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Identifying the Sources of Subsurface Contamination at the Hanford Site in Washington using High-Precision Uranium Isotopic Measurements

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In the mid-1990s, a groundwater plume of uranium (U) was detected in monitoring wells in the B-BX-BY Waste Management Area at the Hanford Site in Washington. This area has been used since the late 1940s to store high-level radioactive waste and other products of U fuel-rod processing. Using multiple-collector ICP source magnetic sector mass spectrometry, high-precision uranium isotopic analyses were conducted of samples of vadose zone contamination and of groundwater. The isotope ratios $^{236}U/^{238}U$, $^{234}U/^{238}U$, and $^{238}U/^{235}U$ are used to distinguish contaminant sources. On the basis of the isotopic data, the source of the groundwater contamination appears to be related to a 1951 overflow event at tank BX-102 that spilled high-level U waste into the vadose zone. The U isotopic variation of the groundwater plume is a result of mixing between contaminant U from this spill and natural background U. Vadose zone U contamination at tank B-110 likely predates the recorded tank leak and can be ruled out as a significant source of groundwater contamination, based on the U isotopic composition. The locus of vadose zone contamination is displaced from the initial locus of groundwater contamination, indicating that lateral migration in the vadose zone was at least 8 times greater than vertical migration. The time evolution of the groundwater plume suggests an average U migration rate of ∼0.7−0.8 m/day showing slight retardation relative to a groundwater flow of ∼1 m/day.

Introduction

Groundwater contamination at the Hanford Site, in south-central Washington, resulted from decades of nuclear fuel production and processing. Understanding the fate and transport of contamination is hindered by the presence of multiple potential contamination sources within relatively small areas and the extended 50-yr duration of activity. Natural sources of uranium have a uniform $^{238}U/^{235}U$ ratio (with the rare exception of the Oklo natural fission reactor; *1*) but can have variable $^{234}U/^{238}U$ depending on natural processes that can disturb the secular equilibrium of the ^{238}U decay chain. In contrast, processed U can have altered $^{238}U/^{235}U$ due either to ^{235}U enrichment for nuclear applications (which also produces residual U depleted in ^{235}U) or to changes resulting from the nuclear modification of natural or enriched uranium in nuclear reactors. The consumption of uranium fuel rods in reactors also produces ^{236}U (half-life = 23 million yr) through neutron capture by ^{235}U. ^{236}U does not occur naturally to any significant degree. These contrasts in the isotopic compositions of natural and processed uranium, as well as the wide variation in the isotopic composition of different anthropogenic uranium sources, promote the measurement of uranium isotopic composition as a tracer of uranium contamination in the environment (e.g., refs *2*−*5*).

Multiple-collector ICP source magnetic sector mass spectrometry (MC-ICPMS) provides high precision isotopic analyses of a wide range of elements (*6*−*8*). MC-ICPMS has been used for high-precision $^{234}U/^{238}U$ measurements (*9*) for U-series disequilibrium dating (e.g., refs *10* and *11*) and for $^{238}U/^{235}U$ and Pu isotopic measurements of atomic bomb fallout (*12*). For environmental applications, MC-ICPMS has the advantage of high sensitivity, high precision in isotopic measurement and, unlike α-spectroscopy, the ability to distinguish between ^{236}U and ^{235}U. Our purpose here is to demonstrate the application of high-precision measurement via MC-ICPMS of the isotopic composition of U in environmental samples.

We report high-precision measurements of $^{234}U/^{238}U$, $^{238}U/^{235}U$, and $^{236}U/^{238}U$ of uranium from vadose zone samples obtained from two contaminated cores in the B-BX-BY Waste Management Area (WMA) at the Hanford site as well as U from groundwater samples (Figure 1). The isotopic analyses are used to investigate the link between vadose zone and groundwater contamination, to identify contamination sources, and to provide estimates of the relative proportions of contaminant uranium in the analyzed samples. In addition, the uranium isotopic compositions measured in the vadose zone and groundwater samples are compared to estimates of the uranium isotopic compositions of different waste fluids to constrain the history of contamination events in the B-BX-BY tank farm.

Geologic and Hydrogeologic Settings. The Hanford Site is on the Columbia Plateau within the Pasco Basin, which was formed by broad folding and faulting of the Columbia River Basalts and overlying sediments. The geology and hydrogeology of the Hanford Site have been summarized by Hartman (*13*). The stratigraphy underlying the site consists of Miocene age Columbia River basalts; Pliocene fluvial and lacustrine sedimentary deposits of the Ringold Formation; a zone of pedogenic carbonate development at the top of the Ringold Formation, called the Cold Creek Unit; and Pleistocene episodic catastrophic flood deposits of the Hanford Formation. In the B-BX-BY WMA, the water table is currently at ∼78 m depth in the coarse gravels of the Cold Creek Unit (Figure 2) where the unconfined aquifer is only about 2−4 m thick. The vadose zone is within sands and gravels of the Hanford Formation and contains thin (tens of centimeter to millimeter scale) intervals of fine sand to silt.

In the B-BX-BY WMA, the hydraulic gradient is small, making the local groundwater flow direction difficult to determine (*14*). Past site activities artificially increased local

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TABLE 1. Uranium Isotopic Data for Pore Water

