

Mechanisms of Thorium Migration in a Semiarid Soil

A. J. Bednar,* D. B. Gent, J. R. Gilmore, T. C. Sturgis, and S. L. Larson

ABSTRACT

Thorium concentrations at Kirtland Air Force Base training sites in Albuquerque, NM, have been previously described; however, the mechanisms of thorium migration were not fully understood. This work describes the processes affecting thorium mobility in this semiarid soil, which has implications for future remedial action. Aqueous extraction and filtration experiments have demonstrated the colloidal nature of thorium in the soil, due in part to the low solubility of thorium oxide. Colloidal material was defined as that removed by a 0.22- μm or smaller filter after being filtered to nominally dissolved size (0.45 μm). Additionally, association of thorium with natural organic matter is suggested by micro- and ultrafiltration methods, and electrokinetic data, which indicate thorium migration as a negatively charged particle or anionic complex with organic matter. Soil fractionation and digestion experiments show a bimodal distribution of thorium in the largest and smallest size fractions, most likely associated with detrital plant material and inorganic oxide particles, respectively. Plant uptake studies suggest this could also be a mode of thorium migration as plants grown in thorium-containing soil had a higher thorium concentration than those in control soils. Soil erosion laboratory experiments with wind and surface water overflow were performed to determine bulk soil material movement as a possible mechanism of mobility. Information from these experiments is being used to determine viable soil stabilization techniques at the site to maintain a usable training facility with minimal environmental impact.

A THOROUGH UNDERSTANDING of contaminant mobility is required for successful immobilization and soil remediation (Dutre et al., 1998; Tome et al., 2002). The work presented in this article describes the chemical and physical mechanisms of thorium migration at Test Site 4, Kirtland Air Force Base, Albuquerque, NM. This training site has historically been amended with thorium oxide to simulate a plutonium spill from a nuclear weapons accident (August et al., 1999; Larson et al., 2004). The training site has restricted access and operations are conducted in compliance with a current Nuclear Regulatory Commission license. Previous work by various researchers characterized the extent of thorium distribution but did not investigate the potential mechanisms of thorium migration at the site (Larson et al., 2004; August et al., 1999). Radionuclide-containing soils have been studied, yet individual site characteristics and radionuclide chemistries require specific investigations, even at similar sites (Mortvedt, 1994; Zararsiz et al., 1997; McClellan et al., 2003; Martinez-Aguirre and Perianez, 2001). Presented here is a series of aqueous extraction and digestion, electrochemical, plant uptake, and wind and water erosion experiments determining the

most likely processes affecting thorium mobility at this semiarid site. This information is critical to determining a remediation technique to prevent mobilization of thorium off-site.

Because of its location relative to civilian populations, it is important to understand the mechanisms of thorium migration and prevent the migration of radioactive thorium (Larson et al., 2004). Details of the site have been previously described (August et al., 1999; Larson et al., 2004). Training Site 4 was studied to determine the mode of thorium migration so that suitable soil stabilization methods may be employed to keep the site available for training while posing minimal environmental risk.

The previous field studies noted that radiation levels approaching 10 times background were found near the site boundaries, sometimes more than 100 m from the point of application yet still within the site, thereby suggesting some thorium migration has occurred (Larson et al., 2004). Simple dissolution reactions cannot explain mobility of inorganic thorium dioxide, which has a K_{sp} of approximately 10^{-53} (Neck et al., 2003); however, thorium is known to complex with simple inorganic ligands and natural organic matter (Murphy et al., 1999). The insoluble nature of thorium oxide prevents transport as a traditional dissolved species and therefore requires further investigations into the mechanisms of mobilization (Hyde, 1960; Neck et al., 2003).

The region is classified as semiarid, receiving approximately 250 mm of precipitation per year. Much of the region's rainfall occurs during the summer months (National Weather Service, 2004), often in short storm events, during which time surface runoff would be expected to contribute significantly to thorium migration. However, due to the extremely low solubility of thorium oxide, transport is most likely to occur in colloidal or suspended phases or complexed with natural organic matter (NOM) (Zhang et al., 1997; Murphy et al., 1999; Baumann et al., 2002). Low solubility also reinforces the explanation for why vertical migration at the site has been less than 1 m, even in the highest thorium concentration areas (Larson et al., 2004). Additionally, the dry climate is likely to support wind transport of soil particles or detrital plant material (Zararsiz et al., 1997; Rodriguez et al., 2002; McClellan et al., 2003).

The area is sparsely vegetated with desert plants, which can aid in both mobilization by uptake into plant tissue and immobilization by reduction of soil erosion by wind and water (Zararsiz et al., 1997; Burlo et al., 1999; Rodriguez et al., 2002; McClellan et al., 2003). A series of plant uptake experiments was also performed to determine the extent of thorium uptake by native plants to determine if this is a possible mode of migra-

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Published in J. Environ. Qual. 33:2070–2077 (2004).
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Abbreviations: ICP–MS, inductively coupled plasma–mass spectrometry; NOM, natural organic matter.

tion after the plants die, desiccate, and are moved by wind.

Thorium geochemistry is relatively straightforward, with only the +4 oxidation state known in nature (Hyde, 1960; Korobkov et al., 2003); however, radionuclides and their decay progeny are known to complex with NOM and accumulate in plants (Zararsiz et al., 1997; Murphy et al., 1999; Morton et al., 2002; Tome et al., 2002; McClellan et al., 2003). The complexity of the field site suggests that multiple mechanisms, rather than simple dissolution and dissolved transport, are responsible for thorium migration. As an example, migration of thorium has been observed up-gradient from the point of thorium application (Larson et al., 2004), possibly as the result of wind transport. Results presented here describe possible modes of thorium transport and are currently being used to formulate viable soil stabilization techniques to maintain the site for future training purposes.

