

# Using Tracer Tests to Assess Natural Attenuation of Contaminants along a Channelized Coastal Plain Stream



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## ABSTRACT

Tracer tests have been widely used in studies of solute transport, gas exchange, and nutrient cycling in streams. However, the use of tracer tests to assess natural attenuation of ground-water-derived contaminants in streams, particularly from point sources, has been limited. We used tracer tests in conjunction with stream gauging and contaminant analyses to study the fate of trichloroethene (TCE) and technetium-99 ( $^{99}\text{Tc}$ ), which seep from industrial contaminant plumes into a channelized, first-order stream in the Coastal Plain of western Kentucky. Six tests were conducted over a 20-month period along a 300-m reach downstream of contaminated springs. Bromide, rhodamine WT, and nitrate were introduced as slug tracers to assess dilution, sorption, and reduction, respectively. Propane was added as a continuous, volatile tracer. Tracer transport was modeled as one-dimensional, with transient storage and first-order mass loss. Results indicate that (1) TCE is attenuated by volatilization; (2) TCE sorption, TCE reduction, and  $^{99}\text{Tc}$  reduction are negligible or absent; and (3) dilution is negligible along the study reach.

## INTRODUCTION

Tracer tests have become well-established tools for assessing mass transport and reactions in streams. Fluorescent dyes, which tend to have low background concentrations and low detection limits, and salt solutions are commonly used to determine flow rates and solute travel times (Kilpatrick and Cobb, 1985; Kilpatrick and Wilson, 1989; and Zellweger et al., 1989). Volatile tracers such as propane and sulfur hexafluoride are used to measure gas

exchange and re-aeration coefficients (Grant and Skavronck, 1980; Yotsukura et al., 1983; Kilpatrick et al., 1989; Wanninkhof et al., 1990; Genereux and Hemond, 1992; and Hibbs et al., 1998). Nitrate, ammonium, and phosphate have been added to measure rates of nutrient uptake and transformation in the hyporheic zone (Triska et al., 1989; Munn and Meyer, 1990; Valett et al., 1996; Peterson et al., 2001; Dodds et al., 2002; and Mulholland et al., 2004).

During the past decade, awareness of the potential for ground-water contaminants to discharge to streams, and thereby affect aquatic ecosystems, has become heightened (Ward, 1996; Winter et al., 1998; Lorah and Olsen, 1999; Church et al., 2002; and Conant et al., 2004). However, studies of the fate of contaminants that have passed through the discharge zone into streams have been limited. A few studies have used stream-tracer techniques to delineate influxes and fate of non-point-source contaminants, such as those from mining activity (Kimball et al., 1994, 2001; Broshears et al., 1996) and agriculture (Böhlke et al., 2004). We know of only one previous study that applied such techniques to ground-water-derived contaminants from industrial point sources (Kim et al., 1995; Kim and Hemond, 1998).

This article describes potential processes of natural attenuation in Little Bayou Creek, a first-order perennial stream in McCracken County, KY. Little Bayou Creek is fed by springs containing trichloroethene (TCE) and technetium-99 ( $^{99}\text{Tc}$ ) from past activities at the U.S. Department of Energy's (DOE) Paducah Gaseous Diffusion Plant (PGDP), a uranium-enrichment facility (Fryar et al., 2000; LaSage, 2004). Observed TCE concentrations decrease downstream of the springs, suggesting natural attenuation by one or more processes, including dilution, volatilization, sorption, and microbially mediated reduction within anaerobic microsites of the otherwise oxygenated streambed sediments. During a 20-month period, we examined variability in stream flow and contaminant concentrations along a channelized, 300-m

reach of the creek. We used these data and tracer tests to assess the roles of dilution, volatilization, sorption, and reduction in attenuating TCE and  $^{99}\text{Tc}$  in the stream.

## BACKGROUND AND METHODS

The study site is located within the Mississippi Embayment region of the Coastal Plain physiographic province (latitude  $37^{\circ}09'N$ , longitude  $88^{\circ}47'W$ ). Little Bayou Creek was a tributary to the Ohio River, but between 1953 and 1971, the creek was rerouted around the Tennessee Valley Authority's Shawnee Fossil Plant, a coal-fired generating station (Fryar et al., 2000). Little Bayou Creek now flows into Bayou Creek  $\sim 340$  m upstream of the Ohio River, and the lower 2.5 km of Little Bayou Creek have been channelized. Land use in the Little Bayou Creek watershed, which occupies an area of  $\sim 4$  km<sup>2</sup> (Fryar et al., 2000), includes rural residences and farms in addition to PGDP and the Shawnee Fossil Plant. Most of the creek itself lies within the public-access West Kentucky Wildlife Management Area. The watershed is underlain by Mississippian limestone bedrock and unconsolidated sediments of Cretaceous to Holocene age. Ground water flows primarily within the informally named Regional Gravel Aquifer (RGA), which is comprised of the Pliocene-Pleistocene Lower Continental Deposits (Clausen et al., 1992). The RGA is semi-confined and sub-crops at a depth of  $\sim 1$  m beneath the monitored reach of Little Bayou Creek (Science Applications International Corporation, 2001).

Plumes of ground water contaminated with TCE, which was used primarily as a degreaser at PGDP, and  $^{99}\text{Tc}$ , which was a byproduct of the reprocessing of spent nuclear fuel, extend several kilometers within the RGA and pass beneath Little Bayou Creek (Figure 1). Springs with TCE concentrations as high as  $450$   $\mu\text{g/L}$  and  $^{99}\text{Tc}$  concentrations as high as  $461$  pCi/L discharge from parts of the Northwest Plume and the Offsite  $^{99}\text{Tc}$  Plume along the upper 410 m of the channelized segment of the creek (LaSage, 2004). Baseflow upstream of these springs is sustained by discharge of process water from PGDP outfall 10, located  $\sim 5.2$  km upstream (Fryar et al., 2000). Measured TCE and  $^{99}\text{Tc}$  concentrations for Little Bayou Creek upstream of the springs are usually near or below laboratory reporting limits ( $\sim 1$   $\mu\text{g/L}$  for TCE and  $\sim 10$  pCi/L for  $^{99}\text{Tc}$ ; LaSage, 2004).

In May 2001, January 2002, June 2002, August 2002, October 2002, and January 2003, we gauged stream flow, collected stream-water samples for analyses of contaminants, and conducted tracer tests along a 300-m reach beginning 14 m downstream of the contaminated springs. Gauging and sampling for contaminants were conducted at three sites: LBC-4, LBC-3B (59 m downstream of LBC-4), and LBC-3 (300 m downstream of LBC-4) (Figure 1). The bed and bank sediment along the reach is

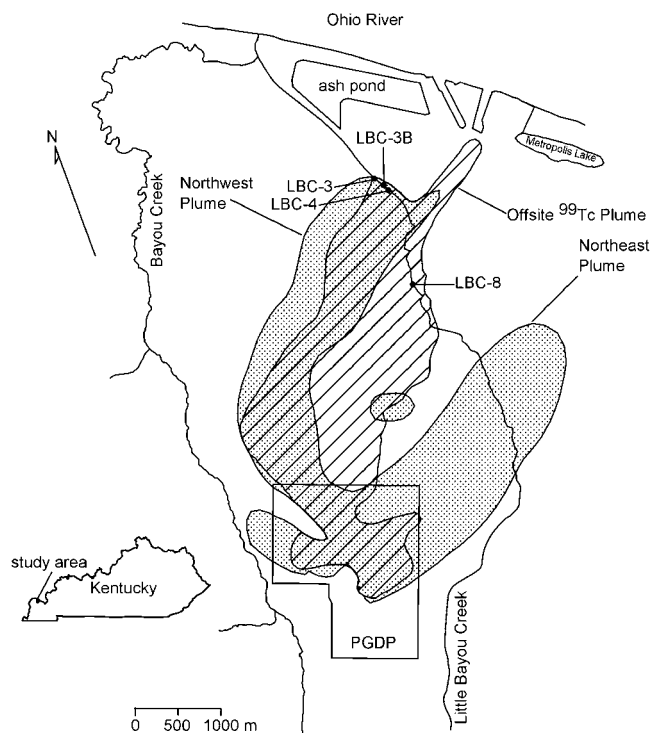


Figure 1. Study-area map with monitoring locations and ground-water contaminant plumes. Stippled areas indicate TCE concentrations in ground water  $\geq 5$   $\mu\text{g/L}$  (Safe Drinking Water Act maximum contaminant level); hatched areas indicate  $^{99}\text{Tc}$  concentrations in ground water  $\geq 25$  pCi/L. Modified from Fryar and others (2000).

