

MPNE1D

ANALYTICAL SOLUTION FOR ONE-DIMENSIONAL SOLUTE TRANSPORT WITH MULTIPROCESS NONEQUILIBRIUM

USER'S GUIDE

Version 4.1

Christopher J. Neville

August 2004

Last update: 2004/Aug/27

Table of Contents

1. Program information
2. Terminology
3. Theory
 - 3.1. Conceptual model
 - 3.2. Governing equations
 - 3.3. Special cases
 - 3.4. Initial and boundary conditions
4. Evaluation of the solution
5. Testing of the solution
6. Instructions for using the computer program
 - 6.1. Running the computer program
 - 6.2. Input data file
 - 6.3. Specification of the inflow reservoir concentration history
 - 6.4. Example analysis
7. References
8. Appendices
 - A1. Derivation of the analytical solution
 - A2. Source code listing
 - A3. Listing of files for example analysis (Experiment 3-5)

1. Program information

Program Names: MPNE1D_41.FOR

Author: Christopher J. Neville

Language: FORTRAN90 (ANSI standard)

Version: 4.1

Date: August 2004

Abstract:

This manual documents a general analytical solution for one-dimensional solute transport with multiprocess nonequilibrium. The solution is described in *Neville et al. (2000)*.

The solution is capable of representing the following physical transport processes:

- One-dimensional advection;
- One-dimensional dispersion;
- Dual porosity mobile-immobile mass transfer;
- Combined equilibrium and kinetic sorption; and
- First-order transformation reactions.

The solution is capable of simulating general initial and boundary conditions, including:

- An initially contaminated domain;
- Specified concentration or flux-type inflow boundary conditions, with a general time-varying reservoir concentration; and
- A semi-infinite domain, or a finite domain with zero gradient of specified concentration at the outflow boundary.

The solution is evaluated by numerical inversion of the Laplace-transformed solution, using the accurate and robust algorithm of *De Hoog et al. (1982)*. The solution is coded in standard FORTRAN77 with updating to FORTRAN90. The code has been compiled without modifications with PC (MS, Lahey F77L3, Salford FTN77), VAX and UNIX-based compilers.

This version of the code has been extended to simplify the generation of concentration distributions at specified times (i.e., profiles) and concentration histories at specified locations (i.e., breakthrough curves). The code has also been modified to report dissolved concentrations in both the mobile and immobile regions.

2. Terminology

C_m : concentration in mobile region dissolved phase [ML^{-3}]

C_{im} : concentration in immobile region dissolved phase [ML^{-3}]

S_{m1} : concentration at instantaneous sorption sites in mobile region [MM^{-1}]

S_{m2} : concentration at rate-limited sorption sites in mobile region [MM^{-1}]

S_{im1} : concentration at instantaneous sorption sites in immobile region [MM^{-1}]

S_{im2} : concentration at rate-limited sorption sites in immobile region [MM^{-1}]

t : time elapsed since beginning of solute release [T]

p : Laplace transformed variable for time [T^{-1}]

x : distance from inflow boundary [L]

L : length of the domain for finite case [L]

ρ : bulk density of porous medium [ML^{-3}]

q : Darcy flux [LT^{-1}]

D : hydrodynamic dispersion coefficient [L^2T^{-1}]

θ : total water content [-]

ϕ : proportion of pore water that is mobile

$$\phi = \frac{\theta_m}{\theta}$$

θ_m : mobile water content [-] ($\theta_m = \phi \theta$)

θ_{im} : immobile water content [-] ($\theta_{im} = (1-\phi) \theta$)

f : mass fraction of sorbent in contact with the mobile region dissolved phase [-]

α : first-order mass transfer coefficient [T^{-1}]

- F_m : mobile region fraction of instantaneous sorption sites [-]
- F_{im} : immobile region fraction of instantaneous sorption sites [-]
- K_m : mobile region equilibrium sorption coefficient [L^3M^{-1}]
- K_{im} : immobile region equilibrium sorption coefficient [L^3M^{-1}]
- K_P : weighted-average sorption coefficient ($K_P = fK_m + (1-f)K_{im}$) [L^3M^{-1}]
- k_{m2} : mobile region first-order kinetic desorption coefficient [T^{-1}]
- k_{im2} : immobile region first-order kinetic desorption coefficient [T^{-1}]
- λ_m : mobile region dissolved phase first-order decay rate [T^{-1}]
- λ_{Sm1} : mobile region instantaneous sorption sites first-order decay coefficient [T^{-1}]
- λ_{Sm2} : mobile region rate-limited sorption sites first-order decay rate [T^{-1}]
- λ_{im} : immobile region dissolved phase first-order decay rate [T^{-1}]
- λ_{Sim1} : immobile region instantaneous sorption sites first-order decay rate [T^{-1}]
- λ_{Sim2} : immobile region rate-limited sorption sites first-order decay rate [T^{-1}]
- $C_0(t)$: solute concentration in inflow reservoir [ML^{-3}]
- δ : inflow boundary coefficient
 = 0 : Type I inflow boundary condition
 = 1 : Type 3 inflow boundary condition
- C_L : solute concentration in outflow reservoir [ML^{-3}], for a finite column with specified outflow concentration

3. Theory

3.1. Conceptual model

The theory implemented in the analytical solution is defined in *Brusseau et al.* [1989] and *Brusseau et al.* [1992] as the multiprocess nonequilibrium model (MPNE). A discussion of the conceptual model for the analytical solution is given in *Neville* [1992]. The physical system represented is shown in Figure 1. The solution is based on the following assumptions:

- The domain is represented as a dual porosity continuum. Mass transfer between the mobile and immobile regions is modelled as a first-order mass transfer reaction.
- Sorption occurs at both equilibrium and rate-limited sites. At the equilibrium sites, sorption is instantaneous and reversible and is governed by a linear isotherm. At the rate-limited sites, sorption is represented as a first-order reaction. The mobile and immobile regions are characterized by separate sorption properties.
- Transformation reactions are modelled as first-order decay processes. If microbially-mediated reactions are represented using this approach, then it is tacitly assumed that they are not limited by substrate availability (e.g. oxygen is in unlimited supply) and that contaminant concentrations are relatively low (*Criddle et al.* [1991]). For maximum generality, the dissolved and sorbed phases in the mobile and immobile regions are characterized by separate decay properties.
- The behaviour of the transformation products or their impact on the parent chemical are neglected.

Several additional assumptions are invoked for the derivation of the one-dimensional analytical solution presented here:

- The material properties are spatially uniform and temporally constant.
- The Darcy flux is steady, one-dimensional and spatially uniform. The solution has been revised to accommodate no Darcy flux.
- Longitudinal dispersion is assumed to be a Fickian process, characterized by a constant dispersion coefficient. Dispersion in the transverse directions is neglected.
- The initial concentrations in the domain are uniform and are specified separately for the dissolved and sorbed phases.

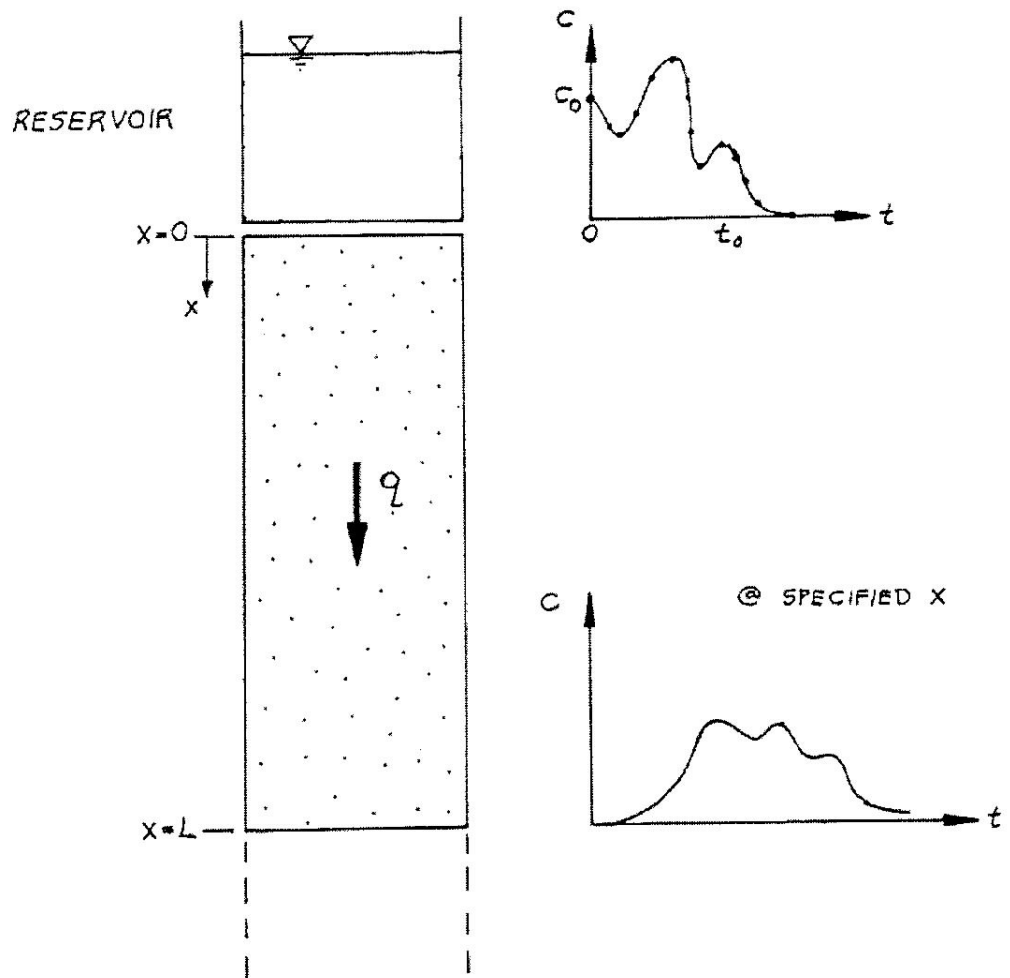


Figure 1. Definition sketch

3.2. Governing equations

The MPNE model is cast in terms of six concentrations: one dissolved phase and two sorbed phase concentrations for each of the mobile and immobile regions. In the following development, use is made of mass balance equations and constitutive relations to derive the six equations, which comprise the MPNE model.

Mobile region

Within the mobile region, the MPNE model accounts for advective-dispersive transport, mobile-immobile mass transfer, equilibrium and rate-limited sorption and first-order transformation reactions. The statement of mass conservation for the dissolved phase in the mobile region is written as:

$$\frac{\partial(\theta_m C_m)}{\partial t} + \frac{\partial(f\rho S_m)}{\partial t} = - \frac{\partial J_m}{\partial x} - G_{\lambda m} - G_{\lambda S_m} - G_{im}$$

The left-hand side of the mass balance equation represents the time rate of change of mass in the dissolved and sorbed phases in the mobile region. In this expression the term f designates the mass fraction of sorbent that is accessible to the dissolved phase in the mobile region. Solute in the sorbed phase is partitioned between the equilibrium and rate-limited sorption sites:

$$S_m = S_{m1} + S_{m2}$$

The first term on the right-hand side, J_m , is the advective-dispersive mass flux in the dissolved phase and is defined as:

$$J_m = -\theta_m D \frac{\partial C_m}{\partial x} + q C_m$$

For the first-order mass transfer model, the sink term representing mobile-immobile interaction is expressed as:

$$G_{im} = \alpha (C_m - C_{im})$$

The second and third terms on the right-hand side, $G_{\lambda m}$ and $G_{\lambda Sm}$, are sinks representing first-order transformation reactions in the dissolved and sorbed phases. The first-order transformation sink terms are written as:

$$G_{\lambda m} = \theta_m \lambda_m C_m$$

$$G_{Sm} = f\rho(\lambda_{Sm1}S_{m1} + \lambda_{Sm2}S_{m2})$$

Assembling all of the terms in the original mass balance equation yields:

$$\frac{\partial}{\partial t}(\theta_m C_m) + f\rho\left(\frac{\partial S_{m1}}{\partial t} + \frac{\partial S_{m2}}{\partial t}\right) = -\frac{\partial}{\partial x}(qC_m) + \frac{\partial}{\partial x}\left(\theta_m D \frac{\partial C_m}{\partial x}\right) - \theta_m \lambda_m C_m$$

The sorbed phase concentration at the instantaneous sorption sites is defined in terms of the following equilibrium constitutive relation:

$$S_{m1} = F_m K_m C_m$$

In this relation F_m represents the mass fraction of sorption sites in the mobile region where sorption is instantaneous. The sorbed phase concentration at the rate-limited sites is defined in terms of a mass balance equation:

$$\frac{\partial S_{m2}}{\partial t} = k_{m2}[(1 - F_m)K_m C_m - S_{m2}] - \lambda_{Sm2}S_{m2}$$

Substituting for the sorbed phase concentrations and invoking the assumption of constant material properties yields the final form of the transport equation for the mobile region:

$$\begin{aligned} (\theta_m + f\rho F_m K_m) \frac{\partial C_m}{\partial t} + f\rho k_2 [(1 - F_m)K_m C_m - S_{m2}] = \\ -q \frac{\partial C_m}{\partial x} + \theta_m D \frac{\partial^2 C_m}{\partial x^2} - (\theta_m \lambda_m + f\rho \lambda_{Sm1} F_m K_m) C_m - \alpha(C_m - C_{im}) \end{aligned}$$

Immobile region

The governing equations for the immobile region are analogous to those presented for the mobile region, with the exception that advection and dispersion are not considered. The statement of mass conservation for the immobile region is written as:

$$\frac{\partial(\theta_{im} C_{im})}{\partial t} + \frac{\partial((1-f)\rho S_{im})}{\partial t} = -G_{\lambda im} - G_{\lambda Sim} + G_{im}$$

The left-hand side of the mass balance equation represents the time rate of change of mass in the dissolved and sorbed phases in the immobile region. In this expression the term $(1-f)$ designates the mass fraction of sorbent that is accessible to the dissolved phase in the immobile region. Solute in the sorbed phase is partitioned between the equilibrium and rate-limited sorption sites:

$$S_{im} = S_{im1} + S_{im2}$$

The mobile-immobile mass transfer term, G_{im} , is defined by equation (6). The remaining terms on the right-hand side are written as:

$$G_{\lambda im} = \theta_{im} \lambda_{im} C_{im}$$

$$G_{\lambda Sim} = (1-f)\rho(\lambda_{Sim1} S_{im1} + \lambda_{Sim2} S_{im2})$$

In these expressions the term $(1-f)$ designates the mass fraction of sorbent that is accessible to the dissolved phase in the immobile region. The expressions for the sinks are similar to those presented for the mobile region, noting that the sign of the mobile-immobile mass transfer term is reversed.

Assembling all of the terms in the mass balance equation for the immobile region yields:

$$\frac{\partial}{\partial t}(\theta_{im} C_{im}) + (1-f)\rho\left(\frac{\partial S_{im1}}{\partial t} + \frac{\partial S_{im2}}{\partial t}\right) = -\theta_{im} \lambda_{im} C_{im}$$

The sorbed phase concentrations at the instantaneous and rate-limited sorption sites are defined by:

$$S_{im1} = F_{im} K_{im} C_{im}$$

$$\frac{\partial S_{im2}}{\partial t} = k_{im2} [(1 - F_{im}) K_{im} C_{im} - S_{im2}] - \lambda_{Sim2} S_{im2}$$

In these relations F_{im} represents the mass fraction of sorption sites in the immobile region where sorption is instantaneous. Substituting for the sorbed phase concentrations and invoking the assumption of constant material properties yields the final form of the transport equation for the immobile region:

$$\begin{aligned} (\theta_{im} + (1 - f) F_{im} K_{im}) \frac{\partial C_{im}}{\partial t} + (1 - f) k_{im2} [(1 - F_{im}) K_{im} C_{im} - S_{im2}] = \\ - (\theta_{im} \lambda_{im} + (1 - f) \rho \lambda_{Sim1} F_{im} K_{im}) C_{im} + \alpha (C_m - C_{im}) \end{aligned}$$

The governing equations presented here differ from equations (4) and (5) of *Brusseau et al.* [1992]. In particular, their equations are missing decay terms for the equilibrium-sorbed phases. The equations defining the concentrations in the equilibrium-sorbed phases are more correctly interpreted here as constitutive relations rather than mass balance equations.

3.3.Special cases

Special care has been taken to ensure that the analytical solution yields correct results when any or all of the MPNE processes are neglected.

Two-region model (Physical nonequilibrium only)

The solution collapses to the two-region model when only equilibrium sorption is considered (setting $F_m = F_{im} = 1.0$ in the governing equations).

Two-site model (Sorption nonequilibrium only)

The solution collapses to the two-site model when all of the pore water is considered to be mobile and all of the sorbent is accessible to the solute (setting $\phi = f = 1.0$ in the governing equations).

LEA (Local Equilibrium Assumption)

The solution collapses to the LEA (one-region/one-site) conceptual model when all of the pore water is considered to be mobile and all of the sorbent is accessible to the solute (i.e., $\phi = f = 1.0$) and when only equilibrium sorption is considered (i.e., $F_m = F_{im} = 1.0$).

3.3.Initial and boundary conditions

Initial conditions

The model of *Brusseau et al.* [1992] assumes that the domain is initially devoid of contaminants. The initial conditions considered by the analytical solution are somewhat more general. It is assumed that the domain is uniformly contaminated and that the initial concentrations in each of the compartments are specified independently:

$$C_m(x,0) = C_m^0$$

$$C_{im}(x,0) = C_{im}^0$$

$$S_{m2}(0) = S_{m2}^0$$

$$S_{im2}(0) = S_{im2}^0$$

If the initial condition of the domain is such that $C_m^0 \neq 0$, and has existed as such for a long period of time, then the following initial concentrations may be assigned:

$$C_m(x,0) = C_m^0$$

$$C_{im}(x,0) = C_{im}^0$$

$$S_{m2}(0) = K_m C_m^0$$

$$S_{im2}(0) = K_{im} C_{im}^0$$

Inflow boundary condition

The inflow boundary condition is represented by a general form capable of representing either specified concentration or specified mass flux conditions. Adopting the notation of *Leij et al.* [1991], the inflow boundary condition is expressed as:

$$qC_m(0,t) - \theta_m \delta D \frac{\partial C_m}{\partial x}(0,t) = qC_o(t)$$

where:

$\delta = 0$, specified concentration (Dirichlet) condition at the inflow boundary

$\delta = 1$, specified mass flux (Cauchy) condition at the inflow boundary

and

$C_o(t)$ = concentration in the influent reservoir

Outflow boundary condition

The analytical solution is capable of representing transport in either semi-infinite or finite domains.

A semi-infinite domain is specified by the following outflow boundary condition:

$$C_m(\infty, t) = C_m^0 \text{EXP}\{-\lambda_m t\}$$

In the original version of the solution, a finite domain could be specified with a Type II (specified-gradient) boundary condition at the outlet:

$$\frac{\partial C_m}{\partial x}(L, t) = 0$$

The solution has been revised to accommodate the additional case of a finite column with a Type I (specified-concentration) boundary condition at the outlet:

$$C_m(L, t) = C_L$$

4. Evaluation of the solution

The final solution is evaluated by numerical inversion of the analytical solution in Laplace-transform space. The inversion is carried out using the algorithm of *De Hoog et al.* (1982). Extensive testing of this algorithm indicates that it yields accurate and robust solutions.

The De Hoog et al. algorithm approximates the inverse Laplace transform in the form of a Fourier series according to the formula:

$$C_m(x, t) = \frac{1}{T} \text{EXP}\{at\} \times \text{Re} \left[\frac{\bar{C}_m(x, a)}{2} + \sum_{k=1}^{2M} \bar{C}_m(x, a + \frac{ik\pi t}{T}) \right]$$

The approximate inverse is a function of two parameters, T and a . The parameter T defines the period of the approximating Fourier series. Our experience indicates that the greatest accuracy is achieved when T is re-calculated for every time t according to the following formula:

$$T = 0.8t$$

The parameter a is related to the singularities in the transformed solution. Our implementation utilizes the estimator of Crump (1976):

$$a = \alpha - \frac{\ln(E_r)}{2T}$$

As implemented here, the inversion algorithm requires four inversion parameters, α , E_r , T , and the number of terms in the series, M . Following the suggestions of *De Hoog et al.* (1982) and our own extensive numerical experiments, the following parameter values are considered to be nearly optimal.

Parameter	Value
α	0.0
E_r	1.E-4
T	0.8 t
M	7

In order to simplify use of the solution, the parameters for the inversion are calculated internally within a "driver" subroutine for the main inversion subroutine. The parameters listed above are presently hard-wired in the inversion driver routine. The inversion code is attached here as a separate code to the analytical solution, using the Fortran INCLUDE statement. This simplifies the use of alternative inversion routines; for example, only minor modifications are required to use the inversion algorithms of Stehfest and Talbot.

5. Testing of the solution

The analytical solution has been tested against the results of other analytical and numerical solutions. For the simple cases without rate-limiting transport processes, the solution has been compared with exact analytical solutions for finite and semi-infinite domains. In all cases, the results obtained with MPNE1D matched the analytical solutions very closely. The results of these tests are not presented here, but are available upon request.

For the full implementation of the MPNE formulation, the solution is tested against previously published numerical simulations of the column experiments of van Genuchten (*van Genuchten* [1974], *van Genuchten and Wierenga* [1976] and [1977], *van Genuchten et al.* [1977]). *Brusseau et al.* [1989 and 1992] simulated the column experiments of van Genuchten using a one-dimensional finite difference implementation of the model. The numerical model employed centered-in-time weighting. In this report we reproduce Brusseau and co-workers' results for only one of the column experiments, #1-4. Figure 2 shows the results of the analytical solution and the numerical results of *Brusseau et al.* [1989] for the experiment. The results demonstrate excellent agreement between the present solution and the numerical solution.

