

## Conditional moments of the breakthrough curves of kinetically sorbing solutes

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**Abstract** We present a methodology for calculating the conditional temporal moments of kinetically sorbing solutes based on the conditional temporal moments of non-reactive tracers. The methodology is based on a Lagrangian description of solute transport in heterogeneous media, and it can be applied to a large variety of flow configurations and mass-transfer rate-limited processes. A stochastic approach is needed, as a deterministic description of the velocity field is usually not available. Conditioning the temporal moments on hydraulic conductivity or transmissivity measurements improves the accuracy and reduces the uncertainty in the results, as shown by a reduction in the variance of the travel time. We present results showing the effect of the geochemical parameters on the reduction in uncertainty obtained by conditioning.

### INTRODUCTION

The moments of breakthrough curves (BTCs) in heterogeneous domains are usually analyzed using the travel time approach. Temporal moments are useful when characterizing subsurface transport, because concentrations measured in field tracer experiments are usually measured at various times at one or several locations downstream. In addition, regulations often concern the probability of exceeding a certain concentration before a certain time. Due to imperfect knowledge of the subsurface, the travel time,  $\tau$ , that is, the time for a particle to move from the input to the measurement location, cannot be fully predicted. The stochastic approach consists of considering  $\tau$  as a Space Random Function (SRF) and deriving its statistical moments. Uncertainty in  $\tau$  can be reduced by conditioning on hydrogeological or geophysical data.

In Lawrence et al. (submitted), we present a concise methodology for estimating the conditional moments of BTCs for non-conservative solutes as a function of the conditional temporal moments of conservative solutes based on a Lagrangian methodology. We consider heterogeneous hydrological parameters, and homogeneous geochemical parameters. We find a general expression for the expected BTC of a reactive solute undergoing chemical reactions in a heterogeneous hydraulic conductivity field. The conditional temporal moments, valid independently of flow configuration, are derived for the general model proposed by Haggerty and Gorelick (1998), which considers a continuous distribution of mass transfer rate coefficients. This paper briefly summarizes the method used in Lawrence et al. (submitted) and shows the effect of the geochemical parameters in the two-site kinetics model on the reduction of uncertainty due to conditioning.

## MATHEMATICAL STATEMENT OF THE PROBLEM AND GENERAL SOLUTION

We consider a non-conservative solute traveling from an injection point to a discharge location. The solute follows a certain streamline, which is unknown due to heterogeneity. Along this streamline, we can write the advection-dispersion equation, which includes a term that accounts for mass transfer between a mobile and an immobile phase. We use the general model proposed by Haggerty and Gorelick (1998), which considers a continuous distribution of mass transfer rate coefficients. Several common models, such as instantaneous equilibrium, two-site kinetics, and a lognormal distribution of rate parameters, can be obtained as special cases of this model. Disregarding the influence of pore-scale dispersion, the resulting equations are:

$$\frac{\partial C_1}{\partial T} + \beta_{\text{tot}} \int_0^{\infty} p(\alpha) \frac{\partial C_2(\alpha)}{\partial T} d\alpha + V \frac{\partial C_1}{\partial \eta} = 0, \quad (1)$$

$$\frac{\partial C_2(\alpha)}{\partial T} = \alpha(C_1 - C_2(\alpha)), \quad (2)$$

where  $C_1$  is the mobile concentration per unit volume of fluid;  $C_2$  is the immobile concentration per unit mass of soil;  $V$  is dimensionless velocity ( $V = v / U$ , where  $v$  is the actual velocity, and  $U$  is the mean velocity);  $T$  is dimensionless time ( $T = U t / I_Y$ , where  $t$  is actual time, and  $I_Y$  is the integral scale of the log-hydraulic conductivity,  $Y$ , in the mean flow direction);  $\eta$  is the coordinate along the streamline, non-dimensionalized by  $I_Y$ ;  $\beta_{\text{tot}}$  is the dimensionless total capacity coefficient; and  $p(\alpha)$  represents the volumetric fraction of the solid that reacts at a particular rate,  $\alpha$ , where  $\alpha$  is a dimensionless mass transfer rate coefficient.