sandy to clayey, and, except for a pool between the injection point and site LBC-3B, the stream was  $< 0.5$  m deep along the reach. Each round of field work was performed within a 48-hour period except in May 2001, when monitoring preceded the tracer test by 17 days, and in August 2002, when monitoring preceded the tracer test by 11 days. Field work occurred when no more than 1 mm of rain had been recorded within the previous 24 hours at the Paducah office of the National Weather Service, located 9 km south of the study site (University of Kentucky Agricultural Weather Center [UKAWC], 2005). The creek was gauged using a current meter with a top-setting rod (Marsh-McBirney, Inc., Frederick, MD) along a measuring tape perpendicular to the channel. Total stream flow at each site was calculated according to the mid-section method of Rantz and others (1982). Samples for analysis of TCE and other volatile organic compounds (VOCs) were collected by immersing 40-mL amber glass vials in the stream, adding 2–5 drops of 6 N HCl to each vial as a preservative, and capping the vial with a screw cap containing a Teflon<sup>TM</sup>-lined septum while excluding bubbles. Each sample for  $^{99}\text{Tc}$  analysis was taken by immersing a 1-L high-density polyethylene (HDPE) bottle in the stream and then adding 10 mL of 6 N HNO<sub>3</sub> as a preservative. During each sampling round, we collected a field blank with distilled water for

VOCs, as well as duplicate samples for  $^{99}\text{Tc}$  (except in October 2002). VOC samples were chilled during storage and transport. Samples were shipped to Severn Trent Laboratories (Earth City, MO), where VOCs were analyzed by gas chromatograph-mass spectrometer according to U.S. Environmental Protection Agency method SW846/8260B, and  $^{99}\text{Tc}$  was analyzed by liquid-scintillation counting.

For each test, up to four tracers were injected into the stream 10 m downstream of LBC-4. The tracers were  $\text{Br}^-$  (added as  $\text{NaBr}$ ), a fluorescent dye (rhodamine WT or another xanthene compound),  $\text{NO}_3^-$  (added as  $\text{NaNO}_3$ ), and propane (Table 1). Bromide was assumed to be a conservative tracer (i.e., concentrations would be affected only by dilution). We used an aqueous xanthene dye solution (Liquid Powder Tracing Dye, Norlab Inc., Amherst, OH) in May 2001 as a qualitative, visual indicator of the arrival of the tracer cloud. Subsequently, we used rhodamine WT both as a visual indicator and as a quantitative tracer. Although rhodamine WT has been treated as quasi-conservative in stream tracing studies (Kilpatrick and Cobb, 1985), sorption to sediment can occur (Bencala et al., 1983; Sabatini and Austin, 1991; and Vasudevan et al., 2001). TCE preferentially sorbs to organic matter when the fraction of organic carbon ( $f_{\text{OC}}$ ) in the sediment is greater than  $\sim 0.001$  (Fetter, 1999). However, the low  $f_{\text{OC}}$  of sediment samples from the bed of Little Bayou Creek (average 0.000334) suggests that sorption primarily occurs on mineral surfaces (LaSage, 2004). Therefore, the breakthrough curves of rhodamine WT, which also sorbs to both mineral surfaces and organic matter, were compared with those of  $\text{Br}^-$  to assess TCE sorption. Nitrate was used as an indicator of the redox state of the stream reach. A decrease in  $\text{NO}_3^-$  mass between the injection point and sampling locations, or delayed arrival of  $\text{NO}_3^-$  relative to a conservative tracer, could indicate reducing conditions where downwelling stream water flows within the bed or banks. Anoxia within the hyporheic zone of first-order perennial streams has been documented elsewhere (Dahm et al., 1991; Mulholland et al., 2004). Understanding the redox state along Little Bayou Creek is important because Tc can be reduced from  $\text{TcO}_4^-$ , the dominant form in near-surface waters (Wildung et al., 1979), to Tc(V) or Tc(IV) precipitates by metal- and sulfate-reducing bacteria (Lloyd and Macaskie, 1996; Lloyd et al., 1998; Lloyd et al., 2000; and Wildung et al., 2000). Moreover, TCE can be biodegraded to *cis*-1,2-dichloroethene (cDCE) under sulfate-reducing conditions (DeWeerd et al., 1998). Propane was used to simulate TCE volatilization. Although the calculated value of the Henry's law constant for TCE at 25°C (10.7 L atm/mol) is almost two orders of magnitude less than that for propane (708 L atm/mol) (Schwarzenbach et al., 1993, pp. 618, 622), the ratio of their measured volatilization coefficients ( $k_v^{\text{TCE}}/k_v^{\text{propane}}$ ) is only 0.79 (Smith et al., 1980).

Specified amounts of the tracers other than propane were dissolved in 20 L of stream water in each of two HDPE carboys. The carboys were then shaken for  $\sim 1$  minute and poured simultaneously into the stream as a slug at the beginning of each test. Propane gas was injected by continuous bubbling into the stream from a tank attached to a regulator, with the delivery pressure set at  $\sim 100$  kPa. The regulator was connected to a 0.97-m-long diffuser made of 1-in. nominal, schedule-40 PVC pipe studded with six porous stainless-steel frits (diameter 2.3 cm) placed at 10.2-cm intervals. The diffuser was anchored to the stream bed and covered with a plastic tarpaulin or bubble wrap to inhibit degassing from the stream surface.

Samples for the tracers were collected at specified time intervals at LBC-3B and -3. Beginning in June 2002, sampling at each location occurred where the highest velocity had been measured during gauging. To determine the background concentrations of the tracers in the stream, one set of samples was taken before the visible dye cloud arrived at LBC-3B and -3. Sampling continued until the cloud was no longer visible, with the time intervals between samples increasing over time to account for tailing of the slug. Generally, the intervals ranged from 2 to 5 minutes immediately following dye arrival and 6–15 minutes thereafter, depending on the stream velocity. Samples for  $\text{Br}^-$  and  $\text{NO}_3^-$  analyses were collected in 125-mL HDPE bottles. Bromide was analyzed by ion-specific electrode (for May 2001 samples) or by ion chromatograph at the Kentucky Geological Survey or in the University of Kentucky (UK) Department of Forestry. Nitrate samples were frozen to inhibit denitrification during storage (Avanzino and Kennedy, 1993) and were analyzed by autoanalyzer in the UK Department of Forestry or by ion chromatograph at the Kentucky Geological Survey. Rhodamine WT samples were collected in 40-mL amber glass vials to limit photodegradation and were chilled and stored in the dark. They were analyzed within 11 days of collection using a fluorescence spectrophotometer at the Kentucky Geological Survey. Propane samples were collected in the same fashion as VOC samples (except without acidification) and were stored for a maximum of 9 days before headspace analysis by gas chromatograph (GC) with a flame-ionization detector in the UK Department of Agronomy. Additional information on sampling and analytical techniques can be found in Mukherjee (2003) and LaSage (2004).

