

Sources and migration of plutonium in groundwater at the Savannah River Site

Minhan Dai¹, James M. Kelley² and Ken O. Buesseler^{1*}

1. Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

2. Pacific Northwest National Lab, Richland, WA 99352, USA

*corresponding author information:

phone: 508-289-2309; fax; 508-457-2193; email: kbuesseler@whoi.edu

Abstract

We examined the isotopic composition, size distribution and redox speciation of plutonium (Pu) in the groundwater of the F-area seepage basins at the US Department of Energy Savannah River Site (SRS). Sampling was designed to follow a groundwater plume downstream from the seepage basins. A control monitoring well upstream from the basins was used as a baseline. A low $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in the control well signifies a Pu source other than global fallout and indicates reactor-produced Pu. Elevated $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios downstream from the seepage basins are due to the decay of transplutonium isotopes mainly ^{244}Cm to ^{240}Pu , which were generated at the SRS. Evidence suggests that migration of basin-released Pu isotopes are minor. Rather, it is the transplutonium isotopes that migrate preferentially downstream and in the process decay to yield progeny Pu isotopes.

Size fractionation studies with cross-flow ultrafiltration show that <4% of the ^{239}Pu or ^{240}Pu are found in the colloidal fraction (1 kD-0.2 μm), a finding is consistent with the higher Pu oxidation states we observed in the SRS groundwater. The observation of low abundance of colloid associated Pu in groundwater cannot be extrapolated to all sites, but is in contrast to the conclusions of prior groundwater Pu studies at the SRS and elsewhere. This work is unique in its

application of a novel combination of sampling and processing protocols as well as high resolution and ultra-sensitive thermal ionization mass spectrometry. This allows us to quantify the Pu source terms and to better determine the ambient Pu size and redox speciation representative of *in situ* conditions.

Introduction

Increasing concerns have been raised regarding the distribution and fate of actinides, such as plutonium (Pu) in subsurface waters since their introduction into the environment^{1,2}. Migration of Pu from waste-disposal basins had been thought to be insignificant given that Pu was believed to be particle reactive, and hence would be transported in groundwater at a much slower rate than in cases of clearly mobile radiological pollutants such as tritium (³H). Recently, however, concerns have increased due to speculation that Pu migration might be enhanced through colloid-facilitated transport³⁻⁷. Unfortunately, we are limited in our fundamental understanding of Pu sources and *in situ* speciation, factors which ultimately determine Pu migration in groundwater. Gaining an understanding of these factors is a prerequisite for long term predictions of Pu mobility and the subsequent design of efficient restoration programs.

This study was undertaken to help clarify the transport mechanisms and migration patterns of Pu from unlined seepage basins that until their closure in 1988 had received the waste discharges from the F-Area chemical separation facilities at the U. S. Department of Energy Savannah River Site (SRS). Our work sought to compliment prior studies of Pu in SRS F-Area groundwater by employing a combination of methods featuring low flow rate sampling in order to prevent remobilization of Pu that would otherwise be stationary, and immediate *on site* cross-flow ultrafiltration (CFF) to avoid Pu phase distribution changes. This was followed by redox

(oxidation state) separations in the field and subsequent Pu isotopic composition measurements with high resolution and ultra-sensitive thermal ionization mass spectrometry (TIMS) in the laboratory.

The relative abundances of ^{239}Pu , ^{240}Pu , and other minor Pu isotopes such as ^{241}Pu and ^{242}Pu , can be used to trace the specific Pu source because Pu isotopic ratios can vary with reactor type, nuclear fuel burn-up time, neutron flux and energy, and for fallout from nuclear detonations, weapon type and yield⁸. Weapons-grade Pu is characterized by a low content of ^{240}Pu with $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios usually <0.07 ⁸. Global weapons testing fallout has an average $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of 0.18⁹. High and low irradiation conditions in reactors would result in $^{240}\text{Pu}/^{239}\text{Pu}$ ratios ranging from <0.06 to >0.65 , respectively¹⁰. In addition, Pu isotopes can originate from the decay of transplutonium isotopes such as curium (Cm) and americium (Am). With TIMS measurements, this study is able to quantify the relative contributions of multiple plutonium/transplutonium source terms, as manifested by perturbations of the Pu isotopic composition from their source signatures.

Experimental Section

Savannah River Site. The Savannah River Site (Figure 1) was constructed in the early 1950's in western South Carolina in the Southeast United States for the production of nuclear materials, mainly ^3H and ^{239}Pu for defense purposes, but also ^{238}Pu and various transplutonium radionuclides for medical, industrial, and scientific applications^{11,12}. The facilities that produced these radionuclides have been shut down or placed on standby status and the main mission at this site has been directed towards the cleanup of chemical and radioactive pollutants generated at the site.

F-Area was one of two main locations at the SRS where chemical separation facilities were located. Starting in late 1954, the Purex (Plutonium and Uranium Extraction) process was used in the F-area to recover ^{239}Pu , ^{237}Np (neptunium) and ^{238}U (uranium) from irradiated ^{238}U targets. The seepage basins in this area received waste effluents from the separation facilities, including waste from the nitric acid recovery unit and the evaporators that concentrated the dilute uranium nitrate solutions. In November 1988, discharges to the F-Area seepage basins ceased and in 1990, low-permeability clay closure caps were placed over the basins¹³. Throughout the 33-year period during which the basins received waste, discharges were extensively described, inventoried and documented^{11,12,14,15}.

Most of the Pu discharged to the F-Area seepage basins originated from five SRS heavy water moderated production reactors. These reactors produced Pu with a characteristic low $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.062¹⁶. The total reported release of ^{239}Pu to the seepage basins was 209 GBq (1 GBq = 10^9 Bq)¹⁴. Releases of minor Pu isotopes may be calculated from this value and the average isotopic composition of SRS-produced Pu. This minor isotopic composition in terms of atom ratios, decay corrected to May 1998, is estimated to be 0.002 for $^{241}\text{Pu}/^{239}\text{Pu}$ and 0.0003 for $^{242}\text{Pu}/^{239}\text{Pu}$ ¹⁶.

Other sources of Pu isotopes in the F-Area seepage basins are transplutonium radionuclides that were discharged as the result of campaigns initiated in the mid-1960's to produce large quantities of ^{244}Cm (~5 kg) and heavier nuclides by high-flux irradiation of targets containing ^{239}Pu or Pu enriched in ^{242}Pu ^{12,16,17}. Of these progenitor radionuclides, those that bear most on this work are ^{243}Am , ^{244}Cm , ^{245}Cm and ^{246}Cm , which decay to ^{239}Pu , ^{240}Pu , ^{241}Pu and ^{242}Pu , respectively. The total release to the seepage basins of ^{244}Cm , the most abundant and shortest lived ($t_{1/2} = 18.10$ y) of these progenitor radionuclides, was reported to be 12.8 GBq¹⁴.

Because of decay of this isotope to ^{240}Pu , ~6 GBq of ^{244}Cm remained in May 1998. The ratio of the ^{240}Pu generated in total by this decay process, relative to the reactor-produced ^{240}Pu , was minor (~0.0008)^{14,16}.

Beyond the confines of the seepage basins, on the other hand, the transplutonium radionuclides are migrating from the seepage basins at a far greater rate than Pu, causing down gradient wells to become enriched in these radionuclides relative to Pu. The fact of this enrichment was noted by Kaplan *et al.*¹⁸ and is further supported by monitoring results documented in SRS groundwater reports¹⁹⁻²⁴.

Well sampling. Groundwater samples were collected in May 1998 from four of the F-Area wells used to monitor the uppermost aquifer beneath the area (Figure 1). The Westinghouse Savannah River Company's designated names for Wells 1 through 4 are FSB-108D, FSB-92D, FSB-78 and FSB-79, respectively. Well 1 lies upgradient from the basins and hence should be minimally influenced by the seepage basins. The other wells, Wells 2 through 4, roughly define a transect along the contaminant plume and general direction of groundwater flow. The groundwater flow rate varies from almost static to within a 100 – 200 m/y range^{18, 25}. The direction of flow is towards Fourmile Branch, a tributary of the Savannah River that is located ~600 m downstream from the basins. Approximately 30 m downstream from Well 4, before Fourmile Branch, the groundwater surfaces at a seep line.

Most plumbing in our sampling system was made of Teflon and was acid cleaned prior to use. Groundwater was purged and sampled from the wells with an all-Teflon bladder pump at a flow rate of ~0.15 L/min. This low sampling rate is a precaution against the mobilization of particles within the aquifer, and subsequent introduction of colloidal artifacts that in the absence of pumping would be stationary^{26,27}. Purge water was monitored with an in-line multiprobe flow

cell until monitoring parameters (i.e., pH, electrical conductivity and dissolved oxygen) stabilized. Following well purging, unfiltered sample fractions were collected first, followed by filtered fractions (through an in-line 0.2 μm pore size and 142 mm diameter polycarbonate membrane), and CFF-processed sample fractions, namely permeate (< 1 kilo Dalton, kD) and retentate (the solution which is retained by the CFF membrane, see below).

CFF processing. CFF is currently the best available method for concentrating colloids from the large sample volumes²⁸, typically 200 L required for this study. The CFF techniques adapted for this study have been used previously for studies of trace constituents in both fresh water and marine environments²⁸⁻³¹. The CFF membranes used for this study (consisting of 3 parallel-configured, spiral-wound CFF membranes, Prep/ScaleTM PLAC, Millipore Corp.) are composed of regenerated cellulose and are rated by the manufacturer to exhibit a nominal molecular weight cutoff of 1 kD³⁰⁻³². The concentration of colloid associated Pu ($\text{Pu}_{\text{colloidal}}$, 1 kD-0.2 μm) is calculated from the Pu concentrations measured in the permeate ($\text{Pu}_{\text{permeate}}$) and retentate ($\text{Pu}_{\text{retentate}}$) sample fractions and a concentration factor term (cf) which is the ratio of the initial mass of the sample to the mass of the retentate fraction at the conclusion of CFF processing:

$$[\text{Pu}_{\text{colloidal}}] = ([\text{Pu}_{\text{retentate}}] - [\text{Pu}_{\text{permeate}}])/cf \quad (1)$$

To help preserve sample integrity, our CFF experiments were undertaken *on site* and simultaneously with the well pumping by balancing the well pumping and CFF flow rates. Prior to CFF sample collection, the CFF system was preconditioned in two steps: 1.) Processing ~ 6 L of filtered groundwater under typical sampling mode, after which the CFF reservoirs were drained, and then 2.) flushing 4 L of filtered groundwater through the system with zero backpressure, in order to eliminate concentrated residues from the first preconditioning step. The

CFF then commenced, with the permeate fraction collected in a 200 L acid cleaned Teflon barrel, and the retentate recirculated back into an acid-cleaned 4 L fluorinated polyethylene bottle. To maintain the ambient redox condition during CFF processing, the CFF system was continuously purged with N₂ gas. Our experience is that if such steps are not taken, colloid precipitation and contamination can occur³³. In addition, HEPA filtered air was directed over the entire CFF system to prevent particulate contamination.