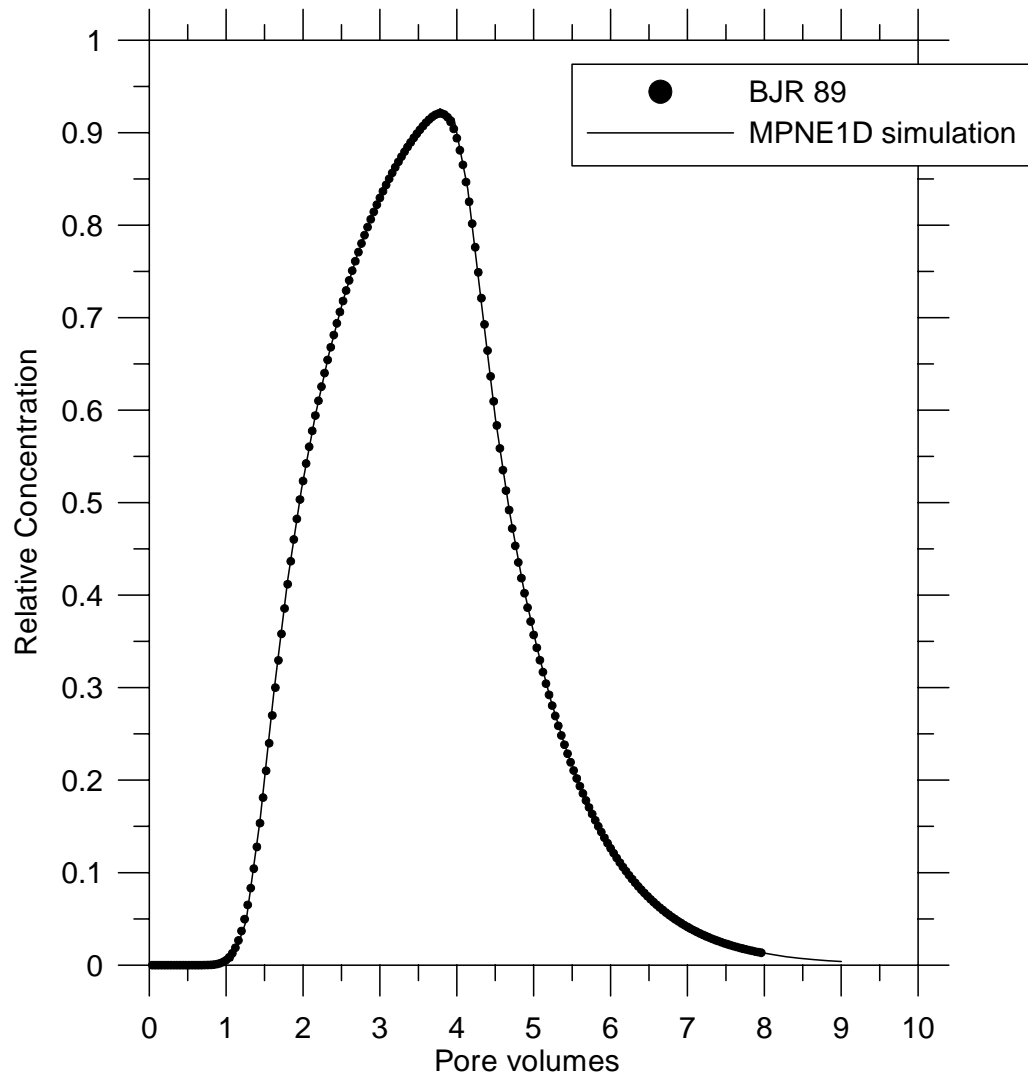


Figure 2. Benchmarking MPNE1D solution
van Genuchten (1974) : Expt. 1-4

6. Instructions for using the computer programs

6.1. Running the computer program

The source code can be compiled using any FORTRAN90 compiler. The executable version of the program distributed with this manual was generated with the Lahey LF90 compiler.

The code is most easily executed from the Command Line (also referred to as the DOS-prompt). At the DOS-prompt, type:

```
mpneld_41
```

The user is then prompted for the **JOBID**, which is the name of the data file - without any extension. The program automatically uses the following file names and extensions:

JOBID.inp	:	data file
JOBID.out	:	output listing, including a full listing of the input parameters
JOBID.dat	:	output listing for concentrations profiles or breakthrough curves stripped of all comments and headings (plot file).

All three of these files are ASCII files.

The plot file can be imported directly into any graphics or spreadsheet program for plotting. The format of the file is:

COL 1: time; **COL 2:** distance; **COL 3:** mobile concentration; **COL 4:** immobile concentration.

6.2. Input data file

All input is in free-format.

1. Basic data

1. TITLE: up to 70 alphanumeric characters
2. RHOB (ρ_b): dry bulk density [ML^{-3}]
3. THETA (θ): total water content [L^3L^{-3}]
4. Q (q): Darcy flux [LT^{-1}]
5. D (D): longitudinal dispersion coefficient [L^2T^{-1}]

2. MPNE parameters

6. PHI (ϕ): fraction of pore water that is mobile [-]
i.e., $\theta_m = \phi\theta$; $\theta_{im} = (1-\phi)\theta$
7. F (f): fraction of sorbent accessible to dissolved phase in mobile region [-]
8. ALFA (α): first-order mass transfer coefficient [T^{-1}]
9. FM (F_m): fraction of sites in mobile region where sorption is instantaneous [-]
10. FIM (F_{im}): fraction of sites in immobile region where sorption is instantaneous [-]
11. KM (K_m): sorption partitioning coefficient for mobile region [L^3M^{-1}]
12. KIM (K_{im}): sorption partitioning coefficient for immobile region [L^3M^{-1}]
13. KM2 (k_{m2}): sorption rate constant for mobile region [T^{-1}]
14. KIM2 (k_{im2}): sorption rate constant for immobile region [T^{-1}]

3. Decay parameters

- 15. LM (λ_m): decay rate, dissolved phase in mobile region [T^{-1}]
- 16. LM1 (λ_{Sm1}): decay rate, instantaneous sorption sites in mobile region [T^{-1}]
- 17. LM2 (λ_{Sm2}): decay rate, rate-limited sorption sites in mobile region [T^{-1}]
- 18. LIM (λ_{im}): decay rate, dissolved phase in immobile region [T^{-1}]
- 19. LIM1 (λ_{Sim1}): decay rate, instantaneous sorption sites in immobile region [T^{-1}]
- 20. LIM2 (λ_{Sim2}): decay rate, rate-limited sorption sites in immobile region [T^{-1}]

4. Boundary condition data

- 21. IBC: inflow boundary condition type
 - = 1: Type I - specified concentration ($\delta = 0$)
 - = 3: Type III - specified mass flux, well-mixed reservoir ($\delta = 1$)
- 22. NP: number of points defining inflow concentration history $c_0(0,t)$
- 23. TI(n), CI(n): (time, concentration) inflow concentration point; [T],[ML^{-3}]
 - time elapsed since start of injection
 - NP values, Specify one pair per line of the input file
- 24. OBC: outflow boundary condition
 - = 1: Semi-infinite domain
 - = 2: Finite domain, Type II
 - = 3: Finite domain, Type I
- 25. LENGTH: length of domain
 - A value must be supplied, but is used only when a finite domain is specified (OBC=2 or 3)
- 26. CL: concentration at outflow boundary, [ML^{-3}]
 - A value must be supplied, but is used only when a finite domain with Type I outflow boundary condition is specified (OBC=3)

5. Locations and times for calculation of solution

Note: This version of MPNE1D has been extended to simplify the calculation of concentration profiles at selected times, and the calculation of concentrations histories at selected locations (breakthrough curves). The input requirements have been modified slightly relative to previous versions of MPNE1D.

27. NPRO: number of times when a concentration profile is to be computed

28. xmin,xmax,dx: minimum x-coordinate where solution is computed [L]
 maximum x-coordinate where solution is computed [L]
 x-coordinate increment [L]

29. T(i): time since injection began [T]
 - NPRO values are specified, free-format

30. NBTC: number of times when a breakthrough curve is to be computed

31. tmin,tmax,dt: minimum time when solution is computed [T]
 maximum time when solution is computed [T]
 time increment [T]

32. X(i): distance along column [L]
 - NBTC values are specified, free-format

6.3. Specification of the inflow reservoir concentration history

The analytical solution is capable of simulating a general time-varying concentration in the influent reservoir. The inflow concentration history is represented as a discrete set of points, illustrated schematically in Figure 3. The computer program automatically converts the punctual history into a set of discrete steps, also shown in Figure 3.

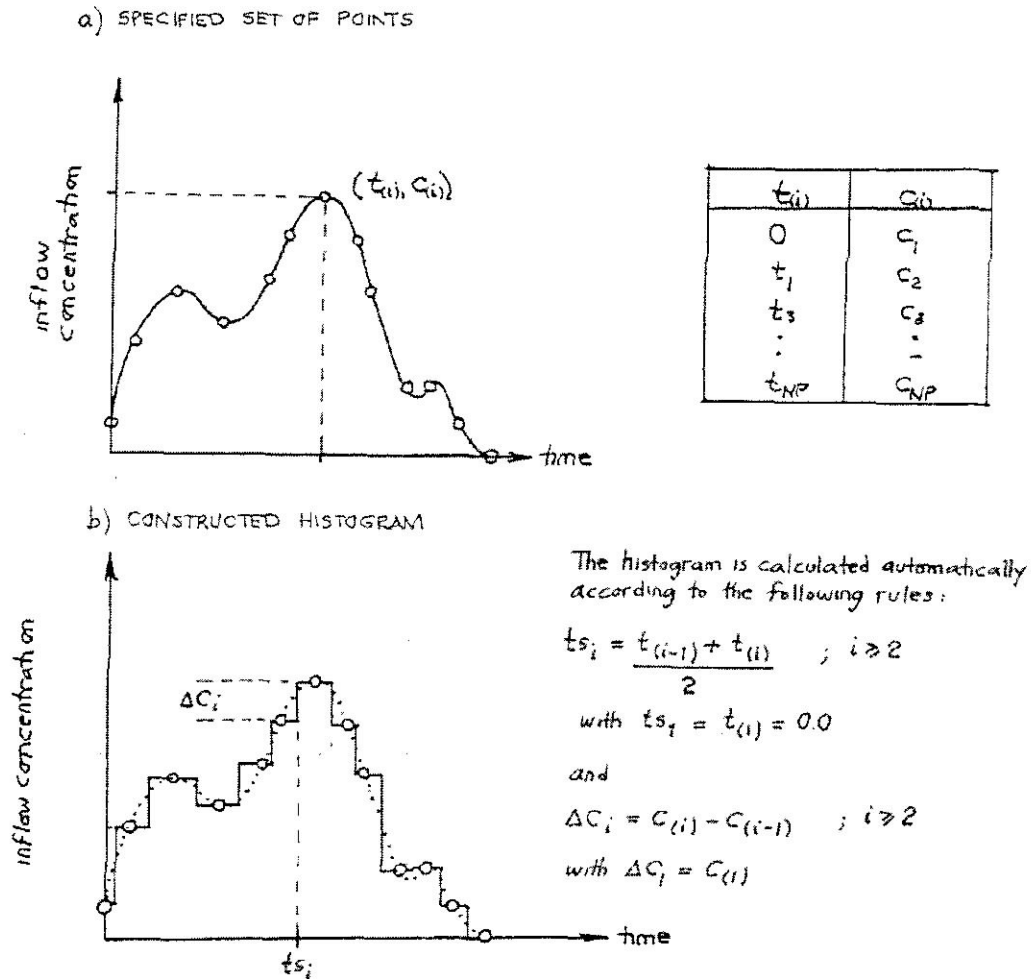


Figure 3. Representation of the inflow concentration history

To represent a concentration history that is already a set of steps it is necessary to "override" the program. The user must specify an artificial set of concentration history points that yield the desired history. The rules for specifying the artificial points are derived from the histogram generation rules shown in Figure 3.

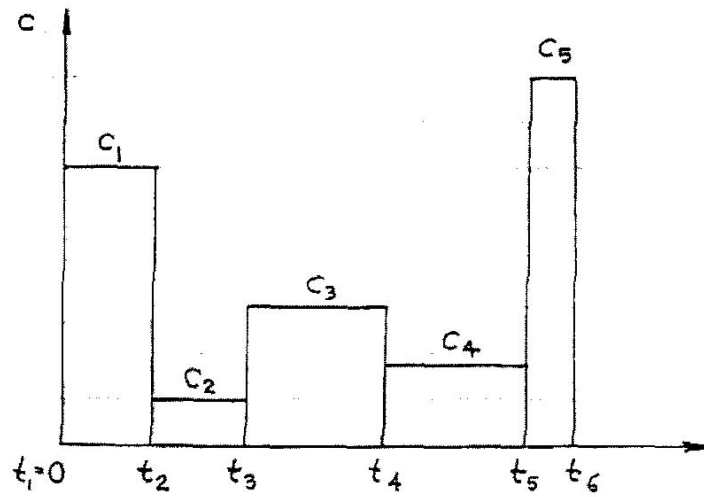
$$\textcircled{1} \quad t_{(1)} = 0.0$$

$$t_{(i)} = 2 \, t_{s_i} - t_{(i-1)} \quad ; \quad i \geq 2$$

$$\textcircled{2} \quad C_{(1)} = \Delta C_{(1)}$$

$$C_{(i)} = \sum_{j=1}^i \Delta C_{(j)} \quad ; \quad i \geq 2$$

The calculation of the required set of points for an arbitrary set of steps is indicated in Figure 4a. Special cases are illustrated in Figure 4b.



FOR AN ARBITRARY SET OF STEPS THE FOLLOWING
POINTS MUST BE SPECIFIED:

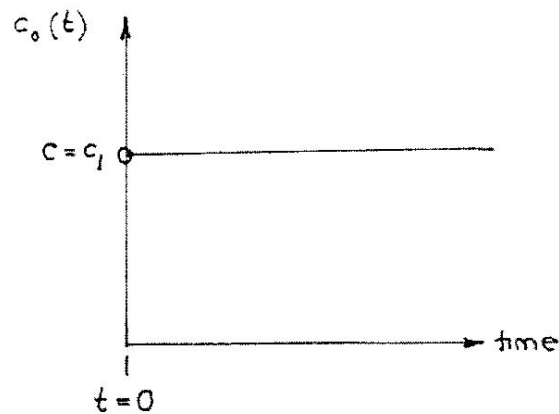
$t(i)$	$C(i)$
0	C_1
$2t_2 - t_{(1)} = 2t_2$	C_2
$2t_3 - t_{(2)} = 2(t_3 - t_2)$	C_3
$2t_4 - t_{(3)} = 2(t_4 - t_3 + t_2)$	C_4
$2t_5 - t_{(4)} = 2(t_5 - t_4 + t_3 - t_2)$	C_5
$2t_6 - t_{(5)} = 2(t_6 - t_5 + t_4 - t_3 + t_2)$	C_6

Figure 4a. Representation of a discrete inflow concentration history

SPECIAL CASES

1. CONSTANT CONCENTRATION

For a constant inflow concentration, the inflow concentration is specified by a single point:



2. FINITE DURATION PULSE

For a finite duration pulse the inflow concentration history is specified by two points:

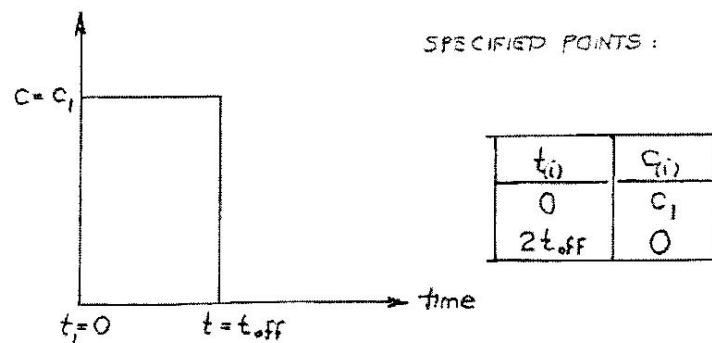


Figure 4b. Representation of a discrete inflow concentration history: Special cases

6.4. Example analysis

The use of the MPNE1D solution is demonstrated by reproducing the *Brusseau et al.* [1992] simulation of *van Genuchten* [1974] Experiment 3-5. The column experiment investigated the transport of the herbicide 2,4,5-D in the aggregated soil Glendale loam. Tritium was used as the conservative tracer. The sources of the input parameters for this simulation are reviewed in the following discussion.

(1) Basic data

The basic data for the simulation are taken from *van Genuchten* [1974]. These data correspond to the preliminary measurements required for any simulation.

Parameter		Value
1	bulk density: ρ_b	1.222 g/cm ³
2	total water content: θ	0.456
3	Darcy flux: q	3.975 cm/d
4	pulse period: t_o	9.653 d
5	column length: L	30.000 cm

(2) Dispersion coefficient, physical nonequilibrium parameters

The advective-dispersive transport parameters were estimated by fitting the breakthrough data from the tritium tracer. For short duration column experiments tritium may be assumed to be nonreactive. According to the conceptual model of multiprocess nonequilibrium, physical nonequilibrium affects both sorbing and nonsorbing solutes. Therefore, the tritium data can also be analysed to identify the characteristics of the mobile-immobile mass transfer processes, using a two-region model. The mass transfer coefficient obtained by fitting the tritium data is adjusted for 2,4,5-D to account for the different free-solution diffusion coefficients of the two solutes.

Parameter		Value
6	dispersion coefficient: D	5.313 cm ² /d
7	proportion of mobile pore water, ϕ	0.88
8	mass transfer coefficient: α	0.03 /d

(3) Sorption parameters

van Genuchten reported the results of batch sorption tests with 2,4,5-D. For this simulation, the mild nonlinearity of the observed sorption isotherm was accounted for by using a linearized sorption coefficient. It is assumed that the sorption coefficient is the same for the mobile and immobile regions, $K_m = K_{im}$.

A correlation with the batch sorption coefficient presented by *Brusseau et al.* [1992] is used to estimate the rate constant for nonequilibrium sorption. It is assumed that the mobile and immobile rate constants are the same, $k_{m2} = k_{im2}$.

The fractions of instantaneous sorption sites in the mobile and immobile regions are assigned the same assumed value, $F_m = F_{im} = 0.5$.

Finally, the proportion of sorption sites that are accessible to the solute in the mobile region is assumed to be equal to the proportion of the pore water that is mobile, i.e., $f = \phi = 0.88$.

Parameter		Value
9	sorption coefficient: K_m	0.426 cm ³ /g
10	sorption coefficient: K_{im}	0.426 cm ³ /g
11	sorption rate constant: k_{m2}	0.66 d ⁻¹
12	sorption rate constant: k_{im2}	0.66 d ⁻¹
13	fraction of equilibrium sorption sites: F_m	0.500
14	fraction of equilibrium sorption sites: F_{im}	0.500
15	fraction of mobile sorption sites: f	0.88

(4) Decay coefficients

Brusseau et al. [1992] estimated the decay coefficient for the dissolved phase in the mobile region. For the simulation it is assumed that decay only occurs in the dissolved phase in the mobile region.

Parameter		Value
16	decay coefficient: λ_m	0.058 /d
17	decay coefficient: λ_{Sm1}	-
18	decay coefficient: λ_{Sm2}	-
19	decay coefficient: λ_{im}	-
20	decay coefficient: λ_{Sim1}	-
21	decay coefficient: λ_{Sim2}	-

Results

The results of the analysis are plotted in Figure 5. The results shown indicate a good match to van Genuchten's experimental observations.

Listings of the contents of all files for this example are included in Appendix A3. The input file for the analysis is `expt35.inp`. The echo of the input parameters, calculation of dimensionless parameters, and annotated results are included in the output file `expt35.out`.

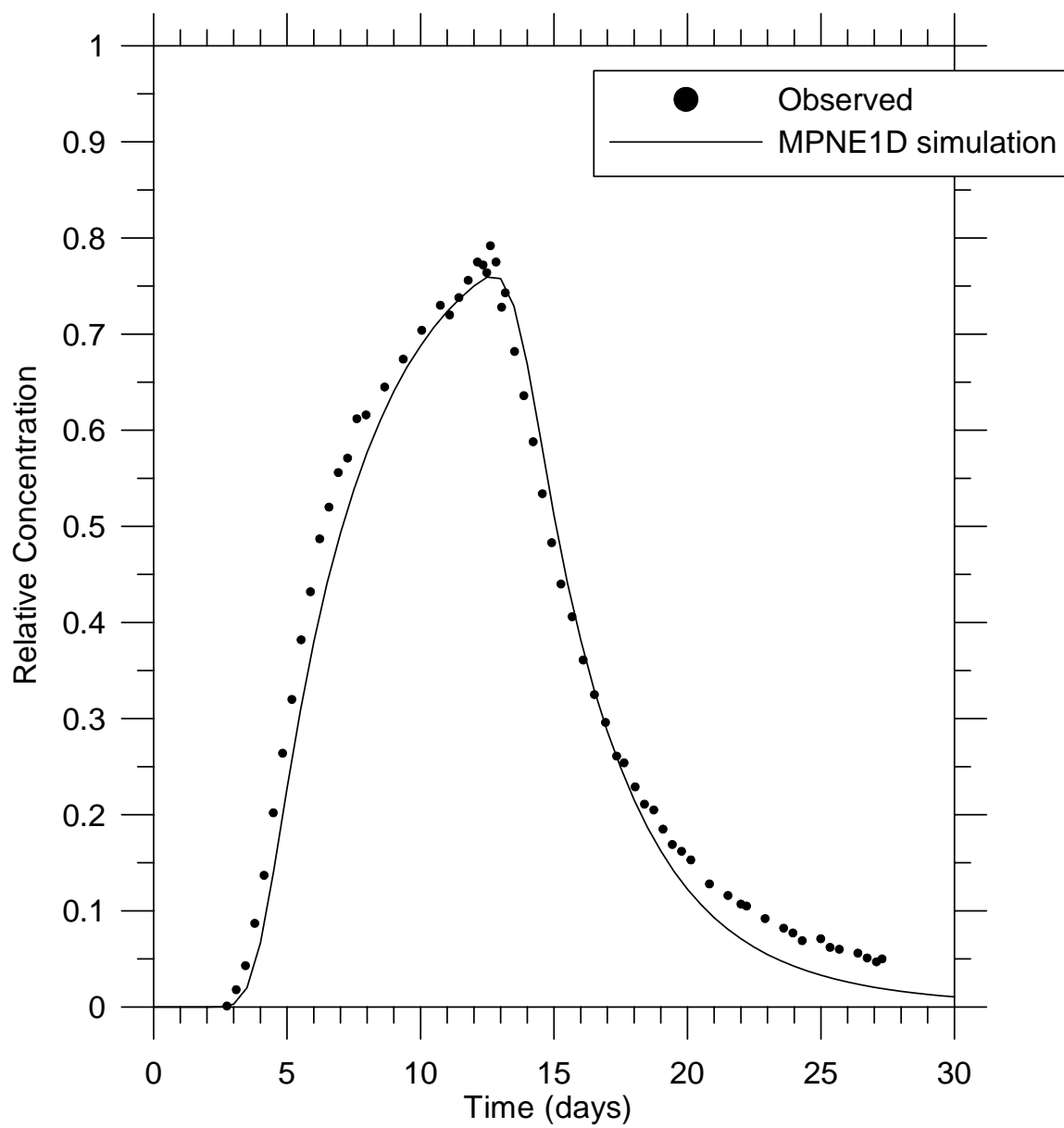


Figure 5. MPNE1D Example analysis
van Genuchten (1974) : Expt. 3-5

7. References

- Brusseau, M.L., R.E. Jessup and P.S.C. Rao, 1989: Modeling the transport of solutes influenced by multi-process nonequilibrium, *Water Resour. Res.*, 25(9), 1971-1988.
- Brusseau, M.L., R.E. Jessup and P.S.C. Rao, 1990: Correction to "Modeling the transport of solutes influenced by multi-process nonequilibrium", *Water Resour. Res.*, 26(1), 165.
- Brusseau, M.L., R.E. Jessup and P.S.C. Rao, 1992: Modeling solute transport influenced by multiprocess nonequilibrium and transformation reactions, *Water Resour. Res.*, 28(1), 175-182.
- Criddle, C.S., L.M. Alvarez, and P.L. McCarty, 1991: Microbial processes in porous media, in *Transport in Porous Media*, J. Bear and Y. Corapcioglu (eds.), NATO Series E - v. 202, Kluwer Academic Publishers, Dordrecht, 641-691.
- de Hoog, F.R., J.H. Knight, and A.N. Stokes, 1982: An improved method for numerical inversion of Laplace transforms, *SIAM Jl. Sci. Stat. Comput.*, 3(3), 357-366.
- Leij, F.J., T.H. Skaggs, and M. Th. van Genuchten, 1991: Analytical solutions for solute transport in three-dimensional semi-infinite porous media, *Water Resour. Res.*, 27(10), 2719-2733.
- Neville, C.J., M. Ibaraki, and E.A. Sudicky, 2000: Solute transport with multiprocess Nonequilibrium: A semi-analytical approach, *Journal of Contaminant Hydrology*, 44, 141-159.
- van Genuchten, M. Th., 1974: Mass transfer studies in sorbing porous media, Ph. D. thesis, New Mexico State University, Las Cruces, NM.
- van Genuchten, M. Th., and P.J. Wierenga, 1976: Mass transfer studies in sorbing porous media: I. Analytical solutions, *Soil Sci. Am. Jl.*, 40, 473-480.
- van Genuchten, M. Th., and P.J. Wierenga, 1977a: Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$), *Soil Sci. Am. Jl.*, 41, 272-278.
- van Genuchten, M. Th., P.J. Wierenga and G.A. O'Connor, 1977b: Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,4,5-T, *Soil Sci. Am. Jl.*, 41, 278-285.