sample	avg depth (m)	PW [U] (ppm)[a]	^{234}U/^{238}U ($\times 10^6$)	$\pm 2\sigma$ ($\times 10^6$)	^{238}U/^{235}U	$\pm 2\sigma$	^{236}U/^{238}U ($\times 10^6$)	$\pm 2\sigma$ ($\times 10^6$)	contaminant (%)[b]
Section A: From Core E33-45 (near Tank BX-102)									
S01014-01A	3.2	0.044	59.84	0.06	138.142	0.067	0.662	0.012	0.9
S01014-06A	6.4	0.015	60.19	0.10	138.116	0.059	0.552	0.019	0.8
S01014-33A	22.4	29.7	54.12	0.12	147.900	0.054	78.92	0.10	100
S01014-35A	23.8	22.4	54.12	0.14	147.888	0.061	78.46	0.09	100
S01014-40A	27.0	9.02	54.00	0.12	147.902	0.087	78.89	0.12	100
S01014-54A	36.9	661.0	53.98	0.04	147.861	0.046	78.77	0.15	100
S01014-72A	46.2	92.9	53.96	0.13	147.888	0.108	78.69	0.16	100
S01014-78A	49.0	70.4	54.12	0.16	147.906	0.068	78.67	0.11	100
S01014-82A	51.4	5.32	54.04	0.11	147.924	0.082	78.50	0.11	100
S01014-83A	52.1	4.80	53.87	0.07	147.99	0.15	78.76	0.13	100
S01014-93A	58.1	47.9	53.95	0.12	147.881	0.042	78.73	0.09	100
S01014-116A	70.5	0.017	57.48	0.11	138.950	0.040	8.17	0.04	10.4
Section B: From Core E33-46 (near Tank B-110)									
S01052−06A	6.4	0.024	62.45	0.12	138.051	0.071	0.739	0.011	1.5
S01052−18A	14.1	0.035	59.98	0.11	140.098	0.083	17.15	0.05	32.0
S01052−21A	16.2	0.069	56.33	0.11	142.496	0.052	35.14	0.08	65.7
S01052−26A	18.5	0.560	54.44	0.06	144.368	0.036	52.10	0.07	97.3
S01052−36A	24.4	2.16	54.35	0.04	144.470	0.120	53.59	0.07	100
S01052−38A	25.3	3.43	54.34	0.04	144.510	0.110	53.41	0.12	100
S01052−42A	27.6	0.160	56.24	0.12	142.333	0.074	35.74	0.07	66.8
S01052−47A	30.1	0.580	55.96	0.05	142.974	0.044	39.41	0.04	73.6
S01052−53A	34.0	0.150	60.27	0.12	138.724	0.020	6.73	0.05	12.7
S01052−57A	36.6	0.141	60.81	0.06	137.881	0.051	0.383	0.004	0.8
S01052−74A	45.8	0.032	59.89	0.09	137.975	0.082	0.585	0.007	1.1
S01052−82A	50.2	0.043	60.39	0.12	137.966	0.070	0.159	0.005	0.4
S01052−90A	54.8	0.027	59.87	0.08	137.901	0.041	0.249	0.005	0.6

[a] Pore water U concentrations from refs *18* and *19*. [b] Percent contaminant U in pore water based on ^{236}U/^{238}U, see text.

recharge and disturbed the water table over much of the site. Since the end of production in the late 1980s, the water table has dropped by as much as 8 m locally, while in the B-BX-BY WMA it has dropped by 2 m. From the geometry of contaminant plumes, it appears that groundwater flow has been to the northwest, consistent with the flow regime during site operations. Recent studies of flow directions in the northern 200-East Area have provided widely varying results (*14*).

Sampling Context. The analyzed vadose zone samples come from two sediment cores taken by CH2M HILL Hanford Group, Inc. for the U.S. Department of Energy to characterize contamination plumes and sediments within the vadose zone in the B-BX-BY WMA (Figure 1). Core E33-45 is near tank BX-102, which in 1951 was involved in a large overflow event that released over 340,000 L of high-level waste to the vadose zone (*15*). Core E33-46 is from near tank B-110 that is estimated to have leaked approximately 94,000 L to the vadose zone via a transfer line around 1965−1969 (*15*).

Analyzed water samples come from groundwater monitoring wells in the vicinity of the B-BX-BY WMA (Figure 1). At the times of well sampling for this study (mid-2001), the groundwater plume (>20 ppb U) was known to be approximately 250 m wide and at least 900 m long with U concentrations up to 525 ppb (*16*). Subsequent sampling indicates that concentrations in the most contaminated wells (E33-9 and E33-44) peaked in 2001 (*17*). The vadose zone source of this groundwater plume is uncertain.

Analytical Methods

Depths of the analyzed core samples are provided in Table 1, Sections A and B, and shown in Figure 2. Isotopic analyses were conducted on aliquots of pore water extracts from sediment samples created using a 1:1 (by weight) deionized water (DI) rinse (*18*, *19*). Concentrations of total U for the rinses are from Serne et al. (*18*, *19*). Aliquots of groundwater samples collected during mid-2001 (see ref *16* for sampling protocols) were analyzed. U isotopic analyses of groundwater samples presented here replicate at higher precision (~20 times better) most of the analyses reported by Dresel et al. (*16*) for the B-BX-BY area. Well locations are shown in Figure 1 and sampling dates are given in Table 2. For the isotopic

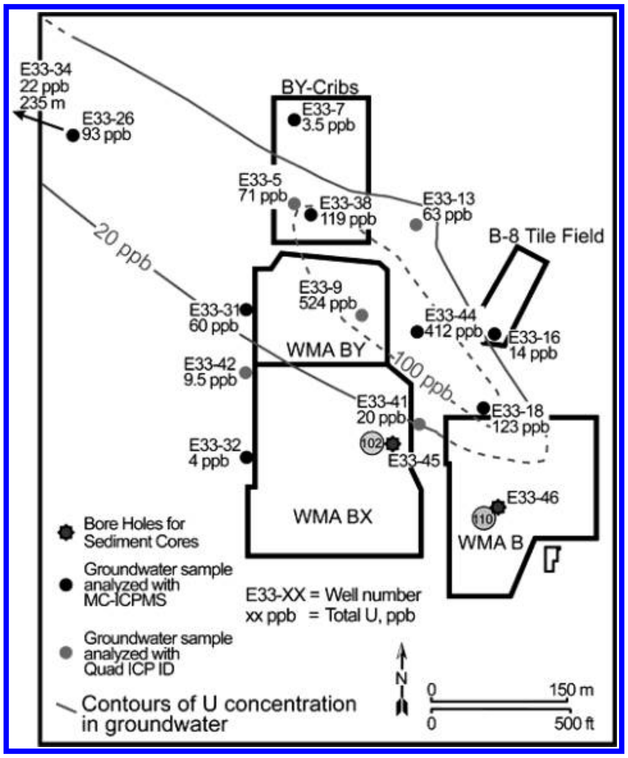

FIGURE 1. Map of the B-BX-BY Waste Management Area in the 200 East Area, Hanford, WA. Shown are locations of sampled monitoring wells and two bore holes, E33-45 near tank BX-102 and E33-46 near tank B-110, that provided sediment cores through the vadose zone. Well E33-34 is off the map, approximately 235 m to the NW of well E33-26. Grey circles represent well samples analyzed by Quad ICP ID only (*16*).

