

URANIUM PARTITION COEFFICIENTS (K_d) IN FOREST SURFACE SOIL REVEAL LONG EQUILIBRIUM TIMES AND VARY BY SITE AND SOIL SIZE FRACTION

Jeffrey J. Whicker,* John E. Pinder III,^{†‡} Shawki A. Ibrahim,[†] James M. Stone,[†] David D. Breshears,[§] and Kristine N. Baker*

Abstract—The environmental mobility of newly deposited radionuclides in surface soil is driven by complex biogeochemical relationships, which have significant impacts on transport pathways. The partition coefficient (K_d) is useful for characterizing the soil-solution exchange kinetics and is an important factor for predicting relative amounts of a radionuclide transported to groundwater compared to that remaining on soil surfaces and thus available for transport through erosion processes. Measurements of K_d for ^{238}U are particularly useful because of the extensive use of ^{238}U in military applications and associated testing, such as done at Los Alamos National Laboratory (LANL). Site-specific measurements of K_d for ^{238}U are needed because K_d is highly dependent on local soil conditions and also on the fine soil fraction because ^{238}U concentrates onto smaller soil particles, such as clays and soil organic material, which are most susceptible to wind erosion and contribute to inhalation exposure in off-site populations. We measured K_d for uranium in soils from two neighboring semiarid forest sites at LANL using a U.S. Environmental Protection Agency (EPA)-based protocol for both whole soil and the fine soil fraction (diameters $<45\ \mu\text{m}$). The 7-d K_d values, which are those specified in the EPA protocol, ranged from 276–508 mL g^{-1} for whole soil and from 615–2249 mL g^{-1} for the fine soil fraction. Unexpectedly, the 30-d K_d values, measured to test for soil-solution exchange equilibrium, were more than two times the 7-d values. Rates of adsorption of ^{238}U to soil from solution were derived using a 2-component (FAST and SLOW) exponential model. We found significant differences in K_d values among LANL sampling sites, between whole and fine soils, and between 7-d and 30-d K_d measurements. The significant variation in soil-solution exchange kinetics among the soils and soil sizes promotes the use of site-specific data for

estimates of environmental transport rates and suggests possible differences in desorption rates from soil to solution (e.g., into groundwater or lung fluid). We also explore potential relationships between wind erosion, soil characteristics, and K_d values. Combined, our results highlight the need for a better mechanistic understanding of soil-solution partitioning kinetics for accurate risk assessment.

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Key words: uranium; depleted uranium; dose assessment; risk analysis

INTRODUCTION

RISK ASSESSMENTS are the main scientific drivers for decisions regarding cleanup criteria and long-term stewardship at sites with legacy environmental contamination, and there can be huge financial, public health, and ecological implications (Whicker et al. 2004). The U.S. Department of Energy (U.S. DOE) manages numerous sites that have large areas with low levels of radioactively contaminated soils (NAS 1989). One specific concern at the DOE managed Los Alamos National Laboratory (LANL) in New Mexico is soil contaminated with environmentally mobile uranium, mostly ^{238}U or depleted uranium (DU), which is introduced into the environment during test explosions (Fresquez et al. 1998; LANL 2002). The DU is dispersed across the soil surface as shrapnel and aerosol particles where it may constitute a potential ecological and human hazard. The concern is manifest not only at LANL, but also across landscapes where there has been heavy use of DU munitions during war times (WHO 2001).

Once a DU particle is deposited on the surface of a soil particle, it can remain on the soil surface where it is subject to wind and water erosion or it can be transported downward through the soil profile and become available for groundwater transport or plant uptake (Breshears et al. 1993, 2003) resulting in three possible and potentially competing pathways (Fig. 1). Radionuclides that have low affinities for binding to soil particles remain in the

* Los Alamos National Laboratory, Radiation Protection Division, Mail Stop G761, Los Alamos, NM 87544; [†] Colorado State University, Dept. Environmental and Radiological Health Science, 1618 Campus Delivery, Ft. Collins, CO 80523; [‡] Texas Christian University, 3023 S. University Drive, PMB 228, Ft. Worth, TX 76109; [§] University of Arizona, School of Natural Resources and Institute for the Study of Planet Earth and Department of Ecology and Evolutionary Biology, Biological Sciences East 325, P.O. Box 210043, Tucson, AZ 85721-0043.

For correspondence contact: Jeffrey J. Whicker, Los Alamos National Laboratory, Radiation Protection Division, Mail Stop G761, Los Alamos, NM 87544, or email at jjwhicker@lanl.gov.

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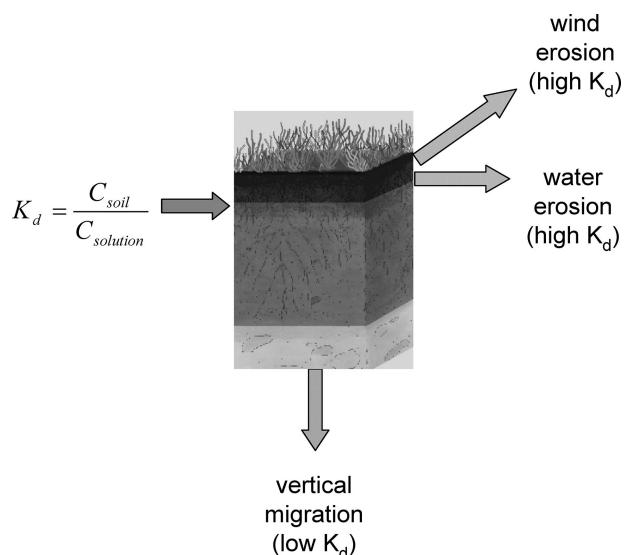


