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Initial Report Aquifer Background Study: Summary of Uranium and Plutonium Data from INEEL Groundwater Samples

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ABSTRACT

As part of the "Aquifer Background Study," Los Alamos National Laboratory (LANL) under contract with the Idaho National Engineering and Environmental Laboratory (INEEL) has undertaken a study to determine uranium and plutonium abundances and isotopic composition in groundwater samples collected at the INEEL. To date, four samples have been analyzed for uranium and plutonium and an additional nine samples have been analyzed for uranium. It is expected that several more samples will be analyzed for this study. This report summarizes the results from this initial set of samples.

Of the 13 samples analyzed for uranium, four samples have ^{238}U/^{235}U ratios that differ from the natural value of 137.88. These four samples and two additional samples also contain ^{236}U at 3-sigma level above detection limits. The presence of ^{236}U and the non-natural ^{238}U/^{235}U ratios unequivocally indicate the presence of anthropic uranium in four of the samples. A small component of anthropic uranium is also present in two additional samples with positive ^{236}U detection but natural ^{238}U/^{235}U isotope ratios. Two of the samples with anthropic uranium, as well as two samples with no detectable anthropic uranium were analyzed for plutonium. No plutonium was detected in these four samples at detection limits of approximately 5E7 ^{239}Pu atoms for three of the samples and approximately 1E8 ^{239}Pu atoms for the forth sample. These detection limits correspond to $^{(239+240)}$Pu activity ratios (assuming a ^{240}Pu/^{239}Pu atom ratio of 0.18) of 0.002 and 0.004 pCi/L respectively.

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1. INTRODUCTION AND BACKGROUND

To document possible radionuclide migration into the subsurface, INEEL contracted LANL to analyze groundwater samples for plutonium and uranium concentration and isotopic composition by Isotope Dilution-Thermal Ionization Mass Spectrometry (ID-TIMS). This report summarizes data from the first set of samples analyzed. This initial set was selected for the following reasons: 1) the four samples selected for plutonium analyses had positive detections of ^{238}Pu in alpha spectrometric analyses; 2) Two of these samples are located in a proximal, down gradient position with respect to the Idaho Nuclear Technology Engineering Center (INTEC), a possible source of plutonium; and, 3) the additional samples analyzed for uranium are also located in a proximal, and/or down gradient position with respect to potential sources of uranium. Thus, the samples were selected to maximize the likelihood of identifying actinide contaminants in the aquifer.

2. METHODS

2.1 Sample Collection

Samples were collected from regional aquifer wells with dedicated pumps by INEEL personnel using established sampling protocol (Burgess, 2000). All samples were collected in pre-cleaned 1-Chem HDPE bottles to minimize the potential for contamination. The samples were acidified in the field with high-purity HNO_3 acid to a pH of less than 2 and shipped to LANL.