The distance from the injection point to the control point or plane, non-dimensionalized by  $I_Y$ , is  $L$ . For a pulse of concentration injected at time zero into a clean aquifer, the initial conditions are  $C_1(\eta, T=0) = C_2(\eta, T=0) = 0$ , and the boundary conditions are  $C_1(\eta \rightarrow \infty, T) = 0$ , and  $C_1(\eta = 0, T) = \delta(t)$ . After applying the Laplace transform to equations (1) and (2) under these conditions, the resulting equation for  $C_1(\eta, t)$  is (after Rubin et al., 1997):

$$s \bar{C}_1(\eta, s)(1 + H(s)) = -V \frac{\partial \bar{C}_1(\eta, s)}{\partial \eta}, \quad (3)$$

$$\text{with } H(s) = \beta_{\text{tot}} \int_0^{\infty} \frac{\alpha p(\alpha)}{\alpha + s} d\alpha, \quad (4)$$

where  $s$  is the Laplace variable, and an overbar indicates the Laplace transform of a variable. Because the geochemical parameters are considered homogeneous,  $H$  does not

depend on location, but only on  $s$  and the parameters used to characterize  $p(\alpha)$ . For a unit pulse injection, the concentration at the control point or plane at a distance  $L$  downstream is

$$\bar{C}_1(L, s) = \exp(-s\tau(L)(1 + H(s))). \quad (5)$$

where  $\tau(L) = \int_0^{\eta(L)} \frac{d\eta'}{V(\eta')}$  corresponds to the travel time of a conservative tracer along the trajectory from the injection point ( $\eta=0$ ) to the control point or plane ( $\eta(L)$ ). In this approach  $V$  and  $\eta$ , and thus  $\tau$ , are SRFs. Therefore, it is better to work with the conditional expectation of the breakthrough curve, given by

$$\langle \bar{C}_1(L, s) \rangle^C = \langle \exp(-s\tau(L)(1 + H(s))) \rangle^C, \quad (6)$$

where  $^C$  stands for conditional. By Aris (1958), the non-central reactive moments of the expected breakthrough curve,  $t_i^R(L) = \int_0^\infty t^i \langle C_1(L, t) \rangle dt$ , are given by  $t_i(L) = (-1)^i d^i \langle \bar{C}_1(L, s) \rangle / ds^i \Big|_{s=0}$ . Using this and the relationships between central and non-central moments,

$$\langle \tau^R \rangle = t_1^R(L) \quad (7)$$

$$\text{and } \sigma_\tau^{2,R} = t_2^R(L) - [t_1^R(L)]^2, \quad (8)$$

the first two conditional reactive central temporal moments (mean and variance) are obtained:

$$\langle \tau^R \rangle^C = (1 + \beta_{\text{tot}}) \langle \tau^{\text{NR}} \rangle^C, \quad (9)$$

$$\sigma_\tau^{2,R,C} = \sigma_\tau^{2,\text{NR},C} (1 + \beta_{\text{tot}})^2 + 2\beta_{\text{tot}} \langle \tau^{\text{NR}} \rangle^C \int_0^\infty \frac{p(\alpha)}{\alpha} d\alpha, \quad (10)$$

where  $^R$  and  $^{\text{NR}}$  stand for reactive and non-reactive solutes, respectively. Notice that the derivation is general, and therefore valid regardless of flow configuration or dimensionality of the problem. The non-central conditional temporal moments for conservative tracers  $t_i^C(L)$  can be obtained from the conditional cumulative distribution function (CDF) of  $\tau$ ,  $G^C(L, \tau)$ , as:

$$t_i^C(L) = \int_0^\infty i\tau^{i-1} (1 - G^C(L, \tau)) d\tau, \quad (11)$$

$$\text{with } G^c(L, \tau) = \frac{1}{2} \operatorname{erfc} \left\{ \frac{L - \langle X_1(\tau) \rangle^c}{\sqrt{2X_{11}^c(\tau)}} \right\}, \quad (12)$$

where  $\langle X_1(\tau) \rangle$  is the mean displacement, and  $X_{11}(\tau)$  is the second moment of the longitudinal displacement. Conditioning can take into account all available measurements, such as transmissivity values, heads, velocities, and geophysical data.