Fig. 1. Schematic showing the relationship between the partition coefficient (K_d), defined as the ratio of the concentration of a contaminant in soil (C_{soil}) and solution ($C_{solution}$), and each transport process for soil-bound contaminants.

soil water and have greater vertical migration rates. With sufficient water infiltration, these radionuclides can pass downward in the soil profile and become less available for transport through wind and water erosion and more available for transport by groundwater flows. Conversely, radionuclides that have a high affinity for binding to soil stay on or near the soil surface and are available for transport by wind and water erosion, especially in arid or ecologically disturbed locations where the vegetation cover is low (Shinn et al. 1989; Johansen et al. 2003; Whicker et al. 2002, 2005, 2006a and b).

A key parameter that describes the propensity for radionuclides to either migrate downward with infiltrating water or remain on the soil surface is the soil partition coefficient (K_d). Mathematically, the K_d equals the ratio of the concentration in the solid phase (such as soil) divided by the concentration in the liquid phase with units of mL g^{-1} . A large K_d implies rapid adsorption and retention of a radionuclide onto soil particles with subsequent availability for erosional transport; whereas, a small K_d implies little retention by surface soils and more rapid downward leaching to groundwater (Fig. 1). Studies have shown that K_d values for uranium can range over several orders-of-magnitude and are highly dependent on important characteristics of the soil such as clay content, texture, pH, and the amount of organic material (U.S. EPA 1999; Sheppard and Thibault 1990). These soil characteristics are highly variable in time and space and help explain why K_d values for uranium can range over many orders-of-magnitude. The K_d measurements are also influenced by the initial chemical form of the

uranium, including the oxidation state, and by laboratory protocol such as equilibrium time and whether the K_d measurement is based on adsorption (solution-to-soil) or desorption (soil-to-solution) (U.S. EPA 1999).

Risk assessments are often limited to using K_d values from a table, or if from measurements made with soils from a site, are often based on soils collected from a small number of sites. Yet soil characteristics can vary dramatically in short distances, especially in lands with complex terrain and geology such as those at LANL (Nyhan et al. 1978). Variation among soils within sites could significantly alter the K_d value and subsequently add to the uncertainty of the risk value. Risk assessment for soil-bound contaminants is further complicated by remaining questions regarding the complex relationships between the K_d and physical processes such as erosion that alter soil characteristics by preferentially removing soil fines and organics (Hennessy et al. 1986; Toy et al. 2002; Lal et al. 2004), which are critical soil components that drive many biogeochemical processes. Perhaps because of the lack of information on these complex relationships, radiological dose assessments most often assume that the transport mechanisms in Fig. 1 are primarily independent of each other and, in a sense, competing with each other for the transport of the radionuclide (Yu et al. 2001; Breshears et al. 2003). However, there are likely important feedbacks between each of these transport mechanisms, and they are not necessarily independent from each other. Few studies, if any, have linked these relationships together, even in a preliminary way.

Most measurements of K_d focus on the soil that is not sifted by particle size (U.S. EPA 1999), hereafter called whole soil, but it is also important to consider the fine fraction of soil (e.g., particles with physical diameter $<45 \mu\text{m}$), especially for surface soils. Radionuclides can concentrate on these fine particles (Whicker and Schultz 1982), and these small soil particles are most available for long-distance transport through wind erosion and subsequent inhalation. Therefore, there is a need to assess the adsorption of uranium to this fine soil fraction relative to the whole soil, and ultimately to relate these findings to wind transport, inhalation, and lung solubility.

Specific to this study, greater airborne concentrations of depleted uranium (DU) have been recently observed at LANL, especially in areas near the firing sites (LANL 2002), and the timing of the increases corresponds to documented increases in wind erosion of soil in burned and recently thinned ponderosa pine forest areas (Whicker et al. 2006b). Because of the potential for DU exposures to workers and the public, the primary objectives of this study were to measure site-specific K_d values for whole soil and the fine soil fraction from two LANL sites and evaluate the results in context of environmental transport pathways and risk assessment.

MATERIALS AND METHODS

General characteristics of forest sampling sites

The study sites are located in the Jemez Mountains in North Central New Mexico (at general area coordinates of 35°52' N; 106°21' W) at an elevation of about 2,300 m (Fig. 2). These sites are located along the western edge of LANL about 10 km southwest of Los Alamos, NM. Average annual precipitation in the area is about 500 mm, and the prevailing wind direction is from the southwest (Bowen 1990). Woody vegetation is comprised mostly of ponderosa pine (*Pinus ponderosa* Laws.

Var. *Scopulorum* Engelm.; nomenclature follows Martin and Hutchins 1980) and gamble oak (*Quercus gambelii*). Ground vegetation consists of a variety of grasses and flowering plants (Foxx and Hoard 1995).

