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Exact analytical solutions for contaminant transport in rivers
1. The equilibrium advection-dispersion equation

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Abstract: Analytical solutions of the advection-dispersion equation and related models are indispensable for predicting or analyzing contaminant transport processes in streams and rivers, as well as in other surface water bodies. Many useful analytical solutions originated in disciplines other than surface-water hydrology, are scattered across the literature, and not always well known. In this two-part series we provide a discussion of the advection-dispersion equation and related models for predicting concentration distributions as a function of time and distance, and compile in one place a large number of analytical solutions. In the current part 1 we present a series of one- and multi-dimensional solutions of the standard equilibrium advection-dispersion equation with and without terms accounting for zero-order production and first-order decay. The solutions may prove useful for simplified analyses of contaminant transport in surface water, and for mathematical verification of more comprehensive numerical transport models. Part 2 provides solutions for advective-dispersive transport with mass exchange into dead zones, diffusion in hyporheic zones, and consecutive decay chain reactions.

Keywords: Contaminant transport; Analytical solutions; Surface water; Advection-dispersion equation.

INTRODUCTION

Mathematical models have long proved useful for analyzing or predicting the fate and transport of contaminants in streams and rivers (Bencala, 1983; Fischer et al., 1979; Runkel, 1998; Thomann, 1973), including contaminant exchange with fluvial sediments and the surrounding stream bed (Thackston and Schnelle, 1970; Bencala and Walters, 1983; Wörman, 1998; Anderson and Phanikumar, 2011), often referred to as the hyporheic zone (Wörman, 1998; Runkel et al., 2003; Bencala, 2005; Gerecht et al., 2011). Such models may be used also for subsurface streams and karst systems (Field, 1997). Constituents in surface waters may involve a range of specific natural and anthropogenic chemicals, including toxic trace elements, radionuclides, industrial solvents, pesticides, nutrients, pathogenic microorganisms, pharmaceuticals, and a variety of water quality variables such as total salinity or dissolved oxygen. Because of the many complex and often nonlinear physical, chemical and biological processes affecting contaminant transport in streams and rivers, numerical models are now increasingly used for prediction purposes (e.g., Anderson and Phanikumar, 2011; O'Connor et al., 2009; Runkel, 1998; Runkel and Chapra, 1993). Still, analytical and quasi-analytical approaches are useful for simplified analyses of a variety of contaminant transport scenarios, especially for relatively long spatial and time scales, when insufficient data are available to warrant the use of a comprehensive numerical model, and for testing numerical models. The application of analytical approaches is greatly facilitated now also by mathematical software such as Maple, Mathematica and Matlab.

Although the literature contains many analytical solutions that are applicable to transport in rivers and streams, most of the solutions originated in other disciplines using mathematically equivalent equations, and hence their existence may not be familiar to many in the surface-water hydrology community (e.g. De Smedt et al., 2006; Huang, 2006). In this two-part series we assembled a large number of one- and multi-dimensional solutions for contaminant transport in streams and rivers. The solutions are for one-dimensional advective-dispersive transport, longitudinal transport and lateral dispersion, transport with simultaneous first-order exchange with relative immobile or stagnant water zones (transient storage models), advective-dispersive transport with simultaneous diffusion into and out of hyporheic zones, and transport of solutes subject to consecutive decay chain reactions. Most of the solutions were derived from solutions to mathematically very similar problems in subsurface contaminant transport, on which the authors have worked for many years (e.g., Leij et al., 1991, Toride et al., 1993a, 1999; van Genuchten, 1981). Except for solutions pertaining to diffusion in hyporheic zones as presented in part 2 (van Genuchten et al., 2013), most or all models have been incorporated in the public-domain windows-based STANMOD software package (Šimůnek et al., 2000). In this part 1 we first start with a brief introduction of the advection-dispersion equation governing transport in surface water bodies, applicable initial and boundary conditions, and a brief overview of analytical solution techniques.

GOVERNING TRANSPORT EQUATION
Formulation of the Advection-Dispersion equation

The transport of contaminants in surface and subsurface waters is generally described with the Advection-Dispersion Equation (ADE), or appropriate modifications or extensions thereof. The ADE distinguishes two transport modes: advective transport as a result of passive movement along with water, and dispersive/diffusive transport to account for diffusion and small-scale variations in the flow velocity as well as any other

processes that contribute to solute spreading. Solute spreading is generally considered to be a Fickian or Gaussian diffusion/dispersion process. A considerable body of literature on dispersion processes now exists for both surface and subsurface contaminant transport (e.g., Bear and Verruijt, 1987; Fischer et al., 1979; Jury and Horton, 2004).

For one-dimensional transport, the solute flux J_s ($ML^{-2}T^{-1}$) can be written as

$$J_s = uC - D_x \frac{\partial C}{\partial x}, \tag{1}$$

where u is the longitudinal fluid flow velocity (LT^{-1}), C is the solute concentration expressed as mass per unit volume of water (ML^{-3}), D_x is the longitudinal dispersion coefficient accounting for the combined effects of ionic or molecular diffusion and hydrodynamic dispersion ($L^{-2}T^{-1}$), and x is the longitudinal coordinate (L).

The mass balance equation can be formulated in a general manner by considering the accumulation or depletion of solute in a control volume over time as a result of the divergence of the flux (i.e., net inflow or outflow), possible reactions, and the injection or extraction of solute along with the fluid phase:

$$\frac{\partial C}{\partial t} = -\nabla \cdot J_s - R_s + R_w C_e, \tag{2}$$

where t is time (T), and R_s represents arbitrary sinks (< 0) or sources (> 0) of solute ($ML^{-3}T^{-1}$), while the last term denotes injection (> 0) or pumping (< 0) of water with constituent concentration C_e at a rate R_w ($L^3L^{-3}T^{-1}$).

The use of analytical methods requires that some of the underlying processes affecting transport are simplified or approximated. Such simplifications include the use of constant values for u and D_x with respect to time and position, adopting idealized initial and boundary conditions, assuming that production and degradation are limited to zero- or first-order processes, and describing solute sorption by fluvial sediments using a linear equilibrium isotherm (or neglecting sorption altogether). If the last two terms of the mass balance equation are ignored, substitution of the advective-dispersive flux, J_s, yields the popularly used advection-dispersion equation (ADE) for one-dimensional transport as follows

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}. \tag{3}$$

A variety of solute source or sink terms may need to be implemented in the ADE. One possible process during transport in rivers is sorption of contaminants on sediment along the main channel. The source/sink term for sorption may then be written as (e.g., Bencala, 1983)

$$R_s = \rho_s \frac{\partial S}{\partial t}, \tag{4}$$

where S is the sorbed concentration expressed as mass of solute per mass of sediment readily accessible for sorption (MM^{-1}), and ρ_s is the mass of sediment per unit volume of river water (ML^{-3}). For binary exchange in a system with a constant total solute concentration, linear equilibrium exchange is given by

$$S = K_d C \tag{5}$$

in which the distribution coefficient K_d (L^3M^{-1}) may be viewed as the ratio of the sorbed (sediment) concentration and the dissolved (stream) concentration at equilibrium (Bencala et al., 1983). Substituting (1), (4) and (5) into (2) allows the ADE to be formulated in terms of one dependent variable (i.e., the stream solute concentration) according to

$$R \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} \tag{6}$$

in which the retardation factor R is given by

$$R = 1 + \rho_s K_d. \tag{7}$$

Sorption onto the sediments reduces the apparent advective and dispersive fluxes by a factor equal to R. This sorption is often considered negligible, in which case $K_d = 0$ and the value for R becomes equal to one. Analytical expressions for the concentration can generally be obtained only for linear sorption. Because the mathematical problem is trivial with regard to the value for R (the values of time t in the analytical solutions are to be divided by R), sorption will not be considered explicitly in the remainder of our study.

Many other processes such as biodegradation or inactivation, radioactive decay, and production may affect the contaminant concentration. They can all be included in the sink/source term, R_s, in Eq. (2). The transport problem can still be solved analytically if this term is described in terms of linear processes. For example, for relatively simple transport scenario's involving one or several sets of zero- and first-order rate expressions, the governing equation can always be represented in the form:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \mu C + \gamma, \tag{8}$$

where μ is a general first-order decay rate (T^{-1}) and γ a zero-order production term ($ML^{-3}T^{-1}$). We assume in this study that μ and γ are either zero or always positive. Additional processes such as nonlinear exchange, precipitation/dissolution, and sorption or chelation of constituents by moving sediment, are not considered here since the resulting transport problem generally will require numerical solution techniques.

