

Lanthanide Field Tracers Demonstrate Enhanced Transport of Transuranic Radionuclides by Natural Organic Matter

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Transuranic (TRU) radionuclides buried 25 years ago in shallow unlined disposal trenches in a fractured shale saprolite had been detected in groundwater from downgradient monitoring wells and in surface water seeps. Field observations had suggested the actinide radionuclides were mobilized by natural organic matter (NOM) and rapidly transported with little retardation. A 73-day natural gradient tracer experiment injected trivalent lanthanides (Nd and Eu) as analogues to determine the mechanisms and rates of actinide transport at the field scale. Adsorption isotherms for ²⁴¹Am and Eu with saprolite from the site confirmed a very high affinity for adsorption ($R > 50\,000$) in the absence of NOM. However, reactive and nonreactive tracers arrived at approximately the same time along a 10-m long deep flow path, and anion-exchange chromatography and filtration suggested that the mobile lanthanides in groundwater were a NOM complex. Although flow through a shallow flow path was intermittent, reflecting transient recharge events, large storms resulted in coincident peaks of both reactive and nonreactive tracers, suggesting that they migrated at similar rates over distances of 78 m. We conclude that NOM facilitated the almost-unretarded transport of lanthanide tracers and, by analogy, that NOM is facilitating the mobilization and rapid migration of the TRU radionuclides.

Introduction

Transuranic (TRU) radionuclides were buried 25 years ago in shallow unlined disposal trenches in groundwater at Waste Area Group 5-North (WAG-5N) of the Oak Ridge National Laboratory (ORNL, Tennessee; Figure 1). Actinides (²⁴⁴Cm(III) and ²⁴¹Am(III)) have been detected in groundwater from downgradient monitoring wells and in surface water seeps (1). The hydrogeology of the site permits seasonal and storm-related contact of the TRU waste with the groundwater; however, migration should be very limited because the expected inorganic species of the actinides strongly adsorb

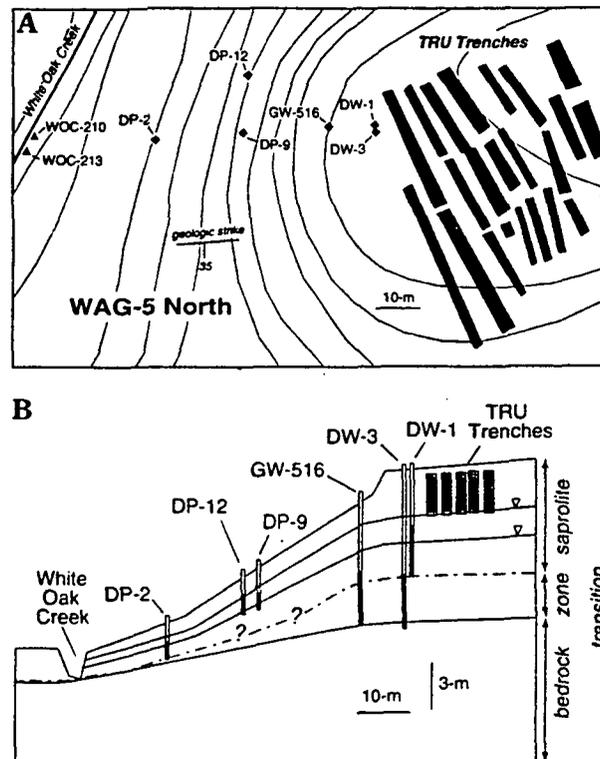


FIGURE 1. The plan view of the WAG-5N site (A) and a cross-section through the transect between the injection wells and White Oak Creek (B). In panel A, the long, shaded rectangles show the location of TRU disposal trenches. Injection and monitoring wells are designated with diamonds. Seeps occur seasonally along the steep bank of White Oak Creek and are designated by triangles and numbers beginning with the prefix "WOC". Surface contours are at 5-ft (1.52 m) intervals. In panel B, the locations of the highest and lowest water table elevation during the experiment are shown. The approximate locations of the bedrock, transition zone, and overlying saprolite are shown. The location of the transition zone is not well-known in the lower portions of the site, as indicated by the question marks.

