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A Survey for Elevated Levels of Uranium North of the 300 Area on the Hanford Site

T. M. Poston

April 1990

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

A comprehensive survey of soil uranium (U) concentrations in a study area due north of the 300 Area on the Hanford site has been conducted by Pacific Northwest Laboratory (PNL). The objective of the study was to determine the spatial distribution of uranium in the study area and to ascertain if background levels of uranium have been increased by Hanford operations. Based on the spatial distribution of ^{238}U, the highest concentrations of uranium are located in the southern portion of the study area adjacent to the 300 Area complex and in the most eastern zone of the study site bordering the Columbia River. Concentrations of ^{238}U in the southern portion of the study area are higher than mean concentrations of ^{238}U reported in control areas of the Hanford Site; that is, environmental monitoring sites at the Prosser and Wye barricades.

Uranium-236, an isotopic marker of fuel processing activities in the 300 Area, was detected in all eight samples selected from the study. A significant and positive regression was demonstrated between the ratios of $^{236}U/^{238}U$ in these eight samples and proximity to the 300 Area.

While no Federal or Washington State guidelines existed for levels of uranium in soil, Westinghouse Hanford Company has instituted operational guidelines for management of contaminated soil. Levels of uranium isotopes detected in soil collected from the study area routinely fall at least an order of magnitude below these guidelines.

ACKNOWLEDGMENTS

This study was funded through the Surface Environmental Monitoring Program under the supervision of Richard E. Jaquish. The author acknowledges assistance provided by US Testing for radiochemical analysis of soil samples: James M. Kelly of Pacific Northwest Laboratory (PNL) conducted high-resolution mass spectroscopy analysis for ^{236}U. Kaiser Engineering Company and Michael Thiede (PNL) assisted with sample site surveys, and Larry Belt collected the soil samples. The manuscript was critically reviewed by Keith Price and edited by Sue Gano.

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INTRODUCTION

The U.S. Department of Energy has conducted defense missions for over 44 years at the Hanford Site. These activities have been supported by extensive environmental monitoring programs. Recently, monitoring of uranium (U) levels at selected environmental monitoring stations has revealed a small increase in uranium levels in air and soil samples collected from locations north of the 300 Area. Levels of ^{238}U in soil collected from the Environmental Monitoring station located north of the 300 Area ranged from 0.5 to 5.4 pCi/g, an increase over a single value of 0.26 pCi/g reported in 1976 (Price 1988). A potential source of the uranium in the environmental samples could be the processing (burning) of uranium fuel shavings to UO_2, which was conducted in the 303L Building (early 1960s to 1971) and 303M Building (1983 to date). From 1972 to 1982, uranium shavings were sealed in concrete and disposed of offsite. Prevailing winds from the southwest, as indicated by wind roses (Price and Kinneson 1982), could have deposited trace amounts of particulate uranium to the north and east of the 300 Area.

Irradiated uranium fuel contains ^{236}U, which is formed by neutron absorption of ^{235}U. The presence of ^{236}U would support the hypothesis that the recent trend in elevated uranium in the 300 Area is a result of uranium fuel processing.

Pacific Northwest Laboratory (PNL)(a) has conducted a study to address possible dissemination of uranium to the environment from uranium fuel processing in the 300 Area. We determined the distribution of uranium in surface soil samples collected north of the 300 Area and identified locations of highest uranium concentrations. Selected samples that indicated elevated levels of uranium were analyzed by mass spectroscopy for ^{236}U. Moreover, samples were collected from the lee side, floor, and far side of a gully in the study area to see if preferential deposition occurred as a result of local topography. These special samples also served as a quality control validation of sample variability. A comparison was also made of sample processing and analysis for uranium isotopes.

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

METHODS

The study involved establishing a sample grid, randomly determining sample sites within the grid, and collecting soil samples and having them analyzed.

STUDY ARFA

The study area was bounded by the Columbia River to the east, the 300 Area to the south, and Highway 4S (Stevens Drive) to the west (Figure 1). To the north lie the open expanses of steppe vegetation that dominate the Hanford Site.

SAMPLING GRID

A method for concentrating sampling efforts in areas with the greatest probability of high levels of contamination has been developed (Skalski and Thomas 1984). This method relies on reconaissance-level information for identifying potential hot spots. An attempt was made in this study to locate hot spots by measuring dose rates with a portable NaI crystal at random locations throughout the study area. The results of this effort were inconclusive.

Because localized areas of contamination could not be estimated, random assignment of sampling sites was used on an 8-row x 4-column grid (Cochran 1977). The grid measured 2000 by 1000 m and consisted of 32 plots each measuring 250 m x 250 m. Sample sites were located in each plot by assigning two random numbers between 0 and 250 for southerly and easterly coordinates. The grid's orientation on the study area placed three plots located in the southern half of the fourth column in the Columbia River. Consequently, those three plots were dropped from the study design, leaving 29 plots.

A witness post (identified as "IDA") located on the study site was used as a reference point for the grid. A north-to-south transect was surveyed by Kaiser Engineering Company, a Hanford contractor. Set hubs with lathes were located at 250 and 750 m to the north and the south of the witness post. This transect formed the line of demarcation between Zones I and II of the sampling

FIGURE 1. Aerial Photograph of the Study Area (July 1989)

grid (Figure 2). Coordinates for the transect were based on the City of Richland grid system.[a] The four hubs, located 500 m apart; the witness post; and a fifth reference point located 500 m east of reference point D were used to locate sample site locations. Sample sites were marked with a stake and a red surveyor's flag.

SPECIAL SAMPLES

Twelve additional soil samples were collected from the study area. Nine samples, designated 31S to 39S, were collected in a shallow gully located in Plot 14 (Figure 2). The orientation of the gully on a SW to NE line allowed samples to be collected from the south side of the gully, the floor of the gully, and the north side of the gully. Samples were taken at three sites along each of three 50-m transects at 0, 25, and 50 m (Figure 3). Additional soil samples were taken at a site in the lee of a slope located in Plot 15, some dark material that appeared to be coal in Plot 23, and at the routine environmental monitoring site, also located in Plot 23.

SOIL SAMPLING

Surface soil samples were collected at each site by compositing four 1-in.-deep by 4-in.-diameter cores taken from within a radius of 5 m or less of the site identification stake. Samples were double bagged with identification labels and transferred to U.S. Testing Company, Richland, Washington, for drying and radiochemical analysis. In contrast to the routine samples (Plots 1-29), special samples 31S to 39S collected in Plot 14 were collected within a radius of 0.5 m of the sample site marker because of the relatively close proximity of the nine sites to each other. These nine samples collected were used to determine variability within a small sample area (0.275 ha).

(a) Kaiser Engineering Company. Manual CP-19, Rev. 0, Richland. Washington. 1989.