Concentration modes and boundary conditions

The mathematical solution of Eq. (8) and related transport equations requires auxiliary conditions specifying the initial and boundary condition of the transport problem. It is important that the boundary conditions accurately describe the adopted modes of solute injection and detection. Concentrations are usually expressed in terms of the amount of solute per unit volume of water. Although the microscopic concentration is based on an infinitesimally small liquid volume, for practical purposes a much larger finite averaging scale must be used. In this way a macroscopic volume-averaged or resident concentration, C^V, can be defined as

$$C^V = \frac{1}{\Delta V} \iiint c \, dV, \tag{9}$$

where c is the local concentration (ML^{-3}) in a microscopic volume element, V, and ΔV is the representative elementary volume (Bear and Verruijt, 1987). Spatial or temporal averages beyond the REV scale may also be employed (Leij and Toride, 1995). Unless stated otherwise, we will assume that all concentrations are macroscopic and are of the volume-averaged or resident type.

Flux-averaged concentrations, C^F, may arise when the concentration is determined as the ratio of the solute flux, J_s, and the water flux, u, passing through a given cross section during an arbitrary time interval (Kreft and Zuber, 1978; Parker and van Genuchten, 1984a), i.e.,

$$C^F = J_s / u. \tag{10}$$

A relationship between the volume- and flux-averaged concentrations can be established by substituting the one-dimensional advective-dispersive flux (Eq. (1)) into (10) to give

$$C^F = C^V - \frac{D_x}{u}\frac{\partial C^V}{\partial x}. \tag{11}$$

Notice that C^V and C^F become similar for small values of D_x/u, i.e., when dispersion is negligible as compared to advection. We emphasize that C^F is a mathematical entity that depends on the formulation of the contaminant flux. As will be discussed shortly, the selection of boundary conditions is related to the concentration mode.

The initial condition can be formulated as

$$C(x,0) = f(x), \tag{12}$$

where $f(x)$ is an arbitrary function versus distance, the simplest case being the situation where the stream has a constant (zero or positive) background concentration. An alternative initial condition, often assumed for one-dimensional stream transport, is the Dirac condition specifying instantaneous release of a prescribed mass. This relatively hypothetical condition assumes that a contaminant mass, m, can be distributed instantaneously over an infinitely small region, for example a thin plane of area A across the main channel at some longitudinal position x_o, i.e.,

$$f(x) = \frac{m}{A}\delta(x - x_o), \tag{13}$$

where $\delta(x–x_o)$ is the Dirac function (L^{-1}) having the property

$$\int_{-\infty}^{\infty} \delta(x - x_o)dx = 1$$
$$\text{with } \delta(x - x_o) = 0 \text{ for all } x \neq x_o. \tag{14}$$

Proper selection of boundary conditions is a somewhat esoteric topic that has received considerable attention in the literature on transport in porous media (e.g., Batu et al., 2013; van Genuchten and Parker, 1984). Many transport problems involve the application of a solute with a concentration described by a spatially independent function, $g(t)$, to a surface water body that, for modeling purposes, can have a finite, semi-infinite, or infinite length. The method of application (or the contaminant source) may also vary widely (pumping or spraying, line or point sources, continuous or finite pulse type applications).

Boundary conditions are simplest for transport problems defined over infinite domains ($-\infty < x < \infty$). To ensure that the concentration remains bounded, the inlet and outlet conditions can be written in the form

$$\frac{\partial C}{\partial x}(\pm\infty, t) = 0. \tag{15}$$

Two types of conditions are often used at the inlet of semi-infinite media ($0 \le x \le \infty$) or finite media ($0 \le x \le L$). These conditions are based on continuity of either the concentration or the solute flux across the inlet boundary. We do not discuss here the simultaneous use of both conditions since this situation is generally too complicated for deriving relatively simple analytical solutions.

First- or concentration-type inlet boundary conditions, also referred to as Dirichlet conditions, require the concentration to be continuous across the interface at all times, i.e.,

$$C(0,t) = g(t) \qquad t > 0. \tag{16}$$

The drawback of this condition is that the (macroscopic) concentration at the interface just inside the river system will, in reality, not respond instantaneously to changes in the influent concentration. Condition (16) generally leads to discrepancies in the mass balance when considered over a finite or semi-infinite system (Batu and van Genuchten, 1990; Parker and van Genuchten, 1984a). Mass conservation can be ensured by using a third- or flux-type condition at the inlet (often referred to also as a Robin or Cauchy type condition):

$$\left(uC - D_x\frac{\partial C}{\partial x}\right)_{x=0^+} = ug(t), \tag{17}$$

where 0^+ indicates a position just inside the system being considered. Analytical solutions for first-type conditions are generally somewhat simpler than those for third-type inlet conditions. This probably explains the popularity of first-type conditions despite mass balance errors in the predicted resident concentration distributions.

Some commonly-used functions for the influent concentration, $g(t)$, in (16) or (17) are the Dirac function, a finite square pulse, and a Heaviside or step function. An instantaneous application of a solute amount m at the inlet, $x = 0$, at an arbitrary time, t_o, across an area A is given by

$$g(t) = \frac{m}{uA}\delta(t - t_o), \tag{18}$$

where $\delta(t–t_o)$ is the Dirac delta function in time (T^{-1}). Instantaneous release into a stream at $x = 0$ can be described alternatively also with a Dirac type initial condition.

The application of a finite pulse can be formulated as

$$g(t) = \begin{cases} C_o & 0 < t \le t_o \\ 0 & t > t_o \end{cases} \tag{19}$$

where t_o is the time duration of the applied pulse having concentration C_o. Note that t_o approaches infinity for a single step change. Because of the linearity of the ADE, solutions for problems involving an arbitrary number of finite pulses of different durations (t_o) and strengths (C_o) can be readily inferred

from the single step solution; the Heaviside function is convenient for this purpose.

The exit boundary condition can be defined in terms of a zero gradient at a finite or infinite distance from the inlet, leading to the assumption of having a finite or semi-infinite medium, respectively. The infinite outlet condition is mathematically far more convenient than the finite condition, and hence has been far more popular in analytical transport studies, even when finite systems are simulated. The infinite outlet condition is given by

$$\frac{\partial C}{\partial x}(\infty,t)=0. \tag{20}$$

The use of this condition for a finite system implies that a semi-infinite fictitious medium with identical properties is placed beyond the system of interest. No assumptions have to be made regarding the physical processes at the outlet, $x = L$, other than that the ADE is applicable just like everywhere else at $x > 0$.

The domain for most transport problems involving rivers is best described with a semi-infinite or infinite system, rather than a finite system. However, we shall provide in this paper also several analytical solutions for finite systems since numerical solutions, by their very nature, can be applied only to finite domains. Assuming that no dispersion occurs for $x > L$, the approximate condition for a finite system is

$$\frac{\partial C}{\partial x}(L,t)=0. \tag{21}$$

This conditions implies both flux and concentration continuity at the downstream boundary of the finite transport domain. A zero-gradient outlet condition is also appealing when no transport occurs across a boundary, such as is the case for solute diffusion or heat transport problems involving insulated media.

The choice of the boundary conditions is affected by the concentration mode (Kreft and Zuber, 1978). In practice only the dependency of the inlet condition is considered (cf. Parker and van Genuchten, 1984a). A typical problem in terms of the usual resident concentration can be formulated as

$$\frac{\partial C^V}{\partial t}=D_x\frac{\partial^2 C^V}{\partial x^2}-u\frac{\partial C^V}{\partial x} \tag{22}$$

subject to a uniform initial condition

$$C^V(x,0)=f(x)=C_i \tag{23}$$

a third-type inlet boundary condition to avoid mass balance problems

$$\left(uC^V-D_x\frac{\partial C^V}{\partial x}\right)_{x=0^+}=ug(t) \tag{24}$$

and a semi-infinite or finite outlet condition

$$\frac{\partial C^V}{\partial x}(\infty,t)=0, \qquad \frac{\partial C^V}{\partial x}(L,t)=0. \tag{25a, b}$$

As shown by Parker and van Genuchten (1984b) this problem can be readily transformed to the flux-averaged mode using Eq. (11) to give

$$\frac{\partial C^F}{\partial t}=D_x\frac{\partial^2 C^F}{\partial x^2}-u\frac{\partial C^F}{\partial x} \tag{26}$$

subject to

$$C^F(x,0)=C_i \tag{27}$$

$$C^F(0,t)=g(t), \tag{28}$$

$$\frac{\partial C^F}{\partial x}(\infty,t)=0 \quad \text{or}$$
$$\frac{\partial C^F}{\partial x}(L,t)=-\frac{D_x}{u}\frac{\partial^2 C^V}{\partial x^2}(L,t). \tag{29}$$

Notice that the mathematical problem in terms of C^F involves the simpler first-type inlet condition with mass now being conserved, unlike the use of a first-type condition for transport problems in terms of C^V. This shows that solutions for a semi-infinite system involving a first-type inlet condition represent mass-conserving solutions if the concentration, inside and outside the solution domain, is interpreted as being of the flux-averaged type (Batu et al., 2013; Parker and van Genuchten, 1984a). The transformations leading to Eqs (26) through (29) are less convenient for finite systems as well as for semi-infinite systems having nonuniform initial conditions (Toride et al., 1993b).

