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Journal of Contaminant Hydrology 41 (2000) 155–173

www.elsevier.com/locate/jconhyd

JOURNAL OF
**Contaminant
Hydrology**

Solute transport modeled with Green's functions with application to persistent solute sources

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Received 25 November 1998; received in revised form 23 April 1999; accepted 29 June 1999

Abstract

Analytical models can be valuable tools to investigate solute transport in porous media. The application of analytical solutions is limited by the perception that they are too cumbersome to derive while their implementation rests on assumptions that are too restrictive. The Green's function method (GFM) was applied to facilitate analytical solution of the advection–dispersion equation (ADE) for solute transport in uniform porous media with steady one- or two-dimensional flow. The GFM conveniently handles different boundary and initial conditions as well as multi-dimensional problems. Concise expressions are possible for the solute concentration with the GFM. This paper provides a general framework to efficiently formulate analytical solutions for many transport problems. Expressions for the longitudinal and transversal Green's function are presented that can be inserted in the general expression to solve a wide variety of transport problems in infinite, semi-infinite, and finite media. These solutions can be used to elucidate transport phenomena, estimate transport parameters, evaluate numerical solution procedures and simulate the movement and fate of solutes. An illustration of the GFM is provided by the analytical modeling of transport from a planar source of persistent, long-lasting contamination. Such a source may be used to represent dissolution from a pool of a non-aqueous phase liquid (NAPL). Analytical solutions are obtained for a first-, second-, and third-type condition in case of a planar source; the third-type condition is due to downward flow or rate-limited dissolution. Several examples are presented to show the effect of source conditions, the sensitivity of NAPL

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dissolution to transport parameters included in the Damköhler and Peclet numbers, and upstream dispersion. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Green's functions; Advection–dispersion equation; Solute transport; Persistent contamination; Analytical modeling

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 to monitor and improve the quality of the subsurface environment. This is usually done numerically. For idealized conditions, however, we may employ analytical solutions. Such solutions are useful to assess the performance of numerical solution techniques, to gain a better understanding of the importance of different transport parameters and mathematical conditions, to estimate model parameters with inverse methods, and to study transport for conditions where numerical methods may not yield accurate or reliable results.

Analytical solutions of the advection–dispersion equation (ADE) have typically been obtained using techniques such as Laplace and Fourier transforms (e.g., Leij et al., 1993), finite integral transforms (e.g., Cleary and Adrian, 1973), and Fourier series (e.g., Güven et al., 1984). Relatively little direct use has been made of the Green's functions method (GFM) although this method is in principle well suited for solving boundary value problems including those for the ADE (Neuringer, 1968; Yeh and Tsai, 1976; Galya, 1987). Appropriate expressions for Green's functions can often be obtained from existing solutions of the ADE or by adopting Green's functions that have been published for the diffusion equation (Tikhonov and Samarskii, 1963; Beck et al., 1992). The GFM is particularly attractive to deal with transport problems involving arbitrary initial or inlet solute profiles, several dimensions, irregular geometries (Greenberg, 1971), fractured media (Fogden et al., 1988), or water flow that is not parallel to the stratification of the porous medium (Ellsworth and Butters, 1993). This study was partly motivated by the potential application of the GFM to solve transport in a medium with a continuous or persistent source.

Persistent sources of contaminants in the subsurface environment may pose a serious threat to the quality of soil and groundwater. Spills of hydrocarbon solvents can create hazardous and long-lasting sources of groundwater contamination. Due to its density and viscosity, a dense nonaqueous phase liquid (DNAPL) will sink to the bottom of aquifers and 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. Solutions may be derived by integrating instantaneous sources with time or space. However, it is desirable that the mathematical model allows the specification of different types of time-dependent conditions at the interface of source and porous medium.

Problems of persistent DNAPL or LNAPL contamination were described as boundary value problems by Chrysikopoulos et al. (1994) and Holman and Javandel (1996), respectively. Solutions for transport of the NAPL pool were obtained with integral transforms. Shan and Javandel (1997) solved a similar problem with several integral transforms by dividing the medium into three regions, with the source located on top of the center region. The GFM facilitates the solution of transport problems involving persistent sources and different source conditions.

The first objective of this study is to formulate the GFM for three-dimensional transport problems and to provide Green's functions for finite, semi-infinite, and infinite media and several boundary conditions. The second objective is to illustrate how the GFM can be used to quantify dissolution and movement in the aqueous of a solute species with a low solubility.

2. Green's function method

2.1. General formulation

A brief introduction will be given to the GFM for solving the ADE. Further information on the GFM can be found in several books on Green's functions (Greenberg, 1971; Stakgold, 1979; Roach, 1982; Beck et al., 1992). The ADE will be used to model equilibrium solute transport in a porous medium whose transport properties are constant with time and space. For a Cartesian coordinate system, the three-dimensional ADE is given by:

$$R \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - R\mu c + \lambda \quad (1)$$

where c is the solute concentration (ML^{-3}); R is the solute retardation factor; t is time (T); x denotes the position (L) along the longitudinal coordinate in the direction of flow; y and z are positions (L) along the transversal coordinates; v is the pore-water velocity (LT^{-1}); D_x is the longitudinal dispersion coefficient ($\text{L}^2 \text{T}^{-1}$); D_y and D_z are the transversal dispersion coefficients ($\text{L}^2 \text{T}^{-1}$); μ is a first-order degradation factor (T^{-1}) and λ is a zero-order source or production term ($\text{ML}^{-3} \text{T}^{-1}$), which may depend on time or position. The corresponding problem in terms of the differential operator, $\mathcal{L}$, is

$$\mathcal{L}(c) = -\frac{D_x}{R} \frac{\partial^2 c}{\partial x^2} + \frac{v}{R} \frac{\partial c}{\partial x} - \frac{D_y}{R} \frac{\partial^2 c}{\partial y^2} - \frac{D_z}{R} \frac{\partial^2 c}{\partial z^2} + \frac{\partial c}{\partial t} + \mu c = \frac{\lambda}{R} \quad (2)$$

An alternative adjoint problem is obtained through multiplication of Eq. (2) by a Green's function G and subsequent integration over the solution region. This procedure can be schematically represented as (cf. Greenberg, 1971):

$$\iiint G \mathcal{L}(c) = \text{boundary terms} + \iiint c \mathcal{L}^*(G) = \iiint G \frac{\lambda}{R} \quad (3)$$

where the formally adjoint differential operator (Roach, 1982) is defined as:

$$\mathcal{L}^* = -\frac{D_x}{R} \frac{\partial^2}{\partial \xi^2} - \frac{v}{R} \frac{\partial}{\partial \xi} - \frac{D_y}{R} \frac{\partial^2}{\partial \eta^2} - \frac{D_z}{R} \frac{\partial^2}{\partial \zeta^2} - \frac{\partial}{\partial \tau} + \mu \quad (4)$$

