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A Comprehensive Set of Analytical Solutions for Nonequilibrium Solute Transport With First-Order Decay and Zero-Order Production

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Solute transport in the subsurface is often considered to be a nonequilibrium process. Predictive models for nonequilibrium transport may be based either on chemical considerations by assuming the presence of a kinetic sorption process, or on physical considerations by assuming two-region (dual-porosity) type formulations which partition the liquid phase into mobile and immobile regions. For certain simplifying conditions, including steady state flow and linear sorption, the chemical and physical nonequilibrium transport models can be cast in the same dimensionless form. This paper presents a comprehensive set of analytical solutions for one-dimensional nonequilibrium solute transport through semi-infinite soil systems. The models involve the one-site, two-site, and two-region transport models, and include provisions for first-order decay and zero-order production. General solutions are derived for the volume-averaged (or resident) solute concentration using Laplace transforms assuming both first- and third-type inlet conditions, and arbitrary initial conditions, input solute concentrations, and solute production profiles. The solutions extend and generalize existing solutions for equilibrium and nonequilibrium solute transport. The general solutions are evaluated for some commonly used input and initial conditions, and zero-order production profiles. Expressions for the flux-averaged concentration are derived from the general and specific solutions assuming a third-type inlet condition. Typical examples of calculated concentration distributions resulting from several sets of initial and input conditions and zero-order production functions are also presented and briefly discussed.

INTRODUCTION

Solute transport in soil and groundwater systems is governed by a large number of complicated and often interactive physical, chemical, and microbiological processes. Attempts have been made to account for a number of these processes by developing transport models which consider the simultaneous effects of hydrodynamic dispersion, molecular diffusion, convective transport, sorption, zero-order production, and first-order decay [*Jury et al.*, 1991]. A special set of models results when nonequilibrium occurs during the transport process, presumably caused by the presence of different types of sorption sites or flow regions in the medium [*Nielsen et al.*, 1986]. Nonequilibrium transport models may be conveniently grouped into chemical nonequilibrium models which presume that chemical-kinetic processes are causing the nonequilibrium situation, and physical nonequilibrium models which assume that nonequilibrium results from a heterogeneous flow regime. Chemical nonequilibrium models include the familiar one-site and two-site sorption models which consider sorption on some (or none) of the sorption sites to be an instantaneous (equilibrium) process, while sorption on the remaining sites is thought to be governed by first-order kinetics [*Selim et al.*, 1976; *Cameron and Klute*, 1977]. In contrast, physical nonequilibrium is often modeled by using a two-region (dual-porosity) type formulation which partitions the medium into distinct mobile (flowing) and immobile (stagnant) liquid regions [*Coats and Smith*, 1964; *van Genuchten and Wierenga*, 1976]. In this case, solute exchange between the two liquid regions is considered to be a first-order mass transfer process.

Although based on different concepts, the chemical and physical nonequilibrium transport models can be put into the same dimensionless form if certain simplifying assumptions are satisfied, such as having a linear sorption process, steady state water flow, and a spatially uniform soil profile [*Nkedi-Kizza et al.*, 1984; *van Genuchten and Wagenet*, 1989]. These conditions, which imply that the pore water velocity, the soil water content, the dispersion coefficient, and the soil bulk density are constant in time and space, are also needed in order to derive analytical solutions. This situation is in contrast to most field conditions where the flow and transport regimes may be highly variable because of transient flow induced by time-dependent boundary conditions, or because of spatial and temporal variability in the hydraulic and solute transport properties. Hence the applicability of analytical solutions is limited as compared to more flexible numerical solutions. Still, analytical solutions are useful for providing rapid initial estimates of alternative pollution or remediation scenarios, especially when implemented over large spatial and temporal scales, and for validating numerical models. Analytical solutions often also provide more insight into the underlying physicochemical processes than do numerical solutions and are helpful for sensitivity analyses to investigate the effects of various transport parameters. Additionally, analytical solutions can be incorporated more easily in stochastic approaches for describing solute transport in heterogeneous soils [e.g., *Dagan and Bresler*, 1979; *Destouni and Cvetkovic*, 1991].

A large number of analytical solutions for one-dimensional nonequilibrium transport currently exists, mostly for specific models subject to unique initial and boundary conditions. Lindstrom and colleagues [*Lindstrom and Narasimhan*, 1973; *Lindstrom and Stone*, 1974] were the first to derive general solutions of the one-site nonequilibrium transport model for arbitrary initial and/or boundary conditions, but without considering first-order degradation and zero-order production. *Lindstrom* [1976] later extended the solutions to first-order decay for pulse-type solute input conditions as-

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suming an initially solute-free profile. Analytical solutions of the two-region nonequilibrium transport model, assuming pulse-type solute input conditions, were derived by *van Genuchten and Wierenga* [1976]. Their solutions were later generalized by *De Smedt and Wierenga* [1979]. *Lassey* [1988] and *van Genuchten and Wagenet* [1989] subsequently derived solutions for the two-site/two-region models with first-order decay, but without considering zero-order production and restricting the solutions to a zero initial concentration distribution. *Lassey* [1988] extended the solutions to general expressions of the flux-averaged concentration for the boundary value problem. Analytical expressions of the flux-averaged concentration for the initial value and production value problems have thus far not been derived.

The objective of this study was to derive a comprehensive set of solutions for one-dimensional nonequilibrium solute transport with first-order decay and zero-order production in a semi-infinite soil system. We start with a brief outline of the one-site and two-site chemical nonequilibrium models, as well as the two-region (mobile-immobile) physical nonequilibrium model. General solutions for the dimensionless transport equations are subsequently derived using both first- and third-type inlet boundary conditions, and assuming arbitrary input concentrations, initial conditions, and production functions. The general solutions are evaluated for specific and commonly used input concentrations, initial conditions, and zero-order production profiles. We also present expressions for the flux-averaged concentration as derived from the general and specific solutions for the volume-averaged concentration based on a third-type inlet condition using the well known relationship between the flux- and volume-averaged (or resident) concentrations [*Kreft and Zuber*, 1978; *Parker and van Genuchten*, 1984*a*]. The solutions for equilibrium transport are shown to be special cases of the nonequilibrium solutions. The effects of selected transport parameters on predicted solute distributions are also demonstrated.

MODEL

Two-Site Nonequilibrium Transport Model

The two-site sorption model makes a distinction between type-1 (equilibrium) and type-2 (first-order kinetic) sorption sites [*van Genuchten and Wagenet*, 1989]. For steady state flow in a homogeneous soil and assuming a linear sorption process, the two-site solute transport model is given by

$$\left(1+\frac{f\rho k}{\theta}\right)\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2}-v\frac{\partial c}{\partial x}-\frac{\alpha\rho}{\theta}[(1-f)kc-s_k]$$
$$-\mu_l c-\frac{f\rho k\mu_{s,e}c}{\theta}+\gamma_l(x)+\frac{f\rho\gamma_{s,e}(x)}{\theta}\qquad(1)$$

$$\frac{\partial s_k}{\partial t}=\alpha[(1-f)kc-s_k]-\mu_{s,k}s_k+(1-f)\gamma_{s,k}(x)\qquad(2)$$

where c is the volume-averaged concentration of the liquid phase (ML^{-3}); s is the concentration of the sorbed phase (MM^{-1}); D is the dispersion coefficient (L^2T^{-1}); θ is the volumetric water content (L^3L^{-3}); $v = q/\theta$ is the average pore water velocity (LT^{-1}) in which q is the volumetric water flux density (LT^{-1}); ρ is the bulk density (ML^{-3}); μ_l and μ_s are first-order decay coefficients for degradation in the liquid and sorbed phases, respectively (T^{-1}); γ_l ($ML^{-3}T^{-1}$) and γ_s($MM^{-1}T^{-1}$) are zero-order production terms for the liquid and sorbed phases, respectively; k is a distribution coefficient for linear sorption ($M^{-1}L^3$); α is a first-order kinetic rate coefficient (T^{-1}); f is the fraction of exchange sites assumed to be at equilibrium; x is distance (L); t is time (T); and the subscripts e and k refer to equilibrium and kinetic sorption sites, respectively. Equations (1) and (2) implement the customary first-order rate expression to describe kinetic sorption on the type-2 sites. Note that if $f = 0$, the two-site sorption model reduces to the one-site fully kinetic sorption model, i.e., when only type-2 kinetic sites are present.

If we employ the dimensionless parameters listed in Table 1, (1) and (2) reduce to

$$\beta R\frac{\partial C_1}{\partial T}=\frac{1}{P}\frac{\partial^2 C_1}{\partial Z^2}-\frac{\partial C_1}{\partial Z}-\omega(C_1-C_2)-\mu_1C_1+\gamma_1(Z)\qquad(3)$$

$$(1-\beta)R\frac{\partial C_2}{\partial T}=\omega(C_1-C_2)-\mu_2C_2+\gamma_2(Z)\qquad(4)$$

where C_1 is the reduced volume-averaged solute concentration, C_2 is the reduced kinetically adsorbed concentration, μ is a first-order decay coefficient, γ is a zero-order production coefficient, Z and T are space and time variables, respectively, β, R, P, and ω are adjustable model parameters, and the subscripts 1 and 2 on μ and γ refer to equilibrium and nonequilibrium sites, respectively. Table 1 gives definitions of the various dimensionless parameters in terms of the original dimensional coefficients. We shall assume that ω and μ cannot be negative. Notice that the zero-order production terms in (3) and (4) are functions of position Z, but that the first-order rate coefficients are assumed to be constant.

