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Plutonium in groundwater at the 100K-Area of the U.S. DOE Hanford Site

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Abstract

We examined the concentration, size distribution, redox state and isotopic composition of plutonium (Pu) in groundwater at the 100K-Area at the U.S. Department of Energy's (DOE) Hanford Site. Total concentrations of Pu isotopes were extremely low (10^{-4} to 10^{-6} pCi/kg, $\approx 10^4$ to 10^6 atoms/kg) but measurable for the first time in the 100K-Area wells using mass spectrometric analyses that are much more sensitive than alpha spectroscopy methods used previously. Size fractionation data from two wells suggest that 7–29% of the Pu is associated with colloids, operationally defined here as particles between 1 kDa–0.2 μm in size. These colloids were collected using a 1 kDa cross-flow ultrafiltration (CFF) 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 can be well characterized. Pu in this colloidal fraction was exclusively in the more reduced Pu(III/IV) form, consistent with the higher affinity of Pu in the lower oxidation states for particle surfaces. While the overall concentrations of Pu were low, the Pu isotopic composition suggests at least two local sources of groundwater Pu, namely, local Hanford reactor operations at the 100K-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, since groundwater Pu at the F-Area seepage basin at SRS has been found using these same methods, to be characterized by lower colloidal abundances and higher oxidation states. This difference is not directly attributable to groundwater redox potential or geochemical conditions,

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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 the Hanford Site, since downstream wells have both an order of magnitude lower concentrations of Pu and a lower fractional colloidal distribution.

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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 (Pu) in groundwater at the Nevada Test Site (Kersting et al., 1999) detected Pu much further than predicted by existing models, and 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 in groundwater at greater distance than expected from one source may 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 et al., 1993) or formation of colloids due to alterations of ambient redox state prior to ultrafiltration (Buesseler et al., 2003).

Our own data from the Savannah River Site (SRS) suggest 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 and may vary from site to site depending upon geochemical conditions and actinide source characteristics.

In this paper, we investigate the speciation and isotopic composition of Pu: the actinide of greatest concern in groundwater of the 100K-Area at the U.S. Department of Energy's (DOE) Hanford Site on the shoreline of Columbia River. The Hanford Site is engaged in the largest waste cleanup effort ever undertaken in human history (Gerber, 1992), and contaminants in these areas may have a direct impact on the Columbia River's ecosystem. This study uses newly developed methods optimized for the determination of Pu speciation under in situ geochemical conditions in the groundwater at the 100K-Area. While it is challenging to work under these extremely low concentration conditions, our results assist in the long-term risk assessment of the potential for Pu migration. These data,

although limited to a few wells, improves our understanding of actinide speciation, sources and behavior in the environment.

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 (Fig. 1). Construction of the 100K-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 100K-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. Geologic units beneath the 100K-Area from the surface downward include eolian silty sand, Hanford formation (sandy gravel, gravelly sands, sand), Ringold Formation Unit E (sandy gravel, gravelly sand), and Ringold Formation paleosols and overbank deposits (silt, sandy silt) (Harman, 2000). Over most of the area, the depth to groundwater is ~25 m (Johnson et al., 1995). Depending on the time of year, the groundwater flows in slightly different directions. The average of those directions is towards the north to the Columbia River (Harman, 2000) with velocities in the range of 0.01 to 0.24 m/day at the KW-Basin and 0.24 to 0.4 m/day at the KE-Basin (Johnson et al., 1995).

Both basins were used to store ~2100 metric tons uranium (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 1900 L/h and was attributed to a construction joint between

