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Radionuclide Leaching from Residual Soils: Screening Study

Mark Fitch[1] and Ellen England[2]

Abstract: Four soil samples, collected from a National Priorities Listed site contaminated with uranium, thorium, and radium, were leached for two, seven, and 30 days. The nonleached soils, leached soils, and leachates were analyzed using gamma spectroscopy, alpha spectroscopy, and delayed neutron activation. Unleached and leached soils had low radionuclide activities, and four different leaching solutions had no significant observable effect upon the resulting leachate activity. Three of the soils produced leachates with uranium activities below the expected primary drinking water standard of 30 μg/L for uranium, but the leachate from the fourth soil had an unacceptably high concentration of uranium (653 μg/L) despite the low activity of the original, unleached soil. Distribution coefficients calculated for uranium ranged from 100 to 12,000 mL/g, while distribution coefficients for ^{226}Ra, ^{228}Ra, ^{228}Th, ^{137}Cs, and ^{40}K ranged from 1 to 20 mL/g. The uranium distribution coefficient was strongly correlated to the leachate alkalinity, suggesting that conditions resulting in high alkalinity yield a high potential to leach uranium.

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Introduction

The St. Louis Airport Site (SLAPS) was used for storage of uranium-bearing residues from 1942 to 1957. Radionuclide-bearing residues stored there were generated from the separation and purification of uranium from uranium-bearing feed materials (U.S. ACE 1999). Both black oxides and ores were processed at a nearby facility and stored at SLAPS. Processing activities were conducted initially under contract with the Manhattan Engineer District and the U.S. Atomic Energy Commission.

The 22-acre SLAPS is located north of the St. Louis Airport and is bordered by roads on the west, north, and east and a security fence on the south. An important geographic feature is Coldwater Creek, which runs along the west side of the site. The creek empties into the Missouri River and is the dominant feature of concern for ground and surface water contamination. Hydrology studies indicate the direction of groundwater flow and surface water flow is towards Coldwater Creek. The site geology has been extensively characterized as part of the remediation effort (U.S. ACE 1999) and, briefly stated, the soil is a silty loam—a combination of fill and loess supporting a grass-forb and woody shrub vegetation community. Soil permeability is moderate, surface runoff is slow, and the available water capacity is very high. Soil borings show manganese stains and nodules and iron-cemented concretions. Land use in the surrounding area is predominantly commercial and industrial. Remediation oversight and management of the site is currently the responsibility of the U.S. Army Corps of Engineers (U.S. ACE 1999).

The leaching potential of "leave-in-place" or "residual" site soils is the focus of this paper. The objective of this study was four-fold: (1) to evaluate the potential for leaching of radioactive materials from representative soils meeting proposed clean-up standards for the SLAPS using fluids approximating the groundwater anticipated to percolate through SLAPS after remediation; (2) to determine the effect of trichloroethylene (TCE) and the TCLP leaching fluids on uranium, radium, and thorium concentrations in those soils and leachates; (3) to characterize residual soil characteristics and contamination; and (4) to determine the distribution coefficients, K_d, for radionuclides found in SLAPS residual soils.

Materials and Methods

Sample Locations

Representative soil samples were selected from locations where the soil was considered to be residual. Residual soils will remain in place after site remediation goals are achieved. Soils selected for sampling and analysis were anticipated to just meet or modestly exceed proposed site remediation goals of 15, 15, and 50 pCi/g for radium, thorium, and uranium, respectively, and had compositions sufficiently varied to reflect soil characteristics of the overall site (Hempen, personal communication, 1998; U.S. ACE 1999). Thus, soil samples were selected to reflect the most contaminated soil that would remain after the proposed remedial effort at the SLAPS. Sample sites were identified from the existing site characterization for the National Priorities List process and utilizing an existing 3D model of the site based on that sampling. Four sample sites were selected and are shown in Fig. 1; the criteria for selection included accessibility and likelihood of finding soil of the correct contamination level, with one site se-

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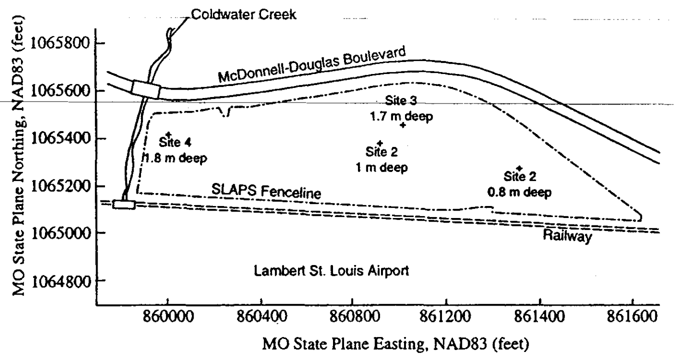

Fig. 1. Sampling locations at St. Louis Airport Site

lected with the expectation of sampling original loess rather than fill. Samples were collected in June and July of 1998.

