

Evaluation of Multidimensional Transport through a Field-Scale Compacted Soil Liner

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Abstract: A field-scale compacted soil liner was constructed at the University of Illinois at Urbana-Champaign by the U.S. Environmental Protection Agency (USEPA) and Illinois State Geological Survey in 1988 to investigate chemical transport rates through low permeability compacted clay liners (CCLs). Four tracers (bromide and three benzoic acid tracers) were each added to one of four large ring infiltrometers (LRIs) while tritium was added to the pond water (excluding the infiltrometers). Results from the long-term transport of Br⁻ from the localized source zone of LRI are presented in this paper. Core samples were taken radially outward from the center of the Br⁻ LRI and concentration depth profiles were obtained. Transport properties were evaluated using an axially symmetric transport model. Results indicate that (1) transport was diffusion controlled; (2) transport due to advection was negligible and well within the regulatory limits of $k_{sat} \leq 1 \times 10^{-7}$ cm/s; (3) diffusion rates in the horizontal and vertical directions were the same; and (4) small positioning errors due to compression during soil sampling did not affect the best fit advection and diffusion values. The best-fit diffusion coefficient for bromide was equal to the molecular diffusion coefficient multiplied by a tortuosity factor of 0.27, which is within 8% of the tortuosity factor (0.25) found in a related study where tritium transport through the same liner was evaluated. This suggests that the governing mechanisms for the transport of tritium and bromide through the CCL were similar. These results are significant because they address transport through a composite liner from a localized source zone which occurs when defects or punctures in the geomembrane of a composite system are present.

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Introduction

Most modern landfills employ a composite liner system consisting of a compacted clay liner (CCL) overlain by a geomembrane (GM). Diffusion is considered the dominant chemical transport mechanism in GMs. However, advection can dominate chemical transport in GMs if holes or punctures are present. These can form in GMs during deployment, during construction of the

leachate collection and recovery system, from defects or weaknesses in the welding process, or from settlement stresses due to waste placement. As a result, GMs are underlain by CCLs, which act as an additional transport barrier to chemicals that penetrate GMs and form localized source zones on the CCL. Giroud and Bonaparte (1989) found that even pinhole punctures in the GM (0.3 mm in diameter) can cause significant flows, e.g., 50 L/day with a 0.3 m head. A composite liner system takes advantage of the low permeation rates of GMs with the long break through times of CCLs.

Chemical migration through CCLs is a result of advection, dispersion, and diffusion (Shackelford 1992; Manassero and Shackelford 1994). Extensive field and laboratory research has focused on one-dimensional (1D) advective flow through soil liners (Daniel 1984; Elsbury et al. 1990; Benson et al. 1999) and 1D diffusive transport in low conductivity soils (Crooks and Quigley 1984; Manassero and Shackelford 1994; Shackelford 1994a, b). However, only a few studies have focused on multidimensional transport in CCLs. Daniel (1989) reported that horizontal hydraulic conductivities (k_h) could be 5–10 times greater than vertical hydraulic conductivities (k_v) in field-scale soil liners based on a Boutwell-type test, suggesting that preferential flow between lifts can affect chemical migration. Benson and Daniel (1994) demonstrate through three-dimensional stochastic modeling that minimizing interlift transmissivity is essential to minimizing the overall hydraulic conductivity of CCLs, indicating that bonding between lifts is a key design and construction parameter. Elsbury et al. (1990) found that preferential flow due to interclod macropores and poor bonding between lifts dominated transport through their field scale compacted liner. In addition, a *prototype*

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liner built for this project displayed preferential transport through lifts along high conductivity zones followed by horizontal transport along lift interfaces (Albrecht et al. 1989). Hence it is not clear if preferential transport occurs in CCLs constructed using best engineering practices, if diffusion dominates transport in horizontal and vertical directions, or if diffusion coefficients for horizontal and vertical transport are different. In light of the failures that can occur in GMs, these are very important questions that must be resolved.

To help evaluate chemical transport through CCLs, the Illinois State Geological Survey (ISGS), in conjunction with the United States Environmental Protection Agency (USEPA), constructed and began monitoring a field scale compacted clay liner at the University of Illinois in Urbana-Champaign in 1987. In April 1988, water was ponded on the liner surface, while concurrently bromide and three benzoic acid tracers were each added to one of four large ring infiltrometers (LRIs). Tritium was added to the pond water (excluding the LRIs) in July 1989. The tracers were then allowed to migrate through the CCL for over 12 years. The ISGS maintained the facility until excavation of the liner in March 2002.

From 1999 to 2001, soil cores both inside and outside of the LRIs were collected and analyzed for tritium, ortho-trifluoromethyl benzoic acid (o-TFMBA) and bromide (Br^-). Concentration profiles and modeling results for tritium were presented in a previous paper (Toupiol et al. 2002), while concentration profiles and modeling results for o-TFMBA were presented in Willingham et al. (2003). Results from the tritium study indicate that: (1) tritium transport was adequately modeled using a 1D analytical solution to the advection-dispersion equation; (2) tritium transport was uniform within the liner (excluding samples taken near LRIs which were affected by lateral diffusive transport); and (3) tritium transport was diffusion dominated. Results from the o-TFMBA study indicate that o-TFMBA was not a conservative tracer over the life of the liner experiment, and hence is not an appropriate tracer for long-term experiments.

In the current study, concentration profiles and modeling results for Br^- are presented. In contrast to tritium, Br^- was only added to a localized region on the liner surface (i.e., inside a LRI), thus allowing assessment of migration in both the vertical and horizontal directions. Our objectives are to determine: (1) vertical and horizontal transport rates through the CCL based on a localized source zone; (2) whether preferential transport occurred in the CCL; (3) the variability in chemical migration rates for different chemical tracers; (4) the validity of an axially symmetric analytical solution to the advection dispersion equation to model vertical and horizontal chemical transport from a localized source zone; and (5) the effect of possible sampling position error on the fitness of estimated parameters. This work is unique because long-term chemical transport in CCLs from localized source zones has not been adequately addressed in the literature and no studies have evaluated radial diffusion rates in a field-scale CCL.

