New solutions for solute transport in a finite column with distance-dependent dispersivities and time-dependent solute sources

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S U M M A R Y

Dispersivity is widely accepted to be scale-dependent. Numerous studies have been published for solute transport in porous media with distance-dependent dispersivities in infinite or semi-infinite domains which set the effluent boundaries to be infinitely far away. However, discussion of finite domains is often overlooked. In this study, two new semi-analytical solutions for solute transport in a finite column are developed with linear-asymptotic (LAF solution) or exponential distance-dependent (EF solution) dispersivities and time-dependent sources. These two solutions are compared with the corresponding solutions for semi-infinite domains (LAI and EI solutions). Results show that breakthrough curves calculated by the LAF/EF solution change faster and possess higher peak values than those calculated by the LAI/EI solution, and the discrepancies increase with the growth rate of the dispersivity and the asymptotic dispersivity. At a specific time, the concentrations calculated by the LAF/EF and the LAI/EI solutions are the same close to the solute source. However, the concentrations calculated by the LAF/EF solution are higher than those calculated by the LAI/EI solution after a certain distance from the source. Such distances decrease with the growth rate of the dispersivity and the asymptotic dispersivity. The performances of the LAF, EF, LAI and EF solutions do not differ much when they are applied to interpret the laboratory column tests conducted in both homogeneous and heterogeneous soil columns.

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1. Introduction

1.1. Scale-dependent dispersivities

An accurate description of solute transport in porous or fractured media is indispensable for groundwater quality monitoring and contamination remediation. In models of solute transport, dispersivity has long been an issue of discussion and debate. Increasing evidences in laboratory and field experiments show that solutions to the classical advection–dispersion equations (ADEs) with constant dispersivities cannot satisfactorily describe the solute transport in the subsurface in many cases. Dispersivity is often found to be scale-dependent (Gelhar et al., 1992). The dispersivities obtained from the analysis of the laboratory breakthrough curves (BTCs) are usually on the order of a few to tens of millimeters, while those obtained from the field can be several orders of magnitude higher (Gelhar et al., 1992). The scale-dependent dispersivity is mainly attributed to the heterogeneity of the natural porous or fractured media at different scales (Barry and Sposito, 1989; Gao et al., 2010; Gelhar et al., 1992; Pickens and Grisak, 1981b). The scale effect of the dispersivity may also be an artifact of using a lower-dimensional model to describe a higher-dimensional system (Domenico and Robbins, 1984; Gao et al., 2010; Moltz et al., 1983; Pickens and Grisak, 1981b; Zhou and Selim, 2003) or by the attempt of representing the spreading process with a diffusive type (Gao et al., 2010; Huang et al., 2006).

The time-dependent dispersivity finds its root in the stochastic analysis (Aral and Liao, 1996; Zhou and Selim, 2003). According to stochastic theories, the dispersivity grows initially with travel time and eventually reaches an asymptotic value after all the scales of heterogeneity have been experienced (Dagan, 1988; Dagan and Bresler, 1985; Gelhar and Axness, 1983). The travel distance required to reach the asymptotic dispersivity is on the order of tens of conductivity integral scales (Dagan, 1984, 1988; Dagan and Bresler, 1985) or of the aquifer thickness if the aquifer is self-affine or self-similar (fractal) (Zhan and Wheatcraft, 1996). Pickens and Grisak (1981a) brought forward four types of time-dependent dispersivity functions (linear, parabolic, asymptotic and exponential), and solved ADEs with these time-dependent dispersivities using a finite element method. Barry and Sposito (1989) obtained a closed-form solution to solute transport in a semi-infinite domain with an arbitrary time-dependent dispersion coefficient and arbitrary initial and boundary flux conditions by variable transformations. Basha and El-Habel (1993) presented analytical solutions with one-dimensional (1D) linear, asymptotic and exponential time-dependent dispersivities in infinite domains. Aral and Liao...
(1996) extended the solutions to two-dimensional (2D) infinite domains with arbitrarily time-dependent dispersivities. However, Chen et al. (2008a) argued that it was easier to get the distance-dependent dispersivity functions, because measuring BTCs at given locations is typically more feasible than measuring spatial distributions of concentration at different times.

Distance-dependent dispersivities are generally described by five types of functions in literature. They are linear, linear-asymptotic, parabolic, exponential and hyperbolic functions. The linear distance-dependent dispersivity has been used in many studies. Examples include the analytical or semi-analytical solutions for 1D solute transport in infinite or semi-infinite domains obtained by Gao et al. (2010), Hunt (1998, 1999), Pang and Hunt (2001), Yates (1999). Chen et al. (2006) and Chen et al. (2007) developed semi-analytical solutions for tracer transport in a convergent flow field using the linear distance-dependent dispersion. Perez Guerrerero and Skaggs (2010) developed a general 1D analytical solution for solute transport in a finite domain with scale-dependent dispersivity, and presented the solution in detail for the linear distance-dependent dispersivity. 2D solutions to solute transport with linear distance-dependent longitudinal and transverse dispersivities have also been developed by Chen (2007) and Chen et al. (2008a) in both radially convergent and uniform flow fields. A parabolic distance-dependent dispersivity is employed in Huang et al. (2006) to solve a 1D fractional ADE. However, the linear and parabolic distance-dependent dispersivities seem to be unphysical, because field observations indicate that some asymptotic constant dispersivity could be eventually reached (Gelhar et al., 1992; Logan, 1996; Pickens and Grisak, 1981a, 1981b). Yates (1992) derived a 1D analytical solution to a generalized ADE with an exponentially varied dispersivity and constant concentration or flux inlet boundary conditions in a semi-infinite domain using the Laplace transform. Logan (1996) extended the study of Yates (1992) to a generalized ADE subjected to periodic boundary conditions. Huang et al. (1996) developed a general analytical solution for 1D solute transport in a semi-infinite domain with the linear-asymptotic distance-dependent dispersivity and constant concentration or flux inlet boundary conditions using two different approaches. The solution to the classical ADE with a constant dispersivity and the solution by Yates (1990) assuming a linearly increasing dispersivity are demonstrated to be the special cases of Huang et al. (1996) solution. Mishra and Parker (1990) developed a numerical model to interpret a field tracer experiment with the hyperbolic distance-dependent dispersivity conducted in an unsaturated zone. By using the power series analysis method, Chen et al. (2008b) developed an analytical solution to solute transport with the hyperbolic distance-dependent dispersivity in a finite column with a length L.

