Semi-Empirical Models Relating Soil Hydraulic Characteristics and Solute Breakthrough Curve

Mohamad Mohamad Hossein, Mohammad Reza Neishabouri and Hosseingholi Rafahi

Department of Soil Science, Faculty of Soil and Water Engineering, University of Teheran, Karadj, Iran
Department of Soil Science, Faculty of Agriculture, University of Tabriz, Tabriz, Iran

Abstract: Since the convection of a fluid in different pores is described by the pore velocity distribution and consequently the pore size distribution, it is possible to connect the BTC to the pore size distribution or the SMC. In this study we presented an approach relating the CDE and Kosugi's SMC model by the simple and easily measured parameters. The BTC and SMC were measured simultaneously on core scale soils under laboratory condition. These two models were connected together with 2 arbitrary constants and 2 empirical coefficients. The obtained SMC and BTC models based on the empirical coefficient were evaluated in wide range of soils. The correlation coefficient between measured and predicted effective saturation and relative effluent concentration were found 0.9215 and 0.9299 respectively. The RMSEs of predicted and experimental data ranged from a low of 0.031 to a high of 0.177, the averaged being 0.0802 for SMC and from a 0.031 to 0.243 and the averaged being 0.0899 for BTC. As the RSMR for BTC and SMC didn't show any correlation with soil physical and hydrodynamic properties, we resulted that these models have enough flexibility in the wide range of soil properties.

Key words: Solute breakthrough curve - water retention characteristic curve - modeling

INTRODUCTION

Because the Soil Moisture Characteristics curve (SMC) is difficult and expensive to measure, many models have been developed to estimate SMC from other soil properties including soil particle size distribution, particle density, ρp and soil morphology [1, 2]. Despite the large number of such studies there is no study estimate the SMC from Solute Breakthrough Curve (BTC). On the other hand, to predict the solute transport events as well as SMC, many investigators have shown that the soil physical properties such as the average pore water velocity [3, 4], the pore size distribution [5, 6, 7] can determine the transport phenomena. Several attempts have been made to relate the soil physical properties with the BTC models parameters. Computer simulations by Vogel, (2000) suggested that solute dispersion is more sensitive to the water-retention curve than the pore-size distribution. Dispersivity is a key parameter in solute transport models and has partially been related to the slope of the SMC [7, 8] and to multiple slope of SMC and the air entry value [9].

Other researcher has proposed an experimental relation between dispersivity and variance of pore water velocity distribution based on the HCC [10]. Databases of soil hydraulic properties are widely available [11, 12, 1]. Similarly if solute breakthrough curves and soil hydraulic properties were measured simultaneously on samples from a wide range of soil types, pedotransfer functions [13] could be developed to predict dispersivity from information stored in existing databases. Goncalves et al. (2001) have developed PTFs to predict transport parameters from basic soil properties and SMC parameters using multiple linear regression and neural network analysis. PTFs are experimental regression equations that are used to predict difficult-to-obtain parameters from more easily measured soil properties.

Wang et al. (2002) successfully have used Brooks and Corey's water retention model to derive a simple model predicting the BTC in disturbed sand columns under saturated conditions.

Since the convection of a fluid in different pores is described by the pore velocity distribution and consequently the pore size distribution, it is possible to connect the BTC to the pore size distribution or the SMC. At the core scale, solute transport is often described by means of the Convection Dispersion Equation (CDE). The hydrodynamic dispersivity in this equation reflects the microscopic variability of solute transport on top of the mean convective flow.

In order to describe the SMC, many models have been developed [14, 15, 16, 17]. The Kosugi's model...
is based on lognormal pore size distribution of soil and it has two physical meaningful parameters. Since the CDE and this model have been used frequently and have similar mathematical form, so relating between these two models and their parameters will be more valuable and useful than complete empirical pedotransfer function which relating soil physical properties and CDE or SMC parameters. Also in many cases at core scale, the measuring of BTC is easier than the measuring of SMC, consequently any reliable relation between the BTC and SMC can result in easily predicting of SMC too. The purpose of the current research are (i) to present an approach that can relate the CDE and Kosugi’s SMC model by the simple and easily measured parameters and (ii) to obtain and evaluate the empirical coefficient of these models in wide range of soils under laboratory conditions.