Background Liner Information

In 1987 a field-scale compacted liner was constructed by the ISGS and the USEPA on the campus of the University of Illinois at Urbana-Champaign. Soil for the field-scale compacted liner was a Batestown Till obtained from the stockpiled borrow material of the Urbana Landfill in Urbana, Ill. The Batestown Till had a mean water content of 10.4%, a specific gravity of 2.74 g/cm^3 , a maximum dry density of 2.08 g/cm^3 , a liquid limit of 21.1%,

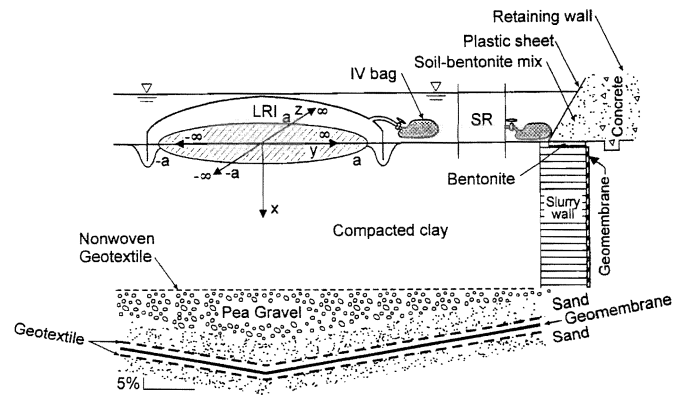


Fig. 1. Cross section of the large ring infiltrometer (LRI)

and a plasticity index of 7.0%. The material is classified as a loam to clay-loam using the unified soil classification system and has a particle size distribution of 33.9% sand, 35.4% silt, and 30.7% clay (Albrecht et al. 1989; Krapac et al. 1991). The liner was constructed wet of optimum; additional compaction information, liner construction procedures, and liner properties can be found in Cartwright and Krapac (1990) and Krapac et al. (1991).

The liner was constructed in seven lifts using a Caterpillar 815B static load padfoot compactor. Each lift was spread at a thickness of 23 cm then compacted to a thickness of 15 cm; to protect the underdrain system and pan lysimeters, the first layer was spread at a thickness of 31 cm. To enhance bonding between lifts and minimize preferential flow paths along lift interfaces, each lift was scarified using a Harvard tiller prior to placement and compaction of the subsequent lift. After construction, the top 0.2 m were removed to provide a uniform surface for testing. The mean moisture content (mass water/mass solids) was $11.44 \pm 0.98\%$ at construction and $10.60 \pm 1.05\%$ at deconstruction, and the mean dry density was $1.83 \pm 0.07 \text{ g/cm}^3$ at construction and $2.01 \pm 0.4 \text{ g/cm}^3$ at deconstruction.

The liner facility consists of a compacted soil liner with dimensions of $10 \times 17 \times 1 \text{ m}$, which includes an instrumented and ponded test area $7.3 \times 14.6 \times 0.9 \text{ m}$. The entire facility is contained inside an enclosed heated shelter, which minimizes weather effects and prevents infiltration from rainfall. Instrumentation includes four sealed double ring LRIs, 32 open small double ring infiltrometers (SRI), eight evaporation pans, 60 pressure-vacuum lysimeters, as well as other monitoring equipment.

Fig. 1 shows a cross section of the liner system including a LRI and SRI. Liner construction also included an underdrain system, pan lysimeters, drainage collection pits, a cutoff wall, and a concrete retaining wall. The underdrain system was divided into four quadrants ($7.3 \text{ m} \times 3.6 \text{ m}$ with one LRI at the center of each quadrant). Each quadrant was graded at a 5% slope toward the center of the quadrant, where a drainage cup was installed to collect any water that passed through the liner. From bottom to top, the underdrain system consists of (1) a 3 cm layer of sand covered by a nonwoven geotextile, (2) a 30-mil (0.076 cm) high-density polyethylene GM, (3) a 3 cm layer of sand covered by a nonwoven geotextile, and (4) pea gravel (10 mm in diameter) filled level to the foundation of the liner.

Large Ring Infiltrometers

The LRIs were 1.5 m in diameter and were imbedded 8 cm into a bentonite-cement slurry filled trench, 13 cm wide by 10 cm deep

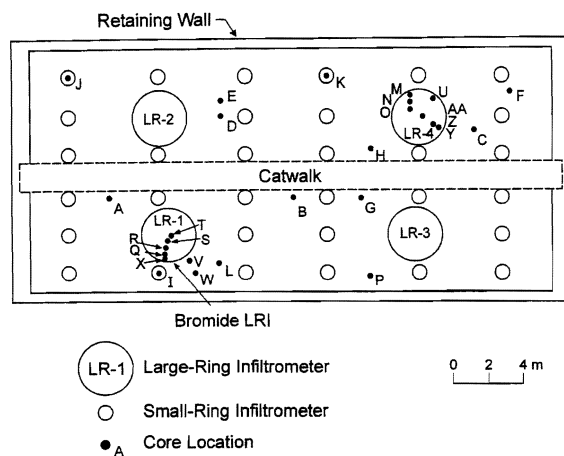


Fig. 2. Location of soil cores

(Krapac et al. 1991). Each LRI was initially filled with water containing one tracer. To maintain an equivalent head between the inside of the LRIs and the pond, a small flexible intravenous (IV) bag was attached to the inner ring of the LRI via a tube as described by Daniel (1989) (Fig. 1). Daniel (1989) reports that sealed double ring infiltrometers are able to reliably measure in situ saturated hydraulic conductivity (k_s) values down to 10^{-8} cm/s. The flux of infiltration water was determined by weighing the IV bags every 2 weeks (Panno et al. 1991); the IV bags were refilled with a solution containing the appropriate tracer to replenish the volume infiltrated as needed during the first 5 years (100 mg/L of Br^- for the Br^- LRI). Based on the initial mass of Br^- added to the LRI and the mass of tracer added over the first 5 years, it was possible to perform a mass balance on the total amount of Br^- added over the life of the liner.