Because of restricted access to the explosives testing areas, which contain soils contaminated with DU, uncontaminated soils were collected at two representative LANL locations, both about 5 km north of the testing areas. The two sampling sites (site 1 and site 2) were separated by about 750 m, and the selected locations were generally similar to the firing sites in terms of dominant vegetation,

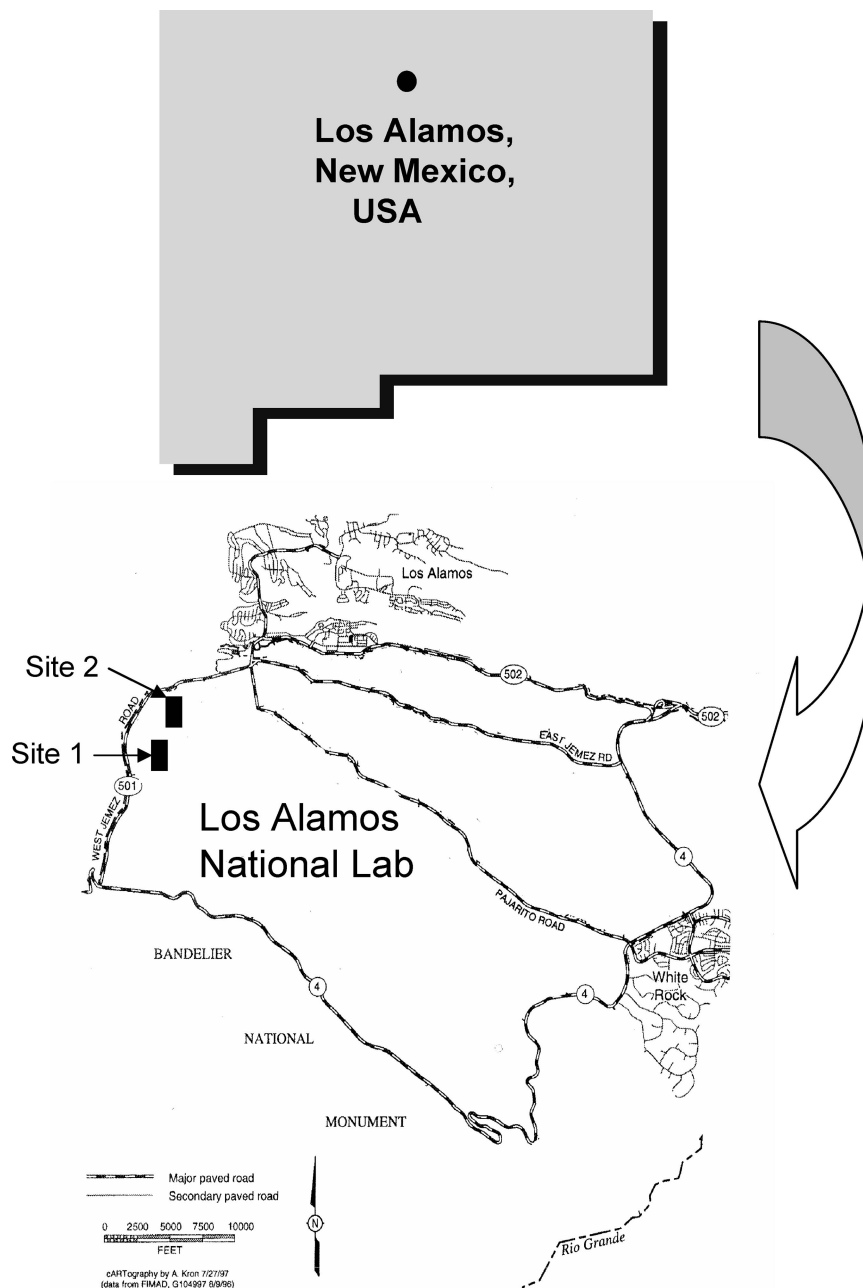


Fig. 2. Map of the sampling sites located within Los Alamos National Laboratory.

elevation, topography, and meteorological conditions. The two sites differed from each other in that the site 1 soil was near the bottom of a long, gentle slope and had greater vegetation cover, which combined could lead to enrichment of fine material such as silts and clays through fluvial and aeolian sedimentation. Site 2 was on a ridge top with less vegetation cover than site 1 and where the fine soil materials were more likely to be lost through erosion (Whicker et al. 2006a).

Soil sampling plan and collection methods

Soil sampling plots were selected by randomly selecting a direction and distance normal to an imaginary line transecting both sites 1 and 2. There were 5 randomly-located plots at the slightly larger site 1 location and three randomly selected plots at the site 2 location. The distance between plots within each site was generally <30 m. A 1-m² frame was placed on the ground at each of the sampling plots and 20 non-overlapping soil cores were obtained around the edge of the frame. Because one of the goals of this and companion studies was to investigate the mobility of depleted uranium in the surface soils, only the top 2 cm of the soil profile was collected. In summary, twenty 38-mm-diameter × 2 cm deep soil cores were obtained at each of the eight sampling plots (5 from site 1 and 3 from site 2). The soils from each plot were air dried and combined with other surface soil from the same site (site 1 or 2). K_d measurements were performed on the composite soil samples.

Sample preparation and K_d measurements

Sample preparation and characterization. A dried 200-g sample from the composite soil from each sampling site (1 and 2) was submitted to the Soil, Water, and Plant Testing Laboratory at Colorado State University for characterization. Analysis of soil texture was performed using a modified pipette method (Indorante et al. 1990) and reported as the percent by mass of sand, silt, and clay (Miller and Gardiner 2001). The soil pH was measured by saturating the soil with deionized water to create a soil paste, waiting 24 h, then measuring the pH of the paste. The content of organic matter in the soil was measured using the Modified Walkely Black Method. Clay mineralogy was also investigated using x-ray diffraction techniques because of the varying cation exchange capacity between different clay types. Sub samples of the fine fraction of the soil (<45 μm) were separated from each of the site 1 and 2 soils using a mechanical sieve to study the partitioning dynamics for the smaller soil particles that provide most of the available surface area for adsorption. In summary, separate

samples of whole and fine soil were prepared for both sites 1 and 2.