## ILLUSTRATIVE EXAMPLES

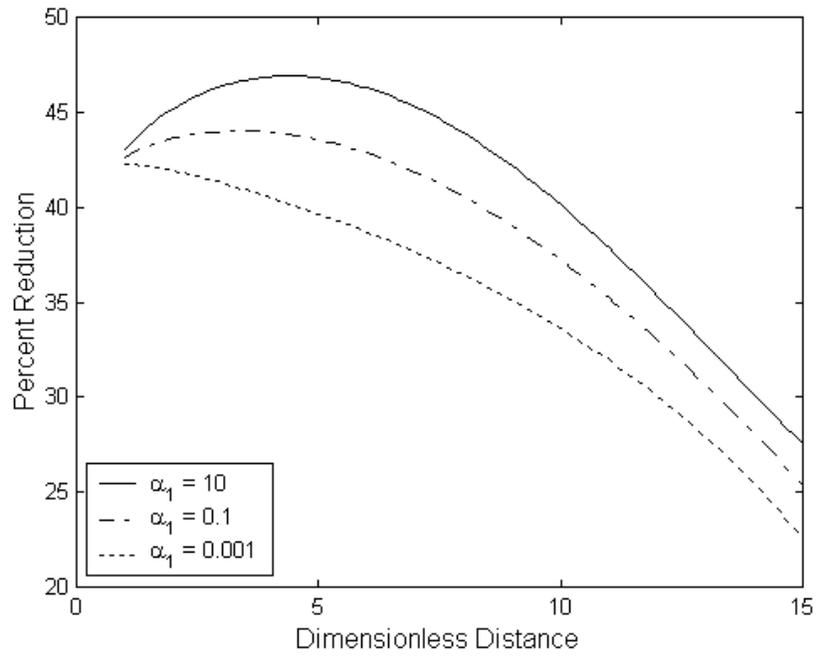
The geochemical model corresponding to a solute that undergoes reactions limited by two-site kinetics depends on four parameters: the capacity coefficients,  $\beta_1$  and  $\beta_2$  ( $\beta_{\text{tot}} = \beta_1 + \beta_2$ ); and the rate parameters,  $\alpha_1$  and  $\alpha_2$ . The function  $p(\alpha)$  is given by

$$p(\alpha) = \frac{\beta_1}{\beta_{\text{tot}}} \delta(\alpha - \alpha_1) + \frac{\beta_2}{\beta_{\text{tot}}} \delta(\alpha - \alpha_2). \quad (13)$$

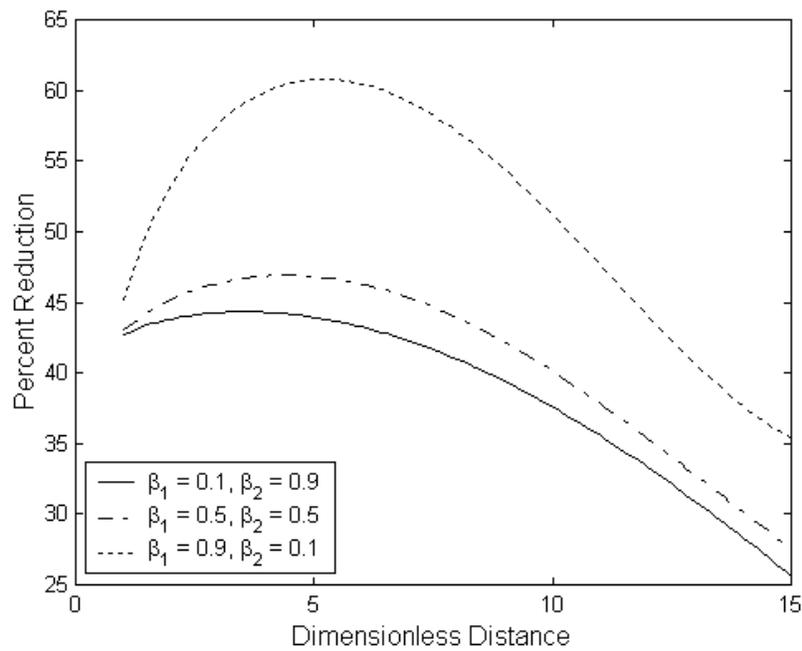
To study the efficiency of conditioning, we use results from Rubin (1991), who gave several examples of the effect of conditioning with transmissivity values on statistical moments of conservative tracers. In particular, we select one example that corresponds to conditioning by 9 transmissivity values located at dimensionless distances  $D=1.25 \times i$  ( $i=0,1,\dots,8$ ) downgradient from the point of injection. The mean and covariance of the longitudinal displacement are given as curve d in Figures 7a and 7b in Rubin (1991). From (12), the conditional CDF of  $t$  is obtained. Then, we can compute the moments in (9) and (10).