A variety of studies have shown that the retention characteristics of different CFF systems vary dramatically due to membrane specific differences, operational procedures and chemical specific properties of the colloid of interest^{28,31,33}. The CFF membranes used in this study were thoroughly evaluated under operating conditions identical to those encountered in the field just prior to sampling. Following a procedure previously described³¹, we found a retention coefficient >91 % for a 3 kD Dextran (Molecular Probes, Eugene, OR) and >94 % for a 14.5 kD protein standard (Molecular Probes, Eugene, OR). It should be noted that CFF membranes even from the same manufacturer can have varying retention properties (unpublished data). It is thus extremely crucial to calibrate each CFF membrane prior to any application.

Prior to changing CFF sampling sites, extensive cleaning protocols were implemented to prevent sample cross contamination³⁰. CFF field blanks consisting of system-processed, nano-pure water were collected following the sampling of Well 2, the nearest well downstream from the seepage basins and the last well sampled. The resulting ²³⁹Pu concentration was $1.0 \pm 0.1 \times 10^5$ atoms/kg, a level that is 1-3 orders of magnitude lower than typical ²³⁹Pu concentrations encountered in this study except in the upstream control well (see **Results and Discussion**).

Typically, CFF system reliability can be checked with is a mass balance approach^{28,31}, in which case, the concentration of Pu isotopes in the filtrate solution is compared with the sum of the permeate and colloidal fractions. Quantifying the mass balance in this study proved difficult, due to the complication of ingrowth corrections (see **Pu ingrowth corrections**). However, we can place an upper limit on losses to or contamination from our CFF of 5 %, based upon the similarity of Pu concentrations in permeate and filtered sample fractions, and the low Pu colloidal abundance (< 4 %, see **Results and Discussion**).

Redox processing. Redox processing was conducted for filtered (< 0.2 μm) and CFF-processed sample fractions. The process consisted of separating the Pu into Pu(III/IV) and Pu(V/VI) subfractions by a method adapted from Lovett and Nelson³⁴, and was carried out immediately upon sample collection in a HEPA filtered laminar flow bench installed in a mobile laboratory. To help maintain redox states, a $\text{Cr}_2\text{O}_7^{2-}/\text{SO}_4^{2-}$ holding oxidant solution was added immediately following the collection. Also added were isotopic tracers for subsequent isotopic dilution TIMS determinations. Pu in the reduced states was traced with $^{244}\text{Pu(III/IV)}$ (SRM-996 Spike Assay and Isotopic Standard) and Pu in the oxidized states was traced with $^{242}\text{Pu(V/VI)}$ (SRM-4334C, calibrated against SRM-996). The amount taken of each tracer was nominally 5×10^6 atoms.

Pu(III/IV) was separated first by coprecipitation from a ~ 1 M acid solution with LaF_3 serving as a carrier. The precipitate, which constituted the reduced sample subfraction, was collected by filtration and retained for further processing and analysis. To retrieve the oxidized subfraction, the Pu(V/VI) retained in the filtrate was reduced by addition of Fe^{2+} , which was likewise coprecipitated, filtered and retained for subsequent processing and analysis.

This method has been widely and successfully used in studies of Pu speciation in environmental samples³⁴⁻³⁷. Moreover, because the method employs two tracers that are isotopically distinguishable as well as by their oxidation states, any possible change of oxidation state of the tracers during processing is ultimately revealed by TIMS results, from which, correction factors can be determined. These correction factors, C_{reduced} and C_{oxidized} , are generally close to 1, and represent the fractions of $^{244}\text{Pu(III/IV)}$ and $^{242}\text{Pu(V/VI)}$ tracers that retain their original oxidation state during processing. In terms of the known $^{242}\text{Pu(V/VI)}/^{244}\text{Pu(III/IV)}$ atom ratio, R_o , and the $^{242}\text{Pu}/^{244}\text{Pu}$ atom ratios that are measured in reduced and oxidized sample subfractions, R_{reduced} and R_{oxidized} , it follows from the definitions given above that

$$C_{\text{reduced}} = (R_o - R_{\text{oxidized}})/(R_{\text{reduced}} - R_{\text{oxidized}}), \quad (2)$$

and that

$$C_{\text{oxidized}} = R_{\text{oxidized}}(R_o - R_{\text{reduced}})/(R_{\text{oxidized}} - R_{\text{reduced}}). \quad (3)$$

Sample purification and TIMS source preparation. Unfiltered, filtered and CFF-processed sample fractions were collected in acid-cleaned 4 L fluorinated polyethylene bottles. Enough of these aliquots were collected so that sample fractions could be analyzed at least in duplicate. Typical aliquot sizes were nominally 4 kg, except for the retentate sample fraction, in which case aliquot sizes ranged from 0.5 to 1.5 kg. Most aliquots were preserved upon collection by acidification to pH=2 with HNO_3 . Throughout all sample processing, ultrapure acids and bases, such as Ultrex, Seastar and Optima brands, were used exclusively.

Processing to separate and purify Pu in various sample fractions was initiated at Woods Hole Oceanographic Institution (WHOI), where aliquots representing fractions that were not redox-processed were spiked with nominally 5×10^6 atoms of SRM-996 ^{244}Pu , after which Pu was reduced by Fe^{2+} , coprecipitated with LaF_3 and filtered. From this point on, all samples, redox-

processed or otherwise, were in the same condition and so were treated identically. All operations were undertaken in a clean room under Class 100 conditions.

Coprecipitated Pu was taken up in 7.5 M HNO₃ and then separated from carrier, transplutonium radionuclides, and other impurities by two sequential anion exchange column chromatography operations. Both operations employed AG1-X4, 100-200 mesh resin (Bio-Rad Laboratories, Richmond, CA), the bed-volume of the first column being 4 mL, and of the second column being 100 μL. Sample was introduced onto column in 7.5 M HNO₃, washed with 9 M HCl and Pu was finally eluted with 1.2 M HCl. Eluate from the final column was taken to incipient dryness and shipped to Pacific Northwest National Laboratory (PNNL). The time at which the first of these column operations was carried out was recorded such that we could infer from measurement results Pu ingrowth between the time of sampling and the time of Pu separation from its transplutonium progenitors.

At PNNL, another anion exchange purification was undertaken, this time as a batch operation for which purpose a single, 800-μm diameter AG1-X4 resin bead was employed. This latter purification operation is particularly stringent and was designed to eliminate trace impurities. Impurities can degrade TIMS measurements by reacting with Pu atoms at TIMS operating temperatures (1700 – 2000°C, TIMS sources containing <10⁸ atoms of Pu) to form dimers with masses that cannot be anticipated much less monitored, thus causing TIMS ion signal quenching, and by forming ion clusters that result in isobaric background interferences. Consequently, stringent sample purification is the key to good TIMS measurements.

The TIMS source consists of a nominally 50-μm diameter carbon sphere incorporating the Pu homogeneously throughout and residing in the center of the trough of a carburized, rhenium filament formed in a V-shape³⁸. Thus configured, such a source is conducive to superior

ion focusing and TIMS measurement efficiency. Carburization increases ionization efficiency by raising the work function of the rhenium filament surface by 0.25 to 0.4 eV^{39,40}, and the bead becomes fixed to the filament because it partially dissolves into the rhenium (carbon forms a solid solution in rhenium) at the carburization temperature.

TIMS measurements. The TIMS instrument used for this study is a three-stage mass spectrometer with a pulse-counting ion detection system. It has an abundance sensitivity (i.e., ratio of the ion counts at mass 237 tailing from a ²³⁸U peak to the counts at mass 238) of 10⁻⁹⁴¹. It is equipped with a unique, sliding-shaft vacuum lock that enables precise positioning of the mass spectrometer source⁴². Instead of internal standards, the Kanno algorithm (a Rayleigh distillation model) is applied to correct for isotopic fractionation⁴³, in which case 0.2 % accuracy is generally achieved. Given a TIMS source prepared as described above, and use of MARZ-grade rhenium filaments (H. Cross Co., Weehawken, NJ) with large grains having a preferred crystalline orientation at the filament surface of the high work function³⁹, the instrument is capable of a measurement efficiency for Pu (i.e., the ratio of Pu⁺ counts to Pu source atoms) of 0.07. Background ion emissions, as ascertained by monitoring of the 243 mass position, can be reduced to the instrument detector noise level of ~0.04 counts/s.

In this work, because sample aliquots seldom contained more than ~10⁸ Pu atoms, most of the TIMS duty cycle was allocated to the measurement of the minor ²⁴¹Pu and ²⁴²Pu isotopes. Isotopic tracers were used for concentration determinations. The precision of atom ratio measurements was typically limited by counting statistics, and the accuracy of concentration determinations was limited by those same statistics, along with the often larger uncertainty (±0.8%) in aliquotting the tracer. Also, because of losses incurred during sample processing and chemical purification operations, efficiencies of 0.07 could not be achieved. Instead, efficiencies

generally ranged between 0.02 and 0.04. Given the TIMS duty cycle allocation for this study, the TIMS detection limit was 10^4 atoms.

Pu ingrowth corrections. Because the samples collected for this study contained transplutonium radionuclides causing ingrowth of Pu isotopes, it was necessary to correct the measurement results to the May 1998 sampling date. These corrections followed from nonlinear regression analyses of replicate TIMS measurements in accordance with the general equation for decay of a progenitor radionuclide, N_1 , to form its progeny, N_2 ⁴⁴.

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^\circ (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^\circ e^{-\lambda_2 t} \quad (4)$$

Here, t is the time elapsed between sample collection and the first separation of Pu from other actinide elements, N_1° and N_2° represent the number of atoms at the time of sample collection (i.e., $t = 0$) of transplutonium progenitor and Pu progeny isotopes, respectively, and λ_1 and λ_2 are the corresponding decay constants for those isotopes. Note that this treatment of the measurement results yields not only ingrowth-corrected concentrations of Pu isotopes, but also decay-corrected concentrations of the transplutonium isotopes that support the ingrowth. In applying these corrections, we assumed for Pu isotopes ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu and ²⁴²Pu half-life values of 24119, 6564, 14.33 and 3.733×10^5 y, respectively. For progenitor isotopes, we assumed ²⁴³Am, ²⁴⁴Cm, ²⁴⁵Cm and ²⁴⁶Cm half-life values of 7370, 18.10, 8500 and 4370 y, respectively⁴⁵.

We also assumed that any possible ingrowth of ²³⁹Pu stems wholly from ²⁴³Am decay. The conditions whereby the Cm isotopes were produced were such that the abundance in the aquifer of ²⁴³Cm, another ²³⁹Pu progenitor, had to be inconsequential⁴⁵. On the other hand, the atom abundance (in May 1998) of ²⁴³Am, an intermediate species in the sequence of neutron

capture reactions leading to ^{244}Cm and heavier isotopes that were discharged to the seepage basins, is estimated to be at least as great as that of ^{244}Cm ¹⁶.

