The STANMOD Computer Software for Evaluating Solute Transport in Porous Media Using Analytical Solutions of Convection-Dispersion Equation

Versions 1.0 and 2.0

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The STANMOD Computer Software for Evaluating Solute Transport in Porous Media Using Analytical Solutions of Convection-Dispersion Equation

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by

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DISCLAIMER

This report documents versions 1.0 and 2.0 of STANMOD, a software package for evaluating solute transport in porous media using analytical solutions of the convection-dispersion equation. The software has been verified against a large number of test cases. However, no warranty is given that the program is completely error-free. If you do encounter problems with the code, find errors, or have suggestions for improvement, please contact one of the authors at

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ABSTRACT

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This report documents versions 1.0 and 2.0 of STANMOD (STudio of ANalytical MODels), a Windows based computer software package for evaluating solute transport in porous media using analytical solutions of the convection-dispersion solute transport equation. Version 1.0 of STANMOD includes at present the following models: CXTFIT 2.0 [*Toride et al.,* 1995], CFITM [*van Genuchten,* 1980], CFITIM [*van Genuchten,* 1981], and CHAIN [*van Genuchten,* 1985]. Version 2.0 of STANMOD, to be released in the spring of 2000, will also include the models 3DADE [*Leij and Bradford,* 1994] and N3DADE [*Leij and Toride,* 1997]. The original manuals of all models included in STANMOD accompany this report.

The software package includes a modified and updated version of the **CXTFIT** code of *Toride et al.* [1995] for estimating solute transport parameters using a nonlinear least-squares parameter optimization method. This code may be used to solve the inverse problem by fitting a variety of mathematical solutions of theoretical transport models, based upon the one-dimensional convection-dispersion (or advection-dispersion) equation (CDE), to experimental results. The program may also be used to solve the direct or forward problem to determine concentrations as a function of time and/or position. Three different one-dimensional transport models are considered: (i) **the conventional CDE**; (ii) **the chemical and physical nonequilibrium CDEs**; and (iii) **a stochastic stream tube model** based upon the local-scale equilibrium or nonequilibrium CDE.

STANMOD also includes an updated version of the **CFITM** code of *van Genuchten* [1980] for analyzing observed column effluent data using analytical solutions of the one-dimensional **equilibrium** convective-dispersive transport equations. The code considers analytical solutions for both semi-finite and finite columns. The model provides an easy to use, efficient and accurate means of determining various transport parameters by optimizing observed column effluent data. CFITM represents a simple alternative to the much more comprehensive, but also more complex, CXTFIT model.

STANMOD also contains an updated version of the **CFITIM** code of *van Genuchten* [1981] for analyzing observed column effluent data using analytical solutions of the one-dimensional equilibrium and **nonequilibrium** convective-dispersive transport equations. The code includes analytical solutions for semi-finite columns. The nonequilibrium solutions for bicontinuum model, the two-region flow model for physical nonequilibrium and the two-site sorption model for chemical nonequilibrium. The model provides an easy to use, efficient and accurate means of determining various transport parameters by optimizing column effluent data.

In addition, STANMOD 1.0 includes the modified and updated **CHAIN** code of *van Genuchten* [1985] for analyzing the convective-dispersive transport of solutes involved in sequential **first-order decay reactions**. Examples are the migration of radionuclides, in which the chain members form first-order decay reactions, and the simultaneous movement of various interacting nitrogen or organic species.

STANMOD 2.0 includes the **3DADE** code of *Leij and Bradford* [1994] for evaluating analytical solutions for **three-dimensional equilibrium** solute transport in the subsurface. The analytical solutions pertain to selected cases of three-dimensional solute transport during steady unidirectional water flow in porous media having uniform flow and transport properties. The transport equation contains terms accounting for solute movement by convection and dispersion, as well as for solute retardation, first-order decay, and zero-order production. The 3DADE code can be used to solve the direct problem, i.e., the concentration is calculated as a function of time and space for specified model parameters, and the indirect (inverse) problem in which the program estimates selected parameters by fitting one of the analytical solutions to specified experimental data.

Finally, STANMOD 2.0 incorporates the **N3DADE** code of *Leij and Toride* [1997] for evaluating analytical solutions for a **three-dimensional nonequilibrium** solute transport in porous media. The analytical solutions pertain to three-dimensional solute transport during steady unidirectional water flow in porous media in systems of semi-infinite length in the longitudinal direction, and of infinite length in the transverse direction. The solutions can be applied also to one- and two-dimensional problems. The flow and transport properties of the medium are again assumed to be macroscopically uniform. Nonequilibrium solute transfer can occur between two domains in either the liquid or the absorbed phase. The transport equation contains terms accounting for solute movement by advection and dispersion, as well as for solute retardation, first-order decay, and zero-order production.