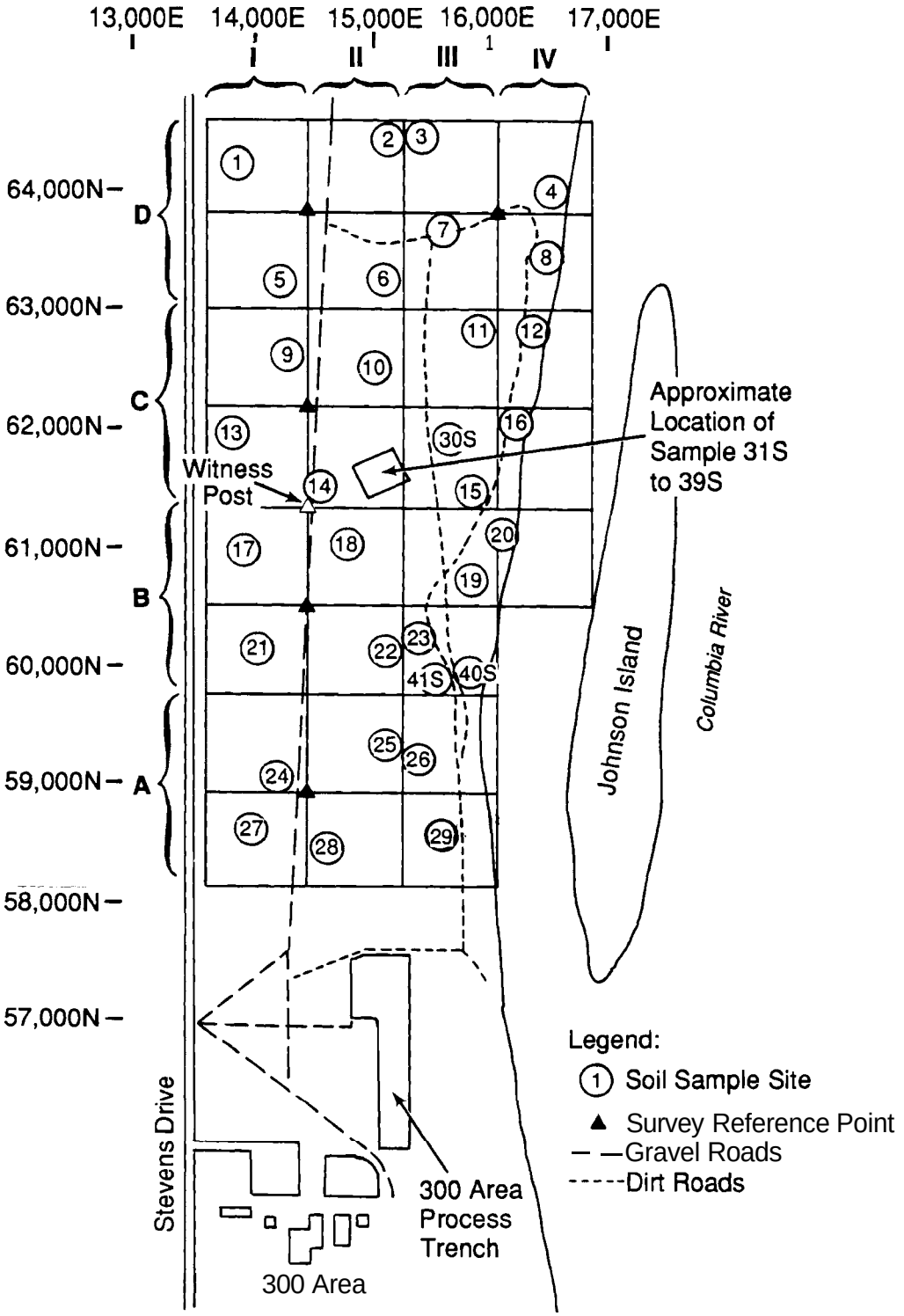

FIGURE 2. Zonation and Sampling Sites in the Study Area

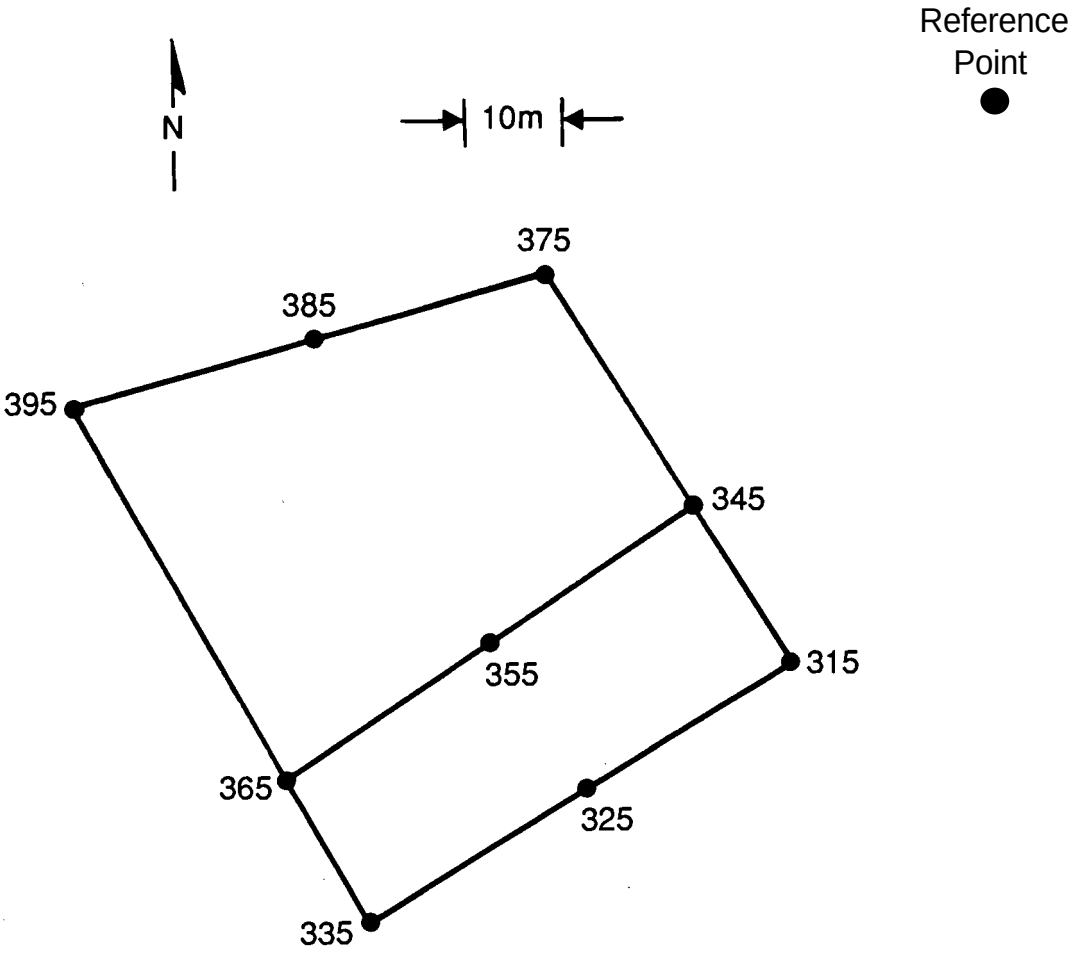

FIGURE 3. Location of Special Sample Sites 31S to 39S in Plot 14

RADIOCHEMICAL ANALYSIS

Soil samples were dried (105°C) and homogenized prior to analysis. Three analytical methods were used to measure uranium isotopes in the study area: low energy photon analysis (LEP), acid leaching (AL) of the dried soil followed by alpha spectroscopy (AS), and microwave bomb dissolution (MBD) of dried soil followed by alpha spectroscopy.