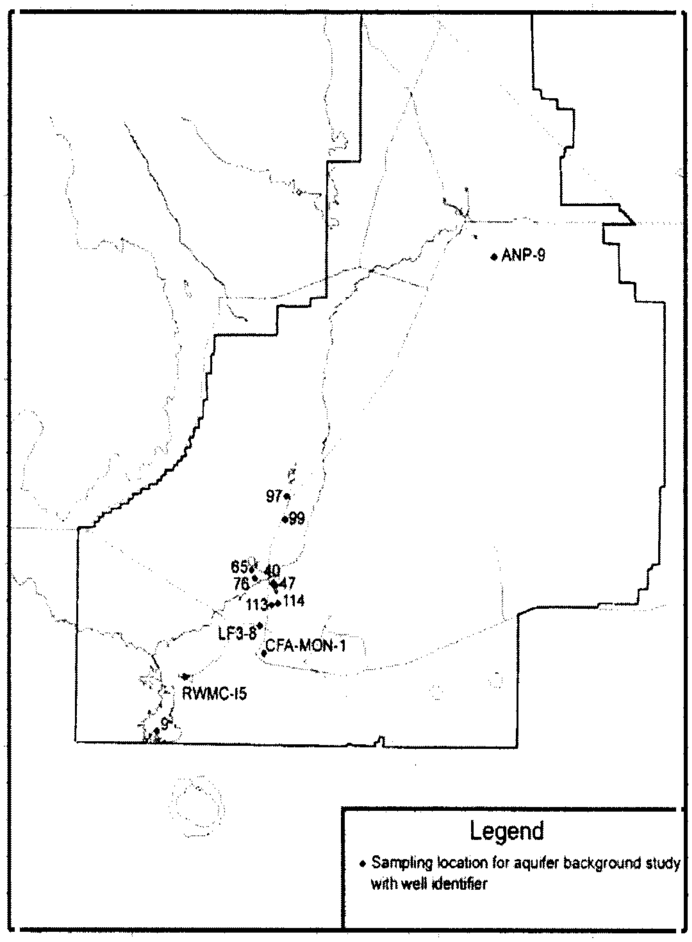

Figure 1. Map of the INEEL showing sample locations. Locations specified only by number are preceded by "USGS."

2.2 Sample Processing

2.2.1 Dissolution and Chemical Separation

All dissolution and chemical separation was performed in clean laboratories at the Clean Chemistry and Mass Spectrometry Facility (TA 48, RC 45*)* at LANL. Ultrapure reagents produced by Seastar™ and Optima™ were used.

Uranium aliquots were weighed, spiked with a ^{233}U tracer, acidified with HNO_3 acid, and evaporated to dryness. The precipitated salts were redissolved in a hydrochloric/hydrofluoric acid mixture, then again in 8M $HCl+H_2O_2$. Uranium was purified by hydrochloric and nitric acid anion exchange column chemistry using BioRad™ MP-1 anion exchange resin and eluted with ultrapure water and dilute hydrochloric acid.

To minimize the possibility that the plutonium had sorbed to the sides of the sample bottle, 10 ml of concentrated nitric acid were added to each sample bottle, and the bottle was warmed on a hot plate for 24 hours. Plutonium aliquots were then weighed (weights were corrected for the addition of the nitric acid), spiked with a ^{242}Pu tracer, and placed on a hot plate for evaporation.

To further ensure against the potential loss of plutonium onto the sides of the sample bottles by sorption, the emptied bottles were "washed" by adding approximately 60 ml of 1.5M nitric acid and placing the bottles, loosely capped on a warm hot plate for 48 hours. This nitric acid wash was added to the samples before they had been completely evaporated. The combined solutions were then evaporated to dryness. The precipitated salts were redissolved in a series of HF, HNO_3 and $HClO_4$ acid digestions. Plutonium was purified with a series of HNO_3 and HCl acid columns and eluted with either a 1:9 mixture of concentrated HI, concentrated HCl, or with concentrated HBr from BioRad™ MP-1 anion exchange resin. Additional details of plutonium chemical processing are given in Efurd et al., 1993.

2.2.2 Analytical Techniques

Mass spectrometric analyses of the U samples were performed on VG Sector 54 equipped with a WARP filter. Uranium was loaded onto outgassed Ta filaments configured in a triple filament assembly with a zone-refined Re center filament. Data acquisition was accomplished by cycling the smaller ^{233}U, ^{234}U, ^{235}U and ^{236}U signals onto the Daly knob while simultaneously measuring ^{238}U and ^{235}U on Faraday collectors. Plutonium analyses were performed using an NBS-type mass spectrometer dedicated to plutonium analyses. These samples were electroplated onto rhenium filaments with a platinum over-plate. For all samples, data were collected in ion counting mode by cycling ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{242}Pu, ^{240}Pu, and ^{239}Pu with background measurements take at the intervening half mass.

