EVALUATING NATURAL ATTENUATION OF CONTAMINANTS ALONG A FIRST-ORDER COASTAL PLAIN STREAM

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ABSTRACT

Little Bayou Creek, a first-order stream in McCracken County, Kentucky, receives discharge of ground water contaminated by past activities at the U.S. Department of Energy's Paducah Gaseous Diffusion Plant. Natural attenuation of trichloroethene (TCE) and technetium-99 (^{99}Tc) along the channelized reach of the creek below the contaminated springs was studied for five consecutive seasons (from January 2002 through January 2003). Bromide, nitrate, and rhodamine WT were injected as slug tracers of baseflow; simultaneously, propane was continuously injected. Tracer concentrations were monitored at two downstream locations. Contaminant concentrations were also monitored and stream flow was gaged prior to tracer injection. Slug tracer peaks tended to coincide for each test, with travel times highest in October and lowest in June. Propane concentrations tended to plateau except in August and at the farther downstream site in October. Simulations with the OTIS-P code showed that solute transport in the stream is predominantly one-dimensional, with insignificant secondary storage in the stream and the hyporheic zone. TCE is attenuated along the studied reach by dilution and volatilization, which increased with ambient temperature and with discharge. TCE volatilization coefficients calculated from modeled values of the first-order loss coefficient for propane are close to the coefficients calculated from TCE concentrations. ^{99}Tc appears to be attenuated only by dilution. Rhodamine WT data suggest that hydrophobic sorption of TCE is insignificant, while nitrate analyses indicate that TCE and ^{99}Tc are not transformed by reduction. These results are consistent with the lack of secondary storage, since sorption and reduction would be likely to occur in low-flow regions within the stream bed and banks.

BACKGROUND

As summarized in Conant (2001), an increasing number of studies during the past decade have focused on natural attenuation of contaminants during ground-water discharge to surface-water bodies. However, fewer studies (e.g., Kim and Hemond, 1998) have examined processes of natural attenuation downstream of plume discharge sites. Since 1997, our research group has been examining discharge of contaminated ground water to Little Bayou Creek, a first-order perennial tributary to the Ohio River in McCracken County, Kentucky (Fig. 1). The lower 2.8 km of Little Bayou Creek were channelized beginning in the early 1950s. Trichloroethene (TCE) and technetium-99 (^{99}Tc) in ground water originate from the Paducah Gaseous Diffusion Plant, a uranium enrichment facility and National Priority List site. Contaminant discharge is associated with springs breaching a clayey confining unit in the bed along the upper 415 m of the channelized reach, while diffuse, cross-gradient seepage occurs through gravels downstream. Stream flow rates and contaminant concentrations in stream water varied both seasonally and spatially (Fryar et al., 2000; Fryar and LaSage, 2001). ^{99}Tc concentrations tended to peak within 300 m downstream of the springs, while TCE concentrations tended to peak immediately downstream of the springs and progressively decrease farther downstream. Dissolved oxygen in spring water and a lack of TCE daughter compounds (dichloroethenes and vinyl chloride) in both spring and stream water suggested that intrinsic anaerobic reduction was limited. The observations of diffuse seepage and the decrease in the TCE/^{99}Tc ratio with distance led us to hypothesize that dilution and TCE volatilization are the dominant mechanisms of natural attenuation downstream of the springs.
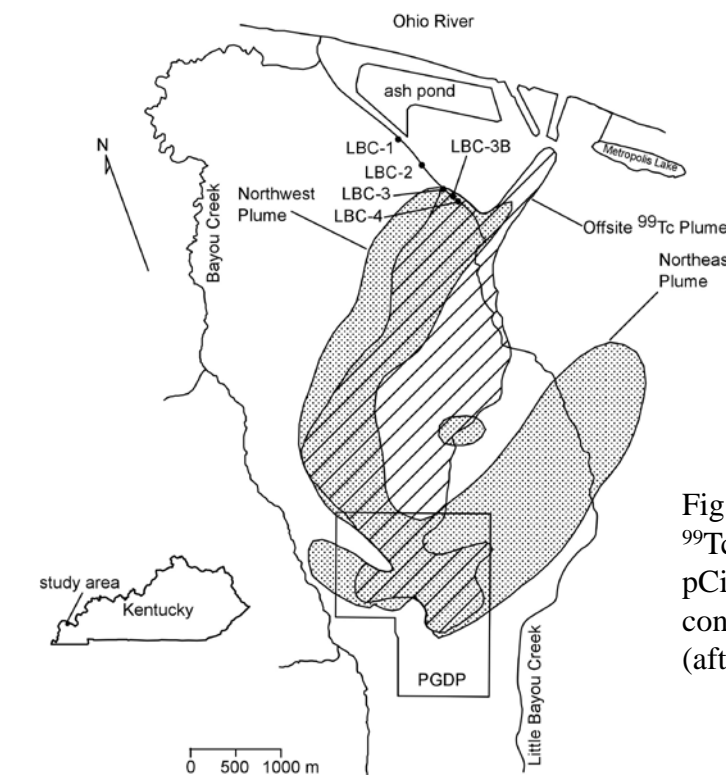

