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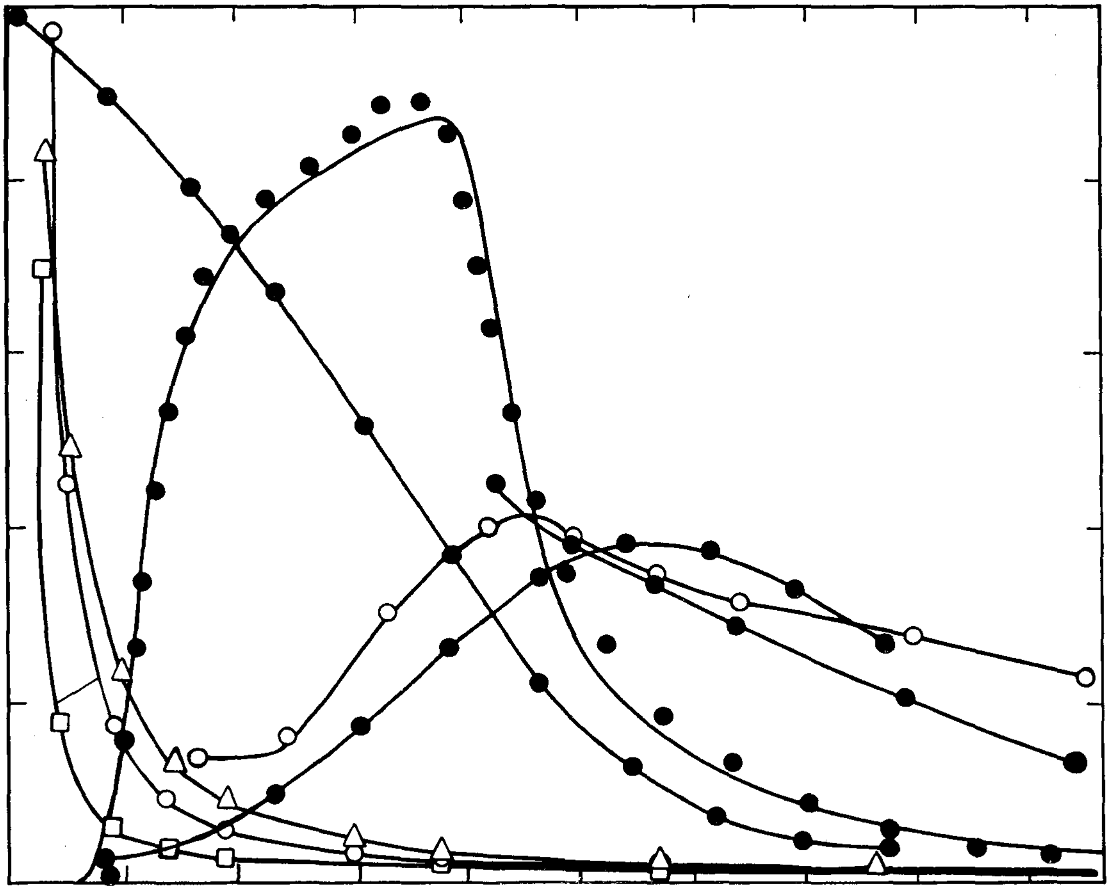

DETERMINING TRANSPORT PARAMETERS FROM LABORATORY AND FIELD TRACER EXPERIMENTS

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The Virginia Agricultural and Mechanical College came into being in 1872 upon acceptance by the Commonwealth of the provisions of the Morrill Act of 1862 "to promote the liberal and practical education of the industrial classes in the several pursuits and professions of life." Research and investigations were first authorized at Virginia's land-grant college when the Virginia Agricultural Experiment Station was established by the Virginia General Assembly in 1886.

The Virginia Agricultural Experiment Station received its first allotment upon passage of the Hatch Act by the United States Congress in 1887. Other related Acts followed, and all were consolidated in 1955 under the Amended Hatch Act which states "It shall be the object and duty of the State agricultural experiment stations . . . to conduct original and other researches, investigations and experiments bearing directly on and contributing to the establishment and maintenance of a permanent and effective agricultural industry of the United States, including the researches basic to the problems of agriculture and its broadest aspects and such investigations as have for their purpose the development and improvement of the rural home and rural life and the maximum contributions by agriculture to the welfare of the consumer . . . "

In 1962, Congress passed the McIntire-Stennis Cooperative Forestry Research Act to encourage and assist the states in carrying on a program of forestry research, including reforestation, land management, watershed management, rangeland management, wildlife habitat improvement, outdoor recreation, harvesting and marketing of forest products, and "such other studies as may be necessary to obtain the fullest and most effective use of forest resources."