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 negative time and velocity. A solution for c may be obtained from the equivalent problem in terms of the adjoint operator. The GFM uses the Dirac delta function for this purpose. The adjoint differential operator on G is equal to the following four-dimensional Dirac delta function

$$\begin{aligned} \mathcal{L}^*(G) &= \delta(x - \xi, y - \eta, z - \zeta, t - \tau) \\ &= \delta(x - \xi) \delta(y - \eta) \delta(z - \zeta) \delta(t - \tau) \end{aligned} \quad (5)$$

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) . For an infinite spatial domain, application of the GFM allows the concentration to be expressed as:

$$\begin{aligned} c(x, y, z, t) &= \frac{1}{R} \int_0^t \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(D_x G \frac{\partial c}{\partial \xi} - D_x c \frac{\partial G}{\partial \xi} - v G c \right) \Big|_{\xi \rightarrow -\infty}^{\xi \rightarrow \infty} d\zeta d\eta d\tau \\ &\quad + \frac{1}{R} \int_0^t \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(D_y G \frac{\partial c}{\partial \eta} - D_y c \frac{\partial G}{\partial \eta} \right) \Big|_{\eta \rightarrow -\infty}^{\eta \rightarrow \infty} d\zeta d\xi d\tau \\ &\quad + \frac{1}{R} \int_0^t \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(D_z G \frac{\partial c}{\partial \zeta} - D_z c \frac{\partial G}{\partial \zeta} \right) \Big|_{\zeta \rightarrow -\infty}^{\zeta \rightarrow \infty} d\eta d\xi d\tau \\ &\quad - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G c \Big|_{\tau=0}^{\tau=t_2} d\zeta d\eta d\xi + \int_0^t \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G \frac{\lambda}{R} d\zeta d\eta d\xi d\tau \end{aligned} \quad (6)$$

Eq. (6) provides the basis for a wide variety of analytical solutions for one- and multi-dimensional problems, which could alternatively be solved with more complicated techniques. 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 an initial value problem where the upper boundary, t_2 , is beyond the time of interest t . These terms may all be dropped for an initially solute free medium while assuming zero concentration gradients at infinite x , y , and z ; only the fifth term remains and the transport problem is essentially a production value problem.

The solution of production value problems is straightforward if λ is expressed in terms of Dirac delta functions. This approach has already been used in conjunction with Green's functions by Yeh and Tsai (1976) and Galya (1987). Yeh (1981) lists results for line and point sources involving different aquifer geometries. Most transport problems, however, are better described as boundary and initial value problems and we will assume $\lambda = 0$.

The appropriate Green's function is determined by solving Eq. (5). This equation is homogeneous except for a discontinuity when ($\xi = x$, $\eta = y$, $\zeta = z$, $\tau = t$). According to the superposition principle, G is often written as the sum of a fundamental and a regular solution (Renardy and Rogers, 1993). The fundamental or free-space solution is obtained by solving Eq. (5) for homogeneous boundary conditions at infinity. The regular or causal solution is obtained by solving the homogeneous version of Eq. (5), i.e., excluding the Dirac source, to ensure that the nonhomogeneous boundary conditions on the concentration can be satisfied.

The fundamental solution, F , may be obtained by transforming Eq. (5) into a diffusion problem, which is solved by Fourier transformation (p. 67, Greenberg, 1971), or by solving the initial value problem for an instantaneous point source (e.g., Prakash, 1984):

$$\begin{aligned}
 F(x, y, z, t; \xi, \eta, \zeta, \tau) &= F_x(x, t; \xi, \tau) F_y(y, t; \eta, \tau) F_z(z, t; \zeta, \tau) \\
 &= \frac{H(t - \tau)}{\sqrt{D_x D_y D_z [4\pi(t - \tau)/R]^3}} \exp \left(-(\mu_x + \mu_y + \mu_z)t \right. \\
 &\quad \left. - \frac{[R(x - \xi) - v(t - \tau)]^2}{4RD_x(t - \tau)} - \frac{R(y - \eta)^2}{4D_y(t - \tau)} \right. \\
 &\quad \left. - \frac{R(z - \zeta)^2}{4D_z(t - \tau)} \right) \quad (7)
 \end{aligned}$$

where the solution for $\tau > t$ is made equal to zero, as mandated by the reverse nature of the adjoint problem, by including the Heaviside step function, H . The solution may be written as the product of functions for the longitudinal and two transversal directions with $\mu = \mu_x + \mu_y + \mu_z$. Because the GFM is based on homogeneous boundary conditions, a well known advantage of higher dimensional Green's functions is that they may be written as a product of lower dimensional functions.

2.2. Specific formulation

The Green's function for a particular problem is formally obtained by solving the adjoint problem for the boundary conditions that are derived from the corresponding advection–dispersion problem. There are several convenient approaches to derive them, namely: (i) deduction from the fundamental solution, (ii) inspection of solutions for the advection–dispersion or diffusion equations (Carslaw and Jaeger, 1959; van Genuchten and Alves, 1982; Javandel et al., 1984), and (iii) adaption of published Green's functions (Tikhonov and Samarskii, 1963; Beck et al., 1992). We will continue with a brief outline of the approach to determine Green's functions for both longitudinal and transversal directions. The concentration for the one-dimensional longitudinal problem (described by the ADE) is denoted as c_x while the concentration for the one-dimensional transversal problems (described by the diffusion equation) are c_y and c_z .

