Final Report
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Speciation, Mobility and Fate of Actinides in the Groundwater at the Hanford Site

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1. Executive Summary

Plutonium and other actinides represent important contaminants in the groundwater and vadose zone at Hanford and other DOE sites. The distribution and migration of these actinides in groundwater must be understood so that these sites can be carefully monitored and effectively cleaned up, thereby minimizing risks to the public. The objective of this project was to obtain field data on the chemical and physical forms of plutonium in groundwater at the Hanford site. We focused on the 100-K and 100-N areas near the Columbia River, where prior reactor operations and waste storage was in close proximity to the river. In particular, a unique set of technical approaches were combined to look at the details of Pu speciation in groundwater, as thus its chemical affinity for soil surfaces and solubility in groundwater, as these impact directly the migration rates off site and possible mitigation possibilities one might undertake to control, or at least better monitor these releases.

Our major findings are that total concentrations of Plutonium isotopes in the groundwater of both the Hanford 100-K and 100-N areas are measurable, but extremely low ($<10^4$ to 10^6 atoms/l). Detectable Pu was found for the first time in these area wells using mass spectrometric analyses techniques that are significantly more sensitive than alpha spectroscopy methods used previously. Total plutonium concentration levels are lower than EPA drinking water standards, so there is no immediate health risk. Isotopic analyses do indicate that the source of the Pu is local, rather than weapons testing fallout or other sources. At the 100-K area at the Hanford Site (HS), colloid-associated Pu is detectable in two wells. This colloidal fraction is essentially 100% in the reduced form (Dai et al., 2003) and accounted for 7-29% of so-called dissolved Pu. The finding of relatively low fractions of Pu in association with colloids is important, as colloid facilitated transport is often invoked to explain more rapid and complete migration of Pu from waste sources in groundwater (see below).

We are more than a generation away from the time period of the major releases of contaminant radionuclides into the environment. We know in general terms something about the quantities of these radionuclides that were produced, the forms of their release, and their distribution and concentrations on land and in surface and subsurface waters. However, despite decades of study, we are not yet able to reconcile many observations with expected transport and speciation of these radionuclides.

For example, a recent study of plutonium in groundwater at the Nevada Test Site (Kersting et al., 1999) detected Pu had migrated much further than predicted by existing models. This finding was attributed to more mobile colloidal forms of Pu in groundwater. Similarly, the detection of Pu in groundwater some 3400 m downstream in Mortandad Canyon at the Los Alamos National Laboratory is widely cited as an example of colloid facilitated transport (Penrose et al., 1990). However, the observation of Pu migration in groundwater at distances greater than expected from one source might also imply additional far field sources (e.g. for Mortandad Canyon see Marty et al., 1997). In addition, a high colloidal association for Pu may be an artifact associated with high flow rate groundwater sampling (Puls, 1990; Ryan and Gschwend, 1990; Kaplan, 1993) or formation of colloids due to alterations of ambient redox state prior to ultrafiltration (Buesseler et al., 2003).

In contrast to prior studies, we do not see direct evidence for rapid far field migration of Pu from the original waste source, or preferential transport of colloidal Pu in groundwater. For example, at HS, we see more than an order of magnitude decrease in groundwater Pu concentrations only a short distance from the source (approx. 300m), and lower relative colloidal Pu abundances in downstream wells (Dai et al., 2003). At Savannah River Site (SRS), where there was enhanced ^{240}Pu (approx. 500m) downstream, the Pu isotopic data suggested that the original Pu discharged to the seepage basins was not the source. Ironically, transplutonium radionuclides, discharges of which were dwarfed by that of Pu, have moved preferentially downstream and it is the in-situ decay of ^{244}Cm which is the largest ^{240}Pu source in F-area wells (Dai et al., 2002). We also attribute the lower colloidal associations at SRS to the ^{244}Cm source. Thus differences in groundwater Pu speciation between HS and SRS in these two examples may be related to both Pu source characteristics (Cm decay) and/or the geochemical properties of the groundwater (most notably pH at F-area wells at SRS are 3-5.5 vs. 8.5 at HS 100-K).

Our results are site specific but have much broader implications. In general, we contend that the degree to which colloids facilitate transport cannot be understood from total concentration data and observations of far field Pu concentrations alone. To understand Pu distributions in the field, we need Pu isotopic data to pinpoint accurately its sources. While ^{244}Cm might not be considered a long-term threat to the environment, its disposal does have long term risks if, as at SRS, it is shown to be generally more mobile given its decay to ^{240}Pu. In other systems, it has also been shown that the physical-chemical form of Pu released to the environment can determine to a large extent the geochemical behavior of Pu (e.g. Buesseler and Sholkovitz, 1987; Smith *et al.*, 1995). Thus, understanding Pu speciation requires an understanding of both source and in-situ geochemical controls.

2. Research Objectives

Our intent was to sample across defined contaminant plumes at the Hanford Site for Pu and other actinides. Samples were collected using a "micro-purge" low pumping rate technique and directly separated into truly dissolved and colloidal size classes with an ultra-clean cross-flow filtration (CFF) system. Pu redox samples were separated immediately in the field and ancillary samples were also carefully collected for supporting organic and basic geochemical analyses. High sensitivity thermal ionization mass spectrometry (TIMS) was used to detect the Pu isotopes in all size and redox fractions, thus providing information not only on Pu concentrations but on the Pu source, which can strongly influence Pu speciation and mobility.

The combination of these state-of-the-art procedures and the demonstrated care taken to process these samples ensures that the data represent the original in-situ speciation. The results of such a careful basic research program: i) provide the basis for accurate modeling and prediction of actinide transport; ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the vadose/groundwater zone, and iii) identify specific Pu sources and the extent of far field, or long-term migration of actinides in groundwater. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies.

To achieve these results, we set the following major goals:

- the determination of the speciation of plutonium and other actinides (Np, U) in groundwater at the 100 area at the Hanford Site. This includes the separation of Pu into particulate, colloidal and <1 kilo-Dalton dissolved phases and the determination of redox states and isotopic composition in each fraction.
- the characterization of groundwater colloids, which includes submicron-sized inorganic particles and organic macromolecules in order to better understand the mechanism and transport of the actinide-colloid complexes
- the prediction of the rate of transport and fate of actinides in the groundwater of the Hanford Site using a three-phase (dissolved-colloid-particulate) model.

The performed work took advantage of sampling and analytical techniques recently developed under a prior EMSP grant entitled "Speciation and structural characterization of Plutonium and Actinide-organic complexes in surface and ground waters" (DE-FG07-96ER14733, granted to K.O. Buesseler and D.J. Repeta), the results of which form the basis for this work. This project included continued collaboration with scientists at the Pacific Northwest National Laboratory (J. Wacker and J. M. Kelley) who assisted in field sampling and provided the technical expertise required for Pu isotopic analyses using ultra sensitive thermal ionization mass spectrometric methods.

3. Methods and Results

Field work under this funding scope included comprehenisive speciation studies at the 100-K (March-April, 1999) and 100-N areas (July, 2001) at the Hanford Site (Figure 1).

3.1 Area description

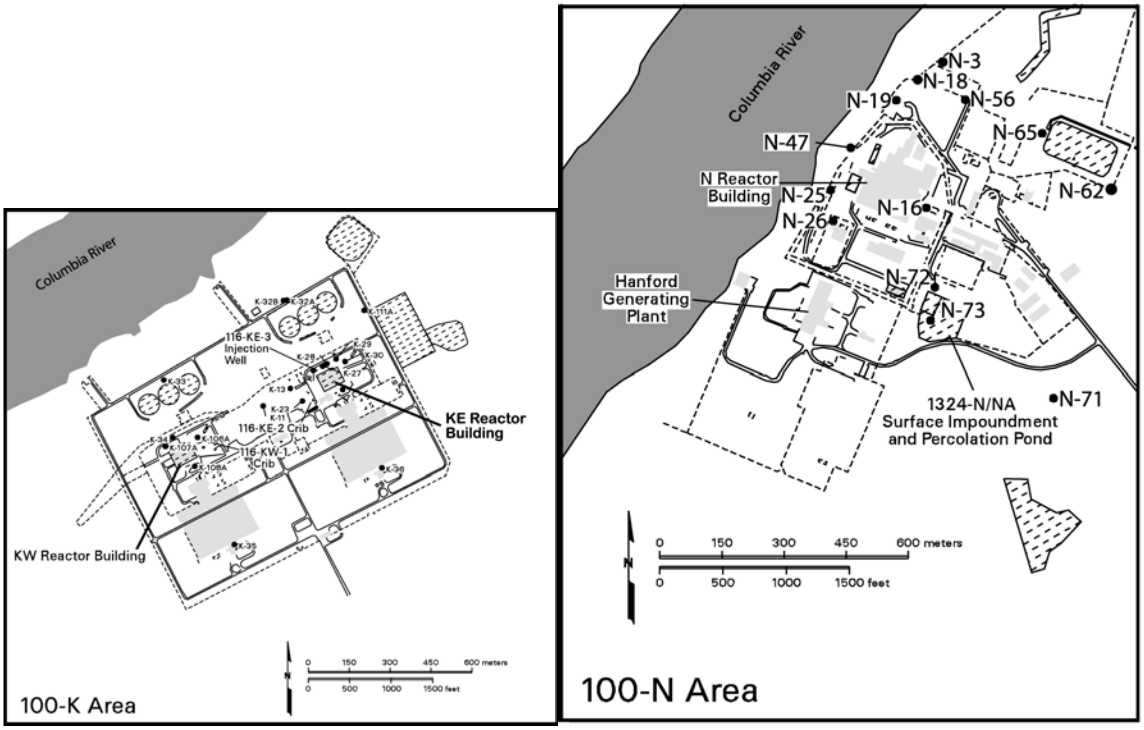

Figure 1. Site maps showing wells atHS 100-K area (left) and HS 100-N area (right) where groundwater Pu studies have been conducted.

The Hanford Site was established in 1943 as the Hanford Engineer Works (HEW) as the world's first Pu production facility constructed for the United States government. The site was remote from major populated areas, had ample electrical power from Grand Coulee Dam and associated transmission facilities, a functional railroad, clean water from the nearby Columbia River, and coarse glacial-fluvial sediments provided sand and gravel aggregate for constructing large concrete structures. Although not an original site requirement, Hanford's arid environment and soil features allowed large amounts of liquid waste to be released to the ground without immediately descending to the groundwater (Gray and Becker, 1993.).

The “100 Area” is a term used to describe a region along the shore of Columbia River where up to nine nuclear reactors were in operation. Construction of the 100-K Area reactors began in September 1953 as part of Project X, a large Cold War expansion effort at the Hanford Site (Carpenter, 1994). The area contains the KE and KW reactor buildings and their support facilities, including water treatment structures. The 100-K Area reactors had more output than the other single-pass reactors because of higher thermal power levels. Reactor operations continued until 1970 when the KW Reactor was deactivated followed by deactivation of the KE Reactor in 1971. The reactors have remained in deactivated status since that date. However, the fuel storage basins and small portions of both reactor buildings remain in use and since early 1975 have been used to store irradiated fuel elements from the N reactor (Johnson et al., 1998; Johnson et al., 1995).

Both the 105-KE and 105-KW basins are 38 m long and 20 m wide. Beneath the 100-K area is unconfined sand and gravel of the Ringold formation which is highly permeable, and over most of the area the depth to groundwater is ~25 m (Johnson et al., 1995). Both basins were used to store ~ 2100 MTU of N-Reactor and 3-4 MTU of Sandia Pulsed Reactor fuel (Garrett and Williams, 1997). The water contained in each of the basins is contaminated by radionuclides that were released from the irradiated fuel. Radionuclide concentrations in KW Basin are much lower than at the KE basin because the fuel stored at KW basin is fully encapsulated. The KE Basin experienced a significant leak in early 1976, which continued until it was isolated near the end of 1979. The leak was on the order of 1893 L/h and was attributed to a construction joint between the main basin and the fuel discharge chute. During Feb 1993, water balance calculations for the KE basin indicated an increase in basin water loss rate. This loss could not be accounted for by increased evaporation alone and is attributed to leakage to the soil column. These episodic and continuous leakages would have released Pu to the groundwater of the basins.

3.2 Sampling and Analytical Techniques

The maintenance of ambient geochemical conditions is crucial to accurate groundwater speciation studies. We believe that the widely variable speciation data for Pu, and its inconsistent transport predictions, are at least partially related to artifacts associated with the sampling protocols employed by different researchers. Therefore, a major effort in our prior EMSP projects has been to optimize and control critical variables that might lead to artifacts in determining colloidal abundances and in-situ redox fractionation of plutonium in groundwater (Dai et al., 2001; Buesseler et al., 2003; Hassellov et al., 2003).

3.2.1 Well sampling and field processing protocols

There are three major issues associated with well sampling that need to be addressed: 1. trace metal cleanliness; 2. pump rate; and 3. redox control. We have addressed each and comment in more detail below on a series of studies designed to elucidate possible artifacts associated with improper groundwater sampling protocols.

Due to the extremely low concentrations of the elements of interest and interferences from possible contaminants, strict protocols with respect to trace-metal and trace-organic clean sampling techniques must be applied during collection and field processing of samples (e.g. Dai et al., 2002; Sanudo-Wilhelmy et al., 2002). Some of the protocols we have adapted include the use of an all Teflon pump-head and Teflon lined purge hoses for groundwater removal. In addition, the cross-flow filtration (CFF) system was constructed with Teflon tubes, and all sample reservoirs were Teflon lined. Field processing of samples was conducted in a mobile lab equipped with two Class 100 laminar flow benches, and sample manipulations made use of acid cleaned Teflon wares.

To minimize the potential for colloid formation and alteration of ambient groundwater characteristics, our well sampling protocols make use of a "micro-purge", low pumping rate procedure for groundwater removal. With this method, we avoid exceeding well recharge rates during purging and sampling (at previous sites, well pumping rates of 0.150 l/min were determined to be appropriate). Wells were purged of fluid prior to sampling, and this step was considered complete when field parameters of temperature, electrical conductivity, pH, dissolved oxygen, redox, and turbidity measured using an in-line flow cell had stabilized.

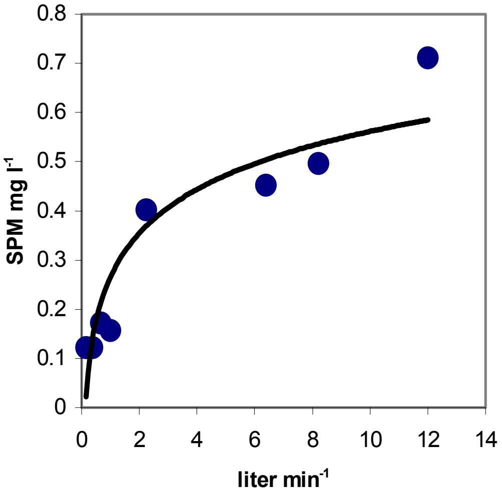

Figure 2. Suspended particulate matter (SMP) results from flow rate experiments conducted at Hanford N-Area, 2001. Experiments were conducted at Well N-26 equipped with a variable speed pump. We began with our normal procedure for CFF with WHOI's bladder pump at a low pumping rate of 150 ml/min, followed by pumping at 370, 667 and 1000 ml/min. The bladder pump was removed and replaced by a Hydrostar variable speed pump with which we pumped at 2000 ml, 6400 ml, 10 l and 12 l/min (unpublished data).

Low flow rate pumping during well purging and sampling is particularly crucial for studies investigating groundwater colloids (Puls, 1990; Ryan & Gschwend, 1990; Ronen, 1992; Kaplan, 1993). As seen in our own experiments (Figure 2) high flow rate pumping can easily mobilize particles that are otherwise stationary. We also observed an overall increase in metal concentration with increased pumping rate and an increase in the abundance of colloidal size particles as viewed with SEM.

To avoid changes in Pu oxidation state during sampling, the CFF tower, CFF reservoirs and the permeate collection barrel were continuously purged with N_2 gas. To further ensure that Pu speciation in all sample fractions remained unchanged, a redox-holding solution was immediately added after collection followed by initial precipitation and filtration of Pu(III) and Pu(IV). The filtrate was collected and further precipitation and filtration of Pu(V) and Pu(VI) were performed (see **Plutonium Oxidation States**, below). Only ultra-pure acids and reagents were used in the separation of Pu oxidation states. All sample processing in the field took place in HEPA filtered laminar flow benches.

3.2.2. On site cross-flow filtration

In cross-flow ultrafiltration, a prefiltered sample solution flows parallel to the CFF membrane. Hydrostatic pressure drives solutes with an effective molecular size less than the cut-off of the membrane, through the membrane (permeate). The remaining solution (retentate) containing both smaller solutes and larger colloids is swept along the membrane surface and recycled through the retentate reservoir. Compounds rejected by the membrane are thus increasingly concentrated in the retentate over time. Colloidal abundances are defined by their retention relative to a given CFF membrane, and the colloidal concentration of a given compound, $[X]^{coll}$, is calculated from:

$$[X]^{coll} = ([X]^{ret} - [X]^{perm})/cf$$

where $[X]^{perm}$ and $[X]^{ret}$ are the concentrations of a given colloid standard in the permeate and retentate, respectively, and cf is the concentration factor calculated from: cf = initial volume/retentate volume.

CFF is an operational procedure with many different designs, operational protocols and associated difficulties (e.g. Buesseler et al., 1996). However, it remains the only method useful for isolating colloidal sized materials from large volume and dilute aqueous environmental samples. The characteristics of each CFF system must be demonstrated for every application of CFF to environmental sampling, and one way we accomplish this is to determine the retention characteristics of each CFF membrane using standard molecules under environmental conditions (Buesseler et al., 1996; Buesseler et al., 2003; Dai et al., 1998). In addition, particular attention must be paid: 1. blanks & sample carryover; 2. sorptive losses to the CFF; and 3. redox control.

Issues of contamination are of great concern and our experience is that each CFF system differs in the extent of cleaning and preconditioning needed. Contamination from CFF materials, carry-over of material between samples and release of even minor levels on organics for example, can all lead to direct contamination of the element of interest, or alteration of ambient properties during processing. We use dilute acid, base and Q-water rinses extensively between samples to reduce blanks and possible carry over (Dai et al., 2002). In the field, we've demonstrated using Q-water blanks, that the CFF blank for Pu is extremely low, and essentially no different than our lab processed Q-water blanks ($< 1.2 \times 10^4$ atoms/kg for ^{239}Pu and $< 0.6 \times 10^4$ atoms/kg for ^{240}Pu; Table 1).

Losses to the CFF system can be evident by mass balance comparisons between the filtered sample and the sum of the permeate and retentate fractions. We find a CFF mass balance for Pu that is generally 100 ± 10% in most of our applications (Dai et al., 2001; 2002), indicating that low or no significant losses or contamination occurred.

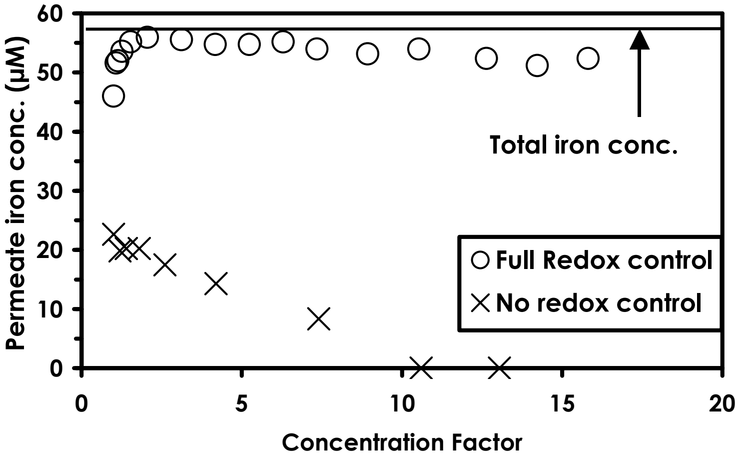

Figure 3. Evolution of Iron concentrations in CFF permeate subsamples with and without redox controls. The reduced, anoxic, ferrous-rich groundwater used in the experiment was sampled from the head of Waquoit Bay (Cape Cod, MA, USA). For the full redox control experiment all samples and CFF system were carefully purged and maintained under N_2 gas to preserve the redox conditions. The samples used for the "no" control experiment were stored overnight with exposure to the atmosphere (Hassellöv et al., 2003).

Groundwater CFF sampling requires strict redox control since groundwater is generally reducing and our goal is to determine in-situ speciation of elements that occur in a variety of redox states. Post sampling alterations to Pu and other redox sensitive elements can bias colloid distributions. As an extreme example of this, an experiment was conducted with reducing waters from a well in Falmouth, MA. In Figure 3 the permeate iron concentration for the experiment with "full redox control" is plotted together with the experiment with "no redox control". Under full redox control, the permeate concentration was quite stable and indicated low colloidal Fe since the total permeate concentrations approach that of total iron (57 μmol/L). As the CFF processing continued, only a slight decrease in total iron was observed indicating minor losses. For the no redox control experiment, the first permeate subsample had a Fe concentration of only 20 μmol/L indicating that without precautions to avoid exposure to ambient air, oxidation of Fe had rapidly occurred forming colloids or microparticulates, thus reducing the permeate concentrations dramatically. With time, the permeate concentrations continued to decrease, and after a concentration factor of 10, iron in the permeate was below our detection limit. This experiment demonstrates how redox control can be crucial, not just for Fe, but any associated elements. In the Falmouth well, we observed even greater losses of phosphorus that accompanied formation of Fe colloids (Hassellov et al., 2003).

3.2.3 Plutonium oxidation states

The redox speciation method separates Pu into Pu(III/IV) and Pu(V/VI) subfractions by a method adapted from Lovett and Nelson(Lovett and Nelson, 1981). To help maintain redox states, a $Cr_2O_7^{2-}/SO_4^{2-}$ holding oxidant solution is added immediately following collection. Pu in the reduced states is traced with added ^{244}Pu(III/IV) and Pu in the oxidized states is traced with ^{242}Pu(V/VI). The amount of each tracer is nominally 5×10^6 atoms. In this procedure, Pu(III/IV) is 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, is collected by filtration and retained for further processing and analysis. To retrieve the oxidized subfraction, the Pu(V/VI) retained in the filtrate is reduced by addition of Fe^{2+}, which is likewise coprecipitated, filtered and retained for subsequent processing and analysis. Because the method employs two tracers that are distinguishable isotopically 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 (Dai et al., 2002). One test of the reliability of these methods is to compare the initial sample concentrations to the sum of the Pu(III/IV) and Pu(V/VI) fractions, for a given Pu isotope and for filtrate, permeate, and retentate. Results of this comparison are good (see data in Figure 7- implications of which are discussed below), lending further confidence in the reliability of our methods, even at these trace level concentrations (10^4 - 10^6 atoms/kg).

