

Field Experiments in a Fractured Clay Till

2. Solute and Colloid Transport

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A field tracer experiment was conducted in a lateral flow field in the weathered and highly fractured upper 6 m of a 40-m-thick clay-rich till plain in southwestern Ontario. In the upper 3 m where fractures are closely spaced (<0.13 m) the advancing front ($C/C_0 = 0.01$) of the nonreactive solute tracers, bromide and ^{18}O , migrated at rates of 0.01 to 0.07 m/d, over distances of 4 and 6 m and under a lateral hydraulic gradient of 0.24. In this same zone, two strains of colloid-sized bacteriophage tracers migrated at rates of 2 to >5 m/d. Simulations with a discrete fracture/porous matrix flow and transport model, which used the cubic law for flow in fractures, showed that diffusion of the solutes, but not the much larger colloids, into the matrix pore water between fractures is sufficient to cause the observed difference in solute and colloid transport rates. Transport-derived and hydraulic conductivity-derived fracture aperture values were similar, within a factor of 3 and falling mainly within a range of 5–40 μm . In the upper 3 m the solute tracers were evenly distributed between pore water in the fractures and the matrix, and as a result, solute transport can be closely approximated with an equivalent porous medium (EPM) approach. Below this depth, fractures are more widely spaced (0.13 to >1 m) with concentration peaks tending to occur near visible fractures, and solute transport cannot be adequately described with an EPM approach.

INTRODUCTION

Clay-rich glacial deposits are generally weathered and fractured near ground surface. The fractured zone has been observed to have a depth ranging from a few meters to tens of meters and can increase both the hydraulic conductivity of the deposit and the potential for rapid migration of contaminants. Flow in individual fractures may be very rapid, of the order of meters per day, and could significantly influence contaminant migration even in deposits where the bulk hydraulic conductivity is relatively low.

A series of recent field investigations was performed in the visibly weathered and fractured zone of a 40-m-thick clay till at the Laidlaw Industrial Waste Disposal Facility near Sarnia, Ontario. In a lateral flow tracer experiment with a hydraulic gradient of 0.4, *D'Astous et al.* [1989] observed that bromide, a nonreactive solute, migrated at 4–6 cm/d. The migration rates are similar to the value of 2 cm/d determined by *Balfour* [1991] for lateral movement (lateral hydraulic gradient of up to 0.2) of a shallow chloride plume which extends up to 40 m from a 4-year-old landfill mound located at the same site. The migration of chloride and bromide in the weathered and fractured zone was much faster than observed at the same site in the unweathered clays at a depth of 18 m, where *Johnson et al.* [1989] determined that chloride had migrated downward only 1 m from the base of a landfill cell which had been filled with hazardous waste 5 years previously. This difference clearly indicates that fractures influenced migration of the contaminants. However, the solute migration rates in the weathered and fractured zone are still several orders of magnitude slower than fracture flow velocities calculated based on

values of lateral hydraulic gradient, fracture spacing, and measured bulk hydraulic conductivity (approximately 10^{-7} m/s) using the cubic equation for flow in smooth parallel fractures [*Snow*, 1969].

The migration of solutes in a fractured clay or porous rock is expected to be retarded relative to the flow velocity in the fractures by diffusion from the fractures into the immobile or much less mobile pore water in the blocks of clay or rock matrix between fractures. *Foster* [1975] first recognized this concept, referred to as matrix diffusion, and offered it as a possible explanation for the retardation of bomb tritium relative to calculated infiltration rates in a fractured chalk aquifer (matrix porosity, 0.15–0.40) in Britain. *Day* [1977], *Grisak et al.* [1980], *Pankow et al.* [1986], and *Rudolph et al.* [1991] later applied this concept to fractured clays (matrix porosity generally >0.25) in field or laboratory studies.

The influence of matrix diffusion on solute transport in fractured clays has not yet been experimentally confirmed in the field. A rigorous test of the conceptual model requires measurement of flow velocity in the fractures as well as measurements of solute concentration in both the fractures and in the pore water of the matrix. Fracture flow velocities cannot be measured directly from solute tracer data because of the influence of matrix diffusion, and in the previous studies velocities were calculated using the cubic law [*Snow*, 1969] from measurements of hydraulic conductivity. As well, the distribution of solute in the matrix pore water was not measured in any of the previous studies, except in the study by *Balfour* [1991].

Colloid-sized tracers are expected to be less influenced by matrix diffusion than solutes due to size exclusion of the colloids from many of the pore throats in the matrix. If the colloids are not strongly retarded by other factors such as filtration or sorption to the walls of the fractures, they should travel at rates faster than solutes and could be used as indicators of flow velocity in the fractures. In laboratory tracer experiments [*Bales et al.*, 1989] in columns of fractured porous tuff (matrix porosity, 0.24), colloid-sized bac-

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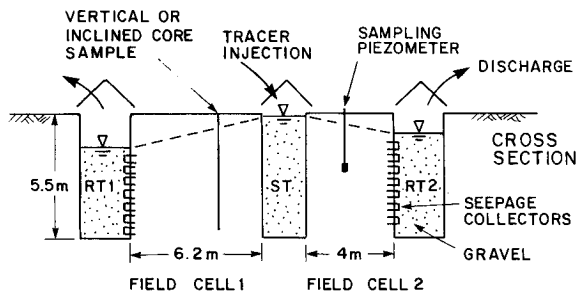


Fig. 1a. Tracer experiment and monitoring methods.

terio-phages were transported at rates up to 3 times faster than nonreactive solute tracers. The difference in transport rates was attributed to diffusion of the solutes but not the much larger bacteriophages into the matrix pore water. In field tracer experiments in fractured crystalline rock [Champ and Schroeter, 1988], colloid-sized bacteria traveled more rapidly than the solutes Na fluorescein and ^{82}Br . The authors did not explain the difference in transport rates, but it is possible that even in this low-porosity medium diffusion of the solutes, but not the colloids, into matrix pore water, microfractures, or small-aperture regions of the main fractures is significant. In a field tracer experiment in a, presumably fractured, sandstone and boulder clay in Wales, Martin and Thomas [1974] observed transport of a colloidal bacteriophage a distance of up to 570 m in 3 days, which indicates that flow velocities in a fractured material can be very high.

The objectives of the study described in this paper are, for a weathered and fractured clay, to determine, at the field scale, the influence of matrix diffusion on transport of nonreactive solutes; to test the feasibility of using colloidal tracers as indicators of flow velocity; to develop and test field monitoring methods; and to assess modeling strategies for application to solute transport.

EXPERIMENTAL METHODS

Experimental Setup

The experiment was performed in the shallow weathered and fractured zone of a thick clay till deposit at the Laidlaw (formerly Tricil) Industrial Waste Disposal Facility near Sarnia, Ontario, Canada. The experimental setup, measurements of hydraulic conductivity and fracture spacing, and calculated values of hydraulic aperture are described by McKay *et al.* [1993a] and are summarized in this section.

A system of three parallel trenches, each 5.5 m deep and 7 m long, with spacings between trenches of 4 and 6.2 m, was constructed (Figure 1a). Along the walls of the trenches, fracture spacings and orientations were mapped, and 70 seepage collectors, each 0.24×0.27 m, were installed to collect lateral infiltration (Figure 1b). The trenches were then backfilled with clean gravel, and roofs and plastic ground covers were constructed to limit infiltration of precipitation into the system. Water levels in the trenches were controlled by adding water to the central, or source trench, and pumping from the two receiver trenches. An overall lateral hydraulic gradient of approximately 0.24 was maintained between the source trench and the receiver trenches.