1.2 Boundary conditions for 1D solute transport in finite domains

Besides the dispersivity, solute transport is also influenced by boundary conditions. For solute transport in a finite column with a length L, the inlet boundary condition is frequently described by (van Genuchten and Parker, 1984)

\[ C(0, t) = C_{in}(t), \]  

(1)

or

\[ \left[ VC - D(x) \frac{\partial C}{\partial x} \right]_{x=0} = VC_{in}(t), \]  

(2)

where x is the distance from the inlet boundary (L); t is time (T); V is the pore water velocity (L T⁻¹); D(x) the distance-dependent dispersion coefficients (L² T⁻¹) in the column; C is the solute concentration in the column (M L⁻³); C_0(t) is the time-dependent source concentration (M L⁻³).

Eq. (2) indicates that the solute concentration at the inlet boundary is discontinuity.

Conservation of mass at the end of the column requires a third-type outlet boundary condition described by (Danckwerts, 1953; van Genuchten and Parker, 1984)

\[ VC - D(x) \frac{\partial C}{\partial x} \bigg|_{x=L} = VC_{out}, \]  

(3)

where L is the length of the finite column (L); C_e is the exit concentration (M L⁻³). However, in order to avoid the unacceptable conclusion that the solute concentration passes through either a maximum or minimum in the interior of the column, it is necessary to supplement the condition C(L, t) = C_e, which leads to the Danckwerts boundary condition (Brenner, 1962; Danckwerts, 1953; Kramer and Alberda, 1953)

\[ \frac{\partial C}{\partial x} \bigg|_{x=L} = 0. \]  

(4)

Another frequently used outlet boundary condition assumes that the solute distributions inside the finite column are unaffected by the presence of an outlet boundary, thus, the outlet boundary condition can be described by (van Genuchten and Parker, 1984)

\[ \frac{\partial C}{\partial x} \bigg|_{x=L} = 0. \]  

(5)

This boundary condition indicates the discontinuity of concentration at the end of the column (van Genuchten and Parker, 1984).

van Genuchten and Parker (1984) studied the physical and mathematical significance of various inlet (Eqs. (1), (2)) and outlet (Eqs. (4), (5)) boundary conditions. They found that only the combination of Eqs. (2) and (4), and Eqs. (2) and (5) conserved mass in the domain. Because of the inconsistencies in the stipulation of concentration continuities at the inlet and outlet boundaries and the numerically more tedious form of Eqs. (2) and (5), van Genuchten and Parker (1984) recommended that Eqs. (2) and (4) were always used in both finite and semi-infinite domains. Danckwerts (1953) also commented Eq. (4) as established on intuitive grounds. However, Wehner and Wilhelm (1956) analyzed the solute transport and reaction in a finite domain taking into account the transport in the fore and after sections. They found that as the diffusivity in the fore section approached zero, the concentration at the inlet boundary was discontinuous. No discontinuity would develop for any period of time at the outlet boundary. Pearson (1959) also justified the discontinuity of the solute concentration at the inlet and continuity at the outlet boundaries by rigorous mathematical derivation using a continuous coefficient of diffusion. Pearson (1959) indicated that Danckwerts boundary condition was resulted from the use of discontinuous diffusion coefficients. Danckwerts boundary condition was also applied to more complicated situations such as diffusion where temperature varied (Pearson, 1959).

Numerous studies have compared the BTCs and concentration distributions for solute transport subjected to various boundary conditions (Brigham, 1974; Novakowski, 1992a, 1992b; Parlane and Starr, 1975, 1978; van Genuchten and Parker, 1984; Wooding, 1972). Unfortunately, most of the published studies for solute transport with scale-dependent dispersivities deal with semi-infinite or infinite domains (or discontinuous concentration at the end of the finite domain), and there are no solutions setting the outlet boundaries at finite distances (continuous concentration at the end of the finite domain). Therefore, the purpose of this study is to derive new solutions for solute transport in 1D finite domains (Eqs. (2) and (4)) with distance-dependent dispersivities and time-dependent sources and to compare the new solutions with the
corresponding solutions for semi-infinite domains to investigate the effect of outlet boundary conditions.

2. Physical and mathematical models

As discussed in the introduction, arbitrarily large dispersivities at large distances appear to be unphysical (Gelhar et al., 1992). Therefore, in this study, we only investigate the linear-asymptotic and exponential models for distance-dependent dispersivities. The hyperbolic distance-dependent dispersivity models will be investigated in the future study.

For solute transport in a 1D finite domain, such as in a laboratory column test, the linear-asymptotic model for dispersivities could be written as

$$z(x) = \left\{ \begin{array}{ll}
\lambda x, & 0 < x < L_0 \\
\lambda_0, & L_0 < x < L,
\end{array} \right. \quad (6)$$

where $z(x)$ is the distance-dependent dispersivity ($L$); $\lambda$ is the growing rate of the dispersivity close to the source (dimensionless) and $\lambda = \lambda_0/L_0$; $\lambda_0$ is the asymptotic dispersivity ($L$); $L_0$ is the distance where the dispersivity reaches the asymptotic value ($L$). This model means that the dispersivity initially increases linearly with the travel distance and stabilizes at some limiting value at the large distance (Zhou and Selim, 2003).

The exponential model for the distance-dependent dispersivity is described as

$$z(x) = z_0(1 - e^{-bx}), \quad (7)$$

where $b$ is a positive constant (dimensionless). According to Eq. (7), the dispersivity is zero at the source. It increases gradually with the distance and approaches a constant value of $z_0$ at the large distance (Zhou and Selim, 2003).

