Isotopic Composition, Speciation and Mobility of Pu in the Groundwater at DOE Savannah River Site

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A. Introduction

Prior studies have revealed that speciation and/or complexation chemistry have dramatic effect on the mobility of many elements in aquifers because sorption onto any solid phase will depend upon the speciation in solution (Choppin, 1988; Choppin, 1992; Moulin and Ouzounian, 1992; Marley *et al.*, 1993; Cooper *et al.*, 1995). Less well understood, is how interactions between source characteristics (i.e. Pu from fallout, underground test debris, liquid vs. vitrified waste) and ambient geochemistry and hydrology interact to change speciation leading to enhanced or retarded actinide migration in groundwater. Total radionuclide activity data are not particularly revealing since speciation, not total activity levels, are needed to predict mobility. Extreme care must be taken not to alter the ambient geochemistry and colloid abundances during sampling. Finally, isotopic information is needed to identify Pu sources which can be linked to the physical-chemical form of Pu and hence its mobility.

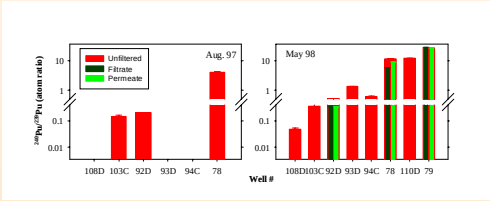
B. Methods

Groundwater samples were collected on two occasions at the Savannah River Site (SRS). The first samples were collected at three groundwater monitoring wells in August 1997 for analysis of total Pu isotopic composition in order to plan a more detailed study the following spring (wells FSB 78, 103C, 92D, see Figure 1). In May 1998, we conducted a more comprehensive sampling using our unique combination of trace metal clean, low flow well sampling, Cross Flow Filtration (CFF), redox speciation and Thermal Ionization Mass Spectrometry (TIMS) techniques. Eight sites were sampled within which four of them (wells FSB 108D, 92D, 78 and 79, see Figure 1) were sampled through CFF in order to obtain size-fractionation samples. Well 108D is located upstream from the seepage basin and thus serves as a "background" well that should be minimally influenced by groundwater discharges associated with the seepage basins. Overall, groundwater is driven by an average hydraulic gradient of 0.014 m/min running approximately from well 92D, towards 93,94, 78, 110, 79 and the Fourmile Branch creek.

We use a "micro-purging", low rate pumping technique and on-site CFF (modified to avoid any redox change during CFF processing) in order to minimize the potential of colloid generation or the alteration of the groundwater characteristics. The prefiltered water samples (0.2 µm Nuclepore) were processed with a CFF system equipped with CFF 1 kiloDalton membranes in order to separate the colloidal fraction. Size fractionated samples were then radiochemically purified and Pu isotopes were analyzed using TIMS. Separation of Pu oxidation states in different size fractions was also performed on site and measurements were made by TIMS. The final efficiency of TIMS measurements was 1-3%.

Figure 1: Groundwater well locations in F-Area at Savannah River Site sampled in 1997 and 1998.

C. Isotopic Composition



a. b.

Figure 2. a) $^{240}Pu/^{239}Pu$ atom ratio in unfiltered well samples collected at SRS in August 1997. b) size fractionated $^{240}Pu/^{239}Pu$ data from samples collected in May 1998. Note two of the well sites are the same, and that for well 108D (Figure 2b), $^{240}Pu/^{239}Pu$ ratio is only available for an unfiltered sample at this time.

Our first results were from unfiltered samples collected in August 1997. In one of the three wells, we were surprised by the elevated $^{240}Pu/^{239}Pu$ atom ratio of 3.9 (well 78) vs. 0.15-0.20 in the other two wells (92D & 103C; see Figure 2a for data). Values typical of fallout and nuclear materials are always <<1, with the global fallout average being 0.18. Hence this high ratio is indeed unusual for most Pu sources. As will become clearer with the 1998 SRS samples, we attribute the highest $^{240}Pu/^{239}Pu$ ratios to samples that have been impacted by the decay of ^{244}Cm (t½ = 18.1 yrs.) to ^{240}Pu in the seepage basin wastes.

We sampled in greater detail in May 1998 at eight sites, four of which were the same wells as in 1997. Note first that the atom ratio of $^{240}Pu/^{239}Pu$ in 1998 is similar to the 1997 results in all of the size classes, and significantly elevated over typical fallout or waste values (wells 92-D and 78; Figure 2b). Note also, that the new well 79 samples from 1998 have the highest $^{240}Pu/^{239}Pu$ ratios. Well 79 is downstream from 78, and we suggest that well 103C, which we sampled only in 1997 is located off the contaminant plume, and thus is not as significantly impacted by the ^{244}Cm source (see map of well sites and groundwater flow-Figure 1). Likewise for the "background" well 108D we measured a very low $^{240}Pu/^{239}Pu$ ratio of 0.05 (0.049 ± 0.005). This well does not appear to be impacted by the Cm source. A low $^{240}Pu/^{239}Pu$ ratio signifies a source other than global fallout and is most likely due to weapons grade Pu waste of some local origin. It is worth noting that the total Pu concentrations are extremely low in this well (0.5 fg/kg ^{239}Pu; 0.03 fCi $^{239,240}Pu$), which is two orders of magnitudes lower than the other wells downstream of the seepage basin (Figures 3a & 3b).