Sample Collection and Preparation

The four soil sampling sites were opened by backhoe and samples taken at a depth of 1–2 m. Prior to sample collection with a hand trowel, the lowest activity section of the pit was identified by a Corps of Engineers subcontractor using their hand-held Geiger counter, and this section of the pit was sampled. Soil samples of approximately 1 kg were immediately placed in resealable plastic bags. Approximately 700 g of soil next to (co-located with) the 1 kg soil sample was placed in aluminum containers for analysis by the on-site Hiss Laboratory, St. Louis.

The co-located soils collected for analysis by the Hiss Lab were not processed in any manner but were sealed in the aluminum cans and sent directly for analysis. Soils collected in the resealable plastic bags were dried and homogenized for leaching studies at Univ. of Missouri-Rolla (UMR) or analysis at the U.S. Geological Survey (USGS). The soil samples for analysis at UMR and the USGS were broken apart by hand, placed on aluminum foil, and dried for one hour at 103°C in a drying oven. After drying, the soil was cut by hand using an aluminum spatula, reduced to very small fines (to the eye), and mixed thoroughly with the same spatula.

Leaching Methodology

Each homogenized soil sample was separated into approximately forty 20 g subsamples. Each subsample was placed into a bottle and treated with a leaching solution as indicated in Fig. 2. Leach-

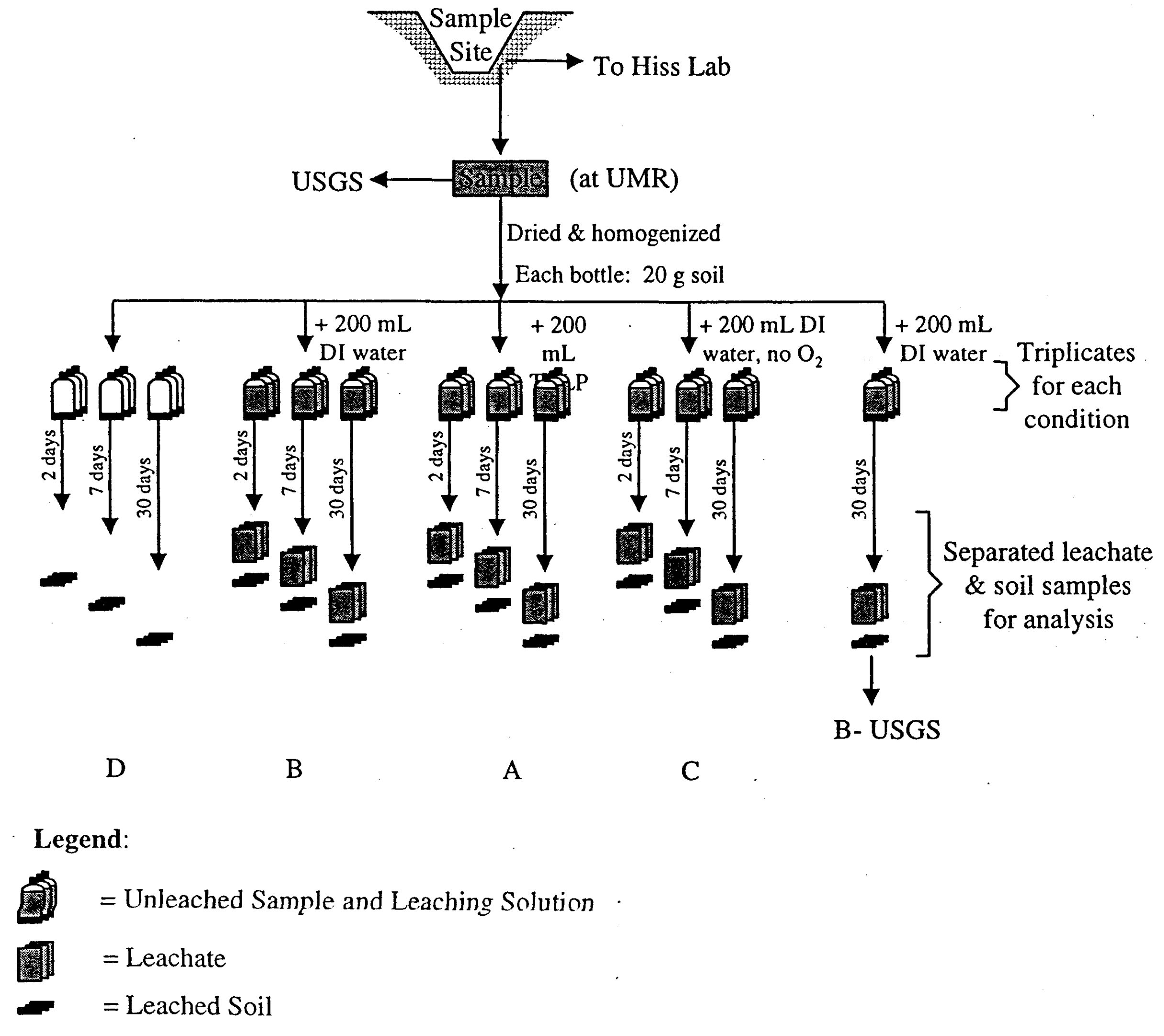

Fig. 2. Leaching methodology for soils: leaching solutions selected to represent anticipated conditions for residual soils

