# Groundwater-derived contaminant fluxes along a channelized Coastal Plain stream

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**Summary** Recent studies in various settings across eastern North America have examined the movement of volatile organic compound (VOC) plumes from groundwater to streams, but few studies have addressed focused discharge of such plumes in unlithified sediments. From 1999 through 2002, we monitored concentrations of trichloroethene (TCE) and the non-volatile co-contaminant technetium-99 ($^{99}$Tc) along Little Bayou Creek, a first-order perennial stream in the Coastal Plain of western Kentucky. Spring flow contributed TCE and $^{99}$Tc to the creek, and TCE concentrations tended to vary with $^{99}$Tc in springs. Contaminant concentrations in stream water fluctuated seasonally, but not always synchronously with stream flow. However, contaminant influxes varied seasonally with stream flow and were dominated by a few springs. Concentrations of $O_2$, $NO_3^-$, and $SO_4^{2-}$, values of $\delta^{37}Cl_{DOCl}$ in groundwater, and the lack of less-chlorinated ethenes in groundwater and stream water indicated that anaerobic biodegradation of TCE was unlikely. Losses of TCE along Little Bayou Creek resulted mainly from volatilization, in contrast to streams receiving diffuse contaminated discharge, where intrinsic bioremediation of VOCs appears to be prevalent.
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## Introduction

During the past two decades, awareness of the movement of groundwater contaminants to surface water has gradually

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increased (Winter et al., 1998). In particular, Ward (1996), Stanley and Jones (2000) have noted the need to assess the impacts of groundwater-derived contaminants on aquatic ecosystems. Stanley and Jones (2000, p. 414) remarked, ''Even though the study of groundwater contaminant movement is well established, investigations of this same topic for near-stream environments and for the transmission of contaminants between groundwater and streams (in either direction) are rare''.

An emerging body of work has addressed the location of zones where plumes of volatile organic compounds (VOCs) discharge to streams. These compounds, which include fuel hydrocarbons and chlorinated solvents, are of concern because they are common groundwater contaminants; they can impact human health at aqueous concentrations as low as micrograms per liter; and some of them are resistant to degradation (National Research Council, 1984; Patrick et al., 1987; Zogorski et al., 2006). VOC plumes discharge to streams in a variety of geologic settings in eastern North America, including clastic sediments in the Atlantic and Gulf Coastal Plains (Vroblesky et al., 1991; Bradley and Chapelle, 1998; Lorah and Olsen, 1999; Fryar et al., 2000), glaciogenic sediments in New England and Canada (Kim et al., 1995; Kim and Hemond, 1998; Lyford et al., 1999; Church et al., 2002; Conant et al., 2004; Chapman et al., 2007), fractured crystalline rocks in the Piedmont and northern Appalachians (Vroblesky et al., 1996; Church et al., 2002), and karstified carbonates in the Interior Low Plateaus (Williams and Farmer, 2003; Vesper and White, 2006). Groundwater discharge at these sites ranges from diffuse in unconsolidated sediments to focused along preferential pathways such as fractures and conduits. Where diffuse discharge occurs, geochemical conditions may promote intrinsic biodegradation of compounds such as chlorinated ethenes along the groundwater-stream interface (Lorah and Olsen, 1999; Conant et al., 2004; Chapman et al., 2007).

Within the literature on interactions of VOC plumes with streams, an underappreciated scenario is that of focused discharge through unlithified sediments. As noted by Lyford et al. (1999) and Conant et al. (2004), springs can develop along heterogeneities such as sand stringers or fractures in clay, thereby enabling plumes to ''short-circuit'' finer-grained zones where biodegradation or sorption might be promoted. Herein, we present a case study of focused discharge of the chlorinated solvent trichloroethene (TCE) and the radionuclide technetium-99 ($^{99}$Tc) to a stream in the northern Gulf Coastal Plain of the USA. This paper builds upon studies of TCE fate in groundwater (Sturchio et al., 1998), TCE and $^{99}$Tc discharge and in-stream attenuation (Fryar et al., 2000; Mukherjee et al., 2005), and groundwater discharge along the stream (Fryar et al., 2000; LaSage et al., 2008). The current study examines indicators of natural attenuation in stream water and groundwater, seasonal variability in contaminant fluxes, and the utility of $^{99}$Tc as a conservative co-contaminant against which TCE attenuation can be compared, as suggested by Fryar et al. (2000).

## Background

Little Bayou Creek is a first-order perennial stream in McCracken County, Kentucky (Fig. 1). Along its lower 2.5 km,

the stream has been channelized around ash ponds at the Tennessee Valley Authority's Shawnee Plant, a coal-fired generating station, and connected to Bayou Creek, a second-order perennial tributary of the Ohio River. Baseflow in both creeks is sustained by process water from outfalls at the Paducah Gaseous Diffusion Plant (PGDP) and by groundwater discharge in the Ohio River floodplain (Fryar et al., 2000; LaSage et al., 2008). The main aquifer in the study area is the informally-named regional gravel aquifer (RGA), which consists of chert pebbles and cobbles in a sandy matrix (the Miocene-Pleistocene-age Mounds Gravel) (Clausen et al., 1992; LaSage et al., 2008). The RGA is underlain by the Porters Creek Clay (Paleocene) and the sandy to clayey McNairy Formation (Upper Cretaceous), and is locally confined by silt and clay of the overlying Metropolis Formation (Pleistocene) and by loess. Groundwater is probably recharged by leakage beneath pipes and lagoons at PGDP as well as by meteoric infiltration (Jacobs EM Team, 1999). Flow in the RGA is north-northeastward toward the Ohio River, although temporary reversals in hydraulic gradient occur when the river is at flood stage (Clausen et al., 1992; Fryar et al., 2000). LaSage et al. (2008) provide additional detail on watershed hydrology, climate, and the geologic setting.

PGDP has enriched uranium since 1952. From 1953 until 1993, TCE was used to decontaminate equipment and waste material at PGDP (Clausen et al., 1997). From 1953 to 1976, the feed plant at PGDP received reprocessed uranium oxide (UO$_2$) and converted it to UF$_6$ in a multi-step process, which resulted in the introduction of over 600 kg of $^{99}$Tc to the plant (Smith, 1984). Since 1988, offsite movement of groundwater contaminated with TCE and $^{99}$Tc has forced the abandonment of several private wells (CH2M Hill, 1992) and the provision of an alternate water supply to affected residents. In May 1994, the site was added to the National Priorities List (USEPA, 2007). Contaminant plumes extend laterally several kilometers within the RGA (Fig. 1). Several sources of TCE contamination exist on the site, including a residual pool of ~795 m$^3$ of dense, non-aqueous phase liquids either at the base of the RGA or within the Metropolis Formation (Sturchio et al., 1998). The plumes are thought to contain ~3200 to 4700 kg of dissolved TCE, with concentrations ranging from near the detection limit (1 μg/L) in the distal portions to near the solubility limit (1100 mg/L) at or close to the source. $^{99}$Tc concentrations in the plumes at PGDP range from near the detection limit (25 pCi/L) at the far edges to 40,000 pCi/L near the source (ATSDR, 1997). Remediation of contaminated groundwater beyond the PGDP property boundary has entailed hydraulic control (via pumping wells) and treatment of pumped water. Coupled flow and transport models (Jacobs EM Team, 1999) indicated that, based on the current remediation strategy, off-site TCE concentrations in the northwest plume would continue to exceed the Safe Drinking Water Act maximum contaminant level (MCL; 5 μg/L) after 30 yr, while $^{99}$Tc concentrations would fall below the derived MCL (900 pCi/L) after 15 yr. Consequently, natural attenuation of TCE is of interest.

