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Reprinted from GROUND WATER, Vol. 36, No. 2, March-April 1998

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Abstract

The single-well, "push-pull" test method is useful for obtaining information on a wide variety of aquifer physical, chemical, and microbiological characteristics. A push-pull test consists of the pulse-type injection of a prepared test solution into a single monitoring well followed by the extraction of the test solution/ground water mixture from the same well. The test solution contains a conservative tracer and one or more reactants selected to investigate a particular process. During the extraction phase, the concentrations of tracer, reactants, and possible reaction products are measured to obtain breakthrough curves for all solutes. This paper presents a simplified method of data analysis that can be used to estimate a first-order reaction rate coefficient from these breakthrough curves. Rate coefficients are obtained by fitting a regression line to a plot of normalized concentrations versus elapsed time, requiring no knowledge of aquifer porosity, dispersivity, or hydraulic conductivity. A semi-analytical solution to the advective-dispersion equation is derived and used in a sensitivity analysis to evaluate the ability of the simplified method to estimate reaction rate coefficients in simulated push-pull tests in a homogeneous, confined aquifer with a fully-penetrating injection/extraction well and varying porosity, dispersivity, test duration, and reaction rate. A numerical flow and transport code (SUTRA) is used to evaluate the ability of the simplified method to estimate reaction rate coefficients in simulated push-pull tests in a heterogeneous, unconfined aquifer with a partially penetrating well. In all cases the simplified method provides accurate estimates of reaction rate coefficients; estimation errors ranged from 0.1 to 8.9% with most errors less than 5%. In an example application, the method is used to estimate reaction rate coefficients for a microbiological process (denitrification) using data from field push-pull tests performed in a petroleum-contaminated, unconfined alluvial aquifer.

Introduction

The single-well, "push-pull" test method (Istok et al. 1997) is useful for obtaining quantitative information on a wide variety of aquifer physical, chemical, and microbiological characteristics in situ. The method consists of the pulse-type injection ("push") of a prepared test solution into a single monitoring well followed by the extraction ("pull") of the test solution/ground water mixture from the same well (Figure 1). A resting phase may also be included between the injection and extraction phases, during which there is no pumping. The test solution contains a conservative tracer and one or more reactive solutes (reactants) selected to investigate a particular aquifer characteristic. During the extraction phase, the concentrations of tracer, reactants, and possible reaction products are measured to obtain breakthrough curves for all solutes. The mass of reactant consumed or product formed during the test and reaction rates are determined from an analysis of these breakthrough curves (Istok et al. 1997).

The push-pull test method was originally developed for use in determining residual oil saturations in petroleum reservoirs (Tomich

et al. 1973). In a typical application the test solution contains a known concentration of ethyl acetate and the test includes an extended resting phase during which a portion of the injected ethyl acetate hydrolyzes to ethanol. The concentrations of both solutes are measured during the extraction phase and residual oil saturation is determined by the delayed arrival of the ethyl acetate breakthrough curve relative to the ethanol breakthrough curve (ethyl acetate transport is retarded relative to ethanol because ethyl acetate partitions into the stationary residual oil phase to a greater extent than ethanol).

Surprisingly, the push-pull test method has received relatively little attention in the hydrology literature despite its apparent usefulness for determining a range of aquifer characteristics. Gelhar and Collins (1971) derived an equation for the breakthrough curve at an extraction well for an initially uniformly distributed tracer that can be used to determine aquifer dispersivity in the absence of regional ground water flow. Hall et al. (1991) derived equations to determine the effective porosity and regional ground water velocity from the results of a push-pull tracer test (which they referred to as a "drift-pumpback" test). Trudell et al. (1986) was perhaps the first to apply a simple form of push-pull test to study microbial processes in the subsurface. In their study, a modified drive sampler was used to inject and extract fluids from a specific depth interval in a specially prepared borehole to assay for denitrification in an alluvial aquifer. Evidence for denitrification was obtained by comparing nitrate, nitrite, and tracer concentrations in water samples collected during the extraction phase. Reinhard et al. (1997) use a methodology similar to push-pull tests to obtain in situ BTEX biotransformation

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Received January 1997, accepted July 1997.

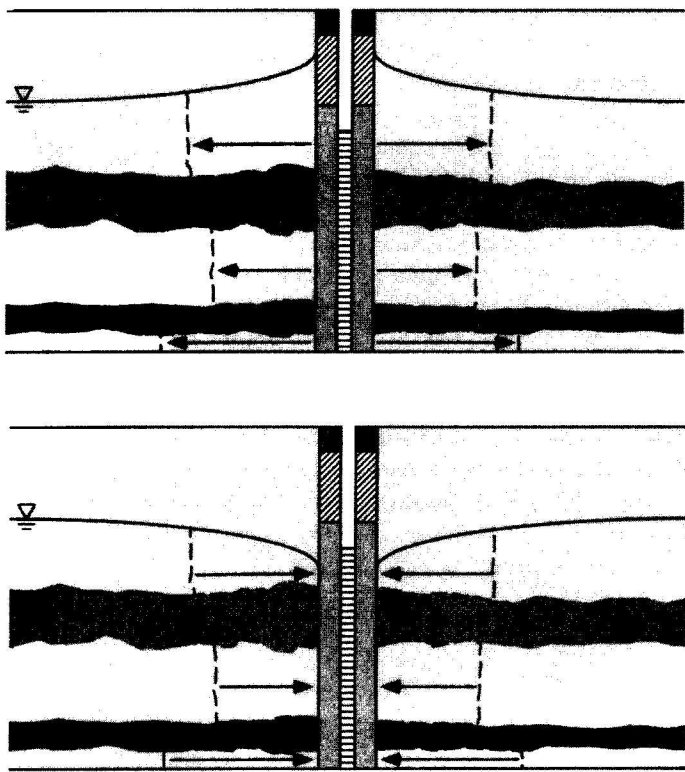


Figure 1. Schematic of a push-pull test in a heterogeneous, unconfined aquifer.

rates, in which a large-volume slug is injected into a gasoline contaminated aquifer. Subsequently, samples of the initial slug mixed with ground water are removed over a two to three month period and analyzed. Most recently, Istok et al. (1997) used push-pull tests to quantify rates of several microbial processes (aerobic respiration, denitrification, sulfate reduction, and methanogenesis) in a petroleum contaminated aquifer. In that paper, zero-order reaction rate coefficients were computed by integrating reactant and product breakthrough curves to obtain the mass of reactant consumed and product formed within the aquifer during the test and dividing this mass by the average residence time for the test solution in the aquifer, which was computed using the tracer breakthrough curve.

The conventional approach to interpreting experimental breakthrough curves to obtain reaction rates requires the construction and use of a numerical or analytical flow and transport model. Model parameters are then found either manually by adjusting parameter values until a satisfactory fit is obtained, or automatically by using a statistical algorithm such as Marquardt (1963). Although this approach is very general, manual implementation requires accurate information on additional aquifer properties (e.g., porosity, dispersivity, and hydraulic conductivity) including their spatial variability, which may not be available at all sites. Automated implementation requires integration of the flow and transport model with a statistical algorithm.