Table 1. Leaching Conditions of Soils

Condition	Solution	Period (days)	Replicates for each period
A	EPA TCLP, 0.2 M acetic acid adjusted to pH 4.9	2, 7, and 30	3
B	Deionized distilled (DI) water equilibrated with air	2, 7, and 30	3
C	DI water, N_2 sparged	2, 7, and 30	3
D	No fluid	30	3
T	20 mg/L TCE in DI water	2, 7, and 30	3
B-USGS[a]	DI water equilibrated with air	30	1

[a] Condition B-USGS was leached at UMR and analyzed at USGS, Denver; all others analyzed at UMR.

ing solutions, leaching periods, and replicate information from batch experiments are shown in Table 1 and Fig. 2. Four batch leaching solutions and conditions were used including the Environmental Protection Agency (EPA) TCLP acetic acid solution (U.S. EPA 1996), distilled, deionized (DI) water equilibrated with air, DI water in a nitrogen (N_2) sparged atmosphere, and 20 mg/L TCE in DI water. Control samples containing only soil were also prepared. The TCLP solution was chosen to represent a worst case acidic environment, the TCE solution a contaminated groundwater environment, and the other solutions to represent groundwater conditions expected after site remediation. The TCLP acetic acid solution (leaching solution A) was prepared using the U.S. EPA's Solid Waste Test Method SW-846 (U.S. EPA 1996). To prepare the solution, 5.7 mL of glacial acetic acid were added to 500 mL of DI water. 64.3 mL of 1 N sodium hydroxide were then added and the solution diluted to one liter with DI water. The resulting pH of the solution was 4.93 ± 0.05. Leaching solutions B and C were DI water equilibrated with air and sparged with nitrogen, respectively. The TCE solution (leaching solution T) was prepared by adding TCE to DI water and mixing for 24 h on a shaker table to form a saturated solution of 1,200 mg/L (Whitten and Gailey 1981). 33.3 mL of the saturated solution was then added to 2 L of DI water, giving a 20 mg/L TCE concentration.

For leaching conditions A, B, and T, 20 g of dried, homogenized soil were placed into 250 mL Teflon-rubber septa capped bottles containing 200 mL of leaching fluid. Control soils (leaching condition D) were transferred to an empty bottle. Leaching condition C soils were prepared in an anaerobic glove bag with continuous nitrogen flow and the bag purged with nitrogen for three minutes after mixing to prevent oxygen contamination. Bottles were tumbled at 5–8 rotations per minute (rpm) for the specified leaching period.

After the leaching period, soils were separated from leachates by centrifugation at 1,000 rpm for 45 min. Soils 1 and 4 had high clay contents contributing to incomplete separation upon initial centrifugation. Leachates from Soils 1 and 4 were subsequently spun at 5,000 rpm for thirty minutes to give a more complete separation. After centrifugation, the supernatant liquid was filtered through a 0.45 micrometer (μm) cellulose nitrate filter. Filtration times for the 200 mL of each liquid ranged from 5 min to 2 h. This separation was designed to remove the soils that would not be transported by groundwater flow from the groundwater. The filters and soils remaining in the bottles were transferred to resealable plastic bags, and the bottles were then rinsed with DI water and the resultant slurry transferred to its respective bag.

pH and Alkalinity Determination

pH and alkalinity were measured for at least one replicate of each 30-day leachate sample. pH was measured using a calibrated Corning 340 pH meter and probe. Alkalinity was measured using 20 mL of leachate in the Standard Method 2320B, end-point titration procedure (APHA 1995).

Gamma Spectroscopy

The three major isotopes present at SLAPS are ^{238}U, ^{230}Th, and ^{226}Ra (U.S. ACE 1999). The decay chain of ^{238}U, the parent isotope, includes ^{230}Th and ^{226}Ra (U.S. DHEW 1970; Lederer and Shirely 1978; Eisenbud 1987). To determine the presence of these and other radioactive elements, leached soils and leachates were examined using gamma spectroscopy at UMR. Gamma ray emissions of decay products were used to detect the presence of the parent isotopes; ^{238}U, ^{230}Th, and ^{226}Ra have long half-lives and emit few or no gammas. For each sample, a spectrum of energies and counts were recorded during a 6-h counting period using an EG & G Ortec gamma spectrometer and the associated software "Maestro." A lead brick shield was constructed around the sample to differentiate the sample emissions, which were in some cases quite low, from the background. The efficiency of the gamma detector was determined with a point source of known activity at a variety of geometries corresponding to the overall geometry of the sample bags. A uranium control standard of 1 mg/mL was assayed as a positive control as 263 pCi/mL, with an expected activity of 328 pCi/mL calculated from the concentration of uranium and the assumption of natural uranium isotope distribution. Detailed discussion of detector efficiency determination may be found elsewhere (Fitch 1999). The limit of detection for the gamma spectrometer for the dominant radionuclides was determined as 2 pCi total activity and 0.01 pCi/mL for the leachates.