3.2.4 Thermal ionization mass spectrometry

The high sensitivity of the TIMS facility at PNNL (collaborative effort with J.M. Kelley) has been extremely important to the success of all of our studies. Subfemtogram ($<10^{-15}$ g) detection limits are critical for following the far-field transport of Pu in the environment, and for determining Pu isotopic abundances in small subfractions of the total groundwater sample. TIMS is advantageous over more commonly used alpha-spectrometric techniques due to its higher sensitivity and its ability to quantify multiple Pu isotopes (see **Plutonium source terms**). Other mass spectrometric techniques such as ICP-MS are less sensitive than TIMS, but more sensitive than alpha-counting, and can be used for sample screening if needed.

With modern TIMS techniques, the limitation for detection is generally not the sensitivity of the TIMS instrument, but rather the researcher's ability to sample, and then chemically extract and purify the element of interest without contamination. At concentrations as low as 10^4-10^6 atoms, it is very important to control and minimize contamination due to reagents, sampling equipment, and air-born particulates, and to frequently monitor one's blanks and standards. As stated earlier, our lab and field processing blanks are on the order of 10^4 atoms/kg ^{239}Pu. We have now shown that we can complete both field sampling and sample processing without introducing a significant blank (Table 1).

Table 1. CFF blank evaluation prior and post Well 199-K-27 sampling at the

	Concentration × 10^4 atoms/kg ± 1σ Error			
	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
sampling CFF blank	2.4 ±0.17	0.24 ---	--- ---	--- ---
Initial Q rinse	60.99 ±1.19	8.57 ±0.32	0.57 ±0.06	0.53 ±0.13
Acid rinse	9.08 ±0.48	1.35 ±0.20	0.51 ---	3.16 ±0.25
Base rinse	6.53 ±0.49	0.78 ---	0.53 ---	1.05 ---
Post-final CFF blank	1.2 ---	0.63 ---	0.63 ---	0.63 ---
Q water	1 ---	0.5 ---	0.5 ---	3.31 ±0.26

Note that measurable levels of Pu carry over and sorptive contamination decrease as we proceed from our initial rinses through the CFF cleaning process. Our final CFF blank is a Q water solution that is recirculated through the CFF and processed in the field. The ^{239}Pu concentrations of this field blank and our lab blank are 1.0-1.2×10^4 atoms/kg. We cannot know whether such low blanks arise from Pu in the Q water itself, or Pu in the reagents or as picked-up during CFF handling and subsequent processing (taken from Dai et al., 2003).

3.3 Major results: Groundwater plutonium sources, speciation and mobility at Hanford Site

3.3.1 100-N basins

In July of 2001, we completed comprehensive field sampling activities at 100 N area of the Hanford Site. During these activities, processing of 6 wells: N-26, N-71, N-72, N-25, and N-16, N-47 was conducted on site using the CFF system. Required sample volumes of 100 l were obtained using low pumping rates (100-200 ml/min) for sampling colloids (see sampling protocols for details). In addition to the comprehensive sampling efforts, we obtained groundwater samples from 7 additional wells (N-73, N-62, N-65, and N-56 and N-3, N-18, N-19) at 100-N area. All samples were processed at the WHOI laboratory in Woods Hole, MA and returned to PNNL for subsequent analysis as performed in the previous Savannah River and Hanford Site sampling efforts.

Table 2. ^{239}Pu concentrations and isotopic ratios in samples taken from Hanford Site 100 N area groundwater monitoring wells.

		Atom Ratio ± 1σ Error	Atom/kg(×10^4) ± 1σError	
Well	Fraction	^{240}Pu/^{239}Pu	^{239}Pu	^{240}Pu
100-N-47	unfiltered	0.0892 ±0.0048	98.44 ±0.79	8.78 ±0.74
100-N-47	Filtrate	0.1006 ±0.0043	52.94 ±0.72	5.32 ±0.72
100-N-26	unfiltered	---	<0.45 ---	<0.30 ---
100-N-26_2	unfiltered	---	<0.46 ---	<0.31 ---
100-N-26	unfiltered	---	<0.94 ---	<0.47 ---
100-N-16	unfiltered	---	<5.28 ---	<1.25 ---
100-N-72	unfiltered	0.139 ±0.014	12.66 ±0.02	1.75 ±0.77
100-N-71	unfiltered	---	<4.26 ---	<0.15 ---

Pu isotopes were detected in unfiltered groundwater samples from the 100-N area monitoring wells for the first time using our TIMS technique (Table 1). However, the absolute levels are extremely low, in general orders of magnitudes lower than in 100-K area (see below). The highest ^{239}Pu concentration was found at Well N-47, on the order of 10^6 atoms/kg, equivalent to 0.00005 pCi/kg, which is ~20,000 times below drinking water standards (1.2 pCi/L).

Given such a low level of Pu isotopes, we are not able to reliably determine in a quantitative viewpoint the size fractionations (and hence speciation) of Pu in these ground water settings. Yet we may conclude that the groundwater at 100-N area has not significantly impacted by the DOE nuclear material prudcution practice.

3.3.2 Results from 100-K basins

3.3.2.1 Pu concentrations and distributions

Table 3. ^{239}Pu concentrations in unfiltered samples taken from Hanford Site 100 K area groundwater monitoring wells.

	[^{239}Pu] $\pm 1\sigma$ error	
Well #	10^5atoms/kg	fCi/kg*
199-K-36	4.06 ± 0.31	1.09 ± 0.08
199-K-110A	21.73 ± 0.49	5.85 ± 0.13
199-K-27	55.90 ± 2.82	15.06 ± 0.76
199-K-28	394.59 ± 11.33	106.28 ± 3.05
199-K-29	$<1.$	<0.3
199-K-30	39.02 ± 1.69	10.51 ± 0.46
199-K-109A	470.98 ± 8.87	126.85 ± 2.39
199-K-32A	6.60 ± 0.42	1.78 ± 0.11
199-K-11	3.14 ± 1.43	0.85 ± 0.38
199-K-106A	6.60 ± 0.61	1.78 ± 0.16
199-K-107A	18.83 ± 1.25	5.07 ± 0.34
Columbia River**	90.06 ± 2.55	24.26 ± 0.69

*A half life of ^{239}Pu of 24131 yrs was used. fCi=10^{-15}Ci

** taken from ~ 60 m from shore downstream well 199-K-32A .

The location is ~46°14'75"N and 119°56'90"E

US EPA Drinking water standard for Pu is 1.2 pCu/L.

Pu isotopes were detected in unfiltered groundwater samples from the 100-K area monitoring wells for the first time using our TIMS technique (Table 3). However, again as 100-N area the absolute levels are extremely low. The highest ^{239}Pu concentration was found at Well K-109A, on the order of 5×10^6 atoms/kg, equivalent to 0.0001 pCi/kg, which is ~10,000 times below drinking water standards (1.2 pCi/L). For comparison, one water sample taken from the Columbia River 60 m from shore downstream of the 100 K area (Table 3 and Fig. 4) revealed an equivalent ^{239}Pu concentration as Well K-27. Since the Columbia River currently has a Pu isotopic composition characteristic of global fallout (see isotope discussion below), this suggests that the highest concentrations of ^{239}Pu in the Hanford Site 100-K area groundwater are on the same order as fallout.

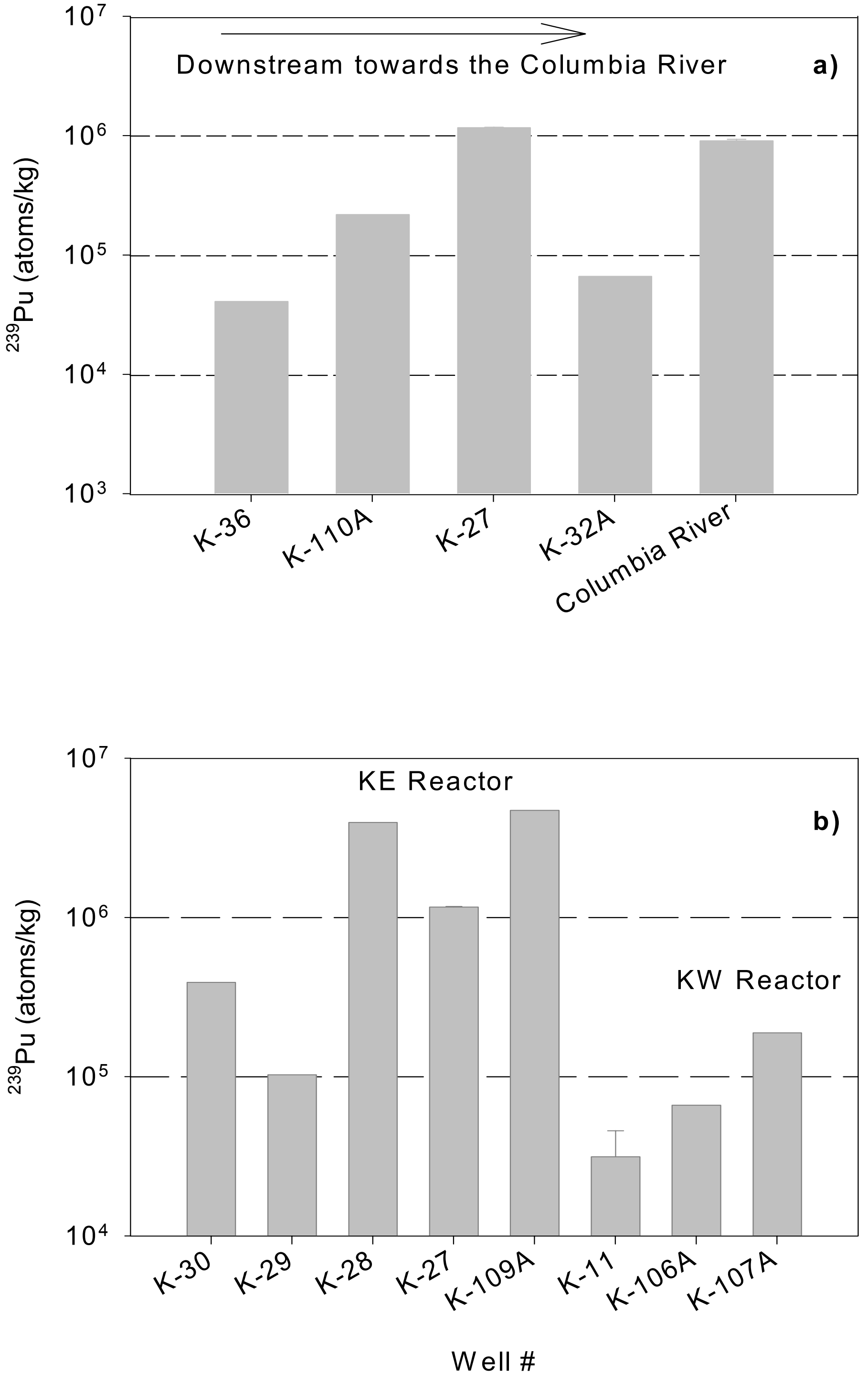

FIGURE 4. ^{239}Pu concentrations in 100K-Area wells of the Hanford Site. Data include both collections in 1997 and 1999.

a) Transect following the groundwater flow towards the Columbia River.

b) Transect cross the reactors

levels in natural surface waters. In contrast to the Columbia River, the origin of Pu in 100-K groundwater is not fallout alone, as will be shown using Pu isotopic information in the following discussion.

Shown in Figure 4 is the distribution pattern of ^{239}Pu measured in the unfiltered samples along two well transects: one towards the Columbia River and the other roughly parallel to the shoreline crossing the KE and KW reactor facilities. Groundwater Pu is highest near the KE reactor and lower near the KW reactor. The lowest level was observed in Well K-11, a well mid-way between both reactors (Figure 1). The lower Pu at KW vs. KE is consistent with previous DOE statements (Johnson et al., 1998) that the KW source activities are much lower because the fuel stored at KW basin is fully encapsulated and undamaged.

Prior to these findings, groundwater Pu had rarely been detected in Hanford Site groundwater. The exception being the 216-B-5 injection well in the 200-E area (Fig 1), a location further from the Columbia River and 100 area, where a maximum ^{239,240}Pu activity of 25.6 pCi/L was observed in 1997 using alpha counting methods (Harman and Dresel, 1998). The finding of detectable Pu in the 100-K area should not be a surprise, but rather a reflection of the enhanced detection capabilities of TIMS over less sensitive alpha spectrometric methods that had been used previously at these sites. While the current groundwater concentrations of Pu are low in these 100-K wells, previous leakages of contaminated groundwater from the 100-K fuel storage basin to the Columbia River are well documented (Heeb et al., 1996). There is also evidence from Pu isotopic data, that suggests previous Hanford Site Pu releases to the River (Beasley et al., 1981). It is therefore important to understand the concentration and forms of Pu in groundwater today, in order to establish the long-term risk assessment for this site. Relevant to this long-term assessment will be questions related to migration of groundwater contaminants from high-level radioactive waste disposed in the 200 area that are approaching the 100 area and Columbia River (Hartman et al., 2002), but the focus of our study is the 100 area only.

3.3.2.2. Plutonium size fractionation results

During our 1999 sampling, we performed both size and redox speciation studies at 4 sites (wells K-27, K-32A, K-36, and K-110A). Results for Pu in the $<0.2\ \mu$m filtrate in Well K-36 and K-110A were at our blank level, thus we can only set $1.0\text{-}1.2\times10^4$ atoms/kg as an upper limit for ^{239}Pu concentrations in these filtered samples. Likewise, the redox subfractions for well K-32A are the same as our blank. We therefore focus our attention on the size fractionated data only from that well K-32A and consider complete size and redox fractionated data from well K-27, which has the highest Pu concentrations in our study (Table 3).

We found 9.8 – 13.3% of the ^{239}Pu was retained by our 1 KD CFF membrane in Wells K-27 and K-32A (Table 4), and is thus classified here as “colloidal” as calculated using equation 1. Also reported in this Table is the CFF mass balance, i.e. how well does the sum of the permeate and retentate fractions compare to the filtrate concentration that is supplied to the CFF system. This allows for a first order check on possible chemical or physical sorptive losses that are common with CFF and evident by a low mass balance (Buesseler et al., 2003). Further evidence for small sorptive losses also shows up as residual Pu removed during acid and base cleaning steps (Table 2). For Well K-27, this mass balance is 84%,suggesting losses of up to 16% for ^{239}Pu during CFF processing (Table 4). For Well K-32A, the mass balance is essentially 100%.

Table 4. Size[a] and redox fractionated ^{239}Pu concentration and isotopic compositions.

				[Pu(III,IV)] ± 1σ error		[Pu(V,VI)] ± 1σ error	
	[^{239}Pu]±1σ error	atom ratio±1σ error		×10^{4} atom/kg		×10^{4} atom/kg	
Sample Fraction	×10^{4} atoms/kg	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu[f]	^{239}Pu	^{240}Pu	^{239}Pu	^{240}Pu
			Well 199-K-27				
Filtrate[b]	92.64 ±1.30	0.1451 ±0.0035	0.0082 ±0.0007	74.01 ±0.93	7.86 ±0.16	41.78 ±0.49	5.79 ±0.16
Permeate[b]	65.57 ±1.33	0.1438 ±0.0056	0.0082 ±0.0017	23.89 ±0.47	3.31 ±0.13	35.46 ±0.49	5.35 ±0.16
Retentate[b]	755.49 ±11.67	0.1447 ±0.0035	0.0081 ±0.0006	757.41 ±10.04	109.38 ±2.35	0.77 ±0.03	0.1 ±0.68
Colloidal[c]	12.38 ±0.21	0.1447 ±0.0041	---	---	---	---	---
Colloidal[d]	27.07 ±1.86						
CFF mass balance[e]	84.10% ±1.9%						
			Well 199-K-32A				
Filtrate[b]	3.17 ±0.39	---	---	---	---	---	---
Permeate[b]	2.96 ±0.26	---	---	---	---	---	---
Retentate[b]	19.84 ±1.17	0.1067 ±0.0258	---	---	---	---	---
Colloidal[c]	0.31 ±0.02	---	---	---	---	---	---
Colloidal[d]	0.21 ±0.04						
CFF mass balance[e]	103.20% ±13.3%						

a) Size fractions: Filtrate (< 0.2 mm); Permeate (< 1 kDa); Retentate (enriched in 1 kDa-0.2 mm colloids); Colloidal (1 kDa-0.2 mm)

b) CFF-processed samples. Concentration factors *(cf)* for Wells K-27 and K-32A were 55.7and 54.6, respectively.

c) [Colloidal]=([retentate]-[Permeate])/*cf*

d) [Colloidal]=[Filtrate]-[Permeate]

e) mass balance = [colloidal] + [permeate] / [filtrate]

f) Decay corrected to 1 Jan 2000.

Losses of particle-reactive elements such as ^{234}Th, to CFF systems are common, and some investigators attribute these losses to the colloidal fraction only, and thus add the lost fraction to the colloidal fraction when estimating colloidal abundances (Baskaran et al., 1992; Sanudo-Wilhelmy et al., 2002). This correction thereby increases the apparent colloidal concentration. Other experiments showed that a large percentage of the ^{234}Th lost during CFF is irrecoverable in weak acid or base rinsing, while the recovered ^{234}Th occurred in both retentive and permeate fractions (Dai and Benitez-Nelson, 2001). Lacking clear evidence on which Pu size fraction is lost during CFF in our study, we take a conservative approach and add any mass balance offset as an error term in our calculations and interpretation of CFF data (Buesseler et al., 2003; Dai et al., 1998; Dai and Benitez-Nelson, 2001). Thus the full range of possible colloidal abundances discussed below, is determined by either the difference between the filtrate and permeate subfractions (i.e. in effect, Pu losses are considered colloidal only), or via equation 1, which does not include the effects of sorptive losses to the CFF system in the calculation of colloid abundances. We are fortunate in this study that the CFF mass balances are close to 100%, however this is not always the case and how one interprets CFF losses can have a large impact on reported colloid data (Buesseler et al., 2003). Using our conservative approach, the full range of possible colloidal ^{239}Pu abundances are 13-29% for Well K-27 and 7–10% for Well K-32A. Size fractionation of ^{240}Pu is well correlated with ^{239}Pu as seen by the similar ^{240}Pu/^{239}Pu ratios in all of the size fractions from Well K-27 (Table 4).

Colloid-facilitated Pu transport has received a great deal of attention for more than two decades, notably within the last few years (Honeyman, 1999; Kaplan et al., 1994; Kersting et al., 1999; Kim, 1994; Kim et al., 1984; Marty et al., 1997; McCarthy and Zachara, 1989; Penrose et al., 1990). In SRS F-area seepage basin groundwater, we found low colloidal Pu (<4%) using this same combination of low-flow rate pumping and on-site CFF processing techniques (Dai et al., 2002). These results at SRS contrast to a prior SRS study, but the earlier data were obtained using very different size fractionation protocols (Kaplan et al., 1994). The Hanford Site 100-K data, thus suggest higher colloid Pu abundances (7-30%) than found at SRS using our same methods and CFF protocols. Differences between the SRS and Hanford Site data must be sought in the redox speciation information and differences in the Pu sources and groundwater characteristics between sites.

3.3.2.3. Redox fractionation results

Redox fractionation data for Hanford Site Well K-27 (the only well with high enough total Pu concentrations to quantify these subfractions) are shown in Fig. 3 and Table 4. As with the CFF fractionation, redox separations are problematic if the Pu concentration in the sum of the reduced and oxidized subfrations, does not total the source water Pu concentration. After sampling, a separate aliquot of each size fractionated sample and the filtrate are used for the redox separations. There are thus 6 subfractions analyzed for both ^{239}Pu and ^{240}Pu concentration: the reduced Pu(III,IV) subfraction of the filtrate, permeate and retentate solutions, and the oxidized Pu(V,VI) in these same 3 sample types. When added together, the sum of Pu(III,IV) and Pu(V,VI) concentrations should independently equal the Pu concentration in the non-fractionated sample. This agreement is shown by the good comparison in Fig. 4 between the concentration of ^{239}Pu and ^{240}Pu in the size fractionated groundwater samples and the separate redox subfractions. This lends further confidence in the reliability of our methods, even at these trace level concentrations (10^6 atoms/kg).

The results of the redox separations are quite consistent between both ^{239}Pu and ^{240}Pu isotopes, with >99% of the Pu being found in the reduced subfraction Pu(III,IV) in the colloid bearing retentate sample (Table 4). In the <1 kDa permeate solution, 40% of the ^{239}Pu was in the reduced subfraction, and in the filtrate, 65% was reduced. This high affinity of the reduced forms of Pu for the colloidal fraction is consistent with the known higher distribution coefficient and hence higher affinity of reduced forms of Pu for particle surfaces (Alberts et al., 1977; Mahara and Matsuzuru, 1989; Nelson et al., 1987; Skipperud et al., 2000).

A major difference between Hanford Site and SRS lies in the overall redox state of Pu. At Hanford Site, much of the Pu is reduced, and these more particle reactive forms are consistent with the higher colloid-associated Pu. At SRS, >90% of the Pu in the <0.2 μm filtrate was oxidized in the well closest to the seepage basins. Complicating the SRS story was evidence that in the downstream wells the primary source of Pu was not migration of ^{239}Pu in groundwater but rather in-situ decay of ^{244}Cm to ^{240}Pu, which results in ^{240}Pu that is preferentially in the oxidized (>90%) and non-colloidal forms (<2% colloidal ^{240}Pu). Thus, looking for geochemical reasons to explain groundwater Pu speciation variability between SRS and Hanford Site is complicated by this ^{244}Cm source of oxidized ^{240}Pu at SRS. Furthermore, environmental and lab based data are not consistent as to the predicted oxidation states of Pu and the geochemical controls thereof (Baxter et al., 1995; Cleveland, 1979; Haschke et al., 2000; Mitchell et al., 1995). While reduced and oxidized Pu may coexist in a same aquatic environment, Pu(IV) is usually a stable form which interacts with anionic species for complexation through ionic bonding (Choppin, 1988; Cleveland, 1979; Dozol and Hagemann, 1993). At the same time, studies have shown a significant percentage of Pu(V) occurs stable in the aquatic environment, such as in seawater (Baxter et al., 1995; McMahon et al., 2000; Mitchell et al., 1995)and groundwater (Dai et al., 2002). Further mechanisms for the formation of Pu(V) dioxide have been uncovered recently (Haschke et al., 2000).

From the contrast between these Hanford Site and SRS data, we thus conclude that higher colloidal abundances for Hanford Site Pu are associated with lower oxidation states. The dominant geochemical control on the relative oxidation state of Pu in groundwater is less certain, and we note that at SRS, ^{240}Pu originating from the decay of ^{244}Cm is preferentially found in the more oxidized and non-colloidal fraction. There are thus geochemical controls on ambient redox conditions in groundwater as well as source controls on the physical-chemical form of Pu released in to the environment, the combination of which appears to determine Pu speciation.