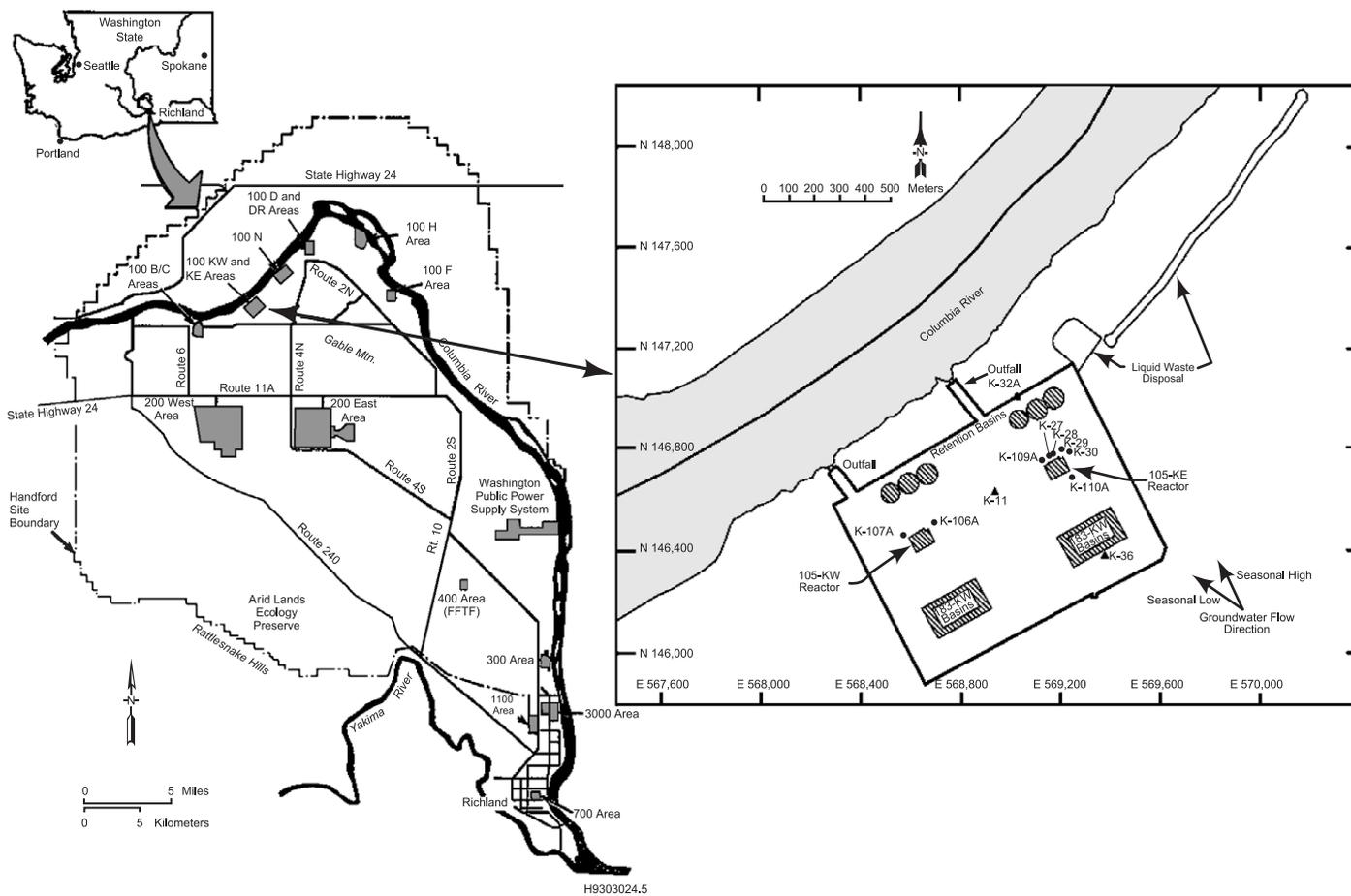


Fig. 1. Locations of the Hanford Site 100K-Area and the monitoring wells sampled in this study. Wells 199-K-36, K-110A, K-27 and K-32A were sampled more comprehensively than the other wells (see text).

the main basin and the fuel discharge chute. During February 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 below the basins (Johnson et al., 1995).

2.2. Well location and settings

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-”; Fig. 1). A more detailed sampling was completed in March 1999 when unfiltered samples were taken from wells K-11 and K-109A for total Pu isotopic composition analysis. In addition, four sites were sampled in greater detail in 1999 (wells K-27, K-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. Wells sampled in this study generally form two cross sections: one towards the Columbia River and the other crosses the two reactor facility areas (Fig. 1). A water sample was also taken from the Columbia River downstream of the 100K-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 exist. 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.

Well K-27 consists of a 6-in. carbon steel casing with perforations starting at 20.4 m to a bottom depth of 27.7 m. From the beginning of the screen to a depth of 25 m, the horizon consists of 60% cobbles/20% pebbles/10% sand/10% silt. K-32A, K-36 and K-110A are all 4-in. stainless steel casings with continuous wrap stainless steel screens at the base. The screen depth for K-32A starts at 14.9 m to a bottom depth of 21.6 m. The horizon over this depth range starts as a gravel/sand/silt/ash mix to a depth of 17 m and progresses to sand/gravel at the base. Well K-36 has a bottom depth of 34.3 m with the screen starting depth of 29.1 m. The horizon over this entire range consists of sand/gravel mix. The screen depth in K-110 began at 22.9 m to a bottom depth of 29.8 m. The horizon over this interval alternates between layers of sand and sand/gravel approximately every 1.7 m.

2.3. Well sampling

Detailed well sampling procedures have been described in Dai et al. (2002). Briefly, groundwater was purged and sampled from the wells with an all-Teflon bladder pump at a flow rate of ~0.15 L/min. This low sampling rate is a precaution against the mobilization of particles within the aquifer and subsequent introduction of colloidal artifacts that in the

absence of pumping would be stationary (Kaplan et al., 1993, 1994). Purge water was monitored with an in-line multiprobe flow cell until monitoring parameters (i.e., pH, electrical conductivity and dissolved oxygen) stabilized. Following well purging, unfiltered sample fractions were collected first, followed by filtered fractions (through an in-line 0.2- μm pore size and 142-mm diameter polycarbonate membrane) and CFF-processed sample fractions, namely, permeate (<1 kDa) and retentate (the solution which is retained by the CFF membrane, see below).