Table 1
Selected longitudinal and transversal Green's functions

Function	Expression	Conditions
$G_x^I(x, t, \xi, \tau)$	$H(t - \tau) / \sqrt{4\pi D_x(t - \tau) / R}$ $\times \exp\left[-\mu_x(t - \tau) - ([R(x - \xi) - v(t - \tau)]^2) / (4D_x R(t - \tau))\right]$	$\partial G_x / \partial \xi(x, t; \pm \infty, \tau) = 0$
$G_x^{S1}(x, t, \xi, \tau)$	$H(t - \tau) / \sqrt{4\pi D_x(t - \tau) / R}$ $\times \left\{ \exp[-\mu_x(t - \tau)] \left\{ \exp\left[-[R(x - \xi) - v(t - \tau)]^2 / (4D_x R(t - \tau))\right] \right\} \right.$ $\left. - \exp\left[vx / D_x - ([R(x + \xi) + v(t - \tau)]^2) / (4D_x R(t - \tau))\right] \right\}$	$G_x(x, t; 0, \tau) = 0, \partial G_x / \partial \xi(x, t; \infty, \tau) = 0$
$G_x^{S3}(x, t, \xi, \tau)$	$H(t - \tau) \exp[-\mu_x(t - \tau)] \left\{ 1 / \sqrt{4\pi D_x(t - \tau) / R} \right.$ $\times \left[\exp\left(-[R(x - \xi) - v(t - \tau)]^2 / (4D_x R(t - \tau))\right) \right.$ $\left. + \exp\left(vx / D_x - [R(x + \xi) + v(t - \tau)]^2 / (4D_x R(t - \tau))\right) \right]$ $\left. - v / (2D_x) \exp(vx / D_x) \operatorname{erfc}\left((R(x + \xi) + v(t - \tau)) / \sqrt{4D_x R(t - \tau)}\right) \right\}$	$\partial G_x / \partial \xi(x, t; 0, \tau) = 0, \partial G_x / \partial \xi(x, t; \infty, \tau) = 0$
$G_x^{F1}(x, t, \xi, \tau)$	$H(t - \tau) \sum_{n=1}^{\infty} (2(\alpha_n^2 + h^2)) / ((\alpha_n^2 + h^2)L + h) \exp[-\mu_x(t - \tau) + h(x - \xi)]$ $- (\alpha_n^2 + h^2) D_x(t - \tau) / R \sin(\alpha_n x) \sin(\alpha_n \xi)$	$G_x(x, t; 0, \tau) = 0, (D_x \partial G_x / \partial \xi + v G_x) _{\xi=L} = 0$
$G_x^{F3}(x, t, \xi, \tau)$	$H(t - \tau) \sum_{n=1}^{\infty} (2 \exp[-\mu_x(t - \tau) + h(x - \xi) - (\beta_n^2 + h^2) D_x(t - \tau) / R]) /$ $((\beta_n^2 + h^2)L + 2h) [\beta_n \cos(\beta_n x) + h \sin(\beta_n x)] [\beta_n \cos(\beta_n \xi) + h \sin(\beta_n \xi)]$	$\partial G_x / \partial \xi(x, t; 0, \tau) = 0, (D_x \partial G_x / \partial \xi + v G_x) _{\xi=L} = 0$
$G_y^I(y, t, \eta, \tau)$	$H(t - \tau) / \sqrt{4\pi D_y(t - \tau) / R} \exp\left(-\mu_y(t - \tau) - (R(y - \eta)^2) / (4D_y(t - \tau))\right)$	$\partial G_y / \partial \eta(y, t; \pm \infty, \tau) = 0$
$G_y^{S1}(y, t, \eta, \tau)$	$H(t - \tau) \exp[-\mu_y(t - \tau)] / \sqrt{4\pi D_y(t - \tau) / R}$ $\times \left[\exp\left(-R(y - \eta)^2 / (4D_y(t - \tau))\right) - \exp\left(-R(y + \eta)^2 / (4D_y(t - \tau))\right) \right]$	$G_y(y, t; 0, \tau) = 0, \partial G_y / \partial \eta(y, t; \infty, \tau) = 0$

$G_y^{S2}(y, t, \eta, \tau)$	$H(t - \tau) \exp[-\mu_y(t - \tau)] / \sqrt{4\pi D_y(t - \tau)} / R$ $\times \left[\exp\left(-R(y - \eta)^2 / (4D_y(t - \tau))\right) + \exp\left(-R(y + \eta)^2 / (4D_y(t - \tau))\right) \right]$	$\partial G_y / \partial \eta(y, t; 0, \tau) = 0, \partial G_y / \partial \eta(y, t; \infty, \tau) = 0$
$G_y^{S3}(y, t, \eta, \tau)$	$H(t - \tau) \exp[-\mu_y(t - \tau)] \left\{ 1 / \sqrt{4\pi D_y(t - \tau)} / R \right.$ $\times \left[\exp\left(-R(y - \eta)^2 / (4D_y(t - \tau))\right) + \exp\left(-R(y + \eta)^2 / (4D_y(t - \tau))\right) \right]$ $- k \exp\{k[y + \eta + kD_y(t - \tau)/R]\} \operatorname{erfc}\left((R(y + \eta) + 2kD_y(t - \tau)) / \sqrt{4D_y R(t - \tau)}\right) \left. \right\}$	$(kG_y - \partial G_y / \partial \eta)_{\eta=0} = 0, \partial G_y / \partial \eta(y, t; \infty, \tau) = 0$
$G_y^{F1}(y, t, \eta, \tau)$	$H(t - \tau) \exp[-\mu_y(t - \tau)] / \sqrt{4\pi D_y(t - \tau)}$ $\times \sum_{n=-\infty}^{\infty} (-1)^n \left[\exp\left(-(y - \eta + 2nL_y)^2 / (4D_y(t - \tau)/R)\right) \right.$ $\left. - \exp\left(-(y + \eta + 2nL_y)^2 / (4D_y(t - \tau)/R)\right) \right] \quad (D_y \tau / L^2 < 0.2)$ $\times (2H(t - \tau)) / L \sum_{n=1}^{\infty} \exp[-\mu_y(t - \tau) - \beta_n^2 D_y(t - \tau) / R] \sin(\beta_n y) \sin(\beta_n \eta)$ $\beta_n = (2n - 1)\pi / (2L) \quad (D_y \tau / L^2 > 0.2)$	$G_y(y, t, 0, \tau) = 0, \partial G_y / \partial \eta(y, t; L, \tau) = 0$
$G_y^{F2}(y, t, \eta, \tau)$	$H(t - \tau) \exp[-\mu_y(t - \tau)] / \sqrt{4\pi D_y(t - \tau)}$ $\times \sum_{n=-\infty}^{\infty} \left[\exp\left(-(y - \eta + 2nL_y)^2 / (4D_y(t - \tau)/R)\right) \right.$ $\left. + \exp\left(-(y + \eta + 2nL_y)^2 / (4D_y(t - \tau)/R)\right) \right] \quad (D_y \tau / L^2 < 0.2)$ $H(t - \tau) \exp[-\mu_y(t - \tau)] \left\{ (1/L) + (2/L) \sum_{n=1}^{\infty} \exp\left[-\beta_n^2 D_y(t - \tau) / R\right] \cos(\beta_n y) \cos(\beta_n \eta) \right.$ $\left. \beta_n = \pi n / L \quad (D_y \tau / L^2 > 0.2) \right.$	$\partial G_y / \partial \eta(y, t; 0, \tau) = 0, \partial G_y / \partial \eta(y, t; L, \tau) = 0$
$G_y^{F3}(y, t, \eta, \tau)$	$(2H(t - \tau) / L) \sum_{n=1}^{\infty} \exp[-\mu_y(t - \tau) - \beta_n^2 D_y(t - \tau) / (RL^2)] (\beta_n^2 + n^2 L^2) /$ $(\beta_n^2 + nL(1 + nL)) \cos[\beta_n(1 - y/L)] \cos[\beta_n(1 - \eta/L)] (\beta_n \tan \beta_n = nL) \quad (D_y \tau / L^2 > 0.2)$	$(kG_y - \partial G_y / \partial \eta)_{\eta=0} = 0, \partial G_y / \partial \eta(y, t; L, \tau) = 0$

The general concentration, resulting from one-dimensional advective–dispersive transport, may be deduced from Eq. (6) as:

$$c_x(x, t) = \frac{1}{R} \int_0^t \left(D_x G_x \frac{\partial c_x}{\partial \xi} - D_x c_x \frac{\partial G_x}{\partial \xi} - v G_x c_x \right) \Big|_{x_l}^{x_u} d\tau + \int_{x_l}^{x_u} G_x(x, t; \xi, 0) c_x(\xi, 0) d\xi \quad (8)$$

where the lower and upper boundaries x_l and x_u are specified depending on the solution domain. This expression is made more specific by applying the boundary conditions for c_x and by subsequently specifying convenient conditions for G_x . The latter should be used when solving the adjoint problem:

$$\mathcal{L}^*(G_x) = -\frac{D_x}{R} \frac{\partial^2 G_x}{\partial \xi^2} - \frac{v}{R} \frac{\partial G_x}{\partial \xi} - \frac{\partial G_x}{\partial \tau} + \mu_x = \delta(x - \xi) \delta(t - \tau) \quad (9)$$

Table 1 lists longitudinal Green's function for boundary and initial value problems in infinite, semi-infinite and finite porous media and conditions on G . The superscripts I, S, and F denote an infinite, semi-infinite, and finite coordinate whereas “1”, “2” and “3” indicate a first-, second- and third-type inlet condition for the ADE. The functions in Table 1 were derived from the fundamental solution (cf. Greenberg, 1971) and published solutions of the ADE.

