

# Exact solutions for one-dimensional transport with asymptotic scale-dependent dispersion

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*A general analytical solution is developed for one-dimensional solute transport in heterogeneous porous media with scale-dependent dispersion. The solution assumes that the dispersivity,  $\alpha$ , increases linearly with distance,  $x$ , that is,  $\alpha(x) = ax$ , until some distance  $xv$ , after which  $\alpha$  reaches an asymptotic value,  $\alpha_L = ax$ . The parameters  $a$  and  $xv$  characterize the nature of the scale-dependent dispersion process. The general solution contains as special cases the solutions of the classical convection-dispersion equation (CDE) assuming a constant dispersivity, and a recent solution by Yates assuming a linearly increasing dispersivity with distance. A simplified solution is also derived for cases where diffusion can be neglected. In addition, a solution for steady-state transport is presented. Results obtained with the proposed solutions demonstrate several features of scale-dependent dispersion in nonhomogeneous media which differ from those predicted with the CDE model and the model of Yates.*

## 1. Introduction

The subsurface transport of chemicals is affected by a large number of processes and porous media properties including convective transport with flowing water, molecular diffusion, hydrodynamic dispersion, equilibrium or nonequilibrium exchange with the solid phase if reactive solutes are involved, and possibly production and decay processes. Most current models for predicting solute transport in soil and groundwater are based on convection-dispersion-type transport equations. For one-dimensional transport of linearly interacting solutes during steady-state water flow, the transport equation may be written as

$$R \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D(x) \frac{\partial c}{\partial x} \right] - \nu \frac{\partial c}{\partial x} - \mu c \quad (1)$$

where  $c$  is the solution concentration,  $R$  is a retardation factor accounting for linear equilibrium sorption,  $D$  is the dispersion coefficient,  $\nu$  is the average steady-state pore-water velocity,  $\mu$  is a first-order decay coefficient,  $t$  is time, and  $x$  is distance. The dispersion coefficient  $D$  in

equation (1) is generally considered to be a linear function of the pore-water velocity as follows:

$$D = D_0 + \alpha \nu \quad (2)$$

where  $D_0$  is the porous medium diffusion coefficient, and  $\alpha$  is the dispersivity. For constant  $\alpha$ , equation (1) reduces to the classical convection-dispersion equation (CDE)<sup>2,3</sup>:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \nu \frac{\partial c}{\partial x} - \mu c \quad (3)$$

The CDE model based on equations (2) and (3) has been quite successful in describing results from laboratory displacement studies involving carefully constructed homogeneous soil columns. The dispersivity,  $\alpha$ , in such studies is usually on the order of a few millimeters or centimeters.<sup>3</sup> These results are in contrast to those from field experiments which indicate that the dispersivity for transport in natural geologic media can be one or several orders of magnitude higher as compared with relatively small laboratory soil columns.<sup>3-7</sup> Moreover, results from field studies suggest that the dispersivity may be scale-dependent, i.e.,  $\alpha$  increases with distance,  $x$ , from the pollution source. The growth with distance of the dispersion process is a consequence of the heterogeneous nature of the subsurface environment. Most geological materials are extremely nonhomogeneous because of the presence of irregular stratifications, fissures and fractures, and lenses of high or low permeability. These nonhomogeneities cause the hydraulic properties to vary spatially, leading to spatial fluctuations in the fluid velocity, and eventually to a dispersivity which increases with distance or time.<sup>5,15</sup>

Attempts to simulate chemical transport in heterogeneous media have been based mostly on stochastic analy-

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ses.<sup>6,9-14</sup> Alternatively, several investigators have incorporated scale-dependent dispersivity functions in numerical solutions of the transport equation.<sup>5,15</sup> Recently, Barry and Sposito<sup>16</sup> developed an analytical solution of the convection-dispersion equation with time-dependent transport coefficients. Yates' subsequently developed analytical solutions for transport with scale-dependent dispersion by assuming that  $\alpha$  increases linearly with distance. According to this model, the increase of  $\alpha$  with distance will be unlimited. However, the results from field experiments at different scales indicate that while the dispersivity initially increases with travel distance,  $\alpha$  eventually may approach a finite asymptotic value.<sup>3-5,17,18</sup> These results, in turn, are consistent with theoretical studies of the dispersion process in heterogeneous media by Gethar," Sposito et al.," Dagan," Shapiro and Cvetkovic,<sup>12</sup> Zhang and Neuman,<sup>14</sup> and Tompson,<sup>19</sup> among others.

The objective of this paper is to develop a set of alternative analytical solutions of the convection-dispersion equation for heterogeneous media assuming scale-dependent dispersion. The solutions assume that the dispersivity increases linearly with  $x$  until some distance  $x_0$ , after which  $\alpha$  reaches an asymptotic value,  $\alpha_L = ax_0$ . The results generalize the earlier solutions by Yates' which form a subset of our solutions for the limiting case when  $x_0 \rightarrow \infty$ .

## 2. Transport model

Similarly as in equation (2), we assume that the dispersion coefficient  $D(x)$  in (1) is linearly proportional to the pore water velocity

$$D(x) = \alpha(x)\nu + D_0 \tag{4}$$

in which  $\alpha(x)$  is now a scale-dependent dispersivity function. Consistent with previous experimental studies,<sup>5,18</sup>  $\alpha(x)$  is assumed to increase linearly with distance until some travel distance  $x_0$  after which the dispersivity becomes constant, i.e.,

$$\alpha(x) = \begin{cases} ax & x \leq x_0 \\ \alpha_L & x > x_0 \end{cases} \tag{5}$$

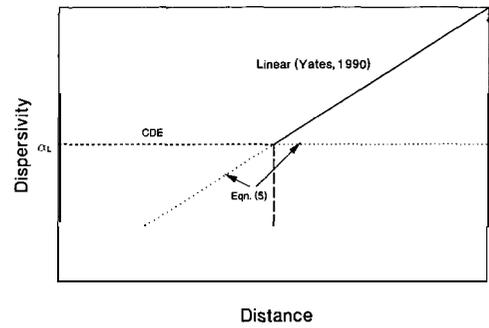
in which  $\alpha_L = ax_0$ , and where  $a$  and  $x_0$  are constants. **Figure 1** compares equation (5) with the dispersivity functions in the CDE model and the formulation of Yates.' With the above assumptions, equation (1) may be restated as follows

$$R \frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x} \left[ (ax\nu + D_0) \frac{\partial c_1}{\partial x} \right] - \nu \frac{\partial c_1}{\partial x} - \mu c_1 \tag{6a}$$

for  $0 \leq x \leq x_0$

$$R \frac{\partial c_2}{\partial t} = D_L \frac{\partial^2 c_2}{\partial x^2} - \nu \frac{\partial c_2}{\partial x} - \mu c_2 \text{ for } x > x_0 \tag{6b}$$

where  $D_L = \alpha_L\nu + D_0$  is the asymptotic dispersion coefficient, and  $c_1$  and  $c_2$  are the solution concentrations in regions 1 (linearly increasing  $\alpha$ ) and 2 (constant asymptotic  $\alpha_L$ ), respectively.