to the shale saprolite. Yet actinide concentrations in groundwater undergo rapid changes that are not consistent with migration of a highly retarded solute. For example, seasonal changes in water elevation that inundate the TRU trenches result in significant increases in gross α -radioactivity levels in monitoring wells. Even more rapid "spikes" of gross α -activity are associated with storm events (1, 2). The timing and relative magnitude of the concentration spikes in wells near the trenches and at surface water seeps 80-m downgradient suggests that the storm events mobilize actinides in the trenches and rapidly transport them with very limited retention by the formation. Based on anion exchange chromatography of the groundwater and geochemical modeling, the mobilization and transport of the actinides were postulated to result from complexation of the actinides by natural organic matter (NOM; 1). The actinide-NOM complexes were believed to migrate with little retention by the formation because NOM binding sites on the formation are saturated due to long-term contact with groundwater NOM (1, 3). It should be noted that liquids, which could have included anthropogenic complexants, were not disposed at WAG-5N, and the chelator EDTA was shown not to be present in the groundwater (1).

The ability of NOM to complex actinide- and lanthanide cations and cationic complexes is well established (4-10),

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TABLE 1. Monitoring Well Details^a

well no.	ORNL well no.	date constructed	surface elevation (m above MSL)	well depth (m BGS)	completed interval (m above MSL)	well construction	comments
DW-1	4380	1995	245.8	7.3	238.5–241.6	2-in (5.1-cm) SS	tracer injection well
DW-2	4381	1995	234.5	9.4	225.1–228.1	2-in (5.1-cm) SS	
DW-3	4382	1995	245.8	9.8	236.1–239.1	2-in (5.1-cm) SS	tracer injection well
DP-2	4384	1995	234.7	2.3	234.1–234.7	1-in (2.5-cm) PVC	
DP-9	4389	1995	239.3	2.0	238.7–239.3	1-in (2.5-cm) PVC	
DP-11	4391	1995	237.2	1.5	236.6–237.2	1-in (2.5-cm) PVC	
GW-516	516	1982	243.7	8.0	235.8–239.8	4-in (10.2-cm) PVC	

^aNote that the companion paper on this field site (7) uses the ORNL well number for identification. MSL, mean sea level; BGS, below ground surface; PVC, polyvinyl chloride; SS, stainless steel.

and several studies have shown that NOM alters the extent of adsorption of actinides and lanthanides to model minerals and can affect their migration in laboratory column experiments (11–14). Under conditions that limited NOM interactions with minerals or in studies with minerals such as silica that have a low affinity for binding NOM, the presence of the NOM decreased binding of the actinides or lanthanides to the mineral phase and enhanced their transport in column studies (11, 14–17).

Although the field observations at WAG-5N (1) are consistent with NOM-enhanced transport, data on the dynamics of contaminants that have been present in the formation for 25 years are inadequate to unequivocally identify mechanisms or rates of transport. For example, are the concentration spikes seen in wells and seeps derived from “old” contaminants stored in the formation or “new” contaminants mobilized from the trenches by storm events and rapidly transported 80-m downgradient to the seeps? Therefore, lanthanides were injected as field-scale tracers to confirm that the mechanism of actinide mobilization involved complexation by NOM and to determine the extent of retardation of the actinide–NOM complex. The lanthanides Nd(III) and Eu(III) (referred to collectively as rare earth elements, REE) have a chemistry and sorption/complexation characteristics analogous to actinides (6–8) and are often used as analogues of the trivalent radionuclides. This study is the first application of lanthanides as geochemical tracers to understand actinide transport at a field scale.

Multiple nonreactive tracers were injected with the REE tracers to provide a basis for comparing the extent of retardation of the REE in the formation. The objectives of this study were (i) to determine if REE tracers were mobile in the groundwater and if the mobile form was a NOM–REE complex; (ii) to determine the extent of retardation of the mobile REE; and (iii) to determine if the storm-related spikes of elevated actinides observed tens of meters downgradient of the TRU trenches could arise from recently mobilized and rapidly transported contaminant.

A natural gradient injection system was employed because transient storm-related hydrological disturbances can affect mobilization and transport, and the injection was sustained over a long period of time to capture responses to several storms. The fractured flow system at WAG-5N is complex, and identification of specific flow paths or the hydrodynamic processes controlling storm-related effects on actinide or tracer migration is beyond the scope of this study.