MATERIALS AND METHODS

Site soils used in the experiments described below were collected in early 2002, composited, and homogenized to a radioactivity of approximately 1.74 Bq/g. Additional clean soil from the site was also collected (background activity approximately 0.074 Bq/g from the natural uranium and thorium in the soil; Larson et al., 2004) for use as a control in all experiments. The soil is a sandy clay loam Aridisol with a paste pH of approximately 8.5 and a cation exchange capacity of 24 cmol/kg. All soils were sieved to 2 mm to remove rocks and large detrital plant material. Chemicals used in all experiments were of reagent grade or higher purity and used without further purification; the deionized water used had a resistivity of 18.3 M Ω -cm.

Thorium Analysis

Inductively coupled plasma-mass spectrometry (ICP-MS) (Elan 6000; PerkinElmer, Wellesley, MA) according to USEPA Method 6020 was used at the U.S. Army Corps of Engineers, Engineer Research and Development Center, Vicksburg, MS, for elemental analysis of all aqueous digestion and extraction samples. A plasma power of 1400 W and a nebulizer flow of 0.8 mL/min were generally used; the relatively high plasma power aided in decomposition of thorium colloids in some samples. Extract samples were prepared for analysis by filtration (0.45 μ m unless otherwise specified) and acidification to pH < 2 with nitric acid. Because of its rarity in most samples, and its similar mass to thorium, bismuth-209 was used as the internal standard for all analyses. We used ICP-MS to determine total thorium because of its higher sensitivity and faster analysis speed than traditional sodium iodide gamma spectroscopy techniques. An estimated detection limit of approximately 0.5 μ g/L for thorium and uranium was determined for the instrumental parameters used. Uranium analysis was also performed in all samples to determine if it would act as a natural internal standard for the site soils (Tome et al., 2002). The results reported below show that the thorium originally used to amend the site most likely contained uranium impurities yielding a slightly higher uranium concentration in the thorium-containing soil compared with the "clean" soil.

Column Leachates

Column experiments were performed to determine the extent of vertical migration of thorium in the soil. Two types of

column experiments, each consisting of 5- \times 15-cm plastic tubes packed with soil with each end capped by a porous frit to allow vertical water flow, were performed. In the first experiment, the columns were packed only with thorium-containing soil. In the second experiment, the columns were packed with a 7.5-cm layer of thorium-containing soil on top of a 7.5-cm layer of clean soil. Both experiments used a deionized water infiltration leachant under fully saturated conditions at steady influent flow rates (approximately 2 mL/d) from a constant head reservoir (approximately 60 cm). Sodium azide (0.5%) was added to the water reservoirs to inhibit microbial growth in the soil columns. The column effluents, which were sampled twice weekly for approximately 3 mo, were filtered, acidified, and analyzed for thorium and uranium by ICP-MS. Dispersion of clay particles was not observed as a result of adding sodium azide to the deionized water because the soil naturally contains sodium; therefore, an equilibrium sodium concentration was established during the leaching of the soils.

Electrokinetic Experiments

Electrokinetic remediation is an in situ process where an electrical field is created in a soil matrix by applying a low-voltage direct current (DC) to electrodes placed in the soil (Pamukcu and Wittle, 1992; Puppala, 1994; Orcino and Bricka, 1998). When DC current is applied to the electrodes, an electrical field develops between the anode and cathode and induces electroosmosis, electromigration, electrophoresis, electrolysis, and pH changes in the soil system.

In electromigration, cations migrate toward the negatively charged cathode, and anions migrate toward the positively charged anode and concentrate in the solutions near the electrodes. Electrophoresis is a similar phenomenon involving charged particles rather than ions. Therefore, the electrode reservoir that accumulates thorium should provide speciation information on the form that is mobile in the soil solution.

Electrolysis reactions occur at the electrodes resulting in changes to the fluid pH. Oxidation of water at the anode generates hydrogen ions (H⁺) and oxygen gas (O₂). Hydrogen ions create an acid front that migrates toward the cathode. Reduction of water at the cathode generates hydrogen gas (H₂) and hydroxyl (OH⁻) ions; the latter then migrate as a base front toward the anode (Acar et al., 1990). These reactive fronts can mobilize soil constituents depending on their respective chemistries.

The experimental design shown in Fig. 1 consisted of a

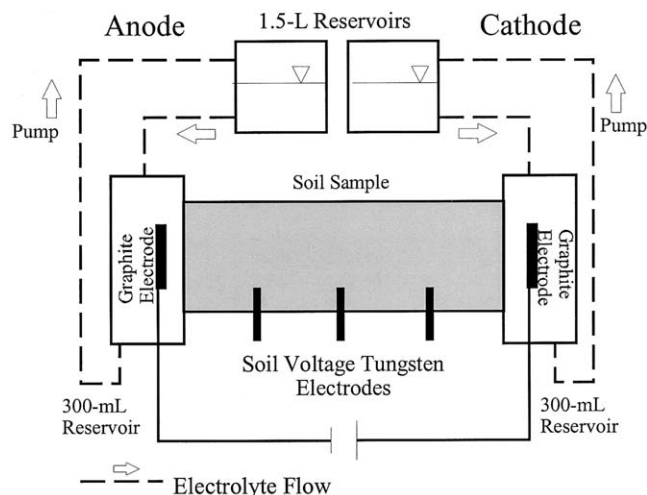


Fig. 1. Schematic of the electrokinetic experimental apparatus.

