Predicting 2,4,5-T Movement in Soil Columns

G. A. O'Connor, M. Th. van Genuchten, and P. J. Wierenga

ABSTRACT

A solute model developed by van Genuchten and Wierenga was used to calculate 2,4,5-T effluent data from soil columns. The model had been previously shown to adequately predict effluent data given model parameters curve fit to a portion of the effluent curve. The present work shows that 2,4,5-T effluent curves may be adequately predicted without prior knowledge of the effluent curves for a particular soil column given: (i) model parameters derived from 2,4,5-T effluent curves for other soil columns, or (ii) model parameters obtained from tritium effluent curves for the same columns. The data suggest that once the physical model parameters have been characterized for a soil, reasonable predictions of 2,4,5-T (and perhaps other solutes) transport can be made given the adsorption coefficient for the solute.

Additional Index Words: pesticides, pesticide mobility, solute transport, effluent curves, breakthrough curves, solute movement models.

The ability to accurately predict solute transport is of major concern to soil scientists today. Accordingly, numerous solute transport models have been suggested but most have been only partially successful, particularly when applied to unconsolidated, heterogeneous, aggregated soils. van Genuchten and Wierenga (1976) described a model that allowed for lateral diffusion of solute and subsequent distribution between dynamic and stagnant regions in the soil. Other models which account for the presence of, and transfer between, mobile and immobile phases in soil have been described by Skopp and Warrick (1974), Krupp et al. (1972), and Coats and Smith (1964). The van Genuchten and Wierenga model was shown to be especially useful in quantitatively describing the early appearance of different chemicals in column effluents, and in describing the slow removal of adsorbed chemicals from soil even after extensive leaching (hereafter referred to as "Cantley".

The model centers around four parameters, three of which are largely a function of the physical properties of the soil and a fourth, the retardation factor, which accounts for adsorption of a particular solute, and which is entirely chemical in nature. The parameters may be determined by curve fitting points from the front side of a solute breakthrough curve (BTC) and then used in the solute model to predict the entire solute BTC (van Genuchten and Wierenga, 1977). This procedure was shown to be very successful in predicting 2,4,5-T BTCs at a variety of fluxes (van Genuchten et al., 1977).

The purpose of this research was to test the suitability of the van Genuchten and Wierenga model to predict 2,4,5-T BTCs in soil columns for which no previous 2,4,5-T BTC data were available. In the first set of calculations, 2,4,5-T BTCs were predicted for three soil columns using model parameters derived from a 2,4,5-T BTC for a fourth soil column. The columns for which predictions were made had bulk densities, water contents, and soil water fluxes different from the column from which the model parameters were derived. In the second set of calculations, 2,4,5-T BTCs were predicted using model parameters derived from irrigated water (9H2O) BTC's on the same columns and adsorption coefficients determined by batch equilibration techniques.

MODEL

The model used in this study to describe solute movement has been described in detail by van Genuchten and Wierenga (1976). Briefly, it is assumed that part of the water during solute transport is immobile. Solute diffuses in and out of this immobile water and adsorption occurs on sites in contact with mobile and with immobile water. Adsorption on soil surfaces in contact with immobile water occurs upon diffusion through the immobile water. The equations describing this system for steady state flow and equilibrium adsorption are:

\[ \theta_m + \frac{1}{a} \ln \left( \frac{C_m}{C_0} \right) = \theta_a + \left( 1 - \frac{1}{a} \right) \ln \left( \frac{C_m}{C_0} \right) \]

where \( \theta_m \) and \( \theta_a \) are the mobile and immobile water contents, respectively (cm³/cm³); \( C_m \) and \( C_a \) are the concentrations of solute in the mobile and immobile liquid phases, respectively (µg/cm³); \( V_m \) is the average pore-water velocity in the soil.

\[ \frac{dC_m}{dt} = -D \frac{d^2C_m}{dx^2} \]

