

***Assessment of Uranium  
and Plutonium in the Saturated  
and Unsaturated Zones  
Beneath the Subsurface Disposal  
Area, INEEL***

*November 2000*

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# **Assessment of Uranium and Plutonium in the Saturated and Unsaturated Zones Beneath the Subsurface Disposal Area, INEEL**

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# Table of Contents

<b>0.0 EXECUTIVE SUMMARY</b> .....	2
<b>1.0 INTRODUCTION AND BACKGROUND</b> .....	3
<b>2.0 METHODS</b> .....	4
2.1 SAMPLE COLLECTION .....	4
2.2 SAMPLE PROCESSING.....	6
2.2.1 Filtration.....	6
2.2.2 Dissolution and Chemical Separation.....	7
2.2.3 Analytical Techniques.....	9
2.2.4 Data Reduction.....	12
<b>3.0 RESULTS</b> .....	15
3.1 URANIUM .....	15
3.1.1 Uranium Concentration.....	15
3.1.2 Uranium Isotopic Ratios.....	16
3.2 PLUTONIUM.....	22
3.2.1 <sup>239</sup> Pu Concentration.....	23
3.2.2 <sup>240</sup> Pu/ <sup>239</sup> Pu Isotopic Ratios .....	26
<b>4.0 DISCUSSION</b> .....	27
4.1 <sup>236</sup> U/ <sup>238</sup> U RATIOS .....	27
4.2 <sup>234</sup> U/ <sup>238</sup> U RATIOS IN WATER SAMPLES .....	28
4.3 COMPARISON OF WATER AND FILTER ISOTOPIC DATA .....	32
<b>5.0 RECOMMENDATIONS</b> .....	34
<b>6.0 LITERATURE CITED</b> .....	36

## 0.0 Executive Summary

Twenty-two groundwater samples from beneath the Surface Disposal Area (SDA), INEEL, were investigated to determine if uranium (U) and/or plutonium (Pu) have migrated from the disposal sites into the subsurface. Groundwater samples include nine aquifer samples, 13 samples from the vadose zone including two samples from perched-water zones. One sample from the Big Lost River was also studied because it is suspected that this water is a potential source for some groundwater beneath the SDA. Each sample was filtered at 0.5  $\mu\text{m}$ . The filtrate and particulate fraction were then processed separately to examine potential modes of actinide transport.

We used Isotope Dilution - Thermal Ionization Mass Spectrometry (ID-TIMS). The method can provide accurate and precise concentration and isotopic composition of U and Pu at much lower detection limits than traditional radioactivity counting techniques.

Uranium concentrations in eight of the nine-aquifer samples are between 0.9 ppb and 2.1 ppb, values that are typical for this aquifer. Sample USGS 120 has a U concentration of 4.3 ppb, a value that is twice the average for this region, but which is still within the range of values for typical groundwater. Uranium concentrations for the vadose zone and perched water samples are extremely variable with values between 0.008 ppb and 143 ppb. The high U concentrations do not appear to be related to anthropogenic input of U, but rather are likely related to natural processes in the vadose zone.

Uranium isotopic data indicate that three samples, TW1 water and filter, and 8802D water unequivocally contain anthropogenic U. Uranium in sample TW1 is enriched with a  $^{238}\text{U}/^{235}\text{U}$  ratio of approximately 18 for both the water and filter samples. Uranium in sample 8802D water

is depleted with a  $^{238}\text{U}/^{235}\text{U}$  ratio of 232. All three samples contain  $^{236}\text{U}$ , which further documents the presence of anthropogenic U. Two additional samples, 8802D filter and W23L08 filter, likely contain a small component of depleted U. All other samples have natural U isotopic composition.

All samples have  $^{239}\text{Pu}$  abundances that are near or below the detection limit for our methods and therefore none of the samples yielded unambiguous evidence for Pu. Plutonium data from two samples, TWI filter and 8802D filter, have statistically higher  $^{239}\text{Pu}$  concentrations than the rest of the samples. It is very likely that these two samples contain  $^{239}\text{Pu}$  at levels of approximately  $5\text{E}7$  atoms/sample (approximately 1.7 femtocuries/sample). Statistical tests on Pu data suggest that sample PA03 filter may contain Pu at detectable levels. The remaining samples do not contain Pu at detectable levels of approximately  $5\text{E}6$  atoms/sample (0.2 femtocuries/sample).

## **1.0 Introduction and Background**

The Radioactive Waste Management Complex (RWMC) is located in the southeastern part of the Idaho National Engineering and Environmental Laboratory (INEEL, Fig. 1). The RWMC was established in 1952 as a disposal site for solid, low-level radioactive waste generated at the INEEL and other DOE sites. The Subsurface Disposal Area (SDA, Fig. 1) is a 97-acre area in the western part of the RWMC dedicated to permanent shallow-land disposal of solid, low-level waste. Transuranic waste generated by national defense programs was disposed of in the SDA from 1954 to 1970 and placed in storage from 1970 to the present. Waste was disposed in 20 pits, 58 trenches, and 21 soil vault rows. Major contaminants include organic chemicals, nitrate salts, metals, and radionuclides.

To evaluate if radionuclides have migrated into the subsurface from the SDA, INEEL contracted Los Alamos National Laboratory (LANL) to analyze groundwater samples collected from beneath the SDA for Pu and U concentration and isotopic composition by ID-TIMS. INEEL personnel and Robert Roback (LANL) collected samples during July 1999. Samples include nine aquifer waters, one sample from the Big Lost River, and 13 water samples from the vadose-zone including two perched saturated zones. Four field blanks were also taken. All samples were filtered at 0.5  $\mu\text{m}$  thus splitting the sample into two aliquots: 1) the dissolved + colloidal phases (referred to as the filtrate or the dissolved phases), and 2) the particulate phases. ID-TIMS for Pu and U was conducted on the filtrate as well as the particulate fractions. Isotopic ratios presented are values corrected as described below. All uncertainties stated in this report are at the 2-sigma level.

## **2.0 Methods**

### ***2.1 Sample Collection***

Samples were collected from wells with dedicated pumps (aquifer samples), bailing (perched water samples), or suction lysimeters by INEEL personnel using established sampling protocol (Burgess, 2000). The Big Lost River sample, BLR-99A, was collected by R. Roback at the INEEL diversion dam. All samples were collected in pre-cleaned Teflon™ bottles to minimize the potential for metals to adsorb onto the walls of the containers. In an effort to minimize the potential for air-borne particulate contamination of the samples, the bottles were transported to the field in sealed plastic (zip-lock) baggies and were removed and left open for the minimum

amount of time required to receive the sample. Collection bottles were returned immediately to the zip-lock baggies, sealed, and placed in coolers for shipment to LANL.

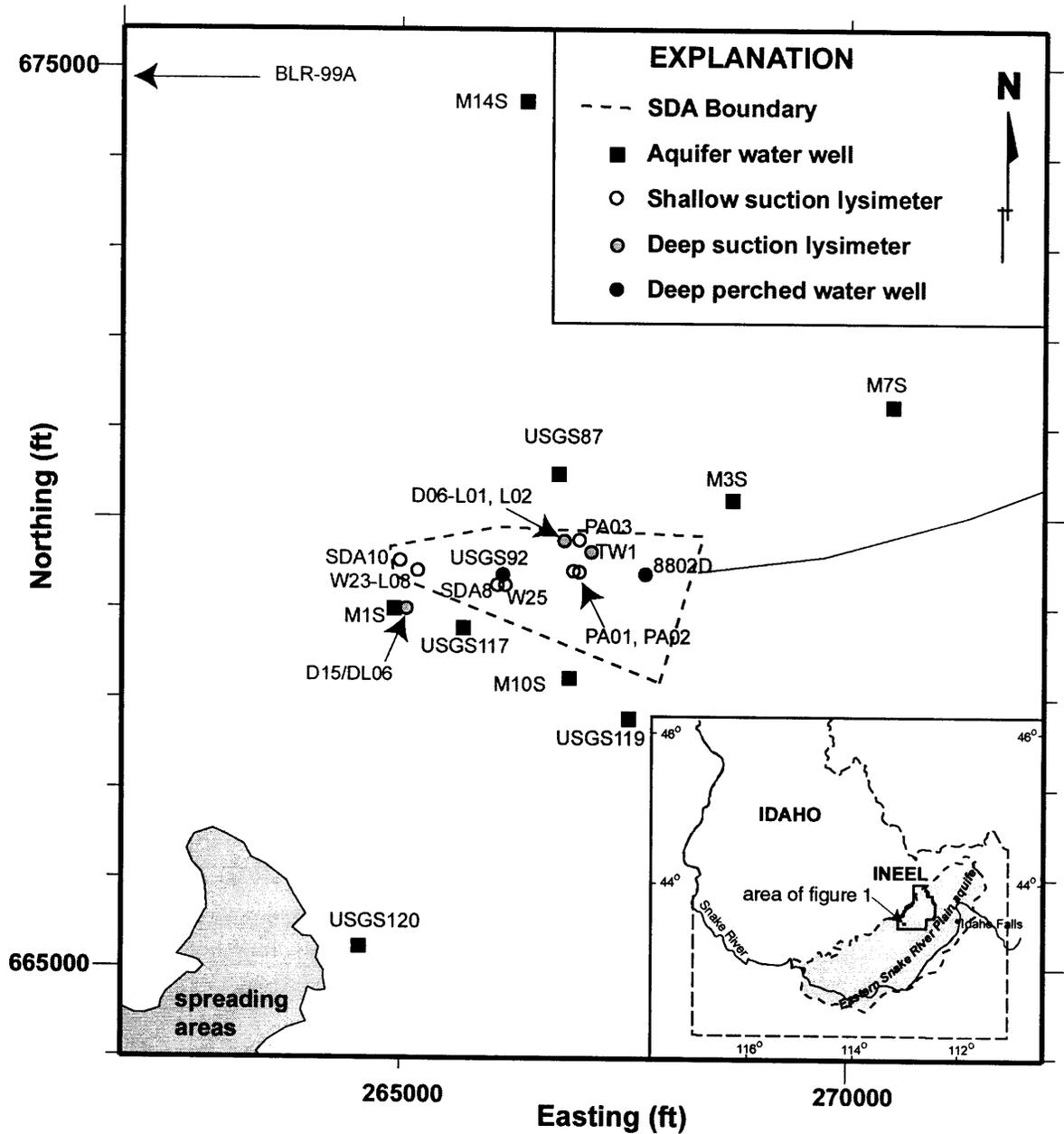


Figure 1. Maps showing locations of INEEL (inset) and of samples collected for this study. The sample of Big Lost River (BLR-99A) was collected to the west of the arrow at easting approximately 262500 ft.

Field blanks were taken at four locations within and surrounding the SDA. Field blanks consisted of ultrapure water (sub-boiling, Teflon™ distilled, 18 mega ohm water) with a known

and very low U content and no measurable Pu that were shipped to INEEL from LANL in double-bagged Teflon™ bottles. The blanks were collected by pouring the ultrapure water into another pre-cleaned Teflon™ bottle at the sampling site. The transfer time approximately equaled the amount of time needed to collect the sample; generally less than a few minutes. Field blanks were handled as samples throughout the subsequent processing and analysis.

## **2.2 Sample Processing**

### **2.2.1 Filtration**

All samples were weighed in the bottles before and after filtration; filtered weights were determined by difference. Samples were filtered in class 100 clean-laboratory conditions using 0.5 µm pre-cleaned Teflon™ filters. The filters were transferred to pre-cleaned Teflon™ vials for further processing (see below). The filtrate was returned to the original collection bottle after the bottle had been rinsed twice with 18 mega ohm water. All subsequent sample processing took place in either class 100 or class 10 clean-laboratory conditions.

