Field-Scale Migration of Colloidal Tracers in a Fractured Shale Saprolite

by L.D. McKaya, W.E. Sanfordb, and J.M. Strongc

Abstract
A field-scale tracer experiment carried out under natural gradient ground water flow conditions showed that colloids can be highly mobile in a fractured and highly weathered shale saprolite. Four colloidal tracers (0.100 μm fluorescent latex microspheres, bacteriophage strains PRD-1 and MS-2, and INAA, a dead strain of Pseudomonas syringae), were introduced to a 6.4 m deep well, and concentrations of the tracers were monitored in the source well and in downgradient monitoring wells at distances of 2 to 35 m. All of the colloidal tracers were detected to distances of at least 13.5 m and two of the tracers (microspheres and INAA) were detected in all of the downgradient wells. In most wells the colloidal tracers appeared as a “pulse,” with rapid first arrival (corresponding to 5 to 200 m/d transport velocity), one to six days of high concentrations, and then a rapid decline to below the detection limit. The colloids were transported at velocities of up to 500 times faster than solute tracers (He, Ne, and rhodamine-WT) from previous tests at the site. This is believed to be largely due to greater diffusion of the solutes into the relatively immobile pore water of the fine-grained matrix between fractures. Peak colloid tracer concentrations in the monitoring wells varied substantially, with the microspheres exhibiting the highest relative concentrations and hence the least retention. Rates of concentration decline with distance also varied, indicating that retention is not a uniform process in this heterogeneous material. Two of the tracers, INAA and PRD-1, reappeared in several monitoring wells one to five months after the initial pulse had passed, and the reappearance generally corresponds with increased seasonal precipitation. This is consistent with subsequent laboratory experiments that showed that colloid retention in these materials is sensitive to factors such as flow rate and ionic strength, both of which are expected to vary with the amount of precipitation.

Introduction
Saprolite, a weathered and thoroughly decomposed rock that retains the original structure of the parent material, is common throughout much of the southeastern United States and in other areas with warm, humid environments. Recent investigations in clayey shale saprolite on the U.S. Department of Energy’s Oak Ridge Reservation (ORR) in eastern Tennessee show that fractures and weathering-related macropores in the saprolite allow for rapid movement of water in what would otherwise be a low hydraulic conductivity material (Jardine et al. 1989; Solomon et al. 1992; Wilson et al. 1993; Shevenell et al. 1994). Results of previous field tracer experiments at ORR show that transport of dissolved contaminants in the saprolite is controlled by advection along the fractures and macropores combined with diffusion into the relatively immobile water in the fine-pore structure of the matrix. This causes solutes to be retarded relative to the calculated flow velocity in the fractures (McKay et al. 1997) and solutes with higher diffusion coefficients tend to experience greater retardation than solutes with lower diffusion coefficients (Sanford et al. 1996). Colloidal particles have much lower diffusion coefficients than most solutes and hence should not be as strongly retarded by matrix diffusion. This suggests that rapid transport of colloidal contaminants, such as pathogenic microorganisms from septic fields or radionuclides attached to mobile particles (McCarthy and Zachara 1989), could occur in these materials. The issue of radionuclide mobility is especially important at ORR, where, during the 1940s to 1970s, radionuclides were disposed of in unlined trenches excavated in the shale saprolite.