Ponding

On April 12, 1988 water was ponded on the liner surface to a depth of 29.5 cm; concurrently, tracers were added to each of the LRIs. The water level was raised to a depth of 31 cm on May 25, 1989 and maintained at that depth until January 30, 1998 (Cartwright and Krapac 1990; Krapac et al. 1991; Panno et al. 1991). After January 1998 the pond depth was allowed to decrease due to evaporation and infiltration; the water depth never reached the liner surface.

Methods

Prior to core sampling from a LRI, the water level inside the LRI was pumped to approximately the same level as the pond, and the top of the LRI was removed by cutting the LRI at an elevation slightly higher than the pond (Fig. 1). The Br^- LRI was opened in June 2000.

The locations of soil cores inside of and adjacent to the Br^- LRI are shown in Fig. 2. To collect core samples, a 50 cm diameter steel pipe was driven 5 cm into the liner surface to create a coffer dam; standing water was removed from within the dam. Three soil cores were taken in 30 cm increments from the same hole using a 76.2 mm i.d. thin-walled aluminum coring tube (ASTM 2000a). The coring tube was driven into the liner using a modified fence-post driver until the desired depth (30, 60, or 90 cm) was reached. Coring tubes were pulled from the liner using a

mechanical jack and sealed on both sides using parafilm and duct tape. After sampling, each hole was filled with bentonite and re-compacted. Soil cores were subsampled within 24 h.

Tracer Analysis

To determine Br^- concentrations in collected soil cores, the coring tubes were cut open and tracer concentrations were measured. Coring tubes were opened by making two axial cuts on opposite sides of each soil core. Once the tube was removed, sections were taken by cutting four to six 2-cm-thick disks from preselected locations along each core length. The sides of each section (disk) were shaved to eliminate smearing effects, and each section was separated into smaller samples. After removing any large rocks (> 6 mm), soil samples (approximately 10 g) were put into pre-weighed 50 ml Nalgene centrifuge tubes and reweighed. 10 mL of deionized water (Barnstead Nanopure De-Ionizer) was added to each centrifuge tube, rapidly mixed for several seconds (vortex mixer), and tumbled end-to-end (NBS rotating tumbler) for 24 h to equilibrate the original pore water with the deionized water (Roy et al. 1991; Shackelford 1991). After tumbling, samples were centrifuged (Beckman J2-HC centrifuge) at 16,000 rpm for 20 min and approximately 6–8 ml of supernatant were removed for analysis.

Br^- was quantified using a Dionex ion chromatograph (IC) with an anion exclusion column (Dionex AS9HC-4mm) and a conductivity detector. Quantification of the tracer concentration in the soil pore-water was determined as follows:

$$C_{pw} = \frac{C_{meas} V_{total} - C_{back} V_{deionized}}{V_{pw}} \quad (1)$$

where C_{meas} = measured tracer concentration; V_{total} = total volume of water ($V_{pw} + V_{deionized}$); C_{back} = background tracer concentration in the deionized water; $V_{deionized}$ = volume of deionized water (i.e., 10 ml); and V_{pw} = original pore water volume. Since C_{back} is negligible for Br^- , Eq. (1) reduces to

$$C_{pw} = \frac{C_{meas} V_{total}}{V_{pw}} \quad (2)$$

The volume of pore-water (V_{pw}) was determined from the following equation:

$$V_{pw} = \frac{1}{\rho_w} \left[M_{wet} - \left(\frac{M_{wet}}{1 + M_c} \right) \right] \quad (3)$$

where ρ_w = density of water; M_{wet} = mass of soil with pore water used in the tracer extraction ($M_{dry-solids} + M_{pore-water}$); and M_c = moisture content ($M_{water} / M_{dry-solids}$). M_c was determined from the weight difference between fresh samples (soil samples before addition of deionized water) and soil samples baked dry after decanting the supernatant (ASTM 2000b). The concentration of Br^- in the pore water was then calculated from Eq. (2). Br^- concentrations in replicate soil samples varied by an average of 3.4%.

Model Information

Bromide concentration profiles were fit using an analytical three-dimensional transport model, 3DADE [3-dimensional advection-dispersion equation (Leij and Bradford 1994)]. The model incorporates 13 different solutions to the advection-dispersion equation depending on initial conditions, boundary conditions, and the coordinate system.

3DADE assumes steady unidirectional flow in a porous medium with homogenous transport properties. Transport from the LRI was modeled using the cylindrical-coordinate form of the advection-dispersion equation:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} + \frac{D_r}{r} \frac{\partial}{\partial r} \left[r \frac{\partial C}{\partial r} \right] - \mu C \quad (4)$$

where C = volume-averaged or resident concentration of the solute; t = time; x = the position in the direction of flow (i.e., vertical); r = radial coordinate perpendicular to the direction of flow; D_x and D_r = dispersion coefficients in the direction of flow and perpendicular to the direction of flow, respectively; V_x = average linear pore-water velocity; and μ = first-order rate decay coefficient.