Results and Discussion

Groundwater chemistry. As a result of the highly acidic wastes discharged to the F-Area seepage basins, groundwater from the downstream wells, Wells 2, 3 and 4, was characteristically acidic (pH ~3-4) and had elevated nitrate levels. This is in stark contrast to Well 1, the upstream control well, which exhibited more natural geochemical properties (Table 1). Other unusual characteristics of the impacted groundwater are high $p\text{CO}_2$ values, resulting from the high acidity, and elevated concentrations of cations, most likely because of the acid-leaching of the aquifer matrix material. There is also a possibility that remediation activities have impacted the groundwater chemistry at this site.

Pu concentration and isotopic composition. Pu measurement results for the various sample fractions (redox subfractions excepted) and representing different times between sample collection and chemical separation of Pu are presented in Table 2. Not surprisingly, ^{239}Pu levels are lowest ($\sim 10^6$ atoms/kg for the unfiltered sample fraction and $\sim 10^5$ atoms/kg for the filtered fraction) in Well 1, a well upgradient from the seepage basins and the first well sampled. This suggests that Well 1 is not significantly impacted by the seepage basins. ^{239}Pu levels are highest in Well 2, the nearest well downstream from the seepage basins.

In contrast to ^{239}Pu , the ^{240}Pu levels are highest in Well 4, the furthest well downstream from the seepage basins. This is evidenced by the much higher $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios indicated for the Well 4 samples. Note also that for each well and each sample fraction, this ratio increased with the time that had elapsed between sample collection and the first separation of Pu

from other actinide elements. This, coupled with the fact that these ratios vary between wells, and are in general too high to attribute to neutron capture events associated with reactor operations, is clear evidence of ^{240}Pu ingrowth from decay of ^{244}Cm present in samples.

The field blank ^{240}Pu concentration ($1.3\pm 0.5\times 10^4$ atoms/kg) was orders of magnitude lower than the ^{240}Pu levels found in the seepage basin plume. The single, very low ^{240}Pu result ($\sim 10^4$ atoms/kg) found for the permeate sample fraction representing the upstream control well, Well 1, is reliable, as Well 1 was sampled first and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio here (0.055 ± 0.009) is consistent with the ratio expected from SRS reactor operations (~ 0.062).

Also shown in Table 2 are ^{241}Pu and ^{242}Pu results. The CFF field blank following Well 2 collections yielded no detectable ^{241}Pu or ^{242}Pu (i.e., typically $< 2,500$ atoms/kg). Unlike ^{240}Pu , it is difficult to discern from a cursory examination of Table 2 possible ingrowth of other Pu isotopes, implying that the ingrowth corrections are smaller. Variations between replicates in Table 2 represents a combination of ingrowth between sampling and separation, and errors greater than the 1σ TIMS measurement error due to variability inherent in groundwater sampling, filtration, CFF processing, weighing etc. Thus only in Well 4, where ingrowth is largest, do statistically significant ingrowth-corrected values emerge for ^{239}Pu , ^{241}Pu and ^{242}Pu with associated uncertainties (see below).

The data selected to construct the ingrowth curves of Figure 2 represent filtered and permeate samples. For Well 4, because it contained the highest concentrations of transplutonium progenitor isotopes relative to Pu isotopes, ingrowth was particularly evident, and it was possible to satisfactorily define ingrowth curves for each Pu isotope (i.e., Eq. 4 regression analysis correlation coefficients ≥ 0.95). These curves are shown as solid lines in Figure 2. For the other wells, it was possible only to define the curve describing ^{240}Pu ingrowth from decay of the most

abundant (in the F-Area aquifer) and shortest lived ($t_{1/2} = 18.10$ y) transplutonium isotope, ^{244}Cm . The other curves, shown as broken lines, are only inferred based on Well 4 results and a well-founded assumption that transplutonium isotope ratios do not vary with location in the aquifer¹⁶.

Somewhat obscured by the logarithmic scale of Figure 2 is the fact that in Well 2, the rate of ingrowth of the ^{241}Pu isotope was slightly exceeded by its rate of decay. This is because the half-life of the ^{241}Pu isotope (14.33 y) is short and the isotopes' concentration was higher in Well 2 ($\sim 10^5$ atoms/kg), relative to its long-lived ^{245}Cm progenitor ($t_{1/2} = 8500$ y, $[^{245}\text{Cm}] \sim 10^7$ atoms/kg), than in the wells further downstream.

Although our focus in this study was on Pu isotopes, the ingrowth corrections indirectly resulted in quantification of transplutonium progenitor isotope concentrations in the F-Area aquifer (Table 3). These transplutonium results are also summarized in Table 3. Moreover, for the ^{244}Cm case, the availability of historical results, derived from $^{243+244}\text{Cm}$ alpha activity measurements^{18, 19-23}, allow a comparison to be made that lends credibility to the inferences of this study. This comparison, shown in Figure 3 in terms of similar alpha activity units (i.e., in the F-Area aquifer 1 Bq $^{244}\text{Cm}/\text{kg}$ is sensibly equivalent to 1 Bq $^{243+244}\text{Cm}/\text{L}$), shows our results to be within an expected range (0– 5 Bq/kg) and that our results mirror a developing trend whereby ^{244}Cm is migrating from the seepage basins and concentrating downstream in Well 4.

Other transplutonium isotope concentration values inferred in this study are likewise reasonable. Although these isotopes in the F-Area aquifer are not determined as part of the SRS groundwater monitoring program, concentrations of ^{243}Am are routinely estimated based on $^{243+244}\text{Cm}$ measurement results and an estimated $^{243}\text{Am}/^{244}\text{Cm}$ atom ratio provided by Holcomb was ~ 1.5 in May 1998¹⁶. The value that we determined for this ratio was 3.2 ± 0.6 . Based on mass spectrometric measurements of Cm isotopes following high flux irradiations of targets

containing in one case $^{239}\text{Pu}^{45}$, and in the other Pu 96 %-enriched in the ^{242}Pu isotope⁴⁶, and assuming a 31 y decay period¹⁶, we can expect that in May 1998 in the F-Area aquifer $^{245}\text{Cm}/^{244}\text{Cm}$ and $^{246}\text{Cm}/^{244}\text{Cm}$ atom ratios should be within ranges of 0.025 - 0.040 and 0.06 - 0.40, respectively. What we found was 0.026 ± 0.002 for the former case, and 0.16 ± 0.03 for the latter.

Relationship between source terms and Pu distributions. In the F-Area aquifer, the relative contributions of the transplutonium source terms to the distribution of Pu isotopes are reflected by perturbations to the atom ratios expected in the absence of ingrowth. To show these perturbations, we have compared the Table 3 atom ratio results with the estimated SRS reactor produced Pu atom ratios provided by Holcomb¹⁶(Figure 4).

As expected, the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in Well 1, is not measurably perturbed, but perturbations at the other wells increase dramatically with distance downstream. This trend is owed as much to the downstream decrease in ^{239}Pu levels as to an increase in ^{240}Pu levels. At Well 4, ~550 m downstream of the basins, the measured $^{240}\text{Pu}/^{239}\text{Pu}$ ratio (13 ± 2) exceeded the estimated ratio of SRS Pu (~0.062) by a factor >200. The reciprocal of this number, 0.005, represents an upper limit estimate of the fraction of the total measured ^{240}Pu in Well 4 that originated from reactor-produced Pu and migrated from the seepage basins; the other 99.5 % of the ^{240}Pu at Well 4 originated from ^{244}Cm decay. This is an upper limit also because small corrections for ^{239}Pu produced locally as a result of the decay of transplutonium isotopes (rather than migrated as ^{239}Pu from the seepage basins), would lower the apparent $^{240}\text{Pu}/^{239}\text{Pu}$ ratio and hence one would underestimate the total ^{240}Pu originated from ^{244}Cm decay. Similarly, the upper limits of the fractions of the total ^{240}Pu in Wells 2 and 3 that migrated from the seepage basins were 0.23 and 0.02, respectively. It is thus clear that discharges of ^{240}Pu to the F-Area seepage

basins, like those of ^{239}Pu , have not rapidly migrated downstream, but mostly remain near Well 2 at the fringe of the seepage basins. On the contrary, it is the ^{244}Cm discharges that, through decay to ^{240}Pu , have caused the downstream appearance of elevated ^{240}Pu .

This finding adds clarity to past findings by Kaplan *et al.*¹⁸, who reported in 1994 on the basis of $^{239,240}\text{Pu}$ (combined ^{239}Pu and ^{240}Pu activity) alpha activity measurements that a Pu plume front had moved more than 300 m downstream, to a well (SRS FSB-110D) located between Well 3 and 4. Not coincidentally, the highest ^{244}Cm level measured by Kaplan *et al.* was also at that well¹⁸. This suggests that what was actually measured by these investigators was predominantly the *in-situ* ingrowth and buildup of the ^{240}Pu isotope tracking the downstream migration of its more mobile ^{244}Cm progenitor. The inference that Pu discharges had moved beyond the seepage basins fringes and migrated so far downstream was erroneous.

^{241}Pu and ^{242}Pu levels at Well 1 were below our detection limits. At the downstream wells, perturbations of the $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ atom ratios from those expected in the absence of ingrowth, although evident, are not nearly as pronounced as in the case of the $^{240}\text{Pu}/^{239}\text{Pu}$ ratios. Note that at Well 2 the $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ atom ratio values that we determined were lower than Holcomb's estimates. Whether this is because the estimates of Holcomb are only nominal values, or the ingrowth rate of ^{239}Pu , integrated over time, exceeded those of ^{241}Pu and ^{242}Pu , or both, is not clear. This uncertainty limits our confidence in the Pu source term for these minor isotopes. The Well 2 $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ atom ratio values that we determined (0.00052 ± 0.00004 and 0.00020 ± 0.00005 , respectively) might be more indicative of the Pu originally discharged to the seepage basins than the estimates provided by Holcomb (nominally 0.002 and 0.0003, respectively). At any rate, we are disinclined to try to infer the relative contributions of source terms to the downstream buildup of the ^{241}Pu and ^{242}Pu

isotopes with the rigor that we applied to ^{240}Pu . Nevertheless, from a qualitative perspective, the fact that the $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{242}\text{Pu}/^{239}\text{Pu}$ atom ratios increase with downstream distance makes it clear that the contributions of transplutonium source terms to the downstream distribution of the ^{241}Pu and ^{242}Pu isotopes were appreciable.

Pu oxidation state distributions. Pu can exist in four oxidation states in the environment^{47,48} with the reduced, Pu(III/IV) forms having a two orders of magnitude higher distribution coefficient, K_d ($K_d=[\text{solid}]/[\text{solution}]$) than the more oxidized, Pu(V/VI) forms^{36,37}.

Pu oxidation states results (Table 4) were corrected for instabilities of tracer oxidation states through applications of Eq. 2 and Eq. 3. The applied C_{reduced} and C_{oxidized} correction factors ranged from 0.74 to 0.97 and from 0.75 to 0.86, respectively, and were typically at the high end of those ranges. The data in Table 4 were ingrowth-corrected to the May 1998 sample collection time (Table 5). However, the chemistry employed in the field to isolate the redox subfractions did not trace the transplutonium isotopes between the reduced and oxidized subfractions, and thus inferences of the concentrations of transplutonium isotopes in these subfractions could not be made.