Two-Region Nonequilibrium Transport Model

The two-region transport model assumes that the liquid phase can be partitioned into mobile (flowing) and immobile (stagnant) regions, and that solute exchange between the two liquid regions can be modeled as a first-order process. Using the same notation as before, and again assuming steady state water flow in a homogeneous medium, the two-region solute transport model is given by [see also *van Genuchten and Wagenet*, 1989]

$$(\theta_m+f\rho k)\frac{\partial c_m}{\partial t}=\theta_m D_m\frac{\partial^2 c_m}{\partial x^2}-q\frac{\partial c_m}{\partial x}-\alpha(c_m-c_{im})$$
$$-(\theta_m\mu_{l,m}+f\rho k\mu_{s,m})c_m+\theta_m\gamma_{l,m}(x)+f\rho\gamma_{s,m}(x)\qquad(5)$$

$$[\theta_{im}+(1-f)\rho k]\frac{\partial c_{im}}{\partial t}=\alpha(c_m-c_{im})-[\theta_{im}\mu_{l,im}+(1$$
$$-f)\rho k\mu_{s,im}]c_{im}+\theta_{im}\gamma_{l,im}(x)+(1-f)\rho\gamma_{s,im}(x)\qquad(6)$$

where the subscripts m and im refer to the mobile and immobile liquid regions, respectively, the subscripts l and s refer to the liquid and sorbed phases, respectively, f represents the fraction of sorption sites that equilibrates with the

TABLE 1. Dimensionless Parameters for the Two-Site and Two-Region Transport Models

Parameter	Two-Site Model	Two-Region Model
T	vt/L	vt/L
Z	x/L	x/L
P	vL/D	$v_m L/D_m$
β	$(\theta + f\rho k)/(\theta + \rho k)$	$(\theta_m + f\rho k)/(\theta + \rho k)$
R	$1 + \rho k/\theta$	$1 + \rho k/\theta$
ω	$\dfrac{\alpha(1-\beta)RL}{v}$	$\dfrac{\alpha L}{\theta v}$
C_1	c/c_0	c_m/c_0
C_2	$\dfrac{s_k}{(1-f)kc_0}$	c_{im}/c_0
μ_1	$\dfrac{(\theta\mu_l + f\rho k\mu_{s,e})L}{\theta v}$	$\dfrac{(\theta_m\mu_{l,m} + f\rho k\mu_{s,m})L}{\theta v}$
μ_2	$\dfrac{(1-f)\rho k\mu_{s,k}L}{\theta v}$	$\dfrac{(\theta_{im}\mu_{l,im} + (1-f)\rho k\mu_{s,im})L}{\theta v}$
γ_1	$\dfrac{L(\theta\gamma_l + f\rho\gamma_{s,e})}{\theta v c_0}$	$\dfrac{L(\theta_m\gamma_{l,m} + f\rho\gamma_{s,m})}{\theta v c_0}$
γ_2	$\dfrac{L(1-f)\rho\gamma_{s,k}}{\theta v c_0}$	$\dfrac{L(\theta_{im}\gamma_{l,im} + (1-f)\rho\gamma_{s,im})}{\theta v c_0}$

Here, c_0 and L represent characteristic concentrations and lengths, respectively.

mobile liquid phase, and α is a first-order mass transfer coefficient (T^{-1}) governing the rate of solute exchange between the mobile and immobile liquid regions. Note that θ is equal to $\theta_m + \theta_{im}$.

It is convenient to also write (5) and (6) in dimensionless form using the parameters listed in Table 1. It can be shown that the resulting dimensionless transport equations are identical to (3) and (4) [see also *Nkedi-Kizza et al.*, 1984]. Hence the subscripts 1 and 2 in (3) and (4) refer to mobile and immobile regions if the dimensionless transport equations are interpreted in terms of the two-region model.

Analytical Solutions

The dimensionless transport equations given by (3) and (4) will be solved for the following general initial and boundary conditions:

$$C_1(Z, 0) = C_2(Z, 0) = C_i(Z) \qquad (7)$$

$$\left.\left(-\frac{\delta}{P}\frac{\partial C_1}{\partial Z} + C_1\right)\right|_{Z=0} = C_0(T) \qquad (8)$$

with $\delta = 0$ for a first-type and $\delta = 1$ for a third-type boundary condition, and

$$\frac{\partial C_1}{\partial Z}(\infty, T) = 0 \qquad (9)$$

where C_i is the initial concentration, and C_0 is the input concentration. Because the governing equations and the initial and boundary conditions are linear in C, the principle of superposition [e.g., *Farlow*, 1982] may be used to express the general solutions into the sum of three independent solutions involving a boundary value problem, an initial value problem, and a production value problem:

$$C_1(Z, T) = C_1^B(Z, T) + C_1^I(Z, T) + C_1^P(Z, T) \qquad (10)$$

$$C_2(Z, T) = C_2^B(Z, T) + C_2^I(Z, T) + C_2^P(Z, T) \qquad (11)$$

where the superscripts B, I, and P denote the boundary, initial, and production value problems, respectively. Each problem was solved using the method of Laplace transforms with respect to T and Z. The solution process is outlined in the appendix. We first present a general solution, and subsequently show several specific solutions for each problem. The separate expressions for C^B, C^I, and C^P given below may be simply added to yield the complete analytical solution for a particular set of input concentrations, initial conditions, and production functions.

BOUNDARY VALUE PROBLEM

General Solution

The following general solution of the boundary value problem was obtained:

$$C_1^B(Z, T) = \int_0^T C_0(T-\tau) f(Z, \tau)\, d\tau \qquad (12)$$

$$C_2^B(Z, T) = \frac{\omega}{(1-\beta)R}\int_0^T C_1^B(Z, \tau) \cdot \exp\left[-\frac{(\omega+\mu_2)(T-\tau)}{(1-\beta)R}\right] d\tau \qquad (13)$$

where

$$f(Z, T) = \Gamma_1(Z, T)\exp\left(-\frac{\omega T}{\beta R}\right) + \frac{\omega}{R}\int_0^T \left(\frac{\tau}{\beta(1-\beta)(T-\tau)}\right)^{1/2} \Gamma_1(Z, \tau) H_1(T, \tau)\, d\tau \qquad (14)$$

Table 2. Expressions for Γ and ψ in the Solutions for the Resident Concentration C^r, Assuming First- and Third-Type Inlet Conditions, and for the Flux Concentration C^f

Γ or ψ	Resident Concentration, C^r		Flux Concentration, C^f
	First Type	Third Type	
$\Gamma_1(Z,\tau)$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\frac{Z}{\tau}\sqrt{\frac{\beta RP}{4\pi\tau}}\exp\left[-\frac{P(\beta RZ-\tau)^2}{4\beta R\tau}\right]$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\{\sqrt{\frac{P}{\pi\beta R\tau}}\exp\left[-\frac{P(\beta RZ-\tau)^2}{4\beta R\tau}\right]$ $-\frac{P}{2\beta R}\exp(PZ)\,\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta RZ+\tau)\right]\}$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\frac{Z}{\tau}\sqrt{\frac{\beta RP}{4\pi\tau}}\exp\left[-\frac{P(\beta RZ-\tau)^2}{4\beta R\tau}\right]$
$\Gamma_2(Z,\eta,\tau)$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\sqrt{\frac{\beta RP}{4\pi\tau}}\{\exp\left[-\frac{P(\beta R(\eta-Z)+\tau)^2}{4\beta R\tau}\right]$ $-\exp(PZ)\exp\left[-\frac{P(\beta R(\eta+Z)+\tau)^2}{4\beta R\tau}\right]\}$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\{\sqrt{\frac{\beta RP}{4\pi\tau}}\exp\left[-\frac{P(\beta R(\eta-Z)+\tau)^2}{4\beta R\tau}\right]$ $+\sqrt{\frac{\beta RP}{4\pi\tau}}\exp(PZ)\exp\left[-\frac{P(\beta R(\eta+Z)+\tau)^2}{4\beta R\tau}\right]$ $-\frac{P}{2}\exp(PZ)\,\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta R(\eta+Z)+\tau)\right]\}$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\sqrt{\frac{\beta RP}{4\pi\tau}}\{\left[1-\frac{\beta R(\eta-Z)+\tau}{2\tau}\right]$ $\times\exp\left[-\frac{P(\beta R(\eta-Z)+\tau)^2}{4\beta R\tau}\right]$ $-\left[1-\frac{\beta R(\eta+Z)+\tau}{2\tau}\right]\exp(PZ)\exp\left[-\frac{P(\beta R(\eta+Z)+\tau)^2}{4\beta R\tau}\right]\}$
$\psi_1(Z,\tau;Z_i)$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\{1-\frac{1}{2}\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta R(Z-Z_i)-\tau)\right]$ $-\frac{1}{2}\exp(PZ)\,\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta R(Z+Z_i)+\tau)\right]\}$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\{1-\frac{1}{2}\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta R(Z-Z_i)-\tau)\right]$ $-\sqrt{\frac{P\tau}{\pi\beta R}}\exp\left[PZ-\frac{P}{4\beta R\tau}(\beta R(Z+Z_i)+\tau)^2\right]$ $+\frac{1}{2}\left(1+P(Z+Z_i)+\frac{P\tau}{\beta R}\right)\exp(PZ)$ $\times\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta R(Z+Z_i)+\tau)\right]\}$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right)\{1-\frac{1}{2}\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta R(Z-Z_i)-\tau)\right]$ $-\frac{1}{2}\exp(PZ)\,\mathrm{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta R(Z+Z_i)+\tau)\right]$ $-\sqrt{\frac{\beta R}{4\pi P\tau}}\exp\left[-\frac{P}{4\beta R\tau}(\beta R(Z-Z_i)-\tau)^2\right]$ $+\sqrt{\frac{\beta R}{4\pi P\tau}}\exp(PZ)\exp\left[-\frac{P}{4\beta R\tau}(\beta R(Z+Z_i)+\tau)^2\right]\}$