TABLE 2. Uranium Isotopic Data for Groundwater Samples, B-BX-BY WMA

well	date	[U] (ppb)[a]	^{234}U/^{238}U ($\times 10^6$)	$\pm 2\sigma$ ($\times 10^6$)	^{238}U/^{235}U	$\pm 2\sigma$	^{236}U/^{238}U ($\times 10^6$)	$\pm 2\sigma$ ($\times 10^6$)
E33-26	8/6/01	92.84	54.613	0.045	147.461	0.026	74.290	0.080
E33-38	8/2/01	119.05	54.517	0.057	147.542	0.034	75.419	0.080
E33-18	8/1/01	122.70	54.316	0.069	147.738	0.064	75.993	0.099
E33-44	8/6/01	411.70	54.092	0.073	147.818	0.041	77.155	0.192
E33-16	5/4/01	14.46	59.204	0.082	143.147	0.080	41.50	0.055
E33-7	8/2/01	3.46	66.955	0.059	137.992	0.040	1.66	0.01
E33-34	3/15/01	22.40	56.441	0.062	146.135	0.036	64.619	0.070
E33-31	7/30/01	60	55.153	0.055	147.092	0.050	71.930	0.109
E33-32	8/2/01	4	66.419	0.070	139.584	0.036	18.108	0.030

[a] U concentrations from ref *16*.

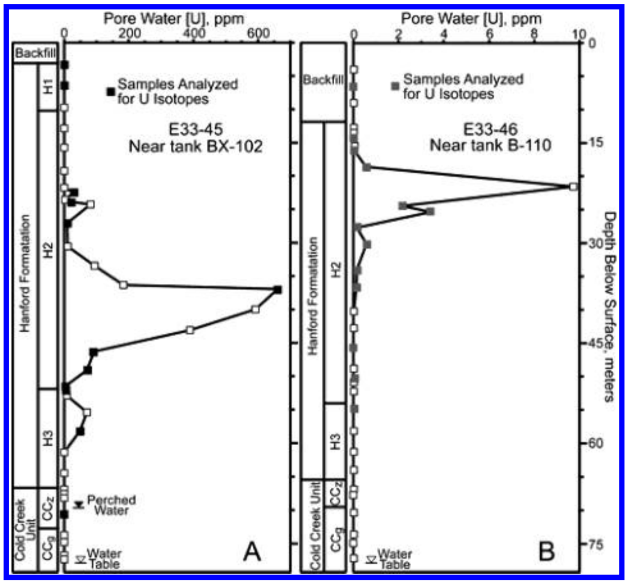

FIGURE 2. Profiles in panel A of core E33-45 and in panel B of core E33-46 showing U concentrations in pore water and stratigraphy of the cores (*18, 19*). Samples analyzed for this paper are represented by black boxes (core E33-45) and gray boxes (core E33-46).

analyses the uranium was chemically separated from the allotted sample aliquots using TRU-SPEC (Eichrom Industries Inc.) resin in small-volume Teflon columns scaled down from the procedure of Luo et al. (*9*). Fresh resin was used for each separation. The separation scheme provided column U yields of ≥95%. Along with batches of the samples, aliquots of natural uranium standard (see below) were passed through the same preparation and separation processes. These aliquots showed no detectable ^{236}U, demonstrating an absence of laboratory cross contamination in sample preparation and analysis.

The uranium isotopic compositions (^{234}U/^{238}U, ^{238}U/^{235}U, and ^{236}U/^{238}U) were measured on a MC-ICPMS (an IsoProbe manufactured by Micromass) at Lawrence Berkeley National Laboratory (LBNL). Uranium isotopes 235 and 238 were measured simultaneously on separate Faraday cups, while 234 and 236 were measured on a Daly ion counting system situated behind a wide-angle retardation potential lens. Two separate static simultaneous measurement routines were used, one for ^{238}U/^{235}U and ^{234}U/^{238}U and a second one for ^{236}U/^{238}U. Corrections for mass fractionation, for Daly–Faraday intercalibration, and for any peak-tail under mass 236 were calculated from bracketed analyses of the secular equilibrium natural uranium standard (U ore from the Schwartzwalder Mine, CO, provided by W. Sharp, Berkeley Geochronology Center, solution diluted to 20 ppb with no chemical separation). Isotopic compositions were normalized to the natural ^{238}U/^{235}U ratio (= 137.88 by convention; *20*) of the standard solution using an exponential mass fractionation law. Sample solutions were introduced to the MC-ICPMS with a desolvation system (Aridus, manufactured by CETAC Inc.) equipped with a low uptake micro-concentric nebulizer. The uranium isotopic compositions are compiled for core E33-45 in Table 1, Section A; for core E33-46 in Table 1, Section B; and for the groundwater samples in Table 2. Statistical analyses and linear regressions were conducted using Isoplot (*21*). Typical precision for ^{238}U/^{235}U is $\leq \pm 0.05\%$ 2σ and for ^{234}U/^{238}U it is $\pm 0.15\%$ 2σ. The ratio ^{236}U/^{238}U can be measured with $\pm 0.15\%$ 2σ precision down to the 10^{-7} range where precision degrades by about a factor of 10. Seven aliquots of the natural uranium standard that were passed through the separation chemistry and analyzed as unknowns yielded weighted average $^{238}\text{U}/^{235}\text{U} = 137.86 \pm 0.03\%$ ($\pm$95% confidence limits; CL) and $^{234}\text{U}/^{238}\text{U} = 5.485 \times 10^{-5} \pm 0.08\%$ ($\pm$95% CL) indistinguishable from expected values for natural U in secular equilibrium.

Results

Borehole 299-E33-45 near Tank BX-102. The uranium concentrations of the pore water rinses outline a distinct vadose zone plume between 22 and 62 m depth in the core, with a peak in U concentration at about 36–40 m depth (*18*) (Figure 2A). The nine samples analyzed from this plume region have virtually identical values of ^{234}U/^{238}U, ^{238}U/^{235}U, and ^{236}U/^{238}U (Table 1, Section A). The weighted average ratios are $^{234}\text{U}/^{238}\text{U} = 5.3979 \times 10^{-5}$ ($\pm$0.097%, 95% CL), $^{238}\text{U}/^{235}\text{U} = 147.889$ ($\pm$0.014%, 95% CL), and $^{236}\text{U}/^{238}\text{U} = 7.870 \times 10^{-5}$ ($\pm$0.16%, 95% CL). The vadose zone plume samples have extremely high U concentrations (from 4.8 to 660 ppm calculated for pore water) as compared to background values of 15–150 ppb, which means that the isotopic ratios are unaffected by the presence of background U. The consistency of the measured U isotopic ratios indicates that the contaminant U is homogeneous and must have come from a single well-mixed source. In contrast, a pore water sample (S01014-116A) from within a perched water body encountered at 70.5 m depth (*18*) has a different isotopic composition (Table 1, Section A). Two samples (S01014-1A and S01014-6A) from near the top of the E33-45 core from depths of 3.2 and 6.3 m have near normal ^{238}U/^{235}U, with small but measurable ^{236}U/^{238}U (Table 1, Section A).