We hypothesized that the mobile form of the REE tracers would be as NOM complexes and that the REE–NOM complex would migrate at rates similar to the nonreactive tracers. We further postulated that episodic concentration spikes of REE tracers would be observed in downgradient wells and seeps, suggesting that episodic releases of TRU radionuclides to White Oak Creek arise at least in part from material recently mobilized from the trenches rather than from a “secondary” source within the formation.

Hydrogeological Setting of WAG-5N. WAG-5N (Figure 1) is underlain by the Dismal Gap Formation, a series of interbedded lenses of limestone, siltstone, and shale. The saprolite, or thoroughly weathered and decomposed bedrock, is clay-rich and retains much of the original bedding and structural features. Mineralogy at the site includes secondary clay minerals such as illite, vermiculite, kaolinite, and calcite cements as well as amorphous iron and manganese oxides coatings (McCarthy and Elless, unpublished data). The groundwater is near-neutral pH dominated by CaCO₃ (alkalinity ~ 350 mg/L as CaCO₃; 1). Annual precipitation is approximately 130 cm per year.

Generally, groundwater flow on the Oak Ridge Reservation (ORR) is dominated by flow near the water table in a zone corresponding to the transition from saprolite to unweathered bedrock (18). Several tracer tests performed in similar media on the ORR have found the predominance of strike-preferential transport along bedding plane fractures under natural gradient conditions (19, 20) with transport directed toward cross-cutting tributary streams. There are permeable intervals that underlie the saprolite-bedrock transition zone by 1–3 m, with a relatively impermeable layer between (21, 22). Recharge to the shallow groundwater varies considerably throughout the year, with most occurring during the winter months when evapotranspiration is at a minimum. Large rain events during this time can cause rapid increases of the elevation of the water table, with a nearly 3-m increase seen in one 24-h period (23), indicative of low fracture porosity. These large water table fluctuations have been shown to bring groundwater in contact with contaminants buried in the numerous disposal trenches on the ORR (18), leading to periodic migration downgradient.

Experimental Section

Tracer Injection Experiment. A 73-day natural gradient injection experiment was conducted from April to June 1995 in two adjacent injection wells, DW-1 and DW-3 (Table 1, Figure 1) located 5 m downgradient from the TRU trenches. Tracers were injected at nearly constant concentrations without altering the natural hydrologic gradient. Groundwater recirculated through a flow cell was maintained at a constant elevated specific conductivity (SC) using a data logger program (Campbell Scientific) that opened a solenoid valve to permit a small volume of concentrated stock solution of the tracers to flow into the well when the SC fell below the target level. For DW-1 and DW-3, stock solutions contained MgBr₂ and EuCl₃, and MgBr₂ and NdCl₃, respectively (Figure 1). Sulfur hexafluoride (SF-6; 24) was also used as a nonreactive dissolved gas tracer in injection well DW-1. The SF-6 gas entered groundwater by diffusion through Teflon capillary tubing located in the well (25).

Groundwater was sampled at low flow rates (<100 mL/min) to minimize mobilization of colloidal particles (26, 27). Cation samples were preserved using HNO₃ to pH < 2 and analyzed by inductively coupled plasma-atomic emission

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spectroscopy (ICP). Total organic carbon (TOC) samples were preserved with HCl to pH 2 and analyzed by high-temperature combustion (Shimadzu Model 5000). SF-6 was determined following equilibration with a known volume of headspace and analysis of the headspace gas by gas chromatograph with electron capture detection. No attempt was made to quantify the absolute concentration of SF-6. It was used to distinguish injection sources and corroborate the arrival time of nonreactive tracers. Some of the groundwater samples were filtered using polycarbonate membrane filters (Nucleopore) with nominal 0.2- or 0.05- μm pore sizes and analyzed as described above.

