



Analytical Modeling of Nonaqueous Phase Liquid Dissolution with Green's Functions

FEIKE J. LEIJ and MARTINUS TH. VAN GENUCHTEN

U.S. Salinity Laboratory, U.S. Department of Agriculture, Agricultural Research Service, 450 W. Big Springs Road, Riverside, CA 92507-4617, U.S.A., e-mail: fleij@ussl.ars.usda.gov

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Abstract. Equilibrium and bicontinuum nonequilibrium formulations of the advection–dispersion equation (ADE) have been widely used to describe subsurface solute transport. The Green's Function Method (GFM) is particularly attractive to solve the ADE because of its flexibility to deal with arbitrary initial and boundary conditions, and its relative simplicity to formulate solutions for multi-dimensional problems. The Green's functions that are presented can be used for a wide range of problems involving equilibrium and nonequilibrium transport in semi-infinite and infinite media. The GFM is applied to analytically model multi-dimensional transport from persistent solute sources typical of nonaqueous phase liquids (NAPLs). Specific solutions are derived for transport from a rectangular source (parallel to the flow direction) of persistent contamination using first-, second-, or third-type boundary or source input conditions. Away from the source, the first- and third-type condition cannot be expected to represent the exact surface condition. The second-type condition has the disadvantage that the diffusive flux from the source needs to be specified a priori. Near the source, the third-type condition appears most suitable to model NAPL dissolution into the medium. The solute flux from the pool, and hence the concentration in the medium, depends strongly on the mass transfer coefficient. For all conditions, the concentration profiles indicate that nonequilibrium conditions tend to reduce the maximum solute concentration and the total amount of solute that enters the porous medium from the source. On the other hand, during nonequilibrium transport the solute may spread over a larger area of the medium compared to equilibrium transport.

Key words: Green's functions, NAPL dissolution, nonequilibrium transport, initial value problem, boundary value problem.

Abbreviations: ADE – advection–dispersion equation; GFM – Green's function method.

Nomenclature

a	auxiliary variable.
b	auxiliary variable.
c	dimensional concentration [ML^{-3}].
C	dimensionless solute concentration ($=c/c_0$).
D	diffusion coefficient [L^2T^{-1}].
f	initial concentration.
G	Green's function.
g	input concentration for NAPL pool.

h	function in convolution integral.
I_0, I_1	modified Bessel function of orders zero and one.
k	dimensionless mass-transfer coefficient.
k^*	mass-transfer coefficient [LT^{-1}].
L	characteristic length.
P	Peclet number.
R	retardation factor.
s	Laplace variable.
s^*	modified Laplace variable.
T	dimensionless time.
u	arbitrary function.
W	dimensionless vertical velocity.
X	dimensionless longitudinal position.
Y	dimensionless transversal position.
Z	dimensionless transversal position.

Greek

β	dimensionless variable for partitioning in nonequilibrium transport models.
Γ	prescribed gradient for second-type condition.
δ	Dirac delta function.
ζ	dummy variable.
η	dummy variable.
μ	first-order degradation term.
ξ	dummy variable.
τ	dummy variable.
ω	dimensionless mass transfer coefficient.
Λ	Auxiliary term in Green's function to quantify nonequilibrium effects.

Subscripts

e	effective value.
L	longitudinal.
0	reference or characteristic value.
s	solubility or upper value.
T	transversal.
u	equilibrium solution for unit input.
X	X-direction.
Y	Y-direction.
Z	Z-direction.
1	mobile region in two-region nonequilibrium model.
2	immobile region in two-region nonequilibrium model.

Superscripts

f	first-type condition.
s	second-type condition.
t	third-type condition.

Special Symbols

\mathbf{L}	differential operator for advection–dispersion equation.
\mathbf{L}^*	adjoint operator for advection–dispersion equation.
\mathcal{L} or $\bar{}$	Laplace transform.

1. Introduction

The deterministic advection–dispersion model has been widely used to describe the movement of dissolved chemicals, heat and other substances in porous media. Mathematical solutions of this model allow us to quantify the spatial and temporal distribution of the solute concentration in porous media, thus providing important information for optimally monitoring or managing the subsurface environment. Whereas, numerical solutions are often used for general problems, analytical solutions may be employed for idealized conditions. Analytical solutions are valuable to evaluate numerical solution techniques, gain a better understanding of the importance of different transport parameters and mathematical conditions, estimate model parameters with inverse methods, and study transport for conditions where numerical methods may not yield accurate or reliable results. Techniques to derive analytical solutions of the advection–dispersion equation (ADE) typically involve Fourier analysis and integral transformation procedures (cf. Cleary and Adrian, 1973; Güven *et al.*, 1984; Leij *et al.*, 1993). Relatively few solutions have been obtained with Green's functions (Yeh and Tsai, 1976; Galya, 1987; Ellsworth and Butters, 1993). Yeh (1981) presented several Green's functions for a source term in the ADE.

The introduction and movement of nonaqueous phase liquids (NAPLs) in the subsurface presents an especially serious threat to the long-term quality of soil and groundwater systems. Spills of hydrocarbon solvents can create hazardous and long-lasting sources of groundwater contamination (Bradford *et al.*, 1998). Due to its density and viscosity, a dense nonaqueous phase liquid (DNAPL) tends to sink to the bottom of aquifers and often remains there as a contamination pool because of its low solubility in water. Similarly, a light nonaqueous phase liquid (LNAPL) may form a relatively immobile pool on top of the aquifer. Pollution from oil tanks, landfills, and other buried sources are further examples of gradual and continuous contamination from a fixed source. In this study we use the advection–dispersion model to describe NAPL movement in the aqueous phase after dissolution from a simple rectangular pool at the top or bottom of the aquifer.

Analytical solutions for such persistent contamination problems can be derived by integrating instantaneous sources with respect to time or space (e.g., Prakash, 1984; Yeh, 1981). This approach does not allow the specification of different types of boundary conditions at the interface of the source and the porous medium. Persistent NAPL contamination has been described as a boundary value problem by, among others, Chrysikopoulos *et al.* (1994), Holman and Javandel (1996), and Shan and Javandel (1997). Solutions in these studies were obtained with a variety of integral transforms. However, the solutions may be obtained far more conveniently with the Green's function method (GFM). This method offers flexibility in terms of handling changes in initial and boundary conditions. Furthermore, very general and concise expressions for the solute concentration are possible with the GFM, particularly for multidimensional problems. Several pertinent texts exist on

the method (Greenberg, 1971; Stakgold, 1979; Roach, 1982; Beck *et al.*, 1992). Expressions for Green's functions have been derived for the standard ADE (Leij *et al.*, 1999). However, bicontinuum transport models may predict solute transport more accurately by distinguishing a 'mobile' or flowing region, with advective and dispersive solute transport, and an 'immobile' or stagnant region (possibly a different fluid phase). Solute exchange between the regions is described by a first-order diffusion equation (Coats and Smith, 1964; Van Genuchten and Wierenga, 1976).

The objectives of this study are to (1) formulate Green's functions for the equilibrium and nonequilibrium ADE, (2) use the GFM to derive analytical solutions for solute movement from a persistent contaminant source, and (3) illustrate the effects of alternative source boundary conditions, mass transfer parameters, and nonequilibrium parameters on the solute distribution.

2. Mathematical Formulation

2.1. EQUILIBRIUM TRANSPORT

The dimensionless ADE for a solute subject to unidirectional flow, three-dimensional dispersion, linear sorption and first-order degradation in a porous medium whose transport properties are constant in time and space, may be given by

$$R \frac{\partial C}{\partial T} = \frac{1}{P_X} \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} + \frac{1}{P_Y} \frac{\partial^2 C}{\partial Y^2} + \frac{1}{P_Z} \frac{\partial^2 C}{\partial Z^2} - \mu C, \quad (1)$$

where R is a solute retardation factor, T is time, X , Y and Z denote the position along the longitudinal and two transversal coordinates with corresponding Peclet numbers P_X , P_Y and P_Z , and μ is a degradation factor. The model may be extended to include a zero-order source/sink term without complicating the solution procedure according to the GFM. The transformation from dimensional to dimensionless parameters has been shown elsewhere (e.g., Toride *et al.*, 1993).

2.1.1. Green's Function Method

The differential operator, \mathbf{L} , for the previously defined ADE is

$$\mathbf{L} = R \frac{\partial}{\partial T} - \frac{1}{P_X} \frac{\partial^2}{\partial X^2} + \frac{\partial}{\partial X} - \frac{1}{P_Y} \frac{\partial^2}{\partial Y^2} - \frac{1}{P_Z} \frac{\partial^2}{\partial Z^2} + \mu. \quad (2)$$

The solution to $\mathbf{L}(C) = 0$ yields the solute concentration C . An alternative adjoint problem, which may be easier to solve, is obtained through multiplication of $\mathbf{L}(C)$ by a Green's function G and subsequent integration over the solution region (X , Y , Z , T). This procedure can be schematically represented as

(cf. Greenberg, 1971)

$$\begin{aligned} & \iiint\limits_V \mathbf{L}(C) \, d\zeta \, d\eta \, d\xi \, d\tau \\ &= \text{boundary terms} + \iiint\limits_V \mathbf{C}\mathbf{L}^*(G) \, d\zeta \, d\eta \, d\xi \, d\tau. \end{aligned} \quad (3)$$

Integration by parts yields the boundary terms and the formally adjoint differential operator, which is defined as

$$\mathbf{L}^* = -R \frac{\partial}{\partial \tau} - \frac{1}{P_X} \frac{\partial^2}{\partial \xi^2} - \frac{\partial}{\partial \xi} - \frac{1}{P_Y} \frac{\partial^2}{\partial \eta^2} - \frac{1}{P_Z} \frac{\partial^2}{\partial \zeta^2} + \mu. \quad (4)$$