The objective of this study is to develop and evaluate a simplified method of push-pull test data analysis that can be used to estimate first-order reaction rate coefficients from tracer and reactant breakthrough curves, but does not require the use of a flow and transport model or knowledge of any other aquifer properties. The method is based on two major assumptions: (1) the injected test solution is completely mixed within the portion of the aquifer assayed by the test; and (2) the retardation factors of tracer and reactant are identical (i.e., the reactant is not sorbed to aquifer solids). Using these assumptions,

first-order reaction rate coefficients can be obtained by fitting a regression line to a plot of normalized concentrations of tracer and reactant versus elapsed time. The ability of the method to estimate first-order reaction rate coefficients for a wide range of simulated aquifer conditions is evaluated for a homogeneous, confined aquifer with a fully penetrating injection/extraction well using a semi-analytical solution to the advective-dispersion equation, written for the radial flow field in the vicinity of the well during a push-pull test. The method is further evaluated for simulated push-pull tests in a heterogeneous, unconfined aquifer with a partially penetrating well using the flow and transport code SUTRA (Voss 1984). In all cases the simplified method provides accurate estimates of reaction rate coefficients; estimation errors range from 0.1 to 8.9% with most errors less than 5%. In an example application, the method is used to estimate reaction rate coefficients for a microbiological process (denitrification) using data from field push-pull tests performed in a petroleum-contaminated, unconfined alluvial aquifer.

Theory of Reactive Solute Transport During a Push-Pull Test

Overview

Our analysis of reactive solute transport during a push-pull test begins with an examination of the radial flow field near the well. In most applications, the injection phase will consist of two parts: the injection of the test solution, followed by the injection of a small volume of clean water "chaser" (no added solutes) to flush the test solution out of the well casing and sand pack (if present) and into the aquifer. If we define the pumping rate and duration of the test solution injection as Q_{inj} and t_{inj} , and the pumping rate and duration of the chaser injection as Q_{chaser} and t_{chaser} , respectively, the total volume of aquifer V investigated by the test is

$$V = \frac{Q_{inj}t_{inj} + Q_{chaser}t_{chaser} - 2\pi r_w b}{\theta} \quad (1)$$

where r_w (L) is the well radius, b (L) is saturated thickness, and θ (dimensionless) is effective porosity. The injected test solution penetrates an approximately cylindrical volume of aquifer centered at the well, but the exact shape of the penetrated zone is never known precisely. It depends on several factors, including the presence of aquifer heterogeneities (e.g., layers or lenses with different hydraulic conductivities), the initial saturated thickness, well screen length, injection rate and duration, and well construction and development methods.

The pore water velocity, v (L/T), in the vicinity of the well during the test is given by:

$$v = \frac{Q}{2\pi b \theta r} \quad (2)$$

where Q (L^3/T) is the pumping rate (positive during the injection phase and negative during the extraction phase), and r (L) is radial distance from the well. The saturated thickness is assumed to remain constant during the test, which is strictly true for tests conducted in confined aquifers and approximately correct for tests conducted in unconfined aquifers if the change in water levels resulting from pumping are small. Temporarily neglecting dispersion, the radial distance that the test solution penetrates into the aquifer can be obtained using

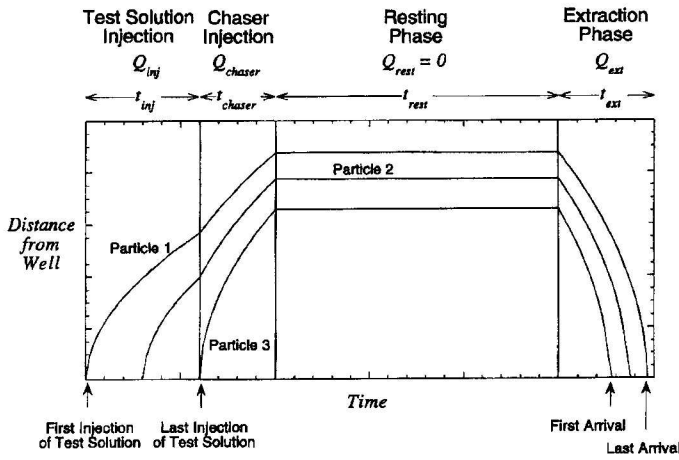


Figure 2. Schematic of the path traveled by particles going away from and returning to an injection/extraction well during a push-pull test.

$$2\pi \int_{r_w}^r b\theta r dr = \int_0^t Q dt \quad (3)$$

where t (T) is time. Performing the integration in Equation 3 for constant Q , b , and θ , gives

$$r = \sqrt{\frac{Qt}{\pi b\theta}} + r_w^2 \quad (4)$$

which reveals the parabolic shape of the radial penetration distance as a function of time due to the non-uniform velocity field. Several important features of solute transport during a push-pull test are summarized graphically in Figure 2. The first injected particle (particle 1) travels a greater radial distance from the well and spends a longer time in the aquifer than the particle that is injected last (particle 3). The first injected particle is therefore the last particle to be extracted and vice versa. As we will see later, this “inversion” process causes push-pull test breakthrough curves to look somewhat different than the more conventional breakthrough curves obtained in laboratory column experiments, or well-to-well field experiments. Note that in Figure 2, the particle trajectories are plotted assuming that the injection phase pumping rates Q_{inj} , Q_{chaser} , and the pumping rate during the extraction phase Q_{ext} are all different.

Mathematical Model

Assuming that transport of injected test solution components is governed by one-dimensional (radial) advection and dispersion, and a first-order (or pseudo-first-order) reaction, the solute transport equation in the vicinity of an injection/extraction well in a homogeneous and confined aquifer can be written (e.g., Hoopes and Harleman 1967)

$$\frac{\partial c}{\partial t} = \alpha_L v \left| \frac{\partial^2 c}{\partial r^2} - v \frac{\partial c}{\partial r} - kc \right. \quad (5)$$

where c (M/L³) is solute concentration, α_L (L) is dispersivity, and k (T⁻¹) is the first-order reaction rate coefficient. Equation 5 is written twice, once for the tracer (with $k = 0$) and once for the reactant (with $k \neq 0$). In Equation 5, the pore water velocity varies with radial distance from the well but is assumed not to change with

time. This assumption is valid when the duration of the injection and extraction phases are long relative to the time required for water levels to adjust to changing pumping rates during the test, which is often the case in practice. For example, using Equation A2 in Harvey et al. (1994), pore water velocities at a radial distance of 1 m from a pumping well in a confined aquifer (with hydraulic conductivity, $K \approx 1 \times 10^{-4}$ m/s and specific storage, $S_s \approx 1 \times 10^{-4}$ m⁻¹) reach 99% of their steady-state values in approximately 25 seconds.

Prior to the start of the test, solute concentrations are assumed to be zero near the well

$$c(r, t = 0) = 0 \quad (6)$$

If initial concentrations are not zero, Equation 6 can still be used if the initial concentrations are subtracted from measured concentrations prior to analysis because Equation 5 is linear in c . During the injection phase, Q and v are positive in Equation 2 and a constant flux boundary condition exists at the well

$$\left(-\alpha_L \frac{\partial c}{\partial r} + c \right)_{r=r_w} = \begin{cases} c_{inj} & 0 \leq t \leq t_{inj} \\ 0 & t > t_{inj} \end{cases} \quad (7a)$$

where c_{inj} (M/L³) is the known solute concentration in the test solution. The right-hand side of Equation 7a is a Heaviside step function. At the outer edge of the region of influence of the injection well the boundary condition is

$$\frac{\partial c(r \rightarrow \infty, t)}{\partial r} = 0 \quad (7b)$$

During the extraction phase, Q and v are negative in Equation 2 and the boundary condition at the well is

$$\frac{\partial c}{\partial r} (r=r_w, t) = 0 \quad (8a)$$

At the outer edge of the region of influence of the injection well the boundary condition is

$$c(r \rightarrow \infty, t) = 0 \quad (8b)$$

Sensitivity Analysis Using a Semi-Analytical Solution

A semi-analytical solution to Equations 5 to 8 was derived (see Appendix) for use in a sensitivity analysis designed to illustrate the effects of porosity, dispersivity, injection time, and first-order (or pseudo-first-order) reaction on push-pull breakthrough curves. A semi-analytical solution is useful for this purpose because it provides a rapid and accurate method for examining the effect of many combinations of parameters on the resulting breakthrough curves. Calculations are performed for a “base case” and for a set of nine additional cases, which have values of a single parameter substantially larger or smaller than in the base case (Figure 3). Values of porosity are varied from 0.01 to 0.30 to represent a wide range of geologic materials and values of dispersivity are varied from 0.013 to 0.35 m, which are between 1 and 30% of the total travel distance (injection plus extraction) (e.g., Gelhar et al. 1992). Injection times are varied from 0.05 to 2.5 hours to match values used in field experiments (Schroth et al. 1997) and reaction rate coefficients are

