Plutonium in groundwater at the 100K-Area of the US 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 US 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 suggests 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 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 for particle surfaces in the lower oxidation states. 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 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 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 suggested 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), 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 US 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, though 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. 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. Beneath the 100K-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 (metric tons uranium) 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 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 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. 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 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 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:

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

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

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 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). 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 co-precipitated, 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; Nelson et al., 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]Pu(III/IV) and [242]Pu(V/VI) tracers that retain their original oxidation state during processing.

2.4 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.

Aliquots representing fractions that were not redox-processed in the field 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, 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 was, 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, so most of the TIMS duty cycle was allocated to the measurement of the minor ^{241}Pu and ^{242}Pu 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 (± 0.8 percent) 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 ±100 percent 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 304-1048 μS•cm^{-1} (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 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 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 distributions

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.

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 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-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 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 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 1.0-1.2×10^4 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 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 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 (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.

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 (7-30%) 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 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 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

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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 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. 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 (9.3 vs 0.3×10^5 atoms/kg ^{239}Pu at K-27 vs. K-32A, respectively, Table 4). 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.

3.5 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 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 of 0.18-0.30. Mixed-oxide fuel has the highest ^{240}Pu content (^{240}Pu/^{239}Pu >0.30) (Pellaud, 2002).

^{240}Pu/^{239}Pu atom ratios 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 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}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 100K-Area (Figure 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 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 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}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 (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}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 atom 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 K-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. 5b). 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 100K-Area using an ultra-sensitive 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).

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 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 and the suggestion that colloidal forms are abundant and might lead to higher mobility in groundwater settings. 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 clean-up 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

Acknowledgements

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

	Unit	199-K-36 Start	End	199-K-110A Start	End	199-K-27 Start	End	199-K-32A 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
pCO_2 [b]	µatm	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	
$NO_3^-+NO_2^-$	µg/L	4970	4750	6440		5980	6520	6910	5120
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	51.80	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) pCO_2 – CO_2 partial pressure, calculated from pH and DIC.

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

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

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

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

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

Well #	[^{239}Pu] ±1σ error	
	10^5 atoms/kg	10^{-2}×fCi/kg*
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**	90.1±2.6	22.2±0.6

*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

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

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

Sample Fraction	[²³⁹Pu]±1σ error ×10⁵atoms/kg	atom ratio±1σ error 240Pu/239Pu	atom ratio±1σ error 241Pu/239Puᵉ	[Pu(III,IV)] ± 1σ error ×10⁵atom/kg 239Pu	[Pu(III,IV)] ± 1σ error ×10⁵atom/kg 240Pu	[Pu(V,VI)] ± 1σ error ×10⁵atom/kg 239Pu	[Pu(V,VI)] ± 1σ error ×10⁵atom/kg 240Pu
Well 199-K-27							
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±0.01	0.01±0.07
Colloidal[c]	1.24±0.02	0.145±0.004	---	---	---	---	---
CFF mass balance[d]	84.1%±1.86%						
Well 199-K-32A							
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 55.7and 54.6, respectively.
c) [Colloidal]=([retentate]-[Permeate])/*cf*
d) mass balance = [colloidal] + [permeate] / [filtrate]
e) Decay corrected to 1 Jan 2000.

Figure Captions

FIGURE 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).