Each tracer test was modeled using the OTIS code of Runkel (1998). This program assumes one-dimensional flow and solute transport with advection, dispersion, lateral inflow, lateral outflow, and transient storage along the main channel. Transient storage entails detention of solutes in small eddies and stagnant zones. The model can account for sorption and first-order mass loss in both

Table 1. Tracer masses added, tracer test durations, stream temperature during tests, and wind speed during tests (UKAWC, 2005).

| Date     | NaBr mass (g) | Rhodamine WT mass (g) | NaNO <sub>3</sub> mass (g) | Start time | End time | Stream T at injection point (°C) and time measured | Wind speed at Paducah NWS office (m/second) |
|----------|---------------|-----------------------|----------------------------|------------|----------|--|---|
| 5/27/01  | 4,000         |                       |                            | 10:29      | ~13:29   |  | 3–4   |
| 1/18/02  | 1,000         | 119                   |                            | 11:50      | 15:03    | 5.3 (13:30)  | 0–2   |
| 6/5/02   | 2,000         | 25.8                  | 2,000                      | 9:31       | 12:07    | 19.3 (12:02)                                       | 3–4   |
| 8/23/02  |               | 20.6                  | 2,000                      | 11:30      | 13:44    | 22.7 (~10:30)                                      | 4–6 (gusts to 8)                            |
| 10/14/02 |               | 20.6                  | 2,000                      | 10:16      | 13:04    | 12.5 (10:41), 13.8 (13:26)                         | 3–4   |
| 1/8/03   |               | 20.6                  | 2,000                      | 10:00      | 12:16    | 6.6 (11:48)  | 6–7   |

the main channel and the storage zone. A version of OTIS that incorporates non-linear least-squares curve fitting (OTIS-P) was used to estimate values of the main-channel cross-sectional area  $A$  and the dispersion coefficient  $D$  for each tracer, as well as the storage-zone cross-sectional area  $A_S$  for slug tracers and the main-channel first-order mass-loss coefficient  $\lambda$  for propane. Values of the storage-zone exchange coefficient  $\alpha$  were varied manually between  $10^{-5}$  and  $10^{-4}$ /second for slug tracers. For propane,  $\alpha$  values were set to zero because the model commonly failed to converge when non-zero values were used. Other variables in the model were kept constant. Because no tributaries enter the reach between LBC-3B and -3, no springs have been observed along the reach, and the stream was assumed to be at baseflow for each test, lateral inflow and outflow were assumed to be negligible. The observed concentrations of each solute at LBC-3B were used to define the upstream boundary condition, and the downstream boundary was set at a distance of 100 m below LBC-3. Continuous injection was specified for propane. Initial values of  $\lambda$  and the storage-zone first-order mass-loss coefficient  $\lambda_2$  were taken from Genereux and Hemond (1992). Further details of the modeling analysis are provided in Mukherjee (2003).

## RESULTS AND DISCUSSION

### Gauging and Contaminant Concentrations

Discharge ( $Q$ ) values measured from stream gauging ranged from 0.028 to 0.067 m<sup>3</sup>/second (Table 2). Maximum values, which were recorded in January 2003, exceeded any measured by LaSage (2004), who gauged flow at sites extending from 3,900 m to 1,660 m upstream of the mouth of Little Bayou Creek between July 1998 and May 2001. At LaSage's farthest upstream site (LBC-8), the U.S. Geological Survey (USGS) maintains stream-gauge number 03611900 (USGS, 2005). Hydrograph separation of daily average discharge using the program iSep (Muthukrishnan et al., 2003) indicated that runoff comprised 38 percent of the flow at this gauge on January 7, 2003, and 34 percent on January 8, 2003. Runoff was less than 5 percent of the flow recorded by USGS at LBC-8 during our other monitoring days except for June 5, 2002, when a thunderstorm

occurred following the tracer test. Consequently, the assumption of baseflow conditions during sampling periods was tenable except for January 2003. Apart from January 2003,  $Q$  values were highest in June 2002, consistent with previous findings that baseflow along Little Bayou Creek is greatest in late spring and early summer (Fryar et al., 2000; LaSage, 2004). Values of  $Q$  usually decreased from LBC-4 to -3, also consistent with observations by LaSage (2004). However, the magnitude of  $\Delta Q$  along that reach was  $<0.001$  m<sup>3</sup>/second on five of seven occasions, including January 2003, which supports the assumption of minimal inflow and outflow in this study. Interestingly, the magnitudes of  $\Delta Q$  values between LBC-4 and -3B and between LBC-3B and -3 were almost always greater than along the entire reach. This may reflect localized downwelling and upwelling (as noted below) or measurement error. The presence of a pool between the injection point and LBC-3B is also consistent with downwelling.

One possible source of error in calculating  $Q$  was shoaling, particularly at LBC-4, which occasionally resulted in portions of the transect across the stream being too shallow to gauge, or caused the top-setting rod to settle in loose sand. For this reason, we gauged several meters downstream of LBC-4 on May 10, 2001. Notwithstanding shoaling, the width of the stream remained relatively uniform, varying by no more than 0.5 m at each gauging location throughout the study (Table 2). We attempted to limit error by gauging over segments as narrow as 3 in. (8 cm), in order to insure that no single segment contained more than 10 percent of the total discharge along a transect. That criterion was met in 17 of 22 gauging runs. To estimate the possible error in calculating  $Q$ , we also varied the reported velocity by  $\pm 0.01$  ft/second ( $\pm 0.003$  m/second, the precision of the current meter) and the reported depth at each measuring point by  $\pm 0.05$  ft ( $\pm 0.015$  m). The top-setting rod was marked in 0.1-ft (0.15-m) increments, although we visually estimated the depth to within 0.01 ft (0.003 m). In estimating error, negative (physically nonsensical) values were taken as 0. The resulting estimated error in  $Q$  was  $\leq 22$  percent of the calculated value at LBC-3,  $\leq 21$  percent at LBC-3B, and  $\leq 30$  percent at LBC-4.

Ranges of contaminant concentrations (Table 3) over-

Table 2. Stream-gauging parameters.

| Date                                 | 5/10/01 | 5/27/01 | 1/17–18/02 | 6/4/02 | 8/12/02 | 8/23/02 | 10/13/02 | 1/7/03 |
|--------------------------------------|---------|---------|------------|--------|---------|---------|----------|--------|
| LBC-4 width (m)                      | 2.50    |         | 5.67       | 6.16   | 5.87    | 5.89    | 5.64     | 5.97   |
| LBC-4 avg. depth (m)                 | 0.16    |         | 0.097      | 0.18   | 0.044   | 0.050   | 0.048    | 0.16   |
| LBC-4 gauged $A$ (m <sup>2</sup> )   | 0.405   |         | 0.550      | 1.12   | 0.258   | 0.294   | 0.272    | 0.944  |
| LBC-4 $Q$ (m <sup>3</sup> /second)   | 0.0332  |         | 0.0321     | 0.0605 | 0.0285  | 0.0366  | 0.0376   | 0.0658 |
| LBC-4 avg. gauged<br>$v$ (m/second)  | 0.0821  |         | 0.0583     | 0.0541 | 0.111   | 0.125   | 0.138    | 0.0697 |
| LBC-3B width (m)                     |         | 5.91    | 6.00       | 6.42   | 6.38    | 6.04    | 6.00     | 6.12   |
| LBC-3B avg. depth (m)                |         | 0.20    | 0.19       | 0.23   | 0.22    | 0.21    | 0.20     | 0.22   |
| LBC-3B gauged $A$ (m <sup>2</sup> )  |         | 1.19    | 1.17       | 1.45   | 1.43    | 1.24    | 1.18     | 1.36   |
| LBC-3B $Q$ (m <sup>3</sup> /second)  |         | 0.0306  | 0.0297     | 0.0622 | 0.0310  | 0.0323  | 0.0384   | 0.0666 |
| LBC-3B avg. gauged<br>$v$ (m/second) |         | 0.0258  | 0.0254     | 0.0429 | 0.0217  | 0.0260  | 0.0326   | 0.0488 |
| LBC-3 width (m)                      | 6.52    | 6.58    | 6.58       | 6.77   | 6.75    | 6.66    | 6.50     | 6.68   |
| LBC-3 avg. depth (m)                 | 0.13    | 0.12    | 0.24       | 0.20   | 0.19    | 0.16    | 0.14     | 0.18   |
| LBC-3 gauged $A$ (m <sup>2</sup> )   | 0.823   | 0.796   | 1.60       | 1.34   | 1.28    | 1.08    | 0.929    | 1.19   |
| LBC-3 $Q$ (m <sup>3</sup> /second)   | 0.0291  | 0.0337  | 0.0328     | 0.0598 | 0.0279  | 0.0367  | 0.0318   | 0.0652 |
| LBC-3 avg. gauged<br>$v$ (m/second)  | 0.0353  | 0.0423  | 0.0205     | 0.0447 | 0.0218  | 0.0339  | 0.0342   | 0.0546 |