There have been relatively few experimental investigations of colloid migration in fractured clay-rich materials, especially at the field-scale, so it is not certain whether migration of colloidal contaminants in fractured shale saprolite poses a significant environmental risk. A preliminary tracer experiment (O’Brien et al., unpublished report) carried out in the laboratory in an undisturbed column of shale saprolite from ORR, showed that bacteriophage strains PRD-1 and MS-2 can be rapidly transported (0.2 to 2.4 m/d using a hydraulic gradient of 0.01), at least over short distances (40 cm). The study also indicated that most of the mass of the colloidal tracers was retained in the column, and hence it was not certain whether these colloids could be transported by flowing ground water over significant distances in the field. Laboratory-scale tracer experiments in other types of fractured or macropore-dominated clay-rich materials also show that colloids can be rapidly transported by flowing ground water, but retention rates tend to vary widely (Smith et al. 1985; Kretzschmar et al. 1995; Hinsby et al. 1996).
The only previous field studies of colloid transport in fractured clay-rich materials were carried out in glacial tills in Canada (McKay et al. 1993) and Denmark (McKay et al. in press). These materials, although of different origin than the saprolite, have similar structure and hydrology, with flow controlled by weathered fractures. In a field-scale tracer experiment in the upper 5.5 m of a weathered till, McKay et al. (1993) observed transport of bacteriophage tracers (PRD-1 and MS-2) at rates of 2 to >5 m/d (for first arrival) over a horizontal distance of 4 m. Peak breakthrough concentrations were all less than 2% of the initial source concentration. In the Danish field experiment, colloid transport rates (first arrival of PRD-1) ranged from <0.5 to 5.5 m/d over vertical distances of 1.5 to 2.3 m. Peak breakthrough concentrations were all less than 0.2% of the initial source concentration. Although the Canadian and Danish experiments indicate that rapid transport of colloids is possible in fractured clay-rich materials, they also show high rates of retention, usually one to three log cycles per meter of travel. Hence, there is still uncertainty as to whether colloids are likely to be mobile in fractured clay-rich materials over environmentally significant distances.

The hypothesis for this study is that many types of colloids are likely to be rapidly transported by advection through fractures and other macropores in a typical shale saprolite, and that transport rates will likely be much faster than for solutes, which are strongly influenced by matrix diffusion. A secondary hypothesis is that colloid retention will be widely variable because of differences in the characteristics of the colloids and variability in properties of the media and the flow system. Specific objectives of this study include: (1) determining whether colloidal tracers are mobile at the field scale (tens of meters) in a typical fractured shale saprolite; (2) comparing the relative mobility of several of the more commonly used colloidal tracers; (3) comparing field-scale colloid transport and retention rates with results from laboratory-scale studies; and (4) comparing field-scale colloid transport with transport of relatively nonreactive solutes from previous field experiments.

Figure 2. Cross section showing injection well and monitoring wells used for colloid tracer experiment.

Hydrogeologic Setting and Previous Field Studies

The field site (Figure 1) is located on the Department of Energy’s Oak Ridge Reservation (ORR) in a hydrogeological setting similar to that of several waste burial grounds associated with activities at Oak Ridge National Laboratory (ORNL) and at a former nuclear weapons plant (Y-12). The field site is underlain by interbedded shales, siltstones, and carbonates of the Dismal Gap Formation of the Cambrian-age Conasauga Group. The deposits are thinly bedded (1 to 5 cm thick), with the average strike and dip of bedding planes at N 55° E and 45° SE (Hatcher et al. 1992; Lee et al. 1992). At the field site saprolite extends to depths of 3 to 10 m, and is thinnest near a perennial stream where much of the saprolite has been eroded. The uppermost saprolite is highly fractured (often >100 fractures/m), with fractures occurring both parallel and perpendicular to bedding. Fracture density decreases with depth and in the underlying bedrock values range from 15 to 30 fractures/m (Lee et al. 1992). The water table is usually located above the transition from saprolite to bedrock and during wet periods rises almost to ground surface. Matrix porosity of the saprolite ranges from 12% to as high as 52%, and is generally much higher than the calculated fracture porosity (Dorsch and Katsube 1996).

