

Sources and Migration of Plutonium in Groundwater at the Savannah River Site

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The isotopic composition, size distribution, and redox speciation of plutonium (Pu) in the groundwater in the vicinity of the F-area seepage basins at the U.S. Department of Energy Savannah River Site (SRS) were examined. A low $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in the upstream 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 the migration of basin-released Pu isotopes is 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 is found in the colloidal fraction, a finding that is consistent with the higher Pu oxidation states observed in the SRS groundwater. The observation of a low abundance of colloid-associated Pu in SRS 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 its use of thermal ionization mass spectrometry for the detection of Pu isotopes. This allows quantification of the Pu source terms and better determination of 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 transport (3–6). Unfortunately, we are limited in our

fundamental understanding of Pu sources and in situ speciation, factors that 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 complement 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 ultrasensitive thermal ionization mass spectrometry (TIMS).

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 yield (7). Weapons-grade Pu is characterized by a low content of ^{240}Pu with $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios usually <0.07 (7). Global weapons testing fallout has an average $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of 0.18 (8). High and low irradiation conditions in reactors would result in $^{240}\text{Pu}/^{239}\text{Pu}$ ratios ranging from <0.06 to >0.65, respectively (9). 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 1950s in western South Carolina in the southeastern 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 (10, 11). 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 toward the cleanup of chemical and radioactive pollutants generated at the site.

Starting in late 1954, the plutonium and uranium extraction (Purex) 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 basins (12). Throughout the 33-year period during which the basins received waste, discharges were extensively described, inventoried, and documented (10, 11, 13, 14).

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 0.062 (15). The total reported release of ^{239}Pu to the seepage basins was 209 GBq

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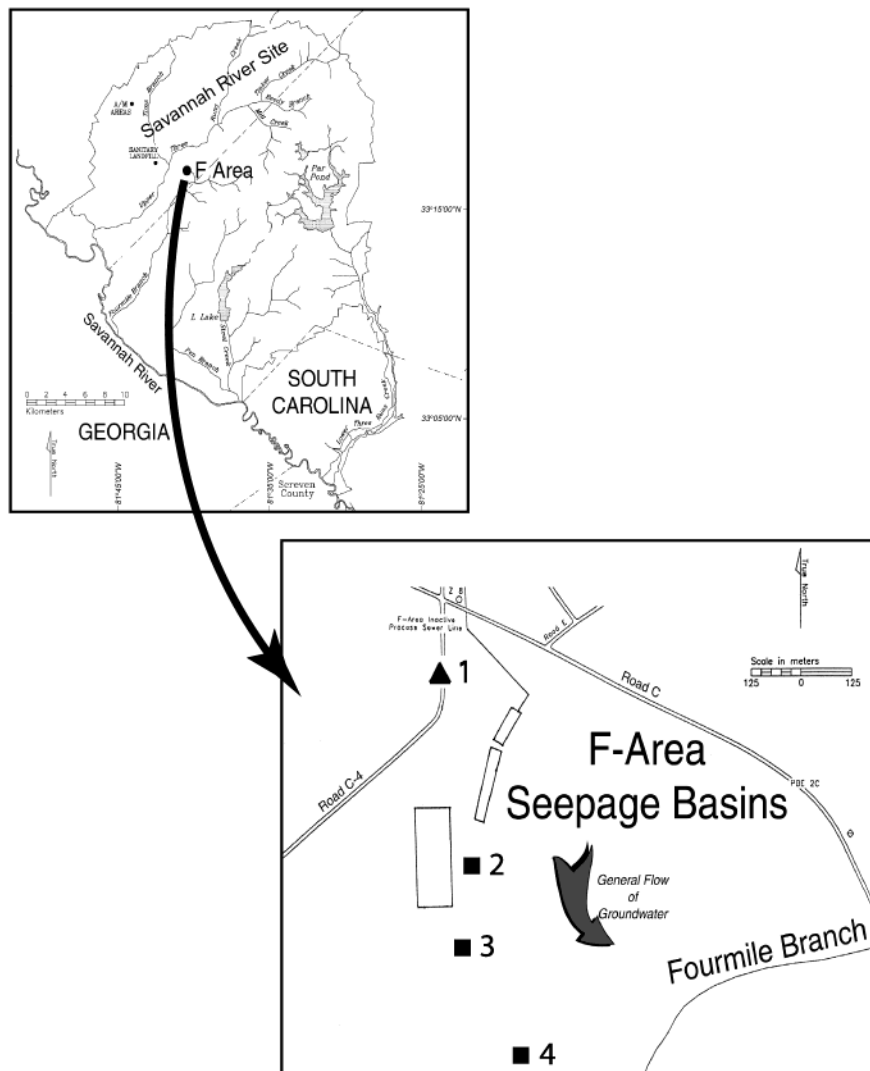


FIGURE 1. Locations of the SRS F-area seepage basins and the four monitoring wells sampled in this study. The Westinghouse Savannah River Co.'s designated names for wells 1–4 are FSB-108D, FSB-92D, FSB-78, and FSB-79, respectively.

(1 GBq = 10^9 Bq) (13). Releases of minor Pu isotopes may be calculated from this value and the average isotopic composition of SRS-produced Pu. This minor isotopic compositions in terms of atom ratios, decay-corrected to May 1998, are estimated to be 0.002 for $^{241}\text{Pu}/^{239}\text{Pu}$ and 0.0003 for $^{242}\text{Pu}/^{239}\text{Pu}$ (15).