$\psi_2(Z,\tau;\lambda)$	$\frac{1}{2}\exp\left(-\frac{\mu_1\tau}{\beta R}+\frac{\lambda^2\tau}{\beta RP}+\frac{\lambda\tau}{\beta R}-\lambda Z\right)$ $\times\left\{2-\operatorname{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}\left[\beta RZ-\left(1+\frac{2\lambda}{P}\right)\tau\right]\right]\right.$ $\left.+\exp(PZ+2\lambda Z)\operatorname{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}\left[\beta RZ+\left(1+\frac{2\lambda}{P}\right)\tau\right]\right]\right\}$	$\exp\left(-\frac{\mu_1\tau}{\beta R}+\frac{\lambda^2\tau}{\beta RP}+\frac{\lambda\tau}{\beta R}-\lambda Z\right)$ $\times\left\{1-\frac{1}{2}\operatorname{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}\left[\beta RZ-\left(1+\frac{2\lambda}{P}\right)\tau\right]\right]\right.$ $\left.+\frac{1}{2}\left(1+\frac{P}{\lambda}\right)\exp(PZ+2\lambda Z)\operatorname{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}\left[\beta RZ+\left(1+\frac{2\lambda}{P}\right)\tau\right]\right]\right\}$ $-\frac{P}{2\lambda}\exp\left(-\frac{\mu_1\tau}{\beta R}+PZ\right)\operatorname{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}(\beta RZ+\tau)\right]$	$\frac{1}{2}\left(1+\frac{\lambda}{P}\right)\exp\left(-\frac{\mu_1\tau}{\beta R}+\frac{\lambda^2\tau}{\beta RP}+\frac{\lambda\tau}{\beta R}-\lambda Z\right)$ $\times\left\{2-\operatorname{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}\left[\beta RZ-\left(1+\frac{2\lambda}{P}\right)\tau\right]\right]\right.$ $\left.+\exp(PZ+2\lambda Z)\operatorname{erfc}\left[\sqrt{\frac{P}{4\beta R\tau}}\left[\beta RZ+\left(1+\frac{2\lambda}{P}\right)\tau\right]\right]\right\}$

with

$$H_j(T,\tau)=\exp\left[-\frac{\omega\tau}{\beta R}-\frac{(\omega+\mu_2)(T-\tau)}{(1-\beta)R}\right]\cdot \mathbf{I}_j\left[\frac{2\omega}{R}\left(\frac{(T-\tau)\tau}{(\beta(1-\beta)}\right)^{1/2}\right]\qquad j=0,1\tag{15}$$

in which $\mathbf{I}_0$ and $\mathbf{I}_1$ denote modified Bessel functions of order zero and one, respectively, and $\Gamma_1(Z,\tau)$ is as given in Table 2. We give here specific solutions assuming Dirac delta and multiple pulse input functions for the input concentration, $C_0(T)$ in (8).

Specific Solutions

Dirac delta input function. The inlet condition for a Dirac delta function is given by

$$C_0(T)=\delta(T)\tag{16}$$

Substitution of (16) into the general solution leads to the following solution:

$$C_1^B(Z,T)=f(Z,T)\tag{17}$$

$$C_2(Z,T)=\frac{\omega}{(1-\beta)R}\int_0^T\Gamma_1(Z,\tau)H_0(T,\tau)\,d\tau\tag{18}$$

where $f(Z,T)$ and $H_0(Z,\tau)$ are given by (14) and (15), respectively, and $\Gamma_1(Z,\tau)$ can be found in Table 2. The solution for a Dirac delta input is often also referred to as the travel time probability density function, or the resident time distribution [e.g., *Jury and Roth*, 1990].

Multiple pulse input conditions. The input concentration for a series of successive applications of rectangular solute pulses may be represented as

$$\begin{aligned}&C_0(T)=f_1 && T_1<T\le T_2 && (T_1=0)\\&C_0(T)=f_2 && T_2<T\le T_3\\&\quad\vdots\\&C_0(T)=f_i && T_i<T\le T_{i+1}\\&\quad\vdots\\&C_0(T)=f_n && T_n\le T\end{aligned}\tag{19}$$

where f_i ($i=1,2,\cdots,n$) is constant. For a single continuous step input function ($n=1$), the solution can be cast in terms of Goldstein's J function [*Goldstein*, 1953] using the same methods as those described in the appendix for solving the general production value problem. Solutions of this type were previously presented by *Lindstrom and Stone* [1974], *De Smedt and Wierenga* [1979], and *Lassey* [1988], among others. Application of the superposition principle to the solution for a single-step input function yields the following multiple pulse input solution for both the equilibrium ($k=1$) and nonequilibrium ($k=2$) concentrations:

$$C_k^B(Z,T)=\sum_{j=1}^{i}(f_j-f_{j-1})A_k(Z,T-T_j)\tag{20}$$

$$i=1,2,\cdots,n\qquad k=1,2$$

where

$$A_1(Z, T) = \int_0^T \Gamma_1(Z, \tau) \exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right] J(a, b)\, d\tau \tag{21}$$

$$A_2(Z, T) = \frac{\omega}{\omega + \mu_2} \int_0^T \Gamma_1(Z, \tau) \cdot \exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right][1 - J(b, a)]\, d\tau \tag{22}$$

$$J(a, b) = 1 - \exp(-b) \int_0^a \exp(-\lambda) \mathrm{I}_0[2(b\lambda)^{1/2}]\, d\lambda \tag{23}$$

$$a = \frac{\omega^2\tau}{(\omega + \mu_2)\beta R} \tag{24a}$$

$$b = \frac{(\omega + \mu_2)(T - \tau)}{(1 - \beta)R} \tag{24b}$$

and where $f_0 = 0$ in (20). In these equations $J(a, b)$ is Goldstein's J function, and $A_k(Z, T)$ is the solution of phase k for a single continuous step input solute distribution [*van Genuchten and Wagenet*, 1989].

Integrating (21) by parts, using the differentiation properties of the J function given by (A31) and (A32) in the appendix, and some rearranging yields the following alternative expression for $A_k(Z, T)$ [see also *De Smedt and Wierenga*, 1979]:

$$A_1(Z, T) = G(Z, T) \exp\left[-\frac{\omega^2 T}{(\omega + \mu_2)\beta R}\right] + \frac{\omega}{R} \int_0^T G(Z, \tau) \exp[-a - b] \cdot \left[\frac{\omega}{(\omega + \mu_2)\beta} \mathrm{I}_0[2(ab)^{1/2}] + \left(\frac{\tau}{\beta(1 - \beta)(T - \tau)}\right)^{1/2} \mathrm{I}_1[2(ab)^{1/2}]\right] d\tau \tag{25}$$

$$A_2(Z, T) = \frac{\omega}{(1 - \beta)R} \int_0^T G(Z, \tau) \exp[-a - b] \cdot \left[\mathrm{I}_0[2(ab)^{1/2}] + \frac{\omega}{\omega + \mu_2}\left(\frac{(1 - \beta)(T - \tau)}{\beta\tau}\right)^{1/2} \mathrm{I}_1[2(ab)^{1/2}]\right] d\tau \tag{26}$$

where

$$G(Z, \tau) = \int_0^\tau \Gamma_1(Z, \sigma) \exp\left[-\frac{\omega\mu_2\sigma}{(\omega + \mu_2)\beta R}\right] d\sigma \tag{27}$$

For a first-type inlet condition, $G(Z, \tau)$ is given by

$$G(Z, \tau) = \frac{1}{2} \exp\left[\frac{P(1 - u)Z}{2}\right] \operatorname{erfc}\left[\frac{\beta RZ - u\tau}{(4\beta R\tau/P)^{1/2}}\right] + \frac{1}{2} \exp\left[\frac{P(1 + u)Z}{2}\right] \operatorname{erfc}\left[\frac{\beta RZ + u\tau}{(4\beta R\tau/P)^{1/2}}\right] \tag{28}$$

where

$$u = \left[1 + \frac{4}{P}\left(\mu_1 + \frac{\omega\mu_2}{\omega + \mu_2}\right)\right]^{1/2} \tag{29}$$

For a third-type inlet condition with $\mu_1 + \omega\mu_2/(\omega + \mu_2) \neq 0$, $G(Z, \tau)$ becomes

$$G(Z, \tau) = \frac{1}{1 + u} \exp\left[\frac{P(1 - u)Z}{2}\right] \operatorname{erfc}\left[\frac{\beta RZ - u\tau}{(4\beta R\tau/P)^{1/2}}\right] + \frac{1}{1 - u} \exp\left[\frac{P(1 + u)Z}{2}\right] \operatorname{erfc}\left[\frac{\beta RZ + u\tau}{(4\beta R\tau/P)^{1/2}}\right] - \frac{2}{1 - u^2} \exp\left[PZ + \frac{P(1 - u^2)\tau}{4\beta R}\right] \cdot \operatorname{erfc}\left[\frac{\beta RZ + \tau}{(4\beta R\tau/P)^{1/2}}\right] \tag{30}$$

whereas for $\mu_1 + \omega\mu_2/(\omega + \mu_2) = 0$:

$$G(Z, \tau) = \frac{1}{2} \operatorname{erfc}\left[\frac{\beta RZ - \tau}{(4\beta R\tau/P)^{1/2}}\right] + \left(\frac{P}{\pi\beta R}\right)^{1/2} \exp\left[-\frac{P(\beta RZ - \tau)^2}{4\beta R\tau}\right] s\frac{1}{2}\left(1 + PZ + \frac{P\tau}{\beta R}\right) \cdot \exp(PZ) \operatorname{erfc}\left[\frac{\beta RZ + \tau}{(4\beta R\tau/P)^{1s2}}\right] \tag{31}$$

We note that when the solutions for a single step input, given by $A_1(Z, T)$ and $A_2(Z, T)$, are differentiated with respect to T, one obtains the solutions for the Dirac delta input function given by (17) and (18), respectively [*De Smedt and Wierenga*, 1979].

INITIAL VALUE PROBLEM

General Solution

The general solution of the inital value problem was found to be

$$C_1^I(Z, T) = \exp\left(-\frac{\omega T}{\beta R}\right) \int_0^\infty C_i(\eta)\Gamma_2(Z, \eta, T)\, d\eta + \frac{\omega}{\beta R} \int_0^T \left(H_0(T, \tau) + \left(\frac{\beta\tau}{(1 - \beta)(T - \tau)}\right)^{1/2} H_1(T, \tau)\right) \cdot \int_0^\infty C_i(\eta)\Gamma_2(Z, \eta, \tau)\, d\eta\, d\tau \tag{32}$$

$$C_2^I(Z,\ T) = C_i(Z)\ \exp\Bigl[\Bigl(-\frac{(\omega+\mu_2)T}{(1-\beta)R}\Bigr] + \frac{\omega}{(1-\beta)R}\int_0^T\Bigl(H_0(T,\ \tau) + \left(\frac{(1-\beta)(T-\tau)}{\beta\tau}\right)^{1/2} H_1(T,\ \tau)\Bigr) \cdot \int_0^\infty C_i(\eta)\Gamma_2(Z,\ \eta,\ \tau)\ d\eta\ d\tau \qquad (33)$$

where $\Gamma_2(Z,\ \eta,\ \tau)$ is listed in Table 2, and $H_0(T,\ \tau)$ and $H_1(T,\ \tau)$ are given by (15). We will present specific solutions for a stepwise and an exponential initial distribution obtained by substituting the initial concentration, $C_i(Z)$, in (32) and (33) and by evaluating the integrals with respect to η.

