

Mobilization of transuranic radionuclides from disposal trenches by natural organic matter

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Abstract

Transuranic (TRU) radionuclides in groundwater at the Oak Ridge National Laboratory migrate rapidly and with little retardation of the radionuclides over distances of 80 m. Several interacting hydrogeochemical processes contribute to the observed releases of actinides (²⁴⁴Cm and ²⁴¹Am) from the shallow unlined disposal trenches, through the highly weathered, fractured shale (saprolite) and to the surface-water seeps at White Oak Creek. Major releases are promoted when seasonal fluctuations in the water table permit groundwater to contact actinide-contaminated waste. Local recharge of stormwater into the trenches appears to permit minor releases, perhaps due to transient saturation within the trenches but above the local water table. Although the hydrogeology of the site permits contact of the TRU waste with the groundwater, the expected inorganic species of the actinides should strongly adsorb to the layer silicates and mineral oxides of the shale saprolite. Yet the timing of the actinide releases relative to when rising groundwater intercepts the trenches suggests that actinide transport is rapid, and the relative magnitude of peak actinide levels in wells near the trenches and at downgradient seeps suggests that there is very limited retention of the actinides by the formation. Based on anion exchange chromatography of the groundwater and geochemical modeling, the mobilization and transport of the actinides is demonstrated to result from complexation of the actinides by natural organic matter (NOM). Storm events contribute to mobilization by promoting hydrologic links between the TRU waste and groundwater, and by increasing the concentration of NOM in the mobile soil and groundwater. This study demonstrates that even in formations characterized by abundant mineral phases

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known to strongly adsorb actinides, the actinides can be transported essentially conservatively as NOM complexes. © 1998 Elsevier Science B.V.

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1. Introduction

The Oak Ridge National Laboratory (ORNL), located in eastern Tennessee, has been operational since 1943 as a multidisciplinary facility for production and research related to nuclear materials. Beginning with the production of materials for nuclear weapons for the Manhattan Project in World War II, and continuing with the production and separation of radioactive isotopes for a variety of weapon- and energy-related activities, the site has been used for the disposal of waste contaminated with an array of radionuclides. While this legacy creates obvious problems and concerns with migration of radionuclides to the biologically accessible environment, it also provides opportunities to examine mechanisms of radionuclide transport at the field-scale that may lead to improved strategies for remediation and for containment of future waste.

The current study focuses on the migration of transuranic (TRU) radionuclides, specifically the actinide elements, curium-244 and americium-241 (Ashwood and Marsh, 1994), from unlined trenches through a shallow fractured groundwater flow system. We postulate that the actinides are mobilized and transported as a result of interacting hydrological and geochemical events, such as (a) seasonal fluctuations in the water table that intercept the shallow disposal trenches and permit contact of groundwater with the actinide-contaminated waste; (b) storm-driven recharge that can lead to transient saturation of trenches above the local water table; and (c) rapid transport and limited retention of the mobilized actinides due to complexation with natural organic matter (NOM) in the groundwater.

The mobilization scenario is initiated by the rising water table that typically occurs in east Tennessee during the winter and early spring due to reduced evapotranspiration after leaf fall, and higher levels of precipitation. The increases in the elevation of the water table can be substantial (several meters) and can permit groundwater to contact the waste. Furthermore, storm-driven recharge not only can lead to transient saturation within trenches, but also mobilizes organic matter in the soil and increases the concentration NOM of the groundwater (Jardine et al., 1990). We postulate that NOM forms an anionic complex with the actinides and that this complex is the mobile form of the radionuclides. Although laboratory studies have shown that both mineral oxides and clays have a high affinity for adsorbing NOM (Davis and Gloor, 1981; Gu et al., 1994; Baham and Sposito, 1994), the actinide–NOM complex is postulated to migrate with minimal adsorption to or retention by the formation because, in the field situation, NOM binding sites on surfaces have been saturated by continuous contact with groundwater NOM (McCarthy et al., 1996a).

This study of actinide transport at WAG-5N constitutes an integrated approach combining field observations, laboratory data and geochemical modeling. Following a

brief description of the study site, we will document the interaction between water elevation and releases of actinides into groundwater. The mobility and limited retention of the actinides will be inferred from the close temporal linkages between storm-driven recharge and spikes in actinide levels in wells and surface water seeps downgradient of the disposal trenches. Finally, the mobile actinides will be shown to be complexed with NOM based on adsorption to and elution from an anion exchange resin as well as geochemical modeling.

2. Hydrogeological setting and contaminant history of WAG-5

Waste Area Group 5 (WAG-5; Fig. 1) lies approximately 0.8 km south of the main plant of ORNL which is one of several sites in the U.S. Department of Energy's Oak

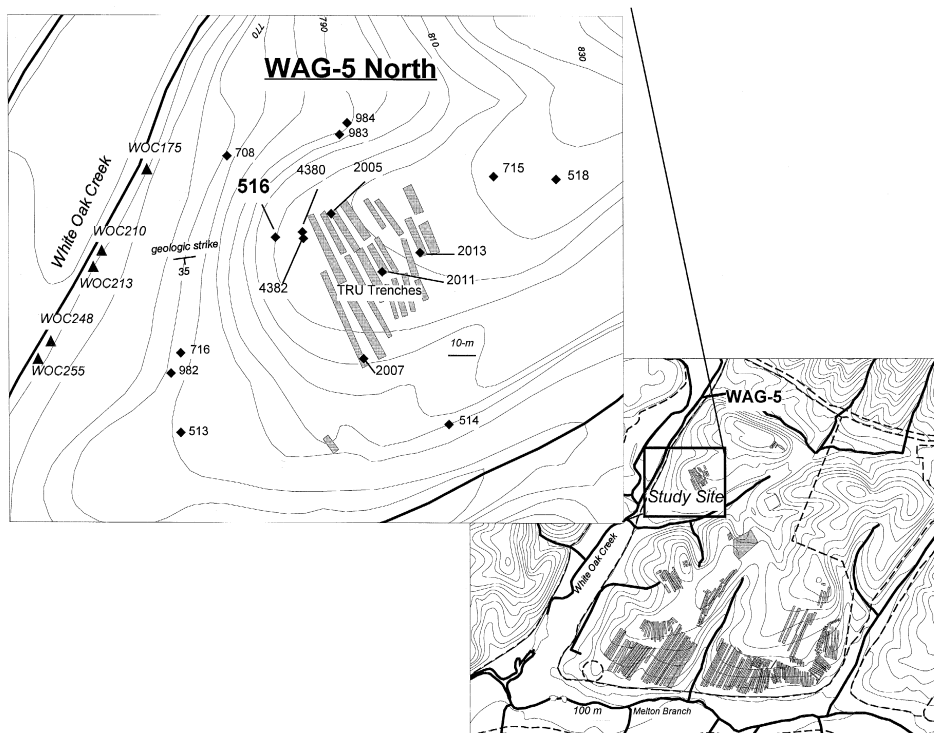


Fig. 1. Map of WAG-5, with an inset showing the location of the WAG-5N study site. The long, shaded rectangles show the location of disposal trenches. The diamonds and numbers shown in the inset identify the monitoring wells at the site. Seeps occur seasonally along the steep bank of White Oak Creek and are designated by triangles and numbers beginning with the prefix 'WOC.' Well 516 is a key monitoring location and is located approximately 15 m from the nearest TRU trench. Surface contours are at 10-ft (3 m) intervals for the large-scale map on the right and at 5-ft (0.52 m) intervals for the inset. The direction of the average strike and dip of the bedding is indicated.

Ridge Reservation (ORR) in Roane and Anderson counties, Tennessee. WAG-5 comprises approximately 32 ha, with 12 ha of forested area and the balance in grassed fields which contain several contaminated source areas, most associated with a solid waste burial ground used from 1959 to 1973 for disposal of low-level radioactive, TRU and fissile wastes, as well as inorganic and organic chemical wastes and biological wastes (Fig. 1).

The ORR is located in the valley and ridge physiographic province in the southern Appalachian fold and thrust belt. The geology of the ORR is dominantly Cambrian and Ordovician siltstones, mudrocks and carbonates. A succession of northeast-trending thrust faults cut across the area, duplicating the Paleozoic sequences. Differential weathering of the carbonates and clastics resulted in a series of alternating valleys and ridges that parallel the surface traces of the thrust faults (Hatcher et al., 1992). WAG-5 is underlain by the interbedded shales and carbonates of the Cambrian-aged Conasauga group. The average strike of the bedding is 35°NE with an average dip of approximately 35°SE, although locally, nearly vertical dips have been observed (USDOE, 1995). Wastes in WAG-5 are buried in the regolith (i.e., the zone between the surface and the unweathered bedrock), and contaminant migration occurs through pathways in, through, or over the soil, saprolite or fill materials that make up the regolith (Solomon et al., 1991; Wilson et al., 1993). Saprolite is the term used for the clay-rich material derived from shale that is thoroughly decomposed by weathering, but retaining much of the original bedding and structural features. The surface and groundwater systems at WAG-5 are closely linked: an active stormflow zone combined with shallow groundwater flow zones creates a system where most of the precipitation that infiltrates the soil is thought to be discharged through shallow flow paths to Melton Branch and White Oak Creek, two streams that border WAG-5 (Fig. 1). The water table varies seasonally and is typically near the bedrock–regolith interface during the late summer and early autumn, and at higher elevations in the regolith during the winter and early spring. Transient-perched water tables can also occur in the upper few meters of the saprolite and there can be significant lateral flow and transport downslope in this so-called stormflow zone (Solomon et al., 1991; Wilson et al., 1993). Annual precipitation is approximately 130 cm/yr.