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-1960s to produce large quantities of ^{244}Cm (~5 kg) and heavier nuclides (11, 15, 16). 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 ($t_{1/2} = 18.10$ year) of these progenitor radionuclides, was reported to be 12.8 GBq (13). Because of decay of this isotope to ^{240}Pu , ~6 GBq of ^{244}Cm remained in May 1998. 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. (17) and is further supported by monitoring results documented in SRS groundwater reports (18–23).

Well Sampling. Groundwater samples were collected in May 1998 from four of the F-area wells (Figure 1). The

Westinghouse Savannah River Co.'s designated names for wells 1–4 are FSB-108D, FSB-92D, FSB-78, and FSB-79, respectively. Well 1 lies up-gradient from the basins, and wells 2–4 define a transect along the contaminant plume. The groundwater flow rate varies from almost static to within a 100–200 m/year range (17, 24). The direction of flow is toward Fourmile Branch, a tributary of the Savannah River that is located ~600 m downstream from the basins.

Groundwater was purged and sampled from the wells using an all-Teflon bladder pump at a flow rate of ~0.15 L/min through acid-cleaned Teflon tubing. 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 (25, 26). Purge water was monitored until 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.

Processing by Cross-Flow Ultrafiltration. CFF is currently the best available method for concentrating colloids from the large sample volumes (27); typically 200 L was required for this study. The CFF techniques adapted for this study have been used previously for studies of trace constituents in both freshwater and marine environments (27–30). The

CFF membranes used for this study (consisting of three parallel-configured, spiral-wound CFF membranes, Prep/Scale PLAC, Millipore Corp.) are composed of regenerated cellulose and are rated by the manufacturer to exhibit a nominal molecular weight cutoff of 1 kDa (29–31). The concentration of colloid-associated Pu ($\text{Pu}_{\text{colloidal}}$, 1 kDa – 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:

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

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 pre-conditioned 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 back-pressure, 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 N_2 gas. Our experience is that if such steps are not taken, precipitation of iron colloids can occur, which leads to very high losses of iron to the membrane (up to 90–100%), which biases the measured colloid abundances (32). 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 (27, 30, 32). The CFF membranes used in this study were thoroughly evaluated under operating conditions identical to those encountered in the field just prior to sampling (30). We found retention coefficients >91% for a 3 kDa dextran (Molecular Probes, Eugene, OR) and >94% for a 14.5 kDa protein standard (Molecular Probes). It should be noted that CFF membranes even from the same manufacturer can have varying retention properties (unpublished data); thus, calibration of each CFF membrane is mandatory.

Prior to changing sampling sites, the CFF system was cleaned by flushing with >20 L of nanopure water followed by 0.01 N NaOH and 0.01 N HCl solutions. The base or acid solution was recirculated for at least 1 h followed by rinsing with nanopure water until pH ~7. These extensive cleaning protocols were implemented to prevent sample cross-contamination (29). CFF field blanks consisting of system-processed, nanopure water were collected following the sampling of well 2, the nearest well downstream from the seepage basins and the last well sampled. The resulting ^{239}Pu concentration was $(1.0 \pm 0.1) \times 10^5$ atoms/kg, a level that is 1–3 orders of magnitude lower than typical ^{239}Pu concentrations encountered in this study, except in the upstream control well (see Results and Discussion). 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 (using ingrowth-corrected data) 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 using

a method adapted from that of Lovett and Nelson (33), which was carried out immediately upon sample collection in a HEPA-filtered laminar flow bench. To help maintain redox states, a $\text{Cr}_2\text{O}_7^{2-}/\text{SO}_4^{2-}$ holding oxidant solution was added following collection. Pu in the reduced states was traced with ^{244}Pu (III/IV) (SRM-996 Spike Assay and Isotopic Standard), and Pu in the oxidized states was traced with ^{242}Pu (V/VI) (SRM-4334C, calibrated against SRM-996). The amount of each tracer was nominally 5×10^6 atoms.

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

This method has been successfully used in studies of Pu speciation in environmental samples (33–36). 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}Pu (III/IV) and ^{242}Pu (V/VI) tracers that retain their original oxidation state during processing. In terms of the known ^{242}Pu (V/VI)/ ^{244}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 sizes were nominally 4 kg, except for the retentate sample fraction, in which case aliquot sizes ranged from 0.5 to 1.5 kg. These sample fractions were large enough to be analyzed at least in duplicate. At the Woods Hole Oceanographic Institution (WHOI), 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 treated identically in a clean room under Class 100 conditions, and throughout all sample processing, ultrapure acids and bases were used exclusively.

Coprecipitated Pu was taken up in 7.5 M HNO_3 and then separated from carrier, transplutonium radionuclides, and other impurities using two sequential anion exchange columns. Both columns employed AG1-X4, 100–200 mesh resin (Bio-Rad Laboratories, Richmond, CA), the bed volume of the first column being 4 mL and that of the second, 100 μL . Sample was introduced onto the column in 7.5 M HNO_3 and washed with 9 M HCl, and Pu was eluted with 1.2 M HCl. Eluate from the final column was taken to incipient dryness and shipped to Pacific Northwest National Laboratory (PNNL).

At PNNL, another anion exchange purification was undertaken using a single, 800- μm diameter AG1-X4 resin bead. This latter purification operation is particularly stringent. The TIMS source was prepared by incorporating the purified Pu sample into a 150- μm diameter AG1-X4 resin bead, placing the bead in the center of the trough of a V-shaped rhenium filament, pyrolyzing the bead, and then carburizing the filament.