2.2.3 Data Reduction

Uranium concentration and isotopic data are summarized in Table 1. Uranium isotopic data were corrected for mass fractionation as determined from repeated runs of NBS U960 standard and samples far from potential sources of anthropic uranium for which natural ^{238}U/^{235}U isotopic ratios are assumed. For analyses performed on the VG Sector 54, a fractionation factor of 0.035%/atomic mass unit (AMU) was applied. Uranium data were also corrected for spike and blank contribution.

Plutonium data were corrected using an in-house program written by Clarence Duffy of LANL (C-INC). For all of the samples, the raw ^{239}Pu and ^{240}Pu instrument signals were extremely low, in all cases statistically indistinguishable from the background taken at the intervening half-mass.

2.3 Quality Control Samples

Uranium samples were processed in two separate batches. Two total procedural blanks were processed along with each sample batch. These blanks average 1.6 picograms, a value that is in good agreement with long-term laboratory uranium procedural blanks. All samples yielded sufficient uranium so that the blank corrections are insignificant. One total procedural plutonium blank was run along with the plutonium samples. No plutonium was detected in the blank.

Table 1. Summary of U and Pu results.

Sample	U Sample Wt(g)	U (ppb)	(+/-) (%)	238U/235U	(+/-) (%)	236U/238U	(+/-) (%)	234U/238U	(+/-) (%)	Pu Sample Wt(g)	239Pu atoms/kg	(+/-) (%)	240Pu atoms/kg	(+/-) (%)
	Uranium Results									Plutonium Results				
USGS 113	290.3	2.08	0.27	**132.86**	0.20	**1.52E-05**	0.48	109.5	0.23	990.4	non-detect		non-detect	
USGS 114	236.8	1.56	0.20	137.76	0.12	**2.14E-07**	5	111.5	0.14	993.7	non-detect		non-detect	
USGS 9	194.4	1.34	0.23	137.95	0.13	-2.26E-09	416	123.3	0.19	979.8	non-detect		non-detect	
ANP 9	199.7	2.39	0.21	137.72	0.09	-9.69E-09	84	164.3	0.13	994.2	non-detect		non-detect	
USGS 40	266.5	2.06	0.20	**131.74**	0.08	**4.63E-05**	0.22	117.8	0.12	Not analyzed				
USGS 97	200.9	2.42	0.22	137.77	0.11	-2.47E-08	60	128.9	0.17	Not analyzed				
LF3-08	247.9	2.16	0.22	**127.17**	0.12	**2.80E-05**	0.30	116.6	0.17	Not analyzed				
USGS 76	211.89	1.57	0.22	137.88	0.12	8.27E-09	91	159.2	0.15	Not analyzed				
USGS 20	130.50	2.06	0.21	137.75	0.11	1.02E-08	55	118.1	0.15	Not analyzed				
CF Mon 001	325.85	1.72	0.24	138.02	0.16	3.51E-09	167	112.1	0.29	Not analyzed				
RWMC I-5	439.25	2.21	0.22	137.96	0.11	2.95E-10	1170	104.8	0.22	Not analyzed				
USGS 47	209.78	2.06	0.20	**125.93**	0.09	**4.37E-05**	0	120.7	0.15	Not analyzed				
USGS 65	221.70	1.96	0.49	138.07	0.46	**1.09E-07**	51	113.7	0.56	Not analyzed				
	Replicates													
USGS 1A-1	198.82	1.64	0.23	137.83						Not analyzed				
USGS 1A-2	195.90	1.64	0.25	137.74						Not analyzed				
Total Process Blanks														
	picograms U													
U Blank 2/4/02 - A	1.40													
U Blank 2/4/02 - B	1.56													
U Blank 3/7/02 - A	1.65													
U Blank 3/7/02 - B	1.62													
Pu Blank 2/15/02 - A											non-detect			

Notes:

All uncertainties are stated at the 2-sigma level.

Minimum detection limit for the $^{236}U/^{238}U$ ratio is approximately 2×E-8.

Minimum detection limit for ^{239}Pu and ^{240}Pu is approximately 5×E7 atoms for USGS 113, USGS 114, USGS 9. Detection for ANP 9 is approximately 1×E8 atoms.