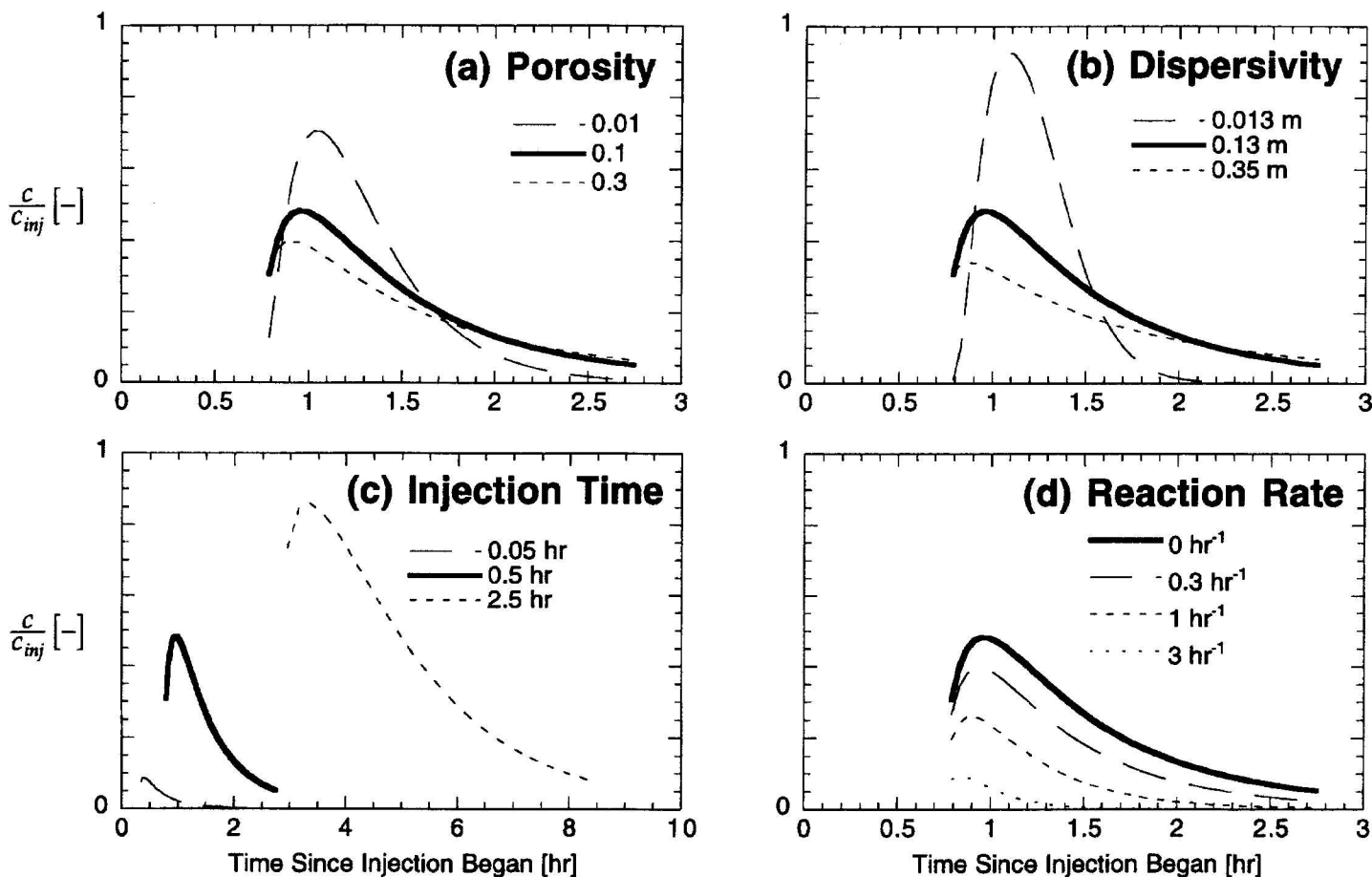


Figure 3. Breakthrough curves at a well during the extraction phase of a push-pull test for various flow and transport characteristics. See Table 1 for additional (constant) parameters. The base case is shown in bold.

Table 1
Constant Parameters Used in Sensitivity Analysis and Evaluation of Simplified Method Performance

Parameter	Value
b [m]	0.30
r_w [m]	0.03
Q_{inj} [m ³ /hr]	0.06
Q_{chaser} [m ³ /hr]	0.06
Q_{ext} [m ³ /hr]	0.06
t_{chaser} [hr]	0.167
t_{rest} [hr]	0.083

varied from 0.0 to 3.0 hr⁻¹. All other parameters are held constant (Table 1).

The results (Figure 3) illustrate three important differences between push-pull test breakthrough curves and those commonly obtained in column studies or well-to-well field experiments, which are attributed to the unique characteristics of the alternating diverging/converging flow field during a push-pull test. First, the curves are highly asymmetric and exhibit long tails. Although such a high degree of asymmetry is typically ascribed to rate-limited mass transfer in other settings, here the asymmetry in these curves is due only to the geometry of the flow field during a test.

Second, we see that varying porosity does not proportionately affect the arrival time of the breakthrough curve peak. For example,

reducing porosity by a factor of 10 (from 0.1 to 0.01) causes the peak arrival time to be reduced by only 13% (from 1.1 to 0.95 hours) (Figure 3a). This behavior is due to porosity equally affecting velocities during both injection and extraction phases of the test; an increase in velocity away from the well caused by reducing porosity is compensated for by an increase in velocity toward the well.

Third, the breakthrough curve scales similarly with porosity and the square of dispersivity; an increase in either parameter causes the curves to display increased asymmetry and tailing (Figures 3a and b). This is expected because porosity and dispersivity are combined in the definition of dimensionless time and reaction rate in the solute transport equation (see Appendix). From this understanding of the dimensionless form of the solution, we should not expect the push-pull test to be able to independently estimate dispersivity, effective porosity, and saturated thickness.

The effect of increasing the reaction rate coefficient, k is, of course, to decrease all concentrations; the peak arrival time and extent of asymmetry and tailing remain approximately the same as k increases (Figure 3d). However, we can see that the effect of an increase in the reaction rate coefficient on the peak concentration is qualitatively similar to an increase in porosity or dispersivity.