This study focuses on the northern quadrant of WAG-5 (WAG-5N), which is currently used for storage of TRU solid waste materials (Fig. 1, inset). The Dismal Gap Formation underlying WAG-5N is a series of interbedded lenses of limestone, siltstone and shale. X-ray diffraction and energy-dispersive X-ray analysis of saprolite recovered by augering at WAG-5N demonstrates that mineralogy includes secondary clay minerals such as illite, vermiculite, kaolinite and calcite cements as well as amorphous iron- and manganese-oxide coatings (McCarthy and Elless, unpublished data). Remotely handled TRU (RH-TRU) solid wastes were buried in unlined trenches from 1972 through 1981 (Fig. 2). Most of the RH-TRU wastes were generated at ORNL by processes related to the production and separation of high specific-activity actinide elements (berkelium, californium, fermium and einsteinium), but also included material from hot-cell operations in other facilities at ORNL (Stewart et al., 1989). Much of the RH-TRU solid waste was packaged in concrete casks and placed in trenches 3-m deep, 1.8-m wide and of variable length (Fig. 2). The containers were buried in unlined trenches and backfilled



Fig. 2. Photographs taken during the burial of the waste in the 1970s show the RH-TRU concrete canisters in the unlined trench with a corrugated metal pipe that became one of the 2000-series wells.

with excavated regolith materials; in some trenches, perforated corrugated metal pipes were placed in the trenches during backfilling, with the bottom at the floor of the trench (the 2000-series wells, Figs. 1 and 2; Table 1). Significant levels of gross-alpha activity has been detected for a number of years in groundwater sampled from monitoring well 516, located approximately 15-m downgradient of the nearest TRU trench (Fig. 1, inset). The primary contributor to the gross-alpha activity is ^{244}Cm , with smaller amounts of

Table 1
Monitoring well details

Well	Date constructed	Surface elevation (m above MSL)	Well depth (m BGS)	Completed interval (m above MSL)	Well construction	Comments
513	1982	237.5	6.1	231.4–234.5	6-in. (15.2-cm) PVC	
514	1982	243.4	9.2	234.3–237.3	6-in. (15.2-cm) PVC	
516	1982	243.7	8.0	235.8–239.8	4-in. (10.2-cm) PVC	
518	1982	250.0	9.8	240.5–243.6	6-in. (15.2-cm) PVC	
715	1986	249.2	12.7	236.7–239.7	2-in. (5.1-cm) PVC	
716	1987	236.5	31.0	205.9–208.9	2-in. (5.1-cm) PVC	
982	1987	236.4	5.0	231.5–234.5	2.1-in. (5.1-cm) SS	RCRA well
983	1987	240.5	7.6	232.9–237.5	2.1-in. (5.1-cm) SS	RCRA well
984	1987	240.6	24.4	216.3–222.4	4-in. (10.2-cm) SS	RCRA well
2005		246.4	3.4	243.1–246.4	perforated CMP	in TRU-trench backfill
2007		244.6	4.0	240.5–244.6	perforated CMP	in TRU-trench backfill
2011		247.0	4.2	242.8–247.0	perforated CMP	in TRU-trench backfill
2013		247.7	3.6	244.1–247.7	perforated CMP	in TRU-trench backfill
4380	1995	245.8	7.3	238.5–241.6	2-in. (5.1-cm) SS	
4382	1995	245.8	9.8	236.1–239.1	2-in. (5.1-cm) SS	

MSL = mean sea level; BGS = below ground surface.

PVC = polyvinyl chloride; SS = stainless steel.

CMP = 9-in. (22.9-cm) diameter corrugated metal pipe.

RCRA = Resource Conservation and Recovery Act.

^{241}Am ; low levels of $^{239/240}\text{Pu}$ and ^{237}Np have also been detected (Ashwood and Marsh, 1994).

3. Methods and materials

Groundwater was sampled from well 516 under two different studies that utilized different methods of sampling. From 1990–1993, the well was sampled under the Active Sites Monitoring Program's documentation of trends in contaminant levels (Ashwood and Marsh, 1994). Under that program, groundwater was retrieved at a high flow rate (several L per minute) following purging of three well volumes using a WaTerra® pump (Solinst, Ontario, Canada). Data from 1994–1996 were collected as part of the current study to evaluate the mechanisms of actinide transport from the TRU trenches. During this study, groundwater samples were obtained from wells using a peristaltic pump and low-flow rates (100 ml/min). Tygon tubing was permanently installed in wells to minimize disturbance prior to sampling. This low-flow-rate sampling method minimizes artifacts due to mobilization of colloidal particles (USEPA, 1994; McCarthy and Shevenell, 1997). Water levels were measured using a water-level meter.

Groundwater samples were analyzed for alkalinity, total organic carbon (TOC), concentrations of cations and anions and gross-alpha radioactivity. Dissolved oxygen (DO) was measured using ChemMetrics ampules with a Hach DR2000 field portable spectrophotometer. TOC samples were preserved by adding HCl to pH 2 and analyzing

with the use of a Shimadzu Model 5000 high-temperature combustion total-organic-carbon analyzer; results are reported as mg-carbon/l. Samples for cation analysis were preserved by using HNO_3 to $\text{pH} < 2$ and analyzed by inductively coupled plasma–atomic emission spectroscopy. Anions were measured using ion chromatography. Alkalinity was measured in the field immediately after sample collection by titration to $\text{pH} 4.5$. Turbidity was measured in the field immediately after collection using a Hach Ratio/XR turbidimeter. Gross-alpha activity was measured by gas proportional counting.

In addition to the analysis of raw unfiltered samples, groundwater was sometimes filtered either by cross-flow filtration using polycarbonate membrane filters (Nucleopore) with nominal $0.2 \mu\text{m}$ pore sizes or tangential flow filtration using Amicon Hollow-Fiber or Spiral Filters with 3000 Dalton molecular weight cut-off. Globular proteins with molecular weights of 3000 Daltons have diameters of approximately 1 nm; this nominal diameter will be referred to in this manuscript. Filtration of water collected from wells was conducted on-line; that is, the groundwater sampling tube was attached to the inlet of the filters, and filtration occurred at the well-head without exposing the sample to the atmosphere. Water samples from seeps in White Oak Creek were collected in the field and filtered in the laboratory using a $0.2\text{-}\mu\text{m}$ Nucleopore filter. Filtrates were analyzed as described above.

Groundwater was also passed through beds of ion-exchange resins. Approximately 1 l of groundwater from well 516 was passed through a large bed of AG-50W-X12 cation-exchange resin (approximately 4-cm diameter and 8-cm high) and the eluent analyzed for gross-alpha activity. Approximately 6 l of groundwater from well 516 were passed through a column (2.5-cm diameter and 6-cm tall) of the weak anion-exchange resin diethylaminoethyl cellulose (DEAE-cellulose), which has been used to isolate humic material in the pH range of 4–8 (Miles et al., 1983; Stuart et al., 1990; Smith et al., 1990). The column was rinsed with distilled water and then adsorbed anions eluted with 0.1 N NaOH, followed by distilled water and 0.1 N HCl. Fractions of the eluent were collected and analyzed for TOC and for gross-alpha radioactivity using a Packard Tri-Carb liquid scintillation counter. Solutions of ^{241}Am (100 ml, with the final ^{241}Am concentration adjusted to approximately 4×10^{-10} M) were also applied to DEAE columns to examine the retention and elution of actinides under controlled conditions. ^{241}Am was prepared either in an artificial groundwater containing an ionic strength, pH and carbonate concentration similar to the well 516 groundwater, or the same solution supplemented with NOM to a concentration of 9.6 mg-C/l, using a well-characterized source of NOM from a wetland pond in South Carolina (McCarthy et al., 1993, 1996a; Gu et al., 1994, 1995).

The effect of storm events on the mobilization of NOM was examined at a subsurface transport facility described by Luxmoore and Abner (1987) and Wilson et al. (1993). The facility is located on a 0.67-ha subcatchment of a proposed solid waste storage area in the Dismal Gap Formation adjacent to WAG-5 and underlain by similar lithology. The facility is unique in that subsurface drainage can be collected and monitored from a 2.5-m deep by 16-m long trench excavated across the outflow region of the subwatershed. In this study, water flow from 1.8- to 2.5-m depth, representing flow in the saprolite below the soil zone, was measured using tipping bucket rain gauges, and samples were analyzed for TOC through several storm events.

4. Geochemical modeling of actinide–NOM interactions

The metal ion-charge neutralization model is used to describe the complexation of the trivalent actinides to humic acid (Kim and Czerwinski, 1996). This model is based on the concept of metal ion-charge neutralization upon complexation to humic acid functional groups. By introducing the operational humic acid concentration and the loading capacity (LC), complexation constants are found which are independent of pH, metal ion concentration and humic acid origin. This is different from a monodentate-binding model. When this model is employed, values are often obtained which vary with metal ion concentration (Bidoglio et al., 1991; Moulin et al., 1992) or pH (Torres and Choppin, 1984). Variations in the conditional complexation constant with experimental conditions from this model can be traced to the definition of the free humic acid concentration. Additionally, many of the evaluations are performed graphically, which tends to preclude speciation. The lack of speciation data complicates intercomparison between different models. When the charge neutralization is not used, the ability to successfully compare data is relegated to calculating the amount of each species from the conditional constants, thereby yielding only conditional results. When the charge neutralization model is used, different conditions can be compared. Therefore, only data derived from the charge neutralization model is applied to this work.

