

A Method to Infer In Situ Reaction Rates from Push-Pull Experiments

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Abstract

A method to evaluate first-order and zero-order in situ reaction rates from a push-pull test is presented. A single-well push-pull test starts with the rapid injection of a well-mixed slug containing a known quantity of a conservative tracer and a reactive solute into the saturated zone. The slug is then periodically extracted and sampled from the same well. For zero- or first-order reactions, in the absence of sorption and assuming negligible background concentrations, these measurements can be used to evaluate reaction rate coefficients directly. The method does not involve computer-based solute transport models and requires no knowledge of regional ground water flow or hydraulic parameters. The method performs well when the dominate processes are advection, dispersion, and zero- or first-order irreversible reactions. Regional flow velocities must be sufficiently low such that the slug stays within the area of the well during the sampling phase. In the case of zero-order reactions, results using the method proposed here are compared with those obtained through the traditional method of calibrating a computer-based transport model. The two methods give similar estimates of the reaction rate coefficient. The method is general enough to work with a broad range of push-pull experiment designs and sampling techniques.

Introduction

Single-well tracer tests have long been used to assess aquifer parameters and have a number of advantages. Single-well push-pull tests are cost effective because only one well needs to be installed and instrumented. The tests can also be completed in less time than multiple-well tests since the practitioner does not need to wait for the slug to reach the other observation wells. Bachmat et al. (1988) present a method for evaluating the longitudinal dispersivity and effective porosity from a single-well conservative tracer test. A technique to estimate regional flow velocity from a single-well tracer test is introduced by Leap and Kaplan (1988). More recently, single-well push-pull tests have been used to assess in situ reaction processes and rates. Reinhard et al. (1997) present results of push-pull experiments used to investigate BTEX degradation and to estimate zero-order reaction rates under a number of reducing conditions. Istok et al. (1997) use push-pull tests to investigate microbial activity at a fuel-contaminated site. These two studies have demonstrated the usefulness of single-well push-pull tests in assessing microbial activity and the biotransformation of solutes in the subsurface.

The purpose of this study is to provide the practitioner of a single-well push-pull test with a simple method for estimating irreversible zero- and first-order reaction rates directly from concentration measurements. These two types of reaction kinetics are among the most common models used to describe solute degrada-

tion (e.g., Morel and Hering 1993; Sparks 1989). It is important to obtain reliable estimates of in situ reaction rates in order to assess remediation strategies and to predict cleanup times. In the estimation of in situ reaction rates, one must take into account that transformation is not the only process that tends to decrease solute concentration. Solute concentrations decrease as a result of dilution caused by molecular diffusion and dispersion. Practitioners often use computer-based models to account for these and other processes. The mathematical model must be accurate enough to compute dilution and must use the appropriate parameters, usually found through model calibration. In this paper, a method for using data gathered in a push-pull test to evaluate zero- and first-order reaction rates without the aid of computer models is presented. The application of the method is illustrated through examples with simulated and experimental data. A full derivation of the method is included in the appendices. Haggerty et al. (1998) present a similar simplified method for obtaining first-order reaction rate coefficients from push-pull tests, but the formulation is based on the specific experimental design of the push-pull tests described in Istok et al. (1997). We develop the method within a more general framework, allowing the practitioner to tailor the method to the specific case of interest. Additionally, we present a method for estimating zero-order reaction rate coefficients.

Push-Pull Test

Push-pull tests to assess in situ reaction rates consist of two stages. In the first stage, the "push," a well-mixed slug of two (or more) completely mixed solutes is injected rapidly into the saturated zone of the aquifer through a single well. One of the solutes is conservative and is only subjected to advection and dispersion. The other

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solute is presumed to be degrading irreversibly under constant-coefficient zero- or first-order reaction kinetics. The background concentrations of the solutes are assumed to be negligible. After the injection, the “pull” stage begins. Water is extracted periodically from the well and the concentrations of the two solutes are measured over time.