lapped those reported for sites LBC-4 and -3 prior to May 2001 by LaSage (2004). TCE concentrations were highest at LBC-4 and gradually decreased downstream to LBC-3 (except for January 2002 and 2003, when values were the same at LBC-4 and -3B). TCE concentrations ranged from a maximum of 63  $\mu\text{g/L}$  at LBC-4 in June 2002 to a minimum of 13  $\mu\text{g/L}$  at LBC-3 in October 2002 and January 2003. Compounds that may have resulted from TCE degradation (e.g., *c*DCE) were not reported at concentrations  $\geq 1$   $\mu\text{g/L}$ . <sup>99</sup>Tc concentrations tended to be highest at LBC-4 but did not consistently decrease with distance downstream. <sup>99</sup>Tc concentrations at LBC-3B were lower than those at LBC-3 on four of five occasions, although the difference was within counting error (Table 3). <sup>99</sup>Tc concentrations were greatest at LBC-4 in January 2003 (average value 100.4 pCi/L) and least at LBC-3B in October 2002 (18.3 pCi/L). However, the maximum <sup>99</sup>Tc value is suspect for several reasons. First, LaSage (2004) observed that contaminant concentrations along Little Bayou Creek tend to be greatest in May or June and least in January, a trend that holds for TCE concentrations in this study. Second, <sup>99</sup>Tc concentrations in January 2003 at LBC-3B (21.9–25.0 pCi/L) and LBC-3 (26.2 pCi/L) are much closer to expected values. Finally, the concentration in the January 2003 sample from LBC-4 changed from 78.8 to 122 pCi/L upon reanalysis, and resampling at LBC-4 on March 14, 2003, resulted in values of 48.8–52.0 pCi/L.

#### Tracer Test Results

Durations of tracer tests ranged from 134 to 193 minutes (Table 1). Breakthrough curves for slug tracers ( $\text{Br}^-$ , rhodamine WT, and  $\text{NO}_3^-$ ) were asymmetric (Figures 2–4), with the ascending limb of each curve

being steeper than the descending limb, as expected (Kilpatrick and Wilson, 1989). Tailing increased and peak concentrations decreased with distance downstream. Secondary peaks were visible in some breakthrough curves, particularly at LBC-3B. Mass recovery of slug tracers was estimated as

$$M_R = (A_C \times Q) / M_i \quad (1)$$

where  $A_C$  is the area under the breakthrough curve and  $M_i$  is the original tracer mass introduced.  $A_C$  was calculated by numerical integration using the trapezoidal rule after subtraction of background values. For a conservative tracer, the total (surface and hyporheic) discharge ( $Q_T$ ) of the stream below the injection point equals the ratio  $M_i/A_C$ , which varies inversely with  $M_R$  (Kilpatrick and Cobb, 1985). Numerical integration was also used to estimate the time of the centroid of each breakthrough curve. Peak-to-peak travel times between LBC-3B and -3 were typically faster than centroid-to-centroid travel times for slug tracers, although the difference between the two methods of calculating travel times for each tracer was less than 20 percent except for nitrate in June 2002 and rhodamine WT in January 2003.

Bromide was used as a tracer in May 2001, January 2002, and June 2002, but was not used thereafter because similar travel times for  $\text{Br}^-$  and rhodamine WT suggested that the latter behaved conservatively. Bromide concentrations peaked at LBC-3B between 15 and 28 minutes after injection and at LBC-3 between 53 and 83 minutes after injection (Table 4; Figure 2). Bromide centroid times ranged from 20.1 to 35.4 minutes at LBC-3B and 60.4 to 99.1 minutes at LBC-3. Bromide centroid velocities between the injection point and LBC-3B were less than

Table 3. Contaminant concentrations in stream water, including results of analyses of duplicate samples. Note that  $\pm$  values =  $^{99}\text{Tc}$  counting errors; \* = results of a two-fold dilution; and \*\* = average of duplicate analyses of a single sample.

| Date     | LBC-4 TCE<br>( $\mu\text{g/L}$ ) | LBC-4 $^{99}\text{Tc}$<br>(pCi/L) | LBC-3B TCE<br>( $\mu\text{g/L}$ ) | LBC-3B $^{99}\text{Tc}$<br>(pCi/L) | LBC-3 TCE<br>( $\mu\text{g/L}$ ) | LBC-3 $^{99}\text{Tc}$<br>(pCi/L) |
|----------|----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|----------------------------------|-----------------------------------|
| 5/10/01  | 33                               | 58.6 $\pm$ 6.7                    |                                   |                                    | 26                               | 56.0 $\pm$ 6.3                    |
|          | 33                               | 54.5 $\pm$ 6.2                    |                                   |                                    |                                  |                                   |
| 1/17/02  | 18                               | 22.4 $\pm$ 3.0                    | 18                                | 23.3 $\pm$ 3.0                     | 16                               | 28.6 $\pm$ 3.5                    |
|          |                                  | 21.4 $\pm$ 2.9                    |                                   |                                    |                                  |                                   |
| 6/4/02   | 63*                              | 82.9 $\pm$ 8.5                    | 59*                               | 70.3 $\pm$ 7.2                     | 45*                              | 74.8 $\pm$ 7.9                    |
| 8/12/02  | 37                               | 58.7 $\pm$ 6.9                    | 33                                | 50.8 $\pm$ 6.5                     | 28                               | 44.5 $\pm$ 6.2                    |
|          |                                  |                                   |                                   | 46.3 $\pm$ 6.5                     |                                  |                                   |
|          |                                  |                                   |                                   | 44.6 $\pm$ 5.7                     |                                  |                                   |
| 10/13/02 | 18                               | 23.6 $\pm$ 3.0                    | 17                                | 18.3 $\pm$ 8.0                     | 13                               | 21.9 $\pm$ 2.9                    |
| 1/7/03   | 15                               | **100.4 $\pm$ 10.8                | 15                                | 25.0 $\pm$ 3.2                     | 13                               | 26.2 $\pm$ 3.5                    |
|          |                                  |                                   |                                   | 21.9 $\pm$ 3.2                     |                                  |                                   |
| 3/14/03  |                                  | **50.4 $\pm$ 6.2                  |                                   |                                    |                                  |                                   |

average velocities measured by gauging at LBC-4, but greater than average gauged velocities at LBC-3B. Bromide centroid velocities between LBC-3B and -3 were greater than average gauged velocities at both LBC-3B and -3. Bromide centroid velocities along both sub-reaches were greatest in June 2002. The  $\text{Br}^- M_R$  value at LBC-3 for May 2001 (120 percent [Table 4]) is nonsensical and may reflect incomplete transverse mixing, as discussed further below. Values of  $M_R$  at LBC-3 for January 2002 (82.0 percent) and June 2002 (86.2 percent) were more realistic than for May 2001, even though  $Q$  values for January 2002 were much closer to May 2001 values than to June 2002 values. Bromide  $M_R$  values were higher for LBC-3 than for LBC-3B, which suggests downwelling between the injection point and LBC-3B, followed by upwelling between LBC-3B and -3. The decrease in  $Q_T$  values from LBC-3B to -3 suggests some infiltration along that sub-reach. Values of  $Q_T$  exceeded  $Q$  by 58.1–105 percent at LBC-3B and by 16.3–22.3 percent at LBC-3 (except for May 2001 at LBC-3, when  $Q$  exceeded the calculated  $Q_T$  by 16.6 percent).