Field hydraulic conductivity values were determined based on measured discharge to the seepage collectors,

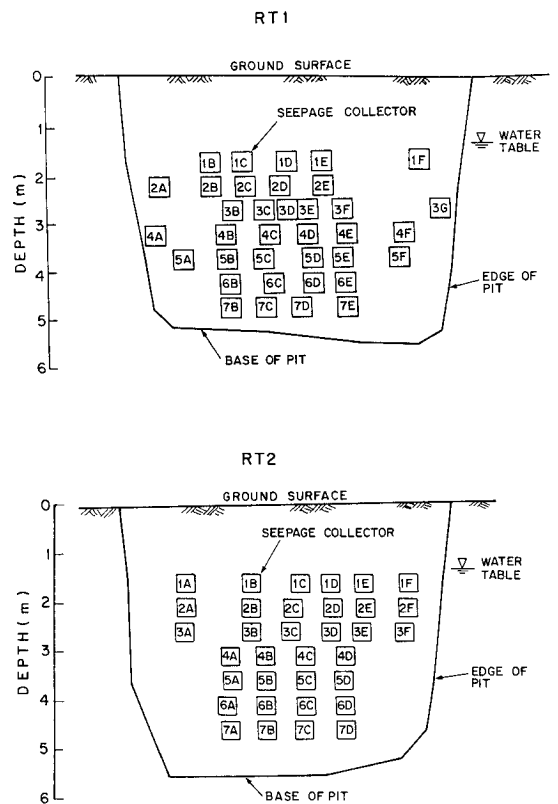


Fig. 1b. Location of seepage collectors.

recovery tests in piezometers installed between the trenches, and measurement of water volumes added to or taken from the trenches. Small-scale hydraulic conductivity values from tests in the seepage collectors and the piezometers ranged from 2×10^{-10} to 10^{-6} m/s. Large-scale hydraulic conductivity values from the trench inflow/discharge data ranged from 1.6 to 2.6×10^{-7} m/s. Values of hydraulic fracture aperture were calculated using the small-scale hydraulic conductivity values and the measured fracture spacing data, assuming an analogy to flow between two smooth parallel plates [Snow, 1969]. The calculated values of hydraulic aperture ranged from <1 to $43 \mu\text{m}$.

Solute Transport Experiments

At the start of the solute tracer experiment on August 5, 1988, the flow system was at steady state due to continuous operation of the trench inflow/discharge system for two months using clean groundwater from the tills. The tracer solution used for the first 300 days of the experiment consisted of NaBr added to water from a confined aquifer which had a natural contrast relative to the till pore water in concentrations of chloride, ^{18}O , and ^2H . From 300 to 695 days, surface water from a local municipal supply, with added NaBr and concentrations of chloride, ^{18}O , and ^2H similar to that of the original till pore water, was used for the tracer solution. The concentrations of the tracers and major ions in the injected solutions and the background pore water are shown in Table 1.

At the start of the tracer experiment, 23,000 L (approximately 1.3 pore volumes assuming porosity of the gravel-filled trench equal to 0.35) of tracer solution was flushed

TABLE 1. Chemistry of Tracer Solution and Background Pore Water in the Weathered and Fractured Till

	Tracer Solution in Source Trench		Background	Analytical Method
	0-300 Days	After 300 Days		
<i>Tracers</i>				
Br ⁻ , mg/L	148	145	<0.5	ion chromatography
Cl ⁻ , mg/L	453	19	9 to 40	ion chromatography
¹⁸ O, ‰	-16.38	-8.5	-8.0 to -8.8	mass spectrometry
² H, ‰	-113.1	-60	-56 to -60	mass spectrometry
<i>Chemistry</i>				
TDS, mg/L	1200	384	620	sum of ions
HCO ₃ ⁻ , mg/L	217	114	231	titration
SO ₄ ²⁻ , mg/L	2	20	222	ion chromatography
Na ⁺ , mg/L	264	53	43	atomic adsorption
Ca ²⁺ , mg/L	58	26	66	atomic adsorption
Mg ²⁺ , mg/L	30	7	38	atomic adsorption
pH	7.5	6.8-7.4	7.4	electrode

TDS denotes total dissolved solids. All analyses were performed by staff of the Environmental Isotope Laboratory and the Aqueous Geochemistry Laboratory at the University of Waterloo.

through the source trench over a 6-hour period at the start of the tracer test, and then the water was mixed by pumping from wells set in the gravel. This provided an abrupt change (Figure 2) in tracer concentration without changing the hydraulic head at the trench boundary. An additional 7500 L (0.4 pore volumes) was flushed through the source trench 5 days later. The tracer solution in the source trench was periodically mixed, weekly for the first 300 days and monthly thereafter, by pumping between wells set in the trench. The concentration of each tracer in the source trench was determined by calculating a time-weighted average of samples from the surface and from shallow (0.9–1.8 m depth) and deeper (4.9 m depth) piezometers within the trench. All subsequent tracer concentrations are presented in terms of relative concentration, C/C_0 , where C is the measured concentration minus the background concentration and C_0 is the concentration in the source trench minus the background concentration.

Concentrations of the solute tracers were determined in the laboratory using a Dionex ion chromatograph. Isotope concentrations were measured in the laboratory using mass spectrometry. McKay [1991] found that concentrations of bromide, chloride, and ¹⁸O in water mixed with samples of

the weathered clay remained constant during batch experiments of up to 1 year in duration. Based on the batch tests these tracers are expected to be essentially nonreactive in the field experiment.

In the "field cells," which are the areas between the trenches, samples from 16 standpipe piezometers located at depths ranging from 1.8 to 4.9 m were analyzed for tracers during the experiment. The piezometers sampled consisted of 0.64-cm-ID polyethylene tubing with a slotted tip completed in a 2.5-cm-diameter quartz sand pack approximately 20 cm in length. The rest of each borehole was filled with a thick bentonite grout. Approximately 60 mL of water was removed from the tip of each piezometer with a dedicated syringe and length of small-diameter polyethylene tubing during weekly sampling episodes for the first 270 days. After 270 days, sampling was approximately once per month, and piezometers were emptied 1 week prior to sampling to ensure that fresh water was drawn from the till.

In the receiver trenches, 65 polyethylene seepage collectors (24 × 27 cm each) were monitored during the solute tracer experiment. Water from the collectors accumulated in polyethylene bags which were sampled, often on a weekly basis, for the first 270 days and monthly thereafter. As well, water samples representing a mixture of all water entering the trench were taken from a discharge sump in each receiver trench.

Nineteen boreholes were drilled and continuously cored to depths of 4.1–6.2 m below ground surface in the field cells between 270 and 277 days after the start of the tracer test. Most (80%) of the soil cores were taken through a hollow stem auger using a CME (Central Mine Equipment) continuous sample core barrel with 7.9-cm-ID polyvinyl chloride core liners. The ends of the 0.75- or 1.5-m-long cores were sealed with plastic caps and tape. The rest of the cores were taken with 7.0-cm-ID steel Shelby tubes, which were then sealed at the ends with beeswax. Six of the boreholes were inclined at either 45° or 60° from vertical and were oriented such that for a given hole the core samples were always the same distance from the source trench. The remaining boreholes were vertical. Each borehole was backfilled with a

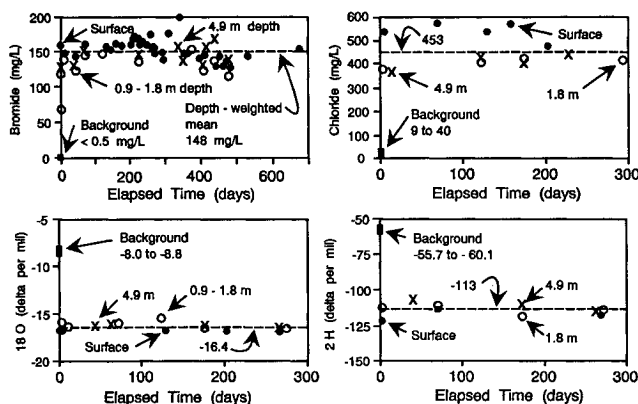


Fig. 2. Source trench solute concentrations.

thick bentonite grout within 2 hours of drilling. A second set of five inclined boreholes, similar to those described above, was drilled and cored 539–540 days after the start of the tracer test.