The concentration in the transversal y direction as result of one-dimensional diffusion may be expressed according to the GFM as (cf. Eq. (6)):

$$c_y(y, t) = \frac{1}{R} \int_0^t \left(D_y G_y \frac{\partial c_y}{\partial \eta} - D_y c_y \frac{\partial G_y}{\partial \eta} \right) \Big|_{y_l}^{y_u} d\tau + \int_{y_l}^{y_u} G_y(y, t; \eta, 0) c_y(\eta, 0) d\eta \quad (10)$$

Explicit expressions for the concentration in the transversal y direction C and also for the transversal z direction C are obtained by imposing a zero-gradient condition for 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

$$\mathcal{L}^*(G_y) = -\frac{D_y}{R} \frac{\partial^2 G_y}{\partial \eta^2} - \frac{\partial G_y}{\partial \tau} + \mu_y = \delta(y - \eta) \delta(t - \tau) \quad (11)$$

and the appropriate conditions as specified in Table 1. These and additional functions have been published elsewhere (Beck et al., 1992).

The functions in Table 1 can be applied to a wide range of initial and boundary value problems involving additional advection terms, different conditions for each boundary, additional impermeable layers. For example, the one-dimensional solutions given by van Genuchten and Alves (1982) for simple initial and input profiles, can all be written down from Eq. (6) after applying the mathematical conditions, inserting the corresponding Green's function from Table 1, and evaluating the resulting integrals with a table of integrals or mathematical software. In the following we hope to illustrate the utility of

the GFM for solving transport problems using a problem involving persistent contamination.

3. Persistent solute sources

Consider solute movement from a planar source as sketched in Fig. 1. This type of problem may arise when an immobile pool of a low-solubility organic is located on top of a saturated soil (for either a laboratory or field setting) or an aquifer (cf. Shan and Javandel, 1997; Hofstee et al., 1998). Other types of solute contamination may also be described by this scenario, as long as Eq. (1) can be used to describe the transport. 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. Note that a mathematically equivalent problem occurs when the pool is located at the bottom of the medium.

The solute may move from the source, which has a negligible thickness, by diffusion or advection. Four different conditions for the concentration in the porous medium at the source boundary are considered, for the time being we will not be overly concerned with their physical merits. A first-type condition should be used if a value can be prescribed for the concentration; an example would be instantaneous dissolution of a low-solubility chemical where the boundary concentration is equal to its solubility. A second-type

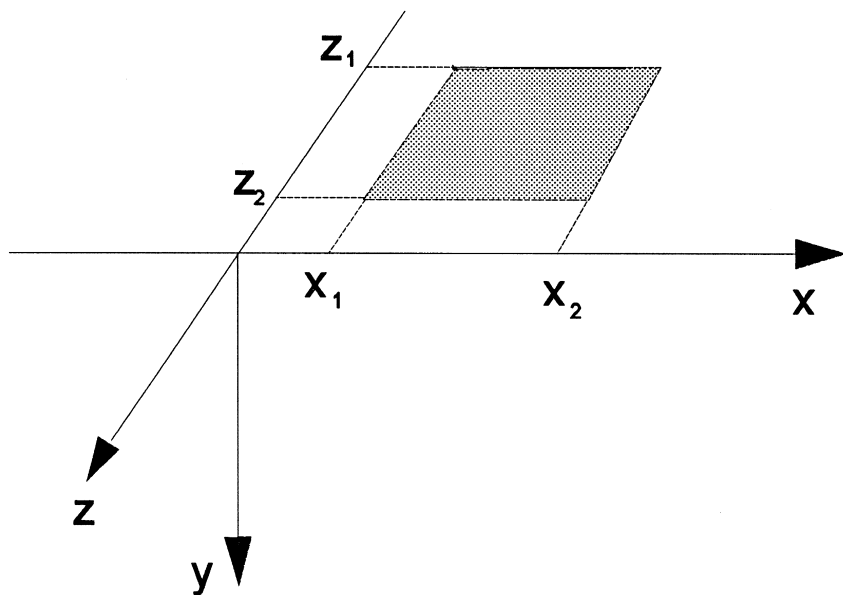


Fig. 1. Schematic of a planar solute source to model transport due to persistent contamination at the exterior of a porous medium.

condition is appropriate if the concentration gradient can be ascertained; this scenario occurs when solute transfer from the source is entirely due to Fickian diffusion and a reliable estimate for the diffusion coefficient is available. The last two conditions pertain to a third-type condition, which includes both the solute concentration and its vertical gradient; the third-type condition is relevant for rate-limited diffusion or for transport by diffusion and vertical advection (rainfall). Mixed-type conditions — such as a first- or third-type condition for the source and a homogeneous second-type condition for the rest of the surface — are more accurate than a uniform surface condition, but will not be considered here since they are mathematically more cumbersome (De Wiest, 1969; Greenberg, 1971).

The general initial and boundary conditions, i.e., excluding the surface, are:

$$c(x, y, z, 0) = 0 \quad (-\infty < x < \infty, 0 < y < \infty, -\infty < z < \infty) \quad (12)$$

$$\frac{\partial c}{\partial x}(\pm \infty, y, z, t) = 0 \quad (0 < y < \infty, -\infty < z < \infty) \quad (13ab)$$

$$\frac{\partial c}{\partial y}(x, \infty, z, t) = 0 \quad (-\infty < x < \infty, -\infty < z < \infty) \quad (14)$$

$$\frac{\partial c}{\partial z}(x, y, \pm \infty, t) = 0 \quad (-\infty < x < \infty, 0 < y < \infty) \quad (15ab)$$

An intermediate result is obtained by substituting the above conditions in Eq. (6):

$$\begin{aligned} c(x, y, z, t) = & \frac{1}{R} \int_0^t \left\{ \int_0^\infty \int_{-\infty}^\infty \left(-D_x c \frac{\partial G}{\partial \xi} - v G c \right) \Big|_{\xi \rightarrow -\infty}^{\xi \rightarrow \infty} d\xi d\eta \right. \\ & - \int_{-\infty}^\infty \int_{-\infty}^\infty \left[D_y c \frac{\partial G}{\partial \eta} \Big|_{\eta \rightarrow \infty} + \left(D_y G \frac{\partial c}{\partial \eta} - D_y c \frac{\partial G}{\partial \eta} \right) \Big|_{\eta=0} \right] d\xi d\xi \\ & \left. - \int_{-\infty}^\infty \int_0^\infty D_z c \frac{\partial G}{\partial \zeta} \Big|_{\zeta \rightarrow -\infty}^\infty d\eta d\xi \right\} d\tau \end{aligned} \quad (16)$$

The Green's function is written as the product of one-directional functions, $G = G_x G_y G_z$. The exact formulation of the concentration will be determined in the following by specifying appropriate conditions on G_x , G_y , and G_z .