The dummy variables (ξ, η, ζ, τ) correspond to the regular independent variables (X, Y, Z, T) . The adjoint operator is similar to the ADE operator except for the sign of the storage and advection terms. A solution for C may be obtained from the equivalent problem in terms of the adjoint operator by requiring that the adjoint differential operator on G is equal to the following four-dimensional Dirac delta function:

$$\mathbf{L}^*(G) = \delta(X - \xi, Y - \eta, Z - \zeta, T - \tau). \quad (5)$$

The Green's function $G(X, Y, Z, T; \xi, \eta, \zeta, \tau)$ denotes the concentration at (X, Y, Z, T) as the result of instant solute release at τ for a unit source located at (ξ, η, ζ) . The concentration for a spatial domain with longitudinal boundaries at X_1, X_2 and transversal boundaries at Y_1, Y_2 , and Z_1, Z_2 , is expressed according to the GFM as

$$\begin{aligned} C(X, Y, Z, T) = & \int_0^T \int_{Y_1}^{Y_2} \int_{Z_1}^{Z_2} \left(\frac{G}{P_X} \frac{\partial C}{\partial \xi} - \frac{C}{P_X} \frac{\partial G}{\partial \xi} - GC \right) \Big|_{\xi \rightarrow X_1}^{\xi \rightarrow X_2} d\zeta \, d\eta \, d\tau + \\ & + \int_0^T \int_{X_1}^{X_2} \int_{Z_1}^{Z_2} \left(\frac{G}{P_Y} \frac{\partial C}{\partial \eta} - \frac{C}{P_Y} \frac{\partial G}{\partial \eta} \right) \Big|_{\eta \rightarrow Y_1}^{\eta \rightarrow Y_2} d\zeta \, d\xi \, d\tau + \\ & + \int_0^T \int_{X_1}^{X_2} \int_{Y_1}^{Y_2} \left(\frac{G}{P_Z} \frac{\partial C}{\partial \zeta} - \frac{C}{P_Z} \frac{\partial G}{\partial \zeta} \right) \Big|_{\zeta \rightarrow Z_1}^{\zeta \rightarrow Z_2} d\eta \, d\xi \, d\tau + \\ & + \int_{X_1}^{X_2} \int_{Y_1}^{Y_2} \int_{Z_1}^{Z_2} RGC \Big|_{\tau=0} d\zeta \, d\eta \, d\xi. \end{aligned} \quad (6)$$

Equation (6) follows from Equation (3) when $\mathbf{L}(C) = 0$ and $\mathbf{L}^*(G)$ is given by (5). The first three terms on the right-hand side arise for boundary value problems in the X, Y and Z directions, while the fourth term is associated with the initial value problem; this expression for C can be further simplified once the boundary and initial conditions are known. The appropriate Green's function is determined by solving Equation (5). This equation is homogeneous except for a discontinuity when $(\xi = X, \eta = Y, \zeta = Z, \tau = T)$. Because the boundary conditions for G are homogeneous, the Green's function may be written as

the product of Green's functions for individual directions (cf. Beck *et al.*, 1992): $G(X, Y, Z, T; \xi, \eta, \zeta, \tau) = G_X(X, T; \xi, \tau) G_Y(Y, T; \eta, \tau) G_Z(Z, T; \zeta, \tau)$. Note that a similar application of the product rule may not be permitted for the concentration (Carslaw and Jaeger, 1959). The degradation factor for three-dimensional transport is partitioned, using somewhat arbitrary contributions for each direction, such that $\mu = \mu_X + \mu_Y + \mu_Z$. In the following, mostly unidirectional Green's functions will be considered for the purpose of constructing a three-dimensional solution for the concentration.

2.1.2. Green's Functions

The following general concentration for the longitudinal direction, resulting from one-dimensional advective–dispersive transport for equilibrium conditions, can be inferred from (6):

$$C_X(X, T) = \int_0^T \left(\frac{G_X}{P_X} \frac{\partial G_X}{\partial \xi} - \frac{C_X}{P_X} \frac{\partial G_X}{\partial \xi} - G_X C_X \right) \Big|_{X_1}^{X_2} d\tau + \int_{X_1}^{X_2} R G_X(X, T; \xi, 0) C_X(\xi, 0) d\xi, \quad (7)$$

where the boundaries X_1 and X_2 are specified depending on the solution domain. A unique solution may be obtained by applying the boundary conditions for C_X , and subsequently imposing conditions on G_X to be used in the solution of the adjoint problem:

$$\mathbf{L}^*(G_X) = -R \frac{\partial G_X}{\partial \tau} - \frac{1}{P_X} \frac{\partial^2 G_X}{\partial \xi^2} - \frac{\partial G_X}{\partial \xi} + \mu_X G_X = \delta(X - \xi, T - \tau). \quad (8)$$

Solutions for G_X can often be readily inferred from existing solutions for the ADE (cf. Van Genuchten and Alves, 1982; Leij *et al.*, 1999).

The concentration in one of the transversal directions, say Y , as a result of one-dimensional dispersion may be expressed according to the GFM as (cf. Equation (6)):

$$C_Y(Y, T) = \int_0^T \left(\frac{G_Y}{P_Y} \frac{\partial C_Y}{\partial \eta} - \frac{C_Y}{P_Y} \frac{\partial G_Y}{\partial \eta} \right) \Big|_{Y_1}^{Y_2} d\tau + \int_{Y_1}^{Y_2} R G_Y(Y, T; \eta, 0) C_Y(\eta, 0) d\eta. \quad (9)$$

Explicit expressions for the concentration in the transversal Y direction are obtained by imposing a zero-gradient condition on C_Y at a finite or infinite distance and by substituting the appropriate Green's function, G_Y . The latter function is derived by solving the adjoint problem given by

$$\mathbf{L}^*(G_Y) = -R \frac{\partial G_Y}{\partial \tau} - \frac{1}{P_Y} \frac{\partial^2 G_Y}{\partial \eta^2} + \mu_Y G_Y = \delta(Y - \eta) \delta(T - \tau), \quad (10)$$

subject to the conditions that eliminate any unknown terms in Equation (9). Expressions for the transverse functions, G_Y and G_Z , can be adapted from the literature on Green's functions for diffusion (Beck *et al.*, 1992).

Table I lists longitudinal (G_L) and transversal (G_T) Green's functions for equilibrium transport – and the conditions on G that they satisfy – that can be used to derive solutions for a variety of boundary and initial value problems in infinite and semi-infinite porous media. The superscripts f, s, and t denote a first-, second- and third-type inlet condition for transport in semi-infinite media. The subscript 1 is used to indicate nonequilibrium conditions. Note that the transverse Green's function contains the nonequilibrium parameter β , which should be set to unity for equilibrium transport.

2.2. NONEQUILIBRIUM TRANSPORT

The porous medium is assumed to consist of two macroscopic continua: one in which transport is always an equilibrium process and the other where access to immobile water or nonequilibrium sorption sites is governed by a first-order rate equation. The dimensionless model for nonequilibrium transport is given by (Toride *et al.*, 1993; Leij *et al.*, 1993)

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P_X} \frac{\partial^2 C_1}{\partial X^2} - \frac{\partial C_1}{\partial X} + \frac{1}{P_Y} \frac{\partial^2 C_1}{\partial Y^2} + \frac{1}{P_Z} \frac{\partial^2 C_1}{\partial Z^2} + \omega(C_2 - C_1) - \mu_1 C_1, \quad (11)$$

$$(1 - \beta)R \frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) - \mu_2 C_2, \quad (12)$$

where C_1 is the dimensionless solution for the part of the aqueous phase where solute transport is described as an equilibrium process, C_2 is the concentration for the rest of the porous medium, β is a coefficient to quantify sorption in the 'equilibrium' phase relative to total sorption, ω is a mass transfer coefficient and μ_1 and μ_2 are dimensionless constants for first-order degradation in the mobile and immobile regions of the medium. The coefficient ω , which quantifies the rate of nonequilibrium exchange to the bulk flow rate, is actually a Damköhler number (Boucher and Alves, 1959). The mathematical equivalency between dimensionless and dimensional transport parameters was illustrated by Toride *et al.* (1993), among others.

Before employing the GFM, the following Laplace transform is applied:

$$\mathcal{L}[C(X, Y, Z, T)] = \bar{C}(X, Y, Z, s) = \int_0^\infty C(X, Y, Z, T) \exp(-sT) dT \quad (13)$$

to Equations (11) and (12). For any arbitrary initial distribution, $f(X, Y, Z)$, the following differential equation may be obtained after some rearrangements, to