From Figure 3 it is apparent that several different combinations of transport parameters can produce similar breakthrough curves. This may limit our ability to estimate reaction rate coefficients from field breakthrough curves, especially when (1) breakthrough data have significant measurement error or the tails of the breakthrough curves are truncated; and (2) one or more parameters are poorly constrained. For example, comparing Figure 3b and 3d it is apparent that

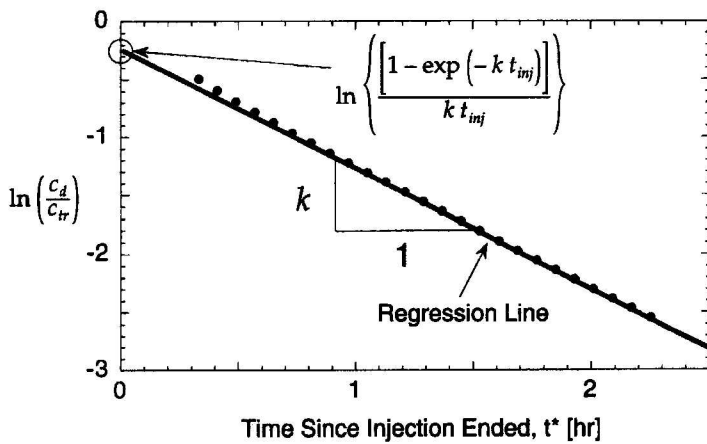


Figure 4. Example application of simplified method of data analysis for estimating first-order and pseudo-first-order reaction rate coefficients. Normalized concentrations (filled symbols) are obtained from tracer ($k = 0 \text{ hr}^{-1}$) and reactant ($k = 1 \text{ hr}^{-1}$) breakthrough curves shown in Figure 3d.

a lowered peak concentration for a reactant could be attributed to either an increased dispersivity or an increased reaction rate. In addition, heterogeneity and other “non-ideal” conditions such as a partially penetrating well or non-zero regional flow velocities may further hinder our ability to accurately estimate reaction rate coefficients under field conditions using a conventional analytical or numerical model. An additional disadvantage of a conventional approach to parameter estimation is that it typically has high costs, because many computer runs are required to estimate model parameters and to calculate estimation errors and construct confidence intervals for estimated parameters.

Simplified Method of Push-Pull Test Data Analysis

Method Development

In developing a simplified method of push-pull data analysis our goals are to develop a method that (1) allows accurate estimation of first-order reaction rate coefficients; (2) is not strongly sensitive to variations in other aquifer parameters (e.g., porosity, dispersivity); and (3) does not require the use of a numerical flow and transport code. The method is based on two simplifying assumptions: (1) the injected test solution is well-mixed within the portion of the aquifer assayed by the test; and (2) retardation factors for tracer and reactant are identical. (As we will see, the first assumption may be relaxed considerably.) These assumptions are identical to those commonly used in the analysis of well-mixed batch reactors. For example, consider the case of an instantaneous Dirac pulse input of a test solution consisting of a tracer and a reactant undergoing a first-order reaction into a well-mixed reactor. The relative concentration (i.e., the measured concentration c divided by c_{inj} , respectively) of the reactant $c_d(t)$ can be computed using (e.g., Jury and Roth 1990)

$$c_d(t) = c_{tr}(t)e^{-kt} \quad (9)$$

where $c_{tr}(t)$ is the relative concentration of the tracer. Equation 9 can be rewritten:

$$\ln\left(\frac{c_d(t)}{c_{tr}(t)}\right) = -kt \quad (10)$$

so that for this simple case, we could obtain an estimate for k by measuring $c_{tr}(t)$, $c_d(t)$ and fitting a line to a plot of $\ln c_d(t)/c_{tr}(t)$ versus

t (e.g., Levenspiel 1989).

For the case of a push-pull test, where the test solution is injected as a pulse with a finite duration (t_{inj}) and then quickly becomes well mixed within the aquifer, the relative concentration of the reactant at the end of the test solution injection is given by

$$c_d(t) = \frac{c_{tr}(t) \int_0^{t_{inj}} Q_{inj} e^{-kt} dt}{\int_0^{t_{inj}} Q_{inj} dt} \quad (11)$$

where Q_{inj} can be a function of t . For constant Q , combining Equation 11 with Equation 9, we obtain:

$$c_d(t^*) = \frac{c_{tr}(t^*)}{kt_{inj}} [e^{-kt^*} - e^{-k(t_{inj}+t^*)}] \quad (12)$$

where t^* is the time elapsed since the end of the test solution injection. Equation 12 can be rewritten in a form that allows us to estimate k solely from the normalized concentration of the tracer and reactant, defined as the ratio of the two relative concentrations, $c_d(t^*)/c_{tr}(t^*)$:

$$\ln\left(\frac{c_d(t^*)}{c_{tr}(t^*)}\right) = \ln\left[\frac{(1 - e^{-kt_{inj}})}{kt_{inj}}\right] - kt^* \quad (13)$$

Using Equation 13, we can obtain an estimate for the rate coefficient, k by measuring $c_{tr}(t^*)$ and $c_d(t^*)$ during a test and then fitting Equation 13 to a plot of $\ln(c_d(t^*)/c_{tr}(t^*))$ versus t^* using a standard least-squares approach. An example application of this procedure is shown in Figure 4, where normalized tracer and reactant concentrations are generated using the semi-analytical solution with $k = 1.0 \text{ hr}^{-1}$ (Figure 3d). For this example, the estimated value of k is 1.017 hr^{-1} with an error of 1.7%.

To summarize, the steps involved in performing this simplified analysis are as follows: (1) conduct a push-pull test using a conservative tracer and a reactant that undergoes a first-order or pseudo-first-order reaction (e.g., Istok et al. 1997); (2) plot the natural log of the ratio of the reactant to tracer concentrations versus the time since the end of injection; and (3) using least-squares, fit Equation 13 to the plot. In fitting Equation 13 to the plot, the only unknown quantity is k .

Evaluation of Simplified Method Performance

Homogeneous, Confined Aquifer

The ability of the simplified method to estimate rate coefficients for a wide range of aquifer and test conditions in a homogenous, confined aquifer is evaluated for a base case and eight additional cases (Table 2). For each case, breakthrough curves are calculated using the semi-analytical solution for a tracer ($k = 0$) and reactant ($k \neq 0$). Constant parameters used in all calculations are in Table 1. Values of $\ln(c_d(t^*)/c_{tr}(t^*))$ are then computed and plotted versus t^* for each case (Figure 5). Estimates of the reactant rate coefficient, k_{est} , the confidence interval of one standard deviation (standard error, or SE), and the percent error of the estimate are obtained by fitting Equation 13 and are given in Table 2.

Several important conclusions can be drawn from these results. First, the shape of the graph of $\ln(c_d(t^*)/c_{tr}(t^*))$ versus t^* is only very weakly dependent on variables other than k (Figure 5). For example, the three different values of dispersivity produce quite differ-

	θ [-]	α_L [m]	t_{inj} [hr]	k [hr^{-1}]	$k_{est} \pm SE$ [hr^{-1}]	% error
Homogeneous, confined aquifer						
Base case	0.1	0.13	0.5	1	$1.017 \pm .003$	1.7
Porosity, θ - Low	0.01	0.13	0.5	1	$1.051 \pm .005$	5.1
Porosity, θ - High	0.3	0.13	0.5	1	$1.008 \pm .002$	0.8
Dispersivity, α_L - Low	0.1	0.013	0.5	1	$1.089 \pm .010$	8.9
Dispersivity, α_L - High	0.1	0.35	0.5	1	$1.003 \pm .002$	0.3
Injection Time, t_{inj} - Low	0.1	0.13	0.05	1	$1.001 \pm 4 \times 10^{-5}$	0.1
Injection Time, t_{inj} - High	0.1	0.13	2.5	1	$1.085 \pm .011$	8.5
Rate coefficient, k - Low	0.1	0.13	0.5	0.3	$0.305 \pm .001$	1.7
Rate coefficient, k - High	0.1	0.13	0.5	3	$3.055 \pm .008$	1.8
Heterogeneous, unconfined aquifer						
	0.1	0.13	0.5	1	$0.993 \pm 7 \times 10^{-4}$	0.7