The field site was the location of several previous hydrogeological investigations related to solute transport in fractured media. In the late 1980s and early 1990s, a series of single and multilevel monitoring wells were installed in the saprolite and underlying bedrock along a transect that sloped downward toward a perennial stream (Figure 2). The wells were used for hydraulic conductivity testing, point dilution tests, and solute tracer experiments (Byard et al. 1989, 1992; Sanford et al. 1994). Hydraulic conductivity values determined from pumping tests and slug tests in the saprolite and bedrock ranged from 2 × 10⁻⁶ to 8 × 10⁻⁹ m/s (Lee et al. 1992). Results of the point dilution tests (using a measured hydraulic gradient of 0.04) yielded geometric mean hydraulic conductivities of 3.7 × 10⁻⁵ m/s for the saprolite and 1.7 × 10⁻⁵ m/s for the upper 3 to 4 m of the bedrock (Sanford and Moore 1994). An important finding of the point dilution tests was that a zone of relatively high specific discharge exists at the base of the saprolite (Sanford and Moore 1994).
Natural gradient tracer tests were carried out using fluorescent rhodamine-WT dye (Lee et al. 1989, 1992) and the dissolved noble gases, helium and neon (Sanford et al. 1996; Sanford and Solomon, 1998), to investigate transport of dissolved contaminants in the saprolite. Important findings from these two tracer tests include: (1) Soluble tracer plumes tend to develop that are elongated along strike, with little transverse dispersion; and (2) solute transport rates are strongly influenced by matrix diffusion. In both tracer tests, transport rates (for a given relative concentration contour) decreased with time and distance from the injection well, and the low concentration “front” of the plumes tended to migrate at rates hundreds of times faster than the high concentration region. Both of these types of behavior indicate a high degree of longitudinal dispersion, which is typical of systems in which matrix diffusion is dominant. For the dye tracer experiment (Lee et al. 1989, 1992) migration rates for the 100 ppb contour (which represents \( C/C_0 = 6 \times 10^{-6} \) relative to the initial pulse concentration) slowed from about 1 m/day during the first 14 days of the experiment, to about 0.04 m/day during the next 230 days. Although this difference may be partly attributable to physical heterogeneity, it is also consistent with greater losses of the tracer pulse with increasing time due to diffusion into the matrix. During the noble gas tracer experiment, breakthrough curves for helium and neon at all the monitored wells show a separation of the tracers with helium, which has a higher diffusion coefficient, migrating slower than neon. This is another indication that matrix diffusion has a strong influence on solute transport in the saprolite (Sanford and Solomon 1998).

**Methods**

**Colloidal Tracers and Analytical Methods**

The following colloidal tracers were used in the experiment: the bacteriophage strains PRD-1 and MS-2; 0.100 \( \mu \)m diameter fluorescent latex microspheres; and INA, which is a dead bacterial strain (*Pseudomonas syringae*), that is assayed based on its ice nucleating activity. PRD-1 and MS-2 are icosahedral bacteriophage with diameters of 0.062 \( \mu \)m and 0.020-0.026 \( \mu \)m, respectively (Olsen et al. 1974; Van Duin 1988). The host bacteria for PRD-1 is *Salmonella typhimurium* LT-2 and the host bacteria for MS-2 is *Escherichia coli*. The bacteriophage concentrations were determined from assays performed using the plaque forming unit (PFU) method described by Adams (1959) and Bales et al. (1991). Dilutions of each ground water sample with Tris buffered saline were prepared and added to test tubes containing molten overlay agar and the host bacteria. It was then poured onto solidified Typtic Soy Agar plates, incubated overnight at 37°C, and the number of plaque forming units was counted. Most of the ground water samples were assayed within 24 hours of collection. The bacteriophage and host bacteria were grown from samples provided by the University of Arizona (Tucson) Department of Microbiology and Immunology and the assays were carried out at the University of Tennessee (Knoxville).

The microspheres used in the field experiment were 0.100 \( \mu \)m diameter Fluoresbrite® yellow-green, latex microspheres that fluoresce at a wavelength of 458 nm (Polysciences Inc., Warrington, Pennsylvania). Serial dilutions of the ground water samples were prepared and filtered onto 0.45-\mu m polycarbonate membrane filters. The filters were then mounted on microscope slides and the number of spheres per sample were determined by counting under an epifluorescent microscope.