Thermal Ionization Mass Spectrometry. The TIMS instrument used for this study is a three-stage mass spec-

trometer 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 ^{238}U peak to the counts at mass 238) of 10^{-9} (37). It is equipped with a unique, sliding-shaft vacuum lock that enables precise positioning of the mass spectrometer source (38). Instead of internal standards, the Kanno algorithm (a Raleigh distillation model) is applied to correct for isotopic fractionation (39), 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 function (40), 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 count/s.

In this work, because sample aliquots seldom contained $> \sim 10^8$ Pu atoms, most of the TIMS duty cycle was allocated to the measurement of the minor ^{241}Pu and ^{242}Pu isotopes. 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 ($\pm 0.8\%$) in aliquoting the tracer. Because of losses incurred during sample processing and chemical purification operations, total efficiencies generally ranged between 0.02 and 0.04 and 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 (41).

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} \quad (4)$$

Here, t is the time elapsed between sample collection and the separation of Pu from other actinide elements on the first anion exchange column, N_1^0 and N_2^0 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 ^{239}Pu , ^{240}Pu , ^{241}Pu , and ^{242}Pu half-life values of 24119, 6564, 14.33, and 3.733×10^5 years, respectively. For progenitor isotopes, we assumed ^{243}Am , ^{244}Cm , ^{245}Cm , and ^{246}Cm half-life values of 7370, 18.10, 8500, and 4370 years, respectively (42). We also assumed that any possible ingrowth of ^{239}Pu stems wholly from ^{243}Am decay. The conditions whereby the Cm isotopes were produced were such that the abundance in the aquifer of ^{243}Cm , another ^{239}Pu progenitor, had to be inconsequential.⁴²

Results and Discussion

Groundwater Chemistry. As a result of the highly acidic wastes discharged to the F-area seepage basins, groundwater from wells 2–4 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 character-

TABLE 1. Basic Groundwater Chemistry near the F-Area Seepage Basins at the Savannah River Site

parameter	unit	well 1 (FSB-108)	well 2 (FSB-92D)	well 3 (FSB-78)	well 4 (FSB-79)
depth to water	m	24.3	19.3	19.3	4.7
sampling depth	m	28	24	24	6
temperature	°C	24.0	24.0	25.4	22.4
conductivity	$\mu\text{S}/\text{cm}$	148.7	744	926	856
pH		6.807	4.034	3.850	4.107
DIC ^a	μM	543	1170	817	631
$p\text{CO}_2^b$	μatm	4007	32492	23738	17499
DO ^c	mg/L		2.70	0.58	3.97
$\text{NO}_3^- + \text{NO}_2^-$	mg/L	1.22	47.60	98.30	139.00
PO_4^{3-}	mg/L	0.40	0.005	0.007	0.006
F ⁻	mg/L		0.30	0.15	0.17
SO_4^{2-}	mg/L	0.56	1.52	14.1	6.01
K	mg/L	0.28	3.60	3.90	1.10
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	27.00	17.00	24.00
Ca	mg/L	4.7	2.9	3.7	2.6
Mn	mg/L	0.01	0.43		
Cu	$\mu\text{g}/\text{L}$	0.34	2.4	5.5	6.2
Zn	$\mu\text{g}/\text{L}$	28.7	61.0	61.0	61.0
Cd	$\mu\text{g}/\text{L}$	0.37	6.90	9.90	3.70
Pb	$\mu\text{g}/\text{L}$	1.32	2.20	1.80	0.56
Fe	$\mu\text{g}/\text{L}$	8.5	15.0	44.0	239.0

^a DIC, dissolved inorganic carbon. ^b $p\text{CO}_2$, CO_2 partial pressure, calculated from pH and DIC. ^c DO, dissolved oxygen.

istics of the affected 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 affected the groundwater chemistry at this site.

Pu Concentration and Isotopic Composition. ^{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 up-gradient from the seepage basins and the first well sampled (Table 2). This suggests that well 1 is not significantly affected by the seepage basins. ^{239}Pu levels are highest in well 2, the well nearest downstream from the seepage basins.

In contrast to ^{239}Pu , the ^{240}Pu levels are highest in well 4, the well furthest downstream. 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 (Table 2). 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 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 < 2500 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.

The data selected to construct the ingrowth curves of Figure 2 represent filtered and permeate samples. Ingrowth was particularly evident in well 4 because it contained the

TABLE 2. Size-Fractionated ²³⁹Pu Concentration and Pu Isotopic Composition (Data Are Not Ingrowth-Corrected)