**Figure 1. Schematic of several dispersivity models: (a) constant dispersivity  $\alpha_L$  (representing the classical CDE); (b) linear function of distance'; (c) the proposed linear-asymptotic dispersivity (LAD) model assuming a linear function of distance for  $0 \leq x \leq x_0$ , and a constant dispersivity  $\alpha_L$  for  $x > x_0$ .**

Equations (6a, 6b) will be solved for a semi-infinite system ( $0 \leq x < \infty$ ) subject to the initial condition

$$c_1(x, 0) = c_2(x, 0) = C_i \tag{7}$$

where  $C_i$  is a constant and a general downgradient ("exit") condition given by

$$\frac{\partial c_2}{\partial x}(\infty, t) = 0 \tag{8}$$

Two different boundary condition can be applied at  $x = 0$ : a first- or concentration-type boundary condition of the form

$$c_1(0, t) = C_0 \tag{9}$$

or a third- or flux-type condition

$$\left[ -D(x) \frac{\partial c_1}{\partial x} + \nu c_1 \right]_{x=0} = \nu C_0 \tag{10a}$$

in which  $C_0$  is a constant. Since  $D(0) = D_0$ , equation (10a) is equivalent to

$$\left[ -D_0 \frac{\partial c_1}{\partial x} + \nu c_1 \right]_{x=0} = \nu C_0 \tag{10b}$$

Notice that the flux boundary condition is identical to the concentration boundary condition when  $D_0 = 0$ , i.e., when the contribution of diffusion to the dispersion coefficient can be neglected.

The development above shows that the scale-dependent dispersion problem, using equation (5) for the dispersivity  $\alpha$ , is reformulated in terms of a two-layer transport problem involving separate concentrations  $c_1$  and  $c_2$  for the two subregions. The approach requires assumptions about how the two regions are coupled. Following Leij et al.,<sup>20</sup> two different approaches will be used to solve equations (6a) and (6b) analytically. In one approach, we assume that region 1 ( $x < x_0$ ) is an effectively semi-infinite system and hence that concentrations in region 1 are not affected by what happens downstream in region 2. With this assumption, the following exit boundary condition can be imposed for  $c_1$ :

$$\frac{\partial c_1}{\partial x} \Big|_{x \rightarrow \infty} = 0 \tag{11}$$

After obtaining the solution for  $c_1$  in this manner, the solution for transport in region 2 can be derived using the concentration of region 1 at  $x = x_0$  as the inlet condition for region 2. One may for this purpose assume either concentration continuity at the interface, i.e.,

$$c_1(x_0, t) = c_2(x_0, t) \tag{12}$$

or continuity in the solute flux as follows

$$\left(-D_L \frac{\partial c_1}{\partial x} + \nu c_1\right)\Big|_{x=x_0} = \left(-D_L \frac{\partial c_2}{\partial x} + \nu c_2\right)\Big|_{x=x_0} \tag{13}$$

In a second approach, we consider region 1 to be finite and invoke both concentration continuity and flux continuity at the interface,  $x = x_0$ , i.e., conditions (12) and (13) are now imposed simultaneously.

### 3. Approach 1: Semi-infinite first region

We will use Laplace transform techniques to solve equations (6a) and (6b) subject to initial condition (7) and several sets of boundary conditions. Taking the Laplace transform of the governing equations and incorporating the initial condition gives

$$R(p\bar{c}_1 - C_i) = \frac{d}{dx} \left[ (ax\nu + D_0) \frac{d\bar{c}_1}{dx} \right] - \nu \frac{d\bar{c}_1}{dx} - \mu\bar{c}_1$$

for  $0 \leq x \leq x_0$  (14a)

$$R(p\bar{c}_2 - C_i) = D_L \frac{d^2\bar{c}_2}{dx^2} - \nu \frac{d\bar{c}_2}{dx} - \mu\bar{c}_2 \text{ for } x > x_0$$
(14b)

where  $p$  is the Laplace transform variable.

#### 3.1 Constant concentration inlet boundary condition

We first solve equations (14a, 14b) subject to equations (8), (9), (11), and (12). The boundary conditions in the Laplace domain are

$$\bar{c}_1(0, p) = C_0/p \tag{15}$$

$$\bar{c}_1(x_0, p) = \bar{c}_2(x_0, p) \tag{16}$$

$$\frac{d\bar{c}_1}{dx}(\infty, p) = 0 \quad \frac{d\bar{c}_2}{dx}(\infty, p) = 0 \tag{17a,b}$$

Equation (14a) may be rewritten as

$$\frac{d}{dx} \left[ (ax\nu + D_0) \frac{dY}{dx} \right] - \nu \frac{dY}{dx} - R(p + \mu/R)Y = 0$$
(18)

where

$$Y = \bar{c}_1 - \frac{C_i}{p + \mu/R} \tag{19}$$

The solution of equation (18) can be written in terms of fractional order Bessel function? :

$$Y = X^{\gamma/2} \left[ A_1 I_\gamma(2\sqrt{KX}) + B_1 K_\gamma(2\sqrt{KX}) \right] \tag{20}$$

where

$$\gamma = 1/a \quad X = x + \delta \tag{21a,b}$$

$$K = \gamma(\mu + Rp)/\nu \quad \delta = \gamma D_0/\nu \tag{21c,d}$$

and  $A$ , and  $B$ , are constants to be determined from the boundary conditions. Because of (17a),  $A$ , is set to zero. Hence the general solution for the physical system  $x \leq x_0$  is

$$\bar{c}_1(x, p) = B_1 X^{\gamma/2} K_\gamma(2\sqrt{KX}) + \frac{C_i}{p + \mu/R} \tag{22}$$

Using boundary condition (15), equation (22) becomes

$$\bar{c}_1(x, p) = \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) \times \left( 1 + \frac{x}{\delta} \right)^{\gamma/2} \frac{K_\gamma[2\sqrt{K(x + \delta)}]}{K_\gamma(2\sqrt{K\delta})} \tag{23}$$