Bolded entries highlight isotopes ratios that indicated the presences of a component of anthropic uranium.

Reproducibility of uranium results is assessed by replicate analyses of New Brunswick Laboratories Certified Reference Material 112A (CRM 112A, formerly NBS Standard Reference Material U960), replicate analysis of INEEL groundwater, and evaluation of $^{238}U/^{235}U$ isotopic data for the data set presented here. Two samples of CRM 112A, which has natural $^{238}U/^{235}U$ isotopic ratio, were spiked with ^{233}U (to mimic actual samples) and run prior to analysis of the samples. For these runs the mass fractionation correction was derived by comparing the measured $^{238}U/^{235}U$ to the natural value of 137.88; this value was then used to correct the $^{234}U/^{238}U$ ratios. Measured $^{234}U/^{238}U$ ratios were: run-1 = 0.0000528 1 ± 0.20%, run- = 2: 0.00005282 ± 0.28% (2-sigma errors). These values are in excellent agreement with values reported for other laboratories (e.g. Cheng et al., 2000) and our long-term laboratory values. A groundwater sample from well USGS 1 located in the southeastern corner of the INEEL has been analyzed previously (Roback et al., 2001) and in this study to assess reproducibility of an actual groundwater sample. These replicates were processed and analyzed alongside and identically to the actual samples. The results of these (Table 1) show: natural $^{238}U/^{235}U$ ratios, ^{236}U below detection, and internally reproducible $^{234}U/^{238}U$ ratios and uranium concentration. Another method of assessing analytical reproducibility is to examine the $^{238}U/^{235}U$ and $^{236}U/^{238}U$ ratios of samples that show no evidence of anthropic uranium under the assumption that these in fact do not contain anthropic uranium (which is likely to be valid for at least many of the samples). A plot of these data along with data from USGS lA is shown in Figure lB. The data form a well-defined cluster with all samples overlapping the values for natural uranium. The mean for these samples is 137.85 ± 0.05% (2-sigma) and $^{236}U/^{238}U$ ratios cluster around zero.

These data also provide a means of assessing the detection limit for ^{236}U. The detection limit for ^{236}U is dependent on the $^{236}U/^{238}U$ ratio because of poorly understood processes in the mass spectrometer (e.g., isobaric interferences, tailing effects from adjacent uranium masses) that are commonly correlated with overall signal intensity. $^{236}U/^{238}U$ ratios from samples with apparently no ^{236}U as well as USGS 1A cluster tightly around zero with a mean of—5.15E-l0 with a 3-sigma standard error of 1.09E-8. This 3-sigma error places the minimum detection limit at a $^{236}U/^{238}U$ ratio of 1E-8. On the basis of these results, results from other ongoing uranium isotopic work at the INEEL, as well as long-term experience, the detection limit for ^{236}U in these samples is conservatively placed at a $^{236}U/^{238}U$ ratio of 2E-8.

3. RESULTS

3.1 Uranium

Uranium concentration and isotopic composition are given in Table 1. Isotope ratios that indicate an anthropic component of uranium are presented as bold text for clarity. Uranium concentrations range from 1.3 to 2.4 ppb, values that are typical for groundwater at INEEL (Roback et al., 2000, and 2001). There is no correlation between uranium concentration and the presence or absence of anthropic uranium. Uranium concentration data, by themselves, do not provide evidence of anthropic uranium for these samples.