well	sampling date	time ^a (days)	[²³⁹ Pu] ± 1σ error (10 ⁶ atoms/kg)	atom ratio ± 1σ error		
				²⁴⁰ Pu/ ²³⁹ Pu	²⁴¹ Pu/ ²³⁹ Pu ^b	²⁴² Pu/ ²³⁹ Pu
Permeate Sample Fraction (<1 kDa) ^c						
1	May 9, 1998	214	0.1401 ± 0.0088			
1	May 9, 1998	894	0.1432 ± 0.0045	0.0548 ± 0.0086		
2	May 12, 1998	241	153.7 ± 2.1	0.33542 ± 0.00097	0.000506 ± 0.000030	0.000265 ± 0.000024
2	May 12, 1998	274	147.8 ± 2.3	0.3419 ± 0.0022	0.000700 ± 0.000090	0.00050 ± 0.00011
2	May 12, 1998	884	142.5 ± 2.0	0.5745 ± 0.0015	0.000459 ± 0.000024	0.000342 ± 0.000023
3	May 9, 1998	226	5.26 ± 0.11	7.216 ± 0.045	0.00130 ± 0.00040	0.00696 ± 0.00054
3	May 9, 1998	368	5.53 ± 0.13	8.686 ± 0.054	0.00226 ± 0.00027	0.00720 ± 0.00053
3	May 9, 1998	887	5.486 ± 0.075	17.05 ± 0.10	0.00199 ± 0.00032	0.01284 ± 0.00063
4	May 11, 1998	232	4.344 ± 0.056	26.75 ± 0.14	0.00306 ± 0.00043	0.01411 ± 0.00082
4	May 11, 1998	760	5.214 ± 0.090	47.41 ± 0.28	0.00401 ± 0.00035	0.0344 ± 0.0011
4	May 11, 1998	892	5.740 ± 0.088	52.48 ± 0.29	0.00378 ± 0.00049	0.02854 ± 0.00097
Retentate Sample Fraction (Enriched in 1 kDa – 0.2 μm Colloids) ^c						
1	May 8, 1998	235	0.161 ± 0.034			
1	May 8, 1998	895	0.2113 ± 0.0094			
2	May 12, 1998	365	151.3 ± 2.1	0.3707 ± 0.0021	0.000423 ± 0.000069	0.000242 ± 0.000092
2	May 12, 1998	884	143.9 ± 1.8	0.5979 ± 0.0027	0.00036 ± 0.00010	0.000743 ± 0.000092
3	May 9, 1998	226	13.15 ± 0.28	3.489 ± 0.033		0.00393 ± 0.00075
3	May 9, 1998	887	12.23 ± 0.19	8.151 ± 0.072	0.00162 ± 0.00040	0.00744 ± 0.00098
4	May 11, 1998	232	9.48 ± 0.12	12.913 ± 0.082	0.00263 ± 0.00045	0.00722 ± 0.00080
4	May 11, 1998	885	14.46 ± 0.20	25.07 ± 0.16	0.00233 ± 0.00034	0.01679 ± 0.00087
Filtered Sample Fraction (<0.2 μm)						
1	May 6, 1998	217	0.1636 ± 0.0088			
1	May 7, 1998	764	0.1394 ± 0.0044			
2	May 12, 1998	241	148.9 ± 5.1	0.3585 ± 0.0013	0.000521 ± 0.000055	0.00028 ± 0.00011
2	May 15, 1998	756	132.9 ± 1.9	0.5462 ± 0.0013	0.000523 ± 0.000030	0.000350 ± 0.000025
3	May 8, 1998	227	6.69 ± 0.13	5.635 ± 0.036		0.01605 ± 0.00069
3	May 9, 1998	762	5.460 ± 0.065	14.327 ± 0.070	0.00218 ± 0.00028	0.00982 ± 0.00059
4	May 10, 1998	233	4.026 ± 0.095	27.09 ± 0.35		0.0149 ± 0.0026
Unfiltered Sample Fraction						
1	May 7, 1998	216	1.145 ± 0.031	0.0489 ± 0.0046		
1	May 8, 1998	895	0.809 ± 0.012	0.0608 ± 0.0027		
2	May 12, 1998	241	96.9 ± 4.0	0.5106 ± 0.0052	0.000577 ± 0.000041	0.000393 ± 0.000043
2	May 12, 1998	884	139.0 ± 1.8	0.5691 ± 0.0013	0.000485 ± 0.000020	0.000584 ± 0.000024
3	May 9, 1998	369	4.858 ± 0.090	11.538 ± 0.054	0.00157 ± 0.00062	0.01087 ± 0.00045
3	May 8, 1998	895	7.56 ± 0.12	16.96 ± 0.10	0.00238 ± 0.00062	0.01085 ± 0.00062
4	May 10, 1998	233	4.158 ± 0.088	26.02 ± 0.19	0.00214 ± 0.00037	0.01423 ± 0.00095
4	May 11, 1998	892	5.83 ± 0.44	49.9 ± 1.9		

^a Elapsed time between sample collection and the first separation of Pu from other actinide elements (used to calculate ingrowth). ^b Decay corrected to the separation date. ^c CFF-processed samples. Concentration factors for wells 1–4 were 48.2, 13.0, 34.4, and 35.5, respectively.

highest concentrations of transplutonium progenitor isotopes relative to Pu isotopes, and it was possible to satisfactorily define ingrowth curves for each Pu isotope (i.e., eq 4 regression analysis correlation coefficients ≥ 0.95). For the other wells, it was possible to define only the curve describing ²⁴⁰Pu ingrowth from decay of the most abundant (in the F-area aquifer) and shortest lived (*t*_{1/2} = 18.10 years) transplutonium isotope, ²⁴⁴Cm (15).