8. Appendices

A1. Derivation of the analytical solution

A2. Source code listing

A3. Listing of files for the example problem (van Genuchten, 1974: Expt. 3-5)

A4. Paper by *Neville, Ibaraki and Sudicky (2000)*

MPNE1D 4.1 Documentation

Appendix A1: Derivation of the analytical solution

Analytical solution for one-dimensional transport with multiprocess nonequilibrium, v.4

1. GOVERNING EQUATIONS

1.1. MASS BALANCE IN MOBILE REGION

$$\begin{aligned} & \frac{\partial(\theta_m C_m)}{\partial t} + \theta_m \lambda_m C_m + f\rho \frac{\partial S_{m1}}{\partial t} + f\rho \lambda_{S_{m1}} S_{m1} \\ & + f\rho \frac{\partial S_{m2}}{\partial t} + f\rho \lambda_{S_{m2}} S_{m2} + \alpha(C_m - C_{im}) \\ & = - \frac{\partial}{\partial x} \left(-\theta_m D \frac{\partial C_m}{\partial x} + q C_m \right) \end{aligned}$$

1.2. MASS BALANCE IN IMMOBILE REGION

$$\begin{aligned} & \frac{\partial(\theta_{im} C_{im})}{\partial t} + \theta_{im} \lambda_{im} C_{im} + (1-f)\rho \frac{\partial S_{im1}}{\partial t} + (1-f)\rho \lambda_{S_{im1}} S_{im1} \\ & + (1-f)\rho \frac{\partial S_{im2}}{\partial t} + (1-f)\rho \lambda_{S_{im2}} S_{im2} - \alpha(C_m - C_{im}) = 0 \end{aligned}$$

1.3. INSTANTANEOUS SORPTION CONSTITUTIVE RELATIONS

$$S_{m1} = F_m K_m C_m$$

$$S_{im1} = F_{im} K_{im} C_{im}$$

1.4. RATE-LIMITED SORPTION EQUATIONS

$$\frac{\partial S_{m2}}{\partial t} + \lambda_{S_{m2}} S_{m2} = k_{m2} \left[(1-F_m) K_m C_m - S_{m2} \right] \quad \text{---}$$

$$\frac{\partial S_{im2}}{\partial t} + \lambda_{S_{im2}} S_{im2} = k_{im2} \left[(1-F_{im}) K_{im} C_{im} - S_{im2} \right] \quad \text{---}$$

— Substituting for S_{m1} and S_{m2} in the mass balance equation for the mobile region (1) :

$$\begin{aligned} & \frac{\partial (\theta_m C_m)}{\partial t} + \theta_m \lambda_m C_m + f_p \frac{\partial (F_m K_m C_m)}{\partial t} + f_p \lambda_{S_{m1}} F_m K_m C_m \\ & + f_p \left(k_{m2} \left[(1-F_m) K_m C_m - S_{m2} \right] \right) + \alpha (C_m - C_{im}) \\ & = - \frac{\partial}{\partial x} \left(- \theta_m D \frac{\partial C_m}{\partial x} + q C_m \right) \end{aligned}$$

Invoking the assumption of constant material properties this becomes :

$$\begin{aligned} & \theta_m \frac{\partial C_m}{\partial t} + \theta_m \lambda_m C_m + f_p F_m K_m \frac{\partial C_m}{\partial t} + f_p \lambda_{S_{m1}} F_m K_m C_m \\ & + f_p k_{m2} \left[(1-F_m) K_m C_m - S_{m2} \right] + \alpha (C_m - C_{im}) \\ & = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \end{aligned}$$

Collecting terms yields :

$$\begin{aligned}
 & \left(\theta_m + f_p F_m K_m \right) \frac{\partial C_m}{\partial t} + \left(\theta_m \lambda_m + f_p \lambda_{s_{m1}} F_m K_m \right) C_m \\
 & + f_p k_{m2} \left[(1-F_m) K_m C_m - S_{m2} \right] + \alpha (C_m - C_{im}) \\
 & = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x}
 \end{aligned}$$

— Substituting for S_{im1} and S_{im2} in the mass balance equation for the immobile region (2) :

$$\begin{aligned}
 & \frac{\partial (\theta_{im} C_{im})}{\partial t} + \theta_{im} \lambda_{im} C_{im} + (1-f) \rho \frac{\partial}{\partial t} (F_{im} K_{im} C_{im}) \\
 & + (1-f) \rho \lambda_{s_{im1}} F_{im} K_{im} C_{im} \\
 & + (1-f) \rho \left(k_{im2} \left[(1-F_{im}) K_{im} C_{im} - S_{im2} \right] \right) \\
 & - \alpha (C_m - C_{im}) = 0
 \end{aligned}$$

Invoking the assumption of constant material properties this becomes :

$$\begin{aligned}
 & \theta_{im} \frac{\partial C_{im}}{\partial t} + \theta_{im} \lambda_{im} C_{im} + (1-f) \rho F_{im} K_{im} \frac{\partial C_{im}}{\partial t} \\
 & + (1-f) \rho \lambda_{sim} F_{im} K_{im} C_{im} \\
 & + (1-f) \rho k_{imz} \left[(1-F_{im}) K_{im} C_{im} - S_{imz} \right] \\
 & - \alpha (C_m - C_{im}) = 0
 \end{aligned}$$

Collecting terms yields :

$$\begin{aligned}
 & \left(\theta_{im} + (1-f) \rho F_{im} K_{im} \right) \frac{\partial C_{im}}{\partial t} + \left(\theta_{im} \lambda_{im} + (1-f) \rho \lambda_{sim} F_{im} K_{im} \right) C_{im} \\
 & + (1-f) \rho k_{imz} \left[(1-F_{im}) K_{im} C_{im} - S_{imz} \right] = \alpha (C_m - C_{im})
 \end{aligned}$$

—(6)

Equations (5), (6), (4a) and (4b) comprise the set of equations governing 1D advective-dispersive transport with multiprocess nonequilibrium.

2. BOUNDARY CONDITIONS

The initial concentrations are specified as :

$$C_m(x, 0) = C_m^0 \quad \text{---(7a)}$$

$$C_{im}(x, 0) = C_{im}^0 \quad \text{---(7b)}$$

$$S_{m2}(0) = S_{m2}^0 \quad \text{---(7c)}$$

$$S_{im2}(0) = S_{im2}^0 \quad \text{---(7d)}$$

The boundary conditions are specified as :

(i) INFLOW BOUNDARY

$$q C_m(0, t) - \Theta_m \delta D \frac{\partial C_m(0, t)}{\partial x} = q C_o(t) \quad \text{---(7e)}$$

where : $C_o(t)$ is a general time-varying concentration history in the influent reservoir

- For $\delta = 0$, (7e) reduces to a Type I inflow boundary condition :

$$C_m(0, t) = C_o(t)$$

- For $\delta = 1$, (7e) reduces to a Type III inflow boundary condition, for a well-mixed reservoir :

$$q C_m(0, t) - \Theta_m D \frac{\partial C_m(0, t)}{\partial x} = q C_o(t)$$

→ These two cases presume that $q \neq 0.0$

When $q = 0.0$ we replace (7e) by :

$$\delta = 0 : C_m(0, t) = C_o(t)$$

$$\delta = 1 : \frac{\partial C_m(0, t)}{\partial x} = 0.0$$

(ii) OUTFLOW BOUNDARY:

a) SEMI-INFINITE

$$C_m(\infty, t) = C_m^0 \exp\{-\lambda_m t\} \quad \text{---(7f)}$$

b) FINITE, TYPE II

$$\frac{\partial C_m}{\partial x}(L, t) = 0 \quad \text{---(7g)}$$

b2) FINITE, TYPE I

$$C_m(L, t) = C_L \quad \text{---(7h)}$$

3. ANALYTICAL SOLUTION IN THE LAPLACE DOMAIN

1. Applying the Laplace transform to the advection-dispersion equation :

$$\begin{aligned}
 & (\theta_m + f_p F_m K_m) \left[p \bar{C}_m - C_m(x, 0) \right] \\
 & + (\theta_m \lambda_m + f_p \lambda_{m1} F_m K_m + f_p k_{m2} (1 - F_m) K_m) \bar{C}_m \\
 & - f_p k_{m2} \bar{S}_{m2} + \alpha (\bar{C}_m - \bar{C}_{1m}) \\
 & = \theta_m D \frac{d^2 \bar{C}_m}{dx^2} - q \frac{d \bar{C}_m}{dx}
 \end{aligned}$$

Substituting in the initial conditions and collecting terms :

$$\begin{aligned}
 & \frac{d^2 \bar{C}_m}{dx^2} - \frac{q}{\theta_m D} \frac{d \bar{C}_m}{dx} - \frac{1}{\theta_m D} \left[p (\theta_m + f_p F_m K_m) \right. \\
 & \left. + \theta_m \lambda_m + f_p \lambda_{m1} F_m K_m + f_p k_{m2} (1 - F_m) K_m + \alpha \right] \bar{C}_m \\
 & = - \frac{1}{\theta_m D} \left[(\theta_m + f_p F_m K_m) C_m^0 + f_p k_{m2} \bar{S}_{m2} + \alpha \bar{C}_{1m} \right]
 \end{aligned}$$

→ The Laplace-transformed boundary conditions are :

$$q \bar{C}_m(0, p) - \theta_m \delta D \frac{d\bar{C}_m(0, p)}{dx} = q \bar{C}_0(p)$$

$$\bar{C}_m(\infty, p) = \frac{1}{p + \lambda_m} C_m^0 \quad \left[\text{SEMI-INFINITE} \right] \quad \text{---(9)}$$

$$\frac{d\bar{C}_m(L, p)}{dx} = 0 \quad \left[\text{FINITE} \right] \quad \text{---(9)}$$

2. Applying the Laplace transform to the mobile-immobile mass transfer reaction :

$$(\theta_{1m} + (1-f)\rho F_{1m} K_{1m}) [p \bar{C}_{1m} - C_{1m}(x, 0)]$$

$$+ (\theta_{1m} \lambda_{1m} + (1-f)\rho \lambda_{1m1} F_{1m} K_{1m} + (1-f)\rho k_{1m2} (1-F_{1m}) K_{1m}) \bar{C}_{1m}$$

$$- (1-f)\rho k_{1m2} \bar{S}_{1m2} = \alpha (\bar{C}_m - \bar{C}_{1m})$$

Substituting in the initial conditions and collecting terms :

$$\alpha (\bar{C}_m - \bar{C}_{1m}) = \left[p (\theta_{1m} + (1-f)\rho F_{1m} K_{1m}) + \theta_{1m} \lambda_{1m} \right.$$

$$\left. + (1-f)\rho \lambda_{1m1} F_{1m} K_{1m} + (1-f)\rho k_{1m2} (1-F_{1m}) K_{1m} \right] \bar{C}_{1m}$$

$$- (1-f)\rho k_{1m2} \bar{S}_{1m2} - (\theta_{1m} + (1-f)\rho F_{1m} K_{1m}) C_{1m}^0$$

Re-arranging :

$$\begin{aligned}
 & \left[p(\theta_{im} + (1-f)p F_m K_{im}) + \theta_{im} \lambda_{im} + (1-f)p \lambda_{sm} F_m K_{im} \right. \\
 & \left. + (1-f)p k_{imz} (1-F_m) K_{im} + \alpha \right] \bar{C}_m \\
 & = \alpha \bar{C}_m + (1-f)p k_{imz} \bar{S}_{mz} + (\theta_{im} + (1-f)p F_m K_{im}) C_{im}^0
 \end{aligned} \tag{10}$$

3. Applying the Laplace transform to the equations for the rate-limited sorption sites :

(i)

$$\left[p \bar{S}_{mz} - S_{mz}(0) \right] + \lambda_{smz} \bar{S}_{mz} = k_{mz} \left[(1-F_m) K_m \bar{C}_m - \bar{S}_{mz} \right]$$

Substituting in the initial conditions and solving for \bar{S}_{mz} yields :

$$\bar{S}_{mz} = \frac{k_{mz} (1-F_m) K_m \bar{C}_m + S_{mz}^0}{p + \lambda_{smz} + k_{mz}} \quad \text{---(11)}$$

(ii)

$$\left[p \bar{S}_{imz} - S_{imz}(0) \right] + \lambda_{simz} \bar{S}_{imz} = k_{imz} \left[(1-F_{im}) K_{im} \bar{C}_{im} - \bar{S}_{imz} \right]$$

Substituting in the initial conditions and solving for \bar{S}_{imz} yields :

$$\bar{S}_{imz} = \frac{k_{imz} (1-F_{im}) K_{im} \bar{C}_{im} + S_{imz}^0}{p + \lambda_{simz} + k_{imz}} \quad \text{---(12)}$$

4. Substituting for \bar{S}_{imz} in the solution for \bar{C}_{im} (ie. (12) \rightarrow (10)) yields :

$$\begin{aligned} & \left[p \left(\theta_{im} + (1-f) \rho F_{im} K_{im} \right) + \theta_{im} \lambda_{im} + (1-f) \rho \lambda_{sim} F_{im} K_{im} \right. \\ & \left. + (1-f) \rho k_{imz} (1-F_{im}) K_{im} + \alpha \right] \bar{C}_{im} \\ & = \alpha \bar{C}_{im} + (1-f) \rho k_{imz} \left(\frac{k_{imz} (1-F_{im}) K_{im} \bar{C}_{im} + S_{imz}^0}{p + \lambda_{simz} + k_{imz}} \right) \\ & \quad + \left(\theta_{im} + (1-f) \rho F_{im} K_{im} \right) C_{im}^0 \end{aligned}$$

Collecting terms in \bar{C}_{im} :

$$\begin{aligned} & \left[p \left(\theta_{im} + (1-f) \rho F_{im} K_{im} \right) + \theta_{im} \lambda_{im} + (1-f) \rho \lambda_{sim} F_{im} K_{im} \right. \\ & \left. + (1-f) \rho (1-F_{im}) K_{im} k_{imz} \cdot \frac{p + \lambda_{simz}}{p + k_{imz} + \lambda_{simz}} + \alpha \right] \bar{C}_{im} \\ & = \alpha \bar{C}_{im} + \frac{(1-f) \rho k_{imz}}{p + k_{imz} + \lambda_{simz}} S_{imz}^0 + \left(\theta_{im} + (1-f) \rho F_{im} K_{im} \right) C_{im}^0 \end{aligned}$$

Solving for \bar{C}_{im} :

$$\bar{C}_{im} = \frac{\alpha}{\left[p(\theta_{im} + (1-f)e F_{im} K_{im}) + \theta_{im} \lambda_{im} + (1-f)e \lambda_{sim} F_{im} K_{im} \right.} \cdot \bar{C}_m$$

$$\left. + (1-f)e (1-F_{im}) K_{im} k_{imz} \cdot \frac{p + \lambda_{simz}}{p + k_{imz} + \lambda_{simz}} + \alpha \right] + G_1^o \quad \text{---(13)}$$

where :

$$G_1^o = \frac{(1-f)e k_{imz} S_{imz}^o + (\theta_{im} + (1-f)e F_{im} K_{im}) C_{im}^o}{p + k_{imz} + \lambda_{simz}}$$

$$\left[p(\theta_{im} + (1-f)e F_{im} K_{im}) + \theta_{im} \lambda_{im} + (1-f)e \lambda_{sim} F_{im} K_{im} \right.$$

$$\left. + (1-f)e (1-F_{im}) K_{im} k_{imz} \cdot \frac{p + \lambda_{simz}}{p + k_{imz} + \lambda_{simz}} + \alpha \right] \quad \text{---(14)}$$

5. Substituting for \bar{C}_{1m} and \bar{S}_{m2} in the transformed advection-dispersion equation (ie. (13), (11) \rightarrow (8)) yields :

$$\begin{aligned}
 & \frac{d^2 \bar{C}_m}{dx^2} - \frac{q}{\theta_m D} \frac{d \bar{C}_m}{dx} - \frac{1}{\theta_m D} \left[p(\theta_m + f_p F_m K_m) \right. \\
 & \quad \left. + \theta_m \lambda_m + f_p \lambda_{sm} F_m K_m + f_p k_{m2} (1 - F_m) K_m + \alpha \right] \bar{C}_m \\
 & = - \frac{1}{\theta_m D} \left\{ (\theta_m + f_p F_m K_m) C_m^0 \right. \\
 & \quad \left. + f_p k_{m2} \left(\frac{k_{m2} (1 - F_m) K_m \bar{C}_m + S_{m2}^0}{p + k_{m2} + \lambda_{sm2}} \right) \right. \\
 & \quad \left. + \alpha \left(\frac{\alpha}{\left[p(\theta_{1m} + (1-f)p F_{1m} K_{1m}) + \theta_{1m} \lambda_{1m} + (1-f)p \lambda_{s1m} F_{1m} K_{1m} \right. \right. \right. \\
 & \quad \left. \left. + (1-f)p (1 - F_{1m}) K_{1m} k_{1m2} \cdot \frac{p + \lambda_{s1m2}}{p + k_{1m2} + \lambda_{s1m2}} + \alpha \right] \right. \right. \\
 & \quad \left. \left. + G_1^0 \right) \right\} \bar{C}_m
 \end{aligned}$$

DEFINE :

$$G_2^0 = (\theta_m + f_p F_m K_m) C_m^0 + \frac{f_p k_{mz}}{p + k_{mz} + \lambda_{smz}} S_{mz}^0 \quad \text{---(1)}$$

THEREFORE, COLLECTING TERMS, THE GOVERNING EQUATION BECOMES :

$$\begin{aligned} \frac{d^2 \bar{C}_m}{dx^2} - \frac{\gamma}{\theta_m D} \frac{d \bar{C}_m}{dx} - \frac{1}{\theta_m D} & \left\{ p(\theta_m + f_p F_m K_m) \right. \\ & + \theta_m \lambda_m + f_p \lambda_{sm1} F_m K_m + f_p (1-F_m) K_m k_{mz} \frac{(p + \lambda_{smz})}{p + k_{mz} + \lambda_{smz}} + \alpha \\ & \left. - \frac{\alpha^2}{\left[p(\theta_{1m} + (1-f)p F_{1m} K_{1m}) + \theta_{1m} \lambda_{1m} + (1-f)p \lambda_{s1m1} F_{1m} K_{1m} \right.} \right. \\ & \left. \left. + (1-f)p (1-F_{1m}) K_{1m} k_{1mz} \frac{(p + \lambda_{s1mz})}{p + k_{1mz} + \lambda_{s1mz}} + \alpha \right] \right\} \bar{C}_m \\ & = - \frac{1}{\theta_m D} \left[G_2^0 + \alpha G_1^0 \right] \quad \text{---(16)} \end{aligned}$$

— THE GOVERNING EQUATION WILL BE RE-WRITTEN IN MORE COMPACT FORM USING NOTATION INSPIRED BY STAUFFER AND HATFIELD (1992).

DEFINING THE FOLLOWING TERMS :

$$\Gamma_1 = \left(1 + \frac{f_p F_m K_m}{\theta_m} \right) p \quad \text{---(17)}$$

$$\Gamma_2 = \frac{1}{\theta_m} \left(f_p (1-F_m) K_m \cdot \frac{k_{mz} (p + \lambda_{smz})}{p + k_{mz} + \lambda_{smz}} \right) \quad \text{---(18)}$$

$$\Gamma_3 = \frac{1}{\theta_m} \left(\frac{\alpha \gamma - \alpha^2}{\gamma} \right) \quad \text{---(19)}$$

$$\Gamma_4 = \lambda_m + \frac{f\rho}{\theta_m} \lambda_{sm1} F_m K_m \quad \text{---(20)}$$

with :

$$\begin{aligned} \gamma = & \rho(\theta_{1m} + \rho(1-f)F_{1m}K_{1m}) + \theta_{1m}\lambda_{1m} + (1-f)\rho\lambda_{s1m1}F_{1m}K_{1m} \\ & + \rho(1-f)(1-F_{1m})K_{1m}k_{1m2} \frac{(\rho + \lambda_{s1m2})}{\rho + k_{1m2} + \lambda_{s1m2}} + \alpha \end{aligned} \quad \text{---(20)}$$

SUBSTITUTING INTO THE GOVERNING EQUATION YIELDS :

$$\begin{aligned} \frac{d^2 \bar{C}_m}{dx^2} - \frac{q}{\theta_m D} \frac{d \bar{C}_m}{dx} - \frac{1}{D} \left[\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 \right] \bar{C}_m \\ = - \frac{1}{\theta_m D} \left[G_2^0 + \alpha G_1^0 \right] \end{aligned}$$

DEFINING $B^* = \Theta_m [\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4]$

The governing equation becomes :

$$\begin{aligned} \frac{d^2 \bar{C}_m}{dx^2} - \frac{a}{\Theta_m D} \frac{d \bar{C}_m}{dx} - \frac{B^*}{\Theta_m D} \bar{C}_m \\ = - \frac{1}{\Theta_m D} [\alpha G_1^0 + G_2^0] \end{aligned}$$

—(2)

6. The transformed advection-dispersion equation for the mobile region is a linear, non-homogeneous, ordinary differential equation.