Because of its widespread industrial use during the 20th century (Bedient et al., 1999), TCE is one of the most prevalent chlorinated VOCs detected in groundwater in North America (Bagley and Gossett, 1990; Stroo et al., 2003). Pro-
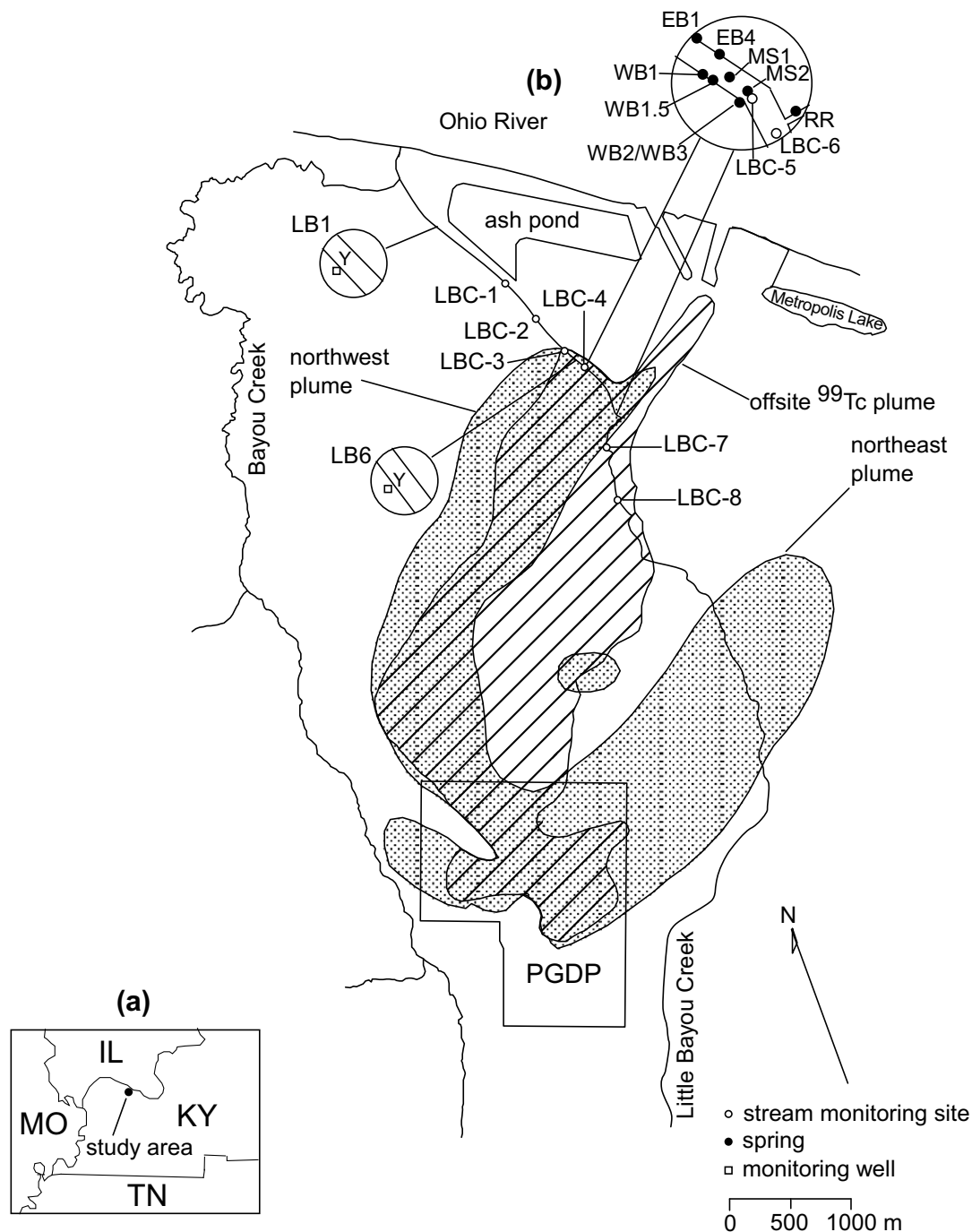
**Figure 1** (a) Inset showing regional location of study area (modified from Fryar et al. (2007)). IL = Illinois; MO = Missouri; KY = Kentucky; TN = Tennessee. (b) Study-area map with monitoring locations and groundwater contaminant plumes. Insets (not to scale) along Little Bayou Creek show relative positions of the stream channel, springs, sites LBC-5 and -6, and wells LB1Y and LB6Y of Fryar et al. (2000). Stippled areas indicate TCE concentrations in groundwater $\geqslant 5\ \mu g/L$ (MCL); hachured areas indicate $^{99}Tc$ concentrations in groundwater $\geqslant 25\ pCi/L$ (approximately $2 \times$ the detection limit). Modified from Mukherjee et al. (2005).

cesses that naturally remove dissolved TCE include volatilization (Rathbun, 1998); sorption to sediments, particularly when the fraction of organic carbon ($f_{oc}$) exceeds $\sim 0.001$ (Fetter, 1999); and bacterially-mediated biodegradation, which is the only one of these processes that actually destroys contaminant mass. Intrinsic biodegradation of TCE typically entails anaerobic reduction, either cometabolic

degradation (Norris, 1994) or direct dehalogenation (halorespiration) (Middeldorp et al., 1999). Under sulfate-reducing conditions, TCE can be cometabolically reduced to one of the dichloroethene (DCE) isomers (*cis*-1,2-DCE [cDCE], *trans*-1,2-DCE, or 1,1-DCE), of which cDCE is the most prevalent (DeWeerd et al., 1998). In turn, the DCE isomers can be reduced under methanogenic conditions to vinyl

chloride (VC) and thence to ethene (Lorah and Olsen, 1999); cDCE can be oxidized in the presence of natural organic matter or $CH_4$ (Bradley and Chapelle, 1998; Bradley et al., 1998a); or VC can be anaerobically oxidized in the presence of Fe(III) (Bradley et al., 1998b).

Unlike TCE, $^{99}Tc$ (the most abundant Tc isotope) is rarely encountered in environmental studies. $^{99}Tc$ decays by beta emission with a half-life of $2.1 \times 10^5$ yr (Lloyd and Macaskie, 1996). $^{99}Tc$ typically enters the environment via effluent at uranium enrichment facilities using reprocessed fuel (Blaylock et al., 1984), often through equipment decontamination (Till, 1984; Liang et al., 1996). Besides PGDP, sites in the USA where $^{99}Tc$ occurs in groundwater have been documented by Beals and Hayes (1995), Ryan and Kipp (1997), Beasley et al. (1998), and the US Government Accountability Office (GAO (2005, 2006)). At all these sites except one (Beasley et al., 1998), $^{99}Tc$ discharge to streams has been either documented or suspected. In oxygenated environments, Tc is rapidly hydrolyzed to $TcO_4^-$, which is relatively mobile (Wildung et al., 1979). Under metal- or sulfate-reducing conditions, $TcO_4^-$ can be reduced to a relatively insoluble (oxyhydr)oxide or sulfide (Lloyd and Macaskie, 1996; Lloyd et al., 1998; Lloyd et al., 2000; Wildung et al., 2000).

## Methods

From June 1999 through May 2001, at 3- to 4-month intervals, we sampled stream water at as many as eight sites (LBC-1 through -8 (Fig. 1)) where LaSage et al. (2008) gauged stream flow. In addition, we sampled as many as eight springs (six along the stream banks and two in the channel (Fig. 1)) studied by LaSage et al. (2008) along the upper ~400 m of the channelized reach of Little Bayou Creek. Typically, sampling began at the farthest downstream point and proceeded upstream, and stream samples were collected during one day of a given trip, while spring samples were collected on a second day. In January, June, August, and October 2002, we again sampled stream water at sites LBC-1 through -4. For comparison, we report analyses of stream and groundwater samples collected quarterly during 1997 at sites LB1 (~750 m downstream of LBC-1) and LB6 (~10 m downstream of LBC-4) of Fryar et al. (2000).

Stream and spring samples were collected by immersing containers except at channel springs, where a seepage meter made from 4-in. nominal (10.2-cm actual inside diameter) PVC pipe was used (Fryar et al., 2000). At sites LB1 and LB6, monitoring wells were sampled using a submersible pump in January 1997 and a peristaltic pump in May, August, and October 1997. Springs, wells and a subset of stream-water sites were monitored for dissolved $O_2$ (DO). All 1997 samples and some from January and August 2000 were analyzed for pH, metals, metalloids, and major anions; the 2000 subset was also analyzed for total organic carbon (TOC). All sites were monitored for VOCs and $^{99}Tc$ except site LB1 in January 1997. For metals, metalloids, anions, and TOC, for VOCs and $^{99}Tc$ during 1997, and for selected $^{99}Tc$ analyses thereafter, samples were passed through disposable 0.45-μm filters to obtain estimates of dissolved concentrations. DO samples were collected in 300-mL BOD bottles. Anion, metal, metalloid, and TOC samples were collected in polyethylene (PE) bottles. Metals and metal-

loids were preserved with 6 N $HNO_3$, while TOC was preserved with 6 N $H_2SO_4$. VOC samples were collected in 40-mL amber glass vials, which were closed with screw caps containing Teflon™-lined septa while excluding bubbles. Two to five drops of 6 N HCl were added to each vial as a preservative. Samples for $^{99}Tc$ were collected in 1-L PE bottles and preserved with 10 mL 6 N HCl or $HNO_3$ except for 2000 and 2001 samples, which were not acidified, following the recommendation of laboratory staff. In May 2001, five springs were sampled for analysis of the Cl stable isotope ratio ($^{37}Cl/^{35}Cl$) of dissolved organic Cl ($\delta^{37}Cl_{DOCl}$) using pre-evacuated 350-mL Schlenk tubes with glass valve barrels and inert O-rings (Holt et al., 1997). Samples for VOCs and $^{37}Cl$ analyses were chilled during transport (except for an overnight shipment in May 2000) and stored at 4 °C prior to analyses.

During July 2000, we collected porewater from streambed sediments at three sites between LBC-5 and -4 to obtain vertical profiles of VOC concentrations. We used multi-chambered acrylic samplers (dialyzers, or ''peepers'') based on the design by Adams (1994). $N_2$ gas was bubbled into boiling deionized water to lower DO concentrations to <1 μg/L. The sampler chambers were then filled with the deaerated, deionized water, a 0.45-μm polysulfonate membrane was placed over the filled chambers, and an acrylic cover with openings aligned with the chambers was placed over the membrane. Following Webster et al. (1998), the peepers were inserted into the stream bed and allowed to equilibrate for 3 weeks. Peeper 1 was inserted into sandy sediment proximal to channel spring MS2. Peeper 2 was in clayey sand adjacent to bank spring WB1.5. Peeper 3 was emplaced at the bend between WB1.5 and MS2, near several mineralized joints. Samples were collected at vertical intervals of 1–4 cm (typically 2 cm) beginning at 6 cm below the bed. Each sample was withdrawn from the chamber using a disposable syringe, injected into a weighed 8-mL glass vial containing a weighed amount of pentane equal to ~4 mL, and mixed gently for 1 min. Samples were chilled during transport and stored at 4 °C.

