A general polynomial solution to convection–dispersion equation using boundary layer theory

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A number of models have been established to simulate the behaviour of solute transport due to chemical pollution, both in croplands and groundwater systems. An approximate polynomial solution to convection–dispersion equation (CDE) based on boundary layer theory has been verified for the use to describe solute transport in semi-infinite systems such as soil column. However, previous studies have only proposed low order polynomial solutions such as parabolic and cubic polynomials. This paper presents a general polynomial boundary layer solution to CDE. Comparison with exact solution suggests the prediction accuracy of the boundary layer solution varies with the order of polynomial expression and soil transport parameters. The results show that prediction accuracy increases with increasing order up to parabolic or cubic polynomial function and with no distinct relationship between accuracy and order for higher order polynomials ($n \geq 3$). Comparison of two critical solute transport parameters (i.e., dispersion coefficient and retardation factor), estimated by the boundary layer solution and obtained by CXTFIT curve-fitting, shows a good agreement. The study shows that the general solution can determine the appropriate orders of polynomials for approximate CDE solutions that best describe solute concentration profiles and optimal solute transport parameters. Furthermore, the general polynomial solution to CDE provides a simple approach to solute transport problems, a criterion for choosing the right orders of polynomials for soils with different transport parameters. It is also a potential approach for estimating solute transport parameters of soils in the field.

1. Introduction

Increasing amounts of agrichemicals produced by industries and agricultural activities enter the ecosystem every day. To minimise the drainage water pollution of groundwater, numerical models are increasingly used in analysing the behaviour of solute transport and quantitatively simulating

the detailed processes of more complex pollution conditions. Approaches have been developed for exact analytical and numerical solutions (Leij *et al.* 1991; Clement 2001; Ross 2003; Ziskind *et al.* 2011; You and Zhan 2013). The parameters of solute transport are critical in determining the composition of chemicals and prioritising plausible solutions, where expert efforts have achieved appreciable

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progress (Yamaguchi *et al.* 1989; Abbaspour *et al.* 1997, 2004; Deng *et al.* 2005; Irsa and Zhang 2012; Wang *et al.* 2013).

The convection–dispersion equation (CDE) is widely used to describe solute transport in both soil column and field soil conditions (Russo *et al.* 1998; Jacques *et al.* 2002; Zhou *et al.* 2011). Dispersion coefficient and retardation factor (two critical parameters of the CDE model) are generally obtained by fitting breakthrough curves (Elprince and Day 1977; Yamaguchi *et al.* 1989). However, CDE transport parameters obtained by this method are not unique and embed uncertainties (Shao *et al.* 1998). Furthermore, the complete measurement of a breakthrough curve is time-consuming with accuracy depending on the technical equipment used, further inducing difficulties in the parameter estimation process. In fact, this fitting approach is not applicable under field conditions because solute breakthrough curve measurements in the field are limited by equipment and observation precisions.

Shao *et al.* (1998) proposed a simple approximate polynomial solution to the CDE model based on boundary layer theory. The boundary layer solutions assume the existence of a chemical boundary layer, the thickness of which increases with time. The solutions based on parabolic and cubic polynomial assumptions are used to predict solute concentration profiles at given transport parameters. This indicates that it is feasible to use boundary layer method as an alternative to CDE parameter estimation. However, the approximate polynomial solutions exist only in parabolic and cubic forms; creating the need for boundary layer solutions with more polynomial terms of higher orders.

Building on the solution suggested by Shao *et al.* (1998), this paper presents a general polynomial solution to the CDE model. The choice of the polynomial order could vastly change the boundary layer solutions and solute concentration profile predictions. By assignment of the n th polynomial order and comparison of the corresponding exact solution, the variation of prediction accuracy with order can be isolated. This study presents a general polynomial solution to the CDE model and shows how to choose the right polynomial order for accurate prediction of solute concentration profiles and estimation of optimal solute transport parameters. The availability of the general polynomial solutions to CDE provides an alternative approach to obtain solute transport parameters of soils in the field.

2. Theory

CDE is the main approach to one-dimensional solute transport in homogeneous porous media

with stationary water flow and is expressed by a partial differential equation as follows:

$$R \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x}, \quad (1)$$

where C_r is solute concentration (g/cm³ of soil solution); D is dispersion coefficient (cm²/h); v is average pore water velocity (cm/h); R is retardation factor; x is distance (cm); and t is time (h). In a semi-infinite system, the initial soil column is free of solutes, as shown in equation (2), to ensure that solutes only enter the transport volume through the entrance surface (Sposito *et al.* 1986):

$$C_r(x, t) = 0. \quad (2)$$

The boundary conditions for solute displacement (van Genuchten and Parker 1984) are defined as:

$$\left(-D \frac{\partial C_r}{\partial x} + v C_r \right) \Big|_{x=0^+} = v C_0 \quad (3)$$

and

$$\left(\frac{\partial C_r}{\partial x} \right) \Big|_{x \rightarrow \infty} = 0. \quad (4)$$

Equation (3) is applicable (i) when the entrance reservoir in the system is not physically connected to the column, or (ii) when the column is connected directly to the entrance reservoir in the system, as long as diffusion across the inlet boundary relative to convective transport by water flow is negligible. Equation (4) is proposed to ensure that the zero gradient boundary condition is not applied at the exit surface, but at a point that is defined as infinity (van Genuchten and Parker 1984).