In the laboratory, cores were removed from the liners and visually logged. Slices of core 1 cm in thickness were taken at intervals ranging from 2 to 50 cm and used for determining gravimetric moisture content and concentration of bromide tracer in the pore water. For the bromide determinations, approximately 50 g of the moist soil was mixed with 18 g of deionized water and shaken overnight. The samples were then centrifuged to separate the solids from the water, which was then analyzed for bromide concentration. In situ concentration of bromide was calculated based on the measured moisture content of the sample and the relative proportions of moist soil and deionized water.

Colloid Transport Experiment

The colloid tracer experiment began on June 20, 1990, 685 days after the start of the solute experiment and is also described by McKay *et al.* [1993b]. A tracer solution was prepared containing two strains of colloid-sized bacteriophage (viruses), MS-2 and PRD-1, provided by researchers at the Department of Microbiology and Immunology at the University of Arizona. The bacteriophages are both roughly spherical with diameters of 0.0260–0.0266 μm for MS-2 and 0.062 μm for PRD-1 [Van Duin, 1988; Olsen *et al.*, 1974]. Two strains were chosen because of uncertainty concerning their degree of sorption in the fractured clay. It was thought that at least one strain would be sufficiently mobile to be useful as a tracer.

The bacteriophages were added to a steel tank on site containing 17,000 L of surface water from the local municipal supply. Sodium thiosulphate (5 mg/L) was added to the tank to reduce residual chlorine from the municipal treatment plant. Iodide (9 mg/L) was also added as a relatively nonreactive tracer and was used mainly to indicate whether there was any cross contamination between the trenches due to the sampling procedure. Approximately 14,000 L of this solution (80% of the trench pore volume) was flushed through the gravel-filled source trench in 4 hours, and then the water in the trench was mixed by pumping between wells set in the gravel. The remaining tracer solution was added to the source trench over the following 9 days to maintain a constant water level.

During the experiment, samples were taken for determining bacteriophage and iodide concentrations from the source trench and from selected seepage collectors in the receiver trenches. Additional samples for determining iodide concentrations were taken from the piezometers. The bacteriophage samples were packed in ice and sent by overnight courier to the University of Arizona for analysis. Assays were performed using a plaque-forming unit (pfu) method with a detection limit of 1 pfu per 10 mL sample (or 0.1 pfu/mL). This method was capable of detecting only the viable bacteriophage and could not detect deactivated (dead) phage.

RESULTS AND DISCUSSION

Bromide Transport and Comparison of Monitoring Methods

Each of the four monitoring methods provides pore water samples in a different portion of the fractured till or at a

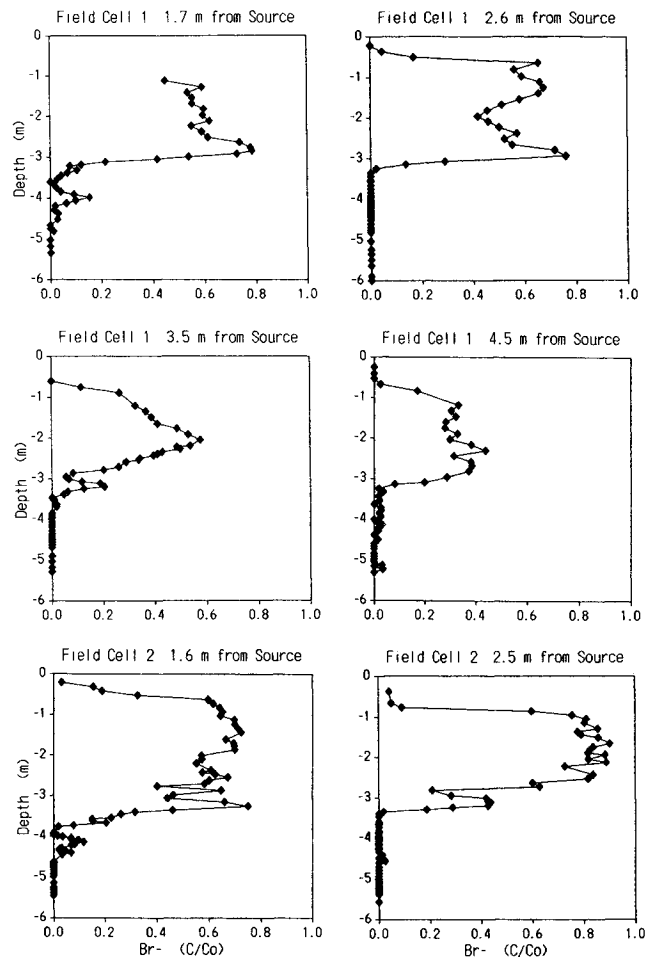


Fig. 3. Bromide in inclined (45° or 60° from vertical) core samples taken 270–277 days after start of tracer injection.

different scale. The bromide value measured for a slice of core was expected to be representative of the concentration in the approximately 15 mL of matrix pore water in a 1 cm thick \times 7.6 cm diameter slice. This would not be significantly affected by water in a fracture intersecting the slice because the volume for a typical 10- μm aperture fracture [McKay *et al.*, 1993a] would be 0.05 mL, or 1/300 of the total pore volume of the slice.

Bromide profiles from core samples taken at 270–277 days after the start of the tracer injection show a continuous plume from the water table (0.5–1.2 m depth) to a depth of approximately 3 m (Figure 3). Each concentration profile was relatively constant in this zone, indicating that bromide had spread throughout the matrix pore water, presumably due to diffusion from the closely spaced (<0.13 m) fractures. The vertical extent of this high-concentration zone closely corresponds to the maximum depth of continuous oxidation staining of the clay matrix as described by McKay *et al.* [1993a]. Concentration values generally decreased in value with distance from the source, although there was also some lateral variability perpendicular to the direction of flow.