In this study, both the first type and third type boundary conditions (Parker and Van Genuchten 1984; Leij and Bradford 1994) were evaluated for the upper boundary (i.e., the liner surface). In order to satisfy the mass flux into the system calculated from a mass balance on the Br^- LRI over the life of the liner, a third type boundary condition would require a Darcy velocity several orders of magnitude higher than the measured LRI velocities. Hence the first-type boundary condition was used to model our system and is represented by

$$C(x=0, r, t) = g(r, t) \quad (5)$$

where g is defined as

$$g(r, t) = \begin{cases} C_0, & r < a, \quad 0 < t < t_0 \\ 0 & \text{otherwise} \end{cases} \quad (6)$$

and where a = radius of the LRI (75 cm), and C_0 = constant concentration of duration t_0 . At the bottom of the liner, the outlet condition is assumed to be semi-infinite, and is given by

$$\left. \frac{\partial C}{\partial x} \right|_{x \rightarrow \infty} = 0 \quad (7)$$

Parker and Van Genuchten (1984) have shown that although liners are finite, the semi-infinite boundary condition at the liner outlet is usually an adequate approximation; Manassero and Shackelford (1994) state that the semi-infinite boundary condition has been shown to result in relatively small error (<5%) when applied to describe miscible transport through finite laboratory columns. At time zero, the liner was assumed to be initially devoid of tracer (Br^-) as the background concentration in the Batestown Till soil was negligible. This is supported by lysimeter pore water samples collected from 1988 to 1990 which were below the detection limit of 0.1 mg/L. The initial condition is expressed as

$$C(x > 0, r, t = 0) = 0 \quad (8)$$

The solution for Eq. (4), with the given boundary (5), (7) and initial (8) conditions, is given by Leij and Bradford (1994) as

$$C(x, r, t) = \frac{C_0}{2} \int_{P(t)}^t \int_0^a \Lambda_1(\tau) \Xi(\rho, \tau) d\rho d\tau + \frac{\lambda}{2} \int_0^t \Lambda_2(\tau) d\tau \quad (9)$$

where

$$\Lambda_1(\tau) = \left[\frac{x^2}{4\pi D_x \tau^3} \right]^{1/2} \exp \left[-\mu\tau - \frac{(x - V_x \tau)^2}{4D_x \tau} \right] \quad (10)$$

$$\Lambda_2(\tau) = \exp[-\mu\tau] \left[\operatorname{erfc} \left[\frac{V_x \tau - x}{(4D_x \tau)^{1/2}} \right] - \exp \left[\frac{V_x x}{D_x} \right] \operatorname{erfc} \left[\frac{x + V_x \tau}{(4D_x \tau)^{1/2}} \right] \right] \quad (11)$$

$$\Xi(\rho, \tau) = \frac{\rho}{D_r \tau} \exp \left[-\frac{(r^2 + \rho^2)}{(4D_r \tau)} \right] I_0 \left[\frac{r\rho}{2D_r \tau} \right] \quad (12)$$

and where $P(t) = 0$ if $0 < t \leq t_0$ and $t - t_0$ if $t > t_0$, I_0 = modified Bessel function, and ρ and τ = dummy variables. 3DADE solves Eq. (9) by numerical evaluation of the integrals.

Model Input Parameters

Model input parameters include the concentration at the liner surface inside the LRI ($C_{x=0}$), the average linear pore-water velocity (V_x), the vertical and radial effective dispersion coefficients (D_x and D_r), and the source zone and liner dimensions. In modeling transport through the liner, advection was assumed to occur only in the vertical direction while dispersion was evaluated in both the vertical and radial directions. The concentration of Br^- at the liner surface (i.e., LRI bulk water) decreased with time due to advective and dispersive transport out of the LRI into the liner. The initial concentration of Br^- inside the LRI bulk water in 1988 was 72.4 mg/L (Krapac et al. 1991), and the final concentration in 2000 was 33.1 mg/L; unfortunately, no measurements were taken in between.

A mass balance approach was used to calculate the change in Br^- concentration at the liner surface with time. As shown in Eq. (13), the mass of tracer in the LRI bulk water at time step k ($M_{\text{LRI},k}$) was calculated from the mass of tracer in the LRI bulk water at the end of the previous time step ($M_{\text{LRI},k-1}$), the flux of tracer leaving the bulk water due to advection and diffusion during the current time step ($M_{\text{flux-out},k}$), and the amount of tracer added to the bulk water via the IV bags for the current step ($M_{\text{add},k}$). Transport through the fiberglass shell of the LRI is assumed to be negligible compared to transport through the liner (Fig. 1). In support of this, Br^- concentrations in pond samples were always below the detection limit of 0.1 mg/L. The mass balance for the Br^- LRI is as follows:

$$M_{\text{LRI},k} = M_{\text{LRI},k-1} - M_{\text{flux-out},k} + M_{\text{add},k} \quad (13)$$

The concentration was evaluated based on 1-year time increments. In order to calculate $M_{\text{flux-out}}$, the circular source corresponding to the LRI was divided into n (375) concentric circles. $M_{\text{flux-out},k}$ was calculated from

$$M_{\text{flux-out},k} = \sum_{i=0}^{n-1} \theta \left[V_x C_{k-1} - D_x \left(\frac{\partial C_{r_i}}{\partial x} \right)_{x=0} \right] [r_{i+1}^2 - r_i^2] \times \pi [t_k - t_{k-1}] \quad (14)$$

where r_i = radius of circle i , $(\partial C_{r_i} / \partial x)_{x=0}$ = concentration gradient at the surface for concentric ring i calculated utilizing concentrations from 3DADE (evaluated by finite difference between $x = 0$ and 10 mm) at the center of each ring with radius $r_i = (r_i + r_{i+1})/2$, θ = volumetric moisture content, V_x and D_x were previously defined, C_{k-1} = concentration of Br^- in the LRI bulk water at the end of previous time step, and t = time. The concentration in the LRI, C_k , is simply equal to $M_{\text{LRI},k}$ divided by the volume of the LRI. The analytical solution (9) assumes a constant value for the input concentration for the time period t_0 and zero afterwards. To extend Eq. (9) to our case where the input concentration varies from year to year, the principal of time superposition was used (Reilly et al. 1984).