The data for E33-45 pore water are presented on a plot of ^{236}U/^{238}U versus ^{238}U/^{235}U in Figure 3A. On this graph, natural U plots on the *x*-axis ($^{236}\text{U}/^{238}\text{U} = 0$) at a value of $^{238}\text{U}/^{235}\text{U} = 137.88 \pm 0.04$ (*20, 22*). The U isotopic compositions representing the vadose zone plume in E33-45 form a tight cluster, while the perched water sample and the two shallow samples fall closer to the ^{238}U/^{235}U axis. A best-fit line through the plume data (nine points) and the data for S01014-116A from the perched water zone gives an intercept of 137.92 ± 0.04 ($\pm 2\sigma$), within error of the ^{238}U/^{235}U of natural uranium (*22, 23*). The data suggest that sample S01014-116A consists of a mixture of natural uranium and contaminant uranium. Assuming the weighted average ^{238}U/^{235}U (= 147.89

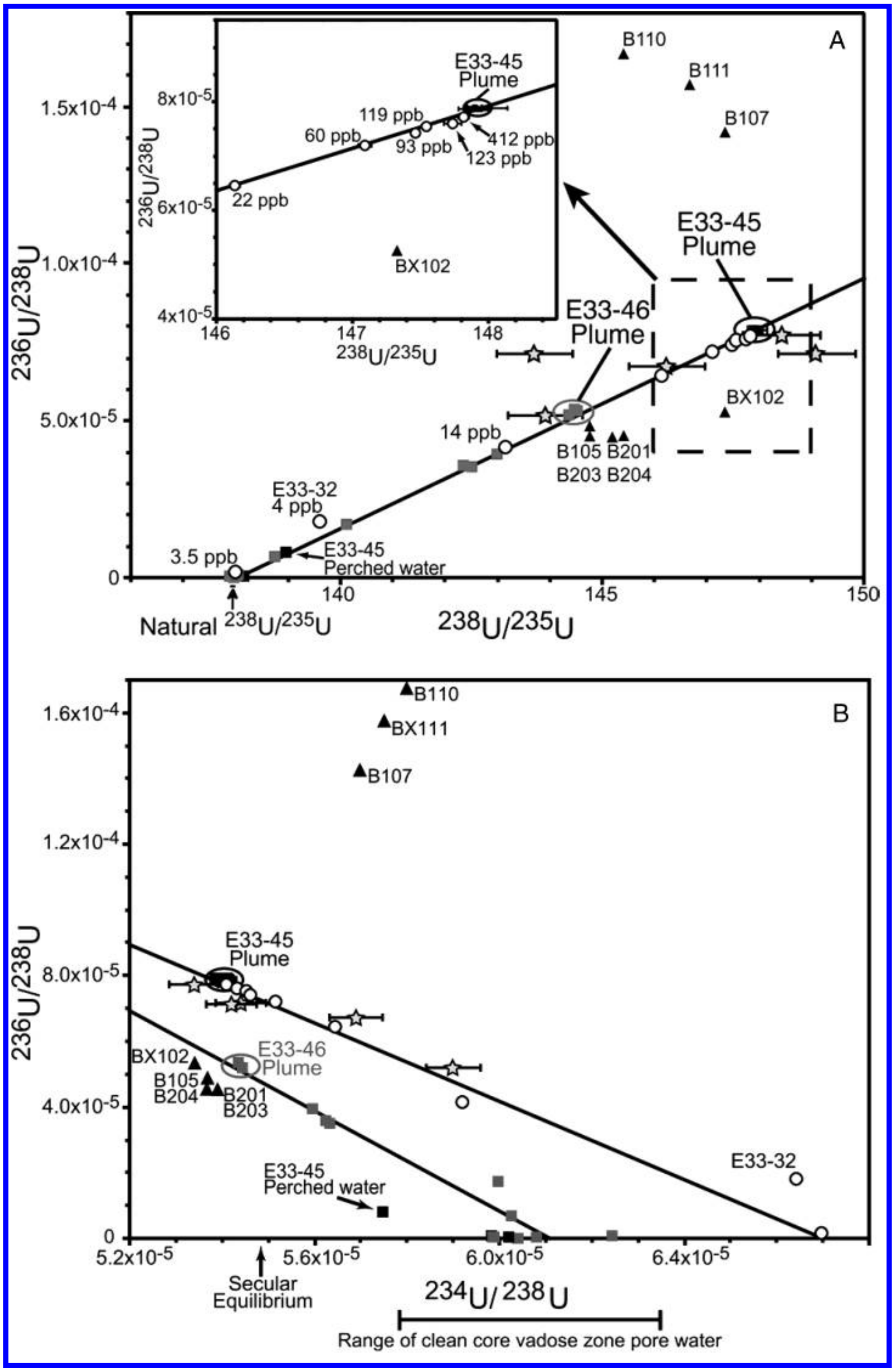

FIGURE 3. Uranium isotopic data: (A) ^{236}U/^{238}U vs ^{238}U/^{235}U; (B) ^{236}U/^{238}U vs ^{234}U/^{238}U. Black squares are data for water extractions from samples from E33-45 (near tank BX-102) contaminated core; gray squares are data for water extractions of samples from E33-46 (near tank B-110) contaminated core. Errors for data are approximately the size of the symbols or smaller. Black triangles are estimates by Jones et al. (*15*) of the uranium isotopic composition of tank leaks in the B-BX-BY area. Open circles are uranium isotopic data for groundwater samples; errors are approximately the size of the symbol or smaller. Grey stars are groundwater data from ref *16* shown with 1% uncertainties.