Let us suppose the existence of a boundary layer, $d(t)$, which is the depth of the solute front as a function of time (figure 1). Then, the solute concentration

Figure 1. A schematic diagram of solute boundary layer.

is complied with equation (5) at the position of boundary layer for the first order polynomial:

$$C_r(d(t), t) = 0. \quad (5)$$

Assuming a linear polynomial solution to CDE as described in equation (1), the resident solute concentration profile is expressed as follows:

$$C_r(x, t) = a_0(t) + a_1(t)x. \quad (6)$$

The application of equation (5) to equation (6) leads to the reduction of coefficients, yielding a substituted expression for C_r as given in equation (7):

$$C_r(x, t) = a_0(t) \left(1 - \frac{x}{d(t)}\right). \quad (7)$$

Equation (7) is applicable for the conditions under $0 < x < d(t)$, when $x > d(t)$, $C_r(x, t) = 0$. Then, substituting equation (7) into equation (3), we get the following:

$$a_0(t) = \frac{vd(t)C_0}{D + vd(t)}. \quad (8)$$

Hence, the linear boundary layer solution to CDE is written as:

$$C_r(x, t) = \frac{vd(t)C_0}{D + vd(t)} \left(1 - \frac{x}{d(t)}\right). \quad (9)$$

Solute transport process satisfies mass balance requirement; in other words, if $I_s(t)$ is cumulated solute added in the column across the surface, then

$$I_s(t) = \int_0^{d(t)} C_r(x, t) dx. \quad (10)$$

Based on the boundary layer conditions in equation (3), integrating the left and right terms of equation (1) from 0 to $d(t)$ yields the following equations:

$$R \int_0^{d(t)} \frac{\partial C_r}{\partial t} dx = R \frac{dI_s(t)}{dt}, \quad (11)$$

$$\int_0^{d(t)} \left(D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \right) dx = vC_0. \quad (12)$$

Hence, equation (1), the initial and boundary conditions imply that

$$I_s(t) = \frac{vC_0}{R}t. \quad (13)$$

The depth of the solute front ($d(t)$) can be obtained by finding the positive root of a parabolic polynomial equation established by the combination of equations (13) and (9) as follows:

$$d(t) = \frac{vt}{R} + \sqrt{\left(\frac{vt}{R}\right)^2 + \frac{2Dt}{R}}. \quad (14)$$

Equations (9) and (14) constitute the boundary layer solution to the CDE model for the case of a linear polynomial concentration profile.

Shao *et al.* (1998) established boundary layer solutions on basin parabolic and cubic polynomial concentration profile assumption, where solute concentration and boundary layer depth are expressed, respectively as the following.

$$C_r(x, t) = \frac{vd(t)C_0}{vd(t) + 2D} \left(1 - \frac{x}{d(t)}\right)^2, \quad (15)$$

$$d(t) = \frac{3vt}{2R} + \sqrt{\left(\frac{3vt}{2R}\right)^2 + \frac{6Dt}{R}}, \quad (16)$$

$$C_r(x, t) = \frac{vd(t)C_0}{vd(t) + 3D} \left(1 - \frac{x}{d(t)}\right)^3, \quad (17)$$

$$d(t) = \frac{2vt}{R} + \sqrt{\left(\frac{2vt}{R}\right)^2 + \frac{12Dt}{R}}. \quad (18)$$

Equations (15) and (16) represent a parabolic polynomial solution and equations (17) and (18), a cubic polynomial solution.