Except as noted, pH was measured in the field using a portable meter and electrode calibrated against pH 4 and 7 buffers, and DO was measured using the azide modification of the Winkler method with a digital titrator (Hach Company, 1997). Bicarbonate alkalinity was measured by digital titration with 1.600 N $H_2SO_4$ to a pH endpoint of ~4.5. Other anions were analyzed by ion chromatography, and metals and metalloids were analyzed by inductively coupled plasma spectrometry, at Severn Trent Laboratories (STL, formerly Quanterra; Earth City, MO, USA) or the Kentucky Geological Survey. TOC was analyzed by oxidation on a TOC analyzer at STL. VOCs were analyzed at STL by gas chromatograph (GC)-mass spectrometer (MS) according to USEPA method SW 846/8260B. $^{99}Tc$ was analyzed by liquid-scintillation counting at Teledyne Brown Engineering (Northbrook, IL, USA) for 1999 samples and at STL for other samples. Detected values for VOCs and $^{99}Tc$ are considered to be those above laboratory reporting limits and, except as noted, $^{99}Tc$ results refer to unfiltered samples. $\delta^{37}Cl_{DOCl}$ was analyzed using a gas-source isotope-ratio MS at the University of Illinois at Chicago. VOCs in porewater were analyzed using a GC with a $^{63}Ni$ electron-capture detector in the Department of Plant and Soil Science at the University of

Kentucky. Further details on $\delta^{37}Cl_{DOCl}$ and porewater analyses are given by Holt et al. (1997) and LaSage (2004), respectively.

## Results and discussion

### Stream water and groundwater chemistry

Stream water shows two distinct spatial groups in terms of major solutes (Table 1). Samples from LBC-4/LB6 and farther upstream tended to have similar concentrations of Ca and Na on a milliequivalent basis, with no dominant anion. In contrast, LBC-1 and LB1 had Ca—$SO_4$ or Ca—Na—$SO_4$ waters, with $SO_4^{2-}$ concentrations as high as 98.6 mg/L (Table 1). The downstream change in chemistry probably resulted primarily from seepage of ash-pond leachate into Little Bayou Creek, as inferred by Fryar et al. (2000) and LaSage et al. (2008). Flue gas desulfurization waste, which is generated at the Shawnee Plant (Hower et al., 1996), contains $CaSO_4$ and is commonly co-disposed with fly ash (US Federal Highway Administration [FHWA], 1998). DO concentrations in stream water (Table 1) approached equilibrium with atmospheric $O_2$ ($\sim$8 mg/L [Langmuir, 1997]). Fe and Mn concentrations, which were <1 mg/L (Table 1), may have been an artifact of metal (oxyhydr)oxide colloids passing through the 0.45-μm filter (Grout et al., 1999).

As in the case of stream water, groundwater samples fall into two groups based on solute chemistry. Concentrations of Na, Ca, Mg, Cl⁻, and $HCO_3^-$ were markedly higher, and $SO_4^{2-}$ concentrations were lower, for the springs and well LB6Y than for well LB1Y (Table 2). Both wells are located on the west bank of Little Bayou Creek opposite the Shawnee Plant ash ponds. Depths from the streambed to the top of the 0.76-m-long well screens are $\sim$4.4 m for LB6Y and $\sim$2.6 m for LB1Y. The springs and LB6Y are located within the northwest plume, whereas LB1Y is cross-gradient to the plume (Fig. 1). In general, groundwater samples were more acidic (pH 5.32—6.79, median 5.83 (Table 2)) than surface water (pH 6.44—7.24, median 6.72 (Table 1)). TOC values for springs, which were near or below the detection limit of 1.0 mg/L (Table 2), were also lower than for stream water (Table 1). DO concentrations in springs, including values from sampling rounds not shown in Table 2, ranged from 2.92 to 5.10 mg/L and were 3.3 to 4.5 mg/L for 45 of 47 samples. These values are similar to those for wells LB6Y and LB1Y (Table 2) and overlap the DO range reported for six upgradient wells (4.4—7.9 mg/L (Clausen et al., 1997; Sturchio et al., 1998)), which are located in the northwest plume at depths as great as 29 m below land surface. Nitrate concentrations for springs and wells ranged from 6.99 to 11.1 mg/L (median 8.9 mg/L) (Table 1). Together, DO and $NO_3^-$ concentrations indicate aerobic conditions in groundwater (Clausen et al., 1997; Sturchio et al., 1998; Wiedemeier et al., 1998). Like for surface water, low but detectable Fe and Mn concentrations in groundwater could be associated with colloidal phases not excluded by filtration (Puls and Powell, 1992).

### Contaminants in stream water and groundwater

TCE was the predominant VOC in stream water. Other VOCs (cDCE, $CS_2$, 2-butanone, methylene chloride, and toluene) were detected occasionally, usually at concentrations <10 μg/L. Some of these trace constituents (2-butanone, methylene chloride, and toluene) were also detected in blanks, which suggests laboratory contamination. TCE concentrations were below the detection limit (1—5 μg/L) at sites LBC-8 through -5 and peaked, except in January 2000, at site LBC-4 (Table 3). All of the springs except for RR were located between LBC-5 and -4. The maximum TCE concentration in stream water was 59 μg/L in June 2002. As noted by Fryar et al. (2000), TCE concentrations tended to decrease with distance downstream of LBC-4 (LB6). However, we do not make quantitative comparisons between contaminant data of Fryar et al. (2000) and our 1999—2002 data because the former values were collected on filtered samples.

Except in June 1999, $^{99}$Tc concentrations in stream water at sites LBC-8 through -5 were near or below the detection limit, which was typically <10 pCi/L (Table 3). We do not know why $^{99}$Tc concentrations at sites LBC-7 through -5 were elevated during the first round of sampling. As observed for TCE, $^{99}$Tc concentrations increased markedly from LBC-5 to -4, but in contrast to TCE, $^{99}$Tc concentrations did not systematically decrease with distance downstream of LBC-4. For seven of 12 sampling rounds between 1999 and 2002, the highest $^{99}$Tc concentration occurred at LBC-3, 300 m downstream of LBC-4. The overall maximum value in stream water (94.8 pCi/L) occurred in June 1999 at LBC-3. However, except for January 2002 (when the concentration was higher at LBC-3) and August 2002 (when the concentration was higher at LBC-4), the difference in concentrations between LBC-4 and -3 was within counting error.

Contaminant concentrations at stream sampling points varied seasonally (Fig. 2a—b). For both TCE and $^{99}$Tc, the highest concentrations occurred during June sampling events (1999 and 2002), while the lowest concentrations occurred in January (2000 and 2002). Stream flow also fluctuated seasonally (LaSage et al., 2008), with maximum values in May or June and minimum values in autumn or winter. However, TCE concentrations increased from May to August 2000, and $^{99}$Tc concentrations increased from May through October 2000, whereas stream flow decreased from May through October 2000. Flow rates from the PGDP outfall sustaining Little Bayou Creek baseflow (K010) did not vary markedly between May and October 2000, averaging 21.5 ± 5.9 L/s (US Enrichment Corporation, unpublished data). Between August and October 2002, TCE and $^{99}$Tc concentrations decreased while stream flow rates increased. Divergent behaviors of contaminant concentrations and stream flow suggest that a seasonal decrease in overall groundwater discharge can coincide with an increase in the proportion of discharge from more contaminated parts of the RGA, and vice versa. Clausen et al. (1995) noted fluctuations of contaminant concentrations and hydraulic head in PGDP monitoring well R-17, upgradient of Little Bayou Creek, indicating seasonal ''wobbling'' in plume orientations. Peaks in TCE and $^{99}$Tc concentrations were out of phase with hydraulic-head peaks, which is consistent with our observations.