Differences between the preferred third-type and first-type solutions for C^V are usually minor except for small values of the dimensionless distance (ux/D_x) and time (u^2t/D_x) (e.g., van Genuchten and Parker, 1984). Since advective transport usually dominates dispersive transport in rivers and streams, the selection of a first- or third-type condition is of secondary importance for most practical river transport problems, except near the inlet. However, the issue should not be overlooked for code verification when small errors in the mass balance are important. Hence, analytical solutions will be presented for both first- and third-type inlet conditions. All concentrations in this study are understood to be of the resident type; flux-averaged concentrations can be derived as needed from the resident solutions using Eq. (11).

SOLUTION TECHNIQUES

Problems in one dimension

Before presenting specific analytical solutions, two different solution techniques will be briefly reviewed. Although a wide variety of solution procedures can be followed, many linear transport problems can be solved by either using a transformation of variables, or implementing Laplace transforms.

Most streams can be considered infinite systems in the longitudinal direction. This makes them quite suitable for making a transformation of variables to cast the ADE in a simpler form. For example, the coordinate transformation

$$\xi=x-ut$$
$$\tau=t \tag{30}$$

transforms Eq. (3) subject to

$$C(x,0)=\begin{cases} C_o & x<0 \\ 0 & x>0 \end{cases} \qquad \frac{\partial C}{\partial x}(\pm\infty,t)=0 \tag{31}$$

into the heat transfer (or solute diffusion) problem

$$\frac{\partial C}{\partial \tau}=D_x\frac{\partial^2 C}{\partial \xi^2} \tag{32}$$

$$C(\xi,0)=\begin{cases} C_o & \xi<0 \\ 0 & \xi>0 \end{cases} \tag{33}$$

Analytical solutions for this and many related problems have been widely reported in the literature (e.g. Carslaw and Jaeger, 1959; Crank, 1975).

An alternative transformation

$$\xi=\frac{x-ut}{\sqrt{4D_x t}} \tag{34}$$

allows the ADE to be written as

$$\frac{d^2C}{d\xi^2}+2\xi\frac{dC}{d\xi}=0, \tag{35}$$

$$C(\xi)=\begin{cases} C_o & \xi<-\infty \\ 0 & \xi>\infty \end{cases} \tag{36}$$

This ordinary differential equation can be solved through a reduction of order according to

$$\frac{d\psi}{d\xi}+2\xi\psi=0 \qquad \text{where} \quad \psi=\frac{dC}{d\xi}. \tag{37}$$

Separation of variables and integration leads to the following solution of (37):

$$\psi=\alpha_1\exp(-\xi^2), \tag{38}$$

where α_1 is an integration constant. Integration of ψ between ξ (corresponding to the desired concentration, C), and ∞, and making use of a zero-concentration as dictated by the infinite boundary condition, leads to

$$C=\int_{\xi}^{\infty}\alpha_1\exp(-w^2)dw+\alpha_2=\frac{\sqrt{\pi}}{2}\alpha_1\operatorname{erfc}\left(\frac{x-ut}{\sqrt{4D_x t}}\right)+\alpha_2 \tag{39}$$

in which w is a dummy integration variable, α_2 is an additional integration constant, and erfc represents the complementary error function (e.g., Gautschi, 1964). The boundary conditions are used to evaluate α_1 and α_2. The final solution is

$$C=\frac{C_o}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_x t}}\right]. \tag{40}$$

More complicated transformations were previously used by Brenner (1962) and Selim and Mansell (1976); several can also be found in Zwillinger (1989).

The complementary error function (erfc) in Eq. (40) frequently occurs in analytical solutions of the ADE. Several approximations can be found in Gautschi (1964). Its evaluation is sometimes not straightforward, especially when erfc occurs in combination with the exponential function and either or both of these functions have unusually large or small arguments. A useful routine for evaluating erfc is listed in van Genuchten and Alves (1982). In some cases, especially for situations with exponentially decaying inflow concentrations, the argument of the erfc function and other terms in the analytical solutions may involve complex variables with real and imaginary parts. An accurate subroutine for such cases is given by van Genuchten (1985b).

Linear partial differential equations are often solved with integral transforms. The transformations generally lead to ordinary differential or even algebraic equations which are much easier to solve than the original partial differential equations. Subsequent inversion of the solution to the regular space-time domain is generally the most complicated part of the solution procedure. The inversion often can be accomplished in several ways (cf. Özişik, 1989; Pérez-Guerrero et al., 2009; Sneddon, 1995; Spiegel, 1965). Laplace transforms traditionally have been the most popular for solving the ADE (Leij et al., 1993; Toride et al., 1993a; van Genuchten, 1981).

Problems in several dimensions

Solutions of transport problems in two and three dimensions are in many cases a direct extension of the one-dimensional solutions. We consider here three-dimensional problems in Cartesian coordinates (x,y,z) with uniform flow and dispersion in the longitudinal direction and dispersion in the transverse direction. We note that solutions for two-dimensional problems follow directly from solution of the more general three-dimensional examples.

The three-dimensional form of the ADE is given by

$$\frac{\partial C}{\partial t}=D_x\frac{\partial^2 C}{\partial x^2}-u\frac{\partial C}{\partial x}+D_y\frac{\partial^2 C}{\partial y^2}+D_z\frac{\partial^2 C}{\partial z^2}, \tag{41}$$

where D_y and D_z are dispersion coefficients (L^2T^{-1}) in the transverse y and z directions. Although the boundary conditions may vary depending upon the assumed geometry of the system, they normally include zero-gradient conditions at the transverse boundaries. Below are the conditions for a somewhat idealized three-dimensional system involving a semi-infinite longitudinal direction and two infinite transverse directions:

$$C(x,y,z,0)=f(x,y,z), \tag{42}$$

$$\left(C-\omega\frac{D_x}{u}\frac{\partial C}{\partial x}\right)_{x=0^+}=g(y,z,t) \qquad \omega=0,1, \tag{43}$$

$$\frac{\partial C}{\partial x}(\infty,y,z,t)=0, \tag{44}$$

$$C(x,\pm\infty,z,t)=0 \qquad \frac{\partial C}{\partial y}(x,\pm\infty,z,t)=0, \tag{45}$$

$$C(x,y,\pm\infty,t)=0 \qquad \frac{\partial C}{\partial z}(x,y,\pm\infty,t)=0, \tag{46}$$

where ω equals 0 or 1 for a first- and third-type boundary condition, respectively. Note that $f(x,y,z)$ and $g(y,z,t)$ are arbitrary initial and influent distributions, respectively. These functions can be specified in a similar manner as for the one-dimensional case except that f and g now depend on multiple coordinates instead of one.

For three-dimensional infinite systems the use of a moving longitudinal coordinate (Eq. (30)) readily transforms the ADE and its auxiliary conditions into a three-dimensional diffusion problem for which a wealth of analytical solutions exist. Another straightforward method of solving multidimensional transport problems is the use of the product rule which states that the product of the solutions of (simpler) one-dimensional problems may directly give the desired three-dimensional solution (e.g., Carslaw and Jaeger, 1959). Consider the three one-dimensional problems

$$\frac{\partial C_x}{\partial t}=D_x\frac{\partial^2 C_x}{\partial x^2}-u\frac{\partial C_x}{\partial x}, \tag{47}$$

$$\frac{\partial C_y}{\partial t}=D_y\frac{\partial^2 C_y}{\partial y^2}, \tag{48}$$

$$\frac{\partial C_z}{\partial t}=D_z\frac{\partial^2 C_z}{\partial z^2}. \tag{49}$$

The product of the solutions of these three one-dimensional problems, i.e.,

$$C(x,y,z,t)=C_x(x,t)\,C_y(y,t)\,C_z(z,t) \tag{50}$$

also satisfies the three-dimensional transport equation. Application of the product rule requires that the boundary conditions be homogeneous and that the initial condition for the three-dimensional problem can be written as a product of the three one-dimensional initial conditions.

Several approaches, in addition to moving coordinate transformation and product rules, have been used in the literature. These include separation of variables and Fourier series (Bruch and Street, 1967), Green's functions (Leij and van Genuchten, 2000; Sagar, 1982; Yeh and Tsai, 1976), or integral transforms (Cleary, 1973; Leij and Dane, 1990; Leij et al., 1993, Pérez Guerrero et al., 2013).

For many river systems at least one direction will be finite, which may complicate the mathematical solutions. Several integral transforms, mostly of the Fourier type, have been used by Özişik (1989) and Sneddon (1995) for such situations. In some cases one or two of the finite directions can be neglected by using a depth-averaged concentration, or by making use of uniformity in the initial and boundary conditions across the stream. Another approach is the use of fictitious constituent sources outside the solution domain to ensure a zero-gradient at the boundaries (e.g., see p. 49 of Fischer et al., 1979). This approach permits one to still use the relatively simple solutions available for infinite outlet conditions.