Measurement of the K_d . K_d measurements were made according to a U.S. Environmental Protection Agency (EPA) protocol (U.S. EPA 1999) with ²³⁸U in uranyl nitrate solution in the +VI oxidation state. The +VI form would be expected from slow oxidation of DU on particle surfaces over time, but some of the larger DU particles may not have fully oxidized and the inside parts could be in metal or other unknown form, which are likely less soluble than the +VI form (U.S. EPA 1999). Assuming that the DU in soil is in the +VI state results in estimates of greater solubility, lower K_d values, and faster infiltration through the soil profile with water flow relative to other forms.

One-gram soil samples were placed into 50-mL plastic test tubes and combined with 30 mL of a 165,000 ppm ²³⁸U solution of UNO₃ at a pH of 5.5. The soil-solution mixtures were agitated using a mixing wheel and the solutions sampled at intervals of 0.17 d (4 h), 1 d, 2 d, 3 d, 7 d, 10 d, 15 d, 20 d, and 30 d. Variability was assessed by sampling two tubes on many of the days, but, because of high analysis costs, the collection of multiple tubes on the same day were alternated between the whole and fine soil after day 1, except for day 30 where multiple samples were taken for whole and fine soil. Specifically, multiple samples from whole soils were collected on days 0.17, 1, 2, 7, 15, and 30, and there was no sample collected on day 3. Single samples were collected on other days. Multiple samples for fine soil were collected on days 0.17, 1, 10, and 30 and single samples on the other days. Means and standard deviations are calculated and reported for days with multiple samples. Results from single measurement days are reported, and variability of single measurements was estimated to be 15% based on analysis history of the Inductively Coupled-Plasma Mass Spectrometry (ICP-MS) technique. Soil and solution were separated by centrifugation, and the supernatant passed through a 0.45- μm filter, tested for pH, and submitted for ICP-MS analysis. The amount of ²³⁸U in the soil was calculated as the difference in the total ²³⁸U in the original spike (165,000 ppm) minus the amount of ²³⁸U measured in the solution for each time period. The amount of the spike was sufficiently high relative to the amount of ^{nat}U in soil expected to desorb into the solution that the background was not measured. Blanks and spiked solutions were submitted for laboratory analysis to assess laboratory procedures. Results for blanks were <0.002% of the spike amount and the measurements for the spiked solutions were <0.3% of the spike.

Table 1. Characteristics of soil for the site 1 and site 2 sampling locations.

	pH	% SOM ^a	% Sand	% Silt	% Clay ^b	Texture class
Site 1	4.8 ± 0	10.2 ± 0.2	34.0 ± 2.1	53.6 ± 1.5	12.4 ± 1.1	Silt loam
Site 2	4.2 ± 0	9.5 ± 1.8	51.3 ± 5.0	39.3 ± 6.7	9.3 ± 2.5	Loam/Sandy loam

^a Soil organic matter.

^b X-ray diffraction results show that the dominant clay types were quartz, illite, and mica.

The partition coefficient values for each measurement time [$K_d(t)$] were calculated using the formula:

$$K_d(t) = \frac{{}^{238}\text{U}(t)_{\text{soil}}}{{}^{238}\text{U}(t)_{\text{solution}}}, \quad (1)$$

where ${}^{238}\text{U}(t)_{\text{soil}}$ is the uranium concentration in the soil at time t , and ${}^{238}\text{U}(t)_{\text{solution}}$ is the uranium concentration in the solution at time t . The results are reported in units of mL g^{-1} .

Statistical analyses

The adsorption rates for whole and fine soil from both sites were determined from the time profiles of ${}^{238}\text{U}$ concentration in the solution. A two-component exponential model was used with the “FAST” component determined from concentrations from the start of the experiment through the end of the first day. The “SLOW” adsorption component was determined from the time profile of the ${}^{238}\text{U}$ concentration in the solution from day 3 to day 30. Linear regression analyses of ln-transformed concentrations were done, and the slopes of the regressions represent the adsorption rates in units of fraction adsorbed per day. The non-parametric Wilcoxon Signed Rank test was used to statistically test for differences in K_d values among size

fractions and sampling sites that were paired by sampling time.

RESULTS

Soil characteristics

Characteristics of the soils from the two sites are given in Table 1, and the results show that the soils from the two sites are different, with site 1 having greater pH, percent soil organic material, and fine soil fraction, as shown by greater clay and silt percentages [Mann-Whitney test ($p \leq 0.05$)]. The differences are consistent with the expectation from field observations and measurements of wind erosion (Whicker et al. 2006a and b) that site 1 could be a place where fine materials accumulate and site 2 is a place where fine materials could be eroding away.

Adsorption kinetics

Fig. 3 shows a time-series plot of the ${}^{238}\text{U}$ concentration in solution for the site 1 and 2 locations in whole soil and the fine soil fraction. These plots show that rapid adsorption occurred in the first hours and then a more moderate adsorption rate occurred after the first day. The