10- × 10-cm acrylic tube packed with soil between two porous frits (Porex polyethylene < 200 μm), similar to the column leach experiments, although positioned horizontally. Inert graphite electrodes were then placed in 300-mL reservoirs at the end of the plastic tube and connected to a DC power supply. A potential of approximately 18 V was applied to the soil samples during the experiments. The fluid in the reservoir ends was circulated with a peristaltic pump to larger 1.5-L reservoirs. Solutions were changed in the reservoirs weekly and replaced with deionized water. Three tungsten wire probes were placed equidistant across the soil sample to measure the potential gradient that developed in the soil between the graphite electrodes. Two cells were set up for the electrokinetic experiments. Cell A was packed with thorium-containing soil only, whereas Cell B contained clean soil on the anode half of the tube. Aqueous samples were taken daily, filtered, and acidified for analysis by ICP–MS. Various filter sizes (0.45-μm and molecular weight cut-off [MWCO] filters) were employed to elucidate the particulate nature of the thorium measured in the electrolyte solutions.

Soil Fractionation

Samples of clean and thorium-containing soil were fractionated using standard dry sieving techniques to determine if the thorium was concentrated in specific grain size fractions. Dry sieving was used to minimize thorium redistribution by particle size that might occur during a wet sieve procedure. Seven 10-cm soil sieves (American Society for Testing and Materials [ASTM] no. 20, 40, 60, 80, 100, 120, and 200) were used to create eight soil fractions for analysis and quantify the soil grain size distribution. These soil fractions were exposed to the same extraction and digestion procedures described below for the bulk soils.

Aqueous Extraction

Batch desorption experiments were conducted at three pH values (low [0.1 M HNO₃], neutral [deionized water], and high [0.1 M KOH]) to determine the solubility of thorium under various pH conditions. In this study, the desorption of thorium from the soil into a neutral aqueous solution at equilibrium was measured and the data used to generate an effective K_d for thorium. The value obtained is termed an “effective” or “apparent” K_d (Langmuir, 1997) because the nature of the thorium measured (as dissolved, 0.45-μm, compared with 0.22-μm filtration) was at least partly colloidal. The concentrations measured were influenced by complexation reactions and colloids; consequently, pure “desorption” phenomena (which the K_d is a measure of) are not dominant in this system.

Thorium-containing soil was combined with the three pH solutions in polyethylene containers. Varying soil to solution ratios indicated that less than 1:20 was required for quantifiable thorium concentrations; therefore, 1:10 was chosen for this work. The solutions were mixed using a reciprocating shaker for 24 h (USEPA, 1999), separated by centrifugation and filtration (0.45-μm), acidified, and analyzed for thorium and uranium using ICP–MS.

Soil Digestions

Digestions were performed to determine concentrations in the bulk thorium-containing (1.74 Bq/g) and clean (0.074 Bq/g) soils and the fractionated soils. The digestion procedure was modified from Method 3050B (USEPA, 1996) and used 1.0 g of soil. The digestion method used 10 mL of concentrated nitric acid + 10 mL of concentrated hydrochloric acid with gentle heating (approximately 40°C) for 1 h in a fluoropolymer

beaker. The samples were then allowed to heat overnight, followed by addition of 10 mL of concentrated nitric acid and dilution to 100 mL with 1% nitric acid. This solution was then filtered and diluted 1:10 for ICP–MS analysis. The digestion method yielded thorium concentrations > 80% of that from a total dissolution method using hydrofluoric acid that digests refractory silicates.

Wind and Water Erosion

To determine the extent of bulk soil movement on the migration of thorium, the contaminated soil was exposed to wind and surface water erosion in a fabricated laboratory erosion box (30 × 30 × 60 cm). For these experiments, a 10- × 10- × 2.5-cm galvanized container was packed with moist soil (approximately 20% moisture) to approximately 0.5 cm above the container edge and allowed to dry and cure for several days. Air-drying before wind erosion experiments also minimized mass lost from evaporation. The sample was then subjected to wind from a 10- × 0.2-cm tube that generated air speeds up to 100 km/h. The wind tube impinged on the soil sample at approximately 20 degrees (Grau, 1993). Corresponding mass loss from the sample was determined by weighing before and after erosion with the eroded material captured in a laboratory vacuum/filter system. The material eroded by the wind treatment captured in the filter system was recovered for subsequent water extraction experiments.

The water erosion experiments used a similar design to deliver the water to the sample set at an angle of 5 degrees, with total inundation rates of up to 2.5 cm/h, which should simulate storm conditions of the field site. This would approximate conditions in erosion gullies of the field site (Larson et al., 2004). The runoff was collected for thorium analysis in filtered and unfiltered samples. Between erosion experiments, samples were also weathered by freezing (dry, and moist approximately 10% water added), heating (100°C for 12 h), and exposure to UV light (1200 mol photons/m²/s for 12 h), to simulate field site conditions (Albuquerque, NM; 100°C represented accelerated weathering conditions).

Plant Uptake

Plant uptake studies were conducted to ascertain whether indigenous plant species would take up thorium from soil (Zararsiz et al., 1997; Sturgis and Lee, 1999; Sturgis et al., 2001, 2002; Tome et al., 2002; McClellan et al., 2003). Three perennial, drought-tolerant, low-water-use species were grown from seed in clean and thorium-containing site soil to evaluate seed germination and plant thorium uptake. The species were Indian ricegrass [*Achnatherum hymenoides* (Roemer & J.A. Schultes) Barkworth], alkali sacaton [*Sporobolus airoides* (Torr.) Torr.], and New Mexico feathergrass [*Hesperostipa neomexicana* (Thurb. ex Coult.)]. All seeds were purchased from Sharp Bros. Seed Company (Healy, KS).