2.1. 1D column test with linear-asymptotic distance-dependent dispersivities

The origin of the $x$ coordinate is set at the solute source. Eq. (6) indicates that the column should be divided into two zones: zone-1 between $x = 0$ and $x = L_0$ with a linearly increasing dispersivity, and zone-2 between $x = L_0$ and $x = L$ with a constant dispersivity. Therefore, the governing equations for this 1D solute transport during steady-state flow with linear equilibrium adsorption can be written as

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left[ D_1(x) \frac{\partial C_1}{\partial x} \right] - Y \frac{\partial C_1}{\partial x} - \mu C_1, \quad 0 < x < L_0, \quad (8a)$$

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x} \left[ D_2 \frac{\partial C_2}{\partial x} \right] - \mu C_2, \quad L_0 < x < L, \quad (8b)$$

where $C_1$ and $C_2$ are the solute resident concentrations ($M \cdot L^{-3}$) in zone-1 and zone-2, respectively; $R$ is the retardation factor (dimensionless); $\mu$ is the first-order decay coefficient ($T^{-1}$); $D_1$ and $D_2$ are the dispersion coefficients ($L^2 \cdot T^{-1}$) in zone-1 and zone-2, respectively. According to Eq. (6), $D_1$ and $D_2$ could be described as

$$D_1(x) = \lambda x \nu + D_0, \quad (9a)$$

$$D_2 = \lambda_0 \nu + D_0, \quad (9b)$$

where $D_0$ is the molecular diffusion coefficient ($L^2 \cdot T^{-1}$). Molecular diffusion is usually neglected in the field experiments and sometimes in the laboratory column tests (Pang and Hunt, 2001), because it is usually much smaller than the mechanical dispersion coefficient. However, we keep the molecular diffusion in this study, because it sometimes is non-negligible in a laboratory column test. Besides, the distance-dependent dispersivity increases from zero at the source and is quite small at the distance very close to the source; thus, the molecular diffusion should play a major role there.

We use Eq. (2) to describe the inlet boundary condition and Eq. (4) to describe the outlet boundary condition.

Assuming initially the soil column is free of tracer, one obtains

$$C_1(t = 0, x) = C_2(t = 0, x) = 0, \quad (10)$$

The concentration and the mass flux are continuous at the interface of zone-1 and -2, therefore, one has

$$C_1(t, x = L_0) = C_2(t, x = L_0), \quad (11a)$$

$$\left( -D_1(x) \frac{\partial C_1}{\partial x} + V C_1 \right)_{x = L_0} = \left( -D_2 \frac{\partial C_2}{\partial x} + V C_2 \right)_{x = L_0}, \quad (11b)$$

For the purpose of mathematical convenience, the following dimensionless parameters are defined:

$$C_{1D} = \frac{C_1}{C_0}, \quad C_{2D} = \frac{C_2}{C_0}, \quad C_D = \frac{C_D}{C_0}, \quad C_{2D} = \frac{C_{2D}}{C_0}, \quad X_D = \frac{X_D}{L}, \quad \beta = \frac{\beta L}{V}, \quad \mu = \frac{\mu L}{V}. \quad (12)$$

where $C_D$ is an arbitrary constant concentration ($M \cdot L^{-3}$); concentration $C$ ($M \cdot L^{-3}$) and the Peclet number $P_e$ (dimensionless) will be used in Section 2.2. According to the dimensionless parameters defined in Eq. (12), one obtains $C_1 = C_1 C_0 D_1$, $C_2 = C_2 C_0 D_2$, $C_D = C_D C_0 D_0$, $X_D = X_D D_0$, $\beta = \frac{\beta L}{V}$, $\mu = \frac{\mu L}{V}$. Substituting them into Eqs. (2), (4), (8)–(11) and rearranging the equations, one obtains the dimensionless form as follows:

$$\frac{\partial C_{1D}}{\partial \tau} + (\lambda_0 + D_0) \frac{\partial^2 C_{1D}}{\partial x^2} + (\lambda - 1) \frac{\partial C_{1D}}{\partial x} - \mu C_{1D} = 0, \quad (13a)$$

$$\frac{\partial C_{2D}}{\partial \tau} + (\beta_0 + D_0) \frac{\partial^2 C_{2D}}{\partial x^2} - \mu C_{2D} = 0, \quad (13b)$$

$$\left[ C_{1D} - D_0 \frac{\partial C_{1D}}{\partial x} \right]_{x = 0} = C_{0D}, \quad (14)$$

$$\left[ C_{1D} - D_0 \frac{\partial C_{1D}}{\partial x} \right]_{x = 0} = C_{0D}, \quad (15)$$

$$\left[ C_{1D} - D_0 \frac{\partial C_{1D}}{\partial x} \right]_{x = 0} = C_{0D}, \quad (16)$$

$$\left[ C_{1D} - D_0 \frac{\partial C_{1D}}{\partial x} \right]_{x = 0} = C_{0D}, \quad (17a)$$

$$\left[ (\lambda_0 + D_0) \frac{\partial C_{1D}}{\partial \tau} + C_{1D} \right]_{\tau = 0} = \left[ (\beta_0 + D_0) \frac{\partial C_{2D}}{\partial \tau} + C_{2D} \right]_{\tau = 0}, \quad (17b)$$

where the subscript “D” denotes the dimensionless terms. One should note that, according to Eq. (13a), $\lambda$ should be less than 1. If $\lambda$ is equal to or larger than 1, the backward dispersion would be so strong that it would equal or exceed the forward dispersion and advection, which is unphysical (Zhou and Selim, 2003). Mathematically, one can see from Eq. (13a) that, $(\lambda - 1)$, which is the coefficient in front of the advective term, should always be negative to make Eq. (13a) physically sound.

The solution to Eqs. (13)–(17) is obtained by the Laplace transform derived in detail in the Supplementary Material. The solution in the Laplace domain is as follows:

$$\Upsilon_{1D} = A e^{-l_1} K_0(2r \sqrt{S + \mu_1 \beta}) + B e^{l_1} L_0(2r \sqrt{S + \mu_1 \beta}), \quad (18a)$$

$$\Upsilon_{2D} = E e^{l_2 \nu_0} + F e^{l_2 \nu_0}, \quad (18b)$$
where $s$ is the dimensionless Laplace transform parameter in respect to the dimensionless time, and over bar means a variable in Laplace domain; $I$, and $K$, are the rth-order modified Bessel function of the first kind and second kind, respectively; $r = 1/2$; $\varepsilon = \sqrt{\varepsilon_0} + D_{DB}/a_1$; $a_1 = 1 + \sqrt{1 - 4\varepsilon_0(\varepsilon_0 + 1) + \varepsilon_0^2}$; the expressions for $A$, $B$, $E$, $F$ and $G$ are listed in Table 1. This solution is hereinafter called the LAF solution, which means the solution for solute transport with a linear-asymptotic distance-dependent dispersivity and with the outlet boundary set at the end of the finite column.