Background counts were subtracted from the sample measurements and prominent peaks catalogued from the gamma spectroscopy. Cataloguing involved identifying the isotope corresponding to the observed peak energy. Concentrations of parent nuclides were calculated from the activity of short-lived daughters using the assumptions of secular equilibrium. Secular equilibrium was applied to elements with half-lives of not more than a few years and activity ratios calculated (Langmuir 1997); that is, ^{226}Ra was assumed to be the source of all measured ^{214}Pb (27 min half-life) and ^{214}Bi (20 min half-life), but ^{234}U was not assumed the parent of ^{230}Th (80,000 year half-life). The specific parent/daughters thus used were ^{226}Ra parent (also directly detected), ^{214}Pb and ^{214}Bi; ^{227}Ac parent, ^{227}Th, ^{223}Ra, and ^{219}Rn; ^{228}Th, ^{212}Pb, and ^{208}Tl; and ^{137}Cs and ^{137m}Ba. From these calculations, the activity of each isotope in the sample was found and reported in units of Ci/mL for liquids or Ci/g for soils.

Gamma spectroscopy was also performed on co-located soil samples at the Hiss Laboratory. An analysis of gamma spectroscopy results similar to that used at UMR was applied for determination of soil activities at the Hiss Lab. Results reported by this U.S. ACE subcontractor are shown here as reported to UMR.

Alpha Spectroscopy

Alpha spectroscopy was performed on co-located soil samples at the Hiss Laboratory. Methods comply to U.S. ACE standards, but were not disclosed.

Table 2. Co-located Soil Site Activities and Measurement Error, Hiss Laboratory Analysis (Units in pCi/g)

Site	Method	^{40}K	^{226}Ra	^{228}Ra	^{228}Th	^{232}Th	^{230}Th	^{235}U	^{238}U	^{234}U	Total
1	γ	12.6±1.8	2.4±0.2	1.0±0.1	1.0±0.1	1.0±0.1	64.9±12.8	0.9±0.3	8.2±1.2	NA	92.7
	α	NA	8.3±1.4	NA	0.8±0.5	0.9±0.5	37±8	ND	8.3±2.1	8.2±2.1	63.5
2	γ	16.7±2.2	2.9±0.2	1.1±0.1	1.0±0.1	1.0±0.1	166±34	1.6±0.3	4.7±1.9	NA	198.8
	α	NA	6.3±1.3	NA	1.5±0.8	1.9±0.7	172±42	ND	4.4±1.4	6.5±1.9	192.6
3	γ	16.2±2.4	0.8±0.1	1.0±0.1	1.0±0.1	1.0±0.1	ND	ND	2.6±1.4	NA	22.6
	α	NA	2.3±1.8	NA	1.6±0.8	1.6±0.7	4.7±1.5	ND	2.8±1.0	3.5±1.2	16.5

Note: ND=not detected, sample activity below detection limit. NA=not analyzed for this isotope. ± values are one standard error. ^{241}Am and ^{137}Cs searched for but not detected; ^{227}Ac found at low levels by gamma spectroscopy, 3.8±0.3 pCi/g at site 2 and at lower levels, 0.7±0.2 pCi/g, at site 1. ^{231}Pa was detected at site 2, at 4.9±0.9 pCi/g.

Delayed Neutron Activation

Original and leached soil samples were analyzed by delayed neutron activation at the USGS in Denver (Millard and Keaten 1982).

Elemental Analysis

Some 30-day DI water leachates were analyzed for metallic elements at the USGS facility. Analysis was completed using U.S. EPA methods of ion coupled plasma and mass spectroscopy (ICP/MS) (Keith 1996). The detection limits for elements are on the order of 1 μg/L.

Results

Original Soils

During sampling, the first 25–50 cm of soil was found to be pale brown in color and silty, while the remaining soil was a rich black color. The darker soil displayed some reddish streaks, possibly indicating a larger amount of iron complexes. Gross measurements using the Geiger counter varied widely, possibly suggesting activity variations in the buried wastes contained within the residual soils.

Results of gamma and alpha spectroscopy, performed at the Hiss Laboratory on co-located soil samples for soils 1, 2, and 3 are shown in Table 2. The co-located sample for Soil 4 was not analyzed. The Hiss lab did not explain the apparent difference in ^{226}Ra and ^{230}Th for the co-located soil from Site 1. Co-located soils had total activities ranging from 17–200 pCi/g. Most of the activity was from ^{230}Th, ^{238}U, and ^{40}K (13–17 pCi/g), with minor amounts of associated decay products and small amounts of ^{226}Ra and ^{228}Ra (1–8 pCi/g). These measurements were required prior to official acceptance of the soil samples by the Univ. of Missouri-Rolla.