Somewhat obscured by the logarithmic scale of Figure 2 is the fact that in well 2, the rate of ingrowth of the ²⁴¹Pu isotope was slightly exceeded by its rate of decay. This is because the half-life of the ²⁴¹Pu isotope (14.33 years) is short and the isotopes' concentration was higher in well 2 (~10⁵ atoms/kg), relative to its long-lived ²⁴⁵Cm progenitor (*t*_{1/2} = 8500 years, [²⁴⁵Cm] ~ 10⁷ 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 isotopes in the F-area aquifer (Table 3). Moreover, for the ²⁴⁴Cm case, the availability of historical results, derived from ²⁴³⁺²⁴⁴Cm α-activity measurements (17, 18–22) allows a comparison to be made that lends credibility to the inferences of this study. This comparison, shown in Figure 3 in terms of similar α-activity units (i.e., in the F-area aquifer 1 Bq ²⁴⁴Cm/kg is sensibly equivalent to 1 Bq ²⁴³⁺²⁴⁴Cm/L), shows our results to be within an expected range

(0–5 Bq/kg) and that our results mirror a developing trend whereby ²⁴⁴Cm 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 ²⁴³Am are routinely estimated on the basis of ²⁴³⁺²⁴⁴Cm measurement results, and an estimated ²⁴³Am/²⁴⁴Cm atom ratio provided by Holcomb was ~1.5 in May 1998 (15). The value that we determined for this ratio was 3.2 ± 0.6. On the basis of mass spectrometric measurements of Cm isotopes following high flux irradiations of targets containing, in one case, ²³⁹Pu (42) and, in the other, Pu 96%-enriched in the ²⁴²Pu isotope (43) and assuming a 31-year decay period (15), we can expect that in May 1998 in the F-area aquifer ²⁴⁵Cm/²⁴⁴Cm and ²⁴⁶Cm/²⁴⁴Cm 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 alteration of the original atom ratio expected in the absence of ingrowth. To show these perturbations, we have compared the Table 3 atom ratio

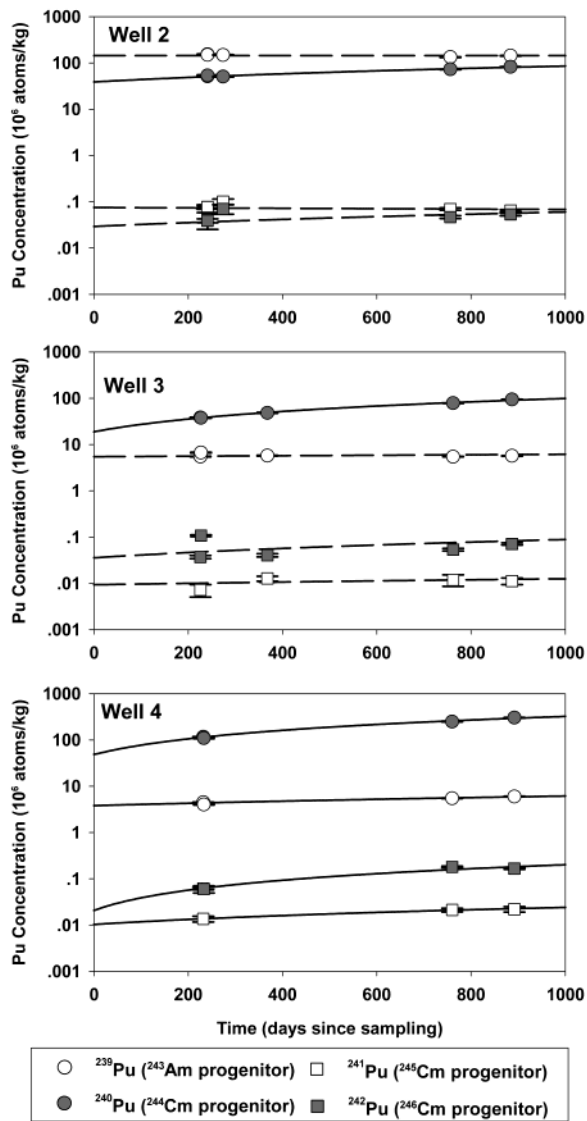


FIGURE 2. Plots of ingrowth of Pu isotopes in permeate (<1 kDa) and filtered (<0.2 μm) groundwater samples from SRS F-area wells. This ingrowth resulted from decay of accompanying transplutonium progenitor isotopes in the samples in accordance with the general equation for decay (eq 4, see text), yielding 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 on the basis of well 4 results and an assumption that transplutonium isotope ratios remain constant throughout the aquifer (15).

results with the estimated SRS reactor-produced Pu atom ratios provided by Holcomb (15) (Figure 4).

As expected, the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in well 1 is not measurably different from the original ratio, but perturbations at the other wells increase dramatically with distance downstream. This trend is due to the downstream decrease in ^{239}Pu levels as well as to an increase in ^{240}Pu levels. At well 4, 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 originating from ^{244}Cm decay. Similarly, the upper limits for the fractions of 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. (17), who reported in 1994 on the basis of $^{239,240}\text{Pu}$ (combined ^{239}Pu and ^{240}Pu) α -activity measurements that a Pu plume front had moved >300 m downstream to a well (SRS FSB-110D) located between wells 3 and 4. Not coincidentally, the highest ^{244}Cm level measured by Kaplan et al. was also at that well (17). 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). 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 (44, 45) with the reduced, Pu(III/IV), forms having a 2 orders of magnitude higher distribution coefficient, K_d ($K_d = [\text{solid}]/[\text{solution}]$) than the oxidized, Pu(V/VI), forms (35, 36).