When the slug enters the ground water it is dispersed and diluted as it mixes with the native ground water. Further mixing and dilution occurs as the slug sits or is extracted. Thus, the measured concentration of the reactive solute is being decreased by two mechanisms, dilution and transformation. From the measured concentration of the reactive solute alone, it is impossible to determine how much of the decrease in concentration is due to degradation as opposed to dilution. If dilution is not accounted for, erroneously large reaction rate coefficients may be calculated. Traditionally, reaction rates have been estimated by fitting parameters in a numerical transport model to the data. This procedure consists of two parts. First the hydraulic parameters, such as conductivity, regional flow, and dispersivity, are adjusted such that the tracer data are reproduced. Then, using these hydraulic parameters, the reaction rate constant is adjusted to reproduce the reactive solute concentration measurements. This procedure is followed by Reinhard et al. (1997) to estimate zero-order reaction rate coefficients for the anaerobic degradation of BTEX compounds.

We present a method which allows the practitioner to calculate reaction rates directly from the concentration measurements without the need to calibrate and run a numerical flow and transport model. The method is derived analytically from the transport equations and the same boundary conditions which would be used in a numerical model. Since the method does not involve a numerical model, no knowledge of aquifer parameters is needed. The only requirements are that both the solutes be injected as a well-mixed slug and experience the same boundary conditions, and that the injection time is short compared to the time during which the reactive solute degrades. The method we present will not work if other processes, such as sorption, are important. However, it may still be useful as a preliminary analysis tool.

Case 1: Zero-Order Reaction Kinetics

The goal is to derive a quantity which behaves as the reactive solute concentration would in a well-mixed batch reactor, i.e., a quantity which is not affected by dilution and whose decrease in concentration is due only to degradation. In the case of zero-order reactions, the following equations describe the transport of the two solutes:

$$\frac{\partial C_t}{\partial t} + L(C_t) = 0 \quad (1)$$

and

$$\frac{\partial C_r}{\partial t} + L(C_r) = -\alpha \quad (2)$$

where L is the advection-dispersion operator

$$L(\cdot) = \mathbf{u} \cdot \nabla - \nabla \cdot D \nabla \quad (3)$$

The concentrations of the reactive solute and the conservative tracer are C_r and C_t , respectively; α is the zero-order reaction rate

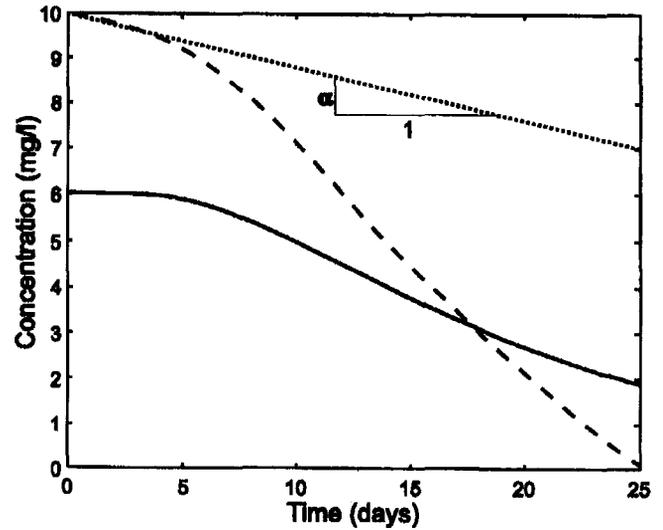


Figure 1. Simulated data. The solid line is the measured conservative solute concentration and the dashed line is the concentration of a reactive solute undergoing zero-order decay. The transformed reactive solute concentration in the case of zero-order reaction kinetics,

$$\hat{C}_r(t) = C_r^0 \left(\frac{C_r^m(t)}{C_r^0} - \frac{C_t^m(t)}{C_t^0} + 1 \right), \text{ is the dotted line.}$$

coefficient (positive for $C_r > 0$ and zero elsewhere); \mathbf{u} is the velocity vector; and D is the dispersion tensor. In this case, the following transformation of the reactive solute concentration measurements may be used

$$C_r(t) = C_r^0 \left(\frac{C_r^m(t)}{C_r^0} - \frac{C_t^m(t)}{C_t^0} + 1 \right) \quad (4)$$

where C_r^0 and C_t^0 are the concentrations at which the two solutes are injected and $C_r^m(t)$ and $C_t^m(t)$ are the concentrations measured at the well at time t . Time $t = 0$ corresponds to the beginning of the pull stage. This transformation removes the effect of dilution from the reactive solute concentration. The quantity $\hat{C}_r(t)$, no matter what the advection or dispersion, is described by the zero-order decay equation

$$\frac{\partial \hat{C}_r(t)}{\partial t} = -\alpha \quad (5)$$

or

$$\hat{C}_r(t) = C_r^0 - \alpha t \quad (6)$$

(See Appendix A for the derivation.) If the reactive solute is decaying at zero-order, a plot of time versus $\hat{C}_r(t)$ will fall on a straight line with a slope equal to the zero-order reaction rate.