Similarly the Laplace transform solution of  $c_2$  for  $x > x_0$ , based on equations (14b), (16), and (17b), becomes

$$\bar{c}_2(x, p) = \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) e^{r(x-x_0)} \times \left( 1 + \frac{x_0}{\delta} \right)^{\gamma/2} \frac{K_\gamma[2\sqrt{K(x_0 + \delta)}]}{K_\gamma(2\sqrt{K\delta})}$$
(25)

where

$$r = \frac{\nu - \sqrt{\nu^2 - 4D_L R(p + \mu/R)}}{2D_L} \tag{25a}$$

Following procedures similar to those used by Carslaw and Jaeger<sup>22</sup> (pp. 334-339) and Yates,<sup>7</sup> the inverse transform of equation (22) is (see the Appendix for details)

$$c_1(x, t) = C_0 \xi^{\gamma/2} \left[ \frac{K_\gamma(2\gamma\sqrt{\beta\xi})}{K_\gamma(2\gamma\sqrt{\beta})} - \frac{2}{\pi} I_c(\xi, t, \beta) \right] + \frac{2}{\pi} C_i \xi^{\gamma/2} e^{-\mu t/R} I_c(\xi, t, \beta) \tag{26}$$

where

$$I_c(\xi, \tau, \beta) = \int_{\sqrt{\beta}}^{\infty} \frac{e^{-\chi^2 \tau} [J_\gamma(\xi\epsilon)Y_\gamma(\epsilon) - J_\gamma(\epsilon)Y_\gamma(\xi\epsilon)]}{\chi [J_\gamma(\epsilon)^2 + Y_\gamma(\epsilon)^2]} d\chi$$
(27a)

$$\beta = \mu D_0/\nu^2 \quad \xi = 1 + x/\delta \tag{27b,c}$$

$$T = R\nu^2 t/D_0 \quad \epsilon = 2\gamma(\chi^2 - \beta)^{1/2} \tag{27d,e}$$

Using the convolution and shifting properties of the Laplace transform, we obtain the following solution for  $x > x_0$  (details are given in the Appendix)

$$\begin{aligned}
 c_2(x, t) &= C_i e^{-\mu t/R} \\
 &+ \frac{C_0 \mu \xi_0^{\gamma/2}}{R} \int_0^t e^{-\mu\tau/R} A(x - x_0, \tau) \\
 &\times \left[ \frac{K_\gamma(2\gamma\sqrt{\beta\xi_0})}{K_\gamma(2\gamma\sqrt{\beta})} - \frac{2}{\pi} I(\xi_0, t - \tau, \beta) \right] d\tau \\
 &+ \frac{C_0 - C_i}{2} \sqrt{\frac{R}{\pi D_L}} (x - x_0) \\
 &\times \exp\left[ \frac{\nu}{2D_L} (x - x_0) - \frac{\mu t}{R} \right] \\
 &\times \int_0^t \frac{1}{\tau^{3/2}} \left[ 1 - \frac{2}{\pi} \xi^{\gamma/2} I_c(\xi_0, t - \tau, 0) \right] \\
 &\times \exp\left[ -\frac{R(x - x_0)^2}{4D_L\tau} - \frac{\nu^2\tau}{4RD_L} \right] d\tau \quad (28)
 \end{aligned}$$

where

$$\xi_0 = 1 + x_0/\delta \quad (29a)$$

$$\begin{aligned}
 A(x, \tau) &= \frac{1}{2} \operatorname{erfc}\left( \frac{Rx - \nu\tau}{2\sqrt{D_L R\tau}} \right) \\
 &+ \frac{1}{2} e^{\nu x/D_L} \operatorname{erfc}\left( \frac{Rx + \nu\tau}{2\sqrt{D_L R\tau}} \right) \quad (29b)
 \end{aligned}$$

The solutions above assume concentration continuity across the interface at  $x = x_0$ . This condition is probably the most realistic if the concentration is viewed as a flux-averaged variable.<sup>20</sup> Alternatively one could also impose a continuity in the solute flux across the interface. In that case, interface condition (12) at  $x = x_0$  is replaced by (13) and the Laplace solution for  $c_2$  becomes

$$\begin{aligned}
 \bar{c}_2(x, p) &= \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) \xi_0^{\gamma/2} \\
 &\times \frac{D_L \sqrt{K/X_0} K_{\gamma-1}(2\sqrt{KX_0}) + \nu K_\gamma(2\sqrt{KX_0})}{K_\gamma(2\sqrt{K\delta})} \\
 &\times \frac{e^{r(x-x_0)}}{\nu - D_L r} \quad (30)
 \end{aligned}$$

where

$$X_0 = x_0 + \delta \quad (31)$$

No exact inverse Laplace solution for  $c_2$  could be obtained, and hence the equation should be inverted numerically.

### 3.2 Constant flux inlet boundary condition

Following the same techniques as before, the Laplace transform solutions for the constant flux boundary condition (10b), i.e., the solutions of equations (14a) and (14b) subject to equations (10b), (16) and (17a, 17b), are

$$\begin{aligned}
 \bar{c}_1(x, p) &= \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) \\
 &\times \frac{\xi^{\gamma/2}}{\sqrt{KD_0/\gamma\nu}} \frac{K_\gamma[2\sqrt{K(x+\delta)}]}{K_{\gamma+1}(2\sqrt{K\delta})} \quad (32)
 \end{aligned}$$

$$\begin{aligned}
 \bar{c}_2(x, p) &= \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) e^{r(x-x_0)} \\
 &\times \frac{\xi_0^{\gamma/2}}{\sqrt{KD_0/\gamma\nu}} \frac{K_\gamma[2\sqrt{KX_0}]}{K_{\gamma+1}(2\sqrt{K\delta})} \quad (33)
 \end{aligned}$$

These solutions were obtained by making use of the expression<sup>23</sup> (p. 460)

$$z \frac{dK_\gamma(z)}{dz} = \gamma K_\gamma(z) - z K_{\gamma+1}(z) \quad (34)$$

Following methods outlined by Yates' and Chrysikopoulos,<sup>24</sup> the inverse Laplace transforms were found to be

$$\begin{aligned}
 c_1(x, t) &= C_0 \xi^{\gamma/2} \left[ \frac{K_\gamma(2\gamma\sqrt{\beta\xi})}{\sqrt{\beta} K_{\gamma+1}(2\gamma\sqrt{\beta})} - \frac{2}{\pi} I_f(\xi, t, \beta) \right] \\
 &+ 2C_i \frac{\xi^{\gamma/2}}{\pi} e^{-\mu t/R} I_f(\xi, t, 0) \quad (35)
 \end{aligned}$$

$$\begin{aligned}
 c_2(x, t) &= C_i e^{-\mu t/R} + \frac{C_0 \mu \xi_0^{\gamma/2}}{R} \int_0^t e^{-\mu\tau/R} A(x - x_0, \tau) \\
 &\times \left[ \frac{K_\gamma(2\gamma\sqrt{\beta\xi_0})}{\sqrt{\beta} K_{\gamma+1}(2\gamma\sqrt{\beta})} - \frac{2}{\pi} I_f(\xi_0, t - \tau, \beta) \right] d\tau \\
 &+ \frac{C_0 - C_i}{2} \sqrt{\frac{R}{\pi D_L}} (x - x_0) \\
 &\times \exp\left[ \frac{\nu}{2D_L} (x - x_0) - \frac{\mu t}{R} \right] \\
 &\times \int_0^t \frac{1}{\tau^{3/2}} \left[ 1 - \frac{2}{\pi} \xi_0^{\gamma/2} I_f(\xi_0, t - \tau, 0) \right] \\
 &\times \exp\left[ -\frac{R(x - x_0)^2}{4D_L\tau} - \frac{\nu^2\tau}{4RD_L} \right] d\tau \quad (36)
 \end{aligned}$$

in which

$$\begin{aligned}
 I_t(\xi, \tau, \beta) &= \int_{\sqrt{\beta}}^{\infty} \gamma e^{-x^2 \tau} \\
 &\times [Y_\gamma(\xi \epsilon) J_{\gamma+1}(\epsilon) - J_\gamma(\epsilon) Y_{\gamma+1}(\xi \epsilon)] \\
 &\times \left\{ \epsilon \chi [J_{\gamma+1}(\epsilon)^2 + Y_{\gamma+1}(\epsilon)^2] \right\}^{-1} d\chi \quad (37)
 \end{aligned}$$