The amount of visible particulate material collected on the filters was variable (Table 1). Approximately half of the filters showed no visible material. Of the other half, most showed only a slight yellow to brown stain. Three of the samples yielded significant material that was yellow to deep red and spongy in character and likely consisted largely of Fe-hydroxides. A small piece representing approximately 5 percent of each sample was cut from the filter using a cleaned scalpel and stored for mineralogical analysis. The mass of the particulate material was not determined; therefore, the amount of U and Pu on the filter is reported (Table 1) as the total mass and the mass per mass of water filtered.

Sample USGS 92 differed from the remaining samples in that it was quite muddy; containing approximately one-quarter sediment estimated by volume. This sample was shaken and then set aside to allow the sediment to settle. The water was then carefully decanted from the bottle to minimize resuspension of the sediment. Regardless, a significant amount of sediment was decanted to the filter. Two filters were required to filter sufficient water for analysis. The filters were dried in a clean hood and an approximately 1-gram aliquot for U and Pu analysis was removed, weighed, and processed as described below.

### **2.2.2 Dissolution and Chemical Separation**

All dissolution and chemical separation was performed in class 100 or class 10 clean rooms at the Clean Chemistry and Mass Spectrometry Facility (TA 48, RC 45) at LANL. Ultrapure reagents produced by Seastar™ and Optima™ were used. For all samples except 8802D, the filtrate was split into separate aliquots for U and Pu analyses.

Uranium aliquots were weighed, spiked with a  $^{233}\text{U}$  tracer, acidified with  $\text{HNO}_3$  acid, and evaporated to dryness. The precipitated salts were redissolved in  $\text{HNO}_3$  acid, some samples required dissolution in a nitric acid/hydrofluoric acid mixture. Uranium was purified by nitric acid, hydrochloric and/or sulfuric acid anion exchange column chemistry using BioRad™ MP-1 anion exchange resin and eluted with ultrapure water.

Plutonium aliquots were weighed, spiked with a  $^{242}\text{Pu}$  tracer, acidified with  $\text{HNO}_3$  and  $\text{HClO}_4$  acid, and evaporated to dryness. The precipitated salts were redissolved in  $\text{HNO}_3$  and  $\text{HClO}_4$  acid, some samples required dissolution in a nitric acid/hydrofluoric acid mixture. Plutonium was purified with a series of  $\text{HNO}_3$  and  $\text{HCl}$  acid columns and eluted with either a 1:9 mixture of

concentrated HI acid and concentrated HCl acid or with concentrated HBr acid from BioRad™ MP-1 anion exchange resin. Additional details of Pu chemical processing are given in Efurd et al., 1993.

Due to low volume collected and the low U concentration (as determined by ICP-MS, see below), U and Pu were processed together for sample 8802D. This sample was weighed and spiked with  $^{233}\text{U}$  and  $^{242}\text{Pu}$  tracers, acidified with  $\text{HNO}_3$  and  $\text{HClO}_4$  acid, and evaporated to dryness. The precipitated salts were redissolved in  $\text{HNO}_3$  acid. Uranium was separated from the Pu by collecting approximately 23 column volumes of 7M  $\text{HNO}_3$  passed through an anion exchange column. The U was purified further as above. Plutonium was eluted with a 1:9 mixture of concentrated HI/HCl acid mixture and further purified as described above.

Solids were dissolved from the Teflon™ filters by placing the filters in a 1:1 mixture of concentrated HF and concentrated  $\text{HNO}_3$ , and warmed for approximately 24 hours. The filters were removed from the solution with cleaned plastic forceps, rinsed three times with 4N  $\text{HNO}_3$ , and discarded. In all cases this treatment produced colorless filters. Subsequent processing of the filters follows the same procedure as sample 8802D described above except for samples USGS 92, which is described below, and sample M10S. Sample M10S yielded sufficient U so that it could be split into separate U and Pu aliquots. Sample M10S was then processed as the waters described above.

Solid material from sample USGS 92 was dissolved in a cleaned Teflon 100 ml beaker in a 1:1 mixture of concentrated HF and  $\text{HNO}_3$  acid and a few ml of  $\text{HClO}_4$  acid. The sample was dried,

fumed and redissolved in 7M HNO<sub>3</sub>. The sample was then weighed and split into separate U and Pu aliquots.

Small aliquots of the filtrate and the solid material dissolved from the filters (and USGS 92 sediment) were removed for semi-quantitative determination of U concentration by Inductively Coupled Plasma Mass Spectrometer (ICPMS) to determine appropriate mass of U spike for each sample. In all cases, the volume of sample removed represented less than 1% of the total. This initial determination of U concentration also helped to determine subsequent sample processing and mass spectrometric procedures. This 1% reduction in volume does not affect concentration data for the water samples or for USGS 92 filter, but it does reduce the total U and Pu on the rest of the filter samples by 1% or less.

### **2.2.3 Analytical Techniques**

Mass spectrometric analyses of most U samples and Pu for sample M7S were performed on VG Sector 54 equipped with a WARP filter. Initial U concentration measurements by ICP-MS, revealed that eight of the filters contained very small amounts of U. These samples were analyzed on a modified NBS-type (12/90) mass spectrometer with ion counting capabilities.

For most analyses performed on the VG Sector 54, U was loaded onto outgassed Ta filaments configured in a triple filament assembly with a zone-refined Re center filament. For most samples, data acquisition was accomplished by cycling the smaller <sup>233</sup>U, <sup>234</sup>U, <sup>235</sup>U and <sup>236</sup>U signals onto the Daly knob while simultaneously measuring <sup>238</sup>U and <sup>235</sup>U on Faraday collectors. Each reported isotopic measurement consisted of an average of 100 ratios. Measuring both spike and unspiked NBS U960 standards regularly over the last three years assessed reproducibility.

$^{234}\text{U}/^{238}\text{U}$  are in excellent agreement for both spike and unspiked standards. The mean  $^{234}\text{U}/^{238}\text{U}$  using this procedure is  $54.86 \text{ ppm} \pm 0.03$ . Some samples with low U concentrations were analyzed by loading the sample onto single carburized Re filaments in a graphite slurry and collecting ratios solely in ion counting mode. Eight filter samples with the lowest U contents were analyzed on the NBS-type instrument. These samples were loaded onto Re filaments with a graphite slurry and data were collected solely in ion-counting mode. For these analyses, ratios for the more abundant masses,  $^{233}\text{U}$  (spike mass),  $^{235}\text{U}$  and  $^{238}\text{U}$  were measured at temperatures between  $1600 - 1680 \text{ }^\circ\text{C}$ . The temperature was increased to between  $1680 - 1740 \text{ }^\circ\text{C}$  to obtain sufficient signal intensity to measure the minor isotopes  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{236}\text{U}$ . Six analyses of a  $1.6 \text{ ng NBS U960} + ^{233}\text{U} - ^{236}\text{U}$  spike mix using this data collection routine yielded a fractionation corrected mean  $^{238}\text{U}/^{235}\text{U}$  of  $137.61 \pm 0.5\%$  and  $^{234}\text{U}/^{238}\text{U}$  of  $52.70 \pm 0.5\%$ .

With the exception of sample M7S, all Pu analyses were performed using an NBS-type mass spectrometer dedicated to Pu analyses. These samples were electroplated onto Re filaments with a Pt overplate. For all samples, data were collected in ion counting mode by cycling  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{239}\text{Pu}$ . Pu analysis for sample M7S was performed on the VG Sector in ion-counting mode.

TABLE 1. Uranium and Plutonium data summary. See table footnotes and text for explanation.

Sample	Depth of well (ft)	Total Mass Filtered (g)	Filter Description	Uranium Data				Plutonium Data <sup>1</sup>						
				Water [U] in Sample (ppb)	U on filter (ng) <sup>3</sup>	U(ng) on filter/g water filtered	238U/235U <sup>4</sup> (%)	236U/238U <sup>5</sup> (%)	234U/238U (ppm)	239Pu atoms in sample	240Pu/239Pu (%)			
<b>AQUIFER SAMPLES</b>														
1 M1S	a6	258.45	1.230	0.63	1.71	5.7E-04	5.00	0.32	4.2E-07	101	116.1	2.00	1739.9	
2 M1S Filter								0.56	-1.5E-06	95.1	96.1	1.69		
3 M3S	a	262.07	1.956	0.25	0.802	2.6E-04	10.6	0.20	2.6E-08	38	122.0	0.25	1761.5	
4 M3S Filter								0.58	-8.5E-07	29	108.6	1.21		
5 M7S	a	264.20	1.892	0.51	8.807	3.1E-03	0.89	0.34	1.7E-07	90	121.1	0.54	1743.8	
6 M7S Filter								0.28	-8.8E-08	562	121.1	1.60		
7 M10S	a	265.35	0.922	0.50	288.6	1.0E-01	0.31	0.47	2.9E-07	83	115.9	0.49	1936.5	
8 M10S Filter								0.25	3.9E-08	30	49.0	0.38		
9 M14S	a	344.17	2.060	0.28	8.24	2.8E-03	0.89	0.22	1.6E-07	102	120.8	0.35	1696.7	
10 M14S Filter								0.22	3.2E-07	51	87.5	1.22		
11 USGS 87	a	334.23	1.858	0.47	4.315	1.5E-03	1.68	0.42	-3.2E-09	600	120.0	0.68	1650.4	
12 USGS 87 Filter								0.20	6.9E-07	70	118.2	1.61		
13 USGS 117	a	310.38	1.248	0.19	3.136	1.1E-03	2.31	0.20	4.3E-08	45	117.0	0.35	1697.4	
14 USGS 117 Filter								0.30	1.4E-06	82	117.0	1.91		
15 USGS 119	a	323.64	1.013	0.28	1.992	6.8E-04	4.33	0.22	8.3E-08	160	116.9	0.36	1633.5	
16 USGS 119 Filter								0.51	3.2E-07	16	100.6	0.81		
17 USGS 120	a	313.34	4.270	0.28	41.53	1.5E-02	0.56	0.22	7.0E-08	126	108.7	0.30	1678.8	
18 USGS 120 Filter								0.25	-6.5E-09	2000	109.4	1.10		
<b>RIVER SAMPLE</b>														
19 BLR-99A		326.48	2.200	0.22	13.039	4.9E-03	0.58	0.2	4.4E-09	140	116.4	0.21	1623.6	
20 BLR-99A Filter								0.2	2.9E-07	30	60.8	1.18		
<b>VADOSE ZONE SAMPLES</b>														
21 PA 01	14.5	9.45	68.02	0.23	0.81	1.1E-03	10.4	0.15	1.5E-07	8	96.0	0.22	627.40	
22 PA 01 Filter								0.48	1.1E-06	28	98.3	1.55		
23 PA 02	8.5	9.55	46.29	0.28	0.294	5.1E-04	29	0.21	7.9E-08	15	111.1	0.30	490.90	
24 PA 02 Filter								0.74	1.6E-06	21	111.2	1.53		
25 PA 03	9.5	8.95	128.2	0.27	7.97	2.7E-02	1	0.20	7.3E-08	14	78.2	0.34	222.96	
26 PA 03 Filter								0.23	1.0E-06	31	78.9	2.52		
27 W23L08	12	10.71	123.9	0.35	12.441	3.1E-02	0.62	0.20	2.8E-08	14	97.1	0.36	312.66	
28 W23L08 Filter								0.20	1.8E-07	66	96.0	0.96		
29 D06L01	88	9.74	134.9	0.38	15.8	3.9E-02	0.53	0.33	2.2E-08	49	111.9	0.41	338.83	
30 D06L01 Filter								0.09	2.9E-07	32	110.0	0.67		
31 D06L02	44	5.21	143.6	0.27	23.928	1.0E+00	0.4	0.20	-5.1E-07	94	98.0	0.29	17.98	
32 D06L02 Filter								0.20	5.9E-08	20	95.9	0.30	246.56	
33 SDA 8	17	70.09	7.900	0.27	0.165	4.4E-04	46	1.02	4.4E-07	23	95.9	6.35	489.82	
34 SDA 8 Filter								0.80	-6.4E-08	25	91.0	2.35		
35 SDA 10	10.5	15.15	30.24	0.31	0.877	1.5E-03	9.7	0.03	2.11E-04	0.18	612	0.10	256.09	
36 SDA 10 Filter								2.44	2.07E-04	3.3	597	2.40		
37 TW 1	102	18.69	26.90	0.18	2.944	9.2E-03	2.44	2.20	2.07E-04	0.18	612	0.10	256.09	
38 TW 1 Filter								0.25	2.6E-08	58	139.1	0.31	230.59	
39 D15DL06	98	98.73	2.200	0.3	2.84	7.2E-03	2.53	0.29	1.5E-06	68	139.0	1.98		
40 D15DL06 Filter								0.32	1.2E-07	18	78.5	0.51	275.94	
41 W25	12	65.28	9.901	0.38	0.043	8.7E-05	198	3.50	2.7E-06	20	119.5	18.00		
42 W25 Filter														
<b>PERCHED WATER SAMPLES</b>														
43 USGS 92	220	59.98	7.077	0.31	13.039	4.9E-03	0.58	0.25	1.8E-07	8	89.96	0.34	93.95	
44 USGS 92 Filter <sup>7</sup>								0.19	3.2E-07	8	53.5	0.36	0.5656	
45 802D	220	66.36	0.0079	0.76	15.503	2.9E-01	0.52	1.39	4.4E-05	30	47.15	1.7	66.38	
46 802D Filter								0.15	5.2E-07	78	83.41	1.31	4.9E+07	6.5E+06
47 802D Filter								0.15	5.2E-07	78	83.41	1.31	4.9E+07	6.5E+06