Low energy photon (LEP) analysis was used to measure ^{235}U and ^{238}U on all samples. One hundred gram amounts were counted for 500 min in a LEP detector. Uranium-238 was determined by measurements of the 63 keV peak of the ^{234}Th daughter.

Eight samples were subjected to isotopic analysis [alpha spectroscopy (AS)] following two methods of sample preparation. The AL method involves 10 g of soil milled to a 50-mesh particle size followed by two extractions with 8.0 N and 2.0 N nitric acid. The extract was purified and electrodeposited on a stainless steel planchet for alpha energy analysis of ^{234}U, ^{235}U, and ^{238}U.

The MBD involves dissolution of 1 g of soil followed by purification. electrodeposition, and alpha energy analysis. The soil sample is milled to a 120 mesh size. The milled soil sample is dissolved in a mixture of hydrochloric, nitric, and hydrofluoric acid in a microwave oven. Extracts from the microwave bomb digestion were split in two and one portion was used for electrodeposition and AS; the other fraction was analyzed by PNL with high-resolution mass spectroscopy (MS) for ^{234}U, ^{235}U, ^{236}U, and ^{238}U.

Several evaluations were conducted to determine the variability associated with sample analysis. The sampling method of compositing four sub-samples from a given area reduces the probability of a contaminated "hot spot" from overly biasing a sample result. Five samples were selected from which five 100-g sub-samples were counted for 500 min to determine the variability associated with LEP analysis of ^{238}U. The five counts were combined with the original LEP analysis to give six replicated readings.

Eight samples were selected that covered the range of concentrations of ^{238}U as determined by LEP analysis. The eight samples also were selected to equally represent study zones A through D on a south-to-north orientation (Figure 2). The data were analyzed with Statview 512+, a statistical software package (Brainpower 1986), by regression analysis and two tailed t tests to test for significant differences among methods. These additional methods were used as a reference for quality control because past environmental sampling of soil used the acid leaching methodology for isotopic analysis.

STATISTICAL ANALYSIS

The study area was divided into two analysis schemes of four zones. One scheme was established on a south-to-north orientation and was designated as Zones A through D. The other scheme consisted of four zones identified as I through IV, which were oriented on a west-to-east orientation. In general

terms, the four south-to-north zones cover a distance of roughly 2000 m and the west-to-east zones cover a distance of from 750 m in the three most southern rows in the study design to 1000 m in the five most northerly rows (Figure 2).

These analysis schemes were developed to test for patterns of ^{238}U soil concentrations as a function of location. Zone borders for each of these schemes and samples contained therein are summarized in Table 1.

Descriptive statistics and confidence intervals were calculated for ^{238}U (LEP analysis) for each zone. A Student's t test was used to compare zones within each scheme to determine if there were statistically significant differences between zones (Snedecor and Cochran 1967). Simple and multiple regression analysis was performed on the uranium data as a function of location by coordinates as indicators of relative easterly or northerly distance. Statview 512+ (trademark of Brainpower. Inc.. Calabasas. California) was used on a Macintosh Plus (trademark of Apple Computer. Inc., Cupertino, California) for all regression analyses.

TABLE 1. Summary of Zonation Schemes for Analysis of ^{238}U Soil Data

South to North Scheme (A-D)

	Border Coordinates(a)				
I.D.	North	East	South	West	Sample Sites
A	59,689.4	16,941.1	58,048.6	13,660.3	24,25,26,27,28,29
B	61,329.4	16,941.1	59,689.4	13,660.3	17,18,19,20,21,22,23,24
C	62,969.8	16,941.1	61,329.4	13,660.3	9,10,11,12,13,14,15,16
D	64,610.2	16,941.1	62,969.8	13,660.3	1,2,3,4,5,6,7,8

West to East Scheme (I-IV)

	Border Coordinates(a)				
I.D.	North	East	South	West	Sample Sites
I	64,610.2	14,480.5	58,048.6	13660.3	1,5,9,13,17,21,24,27
II	64,610.2	15,300.7	58,048.6	14,480.5	2,6,10,14,18,22,25,28
III	64,610.2	16,120.9	58,048.6	15,300.7	3,7,11,15,19,23,26,29
IV	64,610.2	16,941.1	60,509.2	16,120.9	4,8,12,16,20

(a) City of Richland coordinate system.

RESULTS

URANIUM-238 ANALYSIS BY LEP SYSTEM

Twenty-nine samples were collected from the study area in July 1989. Concentrations of ^{238}U ranged from a low value of 0.38 pCi/g to 1.21 pCi/g. Levels of ^{235}U were too low for consistent detection above the overall 2 σ error by LEP analysis. Visual inspection of the data indicated that samples collected in the eastern and southern portions of the study area appeared to have slightly elevated concentrations of ^{238}U (Table 2). Several approaches were taken to analyze for this trend. Simple regression analysis was performed by easting and northing coordinates; however, neither analysis yielded significant results (Table 3). The easting coordinate analysis was strong as indicated by a probability value of 0.111. A value of 0.1 in the probability column would indicate that a regression of the magnitude indicated by the analysis would occur randomly 10% of the time.

To further analyze the data, the study area was divided into two sets of zones, one set on a south-to-north orientation (A-D), and the other on a west-to-east orientation (I-IV). Mean soil ^{238}U concentrations (with 90% confidence intervals) by zone for northing and easting coordinates suggest that levels of ^{238}U are relatively higher in Zone A located closest to the 300 Area (Figure 4) and in Zone IV closest to the Columbia River (Figure 5).

Student's t tests were performed that compared each zone in the study area (Table 4). The null hypothesis was that the concentration of ^{238}U in the southerly or westerly zones was no different from the zones to the north or east, respectively. The alternative hypothesis was that the northerly or easterly levels of ^{238}U were greater than the southerly or westerly zones. Probability values in Table 4 indicate the likelihood that the observed difference in mean ^{238}U values between zones occurs as a random process.