A comparison of co-located soil activities measured at the three laboratories is shown in Table 3. Gamma spectroscopy was performed at UMR and the Hiss Laboratory, alpha spectroscopy at the Hiss Laboratory, and delayed neutron activation at the USGS. The tabular data shows differences, sometimes large, between the laboratories' results. Minor discrepancies are anticipated because the laboratories performed assays on separate subsamples of soils, rather than on the same soil samples; particularly, the co-located samples assayed by the Hiss laboratory, while directly adjacent to the UMR samples, were not homogenized with the UMR samples. Major discrepancies are possible if particles of high activity were insufficiently homogenized among subsamples. The large difference in Th values may be

Table 3. Soil Concentrations (Combined Isotopes for Each Element) Reported by Separate Analytical Laboratories

	Radium	Thorium		Uranium		^{40}K
Soil type	(pCi/g)	(pCi/g)	(mg/kg)^4	(pCi/g)	(mg/kg)^4	(pCi/g)
Proposed goal[a]	15	15		50		
Typical soil[b]	1	1.1	10	0.6	1.8	22
Soil 1: Hiss[c]	6.5	53	8.6	17	25	12.6
UMR	14	14	8×10^{-9}	11	13	75
USGS			6.1		22	
Soil 2: Hiss[c]	5.7	172	13	13	14	16.7
UMR	9.6	8	9×10^{-9}	7	4.4	51
USGS			4.7		14.8	
Soil 3: Hiss[c]	2.6	7.3	12	6.2	8.1	16.2
UMR	11	8	8×10^{-9}	7	2.5	63
USGS			10.3		8.96	
Soil 4: Hiss[c]						
UMR	11	13	9×10^{-9}	9	37	67
USGS			16		81.8	

[a] Proposed goal (U.S.ACE 1999).

[b] Typical soil values (Eisenbud 1987).

[c] Hiss analysis was on co-located samples; values averaged from gamma and alpha spectroscopy; soil 4 data not available from Hiss.

[d] Hiss and UMR mass calculated from isotopic activity; UMR's measurement method was unable to detect ^{232}Th, which is the majority of calculated thorium mass due to low activity.

Table 4. Total U and Th Concentrations in Soil Samples, Before and After Leaching, Determined by Delayed Neutron Activation, USGS

	Th, mg/kg			U, mg/kg		
Soil	Before	After	Loss	Before	After	Loss
1	6.1[a]	7.5	−1.4	22	29.8	−7.8
2	4.7	4.5	0.2	14.8	13.9	0.9
3	10.3	10.9	−0.6	8.96	9.33	−0.37
4	16	15	1	81.8	77.4	4.4
Typical[b]	10			1.8		

[a] Standard deviations, based on counting statistics, were 10% of measured concentrations for thorium and 1–2% of measured concentrations for uranium.

[b] Typical soil values (Eisenbud 1987).

Table 5. Uranium Levels in Soil Leachate Determined by Delayed Neutron Activation, USGS

Soil	Concentration (μg/L)
1	2.54
2	13.01
3	1.15
4	653.2

attributed to the low sensitivity of the UMR gamma spectrometer at the low energies of the ^{232}Th isotope, which is nearly invisible to gamma spectroscopy as performed at UMR if ^{232}Th is present at the levels indicated by alpha spectroscopy performed at the Hiss lab. In general, the original concentration of each isotope was low in the original soils, making detection difficult and requiring long counting periods. Additionally, gamma spectroscopy observes only gammas that are emitted at a low rate, giving a small signal to noise ratio, while delayed neutron activation used at USGS gives a higher signal to noise ratio, resulting in more accurate data. Thus the discrepancies may be attributed to a lack of homogeneity across a very small section of the soil, differences in detector sensitivities, and the generally low activities of the samples.

The four soils met the proposed residual soil standards for uranium and radium (U.S. ACE 1999), while Soils 1 and 2 exceeded the standard for thorium based on Hiss Laboratory results. Based upon analysis results, Soils 3 and 4 could be left at the site given the proposed remediation standards.

Leached Soils and Leachates

Forty-six of a potential 246 total subsamples of leached soils and leachate were analyzed using gamma spectroscopy at UMR. All 246 samples were not analyzed because of very similar initial analysis results and the relatively long counting times, 6 h, associated with gamma spectroscopy for these low concentration samples. Gamma spectroscopy indicated that isotopes from the decay chains of ^{238}U, ^{235}U, and ^{232}Th were present in virtually all leached soil samples and leachates. A natural soil constituent, ^{40}K, and a nuclear weapons testing fallout residue, ^{137}Cs, were also present. Agreement between leached soil and leachate replicates was typically within 20%. However, the unleached Soil 4 samples showed a wide variability in ^{238}U activity. An explanation for this variability might be that the subsamples were insufficiently homogenous.

Table 4 shows U and Th concentrations in soil samples before and after leaching as determined by the USGS. Thorium losses were within the measurement error, but given the low reported standard deviation for the uranium detection, uranium appears to have, surprisingly, increased. However, additional analyses of leachates did indicate that substantial leaching took place. The likely cause of the unexpected values in Table 4 is the inherent variability within the soil samples despite initial homogenization. Soil samples can demonstrate large inhomogeneity; the soil subsamples may have had different starting concentrations of the radionuclides (Winegardner 1996).