Table I. Selected longitudinal and transversal Green's functions*

Function	Expression	Conditions
$G_L(X, T; \xi, \tau)$	$\sqrt{\frac{RP_X}{4\pi(T-\tau)}} \times \exp\left[-\frac{\mu_X(T-\tau)}{R} - \frac{P_X[R(X-\xi) - (T-\tau)]^2}{4R(T-\tau)}\right]$	$\frac{\partial G}{\partial \xi} = 0, \xi \rightarrow \pm\infty$
$G_L^f(X, T; \xi, \tau)$	$\sqrt{\frac{RP_X}{4\pi(T-\tau)}} \exp\left[-\frac{\mu_X(T-\tau)}{R}\right] \times \left\{ \exp\left[-\frac{P_X[R(X-\xi) - (T-\tau)]^2}{4R(T-\tau)}\right] - \exp\left[P_X X - \frac{P_X[R(X+\xi) + (T-\tau)]^2}{4R(T-\tau)}\right] \right\}$	$G = 0, \xi = 0$ $\frac{\partial G}{\partial \xi} = 0, \xi \rightarrow \infty$
$G_L^i(X, T; \xi, \tau)$	$\exp\left(-\frac{\mu_X(T-\tau)}{R}\right) \left\{ \sqrt{\frac{RP_X}{4\pi(T-\tau)}} \times \left[\exp\left(-\frac{P_X[R(X-\xi) - (T-\tau)]^2}{4R(T-\tau)}\right) + \exp\left(P_X X - \frac{P_X[R(X+\xi) + (T-\tau)]^2}{4R(T-\tau)}\right) \right] - \frac{P_X}{2} \exp(P_X X) \operatorname{erfc}\left[\frac{R(X+\xi) + (T-\tau)}{\sqrt{4R(T-\tau)/P_X}}\right] \right\}$	$\frac{\partial G}{\partial \xi} = 0, \xi = 0, \xi \rightarrow \infty$
$G_{L1}(X, T; \xi, \tau)$	$\int_0^{T-\tau} \Lambda(T-\tau, \tau') G_L(X, \frac{\tau'}{\beta}; \xi, 0) d\tau'$	$\frac{\partial G_1}{\partial \xi} = 0, \xi \rightarrow \pm\infty$
$G_{L1}^f(X, T; \xi, \tau)$	$\int_0^{T-\tau} \Lambda(T-\tau, \tau') G_L^f(X, \frac{\tau'}{\beta}; \xi, 0) d\tau'$	$G_1 = 0, \xi = 0$ $\frac{\partial G_1}{\partial \xi} = 0, \xi \rightarrow \infty$
$G_{L1}^i(X, T; \xi, \tau)$	$\int_0^{T-\tau} \Lambda(T-\tau, \tau') G_L^i(X, \frac{\tau'}{\beta}; \xi, 0) d\tau'$	$\frac{\partial G_1}{\partial \xi} = 0, \xi = 0, \xi \rightarrow \infty$
$\Lambda(T-\tau, \tau')$	$\frac{1}{\beta R} \exp\left(\frac{\mu_X \tau'}{\beta R} - \frac{\omega + \mu_{X1}}{\beta R} \tau'\right) \times \left[\delta(T-\tau-\tau') + \frac{\omega}{R} \sqrt{\frac{\tau'}{\beta(1-\beta)(T-\tau-\tau')}} \times I_1\left(\frac{2\omega}{R} \sqrt{\frac{\tau'(T-\tau-\tau')}{\beta(1-\beta)}}\right) \exp\left(-\frac{\omega + \mu_2}{(1-\beta)R} (T-\tau-\tau')\right) \right]$	
$G_T(Y, T; \eta, \tau)$	$\sqrt{\frac{\beta RP_Y}{4\pi(T-\tau)}} \exp\left(-\frac{\mu_Y(T-\tau)}{R} - \frac{\beta RP_Y(Y-\eta)^2}{4(T-\tau)}\right)$	$\frac{\partial G}{\partial \eta} = 0, \eta \rightarrow \pm\infty$
$G_T^f(Y, T; \eta, \tau)$	$\sqrt{\frac{\beta RP_Y}{4\pi(T-\tau)}} \exp\left(-\frac{\mu_Y(T-\tau)}{R}\right) \times \left[\exp\left(-\frac{\beta RP_Y(Y-\eta)^2}{4(T-\tau)}\right) - \exp\left(-\frac{\beta RP_Y(Y+\eta)^2}{4(T-\tau)}\right) \right]$	$G_1 = 0, \eta = 0$ $\frac{\partial G_1}{\partial \eta} = 0, \eta \rightarrow \infty$
$G_T^s(Y, T; \eta, \tau)$	$\sqrt{\frac{\beta RP_Y}{4\pi(T-\tau)}} \exp\left(-\frac{\mu_Y(T-\tau)}{R}\right) \times \left[\exp\left(-\frac{\beta RP_Y(Y-\eta)^2}{4(T-\tau)}\right) + \exp\left(-\frac{\beta RP_Y(Y+\eta)^2}{4(T-\tau)}\right) \right]$	$\frac{\partial G_1}{\partial \eta} = 0, \eta = 0, \eta \rightarrow \infty$

Table I. continued

Function	Expression	Conditions
$G_1^t(Y, T; \eta, \tau)$	$\exp\left(-\frac{\mu_Y(T-\tau)}{R}\right) \left\{ \sqrt{\frac{\beta R P_Y}{4\pi(T-\tau)}} \times \right.$ $\times \left[\exp\left(-\frac{\beta R P_Y(Y-\eta)^2}{4(T-\tau)}\right) + \exp\left(-\frac{\beta R P_Y(Y+\eta)^2}{4(T-\tau)}\right) \right] +$ $-k \exp\left[\frac{k^2(T-\tau)}{\beta R P_Y} + k(Y+\eta)\right] \times$ $\times \operatorname{erfc}\left(\frac{\beta R P_Y(Y+\eta) + 2k(T-\tau)}{\sqrt{4\beta R P_Y(T-\tau)}}\right) \left. \right\}$	$kG_1 - \frac{\partial G_1}{\partial \eta} = 0, \eta = 0$ $\frac{\partial G}{\partial \eta} = 0, \eta \rightarrow \infty$

* $G = 0$ if $\tau > T$.

express the problem in a single dependent variable, \bar{C}_1 :

$$\frac{1}{P_X} \frac{\partial^2 \bar{C}_1}{\partial X^2} - \frac{\partial \bar{C}_1}{\partial X} + \frac{1}{P_Y} \frac{\partial^2 \bar{C}_1}{\partial Y^2} + \frac{1}{P_Z} \frac{\partial^2 \bar{C}_1}{\partial Z^2} -$$

$$- \left(\beta R s + \omega + \mu_1 - \frac{a\omega}{s+b} \right) \bar{C}_1 + \left(\beta R + \frac{\omega}{s+b} \right) f = 0, \quad (14)$$

where

$$a = \frac{\omega}{1-\beta}, \quad (15a)$$

$$b = \frac{\omega + \mu_2}{1-\beta}. \quad (15b)$$

Appendix A shows how solutions for C_1 may be derived for different boundary and initial value problems from the solution for the equilibrium problem (C). Solutions for C_2 will not be presented since they directly follow from those for C_1 (cf. Toride *et al.*, 1993).

2.2.1. Green's Function Method

The same procedure is followed as for the equilibrium problem except that the GFM is applied to the transport equation in the Laplace domain given by Equation (14) rather than the regular time domain. The corresponding differential operator, \mathbf{L}_1 , is

$$\mathbf{L}_1 = -\frac{1}{P_X} \frac{\partial^2}{\partial X^2} + \frac{\partial}{\partial X} - \frac{1}{P_Y} \frac{\partial^2}{\partial Y^2} - \frac{1}{P_Z} \frac{\partial^2}{\partial Z^2} +$$

$$+ \left(\beta R s + \omega + \mu_1 - \frac{a\omega}{s+b} \right). \quad (16)$$

The concentration in the Laplace domain is found by solving

$$\mathbf{L}_1(\bar{C}_1) = \left(\beta R + \frac{\omega}{s+b} \right) f. \quad (17)$$

The following adjoint differential operator can be derived after multiplying this equality by the Green's function \bar{G}_1 and subsequently integrating with respect to the spatial coordinates:

$$\mathbf{L}_1^* = -\frac{1}{P_X} \frac{\partial^2}{\partial \xi^2} - \frac{\partial}{\partial \xi} - \frac{1}{P_Y} \frac{\partial^2}{\partial \eta^2} - \frac{1}{P_Z} \frac{\partial^2}{\partial \zeta^2} + \left(\beta R s + \omega + \mu_1 - \frac{a \omega}{s + b} \right). \quad (18)$$

The adjoint differential operator on \bar{G}_1 should now satisfy the problem

$$\mathbf{L}_1^*(\bar{G}_1) = \delta(X - \xi, Y - \eta, Z - \zeta). \quad (19)$$

The GFM yields the following expression for the transformed concentration in case of unspecified initial and boundary conditions:

$$\begin{aligned} \bar{C}_1(X, Y, Z, s) = & \int_{Y_1}^{Y_2} \int_{Z_1}^{Z_2} \left(\frac{\bar{G}_1}{P_X} \frac{\partial \bar{C}_1}{\partial \xi} - \frac{\bar{C}_1}{P_X} \frac{\partial \bar{G}_1}{\partial \xi} - \bar{G}_1 \bar{C}_1 \right) \Big|_{\xi \rightarrow X_1}^{\xi \rightarrow X_2} d\zeta d\eta + \\ & + \int_{X_1}^{X_2} \int_{Z_1}^{Z_2} \left(\frac{\bar{G}_1}{P_Y} \frac{\partial \bar{C}_1}{\partial \eta} - \frac{\bar{C}_1}{P_Y} \frac{\partial \bar{G}_1}{\partial \eta} \right) \Big|_{\eta \rightarrow Y_1}^{\eta \rightarrow Y_2} d\zeta d\xi + \\ & + \int_{X_1}^{X_2} \int_{Y_1}^{Y_2} \left(\frac{\bar{G}_1}{P_Z} \frac{\partial \bar{C}_1}{\partial \zeta} - \frac{\bar{C}_1}{P_Z} \frac{\partial \bar{G}_1}{\partial \zeta} \right) \Big|_{\zeta \rightarrow Z_1}^{\zeta \rightarrow Z_2} d\eta d\xi + \\ & + \int_{X_1}^{X_2} \int_{Y_1}^{Y_2} \int_{Z_1}^{Z_2} \left(\beta R + \frac{\omega}{s + b} \right) \bar{G}_1 f(\xi, \eta, \zeta) d\zeta d\eta d\xi. \end{aligned} \quad (20)$$

The Green's function, $\bar{G}_1(X, Y, Z, s; \xi, \eta, \zeta)$, can again be written as the product of unidirectional Green's functions. At this stage only the longitudinal part remains of interest since this part entirely reflects the change in previously reported equilibrium Green's functions due to nonequilibrium effects. Rather than solving Equation (19) for \bar{G}_1 , and hence $\bar{G}_{X_1}(X, s; \xi)$, expressions for $\bar{G}_{X_1}(X, T; \xi, \tau)$ will be obtained from the results of Appendix A for a boundary value problem with input function $g(T)$, and for an initial value problem with initial distribution $f(X)$.