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in the second set of experiments, \( \Delta \text{MO} \) BTC data were used to derive three model parameters \((D, k, \alpha)\) for each of four columns. Properties of the soil columns during the \( \Delta \text{MO} \) displacements were very similar to the properties shown in Table 1. 2,4,5-T BTC's were then predicted for each soil column using the parameters from tritium displacement experiments and from retardation factors calculated from batch equilibration determined adsorption coefficients. A value of the Freundlich adsorption coefficient of 0.50 was used based on work described previously (O'Connor and Anderson, 1978). Other independent measurements of the linearized adsorption coefficient yielded similar values to the value assumed herein (M. Th. van Genuchten. 1974). Mass transfer studies in soilless porous media, Ph. D. Dissertation. New Mexico State University, Las Cruces, N. M.). Observed 2,4,5-T BTC data for these columns were also reported by van Genuchten et al. (1977). RESULTS AND DISCUSSION Observed and calculated 2,4,5-T BTC data for columns I-IV are compared in Fig. 1-4. The model parameters used to construct the calculated curves were obtained by fitting the solute model to the front side of the BTC for column I (Fig. 1). The agreement between observed and predicted results for column I is good considering that data from only the front side of the BTC were used to generate the entire BTC. No hysteresis was assumed in the predictive model, and yet both peak height (relative concentration, C/Co) and tailing portions of the curve were adequately described. van Genuchten et al. (1977) reported similar success predicting 2,4,5-T BTC's using the same technique. Model parameters derived from column I were used to predict 2,4,5-T BTC's for soil columns of different physical properties (columns II-IV). Predicted and observed results for these columns are given in Fig. 2-4. Agreement between predicted and observed results is reasonable in all cases, particularly with respect to peak height (C/Co) and peak position (the relative pore volume at which C/Co is maximized). Both factors were predicted within 5% of the observed values. Maximum solute concentrations (peak height) and relative pore volume (peak position) predictions would be of major importance in environmental concerns of solute transport in soils. A predictive error of 5-10% in either factor may be sufficiently accurate for many purposes. The model also does a reasonable job of describing the tailing portion of the BTC's which would be important in determining how long 2,4,5-T would continue to be eluted from a soil even with extensive leaching. Column II was very similar in properties to the reference column I (Table 1) so that the very good agreement between predicted and observed results (Fig. 2) was not surprising. Model parameters, however, are known to vary somewhat with soil physical properties (M. Th. van Genuchten. 1974). Mass transfer studies in soilless porous media, Ph. D. Dissertation. New Mexico State University, Las Cruces, N. M.). Columns III and IV were used to calculate 2,4,5-T BTC's for columns II-IV. Table 1—Selected properties of soil columns utilized in the first set of experiments on 2,4,5-T movements in soil

<table>
<thead>
<tr>
<th>Column</th>
<th>Density</th>
<th>Volumetric aggregate size</th>
<th>Flume</th>
<th>Largest aggregate size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/cm³</td>
<td>cm³/cm⁴</td>
<td>µm</td>
<td>mm</td>
</tr>
<tr>
<td>I</td>
<td>1.26</td>
<td>0.47</td>
<td>5.11</td>
<td>2.0</td>
</tr>
<tr>
<td>II</td>
<td>1.26</td>
<td>0.49</td>
<td>4.39</td>
<td>2.0</td>
</tr>
<tr>
<td>III</td>
<td>1.22</td>
<td>0.46</td>
<td>17.06</td>
<td>6.3</td>
</tr>
<tr>
<td>IV</td>
<td>1.23</td>
<td>0.46</td>
<td>14.01</td>
<td>6.3</td>
</tr>
</tbody>
</table>

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relate to the average pore water velocity, a more appropriate value of $D$ for columns III and IV would be about 27 cm$^2$/day rather than the assumed value of 8.36 cm$^2$/day. When the observed data in Fig. 3 and 4 were predicted assuming a value of $D = 27.0$, the agreement between predicted and observed results was improved. An even better fit is obtained by assuming $D = 60$ cm$^2$/day (data not shown) which probably reflects the influence of the larger aggregate sizes used in columns III and IV on the uniformity of the porous media, and hence on $D$.