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LIST OF VARIABLES

c	concentration
c_f	flux concentration
c_r	resident concentration
D	dispersion coefficient
D_x	dispersion coefficient in the x-direction
D_y	dispersion coefficient in the y-direction
f	fraction of sorption sites that equilibrate with the mobile region
K_d	distribution coefficient
P	Peclet number
R	retardation factor
r	radial coordinate
t	time
t_0	pulse time
T	dimensionless time
T_0	dimensionless pulse time
v	pore-water velocity
x, y, z	spatial coordinates
α	mass transfer coefficient
β	dimensionless variable for partitioning in nonequilibrium transport models
μ	first-order rate coefficient for decay
λ	zero-order rate coefficient for production
θ_{im}	immobile water content
θ_m	mobile water content
σ_D	standard deviation of the logtransform of dispersion coefficient
σ_v	standard deviation of the logtransform of pore-water velocity
ρ_{vKd}	correlation between the pore-water velocity, v, and the distribution coefficient, K_d
ω	dimensionless mass transfer coefficient
$<.>$	ensemble average, e.g., $<v>$ is mean pore-water velocity

1. INTRODUTION

The fate and transport of dissolved substances in soils and groundwater is generating considerable interest because of concerns for the quality of the subsurface environment. The behavior of solutes over relatively long spatial and temporal scales must generally be assessed with the help of theoretical models since it is usually not feasible to carry out experimental studies over sufficiently long distances and/or time periods. Mathematical models are often also used to predict solute concentrations before management strategies are implemented. Advances in software and hardware now permit the simulation of subsurface transport using sophisticated mathematical models. Unfortunately, it is generally difficult to obtain reliable values for transport parameters such as the pore-water velocity, the retardation factor, the dispersion coefficient, and/or degradation or production parameters.

A large number of computer programs now exists for evaluating solute transport in porous media using analytical solutions of the convection-dispersion equation. The purpose of this project was to integrate the most widely used models into a one software package. We developed for this purpose a suite of analytical models STANMOD (Versions 1.0) that includes, at present, the following models for one-dimensional transport: CFITM [*van Genuchten,* 1980], CFITIM [*van Genuchten,* 1981], CHAIN [*van Genuchten,* 1985], and CXTFIT (2.0) [*Toride et al.,* 1995]. The models 3DADE [*Leij and Bradford,* 1994] and N3DADE [*Leij and Toride,* 1997] for multi-dimensional transport problems will be available in version 2.0 of STANMOD to be released in the spring of 2000. In this report we briefly describe the different analytical models included in STANMOD and review some typical examples that were included with the software. Detailed descriptions of all models are given in the original manuals, which are included as PDF files on the STANMOD CD. The manuals provide the governing transport equations, boundary and initial conditions, the derived analytical solutions, as well as description of several illustrative examples.

The graphics-based user-interface of STANMOD is for the MS Windows environment and is largely based on libraries developed for the HYDRUS-1D and HYDRUS-2D software packages [*Simunek et al.*, 1998, 1999]. All computational programs were written in FORTRAN, and the graphic interface in MS Visual C++.

2. OVERVIEW OF INCLUDED MODELS

2.1. CFITM

The **CFITM** code of *van Genuchten* [1980] can be used for analyzing observed column effluent data using analytical solutions of the one-dimensional **equilibrium** convection-dispersion transport equations. The code includes analytical solutions for both infinite and finite columns. The model provides a convenient, efficient and accurate means of determining transport parameters by fitting analytical solutions to observed column effluent data. The unknown parameters include the column Peclet number, P, the retardation factor, R, and the dimensionless pulse time, T_0. CFITM represents an easy to use, simple alternative to the more complex CXTFIT model reviewed in section 2.4.

2.2. CFITIM

The **CFITIM** code of *van Genuchten* [1981] can be used for analyzing observed column effluent data using analytical solutions for one-dimensional equilibrium and **nonequilibrium** convective-dispersive transport. The code includes analytical solutions for infinite columns. The nonequilibrium models are based on the assumption that, either for physical or chemical reasons, adsorption does not proceed at an equal rate in all parts of the soil medium. The model provides an easy to use, efficient and accurate means of fitting various transport parameters to observed column effluent data. Depending upon the exact form of the transport model, the program allows up to five different parameters to be estimated simultaneously. The unknown parameters include the column Peclet number, P, the retardation factor, R, the dimensionless pulse time, T_0, and the dimensionless parameters β (a nonequilibrium partitioning coefficient), and ω (a transfer coefficient).

2.3. CHAIN

The **CHAIN** code of *van Genuchten* [1985] can be used to analyze the convective-dispersive transport of solutes involved in sequential first-order decay reactions. The problem of solute transport involving sequential first-order decay reactions frequently occurs in soil systems. Examples are the migration of radionuclides in which the chain members form first-order decay reactions, and the simultaneous movement of various interacting nitrogen [*Cho,* 1972] or organic (e.g., pesticide) species. CHAIN is based on analytical solutions of the CDE that describe the simultaneous convective-dispersive transport of up to four species involved in such consecutive chain reactions. This program only considers the forward problem.