2.2.2. Boundary Value Problem

The concentration in the Laplace domain for a one-dimensional semi-infinite medium which is initially solute free ($f = 0$) may be deduced from Equation (20):

$$\bar{C}_{X_1}(X, s) = \left(\frac{\bar{G}_{X_1}}{P_X} \frac{d\bar{C}_{X_1}}{d\xi} - \frac{\bar{C}_{X_1}}{d\xi} \frac{d\bar{G}_{X_1}}{d\xi} - \bar{G}_{X_1} \bar{C}_X \right) \Big|_{\xi \rightarrow 0}^{\xi \rightarrow \infty}. \quad (21)$$

For a *first-type condition*, the solute concentration at the inlet is given by the Laplace transform of a time-dependent input concentration, $g(T)$, and a zero-gradient outlet condition:

$$\bar{C}_{X1}(0, s) = \bar{g}(s), \quad \frac{d\bar{C}_{X1}}{dX}(\infty, s) = 0. \quad (22)$$

The conditions for the Green's function, $\bar{G}_{X1}(X, s; \xi)$ become apparent after inserting (22) into (21):

$$\bar{G}_{X1}(X, s; 0) = \frac{d\bar{G}_{X1}}{d\xi}(X, s; \infty) = 0, \quad (23)$$

where it is assumed that \bar{G}_{X1} also becomes zero for the infinite outlet condition. In analogy with the equilibrium solution, the transformed concentration may be written according to (21) and (A6):

$$\begin{aligned} \bar{C}_{X1}(X, s) &= \frac{\bar{g}(s)}{P_X} \frac{d\bar{G}_{X1}}{d\xi}(X, s; 0) = \bar{g}(s) \bar{C}_u(X, s^*), \\ s^* &= \beta R s + \omega + \mu_{X1} - \frac{a\omega}{a+b}, \end{aligned} \quad (24)$$

where, using Duhamel's theorem, the transformed concentration for an arbitrary input is related to the corresponding equilibrium concentration for one-dimensional transport resulting from a unit input concentration with no degradation, C_u (i.e., $g(T) = 1$ and $\mu_X = 0$). The degradation coefficient μ_1 is partitioned according to $\mu_1 = \mu_{X1} + \mu_Y + \mu_Z$, while μ_2 only occurs in the longitudinal problem. The Laplace variable is modified to formulate the nonequilibrium concentration in terms of the equilibrium solution. From (24) it follows that

$$C_{X1}(X, T) = \int_0^T \frac{g(\tau)}{P_X} \frac{\partial G_{X1}}{\partial \xi}(X, T; 0, \tau) d\tau. \quad (25)$$

The Green's function, listed as $G_{L1}^f(X, T; \xi, \tau)$ in Table I, can be determined from inspection of the solution for $C_{X1}(X, T)$ given by (A.10) using the spatial derivative of equilibrium Green's functions. Note that solutions for the nonequilibrium problem are written in terms of the Dirac delta function, $\delta(\cdot)$, and the zero- and first-order modified Bessel functions, I_0 and I_1 .

The transformed boundary conditions for a third-type condition are

$$\bar{C}_{X1}(0, s) - \frac{1}{P_X} \frac{d\bar{C}_{X1}}{dX}(0, s) = \bar{g}(s), \quad \frac{d\bar{C}_{X1}}{dX}(\infty, s) = 0. \quad (26)$$

The following conditions need to be imposed on $\bar{G}_{X1}(X, s; \xi)$ to obtain a unique solution according to Equation (21):

$$\frac{d\bar{G}_{X1}}{d\xi}(X, s; 0) = \frac{d\bar{G}_{X1}}{d\xi}(X, s; \infty) = 0. \quad (27)$$

The solution in the Laplace domain, again written according to the GFM, is based upon the corresponding solution to the equilibrium problem:

$$\bar{C}_{X1}(X, s) = \bar{g}(s)\bar{G}_{X1}(X, s; 0) = \bar{g}(s)\bar{C}_u(X, s^*). \quad (28)$$

The concentration in the regular time domain becomes

$$C_{X1}(X, T) = \int_0^T g(\tau)G_{X1}(X, T; 0, \tau) d\tau. \quad (29)$$

Since the boundary condition does not affect the ‘nonequilibrium’ part of the solution, the Green’s function follows from the nonequilibrium solution and is given as $G_{L1}^t(X, T; \xi, \tau)$ in Table I.

2.2.3. Initial Value Problem

By judiciously specifying the two boundary conditions for $\bar{G}_{X1}(X, s; \xi)$ to cancel unknown terms, the concentration in the Laplace domain for a one-dimensional semi-infinite medium with an arbitrary initial distribution and a zero solute concentration or flux at the inlet ($g = 0$), is given according to Equation (20) as

$$\bar{C}_{X1}(X, s) = \int_0^\infty \left(\beta R + \frac{\omega}{s+b} \right) f(\xi)\bar{G}_{X1}(X, s; \xi) d\xi. \quad (30)$$

Inversion to the real time domain yields

$$C_{X1}(X, T) = \int_0^\infty f(\xi) \left\{ \beta R G_{X1}(X, T; \xi, 0) + \int_0^T \omega \exp[-b(T-\tau)] G_{X1}(X, \tau, \xi, 0) d\tau \right\} d\xi. \quad (31)$$

The Green’s functions were already derived for the boundary value problem.

In case of a *first-type inlet condition*, the transformed boundary conditions are

$$\bar{C}_{X1}(0, s) = 0, \quad \frac{d\bar{C}_{X1}}{dX}(\infty, s) = 0. \quad (32)$$

To arrive at (30), the Green’s function should satisfy (24). It can be shown that inserting $G_{X1}^f(X, T; \xi, \tau)$ yields the solution given by Equation (A.10).

For a third-type condition, the transformed boundary conditions for a zero flux input are

$$\bar{C}_{X1}(0, s) - \frac{1}{P_{X1}} \frac{d\bar{C}_{X1}}{dX} = 0, \quad \frac{d\bar{C}_{X1}}{dX}(\infty, s) = 0 \quad (33)$$

with corresponding Green’s function conditions (27). The solution given by (A.10), including the equilibrium solution for a third-type inlet condition, is obtained by using $G_{X1}^t(X, T; \xi, \tau)$ of Table I.

3. Persistent Solute Sources

Consider solute movement from a planar source as sketched in Figure 1. This type of problem arises when a contaminant pool is located at the top (LNAPL source) or bottom (DNAPL source) of an aquifer. The longitudinal X -domain is infinite, the horizontal transversal Z -coordinate is infinite while the vertical Y -coordinate is semi-infinite, although the analysis can be readily applied to a finite impermeable layer (cf. Leijet *al.*, 1999) or other geometries. Three different types of conditions were applied at the NAPL pool, which has a negligible thickness.

First- and second-type conditions are used for a prescribed concentration and a diffusive mass flux, respectively, while a third-type scenario may be applicable for rate-limited diffusion from the source. Problems with mixed boundary conditions, such as a first- or third-type condition for the source and a homogeneous second-type condition elsewhere at the surface, are more complicated and will not be considered here.

The general initial and boundary conditions (i.e., excluding the source condition) are

$$C(X, Y, Z, 0) = 0 \quad (-\infty < X < \infty, 0 < Y < \infty, -\infty < Z < \infty), \quad (34)$$

$$\frac{\partial C}{\partial X}(\pm\infty, Y, Z, T) = 0 \quad (0 < Y < \infty, -\infty < Z < \infty), \quad (35)$$

$$\frac{\partial C}{\partial Y}(X, \infty, Z, T) = 0 \quad (-\infty < X < \infty, -\infty < Z < \infty), \quad (36)$$

$$\frac{\partial C}{\partial Z}(X, Y, \pm\infty, T) = 0 \quad (-\infty < X < \infty, 0 < Y < \infty). \quad (37)$$

An intermediate result for the concentration is obtained by substituting the above conditions in (6):

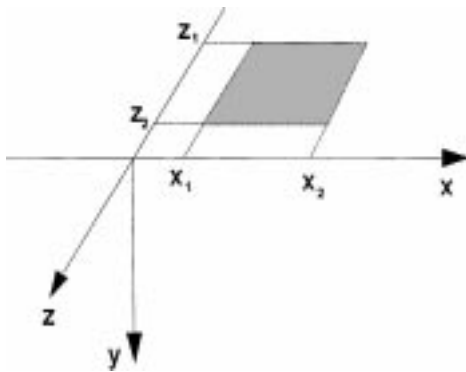


Figure 1. Schematic of a planar solute source.

$$\begin{aligned}
C(X, Y, Z, T) = & \int_0^T \left\{ \int_0^\infty \int_{-\infty}^\infty \left(-\frac{C}{P_X} \frac{\partial G}{\partial \xi} - GC \right) \Big|_{\xi \rightarrow -\infty}^{\xi \rightarrow \infty} d\zeta d\eta - \right. \\
& - \int_{-\infty}^\infty \int_{-\infty}^\infty \left[\frac{C}{P_Y} \frac{\partial G}{\partial \eta} \Big|_{\eta \rightarrow \infty} + \right. \\
& \left. \left. + \left(\frac{G}{P_Y} \frac{\partial C}{\partial \eta} - \frac{C}{P_Y} \frac{\partial G}{\partial \eta} \right) \Big|_{\eta=0} \right] d\zeta d\xi - \right. \\
& \left. - \int_{-\infty}^\infty \int_0^\infty \frac{C}{P_Z} \frac{\partial G}{\partial \zeta} \Big|_{\zeta \rightarrow -\infty}^\infty d\eta d\xi \right\} d\tau. \quad (38)
\end{aligned}$$