Thus although model parameters for 2,4,5-T may vary with soil physical properties, the variations did not induce large errors in our calculations. The soil property variation studied herein reflect practical ranges of soil property values for the Glendale soil, but care should be taken in overextending the data. Predictions should probably be confined to soil in which the physical properties do not vary dramatically from those soils for which model parameters were determined.

2,4,5-T BTC Predicted from $^{18}$O Data

The dispersion coefficient $D$, and the parameter $B$, which defines the homogeneity of the soil, represent purely physical soil properties and should be essentially independent of the solute being transported. A third parameter, the mass transfer coefficient $\alpha$, depends on both soil physical properties and on the solute transported, primarily through the solute diffusion coefficient. Neglecting the influence of the diffusion coefficient on $\alpha$, one may obtain three of the model parameters ($D$, $B$, and $\alpha$) by curve-fitting $^{18}$O BTC for various columns. Values of the curve fit parameters and column physical properties have been presented previously (van Genuchten and Wierenga, 1977). The fourth parameter $K$ was determined from 2,4,5-T batch equilibration adsorption studies. The four parameters were then utilized in the solute movement model to predict 2,4,5-T BTC on the same columns (Fig. 5-8).

The agreement between predicted and observed results is reasonable in all cases, particularly again with respect to peak height ($C/C_0$) and peak position. Both factors were predicted within 10% of the observed values. Much, but not all, of the error associated with predicting 2,4,5-T BTCs from $^{18}$O data appears to be related to differences in mass transfer coefficients of the two compounds. van Genuchten and Almond (1977) suggested that the mass transfer coefficient for the larger 2,4,5-T molecule would be smaller than the coefficient for $^{18}$O primarily as a result of a smaller diffusion coefficient for 2,4,5-T. An approximate average value of the transfer coefficient for 2,4,5-T in the Glendale soil is $\alpha = 0.10$ (van Genuchten et al., 1977). When this smaller value of $\alpha$ is used instead of the $^{18}$O derived values the predicted curves more closely approximate the observed data in some (Fig. 5 and 6), but not all (Fig. 7) cases. The value of $\alpha$ for column IV (Fig. 8) derived from the $^{18}$O BTC was only 0.125 so that no predictions with $\alpha = 0.10$ were made. The 2,4,5-T BTC for column IV (Fig. 8) was ade-
Fig. 5 – 2,4,5-T effluent data predicted using model parameters obtained from a 3 % HgO BTC in column I. Open circles represent observed data points.

Fig. 6 – 2,4,5-T effluent data predicted using model parameters obtained from a 3 % HgO BTC in column II. Open circles represent observed data points.

Fig. 7 – 2,4,5-T effluent data predicted using model parameters obtained from a 5 % HgO BTC in column III. Open circles represent observed data points.

Fig. 8 – 2,4,5-T effluent data predicted using model parameters obtained from a 5 % HgO BTC in column IV. Open circles represent observed data points.

quately predicted using parameters determined directly from the HgO BTC although using α = 0.10 would have improved the prediction. No explanation is offered for the low value of α derived from the column IV HgO BTC as compared to values determined from columns I-III. The approach used to calculate the curves in Fig. 5-8 thus represents an oversimplified, but apparently reasonable, procedure for estimating 2,4,5-T mobility in soil.

The data in Fig. 5-8 indicate that physical properties of a soil which affect 2,4,5-T movement may be moderately independent of the solute being leached. Thus, it appears that once the physical model parameters have been characterized for a soil (such as by curve-fitting HgO data), reasonable predictions of 2,4,5-T (and perhaps other solutes) transport can be made given the adsorption coefficient for the solute.

The solute movement model of van Genuchten and Wierenga (1976) is apparently appropriate for describing 2,4,5-T movement in the Glendale soil, under the conditions of this study. Adequate predictions of 2,4,5-T BTCs were possible given the model parameters derived from other 2,4,5-T or HgO BTCs for a variety of soil physical properties. Field research, however, is still needed to test the possibility of using laboratory soil column data to predict herbicide mobility in the field.

LITERATURE CITED


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