Specific Solutions

Stepwise initial distribution. A stepwise initial concentration distribution may be written in the form

$$\begin{array}{lll} C_i(Z) = U_1 & Z_1 \le Z < Z_2 & (Z_1 = 0) \\ C_i(Z) = U_2 & Z_2 \le Z < Z_3 & \\ \vdots & & \\ C_i(Z) = U_i & Z_i \le Z < Z_{i+1} & \\ \vdots & & \\ C_i(Z) = U_n & Z_n \le Z & \end{array} \qquad (34)$$

where U_i is a constant. When $n = 1$, (34) represents a uniform initial concentration. The solution of the initial value problem assuming initial condition (34) is

$$C_1^I(Z,\ T) = \exp\left(-\frac{\omega T}{\beta R}\right)\sum_{i=1}^{n}(U_i - U_{i-1})\psi_1(Z,\ T;\ Z_i) + \frac{\omega}{\beta R}\int_0^T\Bigl(H_0(T,\ \tau) + \left(\frac{\beta\tau}{(1-\beta)(T-\tau)}\right)^{1/2} H_1(T,\ \tau)\Bigr) \cdot \sum_{i=1}^{n}(U_i - U_{i-1})\psi_1(Z,\ \tau;\ Z_i)\ d\tau \qquad (35)$$

$$C_2^I(Z,\ T) = C_i(Z)\ \exp\left[-\frac{(\omega+\mu_2)T}{(1-\beta)R}\right] + \frac{\omega}{(1-\beta)R}\int_0^T\Bigl(H_0(T,\ \tau) + \left(\frac{(1-\beta)(T-\tau)}{\beta\tau}\right)^{1/2} H_1(T,\ \tau)\Bigr) \cdot \sum_{i=1}^{n}(U_i - U_{i-1})\psi_1(Z,\ \tau;\ Z_i)\ d\tau \qquad (36)$$

where $U_0 = 0$, and ψ_1 is listed in Table 2.

Exponential initial distribution. The initial value problem was solved for an exponential initial condition of the form

$$C_i(Z) = U_1 + U_2\ \exp\ (-\lambda^I Z) \qquad (37)$$

where U_1, U_2, and λ^I are constants. The specific solutions for this condition is given by

$$C_1^I(Z,\ T) = \exp\left(-\frac{\omega T}{\beta R}\right)[U_1\psi_1(Z,\ T;\ 0) + U_2\psi_2(Z,\ T;\ \lambda^I)] + \frac{\omega}{\beta R}\int_0^T\Bigl(H_0(T,\ \tau) + \left(\frac{\beta\tau}{(1-\beta)(T-\tau)}\right)^{1/2} H_1(T,\ \tau)\Bigr) \cdot [U_1\psi_1(Z,\ \tau;\ 0) + U_2\psi_2(Z,\ \tau;\ \lambda^I)]\ d\tau \qquad (38)$$

$$C_2^I(Z,\ T) = C_i(Z)\ \exp\left[-\frac{(\omega+\mu_2)T}{(1-\beta)R}\right] + \frac{\omega}{(1-\beta)R}\int_0^T\Bigl(H_0(T,\ \tau) + \left(\frac{(1-\beta)(T-\tau)}{\beta\tau}\right)^{1/2} H_1(T,\ \tau)\Bigr) \cdot [U_1\psi_1(Z,\ \tau;\ 0) + U_2\psi_2(Z,\ \tau;\ \lambda^I)]\ d\tau \qquad (39)$$

where ψ_1 and ψ_2 are listed in Table 2.

PRODUCTION VALUE PROBLEM

General Solution

As outlined in detail in the appendix, the following general solution for arbitrary production profiles $\gamma_1(Z)$ and $\gamma_2(Z)$ can be obtained:

$$C_1^P(Z,\ T) = \frac{1}{\beta R}\int_0^T \exp\left[-\frac{\omega\mu_2\tau}{(\omega+\mu_2)\beta R}\right] J(a,\ b) \cdot \int_0^\infty\left(\gamma_1(\eta) + \frac{\omega}{\omega+\mu_2}\gamma_2(\eta)\right) \cdot \Gamma_2(Z,\eta,\tau)\,d\eta\,d\tau - \frac{1}{\beta R}\int_0^T H_0(T,\ \tau) \cdot \int_0^\infty \frac{\omega}{\omega+\mu_2}\gamma_2(\eta)\Gamma_2(Z,\ \eta,\ \tau)\ d\eta\ d\tau \qquad (40)$$

For $\omega + \mu_2 > 0$, the nonequilibrium concentration is given by

$$C_2^P(Z,\ T) = \frac{\gamma_2(Z)}{\omega + \mu_2}\left\{1 - \exp\left[-\frac{(\omega + \mu_2)T}{(1-\beta)R}\right]\right\}$$

$$+ \frac{\omega}{\beta R(\omega + \mu_2)}\int_0^T \exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right]$$

$$\cdot [1 - J(b,\ a)]\int_0^\infty \left(\gamma_1(\eta)\right.$$

$$\left.+ \frac{\omega}{\omega + \mu_2}\gamma_2(\eta)\right)\Gamma_2(Z,\ \eta,\ \tau)\ d\eta\ d\tau$$

$$- \frac{1}{\beta R}\int_0^T \left(\frac{\beta(T-\tau)}{(1-\beta)\tau}\right)^{1/2} H_1(T,\ \tau)$$

$$\cdot \int_0^\infty \frac{\omega}{\omega + \mu_2}\gamma_2(\eta)\Gamma_2(Z,\ \eta,\ \tau)\ d\eta\ d\tau \qquad (41)$$

whereas for $\omega = \mu_2 = 0$

$$C_2^P(Z,\ T) = \frac{\gamma_2(Z)T}{(1-\beta)R} \qquad (42)$$

where $H_0(T,\ \tau)$ and $H_1(T,\ \tau)$ are again given by (15), Γ_2 is the same as in the solution of the initial value problem listed in Table 2, $J(a,\ b)$ is Goldstein's J function given by (23), and a and b are given by (24). As for the initial value problem, we also selected stepwise and exponential distributions for the production profiles, $\gamma_1(Z)$ and $\gamma_2(Z)$, and evaluated the integrals in the general solutions given by (40) and (41). Specific solutions are presented here only for the case when $\omega + \mu_2 > 0$. The solution of phase 2 for $\omega + \mu_2 = 0$ is given by (42).

Specific Solutions

Stepwise production profile. A production distribution consisting of n distinct steps can be expressed as

$$\begin{array}{lll}
\gamma_1(Z) = \zeta_1 & \eta_1 \le Z < \eta_2 & (\eta_1 = 0) \\
\gamma_1(Z) = \zeta_2 & \eta_2 \le Z < \eta_3 & \\
 & \vdots & \\
\gamma_1(Z) = \zeta_i & \eta_i \le Z < \eta_{i+1} & \\
 & \vdots & \\
\gamma_1(Z) = \zeta_n & \eta_n \le Z &
\end{array} \qquad (43a)$$

$$\begin{array}{lll}
\gamma_2(Z) = \nu_1 & \xi_1 \le Z < \xi_2 & (\xi_1 = 0) \\
\gamma_2(Z) = \nu_2 & \xi_2 \le Z < \xi_3 & \\
 & \vdots & \\
\gamma_2(Z) = \nu_j & \xi_j \le Z < \xi_{j+1} & \\
 & \vdots & \\
\gamma_2(Z) = \nu_m & \xi_m \le Z &
\end{array} \qquad (43b)$$

where ζ_i, η_i, ν_j and ξ_j are constants ($i = 1, 2, \cdots, n$ and $j = 1, 2, \cdots, m$). For single steps in both phases ($n = 1$ and $m = 1$), the production terms are constant throughout the soil profile. Inserting (43) into the general solution and subsequent integration with respect to η leads to

$$C_1^P(Z,\ T) = \frac{1}{\beta R}\int_0^T \exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right] J(a,\ b)$$

$$\cdot \sum_{i=1}^{n} (\zeta_i - \zeta_{i-1})\psi_1(Z,\ \tau;\ \eta_i)\ d\tau$$

$$+ \frac{\omega}{\beta R(\omega + \mu_2)}\int_0^T \left\{\exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right]\right.$$

$$\left.\cdot J(a,\ b) - H_0(T,\ \tau)\right\}$$

$$\cdot \sum_{j=1}^{m} (\nu_j - \nu_{j-1})\psi_1(Z,\ \tau;\ \xi_j)\ d\tau \qquad (44)$$

$$C_2^P(Z,\ T) = \frac{\gamma_2(Z)}{\omega + \mu_2}\left\{1 - \exp\left[-\frac{(\omega + \mu_2)T}{(1-\beta)R}\right]\right\}$$

$$+ \frac{\omega}{\beta R(\omega + \mu_2)}\int_0^T \left\{\exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right]\right.$$

$$\cdot [1 - J(b,\ a)] \sum_{i=1}^{n} (\zeta_i - \zeta_{i-1})\psi_1(Z,\ \tau;\ \eta_i)$$

$$+ \left[\frac{\omega}{\omega + \mu_2}\exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right][1 - J(b,\ a)]\right.$$

$$\left.- \left(\frac{\beta(T-\tau)}{(1-\beta)\tau}\right)^{1/2} H_1(T,\ \tau)\right]$$

$$\left.\cdot \sum_{j=1}^{m} (\nu_j - \nu_{j-1})\psi_1(Z,\ \tau;\ \xi_j)\right\} d\tau \qquad (45)$$

where $\zeta_0 = \nu_0 = 0$, and ψ_1 is listed in Table 2.