As in stream water, TCE was the predominant VOC in spring samples. TCE concentrations in springs ranged from 25 μg/L (EB1, May 2001) to 440 μg/L (MS2, May 2001) (Table

**Table 1** Temperature, pH, and solute concentrations for stream monitoring sites along Little Bayou Creek

| | $T$ (°C) | pH | Ca (mg/L) | Na (mg/L) | Mg (mg/L) | K (mg/L) | Fe (mg/L) | Mn (mg/L) | Si (mg/L) | Cl (mg/L) | $HCO_3^-$ (mg/L) | $SO_4^{2-}$ (mg/L) | $NO_3^-$ (mg/L) | DO (mg/L) | TOC (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **LB1S** | | | | | | | | | | | | | | | |
| January 1997 | 9.3 | 6.55 | 34.1 | 15.6 | 3.95 | 3.16 | 0.083 | 0.529 | 6.01 | 16.7 | | 77.3 | 3.8 | 7.57[b] | |
| May 1997 | 16.0 | 7.07[a] | 40.8 | 23.4 | 5.54 | 3.38 | 0.131 | 0.563 | 5.54 | 22.8 | 72 | 85.2 | 4.5 | 7.74 | |
| August 1997 | 21.0 | 6.44 | 41.0 | 19.3 | 5.23 | 3.47 | 0.154 | 0.452 | 5.30 | 18.9 | 66 | 84.2 | 4.9 | 6.96 | |
| October 1997 | 20.4 | 6.70 | 37.6 | 22.6 | 5.18 | 3.26 | 0.106 | 0.368 | 4.79 | 21.5 | 54 | 98.6 | 3.3 | 6.96 | |
| **LB6S** | | | | | | | | | | | | | | | |
| January 1997 | 5.1 | 6.80 | 18.0 | 17.8 | 4.66 | 2.40 | 0.0287 | 0.153 | 5.10 | 16.0 | | 22.5 | 2.2 | | |
| May 1997 | 18.2 | 7.07[a] | 21.5 | 30.1 | 6.34 | 2.57 | 0.075 | 0.080 | 5.15 | 30.0 | 85 | 29.7 | 4.2 | 9.36 | |
| August 1997 | 22.7 | 6.78 | 28.0 | 34.5 | 8.43 | 4.02 | 0.034 | <0.002 | 4.23 | 36.0 | 74 | 77.3 | 2.9 | 7.62 | |
| October 1997 | 21.4 | 6.74 | 17.8 | 31.9 | 7.18 | 2.87 | 0.159 | <0.002 | 2.88 | 30.2 | 60 | 54.2 | 1.6 | 8.28 | |
| **LBC-1** | | | | | | | | | | | | | | | |
| January 2000 | 1.3 | 6.52 | 26.6 | 29.7 | 6.04 | 3.75 | 0.421 | | 3.44 | 25.3 | 57 | 66.8 | 6.2 | | 2.6 |
| **LBC-4** | | | | | | | | | | | | | | | |
| January 2000 | 3.2 | 7.24 | 18.7 | 19.7 | 4.88 | 4.31 | 0.131 | | 1.98 | 18.4 | 49 | 33.7 | 1.2 | | 6.0 |
| August 2000 | 26.4 | | 21.9 | 23.7 | 6.04 | 1.99 | 0.440 | | 3.34 | 28.4 | 67 | 35.0 | 2.1 | | 1.7 |
| **LBC-6** | | | | | | | | | | | | | | | |
| January 2000 | 2.4 | 6.54 | 17.7 | 20.0 | 4.64 | 4.06 | 0.499 | | 1.83 | 18.9 | 39 | 43.0 | <0.089 | 4.0 | |
| **LBC-8** | | | | | | | | | | | | | | | |
| January 2000 | 2.1 | 6.47 | 21.7 | 39.9 | 6.99 | 4.07 | 0.130 | | 2.28 | 27.1 | 48 | 64.0 | 2.5 | 12.68 | 2.8 |

Blank = no data.
[a] pH measured at start of alkalinity titration because of meter malfunction in field.
[b] DO measured using electrode.

**Table 2**  Temperature, pH, and solute concentrations for wells and springs along Little Bayou Creek

| | $T$ (°C) | pH | Ca (mg/L) | Na (mg/L) | Mg (mg/L) | K (mg/L) | Fe (mg/L) | Mn (mg/L) | Si (mg/L) | Cl (mg/L) | $HCO_3^-$ (mg/L) | $SO_4^{2-}$ (mg/L) | $NO_3^-$ (mg/L) | DO (mg/L) | TOC (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **LB1Y** | | | | | | | | | | | | | | | |
| January 1997 | 14.7 | 5.50 | 13.2 | 9.88 | 3.18 | <1.21 | <0.006 | <0.002 | 7.60 | 12.7 | | 26.2 | 9.3 | 3.64[b] | |
| May 1997 | 14.7 | 5.71[a] | 12.0 | 10.3 | 3.05 | <1.21 | 0.049 | <0.002 | 8.27 | 11.8 | 28 | 19.7 | 8.0 | 3.24 | |
| August 1997 | 15.5 | 5.32 | 10.9 | 9.78 | 3.14 | 1.72 | <0.006 | <0.002 | 7.62 | 12.1 | 28 | 17.7 | 8.9 | 3.58 | |
| October 1997 | 16.2 | 5.61 | 9.68 | 9.80 | 2.80 | 1.36 | <0.006 | <0.002 | 7.65 | 12.3 | 21 | 17.5 | 8.6 | 3.42 | |
| **LB6Y** | | | | | | | | | | | | | | | |
| January 1997 | 9.8 | 6.02 | 21.7 | 31.2 | 7.57 | <2.33 | 0.239 | 2.05 | 7.58 | 32.5 | | 10.4 | 6.99 | 4.11[b] | |
| May 1997 | 14.8 | 6.28[a] | 19.4 | 29.4 | 6.94 | <1.21 | <0.006 | 0.130 | 7.06 | 34.6 | 98 | 13.2 | 8.8 | 3.78 | |
| August 1997 | 16.3 | 5.83 | 17.9 | 29.4 | 7.04 | 2.36 | <0.006 | 0.233 | 6.77 | 32.4 | 101 | 10.0 | 9.2 | 4.20 | |
| October 1997 | 17.0 | 6.20 | 17.4 | 30.4 | 6.79 | 2.02 | 0.030 | 0.551 | 7.19 | 34.3 | 95 | 10.8 | 8.4 | 3.94 | |
| **EB1** | | | | | | | | | | | | | | | |
| January 2000 | 13.4 | 5.97 | 24.3 | 31.6 | 8.92 | 2.03 | 0.121 | | 6.65 | 33.5 | 103 | 12.9 | 9.3 | 3.90 | <1.0 |
| August 2000 | 15.0 | 6.79 | 25.1 | 31.5 | 9.22 | <5.00 | 0.0199 | | 6.45 | 36.1 | 112 | 9.90 | 10.2 | 3.80 | <1.0 |
| **EB4** | | | | | | | | | | | | | | | |
| January 2000 | 11.8 | 5.65 | 26.8 | 31.2 | 9.44 | 1.85 | 0.101 | | 6.53 | 37.8 | 107 | 10.3 | 11.1 | 3.82 | <1.0 |
| August 2000 | 15.5 | 6.08 | 26.9 | 30.7 | 9.79 | 2.95 | 0.111 | | 6.58 | 38.4 | 119 | 10.1 | 10.6 | 3.50 | <1.0 |
| **WB1** | | | | | | | | | | | | | | | |
| January 2000 | 12.7 | 5.77 | 24.1 | 32.5 | 8.38 | <5.00 | 0.162 | | 7.09 | 35.0 | | 10.6 | 10.2 | 3.94 | 1.2 |
| August 2000 | 15.5 | 6.13 | 24.6 | 31.5 | 8.65 | <5.00 | 0.0234 | | 6.85 | 36.0 | 114 | 10.0 | 10.2 | 3.72 | <1.0 |
| **WB2** | | | | | | | | | | | | | | | |
| January 2000 | 12.1 | 5.35 | 20.9 | 30.5 | 6.64 | 2.48 | <0.100 | | 6.92 | 24.3 | 94 | 15.4 | 7.1 | 2.92 | <1.0 |
| **WB3** | | | | | | | | | | | | | | | |
| August 2000 | 14.9 | 6.29 | 23.9 | 34.0 | 7.76 | <5.00 | 0.0280 | | 7.15 | 29.5 | 122 | 14.6 | 8.4 | 3.50 | <1.0 |
| **RR** | | | | | | | | | | | | | | | |
| January 2000 | 10.6 | 5.75 | 21.5 | 30.3 | 7.36 | 2.60 | 0.0641 | | 9.37 | 29.5 | 91 | 13.5 | 7.5 | 3.90 | <1.0 |

Blank = no data.

[a] pH measured at start of alkalinity titration because of meter malfunction in field.

[b] DO measured using electrode.

