Demonstrations in Solute Transport Using Dyes: II. Modeling

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ABSTRACT

The numerical representation of flow and solute transport is often intimidating to the introductory student. Quantifying the results of simple demonstrations in chemical movement is a valuable introduction to transport modeling and parameter estimation. A solution of the convection-dispersion equation (CDE) is used to describe the solute breakthrough curves generated in the demonstrations suggested in the companion paper. Estimation of the best fit model parameters (solute velocity, dispersion, and retardation) is illustrated step-by-step using the method of moments for an example data set. In addition to the model fitting exercise, the predictive merits of the CDE are demonstrated by employing secondary measurements to estimate the parameters. The most important of these supportive measurements is characterization of the soil-dye adsorption isotherm. The blue dye displays linear adsorption in the sand and clay loam (K_o of 0.25 m^3 Mg^-1 and 2.19 m^3 Mg^-1, respectively) while the yellow dye is nonadsorbed. It is found that the CDE predicts the dye movement fairly well in a sand, but performs poorly in a clay loam with organic matter. The poor prediction in the clay loam is attributed to the idealized nature of the isotherm measurement and shuttling of the dye with mobile organic material.

THEORETICAL CONSIDERATIONS

The Model

Solute transport in soil columns is commonly modeled using a partial differential equation known as the convection-dispersion equation (or advection-dispersion in the engineering literature). For steady-state water flux, \( q \) (m s\(^{-1}\)), in a homogeneous medium at water content \( \theta \), the governing equation for transport of a conservative solute undergoing linear, equilibrium adsorption has the form

\[
\frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} - V^* \frac{\partial C}{\partial x} \quad [1]
\]

where \( C \) (mol m\(^{-3}\)) is solute concentration, \( V^* \) (m s\(^{-1}\)) is the mean pore-water velocity, \( D^* \) (m\(^2\) s\(^{-1}\)) is the dispersion coefficient, \( x \) (m) is distance, and \( t \) (s) is time. The dimensionless \( R \) parameter is called the retardation factor and accounts for reversible adsorption of the solute to the solid phase and is given by

\[
R = 1 + \rho_B K_D/\theta \quad [5]
\]

where \( \rho_B \) is the bulk density (Mg m\(^{-3}\)) and \( K_D \) is the linear partition coefficient of the solute adsorption isotherm.

Numerous analytical solutions of Eq. [1] for a variety of initial and boundary conditions are available (Kreft and Zuber, 1978; van Genuchten and Alves, 1982). For a very narrow pulse input to a soil column of length \( L \) (m), the solute concentration exiting the column as a function of time (called the solute breakthrough curve, BTC) is given by

\[
C(L, t) = \frac{M_0 L}{2q \sqrt{\pi D^* t^3}} \cdot \exp \left( - \frac{(L - V^* t)^2}{4D* t} \right) \quad [6]
\]

where \( M_0 \) (mol m\(^{-2}\)) is the input mass/area (Barry and Sposito, 1988). Because of the imprecision in flux control inherent with simple setups, it is advisable to plot concentration vs. cumulative drainage, \( I \) (m), when presenting the breakthrough curves. To rewrite Eq. [6] in terms of \( I \), simply replace \( t \) with \( I/q \). The result is

Abbreviations: CDE, convection-dispersion equation; BTC, breakthrough curve.


\[ C(L, I) = \frac{M_0 L}{2\pi D\tau} \exp\left(-\frac{(L - V\tau I)^2}{4D\tau}\right) \]  

where the parameters in Eq. [6] and [7] are related such that

\[ V\tau = \frac{V^*}{q} \]  

\[ D\tau = \frac{D^*}{q} \]  

Note that \( V\tau \) is dimensionless and \( D\tau \) has units of length. While Eq. [6] is a steady state solution of the CDE, modeling solute concentrations as a function of cumulative drainage instead of time (Eq. [7]) is a simplified but useful approach to analyzing solute transport under nonsteady flow conditions (Wierenga, 1977; Jury et al., 1982; Butters et al., 1990).

**Parameter Estimation**

It is convenient when quantifying the results of demonstrations to determine values of \( V, D, \) and \( R \) in Eq. [7] that best represent the experimental breakthrough curves. Computer programs are available (for example, see Parker and van Genuchten, 1984) to accomplish this using nonlinear least squares methods. However, such techniques are generally beyond the undergraduate level. Alternatively, moments analysis (Himmelblau, 1970) is a straightforward method of parameter estimation and is well suited for Eq. [7] (Jury and Sposito, 1985).