2.4. CXTFIT

The program **CXTFIT** 2.1 may be used to estimate parameters in several analytical models for solute transport during steady one-dimensional flow by fitting analytical solutions for the models to observed laboratory or field solute transport data. The inverse problem is solved by minimizing an objective function that consists of the sum of the squared differences between observed and fitted concentrations. The objective function is minimized using a nonlinear least-squares inversion method according to *Marquardt* [1963]. In addition, CXTFIT 2.1 may be used for the direct problem to predict solute distributions versus time and/or space for specified model parameters.

CXTFIT 2.1 is an extension and update of earlier versions published by *van Genuchten* [1979, 1981], *Parker and van Genuchten* [1984] and *Toride et al.* [1995]. CXTFIT 2.1, as before, uses the convection-dispersion equation, but with a larger number of analytical solutions pertaining to various initial, boundary, and production value problems. The nonequilibrium transport models also contain terms for zero-order production and first-order decay. Considerably more attention is being paid to the use of stream tube models for simulating transport in heterogeneous fields, thus reflecting the growing popularity of stochastic approaches for modeling field-scale solute transport. A bivariate lognormal probability density function is used to quantify stochastic pore-water velocity

and either stochastic dispersion, adsorption, or nonequilibrium solute transfer. Solute concentrations across the field can be either in the resident mode or in two different types of flux-averaged modes.

2.5. 3DADE

The **3DADE** code of *Leij and Bradford* [1994] is intended for evaluating analytical solutions for **three-dimensional equilibrium** solute transport in the subsurface. The analytical solutions pertain to selected cases of three-dimensional solute transport during steady unidirectional water flow in porous media having uniform flow and transport properties. The transport equation contains terms to account for solute movement by convection and dispersion, as well as for solute retardation, first-order decay, and zero-order production. The 3DADE code can be used to solve the direct problem, i.e., the concentration is calculated as a function of time and space for specified model parameters, and the indirect (inverse) problem in which the program estimates selected parameters by fitting one of the analytical solutions to specified experimental data. Transient analytical solutions are evaluated for five different transport scenarios (three boundary value problems and two initial value problems) in either a Cartesian or cylindrical coordinate system. Simple steady-state solutions are also provided for three initial value problems.

2.6. N3DADE

The **N3DADE** code of *Leij and Toride* [1997] can be used to evaluate analytical solutions for **three-dimensional nonequilibrium** solute transport in porous media. The analytical solutions hold for three-dimensional solute transport during steady unidirectional water flow in porous media of semi-infinite length in the longitudinal direction, and of infinite length in the transverse directions. The solutions can be also applied to one and two-dimensional problems. The flow and transport properties of the medium are assumed to be macroscopically uniform. Nonequilibrium solute transfer can occur between two domains in either the liquid or the absorbed phase. The transport equation contains terms accounting for solute movement by advection and dispersion, as well as for solute retardation, first-order decay, and zero-order production. Unlike 3DADE, the

N3DADE code can be used only to solve the direct problem, i.e., concentrations are calculated as a function of time and space for specified model parameters. A comprehensive set of specific solutions is presented using Dirac, Heaviside and exponential functions to describe a variety of initial, boundary and production profiles. A rectangular or circular inflow area is specified for the boundary value problem, while for the initial and production value problems the respective initial and production profiles are defined for parallelepipedal, cylindrical, or spherical regions of the soil. Solutions are given for volume-averaged or resident concentrations, as well as for flux-averaged or flowing concentrations.

3. EXAMPLES

STANMOD is installed with numerous examples that are divided into eight groups (*workspaces*): CFITM, CFITIM, CHAIN, Direct, Inverse, Stochast, 3DADE, and N3DADE. The first three workspaces CFITM, CFITIM, and CHAIN contain examples of the corresponding models. The next three workspaces Direct, Inverse, and Stochast contain examples of the direct, inverse, and stochastic problems solved with the CXTFIT model. The last two workspaces 3DADE and N3DADE contain examples of the 3DADE and N3DADE models. Users are advised to select an example closest to their particular problem, copy this example and then simply modify the input data. A list of all examples, together with brief descriptions, is given in Table 1 at the end of this chapter.

3.1. Examples of the CFITM model

The CFITM workspace contains two examples for the CFITM model. Both examples pertain to the transport of chromium through a sand [*Wierenga*, 1980, unpublished data; *van Genuchten*, 1980]. Observed effluent data from a 5-cm long soil column are fitted using an analytical solution of the convection-dispersion solute transport equation. Example1 uses the analytical solution for a semi-infinite system, while Example2 holds for a finite system. Peclet numbers, P, and retardation factors, R, were fitted in both examples.