One measure of the reliability of the Pu redox results summarized in Table 5 is the degree to which the sums of Pu(III/IV) and Pu(V/VI) subfraction concentrations agree with the filtered samples for the same well (Table 3). Agreement is with two exceptions within the 1σ TIMS measurement error for both ^{239}Pu and ^{240}Pu , the two exceptions being a difference of 10 % for ^{240}Pu for Well 3 and 35 % for ^{239}Pu in the control Well 1 where Pu levels are lowest.

Downstream from the seepage basins, the fractional abundance of $^{239}\text{Pu(V/VI)}$ is very high at Well 2 (0.92), falls at Well 3 (0.25), and then rises again at Well 4 (0.50). Throughout the aquifer, ^{240}Pu is almost exclusively in the oxidized form, the fractional abundance of

$^{240}\text{Pu}(\text{V/VI})$ diminishing only slightly between Well 2 (~1) and Well 4 (0.9). A similarly high $\text{Pu}(\text{V/VI})$ fractional abundance is also seen at the upstream control well (0.85). The reason that at each well the $^{239}\text{Pu}(\text{V/VI})$ and $^{240}\text{Pu}(\text{V/VI})$ fractional abundances were measurably different remains to be explained, although this difference may be related to the fact that, because most of the ^{240}Pu in the aquifer was born *in-situ* and with recoil energy, an electron-stripping Szilard-Chalmers process may have resulted in production of more oxidized forms⁴⁴.

To offer another perspective of the Pu oxidation state distributions in the F-Area aquifer – this time in terms of alpha activities ($\mu\text{Bq/kg}$ units) – and at the same time to further clarify the ^{239}Pu and ^{240}Pu isotope distributions discussed earlier, the results of Table 5 are presented as a bar chart, in Figure 6. The linear scale of this chart emphasizes how little of the Pu in the F-Area aquifer was in the reduced form, how little of the ^{239}Pu isotope migrated beyond Well 2, and how downstream of Well 2 the preponderance of the Pu present was *in-situ* born ^{240}Pu .

The overall high abundances of oxidized Pu we observed in all wells was consistent with the oxidized form $\text{Pu}(\text{V/VI})$ dominating natural waters, including groundwater^{48,49} as well as with the predominance of Pu in the low molecular weight fraction (permeate) due to the low affinity of oxidized Pu for particles/colloids (i.e., low K_d). Therefore the redox distribution presented above is in agreement with the low abundance of colloid associated Pu at this site, which is discussed below.

Colloid associated plutonium. Measurement results for the permeate and retentate sample fractions indicated that the abundance of colloid associated Pu in the F-Area aquifer was far less than we had expected based on an earlier study by Kaplan *et al.*¹⁸. This was evident, even before applying ingrowth corrections, by the markedly similar concentrations of Pu isotopes in permeate and filtered fractions (Table 2). Only for samples collected from Wells 3 and 4, in

which retentate fraction Pu levels were noticeably elevated above those of the permeate and filtered sample fractions, was it possible to quantify Pu in the colloidal phase.

At no sampling location did the calculated colloid concentration of either the ^{239}Pu or ^{240}Pu isotope exceed 10^6 atoms/kg, nor did the colloid associated Pu fractional abundance (i.e., $\text{Pu}_{\text{colloid}}/\text{Pu}_{\text{filtered}}$) of either isotope exceed 0.04 (Table 6). At Well 1, the ^{239}Pu colloid concentration was lowest ($1.3 \pm 0.5 \times 10^3$ atoms/kg) as was the fractional abundance (0.008 ± 0.003). The colloid associated ^{240}Pu concentration at this well was too low to determine. At the seepage basin fringe, Well 2, we could only establish upper limits for the colloid associated ^{239}Pu and ^{240}Pu concentrations because of insufficient buildup of colloidal Pu in the retentate fraction (Table 6).

The results just described raise a question. Namely, why were the F-Area aquifer colloidal Pu concentrations determined in this study so much lower than those reported in 1994 by Kaplan *et al.*¹⁸? These investigators reported that at Well 4, virtually all of the Pu was associated with colloids. Kaplan *et al.* used sequential filtration to separate colloids, taking up to 3 days to complete their ultrafiltration work. They cautioned that “the recovered colloids may have been sampling artifacts”, since this delay and exposure to ambient surface conditions could have altered the original Pu size distributions. In our own studies, we found that exposure to ambient air during processing can increase colloidal iron distributions in groundwater³³.

Additional factors that might bear on the differences are that Kaplan *et al.* employed different membrane types with different cutoff ratings, one of which was lower (0.5 kD) than that used in the current study. Thus, the differences found likely stem from differences in equipment and protocols and should not in our opinion, be considered controversial, but rather demonstrate the advances that have been made in this field of study.

Elsewhere, at the Nevada Test Site, Kersting *et al.* also reported a high abundance of colloid associated Pu in groundwater (>99 %, ~100 kD – 1 μm size range)⁵. The study itself is not conclusive in terms of colloid mobility due to the high rate of well pumping used (30 L/min), which, as the authors have pointed out, may have generated colloids as an artifact of sampling. Ample evidence exists suggesting that particles that are otherwise stationary in the aquifer may become suspended by increasing the well pumping rate^{26,50,51}.

We conclude that colloid associated Pu concentrations in the F-Area aquifer are much lower than previously reported. How these Pu groundwater distributions compare with other settings is an open question under investigation by this group. Intercomparisons between different groundwater sampling and processing approaches may be needed to conclusively resolve these issues.

One of the main questions that this study sought to answer is: do colloids facilitate Pu transport in groundwater at the SRS? Groundwater colloids were measured, but at very low levels. If those colloids did facilitate Pu transport, it was not very effective, as downstream concentrations of Pu originating from Pu seepage basin discharges were likewise very low.

Taken together, the results of this study have implications that bear on both SRS site-specific issues as well as broader issues. Considering first the site specific issues, a need to identify a mechanism, such as colloid-facilitated Pu transport to explain a higher than anticipated rate of migration of Pu downstream from the F-Area seepage basins no longer exists. Pu discharged to the seepage basins is not migrating rapidly downstream, but has moved only ~30 m downstream to the vicinity of Well 2. Ironically, transplutonium radionuclides, discharges of which were dwarfed by that of Pu, are the concern. These transplutonium radionuclides have moved downstream and in the process decayed to yield progeny Pu isotopes, mainly ²⁴⁰Pu.

Typically, this isotope was not recognized as being different from ^{239}Pu , in part because alpha spectrometric methods measure combined ^{239}Pu and ^{240}Pu activity ($^{239,240}\text{Pu}$), and so all $^{239,240}\text{Pu}$ was mistakenly presumed to derive from Pu seepage basin discharges.

The broader implications stem from the differences noted between this study and earlier efforts. Differences in the technology employed, the care taken in its application and the protocols used to detect Pu and its sources, need to be considered in any examination of the environmental fate of Pu. It is clear that restoration of the environment at the SRS and other facilities needs to include accurate predictions of Pu groundwater transport. This requires reliable estimates of Pu sources and a clearer understanding of *in situ* Pu speciation and phase distributions.

Acknowledgments

This research was supported under Grant No. DOE DE-FG07-96ER14733, Environmental Management Science Program, Office of Science and Technology, Office of Environmental Management, United States Department of Energy (DOE). We thank S. Pike, J.E. Andrews, D.J. Repeta, R.A. Belastock, L. Ball, and R. Nelson from Woods Hole Oceanographic Institution; J. Haffener, K. Johnson from Westinghouse Savannah River Company; J. Wacker, T. C. Maiti, L. Bond from Pacific Northwest National Laboratory and W.J. Cai from the University of Georgia for assistance with sampling, processing and/or analysis. K. A. Orlandini from Argonne National Lab provided valuable suggestions and advice at the initial stage of the redox speciation separation methodology establishment. J. Callahan provided valuable comments on the manuscript. This is contribution #10611 from the Woods Hole Oceanographic Institution.

Literature Cited

- (1) National Research Council *Research Needs in Subsurface Science*; National Academic Press: Washington, D.C., 2000.
- (2) Pockley, P. *Nature* **2000**, 404, 797-797.
- (3) Bates, J. K.; Bradley, J. P.; Teetsov, A.; Bradley, C. R.; ten Brink, M. B. *Science* **1992**, 256, 649-651.
- (4) Moulin, V.; Ouzounian, G. *Appl. Geochem.* **1992**, Suppl., 179-186.
- (5) Kersting, A. B.; Efurud, D. W.; Finnegan, D. L.; Rokop, D. J.; Smith, D. K.; Thompson, J. L. *Nature* **1999**, 397, 56-59.
- (6) Honeyman, B. D. *Nature* **1999**, 397, 23-24.
- (7) Marley, N. A.; Gaffney, J. S.; Orlandini, K. A.; Cunningham, M. M. *Environ Sci Technol* **1993**, 27, 2456-2461.
- (8) Oughton, D. H.; Fifield, L. K.; Day, J. P.; Skipperud, L.; Di Tada, M. L.; Salbu, B.; Strand, P.; Drozcho, E.; Mokrov, Y. *Environ Sci Technol* **2000**, 34, 1938-1945.
- (9) Krey, P. W.; Hardy, E. P.; Pachucki, C.; Rourke, F.; Coluzza, J.; Benson, W. K. In *Transuranium nuclides in the environment*: San Franc., Calif., United States, 1976; pp 671-678.

- (10) Sanders, S. M. J.; Boni, A. L. In *Transuranic Elements in the Environment*; Hanson, W. C., Ed.; National Technical Information Center: Springfield, VA, 1980; Vol. DOE/TIC-22800, pp 107-144.
- (11) Carlton, W. H.; Evans, A. G.; Geary, L. A.; Murphy, C. E.; Pinder, J. E.; Strom, R. N. "Assessment of Plutonium in the Savannah River Site Environment," Westinghouse Savannah River Company, 1993, WSRC-RP-92-879, Rev 1.
- (12) Carlton, W. H. "Assessment of Neptium, Americium, and Curium in the Savannah River Site Environment," Westinghouse Savannah River Company, 1997, WSRC-TR-97-00266.
- (13) Westinghouse Savannah River Site Company "Environmental Summary of the F- and H-Area Seepage Basins Groundwater Remediation Project, Savannah River Site," U.S. Department of Energy, 1997, WSRC-TR-97-0130.
- (14) Cummins, C. L.; Hetrick, C. S.; Martin, D. K. "Radioactive Releases at the Savannah River Site 1954-1989," Westinghouse Savannah River Company, 1991, WSRC-RP-91-684.