If continuity in the solute flux, equation (13), is assumed at  $x = x_0$ , the solution for  $c_2$  in the Laplace domain becomes

$$\begin{aligned}
 \bar{c}_2(x, p) &= \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) \xi_0^{\gamma/2} \\
 &\times \frac{D_L \sqrt{K/X_0} K_{\gamma-1}(2\sqrt{KX_0}) + \nu K_\gamma(2\sqrt{KX_0})}{\sqrt{D_0 \nu K / \gamma} K_{\gamma+1}(2\sqrt{K\delta})} \\
 &\times \frac{e^{r(x-x_0)}}{1 - D_L r / \nu} \quad (38)
 \end{aligned}$$

### 3.3 Solutions for special cases

In the case when molecular diffusion can be neglected, i.e., when  $D_0 = 0$  and hence  $D(x) = \alpha(x)\nu$ , the Laplace domain solutions for the constant concentration and constant flux inlet boundary conditions reduce to the same equations since  $D(0) = 0$ :

$$\begin{aligned}
 \bar{c}_1(x, p) &= \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) \\
 &\times 2(Kx)^{\gamma/2} \frac{K_\gamma(2\sqrt{Kx})}{\Gamma(\gamma)} \quad (39)
 \end{aligned}$$

$$\begin{aligned}
 \bar{c}_2(x, p) &= \frac{C_i}{p + \mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p + \mu/R} \right) \\
 &\times 2e^{r(x-x_0)} (Kx_0)^{\gamma/2} \frac{K_\gamma(2\sqrt{Kx_0})}{\Gamma(\gamma)} \quad (40)
 \end{aligned}$$

Equations (39) and (40) can be readily obtained from equations (23) and (24) by making use of the following asymptotic approximation of  $K_\gamma(z)$  for small  $z$ <sup>23</sup> (p. 400)

$$K_\gamma(z) \approx \frac{2^{\gamma-1} \Gamma(\gamma)}{2^\gamma} z^{-\gamma} \quad (41)$$

The inverse Laplace transforms of equations (39) and (40) are (see Appendix)

$$\begin{aligned}
 c_1(x, t) &= C_i e^{-\mu t/R} + \frac{C_0}{\Gamma(\gamma)} \\
 &\times \int_{\lambda/t}^{\infty} \tau^{\gamma-1} \exp\left[-\left(\tau + \frac{\gamma \mu x}{\nu \tau}\right)\right] d\tau \\
 &- \frac{C_i}{\Gamma(\gamma)} e^{-\mu t/R} \int_{\lambda/t}^{\infty} \tau^{\gamma-1} e^{-\tau} d\tau. \quad (42)
 \end{aligned}$$

$$\begin{aligned}
 c_2(x, t) &= C_i e^{-\mu t/R} \left[ 1 - \frac{\lambda_0^\gamma}{\Gamma(\gamma)} \right. \\
 &\times \left. \int_0^t A(x-x_0, \tau) \frac{e^{-\lambda_0/(t-\tau)}}{(t-\tau)^{\gamma+1}} d\tau \right] \\
 &+ \frac{C_0 \lambda_0^\gamma}{\Gamma(\gamma)} \int_0^t B(x-x_0, \tau) \\
 &\times \frac{\exp[-(\lambda_0/\tau + \mu\tau/R)]}{\tau^{\gamma+1}} d\tau \quad (43)
 \end{aligned}$$

where

$$\begin{aligned}
 B(x, t) &= \frac{1}{2} \operatorname{erfc}\left(\frac{Rx - ut}{2\sqrt{D_L Rt}}\right) \exp\left[\frac{(\nu - u)x}{2D_L}\right] \\
 &+ \frac{1}{2} \operatorname{erfc}\left(\frac{Rx + ut}{2\sqrt{D_L Rt}}\right) \exp\left[\frac{(\nu - u)x}{2D_L}\right] \quad (44a)
 \end{aligned}$$

$$u = \nu \left( 1 + \frac{4\mu D_L}{\nu^2} \right)^{1/2} \quad (44b)$$

$$\lambda = R\gamma x / \nu \quad \lambda_0 = R\gamma x_0 / \nu \quad (44c)$$

Without decay ( $\mu = 0$ ), the solutions further simplify to

$$\begin{aligned}
 c_1(x, t) &= C_0 + C_i \left[ 1 - \frac{\Gamma(\gamma, \lambda/t)}{\Gamma(\gamma)} \right] \\
 &- \frac{C_0 \lambda^\gamma}{\Gamma(\gamma)} \int_0^{1/t} \tau^{\gamma-1} e^{-\lambda\tau} d\tau \quad (45)
 \end{aligned}$$

$$\begin{aligned}
 c_2(x, t) &= C_i + (C_0 - C_i) \frac{\lambda_0^\gamma}{\Gamma(\gamma)} \\
 &\times \int_0^{1/t} A(x-x_0, \tau) \frac{e^{-\lambda_0/(t-\tau)}}{(t-\tau)^{\gamma+1}} d\tau \quad (46)
 \end{aligned}$$

We can similarly derive a solution for  $c_2$  when  $D_0 = 0$  for the continuous flux interface condition at  $x = x_0$  (note

again that  $c_1$  is the same as in equation (42)). The following results were obtained:

$$\bar{c}_2(x, p) = \frac{2(\sqrt{Kx_0})^{\gamma+1}}{\Gamma(\gamma)(\gamma-x_0r)} \left( \frac{C_0}{p} - \frac{C_i}{p+\mu/R} \right) \times K_{\gamma+1}(2\sqrt{Kx_0}) e^{r(x-x_0)} + \frac{C_i}{p+\mu/R} \tag{47}$$

$$c_2(x, t) = C_i e^{-\mu t/R} \left[ 1 - \frac{\lambda_0^{\gamma+1}}{\Gamma(\gamma)} \times \int_0^t F(x-x_0, t-\tau) \frac{e^{-\lambda_0/\tau}}{\tau^{\gamma+2}} d\tau + \frac{C_0 \lambda_0^{\gamma+1}}{\Gamma(\gamma)} \int_0^t E(x-x_0, t-\tau) \times \frac{\exp[-(\lambda_0/\tau + \mu\tau/R)]}{\tau^{\gamma+2}} d\tau \right] \tag{48}$$