2.4. On-site CFF and redox processing

During the comprehensive field work, samples were processed on-site using an ultraclean CFF system with redox control as described previously (Dai et al., 2002) and summarized in the flow chart in Fig. 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, 2004). 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) with regenerated cellulose membranes were calibrated against standard colloidal molecules (Molecular Probes, Eugene, OR). Our CFF system retained >91% of a ~3 kDa 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; 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

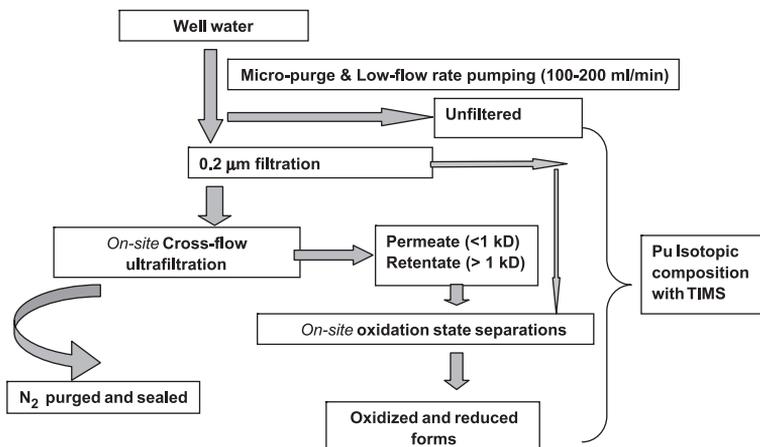


Fig. 2. Flow chart illustrating the collection and processing of groundwater samples from Hanford Site 100K-Area wells.

the membrane and thus becomes increasingly enriched in colloids. The concentration of Pu bound to these colloids ($Pu_{\text{colloidal}}$, units of atoms/kg) is calculated from the Pu concentrations measured in the permeate (Pu_{permeate}) and retentate ($Pu_{\text{retentate}}$) 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:

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

The mass balance or recovery can then be calculated by comparing the sum of $[Pu_{\text{colloidal}}] + [Pu_{\text{permeate}}]$ with the initial solution concentration.

Each well sampling took ~36 h including ~24 h 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, nanopure 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 detail in Dai et al. (2002), which was adapted from Lovett and Nelson (1981). Briefly, Pu in the reduced states was traced with $^{244}\text{Pu(III/IV)}$ and Pu in the oxidized states was traced with $^{242}\text{Pu(V/VI)}$. The amount added of each tracer was nominally 5×10^6 atoms. 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 coprecipitated, filtered and retained for subsequent processing and analysis.

This method has been used widely and successfully in studies of Pu speciation in environmental samples (Lovett and Nelson, 1981; Nelson et al., 1984, 1987; Nelson and Lovett, 1978). Moreover, because the method employs two tracers that are distinguishable isotopically as well as by their oxidation states, any possible alteration of oxidation state of the tracers during processing is revealed by TIMS results from which correction factors can be determined. These correction factors, C_{reduced} and C_{oxidized} , are generally less than, but very close to, one and represent the respective fractions of $^{244}\text{Pu(III/IV)}$ and $^{242}\text{Pu(V/VI)}$ tracers that retain their original oxidation state during processing.

2.5. Analyses

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

Unfiltered, filtered ($<0.2 \mu\text{m}$) 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 HNO₃ 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 U.S. EPA Method (EPA 300.1). Water samples were preserved with HgCl₂ for dissolved inorganic carbon (DIC) and total alkalinity (TAlk) analysis. DIC data were obtained by acidification of 0.5 mL of a water sample and the subsequent quantification of CO₂ 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.

Aliquots representing fractions that were not redox-processed in the field were spiked with nominally 5×10^6 atoms of SRM-996 ²⁴⁴Pu, after which Pu was reduced by Fe²⁺, coprecipitated with LaF₃ and filtered, just like the field-processed redox samples. From this point on, all samples, redox-processed or otherwise, were in the same condition and so were purified identically and sequentially by two anion exchange columns employing AG1-X4, 100–200 mesh resin (Bio-Rad Laboratories, Richmond, CA). The bed-volumes were 4 mL for the first column and 100 μL for the second column. After these operations, another anion exchange purification was undertaken, this time as a batch operation for which purpose a single, 800-μm-diameter AG1-X4 resin bead was employed prior to the final preparation of a TIMS source.

Pu isotopes were analyzed using a three-stage TIMS instrument at the Pacific North National Lab (PNNL; Dai et al., 2002 and references therein). For sample sizes where millions of ion counts are measured using internal standards to correct for isotopic fractionation, the TIMS instrument is capable of measuring these ratios to 1 part per thousand precision and accuracy. Overall, the instrument is capable of a measurement efficiency for Pu (i.e., the ratio of Pu⁺ counts to Pu source atoms) of 0.07. Also, background ion emissions, as ascertained by monitoring of the 243 mass position, can be reduced to the instrument detector noise level of about 0.04 counts/s.