It has been estimated that the groundwater travel time would be less than 10 years between Well K-27 and the downstream well K-32A (Hartman et al., 2002). Despite the relatively high colloid associations in Well K-27 (13-29%) and rapid groundwater flow, there remains a Pu concentration gradient greater than one order of magnitude between these wells (93 vs 3×10^4 atoms/L ^{239}Pu at K-27 vs. K-32A, respectively). Also, we do not see in the downstream well an enrichment in the percent Pu in the colloidal fraction. Therefore, neither the low fraction of colloidal Pu, nor the decreased concentration of Pu in the downstream well supports enhanced transport of groundwater Pu colloids at this site.

3.3.3 Plutonium source terms as revealed by Pu isotopes

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(Oughton et al., 2000). Weapons-grade Pu is characterized by a low content of ^{240}Pu with ^{240}Pu/^{239}Pu atom ratios usually <0.07(Oughton et al., 2000). Global weapons testing fallout has an average ^{240}Pu/^{239}Pu ratio of 0.18(Kelley et al., 1999). High and low irradiation conditions in reactors would result in ^{240}Pu/^{239}Pu ratios ranging from <0.06 to >0.65, respectively(Sanders and Boni, 1980). In addition, Pu isotopes can originate from the decay of transplutonium isotopes such Cm and Am. With TIMS measurements, we are 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.

At Hanford Site 100 K basin, evidence from ^{240}Pu/^{239}Pu points to a mixture of global fallout and local HS wastes as being the source of extremely low Pu concentrations in this groundwater. However, here is a case where determination of the more analytically challenging minor Pu isotopes has also proved enlightening. In the wells nearby the KE reactor, the ^{241}Pu/^{239}Pu ratios are consistently in the range of 0.0081 to 0.0082 (decay corrected to 1 Jan 2000; Figure 5). This small range of ratios was recurrent in all size and redox subfractions at these wells. In contrast, global fallout ratios of ^{241}Pu/^{239}Pu in the Northern hemisphere average at 0.00194 (Kelley et al., 1999) and this ratio was also found in wells near the KW reactor. Our observation of a high ratio for ^{241}Pu/^{239}Pu is clearly another indicator of a second HS waste sources. Typical Hanford site weapons grade material has a ^{241}Pu/^{239}Pu of 0.0054 as of June 1968, which is equivalent to 0.0011 when decay corrected to Jan 2000, i.e. too low for the KE samples. We contend that the high ^{241}Pu/^{239}Pu measured near the KE reactor must come from the materials associated with N Reactor production (with some possible mixture of other HS sources). N Reactor was the only HS reactor ever involved with reactor grade material production whose ^{241}Pu composition may have been up to 10%. It has been documented that N Reactor wastes were stored at the KE reactor basins, consistent with the Pu isotopic composition of wells nearest to the KE reactor (Dai et al., 2003).

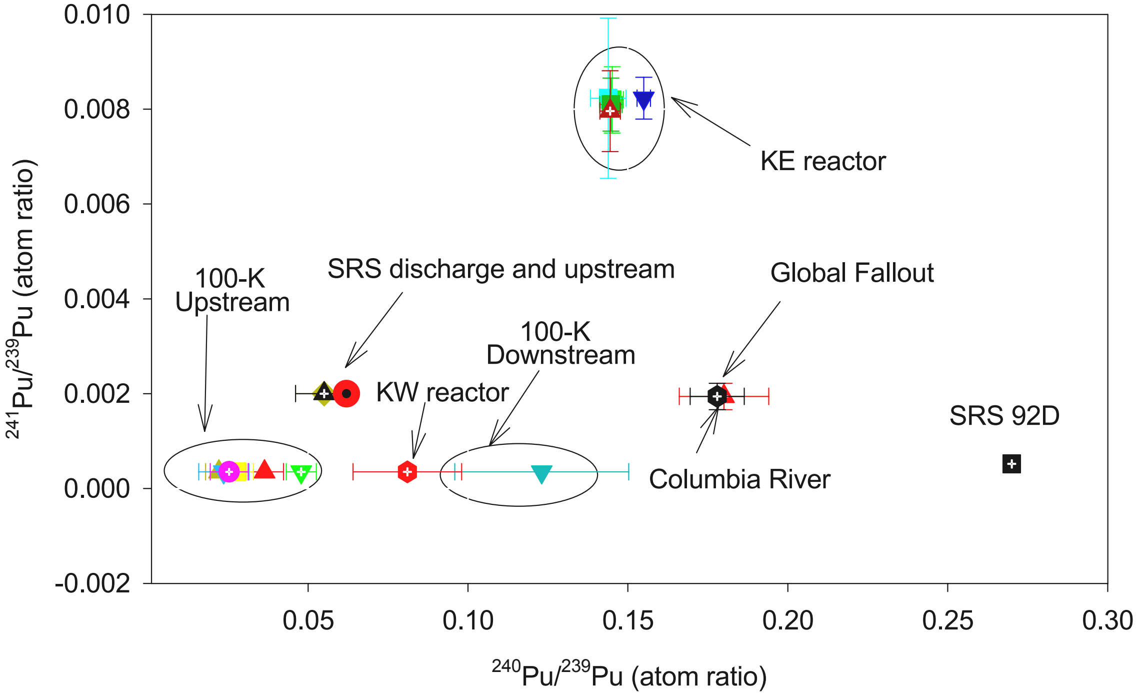

Figure 5. Summary of Pu isotopics from DOE Hanford Site (100-K area transects, and as specified near KW and KE reactor) and Savannah River Site (F area ground water near seepage basin, 92D, and from upstream site). Not shown in the Figure are extremely high ^{240}Pu/^{239}Pu ratios of >3 enriched from ^{244}Cm decay in downstream wells at SRS, wells 78 and 79. Global fallout ratio from Kelley et al. (1999). Compilation of data in Dai et al., 2002; 2003.

The Pu isotopic results obtained at SRS F area seepage basins and Hanford Site 100-K area are compared for ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu in Figure 5. The wide range of Pu atom ratios demonstrates that rather than thinking of all Pu sources as being uniform, we must consider Pu contamination in the context of specific source information. As demonstrated at SRS, we have also shown that Pu oxidation states and colloidal abundances can vary depending upon the specific Pu source (see below; Dai et al., 2002). This is quite important for predicting Pu speciation in groundwater at SRS.

4.Relevance, Impact, and Technology Transfer

Migration of plutonium in the environment is a major issue at several DOE sites (Riley and Zachara, 1992). As such, fundamental data concerning the interactions between various chemical forms of plutonium with compounds in the environment are essential for predicting Pu's behavior in the aqueous environment. Our research over the past 6 years, has focused on two important DOE sites, namely the Savannah River Site and the Hanford Site, and at both sites we see no need to invoke colloid facilitated transport to explain Pu groundwater distributions. This conclusion has important practical implications because much of the uncertainty associated with Pu subsurface transport, including at the Hanford Site (Mann et al. 1998) and the SRS (McDowell et al., 2000) is attributed directly to the uncertainty associated with role that mobile colloids may or may not play in transporting Pu. This conclusion however is based upon only a few wells in the F-area at SRS and 100-K area at HS under a limited range of groundwater conditions.

At this point in time, extensive cleanup and stabilization programs are underway at many DOE sites. These important DOE activities are challenged by the immense scope of the cleanup and the overriding need for more streamlined and focused solutions to the cleanup problem. The results of our research program: i) provide the basis for accurate modeling and prediction of actinide transport; ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the groundwater zone; iii) identify specific Pu sources and the extent of far field, or long-term migration of transuranics in groundwater; iv) reduce costly uncertainty in performance and risk assessment calculations. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies.

The original definition of the transuranic waste category, TRU, was created in 1970 by the Atomic Energy Commission (AEC) to define those wastes with concentrations of **long-lived** transuranics greater than 10 nanocuries per gram (AEC raised this limit to 100 nanocuries per gram in 1984). Waste below this ceiling and the shorter lived transuranics, can be treated as low-level waste and disposed of with much less consideration. At SRS, we have shown that ^{244}Cm, a short-lived transuranic, is the dominant source of the long-lived ^{240}Pu that is of concern in TRU wastes. TRU wastes are common to many DOE sites and the releases are often poorly documented in terms of total radioactivity and relative transuranic activities (Fioravanti et al., 1997). Since little quantitative field data exists documenting in-situ speciation and forms of transuranics in groundwater, the data collected in this study will go a long way to test predictive models of long-term migration patterns and thus assess risk and design containment strategies appropriate for transuranics in groundwater originating from the many differing sources on DOE sites.

5. Project Productivity

We have successfully fulfilled the tasks proposed. Due to the time consuming lab work during our sample processing for TIMS measurements, and difficulties associated with field sampling, we applied for and were granted a no cost extension which ended in July of 2003 instead of Sept 2002 as scheduled during the initial proposal. Given the extremely low concentrations of Pu isotopes found in the 100-K and 100-N areas, we also did not obtain full speciation results that warranted for more complex modeling of groundwater geochemistry and transport.

6. Personnel Supported- WHOI

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7. Publications

Journal Articles - published

Buesseler, K.O., M. Hassellöv, and M.H. Dai, 2003. Comment on "Trace Metal Levels in Uncontaminated Groundwater of a Coastal Watershed: Importance of Colloidal Forms". *Environmental Science & Technology*, 37: 657-658.

Dai, Minhan, James M. Kelley and Ken O. Buesseler, 2002, Sources and migration of plutonium in groundwater at the Savannah River Site. *Environmental Science and Technology* 36, 3690 – 3699.

Repeta, DJ, TM Quan, LI Aluwihare, and AM Accardi, 2002, Chemical characterization of high molecular weight dissolved organic matter in fresh and marine waters, *Geochimica et Cosmochimica Acta* 66: 955-962

Dai, M.H., K.O. Buesseler, J.M. Kelley, J.E. Andrews, S. Pike and J.F. Wacker, 2001, Size Fractionated Plutonium Isotopes in a Coastal Environment, *Journal of Environmental Radioactivity,* 53, 9-25.

Journal Articles - submitted and in preparation

M. Dai, K.O. Buesseler, S.M. Pike (2003) Speciation and isotopic composition of plutonium in the groundwater at the DOE Hanford Site, *Journal of Contamination Hydrology*, in review.

8. Interactions

a. Conference Presentations

Hassellöv, M.; K.O. Buesseler, M.A. Charette, C. Herbold, S.M. Pike (2001) The application of cross flow ultrafiltration to determine the abundance of colloids and associated elements in anoxic ferrous-rich ground waters. In American Geophysical Union Spring Meeting; AGU: Boston, 2001.

Dai, M.H., J.M. Kelley, S. Pike, K.O. Buesseler, T.C. Maiti and J.F. Wacker (2000) Isotopic composition, speciation and mobility of Pu in groundwater at the DOE Savannah River Site, DOE EMSP national workshop, April 2000, Atlanta.

Buesseler, K.O., M.H. Dai and J.M. Kelley, S. Pike, R. Nelson, S. Goodwin and J.F. Wacker (2000), Speciation and isotopic composition of plutonium in the groundwater at the Hanford Site, DOE EMSP national workshop, April 2000, Atlanta.

Kelley, J.M., M.H. Dai, K.O. Buesseler, S. Pike, and J.F. Wacker (2000) Speciation, mobility and fate of actinide element isotopes in groundwater, DOE EMSP vadose zone workshop, November 2000, Richland, WA

Dai, M., J.M. Kelley, K.O. Buesseler et al. (1999) Isotopic composition, speciation and mobility of Pu in the groundwater at DOE Savannah River Site, AGU Spring meeting, May 1999, Boston.

Buesseler, K.O., M. Dai, et al. (1999) Speciation, mobility and fate of actinides in the groundwater at the Hanford Site, EMSP PI workshop, Nov. 16-18, Hanford.

Repeta, D.J., T.M. Quan, L.I. Aluwihare and A. Accardi (1999) Dissolved organic matter in fresh and marine waters. Amer. Soc. Limnol. Oceanogr. Annual meeting, Santa Fe, N.M.

b. Advisory functions directly related to this project

"Research Opportunities for Studies of Contaminant Transport in Fluvial Systems at the Tims Branch-Steeds Pond System, Savannah River Site" March 4 and 5, 2003. Participant in Environmental Remediation Sciences Division Workshop

c. Collaborations

Argonne National Laboratory: K. Orlandini
BHI: J. Borghese, R. Trevino and R. Fabre

Pacific Northwest National Laboratory: J.E. Kelley, T. Marti, L. Bond, S. Goodwin, J. Wacker, P.E. Dresel, S. Conley, S. Peterson, T. Wilson and D. Morgan
Westinghouse Savannah River Company: D. Brown, D. Brooks, J. Haffener, K. Johnson, D. Kaplan, S. Luttrel, L. Peurrung and M. Thomson.
University of Georgia: W-J. Cai
Waste Management Northwest: S. Worley
Woods Hole Oceanographic Institution: J. Andrews, D. Repta, R. Belastock, L. Ball, R. Nelson and M. Hassellöv.

9. Transitions

No specific transitions were made during the project period. This is a basic research proposal, results of which have important implications for transition activities, in particular, in to the fate and monitoring of transuranic wastes at DOE sites. Identification of the chemical and phyisical froms of transuranics in groundwater will allow for better containment strategies and prediction of long term fate of TRU and other wastes. See section 6 for futher details of the relevance of this project to DOE and possible transition activities that are likely to result from this project.

10. Patents

None

11. Future work

We have been recently funded by DOE to return to SRS and test our hypotheses that 1) Cm mobility and its decay to Pu, and not colloidal transport of Pu, is the dominant source of groundwater Pu found downstream from seepage basins at SRS, and that 2) the variability in the extent of groundwater Pu found in association with colloidal size classes will be primarily controlled by ambient geochemistry. SRS is ideal for this study since we have considerable background on expected Pu and transuranic sources and concentrations in groundwater. The combined disposal of Pu and Cm wastes is not unique to SRS, nor are the rain and humid conditions that lead to shallow and significant groundwater flow characteristic of many Eastern DOE sites. We also know that contrasting conditions of pH (and we expect a wider range of Eh and ionic strength), can be found within a small region at SRS with similar Pu and Cm sources so that we can examine Pu speciation under differing geochemical conditions. In addition, we propose to add to our studies direct determination of Cm in groundwater, rather than inferring its concentration via Pu ingrowth (Dai et al., 2002), to confirm that the enhanced ^{240}Pu we found in groundwater downstream from the SRS seepage basins is indeed a result of in-situ ^{244}Cm decay.

To achieve this goals we proposed:

- detailed field study at SRS to determine colloid associations and redox states of Plutonium and other transuranics (Cm, Am) at contrasting SRS groundwater sites. We propose work at F-area and H-area wells in early 2004. These adjoining sites have similar but separate contaminant sources (seepage basins), however the pH range in the F-area plume is more acidic, pH 3 to 5.5, than the H-area plume, pH 4.5 to 7.5.

- the direct measurement of Cm in groundwater (our prior work relied on Cm estimation from ^{240}Pu ingrowth considerations). In addition to Cm being a direct Pu source, contrasts between Pu and Cm in groundwater will tell us something about the relative mobility of transuranics in differing geochemical & redox sensitive forms.

- to support our groundwater observations, selected lab sorption experiments will be used to corroborate the relative mobilities of Pu and Cm seen in the field, using soils from on-site and studying relative sorption under differing conditions.

- combined lab and field data that will be applied to a simplified, but site specific groundwater model. These predictive capabilities will assist management activities on-site, and will be needed if we are to apply these data to the design of more cost effective monitoring and cleanup strategies at SRS and other sites.

This new 3 year project initiated in September of 2003 continues our long standing relationship with Drs. Kelley and others at the PNNL TIMS facility. It also adds to the group, direct collaboration and funding for Dr. Daniel Kaplan and associates at the Savannah River Technology Center. This SRS group will provide valuable assistance with on site sampling, as well as companion lab and modeling expertise that adds an important new element to the project.

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13. Feedback

Access to DOE sites for this study was complicated and difficult to plan and budget. Issues regarding clearance for US and non-US scientists to sample at Hanford took considerable effort by the WHOI PI to resolve, and it was next to impossible to predict and hence budget in the original proposal for all of the costs associated with on site sampling. These costs were originally budgeted in the PNNL award from DOE, but cost over runs in this category led to cuts in other categories, such as the thermal ionization mass spectrometry costs, which was our primary analytical tool. As such, fewer samples could be analyzed over the duration of the project.

14. Appendices:

The findings from our research have been presented in the papers listed below and are provided as part of this report in separate pdf files .

Dai, M.H., K.O. Buesseler, J.M. Kelley, J. E. Andrews, S. Pike and J.F. Wacker (2001). Size Fractionated plutonium Isotopes in a Coastal Environment. *J. Environ. Radioactivity,* **53 (1)**, 9-25.

Dai, M. H., J. M. Kelley and K. O. Buesseler (2002). Sources and migration of plutonium in groundwater at the Savannah River Site. *Environmental Science and Technology.* **36**, 3690-3699.

Dai, M., K. O. Buesseler, S. M. Pike (2003). Speciation and isotopic composition of plutonium in the groundwater at the DOE Hanford Site, submitted to Journal of Contaminant Hydrology.

Speciation and isotopic composition of plutonium in the groundwater at the DOE Hanford Site

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Abstract

We examined the size distribution, redox state and isotopic composition of plutonium (Pu) in the groundwater of the 100-K area at the DOE's Hanford Site. Total concentrations of Pu isotopes were extremely low (10^{-6} to 10^{-8} pCi/l, ≈ 10^4 to 10^6 atoms/l), but measurable for the first time in the 100-K area wells using mass spectrometric analyses that are much more sensitive than alpha spectroscopy methods used previously. Size fractionation data from two wells suggests that 7-29% of the Pu is associated with colloids. These colloids are collected using a 1 kDa cross-flow ultrafiltration system developed specifically for groundwater actinide studies to include careful controls both in the field and during processing to ensure in-situ geochemical conditions are maintained and size separations are well characterized. Pu in this colloidal fraction was exclusively in the more reduced Pu(III,IV) form, consistent with the higher affinity of Pu for particle surfaces in the lower oxidation states. While the overall concentrations of Pu are low, the Pu isotopic composition suggests at least two local sources of groundwater Pu, namely local Hanford reactor operations at the 100 K area, and spent nuclear fuel from the N reactor, which was stored in concrete pools at this site. Differences between this site and the Savannah River Site (SRS) are noted where groundwater Pu at the latter is characterized by much lower colloidal abundances and higher oxidation states. This difference is not directly attributable to groundwater redox potential or geochemical conditions, but rather the physical-chemical difference in Pu sources, which at SRS appear to be dominated downstream from the seepage basins by decay of ^{244}Cm, resulting in more oxidized forms of ^{240}Pu. There is no clear evidence for colloid facilitated transport of Pu in groundwater at this site, since downstream wells have both an order of magnitude lower concentrations of Pu, but also a lower fractional colloidal distribution.

Keywords

Plutonium, isotopic composition, size fractionation, redox speciation, groundwater, Hanford Site

1. Introduction

There have been many studies of the distributions of man-made actinides in surface and subsurface waters since their introduction into the environment as a result of nuclear weapons production, testing and nuclear power-plant operations (Dozol and Hagemann, 1993; National Research Council, 2000; Nelson et al., 1987; Pockley, 2000). Despite these activities however, we still have a limited ability to predict actinide transport in groundwater (National Research Council, 2000). For example, a recent study of plutonium in groundwater at the Nevada Test Site (Kersting et al., 1999) documented the migration of Pu much further than predicted by existing models. These researchers speculated that Pu transport was enhanced by colloid-facilitated transport in groundwater. Similarly, the detection of Pu in groundwater some 3400 m downstream in Mortandad Canyon at the Los Alamos National Laboratory, is cited widely as an example of colloid facilitated transport (Penrose et al., 1990). More recent review of these data suggests that Pu detected in downstream wells could not have entered through groundwater and thus the potential for Pu migration via colloidal transport may have been overstated (Marty et al., 1997). Our own data from the Savannah River Site (SRS), suggests that groundwater Pu is predominantly in more oxidized forms and not associated with colloids (Dai et al., 2002). Thus, whether to what degree groundwater is enriched in colloids and how they facilitate subsurface transport of actinides, especially those with high particle affinity, is still in debate.

In this paper, we investigated the speciation and isotopic composition of Pu: the actinide of greatest concern in groundwater of the 100 K basin at the US DOE Hanford Site on the shoreline of Columbia River. Since the Hanford Site is engaged in the largest waste cleanup effort ever undertaken in human history (Gerber, 1992) contaminants in these areas may have a direct impact on the Columbia River's ecosystem, and long term risk assessment would be much improved if we had a better understanding of actinide speciation, sources and their potential migration.

2. Sampling and methods

2.1 Area description

The Hanford Site (Fig 1) was established in 1943 as the Hanford Engineer Works (HEW) as the world's first Pu production facility constructed for the United States government. The site was remote from major populated areas, had ample electrical power from Grand Coulee Dam and associated transmission facilities, a functional railroad, clean water from the nearby Columbia River, and coarse glacial-fluvial sediments provided sand and gravel aggregate for constructing large concrete structures. Although not an original site requirement, Hanford's arid environment and soil features allowed large amounts of liquid waste to be released to the ground without immediately descending to the groundwater (Gray and Becker, 1993.).

The "100 Area" is a term used to describe a region along the shore of Columbia River where up to nine nuclear reactors were in operation. Construction of the 100-K Area reactors began in September 1953 as part of Project X, a large Cold War expansion effort at the Hanford Site (Carpenter, 1994). The area contains the KE and KW reactor buildings and their support facilities, including water treatment structures. The 100-K Area reactors had more output than the other single-pass reactors because of higher thermal power levels. Reactor operations continued until 1970 when the KW Reactor was deactivated followed by deactivation of the KE Reactor in 1971. The reactors have remained in deactivated status since that date. However, the fuel storage basins and small portions of both reactor buildings remain in use and since early 1975 have been used to store irradiated fuel elements from the N reactor (Johnson et al., 1998; Johnson et al., 1995).

Both the 105-KE and 105-KW basins are 38 m long and 20 m wide. Beneath the 100-K area is unconfined sand and gravel of the Ringold formation which is highly permeable, and over most of the area the depth to groundwater is ~25 m (Johnson et al., 1995). Both basins were used to store ~ 2100 MTU of N-Reactor and 3-4 MTU of Sandia Pulsed Reactor fuel (Garrett and Williams, 1997). The water contained in each of the basins is contaminated by radionuclides that were released from the irradiated fuel. Radionuclide concentrations in KW Basin are much lower than at the KE basin because the fuel stored at KW basin is fully encapsulated. The KE Basin experienced a significant leak in early 1976, which continued until it was isolated near the end of 1979. The leak was on the order of 1893 L/h and was attributed to a construction joint between the main basin and the fuel discharge chute. During Feb 1993, water balance calculations for the KE basin indicated an increase in basin water loss rate. This loss could not be accounted for by increased evaporation alone and is attributed to leakage to the soil column. These episodic and continuous leakages would have released Pu to the groundwater of the basins.