The general solution for \bar{C}_m can be expressed as the sum of a complementary and a particular solution:

$$\bar{C}_m = \bar{C}_H + \bar{C}_p \quad \text{---(22)}$$

where:

\bar{C}_H = solution of the corresponding homogeneous (complementary or auxiliary) differential equation

\bar{C}_p = particular solution for the non-homogeneous problem

(i) Homogeneous solution

The homogeneous differential equation has the following general solution:

$$\bar{C}_H = E_1 \exp\{H_1 x\} + E_2 \exp\{H_2 x\} \quad \text{---(23)}$$

$$\text{where: } H_1 = \frac{q - \sqrt{q^2 + 4B^*\theta_m D}}{2\theta_m D} \quad \text{---(24a)}$$

$$H_2 = \frac{q + \sqrt{q^2 + 4B^*\theta_m D}}{2\theta_m D} \quad \text{---(24b)}$$

(ii) Particular solution

The particular solution is derived using the method of operators :

$$\bar{C}_p = \text{EXP}\{-p_1, x\} \int^x \text{EXP}\{p_1, \xi\} \left[\text{EXP}\{-p_2, \xi\} \int^{\xi} \text{EXP}\{p_2, \chi\} f(\chi) d\chi \right] d\xi \quad \text{---(25)}$$

here : $p_1 = H_1$

$p_2 = H_2$

$$f(x) = -\frac{1}{\theta_m D} \left[\alpha G_1^0 + G_2^0 \right] \equiv K$$

Therefore, substituting into the expression for the particular solution we obtain :

$$\begin{aligned} \bar{C}_p &= \text{EXP}\{-H_1, x\} \int^x \text{EXP}\{H_1, \xi\} \left[\text{EXP}\{-H_2, \xi\} \int^{\xi} \text{EXP}\{H_2, \chi\} K d\chi \right] d\xi \\ &= K \text{EXP}\{-H_1, x\} \int^x \text{EXP}\{H_1, \xi\} \left[\text{EXP}\{-H_2, \xi\} \right. \\ &\quad \left. \cdot \frac{1}{H_2} \text{EXP}\{H_2, \xi\} \right] d\xi \\ &= \frac{K}{H_2} \text{EXP}\{-H_1, x\} \int^x \text{EXP}\{H_1, \xi\} d\xi \\ &= \frac{K}{H_1 H_2} \end{aligned}$$

Now, substituting for H_1 and H_2 and K :

$$\begin{aligned}\bar{c}_p &= -\frac{\theta_m D}{B^*} \left[-\frac{1}{\theta_m D} (\alpha G_1^0 + G_2^0) \right] \\ &= \frac{(\alpha G_1^0 + G_2^0)}{B^*}\end{aligned}$$

— (2)

— Assembling the complementary and the particular solutions, the general solution becomes:

$$\begin{aligned}\bar{c}_m &= E_1 \exp\{H_1 x\} + E_2 \exp\{H_2 x\} \\ &+ \frac{(\alpha G_1^0 + G_2^0)}{B^*}\end{aligned}$$

— (27)

The coefficients E_1 and E_2 are now evaluated by considering the boundary conditions.

7. TRANSFORMED BOUNDARY CONDITIONS

Re-calling the transformed inflow and outflow boundary conditions from (9a) and (9b):

(i) INFLOW (from 7e)

$$q \bar{C}_m(0, p) - \theta_m \delta D \frac{d\bar{C}_m(0, p)}{dx} = q \bar{C}_0(p)$$

(ii) OUTFLOW :

a. SEMI-INFINITE (from 7f)

$$\bar{C}_m(\infty, p) = \frac{1}{p + \lambda_m} C_m^0$$

b. FINITE, TYPE II (from 7g)

$$\frac{d\bar{C}_m(L, p)}{dx} = 0$$

c. FINITE, TYPE I (from 7h)

$$\bar{C}_m(L, p) = \frac{C_L}{p}$$

8.1. SOLUTION FOR THE SEMI-INFINITE CASE

— Considering the outflow boundary first :

$$\bar{C}_m(\infty, p) = \frac{C_m^0}{p + \lambda_m} = E_1 \text{EXP}\{H_1 x\} + E_2 \text{EXP}\{H_2 x\} \Big|_{x \rightarrow \infty} + \frac{(\alpha G_1^0 + G_2^0)}{B^*}$$

In order for the solution to be bounded we must have :

$$E_2 = 0$$

Therefore, the general solution reduces to :

$$\bar{C}_m = E_1 \text{EXP}\{H_1 x\} + \frac{(\alpha G_1^0 + G_2^0)}{B^*}$$

— In order to evaluate the inflow boundary condition we require the derivative of the general solution :

$$\frac{d\bar{C}_m}{dx} = E_1 H_1 \text{EXP}\{H_1 x\}$$

Substituting for \bar{c}_m and $d\bar{c}_m/dx$ in the inflow boundary condition we obtain:

$$\begin{aligned} & q \left[E_1 \exp\{H_1 x\} + \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right]_{x=0} \\ & - \theta_m \delta D \left[E_1 H_1 \exp\{H_1 x\} \right]_{x=0} \\ & = q \bar{C}_0(p) \end{aligned}$$

Simplifying:

$$\begin{aligned} & q \left[E_1 + \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right] - \theta_m \delta D E_1 H_1 \\ & = q \bar{C}_0(p) \end{aligned}$$

Collecting terms in E_1 :

$$\begin{aligned} E_1 \left[q - \theta_m \delta D H_1 \right] & = q \bar{C}_0(p) \\ & - q \frac{(\alpha G_1^0 + G_2^0)}{B^*} \end{aligned}$$

Solving for E_1 :

$$E_1 = \frac{q}{q - \Theta_m \delta DH_1} \left[\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right]$$

Finally, substituting into the general solution yields:

$$\bar{C}_m = \left(\frac{q}{q - \Theta_m \delta DH_1} \left[\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right] \right) \text{EXP}\{H_1 x\} + \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*}$$

CJN

2004/AUG/18

This solution presumes $q \neq 0.0$.

For $q = 0.0$, the solution accommodates the case of $\delta = 1$ and the inflow boundary condition collapses to a Type II condition:

$$\frac{\partial C_m(0,t)}{\partial x} = 0.0$$

For the case of $\delta = 0$, a Type I boundary condition, the transformed inflow boundary condition is replaced by:

$$\bar{C}_m(0,p) = \bar{C}_o(p)$$

Evaluating the general solution at $x = 0$:

$$\bar{C}_m(0,p) = E_1 \text{EXP}\{H_1 x\} + \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \Big|_{x=0} = \bar{C}_o(p)$$

Solving for E_1 :

$$E_1 = \bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*}$$

Finally, substituting for E_1 in the general solution:

$$\bar{C}_m = \left[\bar{C}_0(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right] \text{EXP}\{H_1 x\} + \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*}$$

Solution for a semi-infinite domain and $q = 0.0$

8.2. SOLUTION FOR THE FINITE CASE, TYPE II B.C.

Differentiating the general solution w.r.t. x :

$$\frac{d\bar{C}_m}{dx} = E_1 H_1 \exp\{H_1 x\} + E_2 H_2 \exp\{H_2 x\}$$

— The transformed inflow boundary condition becomes:

$$q \cdot \bar{C}_0(p)$$

$$= q \left[E_1 \exp\{H_1 x\} + E_2 \exp\{H_2 x\} + \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right]_{x=0}$$

$$- \Theta_m \delta D \left[E_1 H_1 \exp\{H_1 x\} + E_2 H_2 \exp\{H_2 x\} \right]_{x=0}$$

Evaluating the boundary condition yields :

$$q \bar{C}_0(p) = q \left[E_1 + E_2 + \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right]$$

$$- \Theta_m \delta D \left[E_1 H_1 + E_2 H_2 \right]$$

Collecting terms in E_1 and E_2 :

$$\begin{aligned} & (q - \Theta_m \delta D H_1) E_1 + (q - \Theta_m \delta D H_2) E_2 \\ & = q \bar{C}_o(p) - q \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \end{aligned}$$

— The transformed outflow boundary condition is :

$$\left. \frac{dC_m}{dx} \right|_L = \left[E_1 H_1 \exp\{H_1 x\} + E_2 H_2 \exp\{H_2 x\} \right]_{x=L} = 0$$

Evaluating this expression at $x=L$ yields :

$$E_1 H_1 \exp\{H_1 L\} + E_2 H_2 \exp\{H_2 L\} = 0$$

— The coefficients E_1 and E_2 are evaluated using Cramer's rule.

Writing the equations for E_1 and E_2 in matrix form:

$$\begin{bmatrix} q - \Theta_m \delta D H_1 & q - \Theta_m \delta D H_2 \\ H_1 \text{EXP}\{H_1 L\} & H_2 \text{EXP}\{H_2 L\} \end{bmatrix} \begin{Bmatrix} E_1 \\ E_2 \end{Bmatrix} = \begin{bmatrix} q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) \\ 0 \end{bmatrix}$$

Defining the following determinants:

$$D_1 = \begin{vmatrix} q - \Theta_m \delta D H_1 & q - \Theta_m \delta D H_2 \\ H_1 \text{EXP}\{H_1 L\} & H_2 \text{EXP}\{H_2 L\} \end{vmatrix}$$

$$= H_2 (q - \Theta_m \delta D H_1) \text{EXP}\{H_2 L\} - H_1 (q - \Theta_m \delta D H_2) \text{EXP}\{H_1 L\}$$

$$D_2 = \begin{vmatrix} q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) & q - \Theta_m \delta D H_2 \\ 0 & H_2 \text{EXP}\{H_2 L\} \end{vmatrix}$$

$$= q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) H_2 \text{EXP}\{H_2 L\}$$

$$D_3 = \begin{vmatrix} q - \theta_m \delta D H_1 & q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) \\ H_1 \text{EXP}\{H_1 L\} & 0 \end{vmatrix}$$

$$= -q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) H_1 \text{EXP}\{H_1 L\}$$

Using these determinants, the coefficients are given by:

$$E_1 = \frac{D_2}{D_1}$$

$$E_2 = \frac{D_3}{D_1}$$

Therefore, the final solution becomes:

$$\begin{aligned} \bar{C}_m = & \frac{D_2}{D_1} \text{EXP}\{H_1 x\} + \frac{D_3}{D_1} \text{EXP}\{H_2 x\} \\ & + \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \end{aligned}$$

— (2)

CJN
2004/AUG/18

This solution presumes that $q \neq 0.0$

If $q = 0.0$, then the solution will fail
for the case of $\delta = 0$ (Type I inflow boundary condition).

For this case the transformed inflow boundary
condition is:

$$\bar{C}_m(0, p) = \bar{C}_o(p)$$

Evaluating the general solution at $x = 0$:

$$\bar{C}_m(0, p) = E_1 \exp\{H_1 x\} + E_2 \exp\{H_2 x\}$$

$$+ \frac{(\alpha G_1^o + G_2^o)}{B^*} \Big|_{x=0} = \bar{C}_o(p)$$

This reduces to:

$$E_1 + E_2 + \frac{(\alpha G_1^o + G_2^o)}{B^*} = \bar{C}_o(p)$$

$$\rightarrow E_1 + E_2 = \bar{C}_o(p) - \frac{(\alpha G_1^o + G_2^o)}{B^*}$$

The matrix form of the solution for E_1 and E_2 becomes:

$$\begin{bmatrix} 1 & 1 \\ H_1 \exp\{H_1 L\} & H_2 \exp\{H_2 L\} \end{bmatrix} \begin{Bmatrix} E_1 \\ E_2 \end{Bmatrix} = \begin{Bmatrix} \bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \\ 0 \end{Bmatrix}$$

The solution has the same general form as was derived for $q \neq 0.0$, with the following determinants:

$$D_1 = H_2 \exp\{H_2 L\} - H_1 \exp\{H_1 L\}$$

$$D_2 = \left[\bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right] H_2 \exp\{H_2 L\}$$

$$D_3 = - \left[\bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right] H_1 \exp\{H_1 L\}$$

8.3. SOLUTION FOR THE FINITE CASE, TYPE I B.C.

Differentiating the general solution w.r.t. x :

$$\frac{d\bar{C}_m}{dx} = E_1 H_1 \exp\{H_1 x\} + E_2 H_2 \exp\{H_2 x\}$$

— The transformed inflow boundary conditions become:

$$q \cdot \bar{C}_0(p)$$

$$= q \left[E_1 \exp\{H_1 x\} + E_2 \exp\{H_2 x\} + \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right]_{x=0}$$

$$- \theta_m \delta D \left[E_1 H_1 \exp\{H_1 x\} + E_2 H_2 \exp\{H_2 x\} \right]_{x=0}$$

Evaluating the boundary condition yields:

$$q \bar{C}_0(p) = q \left[E_1 + E_2 + \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right]$$

$$- \theta_m \delta D \left[E_1 H_1 + E_2 H_2 \right]$$

Collecting terms in E_1 and E_2 :

$$(q - \theta_m \delta DH_1) E_1 + (q - \theta_m \delta DH_2) E_2$$

$$= q \bar{C}_0(p) - q \frac{(\alpha G_1^0 + G_2^0)}{B^*}$$

- The transformed outflow condition is :

$$\bar{C}_m(L, t) = \left[E_1 \exp\{H_1 x\} + E_2 \exp\{H_2 x\} + \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right]_{x=L}$$

$$= \frac{C_L}{P}$$

Evaluating this expression at $x=L$ yields :

$$E_1 \exp\{H_1 L\} + E_2 \exp\{H_2 L\} + \frac{(\alpha G_1^0 + G_2^0)}{B^*} = \frac{C_L}{P}$$

- The coefficients E_1 and E_2 are evaluated using Cramer's rule.

Writing the equations for E_1 and E_2 in matrix form:

$$\begin{bmatrix} q - \theta_m \delta DH_1 & q - \theta_m \delta DH_2 \\ \text{EXP}\{H_1 L\} & \text{EXP}\{H_2 L\} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \end{bmatrix} = \begin{bmatrix} q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) \\ \frac{C_L}{P} - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \end{bmatrix}$$

Defining the following determinants:

$$D_4 = \begin{vmatrix} q - \theta_m \delta DH_1 & q - \theta_m \delta DH_2 \\ \text{EXP}\{H_1 L\} & \text{EXP}\{H_2 L\} \end{vmatrix}$$

$$= (q - \theta_m \delta DH_1) \text{EXP}\{H_2 L\} - (q - \theta_m \delta DH_2) \text{EXP}\{H_1 L\}$$

$$D_5 = \begin{vmatrix} q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) & q - \theta_m \delta DH_2 \\ \frac{C_L}{P} - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} & \text{EXP}\{H_2 L\} \end{vmatrix}$$

$$= q \left(\bar{C}_o(p) - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) \text{EXP}\{H_2 L\}$$

$$- \left(\frac{C_L}{P} - \frac{(\alpha G_1^\circ + G_2^\circ)}{B^*} \right) (q - \theta_m \delta DH_2)$$

$$D_6 = \begin{vmatrix} q - \theta_m \delta DH_1 & q \left(\bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right) \\ \text{EXP}\{H_1 L\} & \frac{C_L}{P} - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \end{vmatrix}$$

$$= (q - \theta_m \delta DH_1) \left(\frac{C_L}{P} - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right) - q \left(\bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right) \text{EXP}\{H_1 L\}$$

Using these determinants, the coefficients E_1 and E_2 are given by :

$$E_1 = \frac{D_5}{D_4}$$

$$E_2 = \frac{D_6}{D_4}$$

Therefore, the final solution becomes :

$$\bar{C}_m = \frac{D_5}{D_4} \text{EXP}\{H_1 x\} + \frac{D_6}{D_4} \text{EXP}\{H_2 x\} + \frac{(\alpha G_1^0 + G_2^0)}{B^*}$$

—————(29B)

GDN

2004/
AUG/18

The solution presumes that $q \neq 0.0$

If $q = 0.0$, the solution will fail for the case of $\delta = 0$ (Type I inflow boundary condition).

For this case the transformed inflow boundary condition is:

$$\bar{C}_m(0, p) = \bar{C}_o(p)$$

Evaluating the general solution at $x = 0$:

$$\bar{C}_m(0, p) = E_1 \text{EXP}\{H_1 x\} + E_2 \text{EXP}\{H_2 x\}$$

$$+ \left. \frac{(\alpha G_1^o + G_2^o)}{B^*} \right|_{x=0} = \bar{C}_o(p)$$

This reduces to:

$$E_1 + E_2 + \frac{(\alpha G_1^o + G_2^o)}{B^*} = \bar{C}_o(p)$$

$$\rightarrow E_1 + E_2 = \bar{C}_o(p) - \frac{(\alpha G_1^o + G_2^o)}{B^*}$$

The matrix form of the solution for E_1 and E_2 becomes:

$$\begin{bmatrix} 1 & 1 \\ \text{EXP}\{H_1 L\} & \text{EXP}\{H_2 L\} \end{bmatrix} \begin{Bmatrix} E_1 \\ E_2 \end{Bmatrix} = \begin{Bmatrix} \bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \\ \frac{C_L}{P} - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \end{Bmatrix}$$

The solution has the same general form as was derived for $q \neq 0.0$, with the following determinants:

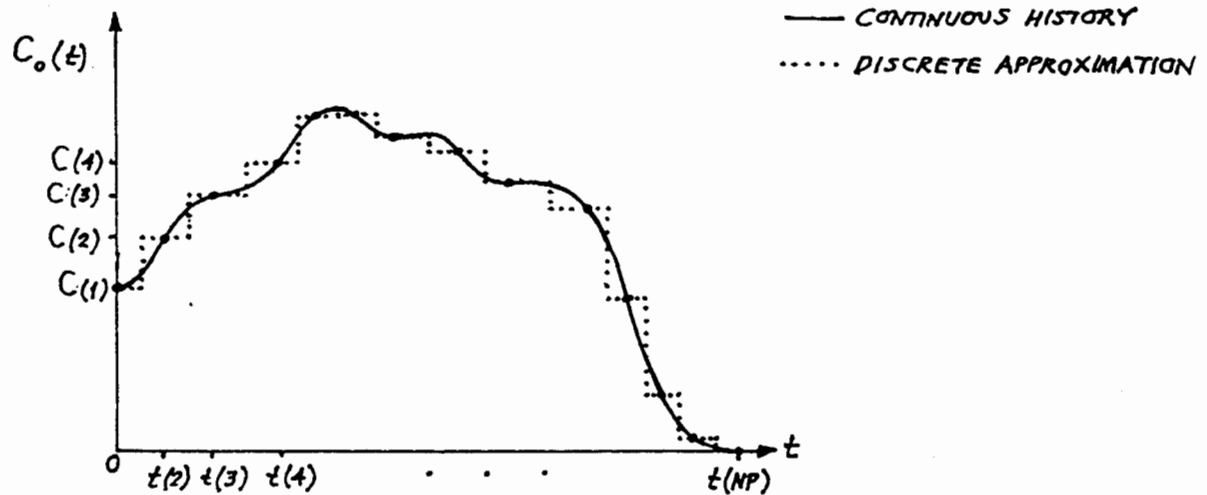
$$D_4 = \text{EXP}\{H_2 L\} - \text{EXP}\{H_1 L\}$$

$$D_5 = \left[\bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right] \text{EXP}\{H_2 L\} - \left[\frac{C_L}{P} - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right]$$

$$D_6 = \left[\frac{C_L}{P} - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right] - \left[\bar{C}_0(p) - \frac{(\alpha G_1^0 + G_2^0)}{B^*} \right] \text{EXP}\{H_1 L\}$$

9. INFLOW CONCENTRATION HISTORY, $C_o(t)$

Consider a general time-varying inflow concentration represented as a set of steps:



$$C_o(t) = \Delta C_1 + \Delta C_2 H(t-t_2) + \Delta C_3 H(t-t_3) + \dots$$

$$= \sum_{i=1}^{NP} \Delta C_i H(t-t_i)$$

—(30)

where $H(t-t_i)$ is the Heaviside step function, defined as

$$H(t-\tau) = \begin{cases} 0 & \text{if } t < \tau \\ 1 & \text{if } t > \tau \end{cases}$$

— The starting times for each change in the influent reservoir concentration are:

$$t_1 = t(1) = 0 \quad ; \quad \Delta C_1 = C(1)$$

$$t_2 = \frac{t(2) + t(1)}{2} \quad ; \quad \Delta C_2 = C(2) - C(1)$$

$$t_3 = \frac{t(3) + t(2)}{2} \quad ; \quad \Delta C_3 = C(3) - C(2)$$

⋮

$$t_{NP} = \frac{t(NP) + t(NP-1)}{2} \quad ; \quad \Delta C_{NP} = C(NP) - C(NP-1)$$

- Applying the Laplace transform to the inflow concentration history :

$$\bar{C}_o(p) = \sum_{i=1}^{NP} \Delta C_i \times \frac{1}{p} \text{EXP} \{-pt_i\} \quad \text{---(31)}$$

MPNE1D 4.1 Documentation

Appendix A2: Source code listing

```

PROGRAM MPNE1D
C *****
C ****
C ****
C ****
C ****
C ****
C ****
C ****
C *****
C
C
C DESCRIPTION
C =====
C ANALYTICAL SOLUTION FOR 1-D ADVECTIVE-DISPERSIVE TRANSPORT
C WITH MULTI-PROCESS NON-EQUILIBRIUM SORPTION.
C (1) DIMENSIONAL SOLUTION
C (2) FIRST-ORDER DECAY REACTIONS
C (3) NON-ZERO INITIAL CONCENTRATIONS
C (4) TYPE I or TYPE III INFLOW BOUNDARY CONDITION WITH
C TIME-VARYING INFLOW CONCENTRATION
C (5) SEMI-INFINITE OR FINITE COLUMN, WITH TYPE I OR TYPE II
C OUTFLOW BOUNDARY CONDITION
C
C REF: BRUSSEAU, M.L., R.E. JESSUP, AND P.S.C. RAO,
C MODELING SOLUTE TRANSPORT INFLUENCED BY MULTIPROCESS
C NONEQUILIBRIUM AND TRANSFORMATION REACTIONS.
C WATER RESOURCES RESEARCH, 28(1), 175-182, 1992.
C
C DEVELOPMENT HISTORY
C =====
C VERSION 1 : C.J. NEVILLE 1992/03
C VERSION 2 : CJN 1992/09
C UPDATED : CJN 1992/09/29
C : CJN 1993/03/16
C : CJN 1993/06/10
C : CJN 1998/11/19
C VERSION 3 : CJN 2000/08
C VERSION 3.1 : CJN 2002/01,
C with modifications for Fortran90 by J.P. KEIZER
C VERSION 3.2 : CJN 2003/01
C VERSION 4.1 : CJN 2004/08/24
C
C DEFINITION OF INPUT PARAMETERS
C =====
C Rhob : BULK DENSITY (M/L**3)
C THETA : TOTAL WATER CONTENT (L**3/L**3)
C Q : DARCY FLUX (L/T)
C D : HYDRODYNAMIC DISPERSION COEFFICIENT (L**/T)
C PHI : PROPORTION OF PORE WATER THAT IS MOBILE
C F : MASS FRACTION OF SORBENT COMPRISING MOBILE REGION (-)
C ALfa : FIRST-ORDER MASS TRANSFER COEFFICIENT (1/T)
C FM : FRACTION OF SORBENT IN MOBILE REGION FOR WHICH SORPTION
C IS INSTANTANEOUS
C FIM : FRACTION OF SORBENT IN IMMOBILE REGION FOR WHICH SORPTION IS
C INSTANTANEOUS
C KM : EQUILIBRIUM SORPTION CONSTANT IN MOBILE REGION (L**3/M)
C KIM : EQUILIBRIUM SORPTION CONSTANT IN IMMOBILE REGION (L**3/M)
C km2 : FIRST-ORDER SORPTION KINETIC COEFF. FOR MOBILE REGION (1/T)