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

FIGURE 5. Pu isotope ratios of Hanford Site 100K-Area groundwater samples. Global fallout ratio from Kelley et al. (1999).
  a) ^{240}Pu/^{239}Pu
  b) ^{241}Pu/^{239}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}Pu/^{239}Pu =0.00117 (Jan 2000).
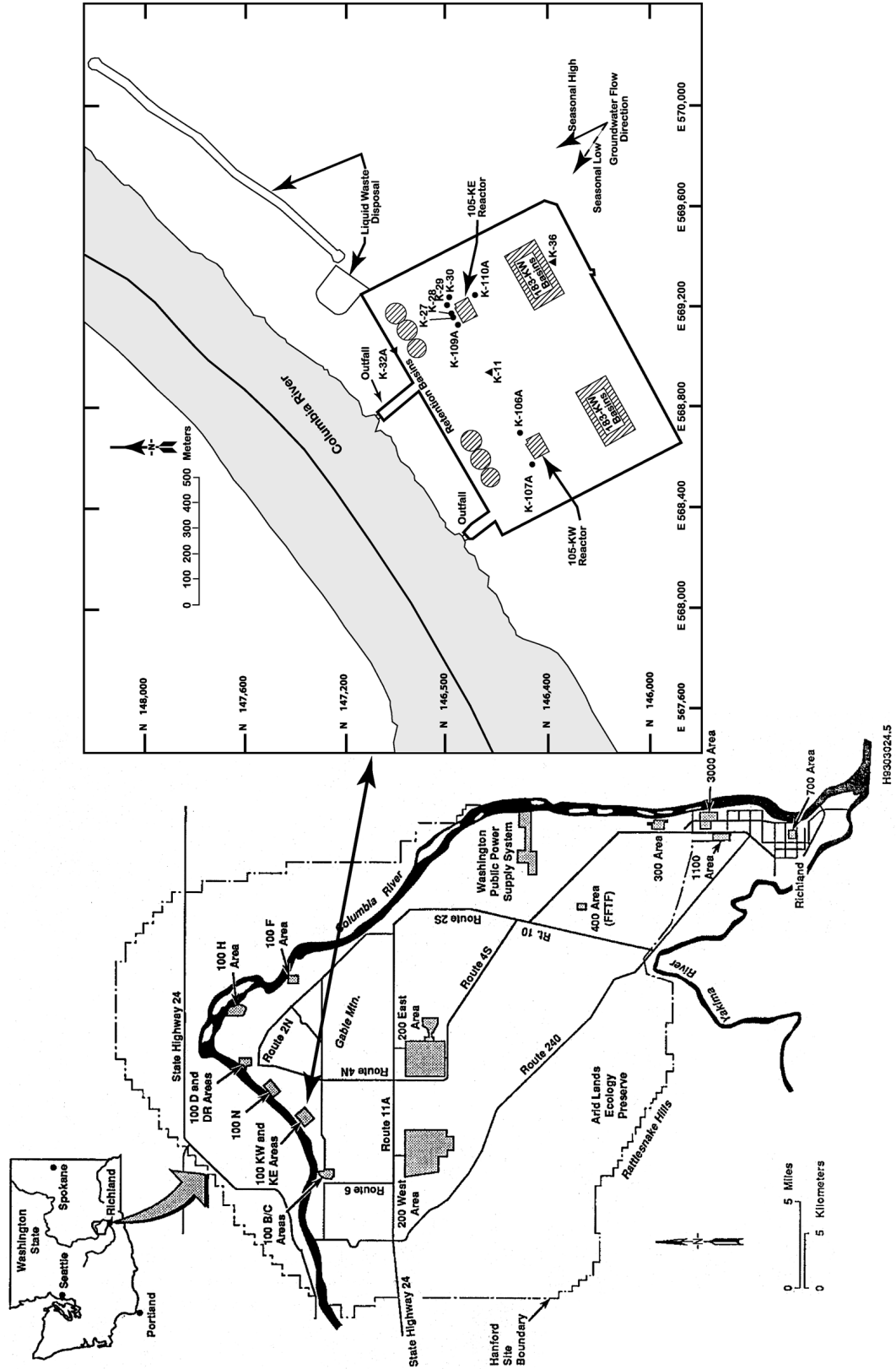
Figure 1.

Figure 2.

Figure 3.