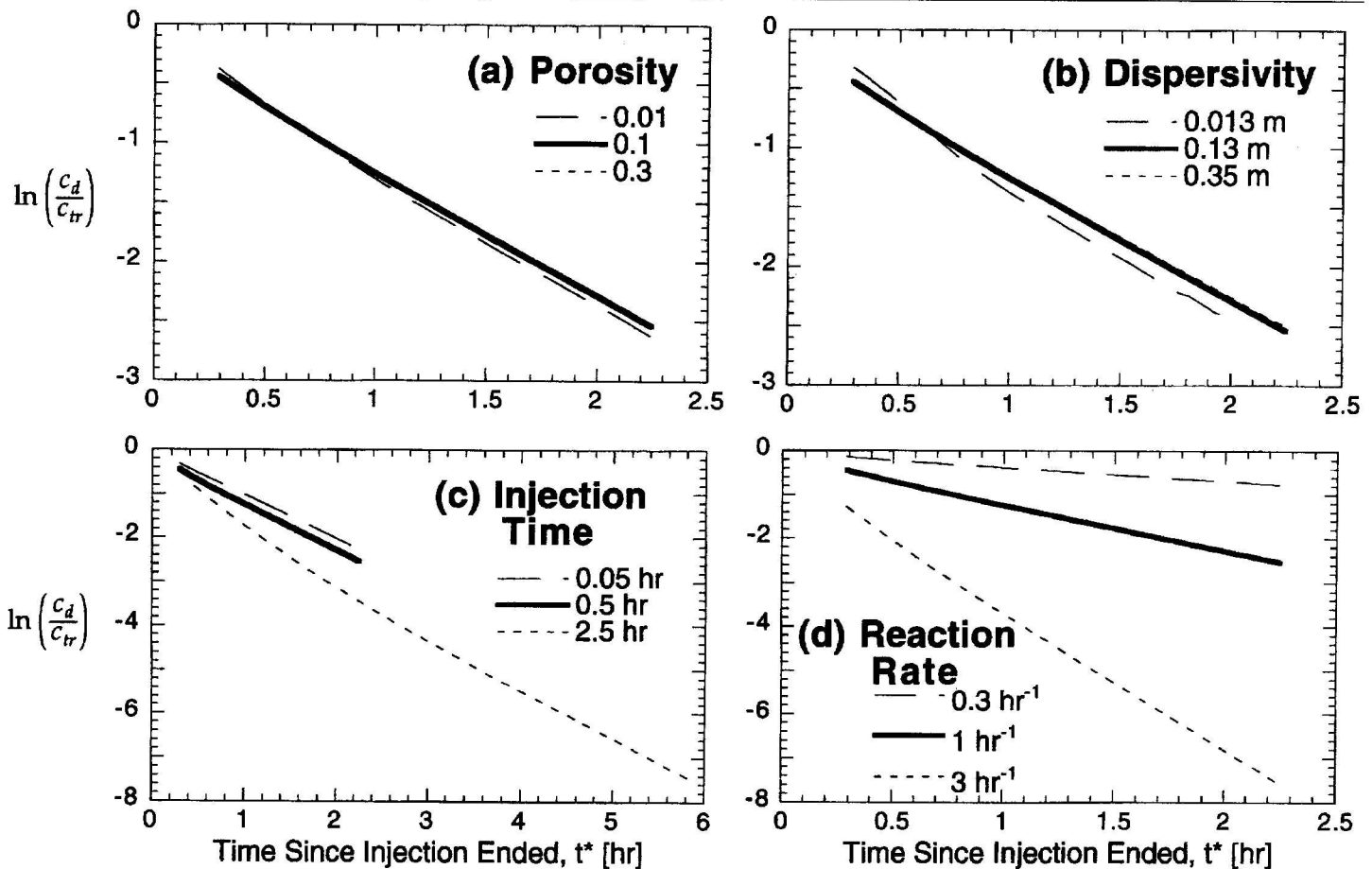


Figure 5. Estimation graphs for all flow and transport conditions (Tables 1 and 2) for the evaluation of simplified method performance under homogeneous conditions.

ent breakthrough curves in Figure 3b, but the graphs in Figure 5b are very similar. In fact, all the graphs in Figures 5 a, b, and c ($k = 1 \text{ hr}^{-1}$) are similar regardless of the value of porosity, dispersivity, or injection time. Additionally, $\ln(c_d(t^*)/c_{tr}(t^*))$ for all plots asymptotically approaches the same slope ($-k$) for large values of t^* . This is because, for large values of t^* , the duration of the injection phase, t_{inj} becomes a smaller fraction of the total time elapsed so that the pulse input more closely resembles the Dirac pulse used to derive Equation 10. This can also be seen in Equation 13 where the first term on the right-hand side goes toward zero as t_{inj} increases.

Second, the method provides estimates for k that are very close to the true value in all cases (Table 2). The smallest errors are

obtained for cases with large dispersivity or short injection time. This is because the assumption of complete mixing of the test solution within the aquifer is more nearly satisfied for these cases. Similarly the worst estimates are obtained for cases with small porosity, small dispersivity, or long injection time. For example, the graph in Figure 5c for an injection time of 2.5 hours is somewhat different from the other graphs in Figure 5c, but the estimate of k is only in error by 8.5%. The maximum error of 8.9% appears to be within a reasonable margin of error for most field studies.

Third, $k_{est} \pm SE$ in Table 2 generally does not encompass the true value of k in these theoretical comparisons. The estimated k is generally greater than true k . This is because a non-linear relationship

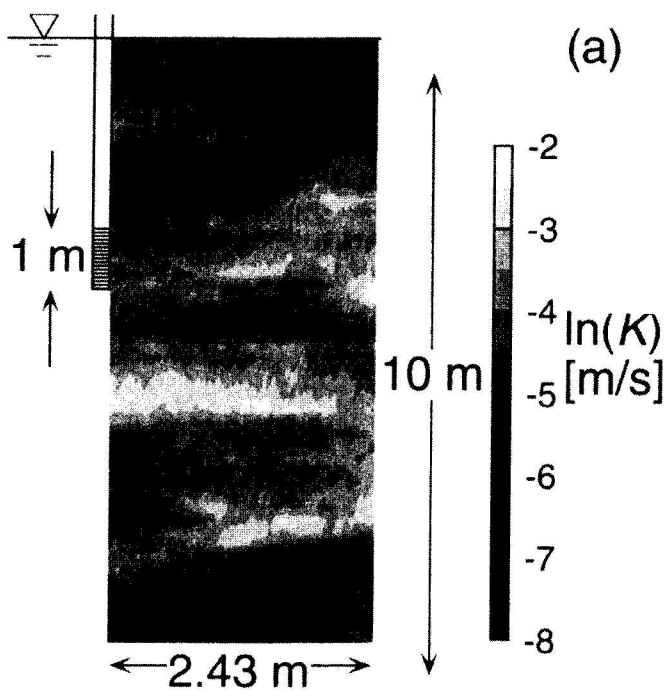


Figure 6a. Evaluation of simplified method for heterogeneous, non-ideal push-pull test. Heterogeneous K field surrounding a partially penetrating well in an unconfined aquifer.