Fig. 1. Site map. Hachured areas represent ^{99}Tc concentrations in ground water > 25 pCi/L; stippled areas represent TCE concentrations in ground water > 5 µg/L (after Fryar et al., 2000).

METHODS

For five consecutive seasons (January 2002 through January 2003), we gaged stream discharge Q and monitored contaminant concentrations downstream of the springs under baseflow conditions. Gaging and monitoring sites were located at intervals of ~ 300 to 400 m along the creek, coincident with previous work. Gaging involved wading with a top-setting rod and Marsh-McBirney flowmeter along a transect across the stream, following the midsection method of Rantz (1982). ^{99}Tc was analyzed by liquid scintillation counting and volatile organic compounds were analyzed by gas chromatography-mass spectrometry, according to EPA method 8260B, at a commercial laboratory (STL, Earth City, MO).

We also conducted tracer tests using Br$^-$ (as NaBr, to mimic dilution), NO$_3^-$ (as NaNO$_3$, to identify reduction), rhodamine WT (to mimic hydrophobic sorption of TCE), and propane (to mimic TCE volatilization). Propane was injected continuously from a cylinder through a diffuser, while known masses of the other tracers were mixed with stream water in two 20-L carboys and added as a slug at the beginning of each test (Fig. 2). Tracer arrival was monitored visually using rhodamine WT at mid-stream locations 59 m (LBC-3B) and 300 m (LBC-3) downstream of the injection point (Fig. 3). Samples were collected at intervals of 2 to 15 minutes beginning immediately before arrival. Br$^-$ was analyzed by ion chromatography, NO$_3^-$ by ion chromatography and by autoanalyzer, rhodamine WT by fluorometry, and propane by gas chromatography (with a flame ionization detector) at the University of Kentucky. The OTIS code (Runkel, 1998), which accommodates one-dimensional transport with inflow, storage, and first-order mass loss, was used to simulate breakthrough curves in both inverse and forward modes and thereby obtain values of solute transport parameters (e.g., dispersion coefficient D, cross-sectional area of the channel A and the storage zone A$_S$, storage-zone exchange coefficient α, and first-order loss coefficient λ).

Fig. 2. View downstream beyond tracer injection point (LBC-4), January 2002.