Since the molecular weight of humic acid varies, the concentration must be determined by other means. In this work, the concentration of humic acid is defined as:

$$[\text{HA}(\tau)]_{\text{total}} = \frac{(\text{HA})(\text{PEC})}{\tau} \quad (1)$$

where $[\text{HA}]$ is the humic acid concentration in g/l, PEC is the humic acid proton exchange capacity in eq/g and τ the charge of the complexing metal ion. From Eq. (1) $[\text{HA}(\tau)]_{\text{total}}$ is evaluated in mol/l and is equivalent to the concentration of a metal species of charge τ that can be neutralized by a given amount of humic substance when all the proton-exchanging sites are involved. For aquo trivalent actinides (An), τ is three. For mixed species, τ is the overall charge of the metal ion and secondary ligand; for AnOH τ is two, for $\text{An}(\text{OH})_2$ and AnCO_3 τ is one. The humic acid concentration is expressed as $[\text{HA}(\text{III})]$, $[\text{HA}(\text{II})]$ and $[\text{HA}(\text{I})]$, where the value in parenthesis represents the charge of the complexed species.

The loading capacity (LC) of humic acid, which is a measure of the amount of humic substances available for binding, increases with increasing pH and decreasing ionic strength. The value for LC, which is experimentally found and used to evaluate free humic acid concentration, has a minimum of zero and a maximum of one. The concept of the LC is explained in more detail in Kim and Czerwinski (1996). The general equation for the free humic acid concentration is:

$$[\text{HA}(\tau)]_{\text{free}} = \text{LC}[\text{HA}(\tau)]_{\text{total}} - [\text{AnHA}(\tau)] \quad (2)$$

The estimate of LC for $\text{HA}(\text{III})$ in this work is (Buckau et al., 1992):

$$\text{LC} = 0.279 \text{ pH} - 1.01 \quad (3)$$

Since LC is between zero and one, values under zero are taken as zero, and values over one are taken as one. For the mixed species, it is assumed LC from Eq. (3) is valid. This

assumption may not be entirely correct, but any introduced errors are limited by the relatively low amount of actinide ion.

The chemical parameters for the calculations are taken from the analysis of groundwater over the pH range of 5–9. It should be noted that fulvic acid (FA) is the major organic component of WAG-5N groundwater (Czerwinski, unpublished data). The important parameters are:

- total fulvic acid concentration $[FA(III)] = 2 \times 10^{-6}$ mol/l
- $[An(III)]_{total} = [Cm(III)] + [Am(III)] = 2 \times 10^{-13}$ mol/l
- aqueous carbonate concentration evaluated from the measured alkalinity
- ionic strength at 0.02 M

The total fulvic acid concentration is found from the TOC, the relative concentration of fulvic acid in the TOC ($\sim 75\%$), amount of C in fulvic acid ($\sim 50\%$), the proton-exchange capacity (7.2 meq/g) and the charge ($z = 3$). A number of different trivalent actinide–humate species is considered. It is known that mixed complexes consisting of a metal ion, humate and a secondary ligand can occur (Panak, 1996; Panak et al., 1996; Glaus et al., 1995; Dierckx et al., 1994; Powell and Town, 1991; Buffle, 1980; Manning and Ramamoorthy, 1973). Generally, consideration is given to species where the metal ion and secondary ligand are cationic. In this regard, An^{3+} , $AnOH^{2+}$, $An(OH)_2^+$ and $AnCO_3^+$ can sorb to humic colloids.

The stability constants of the resulting species are taken from the literature and adjusted for complexation with fulvic acid. From literature data, $\log \beta AnHA(III)$ is 6.39 in 0.02 M $NaClO_4$ (Czerwinski et al., 1996). The difference between $\log \beta AnHA(III)$ and $\log \beta AnFA(III)$ is approximately 0.3 (Buckau et al., 1992); therefore, $\log \beta AnFA(III) = 6.09$. The stepwise formation constants for the mixed fulvic species are assumed to be the same as the humic species and are taken from the literature (Table 2; Panak, 1996).

The nonsorbed species are the trivalent actinide hydroxides, carbonates and free ion. The stability constants at 0.1 M ionic strength for the trivalent actinide hydroxides (Wimmer et al., 1992) and carbonates (Meinrath and Kim, 1991) are evaluated at 0.02 M ionic strength with the specific ion interaction theory (Scatchard, 1936; Grenthe et al., 1992) for chloride media:

$$\begin{aligned}\log \beta AnOH &= 6.03 \pm 0.09 \\ \log \beta An(OH)_2 &= 11.72 \pm 0.2 \\ \log \beta AnCO_3 &= 7.25 \pm 0.07 \\ \log \beta An(CO_3)_2 &= 10.38 \pm 0.24\end{aligned}$$

Table 2

Stepwise stability constants for the mixed fulvic species used in speciation calculations (Panak, 1996)

Species	Stepwise reaction ($\log K$)	Stepwise constant	$\log \beta$
$AnFA(III)$	—	—	6.09 ± 0.12
$An(OH)FA(II)$	$AnFA(III) + OH$	6.95	13.04 ± 0.20
$An(OH)_2FA(I)$	$An(OH)FA(II) + OH$	4.20	17.24 ± 0.30
$An(CO_3)FA(I)$	$AnFA(III) + CO_3$	6.65	12.74 ± 0.30

Using the described species, the total humic substance concentration and trivalent actinide concentration can be written as:

$$[\text{FA(III)}]_{\text{total}} = \frac{[\text{FA(III)}]_{\text{free}} + [\text{AnFA(III)}] + \frac{[\text{AnOHFA(II)}]}{1.5} + \frac{[\text{An(OH)}_2\text{FA(I)}]}{3} + \frac{[\text{AnCO}_3\text{FA(I)}]}{3}}{\text{LC}} \quad (4)$$

$$[\text{An(III)}]_{\text{total}} = [\text{An(III)}]_{\text{free}} + [\text{An(OH)}_x] + [\text{An(CO}_3)_x] + [\text{AnFA(III)}] + [\text{AnOHFA(II)}] + [\text{An(OH)}_2\text{FA(I)}] + [\text{AnCO}_3\text{FA(I)}] \quad (5)$$

where $x = 1$ and 2 . Inclusion of the stability constants and solving for $[\text{FA(III)}]_{\text{free}}$ and $[\text{An(III)}]_{\text{free}}$ yield the concentrations of all the species at a given pH. For calculations of speciation in the absence of NOM, the same constants were used but the humics ignored. A sensitivity analysis was also performed on the fulvate complexation and stepwise formation constants, total fulvic acid concentration and LC to determine the effect of parameter uncertainty on estimates of the fraction of fulvic-bound actinides.

4.1. Site-specific stability constants

Preliminary information on the complexation capacity of the groundwater NOM at WAG-5N was obtained using groundwater collected from the subsurface transport facility at ORNL (Luxmoore and Abner, 1987). Groundwater NOM was concentrated by reverse osmosis (Sun et al., 1995). Preliminary binding studies of Cm(III) to the NOM was measured using time-resolved laser fluorescence spectroscopy at pH 6 and 0.1 M ionic strength, in a CO₂-free atmosphere.

5. Results and discussion

5.1. Water elevation and gross-alpha activity in well 516

The pattern of gross-alpha activity in well 516 between 1990 and 1996 is highly irregular, with sharp but transitory increases early in 1990, 1991 and 1994 (Fig. 3). The levels of radioactivity in 1990 and 1991 appear to be much greater than the peak concentration seen in 1994; however, at least some of that disparity may be due to differences in the sampling technique used during the Active Sites Program sampling from 1990–1993 and the low-flow rate sampling used from 1994–1996. The rapid pumping rates used in the Active Sites Program and the disturbance caused by the operation of the WaTerra[®] pump (a WaTerra[®] pump consists of a check valve at the end of the sample tubing and is operated by rapidly moving the tubing up and down in the well, thus forcing water into and up the tubing during each downstroke) may have entrained particles containing adsorbed radionuclides. Both sampling programs, however, document a sharp drop in gross-alpha levels within a few months of the peak levels, followed by long tailing decreases in 1992–1993 and 1995–1996. The elevated levels of gross-alpha activity correlate with years that had above-average precipitation and appear to be directly related to the increased water elevations in well 516 (Fig. 3). This is particularly evident in 1994–1996 when monitoring was more intense. The peak of gross-alpha activity in the spring of 1994 correlates with a sharp increase in the water