Figure 4.
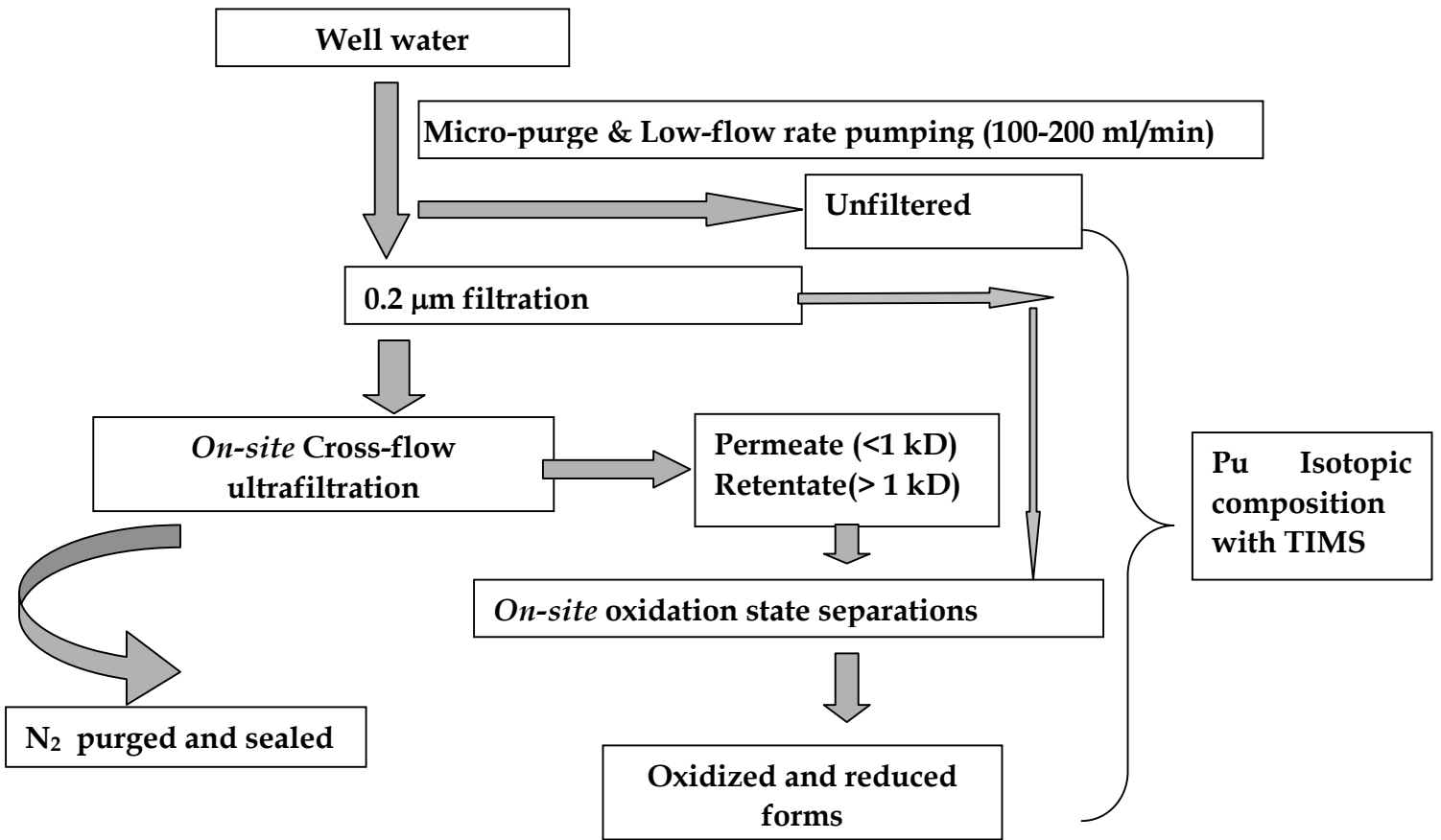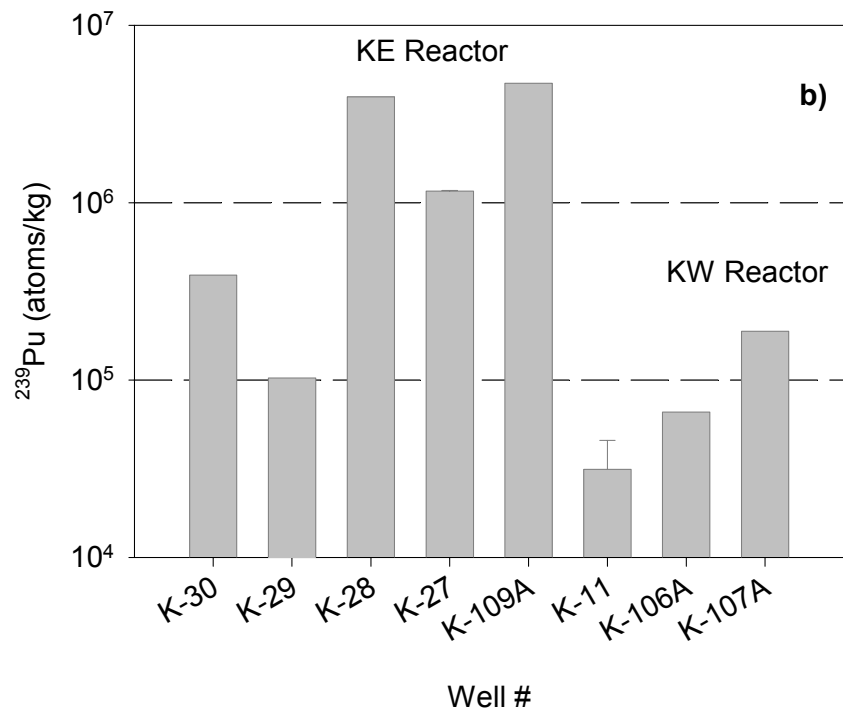