```



```

C      kim2      : FIRST-ORDER SORPTION KINETIC COEFF. FOR IMMOBILE REGION (1/T)
C      LM        : FIRST-ORDER DECAY CONSTANT FOR MOBILE REGION (1/T)
C      LM1       : FIRST-ORDER DECAY CONSTANT FOR INSTANTANEOUS SORPTION
C                  SITES IN MOBILE REGION (1/T)
C      LM2       : FIRST-ORDER DECAY CONSTANT FOR RATE-LIMITED SORPTION
C                  SITES IN MOBILE REGION (1/T)
C      LIM       : FIRST-ORDER DECAY CONSTANT FOR IMMOBILE REGION (1/T)
C      LIM1      : FIRST-ORDER DECAY CONSTANT FOR INSTANTANEOUS SORPTION
C                  SITES IN IMMOBILE REGION (1/T)
C      LIM2      : FIRST-ORDER DECAY CONSTANT FOR RATE-LIMITED SORPTION
C                  SITES IN IMMOBILE REGION (1/T)
C      IBC       : INFLOW BOUNDARY CONDITION
C                  = 1 : TYPE I      (DIRICHLET)
C                  = 3 : TYPE III (CAUCHY)
C      NP        : NUMBER OF POINTS DESCRIBING INFLOW CONCENTRATION HISTORY
C      TI,CI     : INFLOW CONCENTRATION HISTORY POINT
C      OBC       : OUTFLOW BOUNDARY CONDITION
C                  = 1 : SEMI-INFINITE DOMAIN
C                  = 2 : FINITE DOMAIN, TYPE II
C                  = 3 : FINITE DOMAIN, TYPE I
C      LENGTH    : LENGTH OF THE DOMAIN (USED ONLY FOR FINITE DOMAIN)
C      CL        : CONCENTRATION AT OUTFLOW BOUNDARY FOR FINITE DOMAIN-TYPE I
C      CM0       : INITIAL CONCENTRATION IN MOBILE REGION DISSOLVED PHASE
C      CIM0      : INITIAL CONCENTRATION IN IMMOBILE REGION DISSOLVED PHASE
C      SM20      : INITIAL CONCENTRATION IN MOBILE REGION RATE-LIMITED
C                  SORBED PHASE
C      SIM20     : INITIAL CONCENTRATION IN THE MOBILE REGION RATE-LIMITED
C                  SORBED PHASE
C      XX        : DISTANCE FROM COLUMN INLET (L)
C      XMIN      : MINIMUM DISTANCE OF INTEREST (L)
C      XMAX      : MAXIMUM DISTANCE OF INTEREST (L)
C      DX        : DISTANCE INCREMENT (L)
C      T         : TIME SINCE START OF TRANSPORT (T)
C      TMIN      : MINIMUM TIME OF INTEREST (T)
C      TMAX      : MAXIMUM TIME OF INTEREST (T)
C      DT        : TIME INCREMENT (T)
C
C      DECLARATION OF VARIABLES
C      =====
C      IMPLICIT NONE
C      INTEGER MAXPT,MAXP,MAXB
C      PARAMETER(MAXPT=50,MAXP=100,MAXB=100)
C      DOUBLE PRECISION PARAM(19)
C      DOUBLE PRECISION CM0,CIM0,SM20,SIM20,DELTA,LENGTH
C      DOUBLE PRECISION CL
C      DOUBLE PRECISION TI(MAXPT),CI(MAXPT),TS(MAXPT),DELC(MAXPT)
C      DOUBLE PRECISION RHOB,THETA,Q,D,PHI,F,ALFA,FM,FIM,
1      KM,KIM,KM2,KIM2,LM,LM1,LM2,LIM,LIM1,LIM2
C      DOUBLE PRECISION R,P,OMEGA,BETA(4),KM0,KIM0,EM1,EM2,EIM1,EIM2
C      DOUBLE PRECISION XMIN,XMAX,DX,XX,XB(MAXB)
C      DOUBLE PRECISION TMIN,TMAX,DT,TIME,TP(MAXP)
C      DOUBLE PRECISION CM,CIM
C      INTEGER IBC,OBC,NP,I,J,N,LENFIL
C      INTEGER NPRO,NXP,NBTC,NTB
C      INTEGER IC
C      CHARACTER*70 JOBID,TITLE

```

```

COMMON /ICS/CM0,CIM0,SM20,SIM20
COMMON /BCS/TIME,DELTA,TS,DELC,NP,OBC,LENGTH,CL,XX
COMMON /MPNE/PARAM
COMMON /CSWITCH/IC

C
C OPEN INPUT, OUTPUT AND PLOT FILES
C =====
WRITE(*,*) 'input JOBID for file definitions: '
READ(*,100) JOBID
WRITE(*,*)

C
LENFIL=INDEX(JOBID,' ')-1

C
OPEN(UNIT=55,FILE=JOBID(:LENFIL)//'.inp',STATUS='OLD')
OPEN(UNIT=66,FILE=JOBID(:LENFIL)//'.out',STATUS='UNKNOWN')
OPEN(UNIT=67,FILE=JOBID(:LENFIL)//'.dat',STATUS='UNKNOWN')

C
C READ TITLE OF SIMULATION
C =====
READ(55,100) TITLE

C
C READ INPUT PARAMETERS
C =====
C BASIC PROBLEM DATA
C -----
READ(55,*) Rhob
READ(55,*) THETA
READ(55,*) Q
READ(55,*) D

C
C MPNE DATA
C -----
READ(55,*) PHI
READ(55,*) F
READ(55,*) ALFA
READ(55,*) FM
READ(55,*) FIM
READ(55,*) KM
READ(55,*) KIM
READ(55,*) KM2
READ(55,*) KIM2

C
C FIRST-ORDER DECAY COEFFICIENTS
C -----
READ(55,*) LM
READ(55,*) LM1
READ(55,*) LM2
READ(55,*) LIM
READ(55,*) LIM1
READ(55,*) LIM2

C
C INFLOW BOUNDARY CONDITION DATA
C -----
READ(55,*) IBC
READ(55,*) NP
READ(55,*) (TI(N),CI(N), N=1,NP)

```

```

C      OUTFLOW BOUNDARY CONDITION DATA
C      -----
C      READ(55,*) OBC
C      READ(55,*) LENGTH      ! used only for OBC=2 or 3
C      READ(55,*) CL          ! used only for OBC=3
C
C      INITIAL CONCENTRATIONS
C      -----
C      READ(55,*) CM0
C      READ(55,*) CIM0
C      READ(55,*) SM20
C      READ(55,*) SIM20
C
C      OUTPUT SPECIFICATIONS
C      -----
C      READ(55,*) NPRO
C      IF(NPRO.GT.0) THEN
C          READ(55,*) xmin,xmax,dx
C          READ(55,*) (TP(I),I=1,NPRO)
C      END IF
C
C      READ(55,*) NBTC
C      IF(NBTC.GT.0) THEN
C          READ(55,*) tmin,tmax,dt
C          READ(55,*) (XB(I),I=1,NBTC)
C      END IF
C
C      ECHO INPUT PARAMETERS
C      =====
C      WRITE(66,210)
C      WRITE(66,211) TITLE
C      WRITE(66,220) Rhob,THETA,Q,D
C      WRITE(66,221) PHI,F,ALFA,FM,FIM,KM,KIM,KM2,KIM2
C      WRITE(66,222) LM,LM1,LM2,LIM,LIM1,LIM2
C      WRITE(66,231) CM0,CIM0,SM20,SIM20
C
C      SET INFLOW BOUNDARY CONDITION
C      =====
C      IF(IBC.EQ.3) THEN
C          DELTA = 1.D0                ! TYPE III INFLOW B.C.
C      ELSE
C          DELTA = 0.D0                ! TYPE I INFLOW B.C.
C      END IF
C
C      "LOAD" MPNE PARAMETER ARRAY
C      =====
C      PARAM( 1) = RHOB
C      PARAM( 2) = THETA
C      PARAM( 3) = Q
C      PARAM( 4) = D
C      PARAM( 5) = PHI
C      PARAM( 6) = F
C      PARAM( 7) = ALFA
C      PARAM( 8) = FM
C      PARAM( 9) = FIM
C      PARAM(10) = KM
C      PARAM(11) = KIM

```

```

PARAM(12) = KM2
PARAM(13) = KIM2
PARAM(14) = LM
PARAM(15) = LM1
PARAM(16) = LM2
PARAM(17) = LIM
PARAM(18) = LIM1
PARAM(19) = LIM2

C
C CALCULATE DIMENSIONLESS PARAMETERS
C =====
R = 1.D0+(RHOB/THETA)*(f*KM+(1.D0-f)*KIM)
P = Q*length/(PHI*THETA*D)

C
IF(DABS(Q).GT.0.D0) THEN
    OMEGA = alfa*length/Q
ELSE
    OMEGA = 1.D6
END IF

C
BETA(1) = (PHI+(F*Rhob/THETA)*FM*KM)/R
BETA(2) = ((F*Rhob/THETA)*(1.D0-FM)*KM)/R
BETA(3) = (1.D0-PHI+((1.D0-F)*Rhob/THETA)*FIM*KIM)/R
BETA(4) = (((1.D0-F)*Rhob/THETA)*(1.D0-FIM)*KIM)/R

C
IF(DABS(Q).GT.0.D0) THEN
    KM0 = (KM2*length*THETA/Q)*(R*BETA(2))
    KIM0 = (KIM2*length*THETA/Q)*(R*BETA(4))

C
    EM1 = (length*THETA/Q)*((PHI*LM)+(F*RHOB*LM1*FM*KM/THETA))
    EM2 = (length*THETA/Q)*(F*RHOB*(1.D0-FM)*KM*LM2/THETA)
    EIM1 = (length*THETA/Q)*(((1.D0-PHI)*LIM)
1      +((1.D0-F)*RHOB*LIM1*FIM*KIM/THETA))
    EIM2 = (length*THETA/Q)*((1.D0-F)*RHOB
1      *(1.D0-FIM)*KIM*LIM2/THETA)
ELSE
    KM0 = 1.D6
    KIM0 = 1.D6

C
    EM1 = 1.D6
    EM2 = 1.D6
    EIM1 = 1.D6
    EIM2 = 1.D6
END IF

C
C PRINT OUT COMPUTED DIMENSIONLESS PARAMETERS
C -----
WRITE(66,240) R,P,OMEGA,KM0,KIM0
WRITE(66,241) (BETA(I),I=1,4)
WRITE(66,242) EM1,EM2,EIM1,EIM2

C
C CALCULATE INFLOW CONCENTRATION HISTORY
C =====
ts(1) = ti(1)
delc(1) = ci(1)
if(np.gt.1) then
    do n=2,np

```

```

        ts(n)    = (ti(n)+ti(n-1))/2.d0
        delc(n) = ci(n)-ci(n-1)
    end do
end if

C
C  ECHO CONCENTRATION HISTORY
C  -----
WRITE(66,230) IBC
write(66,1234)
do n=1,np
    if (n.lt.np) then
        write(66,1235) ts(n),ts(n+1),ci(n)
    else
        write(66,1236) ts(n),ci(n)
    end if
end do

C
C  ECHO OUTFLOW BOUNDARY CONDITION DATA
C  =====
WRITE(66,2231) OBC,LENGTH
WRITE(66,2232) CL

C
C  WRITE OUTPUT HEADING
C  =====
WRITE(66,500)

C
C  CALCULATE CONCENTRATION PROFILES
C  =====
IF(NPRO.GT.0) THEN
    NXP = idint(((XMAX-XMIN)/DX)+0.5d0)
    DO I=1,NPRO
C
C         TIME = TP(I)
C
C         DISTANCE LOOP
C         -----
        DO J=0,NXP
            XX = XMIN+DBLE(J)*DX
C
C             IF(TIME.LE.0.D0) THEN
C                 CM = CM0
C                 CIM = CIM0
C             ELSE
C                 IC = 1
C                 CALL HOOGD(TIME,CM)
C                 IC = 2
C                 CALL HOOGD(TIME,CIM)
C             END IF
C
C             WRITE (66,510) TIME,XX,CM,CIM
C             WRITE (67,510) TIME,XX,CM,CIM
        END DO
    END DO
END IF

C
C  CALCULATE BREAKTHROUGH CURVES
C  =====

```

```

      IF(NBTC.GT.0) THEN
        NTB = idint(((TMAX-TMIN)/DT)+0.5d0)
        DO I=1,NBTC
C
          XX = XB(I)
C
C        TIME LOOP
C        -----
          DO J=0,NTB
            TIME = TMIN+DBLE(J)*DT
C
            IF(TIME.LE.0D0) THEN
              CM = CM0
              CIM = CIM0
            ELSE
              IC = 1
              CALL HOOGD(TIME,CM)
              IC = 2
              CALL HOOGD(TIME,CIM)
            END IF
C
            WRITE (66,510) TIME,XX,CM,CIM
            WRITE (67,510) TIME,XX,CM,CIM
          END DO
        END DO
      END IF
C
C    FORMAT STATEMENTS
C    =====
100  FORMAT(A70)
210  FORMAT(5X,'MPNE ANALYTICAL SOLUTION FOR 1-D TRANSPORT',/,
1      5X,'VERSION 4.1',/,
2      5X,'===== ',/)
211  FORMAT(5X,A60,/)
220  FORMAT(5X,'BASIC INPUT DATA',/,
1      5X,'----- ',/,
1      5X,'RHOb   : BULK DENSITY              ',1PE12.6/,
1      5X,'THETA  : TOTAL WATER CONTENT        ',1PE12.6/,
1      5X,'Q      : DARCY FLUX                  ',1PE12.6/,
1      5X,'D      : HYDRODYNAMIC DISPERSION COEFF. ',1PE12.6)
221  FORMAT(/5X,'MODEL SPECIFIC DATA',/,
1      5X,'----- ',/,
1      5X,'PHI    : PROPORTION OF MOBILE PORE WATER ',1PE12.6/,
1      5X,'f      : MASS FRACTION OF SORBENT COMPRISING',/,
1      5X,'      MOBILE REGION                    ',1PE12.6/,
1      5X,'ALFA   : FIRST-ORDER MASS TRANSFER COEFF. ',1PE12.6/,
1      5X,'FM     : FRACTION OF SORBENT IN MOBILE REGION',/,
1      5X,'      FOR INSTANTANEOUS SORPTION        ',1PE12.6/,
1      5X,'FIM    : FRACTION OF SORBENT IN IMMOBILE REGION',/,
1      5X,'      FOR INSTANTANEOUS SORPTION        ',1PE12.6/,
1      5X,'KM     : MOBILE EQUIL. SORPTION COEFF.    ',1PE12.6/,
1      5X,'KIM    : IMMOBILE EQUIL. SORPTION COEFF.  ',1PE12.6/,
1      5X,'km2    : FIRST-ORDER SORPTION KINETIC COEFF.',/,
1      5X,'      FOR MOBILE REGION                  ',1PE12.6/,
1      5X,'kim2   : FIRST-ORDER SORPTION KINETIC COEFF.',/,
1      5X,'      FOR IMMOBILE REGION                ',1PE12.6)
222  FORMAT(/5X,'FIRST-ORDER DECAY COEFFICIENTS',/,

```

```

1      5X, '-----', /,
1      5X, 'LM      : MOBILE REGION                      ', 1PE12.6/
1      5X, 'LM1     : MOBILE REGION INSTANTANEOUS SITES ', 1PE12.6/
1      5X, 'LM2     : MOBILE REGION RATE-LIMITED SITES  ', 1PE12.6/
1      5X, 'LIM     : IMMOBILE REGION                    ', 1PE12.6/
1      5X, 'LIM1    : IMMOBILE REGION FOR INSTANTANEOUS ', /,
1      5X, '          SORPTION SITES                     ', 1PE12.6/
1      5X, 'LIM2    : IMMOBILE REGION FOR RATE-LIMITED  ', /,
1      5X, '          SORPTION SITES                     ', 1PE12.6)
231  FORMAT(/5X, 'INITIAL CONCENTRATIONS', /,
1      5X, '-----', /,
1      5X, 'CM0     :                      ', 1PE12.6/
1      5X, 'CIM0    :                      ', 1PE12.6/
1      5X, 'SM20    :                      ', 1PE12.6/
1      5X, 'SIM20   :                      ', 1PE12.6)
240  FORMAT(/5X, 'CALCULATED DIMENSIONLESS PARAMETERS', /,
1      5X, '-----', /,
1      5X, 'R       : TOTAL RETARDATION FACTOR           ', 1PE12.6/
1      5X, 'P       : PECLET NUMBER                     ', 1PE12.6/
1      5X, 'OMEGA   : DAMKOLHER # REPRESENTING PNE        ', 1PE12.6/
1      5X, 'KM0     : DAMKOLHER # REPRESENTING MOBILE', /,
1      5X, '          REGION SORPTION NON-EQUILIBRIUM    ', 1PE12.6/
1      5X, 'KIM0    : DAMKOLHER # REPRESENTING IMMOBILE', /,
1      5X, '          REGION SORPTION NON-EQUILIBRIUM    ', 1PE12.6)
241  FORMAT(/, 5X, 'CALCULATED FRACTIONAL RETARDATION FACTORS', /,
1      5X, '-----', /,
1      5X, 'BETA1    :                      ', 1PE12.6/
1      5X, 'BETA2    :                      ', 1PE12.6/
1      5X, 'BETA3    :                      ', 1PE12.6/
1      5X, 'BETA4    :                      ', 1PE12.6)
242  FORMAT(/, 5X, 'CALCULATED DIMENSIONLESS DECAY PARAMETERS', /,
1      5X, '-----', /,
1      5X, 'EM1     :                      ', 1PE12.6/
1      5X, 'EM2     :                      ', 1PE12.6/
1      5X, 'EIM1    :                      ', 1PE12.6/
1      5X, 'EIM2    :                      ', 1PE12.6)
230  FORMAT(/5X, 'INFLOW BOUNDARY CONDITION DATA', /,
1      5X, '-----', /,
1      5X, 'INFLOW BOUNDARY CONDITION TYPE ', I2)
1234 FORMAT(/5X, 'CONSTRUCTED INFLOW CONCENTRATION HISTOGRAM', /,
1      15X, 'TIME INTERVAL', 11X, 'CONCENTRATION', /, 5X, 48('-'))
1235 FORMAT(5X, 1PE12.6, ' - ', 1PE12.6, 6X, 1PE12.6)
1236 FORMAT(5X, 1PE12.6, ' --> INFINITY ', 7X, 1PE12.6)
2231 FORMAT(/5X, 'OUTFLOW BOUNDARY CONDITION DATA', /,
1      5X, '-----', /,
1      5X, 'OUTFLOW BOUNDARY CONDITION TYPE ', I2/
1      5X, 'LENGTH OF DOMAIN (FOR FINITE DOMAIN)          ', 1PE12.6)
2232 FORMAT(5X, 'CONCENTRATION AT OUTFLOW BOUNDARY, CL      ', 1PE12.6)
500  FORMAT(/10X, 'TIME', 13X, 'X', 17X, 'Cm', 18X, 'Cim' /, 5X, 70('-'))
510  FORMAT(5X, 1PE12.6, 5X, 1PE12.6, 5X, 1PE15.6, 5X, 1PE15.6)
C
C      TERMINATE MAIN PROGRAM
C      =====
C      CLOSE(55)
C      CLOSE(66)
C      CLOSE(67)
C      END

```

```

C
C *****
COMPLEX*16 FUNCTION FBAR(P)
C *****
c Laplace-transformed solution
c
c DECLARATION OF VARIABLES
c =====
c IMPLICIT NONE
c INTEGER MAXPT
c PARAMETER(MAXPT=50)
c DOUBLE PRECISION PARAM(19)
c DOUBLE PRECISION CM0,CIM0,SM20,SIM20,DELTA,LENGTH,CL,XX
c DOUBLE PRECISION TIME,TS(MAXPT),DELC(MAXPT)
c DOUBLE PRECISION RHOB,THETA,Q,D,PHI,THM,THIM,F,ALFA,FM,FIM,
1 KM,KIM,KM2,KIM2,LM,LM1,LM2,LIM,LIM1,LIM2
c DOUBLE PRECISION PCHK,FCHK
c COMPLEX*16 P,SUM,TERM,FS,G10,G20,GAM1,GAM2,GAM3,GAM4,B,H1,H2,
1 D1,D2,D3,E1,E2
c COMPLEX*16 D4,D5,D6,CDEXP
c COMPLEX*16 CMB,CIMB
c INTEGER OBC,NP,N,IC
C
C COMMON /ICS/CM0,CIM0,SM20,SIM20
C COMMON /BCS/TIME,DELTA,TS,DELC,NP,OBC,LENGTH,CL,XX
C COMMON /MPNE/PARAM
C COMMON /CSWITCH/IC
C
C "LOAD" MPNE PARAMETERS FROM THE PARAM ARRAY
C =====
C RHOB = PARAM( 1)
C THETA = PARAM( 2)
C Q = PARAM( 3)
C D = PARAM( 4)
C PHI = PARAM( 5)
C F = PARAM( 6)
C ALFA = PARAM( 7)
C FM = PARAM( 8)
C FIM = PARAM( 9)
C KM = PARAM(10)
C KIM = PARAM(11)
C KM2 = PARAM(12)
C KIM2 = PARAM(13)
C LM = PARAM(14)
C LM1 = PARAM(15)
C LM2 = PARAM(16)
C LIM = PARAM(17)
C LIM1 = PARAM(18)
C LIM2 = PARAM(19)
C
C CALCULATE POROSITIES
C =====
C THM = PHI*THETA
C THIM = (1.D0-PHI)*THETA
C
C TRAP POTENTIAL DIVISION BY ZERO FOR CASE OF NO IMMOBILE REGION
C =====

```



```

PCHK = DABS(PHI-1.D0)
FCHK = DABS(F-1.D0)
C
IF((PCHK.LT.1.D-10).AND.(FCHK.LT.1.D-10)) THEN
    ALFA=1.D0
ENDIF
C
C
C CALCULATE TRANSFORMED INFLOW CONCENTRATION HISTORY
C =====
sum = CMPLX(0.d0,0.d0,KIND=8)
do n=1,np
    if(ts(n).lt.time) then
        if(ts(n).le.0.d0) then
            term = delc(n)/p
        else
            term = (delc(n)/p)*(cdexp(-p*ts(n)))
        end if
    else
        term = CMPLX(0.d0,0.d0,KIND=8)
    end if
    sum = sum+term
end do
fs = sum
C
C
C CALCULATE INITIAL CONDITION TERMS
C =====
G10 = (((1.D0-F)*RHOB*KIM2/(P+KIM2+LIM2))*SIM20
1      +(THIM+(1.D0-F)*RHOB*FIM*KIM)*CIM0)/
2      ((P*(THIM+(1.D0-F)*RHOB*FIM*KIM)+(THIM*LIM)
3      +(1.D0-F)*RHOB*LIM1*FIM*KIM)
4      +(1.D0-F)*RHOB*(1.D0-FIM)*KIM*KIM2*(P+LIM2)/
5      (P+KIM2+LIM2) + ALFA))
G20 = (THM+F*RHOB*FM*KM)*CM0
1      +((F*RHOB*KM2)/(P+KM2+LM2))*SM20
C
C
C CALCULATE GAMMA TERMS
C =====
GAM1 = (1.D0+(F*RHOB*FM*KM)/THM)*P
GAM2 = (F*RHOB*(1.D0-FM)*KM*KM2*((P+LM2)/
1      (P+KM2+LM2)))/THM
GAM3 = (ALFA-((ALFA*ALFA)/
1      ((THIM+(1.D0-F)*RHOB*FIM*KIM)*P
2      +(THIM*LIM)+(1.D0-F)*RHOB*LIM1*FIM*KIM)
3      +(1.D0-F)*RHOB*(1.D0-FIM)*KIM*KIM2
4      *((P+LIM2)/(P+KIM2+LIM2))+ALFA)))/THM
GAM4 = LM+(F*RHOB*LM1*FM*KM)/THM
C
C
C CALCULATE COEFFICIENTS
C =====
B = THM*(GAM1+GAM2+GAM3+GAM4)
H1 = (Q-((Q*Q)+4.D0*B*THM*D)**0.5)/(2.D0*THM*D)
H2 = (Q+((Q*Q)+4.D0*B*THM*D)**0.5)/(2.D0*THM*D)
C
C
C CALCULATE SOLUTION FOR SEMI-FINITE DOMAIN
C =====
IF(OBC.EQ.1) THEN
C