3.1. First-type condition

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

$$c(x, 0, z, t) = \begin{cases} g(x, z, t) & (x_1 < x < x_2, z_1 < z < z_2) \\ 0 & \text{otherwise} \end{cases} \quad (17)$$

For pool dissolution, $g(x, z, t)$ can be set equal to the water solubility (Hunt et al., 1988). The boundaries of the source (x_1 , x_2 , z_1 and z_2) were already shown in Fig. 1 while, although not necessary, we assume that the prescribed concentration only depends

on time. Eq. (16) then implies that the following conditions be placed on the Green's function:

$$\frac{\partial G_x}{\partial \xi}(x, t; \pm \infty, \tau) = 0 \quad (18ab)$$

$$G_y(y, t; 0, \tau) = \frac{\partial G_y}{\partial \eta}(y, t; \infty, \tau) = 0 \quad (19ab)$$

$$\frac{\partial G_z}{\partial \zeta}(z, t; \pm \infty, \tau) = 0 \quad (20ab)$$

These conditions are met by respectively selecting G_x^I , G_y^{SI} , and G_z^I from Table 1 for G_x , G_y , and G_z . All conditions and functions are inserted in Eq. (16). The integration with respect to ξ and ζ is possible due to the simple form of G_x and G_z . The resulting solute concentration is given by:

$$\begin{aligned} c(x, y, z, t) &= \frac{1}{R} \int_0^t \int_{x_1}^{x_2} \int_{z_1}^{z_2} D_y g(\tau) G_x(x, t; \xi, \tau) \frac{\partial G_y}{\partial \eta}(y, t; 0, \tau) G_z(z, t; \zeta, \tau) d\zeta d\xi d\tau \\ &= \frac{1}{4} \int_0^t \frac{yg(t-\tau)}{\sqrt{4\pi D_y \tau^3/R}} \exp\left(-\mu\tau - \frac{Ry^2}{4D_y\tau}\right) \left[\operatorname{erfc}\left(\frac{R(x-x_2)-v\tau}{\sqrt{4D_x R\tau}}\right) \right. \\ &\quad \left. - \operatorname{erfc}\left(\frac{R(x-x_1)-v\tau}{\sqrt{4D_x R\tau}}\right) \right] \left[\operatorname{erfc}\left(\frac{z-z_2}{\sqrt{4D_z\tau/R}}\right) - \operatorname{erfc}\left(\frac{z-z_1}{\sqrt{4D_z\tau/R}}\right) \right] d\tau \quad (21) \end{aligned}$$

3.2. Second-type condition

This condition is used when dissolution of the solute can be described as a diffusive process for which the concentration gradient can be specified (e.g., Chrysikopoulos et al., 1994) at the surface while the concentration is unknown. The surface condition becomes:

$$\frac{\partial c}{\partial y}(x, 0, z, t) = \begin{cases} -\Gamma(x, z, t) & (x_1 < x < x_2, z_1 < z < z_2) \\ 0 & \text{otherwise} \end{cases} \quad (22)$$

For solute dissolution, the parameter Γ (ML^{-4}) may be defined as k^*c_o/D_e where k^* is a mass transfer parameter (LT^{-1}), c_o is a reference or saturated solute concentration (ML^{-3}) and D_e is an effective coefficient of molecular diffusion ($\text{L}^2 \text{T}^{-1}$) (cf. Chrysikopoulos, 1995). The ratio of the solute fluxes due to dissolution and diffusion may be quantified by the Sherwood number, $\text{Sh} = kL/D_e$, where L is a characteristic length.

To eliminate the unknown concentrations in the solution according to Eq. (16), the conditions on the Green's function should be given by Eqs. (18ab) and (20ab) as well as:

$$\frac{\partial G_y}{\partial \eta}(y, t; 0, \tau) = \frac{\partial G_y}{\partial \eta}(y, t; \infty, \tau) = 0 \quad (23ab)$$

It can be shown that G_x and G_z are again equal to G_x^I and G_y^I , respectively, whereas G_y is now given by G_y^{S2} . If Γ is assumed to depend solely on time, the concentration can be written as:

$$\begin{aligned} c(x, y, z, t) &= \frac{1}{R} \int_0^t \int_{x_1}^{x_2} \int_{z_1}^{z_2} D_y \Gamma(\tau) G_x(x, t; \xi, \tau) G_y(y, t; 0, \tau) G_z(z, t; \zeta, \tau) d\zeta d\xi d\tau \\ &= \frac{1}{4} \int_0^t \frac{\Gamma(t-\tau)}{\sqrt{\pi \tau R / D_y}} \exp\left(-\mu\tau - \frac{Ry^2}{4D_y\tau}\right) \left[\operatorname{erfc}\left(\frac{R(x-x_2) - v\tau}{\sqrt{4D_x R\tau}}\right) \right. \\ &\quad \left. - \operatorname{erfc}\left(\frac{R(x-x_1) - v\tau}{\sqrt{4D_x R\tau}}\right) \right] \left[\operatorname{erfc}\left(\frac{z-z_2}{\sqrt{4D_z\tau/R}}\right) - \operatorname{erfc}\left(\frac{z-z_1}{\sqrt{4D_z\tau/R}}\right) \right] d\tau \quad (24) \end{aligned}$$

3.3. Third-type condition

3.3.1. Film diffusion

Dissolution of organics into the aqueous phase is often described with a linear driving force model (Abriola et al., 1993; Fortin et al., 1998). The surface condition is formulated with a third-type condition to describe rate-limited dissolution from the source through a boundary layer:

$$\begin{aligned} \frac{\partial c}{\partial y}(x, 0, z, t) &= k(x, z, t) [c(x, 0, z, t) - g(x, z, t)] \text{ with} \\ g(x, z, t) &= \begin{cases} c_0 & (x_1 < x < x_2, z_1 < z < z_2) \\ 0 & \text{otherwise} \end{cases} \quad (25) \end{aligned}$$

where k is a transfer coefficient [L^{-1}], which accounts for film diffusion and thickness, while $c(x, 0, z, t)$ and c_0 represent lower and upper concentration limits as determined by the bulk solution and the solubility value. From now on, we assume that g and k are independent of time and position, although this is not necessary with the GFM. The second-type condition given by Eq. (26ab) is a special case of the third-type condition, which may be obtained by $k = k^*/D_e$ and by setting $c(x, 0, z, t) - g(x, z, t)$ equal to a value that yields the desired concentration gradient. For film diffusion, the Green's function should satisfy Eqs. (18ab) and (20ab) and

$$\left(kG_y - \frac{\partial G_y}{\partial \eta} \right)_{\eta=0} = \frac{\partial G_y}{\partial \eta}(y, t; \infty, \tau) = 0 \quad (26ab)$$