The exact formulation of the concentration will be determined in the following by specifying appropriate conditions on G , written as the product $G_X(X, T; \xi, \tau)$ $G_Y(Y, T; \eta, \tau)$ $G_Z(Z, T; \zeta, \tau)$, depending on the conditions for the source boundary. In all cases the following conditions apply to G :

$$\frac{\partial G}{\partial \xi}(X, Y, Z, T; \pm\infty, \eta, \zeta, \tau) = 0, \quad (39)$$

$$\frac{\partial G}{\partial \eta}(X, Y, Z, T; \xi, \infty, \zeta, \tau) = 0, \quad (40)$$

$$\frac{\partial G}{\partial \zeta}(X, Y, Z, T; \xi, \eta, \pm\infty, \tau) = 0. \quad (41)$$

3.1. FIRST-TYPE CONDITION

The solute concentration is prescribed for the surface ($Y = 0$) according to

$$C(X, 0, Z, T) = \begin{cases} g(X, Z, T), & (X_1 < X < X_2, Z_1 < Z < Z_2), \\ 0, & \text{otherwise.} \end{cases} \quad (42)$$

Equation (38) implies that the following additional condition be placed on the Green's function:

$$G(X, Y, Z, T; \xi, 0, \zeta, \tau) = 0. \quad (43)$$

All of the above conditions on G are met by selecting G_L , G_T^f , and G_T from Table I for G_X , G_Y , and G_Z . After using the conditions and functions in (38), integration with respect to ξ and ζ is possible due to the simple form of G_L and G_T if the prescribed concentration only depends on time. Remaining integrations with time, for this and other solutions, were done numerically using Gauss–Chebyshev

quadrature (Carnahan *et al.*, 1969). The resulting solute concentration is

$$\begin{aligned}
C(X, Y, Z, T) &= \int_0^T \int_{X_1}^{X_2} \int_{Z_1}^{Z_2} \frac{g(\tau)}{P_Y} G_X(X, T; \xi, \tau) \times \\
&\quad \times \frac{\partial G_Y}{\partial \eta}(Y, T; 0, \tau) G_Z(Z, T; \zeta, \tau) d\zeta d\xi d\tau \\
&= \int_0^T \frac{g(T-\tau)}{4} \frac{Y}{\tau} \sqrt{\frac{RP_Y}{4\pi\tau}} \exp\left(-\frac{\mu\tau}{R} - \frac{RP_Y Y^2}{4\tau}\right) \times \\
&\quad \times \left[\operatorname{erfc}\left(\frac{R(X-X_2)-\tau}{\sqrt{4R\tau/P_X}}\right) - \operatorname{erfc}\left(\frac{R(X-X_1)-\tau}{\sqrt{4R\tau/P_X}}\right) \right] \times \\
&\quad \times \left[\operatorname{erfc}\left(\frac{RP_Z}{4\tau}(Z-Z_2)\right) - \operatorname{erfc}\left(\sqrt{\frac{RP_Z}{4\tau}}(Z-Z_1)\right) \right] d\tau.
\end{aligned} \tag{44}$$

Two obvious disadvantages of this formulation are that this condition imposes a sharp discontinuity at the borders of the pool while it is typically not possible to specify $g(T)$ a priori. Furthermore, an upward diffusive mass flux may occur at $Y = 0$, which seems unrealistic away from the pool.

For nonequilibrium transport, the conditions on the solute concentration, C_1 and the Green's function are essentially the same as for the equilibrium problem, except that G_X needs to be replaced by G_{X1} . The concentration now becomes

$$\begin{aligned}
C_1(X, Y, Z, T) &= \int_0^T \int_{X_1}^{X_2} \int_{Z_1}^{Z_2} \frac{g(\tau)}{P_Y} G_{X1}(X, T; \xi, \tau) \times \\
&\quad \times \frac{\partial G_Y}{\partial \eta}(Y, T; 0, \tau) G_Z(Z, T; \zeta, \tau) d\zeta d\xi d\tau \\
&= \int_0^T \frac{g(T-\tau)}{4} \left\{ \frac{Y}{\tau} \sqrt{\frac{\beta RP_Y}{4\pi\tau}} \exp\left(-\frac{\beta RP_Y Y^2}{4\tau}\right) \times \right. \\
&\quad \times \left[\operatorname{erfc}\left(\sqrt{\frac{\beta RP_Z}{4\tau}}(Z-Z_2)\right) - \operatorname{erfc}\left(\sqrt{\frac{\beta RP_Z}{4\tau}}(Z-Z_1)\right) \right] \times \\
&\quad \times \int_0^\tau \exp\left(-\frac{\omega + \mu_1}{\beta R} \tau'\right) \left[\operatorname{erfc}\left(\frac{\beta R(X-X_2)-\tau'}{\sqrt{4\beta R\tau'/P_X}}\right) - \right. \\
&\quad \left. \left. - \operatorname{erfc}\left(\frac{\beta R(X-X_1)-\tau'}{\sqrt{4\beta R\tau'/P_X}}\right) \right] \times \right.
\end{aligned}$$

$$\begin{aligned} & \times \left[\delta(\tau - \tau') + \frac{\omega}{R} \sqrt{\frac{\tau'}{\beta(1-\beta)(\tau - \tau')}} I_1 \right. \\ & \left. \times \left(\frac{2\omega}{R} \sqrt{\frac{\tau'(\tau - \tau')}{\beta(1-\beta)}} \exp\left(-\frac{\omega + \mu_2}{(1-\beta)R}(\tau - \tau')\right) \right) d\tau' \right] d\tau. \end{aligned} \quad (45)$$

3.2. SECOND-TYPE CONDITION

Transport from the surface is in this case described as a diffusive process; the concentration gradient can presumably be specified across the entire surface of the porous medium while the concentration at the surface is unknown. The surface condition is written as

$$\frac{\partial C}{\partial Y}(X, 0, Z, T) = \begin{cases} -\Gamma(X, Z, T), & (X_1 < X < X_2, Z_1 < Z < Z_2), \\ 0, & \text{otherwise.} \end{cases} \quad (46)$$

The diffusive flux Γ may be defined in terms of dimensional parameters using the Sherwood number (Sh) according to $K^*c_sL/(D_e c_0) = \text{Sh} c_s/c_0$. In this expression, k^* is a mass transfer parameter (LT^{-1}), c_s is the solubility concentration (ML^{-3}), L is a characteristic length (L), c_0 is a reference concentration (ML^{-3}) and D_e is an effective diffusion coefficient ($\text{L}^2 \text{T}^{-1}$) (cf. Chrysikopoulos, 1995). Generally, it will be difficult to prescribe the flux, Γ , since it will normally be controlled by the *a priori* unknown NAPL concentration of the aqueous phase. If an excessively high flux is specified, the solution may predict concentrations exceeding the solubility of the NAPL. As will be discussed shortly, the diffusive flux can be constrained with a third-type condition.

To eliminate the unknown concentrations in the solution according to Equation (37), the remaining condition on the Green's function should be

$$\frac{\partial G}{\partial \eta}(X, Y, Z, T; \xi, 0, \zeta, \tau) = 0 \quad (-\infty < X < \infty, -\infty < Z < \infty). \quad (47)$$

The Green's function is the product of G_X , G_Y , and G_Z given by G_L , G_T^s , and G_T of Table 1. The concentration for the equilibrium problem – for a flux that only depends on time – is given by

$$\begin{aligned} C(X, Y, Z, T) &= \int_0^T \int_{X_1}^{X_2} \int_{Z_1}^{Z_2} \frac{\Gamma(\tau)}{P_Y} G_X(X, T; \xi, \tau) \times \\ & \quad \times G_Y(Y, T; 0, \tau) G_Z(Z, T; \zeta, \tau) d\zeta d\xi d\tau \\ &= \frac{1}{4} \int_0^T \frac{\Gamma(T - \tau)}{\sqrt{\pi P_Y \tau / R}} \exp\left(-\frac{\mu\tau}{R} - \frac{R P_Y Y^2}{4\tau}\right) \times \end{aligned}$$

$$\begin{aligned} & \times \left[\operatorname{erfc} \left(\frac{R(X - X_2) - \tau}{\sqrt{4R\tau/P_X}} \right) - \operatorname{erfc} \left(\frac{R(X - X_1) - \tau}{\sqrt{4R\tau/P_X}} \right) \right] \times \\ & \times \left[\operatorname{erfc} \left(\sqrt{\frac{RP_Z}{4\tau}}(Z - Z_2) \right) - \operatorname{erfc} \left(\sqrt{\frac{RP_Z}{4\tau}}(Z - Z_1) \right) \right] d\tau. \end{aligned} \quad (48)$$

The solution for the nonequilibrium problem according to the GFM is obtained by replacing G_X in equilibrium solution (48) by G_{X1} .