SPECIFIC ADE SOLUTIONS

One-dimensional solutions with third-type inlet condition

Consider the ADE for a contaminant subject to a combination of first-order decay and zero-order production to represent a variety of physical, chemical or biological reactions:

$$\frac{\partial C}{\partial t}=D_x\frac{\partial^2 C}{\partial x^2}-u\frac{\partial C}{\partial x}-\mu C+\gamma. \tag{51}$$

Eq. (51) will be solved for the following initial and boundary conditions:

$$C(x,0)=f(x), \tag{52}$$

$$\left(uC-\omega D_x\frac{\partial C}{\partial x}\right)_{x=0^+}=ug(t), \tag{53}$$

$$\frac{\partial C}{\partial x}(\infty,t)=0 \quad \text{or} \quad \frac{\partial C}{\partial x}(L,t)=0. \tag{54a, b}$$

Analytical solutions for a third-type inlet condition (ω = 1) are given below under Case A, while those for a first-type inlet condition (ω = 0) are presented under Case B. The first solution will be for a Dirac delta type initial distribution, from which solutions for arbitrary initial profiles can be derived. The remaining one-dimensional solutions were selected from van Genuchten (1981) and van Genuchten and Alves (1982). The latter publication contains a large number of solutions for situations with and without zero-order production and first-order decay. Most of the semi-infinite solutions, as well as others, were later included in the CXTFIT computer programs (Parker and van Genuchten, 1984b; Toride et al., 1999), which later were incorporated into the windows-based STANMOD software package (Simůnek et al., 2000).

Case A0. Semi-infinite domain with zero initial concentration and a Dirac-type input function $g(t) = m\delta(t)/Au$. Neglecting any production or decay ($\mu = \gamma = 0$), the solution is

$$C(x,t)=\frac{m}{A}\left\{\frac{1}{\sqrt{\pi D_x t}}\exp\left[-\frac{(x-ut)^2}{4D_x t}\right]-\frac{u}{2D_x}\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_x t}}\right]\right\}. \tag{55}$$

As mentioned previously, an alternative solution exists for a Dirac-type initial distribution in an infinite medium.

In case of an arbitrary input function, $g(t)$, the expression for the concentration can be written as the convolution of the input signal and the concentration for the Dirac function:

$$C(x,t)=\int_0^t ug(t-\tau)\left\{\frac{1}{\sqrt{\pi D_x\tau}}\exp\left[-\frac{(x-u\tau)^2}{4D_x\tau}\right]-\frac{u}{2D_x}\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+u\tau}{\sqrt{4D_x\tau}}\right]\right\}d\tau. \quad (56)$$

Fig. 1 shows an example of the Dirac solution given by Eq. (55) using parameter values selected previously by De Smedt et al. (2005) to test their analytical solution for the same Dirac inlet problem but assuming a first-type boundary condition (the solution of which is given by Case B0 below). The example involves an instantaneous injection (or spill) of 1 kg of a solute in the main channel of a river having a cross-section of 10 m^2, an average flow velocity of 1 m/s and a dispersion coefficient of 5 m^2/s. De Smedt et al. (2005) in their analysis also included the effects of a dead storage zone which we ignore here (that case will be discussed in part 2). Fig. 1 shows the solute distributions in the stream after 500, 1000 and 1500 s. The curve for t = 1000 s is essentially the same as the one calculated by De Smedt et al. (2005) assuming no mass transfer into the dead zone (their Fig. 1 with α = 0).

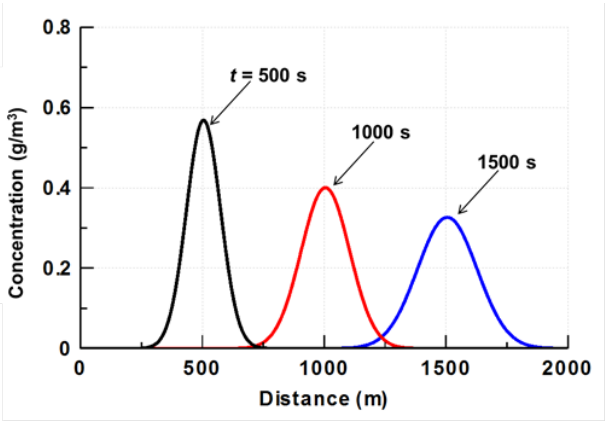


Fig. 1. Calculated concentration distributions obtained with Eq. (55) for instantaneous injection of 1 kg of solute in a stream having a cross-sectional area of 10 m^2 assuming a third-type Dirac input boundary condition (u = 1 m s^{-1}, D_x = 5 m^2 s^{-1}).

Case A1. Semi-infinite domain with uniform initial concentration, $f(x) = C_i$ and no production or decay. The inlet concentration function, $g(t)$, is of the pulse type (a Heaviside type function) with constant concentration C_o, i.e.,

$$g(t)=\begin{cases}C_o & 0<t\le t_o\\ 0 & t>t_o.\end{cases} \quad (57)$$

The solution of this example is

$$C(x,t)=\begin{cases}C_i+(C_o-C_i)A(x,t) & 0<t\le t_o\\ C_i+(C_o-C_i)A(x,t)-C_oA(x,t-t_o) & t>t_o,\end{cases} \quad (58)$$

where

$$A(x,t)=\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_xt}}\right]+\sqrt{\frac{u^2t}{\pi D_x}}\exp\left[-\frac{(x-ut)^2}{4D_xt}\right]-\frac{1}{2}\left(1+\frac{ux}{D_x}+\frac{u^2t}{D_x}\right)\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_xt}}\right]. \quad (59)$$

Here we illustrate one possible application of the above analytical solution by fitting the transport parameters in Eqs. (58) and (59) to observed data obtained by Brevis et al. (2001) as discussed by De Smedt et al. (2005). The data pertain to a tracer experiment in the Chillán River in Chile using a 20% Rhodamine WT solution injected simultaneously at multiple points along a lateral cross-section of the river at x = 0. Fig. 2 shows the observed data of one of their experiments (Exp. I-3), in this case for the application of 157.1 g of tracer at x = 0, with measurements made 4604 m downstream of the injection point. Because of the relative short duration of the experiments, photodegradation and sorption of Rhodamine WT were presumed to be negligible (De Smedt et al., 2005).

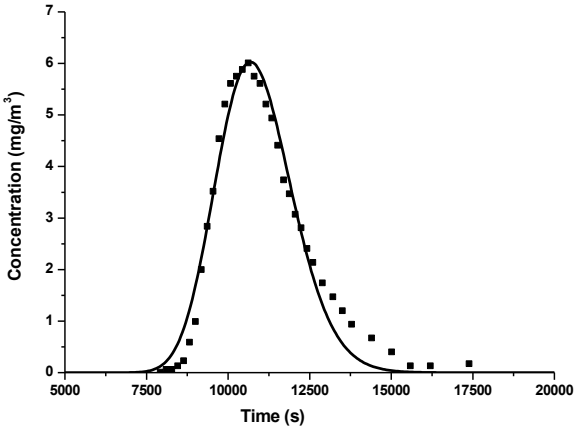


Fig. 2. Observed (solid squares) and fitted (continuous line) concentrations for tracer experiment I-3 of Brevis et al. (2001) and De Smedt et al. (2005).

Fig. 2 shows the data along with the fitted curve based on Eqs (58) and (59). Parameters were estimated using the nonlinear least-squares optimization features of the CXTFIT code (Toride et al., 1999) within STANMOD. The code allows one to estimate not only the longitudinal flow velocity u and the longitudinal dispersion coefficient D_x, but also the concentration C_o of the applied tracer solution for a given value of the injection or pulse time t_o in Eq. (58). Assuming a very short injection period of only 10 s, we obtained the following parameter values (with their 95% confidence intervals): u = 0.426 ± 0.003 m/s, D_x = 11.4 ± 1.4 m^2/s, and C_o = 1729 ± 86 mg/m^3. The coefficient of determination (R^2) of the fit was 0.983, and the root mean square error (RMSE) 0.382 mg/m^3). One may verify that the total amount of solute mass (m) injected per m^2 cross-sectional area hence equals $m = u\,C_o\,t_o$, or 7.37 g/m^2. Given that a total amount of 157.1 g of tracer was applied to the river, this translates to an effective cross-sectional area of 157.1 g/7.37 (g/m^2) or 21.3 m^2 of the channel as calculated with the equilibrium ADE transport model.

The above calculations assume applicability of Eqs. (58) and (59) using a solute injection pulse of 10 s. Exactly the same results were obtained when the total mass was assumed to be applied instantaneously (as estimated with CXTFIT using the

Dirac solution given by Eq. (55)), or spread over a time period t_o of 100 s. We also ran the problem assuming a first-type inlet boundary condition (Cases B0 and B1 given later in this paper). Results were again the same or very close to those obtained with the third-type boundary conditions. For example, for the first-type boundary condition (Case B0) we obtained u = 0.424 ± 0.003 m/s, D_x = 11.3 ± 1.3 m^2/s, and C_o = 1729 ± 860 mg/m^3 (R^2 = 0.970; RMSE = 0.382), which essentially duplicates the results for the third-type solutions. This shows that differences between the first- and third-type boundary conditions for transport problems with relatively large values of the system Peclet number, uL/D_x (van Genuchten and Parker, 1984) generally are very small. The calculated curve in Fig. 2 assuming equilibrium transport provided a reasonable fit of the data, albeit not perfect. In part 2 (van Genuchten et al., 2013) we will analyze the same problem in terms of the transient storage model, similarly as was considered by De Smedt et al. (2005).