Below a depth of 3 m the concentrations from core samples rapidly decreased and were usually below the detection limit ($C/C_0 = 0.005$ for bromide) except for discrete, slightly rounded peaks, a few centimeters or tens of centimeters across. These peaks are believed to be “diffu-

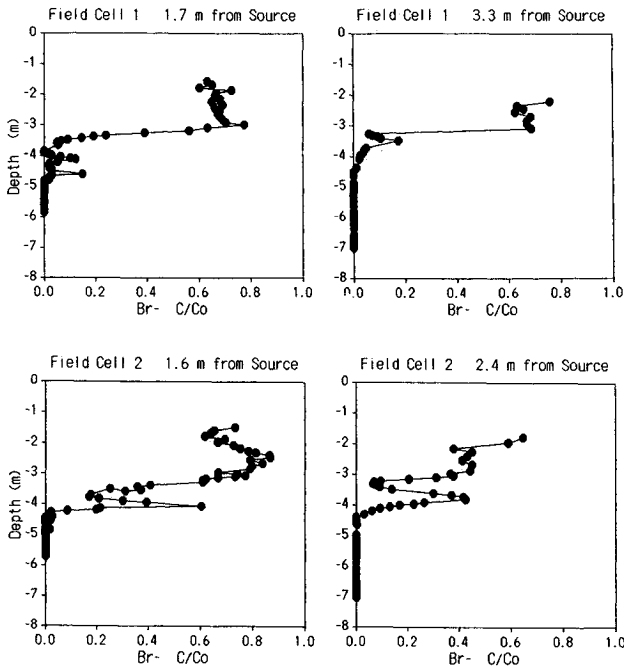


Fig. 4. Bromide in inclined (45° or 60° from vertical) core samples taken 539–540 days after start of injection.

sion halos” occurring around individual fractures or thin silty seams. In approximately half the cases the location of solute concentration peaks corresponded to visibly stained fractures. The other peaks may have been due to transport along thin silty seams, unstained fractures, or nearby features which did not intersect the borehole. Bromide detected below a depth of 3 m could be due to transport through fractures laterally from the source trench or vertically from the overlying high-concentration zone. Generally, core samples from inclined boreholes showed more frequent bromide peaks and greater maximum depth of bromide than core from vertical boreholes. This is believed to be due to the greater probability of intersecting vertical fractures in angled boreholes.

Bromide concentration profiles (Figure 4) from a set of core samples taken at 539 days often had higher values but were otherwise similar to the earlier profiles. The peaks of bromide below a depth of 3 m tended to be more pronounced and persisted to slightly greater depths in the core samples taken at 539 days.

Piezometers, seepage collectors, and discharge from the receiver trenches were expected to sample water almost exclusively from the fractures because of the very low values, average of 2×10^{-10} m/s, of hydraulic conductivity in the clay matrix [McKay et al., 1993a]. As well, since the fracture porosity is very low, 10^{-5} to 10^{-3} , the fracture pore water obtained in any given sample may come from a large volume of till.

Bromide was detected in all piezometers in the upper 2.6 m with first arrival (at $C/C_0 = 0.01$) indicating transport rates of 0.01–0.07 m/d (Figure 5). The concentrations generally decreased with distance from the source, and there were occasional temporary drops in concentration, often corresponding to periods of heavy rain. Concentrations in three piezometers at a depth of 3.2 m were much lower than in the

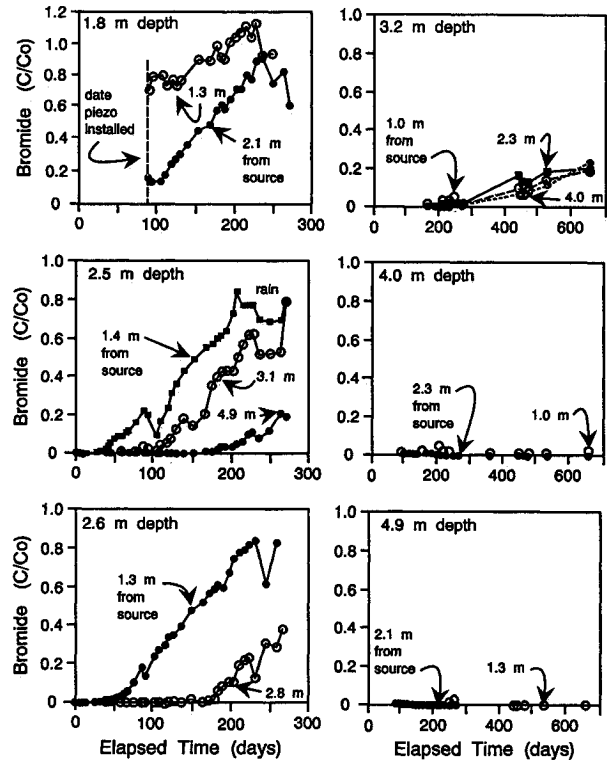


Fig. 5. Bromide breakthrough curves in piezometers.

overlying zone. Samples from piezometers below a depth of 3.2 m had erratic levels of bromide, which were near the detection limit and likely represent contaminants introduced when the piezometers were installed 80 days after the start of the tracer experiment.

Bromide was detected in seepage collectors in both receiver trenches (Figure 6) with transport rates for first arrival (at $C/C_0 = 0.01$) usually in the range of 0.02–0.07 m/d, which are very similar to those observed in piezometers in the upper 3 m. Concentrations decreased sharply below a depth of 3 m but still indicated more widespread occurrence of bromide than was measured in core samples and piezometers. It is likely that during the latter stages of the experiment samples taken in seepage collectors below a depth of 3 m experienced some contamination due to the high levels of bromide that had built up in the receiver trench immediately adjacent to the collectors.

Bromide breakthrough curves in bulk discharge from the receiver trenches (Figure 7) were very similar to those observed in the seepage collectors, but with a time lag of up to 90 days relative to the earliest detection of bromide in the collectors. Trench discharge consists of water entering the trench from the field cell and clean seepage from the end and back walls which mix with the approximately 13 m^3 of water initially in the gravel-filled trenches. The water in the receiver trenches was not expected to be well mixed. In spite of uncertainty concerning the degree of dilution of the tracer after entering the trench these data still provide an order of magnitude measurement of the time at which breakthrough of the solute occurred. In some field situations the uncertainty inherent in using a large-scale infiltration monitoring trench may be acceptable given its advantages, which include that it samples the entire thickness of the fractured

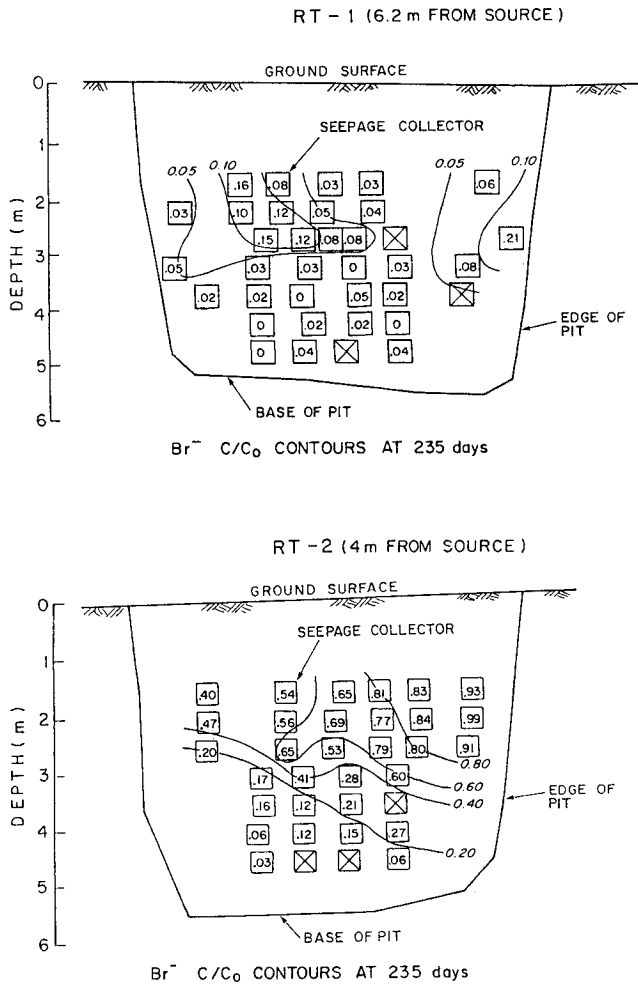


Fig. 6. Bromide distribution in collectors 235 days after start of tracer test.

zone and is more likely to intersect widely spaced major fractures than a smaller-scale method such as a piezometer or a seepage collector, and that it requires much less labor and expense to install and sample than the seepage collectors.