Uranium isotope ratios for seven of the 13 samples are natural; they show no evidence of anthropic uranium. Four samples, USGS 113, USGS 40, LF3-08, and USGS 47, have non-natural $^{238}U/^{235}U$ isotope ratios and clearly contain ^{236}U, with $^{236}U/^{238}U$ ratios up to 0.0000463 (Table 1 and Figure lA). These data unequivocally indicate a component of anthropic uranium. Two other samples, USGS 114 and USGS 65, have $^{238}U/^{235}U$ ratios that are indistinguishable from natural at the 2-sigma level but have detectable ^{236}U (Figure 1B). In Figure 1B $^{236}U/^{238}U$ 2-sigma error bars are shown to demonstrate that the $^{236}U/^{238}U$ for these samples are clearly resolvable from the cluster of samples that define the detection limit for this data set, shown as the dashed line. The $^{236}U/^{238}U$ ratios for USGS 65 and USGS 114 are still above the detection limit of 2E8 at the 3-sigma uncertainty level. The data are therefore interpreted to indicate that USGS 65 and USGS 114 contain a small component of anthropic uranium.

$^{234}U/^{238}U$ ratios for all samples range from 0.000105 to 0.000164 (105 to 164 ppm), values that are within the range of known values of non-contaminated samples (Roback et al., 2000 and 2001). There is no correlation between $^{234}U/^{238}U$ ratios and $^{238}U/^{235}U$ or between $^{234}U/^{238}U$ ratios and $^{236}U/^{238}U$ isotope ratios. It is apparent from this data set and that of previous work (Roback et al., 2000) that most groundwater samples thus far analyzed at INEEL do not contain anthropic ^{234}U enrichments or depletion that are sufficient to distinguish them from the highly variable $^{234}U/^{238}U$ ratios that occur naturally. Significant proportions of anthropic uranium appear to be required before the $^{234}U/^{238}U$ ratios are sufficiently modified to distinguish them from natural. For example groundwater from lysimeter TW-1 with a $^{238}U/^{235}U$ ratio of ~18 and $^{236}U/^{238}U$ ratio of 0.0002 has a $^{234}U/^{238}U$ ratio of 0.000612 a value that is at least 3.5 times higher than values thus far observed at INEEL (Roback et al., 2000, and 2001). Given the $^{238}U/^{235}U$ and $^{236}U/^{238}U$ ratios for this sample, the large $^{234}U/^{238}U$ ratio was reasonably interpreted to reflect anthropic contribution. However, similarly elevated $^{234}U/^{238}U$ ratios are found naturally, and in the absence of additional isotopic data even this elevated value does not unequivocally demonstrate the presence of anthropic uranium. Therefore, due to the wide range of natural variation observed in $^{234}U/^{238}U$ ratios, these data, by themselves, are not good indicators of anthropic uranium. In contrast, $^{238}U/^{235}U$ and $^{236}U/^{238}U$ values are constant in nature; deviations beyond analytical uncertainties unequivocally demonstrate anthropic input.