3.3. THIRD-TYPE CONDITION

The need for a third-type condition arises in case of rate-limited dissolution from the source. The surface condition is then formulated as

$$\frac{\partial C}{\partial Y}(X, 0, Z, T) = k(X, Z, T)[C(X, 0, Z, T) - g(X, Z, T)]$$

with

$$g(X, Z, T) = \begin{cases} c_s/c_0, & (X_1 < X < X_2, Z_1 < Z < Z_2), \\ 0, & \text{otherwise,} \end{cases} \quad (49)$$

where k is a dimensionless transfer coefficient, which is equivalent to k^*L/D_e , and c_s denotes an upper limit for the (dimensional) solute concentration (e.g., as determined by solubility). To simplify the mathematical analysis, it is assumed that k is constant. Away from the source, a homogeneous second-type condition would be more accurate since there is no mass transfer in this case ($k = 0$). The additional condition for the Green's function is given by

$$\left(kG - \frac{\partial G}{\partial \eta} \right)_{\eta=0} = 0. \quad (50)$$

The concentration may now be written as

$$\begin{aligned} C(X, Y, Z, T) &= \int_0^T \int_{X_1}^{X_2} \int_{Z_1}^{Z_2} \frac{kg(\tau)}{P_Y} G_X(X, T; \xi; \tau) \times \\ & \quad \times G_Y(Y, T; 0, \tau) G_Z(Z, T; \zeta, \tau) d\zeta d\xi d\tau \\ &= \int_0^T \frac{kg(T - \tau)}{4} \exp\left(-\frac{\mu\tau}{R}\right) \left[\sqrt{\frac{R}{\pi P_Y \tau}} \exp\left(-\frac{RP_Y Y^2}{4\tau}\right) \right. \\ & \quad \left. - \frac{k}{P_Y} \exp\left(\frac{k^2\tau}{RP_Y} + kY\right) \operatorname{erfc}\left(\frac{RP_Y Y + 2k\tau}{\sqrt{4RP_Y \tau}}\right) \right] \times \\ & \quad \times \left[\operatorname{erfc}\left(\frac{R(X - X_2) - \tau}{\sqrt{4R\tau/P_X}}\right) - \operatorname{erfc}\left(\frac{R(X - X_1) - \tau}{\sqrt{4R\tau/P_X}}\right) \right] \times \end{aligned}$$

$$\times \left[\operatorname{erfc} \left(\sqrt{\frac{RP_Z}{4\tau}} (Z - Z_2) \right) - \operatorname{erfc} \left(\sqrt{\frac{RP_Z}{4\tau}} (Z - Z_1) \right) \right] d\tau. \quad (51)$$

with G_Y equal to G_T^t as defined in Table I. The solution for the nonequilibrium problem follows directly from Equation (51) by substituting G_{X1} for G_X .

4. Examples

The previously derived solutions will be used to illustrate the effect of the surface condition on the solute distribution, and to explore differences between the equilibrium and nonequilibrium transport models. Parameter values were selected for illustrative purposes, they reflect laboratory conditions. In all examples it is assumed that there is neither solute retardation ($R = 1$) nor degradation.

4.1. SURFACE CONDITION

Consider transport from a rectangular source at the surface $Y = 0$ with $X_1 = Z_1 = -1$ and $X_2 = Z_2 = 1$ with $P_X = 20$ (e.g., a pore-water velocity of 10 cm/d and dispersivity of 0.5 cm) and $P_Y = P_Z = 200$. Figure 2 shows steady-state contours of the dimensionless solute concentration in the YX -plane at $Z = 0$ resulting from advection and dispersion as calculated with Equations (45), (48), and (51). These results were obtained with transient Green's functions, which tend to be easier to apply than steady Green's functions (Beck *et al.*, 1992). For a first-type condition, the surface concentration, g , is equal to unity at the source and zero otherwise (Figure 2(a)). The contours for a second-type condition are plotted in Figure 2(b). The parameter Γ was set to 3.3 at the source – this value was based on a dimensional concentration gradient of 0.33 mg/cm⁴ that was normalized using a characteristic length of 10 cm and a concentration of 1 mg/cm³ – and zero for the rest of the surface. Contours for a third-type surface condition are given in Figure 2(c) for $k = 3.3$.

The effects of the boundary conditions can be clearly observed. The first-type condition, with a zero surface concentration away from the source, is probably not realistic (Figure 2(a)). The contours obtained with the second-type condition reveal that the highest concentration for a particular longitudinal distance occurs at the surface; the solute does not move as deep as for the first-type condition. Intermediate surface concentrations were obtained for a third-type condition (Figure 2(c)). Less solute moves from the pool into the medium for rate-limited diffusion (Figure 2(c)) than for a fixed concentration gradient (Figure 2(b)) or instantaneous dissolution (Figure 2(a)).

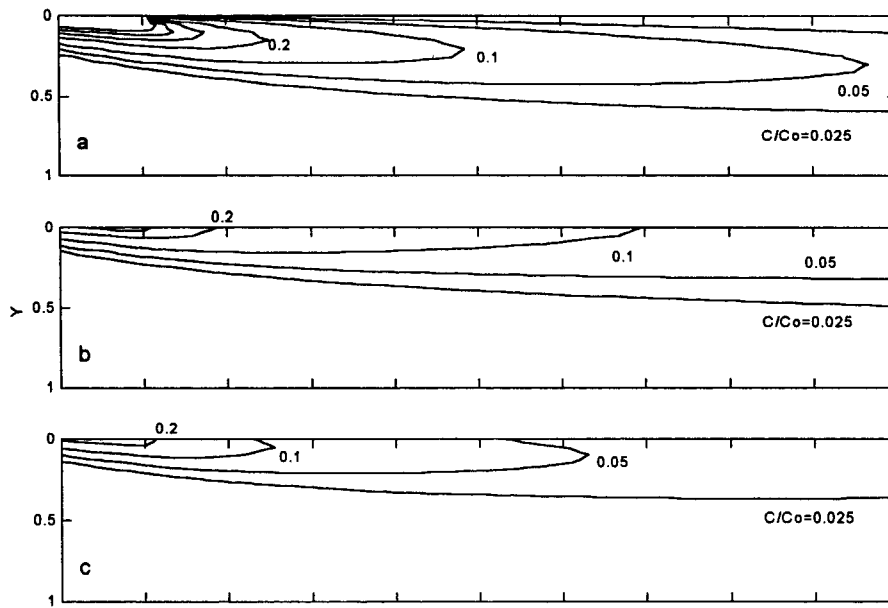


Figure 2. Steady-state contours of the dimensionless concentration ($C = c/c_0$) in the XY -plane at $Z = 0$ as the result of equilibrium transport from a planar source with $X_1 = Z_1 = -1$, $X_2 = Z_2 = 1$, $P_X = 20$ and $P_Y = P_Z = 200$: (a) first-type condition with $g(T) = 1$, (b) second-type condition with $\Gamma = 3.3$, and (c) third-type condition due to rate-limited dissolution with $g(T) = 1$ and $k = 3.3$.

4.2. NONEQUILIBRIUM TRANSPORT

Figure 3 shows contours of the relative concentration as a function of depth, Y , and dimensionless time, T , at $X = 10$ and $Z = 0$ for a first-, second-, and third-type condition. The development of the concentration profile over time is shown in Figures 3(a–c) for the same conditions as used for Figures 2(a–c). Additionally, corresponding profiles were determined for nonequilibrium transport (Figures 3(d–f)). These only pertain to the ‘equilibrium’ concentration. The solute concentration is calculated according to Equations (45), and modifications of (48) and (51), respectively, using $\beta = 0.5$, $\omega = 1.0$, and $\mu_1 = \mu_2 = 0$. Nonequilibrium conditions may decrease the total amount of solute entering the medium and increase the time required to reach the eventual peak solute concentration. Furthermore, steeper concentration gradients may occur because transport is confined to the mobile zone as compared to transport described by the conventional ADE. Both factors increase the opportunity for solute spreading, including downward movement, and the maximum concentrations will consequently be lower.

Figure 4 shows breakthrough curves for C_1 at $X = 2$, $Y = 0.1$ and $Z = 0$ for a third-type condition assuming five different degrees of nonequilibrium. The curves pertain to the same scenario as the contours shown in Figure 3. For a first-type condition, the highest maximum concentration is obtained for the equilibrium

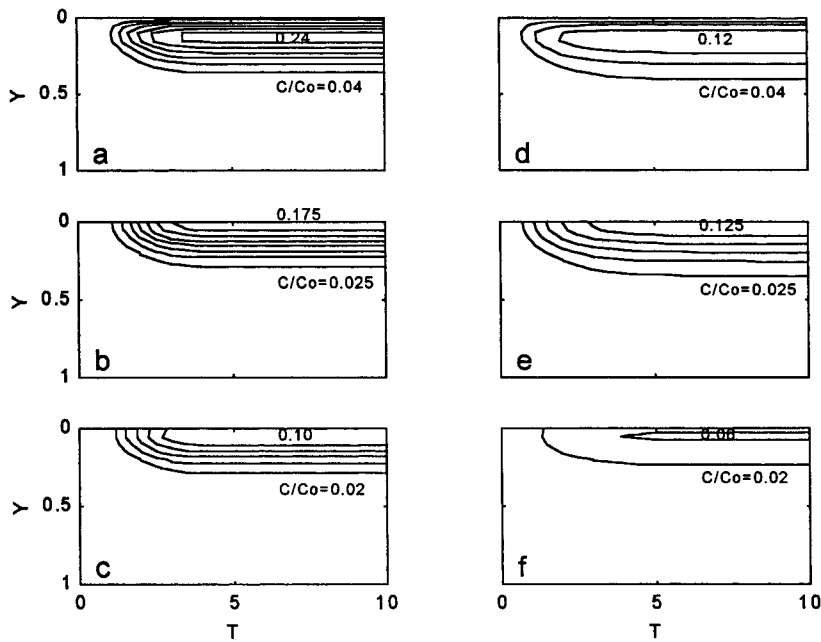


Figure 3. Relative concentration (C or C_1) contours in the YT -plane at $X = 2$ and $Z = 0$ resulting from a planar source with $X_1 = Z_1 = -1$, $X_2 = Z_2 = 1$, $P_X = 20$ and $P_Y = P_Z = 200$ according to the equilibrium model (a,b and c) and nonequilibrium model with $\beta = 0.5$ and $\omega = 1.0$ (d,e,f): (a) and (d) first-type condition with $g(T) = 1$, (b) and (e) second-type condition with $\Gamma = 3.3$, (c) and (f) third-type condition with $g(T) = 1$ and $k = 3.3$.

scenario (Figure 4(a)). The breakthrough curve is apparently more sensitive to the value of the transfer parameter, ω , than the partition coefficient, β . The higher maximum for $\omega = 0.1$ compared to $\omega = 1$ may be due to the fact that less solute has yet moved to the nonequilibrium region in the former case. If a third-type condition is used (Figure 4(b)), the maximum concentration is mostly affected by β while ω determines how soon this maximum is reached. The earliest breakthrough occurs in both cases for the most pronounced case of nonequilibrium ($\beta = 0.25$ and $\omega = 0.1$).