To further explore the accuracy of the boundary layer solutions in describing resident concentrations based on different solute concentration profile assumptions, more polynomial concentration profiles are obtained in a similar way. The solutions based on quartic assumption are obtained using the following equations:

$$C_r(x, t) = \frac{vd(t)C_0}{vd(t) + 4D} \left(1 - \frac{x}{d(t)}\right)^4, \quad (19)$$

$$d(t) = \frac{5vt}{2R} + \sqrt{\left(\frac{5vt}{2R}\right)^2 + \frac{20Dt}{R}}. \quad (20)$$

Based similarly on the use of quintic polynomial concentration profile, the boundary solution is expressed as follows:

$$C_r(x, t) = \frac{vd(t)C_0}{vd(t) + 5D} \left(1 - \frac{x}{d(t)}\right)^5, \quad (21)$$

$$d(t) = \frac{3vt}{R} + \sqrt{\left(\frac{3vt}{R}\right)^2 + \frac{30Dt}{R}}. \quad (22)$$

Upon comparison of the above five boundary layer solutions to CDE in terms of different concentration profile assumptions, a similarity readily emerges among the expressions:

$$C_r(x, t) = \frac{vd(t)C_0}{vd(t) + nD} \left(1 - \frac{x}{d(t)}\right)^n, \quad (23)$$

$$d(t) = \frac{(n+1)vt}{2R} + \sqrt{\left(\frac{(n+1)vt}{2R}\right)^2 + \frac{n(n+1)Dt}{R}}. \quad (24)$$

Equations (23) and (24) combine the general boundary solution to CDE under the n th order polynomial concentration profile assumption.

A proof of the general solution is given in Appendix of this paper. The expressions of C_r and $d(t)$ obtained by boundary layer theory in terms of different assumption polynomial concentration profiles has three main parameters – v , R and D . Usually, v is determined by displacement experiment and R and D are estimated by measuring advancing distance of boundary layer through the use of dye tracers. Tracers such as brilliant blue dye (Flury and Flühler 1994) or TDR (Ward *et al.* 1994) can be used to monitor the advance of the solute front with time for both laboratory soil column and field soil. Lindstrom *et al.* (1967) worked an analytical solution to equation (1) using initial and boundary conditions of equations (2–4) to evaluate resident concentration profiles of semi-infinite systems as:

$$\frac{C_r(x, t)}{C_0} = \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{\frac{1}{2}}} \right] + \left(\frac{v^2 t}{\pi DR} \right)^{\frac{1}{2}} \exp \left[\frac{-(Rx - vt)^2}{4DRt} \right] - f, \quad (25)$$

$$f(x, t) = \frac{1}{2} \left(1 + \frac{vx}{D} + \frac{v^2 t}{DR} \right) \times \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{\frac{1}{2}}} \right]. \quad (26)$$

3. Discussions

3.1 Polynomial order and solute front advance

Polynomial solutions at various orders can describe concentration profiles, resulting in different but similar expressions of resident solute concentrations (C_r) and solute front depths ($d(t)$). Equation (24) shows that the general expression of $d(t)$ is described by dispersion coefficient (D), average pore water velocity (v), retardation factor (R) and polynomial order (n). The ratio of D/v is the dispersivity with a value generally in the range of 0.5–2 cm for packed columns and 5–20 cm for field soils. If the soil column length is l , then the Peclet number (Pe) is defined as lv/D .

Figure 2 shows the sensitivity of $d(t)$ to n for $D = 1.8 \text{ cm}^2/\text{h}$ and $v = 0.18 \text{ cm/h}$ to give a

dispersivity of 10 cm. With D and v held constant, $d(t)$ increases with increasing n at any given time. This indicates that using a higher-order polynomial solution to approximate solute concentration profile results in a faster solute penetration when the solute transport parameters are known.

Figure 3 depicts the sensitivity of boundary layer depth with the Peclet number (Pe) for a fixed value of v and Pe set at 5 and 50, respectively. The soil column length is assumed to be 50 cm. From the plot, boundary layer advances more quickly at a smaller Pe . However, with increasing order of polynomial term, boundary layer depth becomes greater than any time of the same λ . Combining figures 2 and 3 results in a greater order effect on solute front advance than Pe .

Figure 4 plots the effect of pore water velocity (v) on solute front advance. Although, convection influences solute transport more than dispersion (because solute transport by water flow is generally faster than dispersion), the order of the polynomial term still largely drives solute front advance.

Retardation (R) also influences solute front advance as shown in figure 5, where boundary layer depth is inversely related to R at any given time. This is because increased retardation decreases solute transport velocity due to higher increase in liquid-phase solute than in solid-phase solute. Also, the effect of order of the polynomial term on solute front advance is maximal at the same R value.

The above results suggest that the solute transport parameters (v , D and R) in equation (25) influence solute front advance with time. The order (n) of the polynomial has even a greater effect on $d(t)$. Thus, comparisons of prediction accuracies of various orders (n) of polynomial solutions and parameter estimation are critical in choosing the appropriate order for the best prediction and parameter estimation. In fact, $d(t)$ is used for both the prediction of concentration profile and the estimation of parameters.