**Table 3** TCE and $^{99}$Tc concentrations in stream water

|  | LBC-1 | LBC-2 | LBC-3 | LBC-4 | LBC-5 | LBC-6 | LBC-7 | LBC-8 |
|---|---|---|---|---|---|---|---|---|
| **June 1999** | | | | | | | | |
| TCE (µg/L) | 16 | 29 | 44 | 52 | 4J | <5 | <5 | 3J |
| $^{99}$Tc (pCi/L) | 68.6 ± 7.5 | 85.3 ± 8.3 | 94.8 ± 8.8 | 86.7 ± 8.3 | 37.9 ± 6.0 | 23.9 ± 5.1 | 91.8 ± 9.0 | <6.3 |
| **Sep. 1999** | | | | | | | | |
| TCE (µg/L) | 10 | 23 | 27 | 36 | 3J | <5 | <5 | <5 |
| $^{99}$Tc (pCi/L) | 40.4 ± 5.9 | 28.3 ± 6.0 | 61.2 ± 7.0 | 51.5 ± 6.6 | <6.0 | <5.6 | <6.6 | <7.3 |
| **January 2000** | | | | | | | | |
| TCE (µg/L) | 3.5 | 6.7 | 7.8 | 7.5 | 1.3 | 0.52J | <1.0 | <1.0 |
| $^{99}$Tc (pCi/L) | 11.5 ± 4.8[a] | 15.6 ± 2.9 | 13.7 ± 2.8 | 15.2 ± 2.8 | 6.4 J ± 2.2 | 3.5 J ± 2.2 | <0.5 ± 2.1 | <2.7 ± 2.0 |
| $^{99}$Tc(f) (pCi/L) | 11.4 ± 2.5 | 15.0 ± 2.8 | 10.1 ± 2.6 | <13 ± 15 | 5.6 J ± 2.2 | <4.2 ± 2.7 | 6.8 J ± 4.0[a] | <2.3 ± 2.1 |
| **May 2000** | | | | | | | | |
| TCE (µg/L) | 10 | 17 | 22 | 25 | 1.6 | 1.1 | <1.0 | |
| $^{99}$Tc (pCi/L) | 26.4 ± 6.3 | 26.3 ± 4.5 | 27.8 ± 4.1 | 24.6 ± 3.8 | 7.1 J ± 4.0 | 6.3 J ± 3.1 | <3.9 ± 2.7 | |
| **August 2000** | | | | | | | | |
| TCE (µg/L) | | | 23 | 30 | 2.4 | 0.73 J | | |
| $^{99}$Tc (pCi/L) | | | 31.7 ± 4.4 | 30.7 ± 4.3 | <1.7 ± 2.2 | <2.5 ± 3.8 | | |
| **October 2000** | | | | | | | | |
| TCE (µg/L) | 3.7 | 9.6 | 15 | 17[a] | 1.2 | <1.0 | <1.0 | <1.0 |
| $^{99}$Tc (pCi/L) | 32.8 ± 4.4 | 31.6 ± 4.2 | 38.0 ± 4.7 | 34.2 ± 4.6 | 5.7 J ± 2.3 | 5.1 J ± 2.3 | <2.5 ± 1.8 | <2.6 ± 2.3 |
| **January 2001** | | | | | | | | |
| TCE (µg/L) | 4.3 | 6.9 | 9.3 | 12 | 0.81 J | 0.29 J | <1.0 | <1.0 |
| $^{99}$Tc (pCi/L) | 14.7 ± 3.5 | 14.7 ± 3.1 | 17.0 ± 2.8 | 14.5 ± 2.7 | 4.6 J ± 1.9 | 4.7 J ± 2.0 | <4.2 ± 4.3[a] | 4.3 J ± 2.4 |
| **May 2001** | | | | | | | | |
| TCE (µg/L) | 9.9 | 21 | 26 | 33 | 2.6 | 1.2 | <1.0 | <1.0 |
| $^{99}$Tc (pCi/L) | 43.7 ± 6.9[a] | 48.1 ± 5.7 | 56.0 ± 6.3 | 56.6 ± 6.5[a] | 8.1 J ± 2.4 | 6.3 J ± 2.3 | 4.4 J ± 2.2 | <2.4 ± 2.5 |
| **January 2002** | | | | | | | | |
| TCE (µg/L) | 8.2 | 12 | 16 | 18 | | | | |
| $^{99}$Tc (pCi/L) | 23.7 ± 4.2[a] | 24.5 ± 3.2 | 28.6 ± 3.5 | 21.9 ± 3.0[a] | | | | |
| **June 2002** | | | | | | | | |
| TCE (µg/L) | 23 | 37 | 45[b] | 63[b] | | | | |
| $^{99}$Tc (pCi/L) | 73.4 ± 7.7 | 70.1 ± 7.2 | 74.8 ± 7.9 | 82.9 ± 8.5 | | | | |
| **August 2002** | | | | | | | | |
| TCE (µg/L) | 11 | 23[a] | 28 | 37 | | | | |
| $^{99}$Tc (pCi/L) | 42.1 ± 5.8 | 44.6 ± 5.1 | 44.5 ± 6.2 | 58.7 ± 6.9 | | | | |
| **October 2002** | | | | | | | | |
| TCE (µg/L) | 5.4 | 10 | 13 | 18 | | | | |
| $^{99}$Tc (pCi/L) | 20.9 ± 2.7 | 32.7 ± 3.9 | 21.9 ± 2.9 | 23.6 ± 3.0 | | | | |

Blank = no data; ± = $^{99}$Tc counting error; J = value below laboratory reporting limit; < = value below detection limit; For January 2000 $^{99}$Tc values, (f) = filtered sample.
[a] Average of duplicate analyses (on a single sample or on split samples).
[b] Analysis on diluted sample (original analysis out of calibration range).

4). Concentrations tended to be highest within ~200 m of the head of the channelized reach (in the channel spring MS2, west-bank springs WB2 and WB3, and the tributary spring RR). Data are not available for all sampling rounds for all locations because (1) the channel springs (MS1 and MS2) were not always visible; (2) RR did not always flow vigorously enough to be sampled; and (3) flow from WB2 progressively declined between June 1999 and May 2000, while WB3 had emerged ~5 m upstream of WB2 by May 2000 (LaSage et al., 2008). TCE concentrations were lowest in the farthest downstream springs (EB1 and EB4) along the east bank of the creek. We occasionally detected cDCE, $CS_2$, 2-butanone, methylene chloride, toluene, and $CCl_4$. Concentrations of cDCE were <16 µg/L, with the highest values at WB2, WB3, and MS2.

The relative spatial distribution of $^{99}$Tc concentrations in springs was generally similar to that of TCE. There is a strong linear relationship between concentrations of the contaminants (TCE = [1.1$^{99}$Tc] + 8.9; $r^2$ = 0.86) (Fig. 3), as observed by Clausen et al. (1992) for PGDP monitoring wells. $^{99}$Tc ranged from 28.8 pCi/L in EB1 (August 2000) to 461 pCi/L in MS2 (May 2001) (Table 4). Except for September 1999, concentrations were greatest in springs along the uppermost ~200 m of the channelized reach.

In contrast to stream-water sampling sites, springs did not display consistent seasonality with respect to TCE or $^{99}$Tc concentrations, although some fluctuations occurred. $^{99}$Tc concentrations in WB3, WB1, EB4, and EB1 decreased from May to August 2000, increased in October 2000, decreased in January 2001, and increased in May 2001. In con-
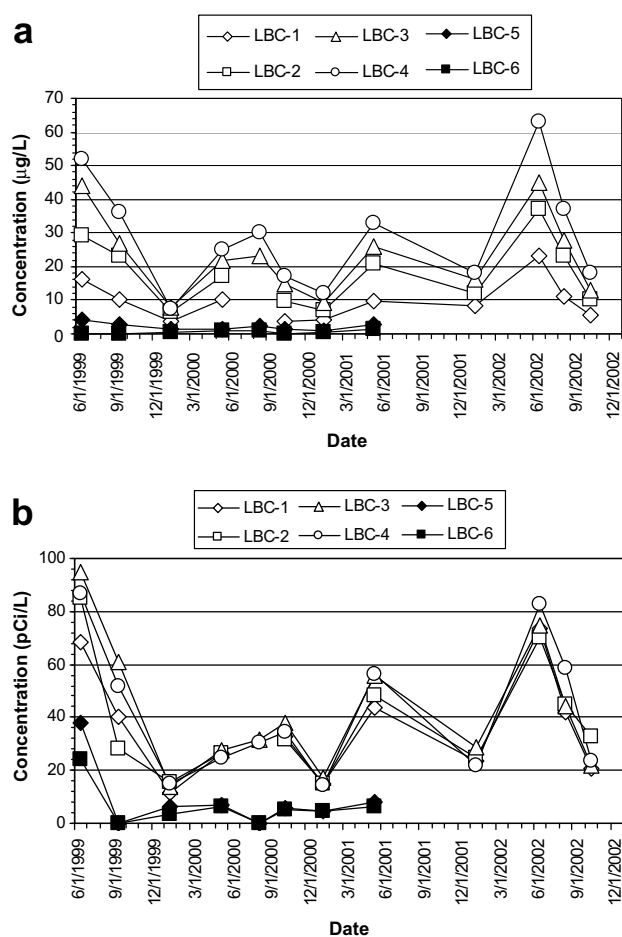
**Figure 2** Concentrations of (a) TCE and (b) $^{99}$Tc in stream water. Values for monitoring locations LBC-7 and -8 are not shown because of a paucity of data. Values below detection limit are shown as 0.

trast, TCE concentrations in WB3 during the same period were relatively invariant (420–430 μg/L). During June 1999 and May 2000, $^{99}$Tc concentrations in channel spring MS1 were comparable to values in west-bank spring WB1, while in September 1999, the $^{99}$Tc concentration in MS1 was similar to that in east-bank spring EB4. No simultaneous shift in TCE values was evident at those sites. However, both TCE and $^{99}$Tc concentrations in channel spring MS2 increased with the shift in discharge from WB2 to WB3.