The concentration may now be written as

$$\begin{aligned}
 c(x, y, z, t) &= \frac{1}{R} \int_0^t \int_{x_1}^{x_2} \int_{z_1}^{z_2} D_y k c_0 G_x(x, t; \xi, \tau) G_y(y, t; 0, \tau) G_z(z, t; \zeta, \tau) d\zeta d\xi d\tau \\
 &= \int_0^t \frac{k c_0}{4R} \exp(-\mu\tau) \left[\sqrt{\frac{D_y R}{\pi\tau}} \exp\left(-\frac{Ry^2}{4D_y\tau}\right) \right. \\
 &\quad \left. - kD_y \exp\left(k(y + kD_y\tau/R)\right) \operatorname{erfc}\left(\frac{Ry + 2kD_y\tau}{\sqrt{4D_y\tau}}\right) \right] \\
 &\quad \times \left[\operatorname{erfc}\left(\frac{R(x - x_2) - v\tau}{\sqrt{4D_x R\tau}}\right) - \operatorname{erfc}\left(\frac{R(x - x_1) - v\tau}{\sqrt{4D_x R\tau}}\right) \right] \\
 &\quad \times \left[\operatorname{erfc}\left(\frac{z - z_2}{\sqrt{4D_z\tau/R}}\right) - \operatorname{erfc}\left(\frac{z - z_1}{\sqrt{4D_z\tau/R}}\right) \right] d\tau \quad (27)
 \end{aligned}$$

with G_y equal to G_y^{S3} as defined in Table 1.

3.3.2. Vertical flow

Consider the scenario where there is a small vertical flow in addition to the horizontal flow. If we ignore cross-dispersion terms, the ADE given by Eq. (1) without the zero-order source term can be modified as follows to include the additional term, w , for vertical flow:

$$R \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} + D_y \frac{\partial^2 c}{\partial y^2} - w \frac{\partial c}{\partial y} + D_z \frac{\partial^2 c}{\partial z^2} - R\mu c \quad (28)$$

The following condition may be selected for the upper boundary:

$$\left(wc - D_y \frac{\partial c}{\partial y} \right)_{y=0} = \begin{cases} wg(t) & (x_1 < x < x_2, z_1 < z < z_2) \\ 0 & \text{otherwise} \end{cases} \quad (29)$$

where w constitutes the downward pore-water velocity. With the GFM, it is relatively straightforward to modify our solution approach for the additional flow term. The following intermediate expression may be obtained for the concentration:

$$\begin{aligned}
 c(x, y, z, t) &= \frac{1}{R} \int_0^t \left\{ \int_0^\infty \int_{-\infty}^\infty \left(-D_x c \frac{\partial G}{\partial \xi} - vGc \right) \Big|_{\xi \rightarrow -\infty}^{\xi \rightarrow \infty} d\zeta d\eta \right. \\
 &\quad \left. - \int_{-\infty}^\infty \int_{-\infty}^\infty \left[\left(D_y c \frac{\partial G}{\partial \eta} + wGc \right) \Big|_{\eta \rightarrow \infty} \right. \right. \\
 &\quad \left. \left. - \left(wg(\tau)G + D_y c \frac{\partial G}{\partial \eta} \right) \Big|_{\eta=0} \right] d\zeta d\xi \right. \\
 &\quad \left. - \int_{-\infty}^\infty \int_0^\infty D_z c \frac{\partial G}{\partial \zeta} \Big|_{\zeta \rightarrow -\infty}^\infty d\eta d\xi \right\} d\tau \quad (30)
 \end{aligned}$$

This suggests that the same conditions be imposed as for the second-type scenario (i.e., Eqs. (28), (20ab) and (23ab)). Again, G_x and G_z are equal to the free-space functions G_x^1 and G_y^1 , respectively, while G_y is equal to the longitudinal G_x^{S3} because of vertical flow. The concentration becomes:

$$\begin{aligned}
 c(x, y, z, t) &= \frac{1}{R} \int_0^t \int_{x_1}^{x_2} \int_{z_1}^{z_2} w g(\tau) G_x(x, t; \xi, \tau) G_y(y, t; 0, \tau) G_z(z, t; \zeta, \tau) d\zeta d\xi d\tau \\
 &= \int_0^t \frac{w g(t - \tau)}{4R} \exp(-\mu\tau) \left[\operatorname{erfc} \left(\frac{R(x - x_2) - v\tau}{\sqrt{4D_x R\tau}} \right) \right. \\
 &\quad \left. - \operatorname{erfc} \left(\frac{R(x - x_1) - v\tau}{\sqrt{4D_x R\tau}} \right) \right] \left[\operatorname{erfc} \left(\frac{z - z_2}{\sqrt{4D_z R\tau}} \right) \right. \\
 &\quad \left. - \operatorname{erfc} \left(\frac{z - z_1}{\sqrt{4D_z R\tau}} \right) \right] \left[\sqrt{\frac{R}{\pi D_y \tau}} \exp \left(-\frac{(Ry - w\tau)^2}{4D_y R\tau} \right) \right. \\
 &\quad \left. - \frac{w}{2D_y} \exp \left(\frac{wy}{D_y} \right) \operatorname{erfc} \left(\frac{Ry + w\tau}{\sqrt{4D_y R\tau}} \right) \right] d\tau
 \end{aligned} \quad (31)$$

4. Examples

The previously derived solutions will be used to obtain the solute concentration as a function of time and position for several examples assuming $R = 1$ and $\mu = 0$. For this purpose, a computer program was written, which is available upon request. The following two examples are generic and the units that are provided for constants and parameters may be replaced by any other set of consistent units.

The first example concerns transport from a rectangular source at the surface $y = 0$ with $x_1 = z_1 = -10$ cm and $x_2 = z_2 = 10$ cm. The horizontal pore-water velocity $v = 10$ cm day⁻¹, the dispersion coefficients were selected according to $D_x = 5$ cm² day⁻¹ and $D_y = D_z = 0.5$ cm² day⁻¹ while $c_0 = 1$ mg cm⁻³. Fig. 2 shows the steady-state contours of the solute concentration in the yx -plane at $z = 0$ as the result of advection and dispersion in the porous medium. For a first-type condition shown in Fig. 2a, the surface concentration is equal to 1 mg cm⁻³ at the source and zero otherwise. The contours resulting from a second-type condition are plotted in Fig. 2b. The concentration gradient, Γ , was set to 0.33 mg cm⁻⁴ at the source and zero for the rest of the surface. We noticed that the numerical results were very sensitive to the imposed gradient, this condition should only be used if the gradient can be specified correctly a priori. Contours resulting from a third-type surface condition are displayed in Fig. 2d, assuming a downward flow $w = 0.2$ cm day⁻¹, and Fig. 2c for $k = 0.33$ cm⁻¹.