The total activity of each isotope (pCi, not per volume or mass) in a given leachate was generally equal to the total activity of that isotope in the corresponding leached soil. However, ^{238}U was present in several soil samples, yet was not observed in the leachates. Leachates also did not contain, within the detection limit, ^{235}U or ^{227}Ac, despite the presence of ^{235}U in most of the soil samples. Overall, the radium activity of the leachates was greater than the drinking water standards for radium. Results of the UMR leachate analysis indicate there was no significant leaching of uranium, thorium, or actinium.

Leachate concentrations of uranium, as determined by delayed neutron activation, are shown in Table 5. Soil 4, containing the highest initial soil concentrations of uranium and thorium, produced a leachate with a large concentration of uranium, 653 μg/L. For comparison, the expected primary drinking water standard is 30 μg/L for uranium (Pontius 1999).

Leaching Period

Initial leachate activities (at two days of leaching) were higher for the TCLP leaching fluid samples; the TCLP solution rapidly leached radionuclides from the soils. The activity of the TCLP leachates declined with increasing leaching period; after 7 days the TCLP leachates were indistinguishable from the other leachates. The TCLP solution may have initially strongly leached the soil, but possibly with time an equilibrium was established resulting in a decrease in leaching activity. Anoxic and oxic leaching conditions had no observable effect on the leaching rates or the resulting leachate activity. The presence of 20 mg/L TCE also had no appreciable effect upon the radionuclide distribution between leachate and leached soil.

For 2, 7, and 30 day leaching periods, no appreciable changes in soil or leachate radionuclide were observed except for ^{40}K. Leaching of ^{40}K is shown in Fig. 3. Less ^{40}K activity with time was measured for some soil leachates while others showed no change, even after 30 days. These results may indicate a long time scale to equilibrium for some of the soils.

Metals by Ion Coupled Plasma

A variety of other metallic elements were found to be present in soils with metal concentrations varying among the soil samples, as shown in Table 6. For example, Soil 1 contained higher quantities of aluminum, nickel, and molybdenum than other soil samples. There were no identified correlations between various metal concentrations.

Determination of K_d

K_d values for uranium calculated from the USGS analyses are shown in Table 7, while K_d values from UMR gamma spectroscopy are shown in Table 8. It should be noted that the confidence associated with the values reported in Table 8 is quite limited due

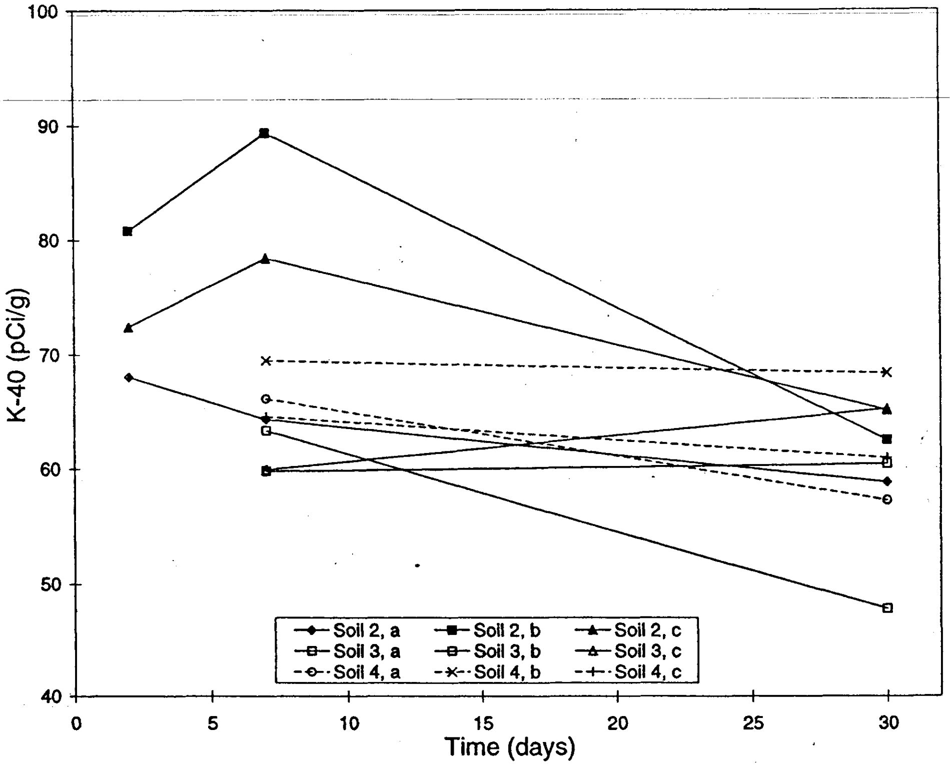

Fig. 3. Leaching of ^{40}K; ^{40}K showed decreasing activity with time for several soils