TABLE 7. ^{235}U and ^{238}U (LEP Analysis) in Soil Samples Collected in the Study Area North of the 300 Area. July 1989

Plot	Sample #	Coordinates(a) North	Coordinates(a) East	Isotope (pCi/g dry wt) ^{235}U	Isotope (pCi/g dry wt) ^{238}U	Isotope (pCi/g dry wt) 2 σ Error
1	89-051	64,419.5	13,857.1	1.15E-2(b)	7.38E-1	2.15E-1
2	89-052	44,662.3	15,235.1	1.14E-1	5.70E-1	1.32E-1
3	89-053	64,685.3	15,327.0	9.44E-4(b)	7.31E-1	1.98E-1
4	89-055	64,104.5	16,639.4	8.86E-2	6.21E-1	1.57E-1
5	89-059	63,310.5	14,247.5	1.75E-2(b)	5.94E-1	2.72E-1
6	89-060	63,402.4	15,018.6	4.36E-2(b)	5.11E-1	2.07E-1
7	89-054	63,966.7	15,674.8	5.28E-2	6.90E-1	1.49E-1
8	89-056	63,701.0	16,728.0	6.47E-3(b)	9.44E-1	2.20E-1
9	89-061	62,592.5	14,408.3	1.20E-1	4.93E-1	2.67E-1
10	89-062	62,458.0	15,090.8	1.43E-2(b)	5.37E-1	2.37E-1
11	89-057	62,704.1	16,222.6	3.56E-2(b)	6.69E-1	1.98E-1
12	89-058	62,753.5	16,508.0	-3.51E-3(b)	6.86E-1	3.06E-1
13	89-076	61,782.1	13,850.5	7.57E-2	6.76E-1	2.12E-1
14	89-063	61,372.0	14,513.3	1.78E-2(b)	3.81E-1	2.10E-1
15	89-077	61,408.1	15,822.4	5.05E-2(b)	6.55E-1	2.00E-1
16	89-079	62,100.4	16,170.2	4.42E-2(b)	9.03E-1	2.21E-1
17	89-064	60,962.0	13,958.8	7.51E-2	5.73E-1	2.06E-1
18	89-065	60,988.2	14,831.6	3.15E-2(b)	5.41E-1	2.10E-1
19	89-072	60,666.7	15,917.6	1.30E-2(b)	3.69E-1	2.82E-1
20	89-078	61,096.5	16,436.0	1.03E-2(b)	6.41E-1	2.17E-1
21	89-066	60,118.8	14,145.8	3.10E-2(b)	4.88E-1	2.48E-1
22	89-067	60,168.0	15,251.5	8.89E-2	7.22E-1	2.03E-1
23	89-068	60,243.4	15,412.3	1.26E-2(b)	3.58E-1	1.70E-1
24	89-069	58,924.6	14,270.5	3.96E-2(b)	4.65E-1	1.96E-1
25	89-074	59,233.0	15,195.8	1.01E-1	9.54E-1	3.20E-1
26	89-073	59,151.0	15,366.4	2.37E-2(b)	8.78E-1	2.62E-1
27	89-070	58,524.3	14,060.5	2.35E-2(b)	8.19E-1	2.84E-2
28	89-075	58,448.8	14,647.8	-5.29E-2(b)	6.46E-1	2.51E-1
29	89-071	58,622.7	15,924.1	9.44E-2(b)	1.21E00	3.26E-1

(a) City of Richland coordinate system.
(b) Value is less than overall error at 2 a.

TABLE 3. Simple and Multiple Regression Analysis of ^{238}U Levels (LEP System) in the Study Area

Dependent Variable	Simple Resression: Degrees of Freedom	Coefficient of Rearession (R^2)	ANOVA: F-Test	ANOVA: Probabilitv
Northerly	28	0.020	0.543	0.4676
Easterly	28	0.091	2.71	0.1113
Multiple Resression of Easterlv & Northerlv Coordinates				
---	28	0.136	2.049	0.1492

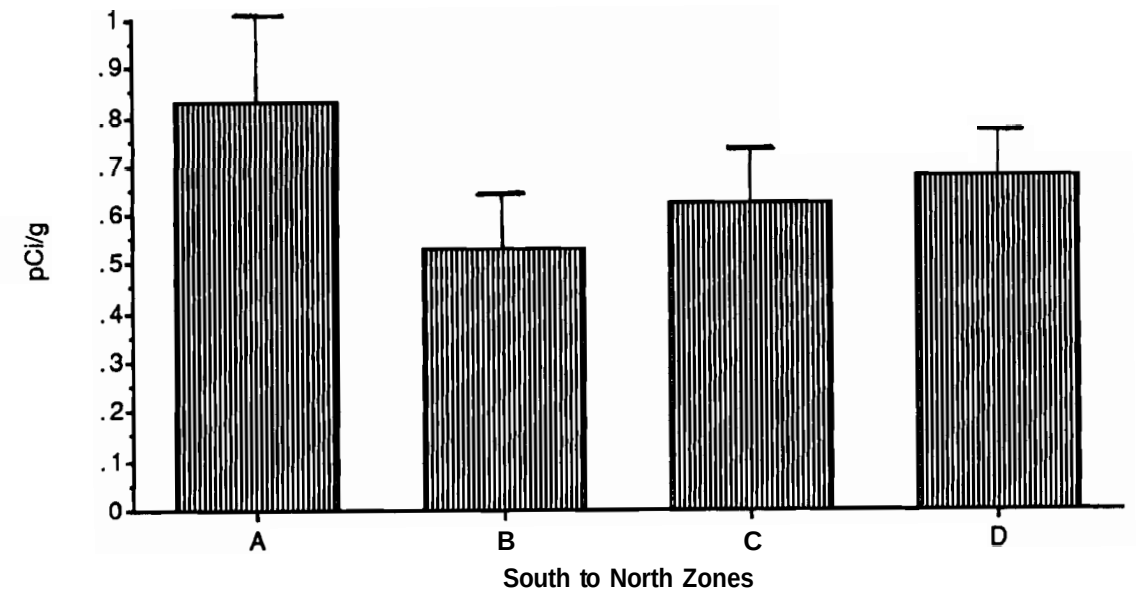

FIGURE 4. Mean (±90% Confidence Intervals) Concentrations of ^{238}U by Zone. South-to-North Orientation

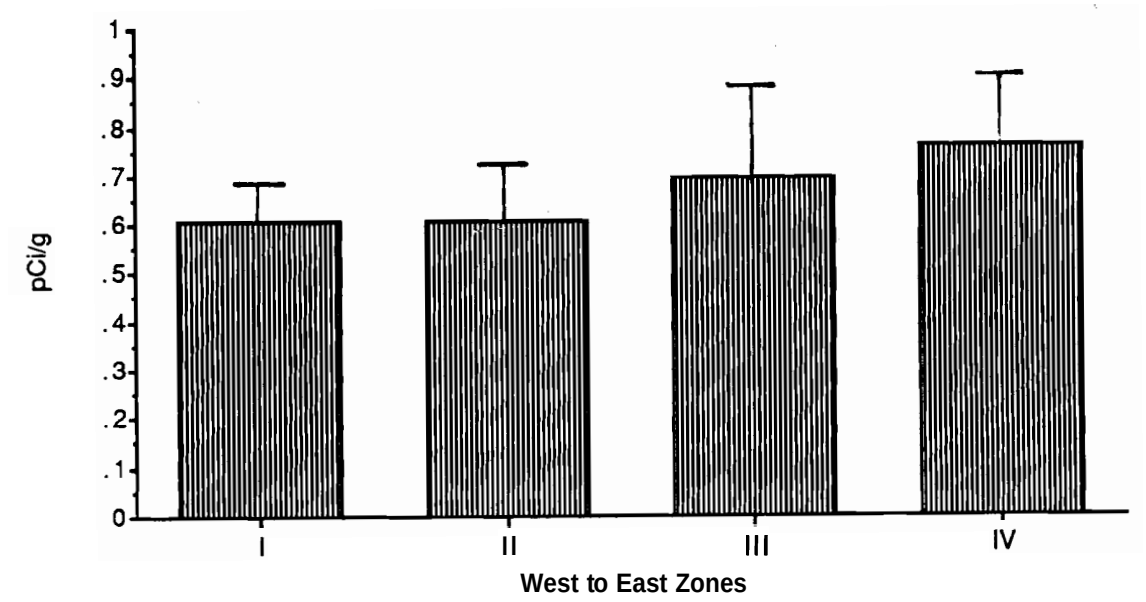

FIGURE 5. Mean (±90% Confidence Intervals) Concentrations of ^{238}U by Zone. West-to-East Orientation