Exponential production profile. The production terms can also be expressed in terms of exponential functions:

$$\gamma_1(Z) = \zeta_1 + \zeta_2 \exp(-\lambda_1^P Z) \qquad (46a)$$

$$\gamma_2(Z) = \nu_1 + \nu_2 \exp(-\lambda_2^P Z) \qquad (46b)$$

where ξ_1, ξ_2, ν_1, ν_2, λ_1^P, and λ_2^P are constants. The concentrations of phases 1 and 2 are now given by

$$C_1^P(Z,\ T) = \frac{1}{\beta R}\int_0^T \exp\left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R}\right] J(a,\ b)$$

$$\cdot [\zeta_1\psi_1(Z,\ \tau;\ 0) + \zeta_2\psi_2(Z,\ \tau;\ \lambda_1^P)]\ d\tau$$

$$
\begin{aligned}
&+ \frac{\omega}{\beta R(\omega + \mu_2)} \int_0^T \bigg\{ \exp\left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] \\
&\cdot J(a, b) - H_0(T, \tau) \bigg\} [\nu_1 \psi_1(Z, \tau; 0) \\
&+ \nu_2 \psi_2(Z, \tau; \lambda_2^P)] \, d\tau
\end{aligned} \tag{47}
$$

$$
\begin{aligned}
C_2^P(Z, T) = {} & \frac{\gamma_2(Z)}{\omega + \mu_2} \left\{ 1 - \exp\left[-\frac{(\omega + \mu_2)T}{(1 - \beta)R} \right] \right\} \\
&+ \frac{\omega}{\beta R(\omega + \mu_2)} \int_0^T \bigg\{ \exp\left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] \\
&\cdot [1 - J(b, a)][\zeta_1 \psi_1(Z, \tau; 0) \\
&+ \zeta_2 \psi_2(Z, \tau; \lambda_1^P)] \\
&+ \bigg[\frac{\omega}{\omega + \mu_2} \exp\left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] \\
&\cdot [1 - J(b, a)] - \left(\frac{\beta(T - \tau)}{(1 - \beta)\tau} \right)^{1/2} H_1(T, \tau) \bigg] \\
&\cdot [\nu_1 \psi_1(Z, \tau; 0) \\
&+ \nu_2 \psi_2(Z, \tau; \lambda_2^P)] \bigg\} \, d\tau
\end{aligned} \tag{48}
$$

Notice that the solutions of the production value problem contain several terms which are the same as, or very close to, those appearing in the solutions of the initial value problem.

EQUILIBRIUM TRANSPORT

The above general and specific solutions for nonequilibrium transport can be readily used to describe equilibrium transport, subject to the same phase 1 boundary, initial, and production conditions. Assuming $\omega = 0$ and subsequently setting $\beta = 1$, the general solution for nonequilibrium transport reduces to the general solution for equilibrium transport:

$$
\begin{aligned}
C_1(Z, T) &= C_1^B(Z, T) + C_1^I(Z, T) + C_1^P(Z, T) \\
&= \int_0^T C_0(T - \tau)\Gamma_1(Z, \tau) \, d\tau \\
&\quad + \int_0^\infty C_i(\eta)\Gamma_2(Z, \eta, T) \, d\eta \\
&\quad + \frac{1}{R} \int_0^T \int_0^\infty \gamma_1(\eta)\Gamma_2(Z, \eta, \tau) \, d\eta \, d\tau
\end{aligned} \tag{49}
$$

where Γ_1 and Γ_2 are the same as before (Table 2). The equilibrium solutions were verified to be consistent with those given recently by *Lindstrom and Boersma* [1989] for a slightly different (space- and time-dependent) zero-order production term.

VOLUME-AVERAGED AND FLUX-AVERAGED CONCENTRATIONS

The transport equations and general solutions above were formulated in terms of volume-averaged or resident concentration, subject to both first- and third-type inlet boundary conditions. The initial concentrations and production profiles were also assumed to be of the resident type. As shown previously [e.g. *van Genuchten and Parker*, 1984; *Parker and van Genuchten*, 1984*a*], a third-type inlet condition is generally to be preferred for resident concentrations since this condition ensures that mass balance requirements are satisfied. Flux-averaged or flowing concentrations are generally encountered at medium exit boundaries, for example, when effluent curves are obtained from solute displacement experiments involving finite columns. The flux-averaged concentration is defined as the ratio of the solute flux to the water flux and is related to the resident concentration through the transformation [*Kreft and Zuber*, 1978]:

$$
C^f = C^r - \frac{1}{P} \frac{\partial C^r}{\partial Z} \tag{50}
$$

where the superscript f refers to flux-averaged concentration, and r to resident concentration (the superscript r was omitted in the previous section). Substituting solutions for C^r assuming a third-type inlet condition into (50) leads to general and specific expressions for C^f which are the same as before, except for some changes in the equations for Γ and ψ as shown in Table 2.

The equations in Table 2 indicate that the general solution of the boundary value problem for the flux-averaged concentration is identical to C^r assuming a first-type boundary condition, i.e., $\Gamma_1(Z, \tau)$ in Table 2 is the same for these two cases. This result is consistent with previous studies [e.g., *Parker and van Genuchten*, 1984] which have shown that the transformation of C^r to C^f using (5) yields a mathematically identical set of equations, except for the inlet boundary condition which changes from a third-type condition for C^r to a first-type for C^f. However, the transformation leads to different solutions for the initial value and production value problems for which the terms $\Gamma_2(Z, \tau)$, $\psi_1(Z, \tau; Z_i)$, and $\psi_2(Z, \tau; \lambda)$ in the C^f solution contains additional terms as compared to C^r for the first-type solution. We will now shown that these additional terms vanish only when the initial conditions or production terms are constant versus distance in the medium, in which case the solution for C^f becomes again identical to the solution for C^r for a first-type condition.

Applying transformation (50) to transport equations (3) and (4) for C^r, and the initial and boundary conditions (7), (8) and (9) assuming a third-type condition ($\delta = 1$), yields the following transport equation in terms of C^f:

$$
\beta R \frac{\partial C_1^f}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1^f}{\partial Z^2} - \frac{\partial C_1^f}{\partial Z} - \omega(C_1^f - C_2^f) - \mu_1 C_1^f + \gamma_1^f(Z) \tag{51}
$$

$$
(1 - \beta)R \frac{\partial C_2^f}{\partial T} = \omega(C_1^f - C_2^f) - \mu_2 C_2^f + \gamma_2^f(Z) \tag{52}
$$

subject to

$$
C_1^f(Z, 0) = C_2^f(Z, 0) = C_i^f(Z) \tag{53}
$$

$$C_1^f(0, T) = C_0(T) \tag{54}$$

$$\frac{\partial C_1^f}{\partial Z}(\infty, T) = 0 \tag{55}$$

where

$$C_k^f = C_k^r - \frac{1}{P}\frac{\partial C_k^r}{\partial Z} \qquad k = 1, 2 \tag{56a}$$

$$\gamma_k^f = \gamma_k^r - \frac{1}{P}\frac{\partial \gamma_k^r}{\partial Z} \qquad k = 1, 2 \tag{56b}$$

$$C_i^f = C_i^r - \frac{1}{P}\frac{\partial C_i^r}{\partial Z} \tag{56c}$$

This problem is mathematically identical to the original transport problem in terms of C^r for a first-type inlet condition. However, notice that the initial conditions C_i and the production functions γ_k are affected by the transformation: the initial flux and resident concentrations in phase 2 are not the same even though there is no convective and dispersive transport in this phase. The transformed initial and production profiles in terms of the flux-averaged mode are identical to the initial and production profiles in terms of the resident mode only in case of uniform distributions of C_i^r and γ_k^r versus Z. Hence the transport problem in terms of C^r subject to a first-type inlet condition will therefore not automatically be equivalent to the problem for C^f subject to a third-type inlet condition. Flux-averaged concentrations for nonuniform C_i^r and γ_k^r can be derived only according to (50).

Finally, we note that current measurement techniques are probably not sophisticated enough to accurately measure resident concentrations in phases 1 and 2 separately. By comparison, the total resident concentration C_T^r defined as

$$C_T^r = \beta R C_1^r + (1 - \beta) R C_2^r \tag{57}$$

i.e., the total amount of solute in phases 1 and 2 combined per unit soil solution at a given point in time and space [*Parker and Valocchi*, 1986], is much more easily measured, for example, by soil coring or using in-situ geophysical measurement devices.

EXAMPLES

A computer code similar to the CFITIM and CXTFIT programs of *van Genuchten* [1981] and *Parker and van Genuchten* [1984*b*] was written to evaluate the various nonequilibrium solutions listed in this paper. Rather than using the Romberg and Gaussian quadrature integration subroutines of CFITIM and CXTFIT, we employed Gauss-Chebyshev formula [e.g., *Carnahan et al.*, 1969] to evaluate the integrals in our solutions. Gauss-Chebyshev quadrature offers greater flexibility in selecting the number of intgration points. We obtained accurate results with 50 integration points for most cases (generally 4 to 5 significant digits, except for cases when β and Z approach 0 and T becomes relatively large). The modified Bessel functions of orders zero and one were evaluated using equations (9.8.1), (9.8.2), (9.8.3), and (9.8.4) of *Abramowitz and Stegun* [1970], while the J function was evaluated using the approximations for the modified Bessel function given by *van Genuchten* [1981]. The equilibrium and nonequilibrium solutions were verified mathematically by means of a series of comparisons with existing simpler formulations [*Parker and van Genuchten*, 1984*b*; *van Genuchten and Wagenet*, 1989], as well as with several numerical solutions. The computer program used to evaluate the above specific solutions (a modified version of CXTFIT) is available upon request.

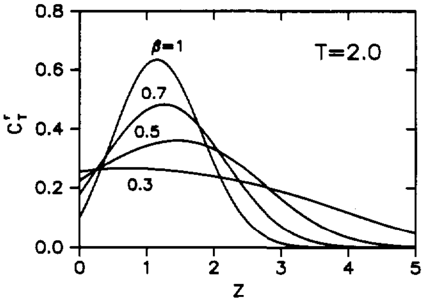

Fig. 1. Calculated total resident concentration distributions $C_T^r(Z)$ versus distance Z at $T = 2$ for four values of β assuming a third-type inlet condition and a Dirac delta concentration input ($P = 4$, $R = 2$, $\omega = 0.5$, $\mu_1 = \mu_2 = 0$).