Sample aliquots seldom contained more than $\sim 10^8$ Pu atoms; thus, most of the TIMS duty cycle was allocated to the measurement of the minor ²⁴¹Pu and ²⁴²Pu isotopes, and isotopic tracers were used for concentration determinations. The precision of atom ratio measurements was typically limited by counting statistics and the accuracy of concentration determinations was limited by those same statistics along with the often larger uncertainty ($\pm 0.8\%$) in aliquoting the tracer. Also, because of losses incurred during sample processing and chemical purification operations, efficiencies of 0.07 could not be achieved and generally ranged between 0.02 and 0.04. In a few instances, background ion emissions above the detector noise level were seen. However, these did not exceed about 0.25 counts/s and appeared only in the first few mass scans. These first scans were either discarded entirely or corrections were made based on the observed counts at mass 243 and an assumption of a $\pm 100\%$ uncertainty as to whether corresponding counts might have also appeared at plutonium mass positions. Given the TIMS duty cycle allocation for this

study, the TIMS detection limit realized in this work did not exceed about 10^4 atoms, the lower Pu concentration limit reported in this study. At each Pu mass, this limit is derived from a doubling of the error associated with a measurement of a Pu-free source (tracer excepted), the error being dictated by the TIMS noise level coupled with uncertainties associated with corrections for minor isotopes present in the SRM-996 ^{244}Pu tracer that was used.

The results of the TIMS measurements of this study are presented as the measured atom ratios, units of which are dimensionless, or, when concentrations are reported, in units of atoms/kg.

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 to 1048 $\mu\text{S cm}$ (Table 1). The highest conductivity is observed at Well K-110A, 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 DIC (8.9 vs. ~2.0 mmol/L at other wells) as well as high alkalinity (8.3 vs. 2.0–3.0 mmol/L at other wells), accompanied by low pH and low DO values.

Nitrate levels seem evenly distributed in the 100K-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 distribution

Pu isotopes were detected in unfiltered groundwater samples from the 100K-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 100K-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 100K-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 100K groundwater is not fallout alone, as will be shown using Pu isotopic information in the following discussion.

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

	Unit	199-K-36		199-K-110A		199-K-27		199-K-32A	
		Start	End	Start	End	Start	End	Start	End
Sampling date		30 March 99	31 March 99	1 April 99	2 April 99	3 April 99	4 April 99	25 March 99	27 March 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	mmol/L	2.76	2.73	8.88	8.38	2.98	2.73	1.83	1.81
Alk	mmol/L	2.81	2.88	8.32	7.48	2.94	2.64	1.86	1.83
SPM	mg/L	4.87	0.11	14.75	–	0.49	0.06	0.38	0.04
DO ^b	mg/L	9.8±0.6		6.52		10.6±1.9		9.8±0.9	
NO ₃ ⁻ +NO ₂ ⁻	mg/L	4.97	4.75	6.44		5.98	6.52	6.91	5.12
PO ₄ ³⁻	µM	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	51.8	63.6	6.2		21.9	20.7	33.0	30.0
K	mg/L	10.0	9.0	15.0		13.0	11.0	3.0	2.9
Ca ^c	mg/L	49.6		112.1		92.9		39.8	
Mg ^c	mg/L	19.0		28.9		31.3		7.7	
Al ^c	mg/L	1.67		0.67		0.52		6.31	
Fe ^c	µg/L	29.7		7.9		20.5		0.2	
Mn ^c	mg/L	1.9		19.9		3.1		0.02	
Cu ^c	µg/L	0.4		6.5		0.6		0.2	
Zn ^c	µg/L	2.2		2.8		1.2		4.1	
Cd ^c	ng/L	9.7		24.3		6.8		6.8	
Pb ^c	ng/L	48.5		16.6		4.3		3.7	

^a DIC—Dissolved inorganic carbon.

^b DO—Dissolved oxygen.

^c From filtrate (<0.2 µm).