where<sup>25</sup> (equations (A2) and (C6))

$$E(x, t) = \frac{\nu}{\nu+u} \operatorname{erfc} \left( \frac{Rx-ut}{2\sqrt{D_L Rt}} \right) \exp \left[ \frac{(\nu-u)x}{2D_L} \right] + \frac{\nu}{\nu-u} \operatorname{erfc} \left( \frac{Rx+ut}{2\sqrt{D_L Rt}} \right) \exp \left[ \frac{(\nu+u)x}{2D_L} \right] + \frac{\nu^2}{2\mu D_L} \exp \left[ \frac{\nu x}{D_L} - \frac{\mu t}{R} \right] \operatorname{erfc} \left( \frac{Rx+\nu t}{2\sqrt{D_L Rt}} \right) \tag{49a}$$

$$F(x, t) = \frac{1}{2} \operatorname{erfc} \left( \frac{Rx-\nu t}{2\sqrt{D_L Rt}} \right) + \sqrt{\frac{\nu^2 t}{\pi D_L R}} \exp \left[ -\frac{(Rx-\nu t)^2}{4D_L Rt} \right] - \frac{1}{2} \left( 1 + \frac{\nu x}{D_L} + \frac{\nu^2 t}{D_L R} \right) e^{\nu x/D_L} \times \operatorname{erfc} \left( \frac{Rx+\nu t}{2\sqrt{D_L Rt}} \right) \tag{49b}$$

**4. Approach 2: Finite first region**

Approach 1 assumed that region 1 can be treated as an effectively semi-infinite system, and hence that transport in region 1 is not affected by what happens in region 2. Alternatively one can also derive analytical solutions by assuming that both the concentration and the solute flux

are continuous across the interface at  $x = x_0$ . The general solutions of equations (14a) and (14b) subject to initial condition (7) and interface conditions, (12) and (13), are

$$\bar{c}_1(x, p) = \left( \frac{C_0}{p} - \frac{C_i}{p+\mu/R} \right) \xi^{\gamma/2} B_2 \times \left[ -\frac{b_1}{a_1} I_\gamma(2\sqrt{KX}) + K_\gamma(2\sqrt{KX}) \right] + \frac{C_i}{p+\mu/R} \tag{50}$$

$$\bar{c}_2(x, p) = \frac{C_i}{p+\mu/R} + \left( \frac{C_0}{p} - \frac{C_i}{p+\mu/R} \right) B_2 \times \left[ -\frac{b_1}{a_1} I_\gamma(2\sqrt{KX_0}) + K_\gamma(2\sqrt{KX_0}) \right] \times \xi_0^{\gamma/2} e^{r(x-x_0)} \tag{51}$$

respectively, in which the coefficients **a**, and **b**, are

$$a_1 = \sqrt{K/X_0} I_{\gamma-1}(2\sqrt{KX_0}) - r I_\gamma(2\sqrt{KX_0}) \tag{52a}$$

$$b_1 = -\sqrt{K/X_0} K_{\gamma-1}(2\sqrt{KX_0}) - r K_\gamma(2\sqrt{KX_0}) \tag{52b}$$

and where  $B_2$  depends on the inlet boundary conditions. Solving equations (50) and (51) for concentration boundary condition (9) yields

$$B_2 = \frac{a_1}{a_1 K_\gamma(2\sqrt{K\delta}) - b_1 I_\gamma(2\sqrt{K\delta})} \tag{53}$$

whereas for flux boundary condition (10b)  $B_2$  becomes

$$B_2 = \frac{a_1 \gamma}{\sqrt{K\delta} [K_{\gamma+1}(2\sqrt{K\delta}) a_1 + b_1 I_{\gamma+1}(2\sqrt{K\delta})]} \tag{54}$$

Equations (53) and (54) for the first- and third-type inlet boundary conditions, respectively, become identical when  $D_0 \rightarrow 0$ . In this case we have

$$\bar{c}_1(x, p) = \left( \frac{C_0}{p} - \frac{C_i}{p+\mu/R} \right) \frac{2(Kx)^{\gamma/2}}{\Gamma(\gamma)} \times [A_2 I_\gamma(2\sqrt{Kx}) + K_\gamma(2\sqrt{Kx})] + \frac{C_i}{p+\mu/R} \tag{55a}$$

$$\bar{c}_2(x, p) = \left( \frac{C_0}{p} - \frac{C_i}{p+\mu/R} \right) \frac{2(Kx_0)^{\gamma/2}}{\Gamma(\gamma)} \times [A_2 I_\gamma(2\sqrt{Kx_0}) + K_\gamma(2\sqrt{Kx_0})] \times e^{r(x-x_0)} + \frac{C_i}{p+\mu/R} \tag{55b}$$

where

$$A_2 = \frac{\sqrt{K/x_0} K_{\gamma-1}(2\sqrt{Kx_0}) + \frac{\nu-u}{2D_L} K_\gamma(2\sqrt{Kx_0})}{\sqrt{K/x_0} I_{\gamma-1}(2\sqrt{Kx_0}) - \frac{\nu-u}{2D_L} I_\gamma(2\sqrt{Kx_0})} \quad (55c)$$

If it is assumed that the dispersivity  $\alpha(x)$  increases linearly with distance without an asymptotic limit, i.e.,  $x_0 \rightarrow \infty$  (Figure 1). Only the first part,  $c_1$ , of each general solution is needed to describe fully the scale-dependent transport problem. The solutions for  $c_1$  in this paper are the same as those by Yates,<sup>1</sup> provided that the initial concentration  $C_1$  in our solutions is taken to be zero.

### 5. Solutions for steady-state transport

For steady-state transport, the solution for  $x \leq x_0$  can be directly obtained from equation (27) by letting  $t \rightarrow \infty$ , i.e.,

$$c_1(x) = C_0 \xi^{\gamma/2} \frac{K_\gamma(2\gamma\sqrt{\beta\xi})}{K_\gamma(2\gamma\sqrt{\beta})} \quad (56)$$

When  $D_0 = 0$ , this solution further reduces to

$$c_1(x) = 2C_0 \frac{(\zeta x)^{\gamma/2}}{\Gamma(\gamma)} K_\gamma(2\sqrt{\zeta x}) \quad (57)$$

where

$$\zeta = \gamma\mu/\nu \quad (57a)$$

When  $t \rightarrow \infty$ ,  $p \rightarrow 0$  and equation (24) can be approximated by

$$\bar{c}_2(x, p) \sim \frac{C_i}{p + \mu/R} + \frac{C_0}{p} \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \times \xi_0^{\gamma/2} \frac{K_\gamma(2\gamma\sqrt{\beta\xi_0})}{K_\gamma(2\gamma\sqrt{\beta})} \quad (58)$$

The inverse Laplace transform of equation (58) gives

$$c_2(x, t) = C_i e^{-\mu t/R} + C_0 \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \times \xi_0^{\gamma/2} \frac{K_\gamma(2\gamma\sqrt{\beta\xi_0})}{K_\gamma(2\gamma\sqrt{\beta})} \quad (59)$$