**Model development:** We assume that at any time, the C/C0 in outlet point is a function of relative portion of the pores discharging the solute to the all pores contributing in water transport. According to their sizes, coarser pores carry the applied pulse concentration to outlet point sooner than fine pores and with increasing time the solute of finer pores reaches to outlet point too. i.e. At any depth the portion of solute carrying pores increases with time where the arriving time of the each pore solution depends on its size, consequently we assume the C/C0 at outlet point is function of pore size distribution or SMC. This may be expressed as:

$$\frac{C}{C_0}(t) = f(Se)$$  \hspace{1cm} (1)

One dimensional transport of solute through homogeneous soil during steady water flow is traditionally described by CDE:

$$R \frac{∂C}{∂t} = D \frac{∂^2 C}{∂x^2} - V \frac{∂C}{∂x}$$  \hspace{1cm} (2)

Where C(x, t) is solute concentration in soil solution, V is average pore water velocity, D is convection dispersion coefficient, t is time, x is space coordinate and R is retardation factor. Initial and boundary condition for semi-infinite column experiment are

$$C(0, t) = C_0 \hspace{1cm} C(8, t) = 0 \hspace{1cm} C(x, 0) = 0$$  \hspace{1cm} (3)

Where C0 represents a constant concentration of solute supplied at column inlet. The solution of Eq. (2) under condition of Eq. (3) is well known [18]:

$$\frac{C}{C_0} = \frac{1}{2} \text{erfc} \left( \frac{R - Pv}{(4RPv/Pc)^{1/2}} \right) + \frac{1}{2} \exp(Pc) \text{erfc} \left( \frac{R + Pv}{(4RPv/Pc)^{1/2}} \right)$$  \hspace{1cm} (4)

Where erfc is complementary error function, ‘Pv’ is number of pore volume equal to Vt/L, L is soil column length, Pc is column Peclet number that equal to Vt/D and R is given by:

$$R = 1 + \rho_b K_d / \theta$$  \hspace{1cm} (5)

ρ_b is soil bulk density and K_d is linear adsorption coefficient.

As the percentage contribution of second term in right hand of Eq. (3) to total relative concentration is negligible [19] so we can consider only the first term as BTC model.

The soil moisture characteristics curve model developed by Kosugi, (1996) is:

$$Se = \frac{1}{2} \text{erfc} \left( \frac{\ln(\psi) - \ln(\psi_s) - \sigma^2}{2^{1/2} \sigma} \right)$$  \hspace{1cm} (6)

Where \(\psi_s\) is pressure at inflection point of pore size distribution curve, \(\sigma^2\) is variance of pore size in lognormal distribution,

$$Se = \frac{\theta - \theta_s}{\theta_i - \theta_s}$$

Which \(\theta_s\) and \(\theta_i\) are saturated and residual water content respectively.

Substituting the Eq. (4) and Eq. (6) in Eq. (1) yields;

$$\frac{C}{C_0} = \frac{1}{2} \text{erfc} \left( \frac{R - Pv}{(4RPv/Pc)^{1/2}} \right) + \frac{1}{2} \exp(Pc) \text{erfc} \left( \frac{R + Pv}{(4RPv/Pc)^{1/2}} \right)$$  \hspace{1cm} (7)

Consequently the function between SMC and BTC expressed in Eq. (7) can be represented as:

$$F \left( \frac{R - Pv}{(4RPv/Pc)^{1/2}} \right) = \frac{\ln(\psi) - \ln(\psi_s) - \sigma^2}{2^{1/2} \sigma}$$  \hspace{1cm} (8)