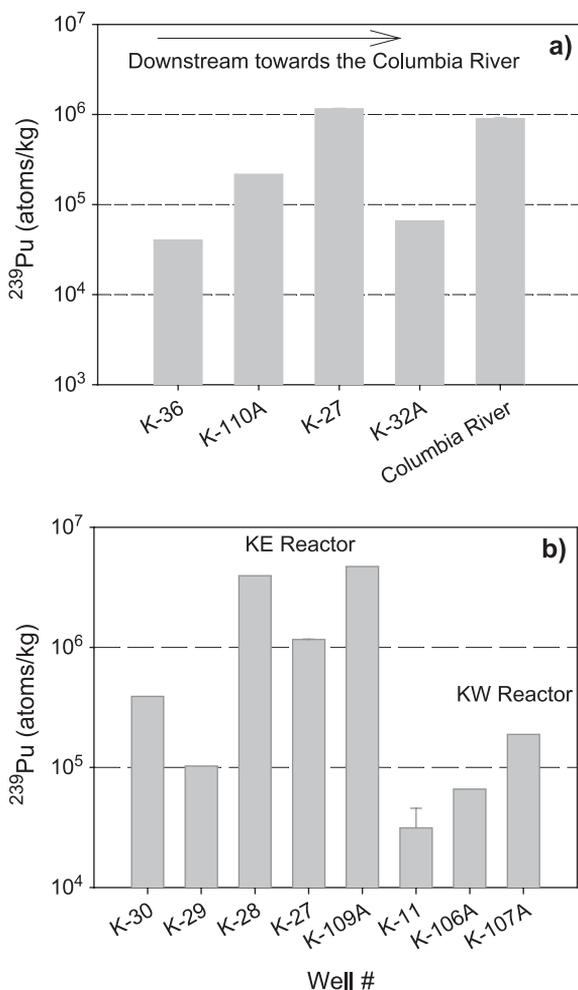


Fig. 3. ^{239}Pu concentrations in 100K-Area wells of the Hanford Site. Data include both collections in 1997 and 1999. (a) Transect following the groundwater flow towards the Columbia River. (b) Transect across the reactors.

Shown in Fig. 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 midway between both reactors (Fig. 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 $^{239,240}\text{Pu}$

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 100K-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 100K wells, previous leakages of contaminated groundwater from the 100K 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 were so low that it became 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-borne particulates and to frequently monitor one's blanks and standards.

To quantify these blank levels, we process not only Nanopure water (*Q*-water hereafter) 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 were observed to decrease as expected, as we proceeded 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 – 1.2×10^4 atoms/kg. We cannot

Table 2
CFF blank assessment prior and post-Well 199-K-27 sampling at the Hanford 100K-Area

	Concentration, $\times 10^5$ atoms/kg $\pm 1\sigma$ error			
	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Prior sampling CFF blank	0.24 \pm 0.02	0.02	–	–
Initial <i>Q</i> -water rinse	6.10 \pm 0.12	0.86 \pm 0.03	0.06 \pm 0.01	0.05 \pm 0.01
Acid rinse	0.91 \pm 0.05	0.14 \pm 0.02	0.05	0.32 \pm 0.03
Base rinse	0.65 \pm 0.05	0.08	0.05	0.11
Post-final CFF blank	0.12	0.06	0.06	0.06
<i>Q</i> -water	0.10	0.05	0.05	0.33 \pm 0.03

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

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 fractionation 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 four sites (wells K-27, K-32A, K-36, and K-110A). Results for Pu in the $<0.2\ \mu\text{m}$ filtrate in Well K-36 and K-110A were at our blank level; thus, we can only set $1.0\text{--}1.2 \times 10^4$ 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 well K-32A and consider complete size and redox-fractionated data from the single well K-27, which has one of the higher Pu concentrations in our study (Table 3).

We found 9.8–13.3% of the ^{239}Pu was retained by our 1 kDa CFF membrane in Wells K-27 and K-32A (Table 4) and is thus classified here as “colloidal” as calculated using Eq. (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

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

Well #	$[^{239}\text{Pu}] \pm 1\sigma$ error	
	10^5 atoms/kg	$10^{-2} \times \text{fCi/kg}^{\text{a}}$
199-K-36	4.1 ± 0.3	1.0 ± 0.1
199-K-110A	21.7 ± 0.5	5.4 ± 0.1
199-K-27	55.9 ± 2.8	13.8 ± 0.7
199-K-28	394.6 ± 11.3	97.1 ± 2.8
199-K-29	<1	<0.3
199-K-30	39.0 ± 1.7	9.6 ± 0.4
199-K-109A	471.0 ± 8.9	115.9 ± 2.2
199-K-32A	6.6 ± 0.4	1.6 ± 0.1
199-K-11	3.1 ± 1.4	0.8 ± 0.4
199-K-106A	6.6 ± 0.6	1.6 ± 0.2
199-K-107A	18.8 ± 1.3	4.6 ± 0.3
Columbia River ^b	90.1 ± 2.6	22.2 ± 0.6

The location is $\sim 46^\circ 14' 75''\text{N}$ and $119^\circ 56' 90''\text{E}$. U.S. EPA drinking water standard for Pu is 15 pCi/L.

^a A half-life of ^{239}Pu of 24,131 years was used. $\text{fCi} = 10^{-15}$ Ci.

^b Taken from ~ 60 m from shore downstream well 199-K-32A.