<sup>1</sup> Plutonium data presented here are only for samples with likely or possible <sup>239</sup>Pu detections. Table 2 presents data for all samples.

<sup>2</sup> All uncertainties are given at the 2-sigma level.

<sup>3</sup> Represents approximately 95% of the total because a portion was removed for mineralogical analysis. For sample M10S, the amount represents 48% of total because sample was split into separate U and Pu aliquots.

<sup>4</sup> Uranium isotopic ratios that are interpreted to include a component of anthropogenic uranium are bolded and discussed in the text.

<sup>5</sup> Only the four bolded results are considered above background, or possibly above background. See text for discussion.

<sup>6</sup> Depth to the aquifer for these wells is approximately 690 ft below land surface.

<sup>7</sup> USGS 92 contained a large amount of sediment. The filtered sediment was dried and weighed, weights are given for the dry sediment. This is the only filter sample that was weighed.

#### 2.2.4 Data Reduction

Uranium concentration and isotopic data are summarized in Table 1. Uranium isotopic data were corrected for mass fractionation. The fractionation factors were determined from repeated runs of the NBS U960 standard, which mimicked run conditions of the samples. For analyses performed on the VG Sector 54, a fractionation factor of 0.05%/atomic mass unit (AMU) was applied. For U analyses performed on the NBS-type instrument a fractionation factor of 0.2%/AMU was applied to the  $^{233}\text{U}/^{235}\text{U}$  and  $^{233}\text{U}/^{238}\text{U}$  ratios collected during the lower temperature data collection. For the higher temperature collection of  $^{234}\text{U}/^{235}\text{U}$  and  $^{236}\text{U}/^{235}\text{U}$  data, zero fractionation correction was applied. Uranium data were also corrected for spike and blank contribution. Blanks for processing of water samples, including the field blanks, averaged 0.04 pico moles (9.5 pico grams), a value that is in good agreement with long-term laboratory U procedural blanks. Filtration added an additional 0.65 pico moles (155 pico grams) of U blank to the sample. All water samples and most of the filter samples yielded sufficient U so that the spike and blank corrections are insignificant. However, for the few filter samples that yielded little U, these corrections are important. In particular, for the eight filters that yielded less than 2 nano grams of total U (Table 1) corrections to the concentration isotopic data become important. Uncertainties for the U blank correction are estimated at 50%. Propagation of these uncertainties results in greatly elevated overall errors for samples with low U yields.

Plutonium data were corrected using an in-house program written by Clarence Duffy of LANL (CST-11). Table 1 presents a summary of the data for those samples in which  $^{239}\text{Pu}$  may have been detected. For all of the samples, the raw  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  instrument signals were extremely low, in all cases less than a few counts per second. Given such low instrument signals, it is crucial to separate signal due to Pu atoms from other compounds that may form isobaric

interferences. Isobaric interferences will typically ionize with different efficiency than true Pu signals. Therefore the relative contribution of isobaric interference to a low Pu signal commonly changes throughout the run, resulting in changing  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  abundances when compared to the relatively large signal of the spike mass  $^{242}\text{Pu}$ . The program written by C. Duffy processes raw count data, examines the changing effects of isobaric interferences through the course of the analysis, and extrapolates these changes to an infinite time to arrive at the final isotopic ratio. Plutonium data for all samples and results of statistical processing are given in table 2.

Table 2, gives the blank corrected  $^{239}\text{Pu}$  abundance. For this study 13 blanks, including field blanks, were evaluated. With two exceptions, they are statistically equal to most of the true samples indicating that the measured values are due to interferences that are shared by samples and blanks. The blank correction and uncertainty were derived from the weighted mean of the blanks and samples that form the statistical bulk of the samples. For this analysis, the weighted mean of analyses 11-55, Table 2 was used. The weighted uncertainty of these analyses was propagated along with counting statistics to arrive at the total uncertainty for the  $^{239}\text{Pu}$  abundance.

TABLE 2. Plutonium data for all samples and summary of statistical tests. See text and notes for explanation.

Sample <sup>1</sup>	239 Pu atoms, 2 Sigma blank corrected		Sample <sup>1</sup>	Inverse of the Normal Cumulative Distribution	Sample <sup>1</sup>	# of Occurrences Expected <sup>2</sup>
1 TWI FILT	5.13E+07	1.1E+07	1 TWI FILT	0.012	1 8802D FILT	2.32E-12
2 8802D FILT	4.87E+07	6.5E+06	2 8802D FILT	0.080	2 TWI FILT	1.31E-04
3 PA02 FILT	1.16E+07	5.5E+06	3 PA02 FILT	0.124	3 <i>BLANK 1</i>	8.54E-04
4 PA03 FILT	9.83E+06	3.6E+06	4 PA03 FILT	0.157	4 PA03 FILT	1.65E-01
5 SDA8 FILT	8.12E+06	4.1E+06	5 SDA8 FILT	0.184	5 M1S FILT	8.26E-01
6 W23L08 FILT	7.70E+06	6.3E+06	6 W23L08 FILT	0.207	6 PA02 FILT	1.01E+00
7 M1S FILT	4.13E+06	1.9E+06	7 M1S FILT	0.228	7 SDA8 FILT	1.40E+00
8 M14S FILT	3.92E+06	5.5E+06	8 M14S FILT	0.247	8 USGS 119 FILT	1.62E+00
9 USGS 119 FILT	3.70E+06	1.9E+06	9 USGS 119 FILT	0.264	9 SDA08	2.74E+00
10 SDA08	2.76E+06	1.7E+06	10 SDA08	0.280	10 USGS 120 FILT	4.28E+00
11 USGS 87 FILT	2.74E+06	5.2E+06	11 USGS 87 FILT	0.295	11 <i>BLANK 2</i>	4.78E+00
12 USGS 120 SOLIDS	2.63E+06	5.5E+06	12 USGS 120 SOLIDS	0.309	12 W23L08 FILT	6.40E+00
13 USGS 120 FILT	2.32E+06	1.6E+06	13 USGS 120 FILT	0.323	13 W23L08	9.50E+00
14 D06/DL02 FILT	2.05E+06	6.4E+06	14 D06DL02 FILT	0.336	14 M3S	9.90E+00
15 D06/DL01 FILT	1.35E+06	1.1E+07	15 D06DL01 FILT	0.348	15 <i>M7S FIELD BLANK</i>	9.96E+00
16 BLR 99A FILT	1.32E+06	6.1E+06	16 BLR 99A FILT	0.360	16 USGS 120	1.05E+01
17 SDA10	1.28E+06	2.7E+06	17 SDA10	0.371	17 USGS 119 SOLIDS	1.14E+01
18 TWI	1.09E+06	3.3E+06	18 TWI	0.383	18 <i>EFURD BLANK 6</i>	1.17E+01
19 PA03	1.01E+06	1.5E+06	19 PA03	0.394	19 M14S FILT	1.39E+01
20 USGS 92 FILT	8.89E+05	1.2E+07	20 USGS 92 FILT	0.404	20 PA03	1.44E+01
21 PA01 FILT	7.03E+05	6.7E+06	21 PA 01FILT	0.415	21 W25	1.50E+01
22 D06DL01	5.86E+05	1.9E+06	22 D06DL01	0.425	22 <i>BLANK 3</i>	1.54E+01
23 USGS 120	5.73E+05	6.3E+05	23 USGS 120	0.436	23 <i>Field Blank 7-28-99 9:30</i>	1.57E+01
24 USGS 119	4.77E+05	2.5E+06	24 USGS 119	0.446	24 USGS 87 FILT	1.74E+01
25 <i>Field Blank 7-28-99 11:20</i>	4.57E+05	1.2E+06	25 <i>Field Blank 7-28-99 11:20</i>	0.456	25 USGS 120 SOLIDS	1.84E+01
26 USGS 87	2.45E+05	6.2E+06	26 USGS 87	0.466	26 SDA10	1.84E+01
27 PA02	4.34E+04	2.3E+06	27 PA02	0.476	27 BLR 99A	1.89E+01
28 D06DL02	-3.48E+04	5.9E+06	28 D06DL02	0.485	28 D15DL06	1.92E+01
29 <i>Filtration Blank</i>	-1.70E+05	1.4E+06	29 <i>Filtration Blank</i>	0.495	29 <i>M10S FIELD BLANK</i>	1.98E+01
30 M3S FILT	-2.29E+05	3.8E+06	30 M3S FILT	0.505	30 W25 FILT	2.00E+01
31 USGS 92	-4.10E+05	3.3E+06	31 USGS 92	0.515	31 <i>BLANK 5</i>	2.02E+01
32 <i>BLANK 5</i>	-4.38E+05	1.1E+06	32 <i>BLANK 5</i>	0.524	32 <i>Field Blank 7-28-99 11:20</i>	2.02E+01
33 M7S FILT	-4.39E+05	2.2E+06	33 M7S FILT	0.534	33 SDA10 FILT	2.08E+01
34 USGS 117 FILT	-4.39E+05	2.6E+06	34 USGS 117 FILT	0.544	34 <i>BLANK 4</i>	2.11E+01
35 M10S FILT	-5.17E+05	5.7E+06	35 M10S FILT	0.554	35 TWI	2.16E+01
36 W25 FILT	-5.46E+05	1.4E+06	36 W25 FILT	0.564	36 <i>FILTER H2O BLANK</i>	2.18E+01
37 D15DL06 FILT	-7.05E+05	3.3E+06	37 D15DL06 FILT	0.575	37 D06DL02 FILT	2.17E+01
38 <i>Field Blank 7-28-99 9:30</i>	-7.33E+05	1.2E+06	38 <i>Field Blank 7-28-99 9:30</i>	0.585	38 D06L01 SOLIDS	2.18E+01
39 <i>BLANK 3</i>	-7.61E+05	1.2E+06	39 <i>BLANK 3</i>	0.596	39 D06DL01	2.21E+01
40 PA01	-9.26E+05	3.7E+06	40 PA01	0.606	40 8802 D	2.26E+01
41 M14S	-9.42E+05	8.1E+06	41 M14S	0.617	41 PA01	2.33E+01
42 USGS 119 SOLIDS	-1.08E+06	1.3E+06	42 USGS 119 SOLIDS	0.629	42 BLR 99A FILT	2.40E+01
43 <i>FILTER H2O BLANK</i>	-1.18E+06	3.7E+06	43 <i>FILTER H2O BLANK</i>	0.640	43 D15DL06 FILT	2.41E+01
44 W25	-1.18E+06	1.8E+06	44 W25	0.652	44 M7S FILT	2.44E+01
45 <i>D3-H2O BLANK</i>	-1.31E+06	1.1E+07	45 <i>D3-H2O BLANK</i>	0.664	45 USGS 119	2.46E+01
46 D06L01 SOLIDS	-1.40E+06	4.4E+06	46 D06L01 SOLIDS	0.677	46 USGS 117 FILT	2.51E+01
47 8802 D	-1.59E+06	5.7E+06	47 8802 D	0.691	47 USGS 92	2.61E+01
48 SDA10 FILT	-1.93E+06	5.3E+06	48 SDA10 FILT	0.705	48 D06/DL01 FILT	2.62E+01
49 D15-DL06	-2.08E+06	4.8E+06	49 D15-DL06	0.720	49 <i>Filtration Blank</i>	2.62E+01
50 <i>BLANK 4</i>	-2.53E+06	7.3E+06	50 <i>BLANK 4</i>	0.736	50 <i>D3-H2O BLANK</i>	2.62E+01
51 BLR 99A	-2.78E+06	6.1E+06	51 BLR 99A	0.753	51 M14S	2.63E+01
52 <i>BLANK 6</i>	-3.30E+06	4.0E+06	52 <i>BLANK 6</i>	0.772	52 PA 01 FILT	2.66E+01
53 <i>M10S Field Blank</i>	-3.48E+06	8.5E+06	53 <i>M10S Field Blank</i>	0.793	53 M10S FILT	2.69E+01
54 <i>M7S Field Blank</i>	-4.44E+06	4.7E+06	54 <i>M7S Field Blank</i>	0.816	54 USGS 92 FILT	2.72E+01
55 M3S	-5.63E+06	5.9E+06	55 M3S	0.843	55 M3S FILT	2.76E+01
56 <i>BLANK 2</i>	-1.26E+07	9.1E+06	56 <i>BLANK 2</i>	0.876	56 USGS 87	2.81E+01
57 W23 L08	-1.81E+07	1.8E+07	57 W23 L08	0.920	57 PA02	2.86E+01
58 <i>BLANK 1</i>	-9.46E+07	2.3E+07	58 <i>BLANK 1</i>	0.988	58 D06DL02	2.89E+01