Concentration values from all of the different solute-monitoring methods are compared for samples taken in the main portion of the plume (upper 3 m) at 270 days (Figure 8). All the methods show two trends: a trend toward decreasing concentration with distance from the source; and values in the fractures (piezometers, collectors and trench discharge) which are similar, often within a factor of 2, to values in the matrix (core samples). Below a depth of 3 m, where measurable concentrations are erratic, the core-sampling method, particularly in angled boreholes, provides the most reliable picture of solute distribution.

Transport of ¹⁸O, ²H and Chloride

Samples from 13 piezometers or seepage collectors were analyzed to determine ¹⁸O breakthrough curves, and of these, three were also analyzed for ²H and chloride. Typical breakthrough curves are shown in Figure 9. The isotope concentrations were slightly retarded relative to the bromide and chloride in all but two cases, one of which was clearly

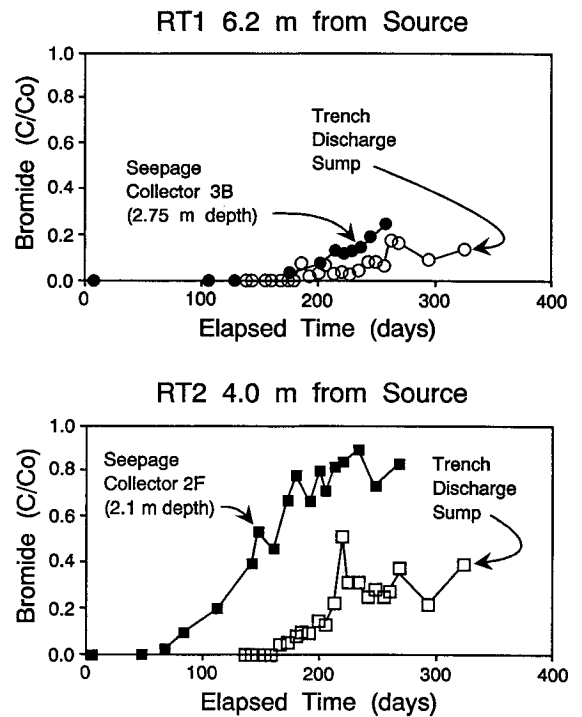


Fig. 7. Bromide breakthrough curves for (bulk) discharge from receiver trenches compared to the earliest detected breakthroughs from seepage collectors in each trench.

due to a leaking piezometer and in the other case all tracers were still at low concentrations ($C/C_0 < 0.2$). It is not clear what caused the retardation of ¹⁸O and ²H. Three possible mechanisms are suggested: reaction of ¹⁸O/²H with mineral or organic solids; repulsion of the anion tracers (but not ¹⁸O/²H) from charged mineral surfaces, resulting in slower diffusion into the matrix pore water; and seasonal infiltration of precipitation enriched with ¹⁸O and ²H.

Each of the three mechanisms was considered, but it is not clear which if any were responsible for the apparent retardation of the isotopic tracers. Laboratory batch experiments up to 350 days in duration showed no significant sorption of bromide, chloride, or ¹⁸O to soil from the experimental site [McKay, 1991]. As well, measured values of effective diffusion coefficients from laboratory column experiments using undisturbed samples of the till by Bedard [1990] showed no appreciable difference between the anion and the isotope

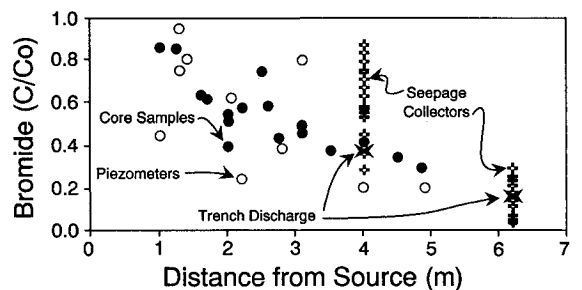


Fig. 8. Comparison of bromide-monitoring methods in the upper 3 m of the fractured till at 270 days after the start of tracer injection. For each core sample the bromide value is the mean of measured values from the water table to a depth of 3 m.

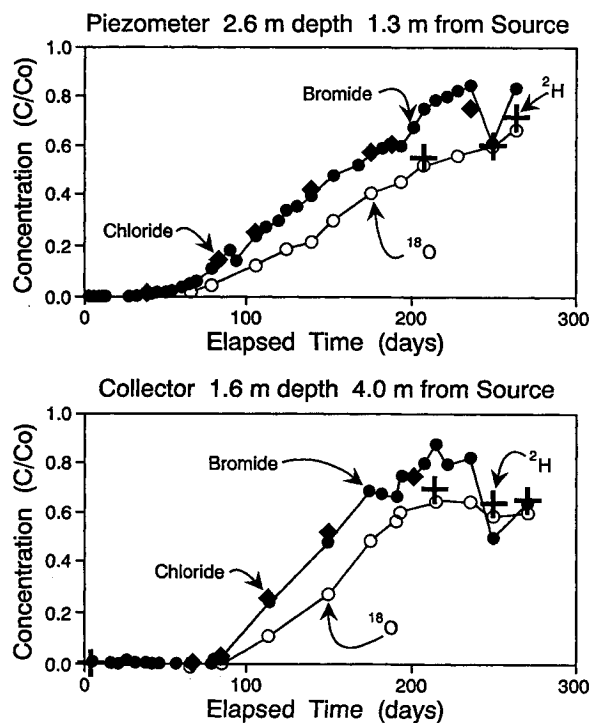


Fig. 9. Comparison of breakthrough curves for ionic and isotopic tracers.

tracers (Table 2). It is possible that infiltration of precipitation enriched with the heavy isotopes is at least partly responsible for the apparent retardation, since seasonal ^{18}O variations of up to 1.5‰ were observed in shallow groundwater in a nearby piezometer nest [McKay, 1991].

Colloid Tracer Experiment

Concentrations of the colloid tracers (also described by McKay *et al.* [1993b]), bacteriophages MS-2 and PRD-1, in the steel storage tank and the source trench are shown in Figure 10. The colloid concentrations in the steel tank remained relatively constant while the source trench values decayed by approximately one log cycle per day, probably due to deactivation or to sorption to mineral or organic solids. Iodide concentrations in the source trench remained

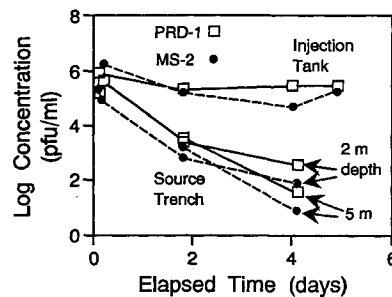


Fig. 10. Colloid concentrations in injection tank and in source trench at depths of 2 and 5 m (adapted from McKay *et al.* [1993b]).

constant at approximately 7 mg/L. Background levels of the colloids and the iodide in pore water from the site were all below the detection limits of 1 pfu/mL and 0.02 mg/L, respectively.

Colloid tracers were detected in trench RT2 (4 m from the source trench) within 1 day of beginning the injection as shown in Figure 11. By the second day the colloid tracers were observed in seven of the 18 seepage collectors sampled in trench RT2 (Table 3). Peak concentrations of the colloids were less than 0.02 of the initial C_0 , but if adjusted for the decay measured in the source trench the values ranged from 0.0004 to 1. In all cases the concentration of PRD-1 was higher than MS-2. No colloids were detected in trench RT1, 6.2 m from the source. This is likely due to inactivation or sorption over the longer travel distance across the 6.2-m-wide field cell. McKay *et al.* [1993a] found that the hydraulic conductivity and the fracture density in the two field cells are very similar, and no differences in phage mobility are expected.