Table 4
Size^a and redox fractionated ²³⁹Pu concentrations and isotopic compositions

Sample fraction	²³⁹ Pu]±1σ error ×10 ⁵ atoms/kg	Atom ratio±1σ error		[Pu(III,IV)]±1σ error ×10 ⁵ atom/kg		[Pu(V,VI)]±1σ error ×10 ⁵ atom/kg	
		²⁴⁰ Pu/ ²³⁹ Pu	²⁴¹ Pu/ ²³⁹ Pu ^c	²³⁹ Pu	²⁴⁰ Pu	²³⁹ Pu	²⁴⁰ Pu
<i>Well 199-K-27</i>							
Filtrate ^b	9.26±0.13	0.145±0.004	0.008±0.001	7.40±0.09	0.79±0.02	4.18±0.05	0.58±0.02
Permeate ^b	6.56±0.13	0.144±0.006	0.008±0.002	2.39±0.05	0.33±0.01	3.55±0.05	0.53±0.02
Retentate ^b	75.55±1.17	0.145±0.004	0.008±0.001	75.74±1.00	10.94±0.24	0.08±0.00	0.01±0.07
Colloidal ^c	1.24±0.02	0.145±0.004	–	–	–	–	–
CFF mass balance ^d	84.1%±1.86%						
<i>Well 199-K-32A</i>							
Filtrate ^b	0.32±0.04	–	–	–	–	–	–
Permeate ^b	0.30±0.03	–	–	–	–	–	–
Retentate ^b	1.98±0.12	0.107±0.026	–	–	–	–	–
Colloidal ^c	0.03±0.002	–	–	–	–	–	–
CFF mass balance ^d	103.21%±13.31%						

^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 55.7 and 54.6, respectively.

^c [Colloidal]=[retentate]–[permeate]/cf.

^d Mass balance=[colloidal]+[permeate]/[filtrate].

^e Decay corrected to 1 January 2000.

the apparent colloidal concentration. 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 (Buessler 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 (that is, in effect, Pu losses are considered colloidal only) or via Eq. (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 (Buessler 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 $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in all of the size fractions from Well K-27.

Colloid facilitated Pu transport has received a great deal of attention (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 in this same area, but the earlier data were obtained using very different size fractionation protocols (Kaplan et al., 1994). The Hanford Site 100K data thus suggest higher colloid Pu abundances (7–29%) than found at the SRS F-Area using our same methods and CFF protocols. Differences between the SRS and Hanford data between these albeit limited number of wells must be sought in the redox speciation information and differences in the Pu sources and groundwater geochemistry and colloid 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. 4 and Table 4. As with the CFF fractionation, redox separations are problematic if the Pu concentration in the sum of the reduced and oxidized subfractions 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 six 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 three sample types. When added together, the sum of Pu(III,IV) and Pu(V,VI) concentrations should independently equal to 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).

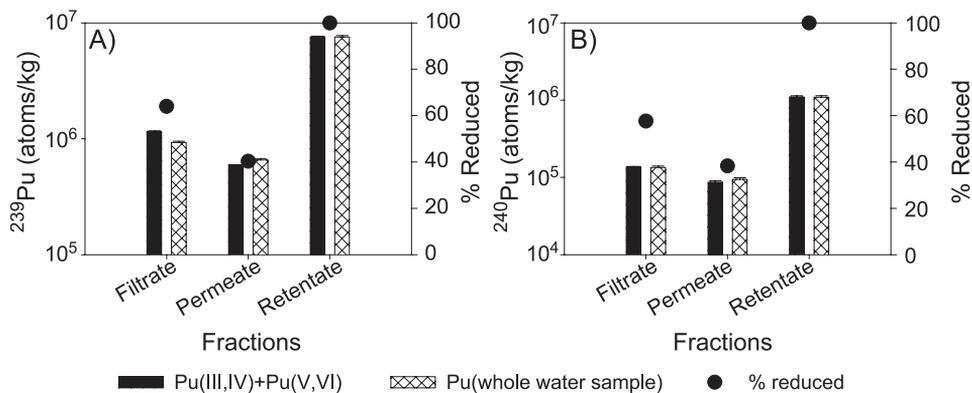


Fig. 4. Comparison of the sum of redox subfractions [Pu(III/IV)+Pu(V/VI)] and the independently measured Pu in whole water samples. Also shown is the percentage of reduced Pu(III/IV) in the filtrate sample fraction from well K-27.

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 Well K-27 and SRS F-Area lies in the overall redox state of Pu. At Well K-27, 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 the SRS study and K-27 is complicated by this ^{244}Cm source of oxidized ^{240}Pu at SRS F-Area. 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; 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 that a significant percentage of oxidized Pu(V) and/or Pu(VI) 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).