Case A2. The same as case A1 (i.e., for a semi-infinite domain with uniform initial concentration C_i and a pulse-type input function with concentration C_o), but now with zero-order production and first-order decay. The solution is

$$C(x,t)=\begin{cases}\left(C_o-\dfrac{\gamma}{\mu}\right)A(x,t)+B(x,t) & 0<t\le t_o\\[2ex] \left(C_o-\dfrac{\gamma}{\mu}\right)A(x,t)+B(x,t) & \\ \qquad -C_oA(x,t-t_o) & t>t_o,\end{cases} \tag{60}$$

where

$$A(x,t)=\frac{u}{u+\xi}\exp\left[\frac{(u-\xi)x}{2D_x}\right]\operatorname{erfc}\left[\frac{x-\xi t}{\sqrt{4D_xt}}\right] +\frac{u}{u-\xi}\exp\left[\frac{(u+\xi)x}{2D_x}\right]\operatorname{erfc}\left[\frac{x+\xi t}{\sqrt{4D_xt}}\right] +\frac{u^2}{2\mu D_x}\exp\left(\frac{ux}{D_x}-\mu t\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_xt}}\right]. \tag{61}$$

$$B(x,t)=\frac{\gamma}{\mu}+\left(C_i-\frac{\gamma}{\mu}\right)\exp(-\mu t)\left\{1-\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_xt}}\right] -\sqrt{\frac{u^2t}{\pi D_x}}\exp\left[-\frac{(x-ut)^2}{4D_xt}\right] +\frac{1}{2}\left(1+\frac{ux}{D_x}+\frac{u^2t}{D_x}\right)\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_xt}}\right]\right\}. \tag{62}$$

in which

$$\xi=u\sqrt{1+4\mu D_x/u^2}\,. \tag{63}$$

Fig. 3 shows an application of this solution using the same problem and parameter values as for Case A0 (Fig. 1), but now assuming that the solute was injected during a finite (pulse) period t_o of 1000 s, and that the solute was subject to first-order decay ($\mu \ge 0$), but without any first-order production ($\gamma = 0$).

Case A3. Steady-state solution for a semi-infinite domain with a third-type inlet concentration C_o, and zero- and first-order decay. The analytical solution can be written as

$$C(x)=\frac{\gamma}{\mu}+\left(C_o-\frac{\gamma}{\mu}\right)\left(\frac{2u}{u+\xi}\right)\exp\left[\frac{(u-\xi)x}{2D_x}\right]. \tag{64}$$

Case A4. Semi-infinite domain with a nonuniform initial concentration, $f(x)=E(x)$, and a pulse-type inlet condition like Case A1 with $g(t)$ given by Eq. (57). As initial condition we use the steady-state profile resulting from continuous application of a solute at background concentration, C_b. This initial profile follows directly from Case A3 as:

$$C(x,0)\equiv E(x)=\frac{\gamma}{\mu}+\left(C_b-\frac{\gamma}{\mu}\right)\left(\frac{2u}{u+\xi}\right)\exp\left[\frac{(u-\xi)x}{2D_x}\right]. \tag{65}$$

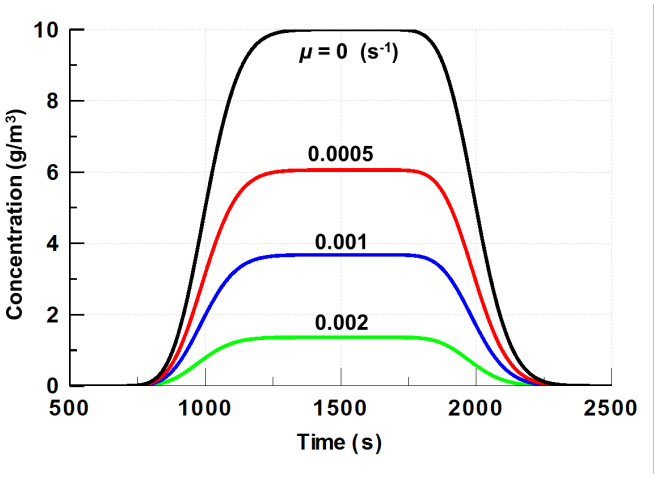


Fig. 3. Effect of first-order degradation (μ) on calculated concentration distributions in a stream after injection of a solute having a concentration of 10 g/m^3 for 1000 s (u = 1 m s^{-1}, D_x = 5 m^2 s^{-1}, γ = 0 g m^{-3} s^{-1}, t_o = 1000 s).

The analytical solution for this case is

$$C(x,t)=\begin{cases}(C_o-C_b)A(x,t)+E(x) & 0<t\le t_o\\[2ex] (C_o-C_b)A(x,t)+E(x)-C_oA(x,t-t_o) & t>t_o,\end{cases} \tag{66}$$

where $A(x,t)$ is given by Eq. (61) and $E(x)$ by (65).

Case A5. Semi-infinite domain with uniform initial concentration, $f(x)=C_i$, no production and decay, and an influent concentration that decreases exponentially with time:

$$g(t)=C_b+C_o\exp(-\lambda t) \tag{67}$$

where λ is a constant (T^{-1}). The solution for this case is

$$C(x,t)=C_i+(C_b-C_i)A(x,t)+C_oB(x,t), \tag{68}$$

where

$$A(x,t)=\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_x t}}\right]+\sqrt{\frac{u^2 t}{\pi D_x}}\exp\left[-\frac{(x-ut)^2}{4D_x t}\right]$$
$$-\frac{1}{2}\left(1+\frac{ux}{D_x}+\frac{u^2 t}{D_x}\right)\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_x t}}\right]. \quad (69)$$

$$B(x,t)=\exp(-\lambda t)\left\{\frac{u}{u+\kappa}\exp\left(\frac{(u-\kappa)x}{2D_x}\right)\operatorname{erfc}\left[\frac{x-\kappa t}{\sqrt{4D_x t}}\right]\right.$$
$$\left.+\frac{u}{u-\kappa}\exp\left(\frac{(u+\kappa)x}{2D_x}\right)\operatorname{erfc}\left[\frac{x+\kappa t}{\sqrt{4D_x t}}\right]\right\}$$
$$-\frac{u^2}{2\lambda D_x}\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_x t}}\right] \quad (70)$$

and

$$\kappa=u\sqrt{1-4\lambda D_x/u^2}\,. \quad (71)$$

Note that this example reduces to Case A1 (only for $t < t_o$) when $C_o = 0$.

Case A6. Finite domain with zero initial concentration, $f(x) = 0$, a third-type inlet condition, and no zero- and first-order rate processes (i.e., $\mu = \gamma = 0$). The inlet condition is again the same as for Case A1, i.e., a pulse type concentration with constant C_o. The outlet condition is now a zero gradient at $x = L$ as given by Eq. (21). The solution for this case is (Brenner, 1962):

$$\frac{C(x,t)}{C_o}=1-\frac{2uL}{D_x}\sum_{m-1}^{\infty}\frac{G(x)\exp\left[\frac{ux}{2D_x}-\frac{u^2 t}{4D_x}+\frac{\beta_m^2 D_x t}{L^2}\right]}{\left[\beta_m^2+\left(\frac{uL}{2D_x}\right)^2+\frac{uL}{D_x}\right]\left[\beta_m^2+\left(\frac{uL}{2D_x}\right)^2\right]}, \quad (72a)$$

where

$$G(x)=\beta_m\left[\beta_m\cos\left(\frac{\beta_m x}{L}\right)+\frac{uL}{2D_x}\sin\left(\frac{\beta_m x}{L}\right)\right] \quad (72b)$$

in which the eigenvalues β_m are the positive roots of

$$\beta_m\cot(\beta_m)-\frac{\beta_m^2 D_x}{uL}+\frac{uL}{4D_x}=0. \quad (73)$$

The above series solution converges very slowly when advection dominates dispersion as is often the case for stream transport problems. For either

$$\frac{uL}{D_x}>5+40\frac{ut}{L} \quad \text{or} \quad \frac{uL}{D_x}>100 \quad (74)$$

the following approximate solution may be used (Brenner, 1962; van Genuchten and Alves, 1982):

$$\frac{C(x,t)}{C_o}=\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_x t}}\right]+\sqrt{\frac{u^2 t}{\pi D_x}}\exp\left[-\frac{(x-ut)^2}{4D_x t}\right]$$
$$-\frac{1}{2}\left(1+\frac{ux}{D_x}+\frac{u^2 t}{D_x}\right)\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_x t}}\right]$$
$$+\sqrt{\frac{4u^2 t}{\pi D_x}}\left[1+\frac{u}{4D_x}(2L-x+ut)\right]\exp\left[\frac{uL}{D_x}-\frac{(2L-x+ut)^2}{4D_x t}\right]$$
$$-\frac{u}{D_x}\left\{\left[2L-x+\frac{3ut}{2}+\frac{u}{4D_x}(2L-x+ut)^2\right]\right.$$
$$\left.\cdot\exp\left(\frac{uL}{D_x}\right)\operatorname{erfc}\left[\frac{(2L-x)+ut}{\sqrt{4D_x t}}\right]\right\}. \quad (75)$$

Although in most cases considerably more complicated, a large number of analytical solutions are also available for finite systems with zero-order production and/or first order decay (Pérez Guerrero et al., 2009; van Genuchten and Alves, 1982).