<sup>1</sup> Filtr = Filter. <sup>2</sup> See text for explanation. Samples bolded are discussed in text regarding the possibility that they may vary statistically from the remainder of the data set. Blanks are italicized, unless otherwise noted all blanks are total procedural. D3-H2O refers to teflon distilled water. Solids refers to the fraction of a sample that remained solid after treatment with heated 7M HNO<sub>3</sub> acid. These were separated from the acid and dissolved with more vigorous acid treatments. The two aliquots were then processed separately to evaluate Pu partitioning between the solution and the solids.

## **3.0 Results**

### **3.1 Uranium**

All natural samples contain U at some level. Dissolved U concentration in groundwater is typically in the parts per billion (ppb) range (Osmond and Cowart, 1992). INEEL aquifer samples have U concentrations ranging from 0.3 to 3.6 ppb with most samples containing between 1 and 2 ppb (Knobel et al., 1991, Roback et al., in review). This project is the first (to the authors' knowledge) to obtain high-accuracy U isotopic measurements for INEEL vadose-zone samples. Natural U has a  $^{238}\text{U}/^{235}\text{U}$  atomic ratio of 137.88 and contains no  $^{236}\text{U}$  (Walker et al., 1989). The  $^{234}\text{U}/^{238}\text{U}$  ratio in nature varies. The  $^{234}\text{U}/^{238}\text{U}$  ratio is approximately 0.000055 (55 ppm) when the  $^{234}\text{U}$  is in secular equilibrium with  $^{238}\text{U}$ . In most groundwaters,  $^{234}\text{U}$  is enriched relative to  $^{238}\text{U}$ . Typical  $^{234}\text{U}/^{238}\text{U}$  ratios for INEEL groundwater range from 0.000086 to 0.000166 (Roback, et al., in review). Results of U analyses for this study are presented in Table 1 and summarized graphically in Figures 1, 2, and 3.

#### **3.1.1 Uranium Concentration**

All but one of the aquifer samples has U concentrations between 0.9 and 2.1 ppb, values that are typical for groundwater at INEEL (Roback et al., in review) and for oxygenated waters globally (Osmond and Cowart, 1992). The only aquifer sample that falls outside of this range is USGS 120, which has a value of 4.3 ppb. This value is the highest known U concentration in parts of the Snake River Plain aquifer in the vicinity of the INEEL *and* away from sources of potential contamination of approximately 73 aquifer samples measured to date (Roback, et al., in review and this report). Although this value is anomalously high for the INEEL region, it is still within the expected range of U concentration for oxygenated groundwater (Osmond and Cowart, 1992).

Uranium concentration of Big Lost River water is 2.2 ppb in close agreement to the value of 2.4 ppb measured previously (Roback, et al., in review).

Uranium concentrations of vadose zone and perched water samples are quite variable with values ranging between 0.008 ppb to 143.6 ppb. With two exceptions, these values are considerably higher than those of the aquifer samples. These high U concentrations likely reflect the greater availability of exchangeable and/or dissolvable uranium in the surficial alluvium relative to the basalt aquifer or the lower water to rock ratios of the vadose zone when compared to the saturated zone or a combination of both. The lower values, and in particular the extremely low value of 0.008 ppb for 8802D, may reflect anomalous reducing conditions. The possibility of such reducing conditions invites the question that they may be caused by leaking of leachates into this sampling site. Additional geochemical studies are needed to address this issue.

The amount of U collected on the filters is also quite variable with values ranging from 0.00009 ng U/g water filtered to 1.0 ng U/g water filtered. The amount of U collected by filtration does not show a consistent correlation among sample types. For example, the amount of U collected on the filters for the aquifer samples vary by over three orders of magnitude, the vadose zone samples encompass the entire range of values. The filtered material for sample USGS 92 has a U concentration of 2172 ppb (2.172 ppm) a value that is typical for common rocks (Faure, 1986).

### **3.1.2 Uranium Isotopic Ratios**

Figures 2-4 show plots of the U isotopic ratios and 2-sigma uncertainties for all of the samples. Nine of the samples plot off of the “natural U” line on a plot of  $^{238}\text{U}/^{235}\text{U}$  ratios (Fig. 2) at the 2-sigma level of uncertainty. Three of the samples, TW1 water and filter and 8802D water, plot

well away from the remainder of the samples. In the following, TW1 and 8802D are discussed first, followed by the samples that plot only slightly off of the natural U line. The samples for which natural U isotopics were determined are discussed last.

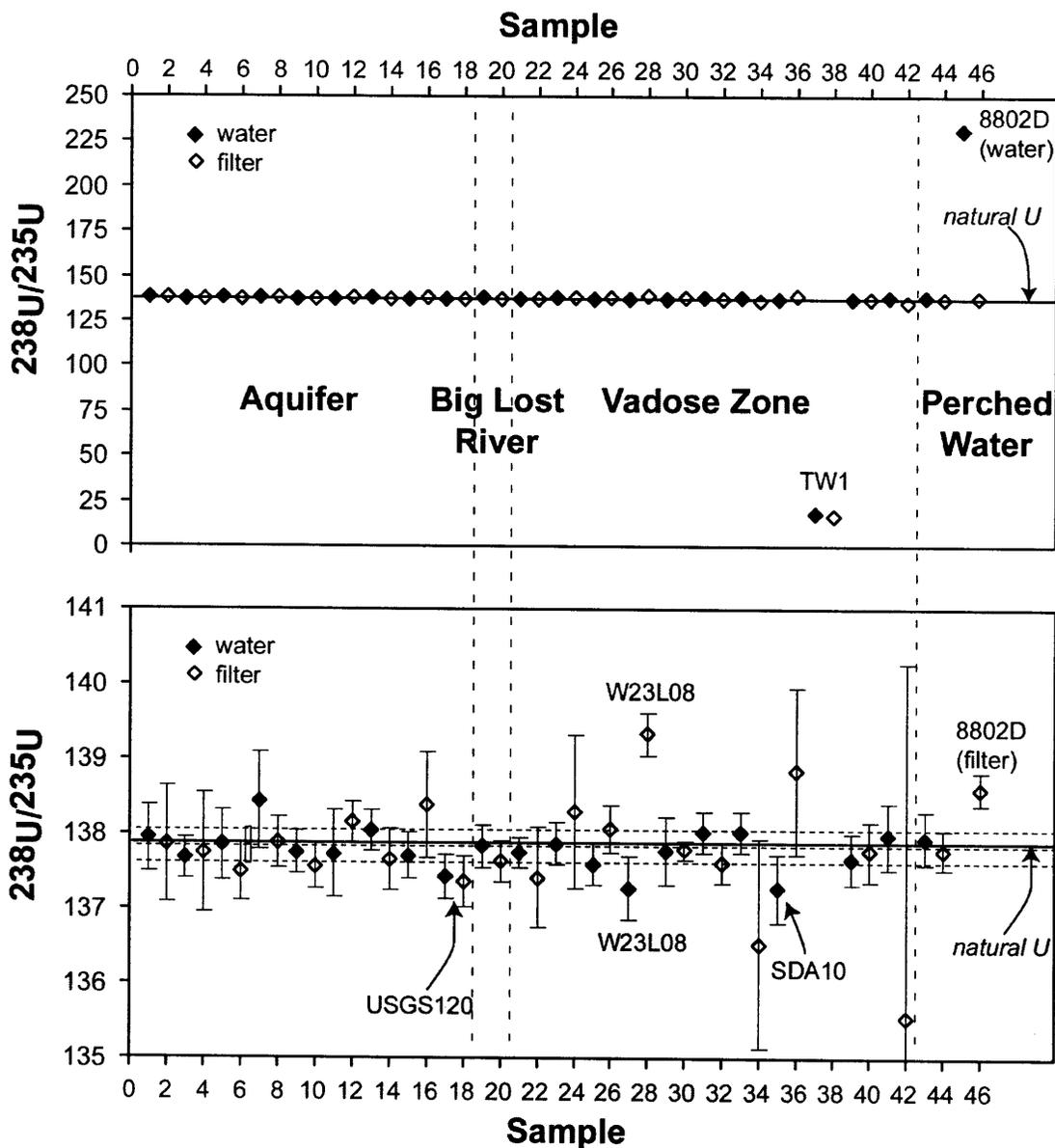


Figure 2. Plot of  $^{238}\text{U}/^{235}\text{U}$  ratios and two-sigma error bars. Upper plot shows all samples; the lower plot is at a greatly expanded scale to facilitate examination of the bulk of the samples, which plot on or near the  $^{238}\text{U}/^{235}\text{U}$  ratio of natural U. Dashed lines are mean and  $\pm$  one standard deviation of reference samples (see text for discussion). Samples labeled are discussed in the text. Sample number identifiers are keyed to Table 1.