For solute transport in an infinite or semi-infinite domain, the outlet boundary is described as

$$\frac{\partial C_D}{\partial x} \bigg|_{x = -\infty} = 0.$$ (19)

The solution to Eqs. (13)–(15), (17) and (19) has the same form as in Eq. (18), except that the expressions for $A$, $B$, $E$, $F$ and $G$ are different. This solution has been obtained by Huang et al. (1996), and will not be repeated here. This solution is hereinafter called the LAI solution, which means the solution for solute transport with a linear-asymptotic distance-dependent dispersivity and with the outlet boundary set at the end of the finite column.

### 2.2. 1D column test with exponential distance-dependent dispersivities

In this section, we will develop the solution for solute transport in a 1D column test with an exponential distance-dependent dispersivity described by Eq. (7). Because such an expression is a smooth and continuous function of the distance $x$, the whole column could be treated as one zone, and the governing equation for solute transport is expressed as

$$K \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D(x) \frac{\partial C}{\partial x} \right] - \nabla \frac{\partial C}{\partial x} - \mu C,$$ (20)

where $D(x)$ is the dispersion coefficient ($L^2 T^{-1}$) and is described as

$$D(x) = a_0(1 - e^{-x/a_0})V + D_0.$$ (21)

The same initial and boundary conditions as those in Section 2.1 are employed.

### Table 1

<table>
<thead>
<tr>
<th>Expression</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$C_{D0}(H_0 M_0 - H_0 M_1)/N$</td>
</tr>
<tr>
<td>$B$</td>
<td>$C_{D0}(H_0 M_1 + H_0 M_0)/N$</td>
</tr>
<tr>
<td>$E$</td>
<td>$C_{D0}(H_0 M_1 + H_0 M_0)/N$</td>
</tr>
<tr>
<td>$F$</td>
<td>$C_{D0}(H_0 M_1 + H_0 M_0)/N$</td>
</tr>
<tr>
<td>$H_1$</td>
<td>$c_1 K(2r_0 a_2 s + \mu_0) + \sqrt{s + \mu_0} c_{11} K_{s-1}(2r_0 a_2 s + \mu_0)$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>$c_1 K(2r_0 a_2 s + \mu_0) + \sqrt{s + \mu_0} c_{11} K_{s-1}(2r_0 a_2 s + \mu_0)$</td>
</tr>
<tr>
<td>$H_3$</td>
<td>$c_1 K(2r_0 a_2 s + \mu_0)$</td>
</tr>
<tr>
<td>$L_1$</td>
<td>$\sqrt{s + \mu_0} c_{11} K_{s-1}(2r_0 a_2 s + \mu_0)$</td>
</tr>
<tr>
<td>$L_2$</td>
<td>$\sqrt{s + \mu_0} c_{11} K_{s-1}(2r_0 a_2 s + \mu_0)$</td>
</tr>
<tr>
<td>$a_0$</td>
<td>$\sqrt{D_0}$</td>
</tr>
<tr>
<td>$a_1$</td>
<td>$\sqrt{F_0}/D_0$</td>
</tr>
<tr>
<td>$M_1$</td>
<td>$e^{\mu x} a_0 e^{\mu x_0} - a_0 e^{\mu x_0} / a_1$</td>
</tr>
<tr>
<td>$M_2$</td>
<td>$a_0 e^{\mu x} - a_0 / a_1$</td>
</tr>
<tr>
<td>$M_3$</td>
<td>$a_0 e^{\mu x} - a_0 / a_1$</td>
</tr>
<tr>
<td>$N$</td>
<td>$(H_0 M_2 + H_0 M_3) - (H_0 M_2 + H_0 M_3) K_1$</td>
</tr>
<tr>
<td>$X$</td>
<td>$-C_{D0 P_1}/(P_2 P_3 - P_1 P_4)$</td>
</tr>
<tr>
<td>$Y$</td>
<td>$-C_{D0 P_1}/(P_2 P_3 - P_1 P_4)$</td>
</tr>
<tr>
<td>$P_1$</td>
<td>$H^n F(n, m + 1; m - n + 1; H^1)$</td>
</tr>
<tr>
<td>$P_2$</td>
<td>$H^n F(n, m + 1; m - n + 1; H^1)$</td>
</tr>
<tr>
<td>$P_3$</td>
<td>$m(H_0)^n F(n, m + 1; m - n + 1; H^1)$</td>
</tr>
<tr>
<td>$P_4$</td>
<td>$m(H_0)^n F(n, m + 1; m - n + 1; H^1)$</td>
</tr>
</tbody>
</table>

Substituting the dimensionless parameters defined in Eq. (12) into Eqs. (2), (4), (10), (20), (21), one obtains the dimensionless form of the model as:

$$\frac{\partial C_D}{\partial \tilde{t}} = \frac{1}{\Phi} \left[ \frac{1 - e^{-b \tilde{t}}} {1 - e^{-\tilde{t}}} \right] \frac{\partial C_D}{\partial \tilde{x}} + \left( \frac{b}{\Phi} e^{-b \tilde{t}} - 1 \right) \frac{\partial C_D}{\partial \tilde{x}} - \mu_0 C_D,$$ (22)

$$C_D(t_0, 0) = 0.$$ (23)

$$\left( \frac{\partial C_D}{\partial \tilde{t}} \right)_{t_0 = 0} = C_{D0}. \quad (24)$$

$$\left( \frac{\partial C_D}{\partial \tilde{x}} \right)_{t_0 = 0} = 0.$$ (25)

Similarly, the solution to Eqs. (22)–(25) could be solved by the Laplace transform. The detailed derivation process can be found in the Supplementary file. The solution in the Laplace domain is as follows:

$$\tilde{T}_D = XZ^{-m} F(m, m + 1; m - n + 1; Z^{-1}) + YZ^{-m} F(n, n + 1; n - m + 1; Z^{-1}).$$ (26)

where $F$ is the Gauss Hypergeometric function $F_1$ (Abramowitz and Stegun, 1972); $z = He^{s \phi}$; $H = 1 + D_{DB}F_1$; $m = \frac{m_0}{m - 1 - 1 + \sqrt{1 + 4 \mu_0 (s + \mu_0)} }; n = \frac{m_0}{m - 1 - 1 + \sqrt{1 + 4 \mu_0 (s + \mu_0)} };$ the expressions for $X$ and $Y$ are listed in Table 1. This solution is hereinafter called the EF solution, which means the solution for solute transport with an exponential distance-dependent dispersivity and with the outlet boundary set at the end of the finite column.