The \( N \)th moment \( M_N \) of Eq. [7] or the BTC (expressed in terms of cumulative drainage) is defined as

\[ M_N = \int_0^\infty I^NC(L, I)dI \]  

The approach is to solve Eq. [10] for \( N = 0, 1, \) and 2 exactly for the model and approximately for BTC data. We then set these solutions equal for \( N = 1, 2, \) which results in two equations and two unknowns (Jury and Sposito, 1985). Substituting Eq. [7] into Eq. [10] and performing the integration results in the exact solutions

\[ M_0 = 1 \]  

\[ M_1 = \frac{L}{V\tau} \]  

\[ M_2 = \left( \frac{L}{V\tau} \right)^2 + 2D\tau L/(V\tau)^3 \]  

For a concentration data set \( C(L, I) \) of \( k \) observations the first step taken by the student is to determine the zeroth moment (denote these numerical estimates as \( \hat{M}_0 \))

\[ \hat{M}_0 = \sum_{j=1}^{k-1} \left( C(L_i, I_j) + C(L_i, I_{j+1}) \right) (I_{j+1} - I_j) \]  

which is simply the trapezoidal rule (Forray, 1978) approximation of Eq. [10] with \( N = 0 \). The zeroth moment is an estimate of the area under the BTC. When plotting solute concentration vs. cumulative drainage, \( M_0 \) serves as a measure of mass recovery. Before calculating the remaining two moments, normalize the concentration data by dividing each value by \( \hat{M}_0 \). The 1st and 2nd moments are then estimated numerically by

\[ \hat{M}_N = \sum_{j=1}^{k-1} \left( \frac{(I_j + I_{j+1})}{2} \right)^N \left( \frac{C^*(L_i, I_j) + C^*(L_i, I_{j+1})}{2} \right) (I_{j+1} - I_j) \]  

where \( C^*(L, I) \) is the normalized concentration \( \left( \text{m}^{-1} \right) \) of the \( j \)th observation of cumulative drainage at distance \( L \). Equations [14] and [15] are calculated by the student using a simple program or hand calculator. These numerical results are equated to Eq. [12] and [13] to obtain

\[ V\tau = \frac{L}{\hat{M}_1} \]  

\[ D\tau = \frac{L^2}{2} \left( \frac{\hat{M}_2 - \hat{M}_1}{\hat{M}_1^3} \right) \]  

which are the parameter estimates for the model solution (Eq. [7]). Plotting Eq. [7] with these values should produce a distribution that looks very much like the experimental BTC.

**Model Prediction**

Parameter estimation finds values for the model parameters that best represent the experimental BTC. These empirical values, however, are not necessarily equal to the values that might be calculated using the definition of the parameters \( V^* \) and \( R \) (Eq. [3]-[5]). Hence, the model-fitting exercise does not by itself test or validate the model's representation of the transport process. A better test of the model is to use secondary measurements such as flux and water content to assign values to the model parameters according to their definitions. For \( V^* \) and \( R \), this means using Eq. [4] and [5], which require \( q, \theta, \rho_b, \) and \( K_p \). The remaining parameter, \( D \), is not easily defined from secondary measurements. Assignment of a value for dispersion is usually accomplished using an empirical relationship,

\[ D = \alpha V \]  

where \( \alpha \) is the so-called dispersivity (Leij and Dane, 1989). In small soil columns, a dispersivity value of about 0.01 m or less is typical (Wierenga and van Genuchten, 1988).

**RESULTS AND DISCUSSION**

**Parameter Estimation**

Table 1 contains a data set of yellow dye concentration vs. cumulative drainage from a short column of sand. For illustration, the following is a step-by-step moments analysis to estimate the \( V\tau \) and \( D\tau \) of Eq. [7] that best represent this data.
Table 1. Yellow dye breakthrough curve data under steady flow rate $q = 6.67 \times 10^5$ m s$^{-1}$ through an unsaturated sand ($\theta = 0.36$). The sand column was 0.05 m in diameter and 0.13 m long. The dye application rate was $12.7 \times 10^{-2}$ g m$^{-2}$.

<table>
<thead>
<tr>
<th>Cumulative drainage (m)</th>
<th>Concentration (g m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0137</td>
<td>0</td>
</tr>
<tr>
<td>0.0245</td>
<td>0</td>
</tr>
<tr>
<td>0.0302</td>
<td>0.09</td>
</tr>
<tr>
<td>0.0332</td>
<td>1.30</td>
</tr>
<tr>
<td>0.0366</td>
<td>3.13</td>
</tr>
<tr>
<td>0.0401</td>
<td>4.70</td>
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<tr>
<td>0.0442</td>
<td>5.92</td>
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<tr>
<td>0.0483</td>
<td>6.43</td>
</tr>
<tr>
<td>0.0526</td>
<td>7.40</td>
</tr>
<tr>
<td>0.0570</td>
<td>8.19</td>
</tr>
<tr>
<td>0.0602</td>
<td>0.55</td>
</tr>
<tr>
<td>0.0639</td>
<td>0.18</td>
</tr>
<tr>
<td>0.0673</td>
<td>0</td>
</tr>
</tbody>
</table>

Step 1: Calculate the zeroth moment using Eq. [14]

$$\bar{M}_0 = \left\{ \frac{0 + 0.09}{2} \right\} (0.302 - 0.0245)$$

$$+ \left\{ \frac{1.3 + 0.09}{2} \right\} (0.0332 - 0.0302) + \ldots$$

$$+ \left\{ \frac{0.18 + 0.0}{2} \right\} (0.0673 - 0.0639)$$

$$= 11.5 \times 10^{-2} \text{ g m}^{-2}$$

The mass/area applied is reported as $12.7 \times 10^{-2}$ g m$^{-2}$. The mass recovery is thus 91%.