Rhodamine WT was added to stream water as a 20 percent stock solution in January 2002 and a 5 percent stock solution thereafter. Although the mass of rhoda-

mine WT added at each time is known (Table 1),  $M_R$  (and thus  $Q_T$ ) could not be accurately quantified from dye analyses, probably because a fluorometer calibration curve was not developed for each tracer test. Using a calibration curve developed prior to January 2002, with a single, higher standard (2,000  $\mu\text{g/L}$ ) added in January 2002, resulted in calculated  $M_R$  values  $>100$  percent in all cases except for LBC-3B in January 2002. Calibration curves developed in December 2004 with dilutions of the original stock solutions still resulted in unrealistically high  $M_R$  values. However, the lack of a calibration curve concurrent with analyses for each test does not preclude determination of travel times and relative  $A_C$  values from rhodamine WT breakthrough curves. The relationship between concentration and fluorescence for each calibration curve is typically linear (Wilson et al., 1986), as we observed, even though slopes may vary among calibrations. Therefore, measured fluorescence intensities can be taken as relative concentrations for each tracer test (Grasso and Williams, 1983). Dissolved organic matter (DOM) in stream water is unlikely to have interfered with our fluorescence measurements because emission wavelengths for DOM tend to be lower than the emission wavelength for rhodamine WT (558 nm) (Mounier et al.,

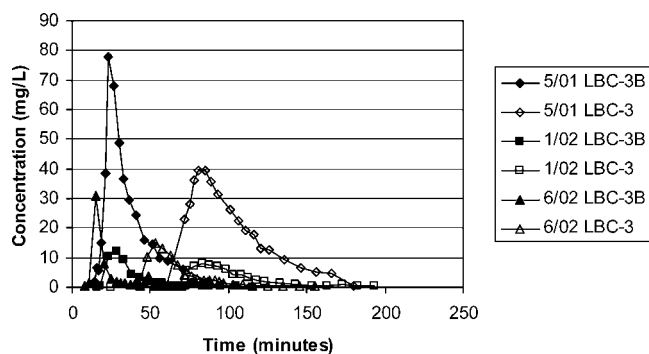


Figure 2. Measured breakthrough curves for  $\text{Br}^-$  at LBC-3B and LBC-3.

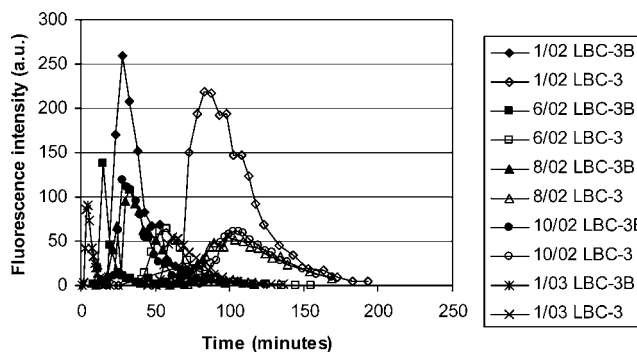


Figure 3. Measured breakthrough curves for rhodamine WT at LBC-3B and LBC-3.

1999; Marhaba, 2000; Alberts et al., 2002; Baker, 2002). The relatively short durations of the tracer tests and the fact that the reach from LBC-3B to -3 is shaded probably limited rhodamine WT photodegradation (Kratzer and Biagtan, 1997).

Rhodamine WT intensities peaked at LBC-3B between 15 and 33 minutes after injection and at LBC-3 between 58 and 106 minutes after injection (Table 4; Figure 3). Final intensities were  $\leq 2$  percent of peak values except for LBC-3 in August and October, when final values were 15 percent of peak values (Kilpatrick and Wilson (1989) recommended  $\leq 10$  percent). Calculated centroid times were 18.9–46.2 minutes at LBC-3B and 63.3–118 minutes at LBC-3. Rhodamine WT centroids were 1.0–2.2 minutes slower than  $\text{Br}^-$  centroids in January 2002. In June 2002, the rhodamine WT centroid was 1.2 minutes faster than the  $\text{Br}^-$  centroid at LBC-3B and 2.9 minutes slower than the  $\text{Br}^-$  centroid at LBC-3. As expected, rhodamine WT centroid velocities tended to increase linearly with  $Q$ , although the correlation was stronger for the sub-reach LBC-3B to -3 than for LBC-4 to -3B. Rhodamine WT centroid velocities between LBC-4 and -3B were greater than average gauged velocities at LBC-3B in January and June 2002 but were less than average gauged velocities at LBC-3B subsequently and were always less than average gauged values at LBC-4. Conversely, rhodamine WT centroid velocities between LBC-3B and -3 were always greater than average gauged values at both LBC-3B and LBC-3. Rhodamine WT centroid velocities along both sub-reaches were greatest in June 2002. Values of  $A_C$  were greater at LBC-3 than at LBC-3B in January and June 2002 (consistent with  $\text{Br}^-$  results) and in January 2003. Because rhodamine WT intensities at LBC-3 did not return to background levels before sampling was completed in August and October 2002, comparisons of  $A_C$  values at LBC-3B and -3 for those dates are inconclusive.

Nitrate travel times, which tended to be similar to those of  $\text{Br}^-$  and rhodamine WT, and  $M_R$  values indicate that  $\text{NO}_3^-$  reduction or uptake was minimal. Nitrate peak times coincided with  $\text{Br}^-$  in June 2002 and with rhodamine WT in January 2003 (Table 4; Figure 4). Nitrate peaks preceded rhodamine WT peaks by 3–6 minutes in August 2002 and lagged rhodamine WT peaks by 0–3 minutes in October 2002. Nitrate centroid calculations are approximate because final sampled concentrations at LBC-3B, LBC-3, or both were not at background, but were within 17 percent of peak values after correction for background. In June 2002, August 2002, and January 2003, calculated  $\text{NO}_3^-$  centroids lagged rhodamine WT centroids by 0.8–14 minutes at LBC-3B, while rhodamine WT centroids lagged  $\text{NO}_3^-$  centroids by 0.7–1.4 minutes at LBC-3. The fact that final sampled concentrations were above background might suggest that  $M_R$  values underestimate actual mass

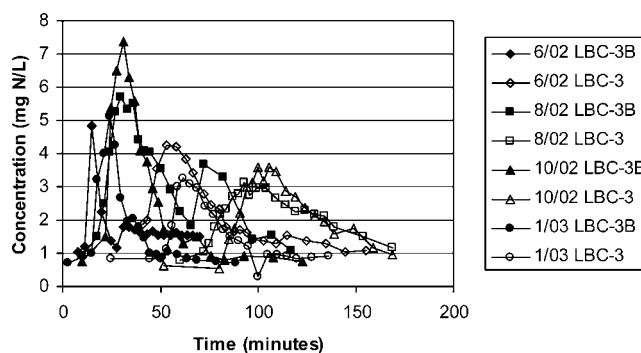


Figure 4. Measured breakthrough curves for  $\text{NO}_3^-$  at LBC-3B and LBC-3.

recoveries for  $\text{NO}_3^-$ . However,  $M_R$  values  $> 100$  percent at LBC-3 in June 2002 and at LBC-3B in August 2002, like the  $M_R$  value for  $\text{Br}^-$  at LBC-3 in May 2001, are clearly overestimates (Table 4). Nonetheless,  $M_R$  values for  $\text{Br}^-$  were less than those for  $\text{NO}_3^-$  in June 2002, which is consistent with relatively conservative behavior for  $\text{NO}_3^-$ . Values of  $Q_T$  for  $\text{NO}_3^-$  were greater than  $Q$  except in August 2002 at LBC-3B and in June 2002 at LBC-3.