We define a parameter that accounts for the reduction in variance of travel time from the unconditional to the conditional case.

$$\text{Percent Reduction} = \frac{|\sigma_{\tau}^{2,R,NC} - \sigma_{\tau}^{2,R,C}|}{\sigma_{\tau}^{2,R,NC}} 100\% \quad (14)$$



**Figure 1:** Effect of  $\alpha_1$  on the percent reduction in the travel time variance due to conditioning for three different cases of the two-site model. For all curves,  $\beta_1 = \beta_2 = 0.5$ ,  $\alpha_2 = 0.1$ , and  $\sigma_Y^2 = 0.5$ .



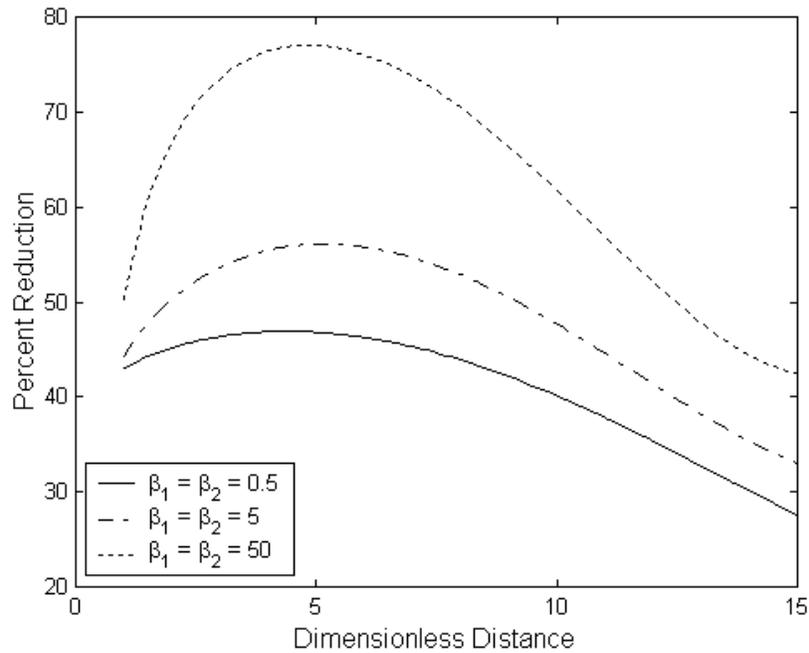
**Figure 2** Effect of  $\beta_1$  and  $\beta_2$  on the percent reduction in the travel time variance due to conditioning for three different cases of the two-site model. For all curves,  $\alpha_1 = 10$ ,  $\alpha_2 = 0.1$ , and  $\sigma_Y^2 = 0.5$ .

Figure 1 shows the effect of changing one of the rate parameters on the percent reduction in the travel time variance due to conditioning. For all three curves,  $\beta_1 = \beta_2 = 0.5$ ,  $\alpha_2 = 0.1$ , and  $\sigma_Y^2 = 0.5$ . As  $\alpha_1$  decreases from 10 to 0.001, conditioning becomes less effective, as shown by the decrease in the percent reduction of the travel time variance. However, even when  $\alpha_1 = 0.001$ , conditioning is still important, reducing uncertainty by over 40% near the source. Because transport of solutes undergoing instantaneous equilibrium reactions are governed by the same equations as non-reactive transport, with only a rescaling of the velocity and diffusion coefficient to account for the retardation factor, the effect of conditioning for the case of instantaneous equilibrium may be similar to the effect on non-reactive transport. Rubin (1991) obtained a percent reduction of travel time variance of over 80% near the source for a conservative tracer using the data that this example uses. The increased effect of conditioning for larger rate parameters can be understood by noting that as the rate parameter increases, the solute can exchange with the immobile phase more quickly, approaching the case of instantaneous equilibrium. Therefore, results for increasingly larger rate parameters would be expected to increase to approach the value found by Rubin (1991) for non-reactive solutes.