TABLE 4. Comparison of Student's t Test Results by Zones in the Study Area

South to North Zones

	C			B			A		
Zone	t* Value	D.F.	Probability	t* Value	D.F.	Probability	t* Value	D.F.	Probability
D	2.72	11	<0.01	1.70	12	<0.10	1.351	12	<0.10
C	---	---	---	-0.102	13	NS(a)	-1.974	13	<0.05
B	---	---	---	--	---	---	-0.641	14	NS

West to East Zones

	II			III			IV		
Zone	t* Value	D.F.	Probability	t* Value	D.F.	Probability	t* Value	D.F.	Probability
I	1.034	11	NS	1.459	11	<0.10	1.736	11	<0.10
II	---	---	---	0.713	14	NS	0.781	14	NS
III	---	---	---	---	---	---	0.025	14	NS

(a) **NS = not significant at an alpha level of 0.01 with a one tailed test.**

On a south-to-north orientation, the southern zone (D) had significantly higher levels of ^{238}U than the three more northern zones (A,B,C). The mean ^{238}U level in Zone C was significantly lower than that in Zone A. On a west-to-east orientation, the only significant differences involved tests of Zone I (westerly) with Zones III and IV. In summary. the analysis indicated that levels of ^{238}U are highest in the southern zone nearest to the 300 Area and along the river (Figure 6). The area on the western border of Zone I indicating uranium levels in excess of 0.6 pCi ^{238}U/g soil may not represent a real zone of elevated uranium soil concentrations.

SAMPLE VARIABILITY AND PRECISION OF LEP ANALYSIS

The nine special samples collected from Plot 14 had a mean concentration (±90% C.I.) of 0.546 (±0.062) pCi ^{238}U/g soil as determined by LEP analysis. The level of precision (about 11% for the 90%C.I.) promotes additional confidence in the statistical analysis of the ^{238}U data. Values of the nine special samples had a range of 0.270 pCi ^{238}U/g. Five soil samples were selected from which five 100-g sub-samples were removed and counted for 500 minutes in addition to the original sample analysis (Table 5). Mean sample values were bounded by a 90%C.I. range of +/- 0.128 to 0.170 pCi/g. Minimum

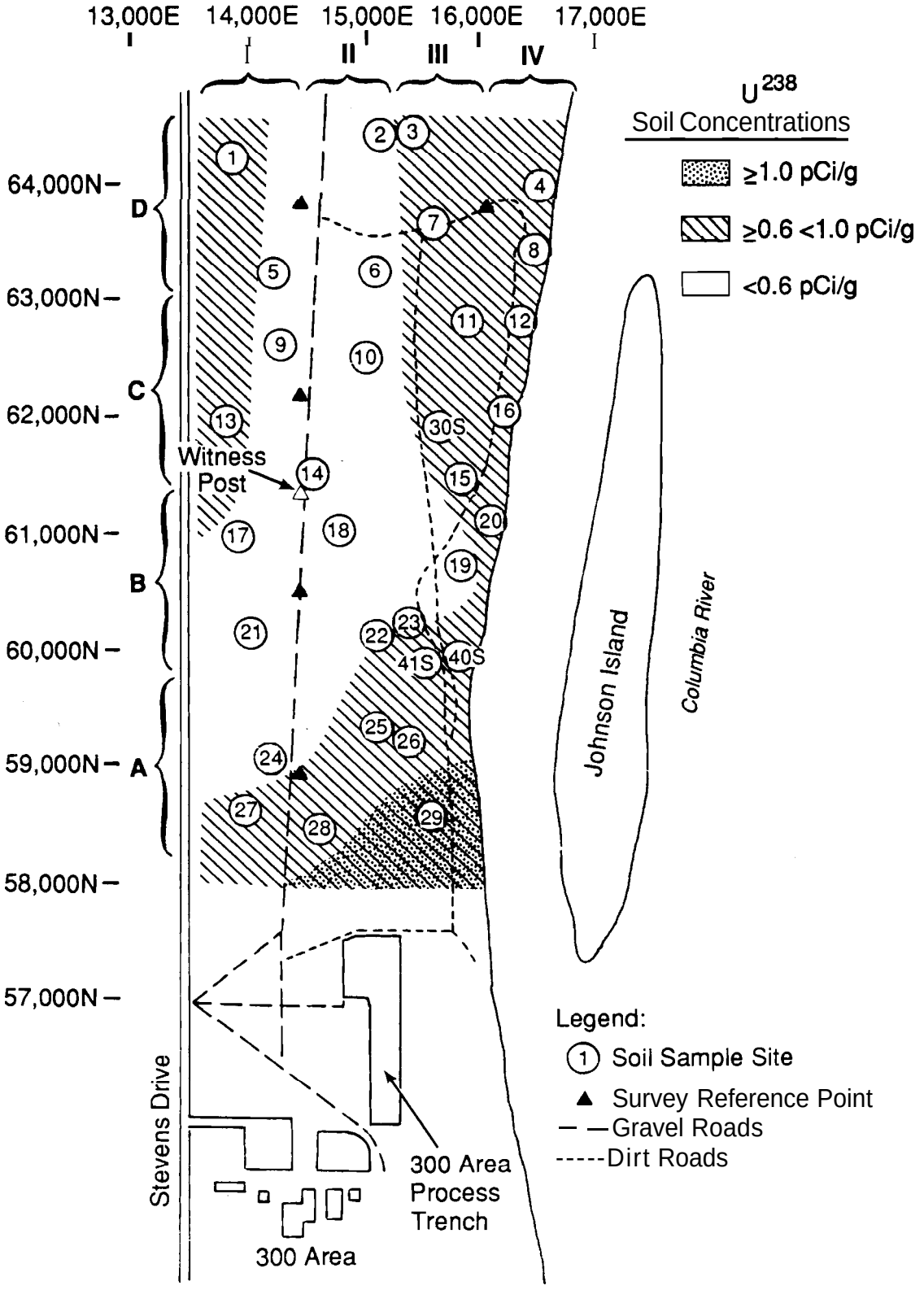

FIGURE 6. Map of Elevated ^{283}U in Soil in the Study Area

TABLE 5. Variability of Replicate LEP Analysis of Selected Soil Samples, Units in pCi ^{238}U/g (dry wt) Soil

Plot	Sample #	Ranae		Mean	95% Confidence Intervals		n
		Minimum	Maximum		Lower	Upper	
3	89-053	0.562	0.868	0.748	0.619	0.876	6
12	89-058	0.640	0.876	0.772	0.664	0.879	6
14	89-063	0.344	0.588	0.452	0.354	0.551	6
22	89-067	0.373	0.722	0.541	0.396	0.686	6
29	89-071	0.944	1.240	1.099	0.977	1.221	6

to maximum values ranged from 0.236 to 0.349 pc ^{238}U/g. A liner regression ($p = 0.03$) of the 2 a error versus the concentration of ^{238}U/g (Figure 7) suggests that a minimum level of detection is around 0.3 pCi ^{238}U/g for LEP analysis. This is the concentration where the upper 95% confidence interval for the 2 a error (about 0.21 pCi/g) approaches the ^{238}U concentration in the sample.