Figure 1 may show the C/C0 as function of second and third term of Eq. (7) in provided that f(x) = x. Figure 1 shows the shape similarity between the SMC and BTC of a nonreactive solute in a soil of our experiments. Figure 1 shows that in addition of soil
Fig. 1: Shape similarity between SMC and BTC in a Loam soil (marked with * in Table 1). C/C0 is drawn as function of 'Pv' and 'y' as described in Eq. (6) provided that the 'a' and 'b' in Eq. (9) are defined. Note to logarithmic scale of 'y'

hydraulic properties, the type of function (f) depends on dimension and scale of 'Pv' and 'y'. So it is necessary to unify and agree between the 'Pv' and 'y' for finding the 'f' or 'F'. i.e. because the Eq. (8) has two variable parameters in both side, fixing one parameter against another is needed to understand the relationship. This agreement between 'Pv' and 'y' can be defined with an exclusive equation such as:

\[ P_v = a y^b \]  

(9)

The 'a' and 'b' in Eq. (9) are arbitrary constant parameters and must be chosen as the Eq. (9) gives the reliable answers in 'Pv' and 'y' given range and leads to simplify the function “f” as possible.

The function (F) may become linear in valid value of a and b. Consequently the Eq. (8) can be represented:

\[ \frac{R-P_v}{(4RP_v/Pe)^{1/2}} = p \left( \frac{\ln(y) - \ln(y_0) - \sigma^2}{2^{1/2}\sigma} \right) + q \]  

(10)

Where, 'p' and 'q' are constant coefficient and depend on soil physical and hydrodynamic properties. For simplification it may express by:

\[ Y = pX + q \]  

(11)

Finding two different point of this line [X1, 0] and [0, Y1] can give the value of 'p' and 'q'.

If X = 0 in Eq. (11) then

\[ \frac{R-P_v}{(4RP_v/Pe)^{1/2}} = q \]  

(12-1)

or

\[ \ln(y) = \ln(y_0) + \sigma \]  

(12-2)

And where Y = 0 then P = R or

\[ \frac{\ln(R) - \ln(a)}{b} = \frac{\ln(y) - \sigma^2}{2^{1/2}\sigma} \]  

(13)

If SMC data be available, 'p' may be estimated with soil physical properties. Since R can be determined from batch studies as described in Eq. (5), 'q' can be calculated with Eq. (13). Consequently predicting of BTC will be possible with using Eq. (10).

On the other part, the 'p' may be estimated when the BTC data is available. Eq. (10) can be represented as:

\[ \frac{R-P_v}{(4RP_v/Pe)^{1/2}} = p \left( \frac{\ln(y) - \sigma^2}{2^{1/2}\sigma} \right) + q \]  

(14)

Considering the defined relationship between 'y' and 'Pv' the measured value of \( \frac{R-P_v}{(4RP_v/Pe)^{1/2}} \) and \( \ln(y) \) may be resolved in Cartesian coordinate with Y and X axis respectively, so for any reliable amount of R, Pe and 'y', this equation gives a line with known slope S and intercept I as:

\[ I = q \cdot \left( \frac{\ln(y) + \sigma^2}{2^{1/2}\sigma} \right) \]  

(15)

\[ S = \frac{Y}{\sqrt{2}\sigma} \]  

(16)

Since the slope can be derive using above resolving and value of 'p' are estimated with BTC, the value of \( \sigma \) can be calculated with Eq. (16).

Combining the Eq. (12-1), Eq. (12-2) and Eq. (9) yields:

\[ q = \frac{R-a(y e^{2\sigma})^b}{(4R(a(y e^{2\sigma})^b)^{1/2} Pe} \]  

(17)
Substituting the Eq. (17) in Eq. (15) gives:

\[
1 - \frac{R - a(\psi, \sigma, \phi)}{4Ra(\psi, \sigma, \phi)} + \frac{\ln(\psi + \sigma^2)}{2 \sigma^2} = 0
\]  

(18)

Only the \( \psi_0 \) is unknown parameter in Eq. (18) and can be calculated easily by a simple numerical method.