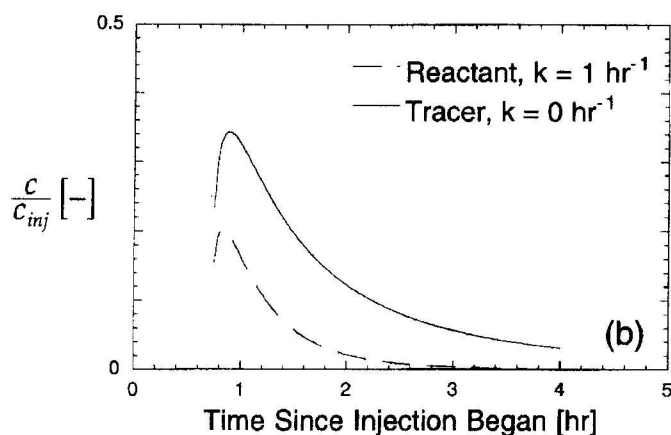


Figure 6b. Breakthrough curves at a well during the extraction phase of the push-pull test.

$(c_d(t^*)/c_{tr}(t^*))$ is being fit by a straight line. The linear relationship assumes instantaneous and complete mixing, whereas complete mixing requires a finite time. A correction factor could be introduced to account for the systematic overestimation of k , but this is not done because the estimation errors are always small, and because the correction factor is a function of aquifer properties that may be unknown (i.e., dispersivity, porosity).

Heterogeneous, Unconfined Aquifer

To further test the simplified method, we conducted a fully transient (i.e., ambient flow) two-dimensional numerical simulation of a push-pull test in an unconfined, heterogeneous aquifer with a partially penetrating injection/extraction well (Figure 6a). We use the numerical flow and transport code SUTRA (Voss 1984) with initial conditions of uniform hydraulic head and solute concentrations of zero. Boundary conditions during the injection phase are constant hydraulic flux defined by the time-varying pumping rates (Table 1) and constant solute flux (Equation 7a) at the well, and constant

hydraulic head and zero gradient solute concentration (Equation 7b) at $r = 2.43$ m from the well. Boundary conditions during the extraction phase are constant hydraulic flux defined by the time-varying pumping rates (Table 1) and zero gradient solute concentration (Equation 8a) at the well, and constant hydraulic head and zero solute concentration (Equation 8b) at $r = 2.43$ m from the well. Other parameters in the simulation are the same as for the homogeneous base case (Tables 1 and 2) with the following exceptions: saturated thickness = 10 m; well screen length = 1 m; specific yield = 0.08; and transverse dispersivity = 0.013 m. The radial grid spacing used in the numerical simulation is 0.03 m and the vertical grid spacing is 0.2 m. The heterogeneous hydraulic conductivity field is generated by sequential Gaussian simulation (Deutch and Journel 1992) using a mean of $\ln(K) = -4$, a variance of $\ln(K) = 0.8$, a spherical variogram with a horizontal range of 0.3 m, a nugget constant of 0.01, and a vertical range of 0.04 m. Units for K are m/s. Our variance lies between values estimated at the Cape Cod site (Garabedian et al. 1991) and the MADE site (Rehfeldt et al. 1992), while the correlation distances in our example are smaller than for either site. Our values of hydraulic conductivity are dominantly within the range of gravel and sand. Figure 6a shows the simulated K field, which is assumed to be identical in all radial directions from the well. In the heterogeneous simulations, concentrations fall to 1% of injected concentration at a maximum distance of 0.6 m from the well.

The simulated relative concentrations of the tracer and reactant at the well during the extraction phase are shown in Figure 6b. The simplified method for the estimation of k is shown in Figure 6c, and good agreement is found between k_{est} ($= 0.993 \text{ hr}^{-1}$) and the true value of k ($= 1.0 \text{ hr}^{-1}$) used in the simulation (Table 2). The error between the estimated and the true value of k is 0.7%.

Example Field Application

An example application of the simplified method of data analysis is presented using breakthrough curve data for field push-pull tests reported by Schroth et al. (1997). The objective of that study was to use the push-pull test to quantify the spatial variability in rates of two microbiological processes, aerobic respiration and denitrification, in an unconfined alluvial aquifer in western Oregon. The results of two representative denitrification tests conducted in different monitoring wells are discussed here. The site had been heavily contaminated by accidental releases of gasoline and diesel fuels at the land surface. The leaking fuels contaminated the unsaturated zone and aquifer to a depth of approximately 5 m, the resulting increase in subsurface microbial activity created widespread anaerobic conditions within the aquifer. Remediation at the site consisted solely of the removal of contaminated surface soils to a depth of approximately 0.5 m. The aquifer consists primarily of unconsolidated silt and sand with some gravel; the hydraulic gradient at the site is ~ 0.01 m/m and the average ground water (Darcy) velocity is ~ 0.001 m/d. The water table elevation fluctuates rapidly in response to seasonally varying recharge from precipitation; water table depth ranged from 1.7 to 2.0 m below land surface during the time of the experiments. Monitoring wells at the site are 0.051 m in diameter, are installed in 0.11 m diameter holes surrounded by a clean sand pack, range in depth from 4.2 to 6.2 m, and are screened over the entire saturated thickness of the aquifer. Identical push-pull tests were performed in each of ten monitoring wells at two depths using an inflatable packer system to isolate a 1 m long test interval within the screened portion of the well. For the denitrification tests, the test solution contained 100 mg/L Br^-

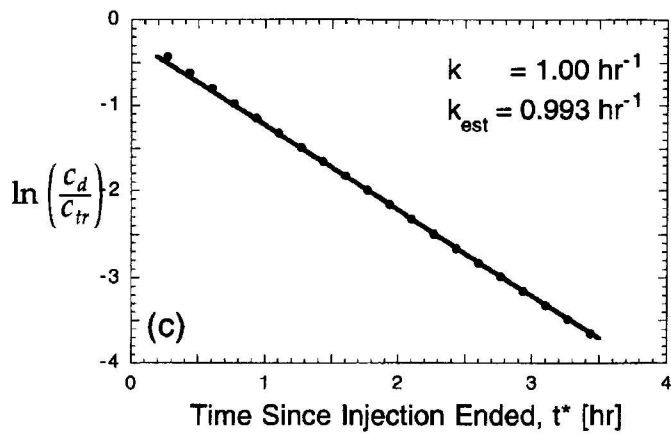


Figure 6c. Estimation graph.

to serve as a tracer and 25 mg/L N-NO₃⁻ as the single reactant. Additional test conditions are given in Table 3; more details about the experimental methods are in Schroth et al. (1997).

Schroth et al. (1997) demonstrated that in this aquifer Br⁻ and NO₃⁻ have similar transport properties and in the absence of denitrification, the breakthrough curves for the two solutes are essentially identical. However, in the contaminated portion of the site denitrification activity was very high and substantial transformation of NO₃⁻ occurred. This resulted in a substantial reduction in the mass of recovered NO₃⁻ relative to Br⁻ (Figures 7 a and b). The mass recovered may be calculated by integrating the breakthrough curve, multiplying

by the injected concentration, and dividing by the pumping rate.

If we assume that the reduction of nitrate proceeds according to a first-order reaction, the rate coefficient can be obtained by fitting Equation 13 as described before. The plots of $\ln(c_d(t^*)/c_{tr}(t^*))$ versus t^* for the two breakthrough curves typically display a larger slope for $t^* < 60$ min than for $t^* > 60$ min. This effect is also seen in the estimations based on semi-analytical solution data (Figure 5), but is much greater in the estimations from field data. The enhancement of this effect may be due to spurious values of $\ln(c_d(t^*)/c_{tr}(t^*))$ greater than 0, which are likely caused by measurement errors for early times when concentrations are near the detection limits used in field measurements. Equation 13 is fit to the later time data (ignoring values greater than 0), which results in estimates for k of 0.265 ± 0.017 hr⁻¹ (Test 1) and 0.285 ± 0.016 hr⁻¹ (Test 2). Experience with the synthetic breakthrough curves indicate that the confidence intervals are likely at least four to five times larger than this. The breakthrough curves suggest that aquifer properties at the Test 1 well are significantly different from the aquifer properties at the Test 2 well (Figures 7a and b). However, the estimation plots and estimated k are very similar for both Test 1 and Test 2 (Figures 7c and d).