- (15) Carlton, W. H.; Murphy, C. E. J.; Evans, A. G. *Health Phys.* **1996**, *71*,, 290-299.
- (16) Holcomb, H. P. "Estimation of ^{63}Ni , ^{241}Pu , ^{242}Pu and ^{243}Am from ^{60}Co , ^{239}Pu , and ^{244}Cm Activities in Groundwater Samples," Westinghouse Savannah River Company, 1993, WSRC-RP-93-723.
- (17) Seaborg, G. T.; Loveland, W. D. *The Elements Beyond Uranium.*; Gohn Wiley & Sons, Inc.: New York, 1990.
- (18) Kaplan, D. I.; Bertsch, P. M.; Adriano, D. C.; Orlandini, K. A. *Radiochim. Acta* **1994**, *66/67*, 181-187.
- (19) Westinghouse Savannah River Company "The Savannah River Site's Groundwater Monitoring Program: Second Quarter 1993," U.S. Department of Energy, 1993, ESH-EMS-930097.
- (20) Westinghouse Savannah River Company "F-Area Seepage Basins Groundwater Monitoring Report: Fourth Quarter 1994," U.S. Department of Energy, 1995, WSRC-TR-94-0487.

(21) Westinghouse Savannah River Company "F-Area Seepage Basins Groundwater Monitoring Report: First and Second Quarters 1995," U.S. Department of Energy, 1995, WSRC-TR-95-0146-2.

(22) Westinghouse Savannah River Site Company "F-area seepage basins groundwater monitoring report (U): first and second quarters 1995," U.S. Department of Energy, 1995, WSRC-TR-95-0146-2.

(23) Westinghouse Savannah River Company "F-Area Hazardous Waste Management Facility Groundwater Monitoring Report: Third and Fourth Quarters 1996," U.S. Department of Energy, 1997, WSRC-TR-96-0146-4.

(24) Westinghouse Savannah River Company "The Savannah River Site's Groundwater Monitoring Program: Third Quarter 1997," U.S. Department of Energy, 1998, ESH-EMS-970490.

(25) Garten Jr., C. T.; Hamby, D. M.; Schreckhise, R. G. *Sci. Total Environ.* **2000**, 255, 55-73.

- (26) Kaplan, D. I.; Bertsch, P. M.; Adriano, D. C.; Miller, W. P. *Environ Sci Technol* **1993**, *27*, 1193-1200.
- (27) Kaplan, D. I.; Hunter, D. B.; Bertsch, P. M.; Bajt, S.; Adriano, D. C. *Environ Sci Technol* **1994**, *28*, 1186-1189.
- (28) Buesseler, K. O.; Bauer, J. E.; Chen, R. F.; Eglinton, T. I.; Gustafsson, O.; Landing, W.; Mopper, K.; Moran, S. B.; Santschi, P. H.; VernonClark, R.; Wells, M. L. *Mar. Chem.* **1996**, *55*, 1-31.
- (29) Dai, M. H.; Martin, J.-M. *Earth Planet. Sc. Lett.* **1995**, *131*, 127-141.
- (30) Dai, M. H.; Buesseler, K. O.; Kelley, J. M.; Andrews, J. E.; Pike, S.; Wacker, J. F. *J. Environ. Radioactiv.* **2001**, *53*, 9-25.
- (31) Dai, M.; Buesseler, K. O.; Ripple, P.; Andrews, J.; Belastock, R. A.; Gustafsson, O.; Moran, S. B. *Mar. Chem.* **1998**, *62*, 117-136.
- (32) Dai, M. H.; Benitez-Nelson, C. R. *Mar. Chem.* **2001**, *74*, 181-196.
- (33) Hassellöv, M.; Buesseler, K. O.; Charette, M. A.; Herbold, C.; Pike, S. M. In *American Geophysical Union Spring Meeting*; AGU: Boston, 2001.

- (34) Lovett, M. B.; Nelson, D. M. In *Techniques for Identifying Transuranic Speciation in Aquatic Environments*; IAEA, Ed., 1981; pp 27-35.
- (35) Nelson, D. M.; Carey, A. E.; Bowen, V., T. *Earth Planet. Sci. Lett.* **1984**, 68, 422-430.
- (36) Nelson, D. M.; Larsen, R. P.; Penrose, W. R. In *Environmental Research on Actinide Elements Process Symposium*; Pinder, J. E. I., Alberts, J. J., K.W., M., Schreckhise, R. G., Eds.; U.S. Department of Energy: Hilton Head, SC, 1987; pp 27-48.
- (37) Nelson, D. M.; Lovett, M. B. *Nature* **1978**, 276, 599-601.
- (38) Stoffels, J. J.; Lagergren, C. R. *Int. J. Mass Spectrom. Ion Processes* **1984**, 55, 217-219.
- (39) Pallmer, P. G.; Gordon, R. L.; Dresser, M. J. *J. Appl. Phys.* **1980**, 51, 3776-3779.
- (40) Smith, D. H. *J. Chem. Phys.* **1971**, 55, 4152-4154.
- (41) Lagergren, C. R.; Stoffels, J. J. *Int. J. Mass Spectrom.* **1970**, 3, 429-438.
- (42) Stoffels, J. J.; Lagergren, C. R., . *Rev. Sci. Instrum.* **1969**, 40, 1288-1290.

- (43) Moore, L. J.; Heald, E. F.; Filliben, J. J. In *Advances in Mass Spectrometry*; Daly, N. R., Ed.; The Institute of Petroleum: London, 1978; Vol. 7A, pp 448-474.
- (44) Friedlander, G.; Kennedy, J. S.; Miller, J. M. *Nuclear and Radiochemistry*; 2nd ed.; John Wiley and Sons, Inc: New York, 1964.
- (45) Hyde, E. K.; Perlman, I.; Seaborg, G. T. *The Nuclear Properties of the Heavy Elements*; Prentice-Hall: New Jersey, 1964; Vol. 2.
- (46) Keller, C. *The Chemistry of the Transuranium Elements*; Verlag Chemie: Berlin, 1971.
- (47) Cleveland, J. M. *The Chemistry of Plutonium*; American Nuclear Society: La Grange Park, IL, 1979.
- (48) Choppin, G. R. *J. Radioanal. Nucl. Ch. Ar.* **1991**, *147*, 109-116.
- (49) Nitsche, H.; Lee, S. C.; Gatti, R. C. *J. Radioanal. Nucl. Ch. Ar.* **1988**, *124*.
- (50) Ryan, J. N.; Gschwend, P. M. *Water Resour. Res.* **1990**, *26*, 307-322.
- (51) Ronen, D. M.; Margaritz, M.; Weber, U.; Amiel, A. J.; Klein, E. *Water Resour. Res.* **1992**, *28*, 1279-1291.

Figure Legends

FIGURE 1. Locations of the SRS F-Area seepage basins and the four monitoring wells sampled in this study. The Westinghouse Savannah River Company's designated names for the Wells 1 through 4 are FSB-108D, FSB-92D, FSB-78, and FSB-79, respectively.

FIGURE 2. Plots of ingrowth of Pu isotopes in permeate (< 1 kD) and filtered (<0.2 μm) groundwater samples from SRS F-Area wells. This ingrowth resulted from decay of accompanying transplutonium progenitor isotopes in the samples in accordance with the general equation for decay (Eq. 4, see text) yielding concentrations of both Pu and transplutonium isotopes corrected to sample collection dates. The time scale indicated in the figure represents the days elapsed between the May 1998 sample collection period and the first separation of Pu from other actinide elements. Solid-line curves followed from nonlinear regression analysis of the replicate measurements. Broken line curves are inferred based on Well 4 results and an assumption that transplutonium isotope ratios remain constant throughout the aquifer.

FIGURE 3. Comparison of ^{244}Cm alpha-activity levels (Bq/kg) found in filtered (<0.2 μm) SRS F-Area well water samples collected between 06- and 15 May 1998 in this study with $^{243+244}\text{Cm}$ levels (Bq/L) in unfiltered samples reported by Westinghouse Savannah River Co.¹⁹⁻²⁴.

FIGURE 4. Comparison of Pu isotopic compositions in filtered (<0.2 μm) SRS F-Area well water samples collected in May 1998 with an estimated composition provided by Holcomb¹⁷ as being indicative of SRS reactor-produced Pu.

FIGURE 5. Comparison of concentrations (alpha activity units of $\mu\text{Bq/kg}$) of ^{239}Pu and ^{240}Pu isotopes in reduced (III/IV) and oxidized (V/VI) forms with the sum of ^{239}Pu and ^{240}Pu in filtered sample fractions (<0.2 μm) that were not redox processed.