Table 1. Br⁻ Diffusion Coefficients in Bulk Solution and Soil

Chemical	Type of medium	Diffusion (10 ⁻⁶ cm ² /s)		Tortuosity		Source
		Minimum	Maximum	Minimum	Maximum	
Br ⁻	Bulk water		18.7			Bowman (1984)
Br ⁻	Bulk water		21.9			Estimate ^a
KBr	Bulk water		20.6 ^b			Shackelford and Daniel (1991)
Br ⁻	Silty clay loam; sandy loam	3.7	6.4	0.18	0.32	Shackelford (1991)
Br ⁻	Soil cores (field)	5.0	7.0	0.25	0.35	Shackelford (1991)
Br ⁻	Kaolinite	4.8	9.9	0.24	0.49	Shackelford (1991)
Br ⁻	Clay soil	1.0	18.0	0.05	0.89	Shackelford (1991)

^aBased on Hayduk and Laudie (1974).

^bFree-solution diffusion coefficient for KBr; KBr was used for the Br⁻ large ring infiltrometer bulk water.

Average Linear Velocity

The average linear pore-water velocity was calculated from infiltration data collected from the LRIs (a water balance method). The water balance method, explained by Panno et al. (1991), uses a linear regression of the cumulative LRI(s) infiltration data to calculate the Darcy velocity. The average linear velocity was calculated by dividing the Darcy velocity (q) by the volumetric water content ($V_x = q/\theta$). The volumetric water content was measured both during liner construction in 1988 and again during final sampling in 2001 and was 21.0 and 22.7%, respectively. The average value was used. The closeness of the values suggests that the effective porosity and the Darcy velocity of the liner were constant with time. The water balance method yielded an average linear velocity of 4.8×10^{-8} cm/s (data not shown) which is in agreement with the modeled upper limit of 4.2×10^{-8} cm/s found by Toupiol et al. (2002) for 1D transport of tritium through the liner.

Dispersion

The dispersion coefficient (D) is a function of the dispersivity (α), the average linear-velocity (V_x), and the effective diffusion coefficient (D^*) as shown in Eq. (15)

$$D = \alpha V_x + D^* \quad (15)$$

In the low permeability soils used for liners, the contribution of mechanical dispersion to total dispersion is negligible (e.g., $\alpha V_x \ll D^*$) (Manassero and Shackelford 1994); hence total dispersion reduces to the effective diffusion coefficient. D^* is a function of the molecular diffusion coefficient in water (D_{mol}) and the tortuosity factor (τ) (Shackelford and Daniel 1991). D^* can be written as

$$D^* = D_{mol} \tau \quad (16)$$

Values of D^* were not measured in this work; instead D^* was adjusted within the range of calculated and published values to obtain the best fit of the data. The model allows for separate input values for radial and vertical effective diffusion coefficients; for

Table 2. Tracer Modeling Results

Tracer	V_x (cm/s)	D^* (cm ² /s)	D_{mol} (cm ² /s)	τ (-)
Tritium	4.2×10^{-8} ^a	6.0×10^{-6} ^a	2.4×10^{-5} ^b	0.25
Bromide	4.0×10^{-9}	5.5×10^{-6}	2.0×10^{-5} ^c	0.27

^aToupiol et al. (2002).

^bPhillips and Brown (1968).

^cAverage bulk diffusion coefficient from Table 1.

initial estimation purposes the two values were assumed to be equal. Calculated and published values of D^* and D_{mol} for Br⁻ in soil and bulk water are shown in Table 1. Tortuosity values calculated from Eq. (16) are shown in Table 2. The soils in Table 1 are similar to the loam to clay loam soil that was used in the construction of the soil liner (Krapac et al. 1991).

Source Zone

The source zone dimension for Br⁻ modeling was set equal to the diameter of the LRI ($d = 150$ cm). Core samples traversed the entire liner depth of 90 cm and were collected out to a radial distance of 121 cm from the center of the LRI. Hence modeled dimensions were evaluated from 0 to 90 cm and from 0 to 120 cm for the depth and radius, respectively.

Bromide Results and Discussion

The Br⁻ concentration profiles obtained from core samples are shown in Fig. 3. Br⁻ concentrations within the LRI ($r \leq 75$ cm)

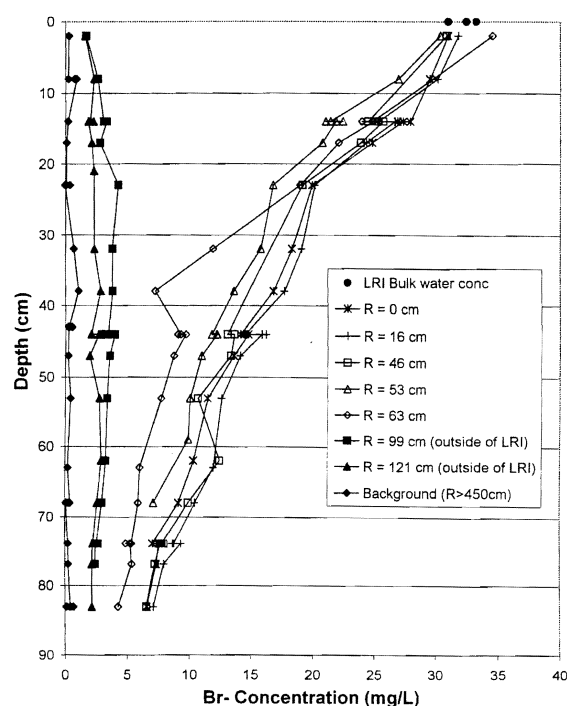


Fig. 3. Br⁻ concentration profiles at different radial locations (R) from the center of the large ring infiltrometer (LRI)