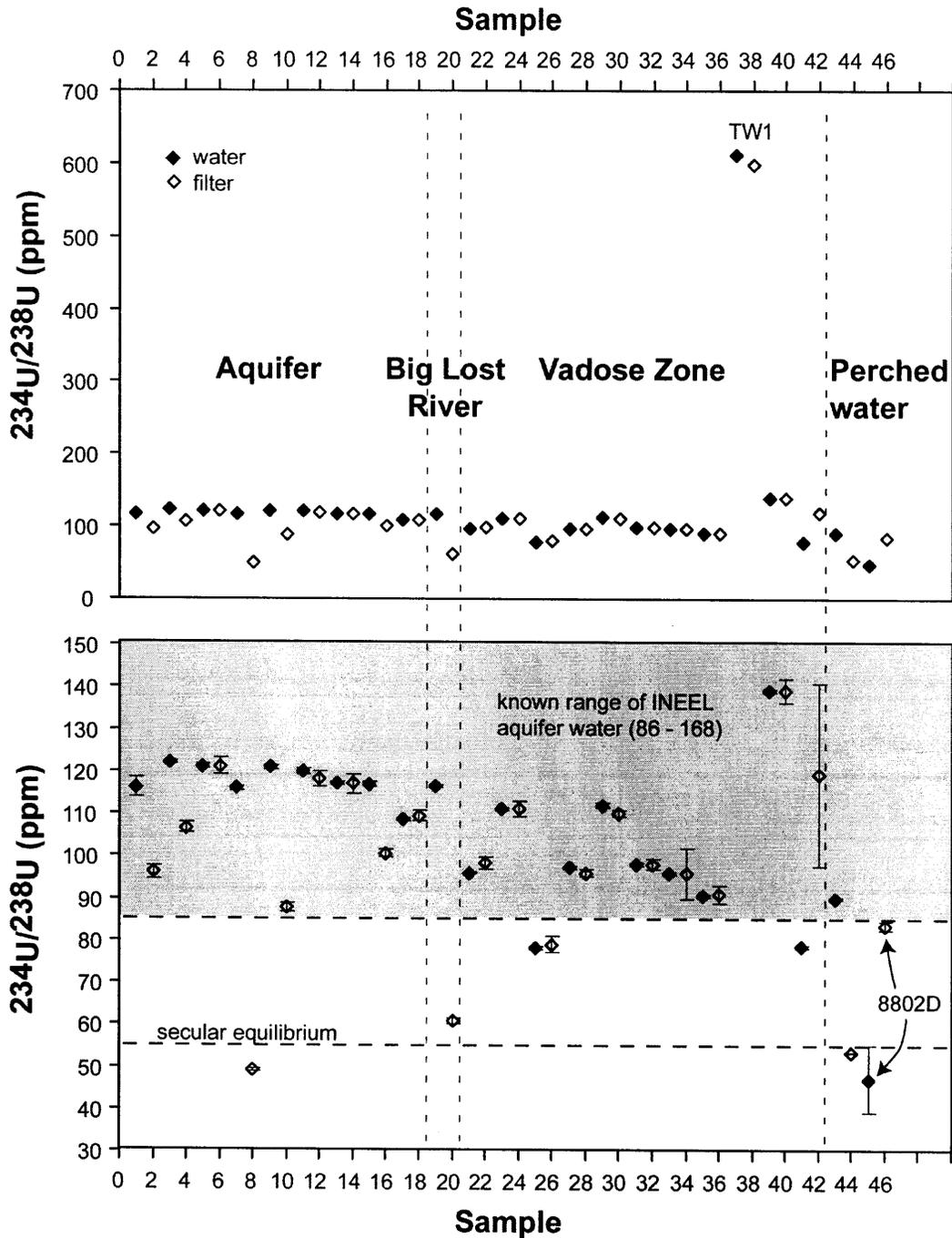


Figure 3. Plot of  $^{234}\text{U}/^{238}\text{U}$  ratios and two-sigma error bars. Upper plot shows all samples; the lower plot is at a greatly expanded scale to facilitate examination of the bulk of the samples. Samples labeled are discussed in the text. Also shown on the plot are  $^{234}\text{U}/^{238}\text{U}$  ratios for secular equilibrium and the range of known values for aquifer samples near INEEL (from Roback et al., in review). Sample number identifiers are keyed to Table 1. See text for discussion.

Approximately 19 grams of water were analyzed from TW1. The U concentration of the sample is about 29 ppb a value that is within the range of concentrations of the other vadose-zone samples. The  $^{238}\text{U}/^{235}\text{U}$  of the sample is  $17.63 \pm 0.03\%$ , clearly indicating that the sample contains a significant percentage of enriched U. The  $^{236}\text{U}/^{238}\text{U}$  ratio is  $0.000211 \pm 0.18\%$ , unequivocally indicating the presence of  $^{236}\text{U}$ . The calculated amount of  $^{236}\text{U}$  present is  $1.6\text{E}10$  atoms of  $^{236}\text{U}$  per gram of sample. The  $^{234}\text{U}/^{238}\text{U}$  of the sample is  $0.000612 \pm 0.10\%$  a value that is anomalously high for all INEEL samples analyzed for this study. Although the  $^{234}\text{U}/^{238}\text{U}$  ratio does not prove anthropogenic input, it is likely that the elevated  $^{234}\text{U}$  is due to addition of enriched U. Particulates filtered from this sample carried 2.94 ng of U, which also have non-natural isotopics. The  $^{238}\text{U}/^{235}\text{U}$  of the particulate material is  $18.13 \pm 2.2\%$ , the  $^{236}\text{U}/^{238}\text{U}$  ratio is  $0.000207 \pm 3.3\%$ , and the  $^{234}\text{U}/^{238}\text{U}$  of the sample is  $0.000597 \pm 2.4\%$ . All of these values are in good agreement with the isotopic ratios from the water sample. These data clearly indicate that anthropogenic U is present in both the particulate fraction and the dissolved or colloidal fractions of this sample.

Approximately 66 grams of water from the perched water at 8802D were analyzed. The U concentration of the sample is about 0.0079 ppb, a value that is the lowest observed for this sample set and, in fact, for all INEEL water analyses performed by the author to date. The  $^{238}\text{U}/^{235}\text{U}$  of the sample is  $231.1 \pm 1.4\%$ , clearly indicating that the sample contains a significant percentage of depleted U. The  $^{236}\text{U}/^{238}\text{U}$  ratio is  $0.000044 \pm 30\%$ , unequivocally indicating the presence of  $^{236}\text{U}$ . The calculated amount of  $^{236}\text{U}$  present is  $8.9\text{E}5$  atoms of  $^{236}\text{U}$  per gram of sample. The  $^{234}\text{U}/^{238}\text{U}$  of the sample is  $0.000047 \pm 17\%$ . Due to the high uncertainty of this analysis, this value overlaps with U in secular equilibrium; however, the value is probably low due to the presence of depleted U (see below).

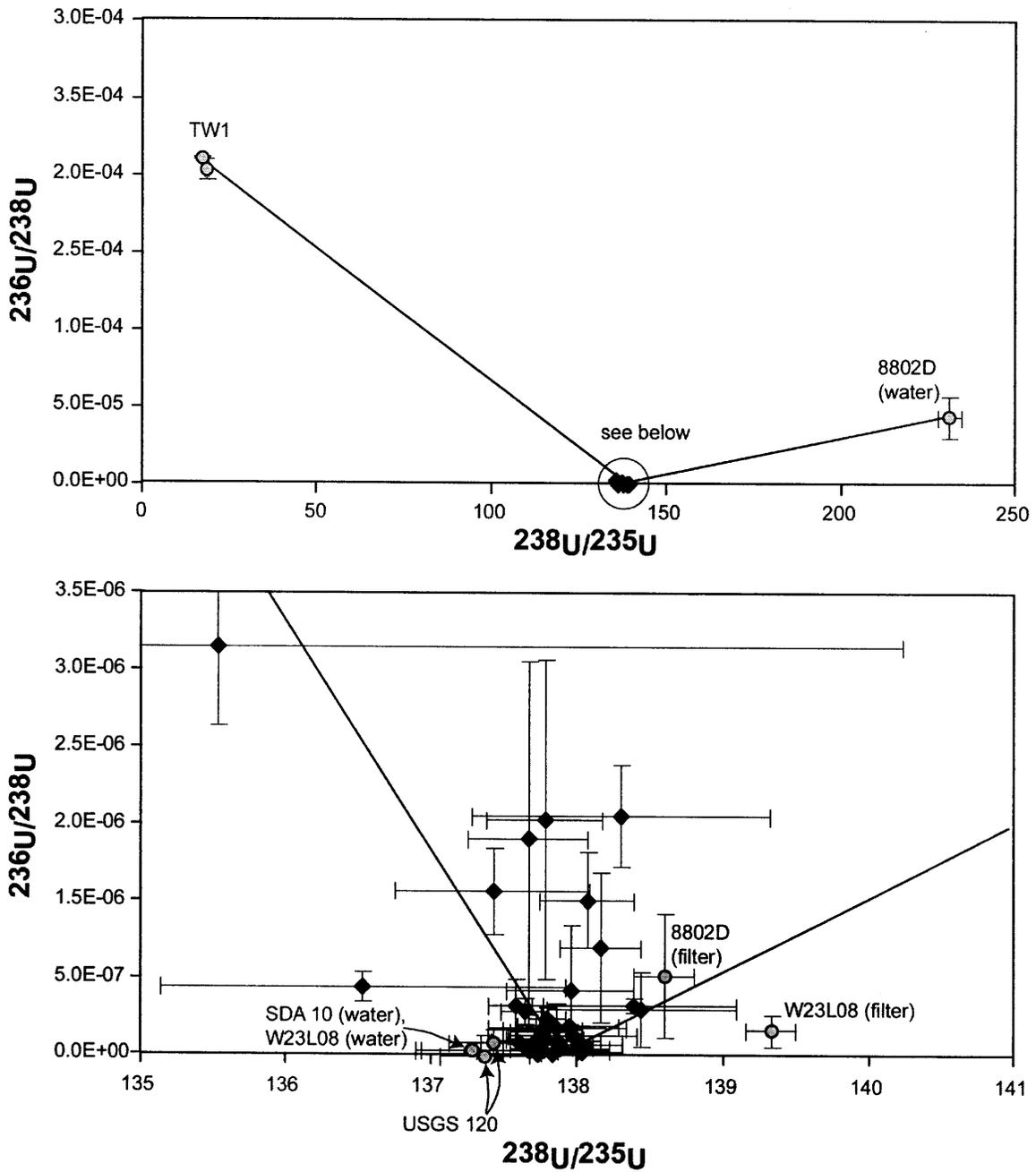


Figure 4. Plots of  $^{236}\text{U}/^{238}\text{U}$  ratios versus  $^{238}\text{U}/^{235}\text{U}$  ratios. Upper figure shows data for all samples, lower figure shows a greatly expanded scale to facilitate examination of the bulk of the data. Two-sigma errors are shown. Samples discussed in the text are labeled. Mixing lines between U with natural isotopic composition and the samples that vary substantially from natural are shown on both figures. Note that 8802D filter in the lower diagram plots along the mixing line between natural U and 8802D water, suggesting that the measured  $^{236}\text{U}/^{238}\text{U}$  ratios are accurate. The  $^{236}\text{U}/^{238}\text{U}$  for the rest of the samples in the lower figure are considered below the detection limit. See text for further discussion.