One-dimensional solutions with first-type inlet condition

Case B0. Semi-infinite domain with zero initial concentration, a first-type ($\omega = 0$) inlet condition, and a Dirac-type input concentration. The solution for the case of no production or decay is

$$C(x,t)=\frac{m}{Au}\frac{x}{\sqrt{4\pi D_x t^3}}\exp\left[-\frac{(x-ut)^2}{4D_x t}\right]. \quad (76)$$

For arbitrary input profiles the expression for the concentration can again be written as the convolution of the input signal and the concentration for the Dirac input:

$$C(x,t)=\int_0^t\frac{xg(t-\tau)}{\sqrt{4\pi D_x\tau^3}}\exp\left[\frac{(x-u\tau)^2}{4D_x\tau}\right]d\tau. \quad (77)$$

Case B1. Semi-infinite domain with uniform initial concentration, $f(x) = C_i$, and a pulse-type solute application (i.e., Eq. (57) as for Case A1). The solution is

$$C(x,t)=\begin{cases}C_i+(C_o-C_i)A(x,t) & 0<t\le t_o\\ C_i+(C_o-C_i)A(x,t)-C_o A(x,t-t_o) & t>t_o\end{cases} \quad (78)$$

where

$$A(x,t)=\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4Dxt}}\right]+\frac{1}{2}\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_x t}}\right]. \quad (79)$$

Case B2. Semi-infinite domain with uniform initial concentration, $f(x) = C_i$, and a pulse-type solute application. The solution for a first-type inlet condition is

$$C(x,t)=\begin{cases}\left(C_o-\dfrac{\gamma}{\mu}\right)A(x,t)+B(x,t) & 0<t\le t_o\\ \left(C_o-\dfrac{\gamma}{\mu}\right)A(x,t)+B(x,t) & \\ \qquad -C_oA(x,t-t_o) & t>t_o,\end{cases} \tag{80}$$

where

$$A(x,t)=\frac{1}{2}\exp\left[\frac{(u-\xi)x}{2D_x}\right]\operatorname{erfc}\left[\frac{x-\xi t}{\sqrt{4D_xt}}\right] +\frac{1}{2}\exp\left[\frac{(u+\xi)x}{2D_x}\right]\operatorname{erfc}\left[\frac{x+\xi t}{\sqrt{4D_xt}}\right] \tag{81}$$

and

$$B(x,t)=\frac{\gamma}{\mu}+\left(C_i-\frac{\gamma}{\mu}\right)\exp(-\mu t) \left\{1-\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_xt}}\right]-\frac{1}{2}\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_xt}}\right]\right\} \tag{82}$$

in which ξ is as defined previously by Eq. (63).

Case B3. Steady-state solution for a semi-infinite domain with uniform initial concentration, $f(x) = C_i$. The analytical solution for a step-type inlet condition with constant concentration C_o is

$$C(x)=\frac{\gamma}{\mu}+\left(C_o-\frac{\gamma}{\mu}\right)\exp\left[\frac{(u-\xi)x}{2D_x}\right]. \tag{83}$$

Case B4. Semi-infinite domain with nonuniform initial concentration, $f(x) = E(x)$, and again a pulse-type inlet condition of Case A1 with constant C_o. As initial condition we use the steady-state profile resulting from a continuous application of the solute at background concentration, C_b. This initial profile follows from Case B2 as

$$C(x,0)\equiv E(x)=\frac{\gamma}{\mu}+\left(C_b-\frac{\gamma}{\mu}\right)\exp\left[\frac{(u-\xi)x}{4D_x}\right], \tag{84}$$

where C_b, as before, represents the background concentration before the pulse of concentration C_o is applied. The solution for this case is

$$C(x,t)=\begin{cases}\left(C_o-C_b\right)A(x,t)+E(x) & 0<t\le t_o\\ \left(C_o-C_b\right)A(x,t)+E(x) & \\ \qquad -C_oA(x,t-t_o) & t>t_o,\end{cases} \tag{85}$$

where $A(x,t)$ is given by Eq. (81) and $E(x)$ by (84).

Case B5. Semi-infinite domain with uniform initial concentration, $f(x) = C_i$, a first-type inlet condition with no production and decay, and an influent concentration that decreases exponentially with time as defined for Case A5 (Eq. (67)). The solution for this case is

$$C(x,t)=C_i+(C_b-C_i)A(x,t)+C_oB(x,t), \tag{86}$$

where

$$A(x,t)=\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_xt}}\right]+\frac{1}{2}\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_xt}}\right], \tag{87}$$

$$B(x,t)=\exp(-\lambda t)\left\{\frac{1}{2}\exp\left(\frac{(u-\kappa)x}{2D_x}\right)\operatorname{erfc}\left[\frac{x-\kappa t}{\sqrt{4D_xt}}\right] +\frac{1}{2}\exp\left(\frac{(u+\kappa)x}{2D_x}\right)\operatorname{erfc}\left[\frac{x+\kappa t}{\sqrt{4D_xt}}\right]\right\} \tag{88}$$

and κ as given by Eq. (71).

Case B6. Finite domain with uniform initial concentration, $f(x) = 0$, a first-type inlet condition, and no zero- or first-order production or degradation processes. The inlet condition is the same as for Case A1 (Eq. (57)), i.e., a pulse type application with constant C_o. The solution is (Cleary and Adrian, 1973):

$$\frac{C(x,t)}{C_0}=1-\sum_{m=1}^{\infty}\frac{2\beta_m\sin\left(\dfrac{\beta_m x}{L}\right)\exp\left[\dfrac{ux}{2D_x}-\dfrac{u^2t}{4D_x}-\dfrac{\beta_m^2D_xt}{L^2}\right]}{\beta_m^2+\left(\dfrac{uL}{2D_x}\right)^2+\dfrac{uL}{2D_x}}, \tag{89}$$

where the eigenvalues β_m are the positive roots of

$$\beta_m\cot(\beta_m)+\frac{uL}{2D_x}=0. \tag{90}$$

As for Case A6, this series solution converges very slowly when advective transport dominates dispersion. For conditions given by (74), the solution is accurately approximated by the much more convenient (van Genuchten and Alves, 1982):

$$\frac{C(x,t)}{C_o}=\frac{1}{2}\operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_xt}}\right]+\frac{1}{2}\exp\left(\frac{ux}{D_x}\right)\operatorname{erfc}\left[\frac{x+ut}{\sqrt{4D_xt}}\right] +\frac{1}{2}\left[2+\frac{u(2L-x)}{D_x}+\frac{u^2t}{D_x}\right]\exp\left(\frac{uL}{D_x}\right)\operatorname{erfc}\left[\frac{(2L-x)+ut}{\sqrt{4D_xt}}\right] -\sqrt{\frac{u^2t}{\pi D_x}}\exp\left[\frac{uL}{D_x}-\frac{(2L-x+ut)^2}{4D_xt}\right]. \tag{91}$$

4.3 Two-dimensional solutions

Case C1. Infinite domain with Dirac-type initial concentration and no zero- and first-order rate processes. The longitudinal flow direction (x) and the transverse direction (y) are assumed to be infinite. An amount m is released instantaneously over the depth the river ($0 < z < d$) at $x = 0$ and $y = 0$. The initial condition for this line source problem can be written as

$$g(x,y)=\frac{m}{d}\delta(x,y) \tag{92}$$

in which the Dirac delta function (δ) has the dimension of L^{-2}. The analytical solution for the concentration can be found with the product rule as

$$C(x,y,t)=\frac{m}{4\pi dt\sqrt{D_xD_y}}\exp\left[-\frac{(x-ut)^2}{4D_xt}-\frac{y^2}{4D_yt}\right]. \tag{93}$$

Arbitrary initial profiles can be viewed as a superposition of instantaneous releases and can therefore be obtained by integrating the analytical solution over time (see also Cases A0 and B0).