Fig. 3. Approach of tracer cloud to first sampling point (LBC-3B), January 2003.
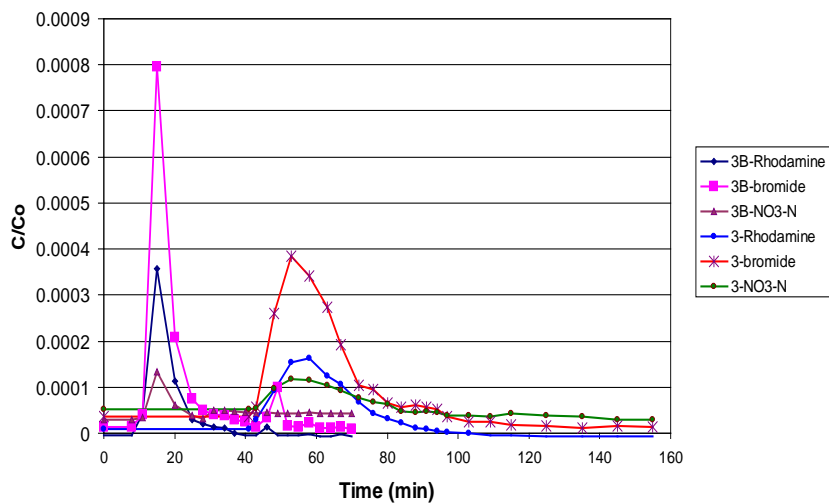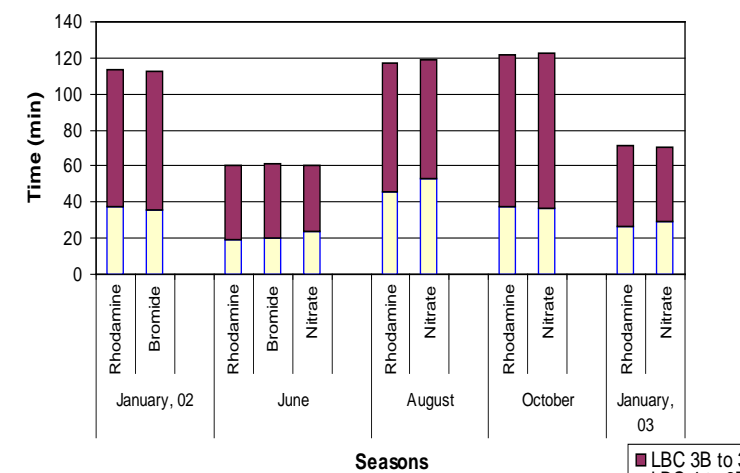
RESULTS

The timing of peak Br$^-$, NO$_3^-$, and rhodamine WT concentrations tended to coincide for each test (Fig. 4). (Consequently, use of Br$^-$ was discontinued after June 2003, when use of NO$_3^-$ began.) Likewise, travel times calculated from breakthrough curve centroids for these three tracers (using MATLAB 6.1) were similar for each test (Fig. 5). Travel times to the downstream location were slightly longer in October than in August and January 2002, and were markedly shorter in June 2002 and January 2003. Seasonal differences in Q mimic those in travel time, but Q values measured by gaging were consistently less (by as much as a factor of four) than those calculated from tracer test results. Gaged values tended to increase with distance downstream in June 2002 and January 2003.

Agreement between simulated and observed concentrations of slug tracers tends to be reasonable, particularly for rhodamine WT (Fig. 6). Modeled values of D for the slug tracers range from 0.015 to 0.29 m^2/s and tend to vary with Q, as expected (lowest in January 2002 and highest in January 2003). Modeled values of A, which range from 0.57 to 0.62 m^2, are about half of those measured during gaging. Modeled values of A$_S$ (on the order of 10^{-3} m^2) and α (ranging from 10^{-5} to 10^{-3} s^{-1}) indicate minimal in-stream storage, which is consistent with the channelized morphology of the stream bed and banks.