Of particular interest are springs WB1 and EB4, which are located opposite each other. WB1 exhibited consistently higher TCE and $^{99}$Tc concentrations than EB4, which might suggest that the east-bank springs discharge a mixture of more-contaminated groundwater and less-contaminated surface water. However, similarities in major solute concentrations for the two springs, and dissimilarities relative to stream water concentrations, suggest that both WB1 and EB4 are composed of groundwater with little or no stream water. An alternative explanation is that contaminated groundwater flowing west to east beneath the stream mixes with uncontaminated groundwater entering the spring along the east bank before discharging into the stream. Likewise, the similarity in solute concentrations between RR and other springs suggests that deeper and shal-

lower groundwater mix before discharging from RR, as suggested by LaSage et al. (2008) based on temperature data.

Analyses of samples from the peepers indicate that TCE concentrations in stream-bed porewater are higher than in stream water, and maximum concentrations in porewater are higher than in groundwater from adjoining springs. No peaks of other VOCs were observed on the chromatograms. TCE concentrations ranged from 149 to 1691 μg/L in peeper 1, 40–505 μg/L in peeper 2, and 16–747 μg/L in peeper 3 (Fig. 4). Discounting obvious outliers (at 9 and 20 cm depth for peeper 1 and 21 cm depth for peeper 3), concentrations tended to decrease as depth decreased at all three sites. At the two downstream sites (peepers 2 and 3), these concentration decreases were more pronounced and appear to reflect dilution of upwelling groundwater by stream water in the hyporheic zone, consistent with the conceptual description of Vroblesky (2002). Concentrations in peeper 1 were generally greater than measured in MS2 and WB3, although differences in the timing of sampling and analytical procedures preclude an exact comparison between peeper and spring samples.

Concentrations of redox-sensitive species (in particular, $O_2$, $NO_3^-$, and $SO_4^{2-}$), TCE concentrations, low to undetectable levels of cDCE (or other putative TCE daughter products) in springs, and the lack of VOCs other than TCE in porewater all indicate that intrinsic biodegradation of TCE via reductive dehalogenation was unlikely at our monitored sites (Wiedemeier et al., 1998). Likewise, $\delta^{37}Cl_{DOCl}$ data do not indicate reductive biodegradation of TCE. We report stable isotope data in ‰ using the conventional δ notation,

$$\delta^{37}Cl_{DOCl}, ‰ = ((R_{sample}/R_{standard}) - 1) \times 1000 \qquad (1)$$

where $R$ is the $^{37}Cl/^{35}Cl$ ratio and the reference material is standard mean ocean chloride (SMOC). The range of $\delta^{37}Cl_{DOCl}$ for the five springs we sampled (RR, WB3, WB1, EB4, and EB1) was +0.3 to +1.3‰, with an analytical uncertainty of ±0.2‰. This range falls within the range for five northwest plume wells sampled by Sturchio et al. (1998) (+0.2 to +1.6‰). Because virtually all of the dissolved organic Cl in the sampled springs and wells occurred as TCE, the isotopic results in effect represent $\delta^{37}Cl$ of dissolved TCE. A plot of $\delta^{37}Cl_{DOCl}$ vs. TCE concentrations (Fig. 5) shows an overall decrease in TCE concentrations between wells and springs (i.e., along the flow path within the northwest plume) without a corresponding change in $\delta^{37}Cl_{DOCl}$. Fractionation of $^{37}Cl$ has been documented for volatilization of TCE ($\alpha = 0.99836$ at 22 °C (Poulson and Drever, 1999) to 0.99818 at 24 °C (Huang et al., 1999)) and anaerobic reductive dehalogenation of TCE ($\alpha = 0.994$–0.995 at 30 °C (Numata et al., 2002)), where

$$\alpha = R_{product}/R_{parent} \qquad (2)$$

The apparent lack of fractionation in our case suggests dilution with water containing less (or no) TCE, which is consistent with other evidence of groundwater mixing in the springs.

## Contaminant fluxes to and from the stream

Analyses of stream water and groundwater indicate that geochemical conditions were not conducive to reductive

**Table 4** TCE and $^{99}$Tc concentrations in springs

| | EB1 | EB4 | WB1 | WB1.5 | MS1 | MS2 | WB2 | WB3 | RR |
|---|---|---|---|---|---|---|---|---|---|
| **June 1999** | | | | | | | | | |
| TCE (µg/L) | 32 | 51 | 120 | | 180 | 280[b] | 305[ab] | | 170 |
| $^{99}$Tc (pCi/L) | 42.4 ± 6.3 | 60.3 ± 7.5 | 131.6 ± 9.9 | | 132.2 ± 11.2 | 257.4 ± 13.6 | 249.2 ± 13.5[a] | | 173.3 ± 11.9 |
| $^{99}$Tc(f) (pCi/L) | | | | | | | 130.7 ± 10.2[a] | | |
| **Sep. 1999** | | | | | | | | | |
| TCE (µg/L) | 38 | 72 | 110 | | 170 | 250 | 325[a] | | 170 |
| $^{99}$Tc (pCi/L) | 45.6 ± 6.6 | 81.2 ± 7.8 | 135.5 ± 10.1 | | 81.7 ± 7.9 | 107.9 ± 9.1 | 314.9 ± 15.2 | | 71.6 ± 7.5 |
| $^{99}$Tc(f) (pCi/L) | | | | | | | 158.7 ± 10.9 | | |
| **January 2000** | | | | | | | | | |
| TCE (µg/L) | 40 | 65 | 110 | | | | 270[b] | | 160 |
| $^{99}$Tc (pCi/L) | 33.8 ± 4.4[a] | 56.4 ± 6.3 | 100 ± 11 | | | | 221 ± 22 | | 118 ± 12 |
| $^{99}$Tc(f) (pCi/L) | 35.1 ± 4.5 | 63.8 ± 7.2 | 91.5 ± 9.9 | | | | 183 ± 19 | | 101 ± 11 |
| **May 2000** | | | | | | | | | |
| TCE (µg/L) | 33 | 57 | 100 | | 130 | 400[b] | | 430[b] | 190 |
| $^{99}$Tc (pCi/L) | 32.0 ± 4.7 | 45.9 ± 4.9 | 80.1 ± 9.0 | | 84.6 ± 9.3 | 325 ± 33 | | 271 ± 28 | 127 ± 13 |
| $^{99}$Tc(f) (pCi/L) | | | | | | | | 271 ± 28 | |
| **August 2000** | | | | | | | | | |
| TCE (µg/L) | 32 | 50 | 97 | 95 | | | | 420 | |
| $^{99}$Tc (pCi/L) | 28.8 ± 3.8 | 34.9 ± 4.7 | 74.5 ± 8.4 | 72.0 ± 8.1 | | | | 267 ± 27 | |
| $^{99}$Tc(f) (pCi/L) | | | | | | | | 381 ± 38 | |
| **October 2000** | | | | | | | | | |
| TCE (µg/L) | 35[a] | 53[b] | 76[b] | 120 | | | | 420[b] | |
| $^{99}$Tc (pCi/L) | 47.7 ± 5.9 | 82.7 ± 8.9 | 116 ± 12 | 116 ± 12 | | | | 450 ± 45 | |
| $^{99}$Tc(f) (pCi/L) | | | | | | | | 379 ± 38 | |
| **January 2001** | | | | | | | | | |
| TCE (µg/L) | 37 | 42[b] | 110 | 110 | | | | 420 | 160[b] |
| $^{99}$Tc (pCi/L) | 34.6 ± 4.4 | 49.1 ± 5.6 | 93 ± 10 | 76.7 ± 8.3 | | | | 249 ± 25[a] | 155 ± 16 |
| $^{99}$Tc(f) (pCi/L) | | | | | | | | 276 ± 28 | |
| **May 2001** | | | | | | | | | |
| TCE (µg/L) | 25[b] | 34[b] | 87[b] | 80[b] | | 450[b] | | 420[b] | 190[b] |
| $^{99}$Tc (pCi/L) | 41.9 ± 5.3 | 54.0 ± 6.3 | 112 ± 12 | 89.1 ± 9.5 | | 461 ± 46 | | 395 ± 40[a] | 229 ± 23 |
| $^{99}$Tc(f) (pCi/L) | | | | | | | | 388 ± 39 | |

Blank = no data; ± = $^{99}$Tc counting error. For $^{99}$Tc values, (f) = filtered sample.

[a] Average of duplicate analyses (on a single sample or on split samples).

[b] Analysis on diluted sample (original analysis out of calibration range).
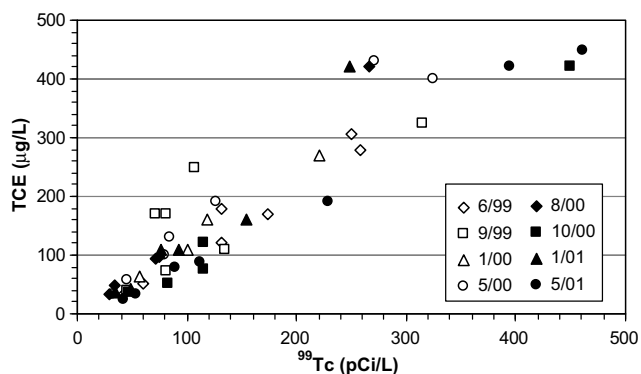
**Figure 3** Variation of TCE with $^{99}$Tc concentrations in springs for different sampling rounds.