When the outlet boundary is set at infinitely far from the inlet boundary, the solution has the same form as in Eq. (26), except that the expressions for $X$ and $Y$ are different. The solution is obtained by Yates (1992) and will not be repeated here. This solution is called the EL solution hereinafter, which means the solution for solute transport with an exponential distance-dependent dispersivity and with the outlet boundary set at infinitely far from the source.

Table 2 shows the specific solutions for the constant source, pulse source, instantaneous source and exponentially declining source with linear-asymptotic and exponential distance-dependent dispersivities.

For the purpose of easy inspection, we summarize the dispersivities, the effluent boundary positions and the references for different solutions defined in this study in Table 3.

As can be seen in Eqs. (18) and (26), the derived solutions contain various forms of special functions. Therefore, simple closed-form expressions for concentration distributions in the real-time domain cannot be obtained easily. We adopted a numerical inverse Laplace transform method developed by de Hoog et al. (1982) to calculate the concentrations in the real-time domain. The de Hoog algorithm is based on the full complex series integration using the trapezoidal rule and the converge acceleration using the epsilon-algorithm. Detailed information about the de Hoog algorithm can be found in de Hoog et al. (1982). Our numerical exercises show that the de Hoog algorithm is accurate enough for the purpose of this study. The code associated with the de Hoog algorithm “invlap” is integrated into our Matlab program Scale_C to assist the computation and the inverse Laplace transform (Press et al., 2007).

### 2.3. Solutions verification

In this section, we will check the accuracy of the semi-analytical LAF and EF solutions developed in Sections 2.1 and 2.2 by compar-
ing them with the published analytical solutions under some special conditions.

If we set both \( L_0 \) and \( L \) to be large enough, the LAF solution in zone-1 close to the source will not be affected by the conditions at the interface of zone-1 and 2, and the outlet boundary condition. The results of the LAF solution in zone-1 close to the source will become essentially the same as the solutions with a linear asymptotic dispersivity, which has been developed analytically by Yates (1990). Fig. 1 shows the BTCs calculated by the LAF and Yates (1990) solutions at different distances from the inlet boundaries with different growth rates of the dispersivities. In Fig. 1, we have set \( L_0 = 500 \text{ m}, L = 100 \text{ m}, R = 1.0, C_0 = 1.0 \text{ g/L}, D_0 = 1.5 \times 10^{-5} \text{ m}^2/\text{day}, V = 15 \text{ m/day} \). The values of \( D_0 \) and \( V \) are revised from Pang and Hunt (2001). Fig. 1 indicates that the difference between the LAF solution and Yates (1990) solution are undetectable at all distances with different growth rates of the dispersivities.

If \( L_0 \) is set to be very small, while \( L \) is set to be large enough, the concentration in zone-2 far away from the interface of zone-1 and zone-2 will not be affected by the linearly increasing dispersivity in zone-1. The concentrations in zone-2 predicted by the LAF solution will become virtually the same as those predicted by the solution to the ADE with a constant dispersivity, which could be found in Brenner (1962) and van Genuchten and Parker (1984) (hereinafter called the ADE solution). Fig. 2 shows the comparisons of the concentrations calculated by the LAF and ADE solutions at different distances with different asymptotic dispersivities \( \lambda_0 \). In Fig. 2, \( L_0 = 0.5 \text{ m}, L = 100 \text{ m}, R = 1.0, C_0 = 1.0 \text{ g/L}, D_0 = 1.5 \times 10^{-5} \text{ m}^2/\text{day}, V = 15 \text{ m/day} \). According to Fig. 2, the results calculated by the LAF solution and the solutions with constant dispersivity values are also indistinguishable at different distances in zone-2 with different asymptotic dispersivity values. Therefore, the LAF solution is sufficiently accurate for the purpose of this study.

Similarly, if we set the column length \( L \) to be large enough in the EF solution, the results calculated by the EF and EI solutions should be the same. Fig. 3 presents the comparisons of the BTCs calculated by the EF and EI solutions at different distances from the inlet boundary with different dispersivity growing rates. The parameters used are \( L = 100 \text{ m}, R = 1.0, C_0 = 1.0 \text{ g/L}, D_0 = 1.5 \times 10^{-5} \text{ m}^2/\text{day}, V = 15 \text{ m/day} \). The results of the EF and EI solutions are the same at different distances from the inlet boundary with different dispersivity growing rates.

### Table 2

<table>
<thead>
<tr>
<th>Solution type</th>
<th>LAF solution</th>
<th>EF solution</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant source ( C_0 = C_a )</td>
<td>Eq. (18)</td>
<td>Eq. (26)</td>
<td>Huang et al. (1996)</td>
</tr>
<tr>
<td>Pulse source ( { C_0 - C_a, t &lt; t_0 } )</td>
<td>{ Eq. (18), ( (1 - e^{-kt}) ) }</td>
<td>{ Eq. (26), ( (1 - e^{-kt}) ) }</td>
<td>Huang et al. (1996)</td>
</tr>
<tr>
<td>Instantaneous source ( C_0 = C_a )</td>
<td>Eq. (18)</td>
<td>Eq. (26)</td>
<td>Huang et al. (1996)</td>
</tr>
<tr>
<td>Exponentially declining source ( C_0 = C_a e^{-kt} )</td>
<td>Eq. (18)</td>
<td>Eq. (26)</td>
<td>Huang et al. (1996)</td>
</tr>
</tbody>
</table>

Note: \( t_0 \) is the time when the solute injection stops (T); \( L_0 \) is the dimensionless form of \( L_0 \), and \( \Sigma_{0d} = \frac{C_a V}{RL} \); \( M \) is the total amount of tracer mass added to a unite area \( (\text{M L}^{-2}); \( \delta(t) \) is the Dirac delta function with respect to \( t \) \( (T^{-1}); \( C_{ia} \) is the initial source concentration \( (\text{M L}^{-3}); k \) is the declining rate of the source concentration \( (T^{-1}).