Adsorption Isotherm. The adsorption of $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ was measured using saprolite from the Dismal Gap Formation adjacent to WAG-5 and a bicarbonate solution similar to the WAG-5 groundwater. The saprolite was pulverized to pass through a 2-mm mesh. ^{241}Am was obtained as a radioactive standard in 1 N HCl and was titrated to pH 7.0 using 0.8 M NaHCO_3 while bubbling with 20% $\text{CO}_2/80\%$ N_2 to a final ionic strength (I) of 0.2 M. EuCl_3 in 0.3 N HCl was similarly titrated to pH 7.0 ($I = 0.06$ M). Solutions were equilibrated with the solids for 2 days with shaking under 20% CO_2 ; adsorption did not increase when the equilibration time was increased to 4 days. The solid-solution ratio was 0.1 for the ^{241}Am isotherms but decreased to 0.001 for the Eu isotherms because of the higher detection limit for the nonradioactive element. Following equilibration, samples were centrifuged, and the solution was analyzed by liquid scintillation counting (for ^{241}Am) or ICP (for Eu).

DEAE Chromatography. Groundwater was passed through a column of the weak anion-exchange resin diethylaminoethyl cellulose (DEAE-cellulose), as described by McCarthy et al. (1). The column was rinsed with deionized water and eluted with 0.1 N NaOH, followed by deionized water and 0.1 N HCl. Fractions of the eluent were collected and analyzed for NOM, cations, and gross α -radioactivity. NOM was measured based on UV absorption at 272 nm.

Results and Discussion

Adsorption Isotherm. Trivalent actinides and lanthanides have a very high affinity for sorption on the saprolite and therefore are expected to be highly retarded. Site-specific isotherms for ^{241}Am and Eu yielded estimated adsorption coefficients (K_d) of 8900 (± 210) and 19 600 (± 1280) dm^3/kg , respectively (Figure 2). Given the bulk density ($1.6 \text{ g}/\text{cm}^3$) and effective porosity (0.26; 17) of the saprolite, the predicted retardation factor (R) of trivalent actinides and REE tracers in this formation is greater than 50 000.

Concentrations and Physicochemical Form of the Tracers in Source Wells. During the 73-day tracer injection, the input concentrations were relatively constant. The time-averaged concentration of Br was 993 (± 206) and 1019 (± 136) mg/L for DW-1 and DW-3, respectively.

Precipitation of hydrolysis products of the REEs in the injection wells resulted in very elevated measurements when a flocculated particle was included in the sample. The colloidal hydrolysis products were unstable due to high concentrations of predominantly divalent cations in the groundwater (1), but flocs remained suspended because water was continuously recirculated in the injection wells. To exclude flocculated material from analyses, samples from the injection wells were filtered (0.2 μm) prior to analysis. The time-averaged source concentration was 0.26 mg/L for Eu and 0.16 mg/L for Nd. None of the tracers had detectable background concentrations.

DEAE Chromatography of Tracer Source Well. McCarthy et al. (1) demonstrated the association of groundwater actinides with NOM by adsorption to and coelution from DEAE-cellulose. Similar DEAE chromatography of groundwater from DW-3 demonstrated that Nd in the source well

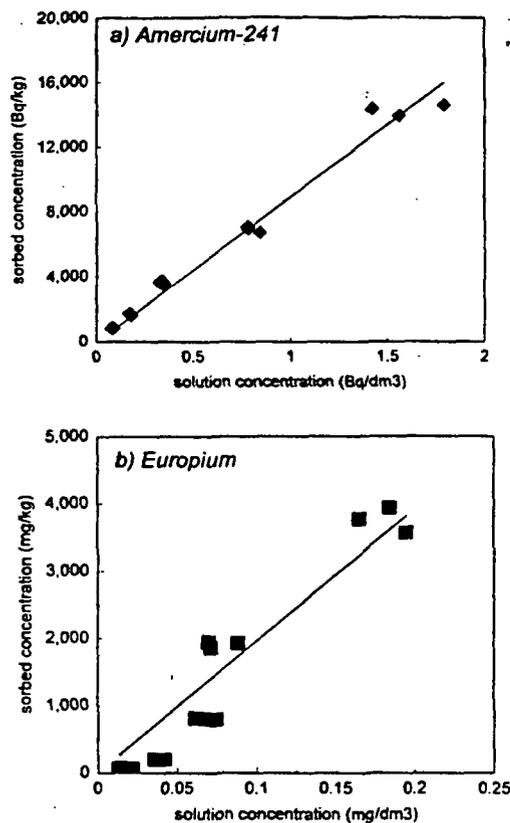


FIGURE 2. Adsorption isotherm for binding of (a) ^{241}Am and (b) Eu to saprolite from the Dismal Gap formation.

was bound to NOM (Figure 3). Neodymium, NOM, and gross α -activity were retained on the DEAE-cellulose column, and when the column was eluted with alkali, the Nd and gross α -activity coeluted with the NOM (Figure 3). Thus, the mobile form of the REE tracers appears to be an NOM complex.