3.2. Examples of the CFITIM model

The CFITIM workspace includes five examples for the CFITIM model. Example1 demonstrates the used of CFITIM on a generated data set using the assumption of physical non-equilibrium solute transport (Figure 1 of *van Genuchten* [1980]). Four parameters (the Peclet number, P, the retardation factor, R, and the dimensionless coefficients β (a nonequilibrium partitioning coefficient) and ω (transfer coefficient)) were fitted simultaneously using the generated effluent curve for a 30-cm long soil column. Example2 and Example3 consider the movement of tritiated water through a Glendale clay loam in a 30-cm long column. The nonequilibrium transport

model with five fitted parameters (P, R, β, ω, and the dimensionless pulse time, T_0) was considered for Example2 (Figure 1 of *van Genuchten* [1980]), while the linear equilibrium adsorption model with three fitted parameters ($P, R,$ and T_0) was used for Example3. Examples Fig79a (Figure 7.9a of *Toride et al.* [1995]) and Fig79b (Figure 5 of *van Genuchten* [1980] and Figure 7.9b in *Toride et al.* [1995]) consider the transport of tritiated water and boron, respectively, through Glendale clay loam in a 30-cm long column. In both examples, parameters of the non-equilibrium transport model are optimized against the effluent curves.

3.3. Examples of the CHAIN model

Two examples are presented here to illustrate typical results that can be obtained with the program. The first example (Nitrogen) applies to the three-species nitrification chain (NH_4^+ - NH_2^- - NH_3^-) (Figure 1 of *van Genuchten* [1985]). The second example deals with the radionuclide decay chain (^{238}Pu - ^{234}U - ^{230}Th - ^{226}Ra) (Figure 2 of *van Genuchten* [1985]), which serves as an illustration of modeling subsurface radionuclide transport.

3.4. Examples of the CXTFIT model

Examples of the CXTFIT model are divided into three workspaces. The first group (Direct) contains direct problems, the second group (Inverse) involves inverse problems, and the third group (Stochast) contains stochastic examples. Most examples were taken from the original CXTFIT manual [*Toride et al.*, 1995], several other examples from a book chapter by *van Genuchten and Cleary* [1979], and two examples from a book chapter by *Leij and Toride* [1998].

3.4.1. Direct problems

The first 2 examples (Fig51 and Fig52) were taken from a book chapter by *Leij and Toride* [1998], the next 9 examples (Fig71 through Fig78) from the original CXTFIT manual [*Toride et al.*, 1995], and the last 15 examples (Fig105 through Fig1012b) from a book chapter by *van Genuchten and Cleary* [1979].

Examples Fig51 and Fig52 demonstrate the use of the nonequilibrium solute transport options in the CXTFIT code. Examples Fig51 (Figure 5.1 of *Leij and Toride* [1998]) and Fig52 (Figure 5.2 of *Leij and Toride* [1998]) use the first-order physical nonequilibrium model to calculate concentrations in the mobile and immobile phases as a function of time at a depth of 50 cm for a 2-d pulse input at the soil surface. Four different combinations of the mobile water content ($\beta = \theta_m/\theta =$ 0.25, 0.5, 0.75, and 0.99) and the transfer rate ($\omega = 0.2, 1, 5, 1000$) are used in example Fig51, while five different fractions of sorption sites ($f = 0, 0.25, 0.5, 0.75, 1$) that equilibrate with the mobile region are used in example Fig52.

3.4.1.1. Examples taken from *Toride et al.* [1995]

The first two examples (Fig71 and Fig72) deal with solutions of the direct problem for **equilibrium** transport. Example Fig71 (Figure 7.1 of *Toride et al.* [1995]) illustrates the effect of the first-order decay constant, μ (=0, 0.25, 0.5, 1 d^{-1}) on solute distribution. Resident concentrations at $t = 7.5$ d were calculated for a single pulse input of duration 5 d starting at $t = 0$ to a solute-free soil profile. Examples Fig72a and Fig72b (Figures 7.2a and 7.2b of *Toride et al.* [1995]) calculate flux (c_f) and resident (c_r) concentrations for two values of the Peclet number, P (= 2, 10), respectively, as a function of relative distance when solute-free water is applied to a soil having a stepwise initial resident distribution.

The next four examples (Fig75 and Fig78) deal with solutions of the direct problem for **nonequilibrium** transport. Examples Fig75 and Fig76 were included to demonstrate differences between the one-site and two-site nonequilibrium sorption models. Example Fig75 (Figure 7.5 of *Toride et al.* [1995]) show the effects of the first-order mass transfer rate coefficient, α (= 0.08, 0.2, 10, 1000 d^{-1}), on breakthrough curves in terms of the flux-averaged concentration, as a result of applying a Dirac delta input function to an initially solute free soil. Example Fig76 (Figure 7.6 of *Toride et al.* [1995]) calculates breakthrough curves according to the two-site nonequilibrium CDE for four values of the fraction of sorption sites ($f = 0, 0.3, 0.7$, and 0.999), and using the same initial and boundary conditions as for Fig75. Values of 0.08 and 0.2 d^{-1} for the first-order mass transfer rate, α, were used in Fig76a and Fig76b, respectively. Examples Fig77a and Fig77b (Figures 7.7a and 7.7b of *Toride et al.* [1995]) calculate breakthrough curves using different sets of R, α, and f values in the two-site nonequilibrium CDE for Dirac delta input and pulse input, respectively. The

last example (Fig78) involving a direct problem concerns deterministic nonequilibrium transport as described by an initial value problem. This case calculates equilibrium and nonequilibrium resident concentrations and total concentration profiles at $T = 1$ for three values of the partitioning coefficient β (= 0.1, 0.5, and 0.9).