Concentration plateaus for propane, which was continuously injected, were observed at some times and locations but not others. In May 2001, propane samples were collected only after the visible dye cloud had passed, at which time propane concentrations were assumed to have reached steady-state, following Kilpatrick and others (1989). Propane breakthrough thus cannot be modeled accurately using May 2001 data. In January 2002, replicate GC injections gave unacceptable variability in propane concentrations. Therefore, we report propane results only for June 2002 onward. At LBC-3B, plateaus were attained at times ranging from 20 minutes in June 2002 to 76 minutes in October 2002 (Table 4; Figure 5). At LBC-3, plateaus were attained at 67 minutes in June 2002 and 100 minutes in January 2003. In both June 2002 and January 2003, plateau concentrations for propane were greater at LBC-3B than at LBC-3. Plateaus were not evident at either site in August 2002 or at LBC-3 in October 2002. Late-time “upticks” in propane concentrations at both sites in June and August 2002 are attributed to changes in delivery pressure resulting from exchange of tanks. Propane plateaus lagged rhodamine WT peaks but occurred before rhodamine WT concentrations returned to background values.

#### Mathematical Modeling and Dimensionality Issues

Modeled breakthrough curves match observed curves at LBC-3 better for some tracer tests than for others. For  $\text{Br}^-$ , modeled curves match observed peak concentrations and peak times (except for January 2002) reasonably well (Tables 4 and 5), but the modeled descending limbs precede the actual ones. Rhodamine WT simulations

Table 4. Measured tracer-test parameters. RWT = rhodamine WT. The  $\lambda_C$  value for 8/23/02 was calculated using TCE concentrations measured 8/12/02. Note that peak  $\text{Br}^-$  and  $\text{NO}_3^-$  concentrations are uncorrected for background values.

| Date  | 5/27/01 | 1/18/02 | 6/4/02 | 8/23/02 | 10/13/02 | 1/7/03 |
|---|---------|---------|--------|---------|----------|--------|
| LBC-3B $\text{Br}^-$ peak concentration (mg N/L)          | 77.93   | 12.3    | 30.9   |         |          |        |
| LBC-3B RWT peak concentration (a.u.)                      |         | 259.9   | 137.6  | 109.3   | 119.2    | 90.23  |
| LBC-3B $\text{NO}_3^-$ peak concentration (mg/L)          |         |         | 4.83   | 5.69    | 7.37     | 5.11   |
| LBC-3B propane plateau concn. ( $\mu\text{mol/L}$ )       |         |         | 24.67  |         | 57.06    | 17.10  |
| LBC-3B $\text{Br}^-$ peak time (minutes)                  | 23      | 28      | 15     |         |          |        |
| LBC-3B RWT peak time (minutes)                            |         | 28      | 15     | 33      | 28       | 24     |
| LBC-3B $\text{NO}_3^-$ peak time (minutes)                |         |         | 15     | 30      | 31       | 24     |
| LBC-3B $\text{Br}^-$ centroid time (minutes)              | 34.5    | 35.4    | 20.1   |         |          |        |
| LBC-3B RWT centroid time (minutes)                        |         | 37.6    | 18.9   | 46.2    | 39.7     | 27.6   |
| LBC-3B $\text{NO}_3^-$ centroid time (minutes)            |         |         | 32.9   | 52.0    | 38.7     | 28.5   |
| LBC-3B propane plateau time (minutes)                     |         |         | 20     |         | 76       | 48     |
| LBC-3B $\text{Br}^- M_R$ (%)                              | 76.1    | 51.6    | 48.8   |         |          |        |
| LBC-3B $\text{NO}_3^- M_R$ (%)                            |         |         | 53.0   | 113     | 99.6     | 83.6   |
| LBC-3B $\text{Br}^- Q_T$ ( $\text{m}^3/\text{second}$ )   | 0.0483  | 0.0576  | 0.128  |         |          |        |
| LBC-3B $\text{NO}_3^- Q_T$ ( $\text{m}^3/\text{second}$ ) |         |         | 0.118  | 0.0286  | 0.0386   | 0.0798 |
| LBC-3 $\text{Br}^-$ peak concentration (mg/L)             | 39.60   | 8.0     | 14.83  |         |          |        |
| LBC-3 RWT peak concentration (a.u.)                       |         | 218.1   | 64.46  | 53.98   | 61.04    | 53.95  |
| LBC-3 $\text{NO}_3^-$ peak concentration (mg N/L)         |         |         | 4.26   | 3.13    | 3.59     | 3.23   |
| LBC-3 propane plateau concn. ( $\mu\text{mol/L}$ )        |         |         | 23.63  |         |          | 15.32  |
| LBC-3 $\text{Br}^-$ peak time (minutes)                   | 81      | 83      | 53     |         |          |        |
| LBC-3 RWT peak time (minutes)                             |         | 83      | 58     | 99      | 106      | 62     |
| LBC-3 $\text{NO}_3^-$ peak time (minutes)                 |         |         | 53     | 93      | 106      | 62     |
| LBC-3 $\text{Br}^-$ centroid time (minutes)               | 99.1    | 97.8    | 60.4   |         |          |        |
| LBC-3 RWT centroid time (minutes)                         |         | 98.8    | 63.3   | 113     | 118      | 73.8   |
| LBC-3 $\text{NO}_3^-$ centroid time (minutes)             |         |         | 62.6   | 113     | 117      | 72.4   |
| LBC-3 propane plateau time (minutes)                      |         |         | 67     |         |          | 100    |
| LBC-3 $\text{Br}^- M_R$ (%)                               | 120     | 82.0    | 86.2   |         |          |        |
| LBC-3 $\text{NO}_3^- M_R$ (%)                             |         |         | 151    | 84.5    | 76.3     | 69.1   |
| LBC-3 $\text{Br}^- Q_T$ ( $\text{m}^3/\text{second}$ )    | 0.0281  | 0.0401  | 0.0696 |         |          |        |
| LBC-3 $\text{NO}_3^- Q_T$ ( $\text{m}^3/\text{second}$ )  |         |         | 0.0396 | 0.0435  | 0.0418   | 0.0945 |
| LBC-4/-3B $\text{Br}^- v$ (m/second)                      | 0.0285  | 0.0278  | 0.0490 |         |          |        |
| LBC-4/-3B RWT $v$ (m/second)                              |         | 0.0261  | 0.0521 | 0.0213  | 0.0248   | 0.0356 |
| LBC-4/-3B $\text{NO}_3^- v$ (m/second)                    |         |         | 0.0299 | 0.0189  | 0.0254   | 0.0346 |
| LBC-3B/-3 $\text{Br}^- v$ (m/second)                      | 0.0621  | 0.0643  | 0.0997 |         |          |        |
| LBC-3B/-3 RWT $v$ (m/second)                              |         | 0.0657  | 0.0904 | 0.0597  | 0.0516   | 0.0871 |
| LBC-3B/-3 $\text{NO}_3^- v$ (m/second)                    |         |         | 0.135  | 0.0662  | 0.0511   | 0.0914 |
| LBC-3B/-3 $\lambda_C$ ( $\text{days}^{-1}$ )              |         | 2.77    | 8.78   | 3.52    | 4.96     | 4.47   |

overestimate the peak time for January 2002 and underestimate peak concentrations for January and June 2002 (Tables 4 and 5). Modeled rhodamine WT curves are more similar to observed curves for subsequent tests. The modeled  $\text{NO}_3^-$  curve for June 2002 closely matches the observed peak time but underestimates the peak concentration, while the modeled  $\text{NO}_3^-$  curve for August 2002 overestimates both the peak time and the peak concentration (Tables 4 and 5). Modeled  $\text{NO}_3^-$  curves for October 2002 and January 2003 are more similar to observed curves. In general, simulations of slug tracers at LBC-3 match peak concentrations more closely than peak arrival times (Figures 6 and 7). The modeled propane curve for June 2002 shows a “stairstep”: the first plateau is synchronous with the actual plateau (Tables 4 and 5), but modeled concentrations are lower, whereas the second plateau approaches observed concentrations (Figure 8). Subsequent modeled curves for propane generally match observed curves. For all tracers, deviations

between modeled and actual curves reflect the extent to which flow in the channel was not one-dimensional.