Simulated Results for Zero-Order Kinetics

In order to illustrate the technique, the computer-based finite-difference transport model described in Reinhard et al. (1997) is used to simulate the transport of a conservative and a reactive solute undergoing zero-order decay with a reaction rate coefficient, $\alpha = 0.12$ mg/L/day. Figure 1 shows the simulated data and the quantity $\hat{C}_r(t)$ (Equation 4). Notice that it falls on a line with slope $-\alpha$.

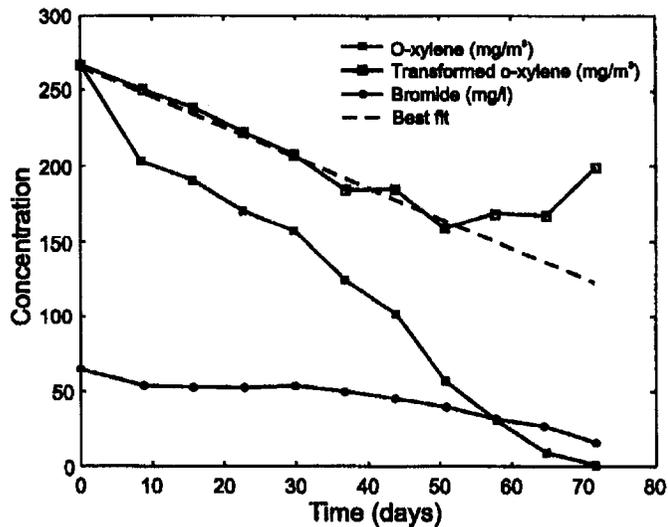


Figure 2. Experimental data from Seal Beach, California.

Thus, the reaction rate can be easily calculated by plotting the data in this manner.

This method allows the practitioner to isolate the effect of transformation from the effect of dilution due to mixing with native ground water. A problem with assessing in situ reaction rates is the inability to distinguish among the many processes affecting the fate and transport of the solute. A reaction rate estimated directly from the raw data would tend to be an overestimate because dilution would be mistaken for transformation. Dilution is accounted for by plotting the transformed data. This is achieved without prior knowledge of aquifer parameters, such as hydraulic conductivity, dispersivity, or regional ground water flow.

Experimental Results for Zero-Order Kinetics

Now we examine data obtained from a push-pull experiment performed at a gasoline-contaminated aquifer in Seal Beach, California. One of the goals of the experiment was to assess the in situ zero-order reaction rates of BTEX compounds. (See Reinhard et al. [1997] for a complete description of the experiment and results.) We present the results for one compound, o-xylene, to illustrate the method and motivate a discussion about some issues that arise when the method is applied to experimental data.

Figure 2 shows the measured bromide (the conservative tracer) concentration and the measured o-xylene concentration. The transformed o-xylene concentration is also plotted along a best fit line with a slope equal to the estimated zero-order reaction rate of approximately $2 \mu\text{g/L/day}$. Reinhard et al. (1997) calculate a degradation rate of $0.1 \mu\text{g/L/hr} = 2.4 \mu\text{g/L/day}$ in the traditional manner of adjusting parameters in a computer-based model. The reaction rate coefficients calculated by the two methods agree well.

Notice that transformed o-xylene measurements fit a line well through day 60. However, at long time, after day 60, the fit deteriorates. This is due, in part, to measurement error. Since the concentration is low at long times, measurement error may be a greater percentage of the measured values. The fit may also break down because the reactive transport of the o-xylene is not described completely by Equation 2. Even though over most of the concentration range the degradation does follow zero-order kinetics, at low concentration the effective reaction may not be zero-order. Also, the reaction rate constant α may not be constant in space. The reaction

rate depends on local geochemical conditions which vary in space. For example, the microbes responsible for the degradation may not be evenly distributed throughout the aquifer, and electron acceptors or other needed compounds may not be present everywhere.