In 1966, the Virginia General Assembly "established within the Virginia Polytechnic Institute a division to be known as the Research Division . . . which shall encompass the now existing Virginia Agricultural Experiment Station . . . "

ABSTRACT

J. C. Parker and M. Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. Bulletin 84-3, Virginia Agricultural Experiment Station, Blacksburg.

This bulletin describes a nonlinear least-squares inversion method that can be used to identify several parameters in a number of theoretical one-dimensional solute transport models. One of the models discussed is the usual convection-dispersion transport equation that includes terms accounting for linear equilibrium adsorption, zero-order production and/or first-order decay. In addition, a two-site/two-region model is described that can be applied to various non-equilibrium transport problems. Also included is a stochastic model that considers the effects of areal variations in hydraulic fluxes on field-scale solute transport. This last model also has provisions for zero- or first-order production and/or decay. The least-squares inversion method can be used to analyze both spatial and temporal distributions of flux or resident concentrations. A detailed description of the computer program, called CXTFIT, is given in one of the appendices of this bulletin. Several example problems illustrating practical applications of the program are discussed in detail.

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1. INTRODUCTION

Concern about the behavior of various chemicals in the subsurface environment has resulted in the development of a number of theoretical models describing the basic processes of solute transport in soils. With the introduction of more and more sophisticated models, an important problem remaining is that of quantifying various model parameters, e.g., dispersion coefficients, retardation factors, and degradation constants. One popular method for determining these parameters is to fit them to observed laboratory or field displacement data. In particular, least-squares inversion methods have proved to be accurate and reliable tools for this identification process. Early examples using least-squares methods are given by Elprince and Day (1977), Laudelout and Dufey (1977), Agneessens et al. (1978) and Le Renard (1979).

In two previous reports we documented relatively simple computer programs that applied nonlinear least-squares inversion methods to deterministic equilibrium (van Genuchten, 1980) and various non-equilibrium adsorption models (van Genuchten, 1981). Those programs are applicable only to breakthrough curves in time, that is, to solute distributions determined at a fixed location downstream of an injection point. In addition, the previous programs ignored any production and decay processes and did not distinguish between analytical solutions applicable to different concentration detection modes. In this report we extend and modify the earlier programs to the analysis of resident- and flux-type concentration distributions that have been determined versus distance or versus time at more than one location in the soil profile. Zero- and first-order production or decay terms are included in the equilibrium adsorption model.

Spatial heterogeneity of medium properties often limits the applicability of deterministic approaches to mass transport for field-scale problems. In this report we also present a stochastic model that considers the effects of areal variations in hydraulic fluxes on transport for a solute subject to linear equilibrium adsorption and zero- and first-order production or decay. Calibration of this model using field observations of spatial and/or temporal resident or flux concentrations can be achieved by application of the least-squares inversion method.

After presenting the different analytical models, a description of the computer program is given, followed by a discussion of several examples that illustrate typical applications of the inversion method. Program listings, input instructions, and example input and output files are presented in various appendices. Machine-readable copies of the FORTRAN IV program are available from the authors upon request.

2. GENERAL FORMULATION OF THE TRANSPORT EQUATION

Transport of a single reactive solute species during steady fluid flow in a one-dimensional homogeneous system may be described by

$$\frac{\rho}{\theta}\frac{\partial s}{\partial t} + \frac{\partial c_r}{\partial t} = D\frac{\partial^2 c_r}{\partial x^2} - v\frac{\partial c_r}{\partial x} - \mu_w c_r - \frac{\mu_s \rho}{\theta} s + \gamma_w + \frac{\gamma_s \rho}{\theta} \qquad [1]$$

where c_r is the volume-averaged resident concentration of the solute in the liquid phase (ML^{-3}), s is the adsorbed concentration per unit mass of the solid phase (MM^{-1}), x is distance (L), t is time (T), D is a dispersion coefficient reflecting the combined effects of diffusion and hydrodynamic dispersion on transport (L^2T^{-1}), v is the average pore-water velocity (LT^{-1}), ρ is the porous medium bulk density (ML^{-3}) and θ is the volumetric water content (L^3L^{-3}). The coefficients μ_w and μ_s are rate constants for first-order decay in the liquid and solid phases of the soil, respectively (T^{-1}). The coefficients γ_w and γ_s represent similar rate constants for zero-order production in the two soil phases ($ML^{-3}T^{-1}$ and T^{-1}, respectively).