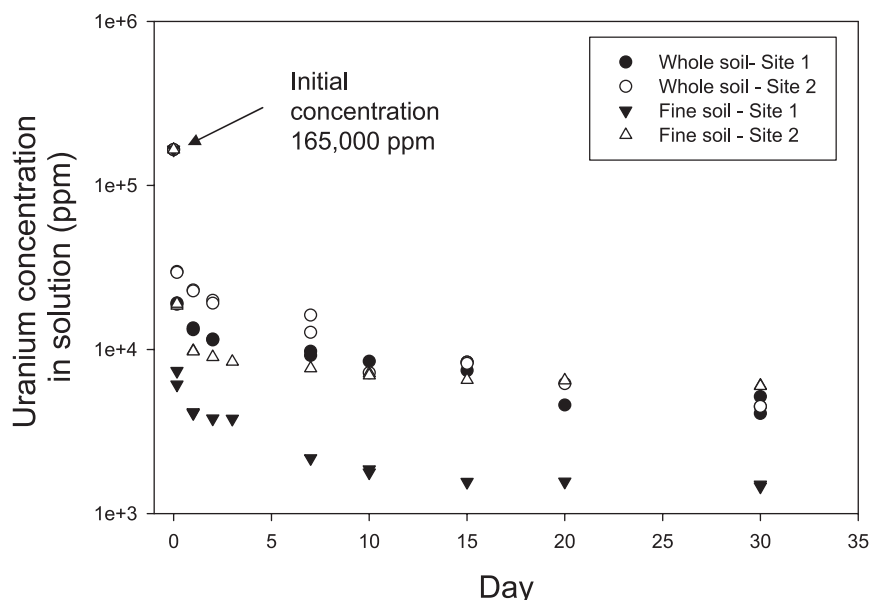


Fig. 3. Time series of concentration of ${}^{238}\text{U}$ in solution categorized by sampling location and by whole or fine soil.

Table 2. Calculated loss rate constants for adsorption rates of ^{238}U to LANL soils in units of d^{-1} . Estimates are based on a two-compartment model using least-square exponential fits of the concentration of ^{238}U in solution over time.

	Whole soil		Fine soil	
	FAST	SLOW	FAST	SLOW
Site 1				
Loss rate (d^{-1})	-1.4 ± 0.9	-0.03 ± 0.004	-2.1 ± 1.4	-0.03 ± 0.008
R^2	0.44	0.89	0.43	0.65
Site 2				
Loss rate (d^{-1})	-1.1 ± 0.74	-0.05 ± 0.006	-1.8 ± 0.9	-0.01 ± 0.002
R^2	0.43	0.89	0.55	0.86

adsorption rates based on a two-component exponential with a “FAST” and a “SLOW” phase were quantified. Table 2 shows the calculated adsorption rates expressed as a fraction per day and categorized by sampling location (sites 1 and 2) and soil type (whole or fine). The results reflect the rapid decline in ^{238}U in solution shown in Fig. 3 with adsorption rates for the FAST phase roughly between 1 and 2 orders-of-magnitude higher than the SLOW phase. The two-component, exponential model was better at predicting solution concentrations during the “SLOW” adsorption phase relative to the “FAST” phase where the R^2 values were lower and the relative variations in slopes were much greater. Results show that a greater number of samples during the first day would be critical toward better characterizing the FAST adsorption phase.

K_d measurements

Differences among sites and whole and fine soil fractions were tested using the K_d values shown in Table 3. This statistical analysis showed highly significant differences between site 1 and site 2 for fine soil ($p < 0.01$) and tending towards significance between sites for whole soil ($p = 0.078$). There were highly significant differences between the whole and fine soil fraction at site 1 ($p < 0.01$), but there was not a statistically significant difference at site 2 ($p = 0.19$). Fig. 4a shows that the K_d values for soil from site 1 were generally

higher than the site 2 location for the whole soils through day 7, after which the K_d values for the whole soil were approximately equal. Fig. 4b shows that the K_d values for the fine soils from site 1 were always higher than the soils from site 2.

Regarding equilibrium, the K_d values for whole soil continued to increase through day 30 for whole soils at both sites (Fig. 4a). Specifically, the whole soil K_d values for day 30 were 2.1 and 3.4 times greater than the 7-d K_d values for site 1 and site 2, respectively. In contrast, the K_d values in fine soil changed little after approximately 15 d (Fig. 4b). Equilibrium levels of adsorption of ^{238}U to whole soil, as indicated by the 30-d K_d mean value, were statistically equal at values of $1,057 \pm 180 \text{ mL g}^{-1}$ and $1,074 \pm 2 \text{ mL g}^{-1}$ for the site 1 and site 2 soils, respectively. However, the U.S. EPA recommended day 7 values showed higher K_d values of $493 \pm 21 \text{ mL g}^{-1}$ at site 1 relative to those at site 2 of $318 \pm 59 \text{ mL g}^{-1}$. These 7-d K_d values are consistent, but on the low end of those reported for other soils where the pH in the K_d measurement was 5.5 (U.S. EPA 1999).

Fig. 5a and b show the time profile of the K_d measurements comparing values for whole and fine soils for both sampling sites, and generally the K_d values were greater for the fine soils compared to the whole soils. The time profile of measurements show that the K_d values

Table 3. Mean and 1 standard deviation for K_d measurements (units mL g^{-1}) through time categorized by soil type and LANL sampling location.

Day	Whole soil		Fine soil	
	Site 1	Site 2	Site 1	Site 2
0.17	230 ± 4^a	137 ± 1.4^a	711 ± 100^a	235 ± 5^a
1	340 ± 6^a	187 ± 2^a	1174 ± 11^a	477 ± 3^a
2	401 ± 3.5^a	249 ± 8^a	1274 ± 191	521 ± 78
3			1281 ± 192	558 ± 84
7	493 ± 21^a	318 ± 59^a	2249 ± 337	615 ± 92
10	554 ± 83	657 ± 99	2698 ± 83^a	673 ± 14^a
15	599 ± 53^a	567 ± 7^a	3151 ± 473	730 ± 110
20	1049 ± 157	769 ± 115	3137 ± 471	735 ± 110
30	1056 ± 180^a	1074 ± 2^a	3318 ± 66^a	795 ± 3^a

^a Standard deviation based on multiple measurements. A 15% measurement error is assumed for all other ICP-MS measurements.