± 0.02) of the vadose zone plume samples as the end member contaminant, then 10.7 ± 0.4% of the uranium in sample S01014-116A is contaminant U. A similar calculation based on ^{236}U/^{238}U gives an indistinguishable but better constrained result of 10.44 ± 0.07%. Likewise, plotting ^{234}U/^{238}U against ^{236}U/^{238}U (see Figure 3B) can give an estimate for the precontamination ^{234}U/^{238}U of sample 116A. The extrapolated ^{234}U/^{238}U is $5.789 \pm 0.022 \times 10^{-5}$ (±95% CL), which corresponds to a slight excess of ^{234}U relative to ^{238}U (^{234}U/^{238}U activity ratio = 1.056 ± 4), as is typical of natural vadose zone pore fluid samples (*24*). Similar calculations based on ^{236}U/^{238}U can be made for samples S01014-1A and S01014-6A, indicating <1% contaminant U in those shallow samples (0.90 ± 0.02% and 0.76 ± 0.03%, respectively). This low level of contamination is not from sample processing at LBNL but could conceivably be due to inadvertent contamination during bore hole operations. The two samples have excesses of ^{234}U (^{234}U/^{238}U activity ratios of 1.092 ± 0.001 and 1.099 ± 0.002).

Borehole 299-E33-46 near Tank B-110. The calculated pore water U concentrations in this core are much lower than in E33-45, with ~9.7 ppm being the highest concentration (*19*). The vadose zone U contamination plume covers a depth range from approximately 15 to 38 m (*19*) (Figure 2B), with a peak concentration at ∼21 m depth. Ten of the analyzed samples are from this contaminated zone, two are from greater depth (samples S01052-82A from 50.2 m and S01052-90A from 54.8 m), and one (S01052-06A) is from within the artificial backfill at a depth of 6.4 m. The sample with the highest U concentration, at 21 m depth, was not available for U isotopic analysis.

The ten samples from the E33-46 vadose zone plume exhibit a significant range in isotopic composition (Table 1, Section B). The U concentrations are sufficiently low in most of the samples that the isotopic ratios reflect a mixture of contaminant U and natural background U. The isotopic composition of the contaminant U can be estimated from the weighted average of the data for the two samples with the highest U concentration (S01052-38A and -36A), which have nearly identical isotopic ratios: ^{234}U/^{238}U = 5.434×10^{-5} (±0.057%, 95% CL), ^{238}U/^{235}U = 144.492 (±0.056%, 95% CL), and ^{236}U/^{238}U = 5.354×10^{-5} (±0.12%, 2σ internal). The best-fit line to the plume data in Figure 3A has an intercept of 137.92 ± 0.18 (±95% CL), indistinguishable from the value for natural uranium. In the plot of ^{236}U/^{238}U versus ^{234}U/^{238}U (Figure 3B), the data for the E33-46 vadose zone plume forms a linear array with an intercept at ^{234}U/^{238}U = $6.119 \pm 0.054 \times 10^{-5}$ (±95% CL). This value falls roughly at the mean of the measured ^{234}U/^{238}U of the samples (S01052-06A, S01052-82A, and S01052-90A) that have very low ^{236}U/^{238}U and natural or near-natural ^{238}U/^{235}U. The E33-46 vadose zone plume data do not all fall on a single line in Figure 3B because they represent mixing between the contaminant composition and background pore water U that has variations in ^{234}U excess. The samples from the plume zone vary from close to 100% contaminant to 0.8% contaminant U (Table 1, Section B), based on the measured ^{236}U/^{238}U and the assumption that samples S01052-38A and S01052-36A represent the ^{236}U/^{238}U of the contaminant uranium (see above, Table 1).

B-BX-BY Area Groundwater Samples. Samples from nine wells were measured, covering the extent of the groundwater plume as known in 2001 and including wells just outside the plume, as defined by the 20 ppb concentration contour. The groundwater U concentrations of the analyzed samples (Figure 1, Table 2) range from 3.5 ppb (well E33-7) to 412 ppb (well E33-44).

The analyzed samples cover a range in isotopic composition (Figure 3A). The ^{236}U/^{238}U and ^{238}U/^{235}U ratios of the groundwater samples fall along a line between the E33-45 vadose zone plume data and the natural isotopic composition of uranium. One sample, E33-32, from a well furthest from the groundwater plume falls off this line. Excluding this sample, the best-fit line to the groundwater data has an intercept of 137.76 ± 0.10 (±95% CL), indistinguishable from natural uranium. This indicates that the groundwater data can be explained by mixing between background natural U and a single end-member contaminant. In the case of the sample from well E33-32, a different or additional component is necessary. The ^{236}U/^{238}U and ^{234}U/^{238}U ratios for the groundwater samples form an array between the E33-45 vadose zone plume composition and a high ^{234}U/^{238}U ratio consistent with natural groundwater U (Figure 3B).

Discussion

Source of the B-BX-BY Area Groundwater Uranium Plume. The uranium isotopic data provide several lines of evidence for the source of the B-BX-BY groundwater U plume. The highest concentration groundwater sample closely approaches the isotopic composition of the E33-45 vadose zone plume, with the other samples falling along the line connecting the samples to natural U composition in decreasing order of concentration (Figure 3A). This systematic relationship is most likely a result of mixing between natural background U and a contaminant composition represented by the E33-45 vadose zone plume rather than each groundwater sample representing contamination from different sources. This conclusion is further supported by the relationships seen in Figure 3B, in which ^{234}U/^{238}U provides additional signatures for natural U and contaminant U due to α-recoil effects that impart to groundwater and pore water a higher ^{234}U/^{238}U than the secular equilibrium ratio. In Figure 3B, the E33-45 and E33-46 vadose zone U plumes are well-separated. The groundwater data form an array between the E33-45 plume and a groundwater component with elevated ^{234}U/^{238}U and zero ^{236}U, eliminating the E33-46 vadose zone plume as a contributor to the contamination. The natural groundwater component is approximated by the sample from well E33-7, which has low ^{236}U/^{238}U (= 1.66×10^{-6}) and nearly normal ^{238}U/^{235}U (= 137.99 ± 0.04) but a high ^{234}U/^{238}U (= 6.695×10^{-5}), indicating that uncontaminated groundwater has ^{234}U/^{238}U further from secular equilibrium than uncontaminated pore waters in the E33-45 and E33-46 cores. The E33-32 well is the sampled well farthest from the groundwater plume and may involve a different contaminant composition and therefore a different source. That it plots to the left of the mixing line in Figure 3A suggests a high ^{236}U/^{238}U as compared to ^{238}U/^{235}U and so a minor component of enriched ^{235}U fuel. Future sampling of this well, along with sampling of additional nearby wells, may resolve this particular issue.