Even if the fate and transport of the reactive solute is described perfectly by Equation 2, the transformation of the measured reactive solute concentration may still break down at long time due to heterogeneity in the flow field. In the derivation we assume that the zero-order reaction rate coefficient, α , is constant in space and time, but because α depends on C_r (i.e., α is zero where C_r is zero), the temporal and spatial derivatives of α will not be zero at the fringes of the plume where C_r —thus, α —goes from a positive value to zero. Heterogeneity in the flow field will tend to increase the area of the interface between the plume and the native ground water, thus increasing the effect of the discontinuity in α . However, away from the interface the transformation is valid. In the case of a homogeneous aquifer in the absence of regional flow, the flow will be radial towards the well. In this case, all the solute affected by the fringes of the plume will arrive at the same long time and Equation 6 will be valid until then. However, in the heterogeneous case, some solute affected by the fringes may arrive sooner, causing Equation 6 to break down earlier. This issue needs to be investigated further but goes beyond the scope of this paper. In general the method will work, although more weight should be given to the earlier measurements. Increasing the injection volume and concentration will tend to minimize the effect of the slug fringe.

Case 2: First-Order Reaction Kinetics

In the case of first-order reactions, the transport of the two solutes is described by the following equations:

$$\frac{\partial C_t}{\partial t} + L(C_t) = 0 \quad (7)$$

and

$$\frac{\partial C_r}{\partial t} + L(C_r) = -\beta C_r \quad (8)$$

where β is the first-order reaction rate constant. Under these conditions the following equation will hold and can be used to estimate the reaction rate constant.

$$\ln \left(\frac{C_r^m(t)}{C_t^m(t)} \right) = \ln \left(\frac{C_r^0}{C_t^0} \right) - \beta t \quad (9)$$

(Haggerty et al. 1996 and 1998 present similar results.) See Appendix B for the derivation of the equation. If a line is fitted to a plot of time versus $\left(\frac{C_r^m(t)}{C_t^m(t)} \right)$, the slope of that line will yield an estimate of the first-order reaction rate constant.

Simulated Results for First-Order Kinetics

Figure 3 shows the simulated data from a computer-based transport model for a conservative solute and a reactive solute undergoing first-order decay with a reaction rate constant of $\beta = 0.012 \text{ day}^{-1}$. (The model described in Reinhard et al. [1997] is modified slightly to include first-order reactions and is used for the

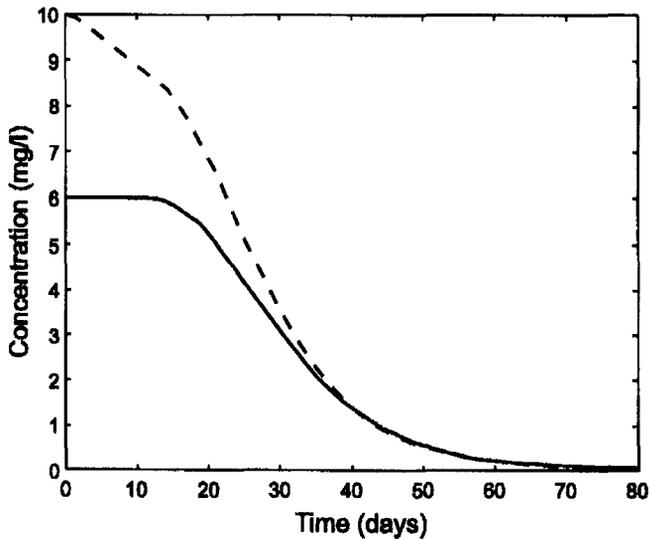


Figure 3. Simulated data. The solid line is the measured conservative solute concentration and the dashed line is the concentration of a reactive solute undergoing first-order decay.

simulation.) Figure 4 shows a plot of $\ln\left(\frac{C_r^m(t)}{C_t^m(t)}\right)$, which is a line with slope $-\beta$. The reaction rate can be calculated directly from the data.

Notice that the quantity $\ln\left(\frac{C_r^m(t)}{C_t^m(t)}\right)$ becomes unstable at long time (Figure 4). This is due to slight numerical errors in the computer-based transport model. No matter how good the numerical algorithm that solves the transport equations may be, there will always be numerical errors associated with it. The longer the simulation, the more these errors will compound. The effect of the error will be most pronounced at long time when the errors are large compared to the concentration. This is another reason for investigating methods that do not require the use of computer-based transport models.