Step 2: Normalize the concentration set by dividing each observation of concentration by $\bar{M}_0$

Step 3: Use Eq. [15] to estimate $\bar{M}_1$ and $\bar{M}_2$ of the normalized concentration

$$\bar{M}_1 = \left\{ \frac{0.0245 + 0.0302}{2} \right\} \left\{ \frac{0 + 0.78}{2} \right\}$$

$$\times (0.0302 - 0.0245) + \ldots$$

$$+ \left\{ \frac{0.0673 + 0.0639}{2} \right\} \left\{ \frac{1.57 + 0}{2} \right\}$$

$$(0.0673 - 0.0639) = 4.61 \times 10^{-2} \text{ m}$$

$$\bar{M}_1 = \left\{ \frac{0.0302 + 0.0245}{2} \right\} \left\{ \frac{0 + 0.78}{2} \right\}$$

$$\times (0.0302 - 0.0245) + \ldots$$

$$+ \left\{ \frac{0.0673 + 0.0639}{2} \right\} \left\{ \frac{1.57 + 0}{2} \right\}$$

$$(0.0673 - 0.0639) = 2.17 \times 10^{-3} \text{ m}^2$$

Step 4: Use Eq. [16] and [17] to estimate $\bar{V}$ (2.82) and $\bar{D}$ (3.95 × 10$^{-3}$ m$^2$ s$^{-1}$)

Figure 1 shows the BTC and the optimized model fit using the $\bar{V}$ and $\bar{D}$ determined above for Eq. [7]. Note the units on the parameters. To convert to the more familiar units of length/time, use Eq. [8] and [9] with the reported water flux to find $V^*$ (1.88 × 10$^{-4}$ m s$^{-1}$) and $D^*$ (2.63 × 10$^{-7}$ m$^2$ s$^{-1}$). The observed retardation is easily determined using Eq. [3] and [4] with the reported flux and water content to find $R = 1.02$. This value is very close to 1, indicating that the yellow dye movement is virtually unretarded.

Model Prediction

The model (Eq. [7]) contains two unknown parameters ($\bar{V}$, $\bar{D}$) that must be assigned values prior to making a prediction of the BTC. By Eq. [4] it is straightforward to determine $V$ and using the adsorption isotherm with Eq. [5] determines $R$. The final parameter, $D$, can be estimated using Eq. [18] with a literature derived value for dispersivity. Dividing these $V$ and $D$ values by $R$ and $q$ yields $\bar{V}$ and $\bar{D}$.

The adsorption isotherms for the blue dye (the yellow dye is not adsorbed) in the clay loam, sand, and sand treated with humic acid are shown in Fig. 2. The isotherms were determined using the batch method wherein known masses of soil and dye were placed in a known volume of water and shaken for 24 h. Each of the isotherms is close to linear with the greatest adsorption occurring in the clay loam. The $K_d$ value is the slope of the best fit line describing the data. Note that the $K_d$ in the sand is lowered slightly by the addition of humic acid. This suggests possible competition between the dye and the humic acid for mineral adsorption sites and/or dye adsorption to the soluble humic acid, and hence retention in the liquid phase. The net result is enhanced mobility of the blue dye in the presence of humic acid (Butters and Bandaranayake, 1993).

As an example of model prediction, consider the yellow and blue dye BTCs from a column of sand (e.g., Fig. ...
Adsorption of blue dye (with best fit line) on a clay loam ($K_D = 2.19 \text{ m}^3 \text{ Mg}^{-1}$), a sand ($K_D = 0.26 \text{ m}^3 \text{ Mg}^{-1}$), and a sand treated with humic acid ($K_D = 0.18 \text{ m}^3 \text{ Mg}^{-1}$). $C_e$ is the liquid phase concentration in equilibrium with the adsorbed phase concentration $C_s$.

Fig. 2. Adsorption of blue dye (with best fit line) on a clay loam ($K_D = 2.19 \text{ m}^3 \text{ Mg}^{-1}$), a sand ($K_D = 0.26 \text{ m}^3 \text{ Mg}^{-1}$), and a sand treated with humic acid ($K_D = 0.18 \text{ m}^3 \text{ Mg}^{-1}$). $C_e$ is the liquid phase concentration in equilibrium with the adsorbed phase concentration $C_s$.