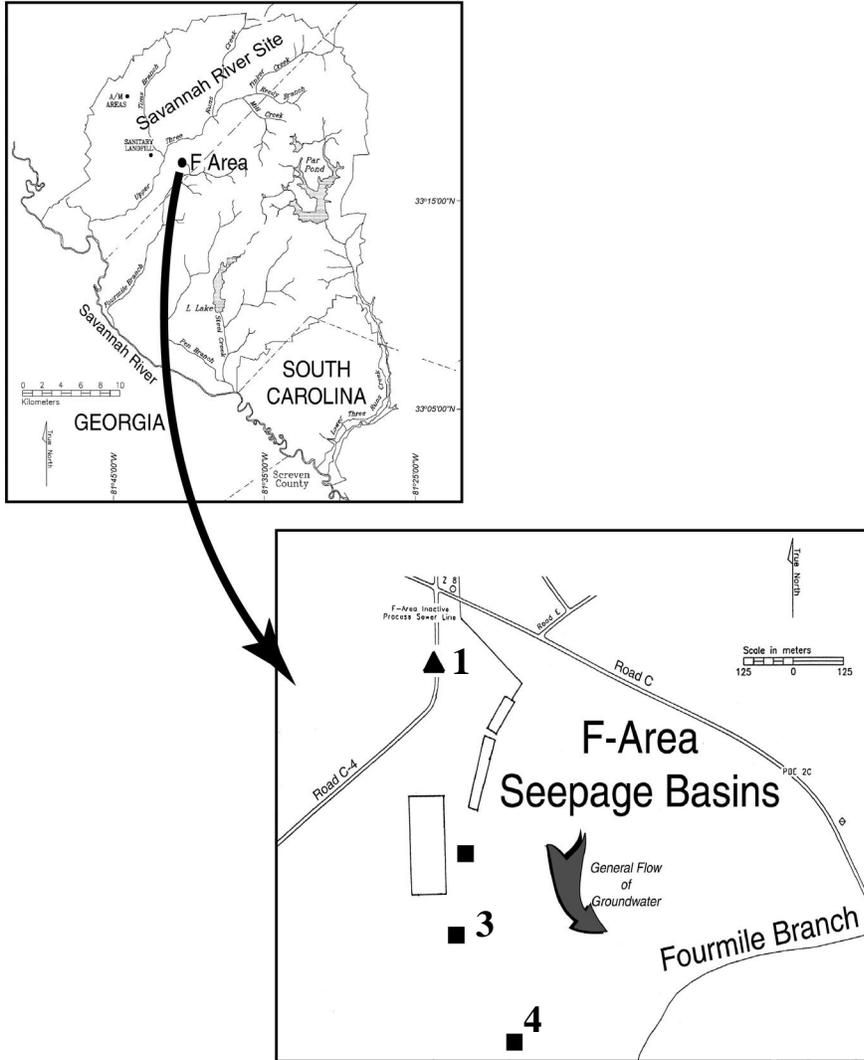


Figure 1

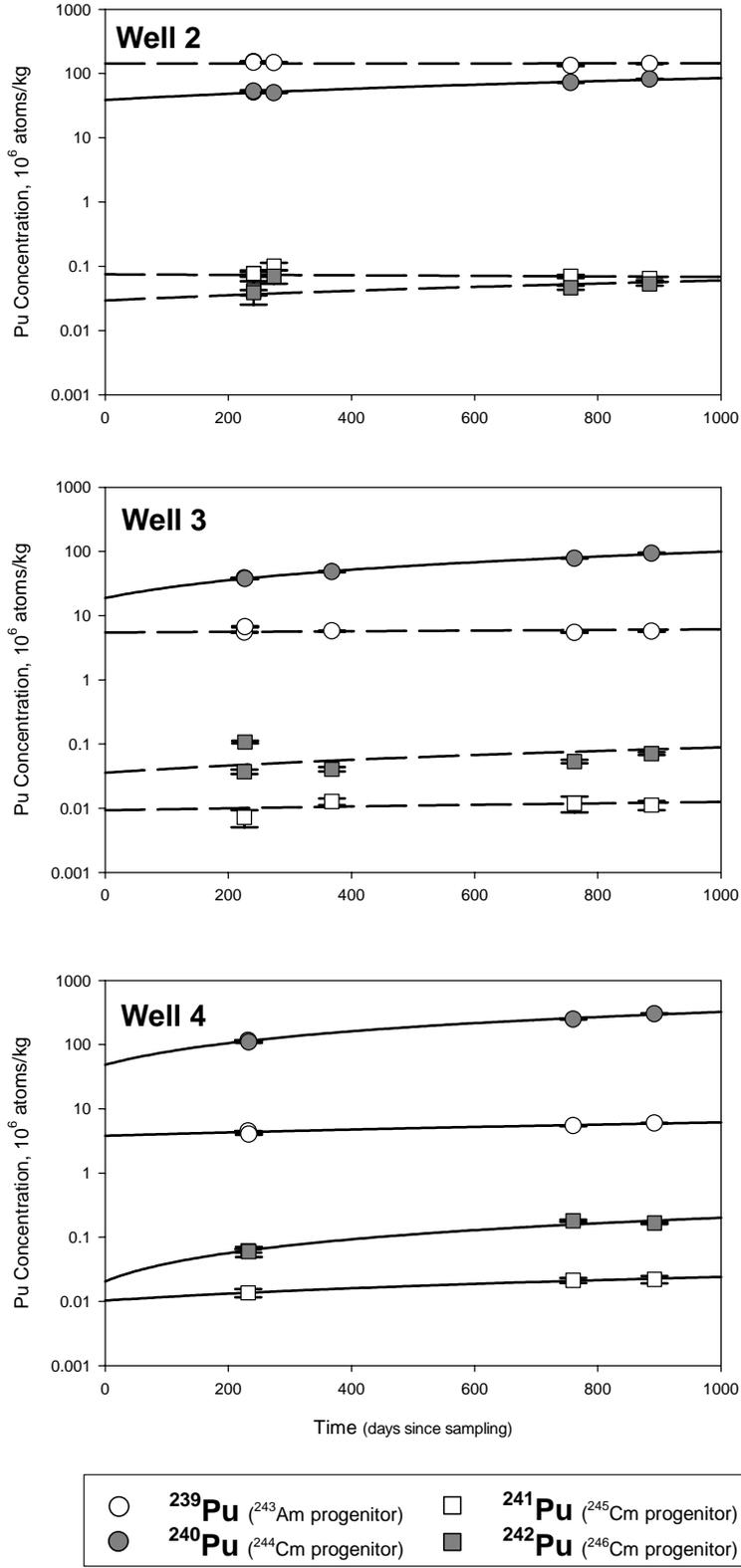


Figure 2

Figure 3

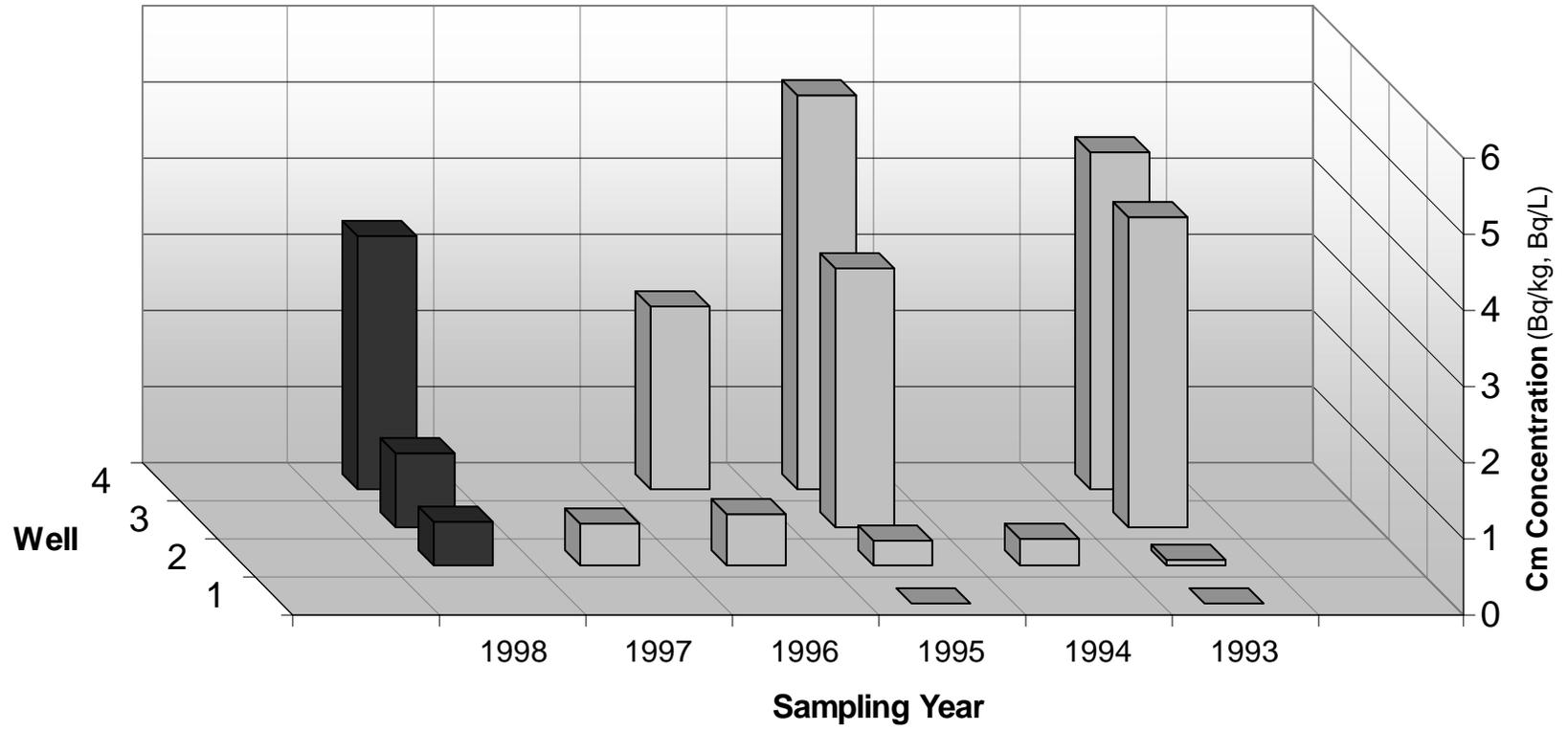
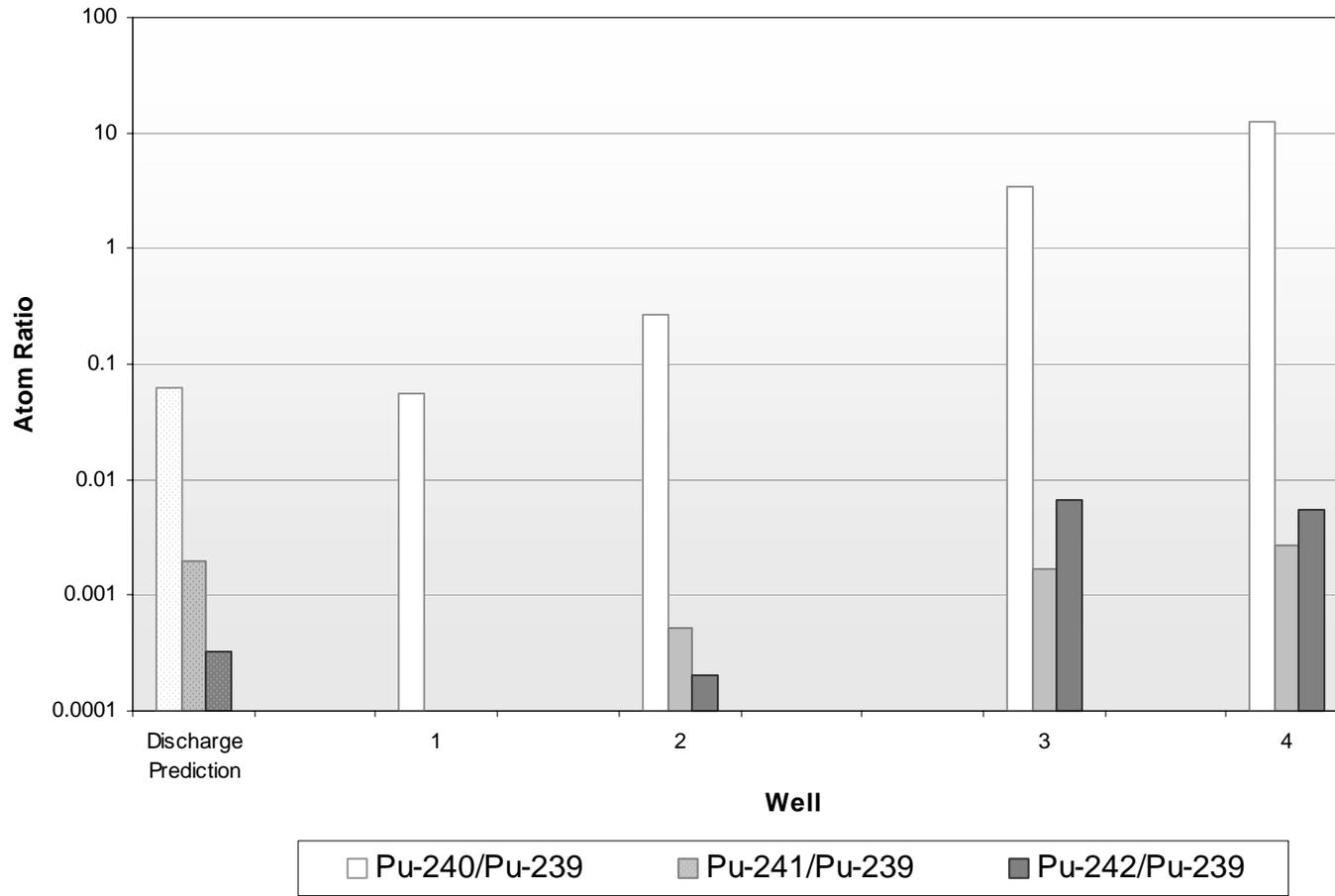