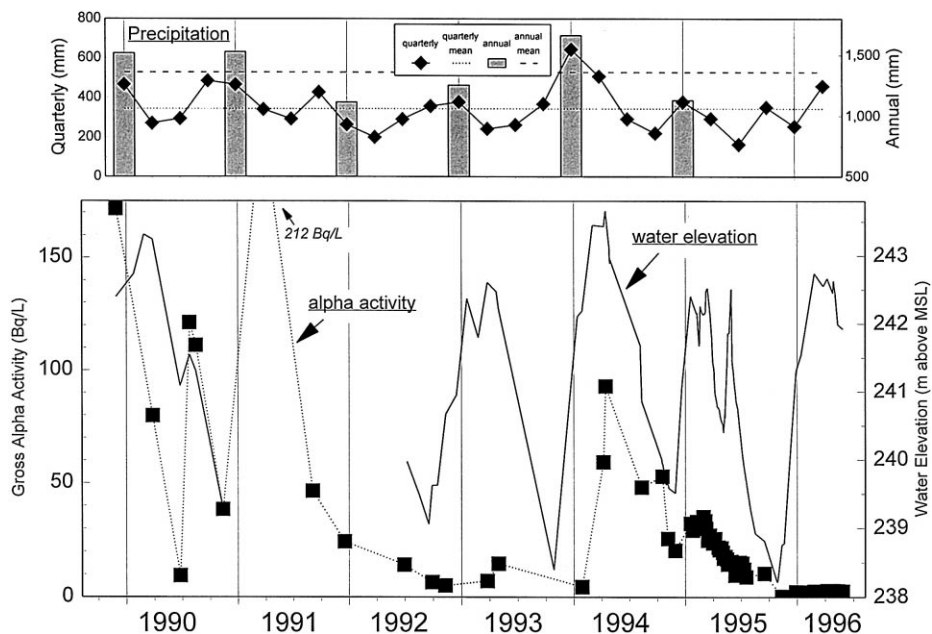


Fig. 3. The temporal pattern of gross-alpha activity and water elevations in well 516 is shown; water elevation was not always recorded when the well was sampled. Also shown is the quarterly and annual precipitation recorded by a National Oceanic and Atmospheric Agency weather station located approximately 6 km from WAG-5. The annual precipitation for a year is shown by the bar at the left grid mark for that year. Quarterly precipitation values are located along the time axis at the beginning of the quarter. The mean annual and quarterly precipitation for the area is also shown by the horizontal line.

elevation, and levels of radioactivity declined later that year as the water level declined. There was another seasonal rise in water elevation at the beginning of 1995, but gross-alpha levels increased only slightly and then resumed a slow tailing decrease. The increasing water elevation in 1996 did not result in any increase in gross-alpha levels. The reasons for this pattern become evident if the water elevation in the TRU trenches upgradient to well 516 is considered.

Contours of the water table in WAG-5N generally reflect the surface contours, with a gentle slope to the water table across the TRU trench area to well 516, and thence with a steeper gradient to White Oak Creek (Fig. 4). Changes in water elevation in well 516 generally reflect changes in the local water table in the TRU trench area (Fig. 5). Water elevations in the trenches (the 2000-series wells) were measured repeatedly only in the winters of 1993 (Fig. 5a) and 1995 (Fig. 5b), years without spikes of elevated gross-alpha activity (note that 'winter of 1993' is intended to refer to the period from approximately November 1992 through the spring of 1993, and so forth for other years). In both those years, no more than few tenths of a meter of water was observed in the wells (the elevation of the bottom of the trenches are shown in dotted lines in Fig. 5b). Similar water elevations were observed in 1996 (data not shown). However, in the spring of 1994, the water elevation in well 516 rose 1.2 m higher than in the winters of

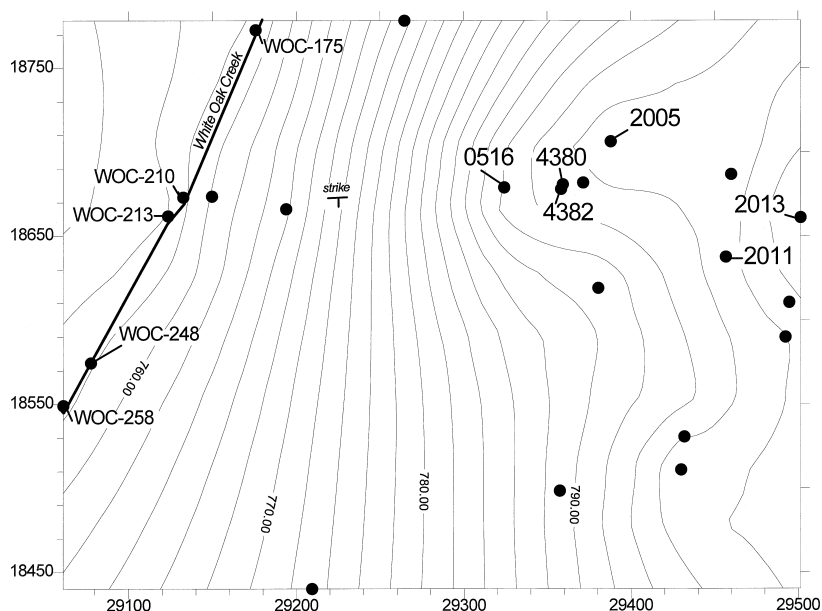


Fig. 4. Contours of the water surface based on water elevation measurements in wells (closed circles) on August 1, 1996. Contours are shown in 2-ft (0.6 m) intervals and were interpolated by kriging using the gridding program in SURFER. The axis are coordinates of the ORNL grid, in feet (0.3 m).

1993, 1995 and 1996 (Fig. 3). The water levels in the trenches would be expected to be correspondingly higher, suggesting that in the spring of 1994, the trenches were inundated to a depth of 1.2 to 2 m. There was one measurement of water elevation in the trenches in April 1994; the water level in well 2005 was at 245.4 m, meaning that 2.1-m tall casks were entirely below the water table.

Most of the RH-TRU casks were fabricated from 4-in. (10 cm) thick concrete drain tiles and are probably not effective at isolating the waste from contact with the groundwater. A worker who had been responsible for burial of the casks reports that he found it impossible to fill an empty cask with water using a garden hose because the water leaked out so rapidly (J. Bolinski, ORNL, personal communication). The integrity of the casks would have been further degraded over the last 25 yrs in the humid soil, especially in the high- SO_4^{2-} environment of the soil and pore water at the site (Atkinson and Hearne, 1990; Rasheeduzzah et al., 1990). The wooden crates can be expected to decay rapidly in the wet soil and the thinner metal canisters could be pierced or crushed as the backfilled material settled, creating opportunities for direct contact between the TRU waste and the groundwater.

Although inundation of the trenches due to the rising water table appears to be the major factor in contaminant mobilization, local recharge may also play a role. The moderate increases in gross-alpha levels in well 516 in early 1995 contrast with the very low levels maintained during the same period in 1996. The discrepancy may be related to differences in the amount and pattern of precipitation in the two years. If precipitation

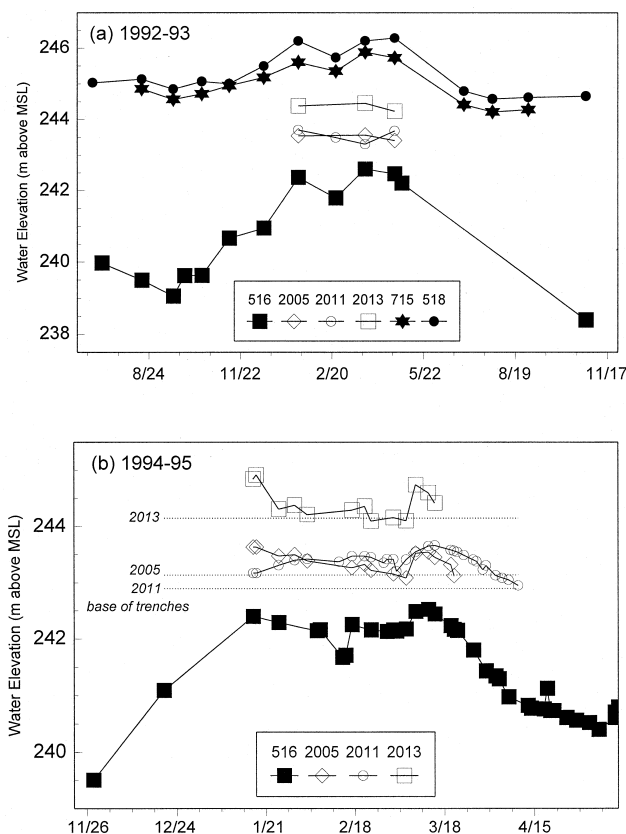


Fig. 5. Water elevations in wells along a transect through the TRU trench area are shown for (a) 1992–1993 and (b) 1994–1995. The absence of data for the 2000-series wells on dates when observations were made for well 516 indicates that the wells were dry. The bottom of the wells is at the floor of the trench and those elevations are shown with the dotted lines in the lower panel.

is faster than the rate of water infiltration through the soil profile, perched water moves laterally downslope through the very shallow stormflow zone. The trenches are oriented perpendicular to the slope of the land surface, and the disturbed backfill material in the trenches could intercept large volumes of stormflow water collected in the recharge area upslope of the trenches (Fig. 1). Since the undisturbed formation surrounding a trench is likely to have a lower hydraulic conductivity than the backfill in the trench, there may be transient periods associated with storm events when the trenches become partially filled with stormwater.

The moderate releases of actinides observed in well 516 in 1995 are likely due to such transient saturation of the trenches above the local water table. There were several large storms in first part of 1995, including a 10-cm event in January 1995. There is some indication of formation of a perched water table within the trenches containing wells 2013 and 2011 in early March, 1995; water levels increased approximately 45 cm

within 3 days following a 5.9 cm rain event and then drained over the next week (Fig. 5b). In 1996, although the total amount of precipitation was only slightly less than the previous year, the pattern of rainfall was different. Precipitation in the first quarter of 1996 tended to be slow, steady rains with no storm involving more than 4 cm of precipitation and most less than 2.5 cm. If the low-intensity rains were able to infiltrate through the soil profile rather than forming a perched stormflow zone, the trenches would remain unsaturated and this could account for the low actinide levels released in 1996.