The solution of [1] requires an expression relating the adsorbed concentration (s) to the solution concentration (c_r). Various expressions for s have been presented in the literature for which analytical solutions of [1] can be obtained. This study considers deterministic solutions of [1] applicable to various linear equilibrium (section 3) and non-equilibrium (section 4) adsorption models. Also presented is a stochastic model that explicitly considers spatial heterogeneity in v and D for the case of linear equilibrium adsorption (section 5).

In addition to the adsorption term, Eq. [1] must be augmented with auxiliary equations describing the initial and boundary conditions of the system under study. In all cases, the initial condition is assumed to be of the simple form

$$c_r(x,0) = C_i \qquad [2]$$

where C_i is a constant.

There has been much discussion in the literature about the type of boundary conditions that are most appropriate for finite and semi-infinite systems. In earlier studies (van Genuchten and Parker, 1984; Parker and van Genuchten, 1984), we showed that a third- or flux-type boundary condition should be used at the inlet position (x=0), i.e.,

$$\left(c_r - \frac{D}{v}\frac{\partial c_r}{\partial x}\right)\Big|_{x=0} = C_{in}(t) \qquad [3]$$

where $C_{in}(t)$ is the concentration of the injection fluid as a function of time. Equation [3] implies a discontinuity in concentration across the injection boundary, which increases with the value of the apparent dispersivity D/v. This discontinuity is a direct consequence of the assumption that at the injection plane a boundary layer of infinitesimal thickness develops in which the system parameters change discontinuously from those of a perfectly mixed inlet reservoir ($x < 0$) to those of the bulk porous medium ($x > 0$). Microscopically, this change always takes place over a finite transition region.

The lower boundary condition for an effectively semi-infinite system can be written as

$$\frac{\partial c_r}{\partial x}(\infty,t) = \text{finite} \qquad [4]$$

For a finite system of length L, a frequently used boundary condition is

$$\frac{\partial c_r}{\partial x}(L,t) = 0 \qquad [5]$$

This condition disregards the development of a boundary transition layer similar to that noted for the injection boundary. In effect, the concentration is forced to be continuous across the exit boundary. Accommodating the presence of a boundary layer at $x = L$ leads to a discontinuous concentration distribution across the lower boundary, and thus to a gradient in c_r interior to the transition zone that is not constrained to be zero. So long as backmixing at the exit boundary is negligible (which generally is the case), Eq. [4] for the semi-infinite case can be used with impunity and the resulting solution for $c_r(x,t)$ applied to the finite region $0 < x < L$ as well (Parker and van Genuchten, 1984; Parker, 1984). Accordingly, all solutions in this report are based on [4].

In many instances, the experimental conditions are such that measured concentrations are flux-averaged rather than volume-averaged. This is the case when effluent concentrations from column tracer experiments, pan lysimeters or subphreatic wells are analyzed. To meaningfully interpret such measurements, it is imperative that the concentrations not be assumed to represent resident concentrations (c_r) at the outflow boundary. Instead, they must be treated as representing flux-averaged concentrations (c_f), which are defined by (Brigham, 1974; Kreft and Zuber, 1978):

$$c_f = J/q \qquad [6]$$

where J and q are the solute and liquid flux densities, respectively:

$$J = qc_r - \theta D \frac{\partial c_r}{\partial x} \qquad [7]$$

and

$$q = \theta v \qquad [8]$$

With [7] and [8], Eq. [6] becomes

$$c_f = c_r - \frac{D}{v} \frac{\partial c_r}{\partial x} \qquad [9]$$

Hence, the flux-averaged concentration, c_f, represents the "mass of solute per unit volume of fluid passing through a given cross-section during an elementary time interval" (Kreft and Zuber, 1978). In this report, we will use analytical solutions of [1] for both the volume-averaged concentration, c_r, and the flux-averaged concentration, c_f.