Values calculated by OTIS-P between LBC-3B and -3 tend to vary more narrowly for  $A$  than for  $A_S$  and  $D$  (Table 5). Values of  $A$  range from 0.44 to 0.82  $\text{m}^2$  and are within 31 percent of each other for different tracers at a given time. By comparison,  $A$  values determined from gauging vary from 1.17 to 1.45  $\text{m}^2$  at LBC-3B and from 0.80 to 1.60  $\text{m}^2$  at LBC-3 (Table 2). Values of  $A_S$  range from  $4.5 \times 10^{-5}$  to 0.028  $\text{m}^2$ , and modeled  $A_S/A$  ratios range from  $6.6 \times 10^{-5}$  to 0.040. These ratios are less than those reported for first-order perennial streams that have not been channelized, including three mountain streams in New Mexico ( $A_S/A \sim 0.08\text{--}4$ ; Valett et al., 1996) and the West Fork of Walker Branch in the Valley and Ridge province of Tennessee ( $A_S/A \sim 0.075\text{--}0.15$ ; Hart et al., 1999). Values of  $D$  range from 0.090 to 0.39  $\text{m}^2/\text{second}$  for slug tracers and from 0.23 to 0.58  $\text{m}^2/\text{second}$  for propane. Because of convergence problems, we could not



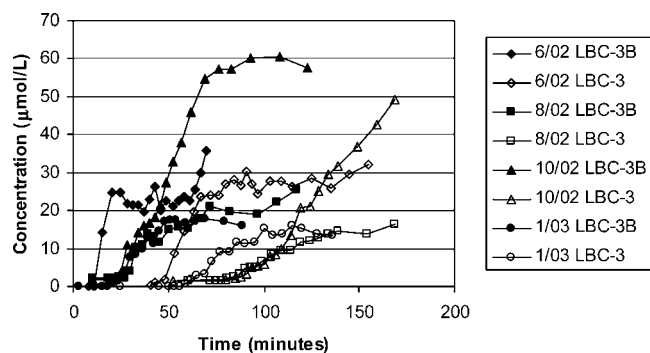


Figure 5. Measured breakthrough curves for propane at LBC-3B and LBC-3.

independently calculate  $A$  and  $D$  for propane in June 2002 or  $A_S$  for  $\text{NO}_3^-$  in October 2002.

Values of  $\lambda$  calculated by OTIS-P (Table 5) range from 0.24 to 7.6/day. These values are about an order of magnitude less than those reported by Genereux and Hemond (1992) for the West Fork of Walker Branch. However, our velocities from tracer tests and gauging are similar to those reported by Hart and others (1999). We attribute the difference in  $\lambda$  values to greater turbulence along the West Fork of Walker Branch because of its more irregular bedrock channel (Schwarzenbach et al., 1999, p. 233). To account for TCE volatilization, values of  $\lambda$  can be multiplied by 0.79 ( $= k_v^C \text{TCE} / k_v^C \text{propane}$ ; Kim and Hemond, 1998). We refer to these corrected values of the volatilization coefficient as  $\lambda_H$ . For comparison, we can directly calculate the TCE volatilization coefficient ( $\lambda_C$ ) as

$$\lambda_C = -1/t \times \ln(C_d/C_u) \quad (2)$$

where  $t$  is centroid travel time (in this case, for rhodamine WT between LBC-3B and -3);  $C$  is TCE concentration; and the subscripts  $d$  and  $u$  refer to the downstream (LBC-3) and upstream (LBC-3B) monitoring points, respectively. Values of  $\lambda_C$  (Table 4) are within a factor of five of  $\lambda_H$  except for October 2002, for which the simulation resulted in singular convergence.

Although the stream had been channelized and tracers were injected across most of its width, several lines of evidence indicate that flow and solute transport were not entirely one-dimensional along the study reach. Evidence includes observations of rhodamine WT retention in stagnant zones along the banks between the injection point and LBC-3B; secondary peaks in breakthrough curves at LBC-3B, which are evident for at least one of the slug tracers in every test except for May 2001; and the underestimation of gauged  $A$  values by OTIS-P. Kilpatrick and Cobb (1985) presented the following equations for estimating the distance downstream from the injection point at which transverse mixing is largely complete:

Table 5. Tracer parameters calculated by OTIS-P between LBC-3B and -3. RWT = rhodamine WT.

| Date   | 5/27/01 | 1/18/02 | 6/4/02  | 8/23/02 | 10/13/02 | 1/7/03  |
|--|---------|---------|---------|---------|----------|---------|
| LBC-3 $\text{Br}^-$ peak concentration (mg/L)          | 37.75   | 7.33    | 12.09   |         |          |         |
| LBC-3 RWT peak concentration (a.u.)                    |         | 153.9   | 52.73   | 52.66   | 60.36    | 54.84   |
| LBC-3 $\text{NO}_3^-$ peak concentration (mg N/L)      |         |         | 2.76    | 3.55    | 4.18     | 3.27    |
| LBC-3 propane plateau concn. ( $\mu\text{mol/L}$ )     |         |         | 20.42   |         |          | 13.51   |
| LBC-3 $\text{Br}^-$ peak time (minutes)                | 84.0    | 102     | 54.0    |         |          |         |
| LBC-3 RWT peak time (minutes)                          |         | 102     | 56.4    | 103     | 106      | 65.4    |
| LBC-3 $\text{NO}_3^-$ peak time (minutes)              |         |         | 54.0    | 120     | 110      | 66.6    |
| LBC-3 propane plateau time (minutes)                   |         |         | 67.2    |         |          | 96.6    |
| $D$ ( $\text{Br}^-$ ) ( $\text{m}^2/\text{second}$ )   | 0.23    | 0.090   | 0.23    |         |          |         |
| $D$ (RWT) ( $\text{m}^2/\text{second}$ )               |         | 0.11    | 0.28    | 0.39    | 0.18     | 0.28    |
| $D$ ( $\text{NO}_3^-$ ) ( $\text{m}^2/\text{second}$ ) |         |         | 0.21    | 0.26    | 0.30     | 0.29    |
| $D$ (propane) ( $\text{m}^2/\text{second}$ )           |         |         |         | 0.23    | 0.46     | 0.58    |
| $A$ ( $\text{Br}^-$ ) ( $\text{m}^2$ )                 | 0.44    | 0.54    | 0.61    |         |          |         |
| $A$ (RWT) ( $\text{m}^2$ )                             |         | 0.51    | 0.62    | 0.54    | 0.71     | 0.62    |
| $A$ ( $\text{NO}_3^-$ ) ( $\text{m}^2$ )               |         |         | 0.58    | 0.67    | 0.74     | 0.69    |
| $A$ (propane) ( $\text{m}^2$ )                         |         |         |         | 0.51    | 0.82     | 0.72    |
| $A_S$ ( $\text{Br}^-$ ) ( $\text{m}^2$ )               | 4.2E-03 | 1.2E-04 | 7.1E-03 |         |          |         |
| $A_S$ (RWT) ( $\text{m}^2$ )                           |         | 8.2E-04 | 1.7E-03 | 7.7E-03 | 8.1E-03  | 8.9E-03 |
| $A_S$ ( $\text{NO}_3^-$ ) ( $\text{m}^2$ )             |         |         | 2.3E-03 | 4.5E-05 |          | 2.8E-02 |
| $\lambda$ ( $\text{days}^{-1}$ )                       |         |         | 2.2     | 7.6     | 0.24     | 5.5     |
| $\lambda_H$ ( $\text{days}^{-1}$ )                     |         |         | 1.7     | 6.0     | 0.19     | 4.4     |