All pots (10 cm) used to grow the plants were prepared by placing muslin cotton cloth in the bottom to prevent the loss of soil. The soil was moistened before being added to the pots. Ten seeds of a single plant species were added to a pot. All seeded pots were placed, in a randomized block design, in a 1.22- × 2.44-m aluminum drying flat lined with sorbent plastic-back paper, on tables in a greenhouse under grow lights. Lights were arranged in a pattern of alternating high-pressure sodium and high-pressure multivapor halide lamps that provided an even photosynthetic active radiation (PAR) distribution pattern of 1200 mol photons/m²/s, and a daylength of 16 h. The temperature in the greenhouse was maintained at 32 ± 5°C during the day and 21 ± 5°C minimum at night. Relative

Table 1. Thorium and uranium concentrations from a nitric-hydrochloric acid digestion and total organic carbon (TOC) as a function of size in Kirtland soil.

ASTM sieve no.	Clean			Thorium-containing				
	Size fraction	Th	U	TOC	Soil fraction	Th	U	Soil fraction
	μm	mg/kg		%	mg/kg		%	
20	bulk†	5.8	0.6	1.7	100	364	7.5	100
	>850	3.0	0.5		1	553	6.2	7
40	425-850	4.1	0.4	3.4	8	1688	25.9	8
60	250-425	5.8	0.6	1.3	7	857	12.4	9
80	180-250	5.1	0.5	0.6	8	476	7.3	7
100	150-180	5.5	0.3	0.6	8	275	4.5	7
120	120-150	4.1	0.3	0.5	31	190	3.2	22
200	75-120	6.0	0.5	0.5	20	161	2.8	21
	<75	4.4	0.4	0.6	17	311	5.1	19

† The bulk soil has an organic carbon content of approximately 0.6%.

humidity was maintained as close to 100% as possible, but never less than 50%.

Emerged seedlings were counted after 7, 14, and 21 d to determine mean seed germination percentages. The plant seedlings were allowed to grow and develop for an additional 5 wk to evaluate plant thorium uptake and appearance. After 8 wk, all plants were photographed and harvested. The plants were cut just above the soil surface, washed (if needed) to remove any soil particles, and then blotted to remove excess water. The plant material was bagged, weighed, dried, and reweighed to determine fresh and dry biomass before digestion (modified from Method 3050B; USEPA, 1996) and thorium analysis by ICP-MS.

RESULTS AND DISCUSSION

Soil Digestions

Thorium and uranium concentrations for the bulk and fractionated soils are given in Table 1. Total thorium concentrations using a hydrofluoric acid total dissolution were approximately 450 and 8.5 mg/kg in the thorium-containing and clean soils, respectively. Also shown in Table 1 are the soil total organic carbon (TOC) concentrations by particle size. There is a relation between TOC values and thorium concentrations (correlation coefficient of 0.952), suggesting an association of thorium with NOM (Murphy et al., 1999). Similar relationships are discussed below in the aqueous extraction and electrokinetic experiment discussions.

Column Leachates

Results of the column leach experiments are summarized in Fig. 2. Figure 2A shows data from the columns packed only with thorium-containing soil, whereas Fig. 2B shows data from the columns packed with a layer of clean soil on the bottom half. As was expected from the insoluble nature of thorium, very little thorium is leached from the soil with deionized water. Because of the low flow volumes from the columns (approximately 2 mL/d) and the ICP-MS volume requirement for analysis (approximately 5 mL), the samples were diluted 1:5 for most analyses. This large dilution resulted in some apparent detections of thorium in the column leachates (approximately 3 $\mu\text{g/L}$); however, on reanalysis of the samples with a 1:1 dilution, it was seen that these concentrations were at or below the estimated detection limit of 0.5 $\mu\text{g/L}$. The major difference be-

tween the two column experiments is that the bottom layer of clean soil appears to retard uranium leaching as shown in Fig. 2B. The lower uranium concentration in Fig. 2B indicates that sorption could be a factor in thorium immobilization in this system; however, the data ultimately show little thorium will be mobilized vertically in the soil.

Aqueous Extractions

Soil extractions were intended to build on the previous column leaching studies to determine the effect of pH on thorium release from the soil. The thorium and uranium concentrations for the three extraction fluids for the bulk and fractionated soils are provided in Table 2.

The data in Table 2 show that low-pH solutions generally extract the most thorium into the "dissolved phase" (0.45- μm filtration), although large concentrations of thorium are also seen in the alkaline extractions of the size fractions containing high total organic C concentrations (see Table 1). Use of 0.2- compared with 0.45- μm filters shows the colloidal nature of the extracted thorium with lower concentrations seen with smaller filter pore sizes. The concentration differences with filter pore

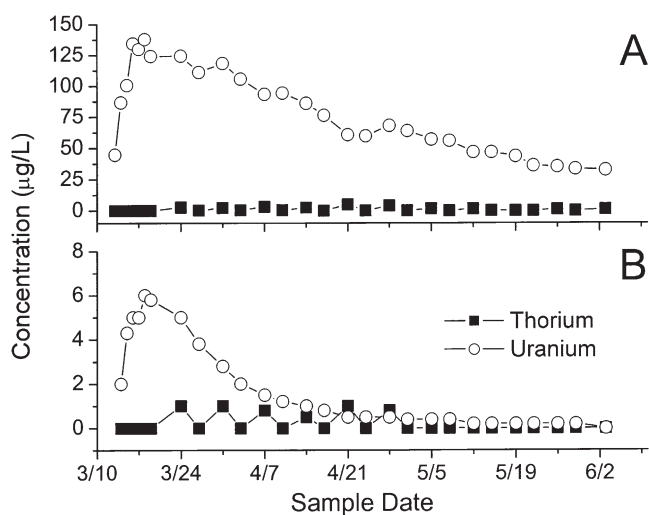


Fig. 2. Thorium and uranium concentrations ($\mu\text{g/L}$) in column leach experiments over approximately 3 mo. (A) Column packed with thorium soil only. (B) Column packed with a layer of clean soil below the thorium soil.