TABLE 3. Calculated Percentage of Contaminant U, Precontamination U Concentrations, and Precontamination ^{234}U/^{238}U for Groundwater Samples

well	contamin (%)	precontamin [U] (ppb ± 2σ)[a]	cor ^{234}U/^{238}U (× 10^6)	±2σ (× 10^6)
E33-26	94	5.2 ± 0.17	65.28	1.1
E33-38	96	5.0 ± 0.22	66.86	1.7
E33-18	97	4.2 ± 0.24	63.75	2.5
E33-44	98	8.1 ± 1.2	59.69	4.28
E33-16	53	6.8 ± 0.02	65.03	0.19
E33-7	2	3.39 ± 0.001	67.23	0.06
E33-34	82	4.0 ± 0.04	67.73	0.42
E33-31	91	5.1 ± 0.12	67.62	0.72
E33-32	∼23	3.08 ± 0.002	70.14	0.08
E33-5[b]	∼91	∼7		
E33-13[b]	∼91	∼6		
E33-9[b]	∼99	∼8		
E33-41[b]	∼84	∼3		

[a] Only includes error in the isotopic measurements, does not include concentration error. [b] Based on data from ref *16*.

Assuming the average ^{236}U/^{238}U found for the E33-45 vadose zone plume, the percentage of contaminant U and the pre-contamination concentration of U in each groundwater sample can be calculated (Table 3). This gives a range of ∼3−8ppb for the precontamination concentration of U and a range of the percentage of contamination of 2% (E33-7) to a high of 98% (E33-44). The range in precontamination concentration is very similar to that seen in background wells outside the B-BX-BY area (*17*). The average ^{236}U/^{238}U and ^{234}U/^{238}U of the E33-45 vadose zone plume can also be used to calculate a precontamination ^{234}U/^{238}U for the groundwater samples (Table 3).

There is a rough negative correlation between the calculated precontamination groundwater ^{234}U/^{238}U and the calculated precontamination groundwater U concentration (Figure 4). This is consistent with the behavior of groundwater U, where natural ^{234}U from α-recoil effects is diluted by secular equilibrium U derived from weathering (*24*). The calculated precontamination ^{234}U/^{238}U provides a potential label for groundwater U for the backtracking of groundwater flow paths (*25*), once a wider survey in the Hanford Site of groundwater ^{234}U/^{238}U is conducted.

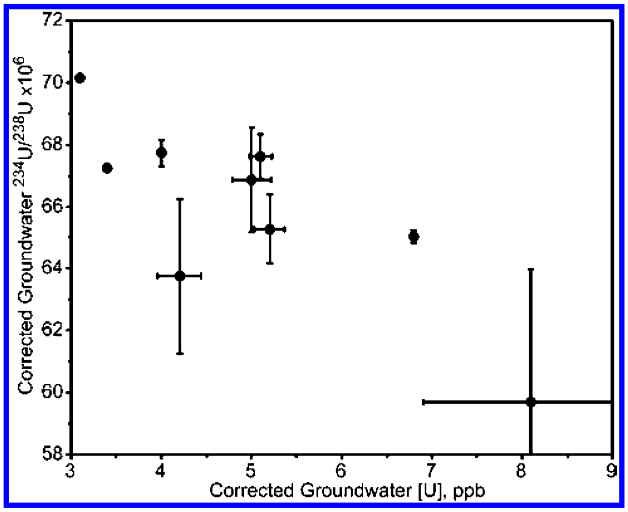

FIGURE 4. Concentration data and $^{234}U/^{238}U$ for groundwater samples corrected for contamination based on the average $^{236}U/^{238}U$ for E33-45 (for concentration) and average $^{236}U/^{238}U$ and $^{234}U/^{238}U$ for E33-45 (for $^{234}U/^{238}U$). Errors are based on the isotopic measurements alone.

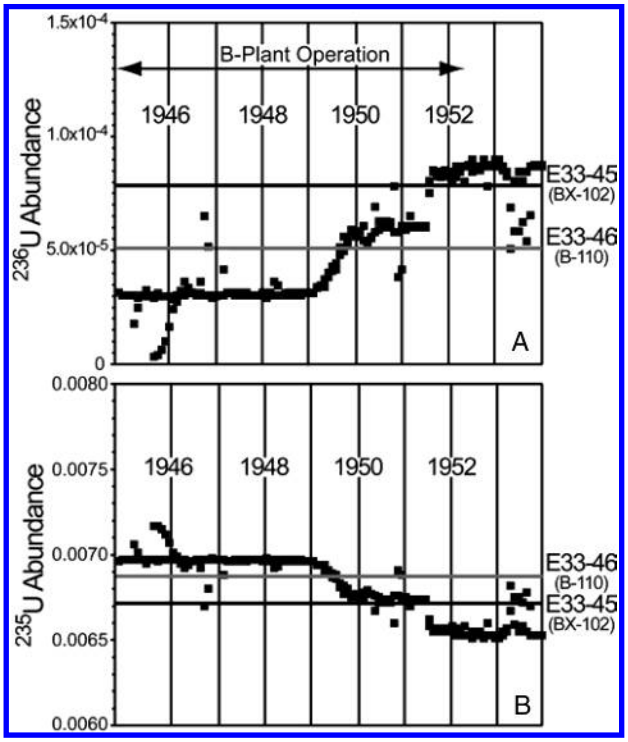

FIGURE 5. Models of the abundances of ^{236}U (A) and ^{235}U (B) for irradiated natural U fuel rods (0.71% 235U-Al) for 1945−1954 from ref *16*. Indicated by horizontal lines are the abundances of ^{236}U and ^{235}U in the contaminants identified in the E33-45 and E33-46 vadose zone plumes. B-plant operated from 1945 to mid-1952 and produced waste that was stored in the B-BX-BY tanks.

Implications for the History of Uranium Contamination. The isotopic compositions of the E33-45 and E33-46 contaminant U are consistent with the model estimates of production from the Al-clad 0.71% ^{235}U (natural uranium) fuel type rather than fuels with enriched ^{235}U contents (*16*). Dresel et al. (*16*) provide model histories of the abundances of ^{234}U, ^{235}U, and ^{236}U of the fuel rods that were processed by the Hanford plants (*26*). The average abundances of ^{235}U (6.72×10^{-3}) and ^{236}U abundance (7.82×10^{-5}) for the E33-45 vadose zone plume are consistent with the composition of natural U fuel rods processed in a fairly narrow time period between 1950 and 1952 (Figure 5). This supports the inference from γ-logs (*15*) that the 1951 BX-102 overflow event is the source of the vadose zone contamination seen in core E33-45. The abundance of ^{234}U only decreased slightly with burn-up of the Al 0.71% ^{235}U fuel, but the average ^{234}U abundance (5.36×10^{-5}) for the E33-45 vadose zone plume is consistent with the A1−0.71% ^{235}U fuel and distinct from other enriched fuel types processed later.