ISOTOPIC ANALYSIS

Uranium isotopic analysis by AS provided data on ^{234}U, ^{235}U, and ^{238}U for soil samples prepared by AL or MBD (Table 6). Low-energy photon analysis provided values for ^{235}U and ^{238}U only. High-resolution MS provided information on relative percentages of ^{234}U, ^{235}U, ^{236}U, and ^{238}U for eight samples prepared by MBD. Two-tailed Student's t tests were performed for each common isotope among LEP. AL, or MBD analyses (Table 7). The null hypothesis was:

$$H_O: = X_{\text{method 1}} - X_{\text{method 2}} = 0$$

where methods 1, 2, and 3 are LEP. AL, or MBD analyses, respectively. The null hypothesis, when rejected, indicates that at a specified probability. sample means were different.

The AL method produced results for ^{234}U, ^{235}U and ^{238}U that were significantly lower than results obtained from MBD or LEP analyses. There was no significant difference for ^{235}U or ^{238}U between LEP and MBD. This analysis

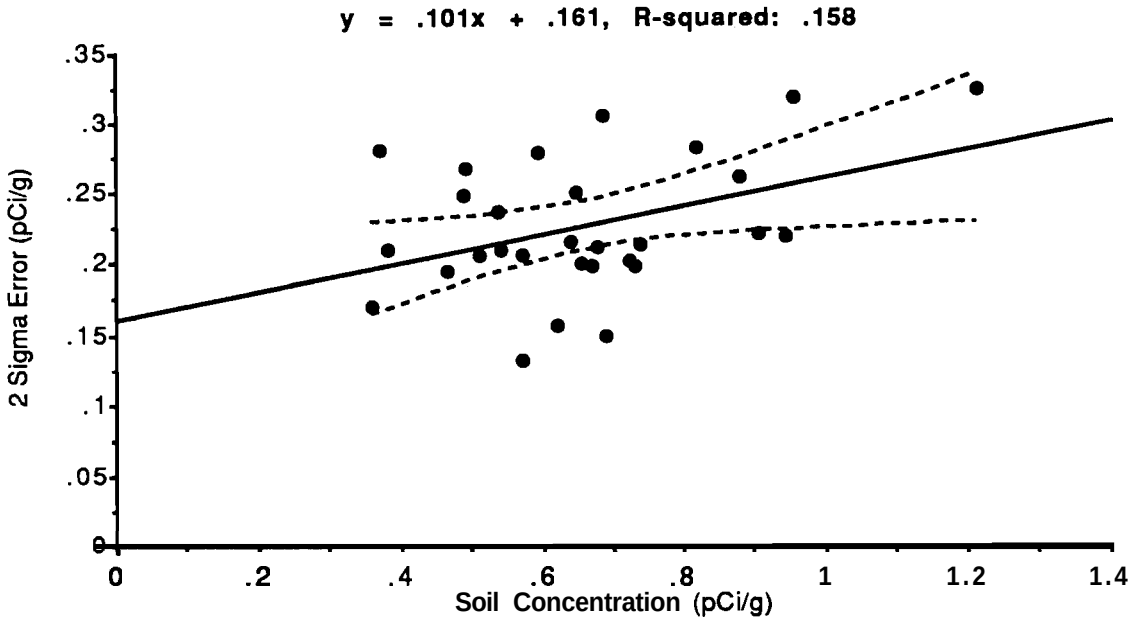

FIGURE 7. Regression Equation Showing Relationship Between 2 σ Analytical Error and 90% Confidence Intervals (Dashed Line) Against Soil Concentration as Determined by LEP Analysis

TABLE 6. Concentrations of Uranium Isotopes in Soil (pCi/g) and 2 σ Error (Below in Italics) Determined by Alpha Spectroscopy Following AL or MBD Sample Preparation

	Acid leached Method			Microwave Bomb Method		
Site	^{234}U	^{235}U	^{238}U	^{234}U	^{235}U	^{238}U
3	1.13E-1	4.47E-3	1.11E-1	7.00E-1	1.38E-2	4.83E-1
	1.55E-2	*2.49E-3*	*1.13E-2*	*9.59E-2*	*1.19E-2*	*8.34E-2*
8	5.28E-1	1.18E-2	4.72E-1	1.19E00	3.20E-2	1.07E00
	8.90E-2	*8.21E-3*	*8.11E-2*	*1.79E-1*	*2.27E-2*	*1.65E-1*
12	2.16E-1	7.02E-3	2.82E-1	5.70E-1	4.65E-2	7.26E-1
	2.60E-2	*3.03E-3*	*3.22E-2*	*1.42E-1*	*3.61E-2*	*1.62E-1*
13	9.51E-2	4.35E-3	9.75E-2	7.56E-1	2.64E-2	7.46E-1
	1.28E-2	*2.19E-3*	*1.29E-2*	*1.27E-1*	*2.23E-2*	*1.24E-1*
20	1.14E-1	5.54E-3	1.20E-1	7.14E-1	2.13E-2	6.98E-1
	1.43E-2	*2.46E-3*	*1.48E-2*	*1.47E-1*	*2.51E-2*	*1.40E-1*
22	2.03E-1	9.25E-3	2.17E-1	3.70E-1	3.32E-2	4.58E-1
	2.22E-2	*3.11E-3*	*2.32E-2*	*8.66E-2*	*2.63E-2*	*9.52E-2*
25	2.23E-1	1.11E-2	2.22E-1	9.82E-1	3.15E-2	9.77E-1
	2.42E-2	*3.44E-3*	*2.39E-2*	*1.83E-1*	*2.99E-2*	*1.77E-1*
29	4.78E-1	1.07E-2	4.18E-1	1.43E00	5.30E-2	1.28E00
	5.03E-2	*4.42E-3*	*4.48E-2*	*1.72E-1*	*2.18E-2*	*1.56E-2*

TABLE 7. Probability of Rejection of the Null Hypothesis in t Tests Performed on Each Method of Uranium Analysis of Eight Samples From the Study Area

	^{234}U		^{235}U		^{238}U	
	MBD	AL	LEP	MBD	MBD	AL
LEP	---(a)	---(a)	---	0.368(b)	0.777	<0.001
AL	<0.001	---	0.049	<0.001	<0.001	---

(a) No test conducted; isotope not analyzed by LEP.
(b) Values indicate the two-tailed probability for failing to reject the null hypothesis, values less than 0.05 indicate differences in analytical results.

indicates that the AL approach does not extract all the uranium isotopes present in the sample; the differences most likely were due to the non-leachable fraction remaining in the undissolved sample matrix. The MBD process dissolves the soil matrix to the point where all uranium is recovered.