![Figure 3. Concentration of colloidal tracers in injection well (GW484): (a) zero to eight days after injection; (b) zero to 300 days after injection. Concentration of bacteriophage strains, PRD-1 and MS-2, are in units of plaque forming units/mL (PFU/mL) and the latex microspheres are given as spheres/mL. The ice nucleating activity (INA) measurements are given as number of positives per 10 subsamples, and these should be considered mainly as indicators of the presence or absence of the INA tracer, rather than as accurate concentrations.](image)

The INA tracer and its usage in ground water is described by Strong-Gunderson et al. (1995). The tracer includes intact and broken fragments of *Pseudomonas syringae*, which have an average particle diameter of approximately 1 \( \mu \)m. The INA tracer is assayed by pipetting 10 droplets (each about 10 \( \mu \)L) of a ground water sample onto a foil pan and then placing the pan into a temperature-controlled glycol bath at -5°C for three minutes. The presence of INA is indicated by freezing of the water droplets (water without a nucleating agent will not freeze at the specified temperature and exposure time). Concentrations of INA are expressed as number of positives per 10 samples (example: a concentration of 6/10 means six drops froze out of the 10 droplets added to foil pan). Values of 10/10 mean that the concentration is greater than or equal to 10 INA particles per 100 \( \mu \)L (or 100 per mL). As a result, INA is used mainly as a qualitative tracer that, if detected, can indicate only whether concentrations are relatively high or low. Most samples were analyzed for INA within 24 hours of collection.
Figure 4. Concentration of colloidal tracers in monitoring well M-3, located 2 m from injection well: (a) zero to eight days after injection; (b) zero to 300 days after injection.

Figure 5. Concentration of colloidal tracers in monitoring well GW-487, located 13.5 m from injection well: (a) zero to eight days after injection; (b) zero to 300 days after injection.

Background Concentrations and Survival Tests
Background samples of ground water from the source well and from the downgradient monitoring wells showed no detectable presence of the bacteriophage tracers (PRD-1 and MS-2), INA, or the fluorescent microspheres. Laboratory survival tests were carried out prior to the field experiment to measure die-off (deactivation) rates for the bacteriophage tracers, PRD-1 and MS-2. A tracer solution containing all of the colloidal tracers at the approximate concentrations used for the field experiment was added to a reservoir containing 5 L of ground water from the source well (GW-484). Two other reservoirs were prepared with ground water from the downgradient wells and “spiked” with the tracer solution to represent dilutions of 0.01 and 0.0001 relative to the initial source reservoir. The reservoirs were stored at 12°C and concentrations of PRD-1 and MS-2 were measured daily for five days (the expected duration of the initial breakthrough portion of the field experiment). The survival tests showed no measurable decline in concentrations of PRD-1 or MS-2 in any of the three reservoirs.

Field Tracer Experiment
Approximately 1200 mL of tracer solution containing PRD-1, MS-2, INA, and fluorescent microspheres were added to the source well (GW-484) over a period of approximately 15 minutes at the start of the tracer experiment (October 4, 1994). As the tracer was slowly added to the source well, an equal volume of water was removed and was recirculated to mix the tracer throughout the water column.

After the tracer injection, water samples were periodically taken from the source well and from five downgradient monitoring wells: M-3 (located 2 m from source well), GW-487 (13.5 m), GW-493 (18 m), GW-499H (27 m), and GW-498 (35 m), and from one upgradient well GW-483 (6 m). These wells are located along the centerline of both the dye and noble gas plumes. The bottoms of wells GW-487, GW-493, GW-499H, and GW-498 correspond to auger refusal and, therefore, are screened entirely in the saprolite (Figure 2). Wells GW-483, GW-484, and M-3 were drilled 0.3 to 0.9 m into the bedrock and their screened sections straddle the transition zone from saprolite to bedrock.