to the sensitivity of the measurement technique, and that a chemical measurement such as done at USGS would give more precise values. The USGS analyses showed appreciable leaching of uranium from Soil 4, resulting in a low K_d value. The UMR gamma spectroscopy, however, indicated ^{238}U, ^{235}U, and ^{227}Ac were not leached to any appreciable degree; the K_d was apparently infinite. Because the minimum detection limit for the elements was nonzero, a reasonable upper limit on the measurable value of K_d for these three isotopes was chosen as 10^3. The differences in the K_d values as determined by the different labs may possibly be explained by detection limit differences. The chemical analyses performed by the USGS are more sensitive (with a ^{238}U detection limit of 3.3×10^{-4} pCi/mL) than the gamma spectroscopy performed at UMR (^{238}U detection limit of 1×10^{-2} pCi/mL). UMR gamma spectroscopy showed the presence in the leachates of low activities of a number of isotopes with relatively long half-lives including ^{226}Ra, ^{228}Ra, ^{228}Th, ^{137}Cs, and ^{40}K. Substantial amounts of other nuclides were leached, yielding low values of K_d; K_d values for these elements ranged from 1 to 75. As a comparison, typical K_d values found in the literature include 10^2–10^5 for cesium; 6,700 for radium; and 3–3,200 mL/g for uranium (Sheppard and Thibault 1991; Smolders et al. 1997; Mollah and Ullah 1998).

Table 6. Dissolved Concentrations of Elements in Leachate

Element (μg/L)	Soil 1	Soil 2	Soil 3	Soil 4
Barium	33.59	33.07	55.04	65.89
Boron	48.689	38.078	44.561	ND
Chromium	1.66	1.5	1.08	2.61
Cobalt	2.14	1	1	1
Copper	5.82	1.67	2.35	4.91
Lead	1.12	1	1	1
Manganese	5.66	1	1	1
Molybdenum	121.17	116.26	39.17	36.8
Nickel	11.21	1.07	1.06	1.53
Zinc	13.41	6.63	12.61	6.22
Aluminum	2552.6	18.78	13.25	52.58
Selenium	11.76	142.78	231.98	3.21
Uranium	2.54	13.01	1.15	653.2

Note: Values determined at USGS Denver lab by ion coupled plasma, except for uranium, determined by delayed neutron activation.

Alkalinity and pH

Soil 4 imparted substantially more alkalinity to the DI water leachate than Soils 1, 2, and 3. The correlation between alkalinity and distribution coefficients is shown in Fig. 4. Fig. 4 shows there is an exponential relationship between alkalinity and K_d, a logarithmic correlation between soil alkalinity and uranium leaching that has been observed previously (Schumacher and Stollenwerk

Table 7. K_d Values for Uranium from USGS Delayed Neutron Activation Analysis

Soil	Soil U (mg/kg)	Soil activity[a] (pCi/g)	Leachate U (μg/L)	Leachate activity[a] (pCi/L)	K_d (mL/g)
1	29.8	9.8–13	2.54	0.84–1.12	11,700
2	13.9	4.6–6.1	13.01	4.29–5.75	1,100
3	9.33	3.1–4.1	1.15	0.38–0.51	8,100
4	77.4	25.5–34.2	653.2	215–289	120

[a] Activity ranges calculated based on ^{235}U/^{238}U activity distributions reported by the Hiss lab, ranging from 0 (lower limit of ND) to 34% ^{235}U activity.

Table 8. K_d Values from UMR Gamma Spectroscopy Analysis

Soil	1	2	2	2	2	2	2	2	3	3	3	4	4	4	Average
Fluid	b	a	b	c	c	c	t	t	a	b	c	a	b	c	—
Period	7/30	2	2	2	7	30	7	30	7	7	7	30	30	30	—
Ra-226	13	20	15	2	75	10	42	11	16	18	12	3	12	10	18
Ra-228	11	6	5	1	23	10	15	9	12	6	13	10	8	11	10
Th-228	6	15	17	2	15	11	18	9	16	15	17	24	14	19	14
Cs-137	10	10	11	2	8	8	8	8	12	11	9	10	15	13	10
Co-60	NA	11	0	NA	NA	NA	NA	NA	NA	0	NA	NA	Inf.	Inf.	
K-40	12	13	18	2	12	9	7	10	13	14	12	11	12	11	11

Note: Inf. = infinite; no evidence of leached isotope (division by zero), $K_d > 1{,}000$. NA = not applicable, no activity for this isotope in both soil and leachate (zero divided by zero).

1991). None of the soil leachates showed any pH extremes. Soil 4 did increase the pH, consistent with the observed alkalinity imparted to leaching solutions.

Discussion

The variability in measurements among the three labs involved in the reported work points out that some of the soil samples appear to have been originally quite nonhomogenous. This lack of homogeneity of the soil at the site may indicate that any attempt to characterize radionuclides in a mass of soil from a site such as SLAPS with subsamples may be completely futile—one might have missed the really hot particle just a foot away from the sample that was taken.