2.2 Well sampling

Samples were collected from the K-Basin groundwater on two occasions. Initial groundwater samples were collected by Hanford Site personnel using typical high speed groundwater pumping procedures at six groundwater monitoring wells in October 1997 for analysis of total Pu isotopic composition (wells 199-K-107A, 199-K-30, 199-K-106A, 199-K-28, 199-K-27, 199-K109A, we hereafter omit the prefix "199-"; Figure 1). A more detailed sampling was completed in March 1999. At this location, unfiltered samples were taken from wells K-11 and K-109A for total Pu isotopic composition analysis. In addition, 4 sites were sampled in greater detail (wells K-27, 32A, K-36, and K-110A) using our combination of low flow rate well sampling, cross-flow ultrafiltration (CFF), redox speciation and thermal ionization mass spectrometry (TIMS) techniques, detailed procedures of which have been described elsewhere (Dai et al., 2002). A water sample was also taken from the Columbia River downstream of the 100-K area.

Well K-36, located upstream from the K-East Reactor Basin, served as a "background" well that should be minimally influenced by groundwater discharges associated with the basins. Yet this well is also located at the southeastern end of the former 183-KE water-treatment plant basins (currently serving as a fish cultivation pond) and thus local waste stream impact could still exit. Well K-27 was installed for monitoring potential leakage from the construction joint in the K-East fuel-storage Basin (Harman and Dresel, 1998) and was located directly downstream from the KE reactor building. Wells sampled in this study generally form two cross sections: one toward the Columbia River and the other crosses the two reactor facility areas (Fig 1). Groundwater flows generally towards the Columbia River, with velocities in the range of 0.01 to 0.24 m/d at the KW basin and 0.24 to 0.4 m/d at the KE basin (Johnson et al., 1995).

2.3 On site CFF and redox processing

During the comprehensive field work, samples were processed on-site using an ultra-clean CFF system with redox control as described previously (Dai et al., 2002) and summarized in the flow chart in Figure 2. 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, colloid precipitation and contamination can occur (Hassellöv et al., 2001). In addition, HEPA filtered air was directed over the entire CFF system to prevent particulate contamination.

Prior to this sampling event, spiral-wound CFF cartridges (Prep/Scale™ PLAC, Millipore Corp.) with regenerated cellulose membranes were calibrated against standard colloidal molecules (Molecular Probes, Eugene, OR). Our CFF system retained >91 % of a ~3 kD dextran carbohydrate colloid and >94% of a 14.5 kDa protein standard. As we have noted (Dai et al., 2002), identical CFF membranes from the same manufacturer can have varying retention properties (unpublished data); thus, calibration of each CFF membrane is mandatory.

In CFF, prefiltered sample solution (<0.2 µm) flows parallel to the CFF membrane. Hydrostatic pressure drives solutes with a molecular size less than the effective cut-off rating of the membrane, through the membrane and into the sample reservoir (permeate sample fraction). The retained solution (retentate sample fraction) is recirculated across the membrane and thus becomes increasingly enriched in colloids. The concentration of Pu bound to these colloids ($Pu_{colloidal}$, units of atoms/kg) is calculated from the Pu concentrations measured in the permeate ($Pu_{permeate}$) and retentate ($Pu_{retentate}$) sample fractions using a concentration factor term (cf) which is the ratio of the initial mass of the sample to the mass of the retentate sample fraction at the conclusion of CFF processing:

$$[Pu_{colloidal}] = ([Pu_{retentate}] - [Pu_{permeate}])/cf \qquad (1)$$

Each well sampling took ~ 36 hours including ~ 24 hours of CFF processing. Between each well sampling and prior to purging and membrane preconditioning, extensive cleaning protocols were implemented to prevent sample cross contamination. These protocols were previously described in Dai et al. (1998; 2002). To enable an assessment of the efficacy of these protocols, a blank consisting of system-processed, nano-pure water was collected and processed following the sampling of Well K-27, the nearest well downstream from KE reactor.

Aliquots taken for redox speciation were also processed in the field immediately following collection. Redox processing consisted of separating the plutonium in the aliquots into Pu(III/IV) and Pu(V/VI) subfractions by a method presented in great detail in Dai et al. (2002) which was adapted from Lovett and Nelson (Lovett and Nelson, 1981). Briefly, Pu in the reduced states was traced with ^{244}Pu(III/IV) and Pu in the oxidized states was traced with ^{242}Pu(V/VI). Pu(III/IV) was separated first and the precipitate, which constituted the reduced sample subfraction, was collected by filtration and retained for subsequent processing and analysis. To retrieve the oxidized sample subfraction, the Pu(V/VI) retained in the filtrate was then reduced by the addition of Fe^{2+} to Pu(III), which was likewise co-precipitated, filtered and retained for subsequent processing and analysis. Because the method employs two tracers that are distinguishable isotopically 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 (Dai et al., 2002).

2.3 Analysis

On site measurements to monitor ambient groundwater conditions included water temperature, pH, dissolved oxygen and specific conductivity using an in-line multi-probe flow cell.

Unfiltered, filtered (<0.2 µm) and CFF-processed sample fractions were collected and retained for subsequent chemical processing and analyses in acid-cleaned 4 L fluorinated polyethylene bottles. Each bottle represented an aliquot, and 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 CFF retentate sample fraction, in which case aliquot sizes ranged from 0.5 to 1.5 kg. Aliquots were preserved upon collection by acidification to pH=2 with ultrapure HNO_3 with the exception of aliquots taken for analysis of basic groundwater chemistry parameters. Major and trace metal concentrations were determined by routine inductively coupled plasma mass spectrometry (ICP-MS, Finnigan Element). Indium was added to acidified samples and used as an internal standard. Anion measurements were run with standard ion chromatography methodology as dictated by US/EPA Method (EPA 300.1). Water samples were preserved with $HgCl_2$ for DIC and Total alkalinity (TAlk) analysis. DIC data was obtained by acidification of 0.5 mL of a water sample and the subsequent quantification of CO_2 with the IR detector (Li-Cor 6252). This method has a precision of 0.1-0.2% (Cai and Wang, 1998). TAlk was determined by Gran titration.

The groundwater size and redox fractionated samples were radio-chemically purified and the Pu isotopes were analyzed using a three-stage TIMS instrument (Dai et al., 2002). For sample sizes where millions of ion counts are measured, and with the use of internal standards to correct for isotopic fractionation, the instrument is capable of returning those ratios to 1 part per thousand precision and accuracy.

3. Results and discussion

3.1. Groundwater chemistry

The groundwater sampled in this study is generally neutral to slightly alkaline calcium-bicarbonate waters (pH ~7.0-8.3), with low specific conductivities ranging from 304-1048 $\mu S \bullet cm^{-1}$ (Table 1). The highest conductivity is observed at Well K110A, a well located upstream of the KE reactor, but downstream of the 183-water treatment plant. This high conductivity is consistent high suspended particulate material (SPM) loads observed at this well. Also at this well, we found very high pCO_2 (15000 μatm vs <2000 μatm in other wells) and DIC (8880 vs. ~ 2000 μmol/L at other wells) as well as high alkalinity (8321 vs 2000-3000 μmol/L at other wells), accompanied by low pH and low DO values.

Nitrate levels seem evenly distributed in the 100-K area groundwater, ranging from 5-7 mg/L. This was documented by Hanford Site routine groundwater monitoring reports and was interpreted as an artifact of site disposal practices to the soil column of decontamination solution, such as nitric acid (Peterson et al., 2000). Major and trace element compositions vary between wells sampled at the site, but fall within typical groundwater ranges (Table 1).

3.2. Pu concentrations and distributions

Pu isotopes were detected in unfiltered groundwater samples from the 100-K area monitoring wells for the first time using our TIMS technique (Table 3). However, the absolute levels are extremely low. The highest ^{239}Pu concentration was found at Well K-109A, on the order of 5×10^6 atoms/kg, equivalent to 0.0001 pCi/kg, which is ~10,000 times below U.S. EPA drinking water standards (15 pCi/L). For comparison, one water sample taken from the Columbia River 60 m from shore downstream of the 100 K area (Table 3 and Fig. 3) revealed an equivalent ^{239}Pu concentration as Well K-27. Since the Columbia River currently has a Pu isotopic composition characteristic of global fallout (see isotope discussion below), this suggests that the highest concentrations of ^{239}Pu in the Hanford Site 100-K area groundwater are on the same order as fallout levels in natural surface waters. In contrast to the Columbia River, the origin of Pu in 100-K groundwater is not fallout alone, as will be shown using Pu isotopic information in the following discussion.

Shown in Figure 3 is the distribution pattern of ^{239}Pu measured in the unfiltered samples along two well transects: one towards the Columbia River and the other roughly parallel to the shoreline crossing the KE and KW reactor facilities. Groundwater Pu is highest near the KE reactor and lower near the KW reactor. The lowest level was observed in Well K-11, a well mid-way between both reactors (Figure 1). The lower Pu at KW vs. KE is consistent with previous DOE statements (Johnson et al., 1998) that the KW source activities are much lower because the fuel stored at KW basin is fully encapsulated and undamaged.

Prior to these findings, groundwater Pu had rarely been detected in Hanford Site groundwater. The exception being the 216-B-5 injection well in the 200-E area (Fig 1), a location further from the Columbia River and 100 area, where a maximum ^{239,240}Pu activity of 25.6 pCi/L was observed in 1997 using alpha counting methods (Harman and

Dresel, 1998). The finding of detectable Pu in the 100-K area should not be a surprise, but rather a reflection of the enhanced detection capabilities of TIMS over less sensitive alpha spectrometric methods that had been used previously at these sites. While the current groundwater concentrations of Pu are low in these 100-K wells, previous leakages of contaminated groundwater from the 100-K fuel storage basin to the Columbia River are well documented (Heeb et al., 1996). There is also evidence from Pu isotopic data, that suggests previous Hanford Site Pu releases to the River (Beasley et al., 1981). It is therefore important to understand the concentration and forms of Pu in groundwater today, in order to establish the long-term risk assessment for this site. Relevant to this long-term assessment will be questions related to migration of groundwater contaminants from high-level radioactive waste disposed in the 200 area that are approaching the 100 area and Columbia River (Hartman et al., 2002), but the focus of our study is the 100 area only.

3.3. Plutonium size fractionation results

Plutonium concentrations in these groundwaters are so low, that it becomes difficult to process unfiltered samples into size fractionated and redox separated subfractions, without approaching the blank levels of our method. With modern TIMS techniques, the limitation for detection is generally not the sensitivity of the TIMS instrument, but rather the researcher's ability to sample, and then chemically extract and purify the element of interest without contamination. At concentrations as low as 10^4-10^6 atoms, it is very important to control and minimize contamination due to reagents, sampling equipment, and air-born particulates, and to frequently monitor one's blanks and standards.

To quantify these blank levels, we process not only Q water samples of equivalent volume in the lab, but also bring to the field Q water that is treated as a sample through our CFF procedures. Our CFF cleaning protocols (Dai et al., 1998; 2002) include Q water, acid and base rinses. We analyzed for one of the higher Pu containing wells (K-27) the Pu concentrations in these rinses (Table 2). Measurable levels of Pu carry over and sorptive contamination decrease as we proceed from our initial rinses through the cleaning process. Our final CFF blank is a Q water solution that is recirculated through the CFF and processed in the field. The ^{239}Pu concentrations of this field blank and our lab blank are $1.0\text{-}1.2\times10^4$ atoms/kg. We cannot know whether such low blanks arise from Pu in the Q water itself, or Pu in the reagents or as picked-up during handling and processing. We can however use this blank to set a lower limit for any Pu subfraction, such that we exclude Pu concentration data from discussion in the size fractionated and redox speciation results if they are at or below 10^4 atoms/kg ^{239}Pu.

During our 1999 sampling, we performed both size and redox speciation studies at 4 sites (wells K-27, K-32A, K-36, and K-110A). Results for Pu in the <0.2 μm filtrate in Well K-36 and K-110A were at our blank level, thus we can only set $1.0\text{-}1.2\times10^4$ atoms/kg as an upper limit for ^{239}Pu concentrations in these filtered samples. Likewise, the redox subfractions for well K-32A are the same as our blank. We therefore focus our attention on the size fractionated data only from that well K-32A and consider complete size and redox fractionated data from well K-27, which has the highest Pu concentrations in our study (Table 2).

We found 9.8 – 13.3% of the ^{239}Pu was retained by our 1 KD CFF membrane in Wells K-27 and K-32A (Table 4), and is thus classified here as "colloidal" as calculated using equation 1. Also reported in this Table is the CFF mass balance, i.e. how well does the sum of the permeate and retentate fractions compare to the filtrate concentration that is supplied to the CFF system. This allows for a first order check on possible chemical or physical sorptive losses that are common with CFF and evident by a low mass balance

(Buesseler et al., 2003). Further evidence for small sorptive losses also shows up as residual Pu removed during acid and base cleaning steps (Table 2). For Well K-27, this mass balance is 84%, suggesting losses of up to 16% for ^{239}Pu during CFF processing (Table 4). For Well K-32A, the mass balance is essentially 100%.

Losses of particle-reactive elements such as ^{234}Th, to CFF systems are common, and some investigators attribute these losses to the colloidal fraction only, and thus add the lost fraction to the CFF retained colloidal fraction when estimating colloidal abundances (Baskaran et al., 1992; Sanudo-Wilhelmy et al., 2002). This correction thereby increases the apparent colloidalconcentration. Other experiments show that a large percentage of the ^{234}Th lost during CFF is irrecoverable in weak acid or base rinsing, and that recovered ^{234}Th occurred in both retentate and permeate fractions (Dai and Benitez-Nelson, 2001). Lacking clear evidence on which Pu size fraction is lost during CFF processing in our study, we take a conservative approach and add any mass balance offset as an error term in our calculations and interpretation of CFF data (Buesseler et al., 2003; Dai et al., 1998; Dai and Benitez-Nelson, 2001). Thus the full range of possible colloidal abundances discussed below, is determined by either the difference between the filtrate and permeate subfractions (i.e. in effect, Pu losses are considered colloidal only), or via equation 1, which does not include the effects of sorptive losses to the CFF system in the calculation of colloid abundances. We are fortunate in this study that the CFF mass balances are close to 100%, however this is not always the case and how one interprets CFF losses can have a large impact on reported colloid data (Buesseler et al., 2003). Using our conservative approach, the full range of possible colloidal ^{239}Pu abundances are 13-29% for Well K-27 and 7–10% for Well K-32A (Table 4). Size fractionation of ^{240}Pu is well correlated with ^{239}Pu as seen by the similar ^{240}Pu/^{239}Pu ratios in all of the size fractions from Well K-27.

Colloid-facilitated Pu transport has received a great deal of attention for more than two decades, notably within the last few years (Honeyman, 1999; Kaplan et al., 1994; Kersting et al., 1999; Kim, 1994; Kim et al., 1984; Marty et al., 1997; McCarthy and Zachara, 1989; Penrose et al., 1990). In SRS F-area seepage basin groundwater, we found low colloidal Pu (<4%) using this same combination of low-flow rate pumping and on-site CFF processing techniques (Dai et al., 2002). These results at SRS contrast to a prior SRS study, but the earlier data were obtained using very different size fractionation protocols (Kaplan et al., 1994). The Hanford Site 100-K data, thus suggest higher colloid Pu abundances (7-30%) than found at SRS using our same methods and CFF protocols. Differences between the SRS and Hanford Site data must be sought in the redox speciation information and differences in the Pu sources and groundwater characteristics between sites.

3.4 Redox fractionation results

Redox fractionation data for Hanford Site Well K-27 (the only well with high enough total Pu concentrations to quantify these subfractions) are shown in Fig. 3 and Table 4. As with the CFF fractionation, redox separations are problematic if the Pu concentration in the sum of the reduced and oxidized subfrations, does not total the source water Pu concentration. After sampling, a separate aliquot of each size fractionated sample and the filtrate are used for the redox separations. There are thus 6 subfractions analyzed for both ^{239}Pu and ^{240}Pu concentration: the reduced Pu(III,IV) subfraction of the filtrate, permeate and retentate solutions, and the oxidized Pu(V,VI) in these same 3 sample types. When added together, the sum of Pu(III,IV) and Pu(V,VI) concentrations should independently equal the Pu concentration in the non-fractionated sample. This agreement is shown by the good comparison in Fig. 4 between the concentration of ^{239}Pu and ^{240}Pu in the size fractionated groundwater samples and the separate redox subfractions. This lends further confidence in the reliability of our methods, even at these trace level concentrations (10^6 atoms/kg).

The results of the redox separations are quite consistent between both ^{239}Pu and ^{240}Pu isotopes, with >99% of the Pu being found in the reduced subfraction Pu(III,IV) in the colloid bearing retentate sample (Table 4). In the <1 kDa permeate solution, 40% of the ^{239}Pu was in the reduced subfraction, and in the filtrate, 65% was reduced. This high affinity of the reduced forms of Pu for the colloidal fraction is consistent with the known higher distribution coefficient and hence higher affinity of reduced forms of Pu for particle surfaces (Alberts et al., 1977; Mahara and Matsuzuru, 1989; Nelson et al., 1987; Skipperud et al., 2000).

A major difference between Hanford Site and SRS lies in the overall redox state of Pu. At Hanford Site, much of the Pu is reduced, and these more particle reactive forms are consistent with the higher colloid-associated Pu. At SRS, >90% of the Pu in the <0.2 μm filtrate was oxidized in the well closest to the seepage basins. Complicating the SRS story was evidence that in the downstream wells the primary source of Pu was not migration of ^{239}Pu in groundwater but rather in-situ decay of ^{244}Cm to ^{240}Pu, which results in ^{240}Pu that is preferentially in the oxidized (>90%) and non-colloidal forms (<2% colloidal ^{240}Pu). Thus, looking for geochemical reasons to explain groundwater Pu speciation variability between SRS and Hanford Site is complicated by this ^{244}Cm source of oxidized ^{240}Pu at SRS. Furthermore, environmental and lab based data are not consistent as to the predicted oxidation states of Pu and the geochemical controls thereof (Baxter et al., 1995; Cleveland, 1979; Haschke et al., 2000; Mitchell et al., 1995). While reduced and oxidized Pu may coexist in a same aquatic environment, Pu(IV) is usually a stable form which interacts with anionic species for complexation through ionic bonding (Choppin, 1988; Cleveland, 1979; Dozol and Hagemann, 1993). At the same time, studies have shown a significant percentage of Pu(V) occurs stable in the aquatic environment, such as in seawater (Baxter et al., 1995; McMahon et al., 2000; Mitchell et al., 1995)and groundwater (Dai et al., 2002). Further mechanisms for the formation of Pu(V) dioxide have been uncovered recently (Haschke et al., 2000).

From the contrast between these Hanford Site and SRS data, we thus conclude that higher colloidal abundances for Hanford Site Pu are associated with lower oxidation states. The dominant geochemical control on the relative oxidation state of Pu in groundwater is less certain, and we note that at SRS, ^{240}Pu originating from the decay of ^{244}Cm is preferentially found in the more oxidized and non-colloidal fraction. There are thus geochemical controls on ambient redox conditions in groundwater as well as source controls on the physical-chemical form of Pu released in to the environment, the combination of which appears to determine Pu speciation.

It has been estimated that the groundwater travel time would be less than 10 years between Well K-27 and the downstream well K-32A (Hartman et al., 2002). Despite the relatively high colloid associations in Well K-27 (13-29%) and rapid groundwater flow, there remains a Pu concentration gradient greater than one order of magnitude between these wells (93 vs 3×10^4 atoms/L ^{239}Pu at K-27 vs. K-32A, respectively). Also, we do not see in the downstream well an enrichment in the percent Pu in the colloidal fraction. Therefore, neither the low fraction of colloidal Pu, nor the decreased concentration of Pu in the downstream well supports enhanced transport of groundwater Pu colloids at this site.

3.4. Isotopic ratios and source provenance

The concentration data alone tell us nothing about the source of Pu in the 100-K area groundwater. For this information, we need to examine the Pu isotopic results in more detail. Note that unlike concentration data, the isotope ratio in the subfractions can still be reliable, even if concentrations are biased by sorptive losses or other processing artifacts, since there is no evidence in this data of measurable isotope fractionation during processing (see Pu isotopic data in all subfractions from Well K-27, Table 4).

The relative abundances of Pu isotopes depend upon the practices and sources of Pu during production. In terms of ^{240}Pu content, super grade Pu has a ^{240}Pu/^{239}Pu atom ratio < 0.03. Nuclear weapon construction requires a ^{240}Pu/^{239}Pu atom ratio lower than 0.07. Upon detonation this ratio increases due to neutron capture with the exact value depending on the test parameters and yield (Taylor et al., 2001). Fuel grade Pu typically has a ^{240}Pu/^{239}Pu ratio between 0.07-0.18 while reactor grade Pu has ^{240}Pu/^{239}Pu ratio 0f 0.18-0.30. Mixed-Oxided fuel has the highest ^{240}Pu content (^{240}Pu/^{239}Pu >0.30) (Pellaud, 2002).

^{240}Pu/^{239}Pu in weapons test fallout can vary between <0.10 and >0.35. For example, characteristic ^{240}Pu/^{239}Pu atom ratios have been found to be <0.04 in Nevada test site fallout (Hicks and Barr, 1984) and as high as 0.36 in the U.S. Mike shots in 1952 at Enewetak (Diamond et al., 1960). However, when averaged over all the weapons tests, the global integrated fallout ^{240}Pu/^{239}Pu ratio in environmental samples is about 0.18 (Kelley et al., 1999; Krey et al., 1976). These isotopic signatures have been successfully used to trace the specific Pu source such as global weapons testing fallout, debris from specific test series or Pu from reprocessing or a local reactor discharge in differing hydro-geochemical regime (Beasley et al., 1981; Buesseler, 1997; Buesseler and Sholkovitz, 1987; Cooper et al., 2000; Dresel et al., 2002; Perkins and Thomas, 1980; Taylor et al., 2001; Warneke et al., 2002).

In this study, we have measured ^{240}Pu/^{239}Pu ratios ranging from <0.04 to >0.15 in the K basin groundwater and 0.18 in the Columbia River downstream of the 100-K area (Figure 5). This isotopic composition range is consistent overall with prior measurements in Hanford Site soils, which were 0.0522±0.0005 within a mile from the PUREX fuel reprocessing plant, 0.0957±0.0013 within 2 miles from the plant and 0.1785±0.0095 at a site 200 miles from the plant (Stoffels et al., 1994).

The Columbia River ^{240}Pu/^{239}Pu ratio today is thus characteristic of global fallout. Past releases of actinides from Hanford Site operations to the Columbia River have been documented in sediment samples taken at approximately this same location. Beasley et al. (1981) reported a mean Columbia River sediment ^{240}Pu/^{239}Pu ratio of 0.126 and estimated that 20-25% of the sedimentary ^{239}Pu was derived from Hanford Site operations between 1944 – 1970. Radionuclide releases to the Columbia River have been well documented (Heeb et al., 1996), but the short residence time of river waters (few months) and fallout ratio today, suggests that current groundwater sources are too small to detect and that sedimentary releases from earlier Pu deposited in the river bed are also minor.