The effects of the boundary conditions can clearly be observed. The first-type condition, with a zero surface concentration away from the source and a jump in surface

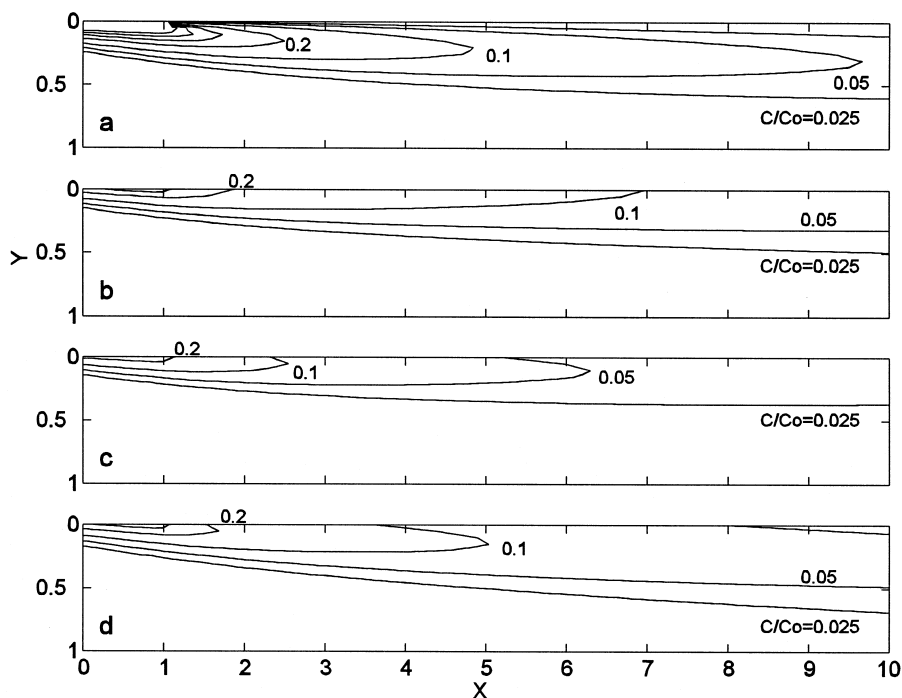


Fig. 2. Steady-state contours of the dimensionless concentration (c/c_0) in the xy -plane at $z = 0$ resulting from a planar source with $x_1 = z_1 = -10$ cm, $x_2 = z_2 = 10$ cm, $v = 10$ cm/day, $D_x = 5$ cm² day⁻¹ and $D_y = D_z = 0.5$ cm² day⁻¹: (a) first-type condition with $g(t) = c_0$, (b) second-type condition with $I = 0.33$ mg cm⁻⁴, (c) third-type condition due to rate-limited dissolution with $g(t) = c_0$, and $k = 0.33$ cm⁻¹, and (d) third-type condition due to downward flow with $g(t) = c_0$ and $w = 0.2$ cm day⁻¹.

concentration at $x = 10$ cm, is not plausible (Fig. 2a). The contours obtained with the second-type condition are symmetric with respect to the surface; the solute does not move as deep as for the first-type condition. The zero-gradient at the surface ($x > 10$ cm), i.e., no diffusion, is more realistic than for the first-type and third-type (film diffusion). The surface concentration for a third-type condition (Fig. 2c and 2d) lies in between that for a first- and second-type condition. In both cases, the diffusive flux at the surface is not zero. The effect of downward flow can clearly be observed (Fig. 2d). Less solute moves from the source into the medium for rate-limited diffusion (Fig. 2c) than for a fixed concentration gradient (Fig. 2b) or instantaneous dissolution (Fig. 2a).

The development of the concentration profile over time is shown in Fig. 3 for the same example as in Fig. 2. Contours of the relative concentration are shown as a function of depth, y , and time, t , at $x = 100$ cm and $z = 0$ for a first-, second-, and third-type condition. For a first-type condition the maximum concentration, which is relatively low, occurs at $y = 3$ cm while solute is again excluded from the surface. For a second-type condition (Fig. 3b), a relatively high maximum concentration occurs at the surface. The solute does not penetrate as deep as for a first-type condition. In case of downward flow, the maximum concentration is again in between the first- and second-

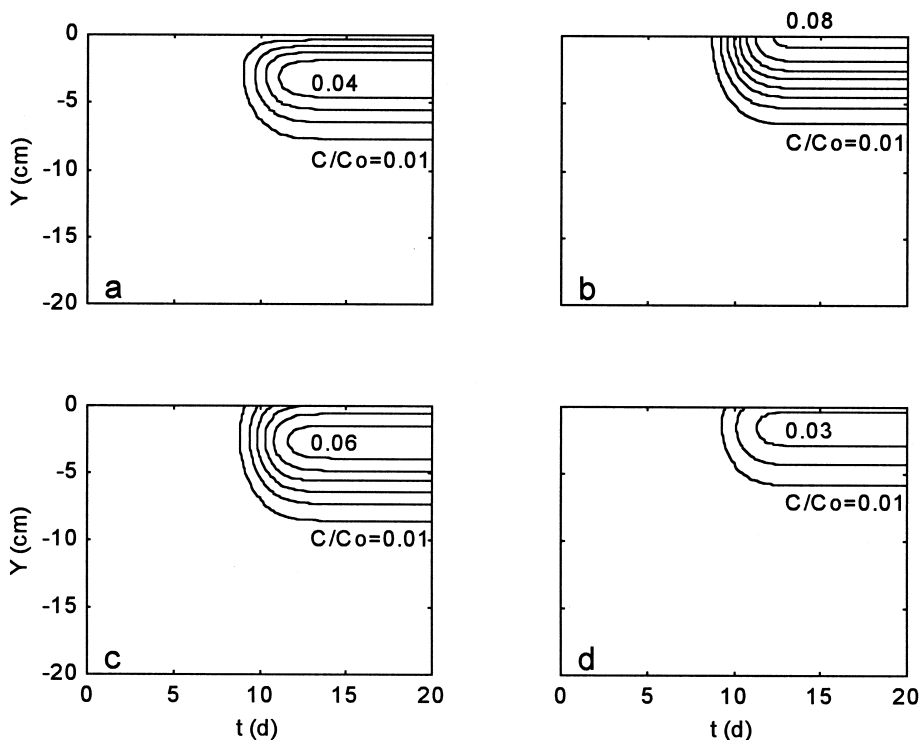


Fig. 3. Contours of the dimensionless concentration (c/c_0) in the yt -plane at $x = 100$ cm and $z = 0$ resulting from a planar source with $x_1 = z_1 = -10$ cm, $x_2 = z_2 = 10$ cm, $v = 10$ cm/day, $D_x = 5$ cm² day⁻¹ and $D_y = D_z = 0.5$ cm² day⁻¹: (a) first-type condition with $g(t) = c_0$, (b) second-type condition with $\Gamma = 0.33$ mg cm⁻⁴, (c) third-type condition due to downward flow with $g(t) = c_0$ and $w = 0.2$ cm day⁻¹, and (d) third-type condition due to rate-limited dissolution with $g(t) = c_0$ and $k = 0.33$ cm⁻¹.

type concentrations. The solute does move to greater depths due to vertical advection. The lowest maximum concentration occurs for rate-limited dissolution (Fig. 3d).