The most intriguing finding of this study relates to the leaching of uranium from residual soils, as determined by delayed neutron activation, and its probable relationship to soil characteristics and soil chemistry. Although all four soils had activities near or below the proposed "leave in place" limits, one soil, Soil 4, leached significant amounts of uranium. This soil met the standards for "leave in place," but would be expected to have become a source of groundwater contamination. For this soil, a K_d of 120 mL/g was observed. Overall, the USGS measurements resulted in distribution coefficients for uranium ranging from 10^2 to 10^4 mL/g, well within the reported literature range of $10-10^6$ (Schumacher and Stollenwerk 1991; Sheppard and Thibault 1991). Distribution coefficients were found to strongly correlate to leachate alkalinity; thus, leaching was not so much a function of specific activity as it was geochemistry.

Because the exact soil geochemistry and uranium mineral speciation were not measured for the sampled soils, and its determination was not the primary focus of this study, no definitive statements can be made about the reason for Soil 4's release of uranium during leaching. However, the difference in Soil 4 leaching is thought to be related to the increased carbonate content of the leachate. In oxidized surface and groundwater, uranium is transported as the highly soluble uranyl ion (UO_2^{+2}) and its complexes, including the carbonate complexes (Garrels and Christ 1965; Langmuir 1997). The carbonate complexes are important, as they increase the solubility of uranium minerals, facilitate U(VI) reduction, and limit adsorption in oxidized waters, increasing uranium mobility (Langmuir 1997). Not only did Soil 4 give the highest observed alkalinity, but it also neutralized the TCLP solution and, when incubated with oxygen-free water, Soil 4 leachate dropped from the initial pH of 8.0 to 5.0. Others have shown that carbonate concentration in leaching solutions, among other factors, may influence uranium extraction and leaching from ore and soils (Langmuir 1978; Longmire 1983; Longmire et al. 1994). Elless and Lee's (1998) work suggests that solubility of uranium-bearing minerals is the critical factor in controlling uranium solubility in soils. For soil where the uranium existed as amorphous coatings on the surface of sand and silt particles or on the surfaces of carbonate minerals present, a strong correlation between uranium and alkalinity was observed. Carbonate-bearing minerals are known to be present at SLAPs and prevalent in the State of Missouri (MDNR 1990; U.S. ACE 1999).

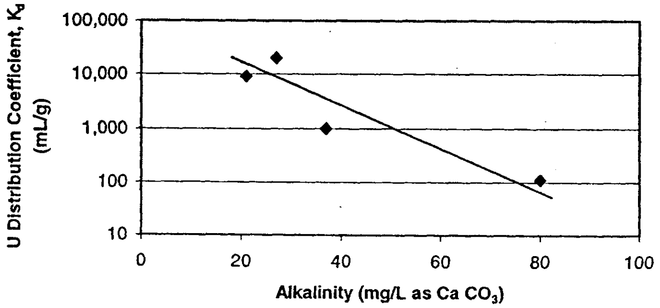

Fig. 4. Correlation of alkalinity and U distribution coefficient

Given the values of the distribution coefficients for uranium cited in the literature, the values determined by gamma spectroscopy are somewhat lower than anticipated. The presence of carbonates can promote the solubility of hexavalent uranium, which then prevents extensive binding to colloidal material (Gaffney et al. 1996). In the case of Soil 4, the high concentration of carbonate most likely did increase the solubility of uranium, resulting in significant leaching.

The uranium present in Soil 4 might have been present as carbonates, allowing it to leach easily from the soils. Batch experiments conducted on soils from Weldon Springs, another Department of Energy site, showed the importance of oxide surfaces in the sorption of uranium (VI) (Schumacher and Stollenwerk 1991). K_d values for uranium found in Weldon Springs batch experiments ranged from 10 to 1,000, with clay till having lower K_d values than the Ferrelview Formation overburden. The current study suggested that K_d values determined using delayed neutron activation ranged from 100 to 12,000. Geochemical modeling simulations have shown that uranium sorption decreases from 100 to 10% as carbonate concentrations increased from 10 to 430 mg/L (Schumacher and Stollenwerk 1991). Modeling simulations also showed that sorption of uranium (VI) was a function of both pH and carbonate concentration (Schumacher and Stollenwerk 1991). Soils that release more carbonate appeared more likely to release uranium.

Implications for Remediation

This study, and several others, suggest parameters other than gross radionuclide concentration or activity should be considered when developing and enacting remediation end-points for soils. Although Soil 4 was designated as a "leave-in-place" soil, this study indicated its leachate contained radionuclides and could subsequently contaminate ground or surface waters. The carbonate complexes present or formed in Soil 4 and its soil pore water have some influence on the leaching of uranium. The presence of carbonates or variations in soil mineralogy might be an additional focus of regulatory organizations in addition to gross soil activities. Perhaps soils with no threat of leaching radionuclides are being removed for sequestration within radioactive burial sites, while soils easily capable of leaching radionuclides are being left in place.

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