3.2 Boundary layer solution and exact solution

As the solution obtained by the boundary layer theory is approximate, there is a need to compare with the exact solution to determine the accuracy of the approach. Different combinations of the three parameters (v , D and R) are used to describe the resident solute concentration profiles at a given time ($t = 5 \text{ h}$) using the two approaches. For this purpose, the initial concentration solution C_0 and soil column length are assumed to be 1 and 50 cm, respectively.

Figure 6 shows the solute concentration profiles calculated by the boundary layer theory based on various orders of the polynomial term and the corresponding exact solutions. Boundary layer

Figure 2. Effect of polynomial order on boundary layer depth with time ($v = 0.18$ cm/h, $D = 1.8$ cm²/h, $R = 1$).

Figure 3. Effects of dispersion coefficient and polynomial order on boundary layer advance with time ($v = 0.18$ cm/h, $R = 1$).

solutions with different polynomial orders are very close to the corresponding exact solutions. However, discrepancies exist for the prediction of resident solute concentration profiles using different polynomial assumptions and different solute transport descriptions. The degree of match between the boundary layer solutions and the exact solution is

determined using maximum error, described as the absolute value of the difference between the two methods.

Figure 7 plots the maximum error of each boundary layer solution against the exact solution based on different polynomial assumptions. The boundary layer solution is closest to the exact

Figure 4. Effect of average pore water velocity on boundary layer depth advance with time ($D = 0.18 \text{ cm}^2/\text{h}$, $R = 1$).

Figure 5. Effect of retardation factor on boundary layer advance with time ($v = 0.18 \text{ cm}^2/\text{h}$, $D = 1.8 \text{ cm}^2/\text{h}$).

solution for the cubic polynomial term of $v = 0.03 \text{ cm/h}$, $Pe = 5$ and $R = 1$, which has a maximum error of 0.0018. The gap between the calculated boundary layer solutions and the corresponding exact solution is widest for $v = 0.3 \text{ cm/h}$, $Pe = 50$

and $R = 0.5$. The comparison indicates that the boundary layer solutions matches very well with the exact solution. When the three parameters (v , D and R) of solute transport are determined, the parabolic or cubic polynomial solution gives the

Figure 6. Comparisons of concentration profiles between boundary layer solutions and the corresponding exact solutions. The combination of parameters are (a) $v = 0.03$ cm/h, $D = 0.3$ cm²/h, $R = 0.5$; (b) $v = 0.03$ cm/h, $D = 0.3$ cm²/h, $R = 1$; (c) $v = 0.03$ cm/h, $D = 0.6$ cm²/h, $R = 0.5$; (d) $v = 0.03$ cm/h, $D = 0.6$ cm²/h, $R = 1$; (e) $v = 0.3$ cm/h, $D = 3$ cm²/h, $R = 0.5$; (f) $v = 0.3$ cm/h, $D = 3$ cm²/h, $R = 1$; (g) $v = 0.3$ cm/h, $D = 6$ cm²/h, $R = 0.5$; and (h) $v = 0.3$ cm/h, $D = 6$ cm²/h, $R = 1$.

best prediction for solute resident concentration profiles. The lowest error is under these two conditions, except for $v = 0.3$ cm/h, $Pe = 50$ and $R = 0.5$. The prediction error of the parabolic polynomial is the second smallest and has tiny discrepancy with the cubic polynomial under this condition. This suggests that for most cases, the parabolic or cubic polynomial solution can accurately predict the solute resident concentration profile.

At a given Pe , an increase of average pore water velocity (v) results in a greater concentration prediction error. For example, the maximum error of parabolic polynomial solutions increases 0.12 folds ($R = 0.5$ and $Pe = 5$) and 0.34 folds ($R = 1$ and $Pe = 5$) when v increases from 0.03 to 0.3 cm/h, respectively. A similar trend is observed for a Pe of 50. Furthermore, Pe is also affected prediction accuracy. The maximum error of cubic polynomial solution increases 7.94 fold ($R = 1$) and 5.27 fold ($R = 0.5$), respectively, when Pe increases from 5

to 50 for $v = 0.03$ cm/h. The same results can be found for the cases of $v = 0.3$ cm/h. Finally, the role of retardation factor (R) in prediction accuracy is determined for a given set of v and Pe . Using the cubic polynomial solutions of figure 6(g and h), a maximum error for $R = 1$ is 5.89% less than that for $R = 0.5$ ($v = 0.03$ cm/h and $Pe = 50$). For other instances, the maximum errors of prediction calculated at $R = 0.5$ are all greater than those calculated at $R = 1$.