Prior to sampling, 30 to 100 mL were purged from each well using a peristaltic pump at rates of about 30 to 100 mL/min to remove stagnant water from the dedicated sample tubing. Four samples (two 15 mL and two 50 mL) were then collected in sterile plastic centrifuge vials. The samples were placed in resealable plastic bags and stored in ice-filled coolers until they were transported to the laboratory for analysis. Sampling frequency near the
start of the experiment ranged from every two to three hours on day 1 to once daily for days 4 through 6. Later samples were taken at irregular intervals (a few weeks or more) and sampling continued for up to 275 days after injection of the tracer solution. Precipitation at the site was monitored daily with an automatic rain gauge and a data logger for the entire tracer monitoring period.

**Results**

**Source Well (GW-484)**

Initial concentrations of the colloid tracers in the source well, immediately after addition and recirculation of the tracer solution were: microspheres = $8 \times 10^8$ spheres/mL; PRD-1 = $3.2 \times 10^9$ PFU/mL; MS-2 = $1.3 \times 10^9$ PFU/mL; and INA ≥ 10/10. During the first day, concentrations of tracers in the source well varied substantially, possibly due to incomplete mixing in the well and sand pack (Figure 3a). After the first few days, the concentration of microspheres in the source well (Figure 3b) declined at a slow but constant rate (approximately one log cycle per 275 days). The bacteriophage concentrations declined at a higher rate, approximately one log cycle per 30 days until about 135 to 200 days after the tracer injection. After this period, bacteriophage concentration values either remained constant or declined slowly. PRD-1, MS-2, and INA were all detectable in the source well at the end of the 275 day monitoring period.
Table 1

<table>
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<th>Time of First Detection (hours)</th>
<th>Velocities (m/day)</th>
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<td>PRD-1</td>
<td>MS-2</td>
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<td>2.3</td>
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<td>18</td>
<td>2.2</td>
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<tr>
<td>499H</td>
<td>27</td>
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<tr>
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<td>35</td>
<td>5.7</td>
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</table>

Figure 9. Decline in peak concentrations of colloidal tracers with distance from injection well. The slope of each graph is indicative of the rate of colloidal losses, which are believed largely due to retention in the saprolite.

Breakthrough Curves in Monitoring Wells

At least one of the colloidal tracers was detected in each of the downgradient wells, and the breakthrough curves are shown in Figures 4 through 8. None of the three colloidal tracers were found in well GW-483 (6 m upgradient), which was monitored during the first 30 days of the experiment. The most noticeable characteristic of the colloidal breakthrough curves for each well is the early time of arrival, and hence the rapid transport of the colloidal tracers, especially the microspheres. The ground water velocity must be at least as fast as the velocity of the tracers, so the data also measures ground water velocity between the source well and each monitoring well. The times of first arrival for the tracers and the calculated transport velocities are shown in Table 1. The calculated velocities of the colloidal tracers range from 5 to 200 m/d, with the greatest velocities (120 to 200 m/d) observed for the microspheres. The well with the slowest colloid transport velocity is M-3, which is closest to the source.

After the rapid first arrival, concentrations of microspheres and bacteriophage in most of the monitoring wells reached a peak lasting from one to six days, and then concentrations rapidly declined to below the detection limit. The only exception was in well M-3, located 2 m from the source well, where the microspheres and bacteriophage were detectable for a much longer period. In M-3, MS-2 was detectable for at least 97 days, and PRD-1 and the microspheres were detectable to the end of the 275 day monitoring period. The persistence of colloidal tracers in M-3 is similar to what was observed in the nearby source well.

The shapes of the INA breakthrough curves are more irregular than for other colloid tracers in most of the wells, which is likely due to the qualitative nature of the INA analyses. INA tended to persist longer than the other tracers, and in many of the downgradient monitoring wells (M-3, GW-487, GW-493, and GW-499H; Figures 4b, 5b, 6b, and 7b) the INA tracer reappeared one to five months after the initial “pulse” of tracer had passed. In GW-487, 13.5 m from the source well, PRD-1 also reappeared in samples taken 29 to 97 days after the start of injection. These tracer reappearances generally correspond with periods of higher rainfall, as shown in Figure 5b, suggesting that INA and PRD-1 may have been remobilized by the infiltrating precipitation.