```

```

      IF((DABS(Q).LE.0.D0).AND.(DELTA.LE.0.D0)) THEN
        E1 = FS-(ALFA*G10+G20)/B
      ELSE
        E1 = (Q/(Q-THM*DELTA*D*H1))*(FS-(ALFA*G10+G20)/B)
      END IF
      CMB = E1*CDEXP(H1*XX) + ((ALFA*G10)+G20)/B
C
      ELSE
C
C      CALCULATE SOLUTION FOR FINITE DOMAIN, TYPE II
C      =====
      IF(OBC.EQ.2) THEN
C
        IF((DABS(Q).LE.0.D0).AND.(DELTA.LE.0.D0)) THEN
          D1 = H2*CDEXP(H2*LENGTH)-H1*CDEXP(H1*LENGTH)
          D2 = (FS-((ALFA*G10)+G20)/B)*H2*CDEXP(H2*LENGTH)
          D3 = -(FS-((ALFA*G10)+G20)/B)*H1*CDEXP(H1*LENGTH)
        ELSE
          D1 = H2*(Q-THM*DELTA*D*H1)*CDEXP(H2*LENGTH)
          1      -H1*(Q-THM*DELTA*D*H2)*CDEXP(H1*LENGTH)
          D2 = q*(FS-((ALFA*G10)+G20)/B)*H2*CDEXP(H2*LENGTH)
          D3 = -q*(FS-((ALFA*G10)+G20)/B)*H1*CDEXP(H1*LENGTH)
        END IF
        E1 = D2/D1
        E2 = D3/D1
        CMB = E1*CDEXP(H1*XX) + E2*CDEXP(H2*XX)
      1      + ((ALFA*G10)+G20)/B
C
      ELSE
C
C      CALCULATE SOLUTION FOR FINITE DOMAIN, TYPE I
C      =====
      IF(OBC.EQ.3) THEN
C
        IF((DABS(Q).LE.0.D0).AND.(DELTA.LE.0.D0)) THEN
          D4 = CDEXP(H2*LENGTH)-CDEXP(H1*LENGTH)
          D5 = (FS-((ALFA*G10)+G20)/B)*CDEXP(H2*LENGTH)
          1      -(CL/P-((ALFA*G10)+G20)/B)
          D6 = -(FS-((ALFA*G10)+G20)/B)*CDEXP(H1*LENGTH)
          1      +(CL/P-((ALFA*G10)+G20)/B)
        ELSE
          D4 = (Q-THM*DELTA*D*H1)*CDEXP(H2*LENGTH)
          1      -(Q-THM*DELTA*D*H2)*CDEXP(H1*LENGTH)
          D5 = q*(FS-((ALFA*G10)+G20)/B)*CDEXP(H2*LENGTH)
          1      -(CL/P-((ALFA*G10)+G20)/B)*(Q-THM*DELTA*D*H2)
          D6 = -q*(FS-((ALFA*G10)+G20)/B)*CDEXP(H1*LENGTH)
          1      +(CL/P-((ALFA*G10)+G20)/B)*(Q-THM*DELTA*D*H1)
        END IF
        E1 = D5/D4
        E2 = D6/D4
        CMB = E1*CDEXP(H1*XX) + E2*CDEXP(H2*XX)
      1      + ((ALFA*G10)+G20)/B
C
      END IF
      END IF
      END IF
C

```

```

C      INVERT LAPLACE-TRANSFORM SOLUTIONS FOR EITHER Cm OR Cim
C      =====
C      IF(IC.EQ.1) THEN
C          FBAR = CMB
C      ELSE
C          IF((PCHK.LT.1.D-10).AND.(FCHK.LT.1.D-10)) THEN
C              CIMB = CMPLX(0.d0,0.d0,KIND=8)
C          ELSE
C              CIMB = CMB*(alfa/
1              (p*(thim+(1.d0-f)*rhob*Fim*Kim)+thim*lim
2              +(1.d0-f)*rhob*lim1*Fim*Kim
3              +(1.d0-f)*rhob*(1.d0-Fim)*Kim*kim2
4              *((p+lim2)/(p+kim2+lim2))
5              +alfa)) + G10
C          END IF
C          FBAR = CIMB
C      END IF
C
C      RETURN
C      END FUNCTION FBAR
C
C      *****
C      FUNCTION CDEXP(Z2)
C      *****
C      COMPLEX DOUBLE PRECISION EXPONENTIAL FUNCTION
C      Coded by JP Keizer, 2002 01
C
C      COMPLEX (KIND=8) :: CDEXP
C      COMPLEX (KIND=8), INTENT(IN) :: Z2
C      REAL (KIND=8) :: A          ! real part of z
C      REAL (KIND=8) :: B          ! imaginary part of z
C
C      A      = REAL(Z2,KIND=8)
C      B      = AIMAG(Z2)
C      CDEXP = DEXP(A)*(CMPLX(DCOS(B),DSIN(B),KIND=8))
C
C      END FUNCTION CDEXP
C
C      *****
C      INCLUDE 'HOOGD.FOR'

```

MPNE1D 4.1 Documentation

Appendix A3: Listing of files for the example problem (van Genuchten, 1974: Expt. 3-5)

```

van Genuchten EXPT. 3-5: 2,4,5-T/Glendale loam
1.222D+0      RHO : BULK DENSITY (G/CM3)
0.4555D+0     THETA : TOTAL WATER CONTENT (CM3/CM3)
3.975D+0      Q : DARCY FLUX (CM/D)
5.313D+0      D : HYDRODYNAMIC DISPERSION COEFFICIENT (CM2/D)
0.880D+0      PHI : PROPORTION OF MOBILE PORE WATER (-)
0.880D+0      f : FRACTION OF ACCESSIBLE SORPTION SITES (-)
3.000D-2      ALPHA : FIRST-ORDER MASS TRANSFER COEFF. (1/D)
0.500D+0      FM : FRACTION OF INST. SORBENT IN MOBILE REGION (-)
0.500D+0      FIM : FRACTION OF INST. SORBENT IN IMMOBILE REGION (-)
0.426D+0      KM : MOBILE-EQUILIBRIUM SORPTION CONSTANT (CM3/G)
0.426D+0      KIM : IMMOBILE-EQUILIBRIUM SORPTION CONSTANT (CM3/G)
0.660D+0      km2 : MOBILE-1ST ORDER SORPTION KINETIC COEFF. (1/D)
0.660D+0      kim2 : IMMOBILE-1ST ORDER SORPTION KINETIC COEFF. (1/D)
0.058D+0      LM : MOBILE/DISSOLVED-1ST ORDER DECAY CONSTANT (1/D)
0.000D+0      LM1 : MOBILE/SORBED-1ST ORDER DECAY CONSTANT (1/D)
0.000D+0      LM2 : MOBILE/R-L SORBED-1ST ORDER DECAY CONSTANT (1/D)
0.000D+0      LIM : IMMOBILE/DISSOLVED-1ST ORDER DECAY CONSTANT (1/D)
0.000D+0      LIM1 : IMMOBILE/SORBED-1ST ORDER DECAY CONSTANT (1/D)
0.000D+0      LIM2 : IMMOBILE/R-L SORBED-1ST ORDER DECAY CONSTANT (1/D)
3             IBC : INFLOW BOUNDARY CONDITION
2             NP : number of points describing inflow concentration
0.000D+0      1.000D+0
19.306D+0     0.000D+0
1             OBC : OUTFLOW BOUNDARY CONDITION
30.000D+0     LENGTH : LENGTH OF COLUMN (FOR TYPE II INFLOW B.C. ONLY)
0.000D+0      CL : CONCENTRATION x=L (FOR OBC=3 ONLY)
0.000D+0      CM0 : MOBILE/DISSOLVED-INITIAL CONCENTRATION
0.000D+0      CIM0 : IMMOBILE DISSOLVED-INITIAL CONCENTRATION
0.000D+0      SM20 : MOBILE/R-L SORBED-INITIAL CONCENTRATION
0.000D+0      SIM20 : IMMOBILE/R-L SORBED-INITIAL CONCENTRATION
0             NPRO : NUMBER OF CONCENTRATION PROFILES
1             NBTC : NUMBER OF BREAKTHROUGH CURVES
0.000      30.000      0.500      : TMIN,TMAX,DT
30.000

```

MPNE ANALYTICAL SOLUTION FOR 1-D TRANSPORT
 VERSION 4.1
 =====

van Genuchten EXPT. 3-5: 2,4,5-T/Glendale loam

BASIC INPUT DATA

```

-----
RHOb  : BULK DENSITY                1.222000E+00
THETA : TOTAL WATER CONTENT         4.555000E-01
Q      : DARCY FLUX                 3.975000E+00
D      : HYDRODYNAMIC DISPERSION COEFF. 5.313000E+00

```

MODEL SPECIFIC DATA

```

-----
PHI    : PROPORTION OF MOBILE PORE WATER  8.800000E-01
f      : MASS FRACTION OF SORBENT COMPRISING
        MOBILE REGION                  8.800000E-01
ALFA   : FIRST-ORDER MASS TRANSFER COEFF.  3.000000E-02
FM      : FRACTION OF SORBENT IN MOBILE REGION
        FOR INSTANTANEOUS SORPTION      5.000000E-01
FIM     : FRACTION OF SORBENT IN IMMOBILE REGION
        FOR INSTANTANEOUS SORPTION      5.000000E-01
KM      : MOBILE EQUIL. SORPTION COEFF.    4.260000E-01
KIM     : IMMOBILE EQUIL. SORPTION COEFF.  4.260000E-01
km2     : FIRST-ORDER SORPTION KINETIC COEFF.
        FOR MOBILE REGION              6.600000E-01
kim2    : FIRST-ORDER SORPTION KINETIC COEFF.
        FOR IMMOBILE REGION            6.600000E-01

```

FIRST-ORDER DECAY COEFFICIENTS

```

-----
LM      : MOBILE REGION                5.800000E-02
LM1     : MOBILE REGION INSTANTANEOUS SITES 0.000000E+00
LM2     : MOBILE REGION RATE-LIMITED SITES 0.000000E+00
LIM     : IMMOBILE REGION              0.000000E+00
LIM1    : IMMOBILE REGION FOR INSTANTANEOUS
        SORPTION SITES                 0.000000E+00
LIM2    : IMMOBILE REGION FOR RATE-LIMITED
        SORPTION SITES                 0.000000E+00

```

INITIAL CONCENTRATIONS

```

-----
CM0     : 0.000000E+00
CIM0    : 0.000000E+00
SM20    : 0.000000E+00
SIM20   : 0.000000E+00

```

CALCULATED DIMENSIONLESS PARAMETERS

```

-----
R        : TOTAL RETARDATION FACTOR      2.142858E+00
P        : PECLET NUMBER                 5.599478E+01
OMEGA    : DAMKOLHER # REPRESENTING PNE  2.264151E-01
KM0      : DAMKOLHER # REPRESENTING MOBILE
        REGION SORPTION NON-EQUILIBRIUM 1.140937E+00
KIM0     : DAMKOLHER # REPRESENTING IMMOBILE
        REGION SORPTION NON-EQUILIBRIUM 1.555823E-01

```

CALCULATED FRACTIONAL RETARDATION FACTORS

```

-----
BETA1    : 6.453332E-01
BETA2    : 2.346668E-01
BETA3    : 8.799998E-02
BETA4    : 3.200002E-02

```

CALCULATED DIMENSIONLESS DECAY PARAMETERS

```

-----
EM1      : 1.754620E-01
EM2      : 0.000000E+00
EIM1     : 0.000000E+00
EIM2     : 0.000000E+00

```

INFLOW BOUNDARY CONDITION DATA

```

-----
INFLOW BOUNDARY CONDITION TYPE 3
```

CONSTRUCTED INFLOW CONCENTRATION HISTOGRAM

```

-----
TIME INTERVAL      CONCENTRATION
-----
0.000000E+00 - 9.653000E+00  1.000000E+00
9.653000E+00 --> INFINITY    0.000000E+00

```

OUTFLOW BOUNDARY CONDITION DATA

```

-----
OUTFLOW BOUNDARY CONDITION TYPE 1
```

LENGTH OF DOMAIN (FOR FINITE DOMAIN) 3.000000E+01
 CONCENTRATION AT OUTFLOW BOUNDARY, CL 0.000000E+00

TIME	X	Cm	Cim
0.000000E+00	3.000000E+01	0.000000E+00	0.000000E+00
5.000000E-01	3.000000E+01	0.000000E+00	0.000000E+00
1.000000E+00	3.000000E+01	2.611927E-08	1.118820E-09
1.500000E+00	3.000000E+01	5.462600E-06	5.828754E-07
2.000000E+00	3.000000E+01	2.659332E-05	5.711387E-06
2.500000E+00	3.000000E+01	1.601337E-04	1.949420E-05
3.000000E+00	3.000000E+01	2.883919E-03	1.828860E-04
3.500000E+00	3.000000E+01	1.994159E-02	1.646798E-03
4.000000E+00	3.000000E+01	6.661045E-02	7.606429E-03
4.500000E+00	3.000000E+01	1.413790E-01	2.172669E-02
5.000000E+00	3.000000E+01	2.271479E-01	4.526387E-02
5.500000E+00	3.000000E+01	3.086689E-01	7.669158E-02
6.000000E+00	3.000000E+01	3.798883E-01	1.133708E-01
6.500000E+00	3.000000E+01	4.407473E-01	1.529397E-01
7.000000E+00	3.000000E+01	4.929360E-01	1.937266E-01
7.500000E+00	3.000000E+01	5.380186E-01	2.346358E-01
8.000000E+00	3.000000E+01	5.771169E-01	2.749438E-01
8.500000E+00	3.000000E+01	6.110494E-01	3.141560E-01
9.000000E+00	3.000000E+01	6.404725E-01	3.519283E-01
9.500000E+00	3.000000E+01	6.659530E-01	3.880243E-01
1.000000E+01	3.000000E+01	6.879139E-01	4.222205E-01
1.050000E+01	3.000000E+01	7.069667E-01	4.545654E-01
1.100000E+01	3.000000E+01	7.234331E-01	4.849547E-01
1.150000E+01	3.000000E+01	7.376621E-01	5.133900E-01
1.200000E+01	3.000000E+01	7.499449E-01	5.399029E-01
1.250000E+01	3.000000E+01	7.593591E-01	5.644894E-01
1.300000E+01	3.000000E+01	7.578125E-01	5.865259E-01
1.350000E+01	3.000000E+01	7.290889E-01	6.035209E-01
1.400000E+01	3.000000E+01	6.684680E-01	6.116990E-01
1.450000E+01	3.000000E+01	5.901281E-01	6.089707E-01
1.500000E+01	3.000000E+01	5.115241E-01	5.962393E-01
1.550000E+01	3.000000E+01	4.416049E-01	5.760906E-01
1.600000E+01	3.000000E+01	3.817834E-01	5.511483E-01
1.650000E+01	3.000000E+01	3.306715E-01	5.233848E-01
1.700000E+01	3.000000E+01	2.866687E-01	4.941348E-01
1.750000E+01	3.000000E+01	2.485861E-01	4.642992E-01
1.800000E+01	3.000000E+01	2.155767E-01	4.345093E-01
1.850000E+01	3.000000E+01	1.869848E-01	4.052220E-01
1.900000E+01	3.000000E+01	1.622562E-01	3.767714E-01
1.950000E+01	3.000000E+01	1.409005E-01	3.493976E-01
2.000000E+01	3.000000E+01	1.224782E-01	3.232666E-01
2.050000E+01	3.000000E+01	1.065967E-01	2.984851E-01
2.100000E+01	3.000000E+01	9.290810E-02	2.751131E-01
2.150000E+01	3.000000E+01	8.110687E-02	2.531734E-01
2.200000E+01	3.000000E+01	7.092654E-02	2.326606E-01
2.250000E+01	3.000000E+01	6.213619E-02	2.135477E-01
2.300000E+01	3.000000E+01	5.453671E-02	1.957920E-01
2.350000E+01	3.000000E+01	4.795707E-02	1.793395E-01
2.400000E+01	3.000000E+01	4.225082E-02	1.641287E-01
2.450000E+01	3.000000E+01	3.729285E-02	1.500932E-01
2.500000E+01	3.000000E+01	3.297645E-02	1.371645E-01
2.550000E+01	3.000000E+01	2.921072E-02	1.252723E-01
2.600000E+01	3.000000E+01	2.591845E-02	1.143491E-01
2.650000E+01	3.000000E+01	2.303389E-02	1.043270E-01
2.700000E+01	3.000000E+01	2.050110E-02	9.514116E-02
2.750000E+01	3.000000E+01	1.827244E-02	8.672937E-02
2.800000E+01	3.000000E+01	1.630730E-02	7.903264E-02
2.850000E+01	3.000000E+01	1.457104E-02	7.199522E-02
2.900000E+01	3.000000E+01	1.303406E-02	6.556474E-02
2.950000E+01	3.000000E+01	1.167100E-02	5.969222E-02
3.000000E+01	3.000000E+01	1.046010E-02	5.433199E-02

MPNE1D 4.1 Documentation

Appendix A4: Paper by *Neville, Ibaraki and Sudicky (2000)*



ELSEVIER

Journal of Contaminant Hydrology 44 (2000) 141–159

www.elsevier.com/locate/jconhyd

JOURNAL OF
**Contaminant
Hydrology**

Solute transport with multiprocess nonequilibrium: a semi-analytical solution approach

Christopher J. Neville^{a,1}, Motomu Ibaraki^{b,*}, Edward A. Sudicky^{c,2}

^a *S.S. Papadopoulos & Associates, Inc., 207 King St. S., Waterloo, Ontario, Canada*

^b *Department of Geological Sciences, The Ohio State University, Columbus, OH 43210, USA*

^c *Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada*

Received 12 November 1999; received in revised form 25 February 2000; accepted 4 April 2000

Abstract

A semi-analytical solution for the simulation of one-dimensional subsurface solute transport incorporating multiple nonequilibrium processes is presented. The solution is based on the theory developed by Brusseau et al. (1992) [Brusseau, M.L., Jessup, R.E., Rao, P.S.C., 1992. Modeling solute transport influenced by multiprocess nonequilibrium and transformation reactions. *Water Resources Research* 28 (1), 175–182.] which is a generalized combination of two-site and two-region model. In addition to developing a semi-analytical complement to their numerical solution, we extend the range of boundary and initial conditions considered. The semi-analytical solution can represent domains of both finite and semi-infinite extent and accommodates nonzero initial concentrations. The solution is derived in Laplace space and final results are obtained using an accurate and robust numerical inversion algorithm. The solution is particularly well suited for interpreting experimental results obtained under controlled laboratory conditions. Identification of the input parameters for the solution is examined by simulating a column experiment by van Genuchten (1974) [van Genuchten, M., 1974. *Mass Transfer Studies in Sorbing Porous Media*. PhD thesis, New Mexico State University, Las Cruces, NM.]. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Solute transport; Sorption; Groundwater; Mathematical models; Laplace transformations

* Corresponding author. Fax: +1-614-292-7688.

E-mail addresses: cneville@sspa.com (C.J. Neville), ibaraki.1@osu.edu (M. Ibaraki), sudicky@sciborg.uwaterloo.ca (E.A. Sudicky).

¹ Fax: +1-519-896-0199.

² Fax: +1-519-746-7484.

1. Introduction

Mathematical models of solute transport are important tools for solving problems involving groundwater contamination. Potential applications of models include planning of site investigations, risk assessment, and design of remedial actions. These models must be capable of representing the most significant processes affecting the transport of solutes. There is evidence to suggest that models based on assumptions of ideal behavior ignore fundamental characteristics of the transport of solutes (reviews are presented by Bouchard et al., 1988 and Brusseau and Rao, 1989a,c).

The transport of sorbing solutes is generally modeled with an idealized model, in which the porous is represented as an interconnected continuum, and sorption is represented as an equilibrium process (instantaneous and reversible) with a linear isotherm. For a pulse input, this approach predicts symmetrical, bell-shaped breakthrough curves. Departures from this ideal behavior have been observed at scales of investigation ranging from column experiments to field-scale tests. Two examples of nonideality are shown in Fig. 1. Fig. 1a plots results from a column experiment with the herbicide 2,4,5-D (2,4,5-trichlorophenoxyacetic acid) reported by van Genuchten et al. (1977). Fig. 1b, taken from Goltz and Roberts (1986a), illustrates concentrations of tetrachloroethene observed during the Stanford–Waterloo natural-gradient tracer test. Of particular importance are the long tails of the breakthrough curves. If tailing is not considered, then the ability to provide quantitative answers to basic questions is severely compromised. For example, in the context of pump-and-treat remediation of contaminated sites, the duration of pumping and the volume of treated water cannot be estimated reliably.

Two general mechanisms have been offered as explanations for nonideal behavior. The first mechanism is adapted from the dual porosity hypothesis and is designated

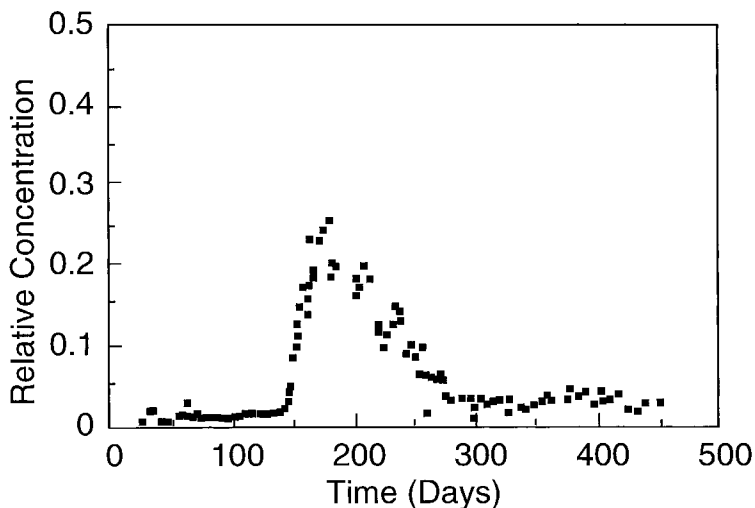


Fig. 1. Evidence of transport nonequilibrium from a field-scale experiment (Goltz and Roberts, 1986a,b).

physical nonequilibrium (PNE). Originally developed to represent flow in densely fractured porous media, the dual porosity hypothesis idealizes the porous medium as two interacting continua. In the first continuum (the mobile region), the pore water is relatively mobile, while in the second (the immobile region), advection is minimal (Coats and Smith, 1964). Solute transport in a dual porosity medium is characterized by early breakthrough resulting from rapid advective transport in the mobile region and tailing resulting from the slow diffusive mass transfer between the mobile and immobile regions.

Different models for dual porosity have been developed based on assumptions about the geometry of the mobile and immobile regions. Geometrical models conceive of the immobile region as an idealized assemblage of simple elements, for example, as uniform slabs and spheres (e.g., Huyakorn et al., 1983). An alternative approach is to represent the diffusive flux between the mobile and immobile regions by a first-order mass transfer reaction. The first-order mass transfer approach has been applied to cases of aggregated porous media (van Genuchten and Wierenga, 1977; van Genuchten et al., 1977), and discrete layering (Brusseau, 1991). The first-order approach has also been applied to simulate transport in heterogeneous aquifers (Brusseau and Rao, 1989b; Brusseau and Srivastava, 1997). In this context, the approach is purely phenomenological and the mass transfer coefficient becomes merely a fitting parameter.