Pu oxidation states results (Table 4) were corrected for instabilities of tracer oxidation states through applications of eqs 2 and 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). 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

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

parameter	unit	ingrowth/decay-corrected average ± 1σ error ^a			
		well 1 ^b	well 2	well 3	well 4
Pu Isotopes					
[²³⁹ Pu]	10 ⁶ atoms/kg	0.144 ± 0.006 (n = 4)	143 ± 4 (n = 5)	5.5 ± 0.3 (n = 5)	3.8 ± 0.2 (n = 4)
²⁴⁰ Pu/ ²³⁹ Pu	atom ratio	0.055 ± 0.009 (n = 1)	0.27 ± 0.01 (n = 5)	3.4 ± 0.4 (n = 4)	13 ± 2 (n = 4)
²⁴¹ Pu/ ²³⁹ Pu	atom ratio	bd ^d	0.00052 ± 0.00004 (n = 5)	0.0017 ± 0.0002 (n = 4)	0.0027 ± 0.0003 (n = 3)
²⁴² Pu/ ²³⁹ Pu	atom ratio	bd	0.00020 ± 0.00005 (n = 5)	0.007 ± 0.003 (n = 5)	0.005 ± 0.004 (n = 4)
Inferred Progenitor Isotopes					
²⁴³ Am/ ²⁴⁴ Cm	atom ratio		<i>3.2^c ± 0.6</i>	<i>3.2^c ± 0.6</i>	<i>3.2 ± 0.6</i> (n = 4)
[²⁴⁴ Cm]	10 ⁶ atoms/kg		468 ± 35 (n = 5)	803 ± 35 (n = 4)	2750 ± 155 (n = 4)
²⁴⁵ Cm/ ²⁴⁴ Cm	atom ratio		<i>0.026^c ± 0.002</i>	<i>0.026^c ± 0.002</i>	<i>0.026 ± 0.002</i> (n = 3)
²⁴⁶ Cm/ ²⁴⁴ Cm	atom ratio		<i>0.16^c ± 0.03</i>	<i>0.16^c ± 0.03</i>	<i>0.16 ± 0.03</i> (n = 4)

^a Pu isotope averages are corrected for ingrowth to the May 6–15, 1998, sampling period (well 1 excepted), and progenitor isotope averages are calculated 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 determined only once; hence, the ²⁴⁰Pu/²³⁹Pu atom ratio shown is from a single measurement. ^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. ^d bd, below detection (i.e., <10⁴ atoms).

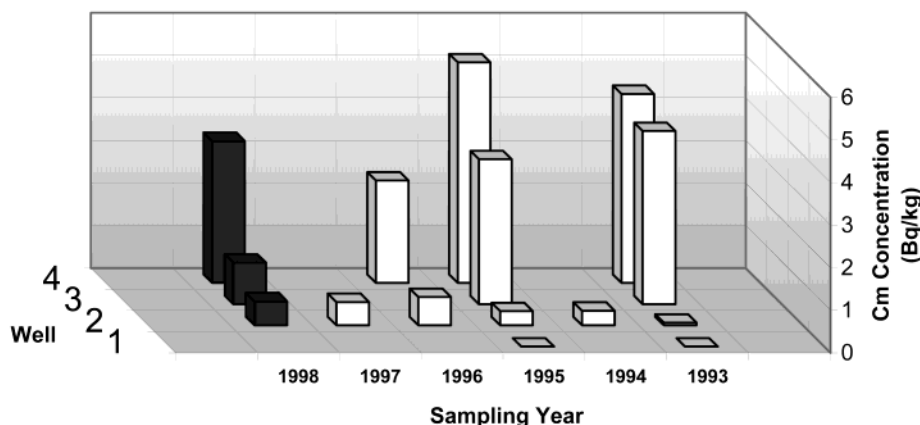


FIGURE 3. Comparison of ²⁴⁴Cm α-activity levels (Bq/kg) found in filtered (<0.2 μm) SRS F-area well water samples collected between May 6 and 15, 1998, in this study with ²⁴³⁺²⁴⁴Cm levels (Bq/L) in unfiltered samples reported by Westinghouse Savannah River Co. (18–23).

differences of 10% for ²⁴⁰Pu for well 3 and 35% for ²³⁹Pu in the control well 1 where Pu levels are lowest.

Downstream from the seepage basins, the fractional abundance of ²³⁹Pu(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, ²⁴⁰Pu is almost exclusively in the oxidized form, the fractional abundance of ²⁴⁰Pu(V/VI) diminishing only slightly between well 2 (~1) and well 4 (0.9). A similarly high Pu(V/VI) fractional abundance is also seen at the upstream control well (0.85). The reason that at each well the ²³⁹Pu(V/VI) and ²⁴⁰Pu(V/VI) fractional abundances were measurably different remains to be explained, although this difference may be related to the fact that most of the ²⁴⁰Pu in the aquifer was formed in-situ from ²⁴⁴Cm decay, and with recoil energy, an electron-stripping Szilard–Chalmers process may have resulted in production of more oxidized forms (41).

To offer another perspective of the Pu oxidation state distributions in the F-area aquifer—this time in terms of α-activities (μBq/kg units)—and at the same time to further clarify the ²³⁹Pu and ²⁴⁰Pu isotope distributions discussed earlier, the results of Table 5 are presented as a bar chart, in Figure 5. 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 ²³⁹Pu isotope migrated beyond well 2, and how downstream of well 2 the preponderance of the Pu present was in-situ-formed ²⁴⁰Pu.

The overall high abundances of oxidized Pu we observed in all wells were consistent with the oxidized form Pu(V/VI) dominating natural waters, including groundwater (45, 46) 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*).