3.4.1.2. Examples adopted from *van Genuchten and Cleary* [1979]

Examples Fig105 and Fig105a (Figure 10.5 of *van Genuchten and Cleary* [1979]) demonstrate the effect of the first-order decay coefficient μ (= 0, 0.1, 0.2, 0.35) on Picloram movement through Norge loam using either a pulse or step input, respectively, and assuming applicability of the equilibrium CDE. Example Fig108 (Figure 10.8 of *van Genuchten and Cleary* [1979]) demonstrates the effect of the dimensionless mass transfer coefficient ω (= 0.001, 0.28, 0.7, 1.7, 2.8, 7.0, 1000000) on calculated effluent curves for 2,4,5-T movement through Glendale clay loam using the two-region physical nonequilibrium CDE model). Example Fig109 (Figures 10.9a and 10.9b of *van Genuchten and Cleary* [1979]) demonstrates the effect of the dimensionless partitioning coefficient β (= 0.2, 0.35, 0.5, 0.65, 0.80, 0.99) on calculated effluent curves from, and spatial concentration distributions in, an aggregated sorbing medium, respectively, assuming two-region physical nonequilibrium transport. Example Fig1010 (Figures 10.10a and 10.10b of *van Genuchten and Cleary* [1979]) demonstrates the effect of the retardation factor R (= 1.0, 1.75, 2.5, 3.5, and 5.0) on calculated effluent curves from, and spatial concentration distributions in, an aggregated sorbing medium, respectively, again assuming two-region physical nonequilibrium transport. Example Fig1011 (Figures 10.11a and 10.11b of *van Genuchten and Cleary* [1979]) calculates solute concentration versus time and distance for an aggregated sorbing medium, respectively, assuming two-region physical nonequilibrium model, as affected by the dimensionless mass transfer coefficient ω (= 0.02, 0.2, 0.5, 1.5, 7.5, 1000). Finally, Example Fig1012 (Figures 10.12a and 10.12b of *van Genuchten and Cleary* [1979]) demonstrates the effect of the Peclet number P (= 5, 15, 40, 100, 10000) on calculated effluent curves from, and spatial concentration distribution in, an aggregated sorbing medium, respectively, assuming two-region physical nonequilibrium transport.

3.4.2. Stochastic problems

Examples presented in this group demonstrate the use of the stochastic stream tube model in the CXTFIT code. The first two example (Fig45a and Fig45b) calculates field-scale resident concentrations, c_r, versus depth resulting from the instantaneous application of a solute to the surface as a BVP (variable mass) and an IVP (constant mass) (Figure 4.5 of *Toride et al.* [1995]). The next two examples (Fig47a and Fig47b) calculate field-scale resident concentrations versus depth as a result of a pulse-type solute application of constant duration (Figure 4.7 of *Toride et al.* [1995]).

The next example (Fig710) demonstrates the effect of variability in the pore-water velocity, v, on the field-scale resident concentration profile and the distribution of the variance for c_r in the horizontal plane (Figure 7.10 of *Toride et al.* [1995]). This example calculates the mean resident concentration and its variance as a function of depth at $t = 3$ d for three values of σ_v (=0.1, 0.3, 0.5) as a result of a 2-d solute application to a solute-free soil. Examples Fig711a, Fig711b, and Fig711c calculate the breakthrough curves for three types of field-scale concentration modes (Figure 7.11 in *Toride et al.* [1995]).

Example Fig713 demonstrates the effect of correlation (ρ_{vKd} = -1, 0, +1) between the pore-water velocity, v, and the distribution coefficient, K_d, on calculated field-scale resident concentration, c_r, profiles (Figure 7.13 of *Toride et al.* [1995]). Field-scale concentrations at $t = 5$ d resulting from a Dirac delta input at $t = 0$ are calculated versus depth for either perfect or no correlation between v and K_d. Finally, examples Fig714a and Fig714b calculate field-scale resident and total concentrations, respectively, assuming stochastic nonequilibrium solute transport. Both examples assume a negatively correlated v and K_d (ρ_{vKd} = -1) using three values of the mass transfer coefficient ω (Figure 7.14 of *Toride et al.* [1995]).

3.4.3. Inverse problems

The parameter estimation option of the CXTFIT model is demonstrated with seven examples. The first three examples (Fig73a, Fig73b, and Fig74) deal with equilibrium solute transport, and the next two examples (Fig79a and Fig79b) with nonequilibrium solute transport. Two additional examples (Fig712 and Fig715) consider field-scale stochastic solute transport.