The above analysis indicates that boundary layer solutions based on polynomial assumptions can predict solute concentration profiles, a prediction accuracy that is influenced by both solute transport parameters and polynomial orders. Firstly, boundary layer solutions match better with exact solutions of smaller values of Pe and average pore water velocity. Secondly, the prediction accuracies vary with polynomial orders (n). Generally, the prediction accuracy of a polynomial boundary

Figure 7. Comparisons of maximum prediction error of boundary layer solutions of different polynomial orders with the corresponding exact solutions.

layer solution reaches the minimum when using parabolic or cubic polynomial function for known solute transport parameters. As the polynomial order increases, the prediction accuracy tends to be constant. Therefore, the parabolic and cubic polynomial solutions are the optimum alternatives for predicting resident solute concentration profiles and estimating solute transport parameters.

3.3 Transport parameter estimation

The above analysis indicates that the boundary layer solution matches well with the corresponding exact solution and it is useful in estimating solute transport parameters such as dispersion coefficient (D) and retardation factor (R). The analytical solution to the CDE approach gives an exact description of solute concentration profiles in soils, while the determination of the parameters in the equation is a critical application factor. Usually, pore water velocity (v) of a soil is obtained from infiltration data. The other two parameters (D and R) can be determined by fitting the solute breakthrough curves (Sardin *et al.* 1991; Padilla *et al.* 1999; Field and Pinsky 2000; Ge and Boufadel 2006). In this section, the values of D and R , determined by boundary layer solutions, are compared with those obtained by CXTFIT analysis – a non-linear least squares optimisation code for estimating transport parameters (Toride *et al.* 1995). The simple fitting approach is used to examine the reliability of the former method of parameter estimation.

With further derivation, equation (24) is written as:

$$\frac{d^2(t)}{t} = \frac{(n+1)v}{R}d(t) + \frac{n(n+1)D}{R}. \quad (27)$$

Here, D/R and v/R are the coefficient and velocity of solute dispersion and convection velocity in real-field conditions, respectively. If $d^2(t)/t$ in equation (27) is used as the variable, then the equation can further be simplified to a linear equation, where the independent variable is $d(t)$. Once the boundary layer depth and the corresponding time are determined, the corresponding linear fitting can be done without difficulty. Then, R can be calculated by the slope and D is obtained from the intercept of equation (27).

The measured breakthrough curves and the solute front advance data for loess soils are analysed further to determine the prediction accuracies of solute transport parameters by different polynomial boundary layer solutions. Loess soil is the typical soil type in the Loess Plateau of China. Zheng (2001) measured the breakthrough curve for chloride (Cl^-) transport in soil columns with different bulk densities. The transport parameters of Cl^- obtained by fitting the breakthrough curve using CXTFIT are listed in table 1. The porosity is greater in soil columns with smaller bulk density, which corresponds with lower D . Then, R tends to increase with decreasing bulk density due to reduced repulsion force between soil colloids. The determination coefficients of the soils with the three bulk densities are very close and with small residual sum of squares, showing that

CXTFIT-calculated parameters can be used to describe solute transport characteristics of the soil. The parameters of the soil can also be considered as reference parameters to test the accuracy of solute transport parameters obtained by polynomial boundary layer solutions.

A set of boundary layer depth and the corresponding time measured using brilliant blue dye are calibrated to match with Cl^- transport. Data for solute front advance are used in fitting equation (27). In order to understand the effects of polynomial orders on parameter estimation accuracy, five values of n are used to estimate D and R for the soils with the different bulk densities, and the results are recorded in table 1. The values of D and R estimated by the boundary layer solutions

are in good agreement with those obtained by CXTFIT procedure for the soils. When the soil bulk density is 1.30 g/cm^3 , the quintic and cubic polynomial solutions yield the most accurate estimates of the two parameters, with errors of 3.57% (D) and 0.74% (R), respectively. While the cubic polynomial solution is slightly better for R , the quintic polynomial solution is better for D for soils with the same bulk density. When the cubic polynomial solution is used to fit the soil parameters ($\rho = 1.25 \text{ g/cm}^3$), the relative error is generally less than that for the other polynomial solutions (18.57% for D and 0.00% for R). As for the soil with the smallest bulk density ($\rho = 1.20 \text{ g/cm}^3$), the two parameters obtained from the cubic solution match best with those calculated by CXTFIT;

Table 1. Estimated transport parameters of Cl^- in the loessial soil with different bulk densities using CXTFIT procedure.

No.	Bulk density (g/cm^3)	Average pore water velocity (cm/h)	Dispersion (cm^2/h)	Retardation factor	Determination coefficient
1	1.30	2.42	0.252	0.812	0.9970
2	1.25	2.49	0.231	0.731	0.9998
3	1.20	2.58	0.130	0.876	0.9999

Table 2. Estimated transport parameters using boundary layer method by fitting equation (27).