From upstream to downstream wells, we observed an overall increase in ^{240}Pu/^{239}Pu ratios (Figure 5) from <0.03 to 0.15, signifying a local Pu source other than global fallout for these K-area groundwaters. It would appear that upstream wells are mostly impacted by Pu from general Hanford Site reactor production, which was characterized by weapons grade Pu possessing with a low ^{240}Pu/^{239}Pu ratio. Downstream, mixing with higher ^{240}Pu/^{239}Pu sources is evident. One possible source for the higher ratio material other than fallout, is the 2,100 metric tons of spent nuclear fuel from the N-reactor stored in the K basins. The N reactors were light-water cooled, graphite-moderated reactors. Among the 9 reactors in operation at Hanford Site, this was the only dual purpose, multi-pass water cooled reactor, and it was designed to supply steam for the production of electricity as a by-product (Garrett and Williams, 1997). Production-wise, N Reactor initially produced weapons-grade Pu (^{240}Pu/^{239}Pu <0.07 ^{240}Pu) from 1964 to 1965. From 1966 to 1973 it produced fuel-grade ^{240}Pu for AEC's breeder reactor program (^{240}Pu/^{239}Pu = 0.09). From 1974 until 1984 it produced fuel-grade ^{240}Pu with an even higher ^{240}Pu/^{239}Pu ratio (0.12). Then in 1984, N reactor was converted to produce weapons-grade Pu until it was shut down in 1986. Therefore, the high ^{240}Pu/^{239}Pu measured downstream from the KE reactor is consistent with a mixture of N reactor waste with fallout Pu (see discussion of ^{241}Pu below).

We can evaluate this N-reactor waste source by consideration of another minor Pu isotope, namely ^{241}Pu. Because of its short half life (14.3 years) the ^{241}Pu/^{239}Pu atom ratios have changed since their release into environment. The ^{241}Pu/^{239}Pu ratio is analytically challenging to measure at these low levels (10^4 – 10^6 atoms), and is rarely reported for environmental samples. Global fallout ratios of ^{241}Pu/^{239}Pu in the Northern hemisphere average 0.00194 (Kelley et al., 1999). In the wells where we had sufficient Pu to quantify ^{241}Pu/^{239}Pu, notably at Well K-27 and 109A, the ^{241}Pu/^{239}Pu ratios are consistently high, in the range of 0.0081 to 0.0082 (decay corrected to 1 Jan 2000; Fig. 5). This small range of ^{241}Pu/^{239}Pu ratios was found for this well in all of the different size and redox subfractions. Our observation of this high ratio for ^{241}Pu/^{239}Pu is clearly another indicator of local waste sources in K-27 and K-109A. In the other wells, ^{241}Pu/^{239}Pu was below detection.

Typical Hanford site weapons grade material has a ^{241}Pu/^{239}Pu ratio of 0.0054 as of June 1968, which is equivalent to 0.0011 when decay corrected to Jan 2000. Thus the high ^{241}Pu/^{239}Pu ratios measured in K-27 and K-109A, are not consistent with this average source material. The N reactor is the only reactor that was ever involved with production of reactor grade material whose ^{241}Pu composition may have been as high as ^{241}Pu/^{239}Pu = 0.10. For these reasons it would appear that the elevated Pu groundwater concentrations are associated with local release of N reactor materials known to be stored at the KE reactor basins and now evident in the Pu isotopic composition of well K-27 and K-109A.

4. Summary and Conclusions

We have detected for the first time extremely low-level plutonium in the groundwater at the Hanford Site 100-K area using ultra-sensitive TIMS technique. Pu isotopic composition has emerged once again as a useful indicator to trace Pu sources. Pu in the groundwater of 100-K area is mainly from general Hanford operations with a mixture of global fallout. Exception to this determination lies in the groundwater near the KE reactor where clear indication occurs for a source from N reactor spent fuel waste. Identifying these sources is important for understanding Pu geochemistry.

Colloid-associated Pu is detectable at least in two wells at the 100-K area, accounting for 7-29% of so-called dissolved Pu, which is higher than what we measured at SRS (<3% colloidal Pu; Dai et al., 2002). This differing colloid association is consistent with measured in situ redox states of groundwater Pu in these studies. We find at HS, essentially 100% of the Pu in the retentate fraction is reduced, which contrasts with the scenario at SRS, where the majority of Pu is found to be in higher oxidation states. At SRS, the major source of Pu downstream from the seepage basins, is ^{240}Pu derived from ^{244}Cm decay, and led to fractionation between ^{240}Pu and ^{239}Pu not seen in this study. Thus differences in groundwater Pu speciation between Hanford Site and SRS in these two examples may be related to both Pu source characteristics (Cm decay) and/or the geochemical properties of the groundwater (most notably pH at F-area wells at SRS are 3-5.5 vs. 8.5 at Hanford Site 100-K).

The groundwater travel time would be less than 10 years between Well K-27 and the downstream well K-32A, yet there remains a Pu concentration gradient greater than one order of magnitude between these wells. Also, we see in the downstream well 32A a decrease in the fraction of colloidal Pu, from 13-29% near the source to 6-9% downstream. Therefore, neither the colloidal abundance changes, nor the decreased concentration of Pu in the downstream well supports rapid or preferential transport of groundwater Pu colloids at the Hanford Site.

Acknowledgements

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Table 1. Basic groundwater chemistry in the monitoring wells sampled at 100-K area of the Hanford Site

		199-K-36		199-K-110A		199-K-27		199-K-32A	
	Unit	Start	End	Start	End	Start	End	Start	End
Sampling Date		30-Mar-99	31-Mar-99	1-Apr-99	2-Apr-99	3-Apr-99	4-Apr-99	25-Mar-99	27-Mar-99
Depth to water	m	31.4		23.9		23.9		17.7	
Sampling depth	m	35.3		28.3		26.6		21.0	
Temperature	°C	12.9±1.1		10.7±1.3		12.7±2.0		12.1±4.2	
Conductivity	µS/cm	489	476	1048	942	859	775	318	304
pH	---	8.00±0.10		7.01±0.10		7.62±0.03		8.34±0.13	
DIC [a]	µmol/L	2764	2727	8881	8380	2976	2728	1833	1809
Alk	µmol/L	2814	2885	8321	7483	2942	2644	1857	1831
$p\text{CO}_2$ [b]	matm	661	376	15065	17701	2214	1795	664	599
SPM	mg/L	4.87	0.11	14.75	---	0.49	0.06	0.38	0.04
DO [c]	mg/L	9.8±0.6		6.52		10.6±1.9		9.8±0.9	
$\text{NO}_3^-+\text{NO}_2^-$	µg/L	4970	4750	6440		5980	6520	6910	5120
PO_4^{3-}	mM	12.01	14.40	9.02		10.52	9.20	10.34	10.62
F^-	mg/L	0.18	0.24			0.13	0.12		0.11
SO_4^{2-}	mg/L	51.80	63.60	6.24		21.90	20.70	33.00	30.00
K	mg/L	10.0	9.0	15.0		13.0	11.0	3.0	2.9
Ca[d]	mg/L	49.60		112.08		92.95		39.83	
Mg[d]	mg/L	19.02		28.88		31.26		7.74	
Al[d]	mg/L	1.67		0.67		0.52		6.31	
Fe[d]	µg/L	29.69		7.28		20.50		0.21	
Mn[d]	mg/L	1.86		19.92		3.11		0.02	
Cu[d]	µg/L	0.43		6.53		0.60		0.19	
Zn[d]	µg/L	2.20		2.84		1.18		4.08	
Cd[d]	µg/L	9.67		24.26		6.77		6.77	
Pb[d]	ng/L	48.49		16.45		4.26		3.69	

a) DIC – Dissolved inorganic carbon. b) $p\text{CO}_2$ – CO_2 partial pressure, calculated from pH and DIC.

c) DO – Dissolved oxygen. d) from filtrate (<0.2 µm)

Table 2. CFF blank evoluation pior and post Well 199-K-27 sampling at the Hanford 100 K area

	Concentration×10^4 atoms/kg± 1σ Error							
	^{239}Pu		^{240}Pu		^{241}Pu		^{242}Pu	
Prior sampling CFF blank	2.40	±0.17	0.24	---	---	---	---	---
Initial Q rinse	60.99	±1.19	8.57	±0.32	0.57	±0.06	0.53	±0.13
Acid rinse	9.08	±0.48	1.35	±0.20	0.51	---	3.16	±0.25
Base rinse	6.53	±0.49	0.78	---	0.53	---	1.05	---
Post-final CFF Q water blank	1.20	---	0.63	---	0.63	---	0.63	---
Q water lab blank	1.00	---	0.50	---	0.50	---	3.31	±0.26

Note: Field blanks and rinses proceeded in order- initial Q rinse, acid, base and final CFF Q water blank

.

Table 3. ^{239}Pu concentrations in unfiltered samples taken from Hanford Site 100 K area groundwater monitoring wells.

	[^{239}Pu]±1σ error			
Well #	**10^5atoms/kg**		**fCi/kg***	
199-K-36	4.06	±0.31	1.09	±0.08
199-K-110A	21.73	±0.49	5.85	±0.13
199-K-27	55.90	±2.82	15.06	±0.76
199-K-28	394.59	±11.33	106.28	±3.05
199-K-29	<1.		<0.3	
199-K-30	39.02	±1.69	10.51	±0.46
199-K-109A	470.98	±8.87	126.85	±2.39
199-K-32A	6.60	±0.42	1.78	±0.11
199-K-11	3.14	±1.43	0.85	±0.38
199-K-106A	6.60	±0.61	1.78	±0.16
199-K-107A	18.83	±1.25	5.07	±0.34
Columbia River**	90.06	±2.55	24.26	±0.69

*A half life of ^{239}Pu of 24131 yrs was used. fCi=10^{-15}Ci

** taken from ~ 60 m from shore downstream well 199-K-32A .

The location is ~46º14'75"N and 119º56'90"E

U.S. EPA Drinking water standard for Pu is 15 pCu/L.

Table 4. Size[a] and redox fractionated ^{239}Pu concentration and isotopic compositions.

							[Pu(III,IV)] ± 1σ error				[Pu(V,VI)] ± 1σ error			
	[^{239}Pu]±1σ error		atom ratio±1σ error				×10^{4}atom/kg				×10^{4}atom/kg			
Sample Fraction	×10^{4}atoms/kg		^{240}Pu/^{239}Pu		^{241}Pu/^{239}Pu[f]		^{239}Pu		^{240}Pu		^{239}Pu		^{240}Pu	
Well 199-K-27														
Filtrate[b]	92.64	±1.30	0.1451	±0.0035	0.0082	±0.0007	74.01	±0.93	7.86	±0.16	41.78	±0.49	5.79	±0.16
Permeate[b]	65.57	±1.33	0.1438	±0.0056	0.0082	±0.0017	23.89	±0.47	3.31	±0.13	35.46	±0.49	5.35	±0.16
Retentate[b]	755.49	±11.67	0.1447	±0.0035	0.0081	±0.0006	757.41	±10.04	109.38	±2.35	0.77	±0.03	0.10	±0.68
Colloidal[c]	12.4	(13%)	0.1447	±0.0041	---		---		---		---		---	
Colloidal[d]	27.1	(29%)[f]												
CFF mass balance[e]	84%	±2%												
Well 199-K-32A														
Filtrate[b]	3.17	±0.39	---		---		---		---		---		---	
Permeate[b]	2.96	±0.26	---		---		---		---		---		---	
Retentate[b]	19.84	±1.17	0.1067	±0.0258	---		---		---		---		---	
Colloidal[c]	0.3	(10%)	---		---		---		---		---		---	
Colloidal[d]	0.2	(7%)												
CFF mass balance[e]	103%	±13%												

a) Size fractions: Filtrate (< 0.2 μm); Permeate (< 1 kDa); Retentate (enriched in 1 kDa-0.2 μm colloids); Colloidal (1 kDa-0.2 μm)

b) CFF-processed samples. Concentration factors *(cf)* for Wells K-27 and K-32A were 55.7and 54.6, respectively.

c) [Colloidal]=([retentate]-[Permeate])/*cf* ; (% colloidal in parenthesis)

d) [Colloidal]=[Filtrate]-[Permeate] ; (% colloidal in parenthesis)

e) mass balance = [colloidal] + [permeate] / [filtrate]

f) Decay corrected to 1 Jan 2000.

Figure Captions

FIGURE 1. Locations of the Hanford Site 100 K area and the monitoring wells sampled in this study. Wells 199-K-36, K-110A, K-27 and K-32A were sampled more comprehensively than the other wells (see text).

FIGURE 2. Flow chart illustrating the collection and processing of groundwater samples from Hanford Site 100 K Area wells.

FIGURE 3. ^{239}Pu concentrations in 100K-Area wells of the Hanford Site. Data include both collections in 1997 and 1999.

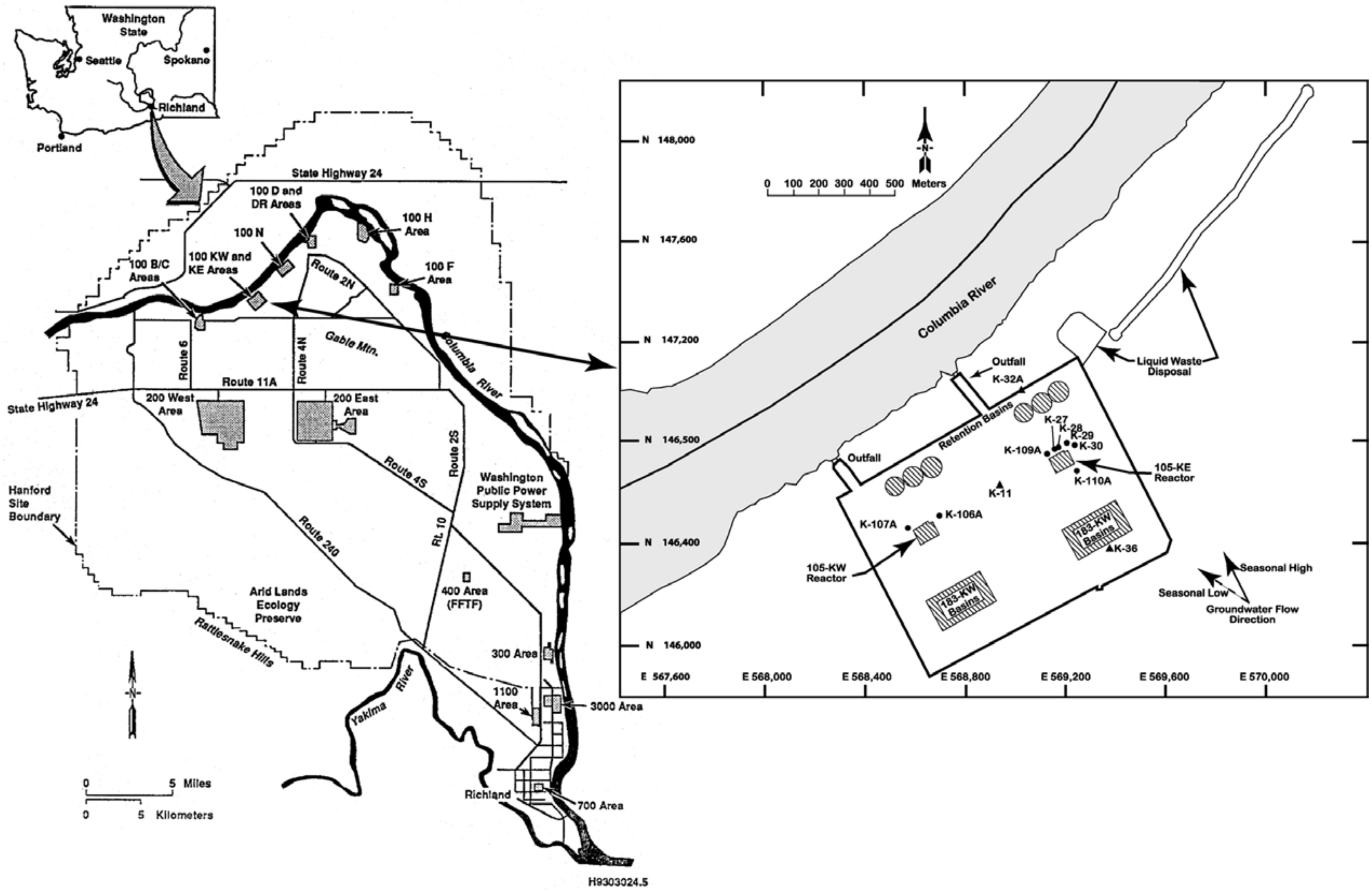
a) Transect following the groundwater flow towards the Columbia River.
b) Transect cross the reactors

FIGURE 4. Comparison of the sum of redox subfraction (Pu(III,IV)+Pu(IV)) and the independently measured Pu in whole water samples. Also shown is the percentage of reduced Pu(III,IV) in the filtrate sample fraction.

FIGURE 5. Pu isotope ratios of Hanford Site 100-K area groundwater samples. Global fallout ratio from Kelley et al. (1999).

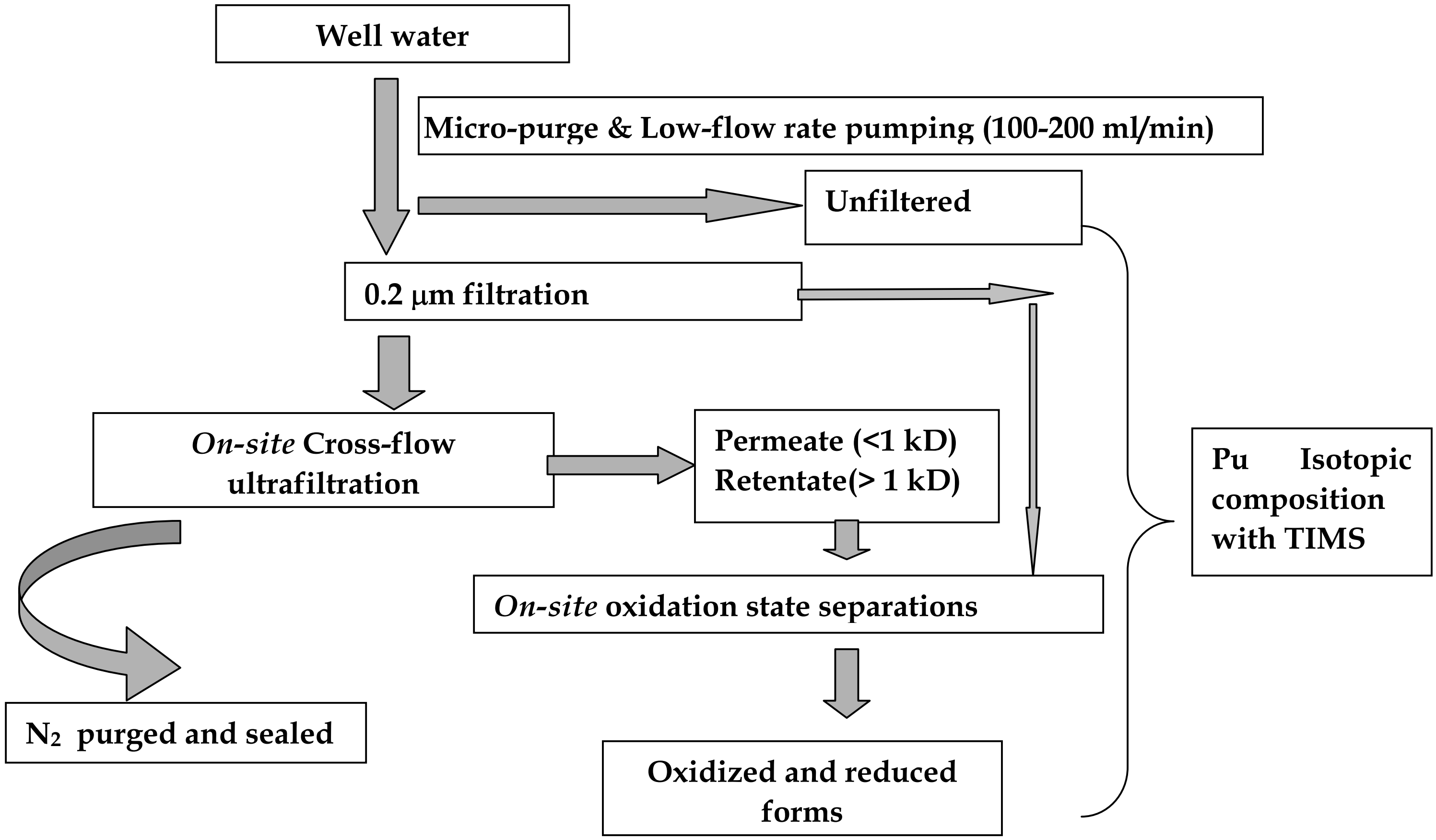
a) ^{240}Pu/^{239}Pu
b) ^{241}Pu/^{239}Pu. Subtraction data from Well K-27 including the ratio in redox fraction. The sample from K-109A is unfitered. Hanford Site refers to typical site operation discharge which contains 0.54% ^{241}Pu as of June 1968, equivalent to ^{241}Pu/^{239}Pu =0.00117 (Jan 2000).

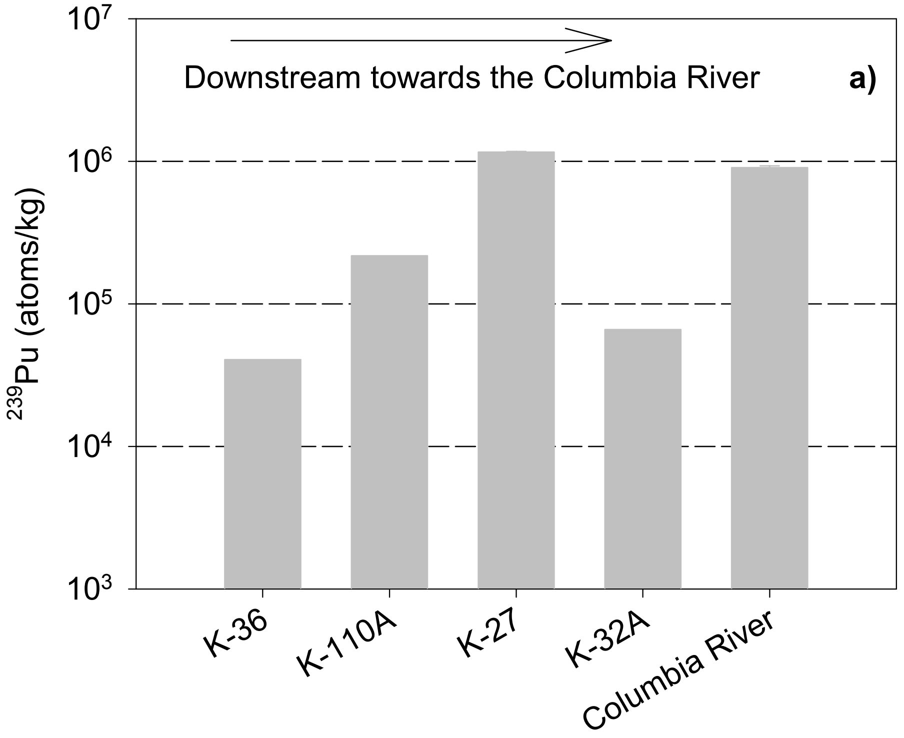
Figure 1.