In the second example, we considered the maximum concentration in the medium resulting from a source at the surface. If solute-free water reaches the source, the solute concentration will gradually increase in the flow direction until a maximum is reached. For one-dimensional transport, this position corresponds to the length of the mass-transfer zone and the maximum concentration follows from the aqueous solubility (cf. Fortin et al., 1998).

Fig. 4 shows c/c_0 according to Eq. (27) (film diffusion) at the center of a downstream strip source boundary with $z_1 = -100$ cm and $z_2 = 100$ cm at $x = x_2$, $y = z = 0$ and $t = 100$ days as a function of the five dimensionless parameters. The latter are defined as k/k_0 ($k_0 = 1$ cm⁻¹), v/v_0 ($v_0 = 40$ cm day⁻¹), D_x/D_{x_0} ($D_{x_0} = 40$ cm² day⁻¹), D_y/D_{y_0} ($D_{y_0} = 10$ cm² day⁻¹), and L/L_0 (with $L = x_2 - x_1$ where x_2 is set at 20 cm with $L_0 = 40$ cm and -20 cm $< x_1 < 20$ cm). For each curve, only one parameter is varied while the four other parameters are constants given by

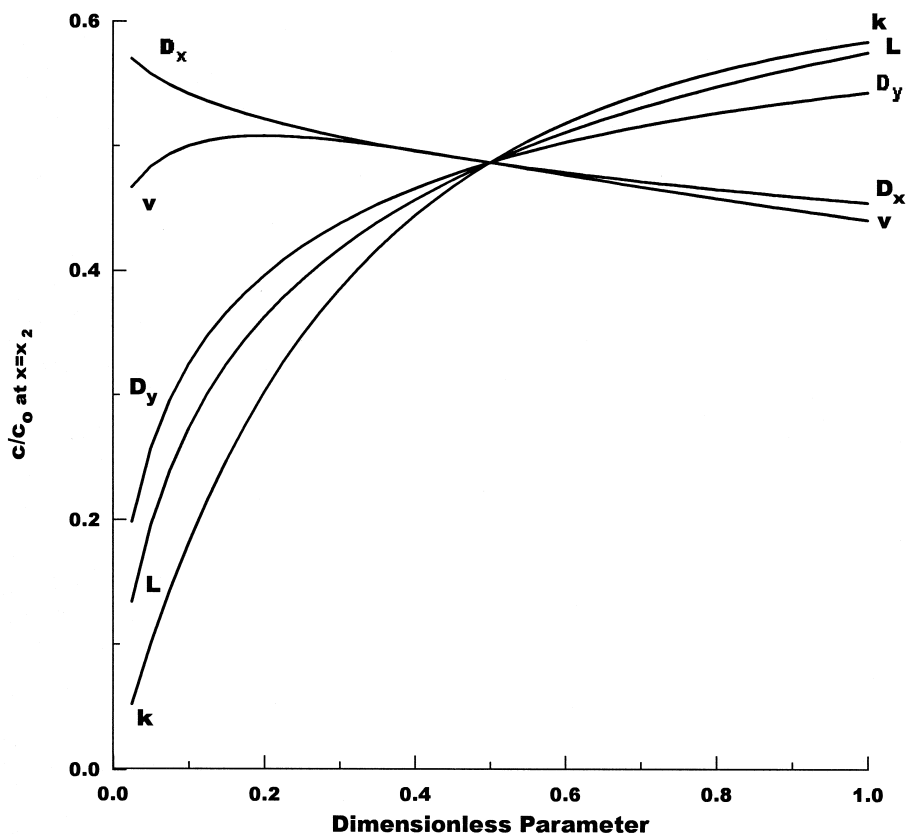


Fig. 4. Relationship between maximum concentration c/c_0 at $x_2 = 10$ cm ($y = z = 0$ and $t = 100$ d) and one of the five dimensionless parameters k/k_0 , v/v_0 , D_x/D_{x0} , D_y/D_{y0} , and L/L_0 (with $L = x_2 - x_1$) where the other four parameters are defined according to $k = 0.5 \text{ cm}^{-1}$, $v = 20 \text{ cm day}^{-1}$, $D_x = 20 \text{ cm}^2 \text{ day}^{-1}$, $D_y = 5 \text{ cm}^2 \text{ day}^{-1}$, and $x_1 = -10$ cm and $x_2 = 10$ cm and additional parameters are: $t = 100$ days, $z_1 = -100$ cm, $z_2 = 100$ cm, and $D_z = 5 \text{ cm}^2 \text{ day}^{-1}$.

$k = 0.5 \text{ cm}^{-1}$, $v = 20 \text{ cm day}^{-1}$, $D_x = 20 \text{ cm}^2 \text{ day}^{-1}$, $D_y = 5 \text{ cm}^2 \text{ day}^{-1}$, and $x_1 = -10$ cm and $x_2 = 10$ cm. Furthermore, D_z is set to $5 \text{ cm}^2 \text{ day}^{-1}$. The concentrations are well below the saturation value ($c/c_0 = 1$). Even for an infinitely long source, c will normally not reach c_0 because of transversal dispersion. The extent of NAPL contamination depends mainly on a Damköhler number, $k^2 D_y (x_2 - x_1)/v$, and the Peclet number vx/D_x . The transfer parameter k is proportional to the diffusive flux and so is the maximum concentration. The maximum c/c_0 is slightly decreased by longitudinal dispersion (D_x). At low velocities the maximum increases somewhat with v (Peclet number), but at larger v the maximum concentration decreases due to reduced opportunity for NAPL to dissolve in a given body of liquid (Damköhler number). The maximum concentration is proportional with D_y and L because these parameters determine the total amount of solute that dissolves. Similar analyses are possible to determine the

influence of transport and pool characteristics on the extent of the solute plume and the total mass flux into the medium.

5. Summary and conclusions

In the first part of this study, we briefly reviewed the GFM to analytical 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. Table 1 lists the longitudinal and transversal Green's function that can be used to formulate the solution for a wide variety of transport problems in infinite, semi-infinite, and finite media.

In the second part of this study, we applied the GFM to solve transport from a planar source of persistent contamination. We obtained solutions for one-dimensional flow for a first-, second-, and third-type condition at the source as well as for two-dimensional flow with a third-type condition. It should be noted that mixed-type conditions at the surface (either a first- or third-type condition for the source and a homogeneous second-type for the rest of the surface) may yield physically more meaningful C albeit mathematically more complicated C solutions.

The solutions were applied to two different examples. The first example illustrated 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 is 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 is predicted, but it occurs at the surface and possible contamination will not extend far into the medium. A third-type condition, either by using a vertical flow term (w) or mass transfer parameter (k), probably leads to more realistic concentration predictions. The second example also involved transport from a planar source; a third-type condition was used to simulate the rate-limited dissolution from a source (e.g., a NAPL pool) at the surface. The sensitivity of the maximum NAPL concentration was quantified as a function of k , v , D_x , D_y and $x_2 - x_1$.

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