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,

but we cannot rule out the possibility of different colloidal composition in two sites having an impact. 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). Yet there remains a Pu concentration gradient greater than one order of magnitude between these wells (9.3 vs. 0.3×10^5 atoms/kg ^{239}Pu at K-27 vs. K-32A, respectively, Table 4), implying that the transport of Pu, if there is any, is not significant. Furthermore, we do not see in the downstream well an enrichment in the percent Pu in the colloidal fraction despite the relatively high colloid associations in Well K-27 (13–29%) and rapid groundwater flow. If those colloids did facilitate Pu transport, it was not very effective, as downstream concentrations of Pu are very low. Therefore, neither the low abundance of colloidal Pu (as compared to the permeate) nor the decreased concentration of Pu in the downstream well supports enhanced transport of groundwater Pu colloids to a significant degree at this site.

3.5. Isotopic ratios and source provenance

The concentration data alone tell us nothing about the source of Pu in the 100K-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 these 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 $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio <0.03 . Nuclear weapon construction requires a $^{240}\text{Pu}/^{239}\text{Pu}$ 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 $^{240}\text{Pu}/^{239}\text{Pu}$ ratio between 0.07 and 0.18, while reactor-grade Pu has $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of 0.18–0.30. Mixed-oxide fuel has the highest ^{240}Pu content ($^{240}\text{Pu}/^{239}\text{Pu} > 0.30$) (Pellaud, 2002).

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in weapons test fallout can vary between <0.10 and >0.35 . For example, characteristic $^{240}\text{Pu}/^{239}\text{Pu}$ 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 $^{240}\text{Pu}/^{239}\text{Pu}$ atom 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 $^{240}\text{Pu}/^{239}\text{Pu}$ ratios ranging from <0.04 to >0.15 in the K-Basin groundwater and 0.18 in the Columbia River downstream of the 100K-Area (Fig. 5A). 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

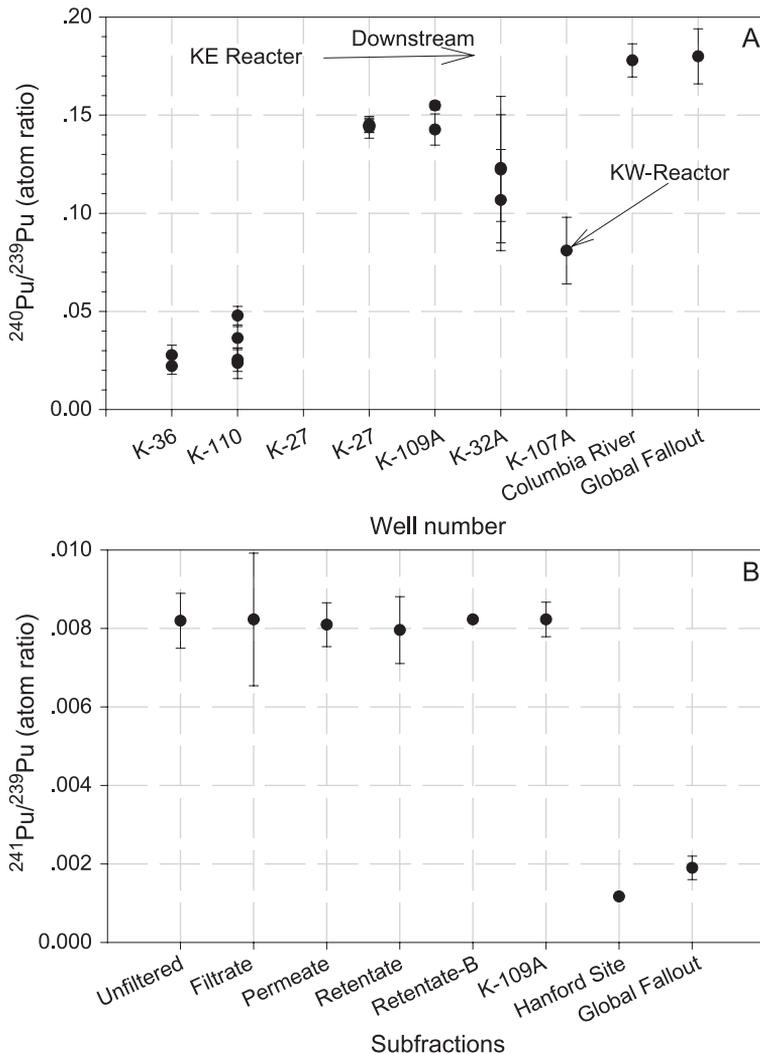


Fig. 5. Pu isotope ratios of Hanford Site 100K-Area groundwater samples. Global fallout ratio from Kelley et al. (1999). (A) $^{240}\text{Pu}/^{239}\text{Pu}$. (B) $^{241}\text{Pu}/^{239}\text{Pu}$. Subfraction data are from Well K-27 including the ratio in the redox fraction (referred to as "retentate-B"). The sample from K-109A is unfiltered. Hanford Site refers to typical site operation discharge which contains 0.54% ^{241}Pu as of June 1968, equivalent to $^{241}\text{Pu}/^{239}\text{Pu}=0.00117$ (January 2000).