5. Summary and Conclusions

The first part of this paper contains a brief review of the use of the GFM to analytically model solute transport as described by the ADE for uniform and steady water flow. The GFM has not been widely employed for this purpose despite some of its advantages. Very concise expressions can be written for the solute concentration. The GFM is well suited to be employed for different boundary and initial conditions. Solutions for multidimensional problems may be obtained by multiplying the Green's functions for separate one-dimensional problems. Of particular interest

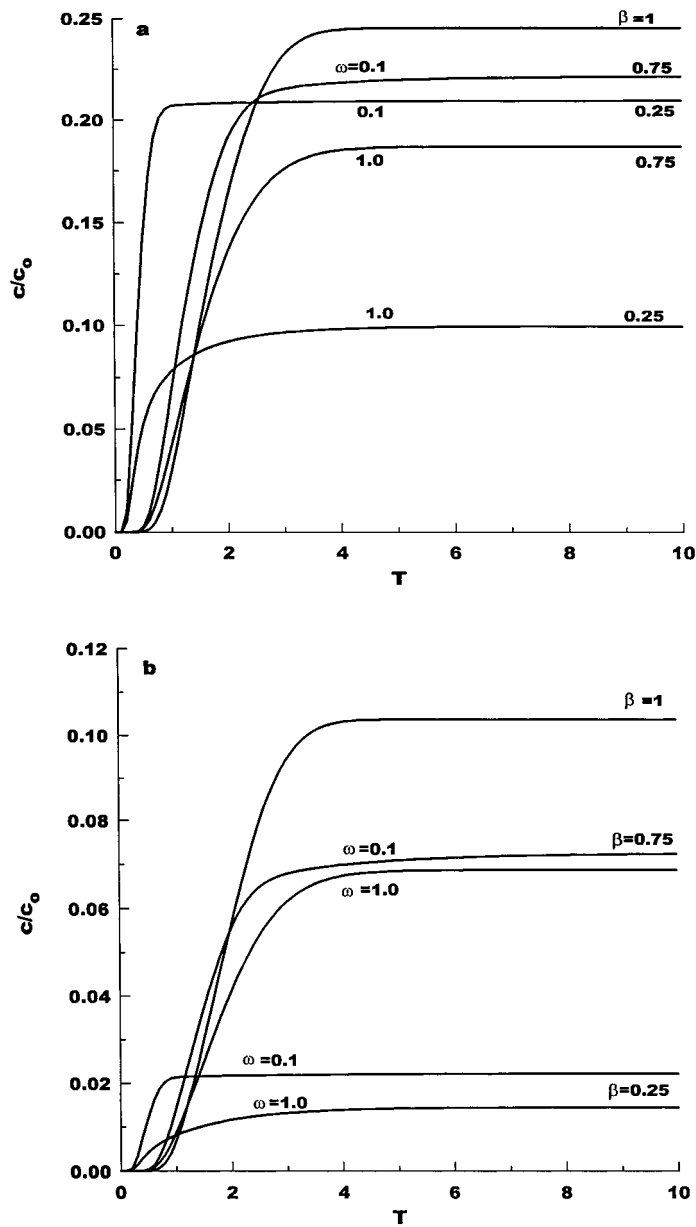


Figure 4. Relative concentration as a function of time (T) at $X = 2$, $Y = 0.1$ and $Z = 0$ resulting from a planar source with $X_1 = Z_1 = -1$, $X_2 = Z_2 = 1$, $P_X = 20$ and $P_Y = P_Z = 200$ predicted for equilibrium conditions and four sets of parameters for nonequilibrium conditions with the following conditions at the source boundary: (a) first-type condition ($g(T) = c/c_0 = 1$) and (b) third-type condition ($g(T) = 1$ and $k = 3.3$).

are the solutions for nonequilibrium transport, which follow in a relatively straightforward manner from those for equilibrium transport. Table I lists longitudinal and transversal Green's functions that can be used to formulate the solution for a wide variety of transport problems in infinite and semi-infinite.

In the second part of this study the GFM was applied to solve transport from a persistent contamination source. Transport took place from a rectangular source located at the bottom or top of an aquifer during one-dimensional equilibrium and nonequilibrium flow for a first-, second-, and third-type condition at the source. The first-type and, particularly, the second-type conditions have the disadvantage that the theoretical solution cannot account for changes in the aqueous phase concentration, which will affect the actual solute flux from the pool. The third-type condition appears more plausible, but leads to errors away from the pool in case of a homogenous third-type condition.

The first example demonstrated the surface condition for transport from a planar source. Solute contours were shown in the XY - and YT -planes. The first-type condition unrealistically mandates that the surface concentration be zero away from the source; the maximum concentration was relatively low. For a second-type condition the problem is that the gradient at the source needs to be specified a priori. A relatively high maximum concentration was predicted, but it occurred at the surface and possible contamination did not extend far into the medium. The second example compared equilibrium and nonequilibrium transport from a planar source using a first-, second-, and third-type condition. Nonequilibrium conditions tended to lower the maximum concentration but enhanced the spreading of the solute over a larger area. Breakthrough curves were shown for a first- and third-type condition involving different degrees of nonequilibrium. These curves exhibited the feature that nonequilibrium promotes earlier breakthrough, as is well known for one-dimensional transport. However, the maximum concentration may be considerably lower due to reduced mass transfer into the medium and increased opportunity for solute spreading.

Appendix A. Derivation of Solutions for Nonequilibrium Transport

The analytical solution procedure will be illustrated for longitudinal transport, which accounts for all nonequilibrium effects. Solutions for the complete problem can be readily obtained with the product rule using appropriate transversal Green's functions for the diffusion problem (Beck *et al.*, 1992). The temporal Laplace transform of the one-dimensional ADE for equilibrium transport yields the following ordinary differential equation for an arbitrary initial distribution, f :

$$\frac{1}{P_X} \frac{d^2 \bar{C}}{dX^2} - \frac{d\bar{C}}{dX} - (R_s + \mu)\bar{C} + f = 0. \quad (\text{A.1})$$

The Laplace transform of the corresponding nonequilibrium Equations (11) and (12) can be combined to yield the following transport problem in terms of one

dependent variable (Toride *et al.*, 1993):

$$\frac{1}{P_X} \frac{d^2 \bar{C}_1}{dX^2} - \frac{d\bar{C}_1}{dX} - \left(\beta R s + \omega + \mu_1 - \frac{a\omega}{s+b} \right) \bar{C}_1 + \left(\beta R + \frac{\omega}{s+b} \right) f = 0. \quad (\text{A.2})$$

This equation has a similar form as the equilibrium problem given by (A.1); this feature facilitates the derivation of solutions for $C_1(X, T)$ as shown below.

A.1. BOUNDARY VALUE PROBLEM

The influent concentration is given by $g(T)$ while the initial concentration $f(X) = 0$. If the solution to the equilibrium problem for $g(T) = 1$ and $\mu = 0$ is given by $C_u(X, T)$, the solutions of the equilibrium and nonequilibrium problems in the Laplace domain are related according to

$$\bar{C}_1(X, s) = \bar{g}(s) \bar{C}_u \left(X, \beta R s + \omega + \mu_1 - \frac{a\omega}{s+b} \right) = \bar{g}(s) \bar{C}_u(X, s^*), \quad (\text{A.3})$$

where s^* is a modified Laplace variable obtained from s without spatially or temporally dependent parameters (cf. de Smedt and Wierenga, 1979; Walker, 1987). The inversion with respect to time is based on the property that the inverse of the iterated Laplace transform of a function is equal to the generalized convolution integral of the function (Sneddon, 1995). The Laplace transform is applied sequentially; in this case, t is replaced by either t_1 or t_2 in the expression for the concentration. The corresponding transformation variable s is split into s_1 and s_2 . The sequential inversion of a function, u , which is transformed in this manner may be written as

$$h(t_1, t_2) = \mathcal{L}_{t_1}^{-1} \{ \mathcal{L}_{t_2}^{-1} [\bar{u}(s_1, s_2)] \}. \quad (\text{A.4})$$

The function in the regular time domain is given by the convolution integral

$$u(x, t) = \int_0^t h(\tau, t - \tau) d\tau. \quad (\text{A.5})$$

Application of this theorem and using the properties of the Laplace transform (Spiegel, 1965) yields

$$\begin{aligned} h(t_1, t_2) &= \mathcal{L}_{t_1}^{-1} \left\{ \mathcal{L}_{t_2}^{-1} \left[\bar{C}_u \left(X, \beta R s_2 + \omega + \mu_1 - \frac{a\omega}{s_1 + b} \right) \right] \right\} \\ &= \mathcal{L}_{t_1}^{-1} \left\{ \exp \left[- \left(\omega + \mu_1 - \frac{a\omega}{s_1 + b} \right) \frac{t_2}{\beta R} \right] \mathcal{L}_{t_2}^{-1} [\bar{C}_u(X, \beta s_2)] \right\} \\ &= \frac{1}{\beta R} C_u \left(X, \frac{t_2}{\beta R} \right) \exp \left[- \left(\omega + \mu_1 \right) \frac{t_2}{\beta R} \right] \times \\ &\quad \times \left[\delta(t_1) + \sqrt{\frac{a\omega t_2}{\beta R t_1}} I_1 \left(2 \sqrt{\frac{a\omega t_2}{\beta R t_1}} \right) \exp(-bt_1) \right]. \end{aligned} \quad (\text{A.6})$$

From (A.6) the following concentration can be written down:

$$\begin{aligned}
C_1(X, T) = & \int_0^T g(T - \tau) \int_0^\tau \frac{1}{\beta R} C_u \left(X, \frac{\tau'}{\beta R} \right) \exp \left[-(\omega + \mu_1) \frac{\tau'}{\beta R} \right] \times \\
& \times \left[\delta(\tau - \tau') + \sqrt{\frac{a\omega\tau'}{\beta R(\tau - \tau')}} I_1 \left(2\sqrt{\frac{a\omega\tau'(\tau - \tau')}{\beta R}} \right) \times \right. \\
& \left. \times \exp[-b(\tau - \tau')] \right] d\tau', \tag{A.7}
\end{aligned}$$

where $\delta(\cdot)$ is the Dirac delta function and I_1 is the first-order modified Bessel function.