Colloid-Associated Plutonium. Measurement results indicated that the abundance of colloid-associated Pu in the F-area aquifer was far less than we had expected on the basis of an earlier study by Kaplan et al. (17). This was evident, even before the application of 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 ²³⁹Pu or ²⁴⁰Pu isotope exceed 10⁶ atoms/kg, nor did the colloid-associated Pu fractional abundance (i.e., Pu_{colloid}/Pu_{filtered}) of either isotope exceed 0.04 (Table 6). At well 1, the ²³⁹Pu colloid concentration was lowest [(1.3 ± 0.5) × 10³ atoms/kg] as was the fractional abundance (0.008 ± 0.003). The colloid-associated ²⁴⁰Pu concentration at this well was too low to determine. At the seepage basin fringe, well 2, we could establish only upper limits for the colloid-associated ²³⁹Pu and ²⁴⁰Pu concentrations

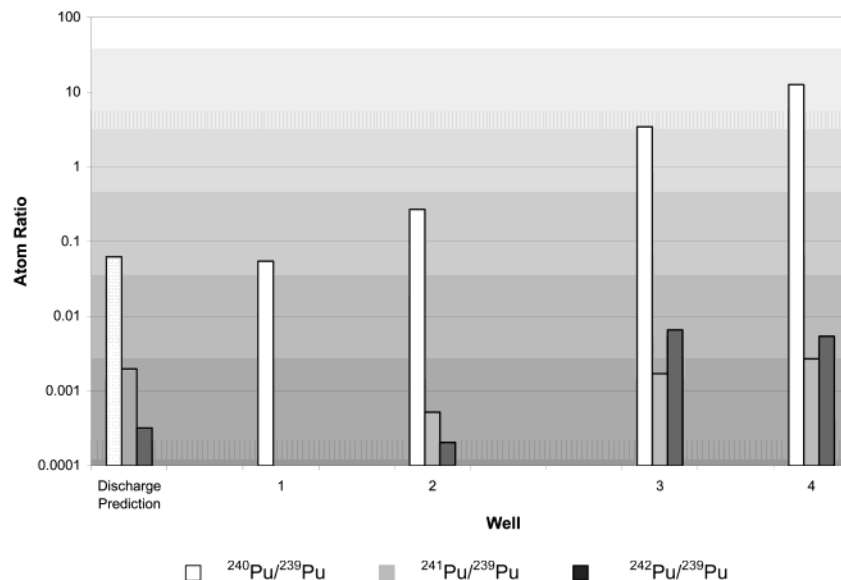


FIGURE 4. Comparison of Pu isotopic compositions in filtered (<0.2 μm) SRS F-area well water samples collected in May 1998 with an estimated composition provided by Holcomb (15) as being indicative of SRS reactor-produced Pu.

TABLE 4. Redox and Size Fractionated ²³⁹Pu and ²⁴⁰Pu Concentrations (Data Are Not Ingrowth-Corrected)

well	sampling date	time ^a (days)	Pu(III,IV) ^b concentration ± 1σ error (10 ⁶ atoms/kg)		time ^a (days)	Pu(V,VI) ^c concentration ± 1σ error (10 ⁶ atoms/kg)	
			²³⁹ Pu	²⁴⁰ Pu		²³⁹ Pu	²⁴⁰ Pu
Permeate Sample Fraction (<1 kDa) ^d							
1	May 8, 1998	24			24	0.179 ± 0.013	
2	May 12, 1998	84	9.70 ± 0.18	0.919 ± 0.024	98	136.3 ± 3.0	35.27 ± 0.78
2	May 12, 1998	581	10.62 ± 0.14	6.046 ± 0.074	581	126.6 ± 1.8	33.74 ± 0.53
3	May 9, 1998	23	3.61 ± 0.14	0.971 ± 0.036	23	1.487 ± 0.036	16.98 ± 0.33
4	May 11, 1998	85	2.39 ± 0.10	7.69 ± 0.25	99	1.68 ± 0.11	46.5 ± 1.6
Retentate Sample Fraction (Enriched in 1 kDa – 0.2 μm Colloids) ^d							
1	May 8, 1998	82			95		
2	May 12, 1998	84	14.72 ± 0.44	1.46 ± 0.10	98	128.6 ± 2.9	35.97 ± 0.82
3	May 9, 1998	81	5.91 ± 0.13	2.031 ± 0.041	94	3.53 ± 0.10	21.75 ± 0.38
4	May 11, 1998	85	7.86 ± 0.30	11.00 ± 0.26	99	2.72 ± 0.14	49.8 ± 1.3
Filtered Sample Fraction (<0.2 μm)							
1	May 6, 1998	84	0.0298 ± 0.0043		97	0.170 ± 0.010	
2	May 12, 1998	84	11.06 ± 0.33	0.933 ± 0.050	98	119.4 ± 3.3	34.23 ± 0.95
2	May 12, 1998	546	13.59 ± 0.16	5.292 ± 0.070	546	119.6 ± 1.9	35.95 ± 0.62
3	May 8, 1998	82	4.856 ± 0.073	3.093 ± 0.038	94	1.224 ± 0.036	10.14 ± 0.21
3	May 9, 1998	549	4.532 ± 0.062	11.69 ± 0.13	549	1.472 ± 0.034	25.73 ± 0.45
4	May 10, 1998	80	1.694 ± 0.092	5.98 ± 0.31	93	2.84 ± 0.11	45.2 ± 1.2
4	May 11, 1998	547	3.058 ± 0.040	23.74 ± 0.19	547	1.821 ± 0.035	62.08 ± 0.95

^a Elapsed time (days) between sample collection and the first separation of Pu from other actinide elements. ^b Reduced sample subfraction. ^c Oxidized sample subfraction. ^d CFF-processed samples.

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. (17)? 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”, because this delay and exposure to ambient surface conditions could have altered the original Pu size distributions. In our own studies, we have found that exposure to ambient air during processing can increase colloidal iron distributions in groundwater (32).

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 kDa) 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 indicative of 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 kDa – 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 (25, 47, 48).