**METHODS AND MATERIALS**

28 columns were filled from the 0 to 18-cm depth (Ap) of different soils. Sampling locations were selected on the basis of textual class to give a wide range of soil hydraulic properties. Soil samples were all obtained from the north and centre of Iran. The 5.0-cm radius by 30-cm long PVC soil columns were filled with dried and sieved by 10 mesh sieve, then soils were saturated from below. Miscible-displacement experiments was determined for each column with continues applying the 0.1 M CaCl\(_2\). SMC were measured using the standard procedure [20], with unifying the bulk density in each column and revealed core sample. SMC and BTC parameters were obtained by MATLAB 7.1 software.

**RESULTS AND DISCUSSION**

In order to obtain any relationship between BTC and SMC, it is necessary to define or find reveal value of ‘a’ and ‘b’. Figure 2 shows the type of relationship (function “F”) between two side of Eq. (8) in different values of ‘a’ and ‘b’. As the shown in Fig. 2b, with decreasing the ‘b’ from 1 to 0.25, the function F in Eq. (7) becomes linear but in low amount of “b” (<0.25) the answers of Eq. (8) and Eq. (9) in any amount of “a” becomes unreliable. So the 0.25 may chosen as the correct value of “b”. Fig. 2a represents the mentioned relationship type as function of “a” with chosen value of “b” (0.25). In high and low value of “a”, the function “F” is nonlinear and it becomes linear when a shifts to 2. Then we consider ‘a’ and ‘b’ as 2 and 0.25 respectively where pressure head expressed as mbar. These constants value gives a linear and reliable relationship between BTC and SMC parameters as described in Eq. (10) in any valid amount of soil physical and hydraulic parameters with \( R^2 > 0.99 \). (Detail is not shown).

As shown in Eq. (13) through (16), ‘p’ is a key parameter and it may be estimated by correlating with soil physical properties. As any strong and significant relation was not observed between ‘p’ and single physical properties, the combination of hydraulic parameters were used. The following relationship were obtained between the parameter ‘p’ and the complex of soil properties and hydraulic parameters (Fig. 3):

\[
\ln(-p) = 0.3362 \frac{R_g^2}{K_0/(\theta_s - \theta_r)} - 0.4666(r^2 = 0.8545^{**})
\]  

(19)

Which the defined unite of \( \sigma \) and \( K_0 \) are cm and cm h\(^{-1} \) respectively.

The parameter ‘p’ was found strongly related to Peclet number ‘Pv’ (Fig. 4) and resulting relationship based on our experimental data is:

\[
\ln(-p) = 0.508 \ln(Pe) - 1.0543 \qquad (r^2 = 0.9057^{**})
\]  

(20)
Fig. 3: The relationship between a defined soil physical parameter \( \frac{R\sigma^2}{K_s/(G_s - Gr)} \) and the parameter ‘p’

\[
y = 0.3962x - 0.4666 \\
r^2 = 0.8545^{**}
\]

Fig. 4: The relationship between the parameter p and Peclet number Pe

\[
\ln(Pe) = 0.6618 \left( \frac{R\sigma^2}{K_s/(G_s - Gr)} \right) + 1.1569
\]  

(21)

This equation can be used for predicting of Pe with \( r^2 = 0.821^{**} \).

Evaluation of models: Simulated and observed BTC for 4 soils are shown in Fig. (5a, b, c, d). As shown the model has simulated well both the SMC and BTC with each other.

The empirically estimated ‘p’ was used in Eq. (10) to independently calculate SMC and BTC of 28 soils.
Table 1: Soil type and Parameters of Eq. (10) that relate the breakthrough curve to soil moisture characteristics curve with their respective Root Mean Square Residuals (RMSR of measured and predicted value of C/C0 and Se respectively)