Soil sample (g/cm^3)		Polynomial order					Determination coefficient
		2	3	5	10	20	
$\rho_v = 1.30$	D^1	0.651	0.434	0.261	0.130	0.065	0.9909
	R^2	0.605	0.806	1.209	2.217	4.232	
$\rho_v = 1.25$	D	0.420	0.280	0.168	0.084	0.042	0.9996
	R	0.548	0.731	1.097	2.011	3.839	
$\rho_v = 1.20$	D	0.161	0.107	0.107	0.032	0.016	0.9992
	R	0.660	0.881	1.321	2.422	4.623	

¹ D is the dispersion coefficient and ² R is the retardation factor.

Figure 8. Concentration profiles observed and fitted by polynomial solutions.

with a relative error of 17.54% for D and 0.45% for R , respectively. Comparison of the estimated parameters by polynomial boundary layer solutions with CXTFIT-fitted ones suggests that the best estimated parameters for soils with a bulk density of 1.30 g/cm^3 is obtained under polynomial order 5. The most appropriate polynomial order for soils with small bulk densities ($\rho = 1.20$ and 1.25 g/cm^3) is 3 (table 2).

The concentration profiles obtained at a time of 2 h using exact solution and polynomial solutions are shown in figure 8. It can be found that the cubic polynomial profiles are closest to the corresponding exact solutions for all the three soils. A higher polynomial order may lead to larger differences between the polynomial profiles and exact profile. Among the three cases, the cubic polynomial profile from the soil with bulk density of 1.20 g/cm^3 matches the exact profile best.

From the above analysis, it is concluded that equation (27) can reliably estimate the solute transport parameters of D and R . This equation is much simpler and therefore easier to use because of the single slope and intercept associated with linear regressions. The method is obviously advantageous over CXTFIT because generally linear fitting method is simpler than that of the exact solution. Also, the measurement of boundary layer depth is easy to perform. Using appropriate boundary layer solution to estimate solute transport parameters provides an alternative method to predict solute concentration profiles of soils.

4. Conclusions

This paper presents a general polynomial solution to the CDE approach based on boundary layer theory for a semi-infinite system. To determine the appropriate order of the polynomial term, the solution is compared with the exact one and transport parameters obtained by the expressions of different polynomial orders are compared with the ones obtained by CXTFIT for three bulk densities of loess soil. Through analysis of the comparisons, the following conclusions are reached:

- (1) Using a higher order polynomial assumption yields a higher boundary layer depth at known solute transport parameters. The orders have more effects on solute front advance $d(t)$ than on solute transport parameters. This suggests that an appropriate choice of order for polynomial solution is critical for precisely predicting solute concentration profile and correctly estimating parameters.
- (2) Boundary layer solutions based on different orders of polynomial expressions match well with exact solutions. While the relative error between boundary layer solutions and the exact

solutions increases with increasing pore water velocity (v), it decreases with increasing dispersion coefficient (D) and retardation factor (R). In most cases, the parabolic or cubic polynomial solution more accurately describes resident solute concentration profiles in soil columns.

- (3) As an example of the application of general polynomial solutions, loess soils of different bulk densities are used to find the appropriate order of polynomial terms for parameter estimation. The results suggest that the linear fitting is much simpler and with a better estimation of solute transport parameters. Order 3 is the most appropriate polynomial order for the estimation of solute transport parameters.

Finally, the general polynomial solution by the boundary layer theory to the CDE approach can potentially be applied in estimating solute transport parameters of field soils. This is because the observation of solute front of a field soil can be done either by TDR system or dye tracer. This makes related studies of field soils promising, calling for more efforts in this direction.

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Appendix

We assume the n th order polynomial approximate concentration profile for a boundary layer solution to CDE to express resident concentration as:

$$C_r(x, t) = a_0(t) + a_1(t)x + a_2(t)x^2 + \dots + a_{n-2}(t)x^{n-2} + a_{n-1}(t)x^{n-1} + a_n(t)x^n. \quad (\text{A1})$$

The boundary-layer conditions assumed in this paper include

$$\begin{aligned} C_r(d(t), t) &= \frac{\partial C_r(d(t), t)}{\partial x} = \frac{\partial^2 C_r(d(t), t)}{\partial x^2} \\ &= \frac{\partial^3 C_r(d(t), t)}{\partial x^3} = \dots \\ &= \frac{\partial^{n-3} C_r(d(t), t)}{\partial x^{n-3}} = \frac{\partial^{n-2} C_r(d(t), t)}{\partial x^{n-2}} \\ &= \frac{\partial^{n-1} C_r(d(t), t)}{\partial x^{n-1}} = 0. \end{aligned} \quad (\text{A2})$$