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.

TABLE 5. Summary of Ingrowth-Corrected Results for Reduced (III/IV) and Oxidized (V/VI) ²³⁹Pu and ²⁴⁰Pu

parameter	ingrowth-corrected average ± 1σ error ^a			
	well 1	well 2	well 3	well 4
	Pu Concentration (10⁶ Atoms/kg)			
[²³⁹ Pu(III/IV)]	0.030 ± 0.004 (n = 1)	11.5 ± 0.8 (n = 4)	4.4 ± 0.4 (n = 3)	1.9 ± 0.5 (n = 3)
[²³⁹ Pu(V/VI)]	0.173 ± 0.008 (n = 2)	125 ± 4 (n = 4)	1.4 ± 0.1 (n = 3)	1.9 ± 0.4 (n = 3)
[²³⁹ Pu] ^b	0.203 ± 0.009	136 ± 4	5.8 ± 0.4	3.8 ± 0.6
[²⁴⁰ Pu(III/IV)]		0.04 ± 0.03 (n = 4)	0.9 ± 0.5 (n = 3)	4 ± 1 (n = 3)
[²⁴⁰ Pu(V/VI)]		34.8 ± 0.5 (n = 4)	18 ± 5 (n = 3)	42.1 ± 0.7 (n = 3)
[²⁴⁰ Pu] ^b		34.9 ± 0.5	19 ± 5	46 ± 1
	Pu(V/VI) Fractional Abundance			
²³⁹ Pu(V/VI)/ ²³⁹ Pu	0.85 ± 0.02	0.915 ± 0.006	0.25 ± 0.02	0.50 ± 0.08
²⁴⁰ Pu(V/VI)/ ²⁴⁰ Pu		0.9987 ± 0.0008	0.95 ± 0.03	0.91 ± 0.02

^a Ingrowth of ²³⁹Pu was evident only in the reduced (III/IV) subfraction of the sample from well 4. Ingrowth of ²⁴⁰Pu was evident only in the reduced subfractions of wells 2–4 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 May 6–15, 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. ^b Sum of the Pu(III/IV) and Pu(V/VI) subfraction concentrations.

TABLE 6. Summary of Ingrowth-Corrected Results for Colloid-Associated ²³⁹Pu and ²⁴⁰Pu (1 kDa – 0.2 μM)

parameter	ingrowth-corrected average ± 1σ error ^a			
	well 1	well 2 ^b	well 3	well 4 ^c
	Colloid-Associated Pu Concentration (10⁶ Atoms/kg)			
²³⁹ Pu	0.0013 ± 0.0005 (n = 2)	<0.5 (n = 5)	0.18 ± 0.02 (n = 4)	0.12 ± 0.02 (n = 4)
²⁴⁰ Pu		<0.2 (n = 5)	0.18 ± 0.03 (n = 4)	<0.8 (n = 4)
	Colloid-Associated Pu Fractional Abundance^d			
²³⁹ Pu _{colloidal} / ²³⁹ Pu _{filtered}	0.008 ± 0.003	<0.004	0.032 ± 0.004	0.031 ± 0.005
²⁴⁰ Pu _{colloidal} / ²⁴⁰ Pu _{filtered}		<0.006	0.010 ± 0.002	<0.02

^a 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 ²³⁹Pu and ²⁴⁰Pu 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. ^b 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 Pu_{colloidal}. However, upper limits were established. These limits are expressed as twice the root-mean-square averages of the individual measurement uncertainties. ^c The ingrowth-corrected concentration of colloid-associated ²⁴⁰Pu in well 4 was determined by nonlinear regression analysis to be (–0.06 ± 0.20) × 10⁶ 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 × 10⁶ atoms/kg, which is the 95% confidence level upper limit derived from the regression analysis. ^d Ratio of colloidal-associated Pu to <0.2 μm filtrate Pu.

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 was, 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 and 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 ²³⁹Pu, in part because α spectrometric methods measure combined ²³⁹Pu and ²⁴⁰Pu activity (^{239,240}Pu), and so all ^{239,240}Pu was mistakenly presumed to derive from Pu seepage basin discharges.

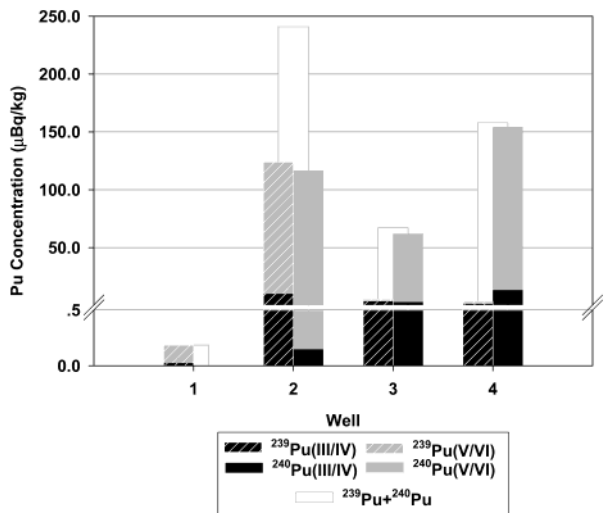


FIGURE 5. Comparison of concentrations (α-activity units of μBq/kg) of ²³⁹Pu and ²⁴⁰Pu isotopes in reduced (III/IV) and oxidized (V/VI) forms with the sum of ²³⁹Pu and ²⁴⁰Pu in filtered sample fractions (<0.2 μm) that were not redox processed.

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.

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