PNE affects the transport of both sorbing and nonsorbing solutes and is commonly associated with aggregated and fractured porous media. However, tailing has also been observed in column studies with sorbing organic solutes in uniform, granular porous media (e.g., Liu et al., 1991). Therefore, a second mechanism has been proposed to explain nonideal behavior of organics. This second mechanism is designated sorption nonequilibrium (SNE). SNE represents the combined effects of intrasorbent (intraorganic or intramineral) diffusion and rate-limited interactions between the solute and sorbent. In the two-site conceptualization, sorption is assumed to occur at two sites: at the first site, sorption is an equilibrium process; at the second site, sorption is a rate-limited process. The rate-limiting sorption reaction is represented as a first-order reaction.

Many analytical solutions based on the mobile–immobile conceptualization, referred to as two-region models, have been developed. Examples included those of van Genuchten and Wierenga (1976) and Goltz and Roberts (1986b). Carnahan and Remer (1984) presented an analytical solution incorporating rate-limited sorption. Analytical solutions based on the two-site model have also been developed by Cameron and Klute (1977) and van Genuchten and Wagenet (1989). It has been long recognized that two-region and two-site models are mathematically identical. Several studies used this identity to develop analytical solutions to handle either physical or chemical nonequilibrium (i.e., two-site or two-region models) (e.g., Leij et al., 1993; Toride et al., 1993; Leij and van Genuchten, 2000). However, none of the existing solutions can be used to handle both nonequilibrium processes simultaneously.

Brusseau et al. (1989) formulated a model that incorporates both physical and sorption nonequilibria, which they called the multiprocess nonequilibrium (MPNE) model. Brusseau et al. (1992) extended the model to consider transformation reactions represented as first-order decay processes. The model integrates the two-region and

two-site conceptualizations. The mobile and immobile regions are each subdivided into three compartments. The first compartment in each region is the dissolved phase and the second and third compartments constitute the two sites of the sorbed phase. The sorption sites are split into a fraction where sorption occurs instantaneously, and a remaining fraction where sorption follows first-order kinetics. Transport between the mobile and immobile regions is modeled with a first-order mass transfer approach.

Several numerical models implementing the MPNE model have been developed. Brusseau et al. (1992) used a one-dimensional finite difference solution to simulate column experiments. Sudicky (personal communication, 1989) developed the first two-dimensional finite element solution to the MPNE equations. The solution is based on the Laplace Transform Galerkin (LTG) technique presented in Sudicky (1989, 1990) and was used by Brusseau et al. (1989) to assess the relative contributions of chemical sorption kinetics, intraparticle diffusion and geologic heterogeneity on plume evolution. Therrien et al. (1990) extended the LTG solution to three dimensions and applied their model to the interpretation of forced-gradient tracer tests in heterogeneous sand aquifers. Recently, Zhang and Brusseau (1999) have published an important field-scale application of the MPNE model with a three-dimensional numerical solution based on the modified method of characteristics.

In this paper, we present an analytical Laplace transform solution for one-dimensional transport with MPNE. Exact analytical or semi-analytical solutions generally can be derived only for problems involving homogeneous media and simple boundary conditions. In light of these restrictions, and the existence of general numerical solutions, the obvious question is: why develop an analytical solution for MPNE? The first answer is that these sophisticated numerical solutions demand verification. Second, there exists a need for simple solutions that can be used as screening tools, particularly for preliminary modeling in the absence of data. Finally, analytical solutions are ideally suited for the interpretation of experimental results obtained under controlled laboratory conditions. For this application, their freedom from spatial and temporal discretization requirements is a significant advantage over numerical solutions.

The solution is derived using the Laplace transform technique, with the final results obtained by numerical inversion of the transformed solution. Special attention is directed towards implementing the solution in a code that is robust and capable of predicting concentrations over a wide range of environmental interest. The solution is verified using the results of a numerical simulation of a column experiment. The identifiability of input parameters for laboratory-scale applications is examined by simulating van Genuchten (1974) experiments 3–5.

2. Mathematical formulation

In this section, we develop the governing equations of the MPNE model in order to clarify each equilibrium/nonequilibrium process which constitute the model. This level of detail in the mathematical formulation is typically missing from the literatures on two-region and/or two-site models (e.g., Brusseau et al., 1989).

2.1. Assumptions

The key assumptions of the MPNE model are summarized below. (1) The domain is represented as a dual porosity continuum. Mass transfer between the mobile and immobile regions is modeled as a first-order mass transfer reaction. (2) Sorption occurs at both equilibrium and rate-limited sites. At the equilibrium sites, sorption is instantaneous and reversible and is governed by a linear isotherm. At the rate-limited sites, sorption is represented as a first-order reaction. The mobile and immobile regions are characterized by separate sorption properties. (3) Transformation reactions are modeled as first-order decay processes. If microbially-mediated reactions are represented using this approach, then it is tacitly assumed that they are not limited by substrate availability (e.g., oxygen is in unlimited supply) and that contaminant concentrations are relatively low (Criddle et al., 1991). For maximum generality, the dissolved and sorbed phases in the mobile and immobile regions are assigned separate decay rates.

Several additional assumptions are required for a tractable one-dimensional analytical treatment:

1. The material properties are spatially uniform and temporally constant.
2. The Darcy flux is steady, one-dimensional, and spatially uniform.
3. Longitudinal dispersion is assumed to be a Fickian process, characterized by a constant dispersion coefficient. Dispersion in the transverse directions is neglected.
4. The initial concentrations in the domain are uniform. For maximum generality, the initial concentrations are specified separately for the dissolved and sorbed phases.

2.2. Governing equations

The MPNE model is cast in terms of six concentrations: one dissolved phase and two sorbed phase concentrations for each of the mobile and immobile regions. In the following development, use is made of mass balance equations and constitutive relations to derive the six equations, which comprise the MPNE model.

2.2.1. Mobile region

Within the mobile region, the MPNE model accounts for advective–dispersive transport, mobile–immobile mass transfer, equilibrium and rate-limited sorption and first-order transformation reactions. The statement of mass conservation for the dissolved phase in the mobile region is written as:

$$\frac{\partial(\theta_m C_m)}{\partial t} + \frac{\partial(f\rho S_m)}{\partial t} = -\frac{\partial J_m}{\partial x} - G_{\lambda_m} - G_{\lambda_{s_m}} - G_{im} \quad (1)$$

The terms appearing in this and all subsequent equations are defined in the Notation. The left-hand side of the mass balance equation represents the time rate of change of mass in the dissolved and sorbed phases in the mobile region. In this expression, the term f designates the mass fraction of sorbent that is accessible to the dissolved phase in

the mobile region. Solute in the sorbed phase is partitioned between the equilibrium and rate-limited sorption sites:

$$S_m = S_{m1} + S_{m2} \quad (2)$$

The first term on the right-hand side in Eq. (1) is the advective–dispersive mass flux in the dissolved phase and is defined as:

$$J_m = -\theta_m D \frac{\partial C_m}{\partial x} + q C_m \quad (3)$$

The second and third terms on the right-hand side, G_{λ_m} and $G_{\lambda_{S_m}}$, are sinks representing first-order transformation reactions in the dissolved and sorbed phases. The first-order transformation sink terms are written as:

$$G_{\lambda_m} = \theta_m \lambda_m C_m \quad (4)$$

$$G_{\lambda_{S_m}} = f\rho(\lambda_{S_{m1}} S_{m1} + \lambda_{S_{m2}} S_{m2}) \quad (5)$$

For the first-order mass transfer model, the sink term representing mobile–immobile interaction is expressed as:

$$G_{im} = \alpha(C_m - C_{im}) \quad (6)$$

Assembling all of the terms in the original mass balance, Eq. (1) yields:

$$\begin{aligned} \frac{\partial(\theta_m C_m)}{\partial t} + f\rho \frac{\partial S_{m1}}{\partial t} + f\rho \frac{\partial S_{m2}}{\partial t} = & \frac{\partial}{\partial x} \left(\theta_m D \frac{\partial C_m}{\partial x} \right) - \frac{\partial}{\partial x} (q C_m) - \theta_m \lambda_m C_m \\ & - f\rho(\lambda_{S_{m1}} S_{m1} + \lambda_{S_{m2}} S_{m2}) - \alpha(C_m - C_{im}) \end{aligned} \quad (7)$$

The sorbed phase concentration at the instantaneous sorption sites is defined in terms of the following equilibrium constitutive relation:

$$S_{m1} = F_m K_m C_m \quad (8)$$

In this relation, F_m represents the mass fraction of sorption sites in the mobile region where sorption is instantaneous. The sorbed phase concentration at the rate-limited sites is defined in terms of a mass balance equation:

$$\frac{\partial S_{m2}}{\partial t} = k_{m2}[(1 - F_m) K_m C_m - S_{m2}] - \lambda_{S_{m2}} S_{m2} \quad (9)$$

Substituting for the sorbed phase concentrations and invoking the assumption of constant material properties yields the final form of the transport equation for the mobile region:

$$\begin{aligned} (\theta_m + f\rho F_m K_m) \frac{\partial C_m}{\partial t} + (\theta_m \lambda_m + f\rho \lambda_{S_{m1}} F_m K_m) C_m + \alpha(C_m - C_{im}) \\ + f\rho k_{m2}[(1 - F_m) K_m C_m - S_{m2}] = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \end{aligned} \quad (10)$$

2.2.2. Immobile region

The governing equations for the immobile region are analogous to those derived for the mobile region, with the exception that advection and dispersion are not considered. The statement of mass conservation for the immobile region is written as:

$$\frac{\partial(\theta_{\text{im}} C_{\text{im}})}{\partial t} + \frac{\partial((1-f)\rho S_{\text{im}})}{\partial t} = -G_{\lambda_{\text{im}}} - G_{\lambda_{S_{\text{im}}}} + G_{\text{im}} \quad (11)$$

The left-hand side of the mass balance equation represents the time rate of change of mass in the dissolved and sorbed phases in the immobile region. In this expression, the term $(1-f)$ designates the mass fraction of sorbent that is accessible to the dissolved phase in the immobile region. Solute in the sorbed phase is partitioned between the equilibrium and rate-limited sorption sites:

$$S_{\text{im}} = S_{\text{im}1} + S_{\text{im}2} \quad (12)$$

The mobile-immobile mass transfer term, G_{im} , is defined by Eq. (6). The remaining components of the right-hand side sink term are analogous to those for the mobile region and are written as:

$$G_{\lambda_{\text{im}}} = \theta_{\text{im}} \lambda_{\text{im}} C_{\text{im}} \quad (13)$$

$$G_{\lambda_{S_{\text{im}}}} = (1-f)\rho(\lambda_{S_{\text{im}1}} S_{\text{im}1} + \lambda_{S_{\text{im}2}} S_{\text{im}2}) \quad (14)$$

The expressions for the sinks are similar to those presented for the mobile region, noting that the sign of the mobile-immobile mass transfer term is reversed.

Assembling all of the terms in the mass balance, Eq. (11) yields:

$$\begin{aligned} \frac{\partial(\theta_{\text{im}} C_{\text{im}})}{\partial t} + (1-f)\rho \frac{\partial S_{\text{im}1}}{\partial t} + (1-f)\rho \frac{\partial S_{\text{im}2}}{\partial t} \\ = -\theta_{\text{im}} \lambda_{\text{im}} C_{\text{im}} - (1-f)\rho(\lambda_{S_{\text{im}1}} S_{\text{im}1} + \lambda_{S_{\text{im}2}} S_{\text{im}2}) + \alpha(C_{\text{m}} - C_{\text{im}}) \end{aligned} \quad (15)$$

The sorbed phase concentrations at the instantaneous and rate-limited sorption sites are defined by:

$$S_{\text{im}1} = F_{\text{im}} K_{\text{im}} C_{\text{im}} \quad (16)$$

$$\frac{\partial S_{\text{im}2}}{\partial t} = k_{\text{im}2}[(1-F_{\text{im}})K_{\text{im}}C_{\text{im}} - S_{\text{im}2}] - \lambda_{S_{\text{im}2}} S_{\text{im}2} \quad (17)$$

In these relations, F_{im} represents the mass fraction of sorption sites in the immobile region where sorption is instantaneous.

Substituting for the sorbed phase concentrations and invoking the assumption of constant material properties yields the final form of the transport equation for the immobile region:

$$\begin{aligned} (\theta_{\text{im}} + (1-f)\rho F_{\text{im}} K_{\text{im}}) \frac{\partial C_{\text{im}}}{\partial t} + (\theta_{\text{im}} \lambda_{\text{im}} + (1-f)\rho \lambda_{S_{\text{im}1}} F_{\text{im}} K_{\text{im}}) C_{\text{im}} \\ + (1-f)k_{\text{im}2} \rho [(1-F_{\text{im}})K_{\text{im}}C_{\text{im}} - S_{\text{im}2}] = \alpha(C_{\text{m}} - C_{\text{im}}) \end{aligned} \quad (18)$$

The governing equations presented here differ from Eqs. (4) and (5) of Brusseau et al. (1992). In particular, their equations are missing decay terms for the equilibrium sorbed

phases. The equations defining the concentrations in the equilibrium sorbed phases are more correctly interpreted here as constitutive relations rather than mass balance equations.

2.3. Initial and boundary conditions

2.3.1. Initial conditions

The model of Brusseau et al. (1992) assumes that the domain is initially devoid of contaminants. The initial conditions considered by our analytical solution are somewhat more general. It is assumed that the domain is uniformly contaminated and that the initial concentrations in each of the compartments are specified independently:

$$C_m(x, 0) = C_m^0 \quad (19a)$$

$$C_{im}(x, 0) = C_{im}^0 \quad (19b)$$

$$S_{m2}(0) = S_{m2}^0 \quad (19c)$$

$$S_{im2}(0) = S_{im2}^0 \quad (19d)$$

If the initial condition of the domain is such that $C_m^0 \neq 0$, and has existed as such for a long period of time, then the following initial concentrations may be assigned:

$$C_m(x, 0) = C_m^0 \quad (20a)$$

$$C_{im}(x, 0) = C_m^0 \quad (20b)$$

$$S_{m2}(0) = K_m C_m^0 \quad (20c)$$

$$S_{im2}(0) = K_{im} C_m^0 \quad (20d)$$

2.3.2. Boundary conditions

Boundary conditions are required only for the dissolved phase in the mobile region. The model developed by Brusseau et al. (1992) considers a third-type inflow boundary condition. For the analytical solution, a “generalized” inflow boundary condition capable of representing either first or third-type conditions is used. Adopting the notation of Leij et al. (1991), the inflow boundary condition is expressed as:

$$qC_m(0, t) - \theta_m \delta D \frac{\partial}{\partial x} C_m(0, t) = qC_0[1 - H(t - t_0)] \quad (21)$$

where H is the Heaviside step function, designating a step input extending from time $= 0$ to t_0 . The reader should note that $\delta = 0$ and $\delta = 1$ specify first-type (Dirichlet) and third-type (Cauchy) boundary conditions, respectively.

The finite difference solution of Brusseau et al. (1992) is necessarily restricted to a finite domain. For analytical solutions, this restriction does not exist and both finite and semi-infinite domains are considered here. A finite domain is specified by the following outflow boundary condition:

$$\frac{\partial}{\partial x} C_m(L, t) = 0 \quad (22)$$

A semi-infinite domain is specified by the following outflow boundary condition:

$$C_m(\infty, t) = C_m^0 \exp(-\lambda_m t) \quad (23)$$

2.4. Analytical solutions in the Laplace domain

The final set of governing equations for the MPNE formulation comprises a set of four linear differential equations involving four unknown concentrations, i.e., C_m , C_{im} , S_{m2} and S_{im2} described in (Eqs. (10), (9), (18) and (17). The linearity of the governing equations is important because it offers the possibility of deriving analytical solutions using integral transform methods. The analytical solution is derived by straightforward application of the Laplace transform. The complete derivation of the solution is given in Neville (1992).

- Step (1): apply the Laplace transform with respect to time to each of the governing equations and to the boundary conditions.
- Step (2): solve the transformed governing equations for the rate-limited phases, expressing \bar{S}_{m2} and \bar{S}_{im2} in terms of \bar{C}_m and \bar{C}_{im} , respectively. The over-bars denote Laplace-transformed quantities.
- Step (3): solve the transformed mass transfer reaction by substituting for \bar{S}_{im2} , expressing \bar{C}_{im} in terms of \bar{C}_m only.
- Step (4): derive the final form of the transformed governing equation in terms of \bar{C}_m by substituting for \bar{C}_{im} and \bar{S}_{im2} . The transformed governing equation is a linear, second order ordinary differential equation.
- Step (5): derive the general solution for \bar{C}_m . For the case of zero initial concentration, the governing equation is homogeneous and the solution is obtained directly. For the case of nonzero initial concentration, the solution is derived as the sum of a complementary and a particular solution.
- Step (6): solve for the undetermined coefficients in the general solution by imposing the transformed boundary conditions. Separate solutions are developed separately for the cases of a semi-infinite and finite domain.

Semi-infinite domain

$$\bar{C}_m = \frac{q}{q - \theta_m \delta D H_1} \left(\frac{C_0}{p} [1 - \exp(-pt_0)] - \frac{\alpha G_1^0 + G_2^0}{B} \right) \exp(H_1 x) + \frac{\alpha G_1^0 + G_2^0}{B} \quad (24)$$

Finite domain

$$\bar{C}_m = \frac{D_2}{D_1} \exp(H_1 x) + \frac{D_3}{D_1} \exp(H_2 x) + \frac{\alpha G_1^0 + G_2^0}{B} \quad (25)$$

where

$$H_1 = \frac{q - \sqrt{q^2 + 4B\theta_m D}}{2\theta_m D} \quad (26a)$$

$$H_2 = \frac{q + \sqrt{q^2 + 4B\theta_m D}}{2\theta_m D} \quad (26b)$$

$$D_1 = H_2 (q - \theta_m \delta DH_1) \exp(H_2 L) - H_1 (q - \theta_m \delta DH_2) \exp(H_1 L) \quad (26c)$$

$$D_2 = \left(\frac{qC_0}{p} (1 - \exp(pt_0)) - q \frac{\alpha G_1^0 + G_2^0}{B} \right) H_2 \exp(H_2 L) \quad (26d)$$

$$D_3 = - \left(\frac{qC_0}{p} (1 - \exp(pt_0)) - q \frac{\alpha G_1^0 + G_2^0}{B} \right) H_1 \exp(H_1 L) \quad (26e)$$

$$B = \theta_m [\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4] \quad (26f)$$

$$\Gamma_1 = \left(1 + \frac{f\rho}{\theta_m} F_m K_m \right) p \quad (26g)$$

$$\Gamma_2 = \frac{1}{\theta_m} \left(f\rho(1 - F_m) K_m \frac{k_{m2}(p + \lambda_{S_{m2}})}{p + k_{m2} + \lambda_{S_{m2}}} \right) \quad (26h)$$

$$\Gamma_3 = \frac{1}{\theta_m} \left(\frac{\alpha\gamma - \alpha^2}{\gamma} \right) \quad (26i)$$

$$\Gamma_4 = \lambda_m + \frac{f\rho}{\theta_m} \lambda_{S_{m1}} F_m K_m \quad (26j)$$

$$\begin{aligned} \gamma = & p(\theta_{im} + \rho(1 - f) F_{im} K_{im}) + \theta_{im} \lambda_{im} + \rho(1 - f) F_{im} K_{im} \lambda_{S_{im1}} \\ & + \rho(1 - f)(1 - F_{im}) K_{im} k_{im2} \frac{p + \lambda_{S_{im2}}}{p + \lambda_{S_{im2}} + k_{im2}} + \alpha \end{aligned} \quad (26k)$$

The terms G_1^0 and G_2^0 are associated with the initial conditions and are defined as:

$$\begin{aligned} G_1^0 = & \left[\frac{\rho(1 - f) k_{im2}}{p + \lambda_{S_{im2}} + k_{im2}} S_{im2}^0 + (\theta_{im} + \rho(1 - f) F_{im} K_{im}) C_{im}^0 \right] \\ & \cdot \left[p(\theta_{im} + \rho(1 - f) F_{im} K_{im}) + \theta_{im} \lambda_{im} + \rho(1 - f) \lambda_{S_{im1}} F_{im} K_{im} \right. \\ & \left. + \rho(1 - f)(1 - F_{im}) K_{im} k_{im2} \frac{p + \lambda_{S_{im2}}}{p + k_{im2} + \lambda_{S_{im2}}} + \alpha \right]^{-1} \end{aligned} \quad (27a)$$

$$G_2^0 = (\theta_m + \rho f F_m K_m) C_m^0 + \frac{\rho f k_{m2}}{p + k_{m2} + \lambda_{S_{m2}}} S_{m2}^0 \quad (27b)$$

2.4.1. Special cases

The advantage of the solution technique described here is its ability to represent a very general physical conceptualization, with flexible boundary and initial conditions. For example, when the SNE parameters, F_m and F_{im} , are set equal to 1.0 (i.e., all sites are equilibrium sites), the solution collapses to the two-region model. Similarly, when the mobile porosity is set equal to the total porosity (i.e., $\theta_m = \theta$) and the sorbent is specified to be completely accessible to the dissolved phase (i.e., $f = 1.0$), the solution reduces to the two-site model. Solutions for these special cases have been presented by van Genuchten and Wagenet (1989).

The solution developed here is also a relatively general model for equilibrium transport (specifying the porosity as entirely mobile and the sorption sites as all equilibrium-controlled). For a first-type (Dirichlet) inflow boundary condition ($\delta = 0$), the solution encompasses those of Ogata and Banks (1951), Lapidus and Amundson (1952), and Bear (1972, p. 630) for a semi-infinite domain, and Cleary and Adrian (1973) for a finite domain. For a third-type (Cauchy) inflow boundary condition ($\delta = 1$), the solution encompasses those of Bastian and Lapidus (1956), Lindstrom et al. (1967), and Gershon and Nir (1969) for a semi-infinite domain, and Brenner (1962) and Dankwerts (1953) for a finite domain.

3. Evaluation and verification

3.1. Evaluation

Final values of the solution are obtained by numerical inversion of the Laplace transform solution. The decision to numerically invert the transformed solution offers two immediate advantages: first, the difficult step of deriving an analytical inverse is eliminated; second, the transformed solution is generally easier to evaluate. This approach was introduced in the hydrogeologic literature by Moench and Ogata (1981), and is now used frequently to evaluate solutions (see for example Goltz and Oxley, 1991). The success of this approach hinges on the ability to carry out the inversion accurately. For diffusion-dominated problems, there are several algorithms that yield accurate results. Unfortunately, for advection-dominated problems involving sharp fronts, these inversion techniques generally fail, yielding spurious results or under/overflow problems.

The groundwater modeling group at the University of Waterloo has obtained excellent results using the inversion algorithm developed by de Hoog et al. (1982). This algorithm has been used for both numerical models (LTG method) and analytical solutions, and has been applied to a broad spectrum of conditions, ranging from pure diffusion to almost pure advection (Therrien et al., 1990; Sudicky and McLaren, 1992). The solution is implemented in a FORTRAN program. A copy of the code with documentation is available from the first author, free upon request.