Discussion

We have demonstrated how data from push-pull tests may be used to infer zero- and first-order reaction rate constants directly. The method is simple and cost effective, as it does not involve the use of numerical models or knowledge of hydraulic parameters. There are a number of difficulties associated with using computer-based transport models to infer reaction rates. Computer models require parameter inputs such as regional ground water flow rates, conductivity values, and dispersion coefficients. None of these parameters can be determined exactly and must be estimated from data. Since the input parameters to the computer-based model are estimates, the solution to the transport equations can only be approximate. Therefore, any estimate of the reaction parameter will contain some error due to errors in the parameter inputs. Additional errors may result from the manner in which the equations are solved numerically. Although numerical errors can be minimized by reducing the time step and grid size, this increases computation time. In the case of a push-pull experiment, the numerical model must accurately account for the dilution of the two solutes. Since the scale of the test slug is relatively small (less than a few cubic meters), a macro-dispersion coefficient may not be used; rather, a small dispersivity is needed. Reinhard et al. (1997) found a dispersivity of 5.0 cm was required to accurately reproduce the

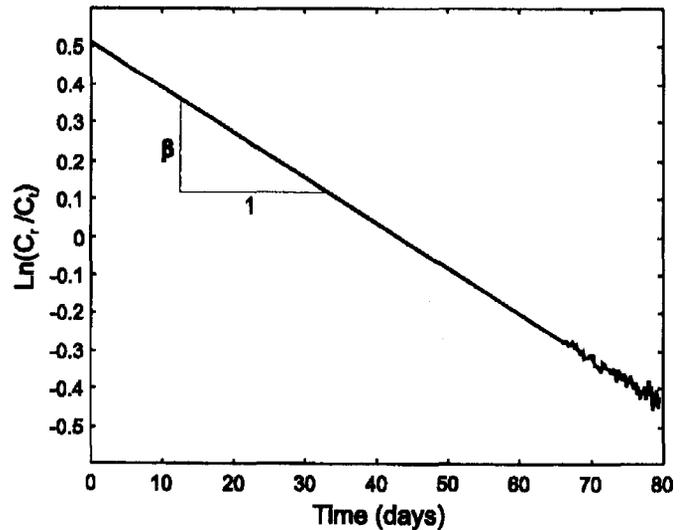


Figure 4. Plot of $\ln\left(\frac{C_r^m(t)}{C_t^m(t)}\right)$ to find the first-order reaction rate.

tracer data. A small dispersivity will require that the transport equations be solved over a fine grid which will increase the computation time. Furthermore, since the goal is to estimate the reaction rate, the computer-based model must be run many times until a good estimate of the reaction rate is achieved. The method presented previously avoids all these problems and is more accurate.

The proposed method is also general enough to perform well under most experimental conditions. The specific experimental design of a push-pull test may be varied to fit the site and compounds of interest. For example, if the reaction rates are slow, the sampling time may be extended. If the regional flow velocities are high, the injected volume may be increased and the extraction time shortened to ensure that the slug does not drift away from the well. Reinhard et al. (1997) and Istok et al. (1997) provide examples of two different approaches to a push-pull test. The method presented in this paper will work with either experimental setup. Therefore, we do not advocate any particular sampling scheme or experimental design. We have presented a simple method for estimating zero- and first-order in situ reaction rate coefficients that will perform well given any push-pull experiment, provided the assumptions made are practically valid.

The push-pull test itself is cost effective, as it involves data from only one well. Thus, only one well needs to be installed and outfitted with the injection/extraction equipment. The usefulness of the tests has been demonstrated by, among others, Istok et al. (1997) and Reinhard et al. (1997). Although regulatory agencies have been hesitant to allow the injection of contaminants into the subsurface for experimental reasons, this attitude is changing. As more studies are performed and our ability to control the injected contaminants is demonstrated, the use of push-pull tests will become more accepted and prevalent. Methods such as those proposed here and the one presented in Haggerty et al. (1998) make the push-pull test all the more useful.