Migration of Reactive and Nonreactive Tracers. Consistent breakthrough was observed along the flow path from DW-3 to GW-516 (Figure 4). Neither Eu nor SF-6 were detected in GW-516. Thus, Br^- present in GW-516 is assumed to originate from the deeper injection well, DW-3. A borehole flow meter test in a well subsequently drilled 4 m from DW-1 and DW-3 indicated the existence of a zone of low hydraulic conductivity between 236 and 238 m above MSL, corresponding to the region where the screened zone of the two injection wells overlapped (Table 1). This zone may have limited downward migration of the tracers in DW-1.

Bromide arrived 10 m downgradient at GW-516 within 2–4 days and reached an initial plateau within approximately 20 days (Figure 4a). The breakthrough of the Nd tracer in GW-516 occurred in a similar time frame as the conservative tracer (Figure 4a), suggesting that retardation was minimal. The Nd in GW-516 groundwater was not retained by a 0.05- μm filter (Table 2), demonstrating that the mobile form of the Nd was not a colloidal hydrolysis product or an inorganic colloid to which the Nd adsorbed or precipitated. The small size of the mobile REE is consistent with the small size expected for a REE-NOM or actinide-NOM complex (20, 1).

The irregularity of the concentration histories for the tracers reflects variability in the hydrologic regime as a result of storm events (Figure 4b). For example, large storms during days 22–29 resulted in increased hydraulic gradients and subsequent declines in tracer concentrations due probably to inputs of dilute recharge water.

Although Br^- levels decline when the injection is terminated, the Nd levels do not. REE flocs remaining in the

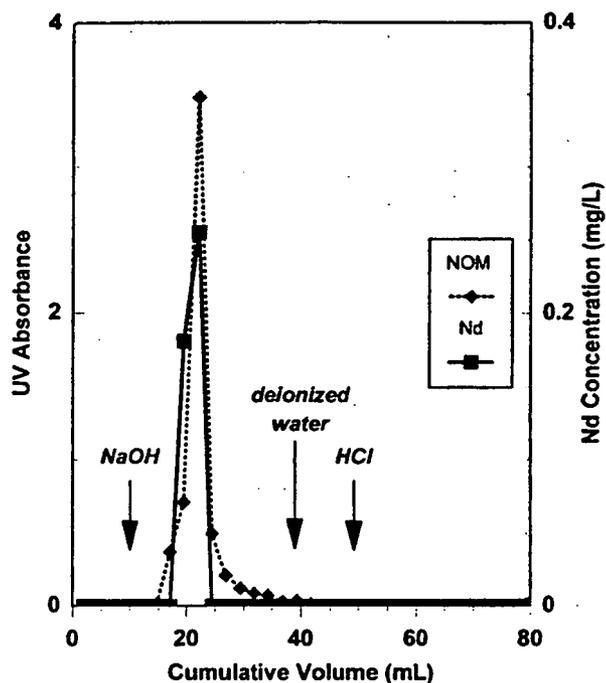


FIGURE 3. DEAE-cellulose chromatography of groundwater from DW-3. The elution of NOM (measured as UV absorbance) and Nd are shown. Gross α -activity also coeluted with the NOM and Nd peak (data not shown). Note that any inorganic species of the actinides or lanthanides that becomes trapped on the column are solubilized and eluted at approximately 20–30 mL after the step input to HCl (7), but no detectable levels of Nd or gross α -activity are observed within this region of the chromatogram.

injection wells after the tracer inputs were terminated may be the source of the continued Nd releases (Figure 4). The Nd in GW-516 after the termination of the injection was not

TABLE 2. Concentrations of Nd (mg/L) in Groundwater Recovered from GW-516, before and after Filtration through a 0.05- μ m Polycarbonate Filter

date (day)	unfiltered	filtered (0.05 μ m)
6/20/95 (day 64)	0.061	0.056
6/27/95 (day 71)	0.076	0.075
7/05/95 (day 79)	0.108	0.106

retained by a 0.05- μ m filter (day 79; Table 2), suggesting that NOM mobilized Nd from the flocculated source in the well. Nd levels in GW-516 had decreased below detection when the well was next sampled at 230 days. The well was sampled eight times from December 1995 to April 1996, but Nd remained below detection except for one observation during a large storm event in March 1996.