Six additional samples plot slightly off of the natural U line (Fig. 2). Samples W23L08 (water and filter) and SDA10 (water) are from the vadose zone, 8802D filter is from a perched water zone and sample USGS 120 (water and filter) is an aquifer sample.

In order to evaluate if the  $^{238}\text{U}/^{235}\text{U}$  ratios of these six samples do actually deviate from that of natural U, the overall accuracy of this data set must be assessed. To do so, we make the assumption that the remainder of the data represents water with natural U. We exclude samples PA02 Filter, SDA8 Filter, SDA10 filter and W25 filter because of the high uncertainties of these analyses. The mean  $^{238}\text{U}/^{235}\text{U}$  of the remaining 36 samples is 137.83 with a standard deviation of 0.23. This mean and  $\pm$  one standard deviation are plotted in Figure 2. This value is taken as a conservative assessment of our accuracy of  $^{238}\text{U}/^{235}\text{U}$  ratio measurements for this study. Given this, then the  $^{238}\text{U}/^{235}\text{U}$  ratios from samples W23L08 water, USGS 120 water and filter, and SDA10 water overlap the natural U line. This evaluation is supported by results of a statistical test using Chauvenet's Criterion, which includes these four samples with the bulk of the data set. In addition, the  $^{236}\text{U}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  ratios, as well as total U concentrations of these samples do not indicate the presence of anthropogenic U. Thus, these data are interpreted to indicate that the measured U isotopic ratios for samples W23L08 water, SDA10 water, and USGS 120 water and filter are natural.

The statistical test using Chauvenet's Criterion identifies two samples, 8802D filter and W23L08 filter, as different from the rest of the data set. These two samples are considered possible candidates for containing a component of anthropogenic U. These two samples plot more than 3-sigma above the natural U line (Fig. 2), with  $^{235}\text{U}/^{238}\text{U}$  ratios of  $138.60 \pm 0.15\%$  and  $139.33 \pm 0.20\%$  respectively. The  $^{234}\text{U}/^{238}\text{U}$  as well as total U concentrations of these samples are well

within the range of values determined for this study. The  $^{236}\text{U}/^{238}\text{U}$  ratios for these samples are low and well within the range of values considered as background for this study. The  $^{236}\text{U}/^{238}\text{U}$  ratio for sample 8802D filter; however, plots on a mixing line between natural U and its water counterpart (Fig. 4) suggesting that the  $^{236}\text{U}/^{238}\text{U}$  ratio measured for this sample may be accurate. Taken together, the  $^{238}\text{U}/^{235}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  ratios for sample 8802D combined with the fact that the counterpart water sample unequivocally contains depleted U argue strongly that this sample also contains a small component of depleted U. Evidence that W23L08 filter contains anthropogenic U comes only from the  $^{238}\text{U}/^{235}\text{U}$  ratio. Whereas we feel that this evidence is strong, we recommend additional analyses to confirm this conclusion.

The rest of the samples have natural  $^{238}\text{U}/^{235}\text{U}$  ratios and  $^{236}\text{U}/^{238}\text{U}$  ratios are considered below detection (see discussion below).  $^{234}\text{U}/^{238}\text{U}$  ratios for the aquifer samples are typical for this part of the INEEL. There are no other equivalently analyzed  $^{234}\text{U}/^{238}\text{U}$  ratios for vadose zone or perched water samples from the INEEL. With the exception of the samples discussed above, the  $^{234}\text{U}/^{238}\text{U}$  ratios of vadose zone and perched water samples collected for this study are considered natural.

### **3.2 Plutonium**

$^{239}\text{Pu}$  is expected to be the most abundant isotope of Pu in this study, and therefore the most readily detectable. The highest  $^{239}\text{Pu}$  abundance measured for all sample is approximately  $5\text{E}7$  atoms (equivalent to approximately 1.7 femtocuries of Pu with a  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of 0.18 [in all subsequent conversions of atoms to curries a  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of 0.18 is assumed]) per sample. Most samples have considerably lower  $^{239}\text{Pu}$  abundances. All of these measurements

are near the detection limits of our procedures. Therefore, none of the samples yield unambiguous evidence for the presence of Pu. The results were therefore rigorously examined to determine the statistical significance of the data and to place reasonable confidence levels regarding the presence of Pu in these samples.

### 3.2.1 $^{239}\text{Pu}$ Concentration

Table 2 and Figure 5 present the results and plots of Pu data reduced as discussed above. In Figure 5a and 5b, the data are ranked in order of decreasing  $^{239}\text{Pu}$  abundances. Figure 5a shows that two samples, TW1 filter and 8802D filter plot well above the rest of the samples even given their two-sigma uncertainties. Another four samples describe a break in the data, plotting above the line described by the rest of the data. However, the two-sigma uncertainties of these data overlap with two sigma uncertainties of the bulk of the data. A plot of  $^{239}\text{Pu}$  atoms versus the inverse of the normal cumulative distribution (Fig. 5b) was constructed to examine if the data set is truly a non-random set of numbers, i.e. that these six data points form a distinct population. In such a plot, a normal Gaussian distribution will follow a straight line. The plot shows a pattern similar to that of Figure 5a with the same two samples (TW1 filter and 8802D filter) plotting well above the rest and the same four samples forming a break in the line formed by the remainder of the samples. It must be pointed out that, in both plots, a few of the samples plot *below* the trend shown by the bulk of the samples. This indicates that our methods have produced anomalously low values, further complicating the significance of the higher values.

Another test was performed to evaluate the statistical significance of the data. Given the calculated  $^{239}\text{Pu}$  and the assigned uncertainty, the test evaluates the number of times a value that is as many or greater number of standard deviations from the mean would be expected to occur.

This test assumes that the measurements all have the same mean (in this case 0) and are normally distributed. Results of the test are presented in Table 2 and shown in Figure 5c. The test shows that the two samples with high Pu are not expected occurrences in this data set. Sample PA03 is expected to occur <0.2 times in this data set. The other samples with suspected high values of Pu (PA02, SDA8, and W23L08) are predicted to occur in this data set and thus are not regarded as anomalous by this statistical test. The test is very sensitive to uncertainties of the data.

Therefore the order of the data changes slightly and, in addition, W23L08 moves down in rank whereas M1S filter and USGS119 filter move up in rank.

The above statistical evaluations yield consistent results that add confidence to the interpretation of the data set. All statistical tests show that samples TW1 filter and 8802D filter contain  $^{239}\text{Pu}$  at levels that are statistically above background for the analytical technique. These two samples, as well as TW1 water also show unambiguous proof of anthropogenic U. The suggestion that Pu has migrated into the vadose zone is consistent with the evidence that U has migrated at these localities. Finally, the Pu detections for these samples are in the particulate phase, which is to be expected due to the low solubility of Pu and its tendency to adsorb onto particulate material (Langmuir, 1997). Therefore, although the Pu results are not unambiguous, several lines of evidence taken together strongly suggest the presence of Pu in these samples.

One additional sample, PA03 filter, consistently ranks highly in all statistical tests.

Anthropogenic U was not detected in this sample. Although the data presented here do not prove the presence of  $^{239}\text{Pu}$  in this sample, they do suggest the possibility that Pu is present.

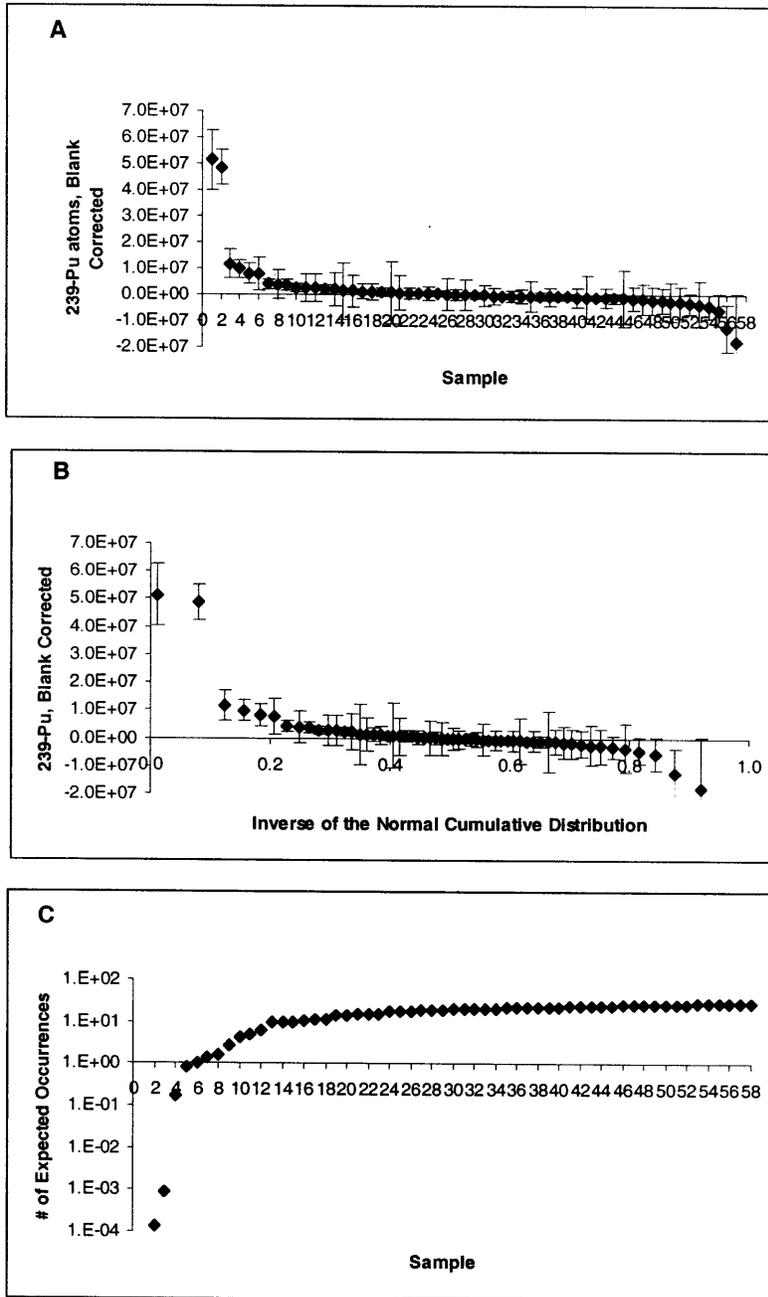


Figure 5. A and B show plots of  $^{239}\text{Pu}$  abundance, ranked in decreasing order for all samples (A) and versus the Inverse of the Normal Cumulative Distribution (B). Two sigma uncertainties are shown. Sample rank is given in Table 2. In both plots, sample 58 plots below the limits of the y axis. Note that TW1 filter and 8802D filter (samples 1 and 2) plot far above the remainder of the samples and the break defined by samples 3-6. C is a plot of the number of expected occurrences for this sample set (see text for description). Sample 1 (8802D) plots well below the minimum value shown on the y axis. Sample number identifiers are keyed to Table 2.

Samples PA02 filter, SDA8 filter, W23L08 filter, M1S filter, and USGS119 filter rank highly in at least one statistical test. Of these, only W23L08 filter shows evidence for anthropogenic U. We conclude that the likelihood that these samples contain  $^{239}\text{Pu}$  is very slight, but recommend that these samples be included in future surveys.