Summary

Let us review the key assumptions used in the analysis. They are:

- Solutes are injected simultaneously as a well-mixed slug.
- Injection time is short compared to the overall length of the experiment.

- Dominant processes are advection, dispersion, and constant coefficient zero- or first-order reactions.
- Other processes such as sorption are negligible.
- Background concentrations are negligible.
- If the flow field is highly heterogeneous, more weight should be given to early measurements.

Given these few assumptions, measurements from a push-pull test can be used to calculate the reaction rates directly. Errors in the calculated value will be due only to measurement error and violations of the assumptions. In many cases encountered in practice, these assumptions will be practically valid and the method may be used.

Appendix A: Derivation for the Zero-Order Case

The equations describing the transport of the two solutes are

$$\frac{\partial C_r}{\partial t} + L(C_r) = -\alpha \quad (10)$$

and

$$\frac{\partial C_t}{\partial t} + L(C_t) = 0 \quad (11)$$

where α is the zero-order reaction rate and L is the operator

$$L(\cdot) = u \cdot \nabla - \nabla \cdot D \nabla \quad (12)$$

Note that α is a positive constant for $C_r > 0$ and zero elsewhere. Let us assume that the solutes are injected at constant concentration and fast compared to the time scale of the reaction, i.e., an insignificant quantity of mass is lost during the injection. Given this assumption, the two solutes will exist in equal proportions everywhere in the aquifer at the end of the injection stage. That is,

$$\frac{C_r(x,0)}{C_r^0} = \frac{C_t(x,0)}{C_t^0} = C_{in}(x) \quad (13)$$

where C_r^0 and C_t^0 are the injection concentrations of the reactive and conservative solutes and $C_{in}(x)$ is the initial concentration distribution with spatial coordinates $x = (x_1, x_2, x_3)$.

During the extraction phase C_r and C_t will satisfy Equations 10 and 11 with initial conditions given by Equation 13 and boundary conditions

$$C_r(x \in \Gamma, t) = 0 \quad (14)$$

$$C_t(x \in \Gamma, t) = 0 \quad (15)$$

$$\frac{\partial C_r(x \in \gamma, t)}{\partial \eta} = 0 \quad (16)$$

$$\frac{\partial C_t(x \in \gamma, t)}{\partial \eta} = 0 \quad (17)$$

where Γ is the far field boundary, γ is the boundary around the well, and η is the vector normal to the boundary. The first two boundary conditions assume that far from the well the concentrations of the

two solutes are zero. This is a reasonable assumption if the background concentrations of the two solutes are negligible. The second two boundary conditions assume that diffusion into the well can be neglected during the extraction phase. This assumption is also reasonable because near the well velocities are high and advection will be the dominant transport mechanism. These are the same boundary conditions used in the transport model employed by Reinhard et al. (1997). We seek a quantity which will behave as the reactive solute concentration would in a batch reactor. We claim this quantity is

$$\hat{C}_r(x,t) = C_r^0 \left(\frac{C_r(x,t)}{C_r^0} - \frac{C_t(x,t)}{C_t^0} + 1 \right) = C_r^0 - \alpha t \quad (18)$$

where α is a positive constant when $C_r > 0$ and 0 when $C_r = 0$. Notice that this will hold if

$$C_r(x,t) = \frac{C_r^0}{C_t^0} C_t(x,t) - \alpha t \quad (19)$$

Thus, we need only to verify that the expression for $C_r(x,t)$ (Equation 19) satisfies the initial condition and boundary conditions for C_r and the transport equation (Equation 10). The initial conditions are satisfied: at time $t=0$, Equation 19 yields $C_r(x,0) = C_r^0$. The boundary conditions are also satisfied as the spatial derivatives of αt are zero and α is zero far from the influence of the slug where the reactive solute concentration is zero. We now need to verify that this expression satisfies the governing equation. Substituting Equation 19 into the left-hand side of Equation 10 yields

$$\begin{aligned} & \frac{\partial \left(\frac{C_r^0}{C_t^0} C_t - \alpha t \right)}{\partial t} + L \left(\frac{C_r^0}{C_t^0} C_t - \alpha t \right) \\ &= \frac{C_r^0}{C_t^0} \left(\frac{\partial C_t}{\partial t} + L(C_t) \right) - \alpha = -\alpha \end{aligned} \quad (20)$$

since the spatial and temporal derivatives of α are always zero within the slug. We have shown that the solution for $C_r(x,t)$ in Equation 19 satisfies the initial and boundary conditions and the governing equation, which is sufficient to prove the relationship. The quantity $\hat{C}_r(x,t)$ is found by rearranging Equation 19.