<table>
<thead>
<tr>
<th>Soil</th>
<th>Texture</th>
<th>p</th>
<th>q</th>
<th>RMSR for predicting SMC</th>
<th>RMSR for predicting BTC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartzipsettment</td>
<td>Sand</td>
<td>-1.067</td>
<td>0.3578</td>
<td>0.117</td>
<td>0.098</td>
</tr>
<tr>
<td>Quartzipsettment</td>
<td>Sand</td>
<td>-0.991</td>
<td>-0.167</td>
<td>0.097</td>
<td>0.073</td>
</tr>
<tr>
<td>Quartzipsettment</td>
<td>Sand</td>
<td>-1.444</td>
<td>-0.079</td>
<td>0.081</td>
<td>0.049</td>
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<tr>
<td>Quartzipsettment</td>
<td>Sand †</td>
<td>-0.426</td>
<td>-0.896</td>
<td>0.115</td>
<td>0.0598</td>
</tr>
<tr>
<td>Quartzipsettment</td>
<td>Sand</td>
<td>-3.372</td>
<td>0.468</td>
<td>0.072</td>
<td>0.127</td>
</tr>
<tr>
<td>Torripsettment</td>
<td>Loamy sand</td>
<td>-0.37</td>
<td>-0.389</td>
<td>0.142</td>
<td>0.07</td>
</tr>
<tr>
<td>Torritorthent</td>
<td>Sandy loam</td>
<td>-0.208</td>
<td>-0.745</td>
<td>0.116</td>
<td>0.117</td>
</tr>
<tr>
<td>Torritorthent</td>
<td>Sandy loam</td>
<td>-2.494</td>
<td>-0.97</td>
<td>0.064</td>
<td>0.087</td>
</tr>
<tr>
<td>Torritorthent</td>
<td>Sandy loam</td>
<td>-1.965</td>
<td>-0.502</td>
<td>0.055</td>
<td>0.056</td>
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<tr>
<td>Haplocacacid</td>
<td>Loam</td>
<td>-1.651</td>
<td>-0.535</td>
<td>0.077</td>
<td>0.09</td>
</tr>
<tr>
<td>Haplocacacid</td>
<td>Loam</td>
<td>-1.825</td>
<td>-0.518</td>
<td>0.058</td>
<td>0.126</td>
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<tr>
<td>Haplocacacid</td>
<td>Loam</td>
<td>-2.727</td>
<td>-0.604</td>
<td>0.031</td>
<td>0.089</td>
</tr>
<tr>
<td>Haplocacacid</td>
<td>Loam †</td>
<td>-0.266</td>
<td>-0.594</td>
<td>0.041</td>
<td>0.031</td>
</tr>
<tr>
<td>Calcixercept</td>
<td>Loam</td>
<td>-0.465</td>
<td>-0.508</td>
<td>0.052</td>
<td>0.062</td>
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<tr>
<td>Calcixercept</td>
<td>Loam †</td>
<td>0.115</td>
<td>-0.637</td>
<td>0.041</td>
<td>0.08</td>
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<td>Calcixercept</td>
<td>Loam</td>
<td>-0.669</td>
<td>-0.675</td>
<td>0.052</td>
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<tr>
<td>Calcixercept</td>
<td>Loam</td>
<td>-0.622</td>
<td>-0.596</td>
<td>0.047</td>
<td>0.059</td>
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<tr>
<td>Calcixercept</td>
<td>Loam</td>
<td>-2.075</td>
<td>-1.33</td>
<td>0.04</td>
<td>0.064</td>
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<tr>
<td>Calciargid</td>
<td>Loam</td>
<td>-0.529</td>
<td>-0.441</td>
<td>0.06</td>
<td>0.156</td>
</tr>
<tr>
<td>Calciargid</td>
<td>Sandy clay loam</td>
<td>-0.368</td>
<td>-0.539</td>
<td>0.045</td>
<td>0.059</td>
</tr>
<tr>
<td>Calciargid</td>
<td>Silty clay loam</td>
<td>-1.017</td>
<td>-0.456</td>
<td>0.094</td>
<td>0.068</td>
</tr>
<tr>
<td>Argixerol</td>
<td>Silty clay loam</td>
<td>-1.238</td>
<td>-0.523</td>
<td>0.07</td>
<td>0.046</td>
</tr>
<tr>
<td>Argixerol</td>
<td>Clay loam</td>
<td>-2.238</td>
<td>-1.244</td>
<td>0.047</td>
<td>0.062</td>
</tr>
<tr>
<td>Argiudol</td>
<td>Clay loam †</td>
<td>-1.1759</td>
<td>-1.005</td>
<td>0.039</td>
<td>0.149</td>
</tr>
<tr>
<td>Calciargid</td>
<td>Clay loam</td>
<td>-2.168</td>
<td>-2.269</td>
<td>0.177</td>
<td>0.161</td>
</tr>
<tr>
<td>Haploxeralf</td>
<td>Silty clay</td>
<td>-1.039</td>
<td>-0.947</td>
<td>0.173</td>
<td>0.057</td>
</tr>
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<td>Argiudol</td>
<td>Clay</td>
<td>-3.44</td>
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<tr>
<td>Argiudol</td>
<td>Clay</td>
<td>-2.727</td>
<td>-0.595</td>
<td>0.081</td>
<td>0.065</td>
</tr>
</tbody>
</table>