The data are interpreted to indicate that all other samples do not contain  $^{239}\text{Pu}$  at detectable levels of about  $5\text{E}6$  atoms per sample (approximately 0.2 femtocuries per sample). For all aquifer samples and the river sample, >1.5 L of water was analyzed and the filter sample consists of material removed from 2.5-3.0 L of water. Thus, the stated upper limit for  $^{239}\text{Pu}$  abundance is actually less when compared to a 1L sample size. Sample volumes for all vadose zone samples were lower, but for most the detection limit for  $^{239}\text{Pu}$  is still less than  $5\text{E}7$  atoms/L of water (approximately 2 femtocuries/L of water).

Four of the samples are not included in the above analysis and plots. As discussed above, sample M7S was run on a different instrument, therefore the data were processed separately. No Pu was detected in this sample. Due to poor chemical yield, a detection limit of approximately  $2.9\text{E}7$  atoms is assigned to this analysis. Three additional samples (M1S water, M10S water, and USGS117 water) also had poor chemical yields so that the data were not processed with the remainder of the samples. These samples also showed no evidence of Pu with a detection limit of approximately  $5\text{E}8$  atoms/sample (approximately 15 femtocuries/sample).

### **3.2.2 $^{240}\text{Pu}/^{239}\text{Pu}$ Isotopic Ratios**

The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio can be useful to fingerprint the source of Pu and, in the case of this study, may possibly help to distinguish true occurrences of Pu from background. The  $^{240}\text{Pu}/^{239}\text{Pu}$  for

most Pu varies between about 0.06 for weapons-grade Pu to about 1.0 for Pu produced in a reactor with high burn-up. Most reactor-produced Pu has a  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of less than 0.5. Plutonium that was released into the atmosphere during nuclear testing has an average isotopic ratio of 0.18 (Shalkovitz, 1983). This is commonly referred to as “fallout Pu” and is found in most surficial soils globally. In this study, all of the  $^{239}\text{Pu}$  measurements are near or below analytical background, therefore measurements of the smaller  $^{240}\text{Pu}$  signal are even less precise and identifying true detections is even more problematic. Therefore only  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios for the two samples with the most likely  $^{239}\text{Pu}$  detections are discussed below. The  $^{240}\text{Pu}$  measured for the remainder of the samples is considered below detection.

Samples TW1 filter and 8802D filter have  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios of  $0.17 \pm 0.14$  and  $0.05 \pm 0.06$  respectively. The high uncertainty of the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio for sample TW1 filter encompasses the range of weapons-grade Pu, fallout Pu and reactor-produced Pu. The  $^{240}\text{Pu}/^{239}\text{Pu}$  for sample 8802D filter is better constrained (0.0 to 0.11) and implies at least a component of weapons-grade Pu. The fact that both ratios fall within the expected range of  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios helps support the contention that the  $^{239}\text{Pu}$  detections are, in fact, real.

## **4.0 Discussion**

### **4.1 $^{236}\text{U}/^{238}\text{U}$ Ratios**

With the exception of sample TW1 water and filter and 8802D water, all the samples have very low measured  $^{236}\text{U}/^{238}\text{U}$  ratios (all less than  $2.7\text{E}-6$ ). These ratios do not necessarily reflect actual abundance of  $^{236}\text{U}$  relative to  $^{238}\text{U}$ . The measured  $^{236}\text{U}$  in these samples (between 0 and about 2 counts per second) may reflect numerous effects, for example transmission of isobaric interferences, which are difficult to accurately quantify. Negative values are due to excessive

background corrections, which are also likely caused by interferences. In some of the samples, the  $^{236}\text{U}/^{238}\text{U}$  ratios are very imprecise indicating variable  $^{236}\text{U}$  count rates that are likely due to variable within-run transmission of isobaric interferences. In other cases, the measured  $^{236}\text{U}/^{238}\text{U}$  ratios were more stable as shown by lower relative uncertainties. Although such data could signal the presence of  $^{236}\text{U}$ , they could also reflect stable transmission of interferences. For this report,  $^{236}\text{U}/^{238}\text{U}$  ratios less than 3E-6, when taken alone, are considered below detection.

The presence of  $^{236}\text{U}$  is unequivocally documented for samples TW1 water and filter and 8802D water. As discussed above, the  $^{236}\text{U}/^{238}\text{U}$  ratio for sample 8802D filter may reflect the presence of very small amounts of  $^{236}\text{U}$ . The fact that  $^{236}\text{U}$  is found in samples that contain both enriched and depleted U is expected and reflects the fact that the U selected for further enrichment and/or depletion was previously modified within a nuclear reactor.

#### **4.2 $^{234}\text{U}/^{238}\text{U}$ Ratios in Water Samples**

$^{234}\text{U}$  ( $t_{1/2}=2.48 \times 10^5$  y) is part of the  $^{238}\text{U}$  ( $t_{1/2}=4.47 \times 10^9$  y) radioactive decay series. The  $^{234}\text{U}/^{238}\text{U}$  ratio in rocks is generally close to the secular equilibrium value of approximately  $55 \times 10^{-6}$  (55 ppm). However,  $^{234}\text{U}/^{238}\text{U}$  ratios in groundwater is typically greater than the secular equilibrium value because of preferential dissolution of  $^{234}\text{U}$  from crystallographic defects created by alpha recoil and because of direct ejection of  $^{234}\text{U}$  into groundwater by recoil (see Gascoyne, 1992 for review and additional hypotheses). Natural variations in groundwater  $^{234}\text{U}/^{238}\text{U}$  reflect the competing effects of decreased  $^{234}\text{U}$  due to radioactive decay, addition of  $^{234}\text{U}$  by selective leaching and recoil, and addition of U with equilibrium  $^{234}\text{U}/^{238}\text{U}$  isotopic ratios by rock and/or mineral dissolution.  $^{234}\text{U}/^{238}\text{U}$  ratios in INEEL groundwater range from 0.000086

to 0.000168 in the shallow aquifer beneath INEEL (Roback et al., in review), but much higher ratios have been observed in groundwater elsewhere (e.g. Osmond and Cowart, 1992). Most rock and especially rock greater than 1 my has  $^{234}\text{U}/^{238}\text{U}$  ratios that are near secular equilibrium.

The high  $^{234}\text{U}/^{238}\text{U}$  ratios measured for samples TW1 water and filter do not by themselves signal the presence of anthropogenic U. However, the  $^{234}\text{U}/^{238}\text{U}$  ratios measured for these samples are a factor of 3.5 times higher than have been thus far measured in a large number of INEEL samples. The  $^{234}\text{U}/^{235}\text{U}$  ratios for these samples range from 0.0079 to 0.011, values that are well within the range of natural samples at INEEL. These data coupled with the  $^{238}\text{U}/^{235}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  data indicate that these high  $^{234}\text{U}/^{238}\text{U}$  ratios are not due to natural enrichment effects, but rather, are due to depletions in  $^{238}\text{U}$  relative to  $^{234}\text{U}$ . The measured  $^{234}\text{U}/^{238}\text{U}$  for TW1 samples most likely reflect mixtures of enriched U and natural U. Mixing calculations using reasonable values for the natural end member suggest that the  $^{234}\text{U}/^{235}\text{U}$  ratios of the enriched end member are not more than 20% from natural values. Thus, processes used to enrich U detected at TW1 did not greatly affect the relative abundances of  $^{234}\text{U}$  and  $^{235}\text{U}$ .

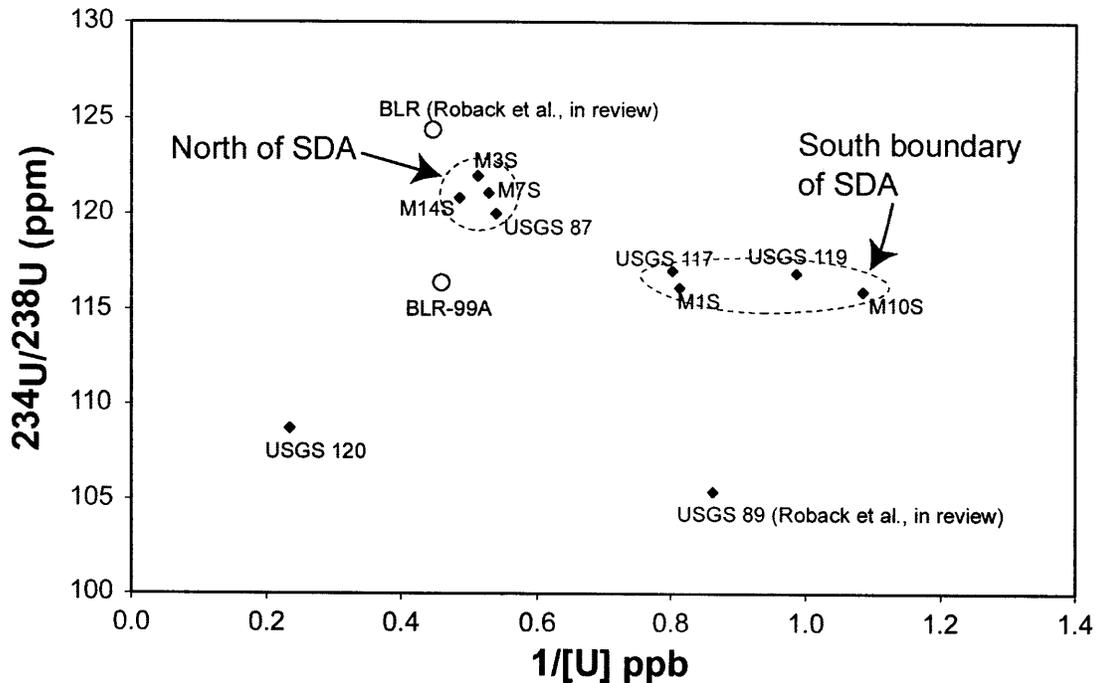


Figure 6. Plot of  $^{234}\text{U}/^{238}\text{U}$  ratios versus the reciprocal of U concentration for aquifer samples near the SDA. Samples north and south of the SDA have distinct U chemistry. It is possible that samples to the north of the SDA were derived largely from the Big Lost River. Samples nearest the spreading areas (USGS 120 and USGS 89) have U chemistry that is distinct from the other samples.

U is readily soluble in oxidizing groundwater (Gascoyne, 1992 and references therein) and therefore it can be used as a relatively conservative tracer, particularly in rapidly flowing aquifers. Roback et al. (in review) used  $^{234}\text{U}/^{238}\text{U}$  ratios to delineate regional flow patterns and mixing relations in the aquifer beneath the INEEL. Most  $^{234}\text{U}/^{238}\text{U}$  ratios determined for this study are in good agreement with values reported in Roback et al. (in review) and help to support their conclusions regarding regional flow patterns.