Downstream from the seepage basins, the $^{240}Pu/^{239}Pu$ ratios increase in all size classes, with the highest ratios being found most distant from the potential source. We speculate that most of the ^{240}Pu in the farthest wells originates from the decay of ^{244}Cm. Curium would be more mobile in groundwater, thus earlier Cm releases should have separated from the original Pu plume. This effect would be most evident the further one moves towards Fourmile Branch. The presence of Cm at this site is not surprising. During the mid 1960's, 3 kg of Cm was produced at the SRS and most relevant to our observations, the Cm produced was primarily ^{244}Cm (Seaborg and Loveland, 1990). It is also estimated that 0.24 Ci of Cm was released into these seepage basins. Assuming discharge in the mid-60's, our results can be used to predict ^{244}Cm levels in well 79 around 4 pCi/kg, which is roughly the same order as observed in well 79 by Kaplan *et al.* (1994).

D. Size Speciation

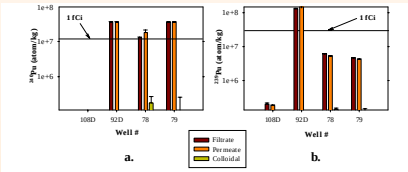


Figure 3. ^{240}Pu (3a) and ^{239}Pu (3b) atom abundances in filtrate (<0.2µm), Permeate (<1kD) and colloidal (1kD-0.2 µm) size fractions.

The Pu concentration data (Figure 3a & 3b) for both ^{239}Pu and ^{240}Pu show that only a small fraction of the total Pu is in the colloidal fraction (<5% in general for both isotopes). A low colloidal abundance is consistent with the higher oxidation states, and with overall low natural colloidal organic carbon levels at this site. In a prior study at well 79 Kaplan *et al.* (1994) observed that 100% of the total $^{239,240}Pu$ was in their 0.5 – 3 kD colloidal fraction (combined ^{239}Pu and ^{240}Pu activities measured using alpha-counting). We can only speculate as to the difference with our results, since we sampled at a different time using different 1 kD cut-off CFF membranes and sampling techniques. Our samples were processed and separated by CFF immediately using an on-line sampling mode in the field, whereas Kaplan *et al.* took up to 3 days to complete their ultrafiltration work. This delay and exposure to ambient surface conditions may have altered the original oxidation state distributions.

E. Oxidation State and Mobility

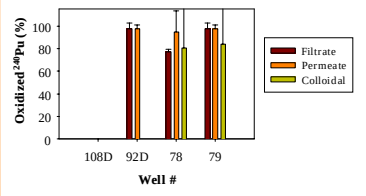


Figure 4. Percent oxidized ^{240}Pu in filtrate (<0.2µm), Permeate (<1kD) and colloidal (1kD-0.2 µm) size fractions.

Our procedures can be used to distinguish between reduced Pu(III or IV) and oxidized Pu(V or VI). For ^{240}Pu, we find that >75-95% of the Pu is in the oxidized form in all of the size classes (Figure 6). Specific isotopic analyses on these oxidized fractions show even higher enrichment in ^{240}Pu than in the bulk permeate and filtrate phases ($^{240}Pu/^{239}Pu$ = 11.2 and 27.1 in oxidized fractions at wells 78 and 79, respectively). Typical groundwater is reducing, and the high abundance of oxidized ^{240}Pu is at first surprising. However, if we consider that the source of much of the ^{240}Pu is from ^{244}Cm decay, it is consistent with known processes. The Pu progeny of the Cm isotopes, by the Szilard-Chalmers process, are born deficient in electrons and hence would be enriched in the penta and hexavalent oxidation states. It should be noted that given these higher valence states, one would predict a significantly lower distribution coefficient (K_d), and hence a lower tendency to adsorb to soil particles and natural colloids.

F. Summary

Overall, our data suggest that redox speciation can vary considerably, and that most of the Pu is in a more oxidized form <1 kD in size in the SRS wells. We attribute this to the unique ^{240}Pu source from ^{244}Cm, but even ^{239}Pu appears less associated with colloids than data from prior studies using different techniques would imply. We note that the forms of Pu found at the SRS would be significantly more mobile than standard models predict. The highly varied $^{240}Pu/^{239}Pu$ ratio can only point to ^{240}Pu being enhanced downstream due to its production from the more mobile Cm precursor and its own enhanced mobility in the oxidized form.

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