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 $^{240}\text{Pu}/^{239}\text{Pu}$ ratio today is 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 river location. Beasley et al. (1981) reported a mean Columbia River sediment $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of 0.126 and estimated that 20–25% of the sedimentary ^{239}Pu was derived from Hanford Site operations between 1944 and 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 suggest 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 $^{240}\text{Pu}/^{239}\text{Pu}$ ratios (Fig. 5A) 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 $^{240}\text{Pu}/^{239}\text{Pu}$ ratio. Downstream, mixing with higher $^{240}\text{Pu}/^{239}\text{Pu}$ sources is evident. One possible source for the higher ratio material other than fallout is the 2100 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 nine reactors in operation at Hanford Site, this was the only dual-purpose, multipass water-cooled reactor, and it was designed to supply steam for the production of electricity as a by-product (Garrett and Williams, 1997). Productionwise, N-reactor initially produced weapons-grade Pu ($^{240}\text{Pu}/^{239}\text{Pu} < 0.07$ ^{240}Pu) from 1964 to 1965. From 1966 to 1973, it produced fuel-grade ^{240}Pu for AEC's breeder reactor program ($^{240}\text{Pu}/^{239}\text{Pu} = 0.09$). From 1974 until 1984, it produced fuel-grade ^{240}Pu with an even higher $^{240}\text{Pu}/^{239}\text{Pu}$ 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 $^{240}\text{Pu}/^{239}\text{Pu}$ 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 $^{241}\text{Pu}/^{239}\text{Pu}$ atom ratios have changed since their release into environment. The $^{241}\text{Pu}/^{239}\text{Pu}$ ratio is analytically challenging to measure at these low levels (10^4 – 10^6 atoms) and is rarely reported for environmental samples. Global fallout atom ratios of $^{241}\text{Pu}/^{239}\text{Pu}$ in the Northern Hemisphere average 0.00194 (Kelley et al., 1999). In the wells where we had sufficient Pu to quantify $^{241}\text{Pu}/^{239}\text{Pu}$, notably at Well K-27 and K-109A, the $^{241}\text{Pu}/^{239}\text{Pu}$ ratios are consistently high, in the range of 0.0081 to 0.0082 (decay corrected to 1 January 2000; Fig. 5B). This small range of $^{241}\text{Pu}/^{239}\text{Pu}$ ratios was found for this well in all of the different size and redox subfractions. Our observation of this high ratio for $^{241}\text{Pu}/^{239}\text{Pu}$ is clearly another indicator of local waste sources in K-27 and K-109A. In the other wells, $^{241}\text{Pu}/^{239}\text{Pu}$ was below detection.

Typical Hanford Site weapons-grade material has a $^{241}\text{Pu}/^{239}\text{Pu}$ ratio of 0.0054 as of June 1968, which is equivalent to 0.0011 when decay corrected to January 2000. Thus, the high $^{241}\text{Pu}/^{239}\text{Pu}$ 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 $^{241}\text{Pu}/^{239}\text{Pu}=0.10$. 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 concentrations in the groundwater at the Hanford Site 100K-Area using an ultrasensitive TIMS technique. Pu isotopic composition has emerged once again as a useful indicator to trace Pu sources. Pu in the groundwater of 100K-Area is mainly from general Hanford operations with a mixture of global fallout. Exception to this are found in the groundwater near the KE reactor where there is a clear indication for a source from N-reactor spent fuel waste.

Colloid-associated Pu is detectable in two wells at the 100K-Area, accounting for 7–29% of so-called dissolved Pu, which is higher than what we measured at F-Area seepage basins of the 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 in one well from the HS 100K-Area, essentially 100% of the Pu in the retentate fraction is reduced, which contrasts with the scenario at SRS, where the majority of Pu was found to be in higher oxidation states. At F-Area seepage basins at the SRS, the major source of Pu downstream from the seepage basins was ^{240}Pu derived from ^{244}Cm decay, which led to fractionation between ^{240}Pu and ^{239}Pu not seen in this study. Thus, differences in groundwater Pu speciation between Hanford Site 100K-Area and SRS F-Area 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 100K) and associated colloidal phases.

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 K-32A a decrease in the fraction of colloidal Pu, from 13–29% near the source to 7–10% 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 100K-Area of Hanford Site.

Finally, our results are site-specific and limited to a few wells, but have much broader implications regarding Pu's fate in the environment. The results suggest that transport of Pu in association with groundwater colloids is not a substantial process. Differences with prior studies can be attributed to improved sampling protocols; however, site-to-site variations in ambient geochemical conditions, colloid abundances and composition and differences in Pu source characteristics are all likely to be important in determining Pu mobility. It must be noted that working at these extremely low concentrations and

striving to maintain ambient geochemical conditions during sample processing is challenging. However, we know of no better way to accurately assess Pu's behavior in the environment and geochemical controls thereof. Such information is required to design strategies to reduce risks and plan effective cleanup and monitoring approaches. In the future, continued work at other sites and comparisons between new methodologies presented here, and those used in the past, are recommended.

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