Equation (A2) is corrected for $n > 1$. When $n = 1$, the boundary-layer condition is

$$C_r(d(t), t) = 0, \quad (\text{A3})$$

and the $(n-1)$ -order derivative of equation (A1) is expressed as:

$$\begin{aligned} \frac{\partial^{n-1} C_r(d(t), t)}{\partial x^{n-1}} &= ((n-1)(n-2)(n-3) \cdots \\ &\quad \times 3 \times 2 \times 1) a_{n-1}(t) \\ &\quad + (n(n-1)(n-2) \cdots \\ &\quad \times 4 \times 3 \times 2) a_n(t) d(t) \\ &= 0. \end{aligned} \quad (\text{A4})$$

Then, $a_n(t)$ is expressed by $a_{n-1}(t)$ as follows:

$$a_n(t) = -\frac{a_{n-1}(t)}{nd(t)}. \quad (\text{A5})$$

Also, the $(n-2)$ -order derivative of equation (A5) is given as:

$$\begin{aligned} \frac{\partial^{n-2} C_r(d(t), t)}{\partial x^{n-2}} &= ((n-2)(n-3)(n-4) \cdots \\ &\quad \times 3 \times 2 \times 1) a_{n-2}(t) \\ &\quad + ((n-1)(n-2)(n-3) \cdots \\ &\quad \times 4 \times 3 \times 2) a_{n-1}(t) d(t) \\ &\quad + (n(n-1)(n-2) \cdots \times 5 \\ &\quad \times 4 \times 3) a_n(t) d^2(t) = 0. \end{aligned} \quad (\text{A6})$$

Substituting equation (A5) to equation (A6), the relationship of $a_{n-1}(t)$ and $a_{n-2}(t)$ is obtained by

$$a_{n-1}(t) = -\frac{2a_{n-2}(t)}{(n-1)d(t)}. \quad (\text{A7})$$

Then, integrating equation (A5) with equation (A7), $a_n(t)$ is expressed in terms of $a_{n-2}(t)$ as follows:

$$a_n(t) = \frac{2a_{n-2}(t)}{n(n-1)d^2(t)}. \quad (\text{A8})$$

In the same way, the k -order derivative of equation (A1) is obtained as follows:

$$\begin{aligned} \frac{\partial^k C_r(d(t), t)}{\partial x^k} &= (k(k-1)(k-2) \times \cdots \times 3 \times 2 \times 1) a_k(t) \\ &\quad + ((k+1)k(k-1) \cdots \\ &\quad \times 4 \times 3 \times 2) a_{k+1}(t) d(t) + \cdots \\ &\quad + ((n-1)(n-2)(n-3) \times \cdots \\ &\quad \times (n-k) a_{n-1}(t) d^{n-1-k}(t)) \\ &\quad + (n(n-1)(n-2) \times \cdots \\ &\quad \times (n-k+1) a_n(t) d^{n-k}(t)). \end{aligned} \quad (\text{A9})$$

Then, equation (A9) is correct when $1 \leq k \leq n-1$. By using boundary layer conditions,

equations (A2) and (A9) are simplified as follows:

$$\begin{aligned} (n-k)! a_k(t) &+ \frac{(k+1)!}{k!} \frac{(n-k)!}{1!} a_{k+1}(t) d(t) + \cdots \\ &+ \frac{(n-1)!}{k!} \frac{(n-k)!}{(n-1-k)!} a_{n-1}(t) d^{n-1-k}(t) \\ &+ \frac{n!}{k!} \frac{(n-k)!}{(n-k)!} a_n(t) d^{n-k}(t) = 0. \end{aligned} \quad (\text{A10})$$

Each term in equation (A10) can be expressed in terms of $a_k(t)$. From this analogy, the n th time coefficients in equation (A1) are reduced to a single coefficient. The coefficient of the k th term of equation (A1) then becomes

$$\begin{aligned} a_k(t) &= (-1)^k \frac{n!}{k!(n-k)! d^k(t)} a_0(t) \\ &= (-1)^k C_n^k a_0(t). \end{aligned} \quad (\text{A11})$$

Equation (A11) is valid for $k \leq n$. Therefore, the alternative expression of equation (A1) with only one coefficient is given as

$$C_r(x, t) = \frac{vd(t)C_0}{vd(t) + nD} \left(1 - \frac{x}{d(t)}\right)^n. \quad (\text{A12})$$

Then, using the same deduction procedure discussed in the main text of the paper, $d(t)$ is obtained as

$$d(t) = \frac{(n+1)vt}{2R} + \sqrt{\left(\frac{(n+1)vt}{2R}\right)^2 + \frac{n(n+1)Dt}{R}}. \quad (\text{A13})$$