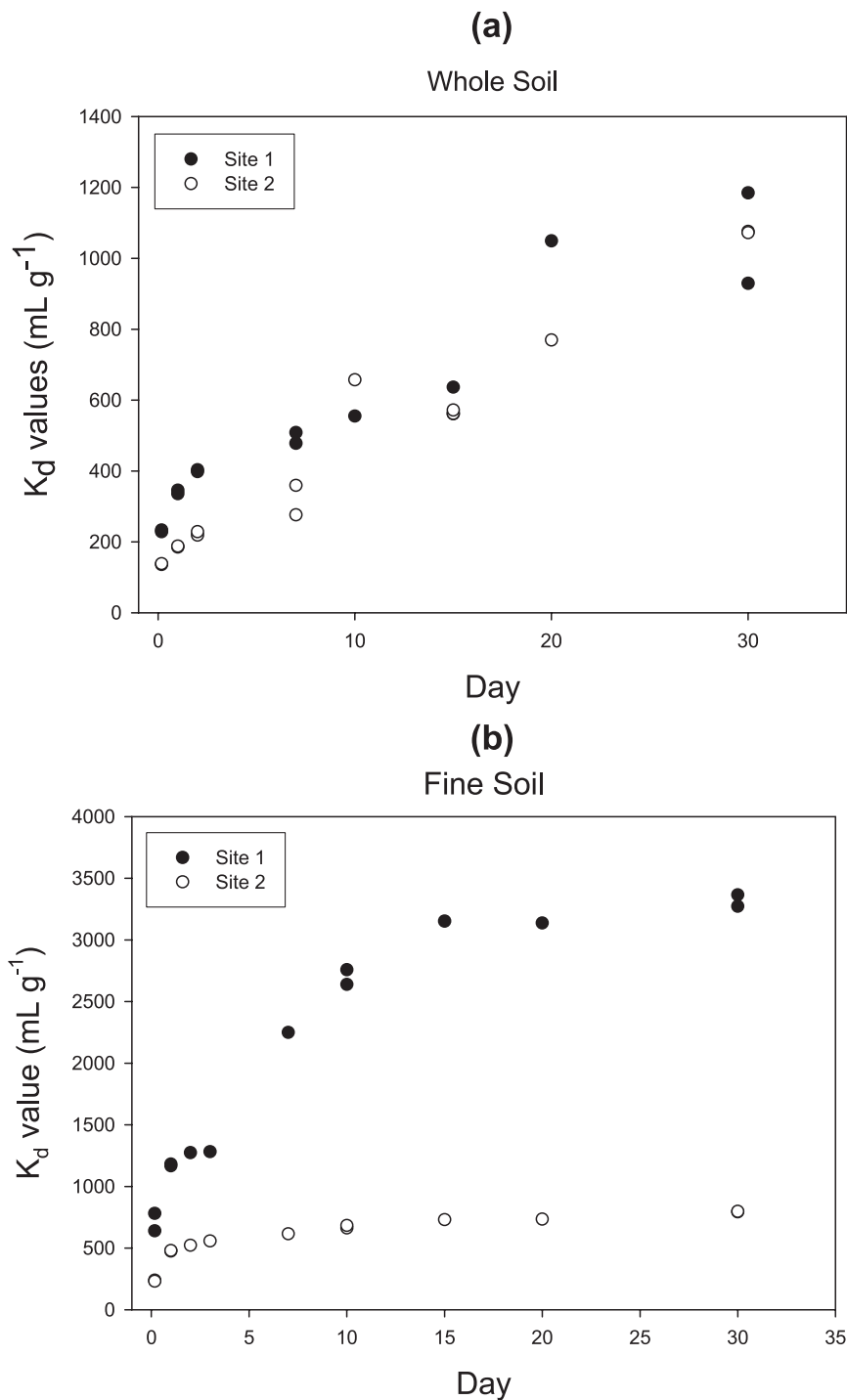


Fig. 4. Time series of K_d values for whole soil (a) and for fine soil (b) contrasting differences between sampling sites.

increased rapidly for both whole soil and the fine fraction of soil through the first 10 d, but the rate of increase slowed dramatically after day 15. The exception was found for the whole soil at site 2 where the K_d value continued to increase through day 30 and eventually approached the K_d value for the fine soil fraction.

DISCUSSION

This study quantified K_d values for ^{238}U in surface soils that were collected from two sites roughly similar in location, elevation, vegetation, geology, and topography to LANL sites contaminated with DU. The objectives