In the first two examples (Fig73a and Fig73b), the pore-water velocity, v, and dispersion coefficient, D, are estimated from breakthrough curves measured at three different depths (11, 17, and 23 cm) with four-electrode electric conductivity sensors. Breakthrough curves were a result of (a) continuous application of a 0.001 M NaCl solution to an initially solute-free saturated sand, and (b) leaching with solute free water during unsaturated conditions, respectively. In the third inverse example (Fig74), the pore-water velocity, v, dispersion coefficient, D, and the duration of the KCl application for a pulse input, t_0, to an undisturbed sandy soil are estimated from breakthrough curves measured at a depth of 10 cm with a TDR probe.

The two examples of nonequilibrium solute transport (Fig79a corresponding to Figure 7.9a of *Toride et al.* [1995], and Fig79b corresponding to Figure 5 of *van Genuchten* [1980] and Figure 7.9b of *Toride et al.* [1995]) consider transport of tritiated water and boron, respectively, through Glendale clay loam in a 30-cm long column. In both examples parameters of the non-equilibrium transport model were optimized against effluent curves. The same examples are also considered using the CFITIM model.

The stochastic option of CXTFIT, together with parameter estimation, is demonstrated with examples Fig712 and Fig715. The first example (Figure 7.12 of *Toride et al.* [1995]) pertains to resident concentrations in a 0.64-ha field to which a bromide pulse was applied for 1.69 d followed by leaching with solute-free water [*Jury et al.,* 1982]. The stream tube model was used to estimate the mean pore-water velocity $<v>$, the mean dispersion coefficient $<D>$, and their standard deviations σ_v and σ_D, respectively. The second example (Figure 7.15 of *Toride et al.* [1995]) demonstrates the estimation of parameters in the stream tube model for reactive transport using a hypothetical data set. The standard deviation, σ_{Kd}, and the coefficient of correlation between v, and K_d, i.e., ρ_{vKd}, were fitted to the hypothetical data, while keeping $<v>$, σ_v, and $<K_d>$ constant.

3.5. Examples of the 3DADE model

Nine examples (Example1 through Example9) are presented here to illustrate the use of the 3DADE model. The first five examples (Example1 through Example5) solve direct problems, while the last four examples (Example6 through Example9) inverse parameter estimation problems.

Example1 calculates steady-state concentration profiles for a diffuse solute source in one quadrant of the soil surface (Figure 2a of *Leij et al.* [1991]). Example2 and Example 3 calculate

transient concentration profiles for transport from a rectangular solute source at the surface using either a first- or third-type boundary condition (Figure 4 of *Leij et al.* [1991]), respectively. Example4 calculates transient concentration profiles for transport from a parallelepipedal initial distribution (Figure 3 of *Leij et al.* [1991]). Finally, Example5 calculates transient concentration profiles for transport from a circular solute source at the surface using a third-type boundary condition (Figure 7 of *Leij et al.* [1991]).

Inverse problems are demonstrated using four examples (Example6 through Example9). The first example (Example6) considers (similarly to Example1) solute application in one quadrant of the soil surface. The parameters R, D_x, and D_y (retardation factor, and dispersion coefficients in the x- and y-directions, respectively) are fitted using a breakthrough curve at a specified position and the steady-state profile at a selected transect. The second inverse example (Example7) involves the estimation of the parameters R, μ, λ, D_x, D_y, and D_z (retardation factor, first-order rate coefficient for decay, zero-order rate coefficient for production, and dispersion coefficients in the x-, y- and z-directions, respectively) for solute transport from a parallelepipedal initial distribution. Breakthrough curves at ten positions along the x coordinate and two transverse profiles were used for the problem. This optimization example was repeated (Example8) for a data set in which errors of ± 10 % were imposed on the transverse concentration profiles (Figure 2 of *Leij et al.* [1994]). The final example (Example9) concerns the application of a solute pulse from a circular area at the soil surface. Parameters t_0, D_x, and D_r (pulse time, and dispersion coefficients in the x- and r-directions, respectively) were estimated using concentrations at several spatial locations at a specific time.

3.6. Examples of the N3DADE model

Five examples are presented here to illustrate the use of the N3DADE model for calculating concentration profiles using the nonequilibrium solute transport CDE. The first two examples demonstrate the use of N3DADE to solve boundary value problems (BVP), the next two examples initial value problems (IVP), and the last example a production value problem (PVP).

The first example (Figures 6, 7a, and 7b of *Leij and Toride* [1997]) calculates breakthrough curves at a depth of 50 cm (Exampl1a) and the flux-averaged spatial concentration distribution (Exampl1b) for instantaneous solute application from a disk having radius of 2.5 cm at the soil surface. The problem involves a circular geometry. The second example (Exampl2a and Exampl2b,

Figures 8 and 9 of *Leij and Toride* [1997]) pertain to flux-averaged concentration profiles resulting from the continuous application of solute to a rectangular surface area (-2.5 < y < 2.5, -2.5 < z < 2.5). Exampl2a calculates equilibrium, nonequilibrium and total concentrations versus longitudinal distance at three different times, while Exampl2b calculates concentrations in the transverse plane at two longitudinal positions.