Data are sparse in 1990 and 1991, but the patterns are consistent with the interpretation above. Both years appeared to have major releases of radionuclides, and both years had greater-than-normal levels of precipitation (Fig. 3, upper panel), especially in the winter and spring when the storms would raise the local water table and possibly cause additional transient increases in the water elevation within the trenches through intercepted stormflow.

Although radionuclide releases from the TRU area are sporadic, it can be reasonably predicted that they will continue. Because of the differences in the sampling methods from 1990–1993 and from 1994–1996, the lower peak levels reported in 1994 compared to peak levels in 1990 and 1991 cannot be interpreted to suggest a trend of decreasing releases over time. Based on the patterns observed over 6 yrs, major releases of actinides can be expected in years with precipitation levels greater than the annual mean precipitation level. Normal precipitation levels in the winter and spring can also be expected to result in moderate actinide fluxes due to the effect of storm-driven recharge through the trenches.

5.2. Spatial orientation of actinide migration pathways

TRU radionuclides appear to follow narrow and discrete flow paths through the subsurface and to seeps in White Oak Creek (Fig. 6). The only wells in the monitoring network (Fig. 1 and Table 1) that demonstrates elevated levels of gross-alpha activity (> 1 Bq/l) are well 516 (Ashwood and Marsh, 1994, USDOE, 1995) and wells 4380 and 4382 installed in 1995, 10-m upgradient and also along geologic strike from well 516 (Fig. 7). Similarly, the only seeps evidencing elevated gross-alpha levels are seeps WOC-210 and WOC-213 located approximately 80-m downgradient from the closest trench and along strike from well 516 (Figs. 1 and 6). The higher levels of actinides are not directly related to discharge rates (Fig. 6, lower panel). The directionality of the migration path is postulated to be related to along-strike flow through preferential flow paths along fractures parallel to the bedding planes of the shale, a phenomena seen elsewhere on the ORR (Sanford and Solomon, 1995; Jardine et al., 1995). The hydraulic gradient is along-strike (Fig. 4), thus reinforcing the directionality of the actinide migration pathway.

5.3. Mobility and retention of the actinides

Although it is difficult to estimate the rates of transport of contaminants that have been in place for 20 yrs, the spiky nature of the pulses of radioactivity provides some

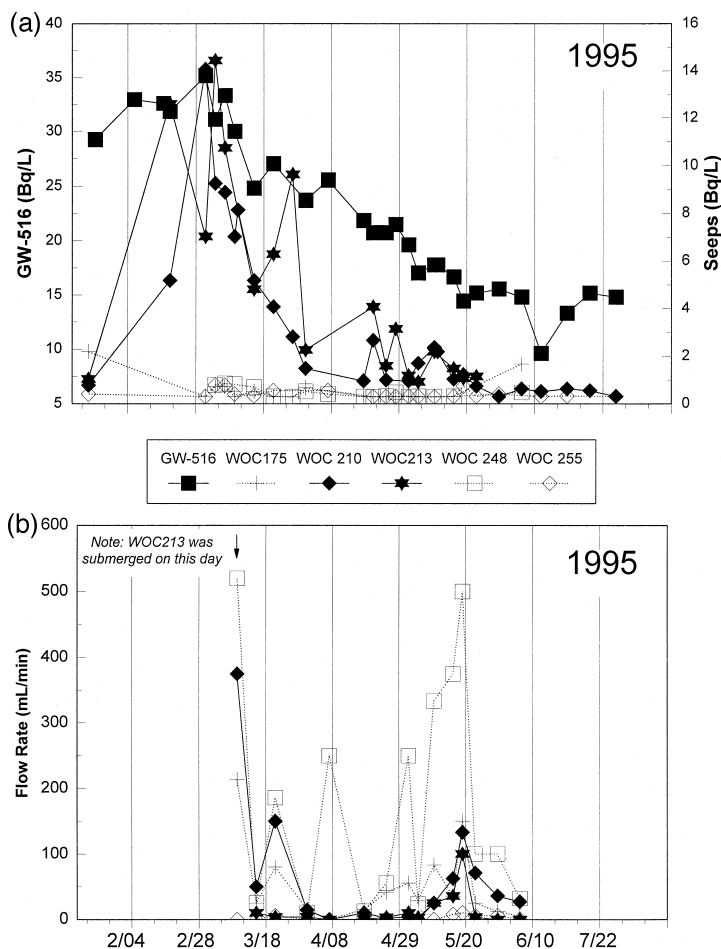


Fig. 6. (a) Gross-alpha activity in well 516 and several seeps in the banks of White Oak Creek are shown for sampling conducted in February through July of 1995, along with (b) the flow rate of water exiting the seeps.

evidence that the actinides at WAG-5N can migrate rapidly and with little retention by the saprolite. In early 1994, for example, there is only a short interval between the time when the rising water elevation intercepted the bottom of the trenches (roughly corresponding to 242.7 m above MSL in well 516; Fig. 5) and the abrupt rise in gross-alpha activity in the groundwater (Fig. 3). This timing suggests that the mobilized actinides migrated 15 m from the closest trench within days to a few weeks. It should be noted that groundwater flow rates in fractured deposits are typically much higher than in granular deposits because most of the flow occurs in fractures, which constitute a relatively small portion of the total porosity of the aquifer. In this context, it is not unreasonable that water could migrate through fractures at rates consistent with these travel times.

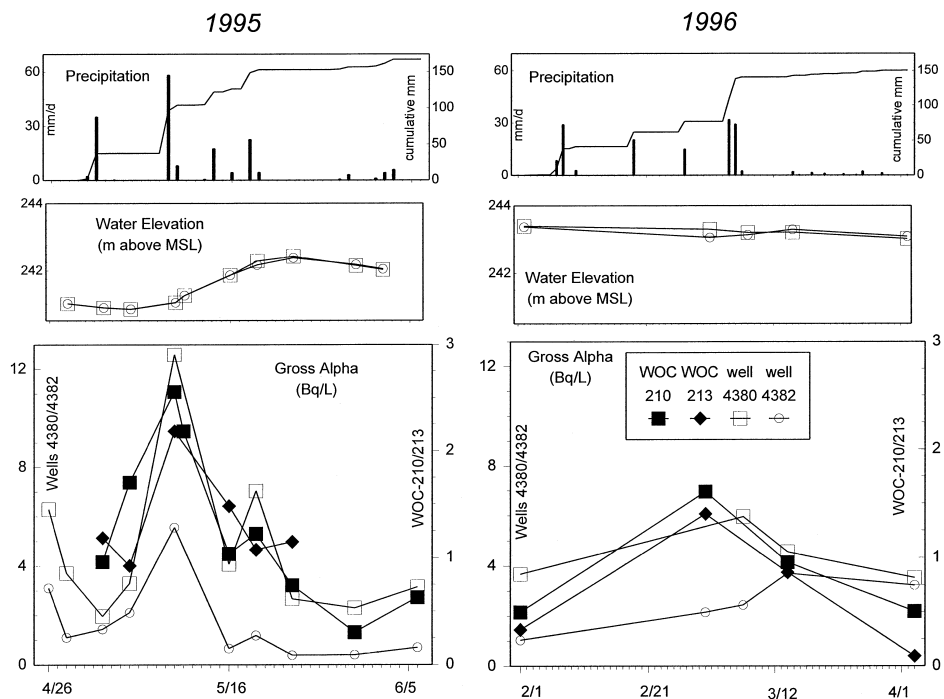


Fig. 7. The gross-alpha activity in groundwater in wells 4380 and 4382 (open squares and circles, respectively) and in water discharging seeps WOC-210 and WOC-213 (closed squares and circles, respectively) are shown in the lower panels for the periods from April through June of 1995 and February through April of 1996. Daily and cumulative precipitation during that period is shown in the upper panels. The changes in water elevation in the wells during those periods are shown in the middle panels.

Even more dramatic and transitory changes in gross-alpha activity were observed in other monitoring wells (wells 4380 and 4382, installed April 1995; Fig. 1), particularly in response to periods of intense storms (Fig. 7). The close temporal linkages between the peaks of alpha activity in these wells near the trenches and at the seeps suggests that actinides exiting the trenches are transported past the monitoring wells and to the seeps rapidly and with little retention by the saprolite.

It is likely that some of the radionuclides may be trapped with water left in fractures or finer pores as water levels declined in the previous year. A rising water table would reconnect this immobilized water to the mobile groundwater system and flush the contaminants further downgradient. However, this does not appear to be the principal source of actinides discharging at the seeps. If the releases are derived primarily from water trapped in the formation the previous season, then some temporal lag might be expected in the magnitude of actinide levels in the seeps compared to upgradient wells. However, the gross-alpha activities at the two locations seem to change yearly in concert with one another. For example, in the spring of 1994, very high concentrations of radionuclides were observed both in seep WOC-213 (36 Bq/l; data not shown) and in well 516 (93 Bq/l; Fig. 3). In contrast, maximum levels were lower in 1995, and the

seeps and well 516 were both approximately 60% less than the previous year (to 15 Bq/l in the seep and 35 Bq/l in well 516). In both years, actinide levels declined by only about half over the 65-m transport distance between well 516 and the seeps. Thus, not only do the actinides appear to move rapidly through the formation, but their concentration is not greatly diminished with distance, especially considering the possibility that some of the decrease in activity of the seep water could be the result of dilution upon convergence of flow paths near the seeps.