References

- Abbaspour K C, Johnson C A and van Genuchten M T 2004 Estimating uncertain flow and transport parameters using a sequential uncertainty fitting procedure; *Vadose Zone J.* 1340–1352.
- Abbaspour K C, van Genuchten M T, Schulin R and Schläppi E 1997 A sequential uncertainty domain inverse procedure for estimating subsurface flow and transport parameters; *Water Resour. Res.* **33**(8) 1879–1892.
- Clement T P 2001 Generalized solution to multispecies transport equations coupled with a first-order reaction network; *Water Resour. Res.* **37**(1) 157–163.
- Deng Z-Q, de Lima J L M P and Singh V P 2005 Transport rate-based model for overland flow and solute transport: Parameter estimation and process simulation; *J. Hydrol.* **315**(1–4) 220–235.
- Elprince A M and Day P R 1977 Fitting solute breakthrough equations to data using 2 adjustable parameters; *Soil Sci. Soc. Am. J.* **41**(1) 39–41.
- Field M S and Pinsky P F 2000 A two-region nonequilibrium model for solute transport in solution conduits in karstic aquifers; *J. Contam. Hydrol.* **44**(3–4) 329–351.
- Flury M and Flühler H 1994 Brilliant blue fcf as a dye tracer for solute transport studies—A toxicological overview; *J. Environ. Qual.* **23**(5).
- Ge Y and Boufadel M C 2006 Solute transport in multiple-reach experiments: Evaluation of parameters and reliability of prediction; *J. Hydrol.* **323**(1–4) 106–119.

- Irsa J and Zhang Y 2012 A direct method of parameter estimation for steady state flow in heterogeneous aquifers with unknown boundary conditions; *Water Resour. Res.* **48**(9).
- Jacques D, Simunek J, Timmerman A and Feyen J 2002 Calibration of Richards' and convection-dispersion equations to field-scale water flow and solute transport under rainfall conditions; *J. Hydrol.* **259**(1–4) 15–31.
- Leij F J, Skaggs T H and van Genuchten M T 1991 Analytical solutions for solute transport in three-dimensional semi-infinite porous media; *Water Resour. Res.* **27**(10) 2719–2733.
- Lindstrom F T, Haque R, Freed V H and Boersma L 1967 The movement of some herbicides in soils: Linear diffusion and convection of chemicals in soils; *Environ. Sci. Technol.* **1**(7) 561–565.
- Padilla I Y, Yeh T C J and Conklin M H 1999 The effect of water content on solute transport in unsaturated porous media; *Water Resour. Res.* **35**(11) 3303–3313.
- Ross P J 2003 Modeling soil water and solute transport – Fast, simplified numerical solutions; *Agron. J.* **95**(6).
- Russo D, Zaidel J and Laufer A 1998 Numerical analysis of flow and transport in a three-dimensional partially saturated heterogeneous soil; *Water Resour. Res.* **34**(6) 1451–1468.
- Sardin M, Schweich D, Leij F J and van Genuchten M T 1991 Modeling the nonequilibrium transport of linearly interacting solutes in porous-media – A review; *Water Resour. Res.* **27**(9) 2287–2307.
- Shao M, Horton R and Miller R K 1998 An approximate solution to the convection–dispersion equation of solute transport in soil; *Soil Sci.* **163**(5) 339–345.
- Sposito G, White R E, Darrah P R and Jury W A 1986 A transfer function model of solute transport through soil. 3: The convection–dispersion equation; *Water Resour. Res.* **22**(2) 255–262.
- Toride N, Leij F and van Genuchten M 1995 The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.0, Research Report No. 137, Laboratory Publication.
- van Genuchten M T and Parker J C 1984 Boundary conditions for displacement experiments through short laboratory soil columns; *Soil Sci. Soc. Am. J.* **48**(4).
- Wang Q, Zhan H and Tang Z 2013 A new parameter estimation method for solute transport in a column; *Ground Water* **51**(5) 714–722.
- Ward A L, Elrick D E and Kachanoski R G 1994 Laboratory measurements of solute transport using time domain reflectometry; *Soil Sci. Soc. Am. J.* **58**(4).
- Yamaguchi T, Yokosi S and Moldrup P 1989 Using breakthrough curves for parameter estimation in the convection–dispersion model of solute transport; *Soil Sci. Soc. Am. J.* **53**(6) 1635–1641.
- You K and Zhan H 2013 New solutions for solute transport in a finite column with distance-dependent dispersivities and time-dependent solute sources; *J. Hydrol.* **487** 87–97.
- Zheng J 2001 Boundary layer method for solute transport in soils; Master Thesis, Northwest A & F University.
- Zhou B B, Shao M A, Wang Q J and Yang T 2011 Effects of different rock fragment contents and sizes on solute transport in soil columns; *Vadose Zone J.* **10**(1) 386–393.
- Ziskind G, Shmueli H and Gitis V 2011 An analytical solution of the convection–dispersion–reaction equation for a finite region with a pulse boundary condition; *Chem. Eng. J.* **167**(1) 403–408.

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