Temporal moments analysis was performed on the Nd breakthrough curves to obtain an estimate of the extent of retardation. Temporal moments provide an integrated perspective of the relative migration of the conservative and reactive tracers (28). The first moment (M1) reflects the average travel time of the center-of-mass along the axis between the injection and sampling wells and can be used to define an empirical retardation factor, R^* , as the ratio of the average travel times (M1) of the reactive REE and conservative Br^- tracers. Since the time span for the step input is relatively large, the mean travel times were corrected by subtracting the mean time of the corresponding step input (3). We recognize that the available data imposes limitations on the accuracy of the estimates of tracer mass. Sampling was relatively sparse, and observations were not equally spaced in time. Nevertheless, since both Br^- and REE were measured at the same time in all samples and since arrival of both tracers occurred within very similar time frames, any bias or errors in the data should be similar for both tracers. The temporal moments analysis should therefore provide a reasonable measure of the magnitude of retardation. Results were calculated based on the first 73 days of the injection

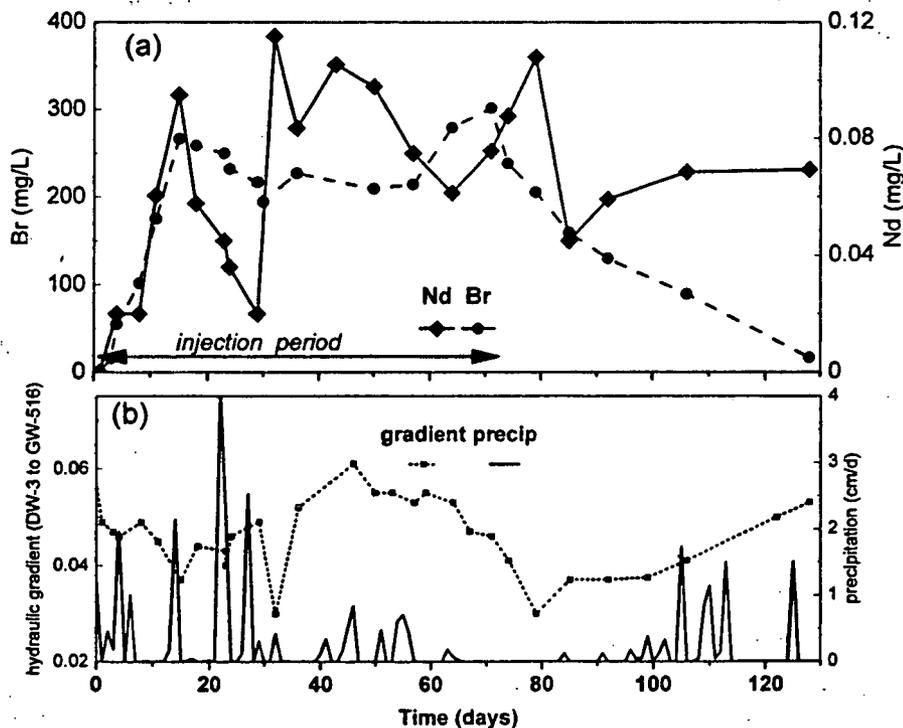


FIGURE 4. Data for GW-516. (a) Concentration history of Br^- and Nd in GW-516. (b) Changes in the hydraulic gradient between DW-3 and GW-516 and the daily precipitation at the WAG-5N site.

because Nd flocs in the injection well may have provided a persistent source that was not comparable to the step termination of the Br⁻ inputs on day 73. The moments analysis confirm that both the reactive and nonreactive tracer migrated at approximately the same rate. The estimated average travel times for the Br⁻ and Nd were 38 and 45 days, yielding an R* of 1.2. Moment calculations based on the entire 120-day observation period yield similar results (R* of 1.3).