Therefore, the steady-state solution for  $x > x_0$  is

$$c_2(x) = C_0 \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \times \xi_0^{\gamma/2} \frac{K_\gamma(2\gamma\sqrt{\beta\xi_0})}{K_\gamma(2\gamma\sqrt{\beta})} \quad (60a)$$

which, for  $D_0 = 0$ , reduces to

$$c_2(x) = 2C_0 \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \frac{(\zeta x_0)^{\gamma/2}}{\Gamma(\gamma)} \times K_\gamma(2\sqrt{\zeta x_0}) \quad (60b)$$

For flux continuity at  $x_0$ , equations (60a) and (60b) must be replaced by, respectively,

$$c_2(x) = \frac{2C_0 \xi_0^{\gamma/2}}{\nu+u} \left( D_L \sqrt{\frac{\mu}{D_0 \xi_0}} K_{\gamma-1}(2\gamma\sqrt{\beta\xi_0}) + \nu K_\gamma(2\gamma\sqrt{\beta\xi_0}) \right) [K_\gamma(2\gamma\sqrt{\beta})]^{-1} \times \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \quad (61a)$$

and

$$c_2(x) = \frac{4C_0 (\zeta x_0)^{\gamma/2}}{\Gamma(\gamma)(\nu+u)} \left[ D_L \sqrt{\zeta/x_0} K_{\gamma-1}(2\sqrt{\zeta x_0}) + \nu K_\gamma(2\sqrt{\zeta x_0}) \right] \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \quad (61b)$$

We obtained similar steady-state solutions for a constant flux boundary condition at the inlet, i.e.,

$$c_1(x) = C_0 \xi^{\gamma/2} \frac{K_\gamma(2\gamma\sqrt{\beta\xi})}{\sqrt{\beta} K_{\gamma+1}(2\gamma\sqrt{\beta})} \quad (62)$$

and

$$c_2(x) = C_0 \xi_0^{\gamma/2} \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \times \frac{K_\gamma(2\gamma\sqrt{\beta\xi_0})}{\sqrt{\beta} K_{\gamma+1}(2\gamma\sqrt{\beta})} \quad (63a)$$

In case of flux continuity at  $x_0$ , the steady-state solutions becomes

$$c_2(x) = \frac{2C_0 \xi_0^{\gamma/2}}{\nu+u} \left( D_L \sqrt{\frac{\mu}{D_0 \xi_0}} K_{\gamma-1}(2\gamma\sqrt{\beta\xi_0}) + \nu K_\gamma(2\gamma\sqrt{\beta\xi_0}) \right) [\sqrt{\beta} K_{\gamma+1}(2\gamma\sqrt{\beta})]^{-1} \times \exp\left[\frac{(x-x_0)}{2D_L}(\nu-u)\right] \quad (63b)$$

Equations (62), (63a), (63b) for a constant flux inlet boundary condition reduce to equations (57), (60b), and (61b), respectively, when the diffusion contribution to the dispersion coefficient is neglected (i.e.,  $D_0 = 0$ ).

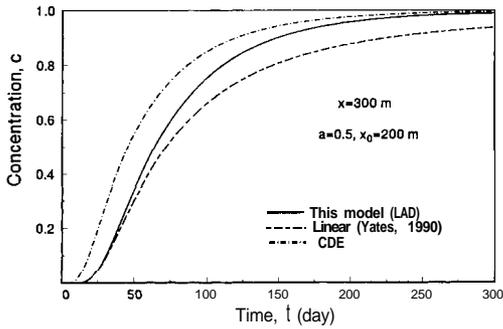


Figure 2. Comparison of breakthrough curves at  $x=300$  m for  $a=0.5$  and  $x_0=200$  m.

For approach 2, in which both the concentration and the solute flux are continuous across the interface at  $x_0$ , the steady-state solution with  $D_0 = 0$  becomes similarly

$$c_1(x) = 2C_0 \frac{(\zeta x)^{\gamma/2}}{\Gamma(\gamma)} \left[ A_3 I_\gamma(2\sqrt{\zeta x}) + K_\gamma(2\sqrt{\zeta x}) \right] \quad (64a)$$

$$c_2(x) = 2C_0 \frac{(\zeta x_0)^{\gamma/2}}{\Gamma(\gamma)} \times \left[ A_3 I_\gamma(2\sqrt{\zeta x_0}) + K_\gamma(2\sqrt{\zeta x_0}) \right] \times \exp\left[ \frac{(x-x_0)}{2D_L}(\nu-u) \right] \quad (64b)$$

where

$$A = \frac{\sqrt{\zeta/x_0} K_{\gamma-1}(2\sqrt{\zeta x_0}) + \frac{\nu-u}{2D_L} K_\gamma(2\sqrt{\zeta x_0})}{\sqrt{\zeta/x_0} I_{\gamma-1}(2\sqrt{\zeta x_0}) - \frac{\nu-u}{2D_L} I_\gamma(2\sqrt{\zeta x_0})} \quad (65)$$

### 6. Illustrative examples

The examples discussed below serve to illustrate several features of the derived analytical solutions. The values of

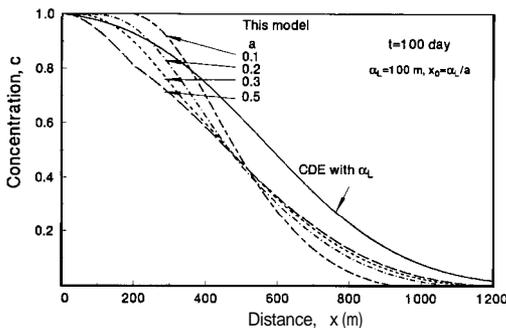


Figure 3. Concentration distributions versus distance at  $t=100$  day for various values of  $a$  and fixed  $\alpha_L=100$  m.

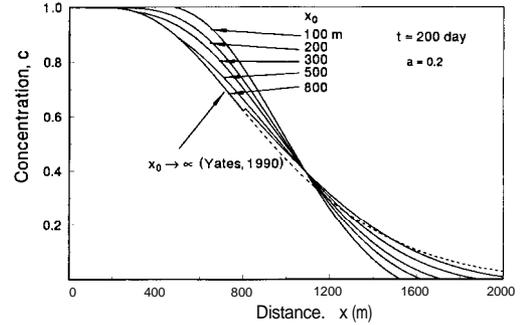


Figure 4. Concentration distributions versus distance at  $t=200$  day for  $a=0.2$ , and  $x_0=100, 200, 300, 500, 800$  m, and  $\infty$ , the later case represents Yates' linear model.'