Iodide concentration was below the detection limit ($C/C_0 = 0.003$) in the seven collectors and four piezometers monitored for up to 13 days after the start of the injection. This lack of iodide migration was expected because of the short duration of this test. Iodide was used to determine cross contamination with the source trench during sampling for the bacteriophages, and none was detected.

The rate (up to 5 m/day) of colloid transport is up to 2 orders of magnitude greater than the rate of bromide transport (0.03–0.07 m/d at $C/C_0 = 0.01$) in the solute tracer test and is within the range of calculated flow velocities (based on

TABLE 2. Measured Values of Effective Diffusion Coefficients for Nonreactive Solutes in Clay From the Laidlaw Site

Reference	Depth of Sample, m	Porosity of Sample	Number of Tests	Tracer Species	Effective Diffusion Coefficient,* $D_e \times 10^{-10} \text{ m}^2/\text{s}$
Bedard [1990]†	4.9	0.38	1	Br^-	5.8
				Cl^-	5.9
				^{18}O	5.5
				^2H	6.0
				$^{36}\text{Cl}^-$	4.9
Desaulniers [1986]†	20	0.40	1	^3H	5.9
Desaulniers [1986]†	36	0.44	1	$^{36}\text{Cl}^-$	5.3
Johnson <i>et al.</i> [1989]‡	17	0.37	1	^3H	6.1
				Cl^-	5.0

*All values normalized to 10°C [Li and Gregory, 1974].

†Values measured in laboratory columns using undisturbed clay samples.

‡Value based on measured Cl^- profile in undisturbed clay beneath landfill cell.

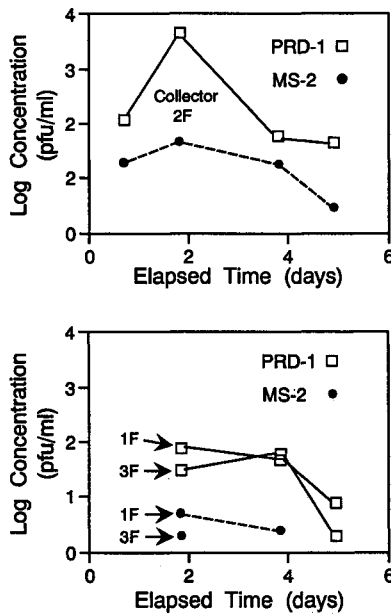


Fig. 11. Examples of colloid breakthrough curves in seepage collectors in trench RT2, 4 m from source trench (adapted from McKay *et al.* [1993b]).

the cubic law) of 1–24 m/d for the same collectors [McKay *et al.*, 1993a]. We attribute the large degree of retardation of the solute tracers to matrix diffusion. The colloids are not expected to diffuse effectively into the matrix because of their large diameter (0.026–0.062 μm) relative to the diameter of matrix pore throats. Pore throat diameters in the weathered clays are expected to be similar to those measured with mercury porosimetry by Fernandez [1989] and Fernandez and Quigley [1988] for samples of weathered clay from a site in the same till deposit several kilometers away. In these samples, approximately 30–50% of the pore throat diameters were smaller than the 0.062- μm diameter of the PRD-1 bacteriophage.

MATHEMATICAL MODELING

Modeling Methods

The objectives of the modeling investigation were, first, to determine if the process of matrix diffusion is potentially sufficient to cause the observed distribution of solute in both the fractures and the matrix, as well as the retardation of the

solutes relative to the colloidal tracers, and second, to test modeling strategies for application to transport in fractured clay.

The first modeling approach is based on an exact analytical solution for flow and advective dispersive transport along discrete, evenly spaced, parallel fractures combined with diffusive transport into the porous matrix [Sudicky and Frind, 1982]. Average flow velocity in the fractures was calculated based on the cubic law for flow between parallel-plate surfaces [Snow, 1969]. The model does not account for the presence of horizontal fractures which, although visible in the field, were not as prominent as the vertical fractures.

The second modeling approach is based on an equivalent porous medium (EPM) analogy. The applicability of an EPM approach depends on the physical scale of the flow system, the factors controlling flow, and their interaction with the factors controlling the rate and degree of diffusion into the matrix [Berkowitz *et al.*, 1988]. Many of these factors are difficult to measure, so there is a large degree of uncertainty in determining whether or not an EPM approach is suitable for a given site. Generally, deposits which are highly fractured are more likely to be suitable for modeling using an EPM approach, but there are very few published field examples with which the groundwater practitioner can compare a given site. Pankow *et al.* [1986] found that for a contaminated site in highly fractured silts (fracture spacing, 0.003 m) the plume was adequately modeled using an EPM approach, but for a contaminated site in fractured shale (spacing, 0.05–0.35 m) the distribution of the plume was very erratic and could not be modeled using the EPM approach.

Discrete Fracture Transport Model

Parametric analysis. A sensitivity analysis for solute transport was performed using the discrete fracture model to determine the influence of input parameters relative to the field scale results (Figure 12). Input parameters (Table 4) were selected for a “base case” using the values determined from the field measurements described by McKay *et al.* [1993a] and then varied over the ranges measured or estimated for nonreactive solutes in fractured clays in the field cells. Values of the two parameters to which the model is most sensitive, fracture aperture and fracture spacing, were chosen as follows: the fracture aperture base value, 20 μm , is at the middle of the range of values (0–43 μm) for the field cells calculated by McKay *et al.* [1993a] using the cubic equation; and the fracture spacing minimum, base, and

TABLE 3. Comparison of Colloid and Solute Transport

Collector	Depth, m	Transit Time, days		Velocity, m/d	
		Colloids at >1 pfu/mL	Bromide at $C/C_0 >0.01$	Colloids at >1 pfu/mL	Bromide at $C/C_0 >0.01$
RT2-1C	1.6	0.7–1.8	130	2–5	0.03
RT2-1D	1.6	0.7–1.8	80	2–5	0.05
RT2-1E	1.6	0.7–1.8	<110	2–5	>0.04
RT2-1F	1.6	0.7–1.8	82	2–5	0.05
RT2-2E	2.1	0.7–1.8	<110	2–5	>0.04
RT2-2F	2.1	<0.7	60	>5	0.07
RT2-3F	2.6	0.7–1.8	<115	2–5	>0.04

Distance from source is 4 m. Here, pfu denotes plaque-forming units. (Adapted from McKay *et al.* [1993b].)

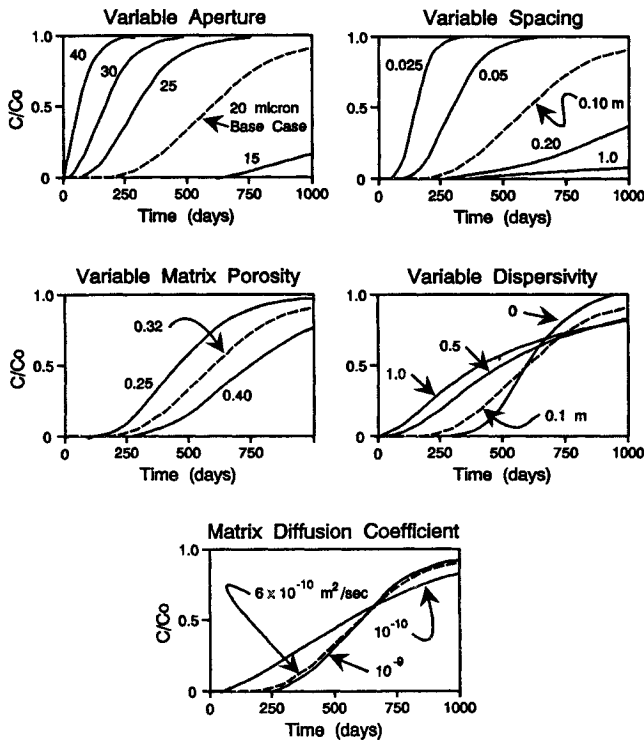


Fig. 12. Parametric analysis using a discrete fracture transport model with diffusion into a porous clay matrix. The simulations are for a nonreactive solute at monitoring point in a fracture 2 m from the source.

maximum values (0.025, 0.10, and 1.0 m) approximately correspond to measured values at the top, middle, and bottom of the field cells.