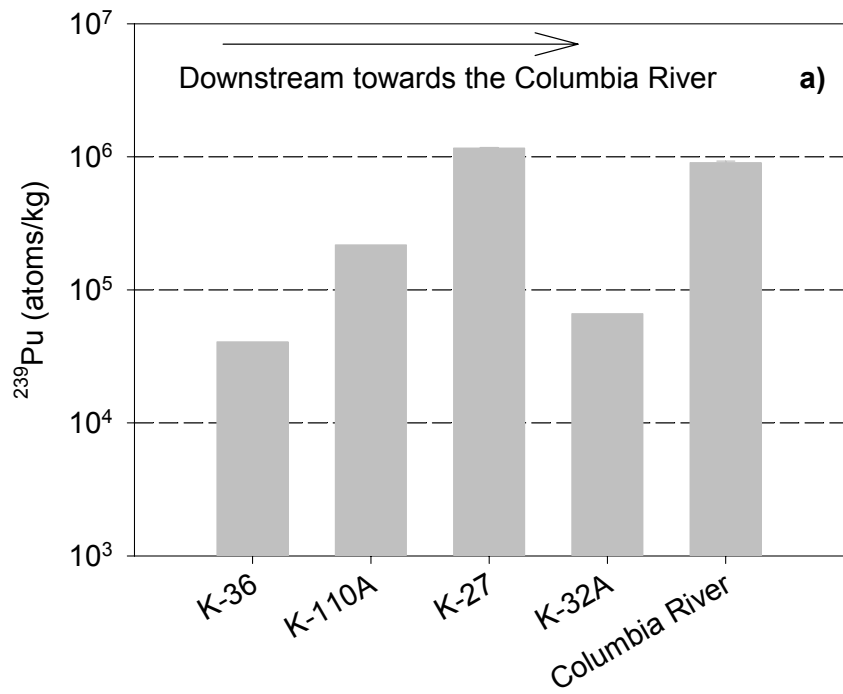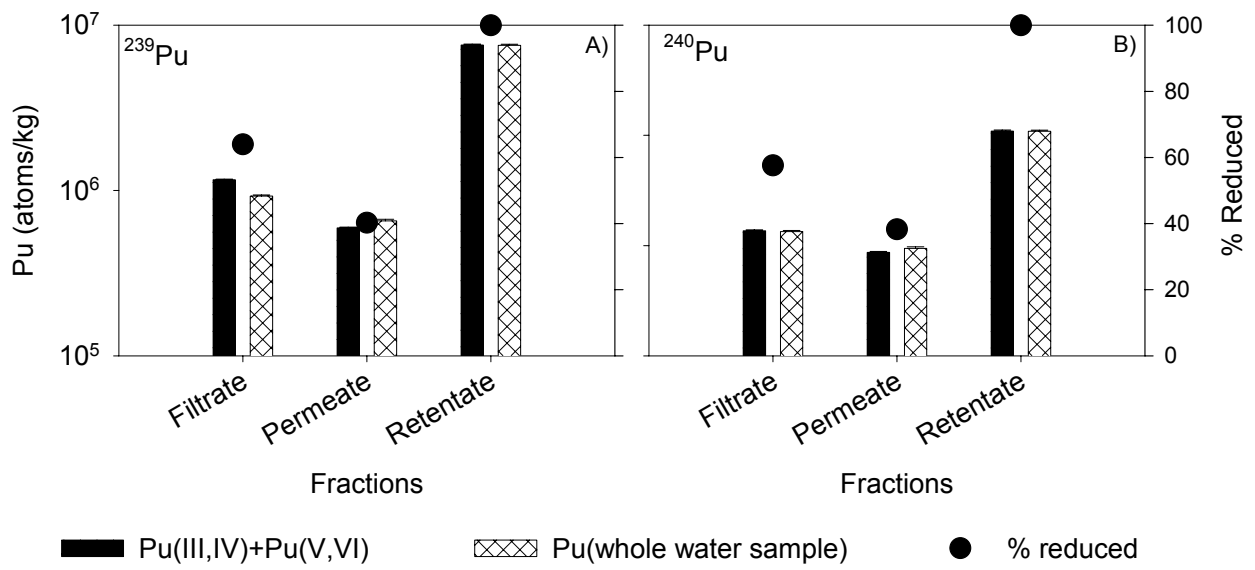