$D_0, \mu, C_i, C_0, \nu$ , and  $R$  were rather arbitrarily fixed at 0.0, 0.0, 0.0, 1.0, 5 m/day and 1.0, respectively. Since  $D_0$  is taken to be zero, the solutions for a flux condition at the inlet boundary will be the same as those obtained using a concentration condition. Values of the model parameters  $a$  and  $x_0$  for each example are shown in the figures. Solutions were obtained by either directly evaluating the analytical expressions or using numerical inversion techniques to evaluate the Laplace domain solutions when no closed-form analytical solution could be obtained. Numerical inversion was accomplished with the method of Stehfest.<sup>26</sup> Integrals in equation (27) and similar expressions were evaluated numerically using 96 Gaussian quadrature points over a finite integration subinterval. Except where mentioned otherwise, all simulations were based on equations (26) and (28), i.e., for an infinite first region subject to concentration conditions at both the inlet and interface locations.

Figure 2 shows calculated breakthrough curves at  $x=300$  m obtained using the proposed linear-asymptotic dispersivity model given by equation (5), further simply referred to as the LAD model. Results are compared with the CDE model (constant dispersivity) and the linear model of Yates. Notice that the LAD results in Figure 2 are initially (at small times) very close to the linear model but later increasingly deviate from this model. Results obtained with the LAD model are much lower than the CDE predictions using a constant asymptotic dispersivity value consistent with equation (5), i.e.,  $D_L = \alpha_L \nu$ .

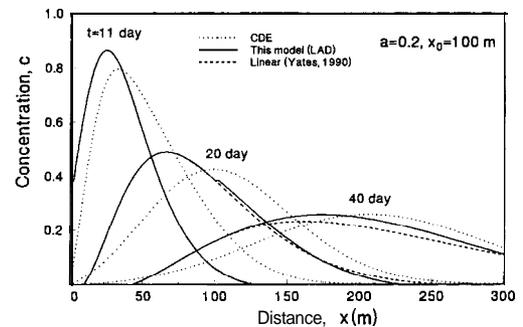
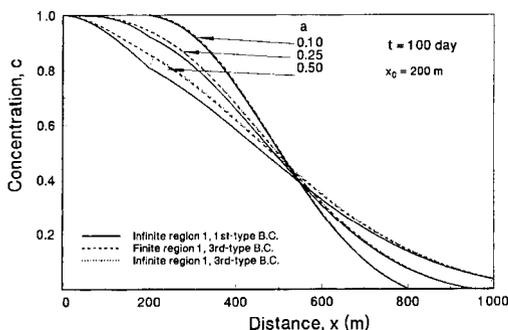


Figure 5. Calculated concentration distributions for a pulse input of solute ( $t_0=10$  day) obtained with equations (42) and (43) (LAD), the CDE assuming  $\alpha_L=20$  m, and the solutions of Yates' which assume that the dispersivity increases linearly with travel distance, respectively.

**Figure 3** shows the effect of changes in the parameter  $a$  in equation (5) on calculated concentration distributions versus distance. The calculations were conducted with a fixed asymptotic dispersivity  $\alpha_L$  of 100 m; hence, the scale-dependence length  $x_0$  changed according to  $x_0 = \alpha_L/a$ . The results in **Figure 3** indicate a much higher concentration near the inlet and less overall dispersion when  $a$  was made smaller. Notice also the relatively large differences between the LAD results and the CDE calculations assuming a constant dispersivity,  $\alpha_L$ . The influence of the scale-dependent length  $x_0$  on computed concentration distributions versus distance at  $t = 200$  day is shown in **Figure 4** for  $a = 0.2$ . As expected, the distributions became more dispersed when  $x_0$  increased because of the higher asymptotic dispersivity value,  $\alpha_L = ax_0$ . Notice that all curves with finite  $x_0$  go through approximately the same point at  $x \approx 1,080$  m which is roughly equal to the convective transport distance,  $\nu t = 1,000$  m. The predicted concentrations obtained with Yates' linear model (infinite  $x_0$ ) are lower than those calculated using the LAD model within the convective transport distance but become higher after this distance.

**Figure 5** compares concentration predictions using the LAD model with CDE results as well as with calculations obtained with the linear model of Yates.' The example involves the application of a solute pulse of duration  $t_0 = 10$  days to an initially solute-free medium. As expected the LAD results duplicated the concentration distributions obtained with Yates' linear model' at  $t = 11$  and 20 days when the travel distance was still less than  $x_0$ , while some relatively small differences become apparent for  $x > 100$  m after 40 days. Relatively large deviations occur between the CDE ( $\alpha_L = 20$  m) predictions and the proposed LAD model results at early times ( $t = 11$  and 20 days); the CDE peaks at those times are ahead of those obtained with LAD. Differences between the CDE and our model LAD models, however, are less pronounced at later times. This fact indicates that it is important also to monitor concentrations at relatively early times if the measured concentration data are to be used for identifying scale-dependent dispersion parameters.

To examine the error introduced by assuming a semi-infinite region 1 using boundary condition (11), we compared the solution for  $D_0 = 0$ , i.e., equations (42), (43),



**Figure 6.** Calculated concentration distributions assuming either concentration or flux continuity at  $x_0$  (Approach 1) or those assuming both flux and concentration continuity at the interface (Approach 2).

and (48), with equations (55a, 55b) based on the presumably more "exact" boundary conditions (12) and (13). The inverse transforms of (55a, 55b) were for this purpose evaluated numerically using the algorithm of Stehfest.<sup>26</sup>

**Figure 6** shows that the different approaches lead to very similar curves for relatively small  $a$  values. For  $a = 0.5$ , the results assuming an infinite region 1 with flux continuity at  $x_0$  also agree well with those obtained with the "exact" boundary conditions except for some deviations when  $x < x_0$ . Overall boundary condition (11) seems to have relatively little effect on the results, especially when the more realistic (and mass-conserving) flux condition at the interface  $x_0$  is adopted. However, notice from **Figure 6** that the distributions for an infinite region 1 assuming solute flux continuity at  $x = x_0$  show an obvious discontinuity at the interface.

Finally we note that the LAD dispersion model discussed in this paper contains two parameters,  $a$  and  $x_0$ , which characterize the scale-dependent dispersion process. The effects of these two parameters are more clearly visible when equation (6a) is rewritten in the form

$$R \frac{\partial c_1}{\partial t} = (ax\nu + D_0) \frac{\partial^2 c_1}{\partial x^2} - (1-a)\nu \frac{\partial c_1}{\partial x} - \mu c_1$$

for  $x \geq x_0$  (66)

We first notice that when  $a > 1$ , the convective transport term of equation (66) becomes negative. As pointed out by Yates,' it seems improbable that the dispersivity will grow so strongly with distance that this increase in  $\alpha$  would cause an apparent negative convective transport process. Moreover, field evidence<sup>5,17,18</sup> suggests that the slope of the dispersivity-distance relationship (i.e., the scale-proportional factor,  $a$ ) should be less than unity. These two factors would indicate that the parameters range  $0 \leq a \leq 1$  is physically more realistic rather than the wider range  $0 \leq a \leq 2$  advocated by Yates.'