### Table 3

Summary of different solutions.

<table>
<thead>
<tr>
<th>Solution name</th>
<th>Distance-dependent dispersivity</th>
<th>Effluent boundary position</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAF solution</td>
<td>Linear-asymptotic</td>
<td>Finite distance</td>
<td>This study</td>
</tr>
<tr>
<td>LA solution</td>
<td>Linear-asymptotic</td>
<td>Infinitely far away</td>
<td>Huang et al. (1996)</td>
</tr>
<tr>
<td>EF solution</td>
<td>Exponential</td>
<td>Finite distance</td>
<td>This study</td>
</tr>
<tr>
<td>EI solution</td>
<td>Exponential</td>
<td>Infinitely far away</td>
<td>Yates (1992)</td>
</tr>
<tr>
<td>ADE solution</td>
<td>Constant dispersivity</td>
<td>Finite distance</td>
<td>Brenner (1962)</td>
</tr>
</tbody>
</table>

Fig. 1. Comparisons between the LAF solution in zone-1 and Yates (1990) solution with the growth rates of the dispersivities equaling 0.1, 0.5, and 0.8, and at distances of \( x = 10 \text{ m}, x = 50 \text{ m}, x = 100 \text{ m}, \) and \( x = 150 \text{ m} \). Lines without circles are calculated by the LAF solution, while lines with circles are calculated by the Yates (1990) solution.
growth rates of the dispersivities and asymptotic dispersivities. Thus, the EF solution is also accurate enough for the purpose of this study.

3. Analysis

In this section, we will investigate the features of the above derived LAF and EF solutions by exploring their sensitivities to the parameters characterizing the dispersivities, and studying their differences from the corresponding LAI or EI solutions. The chemical tracer is assumed to be injected from the time 0 to the time \( t_0 = 1 \) day. For the sake of simplicity, the adsorption of the chemical tracer and the reaction are not considered. Therefore, \( R = 1 \) and \( \mu = 0 \) for all the cases below. The other default parameters are set as \( L = 8 \) m, \( C_0 = 1.0 \) g/L, \( D_0 = 1.5 \times 10^{-5} \) m²/day, \( V = 2 \) m/day.

3.1. Analysis of solutions with linear asymptotic distance-dependent dispersivities

The solutions to the 1D solute transport with linear-asymptotic distance-dependent dispersivities include the LAF solution developed in this study for a finite domain and the LAI solution developed by Huang et al. (1996) for a semi-infinite domain. In both solutions, the parameter \( L_0 \) represents the maximum dispersivity growing distance, and the parameter \( \lambda \) represents the growth rate of the dispersivity. By fixing \( L_0 \) to be 4 m and increasing \( \lambda \) from 0.05, to 0.1, 0.2 and 0.5 in the LAF solution, we find that the peak concentrations for the BTCs at \( x = 8 \) m decrease, and the arrival time for the peak concentrations decrease as well, while the spreading extents for the concentration distributions increase (Fig. 4a). That is because as \( \lambda \) increases, the dispersivities across the distances increase accordingly, which leads to enhanced dispersive effects. Fig. 4b shows the BTCs at \( x = 8 \) m calculated by the LAF solution with a fixed \( \lambda \) (0.1) and varied \( L_0 \) (0.5 m, 2 m, 5 m and 8 m). According to Fig. 4b, increasing \( L_0 \) while fixing \( \lambda \) has the same effect as increasing \( \lambda \) while fixing \( L_0 \), because both of them increase the average dispersivities across the distances and enhance the dispersive effects.

In Fig. 5, we compare the BTCs at \( x = 8 \) m calculated by the LAF and LAI solutions with different maximum dispersivity growing distances \( L_0 \) and growth rates of the dispersivities \( \lambda \). As can be seen from Fig. 5, the concentrations at the increasing limb of the BTCs calculated by the LAF solution are higher than their counterparts by the LAI solution; at the decreasing limb of the BTCs, the concentrations calculated by the LAF solution are lower than those
It sometimes displays the discrepancies among different solutions the time change of the first derivative of the concentration to time. (RTDs) calculated by the LAF and LAI solutions. RTD is defined as the Peclet number increases. BTCs calculated by solutions using different boundary conditions slowly converge to each other with the findings of Parlange and Starr (1975) that only the outlet boundary condition at the end of the column. This is consistent with the findings of Parlange and Starr (1975) that only the boundary condition at the entrance of the column affects the profile within the column, and the outlet boundary condition affects the profiles upstream of the entrance of the column, and the outlet boundary condition affects the profiles upstream of x = 0 for short distance only. As and/or increase, the distances decrease from which the two solutions begin to deviate from each other. For example, if we keep the maximum dispersivity growing distance 0 being 6 m, and increase the growth rate of the dispersivity from 0.05 to 0.5, the dimensionless distance from which the solutions begin to deviate decreases from 0.96 to 0.4. Similar results have been obtained in Perez Guerrero and Skaggs (2010) by comparing their solution setting the outlet boundary condition at the end of the column with the solution of Yates (1990) setting the outlet boundary condition at infinite far.

### 3.2 Analyses of solutions with exponential distance-dependent dispersivities (EF solution)

The solutions to the 1D solute transport with exponential distance-dependent dispersivities include the EF solution developed calculated by the LAF solution. The peak concentrations for the LAF solution are always greater than those for the LAI solution. The differences between the LAF and LAI solutions increase with and/or . As indicated by Brigham (1974), Parlange and Starr (1975) and van Genuchten and Parker (1984), solutions with different boundary conditions slowly converge to each other as the Peclet number increases. BTCs calculated by solutions using boundary conditions of Eqs. (1) and (5), and boundary conditions of Eqs. (2) and (4) are essentially the same when the Peclet number reaches a value of 20 (van Genuchten and Parker, 1984).