3. LINEAR EQUILIBRIUM ADSORPTION MODELS

Consider the case where adsorption is described by a linear or linearized isotherm of the form

$$s = kc_r \qquad [10]$$

where k is an empirical distribution constant $[L^3M^{-1}]$. Substituting [10] in [1] yields

$$R \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v \frac{\partial c_r}{\partial x} - \mu c_r + \gamma \qquad [11]$$

where the dimensionless retardation factor R is defined as

$$R = 1 + \rho k/\theta \qquad [12]$$

and the new rate coefficients μ and γ (T^{-1} and $ML^{-3}T^{-1}$, respectively) are given by

$$\mu = \mu_w + \mu_s \rho k/\theta \qquad [13]$$

$$\gamma = \gamma_w + \gamma_s \rho/\theta \qquad [14]$$

We will consider solutions of [11] for pulse-type input boundary conditions of the form

$$\left(c_r - \frac{D}{v}\frac{\partial c_r}{\partial x}\right)\Bigg|_{x=0} = \begin{cases} C_o & 0 < t \leq t_o \\ 0 & t > t_o \end{cases} \qquad [15]$$

where C_o is a constant. Because solutions for zero values of μ do not follow directly from the more general solutions for non-zero μ, the two cases of zero and non-zero first-order degradation will be considered separately. On the other hand, all solutions for $\gamma = 0$ can be obtained immediately from those for non-zero γ by simply forcing this coefficient to be zero in the analytical solutions.

3.1. Solution for c_r with $\mu \neq 0$.

The analytical solution for this problem is (see case C6 of van Genuchten and Alves, 1982)

$$c_r(x,t) = \begin{cases} \frac{\gamma}{\mu} + (C_i - \frac{\gamma}{\mu})\, A(x,t) + (C_o - \frac{\gamma}{\mu})\, B(x,t) & 0 < t \leq t_o \\ \frac{\gamma}{\mu} + (C_i - \frac{\gamma}{\mu})\, A(x,t) + (C_o - \frac{\gamma}{\mu})\, B(x,t) - C_o B(x,t-t_o) & t > t_o \end{cases}$$

where

$$A(x,t) = \exp(-\frac{\mu t}{R})\ \{1 - \frac{1}{2}\,\mathrm{erfc}[\frac{Rx - vt}{2(DRt)^{1/2}}] - (\frac{v^2 t}{\pi DR})^{1/2} \exp[-\frac{(Rx - vt)^2}{4DRt}]$$

$$+ \frac{1}{2} \left(1 + \frac{vx}{D} + \frac{v^2 t}{DR}\right) \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right] \}$$

$$B(x,t) = \frac{v}{v+u} \exp\left[\frac{(v-u)x}{2D}\right] \operatorname{erfc}\left[\frac{Rx - ut}{2(DRt)^{1/2}}\right]$$

$$+ \frac{v}{v-u} \exp\left[\frac{(v+u)x}{2D}\right] \operatorname{erfc}\left[\frac{Rx + ut}{2(DRt)^{1/2}}\right]$$

$$+ \frac{v^2}{2\mu D} \exp\left(\frac{vx}{D} - \frac{\mu t}{R}\right) \operatorname{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right]$$

and

$$u = (v^2 + 4\mu D)^{1/2} .$$

3.2. Solution for c_r with $\mu = 0$.

Because of a division by zero, the analytical solution above cannot be used for the special case when first-order decay is negligible. For $\mu = 0$, the solution reduces to (case B6 of van Genuchten and Alves, 1982)

$$c(x,t) = \begin{cases} C_i + (C_o - C_i)\, A(x,t) + B(x,t) & 0 < t \leq t_o \\ C_i + (C_o - C_i)\, A(x,t) + B(x,t) - C_o A(x,t-t_o) & t > t_o \end{cases}$$

where

$$A(x,t) = \frac{1}{2} \operatorname{erfc}\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right] + \left(\frac{v^2 t}{\pi DR}\right)^{1/2} \exp\left[-\frac{(Rx - vt)^2}{4DRt}\right]$$