## 7. Summary and conclusions

A scale-dependent LAD was developed to characterize dispersion in a heterogeneous porous medium. The model assumes that the dispersivity increases linearly with distance within a scale-dependent length  $x_0$ , and then retains an asymptotic value  $\alpha_L = ax_0$ . Several solutions based on this model were developed assuming one-dimensional transport in a uniform flow field. The solutions were compared with the CDE assuming a constant dispersivity and solutions by Yates' assuming that the dispersivity increases linearly with distance.

A much stronger scale-dependent effect exists when the parameters  $a$  and  $x_0$  increase in value. However, for the same asymptotic dispersivity  $\alpha_L$  value, the effect of  $a$  on the calculated concentration distribution is relatively small at large distances. The predicted concentration distributions were always the same as those obtained with Yates' linear dispersivity model' when  $0 \leq x \leq x_0$  while generally deviating substantially from that model for  $x > x_0$ . Predicted concentrations obtained with the CDE model in

most cases differed greatly from those calculated with the proposed LAD model as well as the linear model of Yates' except at larger times when an asymptotic dispersivity value was considered.

**Appendix: Derivation of inverse Laplace transforms**

According to Carslaw and Jaeger'' (p. 335, equation (6)) and Yates,' we have

$$L^{-1} \left[ \frac{K_\gamma \left[ 2\sqrt{K(x + \gamma D_0/\nu)} \right]}{pK_\gamma \left( 2\sqrt{K\gamma D_0/\nu} \right)} \right] = \frac{K_\gamma(2\gamma\sqrt{\beta\xi})}{K_\gamma(2\gamma\sqrt{\beta})} - \frac{2}{\pi} I_c(\xi, t, \beta) \tag{A1}$$

where  $L^{-1}$  indicates the inverse Laplace transform, and  $K, \gamma, \xi, \beta,$  and  $I_c(\xi, t, \beta)$  are defined in the text. Using asymptotic expansions of  $K_\gamma(z)$  for small  $z$  (e.g., equation (41)), one can show that

$$\frac{K_\gamma(2\gamma\sqrt{\beta\xi})}{K_\gamma(2\gamma\sqrt{\beta})} \approx \xi^{-\gamma/2} \text{ as } \beta \rightarrow 0 \tag{A2}$$

Thus, when  $\mu \rightarrow 0$  and hence  $\beta \rightarrow 0$  equation (A1) becomes

$$L^{-1} \left[ \frac{K_\gamma \left[ 2\sqrt{K(x + \gamma D_0/\nu)} \right]}{pK_\gamma \left( 2\sqrt{K\gamma D_0/\nu} \right)} \right]_{\mu=0} = \xi^{-\gamma/2} - \frac{2}{\pi} I(\xi, t, 0) \tag{A3}$$

Application of the shifting property of the Laplace transform to equation (A3) leads to

$$L^{-1} \left[ \frac{K_\gamma \left[ 2\sqrt{K(x + \gamma D_0/\nu)} \right]}{(p + \mu/R)K_\gamma \left( 2\sqrt{K\gamma D_0/\nu} \right)} \right] = e^{-\mu t/R} \left[ \xi^{-\gamma/2} - \frac{2}{\pi} I(\xi, t, 0) \right] \tag{A4}$$

Equations (A1) and (A4) are needed to invert the Bessel function terms in equation (23) to yield equation (26) in the main text.

Applying the convolution theorem to equation (A4) and taking the inverse transform of  $\exp[r(x - x_0)]$  from Carslaw and Jaeger<sup>22</sup> (p. 494), we obtain the following result

$$L^{-1} \left[ e^{r(x-x_0)} \frac{K_\gamma \left[ 2\sqrt{K(x_0 + \gamma D_0/\nu)} \right]}{(p + \mu/R)K_\gamma \left[ 2\sqrt{K\gamma D_0/\nu} \right]} \right]$$

$$= \frac{1}{2} \sqrt{\frac{R}{\pi D_L}} (x - x_0) \exp \left[ \frac{\nu(x - x_0)}{2D_L} \right] \times \int_0^t \exp \left[ -\frac{R(x - x_0)^2}{4D_L\tau} - \frac{\nu^2\tau}{4RD_L} \right] \times \frac{\xi^{-\gamma/2} - 2I_c(\xi_0, t - \tau, 0)/\pi}{\tau^{3/2}} d\tau \tag{A5}$$

using equation (A3) and equation (A1) of van Genuchten and Alves<sup>25</sup> (p. 9), we obtain similarly

$$L^{-1} \left[ \frac{e^{r(x-x_0)} K_\gamma \left[ 2\sqrt{K(x_0 + \gamma D_0/\nu)} \right]}{p + \mu/R} \frac{1}{pK_\gamma \left[ 2\sqrt{K\gamma D_0/\nu} \right]} \right] = \int_0^t e^{-\mu\tau/R} A(x - x_0, \tau) \times \left[ \frac{K_\gamma(2\gamma\sqrt{\beta\xi_0})}{K_\gamma(2\gamma\sqrt{\beta})} - \frac{2}{\pi} I(\xi_0, t - \tau, \beta) \right] d\tau \tag{A6}$$

where  $A(x, \tau)$  is defined by equation (29b). Equations (A5) and (A6) are needed in equation (24) to yield the solution for  $c_2(x, t)$  given by equation (28).

The inverse Laplace transform of equation (39) was derived by making use of the equations<sup>22</sup>

$$L^{-1} \left[ p^{\gamma/2} K_\gamma(y\sqrt{\gamma}) \right] = \exp \left( -\frac{y^2}{4t} \right) \frac{y^\gamma}{(2t)^{\gamma+1}} \tag{A7}$$

$$L^{-1} \left[ \frac{p^{\gamma/2} K_\gamma(y\sqrt{\gamma})}{p} \right] = \int_0^t \exp \left( -\frac{y^2}{4\tau} \right) \frac{y^\gamma}{(2\tau)^{\gamma+1}} d\tau \tag{A8}$$

and again applying the shifting property of the Laplace transform.

The inverse transform of equation (40) can be obtained using the convolution theorem and the following equations of van Genuchten and Alves<sup>25</sup>

$$L^{-1} \left[ \frac{e^{r(x-x_0)}}{p + \mu} \right] = e^{-\mu t/R} A(x, t) \tag{A9}$$

$$L^{-1} \left[ \frac{e^{r(x-x_0)}}{p} \right] = B(x, t) \tag{A10}$$

where  $A$  and  $B$  are given by equations (29b) and (44a), respectively.

## Nomenclature

- $c$  solution concentration  
 $R$  retardation factor  
 $D$  dispersion coefficient  
 $\nu$  average steady-state pore-water velocity  
 $\mu$  first-order decay coefficient  
 $t$  time  
 $x$  distance  
 $\alpha_L$  asymptotic dispersivity  
 $C_i$  initial concentration  
 $x_0$  distance where the asymptotic dispersivity value reaches  
 $D_0$  diffusion coefficient of a porous medium

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