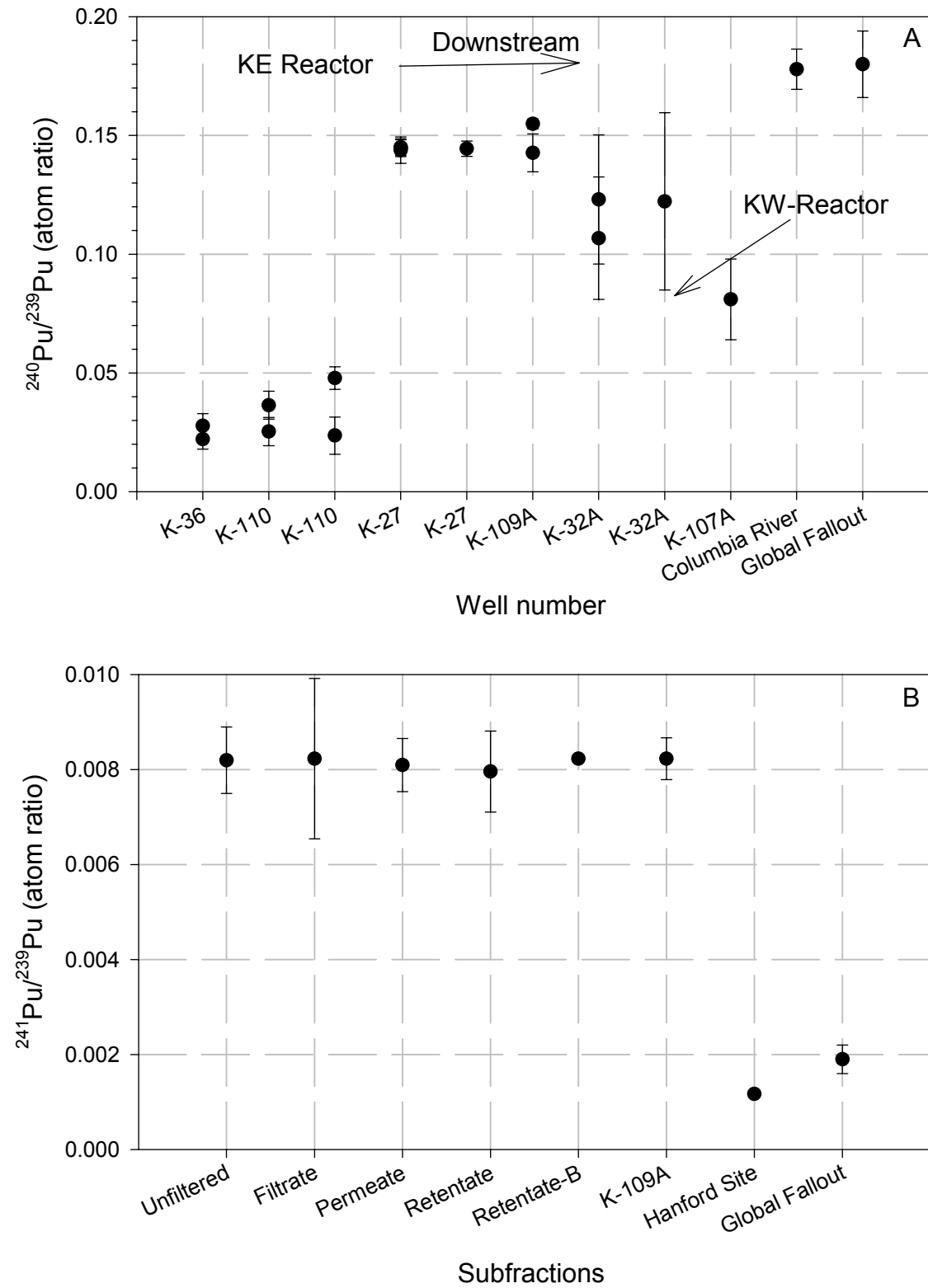
Figure 5.

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