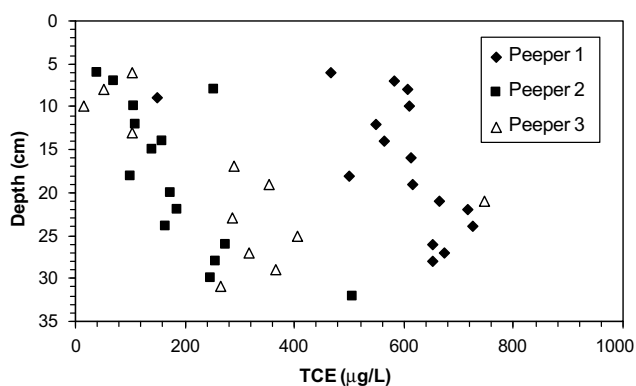**Figure 4** TCE concentrations as a function of depth in porewater samples. Note that the highest concentration (1691 $\mu$g/L at 20 cm depth in peeper 1) is off-scale and thus not shown.

biodegradation of TCE during focused discharge. Additional data suggest that TCE sorption to stream-bed sediment was minimal. The $f_{oc}$ of seven bed-sediment samples collected from three sites between LBC-5 and -4 averaged 0.000152 $\mu$g/$\mu$g (LaSage, 2004), which is below the limit for preferential sorption of TCE to organic matter (Fetter, 1999). These values are slightly lower than $f_{oc}$ values measured for 12 subsoil samples from the Metropolis Formation and possibly loess at PGDP (range 0.0002–0.001 $\mu$g/$\mu$g; mean 0.0005 $\mu$g/$\mu$g) (CH2M Hill, 1992). Schäfer et al. (2000) reported that 10–10$^4$ mg/kg TCE may sorb onto surfaces of minerals, particularly certain clays, but water outcompetes TCE for sorption sites on kaolinite particles. Using X-ray diffraction, LaSage (2004) determined the mineralogy of the fine (<0.075-mm) fraction of stream-bed sediments, which constituted ~10% of the sample mass, to be 38% kaolinite and 37% to 46% illite, with the remaining percentages unresolved.

Similarly, $^{99}$Tc sorption to stream-bed sediment appears to have been minimal. Using the PHREEQC code (Parkhurst, 1995) with solute data from January and August 2000, speciation modeling by LaSage (2004) indicated that Tc occurred in groundwater and stream water as $TcO_4^-$, which is unlikely to sorb to sediment (Blaylock et al., 1984; Meyer

et al., 1989; Gu and Dowlen, 1996). $^{99}$Tc was undetectable (<3.11 pCi/g) in four sediment samples collected between LBC-5 and -4 by LaSage (2004). For stream water collected in January 2000, $^{99}$Tc concentrations were slightly less in filtered than in unfiltered samples from LBC-2, -3, and -4; essentially equal in both samples from LBC-1; and below detection limit in both sets of samples from LBC-5, -6, -7, and -8 (Table 1). For spring WB2, concentrations were lower in filtered than in unfiltered samples in June 1999, September 1999, and January 2000 (Table 2). However, for splits collected subsequently from WB3, filtered values were higher in August 2000 and January 2001, equal in May 2000, and lower in October 2000 and May 2001 (Table 2).

Taken together, water and sediment analyses indicate that reductive dehalogenation of TCE was unlikely in the discharge zone, and sorption of TCE and $^{99}$Tc was unlikely in the discharge zone or downstream sediments. Consequently, given the linear relationship between TCE and $^{99}$Tc concentrations in groundwater, we can use $^{99}$Tc to estimate influxes of TCE, corrected for volatilization, along the reach between LBC-5 and -4 where most of the springs occur. We define flux as

$$F = C_d Q_d - C_u Q_u \tag{3}$$

where $C$ is concentration, $Q$ is the stream-flow rate in L/s (from LaSage et al., 2008), and $d$ and $u$ refer to downstream and upstream monitoring sites, respectively.

Contaminant influxes between LBC-5 and -4 show a strong seasonality, consistent with stream flow (Fig. 6). Maximum values (1910 pCi/s for $^{99}$Tc influxes and 1460 $\mu$g/s for net influxes of TCE [uncorrected for volatilization]) occurred in June 1999. $^{99}$Tc influxes and net influxes of TCE decreased from June 1999 to January 2000, rebounded in May 2000, decreased in October 2000, then rebounded in May 2001. Influx values are not shown for January 2001 because gauged Q at LBC-4 was less than at LBC-5, which results in physically nonsensical flux calculations. As shown by net Q (stream inflows) between LBC-5 and -4 (Fig. 6), contaminant influxes track seasonal fluctuations in stream flow (LaSage et al., 2008) more closely than fluctuations in contaminant concentrations (Fig. 2a–b). Most of the
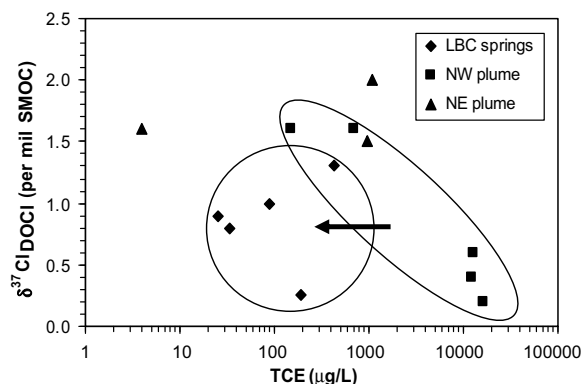


**Figure 5** $\delta^{37}Cl_{DOCl}$ as a function of TCE concentrations for springs sampled in May 2001 and for northwest and northeast plume wells sampled by Sturchio et al. (1998). Arrow shows that compositions of springs can be explained by dilution of northwest plume water.
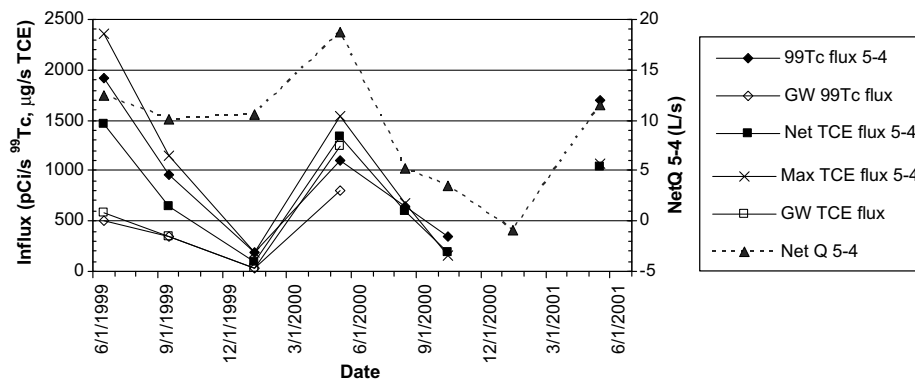
**Figure 6** Net stream flow between LBC-5 and -4, in-stream contaminant fluxes between LBC-5 and -4, and cumulative contaminant fluxes for springs (GW) having both discharge and concentration data. Maximum TCE flux represents net TCE flux between LBC-5 and -4 corrected for volatilization.

spring discharge measurements were made between June 1999 and May 2000 (LaSage et al., 2008). Even though not all springs were gauged, and not all gauged springs were sampled, those that were both gauged and sampled (i.e., those for which point fluxes could be calculated) comprised a substantial proportion of contaminant influxes. These measured point fluxes contributed 18% (in January 2000) to 72% (in May 2000) of the $^{99}$Tc influxes, and 40% (in June 1999) to 93% (in May 2000) of the net TCE influxes. In turn, springs WB2 and WB3, which had both the greatest flow rates and the greatest contaminant concentrations, represented 54% (in January 2000) to 94% (in May 2000) of measured $^{99}$Tc point fluxes, and 55% (in January 2000) to 95% (in May 2000) of measured TCE point fluxes.

Because the linear regression of TCE vs. $^{99}$Tc for all spring samples failed statistical tests of normality and constant variance, we used linear regressions for individual sampling events, which passed those tests (except for May 2001 data, which failed the constant variance test), to correct net TCE influxes for volatilization. The corrected influxes suggest that losses of TCE owing to volatilization between discharge points and LBC-4 could have been as much as 890 μg/s (in June 1999) (Fig. 6). Interestingly, the proportion of mass loss by volatilization did not show the same sort of seasonality: the maximum proportional loss of 49% occurred in January 2000,

when volatilization overall should have been at a minimum because of low temperatures. However, combined errors in stream gauging, concentration measurements, and linear regressions make the TCE loss calculations more qualitatively than quantitatively significant.