In Fig. 6, we compare the residence time distribution curves (RTDs) calculated by the LAF and LAI solutions. RTD is defined as the time change of the first derivative of the concentration to time. It sometimes displays the discrepancies among different solutions better than the BTCs. As evident in Fig. 6, when both and 0 are small, the differences among the results calculated by the LAF and LAI solutions are negligible. As and/or increase, the RTDs calculated by the LAF solution change more rapidly and have greater peak values compared with those calculated by the LAI solution.

Fig. 7 compares the concentration distribution curves with distances calculated by the LAF and LAI solutions at the time of one pore volume (0 = 1). According to Fig. 7, the concentrations calculated by these two solutions are exactly the same close to the inlet boundaries. However, at places close to the outlet boundaries the concentrations calculated by setting the outlet boundary condition infinitely far are always lower than those calculated by setting the outlet boundary condition at the end of the column. This is consistent with the findings of Parlange and Starr (1975) that only the boundary condition at the entrance of the column affects the profile within the column, and the outlet boundary condition affects the profiles upstream of x = L for short distance only. As and/or increase, the distances decrease from which the two solutions begin to deviate from each other. For example, if we keep the maximum dispersivity growing distance 0 being 6 m, and increase the growth rate of the dispersivity from 0.05 to 0.5, the dimensionless distance from which the solutions begin to deviate decreases from 0.96 to 0.4. Similar results have been obtained in Perez Guerrero and Skaggs (2010) by comparing their solution setting the outlet boundary condition at the end of the column with the solution of Yates (1990) setting the outlet boundary condition at infinite far.
in Section 2.2 and the EI solution developed by Yates (1992). The basic difference between the EF and EI solutions is that the EF solution sets the outlet boundary condition at the end of a finite column, while the EI solution sets it at infinitely far. Both the EF and EI solutions have a parameter $b/L$ to characterize the growth rate of the dispersivity and parameter $\alpha_0$ to represent the asymptotic dispersivity. As presented in Fig. 8a, when the growth rate of the dispersivity $b/L$ in the EF solution is fixed at 0.1 m$^{-1}$, and the asymptotic dispersivity $\alpha_0$ is increased from 1 m, to 2 m, 5 m and then 10 m, the BTCs at the end of the finite column $x = 8$ m show increasingly enhanced dispersive effects, which is due to the increased effective dispersivities over the column (The effective dispersivity is defined as the arithmetical average of the dispersivity over the domain). At the same time, if we fix the value of $\alpha_0$ to be 1 m and increase $b/L$ from 0.05, to 0.1, 0.2 and then 0.5 m$^{-1}$, the average dispersivity across the travel distance also increases, leading to a stronger effect of dispersion (Fig. 8b).

Fig. 9 compares the BTCs at $x = 8$ m calculated by the EF and EI solutions with different asymptotic dispersivities $\alpha_0$ and growth rates of the dispersivities $b/L$. Because of the different outlet boundary conditions, the EF and EI solutions differ greatly from each other when $\alpha_0$ and/or $b/L$ are large (Peclet numbers are small). The BTCs calculated by the EF solution rise faster than those calculated by the EI solution, and possess higher peak values. The BTCs calculated by the EI solution have slightly longer tails. These discrepancies increase with $\alpha_0$ and/or $b/L$.

Fig. 10 compares the RTDs at the end of the column calculated by the EF and EI solutions. The RTDs calculated by the EF solutions have larger magnitudes than those calculated by the EI solutions. When both $\alpha_0 = 1$ m and $b/L = 0.05$ m$^{-1}$, the differences between the EF and EI solutions are detectable after about half pore volume. However, when $\alpha_0 = 5$ m and $b/L = 0.5$ m$^{-1}$, their differences become detectable at about 0.1 pore volume, and the magnitude of the difference is as large as 60% at the time of 0.3 pore volume.

In Fig. 11, we compared the concentration distribution curves with travel distances calculated by the EF and EI solutions at the time of one pore volume ($t_D = 1$). The differences between the concentration distribution curves are non-detectable close to the inlet boundaries. These differences increase with travel distances close to the outlet boundaries. The influence distances of the boundary conditions increase with the asymptotic dispersivity $\alpha_0$ and the growth rate of the dispersivity $b/L$. When $\alpha_0 = 5$ m and $b/L = 0.5$ m$^{-1}$, the concentrations calculated by the EI solutions are lower than those calculated by the EF solutions almost across the whole column for the parameters used in this study.

Based on the discussion in Section 3, we may conclude that dispersive effects for solutions using either the linear asymptotic or exponential distance-dependent dispersivities increase with the asymptotic dispersivities. The influence of the outlet boundary conditions are only important when the averaged Peclet numbers across the columns are small (less than 10 for this study).

4. Application

In this section, the developed LAF and EF solutions are used to interpret the laboratory column tracer experiment conducted by Huang et al. (1995). The soil column was 12.5 m in length, with an internal dimension of 10 cm $\times$ 10 cm. A homogenous soil column with medium-textured sand and a heterogeneous soil column with a wide range of soil materials were prepared to investigate the solute transport mechanism. All the soil materials were clean, well-sorted and contained negligible organic matter. Thus, the adsorption of the chemical tracer could be neglected, and $R = 1$. A steady saturated flow was maintained in the columns by using Mariotte bottles and constant head level apparatus. De-aired tap
water was continuously injected into both the homogenous and heterogeneous soil columns for about 1 week, after which, a NaCl solution of concentration $C_0 = 6$ g/L was applied to both columns. NaCl concentrations were measured at 50 cm intervals in the homogenous soil column and 100 cm intervals in the heterogeneous soil column. Detailed information for these column experiments can be found in Huang et al. (1995) and Gao et al. (2010).