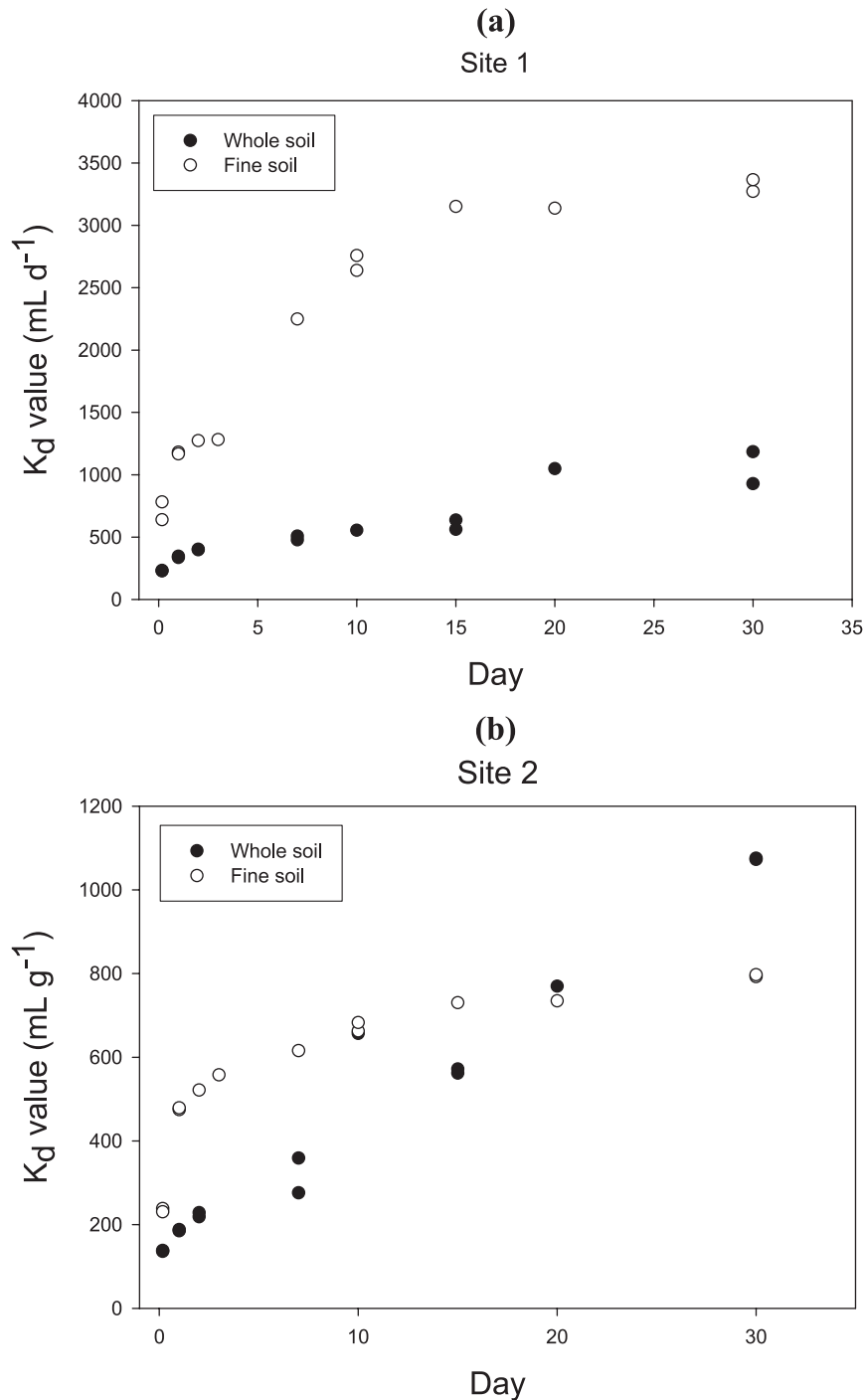


Fig. 5. Time series of the K_d values at site 1 (a) and site 2 (b) contrasting differences between K_d values for whole and fine soils.

and results of this study are categorized into five major areas including 1) quantifying the K_d values for surface soil, 2) testing for equilibrium of ^{238}U exchange between the soil and solution, 3) quantifying ^{238}U adsorption rates based on a two-component model, 4) testing for differences between K_d values for whole and fine fraction of surface soil, and 5) testing for differences in K_d values

between two sites. The details of the findings, their limitations, and the implications of the results are summarized next.

First, the K_d values for the LANL surface soils were quantified and found to be within the range of those reported by the U.S. EPA (1999) for pHs between 4 and 5, though the range of reported values is quite large (0.4

up to 160,000) and this project focused on surface soil whereas other studies included deeper soils. The K_d values were high enough to suggest that deposited DU would remain on the soil surface and generally be available for transport through erosion processes for long periods.

Second, the results document the temporal variation in K_d measurements. The measured K_d values increased quickly for the first couple of days and then the rate of increase in K_d slowed but continued to rise through day 30. The 7-d K_d values were less than the 30-d values by factors of 2.2 to 3.4 in the whole soil and 1.3 to 2.4 in the fine soil fraction. In some cases, the data showed that the K_d may not have reached full equilibrium even after 30 d. It was not possible in this study to extend the measurements beyond 30 d because of budget limitations, but future studies might want to extend the measurements beyond this time length. An important implication of this finding is that unquestioned following of the EPA prescribed 7-d K_d measurements may result in under predicting K_d values in some cases, and data from this study show that longer-term measurements (e.g., >30 d) should be considered to improve the accuracy of uranium-based dose assessments.

Third, the net adsorption rates of ^{238}U were modeled. The adsorption data suggested a two-component model with FAST and SLOW phases, and the loss rate constants for each phase were estimated. The adsorption rates for the FAST component were up to two orders-of-magnitude greater than that found for the SLOW phase. The dramatic differences between the FAST and SLOW adsorption components suggest multiple binding sites for uranium in the soil particles. The two-component model was a better predictor of ^{238}U concentration in solution for the SLOW phase than the FAST phase. Although parameters for a two-component equation were sufficient to model the sorption data, this should not be interpreted as an indication that there are only two sorption processes in these systems. Rather, the two-component equations indicate that the number, variety, and interactions among sorption processes can, when measured on these temporal scales, be approximated by a two-component model. More frequent sorption measurements, especially within the first 24 h, or measurements over a longer duration may identify the need for additional components in the model. However, producing more complex models does not address the more fundamental issue of how differences among these soils and soil fractions in the types and extents of sorption processes affect the short-term and long-term fates of uranium.