3.2. Verification

The implemented solution has been tested extensively. We report here only the testing of the full MPNE formulation. Because no other analytical solutions based on the

Table 1
Parameters for experiments 1–4

Parameter	Value
Bulk density ρ	1.360 g/cm ³
Darcy flux q	5.11 cm/day
Dispersion coefficient D	3.673 cm ³ /day
Total water content θ	0.473
Proportion of mobile pore water ϕ	0.929
Fraction of mobile sorption sites f	0.929
Fraction of equilibrium sorption sites F_m	0.50
Fraction of equilibrium sorption sites F_{im}	0.50
Mass transfer coefficient α	0.075 day ⁻¹
Sorption coefficient K_m	0.429 cm ³ /g
Sorption coefficient K_{im}	0.416 cm ³ /g
Sorption rate constant k_{m2}	0.663 day ⁻¹
Sorption rate constant k_{im2}	0.663 day ⁻¹
Pulse period t_0	7.672 day
Column length L	30.0 cm

MPNE model have been reported, the solution developed here is compared against the results from a numerical solution.

The implementation of the MPNE formulation is verified by comparison with the Brusseau et al. (1989) simulations of the column experiments reported by van Genuchten

Table 2
Parameters for experiments 3–5

Parameter	Value
Bulk density ρ	1.222 g/cm ³
Total water content θ	0.456
Darcy flux q	3.975 cm/day
Pulse period t_0	9.653 day
Column length L	30.0 cm
Dispersion coefficient D	5.313 cm ³ /day
Proportion of mobile pore water ϕ	0.88
Mass transfer coefficient α	0.03 day ⁻¹
Sorption coefficient K_m	0.426 cm ³ /g
Sorption coefficient K_{im}	0.426 cm ³ /g
Sorption rate constant k_{m2}	0.66 day ⁻¹
Sorption rate constant k_{im2}	0.66 day ⁻¹
Fraction of equilibrium sorption sites F_m	0.50
Fraction of equilibrium sorption sites F_{im}	0.50
Fraction of mobile sorption sites f	0.88
Decay coefficient λ_m	0.058 day ⁻¹
Decay coefficient $\lambda_{S_{m1}}$	—
Decay coefficient $\lambda_{S_{m2}}$	—
Decay coefficient λ_{im}	—
Decay coefficient $\lambda_{S_{im1}}$	—
Decay coefficient $\lambda_{S_{im2}}$	—

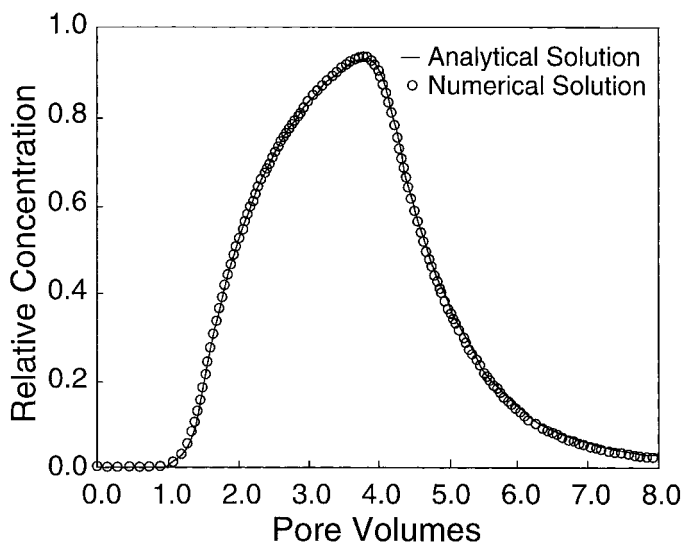


Fig. 2. Verification example: van Genuchten et al. (1977). Experiments 1–4.

et al. (1977). The column experiments were conducted to study the transport of the herbicide 2,4,5-D. The results presented by Brusseau et al. (1989) were obtained using a one-dimensional finite difference model incorporating Crank–Nicolson time-weighting. No information was provided about either the spatial or temporal discretizations used for their simulations, nor was there any indication of the criteria used to select these discretizations.

For the sake of brevity, only the comparison of the analytical and numerical solutions for the calibration of experiments 1–4 is presented here. The dimensionless parameters for the simulation are given in Brusseau et al. (1989, Fig. 6) but the corresponding dimensional parameter values are not reported. The dimensional parameters are listed here in Table 1. Some of the parameter values were obtained from van Genuchten et al. (1977, Tables 1 and 2). The remaining values were deduced from the values of the dimensionless parameters. The results of the analytical and numerical solutions are shown in Fig. 2. In Fig. 2, time is expressed as dimensionless pore volumes, defined as $T = qt/L\theta$.

4. Application of the MPNE model to van Genuchten (1974) experiments 3–5

In this section, we demonstrate the application of the MPNE model by re-visiting another of the van Genuchten and Wagenet (1989) experiments with 2,4,5-D, numbers 3–5. Brusseau et al. (1992) simulated this experiment with their numerical solution, but presented only a brief discussion of the identification of input parameters. We expand upon this discussion in order to clarify the interpretation of the input. The final parameter set is assembled in Table 2.

4.1. Input parameters

4.1.1. Basic data (ρ , θ , q , t_0 , L)

The basic data for the simulation are taken from van Genuchten (1974). These data correspond to the preliminary measurements required for any simulation.

4.1.2. Dispersion coefficient, PNE parameters (D , ϕ , α)

van Genuchten conducted column experiments with tritiated water to provide independent estimates of the dispersion coefficient and PNE parameters. Tritium sorbs relatively weakly, and its half-life of about 12 years is much longer than the duration of the column experiments. Therefore, for the purposes of this analysis, it is assumed to be a nonreactive tracer.

According to the conceptual model of MPNE, PNE affects both sorbing and nonsorbing solutes. Therefore, the tritium breakthrough data are interpreted using a two-region model. The conditions for experiments 3–5 are most similar to those reported for experiments 3–4 by van Genuchten and Wierenga (1977). From their analysis of the data, van Genuchten and Wierenga (1977) estimated a dispersion coefficient, D , of 5.7 cm²/day, a proportion of mobile pore water, ϕ equal to 0.88, and mass transfer coefficient, α of 0.10 day⁻¹. We assume that the dispersion coefficient is dominated by mechanical dispersion, so that the dispersion coefficient for experiments 3–5 can be estimated by scaling the dispersion coefficient with respect to the Darcy flux. The Darcy flux for experiments 3–4 is 4.20 cm/day while the flux for experiments 3–5 is 3.975 cm/day. Hence, the estimated dispersion coefficient for experiments 3–5 is 5.3 cm²/day.

A mass transfer coefficient for tritium was estimated from experiments 3–4. The mass transfer coefficient for 2,4,5-D is estimated by adjusting the fitted value for tritium according to the ratios of the free-solution diffusion coefficients (Brusseau et al., 1992).

$$\alpha = \alpha_{\text{exp. 3-4}} \frac{D_{2,4,5\text{-D}}^0}{D_{3\text{H}}^0}$$

where α and $\alpha_{\text{exp. 3-4}}$ are the mass transfer coefficients for 2,4,5-D and experiments 3–4, respectively, and $D_{2,4,5\text{-D}}^0$ and $D_{3\text{H}}^0$ are the free-solution diffusion coefficients for 2,4,5-D and 3H, respectively.

4.1.3. Sorption parameters (K , k , F , f)

van Genuchten et al. (1977) reported the results of batch sorption tests with 2,4,5-D. The sorption data were found to follow a nonlinear Freundlich isotherm. For an equilibrium porewater concentration C in units of $\mu\text{g}/\text{cm}^3$ and solid phase concentration S in units of $\mu\text{g}/\text{g}$, they obtained the mildly nonlinear relation.

$$S = 0.616C^{0.792}$$

The analytical approach developed for this study does not accommodate nonlinear solution. Hence, we follow the approach adopted by van Genuchten (1974) in using an

equivalent linearized sorption coefficient. For a porewater concentration ranging from 0 to 10 ($\mu\text{g}/\text{cm}^3$), the linearized sorption coefficient, K^1 , is defined by:

$$\int_0^{10} K^1 C dc = \int_0^{10} 0.616 C^{0.792} dC$$

Integrating both sides yields a linearized partitioning coefficient K^1 of $0.426 \text{ cm}^3/\text{g}$. For this simulation, it is assumed that the sorption coefficient is the same for the mobile and immobile regions, i.e., $K_m = K_{im} = K_p$.

The rate constant for nonequilibrium sorption is estimated by using a correlation with batch sorption coefficients presented by Brusseau and Rao (1992):

$$\log k_2 = -1.789 - 0.63 \log K_p$$

where k_2 is the kinetic desorption coefficient, and K_p is the partitioning (sorption) coefficient.

It is assumed that the partitioning (sorption) coefficient in this relation is given by the linearized coefficient K^1 . Using a value of K_p of 0.426, we calculate $k_2 = 0.66 \text{ day}^{-1}$. For this simulation, it is assumed that the mobile and immobile rate constants are the same, i.e., $k_{m2} = k_{im2}$.

The fractions of instantaneous sorption sites in the mobile and immobile regions are assigned the same assumed value, $F_m = F_{im} = 0.5$. It is also assumed that the proportion of sorption sites that are accessible to the solute in the mobile region is equal to the proportion of the pore water that is mobile, i.e., $f = \phi$.

4.1.4. Decay coefficients

A decay rate for the dissolved phase in the mobile region was estimated by Brusseau et al. (1992), $\lambda_m = 0.058 \text{ day}^{-1}$. It is assumed that decay only occurs in the dissolved phase in the mobile region.

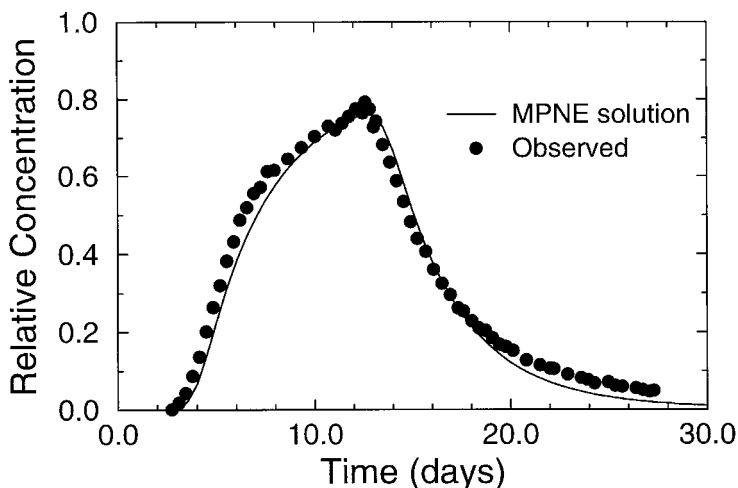


Fig. 3. Application example of the MPNE model for van Genuchten experiments 3–5.

4.2. Results

The observed breakthrough data and results obtained from the analytical solution are shown in Fig. 3.

5. Conclusions

In this paper, it has been demonstrated that the Laplace transform is an effective technique for developing analytical solutions for simulating nonidealities in solute transport. The solution derived here is based on the MPNE model developed by Brusseau et al. (1989, 1992) and is capable of representing a wider range of boundary and initial conditions than their numerical solution. The advantage of the Laplace transform technique is that it allows for straightforward derivation of analytical solutions that incorporate a very general physical conceptualization, with a broad range of boundary and initial conditions. The use of the algorithm of de Hoog et al. (1982) to numerically invert the Laplace-transformed solutions yields a code that is accurate and robust.

Quantitative analysis of field-scale processes is only possible if laboratory data are available to estimate some of the MPNE parameters. The real utility of the solution will be in the analysis of data obtained under controlled laboratory conditions. The analytical solution can be readily incorporated as a subroutine in automated parameter estimation codes. For this application, its freedom from discretization and time-stepping requirements represents a significant advantage over numerical models.

Notation

C_m	concentration in mobile region dissolved phase [ML^{-3}]
C_{im}	concentration in immobile region dissolved phase [ML^{-3}]
S_{m1}	concentration at instantaneous sorption sites in mobile region [MM^{-1}]
S_{m2}	concentration at rate-limited sorption sites in mobile region [MM^{-1}]
S_{im1}	concentration at instantaneous sorption sites in immobile region [MM^{-1}]
S_{im2}	concentration at rate-limited sorption sites in immobile region [MM^{-1}]
t	time elapsed since beginning of solute release [T]
p	Laplace transformed variable for time [T^{-1}]
x	distance from inflow boundary [L]
L	length of the domain for finite case [L]
ρ	bulk density of porous medium [ML^{-3}]
q	Darcy flux [LT^{-1}]
D	hydrodynamic dispersion coefficient [L^2T^{-1}]
θ	total water content [–]
ϕ	proportion of pore water that is mobile [–] $\phi = \theta_m/\theta$
θ_m	mobile water content [–] $\theta_m = \phi\theta$
θ_{im}	immobile water content [–] $\theta_{im} = (1 - \phi)\theta$
f	mass fraction of sorbent in contact with the mobile region dissolved phase [–]
α	first-order mass transfer coefficient [T^{-1}]
F_m	and mobile region fraction of instantaneous sorption sites [–]

F_{im}	immobile region fraction of instantaneous sorption sites [–]
K_m	mobile region equilibrium sorption coefficient [L^3M^{-1}]
K_{im}	immobile region equilibrium sorption coefficient [L^3M^{-1}]
k_{m2}	mobile region first-order kinetic desorption coefficient [T^{-1}]
k_{im2}	immobile region first-order kinetic desorption coefficient [T^{-1}]
t_0	duration of the finite-duration source [T]
λ_m	mobile region dissolved phase first-order decay rate [T^{-1}]
$\lambda_{s_{m1}}$	mobile region instantaneous sorption sites first-order decay coefficient [T^{-1}]
$\lambda_{s_{m2}}$	mobile region rate-limited sorption sites first-order decay rate [T^{-1}]
λ_{im}	immobile region dissolved phase first-order decay rate [T^{-1}]
$\lambda_{s_{im1}}$	immobile region instantaneous sorption sites first-order decay rate [T^{-1}]
$\lambda_{s_{im2}}$	immobile region rate-limited sorption sites first-order decay rate [T^{-1}]
C_0	solute concentration in inflow reservoir [ML^{-3}]
δ	inflow boundary coefficient: = 0 Type 1 inflow boundary condition, = 1 Type 3 inflow boundary condition

Acknowledgements

An early version of the de Hoog inverter was generously provided by Dr. J.H. Knight, CSIRO, Australia. Dr. M.L. Brusseau, University of Arizona, provided the results of the numerical simulations of M.Th. van Genuchten's experiments. We thank the anonymous reviewers for their thoughtful comments.

References

- Bastian, W.C., Lapidus, L., 1956. Longitudinal diffusion in ion exchange and chromatographic columns, finite columns. *Journal of Physical Chemistry* 60, 816–817.
- Bear, J., 1972. *Dynamic of Fluids in Porous Media*. Elsevier, New York.
- Bouchard, D.C., Wood, A.L., Campbell, M.L., Nkedi-Kizza, P., Rao, P.S.C., 1988. Sorption nonequilibrium during solute transport. *Journal of Contaminant Hydrology* 2, 209–223.
- Brenner, H., 1962. The diffusion model of longitudinal mixing in beds of finite length, numerical values. *Chemical Engineering Science* 17, 229–243.
- Brusseau, M.L., 1991. Application of a multiprocess nonequilibrium sorption model to solute transport in a stratified porous medium. *Water Resources Research* 27 (4), 589–595.
- Brusseau, M.L., Rao, P.S.C., 1989a. The influence of sorbate–organic matter interactions on sorption nonequilibrium. *Chemosphere* 18 (9/10), 1691–1706.
- Brusseau, M.L., Rao, P.S.C., 1989b. Sorption nonequilibrium and dispersion during transport of contaminants in groundwater: field-scale processes. In: Kobus, H., Kinzelbach, W. (Eds.), *Contaminant Transport in Ground Water: Proceedings of the International Symposium on Contaminant Transport in Groundwater* Stuttgart, 4–6 April, 1989. A.A. Balkema, Rotterdam; Brookfield, VT.
- Brusseau, M.L., Rao, P.S.C., 1989c. Sorption nonideality during organic contaminant transport in porous media. *Critical Review of Environmental Contaminant* 9 (1), 33–99.
- Brusseau, M.L., Rao, P.S.C., 1992. The influence of sorbate–organic matter interactions on sorption nonequilibrium. *Chemosphere* 9 (9/10), 1691–1706.

- Brusseau, M.L., Srivastava, R., 1997. Nonideal transport of reactive solutes in heterogeneous porous media: 2. Quantitative analysis of the Borden natural-gradient field experiment. *Journal of Contaminant Hydrology* 28 (1–2), 115–155.
- Brusseau, M.L., Jessup, R.R., Rao, P.S.C., 1989. Modeling the transport of solutes influenced by multi-process nonequilibrium. *Water Resources Research* 25 (9), 1971–1988.
- Brusseau, M.L., Jessup, R.E., Rao, P.S.C., 1992. Modeling solute transport influenced by multiprocess nonequilibrium and transformation reactions. *Water Resources Research* 28 (1), 175–182.
- Cameron, D.R., Klute, A., 1977. Convective–dispersive solute transport with a combined equilibrium and kinetic adsorption model. *Water Resources Research* 13 (1), 183–188.
- Carnahan, C.L., Remer, J.S., 1984. Nonequilibrium and equilibrium sorption with a linear sorption isotherm during mass transport through an infinite porous medium: some analytical solutions. *Journal of Hydrology* 73, 227–258.
- Cleary, R.W., Adrian, D.D., 1973. Analytical solution of the convective–dispersive equation for cation adsorption in soils. *Soil Science of America Proceedings* 37, 197–199.
- Coats, K.H., Smith, B.D., 1964. Dead-end pore volume and dispersion in porous media. *Journal of the Society of Petroleum Engineers* 4, 73–84, March.
- Criddle, C.S., Alvarez, L.M., McCarty, P.L., 1991. Microbial processes in porous media. In: *Transport in Porous Media* 202 Kluwer Academic Publishing, Netherlands.
- Dankwerts, P.V., 1953. Continuous flow systems. *Chemical Engineering Science* 2, 1–13.
- de Hoog, F.R., Knight, J.H., Stokes, A.N., 1982. An improved method for numerical inversion of Laplace transforms. *SIAM Journal on Scientific and Statistical Computing* 3 (3), 357–366, (September).
- Gershon, N., Nir, A., 1969. Effects of boundary conditions of models on tracer distribution in flow through porous media. *Water Resources Research* 5, 830–839.
- Goltz, M.N., Roberts, P.V., 1986a. Interpreting organic solute transport data from a field experiment using physical nonequilibrium models. *Transport and Transformations of Organic Contaminants* 1 (1–2), 77–93.
- Goltz, M.N., Roberts, P.V., 1986b. Three-dimensional solutions for solute transport in an infinite medium with mobile and immobile zones. *Water Resources Research* 22 (7), 1139–1148.
- Goltz, M.N., Oxley, M.E., 1991. Analytical modeling of aquifer decontamination by pumping when transport is affected by rate-limited sorption. *Water Resources Research* 27 (4), 547–556.
- Huyakorn, P.S., Lester, B.H., Mercer, J.W., 1983. An efficient finite element technique for modeling transport in fracture porous media: 1. Single species transport. *Water Resources Research* 19 (3), 841–854.
- Lapidus, L., Amundson, N.R., 1952. Mathematics of adsorption in beds: VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. *Journal of Physical Chemistry* 56, 984–988.
- Leij, F.J., van Genuchten, M., 2000. Analytical modeling of nonaqueous phase liquid dissolution with Green's functions. *Transport in Porous Media* 38 (1–2), 141–166.
- Leij, F.H., Skaggs, T.H., van Genuchten, M., 1991. Analytical solutions for solute transport in three-dimensional semi-infinite porous media. *Water Resources Research* 27 (10), 2719–2733.
- Leij, F.J., Toride, N., van Genuchten, M., 1993. Analytical solutions for nonequilibrium solute transport in three-dimensional porous media. *Journal of Hydrology* 151 (2–4), 193–228.
- Lindstrom, F.T., Haque, R., Freed, V.H., Boersma, L., 1967. Theory on the movement of some herbicides in soils: linear diffusion and convection of chemicals in soils. *Environmental Science and Technology* 1, 561–565.
- Liu, K.-H., Enfield, C.G., Mravik, S.C., 1991. Evaluation of sorption models in the simulation of naphthalene transport through saturated soils. *Ground Water* 29 (5), 685–692.
- Moench, A.F., Ogata, A., 1981. A numerical inversion of the Laplace transform solution to radial dispersion in a porous medium. *Water Resources Research* 17 (1), 250–252.
- Neville, C.J., 1992. An analytical solution for multiprocess nonequilibrium sorption. Master's thesis, University of Waterloo, Dept. of Earth Sciences, Waterloo, Ontario.
- Ogata, A., Banks, R.B., 1951. A solution of the differential equation of longitudinal dispersion in porous media. Technical Report P 0411-A.p. A1–A7, US Geological Survey, Reston, VA.
- Sudicky, E.A., 1989. The Laplace transform Galerkin technique: a time continuous finite element theory and application to mass transport in groundwater. *Water Resources Research* 25 (8), 1833–1846.
- Sudicky, E.A., 1990. The Laplace transform Galerkin technique for efficient time-continuous solution of solute transport in double-porosity media. *Geoderma* 6, 209–232.

- Sudicky, E.A., McLaren, R.G., 1992. The Laplace transform Galerkin technique for large-scale simulation of mass transport in discretely-fractured porous formations. *Water Resources Research* 28 (2), 499–514.
- Therrien, R., Sudicky, E.A., Brusseau, M.L., 1990. Three-dimensional analysis of solute transport in heterogeneous aquifers under multiprocess nonequilibrium conditions, The Int. Conf. On Transport and Mass Exchange Processes in Sand and Gravel Aquifers: Field and Modelling Studies, Ottawa, Ontario.
- Toride, N., Leij, F.J., van Genuchten, M., 1993. A comprehensive set of analytical solutions for nonequilibrium solute transport with first-order decay and zero-order production. *Water Resources Research* 2 (7), 2167–2182.
- van Genuchten, M., 1974. Mass Transfer Studies in Sorbing Porous Media. PhD thesis, New Mexico State University, Las Cruces, NM.
- van Genuchten, M., Wierenga, P.J., 1976. Mass transfer studies in sorbing porous media: I. Analytical solutions. *Soil Science of American Journal* 40, 473–480.
- van Genuchten, M., Wierenga, P.J., 1977. Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$). *Soil Science of American Journal* 41, 272–278.
- van Genuchten, M., Wagenet, R.J., 1989. Two-Site/Two-region models for pesticide transport and degradation: theoretical development and analytical solutions. *Soil Science of American Journal* 53, 1303–1310.
- van Genuchten, M., Wierenga, P.J., O'Connor, G.A., 1977. Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,4,5-t. *Soil Science of American Journal* 41, 278–285.
- Zhang, Z.H., Brusseau, M.L., 1999. Nonideal transport of reactive solutes in heterogeneous porous media: 5. Simulating regional-scale behavior of a trichloroethene plume during pump-and-treat remediation. *Water Resources Research* 35 (10), 2921–2935.