Simple linear regression analysis was also performed comparing the results for each analysis. The relationships between LEP and alpha spectroscopy of AL or MBD analysis were again not significant for ^{235}U; however, the simple regressions were significant for ^{238}U (Table 8). Levels of ^{235}U in the soil samples were at or below the limit of detection; hence, it is not surprising that the regression relationships were not significant.

Theoretically. the slope term (beta coefficient) for each regression equation should equal 1.0 if the two methods produce equivalent results for each isotope. Only the relationship between MBD and LEP analysis for ^{238}U had a slope approaching 1 (Table 8). The low slope term for AL versus LEP regression indicates that the AL method does not account for all the ^{238}U in the sample. Slope terms for ^{235}U again indicate no significant relationship due to the low levels of ^{235}U in the samples. Probability values less than 0.10 indicate a significant regression. The coefficient of determination (r^2) indicates the degree of closeness of the linear relationship between the two analytical results. The closer to 1.0, the better the agreement of both methods being regressed. Significant regressions were obtained for predicting ^{238}U by LEP analysis from the MBD method, but not from the AL method. The AL

TABLE 8. Simple Regression Parameters[a] and Measures of Fit and Correlation for Comparing LEP, AL, and MBD Analysis of Soil Samples

Dependent (x) Variable	Independent (y) Variable	Intercept (a)	Beta (b) Coefficient	Probability	r^2
^{235}U LEP	^{235}U AL	0.007	0.025	0.332	0.162
^{235}U LEP	^{235}U MBD	0.028	0.082	0.450	0.098
^{238}U LEP	^{238}U AL	0.097	0.434	0.027	0.587
^{238}U LEP	^{238}U MBD	0.157	0.826	0.044	0.520
^{234}U AL	^{234}U MBD	-0.067	0.373	0.026	0.591
^{235}U AL	^{235}U MBD	0.004	0.136	0.146	0.317
^{238}U AL	^{238}U MBD	-0.054	0.369	0.034	0.557

(a) Regression equation is $y = b(x) + a$.

method, because it does not leach uranium retained in the sample matrix. should produce results less than that determined by LEP and MBD.

COMPARISON OF ISOTOPIC RATIOS

The MS analysis provided results expressed as percentage gram-atom and as gram-atom ratios of ^{234}U, ^{235}U, and ^{236}U to ^{238}U (Appendix A). Gram-atom ratios by alpha spectroscopy of MBD extracts were also calculated for comparison with the MS data (Table 9). The calculations involved converting the pCi amounts of each isotope to gram-atoms for generating ratios. As indicated by the coefficient of variation (CV = 1.0 σ/mean), isotopic ratios based on MS analysis were considerably less variable than ratios derived by MBD-alpha spectroscopy data. The mean ratios. however, differed slightly from expected ratios of 5.53E-5 for $^{234}U/^{238}U$ and 7.35E-3 for $^{235}U/^{238}U$ (Friedlander. Kennedy, and Miller 1964), but are within the error estimates of the sample mean based on alpha spectroscopy. The MS data, which are more accurate than the AS data. indicate a depletion of ^{235}U.

The deviation from expected values is indicative of the presence of an altered source of uranium, a hypothesis supported by the presence of ^{236}U in soil samples. Isotopic ratios of $^{236}U/^{238}U$ were variable with a CV of 110%:

TABLE 9. Comparison of Uranium Isotope Ratios (gram-atom) of Eight Soil Samples Processed by MBD and Analyzed by AS or High-Resolution MS

	Alpha Spectroscopy		Mass Spectroscopy		
Site	234/238	235/238	234/238	235/238	236/238
3	7.90E-5	4.50E-3	5.57E-5	7.26E-3	1.56E-6
8	6.06E-5	4.71E-3	6.20E-5	7.27E-3	2.52E-6
12	4.28E-5	1.01E-2	5.64E-5	7.18E-3	3.22E-6
13	5.52E-5	5.58E-3	5.42E-5	7.24E-3	1.41E-6
20	5.58E-5	4.81E-3	5.74E-5	7.22E-3	3.83E-6
22	4.40E-5	1.14E-2	5.24E-5	7.20E-3	2.92E-6
25	5.48E-5	5.08E-3	5.47E-5	7.27E-3	9.17E-6
29	6.09E-5	6.52E-3	5.94E-5	7.35E-3	1.90E-5
		Summary Statistics			
Mean	5.66E-5	6.59E-3	5.65E-5	7.25E-3	5.46E-6
S.D.	1.13E-5	2.67E-3	3.06E-6	5.33E-5	6.01E-6
C.V.	19.9%	40.6%	5.41%	0.74%	110%

however, a distinct trend was apparent in the ratios. Samples collected closest to the 300 Area (Plots 25 and 29) had the highest $^{236}U/^{238}U$ ratios (Figure 8). This hypothesis was tested by simple and multiple regression analysis of $^{236}U/^{238}U$ ratios and the relative location on the study grid as determined by their easterly and northerly coordinate values (Table 10). The simple regression between $^{236}U/^{238}U$ isotopic ratios and northern coordinate values was significant. The simple regression with easterly coordinates and isotopic ratios was not significant. The sample sites used in this analysis were concentrated in the eastern half of the study grid (Figure 2), and it is not surprising that the analysis failed to produce a significant relationship based on easterly coordinate values.

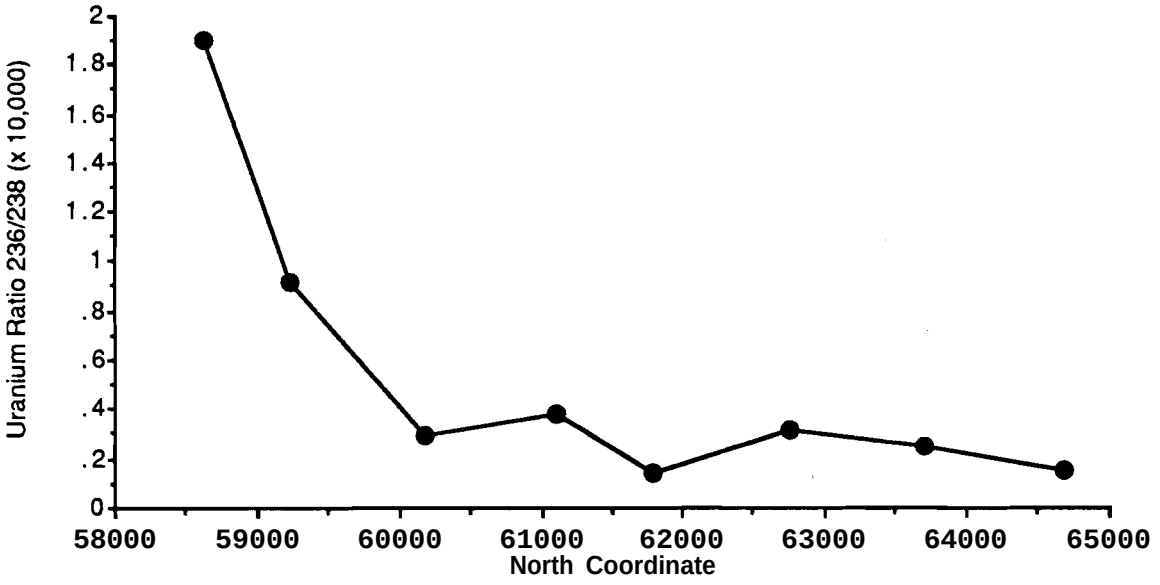

FIGURE 8. Isotopic Ratio of $^{236}U/^{238}U$ as a Function of Northerly Coordinate