While we postulate that the major releases of radionuclides represent the rapid transport of actinides recently mobilized from the waste in the TRU trenches, it is apparent that some of the radionuclides can be stored in the fractures or fine pores during periods of declining water. For example, in 1996, the concentrations in the seeps were higher than those observed in wells 516 (Fig. 3), 4380 or 4382, albeit only half the levels seen in the seeps the previous year (Fig. 7). Remobilization of actinide-contaminated water remaining in the formation as a result of the seasonal rise in the water table could be the source of the modest levels of radionuclides observed in the seeps in 1996.

5.4. Physicochemical form of the mobile actinides

Given inundation of the actinide-containing waste by groundwater and the potential for rapid water movement through fracture flow paths, the high mobility of the Cm(III) and Am(III) is still unexpected. Both actinides are trivalent cations that would be expected to be strongly adsorbed to the layer silicates and mineral oxide coatings that constitute the surfaces of fractures in the saprolite. The groundwater is rich in CaCO_3 due to dissolution of limestone, and the expected geochemical speciation of the actinides, using aqueous chemistry shown in Table 2, is predicted to be as cationic carbonate complexes (Fig. 8a). The free actinide and its expected carbonate complex would also be expected to be strongly retarded. Trivalent actinides and lanthanides have been shown to have a very high affinity for sorption on layer silicates and mineral oxides, with adsorption coefficients (K_d) generally reported in the range of 10^5 – 10^7 cm^3/g (Higgo and Rees, 1986; Higgo, 1987; Kershaw et al., 1986; Meyer et al., 1984; Sanchez et al., 1982). The mass concentration of the actinides is very low (approximately 2×10^{-13} M), and unlikely to have saturated the binding capacity of the clays and mineral oxides in the saprolite (Meyer et al., 1984). Thus, even if the groundwater contacted the TRU waste, the dissolved actinides should have been very strongly retained by sorption sites in the saprolite. Based on literature K_d 's, the actinides would be expected to migrate at rates thousands of times slower than the rate of groundwater flow. Even though fracture flow velocities may be rapid, there is adequate opportunity for reactive solutes to contact sorption sites. Fractures in the saprolite in the Dismal Gap Formation consist of a network of closely spaced fractures with typical fracture apertures of 100 μm or less (L. McKay, University of Tennessee, personal communication; O'Brian et al., 1997). Intimate contact between migrating solutes and the saprolite is demonstrated by the strong attenuation of nonreactive solutes seen in tracer studies at the WAG-5N site (Knowles et al., 1995) and similar saprolite or fractured shale formations (Sanford and Solomon, 1995; Jardine et al., 1995); these losses are attributed

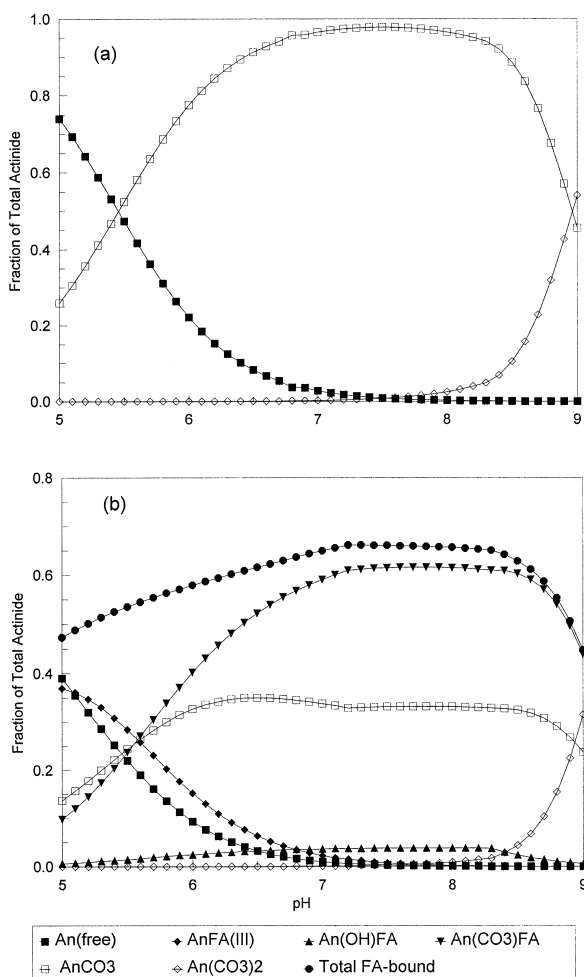


Fig. 8. The predicted speciation of actinides in well 516 groundwater is shown as (a) considering only the inorganic species and (b) considering the actinide complexes with humic acid. Note that three species are not shown ($\text{An}(\text{OH})_2\text{FA}$, AnOH and $\text{An}(\text{OH})_2$) because they are predicted to comprise < 0.003 of the actinides in the pH range shown.

to the diffusion of the nonreactive tracers into the rock matrix, but clearly opportunities exist for reactive actinide species to contact and potentially adsorb to the saprolite.

In an effort to explain the high levels of the actinides in groundwater, we tested the hypothesis that colloid-facilitated transport was enhancing the migration of the actinides, either as mobile colloidal particles (hydrolysis products of the actinides, or actinides adsorbed to or precipitated on natural groundwater colloids) or by complexation of actinides with NOM or synthetic chelators (McCarthy and Zachara, 1989; McCarthy and Degueldre, 1993 and references therein). Field experiments using colloidal tracers (later microsphere) at WAG-5N (McCarthy, unpublished data), as well as field studies using

multiple tracers (including bacteriophage, bacteria and latex microspheres) in a weathered shale saprolite in nearby Bear Creek Valley showed colloid transport rates of tens of meters per day (McKay et al., 1995), thus demonstrating the potential for rapid colloid-facilitated transport in these deposits.

Filtration of groundwater from well 516 over repeated sampling events from 1993–1995 demonstrated that almost none of the gross-alpha activity was retained by a filter with a cut-off of 3000 Dalton molecular weight (approximately 1-nm diameter; Ashwood and Marsh, 1994; Table 3). Almost all of the NOM in the groundwater was also < 1-nm. Similar results were obtained for water from wells and seeps in May and June of 1995 (Table 4). Based on these results, we conclude that the actinides are not migrating as inorganic colloids. It should be noted that there appear to be very low levels of inorganic colloids in the groundwater (see turbidity data in Table 3), perhaps due to the relatively high ionic strength and high levels of Ca, both of which tend to promote coagulation of colloidal particles in groundwater (Degueldre, 1994; McCarthy and Shevenell, 1995).

Table 3

Seasonal changes in aqueous chemistry of groundwater in well 516

Aqueous chemistry	Unit	Sampling date							
		4/14/94		8/10/94	11/4/94	2/6/95	6/27/95*		
		Unfiltered	< 1 nm	Unfiltered	Unfiltered	Unfiltered	Unfiltered	< 1 nm	
Gross alpha	Bq/l	93.0 ± 10	84.4 ± 8.9	48.1 ± 3.7	20.4 ± 0.9	33.0 ± 1.8	15.2 ± 0.9	14.4 ± 0.9	
Temperature	°C	15.6		18.6	15.4				
pH		7.15		6.89	6.98	7.27	6.87		
Eh	mV	203		275	232		257		
Conductivity	mS/cm	0.68		0.66	0.68	0.73	1.05		
Turbidity	NTU	1.358		0.934	0.54	0.007	0.062		
DO	mg/l	3		3	2	2	2		
Water	m above	243.6		240.8	239.6	241.1	240.4		
Elevation	MSL								
TOC	mg-C/l	0.74	0.69	0.5	0.75	0.64	0.65	0.45	
Alkalinity	mg/l CaCO ₃	367			347	361	320		
Aluminum	mg/l	< 0.022	< 0.022	< 0.020	< 0.020	0.023	0.058	0.032	
Barium	mg/l	0.33	0.32	0.33	0.33	0.37	0.5	0.5	
Calcium	mg/l	120	91	110	110	120	170	170	
Chloride	mg/l	2	2.6		2	3	5.2	5.2	
Dissolved solid	mg/l	414	406		416	426	850	852	
Iron	mg/l	0.14	0.012	< 0.0050	0.013	0.0051	< 0.005	0.05	
Magnesium	mg/l	15	15	13	13	13	19	19	
Manganese	mg/l	0.0028	< 0.0011	< 0.0010	0.001	< 0.001	< 0.001	< 0.001	
Nitrate	mg/l	0.32	0.23		0.47	4.7	< 10	< 1	
Potassium	mg/l	1.6	1.5	1.6	1.5	1	1.5	2.2	
Silicon	mg/l	7.1	7.2	6.9	6.7	7.3	6.7	6.8	
Sodium	mg/l	12	12	12	12	13	15	15	
Sulfate IC	mg/l	20.8	20.6		23	21	16	17	

* Note: A tracer experiment involving injection of NaBr upgradient of 516 altered some parameters on this date.