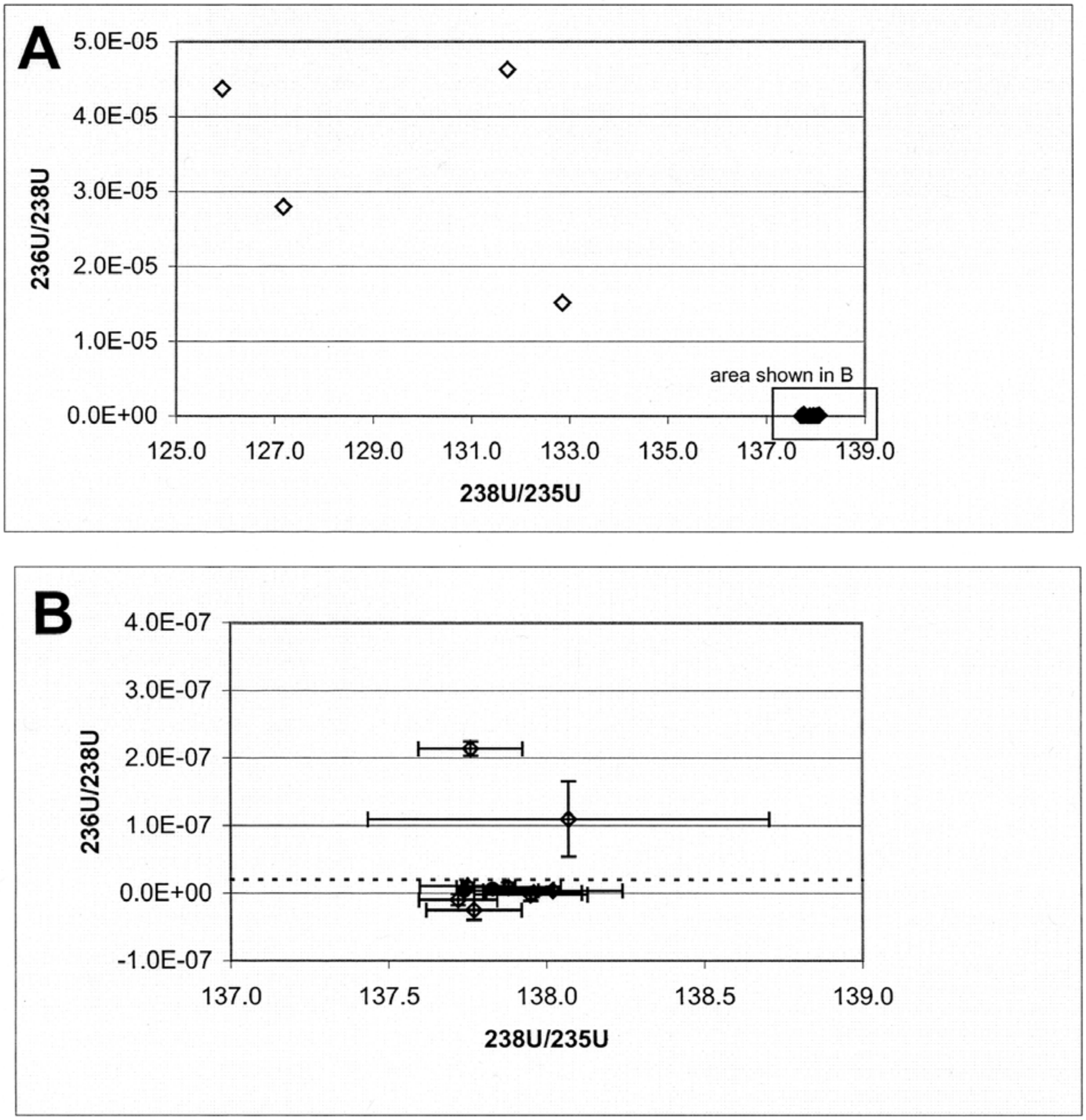

Figure 2. A. Plot of uranium atomic ratios. Errors in ^{238}U/^{235}U are 2-sigma, y-axis error bars are smaller than symbols. B. Blow up of area shown in A to facilitate examination of data. Dashed line is the detection limit for ^{236}U/^{238}U of 2E8 (see text for discussion). All errors are 2-sigma. Natural uranium has ^{238}U/^{235}U ratio of 137.88 and no ^{236}U.

3.2 Plutonium

Plutonium-239 is expected to be the most abundant isotope of Pu in these samples, and therefore the most readily detectable by mass spectrometry. Plutonium-239 was not detected in the four samples analyzed. One total procedural blank was processed along with the samples. No ^{239}Pu was detected in the blank.

Minimum detection limits at the 99% confidence level for the four samples processed thus far are 5E7 atoms total for samples USGS 113, USGS 114 and USGS 9, and 1E8 atoms total for sample ANP-9. Minimum detection limits for plutonium performed by ID-TIMS will vary somewhat depending on sample type and chemistry. Due to the limited number of samples and blanks thus far processed, the stated detection limits are based on the within-run counting statistics for the samples and the blank, as well as previous experience on similar INEEL samples. The higher detection limit for ANP 9 compared to the other three samples is due to poorer quality of the mass spectrometry run. This sample will be reprocessed to achieve a better detection limit.