Case C2. Infinite domain with a continuous line source at $x = 0$ and $y = 0$ from which a nonreactive constituent is released at a rate of W_o (MT^{-1}). The steady-state solution is given by (Sayre, 1973)

$$C(x,y)=\frac{W_o}{2\pi d\sqrt{D_xD_y}}\exp\left(\frac{ux}{2D_x}\right)\mathrm{K}_0\left[\frac{u}{\sqrt{4D_x}}\sqrt{\frac{x^2}{D_x}+\frac{y^2}{D_y}}\right], \tag{94}$$

where $K_0[\ ]$ is the zero-order modified Bessel function of the second kind. If longitudinal dispersion is negligible, the following approximate solution may be used

$$C(x,y)=\frac{W_o}{2d\sqrt{\pi uD_yx}}\exp\left(-\frac{uy^2}{4D_yx}\right)$$
$$\text{if}\quad \frac{y^2D_x}{x^2D_y}\ll 1\quad\text{and}\quad x\gg\frac{2D_x}{u}. \tag{95}$$

Case C3. Semi-infinite longitudinal and finite transverse domain having a continuous line source at $x = 0$ and $y = y_o$ (not necessarily at $y = 0$) from which a contaminant is released at a rate W_o (MT^{-1}). The steady-state solution is very similar to the solution of Case C2; however, part of the contaminant eventually will reach the banks of the river because of its finite width. The mirror-image technique (e.g., Fischer et al., 1979) may be used to ensure that the constituent beyond the river bank, as predicted with the solution of Case C2 (denoted here as C^*) for the infinite transverse condition, is reflected back. The solution can be written in terms of C^* with modified y variable (Sayre, 1973):

$$C(x,y)=C^*(x,y-y_o)+\sum_{n=1}^{\infty}\left[\begin{array}{l}C^*\left(x,nB-y_o+(-1)^n\,y\right)\\+C^*\left(x,-nB-y_o+(-1)^n y\right)\end{array}\right], \tag{96}$$

where B is the channel width (L), with transverse solution domain $-B/2 \le y \le B/2$, and n is the number of reflection cycles. Usually, a value of 4 or 5 for n yields sufficiently accurate results.

Three-dimensional solutions

The governing equation for three-dimensional transport is similar as for two-dimensional transport except that a second transverse dispersion term with coefficient D_z is included. The three-dimensional problem can be readily solved for an infinite z direction.

Case D1. Infinite domain with Dirac-type initial concentration and a first-type inlet condition with no zero- and first order processes. The x, y and z directions are infinite for all practical purposes. An amount m is released instantaneously at $x = y = z = 0$. The initial condition for this point source can be written as

$$g(x,y,z)=m\,\delta(x,y,z) \tag{97}$$

in which the Dirac delta function (δ) now has the dimension of L^{-3}. The expression for the concentration follows again from the product rule as (Onishi et al., 1981; Sayre, 1973)

$$C(x,y,z;t)=\frac{m}{8\pi t\sqrt{\pi D_xD_yD_zt}}$$
$$\exp\left[-\frac{(x-ut)^2}{4D_xt}-\frac{y^2}{4D_yt}-\frac{z^2}{4D_zt}\right]. \tag{98}$$

Solutions for arbitrary initial profiles can again be obtained by integrating the point source solution over time.

Case D2. Semi-infinite domain with a constant water depth, d, for which a nonreactive material is continuously released at a rate W_o (MT^{-1}) from a point source at $x = 0$, $y = y_o$, and $z = z_o$. It is also assumed that longitudinal dispersion is negligible (i.e., $D_x = 0$) as compared to advective transport. The steady-state solution for this case is (Onishi et al., 1981).

$$C(x,y,z)=\frac{W_o}{4\pi x\sqrt{D_yD_z}}\left\{\exp\left(-\frac{(y-y_o)^2u}{4D_yx}\right)+\exp\left(-\frac{(y+y_o)^2u}{4D_yx}\right)\right\}$$
$$\cdot\sum_{m=-\infty}^{\infty}\left\{\exp\left(-\frac{(z-z_o-2md)^2u}{4D_zx}\right)+\exp\left(-\frac{(z+z_o-2md)^2u}{4D_zx}\right)\right\}. \tag{99}$$

Case D3. Semi-infinite domain with the solute initially uniformly distributed in a parallelepipedal region with no inflow of mass at the upstream boundary. The y and z directions are assumed to be infinite. The problem can be solved with the product rule. The longitudinal transport equation, as given by Eq. (56), is solved subject to

$$C_x(x,0)=\begin{cases}C_i^{1/3} & x_1<x<x_2\\ 0 & \text{elsewhere}\end{cases} \tag{100}$$

and

$$\left(C_x-\omega\frac{D_x}{u}\frac{\partial C_x}{\partial x}\right)_{x=0^+}=0\qquad\frac{\partial C_x}{\partial x}(\infty,t)=0, \tag{101}$$

where x_1 and x_2 are two arbitrary locations between which the solute is originally present. The solution can be deduced direct-

ly from examples A5 and A6 in van Genuchten and Alves (1982). The solution for a first-type inlet condition (ω = 0) is given by

$$C_x(x,t)=\frac{C_i^{1/3}}{2}\ \mathrm{erfc}\left(\frac{x-x_2-ut}{\sqrt{4D_xt}}\right)-\mathrm{erfc}\left(\frac{x-x_1-ut}{\sqrt{4D_xt}}\right)+\exp\left(\frac{ux}{D_x}\right)\left[\mathrm{erfc}\left(\frac{x+x_2+ut}{\sqrt{4D_xt}}\right)-\mathrm{erfc}\left(\frac{x+x_1+ut}{\sqrt{4D_xt}}\right)\right] \quad (102)$$

whereas the solution for a third-type inlet condition (ω = 1) is

$$C_x(x,t)=\frac{C_i^{1/3}}{2}\left\{\exp\left(\frac{ux}{D_x}\right)\left[\left(1+\frac{u}{D_x}(x+x_1+ut)\right)\cdot\mathrm{erfc}\left(\frac{x+x_1+ut}{\sqrt{4D_xt}}\right)-\left(1+\frac{u}{D_x}(x+x_2+ut)\right)\mathrm{erfc}\left(\frac{x+x_2+ut}{\sqrt{4D_xt}}\right)\right]+\mathrm{erfc}\left(\frac{x-x_2-ut}{\sqrt{4D_xt}}\right)-\mathrm{erfc}\left(\frac{x-x_1-ut}{\sqrt{4D_xt}}\right)+\sqrt{\frac{4u^2t}{\pi D_x}}\exp\left(\frac{ux}{D_x}\right)\left[\exp\left(-\frac{(x+x_2+ut)}{4D_xt}\right)-\exp\left(-\frac{\left[R(x+x_1)+ut\right]^2}{4D_xt}\right)\right]\right\}. \quad (103)$$

The solution of the transverse one-dimensional transport equation given by Eq. (48) subject to the condition

$$C_y(y,0)=\begin{cases}C_i^{1/3} & -a<y<a\\ 0 & \text{elsewhere}\end{cases}\quad\text{and}\quad\frac{\partial C_y}{\partial y}(\pm\infty,0)=0 \quad (104)$$

can be readily adopted from the literature (e.g., Eq. [2.15] of Crank, 1975):

$$C_y(y,t)=\frac{C_i^{1/3}}{2}\left[\mathrm{erfc}\left(\frac{y-a}{\sqrt{4D_yt}}\right)-\mathrm{erfc}\left(\frac{y+a}{\sqrt{4D_yt}}\right)\right]. \quad (105)$$

The same solution can be used to express C_z in the z-direction where, for example, the solute is initially between $-b$ and b.

The solution of the three-dimensional transport equation given by (41) for solution domain $\{0 < x < \infty, -\infty < y < \infty, -\infty < z < \infty, t > 0\}$, subject to the initial condition

$$C(x,y,z,0)=\begin{cases}C_i & x_1<x<x_2\quad |y|<a,\quad |z|<b\\ 0 & \text{elsewhere}\end{cases} \quad (106)$$

and for homogeneous boundary conditions can now be written as the product of individual solutions as follows

$$C(x,y,z,t)=C_x(x,t)\,C_y(y,t)\,C_z(z,t). \quad (107)$$

Case D4. Semi-infinite domain with zero initial concentration, $f(x) = C_i$, and a third-type inlet condition. The inlet condition is of the pulse type with constant concentration C_o, i.e.,

$$g(y,z,t)=\begin{cases}C_o & |y|<a,\quad |z|<b,\quad 0<t\le t_o\\ 0 & \text{otherwise.}\end{cases} \quad (108)$$