Fourth, we found evidence of higher K_d values for the fine fraction of soil compared to the whole soil. This

finding was expected because of the much larger available surface area per gram of material for adsorption in the fine fraction of the soil and the expected larger amounts of clay and organic material in the fine soil fraction. An exception to this trend is found in the site 2 soils where the K_d for whole soil continued to increase through day 30 suggesting that equilibrium in this soil occurs slowly.

Fifth, we found evidence for differences in measured K_d values between sites 1 and 2; however, it was not possible to identify the specific cause (such as clay content) because the two soils differed in several parameters. Differences in soil characteristics between sites 1 and 2 may account for the differences in whole soil K_d but cannot directly explain the large differences in K_d for the <45- μm soil fractions. These differences imply that the composition of the fine particles had impacts on the uranium K_d that were not obvious from soil measures or clay mineralogy.

Implications for dose assessment and site-specific measurement of K_d

Key to the accuracy and credibility of the dose assessments are relevant measurements of the kinetics of the DU in the local soils (U.S. EPA 1999) as well as the solubility of the soil-bound DU in the lung (Eidson et al. 1989; Eidson 1994; NCRP 1997). The differential partitioning of uranium between the solid and liquid phases in fine and whole soil found in this study is an important consideration for dose assessments from inhaled uranium because 1) the uranium may be concentrated in fine fraction of the soil, 2) the fine soil fraction will be preferentially resuspended by wind and transported to off-site populations, and 3) the solubility of soil-bound uranium in lung fluid is uncertain, though some research has been conducted (Casaceli 2006).

The variability in soil characteristics and related K_d measurements between sites 1 and 2 argues for performing K_d measurements with soils taken at multiple locations to assess this variability at relevant spatial scales. There are several possible explanations for the difference in K_d across the two sites including pH, soil size, and organic content (U.S. EPA 1999), and each of these factors can be altered through erosion (Hennessy et al. 1986; Toy et al. 2002; Lal et al. 2004). Although specific causative factors were not identified, the higher K_d values at site 1 relative to site 2 are consistent with the assessment that site 1 may be an area of fluvial and aeolian accumulation with a relatively low soil erosion rate resulting in greater amounts of soil fines. In contrast, the erosion rate at site 2 could be much faster resulting in a sandier soil with lower amounts of fine soil materials, which could lead to relatively low K_d values. While not

directly tested, this idea is supported by measurements of wind erosion made at the two sampling sites as part of a risk assessment (Whicker et al. 2006a and b). These measurements showed consistently higher wind erosion rates at site 2 relative to site 1 with wind-driven sediment fluxes of $0.43 \pm 0.21 \text{ g m}^{-2} \text{ d}^{-1}$ and $0.91 \pm 0.41 \text{ g m}^{-2} \text{ d}^{-1}$ for sites 1 and 2, respectively.

Combined, the K_d and wind erosion measurements suggest that uranium contamination in LANL surface soils could preferentially adsorb to the fine soil fraction, which is the soil fraction most subject to wind erosion and subsequent off-site transport (Bagnold 1941; Stout and Zobeck 1996). These analyses provide one example of how soil/liquid chemistry and physical processes such as soil erosion might be linked and that this interaction could be worth further investigation.

Implications for cleanup of DU contaminated sites

The relatively large K_d values measured in this study suggest that DU at LANL will largely remain in surface soils for long periods, and the DU could concentrate in erodible soil materials. The DU remaining in the surface soil is significantly less environmentally mobile in an undisturbed ecosystem, but if the vegetation or soil is disturbed (i.e., by fire, forest management practice, or clean up of contaminated sites), DU mobility can increase significantly and increase inhalation doses (Whicker et al. 2006b). This result has important implications for clean-up activities at contaminated sites. One of the major clean-up options used is physical removal of the soils, which is extremely costly. Soil substrate removal only translocates the problem, may add significant health risks to the clean-up workers, can damage ecosystem function, and may actually enhance the dispersion of contamination in the process (Shinn et al. 1989; Whicker et al. 2004). In contrast, if the long-term risks from DU in surface soils of the environment are sufficiently low, contaminants may be safely left in place, providing that soil stability, even during extreme events, is adequately demonstrated (Whicker et al. 2002, 2006a and b).

CONCLUSION

Adsorption K_d values were measured through time for whole and fine surface soils collected at several semiarid forest sites within LANL. Results suggest 1) rapid adsorption onto soils during the first day, 2) increasing K_d values through time with a 30-d K_d value for whole soil more than twice the 7-d value for both sites, 3) potential for greater K_d values for the fine soil fraction that is more susceptible to resuspension and inhalation than the whole soil, and 4) differences between K_d values from two sampling sites whose soil

characteristics differed, possibly due to impacts of soil erosion or other unknown processes.

Clearly, K_d measurements and interpretations of their meaning are complex, but this study confirms other findings showing the importance of obtaining site-specific K_d measurements for risk assessment and that consideration should be given to continuing uranium K_d measurements beyond the EPA recommended 7 d. Otherwise, K_d values could be underestimated and lead to inaccurate predictions of transport pathways and rates. The high cost, both financial and ecological, of cleanup of contaminated sites requires relevant measurements of K_d values and a better mechanistic understanding of soil-solution partitioning kinetics for assessing risk accurately.

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