Table 2. Thorium and uranium concentrations in three different pH aqueous extraction fluids as a function of particle size in clean and thorium-containing Kirtland soil.†

Extractant size fraction	Clean						Soil fraction	Thorium-containing						Soil fraction
	Extractant							Extractant						
	Acid		Neutral		Base			Acid		Neutral		Base		
Th	U	Th	U	Th	U	Th	U	Th	U	Th	U	Th	U	
µm	µg/L												%	
Bulk (0.22 µm)	1.3	4.2	0.5	BDL‡	0.9	BDL	100	15.0	34.7	2.4	1.5	6.6	BDL	100
Bulk (0.45 µm)	1.4	4.3	1.1	BDL	0.9	BDL	100	13.9	34.6	6.5	1.6	10.2	BDL	100
>850	2.9	2.3	1.2	BDL	2.1	BDL	1	569	235	475	9.1	2939	50.5	7
425–850	1.2	3.5	1.2	BDL	1.7	BDL	8	306	86	406	9.2	49.7	1.3	8
250–425	1	2.8	1.1	BDL	1	BDL	7	5.8	17.7	9.9	1.6	3.9	BDL	9
180–250	0.9	2.8	1.3	BDL	1	BDL	8	10.7	32.3	4.9	1.1	3.4	BDL	7
150–180	0.9	2.9	0.9	BDL	0.8	BDL	8	14.3	36.6	7.5	1.3	3.7	BDL	7
120–150	0.9	3.7	0.9	BDL	0.9	BDL	31	14.9	41.8	9.7	1.7	5.6	BDL	22
75–120	0.8	4.2	0.7	BDL	1	BDL	20	17	53.4	13.7	2.1	7	BDL	21
<75	0.9	4.1	0.7	BDL	1.1	BDL	17	25.3	101.4	32.4	3.2	14.4	0.5	19

† Solutions were filtered to 0.45 µm unless specified as 0.22 µm.

‡ Below detection limit (approximately 0.5 µg/L).

sizes were primarily seen in the neutral and alkaline extractions (Table 2). The higher thorium concentrations in the acidic solutions are explained by proton-assisted dissolution of inorganic thorium oxide particles, as is expected with many metals. Substantial thorium concentrations in the alkaline solutions are thought to be the result of thorium associated with natural organic matter extracted from the soil at high pH since thorium oxide is not amphoteric (Lenhart et al., 2000; Hyde, 1960).

Using the thorium concentrations from the neutral aqueous extractions (deionized water) in Table 2, an effective or apparent K_d can be calculated for thorium in this soil system (Langmuir, 1997; Kaplan and Serkiz, 2001). Assuming that desorption processes are entirely responsible for the observed concentrations, and using the method described by Langmuir (1997) for the linear Freundlich isotherm, a value of approximately 7×10^7 mL/g is obtained for this system. This value is approximately three to four orders of magnitude higher than K_d values reported for thorium in pure metal oxyhydroxide systems (Langmuir, 1997; Kaplan and Serkiz, 2001). The

experiments suggest a nondissolved-phase mechanism may be controlling thorium concentration in the system, not pure adsorption–desorption or dissolution phenomena, in addition to complexation with other soil constituents and pH buffering effects (Zhang et al., 1997; Casas et al., 1998).

Electrokinetic Experiments

Data presented in Fig. 3 and 4 show the concentration of thorium in the electrolyte solutions as a function of time. The cyclical nature of the increase is caused by the weekly changing of the cell fluids. Substantial concentrations of thorium are only measured in the anode solution of the cell containing only contaminated soil (Fig. 3). A small amount of thorium is also seen in the anode of Cell B, which contains clean soil on the anode side; this solution also shows cyclical increases, although at an order of magnitude lower concentrations (Fig. 4). This experiment demonstrates the anionic nature of thorium migration in the soil because of the accumulation in the anode solution. It further demonstrates the ability of the clean soil (in Cell B) to retard ion mobility by

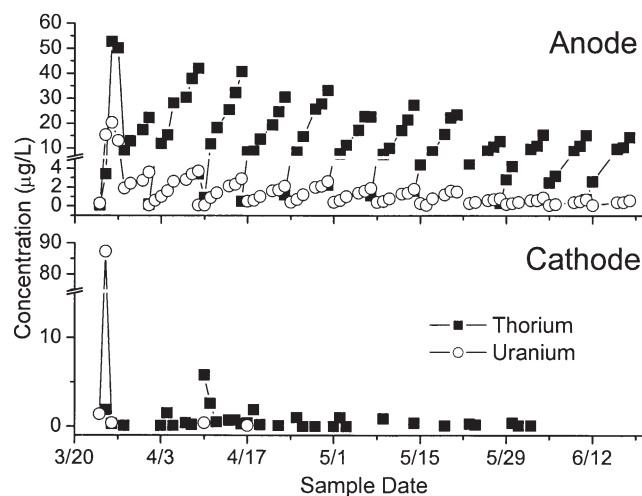


Fig. 3. Thorium and uranium concentrations in electrokinetic experiments over approximately 3 mo in Cell A. Weekly changing of cell fluids produces the observed cyclical increases.