Propane concentrations tended to attain plateau values except in August and at the farther downstream site in October (Fig. 7), while contaminant concentrations in stream water tended to fall within ranges previously observed for each site and season. Values of λ modeled using propane data track seasonal changes in temperature, as expected. Multiplying these λ values by 0.79 (the ratio of TCE and propane volatilization coefficients [Smith et al., 1980]) gives a range of 1.50 to 6.23 d^{-1} for the TCE volatilization coefficient. Values of λ were also calculated independently using the equation:

$$(1) \qquad \lambda = -1/t \ln (C_d/C_u)$$

where t = travel time between sampling points,
C$_u$ = TCE concentration at an upstream sampling point,
and C$_d$ = TCE concentration at a downstream sampling point.

These calculated values are within a factor of two of the modeled values. Contaminant mass fluxes were estimated by:

$$(2) \qquad F = C_d Q_d - C_u Q_u$$

where the subscripts u and d are used as in equation (1) and gaged values were used for Q. ^{99}Tc fluxes tend to cluster around 0 (Fig. 8), whereas TCE fluxes tend to be positive and to increase downstream (Fig. 9).

Fig. 4. Normalized concentrations of Br$^-$, NO$_3^-$, and rhodamine WT versus time at LBC-3B and -3, June 2002.

Fig. 5. Travel times from LBC-4 to -3B and LBC-3B to -3 calculated for different slug tracers.
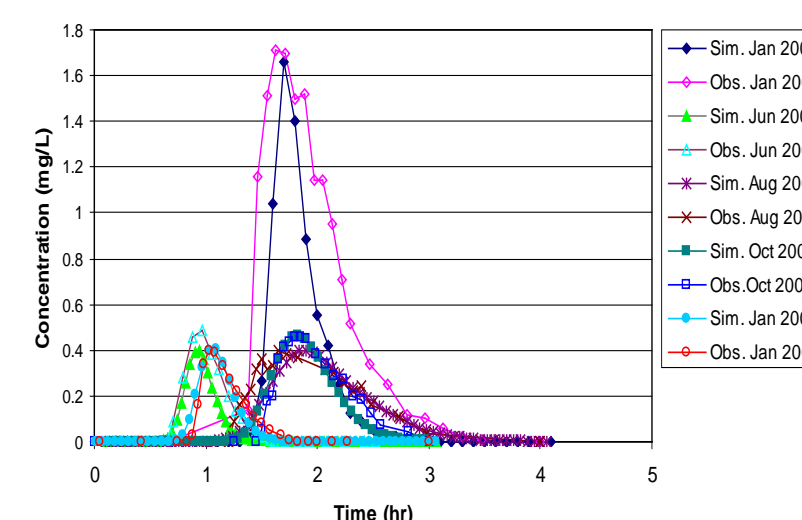

Fig. 6. Simulated and observed rhodamine WT concentrations at LBC-3.
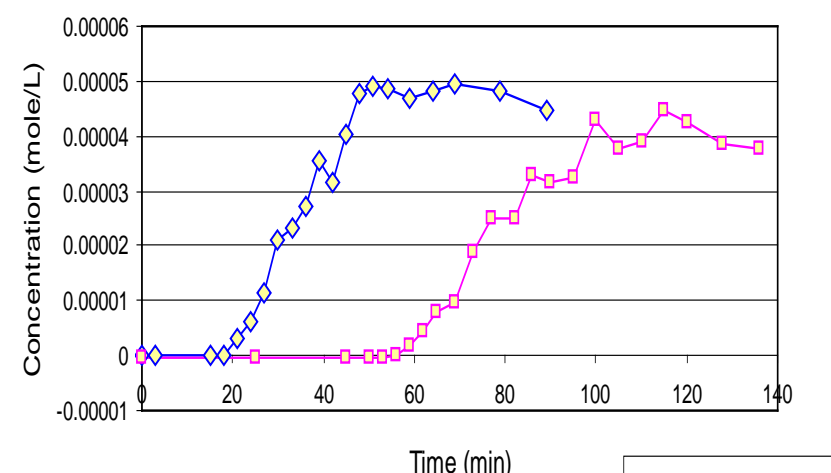