Butters and Bandaranayake, 1993). The dyes were applied to a 0.225 m long column with a soil bulk density of 1.6 Mg m$^{-3}$. An average flow rate (cumulative discharge per unit area per unit time) of $3.03 \times 10^5 \text{ m s}^{-1}$ was used with a water content of 0.33. To predict the BTCs following a narrow pulse input of dyes, use Eq. [4] to estimate the pore water velocity ($9.19 \times 10^{-5} \text{ m s}^{-1}$) and use the adsorption isotherm with Eq. [5] to estimate the blue dye retardation factor (2.26). Selecting a representative dispersivity of 0.005 m, the predicted values of $V^* \text{ and } D^*$ in Eq. [6] are $9.19 \times 10^{-5} \text{ m s}^{-1}$ and $4.59 \times 10^{-7} \text{ m}^2 \text{s}^{-1}$ for the yellow dye and $4.07 \times 10^{-5} \text{ m s}^{-1}$ and $2.03 \times 10^{-7} \text{ m}^2 \text{s}^{-1}$ for the blue dye. Next, divide these estimates by the flow rate to find $V_T$ and $D_T$. (The flow rate, $q$, was used in this sequence of calculations for illustration but actually it is not required to estimate the parameters in Eq. [7]. Note by combining Eq. [2] to [4] with Eq. [8], [9], and [18], you find $V_T = 1/(8R)$ and $D_T = \alpha V_T$. These latter expressions provide the most direct calculation of parameters for Eq. [7].) Figure 3 shows the resulting predictions (by plotting Eq. [7]) compared with the observed BTCs. The model predicts the shape and position of the BTCs fairly well. The peak concentrations are missed because the observed dispersion is different than expected. In this soil, the literature selected dispersivity value is an overestimate for the yellow dye, but an underestimate for the blue dye.

As a second example, consider an experiment in which the blue dye is applied to a clay loam soil. As above, the soil properties and flow rate allow determination of $V_T$, $D_T$, $V^*$, and $D^*$.
$D_f$, and $R$. The results of such an experiment and the model prediction (using $\alpha = 0.01$ m) are shown in Fig. 4. It is clear that the adsorption isotherm leads to a very large over prediction of the retardation. That is, the blue dye moves through the unsaturated clay loam much more rapidly than the model predicts (in particular, $V_{\text{observed}} = 4.2 \times V_{\text{predicted}}$). Of course, the model parameters could be adjusted to improve the model's agreement with the breakthrough data. These after the fact adjustments, however, need to be carefully distinguished from model predictions.

**SUMMARY AND CONCLUSIONS**

The method of moments is a useful and straightforward approach for estimating the parameters of the convection-dispersion model for solute BTCs from soil columns. The parameter optimization serves to quantify the features of the BTC but does not test the process description of the model. A better test of the model is to estimate the parameters independently. We find that the transport of both dyes in the sand is fairly well described by the convection-dispersion model. In the clay loam, however, the blue dye moves faster than predicted based on the adsorption isotherm. As discussed in Butters and Bandaranayake (1993) we believe this results in part from blue dye shuttling with mobile organic matter. Furthermore, the adsorption isotherm is an equilibrium measurement determined in a closed system designed to maximize adsorbent-solute contact. As such, the isotherm is an idealized estimate largely devoid of physical and chemical nonequilibrium effects. These results are useful for stimulating students into a broader discussion of the appropriateness of the batch $K_d$ method and the predictive utility of literature $K_d$ values.

It is important to stress to students that the benefits of parameter estimation (aside from quantifying results) is realized most in the comparison of observed and predicted model parameters. Such analysis improves our understanding of transport processes and leads to model refinements and development of better models. For example, it is worthwhile considering how a researcher might approach the problem of refining the CDE used here to include convection of adsorbed solutes. A $K_d$ value independent of the isotherm may be calculated using the observed $R$ and Eq. [2]. This so-called dynamic partition coefficient, $K_d^*$ (Jury et al., 1986) is strictly empirical, but its deviation from $K_d$ reflects nonideal adsorption behavior and shuttling as discussed above. In the case of the homogeneous sandy soil treated with humic acid, one might cautiously hypothesize that the difference between $K_D$ and $K_d^*$ is due largely to dye adsorption to mobile organic matter since nonequilibrium effects should be minimal. In this simplified system the fraction of applied blue dye adsorbed to mobile material is at most $1 - (K_d^*/K_D)$, or about 47% for the sand plus humic acid treatment. If not taken too literally, the simple result might be used in conjunction with BTCs from sand columns (with and without humic acid) to test solute transport models that account for movement of adsorbed solute.

**REFERENCES**