† BTC and SMC of these soils are presented in Fig. 5a, b, c, d. † BTC and SMC of this soil is presented in Fig. 1

Fig. 6: Comparison of predicted and observed C/C0 and Se. Test results for 28 soil are pooled
These soils are identified in Table 1. Examples of predicted and experimental data are presented in Fig. 5a (sand), 5b (loam), 5c (silt loam) and 5d (clay). Overall, the shapes of the predicted SMC and BTC were similar to those of the measured data in wide range of soil physical properties.

Figure 6 shows a comparison of experimental vs. predicted SMC (Fig. 6a) and BTC Fig. (6b) values for all soils on a 1:1 scale. The regression line between the experimental and predicted values closely matches the 1:1 line with an $r^2$ of 0.9215 and 0.9299 for SMC and BTC respectively. The Root Mean Square Residuals (RMSR) between predicted and measured C/C0 and S values represent respective level of agreement between the model and experimental data. The RMSRs of the predicted and experimental $S_c$ data range from 0.031 to 0.177 (average 0.0802) and for $C/C_0$ ranged from 0.031 to 0.243 (average 0.0899), Table 1. As the RMSR for neither BTC and nor SMC show any correlation with soil physical and hydrodynamic properties, we resulted that the presented models have enough flexibility in the wide range of soil properties.

The scatter in the data in Fig. 6a and 6b is not surprising in view of the many sources of variation in the experimental as well as input data. These variations may be attributed to variations in determining the coefficients ‘p’ and ‘q’ empirically which can be resulted from (i) neglecting the second term of CDE model (ii) lack of fitting in describing of SMC with Kosugi model (iii) differences in mineralogy, microaggregation and organic matter content. We believe that the predictions of the BTC and SMC from each other by a semiempirical model are quite reasonable. Predictions of the model may be further improved if the empirical coefficients using in calculation of ‘p’ found in more wide range of soils.

SUMMARY AND CONCLUSIONS

Research reported here describes a method to relate the BTC to SMC using two empirical coefficients. With using two scaling parameters, which relate $P_v$ to pressure head, the BTC based on CDE model is connected to the SMC based on Kosugi model (1996). The model parameters for 28 soils are determined empirically. Our model requires only two parameters of concern: p and q, while finding the first parameter is sufficient for simulation the BTC or SMC. The behavior of these parameters may be further elucidated as the model is subjected to further tests and scrutiny. Predictions of the SMC or BTC from each other for a number of soils, representing a range in texture, Peetle number, saturated hydraulic conductivity and pore size detritions were reasonable. The RMSEs of predicted and experimental data ranged from a low of 0.031 to a high of 0.177, the averaged being 0.0802 for SMC and from a 0.031 to 0.243 and the averaged being 0.0899 for BTC. As the RMSR for BTC and SMC didn’t show any correlation with soil physical and hydrodynamic properties, we resulted that these models have enough flexibility in the wide range of soil properties. Lack of fit the Kosugi model as well as adjusted CDE to experimental data and variability in mineralogy, microaggregation and organic matter content attributes and hydrophysical behavior of individual soils are believed to be responsible for uncertainties in the model’s predictions. The reported empirical coefficient may be adjusted in future researches with studying on more abundant and undisturbed soils.

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REFERENCES