We now briefly discuss typical examples of nonequilibrium transport for the boundary value problem (example 1), the initial value problem (example 2), and the production value problem (example 3). We emphasize again that these three solution, or any other combination of solutions involving a boundary value problem, an initial value problem and a production value problem, may be combined to obtain more complicated solutions as described by (10) and (11).

Example 1: Boundary Values Problem With Dirac Delta Input

Figure 1 gives a plot versus distance of the total resident concentration C_T^r given by (57) for a third-type Dirac delta inlet condition. Results are for T = 2.0, P = 4, R = 2, ω = 0.5, $\mu_1 = \mu_2 = 0$ (no degradation), and three values of the dimensionless coefficient β. The parameter β accounts for the relative partitioning of the medium into phases 1 and 2. When β increases, more solute transport occurs in phase 1 which constitutes the equilibrium part of the transport system, with the limiting case of equilibrium transport occurring when $\beta = 1$. As expected, the solute profile becomes more symmetrical and has a higher peak concentration when β increases to 1.

Example 2: Initial Value Problem With Stepwise Initial Distribution

Figure 2 gives phase 1 equilibrium (C_1) and phase 2 nonequilibrium (C_2) resident concentration profiles at T = 1.0 for three values of the partitioning coefficient β assuming a third-type inlet condition. The example involves the application of a solute-free solution to a soil having a stepwise initial distribution as shown by the dashed line. The initial condition is given by (24) with $n = 3$, $(U_1, U_2, U_3) = (0.3, 1, 0.1)$, and $(Z_1, Z_2, Z_3) = (0, 0.5, 1)$. Other parameter values are $P = 10$, $R = 2$, $\omega = 1$, and $\mu_1 = \mu_2 = 0.2$. Figure 2 shows that solutes are leached much more gradually (dispersed) when β is relatively small, i.e., when the non-

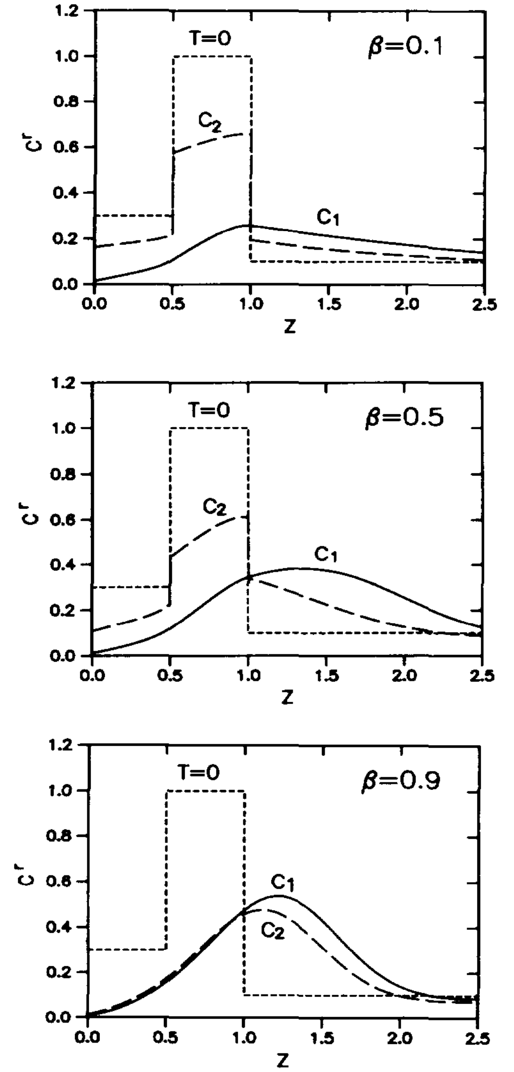

Fig. 2. Calculated resident equilibrium (C_1) and nonequilibrium (C_2) distributions versus distance Z at $T = 1$ for three values of β assuming solute-free input to a soil having a stepwise initial distribution as shown by the dashed line ($P = 10$, $R = 2$, $\omega = 1$, $\mu_1 = \mu_2 = 0.2$).

equilibrium phase 2 dominates relative to the equilibrium phase 1. Hence the leaching process is not as effective in terms of completely removing the chemical from the soil profile when β is small. Notice also that the discontinuity in the nonequilibrium concentration C_2 persists much longer for smaller β values. This is because solute removal and subsequent leaching from phase 2 can only occur indirectly through phase 1 after the solute has kinetically desorbed from phase 2 into phase 1 (the one- or two site sorption models), or has diffused from immobile water in phase 2 to mobile water in phase 1 (the two-region model). For larger β values the nonequilibrium profiles closely resemble the equilibrium profile because of increased opportunity for the relatively small amount of solute in phase 2 to move to phase 1.

Example 3: Production Value Problem With Stepwise Production

Figure 3 shows equilibrium (C_1) and nonequilibrium (C_2) concentration profiles at $T = 3$ after application of solute-free water to an initially solute-free soil profile with a stepwise production function in phase 2 (equation (43*b*) with $\nu_1 = 0.2$ for $0 \leq Z < 1$, $\nu_2 = 0$ for $Z \geq 1$), but no production in phase 1. Other parameter values are $P = 10$, $R = 3$, $\beta = 0.5$, $\omega = 1$, and $\mu_1 = \mu_2 = 0$. Notice the development of a discontinuity in the phase-2 concentration at $Z = 1$. As in example 2, this feature reflects the fact that solutes produced in phase 2 (or initially present in phase 2) can only be removed from the profile after being transferred to phase 1.

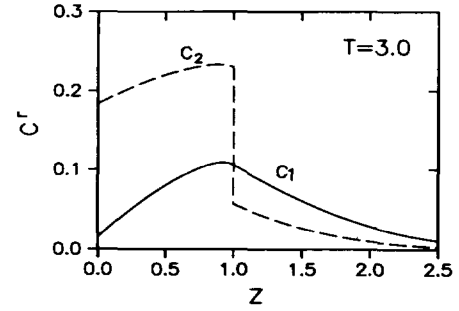

Fig. 3. Calculated resident concentrations profiles for the equilibrium (C_1) and nonequilibrium (C_2) phases at $T = 3$ for a constant production term ($0 \leq Z < 1$) in phase 2, no production in phase 1, a third-type inlet condition and solute-free input to an initially solute-free soil profile ($P = 10$, $R = 3$, $\beta = 0.5$, $\omega = 1.0$, $\mu_1 = \mu_2 = 0$).

CONCLUDING REMARKS

We have derived general analytical solutions for nonequilibrium transport in a one-dimensional semi-infinite soil system. The governing dimensionless equations for one-site, two-site, and two-region solute transport include terms accounting for nonequilibrium adsorption or exchange between mobile and immobile liquid regions, first-order degradation, and zero-order production. Laplace transform techniques were used to derive general solutions to the boundary, initial, and production value problems for resident concentrations using a first- and third-type inlet boundary conditions, and for flux-averaged concentrations. The solutions extend and generalize existing solutions for equilibrium and nonequilibrium transport. Specific solutions included those for Dirac delta and multiple pulse input functions, stepwise and exponential initial distributions, and stepwise and exponential zero-order production profiles. Any combination of these solutions involving the boundary, initial and production value problems may be implemented by simply adding the various solutions. The nonequilibrium solutions can be readily used to describe equilibrium transport by simply setting $\omega = 0$ and $\beta = 1$.

The solutions for C^f were found to be different from the solution for C^r using a first-type inlet condition when the volume-averaged initial and/or production profiles are nonuniform versus distance. Hence C^f needs to be derived from C^r for a third-type inlet condition using transformation (50). Typical examples of calculated concentration distributions, resulting from several sets of initial and input conditions and zero-order production functions were presented and briefly discussed.

The analytical solutions should be helpful for obtaining initial or approximate analyses of field scale transport scenarios, for analyzing underlying physico-chemical and biological transport processes (e.g., in conjunction with laboratory soil column displacement experiments), for sensitivity analyses, and for validating numerical solutions of solute transport, among other applications.

APPENDIX

The purpose of this appendix is to give details of the Laplace transform solution of the general nonequilibrium solute transport problem given by (3) and (4) in the main text. Taking the Laplace transforms with respect to time of (3) and (4), subject to the initial and the boundary conditions given by (7), (8), and (9) yields

$$\frac{1}{P}\frac{d^2\bar{C}_1}{dZ^2} - \frac{d\bar{C}_1}{dZ} - \beta R(s\bar{C}_1 - C_i) - (\omega + \mu_1)\bar{C}_1 + \omega\bar{C}_2 + \frac{\gamma_1}{s} = 0 \qquad \text{(A1)}$$

$$(1-\beta)R(s\bar{C}_2 - C_i) = \omega(\bar{C}_1 - \bar{C}_2) - \mu_2\bar{C}_2 + \frac{\gamma_2}{s} \qquad \text{(A2)}$$

$$\left.\left(-\frac{\delta}{P}\frac{d\bar{C}_1}{dZ} + \bar{C}_1\right)\right|_{Z=0} = \bar{C}_0 \qquad \text{(A3)}$$

with $\delta = 0$ for a first-type and $\delta = 1$ for a third-type boundary condition, and

$$\frac{d\bar{C}_1}{dZ}(\infty) = 0 \qquad \text{(A4)}$$

where the overbar denotes a transform function with respect to time, and s is the corresponding Laplace transform variable. Solving (A2) for C_2 gives

$$\bar{C}_2 = \frac{1}{s + b_1}\left[C_i + \frac{\omega\bar{C}_1}{(1-\beta)R} + \frac{\gamma_2}{(1-\beta)Rs}\right] \qquad \text{(A5)}$$

where

$$b_1 = \frac{\omega + \mu_2}{(1-\beta)R} \qquad \text{(A6)}$$

We restrict the derivation only to nonequilibrium transport ($\omega > 0$). The inverse transformation of (A5) yields the following relationship for C_2 in terms of C_1:

$$C_2(Z, T) = \frac{\omega}{(1-\beta)R}\int_0^T C_1(Z, \tau)\exp\left[-b_1(T-\tau)\right]d\tau + C_i\exp(-b_1T) + \frac{\gamma_2}{\omega + \mu_2}\left[1 - \exp(-b_1T)\right] \qquad \text{(A7)}$$