Table 4

Gross-alpha activity and NOM concentrations before and after filtration

Location	Date	Unfiltered		Filtered (0.2- μ m)		Filtered (1-nm)	
		Gross alpha (Bq/l)	TOC (mg-C/l)	Gross alpha (Bq/l)	TOC (mg-C/l)	Gross alpha (Bq/l)	TOC (mg-C/l)
Seep WOC210	05/10/95	2.55 \pm 0.37	2.8	2.18 \pm 0.34	3.7		
	05/11/95	2.18 \pm 0.37	4.1	1.18 \pm 0.28	4.5		
	05/16/95	1.03 \pm 2.78	0.95	0.32 \pm 0.24	1.3		
Wells 4380/4382 ^a	06/27/95	0.92 \pm 0.37	0.69			1.03 \pm 0.33	0.55

^aEqual volumes from wells 4380 and 4382 were combined and filtered in the laboratory.

The inorganic speciation in the carbonate-rich water is predicted to be an actinide carbonate cation (Fig. 8a), yet none of the gross-alpha activity in groundwater from well 516 was retained when the water was passed through a cation exchange resin (data not shown). The groundwater actinides, therefore, may exist as anionic organic complexes. The radionuclides were retained by an anion exchange resin and coeluted from the resin with the adsorbed groundwater NOM. When several liters of well 516 groundwater was passed through a column of DEAE weak anion-exchange resin, adsorbed NOM could be seen as a light brown band accumulating near the top of the column. The column was rinsed with approximately 50 ml of distilled water and then eluted with base. The brown material at the top of the column was mobilized by the NaOH solution and a peak of color eluted at the breakthrough of the front of elevated pH. Analysis of the eluted fractions for TOC and gross-alpha activity (Fig. 9a) confirmed that the peak of visible color coincided with a sharp peak of TOC and an even sharper peak of gross-alpha activity coeluting at the beginning of the NOM peak. When the column was then rinsed with acid to recover any actinides that may have been immobilized on the column by precipitation or filtration of hydrolysis products of the actinides, only a very small peak of TOC and gross-alpha activity were released (Fig. 9a).

To confirm the effect of NOM on actinide retention and release on the DEAE column, artificial groundwater solutions containing ²⁴¹Am were passed through DEAE columns. When an artificial groundwater containing ²⁴¹Am in a carbonate solution (without organic matter) was passed through the column, elution with base did not mobilize the ²⁴¹Am, but treatment with acid did elute a peak of ²⁴¹Am that appeared to have precipitated or been retained by the column packing (Fig. 9b). In contrast, when the ²⁴¹Am-carbonate input solution was supplemented with NOM to a final concentration of approximately 10 mg-C/l, the ²⁴¹Am coeluted with the peak of NOM (Fig. 9c). A second peak of radioactivity eluting with acid in Fig. 9c is likely due to the much higher concentration of ²⁴¹Am used in that experiment, compared to the groundwater situation. The ratio of ²⁴¹Am to NOM was approximately two orders of magnitude greater in the artificial groundwater (Fig. 9c) than in the natural groundwater (Fig. 9a). Thus, it appears that not all the ²⁴¹Am in the artificial groundwater was organically complexed and a significant fraction eluted with acid (Fig. 9c) as had ²⁴¹Am in the absence of NOM (Fig. 9b).

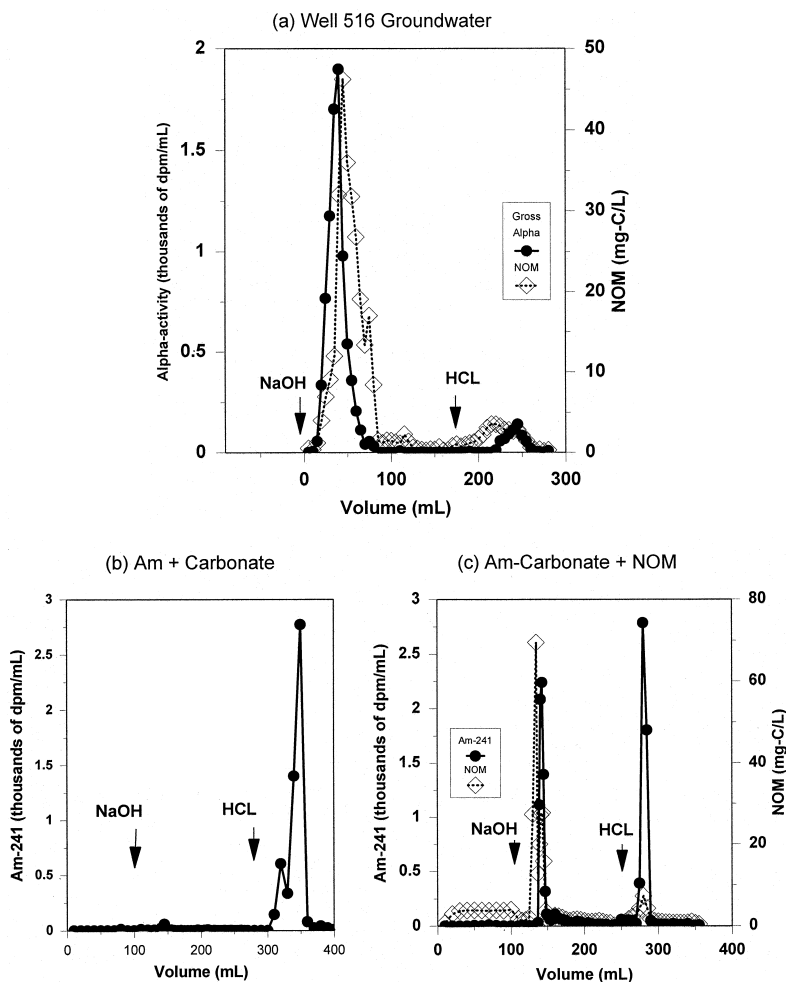


Fig. 9. (a) DEAE-cellulose chromatography of groundwater from well 516. The elution of NOM (measured as TOC) and gross-alpha activity (by liquid scintillation counting) is shown. Similar chromatography was performed using artificial groundwater and ^{241}Am . (b) Elution of TOC and ^{241}Am in an organic-free artificial groundwater. (c) The ^{241}Am -carbonate artificial groundwater was supplemented with NOM.

These results are consistent with the predictions of the humic acid complexation model. The model predicted that at the neutral groundwater pH, approximately 70% of the actinides would be complexed to the groundwater NOM as actinide-FA complexes or as actinide-carbonate or actinide-hydroxyl ternary complexes with FA ($\text{An}(\text{CO}_3)_2\text{FA}$ or $\text{An}(\text{OH})_x\text{FA}$, respectively; Fig. 8b). A sensitivity analysis was performed on the fulvate complexation and stepwise formation constants, total fulvic acid concentration and LC (Table 5). The results indicate where the total amount of actinide bound to fulvic acid varied from pH 6.9 to 7.3 was changed 10% of the original calculated value by independently varying the examined terms. It is found the most sensitive term is $\log \beta$

Table 5

Results of sensitivity analysis performed on the fulvate complexation. Ranges where the calculated mole fraction of fulvic-bound actinides vary by $\pm 10\%$ are shown

Term	Range
$\log \beta$ AnHA(III)	5.97–6.22
$\log K$ AnOHHA(II)	0–7.82
$\log K$ An(OH) ₂ HA(I)	0–7.13
$\log K$ AnCO ₃ HA(I)	6.52–6.79
LC	0.76–1.00
[FA(III)] _{total}	1.53 μ M–2.69 μ M

AnCO₃FA(I). Within the error value of this term, the mole fraction of fulvic-bound actinide varies from 50% to 80%. This strong dependence on the mixed carbonate complex is due to the large amount of carbonate present in the natural water. The value for $\log \beta$ AnFA(III) is also sensitive, but only a 10% variance in the mole fraction of fulvic-bound actinide arises from the error in this term. The LC value and FA(III)_{total} concentrations are linked and both moderately affect the evaluated fulvic-bound mole fraction. The values for the stepwise hydroxide-formation constants have practically no effect on the calculated amount of bound actinides due to the high carbonate concentration of the water.

Initial measurements of the capacity of the groundwater NOM at WAG-5N to bind at Cm(III) indicate the $\log \beta$ for the Cm–NOM(III) complex is 6.00 ± 0.20 , consistent with the estimates used for the simulation. Further characterization of the groundwater NOM and its actinide binding capacity will be described elsewhere (Czerwinski, in preparation).

The organic complexant responsible for actinide mobilization at WAG-5N was not a anthropogenic chelator codisposed with the TRU waste. In another portion of the ORR, the strong complexing agent, ethylenediaminetetraacetic acid (EDTA) had been demonstrated to cause the migration of cobalt-60 (Means et al., 1978); EDTA had been used in decontamination operations and disposed of in radioactive liquid-waste seepage trenches. Codisposed EDTA was also implicated in migration of Pu isotopes and ⁶⁰Co from shallow burial trenches at Maxey Flats, Kentucky (Kirby et al., 1991). However, liquids were not disposed at WAG-5N, and initial results of mass spectral analysis of the groundwater from well 516 confirm that the chelator EDTA could account for no more than 0.2% of the TOC in the sample (Wang Ding, Stanford University, unpublished data).

Thus, both geochemical analyses of groundwater and geochemical modeling are consistent with the hypothesis that the groundwater actinides are migrating as anionic organic complex with groundwater NOM.