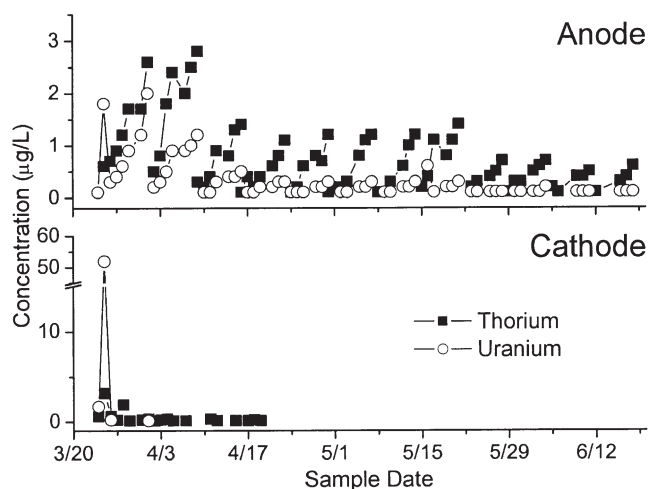


Fig. 4. Thorium and uranium concentrations in electrokinetic experiments over approximately 3 mo in Cell B. Weekly changing of cell fluids produces the observed cyclical increases.

Table 3. Thorium and uranium concentrations using three different filtration sizes in electrokinetic electrode fluids.

	Filter size†					
	0.45 μm		100K MWCO		10K MWCO	
	Th	U	Th	U	Th	U
	$\mu\text{g/L}$					
	21 May 2003 Cell A sample					
Anode	23.4	1.5	19.0	1.5	7.1	1.3
Cathode	BDL‡	BDL	BDL	BDL	BDL	BDL
	21 May 2003 Cell B sample					
Anode	1.4	BDL	1.0	BDL	BDL	BDL
Cathode	BDL	BDL	BDL	BDL	BDL	BDL

† Molecular weight cut-off (MWCO) filter sizes are in amu (100K = 100 000).

‡ Below detection limit (approximately 0.5 $\mu\text{g/L}$).

sorption, as was seen with uranium in the column leach experiments. Uranium concentrations, at much lower levels, mirror those of thorium in the Cell A anode solution. Additionally, the large spike of uranium seen in both cathode solutions on Day 2 possibly represents uranium-carbonate complexes extracted before the infiltration of the hydroxide front into the soil (Chen and Yiacoumi, 2002).

The anionic nature of thorium migration in these experiments at low pH in the anode solutions supports thorium association with natural organic matter, as suggested by the alkaline soil extractions of the fractionated soil described previously (see Table 3). Furthermore, the molecular weight cut-off (MWCO) filtration data in Table 3 also suggest NOM association, with decreased thorium concentrations seen with smaller filter pore sizes, whereas the uranium concentrations reflect what would be expected for a “dissolved” constituent (Lenhart et al., 2000). After approximately 3 mo of applied electric field, only a small fraction (<0.01%) of the thorium had been removed from the soil, thereby suggesting that amending the soil with organic chelating agents may speed up electromigration of thorium in these experiments.

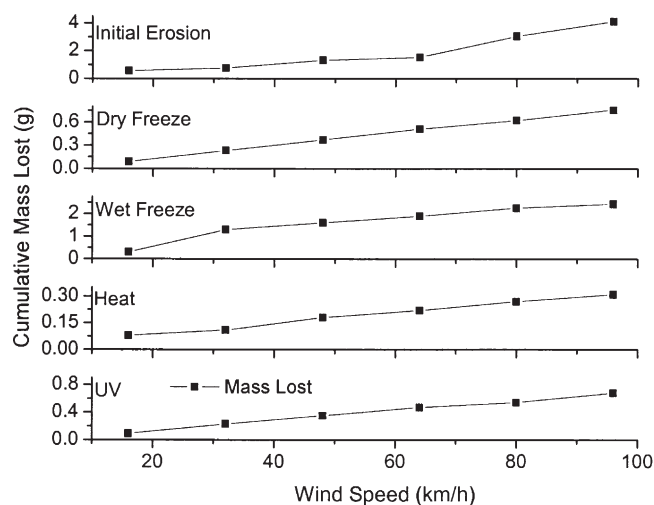
Wind and Water Erosion

Results of the wind erosion experiments are listed in Table 4 with cumulative mass lost shown in Fig. 5. Soil test casts were exposed to various wind speeds for specific time intervals and then weighed to determine mass lost. With wind speeds as low as 30 km/h, substantial amounts of soil are mobilized, particularly after wet freeze-thaw weathering of the soil, which could result in mobilization of thorium. The wet freeze-thaw weathering in Fig. 5 creates the most erodible material; however, UV exposure also tends to promote erosion, possibly by degradation of soil organic matter (Goldstone et al., 2002).

Water erosion data are presented in Table 5. These

Table 4. Mass of soil lost from wind erosion from a single clean Kirtland soil exposed to various weathering treatments.