$$L_m = KvB^2/E_Z \quad (3)$$

$$E_Z = 1.13d^{1.5}s^{0.5} \quad (4)$$

where  $K$  is an empirical coefficient depending on the injection geometry,  $v$  is the average stream velocity (in ft/second),  $B$  is the average stream width (in ft),  $d$  is the average stream depth (in ft), and  $s$  is the stream-surface slope. For slug injection at two points, each between the mid-point of the stream and one bank,  $K = 0.018$  for 90 percent mixing, 0.025 for 95 percent mixing, and 0.035 for 98 percent mixing (Kilpatrick and Cobb, 1985). Using Eqs. 3 and 4 with values of  $v$ ,  $B$ , and  $d$  derived from gauging at LBC-3B, taking  $s$  as 0.0015 (the approximate gradient downstream of LBC-4), and assuming 98 percent mixing, we obtain  $L_m$  values  $< 49$  m

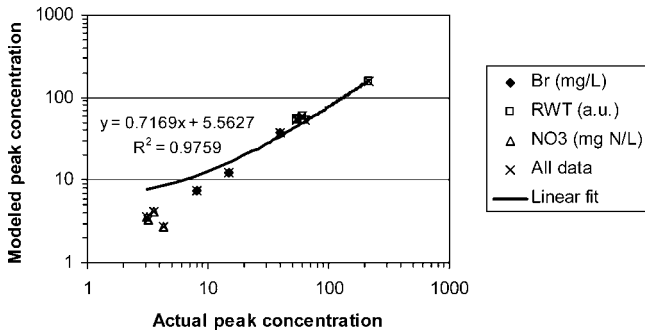


Figure 6. Modeled vs. actual peak concentrations for slug tracers at LBC-3. RWT = rhodamine WT. Note that, because time intervals between tracer samples varied during each test, whereas simulated intervals were uniform for each test, comparisons between modeled and actual results are approximate.

(the distance from the injection point to LBC-3B) (Table 6). However, with values of  $\nu$ ,  $B$ , and  $d$  derived from gauging at LBC-4,  $L_m$  values are  $\geq 290$  m (the distance from the injection point to LBC-3) for 90 percent mixing in August and October 2002 (Table 6). This latter result is consistent with the relatively poor fit between modeled and observed  $\text{NO}_3^-$  breakthrough curves for August; the anomalous  $A_S$  values for  $\text{NO}_3^-$ ; the anomalous  $\lambda$  value for October; and the singular convergence for August  $\text{NO}_3^-$  simulations and October propane simulations.

CONCLUSIONS

This study illustrates the utility of tracer tests, in conjunction with gauging of flow and monitoring of ambient water quality, for assessing the fate of groundwater-derived contaminants in streams. Among the mechanisms of natural attenuation examined, there was substantial evidence only for volatilization of TCE. The similarity between velocities for anionic tracers and for rhodamine WT suggests that TCE sorption is negligible along the study reach. Losses of  $\text{NO}_3^-$ , which appear to be minimal, can result from assimilatory uptake as well as

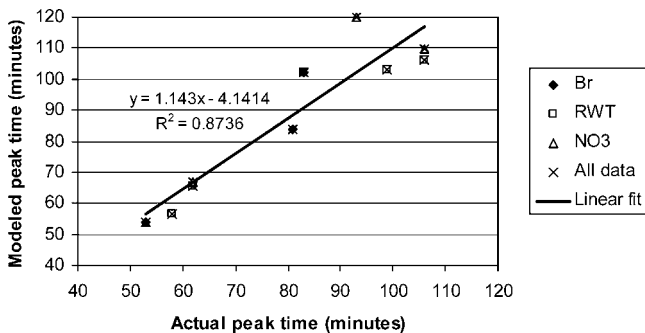


Figure 7. Modeled vs. actual peak times for slug tracers at LBC-3. RWT = rhodamine WT. Note that, because time intervals between tracer samples varied during each test whereas simulated intervals were uniform for each test, comparisons between modeled and actual results are approximate.

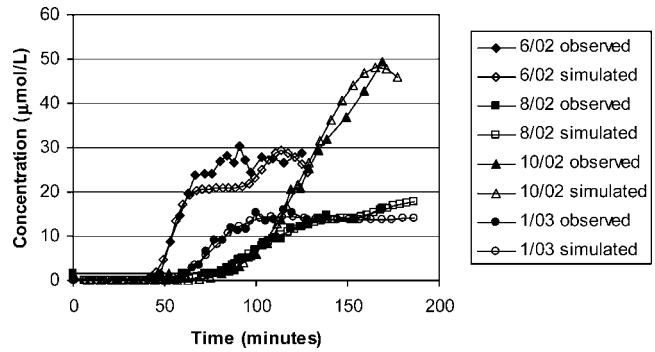


Figure 8. Measured and modeled breakthrough curves for propane at LBC-3.

from denitrification (Peterson et al., 2001; Dodds et al., 2002). Use of  $^{15}\text{N}$ -labeled  $\text{NO}_3^-$  as a tracer can facilitate the delineation of anaerobic conditions in the hyporheic zone (Böhlke et al., 2004; Mulholland et al., 2004), but would not conclusively document the occurrence of metal- or sulfate-reducing conditions necessary for reduction of  $^{99}\text{Tc}$  or TCE. The lack of a consistent decrease in  $^{99}\text{Tc}$  concentrations downstream of LBC-4 and the lack of putative TCE daughter compounds in stream water argue against significant  $^{99}\text{Tc}$  and TCE reduction in our study. Sorption and reduction are probably limited by the small fraction of organic matter in stream sediments (LaSage, 2004) and the small storage area along the study reach. In streams with higher  $f_{\text{OC}}$  sediments, use of rhodamine WT as a tracer could underestimate sorption of TCE and other organic solutes prone to hydrophobic partitioning. The lack of inflow between LBC-4 and -3, as indicated by the tendency of  $Q$  values to decrease, suggests that dilution is insignificant along the reach. Dilution probably occurs farther downstream along Little Bayou Creek, where diffuse discharge from the Regional Gravel Aquifer (beyond the Northwest Plume) and from the Shawnee Fossil Plant ash ponds is evident (Fryar et al., 2000). Notwithstanding the simplifying assumption of one-dimensional flow and transport, the general similarity between  $\lambda_H$  and  $\lambda_C$  values indicates that volatilization causes TCE concentrations to decrease with distance along Little Bayou Creek.

Table 6. Downstream distances from the injection site at which transverse mixing would theoretically have been 90, 95, and 98 percent complete (Kilpatrick and Cobb, 1985). Because the stream was not gauged at the injection site, mixing lengths were estimated using gauging parameters from both LBC-4 and LBC-3B.

| Date     | LBC-4,  | LBC-4,  | LBC-4,  | LBC-3B, | LBC-3B, | LBC-3B, |
|----------|---------|---------|---------|---------|---------|---------|
|          | 90% (m) | 95% (m) | 98% (m) | 90% (m) | 95% (m) | 98% (m) |
| 1/17/02  | 46.1    | 64.0    | 89.6    | 7.9     | 11.0    | 15.4    |
| 6/4/02   | 19.7    | 27.4    | 38.4    | 12.2    | 17.0    | 23.8    |
| 8/23/02  | 290     | 402     | 563     | 7.6     | 10.6    | 14.8    |
| 10/13/02 | 309     | 429     | 600     | 10.0    | 13.9    | 19.4    |
| 1/7/03   | 29.4    | 40.8    | 57.1    | 13.0    | 18.0    | 25.2    |

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