Figure 4



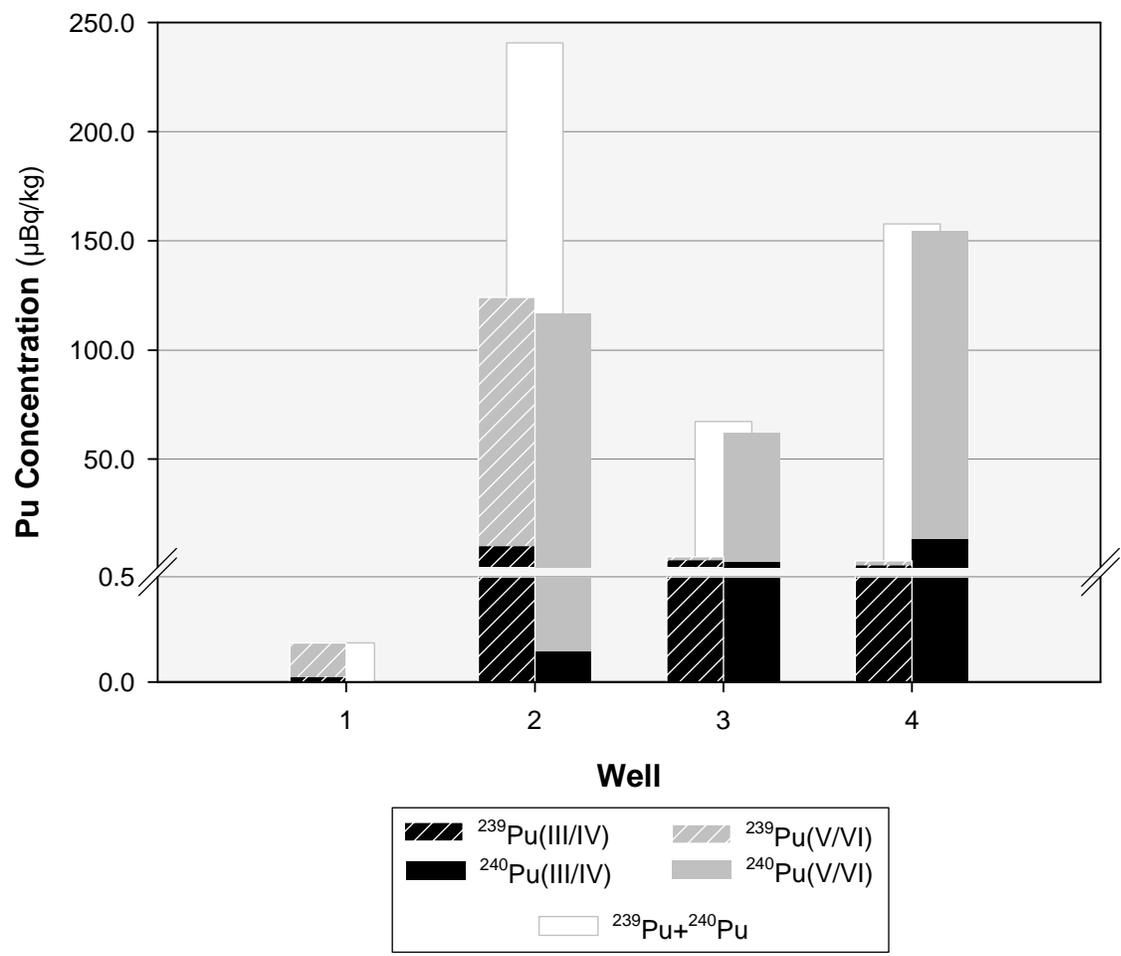


Figure 5

Table 1. Basic groundwater chemistry near the F area seepage basins of the Savannah River Site.

Parameter	Unit	Well 1	Well 2	Well 3	Well 4
		(FSB-108)	(FSB-92D)	(FSB-78)	(FSB-79)
Depth to water	m	24.3	19.3	19.3	4.7
Sampling depth	m	28	24	24	6
Temperature	°C	24	24	25.4	22.4
Conductivity	µS/cm	148.7	744	926	856
pH	---	6.807	4.034	3.850	4.107
DIC ^a	µM	543	1170	817	631
pCO ₂ ^b	Atm	0.004	0.032	0.023	0.017
DO ^c	mg/L	---	2.700	0.580	3.970
NO ₃ ⁻ +NO ₂ ⁻	mg/L	1.22	47.6	98.3	139
PO ₄ ³⁻	mg/L	0.40	0.005	0.007	0.006
F ⁻	mg/L	---	0.3	0.15	0.17
SO ₄ ²⁻	mg/L	0.56	1.52	14.1	6.01
K	mg/L	0.28	3.6	3.9	1.1
Na	mg/L	3.3	11.0	6.6	4.1
Mg	mg/L	0.5	2.4	3.4	1.3
Al	mg/L	0.004	27	17	24
Ca	mg/L	4.7	2.9	3.7	2.6
Mn	mg/L	0.01	0.43	---	---
Cu	µg/L	0.34	2.4	5.5	6.2
Zn	µg/L	28.7	61	61	61
Cd	µg/L	0.37	6.9	9.9	3.7
Pb	µg/L	1.32	2.2	1.8	0.56
Fe	µg/L	8.5	15	44	239

a) DIC – Dissolved inorganic carbon.

b) pCO₂ – CO₂ partial pressure, calculated from pH and DIC.

c) DO – Dissolved oxygen.

Table 2. Results of mass spectrometric measurements of ^{239}Pu concentration and Pu isotopic composition made at different times in different size fractions of groundwater samples collected from wells near the SRS, F-Area seepage basins.

Well	Sampling Date	Separation ^a Date	Time ^b (days)	$[^{239}\text{Pu}] \pm \sigma$ error (10^6 atoms/kg)		Atom Ratio $\pm 1\sigma$ error					
						$^{240}\text{Pu}/^{239}\text{Pu}$		$^{241}\text{Pu}/^{239}\text{Pu}^c$		$^{242}\text{Pu}/^{239}\text{Pu}$	
<u>Permeate Sample Fraction (<1 kD)^d</u>											
1	05/09/98	12/09/98	214	0.1401	0.0088	---	---	---	---	---	---
1	05/09/98	10/19/00	894	0.1432	0.0045	0.0548	0.0086	---	---	---	---
2	05/12/98	01/08/99	241	153.7	2.1	0.33542	0.00097	0.000506	0.00003	0.000265	0.000024
2	05/12/98	02/10/99	274	147.8	2.3	0.3419	0.0022	0.000700	0.00009	0.00050	0.00011
2	05/12/98	10/12/00	884	142.5	2.0	0.5745	0.0015	0.000459	0.00002	0.000342	0.000023
3	05/09/98	12/21/98	226	5.26	0.11	7.216	0.045	0.00130	0.00040	0.00696	0.00054
3	05/09/98	05/12/99	368	5.53	0.13	8.686	0.054	0.00226	0.00027	0.00720	0.00053
3	05/09/98	10/12/00	887	5.486	0.075	17.05	0.10	0.00199	0.00032	0.01284	0.00063
4	05/11/98	12/29/98	232	4.344	0.056	26.75	0.14	0.00306	0.00043	0.01411	0.00082
4	05/11/98	06/09/00	760	5.214	0.090	47.41	0.28	0.00401	0.00035	0.0344	0.0011
4	05/11/98	10/19/00	892	5.740	0.088	52.48	0.29	0.00378	0.00049	0.02854	0.00097
<u>Retentate Sample Fraction (enriched in 1 kD - 0.2 μm colloids)^d</u>											
1	05/08/98	12/29/98	235	0.161	0.034	---	---	---	---	---	---
1	05/08/98	10/19/00	895	0.2113	0.0094	---	---	---	---	---	---
2	05/12/98	05/12/99	365	151.3	2.1	0.3707	0.0021	0.000423	0.00006	0.000242	0.000092
2	05/12/98	10/12/00	884	143.9	1.8	0.5979	0.0027	0.00036	0.00010	0.000743	0.000092
3	05/09/98	12/21/98	226	13.15	0.28	3.489	0.033	---	---	0.00393	0.00075
3	05/09/98	10/12/00	887	12.23	0.19	8.151	0.072	0.00162	0.00040	0.00744	0.00098
4	05/11/98	12/29/98	232	9.48	0.12	12.913	0.082	0.00263	0.00045	0.00722	0.00080
4	05/11/98	10/12/00	885	14.46	0.20	25.07	0.16	0.00233	0.00034	0.01679	0.00087

Table 2. Continued.

Filtered Sample Fraction (<0.2 μm)

1	05/06/98	12/09/98	217	0.1636	0.0088	---	---	---	---	---	---
1	05/07/98	06/09/00	764	0.1394	0.0044	---	---	---	---	---	---
2	05/12/98	01/08/99	241	148.9	5.1	0.3585	0.0013	0.000521	0.00005	0.00028	0.00011
2	05/15/98	06/09/00	756	132.9	1.9	0.5462	0.0013	0.000523	0.00003	0.000350	0.000025
3	05/08/98	12/21/98	227	6.69	0.13	5.635	0.036	---	---	0.01605	0.00069
3	05/09/98	06/09/00	762	5.460	0.065	14.327	0.070	0.00218	0.00028	0.00982	0.00059
4	05/10/98	12/29/98	233	4.026	0.095	27.09	0.35	---	---	0.0149	0.0026
1	05/07/98	12/09/98	216	1.145	0.031	0.0489	0.0046	---	---	---	---
1	05/08/98	10/19/00	895	0.809	0.012	0.0608	0.0027	---	---	---	---
2	05/12/98	01/08/99	241	96.9	4.0	0.5106	0.0052	0.000577	0.00004	0.000393	0.000043
2	05/12/98	10/12/00	884	139.0	1.8	0.5691	0.0013	0.000485	0.00002	0.000584	0.000024
3	05/09/98	05/13/99	369	4.858	0.090	11.538	0.054	0.00157	0.00062	0.01087	0.00045
3	05/08/98	10/19/00	895	7.56	0.12	16.96	0.10	0.00238	0.00062	0.01085	0.00062
4	05/10/98	12/29/98	233	4.158	0.088	26.02	0.19	0.00214	0.00037	0.01423	0.00095
4	05/11/98	10/19/00	892	5.83	0.44	49.9	1.9	---	---	---	---

a) Date of the first separation of Pu from other actinide elements.

b) Elapsed time between sample collection and the first separation of Pu from other actinide elements.

c) Decay corrected to the separation date.

d) CFF-processed samples. Concentration factors for Wells 1, 3, 6 and 8 were 48.2, 13.0, 34.4 and 35.5, respectively.

Table 3. Summary of ingrowth/decay-corrected results for Pu isotopes and inferred Am and Cm progenitor isotopes present in filtered (<0.2 μm) samples collected between 06- and 15 May 1998 from SRS F-Area wells.