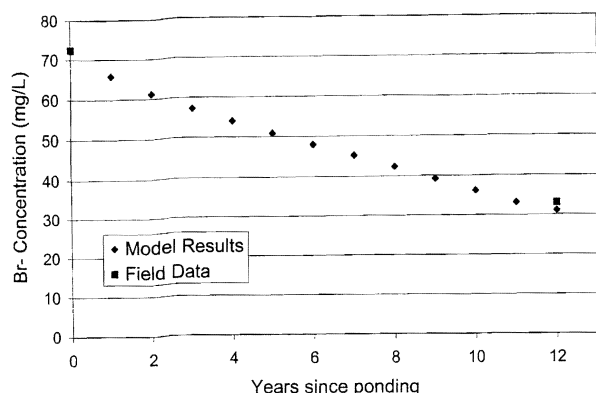


Fig. 4. Modeled Br^- large ring infiltrometer bulk water concentrations with time

decrease with depth, whereas Br^- concentrations outside the LRI increase in concentration to a depth of around 20 cm, and then remain approximately constant. Br^- concentrations measured in cores collected further from the center of the LRI tend to be smaller for a given depth than those collected closer to the center. This is reasonable given that the concentration of Br^- in the pond water outside of the LRI was negligible compared to the concentration inside the LRI.

The radial Br^- concentration gradient between the inside and outside of the LRI (e.g., at $r=75$ cm) decreased with depth. Hence radial diffusion was most significant near the surface of the liner. Concentrations of Br^- in samples taken near the liner surface (i.e., at 2 cm depth) inside the LRI ($r \leq 75$ cm) were close to each other, and within the spread of Br^- concentrations measured in the bulk water. This implies that the concentration of Br^- in the bulk water of the LRI was uniform.

The Br^- concentrations in the LRI bulk water were measured at the beginning and end of this study. As a result, the LRI bulk water concentrations for the last 12 years had to be calculated. This was performed using a mass balance approach [Eq. (13)]; the results are shown in Fig. 4. The LRI bulk water concentrations shown were calculated by setting $D^*=5 \times 10^{-6} \text{ cm}^2/\text{s}$ and $V_x=4.2 \times 10^{-8} \text{ cm/s}$. The value of D^* is in the range of values obtained from the literature $[(3.7-9.9) \times 10^{-6} \text{ cm}^2/\text{s}]$ and is equal to the bulk diffusion rate of Br^- (infinite dilution) times the tortuosity value of 0.25 obtained for tritium transport through the liner (Toupiol et al. 2002). The value of V_x is equal to the upper limit of velocity found by Toupiol et al. (2002) for tritium transport through the liner. The LRI bulk water concentration profile was also calculated at a seepage velocity of $V_x=6.5 \times 10^{-10} \text{ cm/s}$ to determine if the profiles were sensitive to decreases in velocity. The profiles were shown to be coincident (within 0.4% after 12 years), indicating that transport was diffusion controlled, and that lower values of V_x did not result in variations of the input concentration profile.

The calculated Br^- concentration in the LRI bulk water after 12 years was within 6% of the measured Br^- concentration, indicating that the mass balance approach is valid, and that the parameters used (i.e., D^* and V_x) were within the accuracy of the data. An additional check on the accuracy of the model was performed by comparing the mass that entered the system based on 3DADE modeling with the historic LRI field data. These results compare well; the modeled value is 18.2 g of Br^- entering the liner while the measured value based on the mass balance ap-

proach (30.1 g added over the life of the liner minus 12.6 g in the LRI at deconstruction) is 17.5 g of Br^- , a difference of only 4.4%.

The calculated LRI bulk water concentration profile (Fig. 4) was used as input to calculate the Br^- concentration profiles with depth. The fitness of model parameters were evaluated and optimized by minimizing the sum of relative least-squares (SRLS) between model predictions and the field samples over all soil cores. The best-fit average linear velocity was less than $0.4 \times 10^{-8} \text{ cm/s}$, and the best-fit effective diffusion coefficient was between 5×10^{-6} and $6 \times 10^{-6} \text{ cm}^2/\text{s}$.

To evaluate parameter sensitivity, (1) the average linear velocity was fixed at the optimized value and the effective diffusion coefficient was varied (Fig. 5) and (2) the effective diffusion coefficient was fixed at the optimized value and the average linear velocity was varied (Fig. 6). In Figs. 5 and 6, three modeled profiles and the corresponding field data are shown; the modeled profiles were evaluated in 10 cm radial increments, and the nearest profile to the field data is shown. In Fig. 5, values of D^* above and below the best-fit value yield Br^- concentration profiles that are offset from the data in opposite directions and result in greater SRLS values; this demonstrates that the model is sensitive to changes in D^* . In contrast to the profiles in Fig. 5, values of V_x above the best-fit result in profiles (Fig. 6) that are increasingly divergent from the measured field data (based on the SRLS), whereas profiles generated from V_x values less than the best fit are nearly coincident. This indicates that decreases in average linear velocity less than the best-fit value do not have an effect on the resulting model profiles and that transport is diffusion controlled. In support of this, a Peclet number ($P=V_x \cdot L/D^*$) of 6.5×10^{-2} was calculated using the best-fit V_x , D^* , and the depth of the liner, L ; peclet numbers ≤ 1 indicate that diffusion controls mass transport (Shackelford 1994a).

The best-fit model profiles in Figs. 5 and 6 match the data remarkably well, considering that Br^- transport occurred over 12 years and that model parameters were assumed constant for that duration. The closeness of the model fit suggests that (1) our model assumptions are reasonable (i.e., radial advection is negligible, diffusion in the radial and vertical direction are equal), (2) simple analytical models can often be used to simulate transport in soil liners, and (3) three-dimensional transport was uniform in the field-scale compacted clay liner (e.g., no preferential transport through the lifts).