Discussion

The development of the simplified method of data analysis presented in this paper requires two major assumptions and several other minor assumptions. Violation of the major assumptions may cause the method to fail, while violation of the minor assumptions

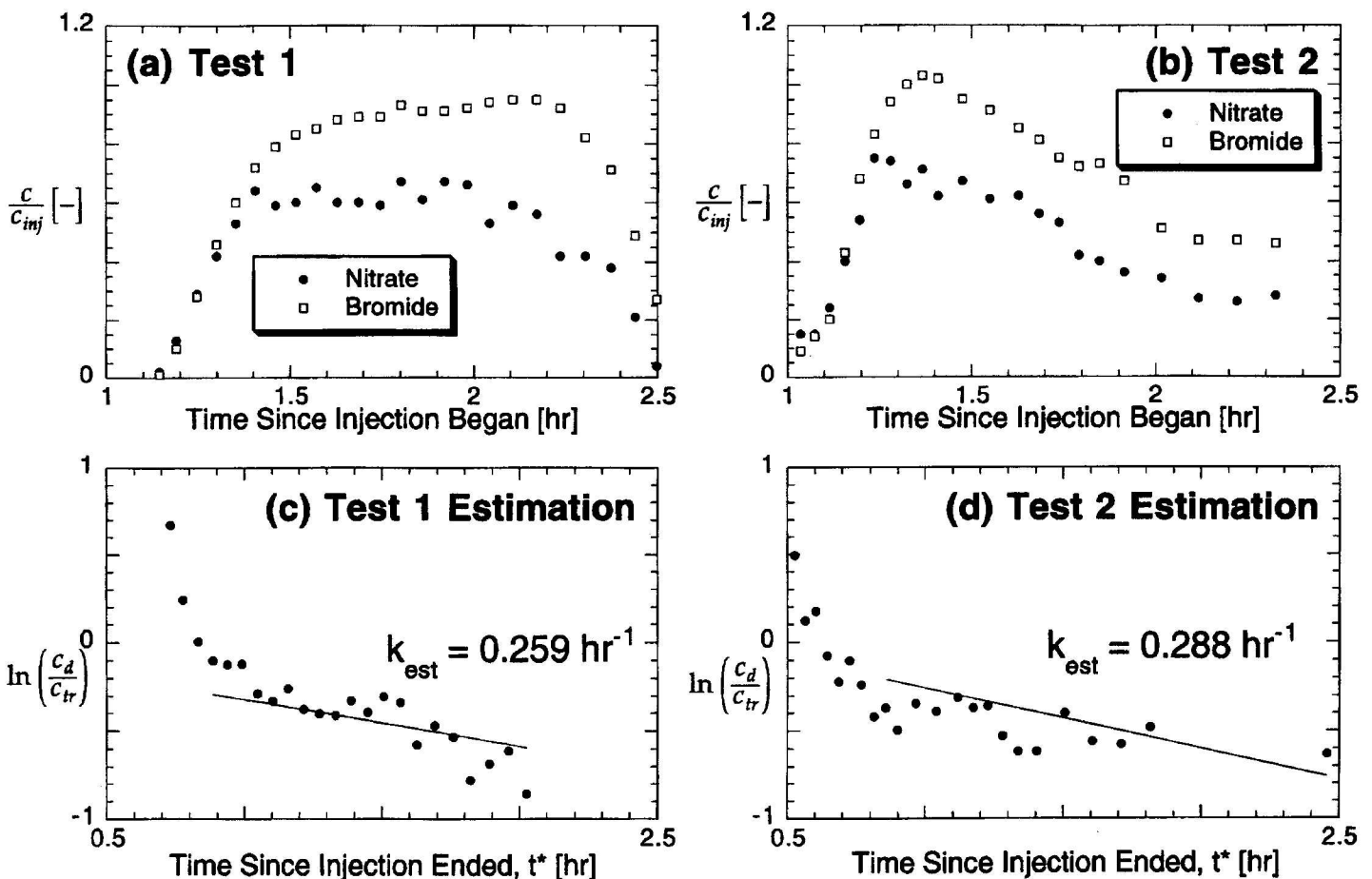


Figure 7. Tracer and reactant breakthrough curves, and corresponding estimation graphs for the determination of denitrification rates for two push-pull tests conducted in different monitoring wells in a petroleum contaminated aquifer (Schroth et al. 1997).

Table 3
Push-Pull Test Conditions for Field Tests Conducted
by Schroth et al. (1997)

Parameter	Test No. 1	Test No. 2
b [m]	1.0	1.0
Q _{inj} [m ³ /hr]	0.090	0.060
Q _{chaser} [m ³ /hr]	0.024	0.054
Q _{ext} [m ³ /hr]	0.036	0.030
t _{inj} [hr]	0.417	0.517
t _{chaser} [hr]	0.450	0.200
t _{rest} [hr]	0.200	0.300
t _{ext} [hr]	1.440	1.500

may lead to smaller inaccuracies. Major assumptions are: (1) complete and instantaneous mixing of the injected test solution in the portion of the aquifer investigated by the test; and (2) injected tracer and reactant have the same retardation factors. Other assumptions include: (3) spatially homogeneous reaction rates; (4) identical reaction rates in mobile and immobile aqueous or sorbed phases; (5) concentrations of tracers that are initially zero in the aquifer; and (6) measurement errors are small, random, independent, and have a mean value of zero.

From our evaluation of the simplified method performance, we see that the first assumption does not have a significant impact on the accuracy of the resulting estimates. Although the assumption is certainly invalid for dispersivities equal to 1% of the travel distance, the method is still able to produce reasonably accurate estimates for these cases.

The second assumption would be violated if the tracer and reactants have different retardation factors due to, e.g., differential sorption of tracer and reactant to aquifer solids. The consequence of violating this assumption would be that the two solutes would chromatographically separated from each other during the test and therefore travel through different parts of the aquifer. The effects of this assumption on estimated reaction rate coefficients are currently being investigated but at present are unknown.

A third source of potential inaccuracy for the method is when reaction rates are spatially heterogeneous, and particularly if k and K are spatially correlated. Miralles-Wilhelm and Gelhar (1996) investigated this problem and found that if k and K are spatially correlated, then an estimate of the effective value of k would always overestimate the true reaction rate. They also found that estimation errors increase with increasing correlation between the two variables and may be as large as 200%.

A fourth concern, related to sorption or diffusion, involves potentially different reaction rates in mobile and immobile aqueous or sorbed phases. If reaction rates between these phases are different, then the overall reaction rate depends on the difference in reaction rates and on the amount of time a reactant spends in each phase. The estimated reaction rate may then be dependent on the specific parameters of the push-pull test, including pulse length and the duration of the experiment, and it is expected that our method would generally overestimate the mean reaction rate for this case.

Fifth, initial concentrations of solutes are not always zero. If the background concentration is known, it can be subtracted from the measured concentrations before any analysis is conducted. In some

situations, however, the background concentration may not be known or it may be spatially variable. In these cases, it is presumed that injected concentrations are much larger than background, and therefore early concentration measurements should be weighted more heavily in the analysis than late measurements.