Episodic Tracer Arrival at Downgradient Locations. Detectable levels of the tracers Eu, Br, and SF-6 from DW-1 were observed intermittently in the shallow wells, DP-9, DP-12, and DP-2 (30–50 m from the injection well), and at seeps in White Oak Creek (78 m from the injection well; Figure 1), the timing probably reflecting transient recharge events that periodically elevated the water table in the shallow fracture system and connected discrete flow paths between the source well and our monitoring locations. Although the hydrodynamics responsible for the intermittent arrival are not known, it is significant to the objectives of this study that both the reactive and nonreactive tracers were detected along the entire 78-m flow path. For example, Eu and Br⁻ were detected in DP-2 and in seeps WOC-210 and WOC-213 (Figure 1) on day 18 of the injection (data not shown). Their arrival may have been related to the large storms on days 1–8 of the injection (Figure 4b). DP-9 and DP-12 were above the water table during this period (Figure 1) and were not sampled.

Likewise, Eu and Br⁻ were detected in DP-12, DP-9, and DP-2 on day 36. The DW-1 tracer, SF-6, was also detected in DP-2. The arrival of the tracers during this period may have been related to the large storms on days 20–29. No detectable levels of tracer were observed in the seeps following that 92-mm storm event, perhaps as a result of dilution by the large volume of recharge water converging on these discharge points at White Oak Creek.

The failure to detect SF-6 except in DP-2 is explained by the fact that the dissolved gas tracer is readily lost from solution if the groundwater contacts gas-filled pores or if samples come into extensive contact with the atmosphere (as happens in sampling of the seeps). Unlike DP-2, DP-12 and DP-9 underwent transient desaturation during the experiment, and this may account for the failure to detect SF-6 except in DP-2. Nevertheless, the presence of this tracer in the shallow wells and seeps and the failure to detect Nd in any of these locations suggest that DW-1 was the source of the tracer observed in these more distant monitoring locations.

Although rates of migration cannot be accurately estimated due to the intermittent arrival and sparse sampling of the more distant monitoring locations (wells were sampled every 4–5 days), the coincident appearance of reactive and nonreactive tracers suggests that the REE tracers can migrate along a strike-parallel transect between the trenches and White Oak Creek within time frames of days to weeks. These observations suggest that at least some of the storm-associated spikes in gross α -radioactivity observed along this flow path represent material mobilized at the TRU trenches and rapidly transported through the formation, likely as minimally retarded NOM complexes. Local nonequilibrium adsorption may also contribute to the Eu and actinide transport during storm events. However, transport times to the more distant wells appear to be on the order of several days to over a week, which is long as compared to the time required for adsorption equilibrium. Given the very high adsorption affinity of the lanthanide and actinide cations, local nonequilibrium processes may be more significant to the mobilization of the actinide–NOM complex than to the transport of the inorganic actinide or lanthanide species.

Environmental Implications. This study injected non-radioactive REE as field tracers to understand the rates and mechanisms of mobilization and transport of transuranic radionuclides at a contaminated site. Despite high adsorption affinity shown in isotherms, the REE tracers injected in the 10-m long flow path arrived at GW-516 at approximately the same time as the conservative tracer. Similarly, detectable levels of the reactive and nonreactive tracers were observed intermittently in association with large storms that create transient hydraulic connections along the shallow flow path from the TRU trenches to White Oak Creek. Evidence that the enhanced mobility is the result of complexation of the tracer by groundwater NOM includes (i) the size of the mobile REE (<0.05 μ m, consistent with the small size expected for a REE–NOM or actinide–NOM complex) and (ii) DEAE chromatography demonstrated that the REE in the source well was present as an NOM complex.

The essentially unretarded transport of the REE tracers at WAG-5N provides strong evidence that the TRU radionuclides can also migrate with little retardation, as suggested by the field observations (1). Although rapid flow in fractured systems, especially during storm events, may create non-equilibrium conditions that facilitate the mobilization of NOM and NOM-contaminant complexes, the sustained migration of the REE tracer during the 73-day injection period suggests that NOM could have comparable effects on contaminant migration at slower flow rates characteristic of granular formations.

The importance of this process to the flux of contaminants at a site will depend on the binding affinity of the contaminant for the groundwater NOM (which may vary between sites) and the NOM concentration. It is evident that assumptions inherent in many risk assessments for existing waste facilities and performance assessments for future repositories must begin to 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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