	Initial mass	Erosion after curing	Erosion after dry freeze	Erosion after wet freeze	Erosion after baking	Erosion after UV exposure
Soil mass, g	590.76	5.23	1.73	4.07	0.55	1.48
% Lost	—	0.88	0.29	0.69	0.09	0.25

**Fig. 5. Mass lost from soil sample after exposure to various weathering events and erosion by different wind speeds.**

water runoff samples were generated by application of 2.5 cm/h of deionized water onto the soil samples resting at an angle of approximately 5 degrees. The samples were eroded in two stages, the first started with the soil initially dry with the second stage starting with saturated soil, to simulate rainfall runoff from two different soil conditions. The results from the unfiltered and 0.22- μm filtered samples (Table 2) indicate that colloidal transport of thorium from the soil is a potentially significant mechanism, whereas “dissolved phase” mechanisms (0.45- μm filtration) may also be important. Similar filtration effects were seen in the electrokinetic results previously discussed.

Plant Uptake

The data listed in Table 6 show the extent of thorium uptake by the three plant species evaluated. In two of the plant species, there was a slight indication of uptake in the thorium-containing soil (8.2 mg/kg) compared with the clean soil (<0.1 mg/kg); however, due to poor germination and growth of Indian ricegrass, the experiment was not conclusive and could not determine if thorium uptake is a major mechanism of migration for all plant species that may be at the site. Additionally, in the field, perennial plants would have many years to accumulate thorium, thereby causing this 8-wk experiment to possibly underestimate plant uptake results (Tome et al., 2002). Therefore, coupling the demonstrated potential for plant uptake with the previously presented wind erosion data, it is possible that windblown detrital plant material is also a mobility mechanism.

CONCLUSIONS

The work presented here shows the importance of nondissolved phase mobility mechanisms for thorium in

Table 5. Thorium concentrations from surface water erosion of Kirtland soils.

Soil	Filtered		Unfiltered	
	Initially dry soil	Initially wet soil	Initially dry soil	Initially wet soil
Clean	1.4	BDL†	0.8	0.8
Thorium-containing	3.6	1.2	15.8	8.0

† Below detection limit (approximately 0.5 µg/L).

Table 6. Plant tissue thorium concentration after 8 wk of exposure to Kirtland soils.

Soil	Plant species		
	Alkali sacaton	New Mexico feathergrass	Indian ricegrass
Clean	BDL†	BDL	IS‡
Thorium-containing	8.2 ± 3.5	4.3 ± 3.7	BDL

† Below detection limit (approximately 0.1 mg/kg).

‡ Insufficient sample for analysis because of poor plant growth.

soil. Complexation with NOM is a likely factor affecting aqueous “dissolved” thorium concentrations. Vertical migration of dissolved thorium through the soil column would most likely be hindered by sorption processes. Vertical colloidal mobility seems to be minimal; however, colloidal transport of thorium in surface water runoff is suggested. Wind and surface water runoff may also be significant transport mechanisms for the site by causing movement of bulk thorium-containing soil and possibly detrital plant material. Complexation with NOM could also explain the plant uptake observed; however, a more in-depth study is required to determine the mechanisms of thorium uptake by plants. Based on the results of experiments reported herein, work is proceeding to develop viable remediation schemes involving soil stabilization techniques to lower thorium bioavailability and bulk soil movement while maintaining the functionality of the training site.

ACKNOWLEDGMENTS

The use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government. The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the RangeSafe and Environmental Quality Technology Programs of the United States Army Corps of Engineers by the USAERDC. Permission was granted by the Chief of Engineers to publish this information. The authors also thank Mr. John Ballard and Ms. Susan Bailey of the USACE for their editorial comments.

REFERENCES

Acar, Y.B., R.J. Gale, G. Putnam, J. Hamed, and R. Wong. 1990. Electrochemical processing of soils: Theory of pH gradient development by diffusion migration and linear convection. *J. Environ. Sci. Health Part A Environ. Sci. Eng.* A25:687–714.

August, R.A., G.W. Phillips, M. Harper, M. Nelson, and S. Gann. 1999. Mixed waste characterization in soil. *Nucl. Instrum. Methods Phys. Res. Sect. A* 422:767–772.

Baumann, T., S. Muller, and R. Niessner. 2002. Migration of dissolved heavy metal compounds and PCP in the presence of colloids through a heterogeneous calcareous gravel and a homogeneous quartz sand—Pilot scale experiments. *Water Res.* 36:1213–1223.

Burlo, F., I. Guijarro, A.A. Carbonell-Barrachina, D. Valero, and F. Martinez-Sanchez. 1999. Arsenic species: Effects on and accumulation by tomato plants. *J. Agric. Food Chem.* 47:1247–1253.

Casas, I., J. de Pablo, J. Gimenez, M.E. Torrero, J. Bruno, E. Cera, R.J. Finch, and R.C. Ewing. 1998. The role of pe, pH, and carbonate on the solubility of UO₂ and uranite under nominally reducing conditions. *Geochim. Cosmochim. Acta* 62:2223–2231.

Chen, J.P., and S. Yiacoumi. 2002. Modeling of depleted uranium transport in subsurface systems. *Water Air Soil Pollut.* 140:173–201.

Dutre, V., C. Kestens, J. Schaep, and C. Vandecasteele. 1998. Study of the remediation of a site contaminated with arsenic. *Sci. Total Environ.* 220:185–194.

Goldstone, J.V., M.J. Pullin, S. Bertilsson, and B.M. Voelker. 2002. Reactions of hydroxyl radical with humic substances: Bleaching, mineralization, and production of bioavailable carbon substrates. *Environ. Sci. Technol.* 36:364–372.

Grau, R.H. 1993. Evaluation of methods for controlling dust. *Tech. Rep. GL-93-25*. U.S. Army Eng. Res. and Development Center, Vicksburg, MS.

Hyde, E.K. 1960. The radiochemistry of thorium. *Natl. Academy of Sci. Publ. NAS-NS 3004*. U.S. Atomic Energy Commission, Washington, DC.