As expected, varying fracture aperture (and hence flow velocity) or spacing over the specified ranges has a strong influence on solute transport. The arrival times (for $C/C_0 = 0.5$) at a hypothetical monitoring point in a fracture 2 m from the source varied over 3 orders of magnitude in response to changes of fracture aperture or spacing values over the ranges indicated. Varying matrix porosity or effective diffusion coefficient over the ranges chosen has little influence.

Longitudinal dispersion in the fractures, which was varied from 0 to 1.0 m, changes the slope of the breakthrough curve but has little influence on arrival time of the tracer (at $C/C_0 = 0.5$). No determinations of longitudinal dispersivity for

TABLE 4. Values for Solute Transport Modeling Parametric Analysis

Parameters	Base Value	Range for Parametric Analyses
Fracture aperture, μm	20	5–40
Fracture spacing, m	0.10	0.025–1.0
Hydraulic gradient	0.24	...
Fracture dispersivity, m	0.10	0–1.0
Viscosity of water, N s/m^2	0.00131	...
Density of water, kg/m^3	1000.0	...
Matrix porosity	0.32	0.25–0.4
Diffusion coefficient in matrix, m^2/s	6×10^{-10}	10^{-9} – 10^{-10}
Fracture retardation factor	1.0	...
Matrix retardation factor	1.0	...

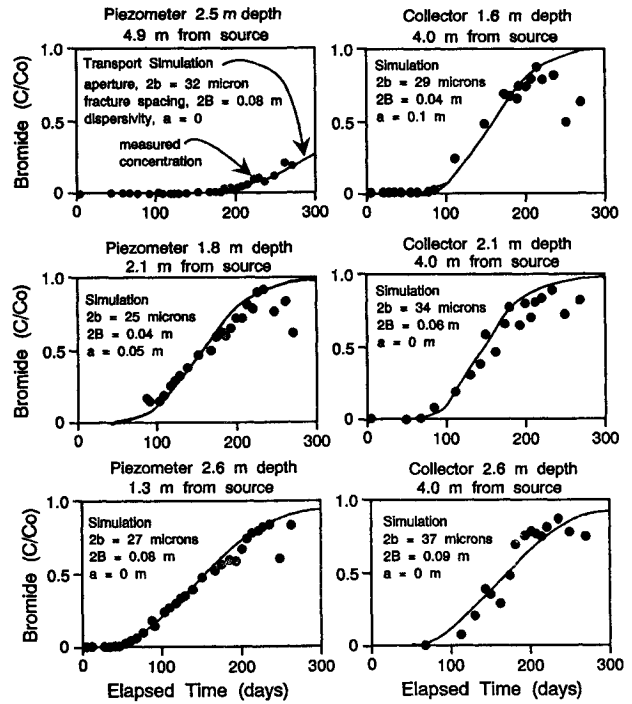


Fig. 13. Examples of measured and simulated bromide breakthrough curves in piezometers and seepage collectors.

fractures in clay exist, so the range of values chosen was based on determinations by Gelhar [1987] for tracer experiments in single horizontal fractures in crystalline rock over distances of 4–30 m (range of dispersivity, 0.2–1.2 m).

Comparison to field data. Simulations of solute concentrations in the fractures using the discrete fracture/matrix diffusion model were fitted to measured bromide breakthrough curves from the piezometers and from selected seepage collectors (examples shown in Figure 13). Fracture spacing values used in the simulations correspond to the best fit of the measured fracture spacing versus depth plot shown by McKay et al. [1993a]. Matrix porosity and diffusion coefficient values were fixed at the base case values (Table 4), and fracture aperture and longitudinal dispersivity were varied to fit the simulation to the data. All values for parameters derived from the solute transport simulations are referred to as “solute transport” values.

For the seven seepage collectors in which colloid breakthrough was observed, aperture and flow velocity values (Table 5) were derived from solute transport and colloid transport data as well as from calculations based on hydraulic conductivity data. The values are similar, falling within ranges of 9–43 μm and 1–24 m/d for aperture and flow velocity, respectively. This clearly shows that matrix diffusion is potentially sufficient to cause the observed 2 orders of magnitude retardation of the nonreactive solute tracers relative to the colloid tracers. Solute transport aperture values (Table 6) from the 13 piezometers (depths of 1.7–3.2 m) in which breakthrough of the bromide tracer was observed fall in approximately the same range as for the seepage collectors. Solute transport–derived dispersivity values in the fractures range from 0 to 0.2 m.

The mean and geometric mean of the solute transport aperture values (Tables 5 and 6) are a factor of 1.5–3 larger

TABLE 5. Fracture and Transport Parameters Derived From Seepage Collectors

	Measured Hydraulic Conductivity, m/s	"Hydraulic" Values*		"Solute Transport"† (and "Colloid Transport"‡) Values			
		Aperture, μm	Flow Velocity, m/d	Hydraulic Conductivity, m/s	Aperture, μm	Flow Velocity, m/d	Longitudinal Dispersivity, m
Minimum	1.0×10^{-8}	9	0.9	3.4×10^{-7} (5×10^{-8})	28 (19–30)	10 (2–5)	0
Maximum	1.3×10^{-6}	43	24	4.2×10^{-7} ($>2 \times 10^{-7}$)	37 (>30)	17 (>5)	0.1
Mean	3.4×10^{-7}	21	7.8	3.9×10^{-7}	32	13	0
Geometric mean	6.7×10^{-8}	18	3.9	3.8×10^{-7}	31	12	...

*"Hydraulic" values calculated from measured hydraulic conductivity and measured fracture spacing using the cubic law.

†"Transport" values based on best fit with discrete fracture/porous matrix transport model

‡Values are determined only for the seven collectors in trench RT2 (4 m from source) in which breakthrough of the bacteriophage tracers was observed.

than values derived hydraulically. Similarly, the mean and geometric mean of solute transport derived hydraulic conductivity values are larger than for measured hydraulic conductivity values, with a greater difference observed for piezometers than for seepage collectors. The differences in "solute transport" and "hydraulic" aperture values, particularly in the piezometers, may be partly due to compaction or smearing shut of fractures along the sides of the boreholes. This could significantly influence hydraulic measurements while having little effect on solutes which could rapidly diffuse through a thin smeared zone.

Differences between "hydraulic" and "transport" aperture values have also been observed in experiments in single fractures in rock, which although very different from the fracture networks in the clays are still worth considering. *Raven et al.* [1988], in a series of field experiments in a single fracture in gneissic rock, found that aperture values based on hydraulic tests were consistently larger than values based on tracer experiments. *Shapiro and Nicholas* [1989] performed a series of experiments in an isolated fracture in a dolomite rock and observed the reverse situation, with transport aperture values larger than hydraulic values. *Silliman* [1989] argued that both of these effects could be due to the presence of larger aperture "channels" within the fractures. For cases where flow is parallel to the direction of channeling he showed that transport aperture values should be larger than hydraulic values. Where flow is perpendicular to the direction of channeling, the transport aperture values should be smaller than the hydraulic values.