Finally, the method assumes that concentration measurement errors are small, random, independent, and have a zero mean. If these assumptions are violated in practice, the error in k could be larger than what we found using this method.

Conclusions

The simplified method of field data analysis presented in this paper appears to be useful and accurate for estimating first-order reaction rate coefficients, k , from push-pull test data without the need for a solute transport model or information on any other aquifer properties. The method is highly accurate provided that the length of injection is not a large fraction of the total experiment time, and the dispersivity or porosity are not too small. Even in cases where one or more of these conditions are violated, the method is still capable of yielding an approximate (error < 10%) estimate for k . The derived semi-analytical solution for tracer and reactant transport during a push-pull test should also be useful for test design and data interpretation. The solutions and method presented in this paper can be extended to cases of both equilibrium and rate-limited mass transfer processes such as sorption, which will be the subject of future work.

The reader is cautioned in using this method in cases where (1) tracer and reactants have different retardation factors; (2) the aquifer is highly heterogeneous and where k and K may be spatially correlated; and/or (3) the reactant has a large retardation factor and has significantly different reaction rates in the mobile and immobile or sorbed phases. The effects of these cases on the method are not yet known.

Acknowledgments

We would like to thank G. Conner and J. Guida for their help obtaining the field data used in the example application. Partial funding for this research was provided by Chevron Research and Technology Co., Richmond, California and by the National Center for Integrated Bioremediation Research and Development. The authors gratefully acknowledge valuable review comments and suggestions provided by John Ward, HydroGeochem Inc., Tucson, Arizona.

Appendix

In this section, we derive a semi-analytical solution to Equations 5 and 8 for a reacting solute in a one-dimensional radial flow field in the vicinity of an injection/extraction well. To simplify subsequent analyses, we define the following dimensionless variables:

$$\rho = \frac{r}{\alpha_L} \quad (A1a)$$

$$\rho_0 = \frac{r_w}{\alpha_L} \quad (A1b)$$

$$T = \left| \frac{Qt}{2\pi b\theta\alpha_L^2} \right| \quad (A1c)$$

$$\kappa = \left| \frac{2\pi b \theta \alpha_L^2 k}{Q} \right| \quad (\text{A1d})$$

$$C = \frac{c}{c_{inj}} \quad (\text{A1e})$$

where ρ and ρ_0 are dimensionless radii (also Peclet numbers), T is a dimensionless time, κ is a dimensionless reaction rate coefficient (also a Damkohler I number) and C is relative concentration. With these definitions Equation 5 can be written:

$$\frac{\partial C}{\partial T} = \frac{1}{\rho} \left(\frac{\partial^2 C}{\partial \rho^2} \pm \frac{\partial C}{\partial \rho} \right) - \kappa C \quad (\text{A2})$$

where the \pm sign is negative during the injection phase and positive during the extraction phase.

Injection Phase

Taking the Laplace transform of (A2) for the injection phase, we get

$$0 = \frac{d^2 \bar{C}}{d\rho^2} - \frac{d\bar{C}}{d\rho} - \rho(s + \kappa)\bar{C} \quad (\text{A3})$$

where s is the Laplace variable and an overbar designates the Laplace transform of a variable. Taking the Laplace transform of the boundary conditions, Equation 7, written in terms of the dimensionless variables defined above, gives:

$$\bar{C} - \frac{d\bar{C}}{d\rho} = 1, \rho = \rho_0 \quad (\text{A4a})$$

$$\frac{d\bar{C}}{d\rho} = 0, \rho \rightarrow \infty \quad (\text{A4b})$$

Modifying the method of Chen (1985), the solution to Equation A3 and A4 in the Laplace domain is

$$\bar{C} = \frac{1 - e^{-sT_{inj}}}{s} \exp\left(\frac{\rho - \rho_0}{2}\right) \frac{Ai(P^{1/3}y)}{\frac{1}{2} Ai(P^{1/3}y_0) - P^{1/3} Ai'(P^{1/3}y_0)} \quad (\text{A5})$$

where

$$P = s + \kappa \quad (\text{A6a})$$

$$y = \rho + (4P)^{-1} \quad (\text{A6b})$$

$$y_0 = \rho_0 + (4P)^{-1} \quad (\text{A6c})$$

$$T_{inj} = \left| \frac{Qt_{inj}}{2\pi b \theta \alpha_L^2} \right| \quad (\text{A6d})$$

Ai is the first Airy function, and Ai' is the derivative of Ai with respect to its argument (Abromowitz and Stegun 1965). The first term in Equation A5 is the Laplace transform of the dimensionless injected concentration from Equation 7a. If the injected concentration is

not a Heaviside step function, then the first term in Equation A5 can be replaced by the respective Laplace transform of the injected concentration. We also note here that if a solution for solute transport in the presence of rate limited mass transfer is desired, the solution is exactly as given in Equation A5, but the definition of P changes slightly (for a similar case, see Harvey et al. 1994).

Resting Phase

During the resting phase, the concentration of a reactant is given everywhere by

$$C(\rho) = C_r(\rho)e^{-\kappa t} \quad (\text{A7})$$

where $C_r(\rho)$ is the concentration at a particular location at the beginning of the resting phase and t is the time since the resting phase began.

Extraction Phase

Taking the Laplace transform of Equation A3 for the extraction phase, we get

$$-\rho C_p(\rho) = \frac{d^2 \bar{C}}{d\rho^2} + \frac{d\bar{C}}{d\rho} - \rho P \bar{C} \quad (\text{A8})$$

where $C_p(\rho)$ is the concentration at the beginning of the extraction phase, as a function of the dimensionless radius ρ . The boundary conditions are

$$\frac{d\bar{C}}{d\rho} = 0, \rho = \rho_0 \quad (\text{A9a})$$

$$\bar{C} = 0, \rho \rightarrow \infty \quad (\text{A9b})$$

Modifying the method of Chen and Woodside (1988) and Harvey et al. (1994), the solution for the Laplace-domain concentrations at the pumping well is

$$\bar{C} = \frac{\pi}{P^{1/3}} e^{-\rho_0/2} [Bi(P^{1/3}y_0) - X Ai(P^{1/3}y_0)] \int_{\rho_0}^{\infty} \xi e^{\xi/2} C^0(\xi) Ai(\sigma) d\xi \quad (\text{A10})$$

where

$$X = \frac{P^{1/3} Bi'(P^{1/3}y_0) - \frac{1}{2} Bi(P^{1/3}y_0)}{P^{1/3} Ai'(P^{1/3}y_0) - \frac{1}{2} Ai(P^{1/3}y_0)} \quad (\text{A11a})$$

$$\sigma = P^{1/3} [\xi + (4P)^{-1}] \quad (\text{A11b})$$

Bi is the second Airy function, Bi' is the derivative of Bi with respect to its argument (Abromowitz and Stegun 1965), and definitions for y_0 and P are given in Equation A6. A solution for a case where rate-limited mass transfer is present is very similar to that given above: P must be changed slightly, as well as the definition of $C_p(\xi)$ (Harvey et al. 1994).

The solution for concentrations at the well during a push-pull test is obtained by using Equations A5, A7, and A10 in sequence. To obtain a solution in the time domain, Equations A5 and A10 are numerically inverted from the Laplace domain using the de Hoog algorithm (de Hoog et al. 1982). This algorithm and the numerical integration in Equation A10 are performed using IMSL (International

Mathematics and Statistics Libraries) algorithms. The complex Airy functions and their derivatives are calculated using SLATEC (Sandia, Los Alamos, Air Force Weapons Laboratory Technical Exchange Committee) algorithms.

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