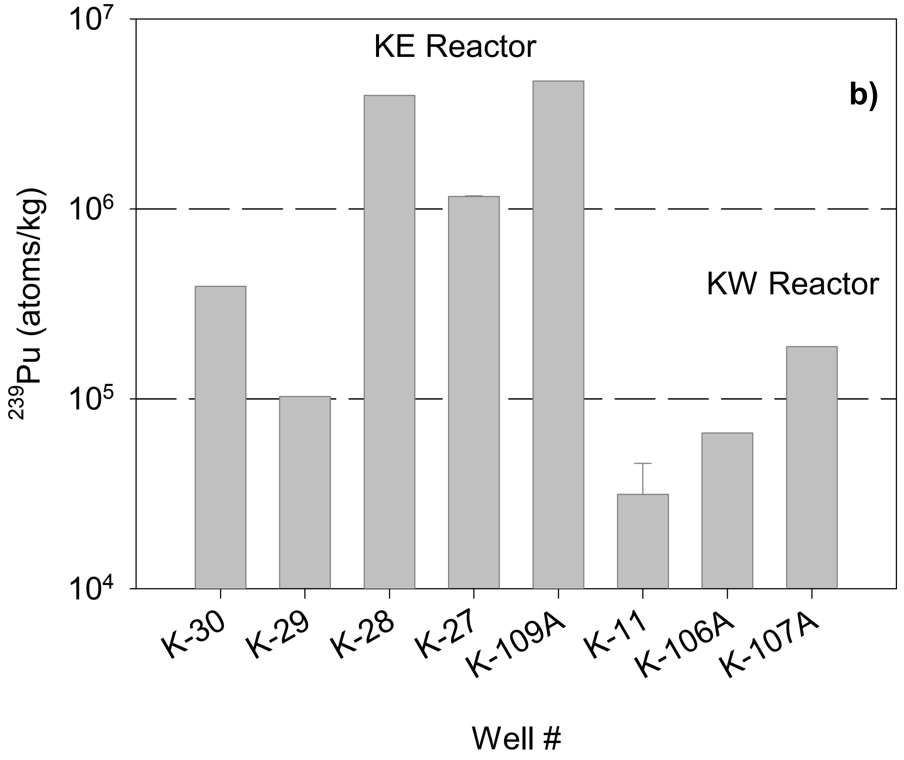
Washington State
Seattle
Spokane
Richland
Portland
State Highway 24
100 D and DR Areas
100 H Area
100 N
100 KW and KE Areas
100 B/C Areas
100 F Area
Route 2N
Gable Mtn.
Columbia River
Route 6
Route 4N
Route 11A
State Highway 24
200 West Area
200 East Area
Route 4S
Route 2S
Washington Public Power Supply System
Hanford Site Boundary
Route 240
RL 10
400 Area (FFTF)
Arid Lands Ecology Preserve
Rattlesnake Hills
300 Area
Yakima River
1100 Area
3000 Area
Richland
700 Area
N
0 5 Miles
0 5 Kilometers
H9303024.5
N 148,000
N 147,600
N 147,200
N 146,500
N 146,400
N 146,000
E 567,600
E 568,000
E 568,400
E 568,800
E 569,200
E 569,600
E 570,000
N
0 100 200 300 400 500 Meters
Columbia River
Outfall
K-32A
Retention Basins
Liquid Waste Disposal
K-27
K-28
K-29
K-30
K-109A
105-KE Reactor
K-110A
Outfall
K-11
K-107A
K-106A
183-KW Basins
K-36
105-KW Reactor
183-KW Basins
Seasonal High
Seasonal Low
Groundwater Flow Direction

Figure 2.


Well water
Micro-purge & Low-flow rate pumping (100-200 ml/min)
Unfiltered
0.2 μm filtration
On-site Cross-flow ultrafiltration
Permeate (<1 kD)
Retentate(> 1 kD)
Pu Isotopic composition with TIMS
On-site oxidation state separations
N_2 purged and sealed
Oxidized and reduced forms

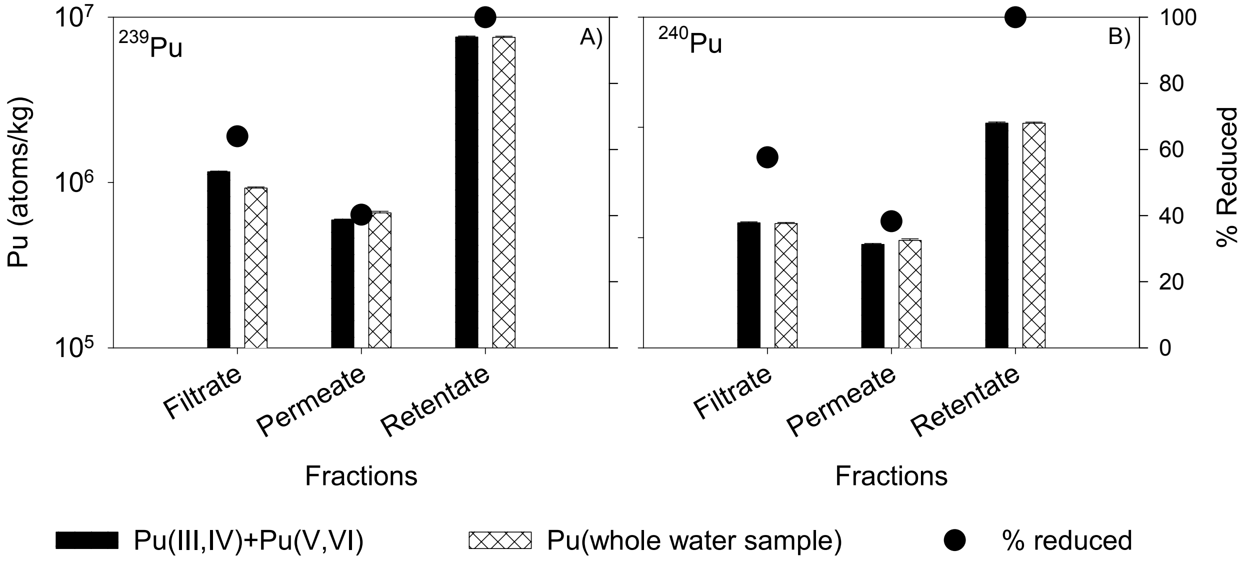


a)
Downstream towards the Columbia River
^{239}Pu (atoms/kg)
10^7
10^6
10^5
10^4
10^3
K-36
K-110A
K-27
K-32A
Columbia River



b)
KE Reactor
KW Reactor
^{239}Pu (atoms/kg)
10^7
10^6
10^5
10^4
K-30
K-29
K-28
K-27
K-109A
K-11
K-106A
K-107A
Well #

Figure 4.


10^7
10^6
10^5
Pu (atoms/kg)
239Pu
A)
240Pu
B)
100
80
60
40
20
0
% Reduced
Filtrate
Permeate
Retentate
Fractions
Filtrate
Permeate
Retentate
Fractions
Pu(III,IV)+Pu(V,VI)
Pu(whole water sample)
% reduced

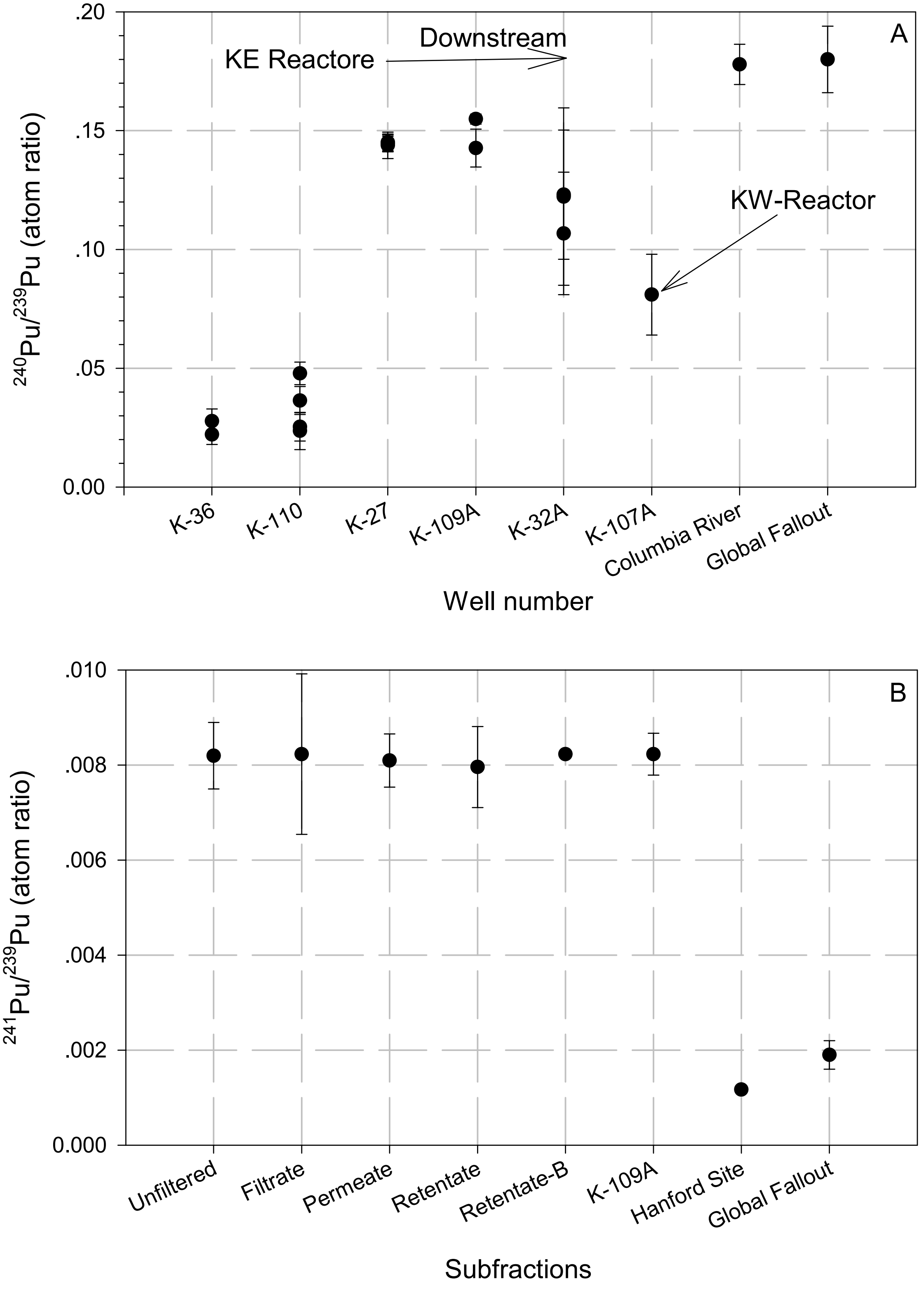

A
^{240}Pu/^{239}Pu (atom ratio)
.20
.15
.10
.05
0.00
KE Reactore
Downstream
KW-Reactor
K-36
K-110
K-27
K-109A
K-32A
K-107A
Columbia River
Global Fallout
Well number
B
^{241}Pu/^{239}Pu (atom ratio)
.010
.008
.006
.004
.002
0.000
Unfiltered
Filtrate
Permeate
Retentate
Retentate-B
K-109A
Hanford Site
Global Fallout
Subfractions

Figure 5.

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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}Pu/^{239}Pu ratio in the upstream control well signifies a Pu source other than global fallout and indicates reactor-produced Pu. Elevated ^{240}Pu/^{239}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 (^{3}H). 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 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 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}Pu/^{239}Pu atom ratios usually <0.07 (*7*). Global weapons testing fallout has an average ^{240}Pu/^{239}Pu ratio of 0.18 (*8*). High and low irradiation conditions in reactors would result in ^{240}Pu/^{239}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 ^{3}H 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}Pu/^{239}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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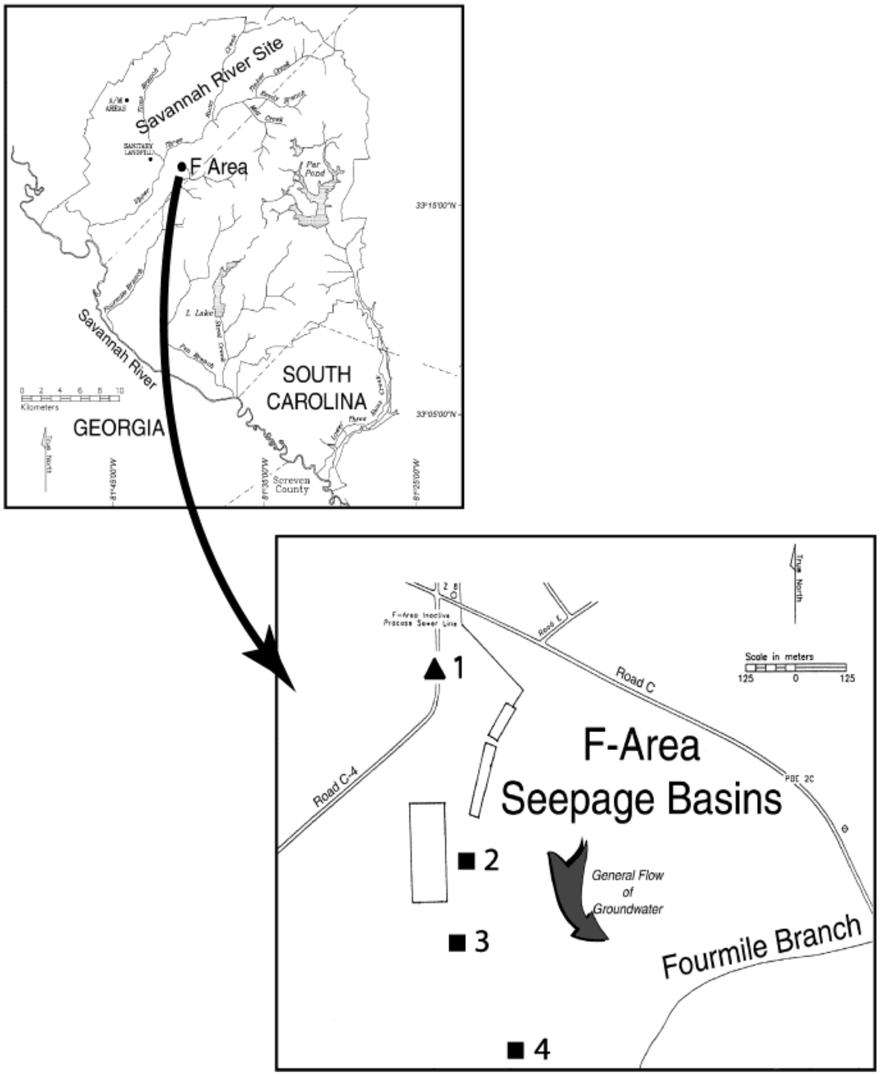

FIGURE 1. Locations of the SRS F-area seepage basins and the four monitoring wells sampled in this study. The Westinghouse Savannah River Co.'s designated names for wells 1−4 are FSB-108D, FSB-92D, FSB-78, and FSB-79, respectively.

(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}Pu/^{239}Pu and 0.0003 for ^{242}Pu/^{239}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 ($Pu_{colloidal}$, 1 kDa − 0.2 μm) is calculated from the Pu concentrations measured in the permeate ($Pu_{permeate}$) and retentate ($Pu_{retentate}$) 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:

$$[Pu_{colloidal}] = ([Pu_{retentate}] - [Pu_{permeate}])/cf \qquad (1)$$

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, 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 $Cr_2O_7^{2-}/SO_4^{2-}$ 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}Pu/^{244}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

$$C_{reduced} = (R_o - R_{oxidized})/(R_{reduced} - R_{oxidized}) \qquad (2)$$

and that

$$C_{oxidized} = R_{oxidized}(R_o - R_{reduced})/(R_{oxidized} - R_{reduced}) \qquad (3)$$

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 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 ^{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 $>\sim10^8$ 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 (±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*).

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

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 characteristics of the affected groundwater are high $p\mathrm{CO_2}$ 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.

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	μS/cm	148.7	744	926	856
pH		6.807	4.034	3.850	4.107
DIC[a]	μM	543	1170	817	631
$p\mathrm{CO_2}$[b]	μatm	4007	32492	23738	17499
DO[c]	mg/L		2.70	0.58	3.97
$\mathrm{NO_3^-} + \mathrm{NO_2^-}$	mg/L	1.22	47.60	98.30	139.00
$\mathrm{PO_4^{3-}}$	mg/L	0.40	0.005	0.007	0.006
$\mathrm{F^-}$	mg/L		0.30	0.15	0.17
$\mathrm{SO_4^{2-}}$	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	μg/L	0.34	2.4	5.5	6.2
Zn	μg/L	28.7	61.0	61.0	61.0
Cd	μg/L	0.37	6.90	9.90	3.70
Pb	μg/L	1.32	2.20	1.80	0.56
Fe	μg/L	8.5	15.0	44.0	239.0

[a] DIC, dissolved inorganic carbon. [b] $p\mathrm{CO_2}$, $\mathrm{CO_2}$ partial pressure, calculated from pH and DIC. [c] DO, dissolved oxygen.

Pu Concentration and Isotopic Composition. ^{239}Pu levels are lowest (∼10^6 atoms/kg for the unfiltered sample fraction and ∼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}Pu/^{239}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 (∼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}Pu/^{239}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 ^{239}Pu 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 ^{240}Pu ingrowth from decay of the most abundant (in the F-area aquifer) and shortest lived ($t_{1/2} = 18.10$ years) transplutonium isotope, ^{244}Cm (*15*).

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 years) 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 years, [^{245}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 isotopes in the F-area aquifer (Table 3). Moreover, for the ^{244}Cm case, the availability of historical results, derived from $^{243+244}$Cm 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 ^{244}Cm/kg is sensibly equivalent to 1 Bq $^{243+244}$Cm/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 on the basis of $^{243+244}$Cm measurement results, and an estimated ^{243}Am/^{244}Cm 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, ^{239}Pu (*42*) and, in the other, Pu 96%-enriched in the ^{242}Pu isotope (*43*) and assuming a 31-year decay period (*15*), we can expect that in May 1998 in the F-area aquifer ^{245}Cm/^{244}Cm and ^{246}Cm/^{244}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 alteration of the original atom ratio expected in the absence of ingrowth. To show these perturbations, we have compared the Table 3 atom ratio

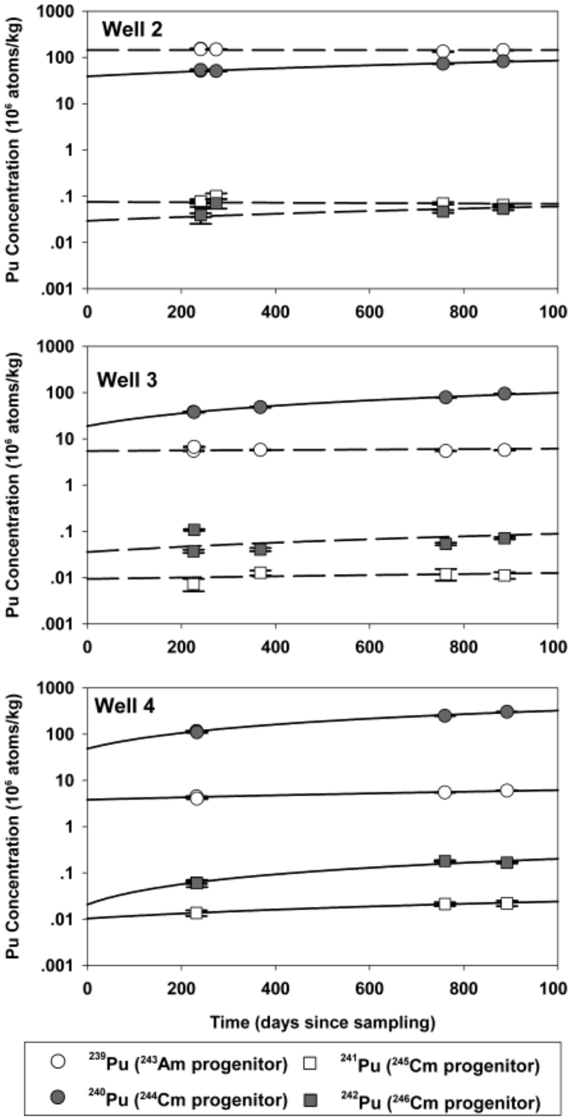

FIGURE 2. Plots of ingrowth of Pu isotopes in permeate ($<$1 kDa) and filtered ($<$0.2 μm) groundwater samples from SRS F-area wells. This ingrowth resulted from decay of accompanying transplutonium progenitor isotopes in the samples in accordance with the general equation for decay (eq 4, see text), 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}Pu/^{239}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}Pu/^{239}Pu ratio (13 ± 2) exceeded the estimated ratio of SRS Pu ($\sim$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}Pu/^{239}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}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 coincidently, 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}Pu/^{239}Pu and ^{242}Pu/^{239}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}Pu/^{239}Pu ratios. Note that at well 2 the ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}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}Pu/^{239}Pu and ^{242}Pu/^{239}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}Pu/^{239}Pu and ^{242}Pu/^{239}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 = [solid]/[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 1 σ 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			*3.2[c] ± 0.6*		*3.2[c] ± 0.6*		3.2 ± 0.6	($n = 4$)
[^{244}Cm]	10^6 atoms/kg			468 ± 35	($n = 5$)	803 ± 35	($n = 4$)	2750 ± 155	($n = 4$)
^{245}Cm/^{244}Cm	atom ratio			*0.026[c] ± 0.002*		*0.026[c] ± 0.002*		0.026 ± 0.002	($n = 3$)
^{246}Cm/^{244}Cm	atom ratio			*0.16[c] ± 0.03*		*0.16[c] ± 0.03*		0.16 ± 0.03	($n = 4$)

[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 ^{239}Pu concentration average is the mean of the four measurement results, weighted to their associated uncertainties. The ^{240}Pu level in this well was determined only once; hence, the ^{240}Pu/^{239}Pu atom ratio shown is from a single measurement. [c] In wells 2 and 3, the levels of progenitor isotopes ^{243}Am, ^{245}Cm, and ^{246}Cm, relative to ^{244}Cm, are indicated in italics and assumed to be the same as in well 4. [d] bd, below detection (i.e., <10^4 atoms).