3.2.1 Implications for detection of ^{238}Pu by alpha spectrometry

As part of environmental monitoring efforts at the INEEL, groundwater samples are routinely analyzed by alpha spectrometry for the presence of plutonium isotopes. Several groundwater samples have yielded possible positive detections of ^{238}Pu during the course of these investigations. These possible detections are all very close to the stated detection limit by 1000-minute alpha spectrometry of 0.02 pCi/L (L. Don Koeppen, INEEL, personal communication). One of the goals of this study is to provide data that may help in evaluating the validity of these possible ^{238}Pu detections.

Plutonium-238 has a short half-life (87.7 yr) relative to ^{239}Pu (half-life of 2.410E4 yr) and ^{240}Pu (half-life of 6.56E3 yr) (Walker et al., 1989). The half-life is related to activity by the following relationships:

$n\lambda c$ = Activity

where *n* is the number of atoms, λ is the decay constant in units of time, and c is the detection coefficient in decays/atom. Units for activity are decays/unit time. The decay constant λ is related to the half-life by the expression:

$\lambda = \ln(2)/\text{half-life}$

Conversion of activity in units of decays/unit time to curies (Ci) follows the following expression:

1Ci = 3.70E10 decays/second

Plutonium-238 abundances are typically determined by alpha spectrometry because the shorter half-life will result in a greater number of decays/unit time compared with the longer-lived ^{239}Pu and ^{240}Pu isotopes. Plutonium-239 is not readily separable from ^{240}Pu by alpha spectrometry because of their similar energy spectra; alpha spectrometric measurements are therefore reported as $^{(239+240)}$Pu. Plutonium isotopic data routinely collected at INEEL are reported in units of pico Curies/L (pCi/L) for ^{238}Pu and $^{(239+240)}$Pu. Plutonium-239 and ^{240}Pu relative abundances can be determined by mass spectrometry and ^{240}Pu/^{239}Pu isotope ratios are generally given as the atom ratio. In this study, ^{239}Pu and ^{240}Pu abundances are given in units of atoms and concentrations in terms of atoms/g.; ^{238}Pu abundances were not determined.

In order to evaluate the implications of the data presented here on the possible ^{238}Pu detection by alpha spectrometry the relative abundance of ^{238}Pu and ^{239}Pu must be known or assumed.

Plutonium isotopic ratios may vary considerably depending on the original production process and age of the material. Over the course of its operation, the INEEL has handled plutonium waste derived from a number of production processes. Thus, the plutonium present at the site may have a wide range of isotopic ratios. Predicting the isotopic ratios of plutonium contamination is further complicated by the possibility that plutonium derived from different production processes may mix in the environment. It is beyond the scope of this study to evaluate the potential range in ^{238}Pu/$^{(239+240)}$Pu that may be present in environmental samples from the INEEL. Rather, Table 2 below presents the number of ^{239}Pu atoms that would be expected given a range of ^{238}Pu/^{239}Pu and ^{240}Pu/^{239}Pu isotopic ratios and assuming a minimum detection limit of 0.02 pCi/L for ^{238}Pu in aquifer samples. The table presents a reasonable range of plutonium isotope ratios for evaluating plutonium based on production processes. Small ^{238}Pu/$^{(239+240)}$Pu activity ratios and ^{240}Pu/^{239}Pu atom ratios correspond to weapons-related plutonium and to average globa1 fallout, which has a ^{238}Pu/$^{(239+240)}$Pu activity ratio of approximately 0.04 and a ^{239}Pu/^{240}Pu atom ratio of approximately 0.18. Larger ^{238}Pu/$^{(239+240)}$Pu activity ratios and ^{240}Pu/^{239}Pu atom ratios will be expected in nuclear fuels, with larger ratios produced with increased burn up of the fuel. In a general sense the ^{238}Pu/$^{(239+240)}$Pu activity ratios should be positively correlated with ^{240}Pu/^{239}Pu atom ratios.
Beasley et al., (1998) presented plutonium isotopic data from shallow soils at INEEL in order to characterize and distinguish fallout plutonium from operations-related plutonium. The reported ^{238}Pu/$^{(239+240)}$Pu activity ratios range from 0.03 to 0.72 and ^{240}Pu/^{239}Pu atom ratios range from 0.07 to 0.18. The authors concluded that most of the plutonium encountered was derived from fallout but a few samples contained mixtures of fallout plutonium and plutonium from facilities at the INEEL. The range of plutonium isotope ratios presented by Beasley et al., (1998) provides reasonable bounds on the isotopic composition of near-surface plutonium at the INEEL.