Downstream of LBC-4, the attenuation of TCE relative to $^{99}$Tc can also be explained by volatilization. Using Br$^-$, rhodamine WT, and NO$_3^-$ as slug tracers, Mukherjee et al. (2005) determined that sorption of TCE and reduction of TCE and $^{99}$Tc were negligible or absent between LBC-4 and -3. Propane tracer tests confirmed that volatilization could account for TCE attenuation (Mukherjee et al., 2005). Effluxes between LBC-4 and -1 were positive for all sampling rounds for TCE but fluctuated around zero for $^{99}$Tc (Fig. 7). Net Q values between LBC-4 and -1 track TCE effluxes more closely than $^{99}$Tc effluxes (Fig. 7). However, because discharge increases with both stream velocity and depth, whereas volatilization increases with stream velocity but decreases with depth (Rathbun, 1998), volatilization should not simply track discharge. Seasonal fluctuations in volatilization are likely to be partly a function of temperature. Because volatilization decreases with decreasing aqueous concentrations (Rathbun, 1998), TCE could still be detected at μg/L levels at LB1 by Fryar et al. (2000), even after dilution by diffuse seepage downstream of LBC-1. Ultimately,



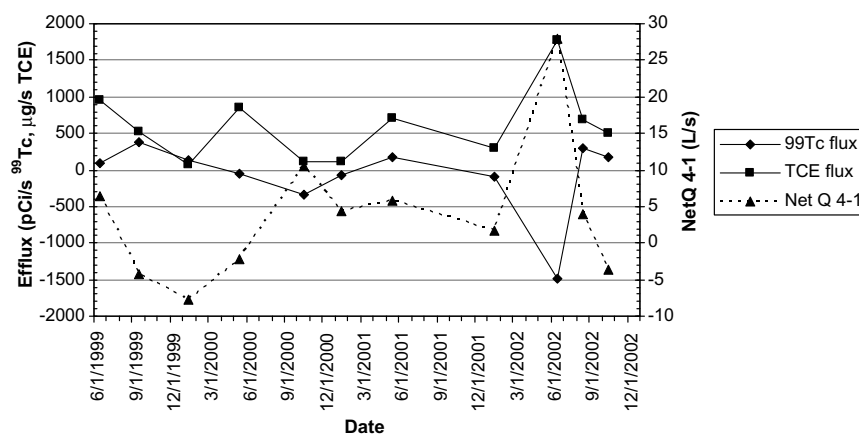**Figure 7** Net stream flow, $^{99}$Tc fluxes, and net TCE fluxes in stream water between LBC-4 and -1.
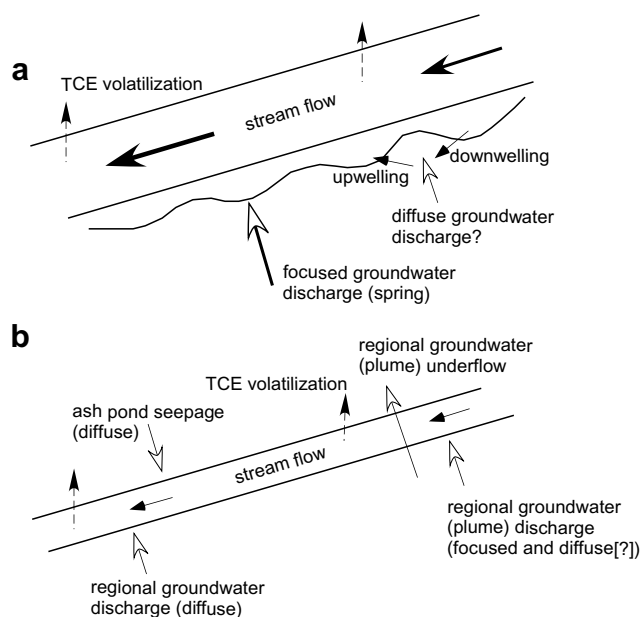
**Figure 8** Schematic diagram (not to scale) showing processes that affect contaminant concentrations (a) along the reach of Little Bayou Creek where springs discharge (between LBC-6 and -4) and (b) along the entire channelized reach of Little Bayou Creek (from LBC-6 to the confluence with Bayou Creek).

dilution by mixing with Bayou Creek and the Ohio River should make TCE and $^{99}$Tc in stream water undetectable.

## Comparison with other sites

Prior studies of chlorinated ethene plumes discharging from unconsolidated aquifers to streams have shown a range of behaviors. At two sites in the Atlantic Coastal Plain, chlorinated ethenes were completely biodegraded during diffuse discharge through the stream bed. Oxidation of cDCE occurred under aerobic conditions (DO ~ 2 mg/L in shallow bed sediments) at Cecil Field, Florida (Bradley and Chapelle, 1998). Reductive dechlorination of TCE occurred along the West Branch of Canal Creek, Maryland, as initially aerobic groundwater (DO > 1 mg/L) discharged through Fe(III)-reducing, sulfate-reducing, and methanogenic zones within 5 m of land surface (Lorah and Olsen, 1999). In contrast, at three sites on glaciogenic sediments, pervasive biodegradation was not observed. At an unidentified site in Connecticut, TCE was biodegraded as groundwater evolved from aerobic to methanogenic along the flowpath, but the primary mechanism of TCE loss from groundwater was discharge to a pond and tributary streams (Chapman et al., 2007). Conant et al. (2004) found that tetrachloroethene (PCE) discharged locally via ''geological windows through...semi-confining deposits'' (p. 263) to the Pine River in Ontario. Degradation of PCE to TCE and less chlorinated daughter compounds occurred in less permeable stream-bed sediments, where redox conditions evolved from nitrate-reducing to methanogenic (Conant, 2001). Lyford et al. (1999) delineated TCE discharge along the Royal River in Maine where erosion had breached a confining unit, but did not report water quality analyses for parameters other than TCE.

Contaminant discharge along Little Bayou Creek appears to have more in common with the sites in glaciated terrain than with the other Coastal Plain sites noted. As in springs along the Pine and Royal rivers, chlorinated ethene concentrations in springs along Little Bayou Creek were as high as several hundred micrograms per liter. TCE concentrations were tens of micrograms per liter in Little Bayou Creek, as in the Royal River and a small stream at the Connecticut site. Apart from the Royal River site, our site differs from those profiled above in that discharge from the northwest plume is primarily focused through springs.

## Summary and conclusions

We have documented that groundwater discharge is responsible for TCE and $^{99}$Tc loading to Little Bayou Creek, a first-order perennial stream in the Gulf Coastal Plain of western Kentucky. Both stream water and groundwater were oxic, and TCE was the predominant VOC detected. TCE and $^{99}$Tc concentrations in stream water typically were undetectable upstream of the springs, near the head of the channelized reach of the stream. TCE concentrations peaked immediately downstream of the springs, then progressively decreased with distance farther downstream, whereas $^{99}$Tc usually peaked within 300 m downstream of the last spring, but did not systematically decrease with additional distance. Contaminant concentrations downstream of the springs appeared to fluctuate seasonally, but those fluctuations were not always in phase with stream-flow fluctuations, which suggests that discharge originates from different parts of the aquifer at different times. $^{99}$Tc concentrations varied linearly with TCE concentrations for springs. Maximum concentrations of TCE (>400 μg/L) and $^{99}$Tc (>400 pCi/L) occurred along the west bank near the head of the channelized reach. Mixing with less-contaminated groundwater appeared to dilute contaminant concentrations in springs, while mixing with downwelling stream water appeared to dilute TCE (and presumably $^{99}$Tc, which was not analyzed) in stream-bed porewater, as conceptualized in Fig. 8a. TCE and $^{99}$Tc concentrations in springs fluctuated over sampling intervals of 3 to 4 months, but no seasonal trends were evident.

Putative daughter products of TCE dehalogenation were detected in stream water, springs, and porewater only at low concentrations or not at all. The lack of these compounds, TCE concentrations, concentrations of redox-sensitive solutes, and the apparent lack of isotopic fractionation of $Cl_{DOCl}$ in springs relative to up-gradient groundwater indicate that anaerobic biodegradation of TCE was insignificant in focused discharge zones. Likewise, reduction of $^{99}$Tc and sorption of TCE and $^{99}$Tc appear to have been minimal in focused discharge zones and stream sediments. Consequently, $^{99}$Tc (which is non-volatile, and which varies with TCE) can be used to correct the net influx of TCE for in-stream volatilization. The $^{99}$Tc influx, the uncorrected net influx of TCE, and the corrected TCE influx fluctuated seasonally with stream flow and were dominated by a few discharge points. Differential attenuation of TCE relative to $^{99}$Tc downstream of the springs is consistent with further volatilization. Dilution by diffuse seepage from the ash ponds and perhaps the RGA (LaSage et al., 2008) lowered concentrations of both

TCE and ^{99}Tc in stream water, as conceptualized in Fig. 8b. Because we did not analyze sediment chemistry except for four ^{99}Tc analyses or porewater chemistry other than chloroethenes in the peepers, we cannot rule out the possibility of reduction or sorption of contaminants in finer-grained sediments along Little Bayou Creek.

Our findings expand prior findings on discharge of VOC plumes to streams elsewhere in eastern North America. Where focused discharge limits the residence time of contaminated groundwater in the riparian or hyporheic zone, reduction or sorption can be limited, and contaminant removal from the aqueous phase may depend substantially on volatilization downstream of the discharge zone. Moreover, because of the dynamic nature of spring discharge in unlithified sediments (LaSage et al., 2008), migration of discharge points where streams flow within such sediments may pose challenges for long-term monitoring.

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