The assumption that the derivatives of α are always zero is not true at the fringes of the slug where C_r and thus α goes from a positive value to zero. However, concentrations measured at the well will not be affected until water (which has been depleted of the reactive solute) is extracted. In the idealized case of a homogeneous aquifer in the absence of regional flow, the injected slug will always maintain a cylindrical shape and all the water affected by the fringes of the slug will arrive at the same time. Thus, the method described here will exactly satisfy the transport equations until all of the reactive solute has been extracted. In heterogeneous aquifers or in the presence of strong regional flow, the method will begin to break down earlier because some water affected by the fringes of the slug will be extracted before all the reactive solute can be recovered. In such cases, increasing the slug volume and concentrations will increase the time and range of concentration over

which the method will be valid.

It should be noted that computer-based numerical models suffer from similar problems due to the discontinuity of the zero-order reaction rate coefficient α . If the fringes of the plume are to be modeled accurately, the time step must be decreased. If the slug concentrations are low at the fringes, a small time step is required to accurately capture the degradation of the reactive solute. Additionally, computer-based transport models tend to overpredict the amount of mixing, and thus degradation, occurring at the fringes of the plume. This is because computer-based models cannot represent all the heterogeneity in the flow field explicitly; rather, they must account for its effect through the use of dispersivity or dispersion coefficients. The use of these effective parameters will cause the model to overpredict the amount of mixing. This effect is most pronounced at the fringes of the plume where concentration gradients are generally the steepest. Therefore, even when using numerical models, concentration values that have been affected by mixing at the interface between the plume and the native ground water may be in error. This method will perform better than computer-based numerical models given the inherent uncertainties in model inputs, such as the hydraulic conductivity field and regional flow velocities, and given grid size and time step requirements to model processes occurring at this scale. Of course, computer-based numerical models are still necessary when practitioners wish to account for other processes, such as sorption or spatially varying reaction rate coefficients.

Appendix B: Derivation for the First-Order Case

The equations describing the transport of the two solutes are

$$\frac{\partial C_r}{\partial t} + L(C_r) = -\beta C_r \quad (21)$$

and

$$\frac{\partial C_t}{\partial t} + L(C_t) = 0 \quad (22)$$

where β is the first-order reaction rate. Let us assume, as before, that the solutes are injected at constant concentration and fast compared to the time scale of the reaction term. Given this assumption, at the end of the injection stage, the two solutes will exist in equal proportions everywhere in the aquifer (Equation 13). Then, during the extraction phase, C_r and C_t will satisfy Equations 21 and 22 with initial conditions given by Equation 13. The boundary conditions are given by Equations 14 through 17. We claim that

$$\ln \left(\frac{C_r(x,t)}{C_t(x,t)} \right) = \ln \left(\frac{C_r^0}{C_t^0} \right) - \beta t \quad (23)$$

or that

$$C_r(x,t) = \frac{C_r^0}{C_t^0} C_t(x,t) \exp(-\beta t) \quad (24)$$

Notice that Equation 24 satisfies the initial and boundary conditions. Let us check that it satisfies the governing transport Equation 21. Substituting Equation 24 into the left-hand side of Equation 21 yields

$$\begin{aligned} & \frac{\partial \left(\frac{C_r^0}{C_t^0} C_t \exp(-\beta t) \right)}{\partial t} + L \left(\frac{C_r^0}{C_t^0} C_t \exp(-\beta t) \right) = \\ & \frac{C_r^0}{C_t^0} \exp(-\beta t) \left[\frac{\partial C_t}{\partial t} + L(C_t) \right] - \beta \left[\frac{C_r^0}{C_t^0} C_t \exp(-\beta t) \right] = \\ & -\beta \left[\frac{C_r^0}{C_t^0} C_t \exp(-\beta t) \right] = -\beta C_r \end{aligned} \quad (25)$$

That is, expression 24 satisfies the governing equation for C_r , which is sufficient to prove the proposed relationship of Equation 23.

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