Kaplan, D.I., and S.M. Serkiz. 2001. Quantification of thorium and uranium sorption to contaminated sediments. *J. Radioanal. Nucl. Chem.* 248:529–535.

Korobkov, I., S. Gambarotta, and G.P.A. Yap. 2003. The first thorium arene complex: A divalent synthon. *Angew. Chem. Int. Ed. Engl.* 42:814–818.

Langmuir, D. 1997. *Aqueous environmental geochemistry*. Prentice Hall, Upper Saddle River, NJ.

Larson, S.L., J.H. Ballard, A.J. Bednar, M.G. Shettlemore, C. Christodoulatos, R. Manis, J.C. Morgan, and M.P. Fields. 2004. Evaluation of thorium-232 distribution at Kirtland Air Force Base, Defense Nuclear Weapons School, Training Site 4. U.S. Army Eng. Res. and Development Center, Vicksburg, MS (in press).

Lenhart, J.J., S.E. Cabaniss, P. MacCarthy, and B.D. Honeyman. 2000. Uranium (VI) complexation with citric, humic, and fulvic acids. *Radiochim. Acta* 88:345–353.

Martinez-Aguirre, A., and R. Perianez. 2001. Sedimentary speciation of U and Th isotopes in a marsh area at the southwest of Spain. *J. Radioanal. Nucl. Chem.* 247:45–52.

McClellan, Y., R. August, J. Gosz, S. Gann, R. Parmenter, M. Nelson, and M. Harper. 2003. Uptake rates of thorium progeny in a semiarid environment. *J. Environ. Qual.* 32:1759–1763.

Morton, L.S., C.V. Evans, and G.O. Estes. 2002. Natural uranium and thorium distributions in podzolized soils and native blueberry. *J. Environ. Qual.* 31:155–162.

Mortvedt, J.J. 1994. Plant and soil relationships of uranium and thorium decay series radionuclides—A review. *J. Environ. Qual.* 23: 643–650.

Murphy, R.J., J.J. Lenhart, and B.D. Honeyman. 1999. The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. *Colloids Surf. A* 157:47–62.

National Weather Service. 2004. National Weather Service Weather Forecast Office, Albuquerque, New Mexico [Online]. Available

- at www.srh.noaa.gov/abq/ (verified 15 June 2004). NWS, Silver Spring, MD.
- Neck, V., M. Altmaier, R. Müller, A. Bauer, T. Fanghänel, and J. Kim. 2003. Solubility of crystalline thorium dioxide. *Radiochim. Acta* 91:253–262.
- Orcino, M.A., and R.M. Bricka. 1998. Electrochemical remediation of heavy metal contaminated soils. *J. Environ. Cleanup Costs Technol. Techniques* 9:23–47.
- Pamukcu, S., and J.K. Wittle. 1992. Electrokinetic removal of selected heavy metals from soil. *Environ. Prog.* 11:241–250.
- Puppala, S.K.V. 1994. Evaluation of saturation effects and selected enhancement techniques in electrokinetic soil remediation. Thesis. Louisiana State Univ. and the Agric. and Mechanical College, Dep. of Civil and Environ. Eng., Baton Rouge.
- Rodriguez, P.B., F.V. Tome, and J.C. Lozan. 2002. About the assumption of linearity in soil to plant transfer factors for uranium and thorium isotopes and ^{226}Ra . *Sci. Total Environ.* 284:167–175.
- Sturgis, T.C., and C.R. Lee. 1999. Manufactured soil screening test. DOER Tech. Notes Collection TN DOER-C-6. U.S. Army Eng. Res. and Development Center, Vicksburg, MS.
- Sturgis, T.C., C.R. Lee, and H.C. Banks, Jr. 2001. Evaluation of Toledo Harbor dredged material for manufactured soil. Phase I: Greenhouse bench-scale. Tech. Rep. ERDC/EL TR-01-25. U.S. Army Eng. Res. and Development Center, Vicksburg, MS.
- Sturgis, T.C., C.R. Lee, H.C. Banks, Jr., K. Johnson, J.P. Langan, S.I. Rees, and C. Dyess. 2002. Evaluation of manufactured soil using dredged material from confined placement facilities in Mobile, Alabama. Phase I: Greenhouse bench-scale test. Tech. Rep. ERDC/EL TR-02-12. U.S. Army Eng. Res. and Development Center, Vicksburg, MS.
- Tome, F.V., P.B. Rodriguez, and J.C. Lozano. 2002. Distribution and mobilization of U, Th, and ^{226}Ra in the plant-soil compartments of a mineralized uranium area in south-west Spain. *J. Environ. Radioact.* 59:41–60.
- USEPA. 1996. Acid digestion of sediments, sludges, and soils. SW-846 Method 3050B. USEPA, Washington, DC.
- USEPA. 1998. Inductively coupled plasma mass spectrometry. SW-846 Method 6020A. USEPA, Washington, DC.
- USEPA. 1999. Understanding variation in partition coefficient, K_d , values. Vol. 1 and 2. EPA 402-R-99-004A and 402-R-99-004B. USEPA, Washington, DC.
- Zararsiz, A., R. Kirmaz, and P. Arikan. 1997. Field study on thorium uptake by plants within and around of a thorium ore deposit. *J. Radioanal. Nucl. Chem.* 222:257–262.
- Zhang, Y.J., N.D. Bryan, F.R. Livens, and M.N. Jones. 1997. Selectivity in the complexation of actinides by humic substances. *Environ. Pollut.* 96:361–367.