Simulations were also fitted to bromide concentration versus distance profiles measured in core samples (Figure

14). On the profile at a depth of 1.5 m, approximately 90% of the measured concentrations fall within the simulated envelope for fracture apertures of 18 and 25 μm where fracture spacing is assigned the measured value of 0.04 m. At a depth of 3.0 m (fracture spacing, 0.13 m) the measured concentrations fall within an envelope for fracture apertures between 22 and 33 μm . Modeling of both profiles showed little difference in aperture values fitted based on concentrations in the fractures or concentrations in the midpoint of the matrix. The aperture values (18–33 μm) determined based on the core samples are very similar to transport aperture values determined for the piezometers (14–33 μm) and for the seepage collectors (28–37 μm).

Hydraulic conductivity values derived from the solute transport simulations range from 5×10^{-8} to 4×10^{-7} m/s. These values are very close to the bulk hydraulic conductivity of the field cells (approximately 2×10^{-7} m/s) calculated based on total flow into or out of the trenches [*McKay et al.*, 1993a]. Based on the depth range of the main plume (Figure 3) it is evident that most of the flow and transport is occurring in the upper 3 m, so the bulk hydraulic conductivity of this zone is actually 4×10^{-7} m/s, which is still within the range of the solute transport values.

Equivalent Porous Medium Transport Model

In the upper 3 m of the till the solute concentrations are similar in both the pore water in the fractures and in the matrix. If this zone is considered as an equivalent porous medium, with the effective porosity, n , equal to the total porosity (0.32), then the bulk hydraulic conductivity, K_b , calculated based on plug flow displacement is

TABLE 6. Fracture and Transport Parameters Derived From Piezometers

	Measured Hydraulic Conductivity, m/s	"Hydraulic" Values*		"Solute Transport" Values†			
		Aperture, μm	Flow Velocity, m/d	Hydraulic Conductivity, m/s	Aperture, μm	Flow Velocity, m/d	Longitudinal Dispersivity, m
Minimum	3.3×10^{-10}	2	0.1	1.2×10^{-8}	14	2.3	0
Maximum	3.0×10^{-7}	34	14.7	2.7×10^{-7}	33	13.7	0.2
Mean	3.5×10^{-8}	11	2.6	1.5×10^{-7}	25	8.0	0.1
Geometric mean	6.1×10^{-9}	9	0.9	1.1×10^{-7}	24	7.2	...

*"Hydraulic" values calculated from measured hydraulic conductivity and measured fracture spacing using the cubic law.

†"Transport" values based on best fit with discrete fracture/porous matrix transport model.

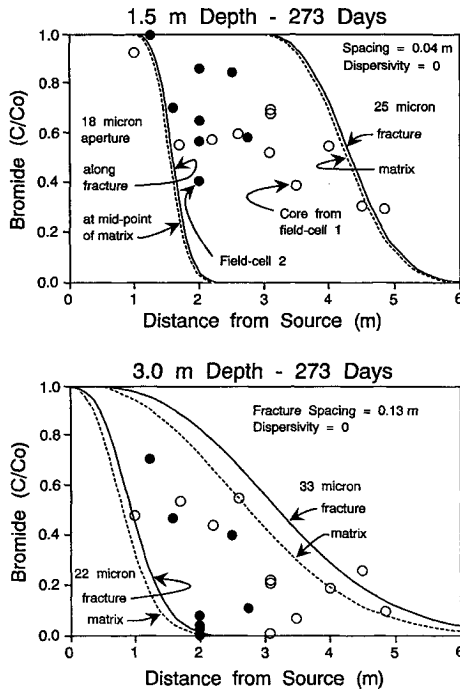


Fig. 14. Measured and simulated bromide distribution in core samples.

$$K_b = vn/i$$

where v is the velocity of the solute front at $C/C_0 = 0.5$ and i is the lateral hydraulic gradient (0.24).

Using the bromide concentration versus distance profiles (Figure 14) the values of K_b range from 6×10^{-8} to 3×10^{-7} m/s. These values are very similar to values from the discrete fracture solute transport simulations and from total trench inflow or outflow, which implies that in the highly fractured zone (upper 3 m) where most of the solute plume exists, lateral transport is controlled by the bulk hydraulic conductivity, total porosity (i.e., matrix porosity), and lateral hydraulic gradient. In the zone from 3 to 5.5 m depth (fracture spacing, 0.13–2.0 m) an EPM approach would not be appropriate at the time of core sampling, 1.5 years after the start of the tracer test, because the bromide distribution is still very erratic (Figure 4), showing that the solute has not spread through the matrix pore water.

The best indicator of whether or not an EPM approach can be successfully applied to solute transport at a given site is the distribution of solutes, either from tracer experiments or from previously existing sources. For example, environmental tracers such as tritium or contaminants from an existing plume could be monitored to measure the contrast in concentrations between fracture pore water and matrix pore water. In cases where they are locally near equilibrium an EPM approach using the total porosity for the value of effective porosity can be used. In cases where there are large variations in concentration the effective porosity is unknown, and the applicability of the EPM approach is limited.

CONCLUSIONS AND IMPLICATIONS

Solute migration in the visibly weathered and fractured zone of the till at the Laidlaw site is controlled by advection

along the fractures combined with diffusion into the matrix pore water. This matrix diffusion is sufficient to cause the observed 2 orders of magnitude retardation of nonreactive solute tracers relative to colloid tracers. Numerical simulations indicate that matrix diffusion is an important factor in retarding migration of dissolved contaminants over the range of fracture parameters and porosity expected in most fractured clay deposits. At the experimental site the representation of flow in the fracture network by the cubic law is a reasonable approximation of the field conditions, as indicated by the similarity between fracture parameters derived from hydraulic conductivity and solute transport and colloid transport data. Although the cubic law provides a good representation of the tracer experiment results, the equivalent porous medium model also provides a good representation in the upper 3 m where fractures are closely spaced (<0.13 m).

Samples of pore water obtained using four different methods, namely, matrix pore water extracted from core samples and fracture pore water obtained from piezometers, seepage collectors, and trench discharge, all gave similar profiles of solute tracer concentration versus elapsed time or distance from the source in the upper 3 m, where fractures are closely spaced (<0.13 m). Below a depth of 3 m, distribution of solute was very erratic, and sampling of matrix pore water from angled boreholes, which increases the probability of intersecting the predominantly vertical fractures, was the most reliable monitoring method used. This illustrates that in the highly fractured upper 3 m, which behaves as an equivalent porous medium, measured values of solute concentration are relatively insensitive to the method of pore water sampling, while in the deeper zone where fractures are more widely spaced, the measured concentration is greatly influenced by the drilling and sampling method.

The experiments clearly show that dissolved contaminants, although strongly retarded by matrix diffusion, can still migrate laterally at environmentally significant rates in some fractured clay deposits. Remediation of a solute plume in fractured clay would also be strongly influenced by matrix diffusion. In a scenario where clean water is flushed through a previously contaminated fractured clay the solute would slowly diffuse out of the matrix and back into the fractures, where it would be advected away. Since most of the solute mass is expected to reside in the matrix, it could take many years, or many pore volumes, to flush out the contaminant. Remediation efforts in fractured clays by the introduction of contaminant-transforming microbes would also be influenced by diffusion. The microbes may be rapidly transported along the fractures but would not likely migrate very far into the matrix. As a result, the rate of remediation of contaminants would still depend on the rate of diffusion from the matrix to the fractures.

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