In order to predict the BTCs for the column experiments, the parameters describing the dispersivities, $L_0$ and $\lambda$ for the LAF solution, $x_0$ and $b$ for the EF solution, and the pore water velocity $V$ are required. In this study, we first use the available concentration data at the largest distances of each column 12.0 m (or 1200 cm) to conduct parameter optimization to search for the optimal values for $L_0$, $\lambda$, $x_0$, $b$, $L$, and $V$. Secondly, we will use the obtained $L_0$, $\lambda$, $x_0$, $b$, $L$, and $V$ values to predict the BTCs at other distances. The simplex method is employed to do the parameter optimization for its simplicity and rapid convergence (You et al., 2010). One noticeable point is that the results for the parameter optimization may be non-unique. However, a good initial guess of the parameters to be optimized would lead to a rapid convergence to a unique pair of results (You et al., 2010). Based on the results in Huang et al. (1995) and Gao et al. (2010), our initial guess for $V$, $L_0$, $\lambda$, $x_0$ and $b$, $L$ are 35 cm/h, 100 cm, 0.25, 25 cm and 0.05 cm$^{-1}$ respectively for the homogenous soil column, and 60 cm/h, 300 cm, 0.2, 60 cm and 0.02 cm$^{-1}$ respectively for the heterogeneous soil column.

Fig. 12 shows the predicted BTCs at different distances from the source for the homogenous soil column. The parameters used here are the best estimated values at 1200 cm, which are listed in Table 4. In Table 4, RMSE is the root mean square error for each solution, which is calculated to quantify the goodness of simulations (You et al., 2010). RMSE is defined as

$$RMSE = \sqrt{\frac{\sum_{n=1}^{N} (R_n - \bar{R}_n)^2}{N}},$$

where $R_n$ and $\bar{R}_n$ are the measured data and simulated results, respectively; $N$ is the number of measurements. Table 4 demonstrates that the performance of the LAF, EF, LAI, and EI solutions, and the solution to the traditional ADE with a constant dispersivity (the ADE solution) are the same at $x = 1200$ cm in the homogenous soil column. In the heterogeneous soil column, the performances of the LAF and LAI solution seem slightly better than the other solutions. The boundary conditions here seem not important in both the homogenous and heterogeneous soil columns, because the length of both columns are very large (1200 cm) and the averaged Peclet numbers are large (greater than 10) as well.

As evident in Fig. 12, the performances of the LAF and EF solutions are the same for all the distances in the homogenous soil column. Because the values for the parameters are estimated from the concentration data at $x = 1200$ cm, the closer to 1200 cm, the better the prediction is (Fig. 12). The same conclusion is obtained in Gao et al. (2010). Our numerical exercise shows that the performances of the LAF, LAI, EF and EI solutions are also similar at other distances in the homogenous soil column. That is because the optimized dispersivities by all these solutions are relatively small.

![Fig. 11. Comparisons of the concentration distribution curves when $t_0 = 1$ calculated by the EF (lines without markers) and EI (lines with markers) solutions with different asymptotic dispersivities $x_0$ and growth rates of the dispersivities $b/L$.](image1)

![Fig. 12. The predicted BTCs in the homogenous soil column at $x = 600$ cm, 800 cm, 1000 cm, and 1200 cm by the LAF and EF solutions using the best estimated parameters at $x = 1200$ cm.](image2)
(around 5 cm) and quite similar across the homogenous soil column.

Fig. 13 presents the calculated BTCs at different distances in the heterogeneous soil column. The parameters employed are also the optimal values obtained from 1200 cm (Table 4). As can be expected, the performances of all the solutions (the LAF, LAI, EF and EI solutions) in the heterogeneous soil column are not as good as that in the homogenous soil column (Table 4), because the heterogeneous soil column has a much wider distribution of soil properties than the homogenous one. The LAF and EF solutions generally work well close to 1200 cm. However, their performances are not good at distances far away from 1200 cm (600 cm for example). Besides, the discrepancies of the predicted concentrations between the LAF and EF solutions increase with the distances away from 1200 cm (Fig. 13).

According to Table 4, the dispersivity is not a constant and increases with the travel distance close to the inlet boundary even in a homogenous soil column. The study by Levy and Berkowitz (2003) shows that even in a carefully packed homogeneous soil column, grain size heterogeneity and preferential flow exist, and will significantly impact the water flow and solute transport. In the homogenous soil column, the asymptotic dispersivity and the travel distance for the dispersivity to reach the asymptotic one are both much smaller than their counterparts in the heterogeneous one. That is because the heterogeneous soil column has a much wider range of soil properties across the travel distance.

5. Summary and conclusions

This study developed two new semi-analytical solutions for the 1D solute transport in a finite domain with time-dependent sources and distance-dependent dispersivities. The dispersivity in the LAF solution increases linearly, and the dispersivity in the EF solution increases exponentially with the travel distance from a zero value at the source until an asymptotic value is reached. The third type inlet and丹克沃茨 outlet boundary conditions were used in both solutions. The developed solutions were demonstrated to be accurate enough for the purpose of this study by comparing with previously published solutions under special conditions.

Comparisons of the LAF and EF solutions with the previously published LAI and EI solutions, which set the outlet boundary condition to be infinitely far, showed that the choice of the outlet boundary conditions significantly influenced the BTCs and concentration distributions when the Peclet numbers were small. Compared with the LAI/EI solution, the BTCs calculated by the LAF/EF solution changed more rapidly and possessed higher peak values for pulse sources. These discrepancies increased with the asymptotic dispersivities. At a fixed time, the concentrations calculated by the LAF/EF solution were the same as those calculated by the LAI/EI solution close to the source. From a certain travel distance the concentrations calculated by the LAF/EF solution became higher than those calculated by the LAI/EI solution. This distance decreased with the asymptotic dispersivity. One should pay special attention to the choice of the boundary conditions to accurately interpret solute transport in finite domains when the Peclet number is small (less than 10 for this study).

Application of the developed solutions to interpret the laboratory column tests conducted by Huang et al. (1995) indicated that all the solutions performed the same in the homogenous soil column because the asymptotic dispersivity in it is small, while the LAF and LAI solutions performed slightly better than the others in the heterogeneous one. The dispersivity was not a constant and increased with the travel distance at the place close to the inlet boundary even in the homogeneous soil column.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2013.02.027.

References