Plutonium-239 detection limits for this study are 5E7 atoms/L, equivalent to a $^{(239+240)}$Pu concentration of 0.002 pCi/L, for samples USGS 113, USGS 114 and USGS 9, and 1E8 atoms/L for sample ANP-9, equivalent to a $^{(239+240)}$Pu concentration of 0.004 pCi/L (conversions of atoms to activity assume a ^{240}Pu/^{239}Pu atom ratio of 0.18). Given these detection limits for ^{239}Pu, it is reasonable to conclude that for plutonium with a ^{238}Pu/$^{(239+240)}$Pu activity ratio of <1, i.e., typical of fallout Pu and weapons-related plutonium, ^{238}Pu concentration would be below 0.02 pCi/L. Plutonium-238 concentration would be above 0.02 pCi/L only if the ^{238}Pu/$^{(239+240)}$Pu activity ratio in these samples is greater than about 5.

Table 2. Number of ^{239}Pu atoms expected for different ^{238}Pu/$^{(239+240)}$Pu activity ratios and ^{240}Pu/^{239}Pu atom ratios given a ^{238}Pu activity of 0.02 pCi.

	Given ^{238}Pu detection limit =	0.02	PCi/L			
	and:					
	^{238}Pu/$^{(239+240)}$Pu activity ratio =	0.01	0.1	1	5	10
	and ^{240}Pu/^{239}Pu atomic ratio =	^{239}Pu atoms/L	^{239}Pu atoms/L	^{239}Pu atoms/L	^{239}Pu atoms/L	^{239}Pu atoms/L
weapons Pu	0.04	7.1E+10	7.1E+09	7.1E+08	1.4E+08	7.1E+07
	0.10	5.9E+10	5.9E+09	5.9E+08	1.2E+08	5.9E+07
Average Global Fallout	0.18	4.9E+10	4.9E+09	4.9E+08	9.8E+07	4.9E+07
reactor fuels	0.50	2.9E+10	2.9E+09	2.9E+08	5.7E+07	2.9E+07
increasing	1.00	1.7E+10	1.7E+09	1.7E+08	3.5E+07	1.7E+07
burn up	1.50	1.2E+10	1.2E+09	1.2E+08	2.5E+07	1.2E+07

4. SUMMARY

Six of the thirteen samples analyzed contain a component of anthropic uranium. In four of these, the uranium is enriched in ^{235}U relative to ^{238}U. The other two samples with detectable ^{235}U have natural ^{238}U/^{235}U ratios. Uranium concentrations and ^{234}U/^{238}U ratios are indistinguishable from natural values and do not by themselves suggest the presence of anthropic contamination. Plutonium-239 was not detected in the four samples analyzed. Minimum detection limits at the 99% confidence level are 5E7 atoms and 1E8 atoms. These correspond to $^{(239+240)}$Pu activities of 0.002 pCi and 0.004 pCi respectively, calculated assuming a ^{239}Pu/^{240}Pu atom ratio of 0.18. Sample acidification and a strong acid leach of each sample bottle were performed to insure that any plutonium that may have adsorbed to the sample bottle was removed and included in the sample. Given that no ^{239}Pu was detected, in order for ^{238}Pu concentration to be greater than 0.02 pCi/L, and therefore above detection limits for 1000-minute alpha spectrometry, the ^{238}Pu/$^{(239+240)}$Pu activity ratios must be greater than about 5. Such large ratios are known from high-burn up nuclear fuel but are not characteristic of weapons-related or fallout plutonium.

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