Effect of Sample Positioning Error on Model Fit

Kim et al. (1997) reported that sampling position error due to compaction of soil samples from coring techniques can have a significant impact on parameter estimation. Kim et al. indicated that hydrodynamic dispersion is relatively insensitive to positioning error while errors in velocity estimation were dependent on the duration of experiment and uniformity of the concentration depth profile.

We evaluated the fitness of parameters based on the SRLS. Two methods of positioning error were evaluated. The first method evaluated sampling position error for each subsample as 6.6% times the distance from the top of the core to that subsample; 6.6% corresponds to the average field compression rate of 2 cm per 30 cm core. With this scenario, subsamples at the bottom of a core have a larger displacement than subsamples at the top of the core. For the second method, a constant offset of 7.5 mm was evaluated for each subsample; this is consistent with the approach used by Kim et al. (1997).

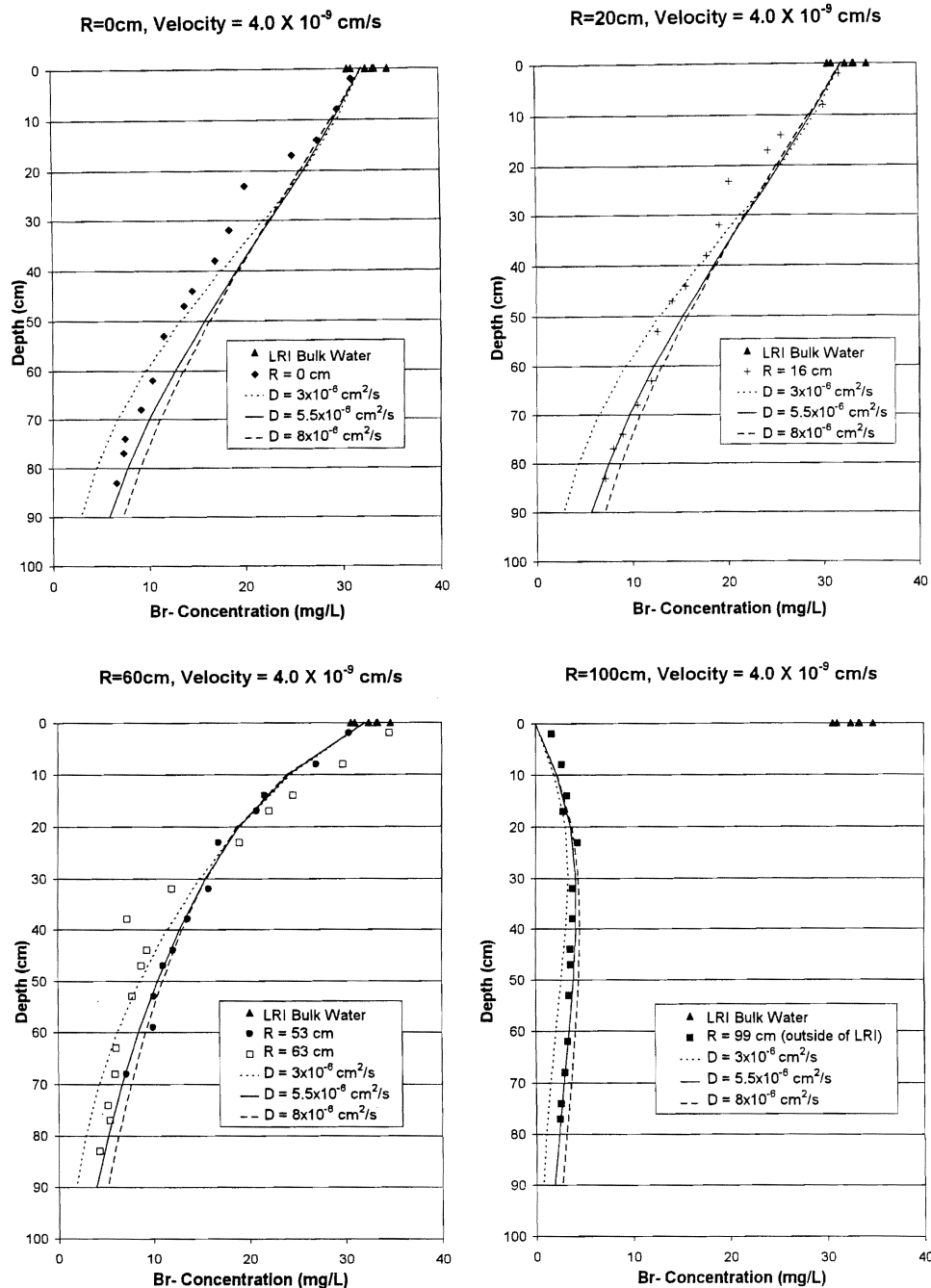


Fig. 5. Sensitivity of Br^- model fits for fixed velocity

For both assumed types of positioning errors, the result of the best fits were the same as reported above; the best-fit velocity was less than $0.4 \times 10^{-8} \text{ cm/s}$ and the best-fit diffusion coefficient was between 5.0×10^{-6} and $6 \times 10^{-6} \text{ cm}^2/\text{s}$. These results are consistent with the findings by Kim et al. (1997).

Comparison with Tritium

Best-fit values of V_x and D^* determined from this work and from the earlier work analyzing tritium transport at the same liner (Toupiol et al. 2002) are shown in Table 2. Values of D_{mol} and τ for Br^- and tritium are also listed. The values of τ for the two tracers are nearly coincident suggesting that the mechanisms controlling the diffusive transport of the two tracers are similar. In contrast to τ , the best-fit value of V_x for Br^- is an order of magnitude less than the best-fit value for tritium. At first this may appear surpris-

ing; however, the *best-fit* values listed are actually an upper limit for velocity (at velocities less than the best fit, profiles are coincident). By examining the effect of velocity and diffusion on the value of the SRLS, it can be seen that velocity values less than the best-fit do not improve this value. In fact, an infinite number of equally good fits can be obtained for velocities less than the reported best-fit value. In addition, Br^- diffusion is slightly slower than that of tritium; hence a lower V_x is required before the simulated profiles are diffusion controlled.