Concentration Loss Rates

Relative concentrations of microspheres were higher than either PRD-1 or MS-2 throughout the experiment in all of the downgradient wells (Figures 4 through 8). Peak concentrations of each tracer declined with distance from the source well, but the rate of decline (log cycles per meter of travel) was not constant (Figure 9). Over the first 2 m of travel, peak concentrations of PRD-1 and MS-2 declined at >2 log cycles/m, but from 2 to 13.5 or 18 m distance, the rate was approximately 0.3 log cycles/m. For the microspheres, the decline in concentration over the first 2 m of travel was approximately 1 log cycle/m, which was half the rate observed for PRD-1 and MS-2. However, from 2 to 18 m, the rate for the microspheres (0.3 log cycles/m) was nearly identical to the rate for PRD-1 and MS-2. From 18 to 35 m distance, the peak microsphere concentrations showed no further decline with travel distance.

Discussion

The experiment clearly shows that at least some types of colloids can be rapidly transported over environmentally significant distances in fractured clay-rich saprolite. In all of the monitoring wells peak concentrations of the tracers were small (4 \times 10^{-3} to 1 \times 10^{-10}) relative to the initial concentration in the source well. The low peak concentrations are at least partly due to dispersion, or spreading of the tracer pulse and mixing with the surrounding ground water. However, much of the decline in concentrations also appears to be due to retention of colloids in the saprolite, although there is some uncertainty in this assessment. The influence of retention is indicated by the large differences in peak concentrations for different colloidal tracers in each downgradient monitoring well, which based on the high bacteriophage survival rates measured in the survival tests, cannot be explained by microbial decay. Differences in the rate of decline of colloid concentrations
in the source well may also be due to differences in attachment and detachment rates in the well casing or the soil around the screen.

The large degree of variation in velocity of first arrival for the colloids at each monitoring well (Table 1) and the variation in colloid loss rates with distance (Figure 9) is most likely due to heterogeneity along the fracture flowpaths between the source well and the monitoring wells. Over the first 2 m of travel, loss rates for all three of the quantitative tracers (PRD-1, MS-2, and the microspheres) are highest and transport velocities lowest, suggesting that fractures connecting the source well and well M-3 have smaller apertures or more tortuous pathways than the fractures further downstream. M-3 is screened over a short interval at the saprolite-bedrock transition, so it is possible that it does not intersect some of the major fracture pathways connecting the other wells. As a result, many of the colloidal tracers detected in the wells further downstream may have bypassed the sampling interval in M-3. The nearly constant peak microsphere concentration from 18 to 35 m distance from the source well is further evidence of heterogeneity; in this case it is likely a large aperture fracture, with fast ground water flow and little colloid retention. The previous field studies (Lee et al. 1992; Sanford and Solomon 1995) confirm that this material is heterogeneous, and the monitoring wells chosen for the colloid tracer experiment were generally those wells that had relatively rapid breakthrough of the solute tracers.