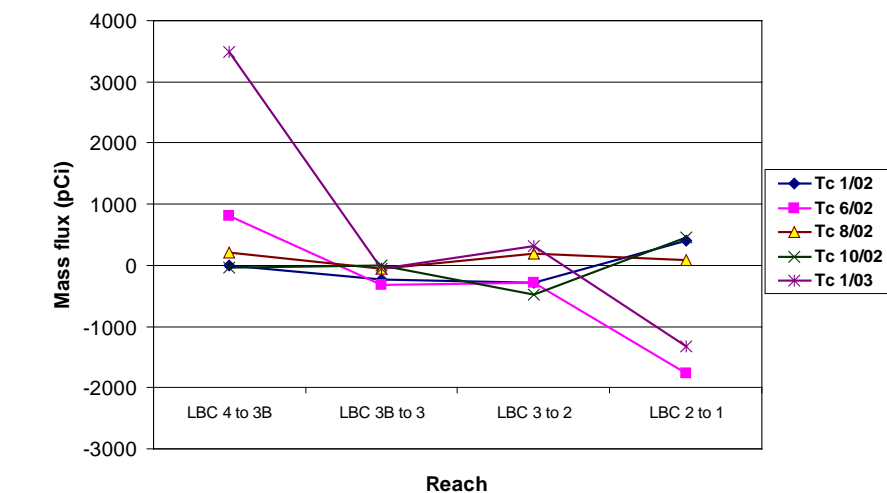Fig. 7. Time-normalized concentration plot for propane at LBC-3B and -3, January 2003.

Fig. 8. Calculated ^{99}Tc fluxes between monitoring sites.
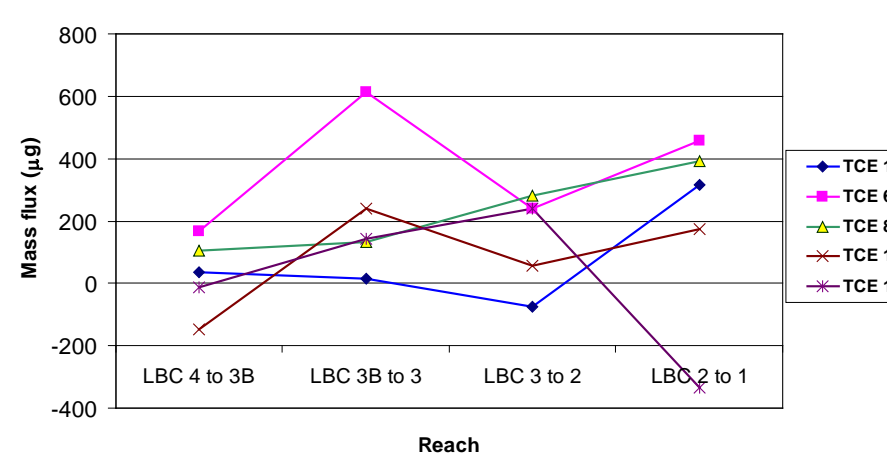

Fig. 9. Calculated TCE fluxes between monitoring sites.

CONCLUSIONS

Comparing results of tracer tests with monitoring of stream flow and contaminant concentrations along Little Bayou Creek indicates that:

1. anaerobic biodegradation of TCE and bioimmobilization of ^{99}Tc are negligible;

2. hydrophobic sorption of TCE to stream sediment is probably insignificant;

3. TCE is attenuated by volatilization, particularly as temperature increases; and

4. contaminant concentrations can be seasonally reduced by downstream dilution.

The first two findings are consistent with a general lack of secondary storage, since reduction and sorption would be likely to occur in low-flow regions within the stream bed and banks. In turn, the lack of secondary storage is likely to be an artifact of the channelization of the creek. However, observations of rhodamine WT retention in stagnant zones and differences between gaged and modeled values of Q and A suggest that treating the channelized reach as a 1-D system is still a simplification.

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