The solution for this case is (Leij et al., 1991)

$$C(x,y,z,t)=\frac{uC_o}{4}\int_{P(t)}^{t}\exp(-\mu\tau)\left\{\frac{1}{\sqrt{\pi D_x\tau}}\exp\left[-\frac{(x-u\tau)^2}{4D_x\tau}\right]-\frac{u}{2D_x}\exp\left(\frac{ux}{D_x}\right)\mathrm{erfc}\left(\frac{x+u\tau}{\sqrt{4D_x\tau}}\right)\right\}\cdot\left[\mathrm{erfc}\left(\frac{y-a}{\sqrt{4D_y\tau}}\right)-\mathrm{erfc}\left(\frac{y+a}{\sqrt{4D_y\tau}}\right)\right]\cdot\left[\mathrm{erfc}\left(\frac{z-b}{\sqrt{4D_z\tau}}\right)-\mathrm{erfc}\left(\frac{z+b}{\sqrt{4D_z\tau}}\right)\right]d\tau+\frac{\gamma}{2}\int_0^t\exp(-\mu\tau)\mathrm{erfc}\left(\frac{u\tau-x}{\sqrt{4D_x\tau}}\right)+\left[1+(x+u\tau)\frac{u}{D_x}\right]\exp\left(\frac{ux}{D_x}\right)\mathrm{erfc}\left(\frac{x+u\tau}{\sqrt{4D_x\tau}}\right)-\sqrt{\frac{4u^2\tau}{\pi D_x}}\exp\left(-\frac{(x-u\tau)^2}{4D_x\tau}\right)\Bigg]d\tau, \quad (109)$$

where

$$P(t)=\begin{cases}0 & 0<t\le t_o\\ t-t_o & t>t_o.\end{cases} \quad (110)$$

Here we illustrate a two-dimensional application of Eq. (109) involving the injection of a solute over a finite horizontal cross-section ($-10 \le y < 10$ m), $0 \le z < \infty$) of an initially solute free river channel or other open surface water body. As before we use a mean transport velocity of 1 m s^{-1}, and longitudinal (D_x) and lateral (D_y) dispersion coefficients of 5 and 0.1 m^2 s^{-1}, respectively. Production or decay processes are neglected ($\mu = \gamma = 0$). The two-dimensional (x, y) concentration distribution at time 1500 s is shown in Fig. 4. Calculations were carried out using the 3DADE code (Leij and Bradford, 1994) within STANMOD assuming a = 10 m and b = 1000 m (the latter large value ensuring a two-dimensional transport geometry).

Fig. 5 further shows for this example the concentration distribution along the longitudinal (x) coordinate in the middle of the channel (i.e., for $y = z = 0$). The width (b) of the solute source along the z-coordinate perpendicular to the river surface (Eq. (108)) was taken to be very large in this example (1000 m), thus creating a two-dimensional (x, y) transport geometry. Smaller values of the source width, b (e.g., 5 or 2 m) would

create a three-dimensional geometry and significantly lower the intermediate concentrations in Fig. 4 (between approximately 200 and 1300 m) because of lateral dispersion away from the center line. The same effect would occur if higher values of the lateral dispersion coefficient (D_y) were used.

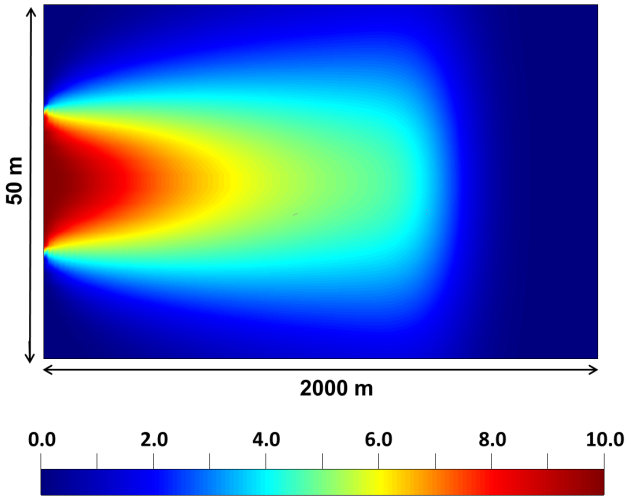


Fig. 4. Two-dimensional (x, y) concentration distributions at the surface of a stream upon continuous injection of a solute having a concentration of 10 g/m^3 into a cross-section $-10 \le y \le 10$ (m), $-1000 \le z < 1000$ m as obtained with Eq. (109) using the 3DADE module within STANMOD (a = 10 m, b = 1000 m, u = 1 m/s, D_x = 5 m^2/s, $D_y = D_z$ = 0.1 cm^2/s, $\mu = \gamma = 0$).

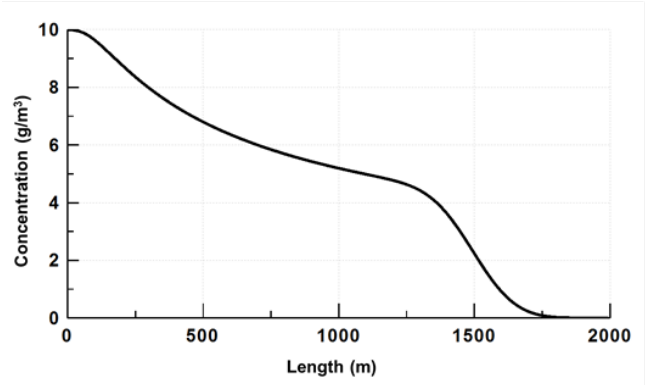


Fig. 5. Concentration distribution along the longitudinal (x) coordinate in the middle of the stream ($y = z = 0$) for the problem depicted in Fig. 4.

The above example is just one possible scenario for predicting two- and three-dimensional transport in streams and larger surface water bodies. We refer to Leij and Dane (1990), Leij et al. (1991), Leij and Bradford (1994) and Weerts et al. (1995) for many other solutions, including for nonequilibrium transport as discussed in Part 2. Many of the solutions are included in the 3DADE (Leij and Bradford, 1994) and N3DADE (Leij and Toride, 1997) modules within the STANMOD software package, which we used for all calculations in this study. Fig. 6 gives an overview of the various geometries that can be considered with this software for multidimensional transport problems.

CONCLUDING REMARKS

The solutions in this paper pertain to one-dimensional longitudinal equilibrium transport in streams and rivers, and longitudinal transport and lateral dispersion in rivers and larger surface water bodies. This ideal situation generally does not occur in streams and rivers because of the presence of relatively immobile or stagnant (dead) zones of water connected to the mean stream. Such stagnant zones include pools and eddies along the river banks, water isolated behind rocks, gravel or vegetation, or relatively inaccessible water along an uneven river bottom. Fluvial sediments and more generally the subsurface hyporheic zone may also contribute to the presence of such relatively stagnant water zones. By providing sinks or sources of solute during transport, stagnant water zones typically cause tailing in observed concentration distributions, which cannot be predicted with the conventional equilibrium ADE formulations. Part 2 of this two-part series (van Genuchten et al., 2013) will focus on nonequilibrium transport caused by the presence of such stagnant water zones (transient storage models), and also includes models that consider simultaneous longitudinal advective-dispersive transport in a river and lateral diffusion into and out of the hyporheic zone. Part 2 additionally provides several solutions for the transport of solutes involved in consecutive decay chain reactions.

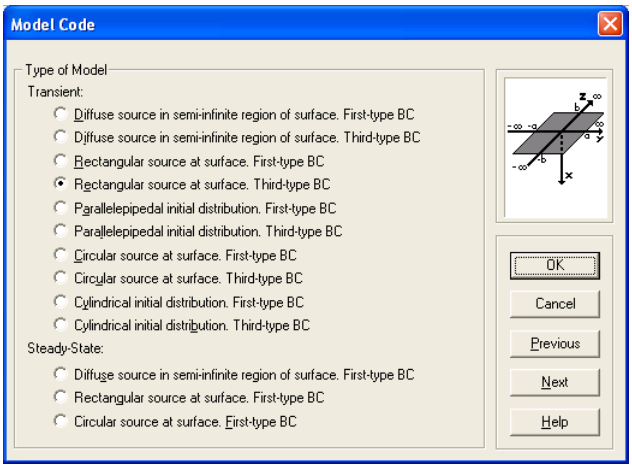


Fig. 6. Available geometries, initial conditions, and inlet boundary conditions (BC's) that can be simulated using the 3DADE module within the STANMOD software package. Both transient (time-dependent) and steady-state (time-independent) problems can be considered.

Most of the analytical solutions presented in this part 1 were derived from solutions to mathematically very similar problems in subsurface contaminant transport. All part 1 solutions have been incorporated in the public-domain windows-based STANMOD software package (Šimůnek et al., 2000). This software package also includes parameter estimation capabilities (e.g., Fig. 2), and hence provides a convenient tool for analyzing observed contaminant concentration distributions versus distance and/or time.

While inherently less flexible than more comprehensive numerical models for contaminant transport in streams and rivers, we believe that the analytical solutions assembled in this study can be very useful for a variety of applications, such as for providing initial or approximate analyses of alternative pollution scenarios, conducting sensitivity analyses to investigate the effects of various parameters or processes on contaminant

transport in rivers and streams, extrapolating results over large times and spatial scales where numerical solutions become impractical, serving as screening models, providing benchmark solutions for more complex transport processes that cannot be solved analytically, and for validating more comprehensive numerical solutions of the governing transport equations.

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