TABLE 10. Simple and Multiple Regression Analysis of $^{236}U/^{238}U$ Ratios (MBD: MS Analysis) in Eight Soil Samples Collected from the Study Area

Dependent Variable	Degrees of Freedom	Coefficient of Rearession (R^2)	ANOVA F-Test	ANOVA Probability
		Simple Regression		
Northerly	7	0.544	7.147	0.0369
Easterly	7	0.017	0.105	0.7572
		Multiple Regression		
---	7	0.610	3.909	0.095

DISCUSSION

Soil levels of uranium have been monitored at Hanford and the surrounding environs since 1972. Generally, reported soil levels within the site boundaries range up to 0.5 pCi ^{238}U/g dry weight for areas that can be considered free of influence of Hanford activities (Price 1988). In 1985. and again in 1987, levels of ^{238}U in soil collected from the environmental monitoring station located north of the 300 Area ranged from 0.5 to 5.4 pCi/g, an increase over the lone value of 0.26 pCi/g observed in 1976 (Price 1988). For all onsite environmental monitoring samples, only three other samples had values in excess of 1.0 pCi U/g; a sample collected in 1984 SSW of PUREX in the 200 East Area. and two 300 Area samples, one collected south of the 300 area, and the other located on the north fenceline of the 300 Area (Price 1988). Background levels measured at the Wye and Prosser Barricades ranged from 0.13 to 0.80 pCi/g with a mean value of 0.3 pc/g for the period of 1982 to 1987.

The systematic analysis of soil samples by LEP analysis from the study area north of the 300 Area did not indicate levels of ^{238}U at levels comparable to the elevated levels observed at the environmental sampling site. There was a strong indication that levels of ^{238}U in soil were highest closest to the Columbia River and the 300 Area enclosure. Based on wind rose patterns for the study area, these observations are consistent with atmospheric dispersion of uranium from uranium processing facility stacks in the 300 Area. A more definitive atmospheric dispersion modeling study would be required to corroborate this observation. Other sources of ^{236}U that can not be discounted include the operation of low-level process waste trenches and low-level solid waste disposal sites near the 300 Area.

The presence of ^{236}U is conclusive proof that uranium of Hanford origin is present in surface soil north of the 300 Area. Ratios of $^{236}U/^{238}U$ may have been higher if AL was used for sample preparation instead of MBD because the uranium contained in the soil matrix mineral base would not contain ^{236}U. Acid leaching could produce a sample with higher ratios of $^{236}U/^{238}U$ because the amount of ^{238}U would be smaller while the amount of ^{236}U would not change.

Jaquish (1989) reported that ratios of $^{235}U/^{238}U$ in ground water collected from the 300 Area ranged from 7.8E-3 to 9.8E-3, indicating the presence of enriched U. Our soil analysis showed a slight depletion of ^{235}U as indicated by the $^{235}U/^{238}U$ ratios. Both ground-water and soil isotopic analyses were performed at PNL by MS. The differences in isotopic ratios may be explained by differences in the source terms for ground water and air resulting from fuel processing activities in the 300 Area, however this topic requires further review.

Because several different methods were used to measure uranium isotopes in soil, summary data comparing the results have been included in this report. The LEP analysis is adequate for screening soil samples for ^{238}U; however. levels of ^{235}U were at or below the detection limit for the majority of samples collected during this study. The MBD method is more efficient at recovering uranium from a sample than the AL method; however, if the objective of the sampling is to investigate atmospheric deposition, the AL method may be adequate. While detection of ^{236}U in soil samples was indicative of contributions by Hanford activities, the isotope ratios used in this report must still be qualified by method as it is likely that ratios of $^{236}U/^{238}U$ would have been higher if acid leaching was used for sample preparation.

The amounts of uranium found in soils in the area north of the 300 Area indicate a slight increase in uranium over the last 15 years of monitoring data. While no federal or Washington State standards or guidelines exist for uranium in soil, Westinghouse Hanford Company has implemented operational guidelines for management of contaminated soil on the Hanford Site. These guidelines were established for disposal operations, stabilization and cleanup, decontamination and decommissioning operations, and posting and control. Threshold levels have been established at 100 pCi $^{234}U/g$, 15 pCi $^{235}U/g$, and 50 pCi $^{238}U/g$ in soil (Westinghouse Hanford Company 1988). In practice, soils containing less than these guideline values do not require control as radioactive materials unless the radioactivity can be detected with portable survey instruments. The levels of uranium isotopes detected in soils collected from the study area do not approach these guidelines.

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APPENDIX

URANIUM ISOTOPIC COMPOSITION OF 300 AREA SOIL SAMPLES

APPENDIX

URANIUM ISOTOPIC COMPOSITION OF 300 AREA SOIL SAMPLES

Plot	Sample Number*			Atom Ratio + 1σ Error			Atom Percent + 1σ Error			
	Customer	UST	NCS	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$	^{234}U	^{235}U	^{236}U	^{238}U
3	89-053	R1304	79170	0.00005569 44	0.007260 18	0.000001557 73	0.00553 4	0.721 2	0.000155 7	99.274 2
8	89-056	R1307	79176	0.00006194 78	0.007277 11	0.00000249 31	0.00615 8	0.722 1	0.00025 3	99.271 1
12	89-058	R1309	79172	0.00005678 12	0.007184 12	0.00000324 33	0.0056 1	0.713 1	0.00032 3	99.281 1
22	89-067	R1318	79174	0.0000528 13	0.007198 13	0.00000293 36	0.0052 1	0.715 1	0.00029 4	99.280 1
29	89-071	R1322	79177	0.0000599 10	0.007351 13	0.00001908 53	0.0059 1	0.730 1	0.00189 5	99.262 1
25	89-074	R1325	79175	0.00005470 87	0.007273 15	0.00000921 37	0.00543 9	0.722 2	0.00091 4	99.272 2
13	89-076	R1333	79173	0.00005421 59	0.007247 16	0.00000143 14	0.00538 6	0.719 2	0.00014 1	99.275 2
20	89-078	R1335	79171	0.0000571 10	0.007223 14	0.00000380 54	0.0057 1	0.717 1	0.00038 5	99.277 1
	---	I21086B	79169	0.0000600 78	0.007134 33	<0.000008	0 0060 8	0.708 3	<0.0008	99.286 3

* The samples as received by the Nuclear Chemistry Section (NCS) were identified by U.S. Testing (UST) numbers.

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