Substituting (A5) into (A1) gives

$$\frac{1}{P}\frac{d^2\bar{C}_1}{dZ^2} - \frac{d\bar{C}_1}{dZ} - \beta R(s\bar{C}_1 - C_i) - (\omega + \mu_1)\bar{C}_1 + \frac{\omega C_i}{s + b_1} + \frac{a_1\bar{C}_1}{s + b_1} + \frac{a_2\gamma_2}{s(s + b_1)} + \frac{\gamma_1}{s} = 0 \qquad \text{(A8)}$$

where

$$a_1 = \frac{\omega^2}{(1-\beta)R} \qquad a_2 = \frac{\omega}{(1-\beta)R} \qquad \text{(A9)}$$

For brevity, only the solution subject to a third-type inlet condition ($\delta = 1$) will be discussed. The solution for a first-type inlet condition ($\delta = 0$) can be derived in a very similar manner. Taking the Laplace transform of (A8) with respect to Z and using (A3) leads to the equation

$$\tilde{\bar{C}}_1(r, s) = \left[\frac{r\bar{C}_1(0)}{P} - \left(\beta R + \frac{\omega}{s + b_1}\right)\tilde{C}_i - \bar{C}_0(s) - \frac{\alpha_2\tilde{\gamma}_2}{s(s + b_1)} - \frac{\tilde{\gamma}_1}{s}\right]\left[\frac{r^2}{P} - r - h_1(s)\right]^{-1} \qquad \text{(A10)}$$

where the tilde denotes a transformation with respect to Z in terms of the corresponding Laplace transform variable r, and where

$$h_1(s) = \beta Rs + \omega + \mu_1 - \frac{a_1}{s + b_1} \qquad \text{(A11)}$$

Note that $\bar{C}_1(0)$ is the Laplace transform with respect to time of the inlet concentration $C_1(0, T)$, which for a third-type boundary condition is an unknown to be determined later from boundary condition (A4). The denominator of (A10) can be factored and separated into partial fractions as follows:

$$\tilde{\bar{C}}_1(r, s) = \frac{P}{r_2 - r_1} \cdot \left[\frac{\dfrac{r_2\bar{C}_1(0)}{P} - \left(\beta R + \dfrac{\omega}{s + b_1}\right)\tilde{C}_i - \bar{C}_0 - \dfrac{a_2\tilde{\gamma}_2}{s(s + b_1)} - \dfrac{\tilde{\gamma}_1}{s}}{r - r_2} - \frac{\dfrac{r_1\bar{C}_1(0)}{P} - \left(\beta R + \dfrac{\omega}{s + b_1}\right)\tilde{C}_i - \bar{C}_0 - \dfrac{a_2\tilde{\gamma}_2}{s(s + b_1)} - \dfrac{\tilde{\gamma}_1}{s}}{r - r_1}\right] \qquad \text{(A12)}$$

where

$$r_1 = \frac{P}{2}(1 - \xi) \qquad r_2 = \frac{P}{2}(1 + \xi) \qquad \xi = \left(1 + \frac{4h_1(s)}{P}\right)^{1/2} \qquad \text{(A13)}$$

Taking the inverse of (A12) with respect to r using standard methods [e.g., *Abramowitz and Stegun*, 1970] leads to

$$\bar{C}_1 = \frac{P}{r_2 - r_1}\left\{\exp(r_2Z)\left\{\frac{r_2\bar{C}_1(0)}{P} - \bar{C}_0 - \int_0^Z\left[\left(\beta R + \frac{\omega}{s + b_1}\right)C_i(\eta) + \frac{a_2\gamma_2(\eta)}{s(s + b_1)} + \frac{\gamma_1(\eta)}{s}\right]\right.\right.$$

$$
\begin{aligned}
&\cdot \exp(-r_2\eta)\, d\eta\Big\} - \exp(r_1 Z)\Bigg\{\frac{r_1\bar{C}_1(0)}{P} - \bar{C}_0 \\
&- \int_0^Z \left[\left(\beta R + \frac{\omega}{s+b_1}\right)C_i(\eta) + \frac{a_2\gamma_2(\eta)}{s(s+b_1)} + \frac{\gamma_1(\eta)}{s}\right] \\
&\cdot \exp(-r_1\eta)\, d\eta\Bigg\}\Bigg\}
\end{aligned}
\qquad (A14)
$$

Because $r_1 < 0$, $\exp(r_1 Z)$ in (A14) vanishes as $Z \rightarrow \infty$. Thus substitution of (A14) into (A4) and solving for $\bar{C}_1(0)$ gives

$$
\begin{aligned}
\bar{C}_1(0) = \frac{P}{r_2}\Bigg\{\bar{C}_0 + \int_0^Z \Bigg[&\left(\beta R + \frac{\omega}{s+b_1}\right)C_i(\eta) + \frac{a_2\gamma_2(\eta)}{s(s+b_1)} \\
&+ \frac{\gamma_1(\eta)}{s}\Bigg] \exp(-r_2\eta)\, d\eta\Bigg\}
\end{aligned}
\qquad (A15)
$$

After inserting (A13) and (A15) into (A14), the general solution for $\bar{C}_1$ for a third-type input boundary condition may be written as

$$
\begin{aligned}
\bar{C}_1 = {} & \frac{2\exp\left[\dfrac{PZ(1-\xi)}{2}\right]}{1+\xi}\bar{C}_0 \\
&+ \int_Z^\infty C_i(\eta)\exp\left[-\frac{P(\eta-Z)}{2}\right]\frac{1}{\xi} \\
&\cdot\left(\beta R + \frac{\omega}{s+b_1}\right)\exp\left[-\frac{P\xi(\eta-Z)}{2}\right] d\eta \\
&+ \int_0^Z C_i(\eta)\exp\left[-\frac{P(\eta-Z)}{2}\right]\frac{1}{\xi} \\
&\cdot\left(\beta R + \frac{\omega}{s+b_1}\right)\exp\left[-\frac{P\xi(Z-\eta)}{2}\right] d\eta \\
&+ \int_0^\infty C_i(\eta)\exp\left[-\frac{P(\eta-Z)}{2}\right]\frac{\xi-1}{\xi(\xi+1)} \\
&\cdot\left(\beta R + \frac{\omega}{s+b_1}\right)\exp\left[-\frac{P\xi(\eta+Z)}{2}\right] d\eta \\
&+ \int_Z^\infty \left(\frac{\gamma_1(\eta)}{s} + \frac{a_2\gamma_2(\eta)}{s(s+b_1)}\right)\exp\left[-\frac{P(\eta-Z)}{2}\right]\frac{1}{\xi} \\
&\cdot\exp\left[-\frac{P\xi(\eta-Z)}{2}\right] d\eta \\
&+ \int_0^Z \left(\frac{\gamma_1(\eta)}{s} + \frac{a_2\gamma_2(\eta)}{s(s+b_1)}\right)\exp\left[-\frac{P(\eta-Z)}{2}\right]\frac{1}{\xi} \\
&\cdot\exp\left[-\frac{P\xi(Z-\eta)}{2}\right] d\eta + \int_0^\infty \left(\frac{\gamma_1(\eta)}{s} + \frac{a_2\gamma_2(\eta)}{s(s+b_1)}\right) \\
&\cdot\exp\left[-\frac{P(\eta-Z)}{2}\right]\frac{\xi-1}{\xi(\xi+1)}\exp\left[-\frac{P\xi(\eta+Z)}{2}\right] d\eta
\end{aligned}
\qquad (A16)
$$

This general solution can be divided into three parts: the first term of the right-hand side is the solution of the boundary value problem, the next three terms containing $C_i(\eta)$ provide the solution of the initial value problem, while the last three terms containing $\gamma_1(\eta)$ and $\gamma_2(\eta)$ constitute the solution of the production value problem.

Before attempting to invert (A16), we first obtain the inverse transform of the function

$$
\bar{F}(s) = \frac{\bar{f}\left(s - \dfrac{\kappa_1}{s}\right)}{s} \qquad (A17)
$$

where $\bar{F}(s)$ and $\bar{f}(s)$ are the Laplace transforms of $F(T)$ and $f(T)$, respectively, and κ_1 is a constant. The inverse is obtained with the help of the following general convolution integral [*De Smedt and Wierenga*, 1979; *Walker*, 1987]:

$$
\mathscr{L}^{-1}[\bar{F}(s, s)] = \int_0^T f(\tau, T-\tau)\, d\tau \qquad (A18)
$$

where $\mathscr{L}^{-1}$ denotes the inverse Laplace transform. This equation states that the iterated Laplace transform of a function is equal to the Laplace transform of the generalized convolution integral of that function. Equation (A18) will be applied to (A17) by rewriting (A17) into the following form involving two separate transform variables, s_1 and s_2:

$$
\bar{F}(s_1, s_2) = \frac{\bar{f}\left(s_1 - \dfrac{\kappa_1}{s_2}\right)}{s_2} \qquad (A19)
$$

The first inversion of A(17) with respect s_1 follows from the shifting theorem:

$$
\mathscr{L}_{s_1}^{-1}[\bar{F}(s_1, s_2)] = \frac{1}{s_2}\exp\left(\frac{\kappa_1 T_1}{s_2}\right) f(T_1) \qquad (A20)
$$

The second inversion with respect to s_2 follows from equation (29.3.81) of *Abramowitz and Stegun* [1970]:

$$
\begin{aligned}
F(T_1, T_2) &= \mathscr{L}_{s_2}^{-1}\mathscr{L}_{s_1}^{-1}[\bar{F}(s_1, s_2)] \\
&= \mathscr{L}_{s_2}^{-1}\left[\frac{1}{s_2}\exp\left(\frac{\kappa_1 T_1}{s_2}\right) f(T_1)\right] = \mathbf{I}_0[2(\kappa_1 T_1 T_2)^{1/2}] f(T_1)
\end{aligned}
\qquad (A21)
$$

Application of (A18) to (A17) hence leads to the following inverse transform of $\bar{F}(s)$:

$$
F(T) \equiv \mathscr{L}^{-1}[\bar{F}(s, s)] = \int_0^T \mathbf{I}_0[2(\kappa_1(T-\tau)\tau)^{1/2}] f(\tau)\, d\tau \qquad (A22)
$$

The following equations may be obtained from (A22) by applying the shifting theorem [see also *Lindstrom and Narasimhan*, 1973]

$$\mathscr{L}\left\{\exp\,(-\kappa_2 T)\int_0^T \mathbf{I}_0[2(\kappa_1(T-\tau)\tau)^{1/2}]f(\tau)\,d\tau\right\}$$

$$=\frac{1}{s+\kappa_2}\bar{f}\left(s+\kappa_2-\frac{\kappa_1}{s+\kappa_2}\right) \qquad \text{(A23)}$$

and, with some additional manipulations,

$$\mathscr{L}\left\{\exp\,(-\kappa_2 T)\,\frac{\partial}{\partial T}\int_0^T \mathbf{I}_0[2(\kappa_1(T-\tau)\tau)^{1/2}]f(\tau)\,d\tau\right\}$$

$$=\bar{f}\left(s+\kappa_2-\frac{\kappa_1}{s+\kappa_2}\right) \qquad \text{(A24)}$$

where κ_2 is a constant.