Conclusions

Construction of the field-scale soil liner used in this study was completed in 1988 at the University of Illinois at Urbana-Champaign; five tracers were ponded on the liner's surface and

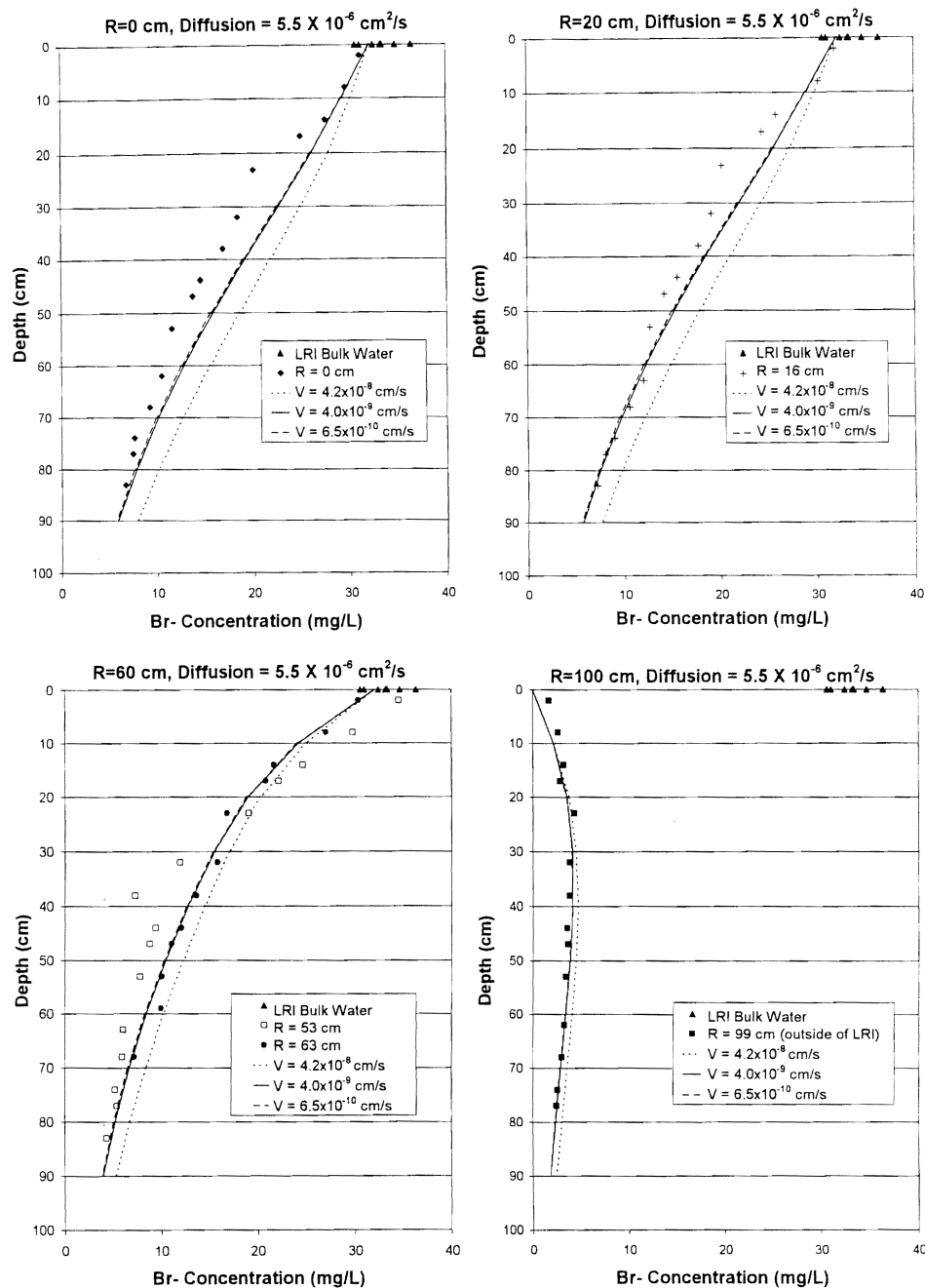


Fig. 6. Sensitivity of Br^- model fits for fixed diffusion coefficient

were allowed to migrate through the liner for over 12 years. Bromide was ponded in a localized source zone (inside a LRI) on the liner surface. At the end of 12 years, soil cores were taken and analyzed for Br^- . A solution to the cylindrical-coordinate form of the advection-dispersion equation was applied to the data. Excellent agreement between measured field concentration depth profiles and modeled concentration depth profiles were obtained by minimizing the sum of relative least-squares.

Results from this study indicate that: (1) compacted clay liners can be constructed as diffusion controlled barriers that are capable of mitigating chemical transport from localized leaks or source zones; (2) in experiments of sufficient duration and profile uniformity, small positioning errors due to sampling compression do not affect the best-fit advection and diffusion values; (3) preferential transport through the liner (lifts) was not observed; (4) Br^- trans-

port through the field-scale earthen liner was controlled by diffusion; and (5) the vertical and horizontal diffusion coefficients were the same.

Evaluation of chemical transport through compacted clay liners is essential to understanding transport through composite liner systems. Defects or holes in the geomembrane of a composite liner system can develop during deployment, construction, or waste settlement, and thereby create a localized source zone on the surface of compacted clay liners. Hence results from this study are especially important because they indicate that compacted clay liners can be constructed to act as diffusion barriers to minimize contaminant flux from a localized source zone. Previous work has not demonstrated this because this is the first time that transport in both the vertical and horizontal directions from a localized source zone has been analyzed in a field-scale liner.

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