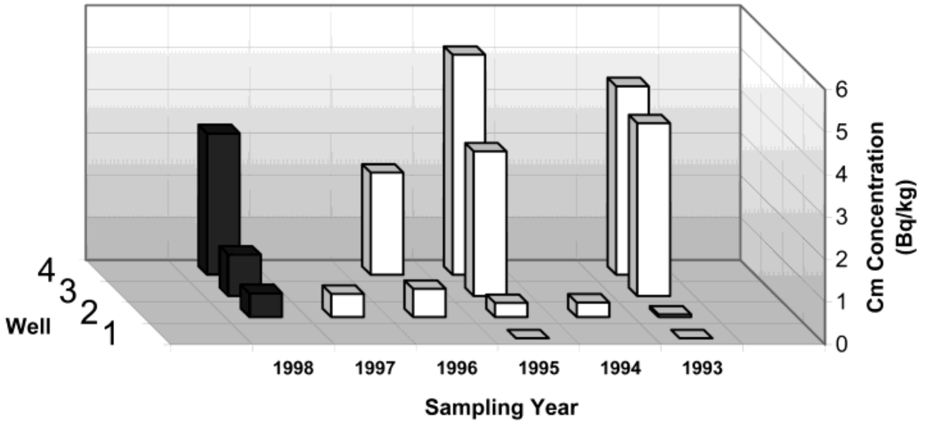

FIGURE 3. Comparison of ^{244}Cm α-activity levels (Bq/kg) found in filtered (<0.2 μm) SRS F-area well water samples collected between May 6 and 15, 1998, in this study with $^{243+244}$Cm levels (Bq/L) in unfiltered samples reported by Westinghouse Savannah River Co. (*18*−*23*).

differences 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}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}Pu(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 ^{239}Pu(V/VI) and ^{240}Pu(V/VI) fractional abundances were measurably different remains to be explained, although this difference may be related to the fact that most of the ^{240}Pu in the aquifer was formed in-situ from ^{244}Cm 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 ^{239}Pu and ^{240}Pu 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 ^{239}Pu isotope migrated beyond well 2, and how downstream of well 2 the preponderance of the Pu present was in-situ-formed ^{240}Pu.

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 ^{239}Pu or ^{240}Pu isotope exceed 10^6 atoms/kg, nor did the colloid-associated Pu fractional abundance (i.e., $\mathrm{Pu_{colloid}/Pu_{filtered}}$) 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 establish only upper limits for the colloid-associated ^{239}Pu and ^{240}Pu concentrations

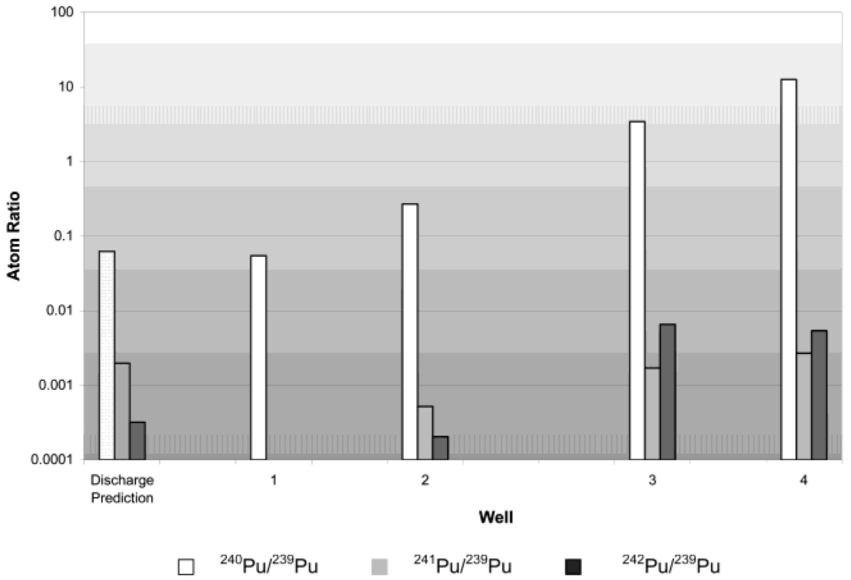

FIGURE 4. Comparison of Pu isotopic compositions in filtered (<0.2 μm) SRS F-area well water samples collected in May 1998 with an estimated composition provided by Holcomb (*15*) as being indicative of SRS reactor-produced Pu.

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

well	sampling date	time[a] (days)	Pu(III,IV)[b] concentration ± 1σ error (10^6 atoms/kg) ^{239}Pu	^{240}Pu	time[a] (days)	Pu(V,VI)[c] concentration ± 1σ error (10^6 atoms/kg) ^{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) ^{239}Pu and ^{240}Pu

parameter	well 1	well 2	well 3	well 4
	ingrowth-corrected average ± 1σ error[a]			
Pu Concentration (10^6 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/IV)]	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 ^{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 2−4 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 ^{239}Pu and ^{240}Pu (1 kDa − 0.2 μM)

parameter	well 1	well 2[b]	well 3	well 4[c]
	ingrowth-corrected average ± 1σ error[a]			
Colloid-Associated Pu Concentration (10^6 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$_{\text{colloidal}}$/^{239}Pu$_{\text{filtered}}$	0.008 ± 0.003	<0.004	0.032 ± 0.004	0.031 ± 0.005
^{240}Pu$_{\text{colloidal}}$/^{240}Pu$_{\text{filtered}}$		<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 ^{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. [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$_{\text{colloidal}}$. 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 ^{240}Pu in well 4 was determined by nonlinear regression analysis to be (−0.06 ± 0.20) × 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 × 10^6 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 ^{240}Pu. Typically, this isotope was not recognized as being different from ^{239}Pu, in part because α spectrometric methods measure combined ^{239}Pu and ^{240}Pu activity (^{239,240}Pu), and so all ^{239,240}Pu was mistakenly presumed to derive from Pu seepage basin discharges.

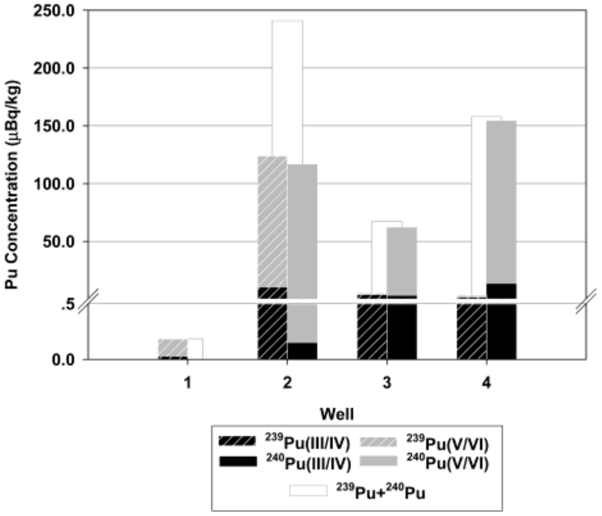

FIGURE 5. Comparison of concentrations (α-activity units of μBq/kg) of ^{239}Pu and ^{240}Pu isotopes in reduced (III/IV) and oxidized (V/VI) forms with the sum of ^{239}Pu and ^{240}Pu in filtered sample fractions (<0.2 μm) that were not redox processed.

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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Size-fractionated plutonium isotopes in a coastal environment

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Abstract

We have examined the distribution of individual Pu isotopes (^{239}Pu, ^{240}Pu, and ^{241}Pu) in seawater from the Gulf of Maine (GOM). Samples were size-fractionated with a 1 kD cross-flow ultrafiltration (CFF) membrane. Subfractioned samples were radiochemically purified and Pu isotopes were analyzed using a three-stage thermal ionization mass spectrometer (TIMS). To our knowledge, this is the first time that both size class and Pu isotopic data have been obtained for seawater samples. Within measurement uncertainties a single ^{240}Pu/^{239}Pu atom ratio of 0.18 was found for all sample collection depths and sample size fractions. This signifies a current, single Pu source in GOM waters, namely global fallout, and suggests that no measurable isotopic fractionation occurred during CFF processing. The majority of Pu was found in the low molecular weight fraction (<1 kD). Colloidal Pu varied from 8% of the total in surface waters to <1% in the deepest (250 m) seawater sample. Evidence suggests that the vertical distribution of Pu in GOM is primarily controlled by conservative mixing processes. The high Pu fraction found in the low molecular size fraction implies that most of the Pu is in the non-particle-reactive oxidized fraction, and is consistent with the conservative Pu behavior. The activity levels are in agreement with other studies which show a slow decrease in Pu with time due to continued mixing and relatively slow particle removal.

Keywords: Plutonium; Isotopes; Colloids; Cross-flow ultrafiltration; Gulf of Maine

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1. Introduction

Plutonium had been spread world-wide through above-ground nuclear weapons testing during the 1950s and early 1960s (Perkins and Thomas, 1980; Harley, 1980; Sholkovitz, 1983) and through various accidental releases and reprocessing of nuclear materials (Johnson, 1984; Kim, 1986; Guéguéniat, Germain & Métivier, 1996). The release of artificial radionuclides in general is of environmental concern, but these radionuclides have also become a useful tool for tracing geochemical processes in marine research (Broecker & Peng, 1982; Kershaw & Woodhead, 1991). Consequently, considerable effort has been devoted to the study of radionuclides in the marine environment. However, as Hamilton (1998) recently stated, "In paying attention to the specific needs of radiological protection and the protection of man and the environment from ionizing radiation, insufficient attention has been paid to the identification of prime processes which control the distributions of radionuclides". Moreover, most of the results for Pu in the environment are based upon the measurement of combined activities of ^{239}Pu and ^{240}Pu by alpha spectrometry. Since alpha spectrometry is not able to distinguish the decay energies of ^{239}Pu and ^{240}Pu, these results can rarely identify local Pu sources (such as close-in fallout or reprocessing waste streams) and must assume an identical geochemical behavior of Pu from its various sources. Source information for Pu is best achieved using high-sensitivity mass spectrometry techniques (e.g. TIMS or the less sensitive inductively coupled plasma mass spectrometry).

It has become increasingly evident that Pu transport in the marine environment depends dramatically on its sources (global fallout vs. close-in fallout, Buesseler and Sholkovitz, 1987; Buesseler, 1997) and its speciation (Baxter, Fowler & Povinec, 1995). While oxidation states of Pu in seawater have been measured (e.g., Nelson and Lovett, 1978, 1981; Orlandini, Penrose & Nelson, 1986; Choppin and Kobashi, 1990; Mitchell et al., 1991, 1995), its size fractionation and partitioning are less commonly studied. The lack of size partitioning data is primarily associated with its extremely low concentration (subfemtogram, or $<10^{-15}$ g/l) in seawater and even lower concentration in the fractionated samples. Thus highly sensitive analytical techniques are required. Size-fractionation utilizing CFF techniques, which allows for processing of multi-liter sample volumes, was only recently introduced to the marine sciences, in the early 1990s (Benner, 1991; Buesseler et al., 1996; Guo & Santschi 1997; Dai et al., 1998). CFF is the only practical technique able to process large-volume samples and, as shown in this paper, low blanks and reasonable mass balances for Pu can be achieved through careful application of this tool. The combination of TIMS and CFF provides us therefore with a unique approach for studying Pu sources and host (e.g., particles, colloids) size distribution in the marine environment.

Aarkrog (1988) summarized existing Pu studies in the ocean and concluded that Pu is highly associated with particles/sediments. Thus, Pu is expected to be rapidly removed from the water column, particularly in highly particle-laden coastal waters. We report in this paper a novel data set from the GOM showing that a dominant fraction of Pu passes through our 1 kD CFF membrane. We suggest that even in coastal waters, Pu is relatively soluble and appears to have a longer residence time in the water column than earlier studies would have predicted.

2. Materials and methods

2.1. Study area

The Gulf of Maine is a semi-enclosed coastal sea on the Northwest Atlantic shelf. Water circulation within the GOM is complex. Within Wilkinson Basin, surface waters generally flow in a cyclonic pattern and Atlantic slope waters enter the GOM through the Northeast channel (Brooks, 1992). This slope water affects the distribution of Pu in the Gulf.

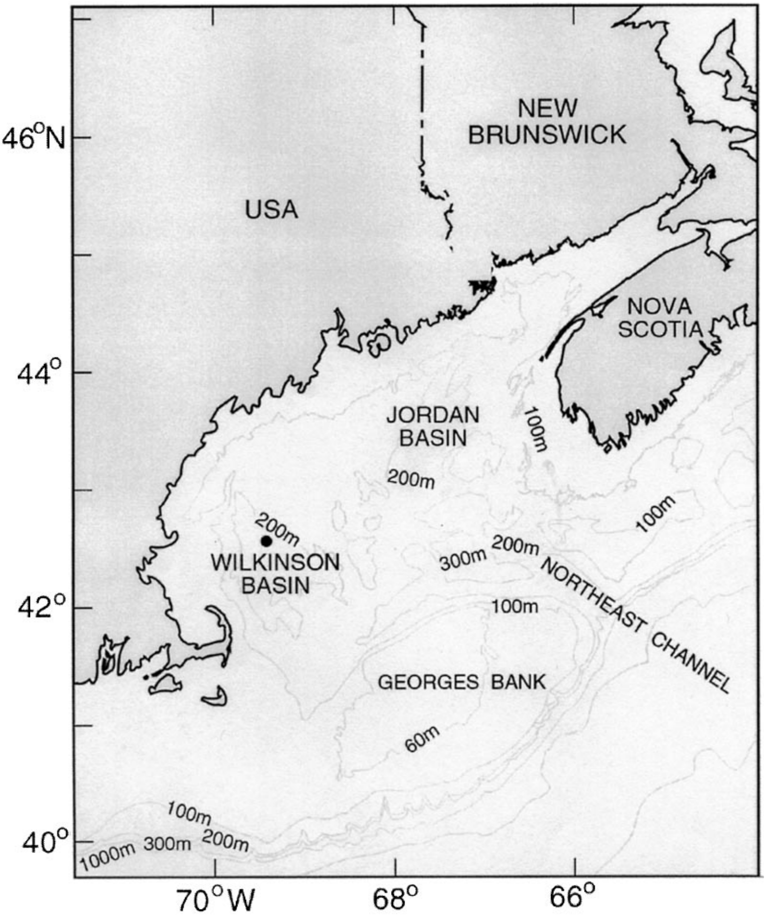

Fig. 1. Map showing the location of the Gulf of Maine and the sampling station at the Wilkinson Basin.

2.2. Sampling

Seawater samples were collected in the GOM from Wilkinson Basin at a station located at 42°29.1N and 69°43.7W (Fig. 1) aboard the R/V *Cape Hatteras* in July, 1997. The total water depth of the sampling station is 272 m. Samples were collected from 30 Niskin bottles and pumped directly via Teflon tubing through acid-cleaned polycarbonate Nuclepore filters (142 mm diameter; 1.0 μm pore size) and subsequently through the CFF system. Unfiltered samples were also collected and particulate Pu concentrations were calculated by difference between the unfiltered and filtered samples.

We shall use the following terms in the text. “Permeate” is the fraction passing through a CFF membrane while “retentate” is the fraction retained by the membrane. We define the colloidal fraction as the material which passes through a 1.0 μm prefilter and is retained by our 1 kD CFF membranes. Particulate is the fraction retained by a 1 μm Nuclepore prefilter. The total dissolved fraction is that which passes through this prefilter.

2.3. CFF processing

Detailed CFF processing procedures are described in Dai et al. (1998). Briefly, our CFF system is composed of a Flojet polypropylene diaphragm pump, plumbing (mostly of Teflon) and Millipore Prep/Scale^{TM}-TFF PLAC regenerated cellulose CFF membranes. We used 3 CFF membranes (nominal molecular weight cutoff = 1 kD) in parallel (surface area 18 ft^2) to increase the ultrafiltration rate to about 150 ml/min. The prefiltered seawater (through 1 μm Nuclepore filters) was continuously fed into a 4 l fluorinated polyethylene bottle. The membrane pressure was maintained at ~14–16 psi during CFF operation.

Before and after a typical sample run, the CFF system was cleaned by flushing with > 20 L nano-pure water (referred to as Q-water hereafter) followed by 0.01 N NaOH and 0.01 N HCl solutions made from the same Q-water. The base or acid solution was recirculated for at least one hour followed by rinsing with Q water until pH~7. These cleaning steps were followed by preconditioning with prefiltered seawater (4–6 l). The cleaning was conducted just prior to each sample run.

“Integrated” refers to samples of permeate and retentate collected from the CFF system for Pu isotopes at the end of sampling.

2.4. Colloidal concentration

The colloidal Pu concentration is calculated based on the Pu concentrations measured in the integrated permeate and retentate samples, and the concentration factor cf.

$$[\mathrm{Pu}_{\mathrm{colloidal}}] = ([\mathrm{Pu}_{\mathrm{retentate}}] - [\mathrm{Pu}_{\mathrm{permeate}}])/\mathrm{cf}, \tag{1}$$

$$\mathrm{cf} = (\text{retentate volume} + \text{permeate volume})/\text{retentate volume} \tag{2}$$

The mass balance, or recovery (R%) can be calculated by comparing the sum of the colloidal and permeate Pu concentrations with the concentration of Pu in the initial source solution (prefiltrate).

2.5. Analysis

Size-fractionated samples were collected in acid-cleaned 4 l fluorinated polyethylene bottles and acidified with ultrapure HNO_3 to pH~2 followed by addition of standardized ^{244}Pu tracers and $FeCl_3$ (~1 mg Fe/1 l sample). Nominal aliquot sizes taken for Pu analyses were about 4 kg except for the retentate fraction, in which case 1.5 kg aliquots were used. Samples were allowed to equilibrate for >48 h while being slowly stirred at ~40°C in order to remove CO_2 in the sample. Carbonates which form soluble complex compounds with Pu must be absent prior to the co-precipitation. Pu was then co-precipitated with iron hydroxide by adjusting the pH to 8–9 with ultrapure NH_4OH (Seastar). Samples were allowed to stand overnight and the precipitates were filtered onto acid-cleaned Duropore filters (47 mm diameter; 0.45 μm pore size, Millipore). After digestion, samples were radiochemically purified by running sequentially through two anion exchange columns (AG1-X4, 100-200 mesh, Bio-Rad Lab., Richmond, CA). The first is a 4 ml bed-volume anion exchange column, and the second is a 100 μl micro-volume column. Pu was eluted with 1.2 M HCl onto a Teflon pad. Next, samples were even more stringently purified by employing, instead of a column, a single 800 μm diameter resin bead. The maximum volume of analyte used in this operation, which is carried out under a microscope, is 20 μl. Finally, Pu was incorporated in a single, nominally 150 μm diameter resin bead from 1 μl of 7.5 M HNO_3. The bead was transferred into the trough of a rhenium filament formed into a V-shape as a mass spectrometry ion source. During all procedures, only ultrapure acids (Seastar or Ultrex) were used.

The mass spectrometer is a three-stage instrument with a pulse-counting ion detection system (Lagergren and Stoffels, 1970). The instrument is equipped with a sliding-shaft vacuum lock that enables precise positioning of the mass spectrometer source. Masses were scanned by sweeping the magnetic field. The bead was pyrolyzed, the filament carburized, and the mass spectrometry measurements conducted using standard Pacific Northwest National Laboratory (PNNL) operating procedures. The high sensitivity associated with TIMS analysis enables detection of extremely low atom concentrations of elements of interest. To insure the absence of measurable ($>10^4$ atoms) contamination, process blanks were liberally interspersed with samples.

3. Results and discussion

3.1. Process blank and CFF mass balance

In the light of our previous experience with the application of CFF to thorium studies (Dai et al., 1998), we carefully evaluated CFF performance. The two crucial

Table 1
CFF system blank of Pu isotopes (μBq/kg)

Sample	^{239}Pu	^{240}Pu	^{241}Pu
Permeate blank	<0.02	<0.02	<0.007
Retentate blank[a]	<0.02	<0.008	<0.008

[a] Retentate blank refers to Q-water being concentrated by a factor of 4 with the CFF.

issues related to CFF's applicability are system blanks and mass balance issues (Buesseler et al., 1996; Dai et al., 1998). After careful cleaning, we achieved Pu blanks that were at or below TIMS detection limits, i.e. 0.02 μBq/kg. The blanks were not significant with respect to Pu isotope levels subsequently measured in samples (see Table 1).

CFF mass balance provides a first-order check on sorptive losses. The recoveries of Pu in this study were generally 100 ± 10% (Table 2), indicating that on balance no significant losses or contamination occurred during the CFF processing of seawater samples. For the 37 m sample, the CFF mass balance was only 86 ± 3% for ^{239}Pu. The concentration factor (cf) for this sample was the highest among the samples processed (12.7 vs. ≤ 10). We have noted previously that losses of high molecular weight material onto the CFF membranes may occur preferentially at higher CFF concentration factors (Dai et al., 1998).

3.2. Pu isotopic ratios

Listed in Table 3 are the Pu isotopic ratios in the different size fractions. The atom ratios of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu were similar in all fractions. We do not expect there to be any fractionation related to CFF processing and these uniform data confirm this expectation. When plotted it is easy to see that the measured ^{240}Pu/^{239}Pu atom ratios are indistinguishable from those observed for global fallout in the Northern Hemisphere (0.18 ± 0.014, Kelley, Bond & Beasley, 1999), indicating that Pu in the GOM originated primarily from global fallout (Fig. 2). This is similar to most other water-column Pu data, except in the vicinity of close-in fallout sources, such as the Marshall Islands (Buesseler, 1997) and Mururoa Atoll (Chiappini, Millies-Lacroix, Le Petit & Poiturier, 1998), where anomalous ^{240}Pu/^{239}Pu ratios have been found. There were only 4 colloidal Pu samples with sufficient signal to quantify ^{240}Pu/^{239}Pu, and two of these (37 and 65 m) are slightly lower than the global fallout average; but within the errors these data overlap with the soil data (Fig. 2). Using the simple two end-member mixing model of Krey et al. (1976), a ^{240}Pu/^{239}Pu ratio of 0.170 requires ~2% of Nevada Pu being contributed (Nevada ^{240}Pu/^{239}Pu = 0.035, Krey et al., 1976). This study shows that most of ^{240}Pu/^{239}Pu ratios in the GOM water column is >0.170, hence there is no evidence that there remains sufficient Nevada Pu in the water column to lower the bulk water-column ^{240}Pu/^{239}Pu ratio while low-ratio Pu has been detected in the sediments off the NE US coast from Nevada fallout (Buesseler and Sholkovitz, 1987).