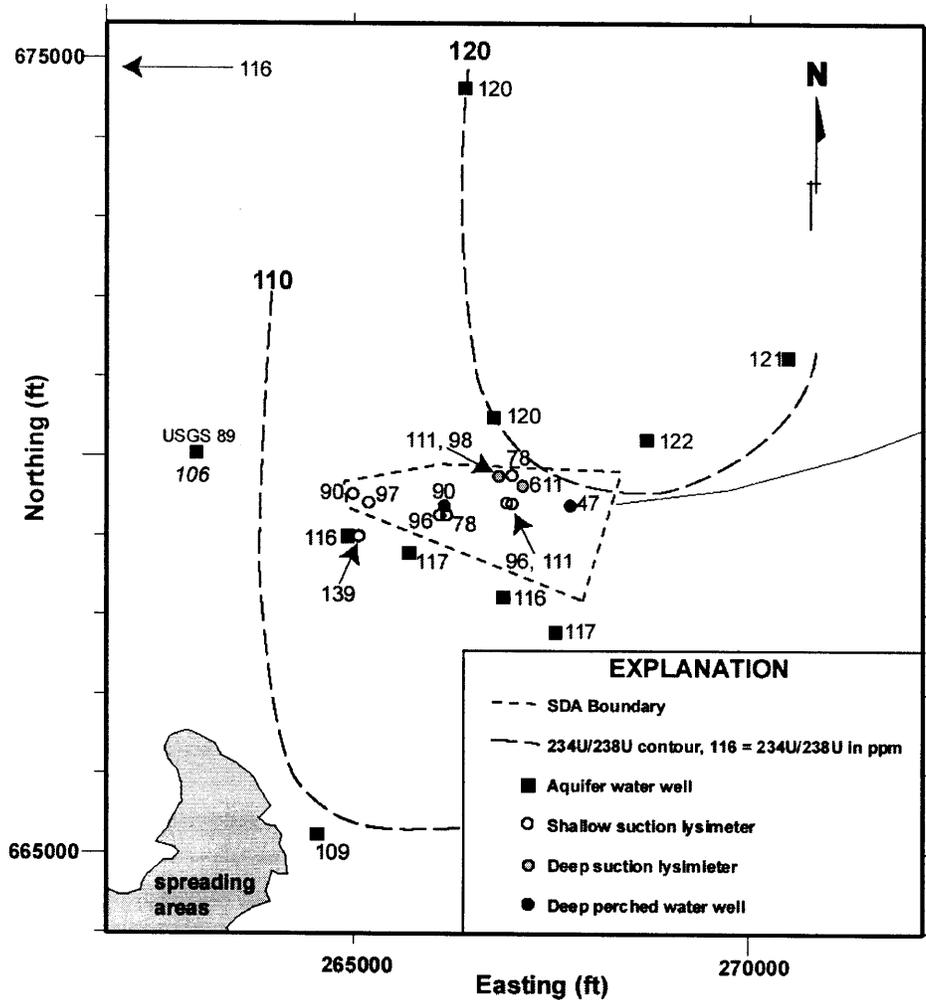


Figure 7. Map showing  $^{234}\text{U}/^{238}\text{U}$  isotopic ratios. Datum from USGS 89 is from Roback et al. (in review). The sample of Big Lost River (BLR-99A) was collected to the west of the arrow at easting approximately 262500 ft. See text for discussion.

U concentration data combined with the  $^{234}\text{U}/^{238}\text{U}$  ratios measured for the aquifer water samples in this study show an interesting and potentially informative geographic pattern (Figs. 6 and 7). Samples to the north and east of the SDA have higher concentrations (1.86 to 2.06 ppb) than do samples just outside of the southern boundary of the SDA (U concentrations of 0.92 to 1.25 ppb). All aquifer samples in this study have a fairly narrow range of  $^{234}\text{U}/^{238}\text{U}$  ratios between 109 ppm and 121 ppm and these ratios generally increase from the southwest to northeast. The four samples to the north and northeast of the SDA have internally consistent  $^{234}\text{U}/^{238}\text{U}$  ratios and U

concentration. These data indicate that the water mass to the north and northeast of the SDA is quite homogeneous in terms of U chemistry, which may point to similar sources, thorough mixing, and/or similar geochemical evolution. The  $^{234}\text{U}/^{238}\text{U}$  ratios and U concentration of the four samples to the north and northeast of the SDA differ from those from wells along the southern boundary of the SDA, which have lower isotopic ratios as well as U concentrations, indicating that this water mass is geochemically distinct from that to the north and east of the SDA, at least in terms of its U chemistry. The differences in U chemistry between these two sample groups may reflect differences in source and/or chemical evolution that is related to their proximity to the spreading areas and/or the Big Lost River. A test of these hypotheses awaits collection and evaluation of additional geochemical and isotopic data from this area.

#### ***4.3 Comparison of Water and Filter Isotopic Data***

Comparison between water and filter isotopic data may shed light on the mode of transport of U and Pu, i.e. whether they are carried as dissolved constituents or as particles. All the samples were filtered at 0.5  $\mu\text{m}$ , thus splitting the sample into two aliquots, 1) constituents greater than 0.5  $\mu\text{m}$  (referred to as the particulate fraction) and 2) constituents less than 0.5  $\mu\text{m}$ . The generally accepted maximum size of colloids is 0.45  $\mu\text{m}$ , and they typically exist as much smaller particles. The methods employed for this study did not attempt to separate dissolved from colloidal constituents and, as a result, data presented herein cannot differentiate between whether U and Pu were carried as a dissolved or colloidal phase. In the following, the combined dissolved and colloidal phases will be simply referred to as the dissolved phase. Uranium isotopic data for the paired water and filter samples are shown in Figures 2, 3, and 4. As concluded above, all possible occurrences of Pu are from the particulate fraction.

Samples TW1 water and filter have analytically indistinguishable U isotopic data indicating that isotopic equilibrium has been achieved between dissolved and particulate fractions. The filter sample from 8802D has  $^{238}\text{U}/^{235}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios that are much closer to that of natural U than data from the counterpart water sample. This likely indicates that the filter sample is dominated by particles with natural U isotopic composition. This is to be expected given that the water from this sample has anomalously low U concentration and therefore low capacity to affect the U isotopics of the particles through adsorptive exchange. The only other sample with a high probability of containing non-natural U is W23L08 filter, which has a  $^{238}\text{U}/^{235}\text{U}$  ratio that is slightly elevated from natural. In contrast, the corresponding water sample has natural U isotopics suggesting that U is being transported in the particulate rather than the dissolved phase at this locality.

In all but two of the samples, the  $^{234}\text{U}/^{238}\text{U}$  ratios of the filter samples are either lower than, or essentially equal to, the corresponding water samples. Lower  $^{234}\text{U}/^{238}\text{U}$  isotopic ratios for the filter samples likely indicates that the waters are carrying rock particles with  $^{234}\text{U}/^{238}\text{U}$  close to secular equilibrium, in addition to U that was adsorbed from the water. Samples for which the  $^{234}\text{U}/^{238}\text{U}$  ratios of the filter and water are nearly identical likely carry most of the particulate U as an adsorbed and therefore readily exchangeable phase. Five of the ten aquifer samples, the river sample, and one of the perched water samples have lower  $^{234}\text{U}/^{238}\text{U}$  ratios for the filter when compared to the water. In contrast, with only two exceptions, all vadose zone filter and water samples have nearly identical  $^{234}\text{U}/^{238}\text{U}$  ratios. This result is expected for a number of reasons: 1) the aquifer and river samples have a higher capacity to carry more and coarser rock fragment than do the vadose zone samples due to greater flow velocities, 2) the vadose zone samples were

collected via suction lysimeters, which filter out some of the coarse particles, and 3) for USGS 92, the collection method entrained a large amount of sediment. Samples W25 and 8802D do not follow this pattern, i.e. the water samples have lower  $^{234}\text{U}/^{238}\text{U}$  than do the corresponding filter samples. Sample W25 yielded the lowest mass of U on the filter of all the samples. The uncertainties of the data for this sample are very high due to the large blank correction, and may in fact be understated. The  $^{234}\text{U}/^{238}\text{U}$  ratio of W25 filter should therefore be treated conservatively. Sample 8802D water has depleted  $^{238}\text{U}/^{235}\text{U}$  isotopics. A likely explanation for the fact that the water sample has a lower  $^{234}\text{U}/^{238}\text{U}$  ratio than the filter is that the  $^{234}\text{U}/^{238}\text{U}$  ratio is lowered due to the presence of enriched U.

All possible Pu detections are from the filter samples indicating that Pu was likely transported as a particle rather than a dissolved constituent. This is to be expected owing to the generally low solubility of Pu in groundwater and its affinity to adsorb onto particles (Langmuir, 1997). This study does not provide evidence that Pu was transported as a colloid (e.g. Kirsting et al., 1999). We cannot rule out the possibilities that true colloids coagulated between collection and processing to form coarser particles, or that the colloids adsorbed onto the filter or filtered particles during filtration.

## **5.0 Recommendations**

This study documents that anthropogenic U and probably Pu are present in two sampling localities: TW1 and 8802D. Continued monitoring of these will help to confirm the presence for Pu as well as document changes in the anthropogenic contribution to the U in the sample. The anomalously low U concentration for sample 8802D may suggest reducing conditions brought on

by contaminant release. Additional geochemical evaluation of this well should be conducted to investigate redox conditions, and the possible role of organic complexing agents in contaminant transport. Two other samples, W23L08 and PA3, yielded probable or possible detections for anthropogenic U and Pu respectively. Additional analyses of samples from these localities are necessary to positively document the presence of anthropogenic U or Pu. In addition to replicate analyses, processing of larger samples would aid in confirming Pu detections in these four samples and possibly in documenting the presence of Pu in other samples.

Natural  $^{234}\text{U}/^{238}\text{U}$  ratios in aquifer groundwater are useful indicators of flow and geochemical evolution. These data give us clues to physical and chemical interactions of the groundwater sources, water rock interactions and mixing relations (e.g. Roback et al., in review). The pattern of U isotopic ratios and concentrations determined for this study reveals distinct special patterns in the vicinity of the SDA. Such data from a more complete coverage of aquifer wells coupled with other data, such as major element concentration data and other isotopic data, would add greatly to our understanding of local groundwater sources, flow patterns, and geochemical evolution in the vicinity of the SDA. Ultimately these data would lead to better prediction of the migration of contaminants from the SDA.

## 6.0 Literature Cited

- Burgess, D., 2000, Sampling and Analysis Plan for Lysimeter and Perched Water Monitoring of Operable Unit 7-13/14, INEEL/EXT-2000-00714.
- Efurd, D.W., Rokop, D.J., and Perrin, R.E., 1993, Characterization of the radioactivity in surface-waters and sediments collected at the Rocky Flats Facility, Los Alamos National Laboratory Report # LA-UR-93-4374, 1-54.
- Faure, G. 1986, Principles of isotope geology, 1986, New York, NY, John Wiley and Sons, 589 p.
- Gascoyne, M., 1992, Geochemistry of the actinides and their daughters, *in* Ivanovich, M. and Harmon, R. S. eds., U-series disequilibrium; applications to Earth, marine, and environmental sciences: Oxford, United Kingdom, Clarendon Press, p. 34-61.
- Kersting, A. B., Efurd, D. W., Finnegan, D. L., Rokop, D. J., Smith D. K., and Thompson, J. L., 1999, Migration of plutonium in groundwater at the Nevada Test Site: *Nature*, v. 397, no. 6714, p 56-59.
- Langmuir, D., 1997, Aqueous environmental geochemistry: Upper Saddle River, NJ, Prentice Hall, 600 p.
- Osmond, J. K. & Cowart, J. B., 1992, Groundwater. *in* Ivanovich, M. and Harmon, R. S. eds., U-series disequilibrium; applications to Earth, marine, and environmental sciences.: Oxford, United Kingdom, Clarendon Press, p. 290-333.

Roback, R.C., Johnson, T.M, McLing, T.L., Murrell, M.T., Luo, Shangde and Ku, Teh-Lung.

Groundwater flow patterns and chemical evolution in the Snake River Plain aquifer in the vicinity of the INEEL: constraints form  $^{234}\text{U}/^{238}\text{U}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios: Submitted to Geological Society of America Bulletin, February 14, 2000.

Shalkovitz, E. R., 1983, The geochemistry of plutonium in fresh and marine water environments:

Earth Science Review, v. 19, p. 95-161.

Walker F. W., Parrington, J. R. and Feiner, F., 1989, Nuclides and Isotopes, (14<sup>th</sup> ed.) General

Electric Corporation, Nuclear Energy Operations, San Jose, CA 95125.