5.5. Mobility of the actinide–NOM complex

We attribute the rapid changes in gross-alpha activity in groundwater at WAG-5N to the formation of highly mobile actinide–NOM complexes. Yet mineral oxides and layer

silicates, both abundant in the saprolite, have been shown to have a very high affinity for adsorbing NOM through both physical adsorption (Baham and Sposito, 1994; Jardine et al., 1989) and ligand exchange (Tipping, 1981; Murphy et al., 1990; Gu et al., 1994). However, we postulate that the adsorption of the NOM and the actinide–NOM complexes is minimal because NOM-binding sites on the formation are saturated due to long-term contact with groundwater NOM.

The field-scale mobility of NOM was examined in an iron oxide-coated sandy aquifer by injection of NOM from a wetland pond along with a nonreactive tracer (chloride; McCarthy et al., 1993, 1996a). Although there was a significant retention and retardation of the injected NOM by the aquifer, different components of the NOM had different mobility. It is significant that the low molecular weight, hydrophilic components of the NOM migrated conservatively, similar to the chloride tracer. This component of the NOM-injection solution was chemically similar to the groundwater NOM, and it was postulated on the basis of these results that the sorption sites on the aquifer capable of binding these components were saturated by the groundwater NOM (McCarthy et al., 1996a). Similarly, we postulate that groundwater NOM at WAG-5N has saturated binding sites, and although individual NOM molecules may adsorb or desorb from sorption sites, the net retention of the NOM during transport through the saprolite is minimal.

Additional evidence of the rapid transport and low retention of the actinide–NOM complex was obtained in a long-term natural gradient tracer studies at WAG-5N (Ketelle et al., 1995; McCarthy et al., 1996b). Trivalent lanthanides (europium and neodymium) were used as reactive tracers whose speciation and migration would be similar to the trivalent actinides. The lanthanides, as well as a nonreactive tracer (bromide), were injected for 73 days into wells 4380 and 4382 (Fig. 1). The lanthanides and bromide arrived at well 516 at approximately the same time (Ketelle et al., 1995), and retardation factors modeled using either temporal moments analysis or a one-dimensional fracture flow model were estimated to be between 2–10 (McCarthy et al., 1996b). Like the actinides (Fig. 9a), the lanthanide tracer in the groundwater adsorbed to a DEAE cellulose anion-exchange column and coeluted with the peak of NOM and of gross-alpha activity (McCarthy et al., 1996b).

It should be noted that two of the conditions that appear to control actinide mobilization–precipitation and the presence of NOM as a complexant are closely linked in these shallow soil–saprolite systems. The effect of storm events on TOC concentrations in the shallow saprolite was monitored at the ORNL subsurface transport facility. Stormflow through the soil and saprolite-mobilized NOM at concentrations over 3-fold greater than during baseflow conditions (Fig. 10). The TOC concentrations changed very rapidly from baseflow concentrations of less than 1 mg-C/l to a maximum of 3.4 mg-C/l. In a series of storms, the TOC concentration rose and fell rapidly in parallel with the changing flow rate of water through the saprolite at a depth corresponding to that of the TRU trenches. Similar increases in the concentration of NOM might be expected in stormflow water entering the TRU trenches. The only well located in a trench that was monitored for TOC in this study was well 2007 (Fig. 1). Baseflow TOC levels observed in 1995–1996 ranged from approximately 0.5 to 1.5 mg-C/l (Fig. 11), but large increases in TOC levels were associated with storm events. For example, TOC

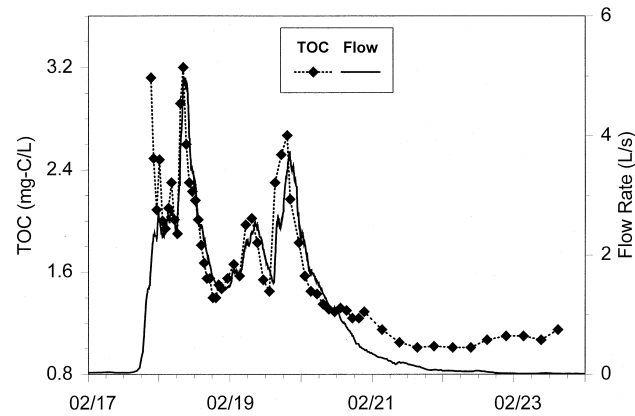


Fig. 10. Changes in TOC concentration of groundwater and the flow rate of groundwater entering the subsurface weir at the 1.8- to 2.5-m depth of the ORNL subsurface transport facility is shown during several storm events.

concentrations increased up to 16 mg-C/l following a 70-mm rain event in May 1995 (Fig. 11a). Storms with lower levels of precipitation resulted in lower TOC levels. TOC concentrations did not rise above approximately 3 mg-C/l in 1996 (Fig. 11b), but storms did not exceed 30-mm of precipitation a day during that period.

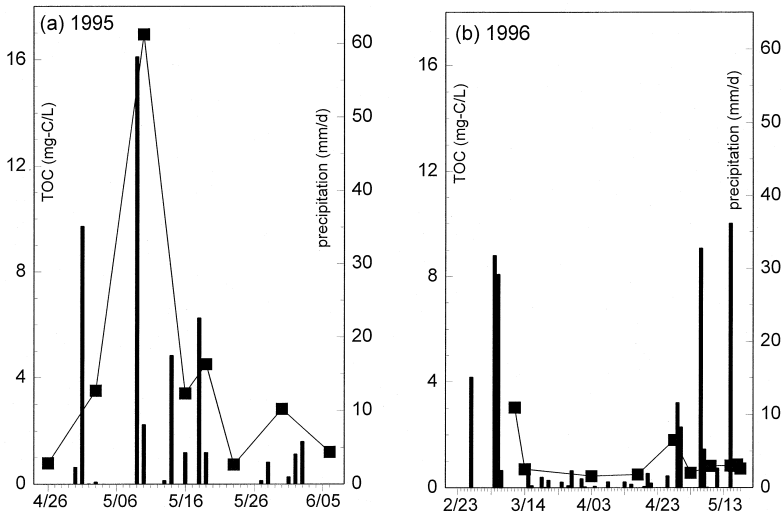


Fig. 11. The TOC concentration in groundwater recovered from well 2007 is shown for the periods of (a) February through May of 1996 and (b) April through June of 1995. Daily precipitation during that period is also shown as the vertical bars.

6. Summary and conclusions

The mechanisms and rates of transport of transuranic radionuclides in groundwater at the Oak Ridge National Laboratory were examined to determine the mechanisms and rates of radionuclide migration. Several interacting hydrogeochemical processes contribute to the observed releases of actinides (^{244}Cm and ^{241}Am) from the shallow unlined disposal trenches, and their transport through the fractured shale saprolite to the surface water seeps at White Oak Creek. Major releases are promoted when seasonal fluctuations in the water table permit groundwater to contact actinide-contaminated waste. Interception by the trenches of upslope recharge moving laterally through the stormflow zone appears to permit minor releases due to transient saturation within the trenches but above the local water table. There is not extensive tailing of the actinide levels following spikes of groundwater concentrations, suggesting that most of the actinide transport is through the more accessible fractures and larger pore space. Thus, secondary storage of contaminants in the rock matrix may not pose a long-term problem as a significant source of continued releases if remedial actions isolate the primary contaminant sources in the trenches.

The spatial distribution of the radioactive contaminants appears to be highly directional, reflecting the orientation of the hydraulic gradient as well as structural features that result in preferential transport of mobilized actinides along geologic strike.

Although the hydrogeology of the site permits contact of the TRU waste with the groundwater, the expected inorganic species of the actinides should strongly adsorb to the layer silicates and mineral oxides of the saprolite. Laboratory adsorption studies with model mineral phases or with subsurface material predict that the actinides should migrate at rates many orders of magnitude slower than the groundwater flow velocities. Yet the timing of the actinide releases relative to when rising groundwater intercepts the trenches suggests that actinide transport is rapid, and the relative magnitude of peak actinide levels in wells near the trenches and downgradient seeps suggests that there is very limited retention of the actinides by the formation. Based on anion exchange chromatography and geochemical modeling, the mobilization and transport of the actinides is demonstrated to result from complexation of the actinides by NOM. We postulate that the actinide–NOM complex migrates with minimal retention by the saprolite because NOM-binding sites on surfaces have been saturated by continuous contact with groundwater NOM (McCarthy et al., 1996a). Storm events contribute to mobilization by promoting hydrologic links between the TRU waste and groundwater, and by increasing the concentration of NOM in the mobile soil and groundwater.

Many studies have examined the mechanisms and extent of humic acid complexation of TRU radionuclides (Bertha and Choppin, 1978; Moulin et al., 1987, 1988; Kim et al., 1991; Maes et al., 1991), and some evidence has been presented that groundwater contaminants at some sites are present as organic complexes (Means et al., 1978; Champ et al., 1984). However, we are aware of no previous study that brings together field observations, laboratory data and geochemical modeling to establish a coherent hydro-geochemical demonstration of the mobilization and field-scale transport of radionuclides by NOM. Clearly, assumptions inherent in many risk assessments for existing waste facilities, and performance assessments for future repositories, must rigorously account

for the role that even typically low levels of groundwater NOM plays in contaminant mobility. This demonstration that NOM can dominate the mobilization, transport and fate of groundwater contaminants, and that NOM-contaminant complexes are not retained even by highly reactive surfaces of the saprolite forces a reevaluation of our approaches to describing contaminant transport.

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