Given the large volume of material spilled from BX-102, it might be supposed that the E33-46 plume is a diluted mixture of BX-102 uranium and background uranium either picked up from pore fluid ($^{234}U/^{238}U > 5.43 \times 10^{-5}$) or leached from the sediment minerals ($^{234}U/^{238}U = 5.43 \times 10^{-5}$) during lateral spreading of the contaminant fluid. But the isotopic evidence does not support either of these possibilities. In Figure 3B, the data for the E33-46 vadose zone plume forms a linear array that represents mixing between contaminant uranium and natural pore water U, as was also concluded from Figure 3A. However, the E33-45 vadose zone plume samples plot off the line defined by the E33-46 samples, eliminating addition of pore water U to the E33-45 contaminant U as a means to produce the E33-46 vadose zone plume U. The E33-46 plume contaminant U isotopic composition does not fall on a common mixing line between natural U and the E33-45 plume composition. In Figure 3A, a best-fit line (not shown) through the E33-45 plume data and the E33-45 contaminant (samples S01052-36A and -38A) has an intercept of 137.29 ± 0.25 (2σ) distinct from natural U. If instead in Figure 3A a line is fit between the E33-45 plume data and the natural U composition and another line is fit between the E33-46 contaminant (again samples S01052-36A and -38A) and the natural U composition, those two lines have distinct slopes ($7.864 \pm 0.018 \times 10^{-6}$ for E33-45 and $8.091 \pm 0.099 \times 10^{-6}$ for E33-46). This is to be expected for different batches of natural U fuel rods that went through burn-up under different reactor power conditions, which varied during the Hanford production history. In addition, it is highly unlikely that the E33-46 uranium isotopic composition can be derived from that of the E33-45 contaminant through wholesale extraction of natural secular equilibrium U from the sediment by the E33-45 contaminant fluid. A mass balance calculation for a contaminant fluid with 660 ppm U and sediment with 1 ppm indicates that a sediment/fluid ratio of at least 200 would be needed, an unreasonably high value. Each of the above points to separate contaminant sources for the U in the E33-45 and E33-46 vadose zone plumes.

Our best interpretation of the isotopic analyses is that most, if not all, of the uranium in the groundwater samples from the B-BX-BY area comes from the 1951 BX-102 overflow event. Recent modeling of the supernatant chemical compositions for the B-BX-BY tanks (*27*) that indicates that BX-102 had the highest supernatant uranium concentration (by several orders of magnitude) supports this conclusion. This, together with the large volume of that leak (>340,000 L of solution with ~0.1 mol/L of U (*15*)), suggests it as an important source of uranium contamination in the area. It should be noted, however, that several liquid waste disposal facilities (cribs) were in operation in close proximity to the B-BX-BY tanks during the late 1940s and early 1950s (*28*). With no vadose zone samples from those facilities, our study cannot entirely rule them out as sources of groundwater contamination.

The isotopic composition of the E33-46 vadose zone U plume does not match the isotopic composition estimated by Jones et al. (*15*) for the 1965/1969 leak from the B-110 tank (Figure 3). The estimate by Jones et al. (*15*) presumes a mixture of processed natural U and enriched fuel rods, as might be expected from the late 1960s. Even if this estimate is in error, the E33-46 vadose zone plume ^{236}U abundance (5.322×10^{-5}) and ^{235}U abundance (6.873×10^{-3}) would appear to be inconsistent with the composition of most natural U fuel processed in the late 1960s (see estimates in ref *16*). Rather, the E33-46 composition is more likely to be natural U fuel from early in the history of processing, possibly before 1950 (Figure 5). Therefore, it appears that the vadose zone plume in the E33-46 core is not related to the 1965/1969 leak from the B-110 tank but related to an earlier unrecorded event or leak. Tank B-110 was placed in service in May 1945 and filled by December 1945, making it one of the first used in the area (*29*). By virtue of the fact that the ^{236}U/^{238}U (or ^{236}U abundance) for E33-46 is lower than that of E33-45, the contaminant appears to be waste generated earlier than the BX-102 overflow event. On the basis of the isotopic differences between the leak and the groundwater contamination, the B-110 leak was probably not a significant source of uranium contamination in groundwater.

Having made a case for the E33-45 vadose U plume (and hence the 1951 BX-102 overflow event) being the source of the B-BX-BY groundwater plume, there are implications for the path and history of U transport. Apparently the initial locus of groundwater contamination was displaced from the vadose zone source by as much as 150 m to the northeast. Comparing this distance to the vertical distance to the water table of the contamination in E33-45 implies more than an 8:1 ratio of horizontal to vertical migration of the contaminant U within the vadose zone before contamination of the groundwater. This may have resulted from the strong anisotropy in the vertical permeability due to the presence of fine sedimentary layers in the stratigraphy (*30*) enhancing horizontal migration, following the slight (<5°) northeast dip of sedimentary layering (*18*). The time of groundwater contamination is also significantly displaced (>40 yr) from the time of the 1951 overflow event that contaminated the vadose zone sediments. From an examination of monitoring well records, the first sign of U contamination appeared in well E33-18 in early 1993 and peaked in mid-1997. Records for other wells are incomplete, especially for E33-9 and E33-44, which showed the highest U concentrations in 2001. For well E33-34, about 775 m downgradient from E33-18 along the axis of the groundwater plume (Figure 1), the first appearance of elevated U concentrations was about mid-1995 to early-1996. Thus about 2.5−3 yr was necessary for the contaminant uranium to migrate from E33-18, presumed to be close to the locus of initial contamination, to E33-34, implying a rate of 0.7−0.8 m/day. This is somewhat less than a groundwater flow rate of 1 m/day calculated from measured data for 2000 (*17*) but is consistent considering that some retardation of U migration relative to groundwater movement is likely (e.g., ref *2*).

The current groundwater contamination appears to have resulted from an episodic event given the relatively limited size of the groundwater plume and declining concentrations near the source area. Since over 40 yr separates the vadose zone spill and the groundwater contamination that was detected in the early 1990s, we cannot say whether there were prior undetected events. It is also not known whether contamination reached the water table in 1951, but if so, it appears that it had dissipated by the early 1990s before the appearance of the current groundwater plume. By about 2001, U concentrations in monitoring wells in the area had begun to diminish (*17*) as the plume migrates and attenuates. But the connection between the still significant U contamination seen in the vadose zone near tank BX-102 and groundwater contamination indicates a continuing potential for future contamination events from this source.