A.2. INITIAL VALUE PROBLEM

The initial solute concentration is given by $f(X)$, while the influent concentration, $g(T)$, is equal to zero. This problem has not been studied as widely as the boundary value problem, but inspection of the ordinary differential equations given by (A.1) and (A.2) suggests that $\bar{C}_1(X, s)$ can be written in terms of the solution of the transformed equilibrium problem without degradation according to

$$\begin{aligned}
\bar{C}_1(X, s) &= \left(\beta R + \frac{\omega}{s + b} \right) \bar{C} \left(X, \beta R s + \omega + \mu_1 - \frac{a\omega}{s + b} \right) \\
&= \left(\beta R + \frac{\omega}{s + b} \right) \bar{C}(X, s^*). \tag{A.8}
\end{aligned}$$

Again, $C_1(X, T)$ is obtained with the iterated Laplace transformation. It may be verified that (cf. Spiegel, 1965; Walker, 1987)

$$\begin{aligned}
h(t_1, t_2) &= \mathcal{L}_{t_1}^{-1} \left\{ \mathcal{L}_{t_2}^{-1} \left[\left(\beta R + \frac{\omega}{s_1 + b} \right) \bar{C} \left(X, \beta R s_2 + \omega + \mu_1 - \frac{a\omega}{s_1 + b} \right) \right] \right\} \\
&= \mathcal{L}_{t_1}^{-1} \left\{ \left(\beta R + \frac{\omega}{s_1 + b} \right) \times \right. \\
&\quad \left. \exp \left[- \left(\omega + \mu_1 - \frac{a\omega}{s_1 + b} \right) \frac{t_2}{\beta R} \right] \mathcal{L}_{t_2}^{-1} [\bar{C}(X, \beta R s_2)] \right\} \\
&= C \left(X, \frac{t_2}{\beta R} \right) \exp \left[-(\omega + \mu_1) \frac{t_2}{\beta R} \right] \{ \delta(t_1) + \exp(-bt_1) \times \\
&\quad \times \left[\frac{\omega}{\beta R} I_0 \left(2\sqrt{\frac{a\omega t_2}{\beta R}} t_1 \right) + \sqrt{\frac{a\omega t_2}{\beta R t_1}} I_1 \left(2\sqrt{\frac{a\omega t_2}{\beta R}} t_1 \right) \right] \}. \tag{A.9}
\end{aligned}$$

The solution in terms of the equilibrium concentration therefore becomes

$$\begin{aligned}
 C_1(X, T) = & \int_0^T C\left(X, \frac{\tau}{\beta R}\right) \left\{ \delta(T - \tau) \exp\left(-\frac{(\omega + \mu_1)T}{\beta R}\right) \right. \\
 & + \frac{\omega}{\beta R} \exp\left[-\frac{\omega + \mu_1}{\beta R}\tau - \frac{\omega + \mu_2}{(1 - \beta)R}(T - \tau)\right] \times \\
 & \times \left[I_0\left(\frac{2\omega}{R} \sqrt{\frac{\tau(T - \tau)}{\beta(1 - \beta)}}\right) + \right. \\
 & \left. \left. + \sqrt{\frac{\beta\tau}{(1 - \beta)(T - \tau)}} I_1\left(\frac{2\omega}{R} \sqrt{\frac{\tau(T - \tau)}{\beta(1 - \beta)}}\right) \right] \right\} d\tau. \quad (\text{A.10})
 \end{aligned}$$

with I_0 as the zero-order modified Bessel function.

References

- Beck, J. V., Cole, K. D., Haji-Sheikh, A. and Litkouhi, B.: 1992, *Heat Conduction Using Green's Functions*, Hemisphere Publ., Washington, DC.
- Boucher, D. F. and Alves, G. E.: 1959, Dimensionless numbers, *Chem. Engng Progr.* **55**, 55–64.
- Bradford, S. A., Abriola, L. M. and Rathfelder, K.: 1998, Flow and entrapment of dense nonaqueous phase liquids in physically and chemically heterogeneous aquifer formations, *Adv. Water. Resour.* **22**, 117–132.
- Carslaw, H. S., Jaeger, J. C.: 1959, *Conduction of Heat in Solids*, Clarendon Press, Oxford.
- Carnahan, B., Luther, H. A. and Wilkes, J. O.: 1969, *Applied Numerical Models*, Wiley, New York.
- Chrysikopoulos, C. V.: 1995, Three-dimensional analytical models of contaminant transport from nonaqueous phase liquid pool dissolution in saturated subsurface formations, *Water Resour. Res.* **31**, 1137–1145.
- Chrysikopoulos, C. V., Voudrias, E. A. and Fyrrilas, M. M.: 1994, Modeling of contaminant transport from dissolution of nonaqueous phase liquid pools in saturated porous media, *Transport in Porous Media* **16**, 125–145.
- Cleary, R. W. and Adrian, D. D.: 1973, Analytical solution of the convective–dispersive equation for cation transport in soils, *Soil Sci. Soc. Am. Proc.* **37**, 197–199.
- Coats, K. H. and Smith, B. D.: 1964, Dead-end pore volume and dispersion in porous media, *Soc. Petrol. Engng J.* **4**, 73–84.
- De Smedt, F. and Wierenga, P. J.: 1979, A generalized solution for solute flow in soils with mobile and immobile water, *Water Resour. Res.* **15**, 1137–1141.
- Ellsworth, T. R. and Butters, G. L.: 1993, Three-dimensional analytical solutions to the advection–dispersion equation in arbitrary Cartesian coordinates, *Water Resour. Res.* **29**, 3215–3225.
- Galya, D. P.: 1987, A horizontal plane source model for ground-water transport, *Ground Water* **25**, 733–739.
- Van Genuchten, M. Th. and Alves, W. J.: 1982, Analytical solutions of the one-dimensional convective–dispersive solute transport equation, *Tech. Bull., U.S. Dep. Agric.*, 1661.
- Van Genuchten, M. Th. and Wierenga, P. J.: 1976, Mass transfer studies in sorbing porous media. I. Analytical solutions, *Soil Sci. Soc. Am. J.* **53**, 1303–1310.
- Greenberg, M. D.: 1971, *Application of Green's Functions in Science and Engineering*, Prentice Hall, Englewood Cliffs, NJ.
- Güven, O., Molz, F. J. and Melville, J. G.: 1984, An analysis of dispersion in a stratified aquifer, *Water Resour. Res.* **20**, 1337–1354.

- Holman, H.-Y. N. and Javandel, I.: 1996, Evaluation of transient dissolution of slightly water-soluble compounds from a light nonaqueous phase liquid pool, *Water Resour. Res.* **32**, 915–923.
- Leij, F. J., Toride, N. and van Genuchten, M. Th.: 1993, Analytical solutions for nonequilibrium solute transport in three-dimensional porous media, *J. Hydrol.* **151**, 193–228.
- Leij, F. J., Priesack, E. and Schaap, M. G.: 1999, Transport from persistent solute sources modeled with Green's functions, *J. Contam. Hydrol.* (in press).
- Prakash, A.: 1984, Ground-water contamination due to transient sources of pollution, *J. Hydraul. Engng* **110**, 1642–1658.
- Renardy, M. and Rogers, R. C.: 1993. *An Introduction to Partial Differential Equations*, Springer-Verlag, New York.
- Roach, G. F.: 1982, *Green's Functions*, Cambridge Univ. Press.
- Shan, C. and Javandel, I.: 1997, Analytical solutions for solute transport in a vertical aquifer section, *J. Contam. Hydrol.* **27**, 63–82.
- Sneddon, I. H.: 1995, *Fourier Transforms*, Dover, New York.
- Spiegel, M. R.: 1965, *Theory and Problems of Laplace Transforms*, Schaum's Outline Ser., McGraw-Hill, New York.
- Stakgold, I.: 1979, *Green's Functions and Boundary Value Problems*, Wiley, New York.
- Toride, N., Leij, F. J. and Van Genuchten, M. Th.: 1993, A comprehensive set of analytical solutions for nonequilibrium solute transport with first-order decay and zero-order production, *Water Resour. Res.* **29**, 2167–2182.
- Walker, G. R.: 1987, Solution to a class of coupled linear partial differential equations, *IMA J. Appl. Math.* **38**, 35–48.
- Yeh, G. T.: 1981, AT123D: Analytical transient one-, two-, and three-dimensional simulation of waste transport in an aquifer system, Rep. ORNL-5602. Oak Ridge National Laboratory, Oak Ridge, TN.
- Yeh, G. T. and Tsai, Y.-J.: 1976, Analytical three-dimensional transient modeling of effluent discharges, *Water Resour. Res.* **12**, 533–540.