Subsequent to the field experiment described in this manuscript, a series of laboratory tracer experiments were carried out in undisturbed columns of shale saprolite from another location on the Oak Ridge Reservation, to investigate colloid retention processes and factors influencing these processes. Tracer experiments by Cumbie and McKay (1999) using five different sizes (0.05 to 4.25 µm diameter) of carboxylate-coated latex microspheres were carried out in a saprolite column, which was then dismantled and inspected. Inspection under UV light showed visible concentrations of fluorescent microspheres on approximately 50% of the bedding plane fractures and almost all of the fractures perpendicular to bedding. The uncoated microspheres used in the field study are expected to have an even greater attraction to mineral surfaces, so this supports our hypothesis that declines in peak tracer concentration with distance from the source well are primarily due to colloid retention rather than dispersion of the tracer pulse. The study by Cumbie and McKay (1999) also showed that there was an optimum colloid size for transport (approximately 0.5 to 1.0 µm). This was confirmed by subsequent experiments by Haun (1998) that indicated an optimum colloid size of approximately 1.0 µm. The existence of an optimum colloid size is consistent with colloid filtration theory developed for granular media (Yao et al. 1971), which predicts greater losses of larger than optimum particles due to gravitational settling and physical straining in small pores, and greater losses of smaller than optimum particles due to their higher diffusion coefficients, which result in more frequent collisions with, and attachment to, the media. This may be partly responsible for the differences observed in breakthrough curves from the field experiment, where peak concentrations tended to decrease as the size of the colloidal tracer decreased (microspheres = 0.100 µm, PRD-1 = 0.062 µm, and MS-2 = 0.026 µm). Although the field data supports this hypothesis, it is not conclusive, because other factors such as differences in surface characteristics of the tracers can also influence retention (Bales et al. 1997).

Two of the laboratory studies (Harton 1996; Haun 1998) showed that changing environmental conditions (increased flow rate and decreased ionic strength) can release previously retained colloids. This is consistent with our hypothesis that reappearance of INA and PRD-1 in several of the monitoring wells approximately one to five months after the tracer injection was due to infiltration of precipitation during the fall and winter rainy period (Figure 5b). Precipitation is expected to have much lower ionic strength than the ground water, and during seasonal wet periods hydraulic gradients and flow rates typically increase, so both of these factors could have contributed to the release of retained colloidal tracers. However, this conclusion is still tentative because there were only a few sampling visits during the rainy season and because other factors, such as arrival of colloids through other more tortuous or slower flowing fracture pathways, may also contribute to the reappearance of colloids.

It is difficult to directly compare loss rates between the field and the laboratory experiments. This is partly because the undisturbed laboratory columns were collected from the upper 1.5 m of a similar saprolite, located several km from the field site, and it is uncertain whether they are sufficiently representative of conditions at the depths where the monitoring wells were located. As well, in the laboratory experiments a different type of coating was used for the microspheres and in one of the studies (Haun 1998) a variety of chemically different influent solutions were used. However, a simple comparison of the rate of decline of peak concentration with distance from source can be carried out for the bacteriophage tracers, PRD-1 and MS-2, which were used in both the field and in the lab (Harton 1996). The laboratory tracer experiments were carried out using a constant concentration influent solution (0.005 M CaCl₂), which has an ionic strength value typical of ground water in this area, and at specific discharge rates (0.008 to 0.95 m/d), which

Figure 10. Comparison of breakthrough curves for colloids and solute tracers in: (a) well 493 and (b) well 498. The solute tracer data is from previous field experiments at the site by Lee et al. (1989, 1992) and by Sanford and Solomon (1998).
span most of the range of values previously measured by Sanford and Moore (1994) in saprolite at the field site. The rate of concentration loss, \( r \), expressed as log cycles per m of travel, for the column tracer experiments, was calculated using

\[
    \log \left( \frac{1}{C / C_0} \right) = \frac{d}{r}
\]

where \( C / C_0 \) is the peak relative concentration in the effluent, and \( d \) is the length of the column. The \( r \) values for bacteriophage tracers (calculated based on data from Barton 1996) in the laboratory experiments ranged from 0.08 to 7.7 log cycles per meter, which is a much wider range than the \( r \) values of 0.3 to 2.3 log cycles per meter, calculated for the same tracers in the field experiment. Much of this difference is likely due to the difference in flow rates. When the comparison is made using tests with approximately the same specific discharge rates (2 \( \times \) 10\(^6\) m/s in lab test #3, compared to approximately 4 \( \times \) 10\(^6\) m/s for the geometric mean of the specific discharge values derived from point-dilution tests at the field site), the lab and field results more closely resemble one another: lab \( r \) values range from 0.08 to 2.4 log cycles per meter, and field \( r \) values range from 0.3 to 2.3 log cycles per meter.