Parameter	Unit	Ingrowth/decay-corrected average ± 1σ error ^a			
		Well 1 ^b (FSB-108D)	Well 2 ^c (FSB-92D)	Well 3 ^c (FSB-78)	Well 4 (FSB-79)
Pu Isotopes					
[²³⁹ Pu]	10 ⁶ atoms/kg	0.144 (n=4) ± 0.006	143. (n=5) ± 4.	5.5 (n=5) ± 0.3	3.8 (n=4) ± 0.2
²⁴⁰ Pu/ ²³⁹ Pu	Atom Ratio	0.055 (n=1) ± 0.009	0.27 (n=5) ± 0.01	3.4 (n=4) ± 0.4	13. (n=4) ± 2.
²⁴¹ Pu/ ²³⁹ Pu	Atom Ratio	---	0.00052 (n=5) ± 0.00004	0.0017 (n=4) ± 0.0002	0.0027 (n=3) ± 0.0003
²⁴² Pu/ ²³⁹ Pu	Atom Ratio	---	0.00020 (n=5) ± 0.00005	0.007 (n=5) ± 0.003	0.005 (n=4) ± 0.004
Inferred Progenitor Isotopes					
²⁴³ Am/ ²⁴⁴ Cm	Atom Ratio	---	3.2 ± 0.6	3.2 ± 0.6	3.2 (n=4) ± 0.6
[²⁴⁴ Cm]	10 ⁶ atoms/kg	---	468. (n=5) ± 35.	803. (n=4) ± 35.	2750. (n=4) ± 155.
²⁴⁵ Cm/ ²⁴⁴ Cm	Atom Ratio	---	0.026 ± 0.002	0.026 ± 0.002	0.026 (n=3) ± 0.002
²⁴⁶ Cm/ ²⁴⁴ Cm	Atom Ratio	---	0.16 ± 0.03	0.16 ± 0.03	0.16 (n=4) ± 0.03

a) Pu isotope averages are corrected for ingrowth to the 06-15 May 1998 sampling period (Well 1 excepted), and progenitor isotope averages are inferred for that same time frame. The corrections followed from nonlinear regression analysis of replicate measurements (n, as indicated in parentheses), in accordance with the general equation for decay (Eq. 4, see text). Uncertainties shown are standard errors derived from the replicate measurements.

b) In Well 1, we saw no evidence of Pu isotope ingrowth nor do we have reason to believe that progenitor isotopes might be present. Consequently, the Well 1 ²³⁹Pu concentration average is the mean of the four measurement results, weighted to their associated uncertainties. The ²⁴⁰Pu level in this well was very low, nominally 10⁴ atoms/kg, and only once were we able to measure this isotope. Hence, the ²⁴⁰Pu/²³⁹Pu atom ratio shown is from a single measurement. The levels of ²⁴¹Pu and ²⁴²Pu isotopes in this well were below our TIMS detection limit for Pu (i.e., <10⁴ atoms).

c) In Wells 2 and 3, the levels of progenitor isotopes ²⁴³Am, ²⁴⁵Cm and ²⁴⁶Cm, relative to ²⁴⁴Cm, are indicated in italics and assumed to be the same as in Well 4.

Table 4. Results of mass spectrometric measurements of ²³⁹Pu and ²⁴⁰Pu concentrations made at different times and in different redox states and size fractions of groundwater samples collected from wells near the SRS, F-Area seepage basins.

Well	Sampling Date	Pu(III,IV) conc. $\pm 1\sigma$ error, 10 ⁶ atoms/kg ^a					Pu(V,VI) conc. $\pm 1\sigma$ error, 10 ⁶ atoms/kg ^b				
		Time, d ^c	²³⁹ Pu		²⁴⁰ Pu		Time, d ^c	²³⁹ Pu		²⁴⁰ Pu	
<u>Permeate Sample Fraction (< 1kD)^d</u>											
1	05/08/98	24	---	---	---	---	24	0.179	0.013	---	---
2	05/12/98	84	9.70	0.18	0.919	0.024	98	136.3	3.0	35.27	0.78
2	05/12/98	581	10.62	0.14	6.046	0.074	581	126.6	1.8	33.74	0.53
3	05/09/98	23	3.61	0.14	0.971	0.036	23	1.487	0.036	16.98	0.33
4	05/11/98	85	2.39	0.10	7.69	0.25	99	1.68	0.11	46.5	1.6
<u>Retentate Sample Fraction (enriched in 1 kD - 0.2 μm colloids)^d</u>											
1	05/08/98	82	---	---	---	---	95	---	---	---	---
2	05/12/98	84	14.72	0.44	1.46	0.10	98	128.6	2.9	35.97	0.82
3	05/09/98	81	5.91	0.13	2.031	0.041	94	3.53	0.10	21.75	0.38
4	05/11/98	85	7.86	0.30	11.00	0.26	99	2.72	0.14	49.8	1.3
<u>Filtered Sample Fraction (<0.2 μm)</u>											
1	05/06/98	84	0.0298	0.004	---	---	97	0.170	0.010	---	---
2	05/12/98	84	11.06	0.33	0.933	0.050	98	119.4	3.3	34.23	0.95
2	05/12/98	546	13.59	0.16	5.292	0.070	546	119.6	1.9	35.95	0.62
3	05/08/98	82	4.856	0.073	3.093	0.038	94	1.224	0.036	10.14	0.21
3	05/09/98	549	4.532	0.062	11.69	0.13	549	1.472	0.034	25.73	0.45
4	05/10/98	80	1.694	0.092	5.98	0.31	93	2.84	0.11	45.2	1.2
4	05/11/98	547	3.058	0.040	23.74	0.19	547	1.821	0.035	62.08	0.95

a) Reduced sample subfraction.

b) Oxidized sample subfraction.

c) Elapsed time (days) between sample collection and the first separation of Pu from other actinide elements.

d) CFF-processed samples.

Table 5. Summary of ingrowth-corrected results for reduced (III/IV) and oxidized (V/VI) ^{239}Pu and ^{240}Pu isotopes present in filtered ($<0.2\ \mu\text{m}$) samples collected between 06- and 15 May 1998 from SRS F-Area wells.

Parameter	Ingrowth-corrected average $\pm 1\sigma$ error ^a			
	Well 1 (FSB-108D)	Well 2 (FSB-92D)	Well 3 (FSB-78)	Well 4 (FSB-79)
Pu concentration (10^6 atoms/kg)				
$^{239}\text{Pu(III/IV)}$	0.030 (n=1) ± 0.004	11.5 (n=4) ± 0.8	4.4 (n=3) ± 0.4	1.9 (n=3) ± 0.5
$^{239}\text{Pu(V/IV)}$	0.173 (n=2) ± 0.008	125. (n=4) $\pm 4.$	1.4 (n=3) ± 0.1	1.9 (n=3) ± 0.4
$^{239}\text{Pu}^{\text{b}}$	0.203 ± 0.009	136. $\pm 4.$	5.8 ± 0.4	3.8 ± 0.6
$^{240}\text{Pu(III/IV)}$	---	0.04 (n=4) ± 0.03	0.9 (n=3) ± 0.5	4. (n=3) $\pm 1.$
$^{240}\text{Pu(V/VI)}$	---	34.8 (n=4) ± 0.5	18. (n=3) $\pm 5.$	42.1 (n=3) ± 0.7
$^{240}\text{Pu}^{\text{b}}$	---	34.9 ± 0.5	19. $\pm 5.$	46. $\pm 1.$
Pu(V/VI) fractional abundance				
$^{239}\text{Pu(V/VI)}/^{239}\text{Pu}$	0.85 ± 0.02	0.915 ± 0.006	0.25 ± 0.02	0.50 ± 0.08
$^{240}\text{Pu(V/VI)}/^{240}\text{Pu}$	---	0.9987 ± 0.0008	0.95 ± 0.03	0.91 ± 0.02

d) Ingrowth of ^{239}Pu was evident only in the reduced (III/IV) subfraction of the sample from Well 4. Ingrowth of ^{240}Pu was evident only in the reduced subfractions of Wells 2, 3 and 4 and in the oxidized (V/VI) subfraction of Well 4. This is because the abundance of transplutonium progenitor isotopes is greatest in Well 4 and, because of the chemistry employed to isolate the subfractions, progenitor isotopes were concentrated in the reduced sample subfractions immediately following sample collection. For the cases in which ingrowth was evident, corrections to the 06-15 May 1998 sampling period were as described in the text and in the footnotes of Table 3. For the other cases, averages shown are means of the replicate measurements (number of replicates indicated in parentheses), weighted to associated uncertainties.

e) Sum of the Pu(III/IV) and Pu(V/VI) subfraction concentrations.

Table 6. Summary of ingrowth-corrected results for colloid associated ^{239}Pu and ^{240}Pu (1 kD - 0.2 μm) present in filtered (<0.2 μm) samples collected between 06- and 15 May 1998 from SRS F-Area wells.

Parameter	Ingrowth-corrected average $\pm 1\sigma$ error ^a			
	Well 1 (FSB-108D)	Well 2 ^b (FSB-92D)	Well 3 (FSB-78)	Well 4 ^c (FSB-79)
<u>Colloid associated Pu concentration (10^6 atoms/kg)</u>				
^{239}Pu	0.0013 (n=2) ± 0.0005	<0.5 (n=5)	0.18 (n=4) ± 0.02	0.12 (n=4) ± 0.02
^{240}Pu	---	<0.2 (n=5)	0.18 (n=4) ± 0.03	<0.8 (n=4)
$^{239}\text{Pu}_{\text{colloidal}}/^{239}\text{Pu}_{\text{filtered}}$	0.008 ± 0.003	<0.00	0.032 ± 0.004	0.031 ± 0.005
$^{240}\text{Pu}_{\text{colloidal}}/^{240}\text{Pu}_{\text{filtered}}$	---	<0.00	0.010 ± 0.002	<0.02

f) The results presented follow from the replicate results (number of replicates indicated in parentheses) for all of the CFF-processed samples (shown in both Tables 2 and 4). Ingrowth of colloid associated ^{239}Pu and ^{240}Pu was evident only for Well 4 samples. Consequently, results indicated for the other wells are simply means of the replicate measurements weighted to associated uncertainties.

g) The Well 2 CFF concentration factor (13.0) was only about one-third as large as the concentration factors for the other wells. That fact, coupled with the unexpectedly low levels of Pu in the colloidal fraction present in the aquifer, prevented quantification of Well 2 $\text{Pu}_{\text{colloidal}}$. However, upper limits were established. These limits are expressed as twice the root-mean-square averages of the individual measurement uncertainties.

h) The ingrowth-corrected concentration of colloid associated ^{240}Pu in Well 4 was determined by nonlinear regression analysis to be $-0.06 \pm 0.20 \times 10^6$ atoms/kg (correlation coefficient = 0.84). Because of the large relative uncertainty associated with this determination, we have instead indicated an upper limit of $<0.8 \times 10^6$ atoms/kg, which is the 95% confidence level upper limit derived from the regression analysis.