The third example (Example3, Figure 10 of *Leij and Toride* [1997]) considers an initial value problem (rectangular) with solute initially located in the regions 5 < x < 15 (c = 1) and 25 < x < 35 (c = 0.5) for 15 < y < 25 and -100 < z < 100. The fourth example (Example4, Figure 11 of *Leij and Toride* [1997]), which also pertains to an initial value problem (in this case spherical), assumes that the solute has initially a maximum value at the point given by x=5, y=0, and z=5, and that the solute concentration decreases exponentially from the maximum.

The last example (Example5, Figure 12 of *Leij and Toride* [1997]) involves solute production in a cylindrical region of the soil (0 < x < 10 and 0 < r < 2.5). The problem is modeled as a production value problem (PVP) with a heaviside function for the longitudinal and transversal directions, with production in the equilibrium phase equal to 0.5, and in the nonequilibrium phase equal to 1.

Table 1. Summary of examples included in STANMOD.

Model/Workspace	Name	Brief Description
CFITM/CFITM	Example1 Example2	Example 2A: Chromium (Column Number 4) - Semi-Finite System Example 2B: Chromium (Column Number 4) - Finite System
CFITIM/CFITIM	Example1 Example2 Example3 Fig79a Fig79b	Generated data, Nonequilibrium model Example 2D: Tritiated water (EXP. 5-2); Nonequilibrim model Example 2H: Tritiated water (EXP. 5-2); Linear adsorption model Tritium effluent curve from Glendale clay loam; Nonequilibrim model Boron effluent [exp. 3-1, *van Genuchten*, 1974]; Nonequilibrim model
CHAIN/CHAIN	Nitrogen Radionuc	Nitrogen chain [*Cho*, 1972] Radionuclide transport
CXTFIT/Direct	Fig51 Fig52 Fig71 Fig72a Fig72b Fig75 Fig76a Fig76b Fig77a Fig77b Fig78 Fig105 Fig105a Fig108 Fig109 Fig109a Fig109b Fig1010 Fig1010a Fig1010b Fig1011 Fig1011a Fig1011b Fig1012 Fig1012a Fig1012b	First-order nonequilibrium model, effect of β and ω First-order nonequilibrium model, effect of β and f Fig.7-1: The deterministic CDE (BVP+PVP) Fig.7-2a: Flux vs. (resident) conc. for the IVP, Cf(Z) (a) P=2 (b) P=10 Fig.7-2b: (Flux) vs. resident conc. for the IVP, Cf(Z) (a) P=2 (b) P=10 Fig.7-5: Nonequilibrium one-site CDE (β=1/R, ω=0.08, 0.2, 1.0, 10) Fig.7-6a: Two-site CDE (ω=0.08, f=0, 0.3, 0.7,0.99875) Fig.7-6b: Two-site CDE (ω=0.2, f=0, 0.3, 0.7,0.99875) Fig.7-7a: Two-site CDE for βR=0.22 - Dirac input Fig.7-7b: Two-site CDE for βR=0.22 - pulse input Fig.7-8: IVP for the nonequilibrium CDE Equilibrium model, Effect of first-order decay, Step Input Equilibrium model, Effect of first-order decay, Pulse Input One-Site Model, Effect of mass-transfer coefficient Two-site model, Effect of mobile/immobile water ratio, $C_f(T)$ Two-site model, Effect of mobile/immobile water ratio, $C_f(Z)$ Two-site model, Effect of mobile/immobile water ratio, $C_r(Z)$ Two-site model, Effect of retardation factor, $C_f(T)$ Two-site model, Effect of retardation factor, $C_f(Z)$ Two-site model, Effect of retardation factor, $C_r(Z)$ Two-site model, Effect of mass transfer coefficient, $C_f(T)$ Two-site model, Effect of mass transfer coefficient, $C_f(Z)$ Two-site model, Effect of mass transfer coefficient, $C_r(Z)$ Two-site model, Effect of Peclet number, $C_f(T)$ Two-site model, Effect of Peclet number, $C_f(Z)$ Two-site model, Effect of Peclet number, $C_r(Z)$

Table 1. (continued).