The effect of conditioning decreases with increasing travel distance. The reason is that the data extends only to a distance of 10 integral scales. One would expect that when the solute has traveled a large number of integral scales without additional conditioning data, the effect of conditioning would be null. In any case, the effect at a distance of 15 integral scales is still quite significant.

Figure 2 shows the effect of changing the proportion of sorption sites associated with each rate parameter, while keeping the total capacity coefficient constant at 1. The combination of rate parameters with the largest reduction in uncertainty from Figure 1 is used, that is  $\alpha_1 = 10$ ,  $\alpha_2 = 0.1$ . Again,  $\sigma_Y^2 = 0.5$ . Notice from Figure 2 that as  $\beta_1$  increases, the percent reduction of variance due to conditioning increases. As  $\beta_1$  increases, more of the sorption sites are associated with  $\alpha_1$ , the higher rate parameter. One would expect the percent reduction of variance to increase when more sorption sites have a high rate parameter, because it increases in Figure 1 when  $\alpha_1$  increases.

Figure 3 shows the effect of the total capacity coefficient on the percent reduction of travel time variance due to conditioning.  $\beta_1 = \beta_2$  for all three curves. Again,  $\alpha_1 = 10$ ,  $\alpha_2 = 0.1$ , and  $\sigma_Y^2 = 0.5$ . As the total capacity coefficient increases, the effect of conditioning increases. Although this may make it appear that there is less uncertainty for large values of the capacity coefficients after conditioning, that is not the case. The larger values of the capacity coefficients result in much larger unconditional and conditional travel time variances. However, conditioning causes a more significant change when the capacity coefficients are large. Therefore, in aquifers with large capacity coefficients, conditioning can be extremely helpful. For example, when the total capacity coefficient is 100, for a distance around five integral scales downgradient from the source, conditioning reduces the travel time variance by over 75%.



**Figure 3:** Effect of total  $\beta$  on the percent reduction in the travel time variance due to conditioning for three different cases of the two-site model. For all curves,  $\alpha_1 = 10$ ,  $\alpha_2 = 0.1$ , and  $\sigma_Y^2 = 0.5$ .

## CONCLUSIONS

Based on a Lagrangian approach to solute transport in heterogeneous media, we develop a concise and integrated methodology for evaluating the conditional temporal moments of a reactive solute. The obtained temporal moments are valid for different flow configurations, including convergent flow. The methodology can also be applied to a very wide range of linear mass-transfer rate-limited processes, which can be considered special cases of the continuous model of Haggerty and Gorelick (1998). The dependence of the temporal moments on only the chemical parameters and the temporal moments of a non-reactive tracer reduces computational effort, because the moments of the non-reactive tracer can be calculated once, and then used repeatedly with the applicable chemical parameters.

For the two-site kinetics model, the effect of conditioning was investigated for different values of the model parameters. Conditioning is most effective when the rate coefficients are high and the capacity coefficients are large. In all cases investigated, conditioning provided significant improvements over the unconditional case, in terms of the percent reduction in the travel time variance.

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## REFERENCES

Aris, R., On the dispersion of linear kinematic waves. *Proc. R. Soc. London A*, 245, 268-277, 1958.

Haggerty, R., and Gorelick, S. M., Modeling mass transfer processes in soil columns with pore-scale heterogeneity. *Soil Sci. Soc. Am. J.*, 62(1), 62-74, 1998.

Lawrence, A. E., X. Sanchez-Vila, and Y. Rubin, Conditional moments of the breakthrough curves of kinetically sorbing solute in heterogeneous porous media using multirate mass transfer models for sorption and desorption. *Water Resour. Res.*, submitted.

Rubin, Y., Prediction of tracer plume migration in disordered porous media by the method of conditional probabilities. *Water Resour. Res.*, 27(6), 1291-1308, 1991.

Rubin, Y., Cushey, M. A., and Wilson, A., The moments of the breakthrough curves of instantaneously and kinetically sorbing solutes in heterogeneous geologic media: Prediction and parameter inference. *Water Resour. Res.*, 33(11), 2465-2481, 1997.