Table 2

^{239}Pu concentrations in different size fractions of Gulf of Maine samples[a]

Depth m	Unfiltered μBq/kg ± 1σ error		Total dissolved μBq/kg ± 1σ error		Permeate μBq/kg ± 1σ error		Colloidal μBq/kg ± 1σ error		% of unfiltered μBq/kg ± 1σ error		% of total dissolved fraction ± 1σ error		Particulate μBq/kg ± 1σ error		% of unfiltered fraction ± 1σ error		CFF recovery % ± 1σ error	
1	3.98	0.05	3.83	0.05	3.72	0.05	0.17	0.01	4.17	0.25	4.34	0.26	0.16	0.07	4.0	1.7	101.5	1.8
15[b]	4.21	0.05	2.81	0.06	**2.46**	**0.32**	0.35	0.03	8.25	0.79	12.35	1.21	1.40	0.08	33.2	1.9	**100.**	**10.**
37	4.76	0.30	4.46	0.12	3.54	0.08	0.28	0.02	5.87	0.50	6.27	0.40	0.30	0.32	< 14	—	85.5	2.9
65	5.58	0.08	5.33	0.08	4.47	0.08	0.41	0.02	7.36	0.40	7.71	0.42	0.25	0.11	4.5	2.0	91.6	2.0
200	8.15	0.08	7.40	0.06	17.48	0.06	0.24	0.01	2.92	0.16	3.22	0.18	0.75	0.10	9.2	1.3	104.3	1.2
250	9.07	0.12	8.01	0.11	7.61	0.14	0.00	0.02	< 0.5	—	< 0.5	—	1.06	0.16	11.6	1.8	94.9	2.0

[a] Size fractions: total dissolved, < 1 μm; permeate, < 1 kD; colloidal, 1 kD–1 μm; particulate, > 1 μm. A ^{239}Pu half-life of 24119 ± 27 y was used to convert the measured atom concentrations to the activity units (Bg/kg water) presented here.

[b] The permeate fraction of the 15 m sample was lost during preparation for measurement. The concentration value for this fraction is shown in bold type and was calculated in accordance with Eq. (1) (see text) from the ^{239}Pu concentration in the retentate fraction, the measured concentration factor, and an assumed value for the CFF recovery of 100 ± 10%, which is also shown in bold type.

Table 3
Pu isotopic ratios in different size fractions of Gulf of Maine samples[a]

Depth m	Unfiltered atom ratio	± 1σ error	Total dissolved atom ratio	± 1σ error	Permeate atom ratio	± 1σ error	Colloidal atom ratio	± 1σ error	Particulate atom ratio	± 1σ error
^{240}Pu/^{239}Pu										
1	0.1892	0.0027	0.1873	0.0030	0.1830	0.0031	0.186	0.023	0.1748	0.0046
15[b]	0.1833	0.0026	0.1801	0.0054	**0.177**	**0.034**	0.204	0.028	0.1794	0.0029
37	0.194	0.010	0.1760	0.0070	0.1831	0.0062	0.157	0.023	0.1809	0.0045
65	0.1808	0.0028	0.1769	0.0032	0.1823	0.0028	0.169	0.017	0.26	0.17
200	0.1837	0.0017	0.1844	0.0015	0.1831	0.0014	0.179	0.019	0.176	0.042
250	0.1803	0.0024	0.1790	0.0025	0.1826	0.0035	—	—	0.190	0.050
^{241}Pu/^{239}Pu[c]										
10.0026	0.0005	0.0025	0.0005	0.0025	0.0006	N/A	N/A	0.0025	0.0012	
15	0.0027	0.0005	0.0025	0.0008	N/A	N/A	N/A	N/A	0.0030	0.0008
37	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
65	0.0026	0.0009	0.0028	0.0007	0.0030	0.0005	N/A	N/A	N/A	N/A
200	0.0025	0.0002	0.0026	0.0003	0.0028	0.0003	N/A	N/A	N/A	N/A
250	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	N/A	N/A	N/A	N/A

[a] Size fractions: Total dissolved, <1 μm; permeate, <1 kD; colloidal, 1 kD–1 μm; particulate, >1 μm.

[b] The permeate fraction of the 15 m sample was lost during preparation for measurement. The ^{240}Pu/^{239}Pu atom ratio value for this fraction is shown in bold type and was calculated in accordance with Eq. (1) (see text) from the ^{239}Pu and ^{240}Pu concentrations in the retentate fraction, the measured concentration factor, and an assumed value for the CFF recovery of $100 \pm 10\%$.

[c] ^{241}Pu was decay corrected to January 1, 1998.

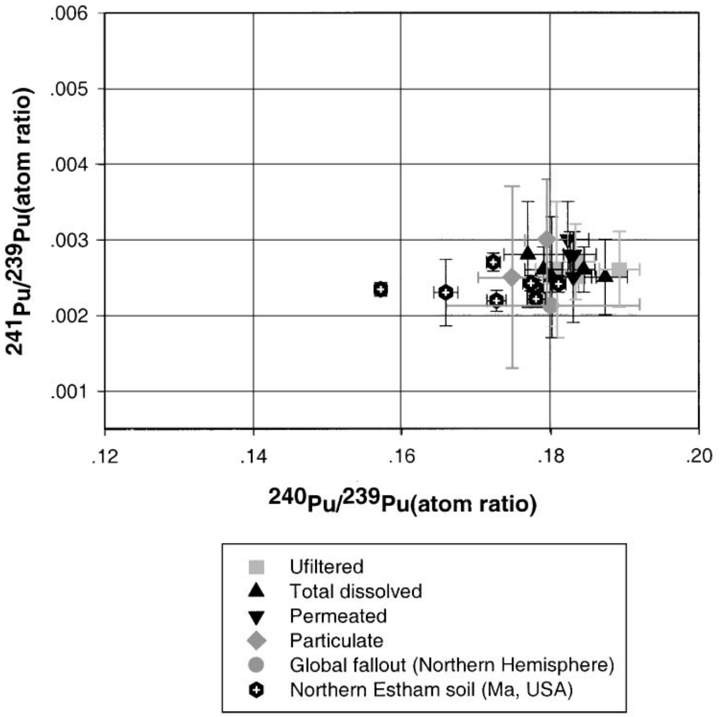

Fig. 2. Plot of ^{240}Pu/^{239}Pu against ^{241}Pu/^{239}Pu atom ratio in fractionated GOM seawater samples. Also shown are the global fallout average ratios (^{240}Pu/^{239}Pu $= 0.18 \pm 0.01$, ^{241}Pu/^{239}Pu $= 2.13 \times 10^{-3} \pm 0.28 \times 10^{-3}$, compiled by Kelley et al., 1999) and ratios in Northern Estham soil samples (data from Kelley).

The ^{241}Pu/^{239}Pu ratio is analytically quite challenging to measure on these small sample sizes (10^4–10^6 atoms), and is rarely reported for Pu. In the fractions where we could quantify ^{241}Pu/^{239}Pu, the mean ratio does not appear to be significantly different from the Northern Hemisphere fallout ratio defined by Kelley et al. (1999) (Fig. 2; decay-corrected to January 1, 1998; $t_{1/2}$ ^{241}Pu $= 14.33$ y). Thus from both the ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios, we conclude that the GOM Pu is derived from global fallout sources.

3.3. Pu concentrations

Pu concentration results of this work are compared in Table 4 with results from previous research. Here, concentrations are presented in terms of ^{239,240}Pu alpha activities. To express our mass spectrometrically determined results as activities, we used half-life values for ^{239}Pu and ^{240}Pu of $24{,}119 \pm 27$ and 6564 ± 11 yr, respectively. The ^{239,240}Pu concentration in GOM surface waters has decreased over

Table 4
Concentration of ^{239,240}Pu in the Gulf of Maine and comparable North Atlantic regions[a]

	Sampling date	^{239,240}Pu mBq/kg	± 1σ error	Reference
Gulf of Maine				
1 m	1997	6.752	0.090	This study
15 m	1997	7.045	0.093	This study
37 m	1997	8.18	0.55	This study
65 m	1997	9.28	0.14	This study
200 m	1997	13.65	0.17	This study
250 m	1997	15.07	0.22	This study
Surface	1975	30.27	N/A	Cochran and Livingston (1987)
260 m	1975	50.45	N/A	Cochran and Livingston (1987)
Narragansett Bay (surface)	1976	31.95	0.34	Santschi et al. (1980)
Sargarsso Sea (surface)	1984	23.2	1.5	Buesseler and Sholkovitz (1987)
Sargarsso Sea (surface)	1984	21.7	1.5	Buesseler and Sholkovitz (1987)
Sargarsso Sea (10 m)	1972	60.5	1.3	Livingston et al. (1985)
Sargarsso Sea (4859 m)	1972	0.84	0.34	Livingston et al. (1985)
SEEP STA-D (454 m)	1984	20.85	0.12	Buesseler and Sholkovitz (1987)
SEEP STA-D (1700 m)	1984	16.7	1.5	Buesseler and Sholkovitz (1987)
Altantic surface(40–50°)	1992–1993	6.9–11.5		Bourlat et al. (1996)

[a] All results presented here represent unfiltered sample collections. To express the mass spectrometrically determined results of this study in terms of alpha activities, we used half-life values for ^{239}Pu and ^{240}Pu of 24,119 ± 27 y and 6,564 ± 11 y, respectively.

the last two decades by a factor of 4, from 30 μBq/kg in 1975 (GOM surface waters reported in Cochran and Livingston, 1987) to 6.7 μBq/kg (mean from this study). ^{239,240}Pu concentrations in 1976 surface-water collections in the Narragansett Bay just south of the GOM (Santschi, Li, Bell, Trier & Kawtaluk, 1980) are also similar to the Cochran and Livingston results, suggesting that the earlier higher activities were representative of the region.

This decrease with time reflects the continuing decline of fallout input after the end of above-ground nuclear tests in 1980, and the corresponding subsequent decrease of stratospheric Pu input (Rosner, Hotzl & Winkler, 1997). In addition, there is continued removal of Pu from surface waters due to mixing and particulate scavenging processes. Long-term observations on Pu in air show a decrease of Pu deposition by a factor >10 between 1978 and 1991 at Munich-Neuherberg, Germany (Rosner, Hotzl & Winkler, 1997). It is reasonable to assume that the change in fallout deposition would be similar in the GOM region, and hence the decline of Pu in surface seawater is slower than the decline in fallout input.

A decline in Pu concentration in surface waters is also seen elsewhere. According to Hirose, Sugimura and Aoyama (1992), Pu had decreased to about one-fifth of the 1979 value by 1987 in Northern Pacific surface waters. Holm, Sugimura & Aoyama (1991) noted a 4–5-fold decline in surface Pu concentrations from 1972 (GEOSECS) to 1988 (Swedish expedition) in Atlantic surface waters between 73°N and 72°S. Papucci et al. (1996) reported a 4-fold decrease in surface Pu in the Western Mediterranean from the early 1970s to the early 1990s. We note that much of the

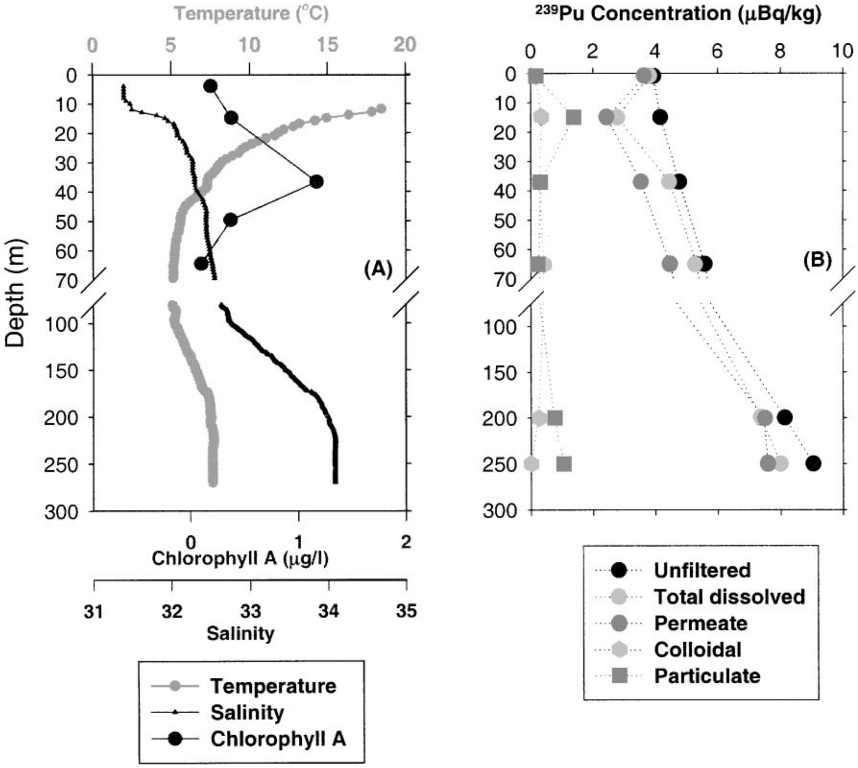

Fig. 3. Profiles of ^{239}Pu fractions and temperature, salinity in the Gulf of Maine seawater. In plots B, total dissolved, <1 µm; permeate, <1 kD; colloidal, 1 kD–1 µm; particulate, >1 µm. See the text for details. Note that all Pu concentrations are in the unit of Bg/kg water.

decline in Pu can be attributed to physical mixing in the Mediterranean. Papucci et al. (1996) reported a decrease in the conservative fallout radionuclide ^{137}Cs by a factor of 1.7 (decay corrected) between 1970 and 1982, at the same time that the Pu decrease was only slightly higher, or a factor of 2.2. It is clear that site-specific variations in the rates of mixing and sedimentation will alter the relative decrease of surface-water Pu and ^{137}Cs with time. Surface GOM Pu concentrations continue to decrease, similar to other regions, but much of the decrease appears to be due to physical mixing rather than local scavenging and sedimentation processes.

3.4. Pu vertical distribution

Fig. 3 shows the vertical distributions of size-fractionated Pu (^{239}Pu data only, since ^{240}Pu/^{239}Pu ratios are constant, see Table 3) along with temperature and salinity. We observed a linear increase in total Pu concentration (unfiltered samples) with depth by a factor of 2 (see Fig. 3B). The total dissolved and permeate Pu concentrations similarly increase with depth, except at 15 m where these concentrations abruptly fall before rising again. At this 15 m depth, we note a clearly related maximum in the particulate Pu concentration. Cochran and Livingston (1987) reported a similar vertical profile in terms of ^{239,240}Pu concentration at this same location. They attributed this pattern to the increase in the concentration of suspended particles (and associated ^{239,240}Pu) near the bottom. While our data show a ^{239,240}Pu concentration increase in the particulate fraction near the bottom, it is too slight to account for the large difference between surface- and bottom-water total Pu levels.

Open ocean Pu concentration profiles are characterized by a depletion in surface waters, an increase with depth in the upper 100–400 m, and a decrease below forming a subsurface maximum (see for example GEOSECS data by Livingston et al., 1985). Many locations also exhibit an increase near the bottom, particularly in the vicinity of the Pacific test sites (Livingston et al., 1985). Shallower sites do not always show these features.

The increase in Pu concentration with depth in the GOM is similar to that found for Pu at shallower stations in the Mediterranean Sea (Papucci et al., 1996), and is characteristic of elements whose distributions are controlled by surface removal and deep regeneration in the ocean. We argue however, that simple conservative mixing between low Pu concentrations in near-shore waters and higher concentrations in off-shore waters would produce a Pu concentration profile similar to the one found here. Indeed, warmer and saline Atlantic slope water was clearly seen at the bottom of the studied region (see Fig. 3A). This Atlantic slope water characterized by higher Pu concentration flows into the GOM through the Northeast Channel (Brooks, 1992). We will further address this mixing phenomenon below.

3.5. *Pu size fractionation and partitioning*

The majority of Pu was found in the low molecular weight fraction (<1 kD) as shown in Table 2. Colloidal Pu varied from 8% of the total in surface waters to <1% in the deepest (250 m) seawater sample. Note that colloidal organic carbon (COC) represents ~20% of the DOC at this depth (Dai & Benitez-Nelson, 2000). Since total Pu is increasing with depth, and near-bottom, colloidal Pu is decreasing, this implies a different Pu partitioning affinity near the bottom. This low Pu affinity to COC in bottom waters may be related to the characteristics of the deep-water COC macromolecules (usually older) and/or the speciation of Pu. Pu is found in both reduced and oxidized forms in the oceans but with a dominant fraction in the oxidized form (Nelson, Carey & Bowen, 1984; Orlandini et al., 1986; Choppin and Kobashi, 1990; Mitchell et al., 1991). The oxidized Pu species are considerably less surface-reactive, hence an increase in oxidized Pu near bottom should correspond to a decrease in particulate and colloidal forms of Pu. An increase in the percentage of oxidized Pu near bottom was reported by Nelson et al. (1984) for the North Pacific Ocean. They suggested that chemical reactions near the sediment–water interface, possibly involving MnO_2 as an active catalyst, would promote the oxidation of Pu.

Particulate Pu concentration is similar to that of colloidal Pu, except at 15 m, and in the deepest samples. At 15 m, particulate Pu represents 33% of the Pu in an unfiltered collection (Table 2; Fig. 3). The high particulate Pu concentration at 15 m does not directly correlate with chlorophyll or particulate organic carbon data, which peak at 37 m; however, this sample is at the base of a shallow pycnocline (Fig. 3A). It is noteworthy that our samples were taken in July right after the spring bloom in the GOM, which might be an aternative reason that both surface colloidal and particulate Pu concentrations were low in the GOM.

Particulate Pu concentration decreases overall with depth until the bottom-water interface, where an increase in particulate Pu concentration to >10% of that of the unfiltered sample is observed (Fig. 3B). The increase near bottom is likely to be related to sediment resuspension. A nepheloid layer at the sediment–water interface caused by sediment resuspension is frequently reported at Wilkinson Basin (Pike, 1998 and references therein). However, as mentioned above, the resuspension of particles is not enough to account for the increase in Pu accumulated at the bottom.

There is no evidence in the study area that Pu forms complexes with organic matter or that Pu is enriched in a high-DOM environment as suggested by Nelson, Penrose, Karttunen and Mehlhaff (1985). Instead, dissolved Pu has a negative correlation with DOC in this study (Fig. 4A). Dissolved and permeate Pu have a positive correlation with salinity (Fig. 4B), with a slight reduction at 15 m where the particulate Pu maximum occurs. Generally, GOM surface waters are thus characterized by low Pu concentrations, low salinities, and relatively high DOC levels. Conservative mixing between these surface waters, and deeper high salinity, low DOC waters can generate the observed Pu concentration increase with depth with the exception of 15 m, where this increase reverses briefly and Pu seems to be more effectively scavenged by particles than at other depths. In the New York Bight, Santschi et al. (1980) also found that nearshore, low-salinity waters were lower in Pu concentration than offshore, higher-salinity samples. Thus, there is an overall pattern of higher Pu removal in particle-rich coastal regimes than in offshore regions, as expected with any particle reactive element. But the relatively constant mixing lines shown for DOC level and salinity versus Pu concentration (Fig. 4) suggest that the removal is slow and that mixing processes govern the vertical distribution of Pu in such regimes more so than particle scavenging considerations.

Buesseler, Livingston and Sholkovitz (1985) estimated that the measured Pu inventories in the sediments of the GOM constituted only 45% of the fallout expected at these latitudes. In the open ocean, even lower Pu inventories are found in marine sediments (Aarkrog, 1988), which might suggest that net residence times of Pu with respect to particle removal are larger than originally estimated.

The actual factors that control the Pu oxidation state distribution in the ocean are not known. Generally speaking, Pu in the coastal seas is believed to exist in an oxidized form. For example, Mitchell et al. (1995) reviewed a large data set on Pu oxidation states in the Irish Sea and concluded that some 87% of the Pu is in the oxidized, pentavalent form, Pu(V). Baxter et al. (1995) reached a similar conclusion. This dominant oxidized Pu form has less of an affinity for either colloids (macromolecules) or particles than the reduced ter- and tetravalent Pu forms. Our

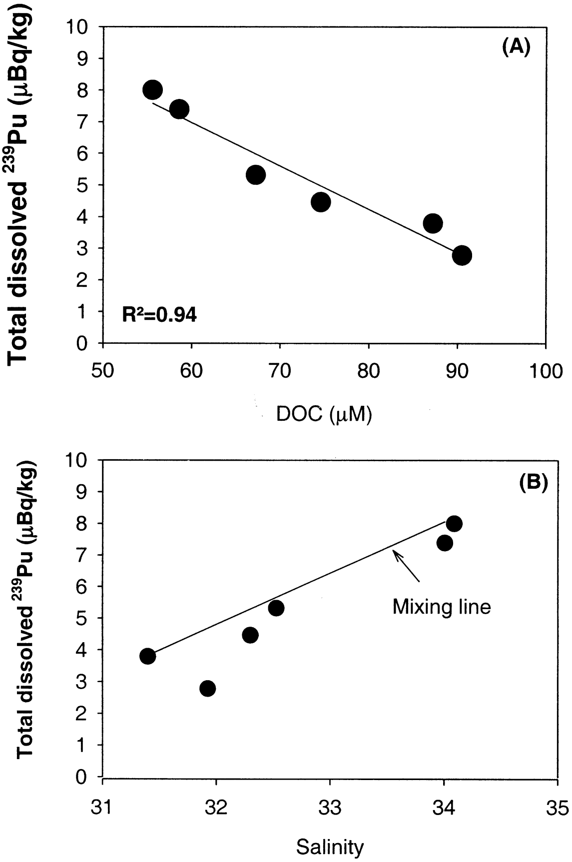

Fig. 4. ^{239}Pu concentration plots against dissolved organic C (DOC), and salinity: (A) ^{239}Pu-DOC; (B) ^{239}Pu-salinity. Plots show mixing as a dominant process controlling the Pu distribution.

observation of low percentages of both colloidal and particulate Pu, and the conservative mixing lines for Pu and salinity found in our results may thus be attributed to the dominance of the less particle reactive oxidized forms of Pu.

4. Summary

This investigation has shown for the first time that a combination of CFF and TIMS can be used for separating dissolved and colloidal forms of ^{239}Pu and ^{240}Pu in seawater. After careful cleaning CFF blanks are negligible and the CFF mass balance for Pu isotopes is acceptable in most cases. The results suggest that colloidal Pu is only a minor fraction of the total, as most of the Pu in the studied area occurs in the low molecular weight fraction (<1 kD). The high Pu fraction found in this low molecular size fraction implies that most of the Pu is conservative, probably due to its redox speciation being in the oxidized fraction. The source of Pu in the GOM is clearly global fallout, as seen in the ^{240}Pu/^{239}Pu and ^{241}Pu/^{240}Pu isotopic ratios, and the activity levels are consistent with other studies which show a slow Pu decrease with time due to continued mixing and particle removal. The increase of Pu with depth is typical of highly scavenged elements in the oceans and the particulate maximum at 15 m suggests enhanced particulate removal at the base of the mixed layer. However, the constant mixing lines between high DOC, low salinity and low Pu surface waters and elevated deep Pu with lower DOC and higher salinity suggests that particle removal rates are slow and that the local vertical distribution of Pu is dominated by physical mixing processes on these time scales.

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