Model/Workspace	Name	Brief Description
CXTFIT/Inverse	Fig73a	Fig.7-3a: Steady saturated flow in a sand column
	Fig73b	Fig.7-3b: Steady saturated flow in a sand column
	Fig74	Fig.7-4: Estimation of duration time (MASS = 1 in Block B)
	Fig79a	Fig.7-9a: Tritium effluent curve from Glendale clay loam
	Fig79b	Fig.7-9b: Boron effluent curve (exp. 3-1, *van Genuchten*, 1974)
	Fig712	Fig.7-12: Field-scale bromide movement (after *Jury at al.*, 1982)
	Fig715	Fig.7-15: Hypothetical field-scale reactive solute transport
CXTFIT/Stochast	Fig45a	Fig4-5: Stream tube model (STM) with random v, BVP vs. (IVP)
	Fig45b	Fig4-5: Stream tube model (STM) with random v, (BVP) vs. IVP
	Fig47a	Fig4-7: STM with random v, Constant and (variable) duration
	Fig47b	Fig4-7: STM with random v, (Constant) and variable duration
	Fig710	Fig.7-10: STM with random v, Effect of σ_v
	Fig711a	Fig.7-11: STM with random v, ensemble-averaged flux conc.
	Fig711b	Fig.7-11: STM with random v, field-scale flux conc.
	Fig711c	Fig.7-11: STM with random v, field-scale resident conc.
	Fig713	Fig.7-13: STM with random v and K_d, effect of ρ_{vKd}
	Fig714a	Fig.7-14: Nonequilibrium field-scale transport, field-scale c_r
	Fig714b	Fig.7-14: Nonequilibrium field-scale transport, field-scale c_t
3DADE/3DADE	Example1	Figure 2A: Diffuse source in semi-infinite region of surface, Steady-state.
	Example2	Figure 4: Rectangular source at surface, First-type BC.
	Example3	Figure 4: Rectangular source at surface, Third-type BC.
	Example4	Figure 3B: Parallelepipedal initial distribution, Third-type BC.
	Example5	Figure 7: Circular source at surface, Third-type BC.
	Example6	Inverse: Diffuse source in semi-infinite region of surface, First-type BC.
	Example7	Inverse: Parallelepipedal initial distribution, Third-type BC.
	Example8	Inverse: Parallelepipedal initial distribution, Third-type BC.
	Example9	Inverse: Circular source at surface, First-type BC.
N3DADE/N3DADE	Exampl1a	BVP: Fig. 6: Instantaneous application from disc (cm,d)
	Exampl1b	BVP: Fig. 7: Instantaneous application from disc (cm,d)
	Exampl2a	BVP: Fig. 8: Heaviside application finite rectangle
	Exampl2b	BVP: Fig. 9: Heaviside application finite rectangle
	Example3	IVP: Fig. 10: Heaviside initial, Finite rectangle
	Example4	IVP: Fig. 11: Exponential distribution about (5,0,0), Spherical coordinate
	Example5	PVP: Fig. 12: Heaviside production, Circular coordinate

4. USERS MANUAL

The computational modules of the STANMOD software package (i.e., CFITM, CFITIM, CHAIN, CXTFIT, 3DADE, N3DADE) were all written in FORTRAN. However, the interactive graphics-based interface for the MS Windows environment was written in C++. In addition to information given in this chapter and the original manuals of the different codes, extensive context-sensitive on-line help is made part of the interface. By pushing the F1 button, or clicking on the Help button while working in any window, the user obtains information about the window content. In addition, context-sensitive help is available using the "SHIFT+F1" help button. In this mode the mouse cursor changes to a help cursor (a combination of arrow + question mark), and the user can proceed by clicking on the object for which help is needed (i.e., a menu item, toolbar button, or other feature). At this point a help file will be displayed, giving information about the item on which the user clicked.

STANMOD is the main program unit defining the overall computational environment of the system. This module controls execution of the program and determines which other optional modules are necessary for a particular application. The module contains a project manager and both the pre-processing and post-processing units. The pre-processing unit includes specification of all necessary parameters to successfully run the FORTRAN codes. The post-processing unit consists of simple x-y plots for graphical presentation of the results and a dialog window that displays an ASCII output file.

The work for a new project should begin by opening the **Project Manager**, and giving a name and brief description of the new project. Users must also decide where to save the project's data (to which workspace). After clicking OK, the user has to select the specific program (e.g., CXTFIT or CFTM) for which the input is to be created. Then select the Type of Problem command from the Input Menu. From this point on the program will navigate the user through the entire process of entering input files. The user may either select particular commands from a menu, or allow the interface to lead him/her through the process of entering input data by repeatedly selecting the Next button. Alternatively, clicking the Previous button will return the user to the previous window.

A **Project Manager** is used to manage data of existing projects, and to help locate, open, copy, delete and/or rename desired projects or their input or output data. A "project" represents any

particular problem to be solved by STANMOD. The project name (8 letters maximum), as well as a brief description of the project, helps to locate a particular problem. Input and output data for each project are placed in a subdirectory with the same name as the project. Projects are represented by a file *project_name.cxt* and the *project_name* subdirectory.

The **Project Manager** gives users considerable freedom in terms of organizing his/her projects. The projects are grouped into **Workspaces** that can be placed anywhere in accessible memory, i.e., on local and/or network hard drives. The **Workspace** can be any existing accessible subdirectory (folder). STANMOD is installed together with several default workspaces. For example, the *Direct, Inverse*, and *Stochast* workspaces located in the STANMOD subdirectory contain test examples for, respectively, direct, inverse, and stochastic problems that can be analyzed with the CXTFIT program. We suggest that the user creates his/her own workspaces, e.g., the *MyDirect* and *MyInverse* workspaces, and keeps the provided examples intact for further reference. Projects can be copied with the **Project Manager** only within a particular workspace. Users can copy projects between workspaces using standard file managing software, e.g., Windows Explorer. In that case users must copy both the subdirectory of a particular project and the *project_name.cxt* file. Another way of copying a project between Workspaces is to first open the project and then using the command Save as to save this project to a new location.

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