As an example, we will now briefly outline how the solution for the production value problem in (A16) can be obtained. Solutions for the boundary and initial value problems can be derived in a very similar manner. Separating the denominator $s(s+b_1)$ from the production value terms (the last three terms) of (A16) and applying (A23) and (A24) to these three terms yields

$$C_1^P(Z,\,T)$$

$$=C_1^{P1}(Z,\,T)+C_1^{P2}(Z,\,T)$$

$$=\left(\frac{P}{4\beta R}\right)^{1/2}\int_0^\infty\bigg(\gamma_1(\eta)$$

$$+\frac{\omega}{\omega+\mu_2}\,\gamma_2(\eta)\bigg)\exp\left[-\frac{P(\eta-Z)}{2}\right]$$

$$\cdot\int_0^T\exp(-b_1\tau)\frac{\partial}{\partial\tau}\int_0^\tau \mathbf{I}_0\bigg[\frac{2\omega}{R}\bigg(\frac{(\tau-\sigma)\sigma}{\beta(1-\beta}\bigg)^{1/2}$$

$$\cdot\,h_2(Z,\,\sigma,\,\eta)\,d\sigma\,d\tau\,d\eta-\left(\frac{P}{4\beta R}\right)^{1/2}$$

$$\cdot\int_0^\infty\frac{\omega}{\omega+\mu_2}\,\gamma_2(\eta)\exp\left[-\frac{P(\eta-Z)}{2}-b_1T\right]$$

$$\cdot\int_0^T \mathbf{I}_0\left[\frac{2\omega}{R}\left(\frac{(T-\tau)\tau}{\beta(1-\beta)}\right)^{1/2}\right]h_2(Z,\,\tau,\,\eta)\,d\tau\,d\eta$$

(A25)

where

$$h_2(Z,\,\tau,\,\eta)=\frac{1}{(\pi\tau)^{1/2}}\exp\left[-\frac{(P/4+\omega+\mu_1-\beta Rb_1)\tau}{\beta R}\right]$$

$$\cdot\bigg\{\exp\left[-\frac{\beta RP(\eta-Z)^2}{4\tau}\right]$$

$$+\exp\left[-\frac{\beta RP(\eta+Z)^2}{4\tau}\right]\bigg\}$$

$$-\left(\frac{P}{\beta R}\right)^{1/2}\exp\bigg[\frac{P(\eta+Z)}{2}$$

$$-\frac{(\omega+\mu_1-\beta Rb_1)\tau}{\beta R}\bigg]\operatorname{erfc}\left[\frac{\beta(\eta+Z)+\tau}{(4\beta R\tau/P)^{1/2}}\right]$$

(A26)

Next, the first term, $C_1^{P1}(Z,\,T)$, of (A25) is integrated by parts with respect to τ, while Fubini's theorem [*Lindstrom and Stone*, 1974]

$$\int_0^T\int_0^\tau\cdots\,d\sigma\,d\tau=\int_0^T\int_\sigma^T\cdots\,d\tau\,d\sigma \qquad \text{(A27)}$$

is used to changed the order of integration. These operations lead to

$$C_1^{P1}(Z,\,T)=\frac{1}{\beta R}\int_0^T\exp\left[-\frac{\omega\mu_2\tau}{(\omega+\mu_2)\beta R}\right]J(a,\,b)$$

$$\cdot\int_0^\infty\left(\gamma_1(\eta)+\frac{\omega}{\omega+\mu_2}\,\gamma_2(\eta)\right)\Gamma_2(Z,\,\eta,\,\tau)\,d\eta\,d\tau$$

(A28)

where

$$J(a,\,b)=\exp\,(-a-b)\mathbf{I}_0[2(ab)^{1/2}]+\exp\,(-a)\int_0^b$$

$$\cdot\exp\,(-\lambda)\mathbf{I}_0[2(a\lambda)^{1/2}]\,d\lambda \qquad \text{(A29)}$$

and where a and b were given by (24). Equation (A28) gives the first term of (40). Equation (A29) may be rearranged into (23) by using the following property of Goldstein's J function [*van Genuchten*, 1981]

$$J(a,\,b)+J(b,\,a)=1+\exp\,(-a-b)\mathbf{I}_0[2(ab)^{1/2}] \qquad \text{(A30)}$$

Finally, changing the order of integration of $C_1^{P2}(Z,\,T)$ yields the second term of (40).

The corresponding expressions for $C_2^P(Z,\,T)$ can be readily obtained by substituting (40) into (A7). Before doing so, the first part of (40), i.e., C_1^{P1} given by (A28), is integrated by parts and further modified using the following differentiation properties of the J function [*van Genuchten*, 1981]:

$$\frac{\partial J(a,\,b)}{\partial a}=\exp\,(-a-b)\mathbf{I}_0[2(ab)^{1/2}] \qquad \text{(A31)}$$

$$\frac{\partial J(a,\,b)}{\partial b}=\exp\,(-a-b)\left(\frac{a}{b}\right)^{1/2}\mathbf{I}_1[2(ab)^{1/2}] \qquad \text{(A32)}$$

The above calculations lead to

$$C_2^{P1}(Z,\,T)$$

$$=\frac{1}{\beta R}\exp\left[-\frac{\omega\mu_2T}{(\omega+\mu_2)\beta R}+\frac{\omega^2T}{(\omega+\mu_2)\beta R}\right]$$

$$\cdot\int_0^T\int_0^\infty\left(\gamma_1(\eta)+\frac{\omega}{\omega+\mu_2}\,\gamma_2(\eta)\right)\Gamma_2(Z,\,\eta,\,\tau)d\eta\,d\tau$$

$$+\frac{\omega}{\beta R^2}\int_0^T\left\{\int_0^\tau \exp\left[-\frac{\omega\mu_2\tau}{(\omega+\mu_2)\beta R}\right]\exp(-a-b)\right.$$
$$\cdot\left[\frac{\omega}{(\omega+\mu_2)\beta}\mathbf{I}_0[2(ab)^{1/2}]+\left(\frac{\tau}{\beta(1-\beta)(T-\tau)}\right)^{1/2}\mathbf{I}_1[2(ab)^{1/2}]\right]$$
$$\left.\cdot\int_0^\infty\left(\gamma_1(\eta)+\frac{\omega}{\omega+\mu_2}\gamma_2(\eta)\right)\Gamma_2(Z,\eta,\sigma)\,d\eta\,d\sigma\right\}d\tau \tag{A33}$$

Finally, substituting (A33) into (A7), integrating by parts, and applying Fubini's theorem (A27) yields the second term of (41).

NOTATION

a	constant defined by (24*a*).
A_k	terms defined by (21) and (22), or (25) and (26) ($k = 1, 2$).
b	constant defined by (24*b*).
C_k or C_k^r	volume-averaged concentrations of phase k ($k = 1, 2$).
C_k^f	flux-averaged concentrations of phase k defined by (56*a*) ($k = 1, 2$).
C_i or C_i^r	volume-averaged initial concentration.
C_i^f	flux-averaged initial concentration defined by (56*c*).
C_0	volume-averaged input concentration.
C_T^r	total resident concentration defined by (57).
$\mathbf{I}_0$, $\mathbf{I}_1$	modified Bessel function of orders zero and one.
f_i	constants for multiple pulse input ($i = 1, 2, \cdots, n$).
$f(Z, T)$	travel time probability density function defined by (14).
$G(Z, \tau)$	term defined by (27).
$H_j(T, \tau)$	terms defined by (15) ($j = 0, 1$).
J	Goldstein's J function defined by (23).
P	Peclet number (Table 1).
R	retardation factor (Table 1).
T	time (Table 1).
T_i	constants for multiple pulse input ($i = 1, 2, \cdots, n$).
u	term defined by (29).
U_i	constants for initial concentration ($i = 1, 2, \cdots, n$).
Z	distance (Table 1).
Z_i	constants for stepwise initial distribution ($i = 1, 2, \cdots, n$).
β	partition coefficient (Table 1).
Γ_i	terms defined by Table 2 ($i = 1, 2$)
γ_k or γ_k^r	volume-averaged zero-order production coefficients in phase k ($k = 1, 2$) (Table 1).
γ_k^f	flux-averaged zero-order production coefficients in phase k ($k = 1, 2$) defined by (56*b*).
ζ_i	constants for production distribution ($i = 1, 2, \cdots, n$).
η_i	constants for stepwise production distribution ($i = 1, 2, \cdots, n$).
λ^I	constant for exponential initial distribution.
λ_k^P	constant for exponential production distribution in phase k ($k = 1, 2$).
μ_k	first-order decay coefficients in phase k ($k = 1, 2$) (Table 1).
ν_j	constants for production distribution ($j = 1, 2, \cdots, m$).
ξ_j	constants for stepwise production distribution ($j = 1, 2, \cdots, m$).
ψ_i	terms defined by Table 2 ($i = 1, 2$).
ω	mass transfer coefficient (Table 1).

Superscripts

B	boundary value problem.
f	flux-averaged concentration mode.
I	initial value problem.
P	production value problem.
r	resident concentration mode.

Dimensional parameters listed in Table 1 for the description of the two-site and two-region models are not included.

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