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Literature Cited

(1) Lancelot, J. R.; Vitrac, A.; Allegre, C. J. *Earth Planet. Sci. Lett.* **1975**, *25*, 189−196.
(2) Beasley, T. M.; Dixon, P. R.; Mann, L. J. *Environ. Sci. Technol.* **1998**, *32*, 3875−3881.
(3) Ketterer, M. E.; Wetzel, W. C.; Layman, R. R.; Matisoff, G.; Bonniwell, E. C. *Environ. Sci. Technol.*, **2000**, *34*, 966−972.
(4) Yoshida, S.; Muramatsu, Y.; Tagami, K. *Environ. Sci. Technol.* **2001**, *35*, 4174−4179.
(5) Croudace, I. W.; Warwick, P. E.; Taylor, R. N.; Cundy, A. B. *Environ. Sci. Technol.* **2000**, *34*, 4496−4503.
(6) Walder, A. J.; Freedman, P. A. *J. Anal. At. Spectrosc.* **1992**, *7*, 571−575.
(7) Walder, A. J.; Platzner, I.; Freedman, P. A. *J. Anal. At. Spectrosc.* **1993**, *8*, 19−23.
(8) Halliday, A. N.; Lee, D.-C.; Christensen, J. N.; Rehkämper, M.; Yi, W.; Luo, X.; Hall, C. M.; Ballentine, C. J.; Pettke, T.; Stirling, C. *Geochim. Cosmochim. Acta* **1998**, *62*, 919−940.
(9) Luo, X. Z.; Rehkämper, M.; Lee, D.-C.; Halliday, A. N. *Int. J. Mass Spectrom. Ion Processes* **1997**, *171*, 105−117.
(10) Stirling, C. H.; Lee, D.-C.; Christensen, J. N.; Halliday, A. N. *Geochim. Cosmochim. Acta* **2000**, *64*, 3737−3750.
(11) Stirling, C. H.; Esat, T. M.; Lambeck, K.; McCulloch, M. T.; Blake, S. G.; Lee, D.-C.; Halliday, A. N. *Science* **2001**, *291*, 290−293.
(12) Warneke, T.; Croudace, I. W.; Warwick, P. E.; Taylor, R. N. *Earth Planet. Sci. Lett.* **2002**, *203*, 1047−1057.
(13) Hartman, M. J., Ed. *Hanford Site Groundwater Monitoring: Setting, Sources and Methods*; PNNL-13080; Pacific Northwest National Laboratory: Richland, WA, 2000.
(14) Hartman, M. J., et al., Eds.; *Hanford Site Groundwater Monitoring for Fiscal Year 2002*; PNNL 14187; Pacific Northwest National Laboratory: Richland, WA, 2003.
(15) Jones, T. E.; Simpson, B. C.; Wood, M. I.; Corbin, R. A. *Preliminary Inventory Estimates for Single-Shell Tank Leaks in B, BX, and BY Tank Farms*; RPP-7389; CH2M HILL Hanford Group, Inc.: Richland, WA, 2001.
(16) Dresel, P. E.; Evans, J. C.; Farmer, O. T. III. *Investigation of Isotopic Signatures for Sources of Groundwater Contamination at the Hanford Site*; PNNL-13763; Pacific Northwest National Laboratory: Richland, WA, 2002.
(17) Hartman, M. J., et al., Eds. *Hanford Site Groundwater Monitoring for Fiscal Year 2001*; PNNL 13788; Pacific Northwest National Laboratory: Richland, WA, 2002.
(18) Serne, R. J.; et al. *Characterization of Vadose Zone Sediment: Borehole 299-E33-45 near BX-102 in the B-BX-BY Waste Management Area*; PNNL-14083; Pacific Northwest National Laboratory: Richland, WA, 2003.
(19) Serne, R. J.; et al. *Characterization of Vadose Zone Sediment: Borehole 299-E33-46 near B-110 in the B-BX-BY Waste Management Area*; PNNL-14119; Pacific Northwest National Laboratory: Richland, WA, 2003.
(20) Steiger, R. H.; Jäger, E. *Earth Planet. Sci. Lett.* **1977**, *36*, 359−362.
(21) Ludwig, K. *Isoplot/Ex Version 2.49*; Berkeley Geochronology Center: Berkely, CA, 2002.
(22) Cowan, G. A.; Adler, H. H. *Geochim. Cosmochim. Acta* **1976**, *40*, 1487−1490.
(23) Cheng, H.; Edwards, R. L.; Hoff, J.; Gallup, C. D.; Richards, D. A.; Asmerom, Y. *Chem. Geol.* **2000**, *169*, 17−33.
(24) Osmond, J. K.; Cowart, J. B. In *Uranium Series Disequilibrium: Applications to Earth, Marine and Environmental Sciences*; Ivanovich, M., Harmon, R. S., Eds.; Clarendon Press: Oxford, U.K., 1992; pp 290−333.

(25) Roback, R. C.; Johnson, T. M.; McLing, T. L.; Murrell, M. T.; Luo, S.; Ku, T.-L. *Geol. Soc. Am. Bull.* **2001**, *113*, 1133−1141.

(26) Watrous, R. A.; Wootan, D. W. *Activity of Fuel Batches Processed through Hanford Separations Plants, 1944 through 1989*; HNF-SD-WM-TI-794, Rev. 0; Lockheed Martin Hanford Corporation: Richland, WA, 1997.

(27) Lichtner, P. C. *Simulated B-BX-BY Tank Farms Supernate Compositions*; RPP-10098; Pacific Northwest National Laboratory: Richland, WA, 2003.

(28) Narbutovskih, S. M. *Results of Phase I Groundwater Quality Assessment for the Single-Shell Tank Waste Management Areas B-BX-BY at the Hanford Site*; PNNL-11826; Pacific Northwest National Laboratory: Richland, WA, 1998.

(29) Anderson, J. D. *A history of the 200 Area Tank Farms*; WHC-MR-0132; Westinghouse Hanford Company: Richland, WA, 1990.

(30) Pruess, K.; Yabusaki, S. *Modeling Studies of Fluid Flow and Solute Transport at Tank BX-102 in the Hanford Vadose Zone*; RPP-10098; Pacific Northwest National Laboratory: Richland, WA, 2003.

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