The breakthrough curves for the colloid tracers in the field experiment can be compared to solute tracers (He, Ne, and rhodamine-WT dye) from previous experiments at the same site (Sanford and Solomon 1998; Lee et al. 1989, 1992). For all of the wells, the colloidal tracers arrived before the solute tracers, and the difference between tracer arrival times increased with distance from the source, as shown in the two examples in Figure 10. The ratio of colloid velocity to solute velocity, determined by dividing the time of arrival of the fastest colloidal tracer by the time of arrival of the fastest solute tracer at each well, also increased with distance from the source. For well 487 (13.5 m from the source), the velocity ratio was <44, and for well 498 (35 m from the source), the ratio was approximately 500. These velocity ratios are affected by tracer detection limits, sampling frequency, and possibly by some sorption of the dye, but it is evident that on average the colloid pulse is traveling much faster than most of the solute. This is consistent with our matrix diffusion conceptual model, which predicts that as transport distance or residence time increases there should be increased retardation of tracers with higher diffusion coefficients (in this case, the solutes). The behavior of the receding limb or “tail” of the colloid and solute breakthrough curves can also be compared. For all the monitoring wells, except M-3, the breakthrough of each of the colloidal tracers occurred mainly as a discrete pulse, which largely disappeared within one to six days. By comparison, the dye tracer, which was also injected as a small volume pulse, is still present in most of the wells at the site more than 10 years after the initial injection. Again, this is consistent with the matrix diffusion conceptual model, because once a solute has entered the matrix it can slowly diffuse back into the fast-flowing water in the fractures, resulting in long-term contamination of the system.

Conclusions and Implications

The field-scale colloid tracer experiment described in this paper shows that a variety of different colloid types can be transported rapidly (tens to hundreds of m/day) over distances of up to 35 m, by ground water flowing under natural gradient conditions in a typical fractured shale saprolite. Transport and retardation rates varied substantially between different tracers and with distance along the flowpath. The variations are believed due to both heterogeneity in properties of the media (principally fracture aperture and degree of fracture interconnection) and to differences in properties of the colloids, including but not limited to the diameter of the tracer particles. The experiment shows that the colloidal tracers, which are analogs for colloidal contaminants, can remain in suspension in the saprolite for tens of days, and, in the case of the bacteriophage, can remain viable during this period. The reappearance of INA in several of the monitoring wells and reappearance of PRD-1 in one of the wells several months after the initial pulse had passed, suggests that retained colloids in this material can be remobilized by changes in flow rate or chemical composition of the infiltrating ground water. Comparison of the results of the field experiment with laboratory-scale experiments indicate that although the lab studies may be useful for investigating transport processes, there is a high degree of uncertainty in attempting to use lab results to predict colloid transport behavior in the field. Comparison of the colloid breakthrough curves to results of previous tracer experiments using relatively nonreactive solutes also indicates substantial differences in tracer behavior, with the colloidal tracers migrating much faster than the solutes, and being flushed out of the system much earlier. This is believed to be largely due to greater diffusion of the solutes into the relatively immobile pore water in the fine-grained matrix.

The experiment suggests that there is potential for environmentally significant migration of colloidal contaminants, such as pathogenic microorganisms or radionuclides attached to mobile particles, in fractured saprolite and other clay-rich materials. Since these materials are widespread, it is possible that there may be many instances where contaminants from sources such as septic fields, leaking sewer pipes, or waste disposal pits are causing degradation of water quality in nearby aquifers or streams. Finally, the experiment shows that colloidal tracers are sufficiently mobile, at least in some cases, to be used to detect fracture flow pathways and indicate flow velocities in fractured saprolite. For these purposes colloidal tracers have major advantages over dissolved tracers because of their low detection limits and their expected low sensitivity to retardation by matrix diffusion.

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