$$- \frac{1}{2} \left(1 + \frac{vx}{D} + \frac{v^2 t}{DR}\right) \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right]$$

$$B(x,t) = \frac{\gamma}{R}\{t + (\frac{Rx}{2v} - \frac{t}{2} + \frac{DR}{2v^2})\,\mathrm{erfc}[\frac{Rx - vt}{2(DRt)^{1/2}}]$$

$$- (\frac{t}{4\pi DR})^{1/2}(Rx + vt + \frac{2DR}{v})\exp[-\frac{(Rx - vt)^2}{4DRt}]$$

$$+ [\frac{t}{2} - \frac{DR}{2v^2} + \frac{(Rx + vt)^2}{4DR}]\exp(\frac{vx}{D})\,\mathrm{erfc}[\frac{Rx + vt}{2(DRt)^{1/2}}]\}.$$

3.3. Solution for c_f with $\mu \neq 0$.

The solutions for the flux-averaged concentrations (c_f) follow immediately from those of the volume-averaged concentrations (c_r) above by making use of definition [9]. Alternatively, the desired expressions for c_f can be found by first using [9] to redefine transport equation [11] and its initial and boundary conditions in terms of the flux-averaged concentration, and subsequently solving the transformed set of equations. To accomplish the latter, let us first differentiate [9] with respect to x and t, to give respectively

$$\frac{\partial c_f}{\partial x} = \frac{\partial c_r}{\partial x} - \frac{D}{v}\frac{\partial^2 c_r}{\partial x^2} \qquad [16]$$

$$\frac{\partial c_f}{\partial t} = \frac{\partial c_r}{\partial t} - \frac{D}{v}\frac{\partial^2 c_r}{\partial t \partial x} \qquad [17]$$

Combining [11] and [16] gives

$$R\frac{\partial c_r}{\partial t} = - v\frac{\partial c_f}{\partial x} - \mu c_r + \gamma \qquad [18]$$

Next we use [17] to eliminate $\partial c_r/\partial t$ from [18]:

$$R\frac{\partial c_f}{\partial t} = - \frac{RD}{v}\frac{\partial^2 c_r}{\partial t \partial x} - v\frac{\partial c_f}{\partial x} - \mu c_r + \gamma$$

$$= - \frac{D}{v} \frac{\partial}{\partial x} (R \frac{\partial c_r}{\partial t}) - v \frac{\partial c_f}{\partial x} - \mu c_r + \gamma \qquad [19]$$

which, again with [18] and some rearranging, yields

$$R \frac{\partial c_f}{\partial t} = D \frac{\partial^2 c_f}{\partial x^2} - v \frac{\partial c_f}{\partial x} - \mu(c_r - \frac{D}{v} \frac{\partial c_r}{\partial x}) + \gamma. \qquad [20]$$

Finally, sustitution of [9] into [20] leads to

$$R \frac{\partial c_f}{\partial t} = D \frac{\partial^2 c_f}{\partial x^2} - v \frac{\partial c_f}{\partial x} - \mu c_f + \gamma \qquad [21]$$

which is identical to [11], except that the volume-averaged concentration, c_f, is replaced by the flux-averaged concentration, c_f.

The initial and boundary conditions are transformed in the same manner to give

$$c_f(x,0) = C_i \qquad [22]$$

$$\frac{\partial c_f}{\partial x}(\infty,t) = \text{finite} \qquad [23]$$

$$c_f(0,t) = \begin{cases} C_o & 0 < t \leq t_o \\ 0 & t > t_o \end{cases} \qquad [24]$$

The transformation from [4] to [23] formally requires that the second spatial derivative of c_r also be finite when $x \to \infty$. Using the different solutions for c_r, one may verify that this criterion is indeed always met. Note that the transport model for c_f is exactly the same as the model for c_r, except that the third-type input boundary condition for c_r has been transformed into a first-type condition for c_f.

The complete solution of Eqs. [21] through [24] is (case C5 of van Genuchten and Alves, 1982)

$$c_f(x,t) = \begin{cases} \frac{\gamma}{\mu} + (C_i - \frac{\gamma}{\mu})\ A(x,t) + (C_o - \frac{\gamma}{\mu})\ B(x,t) & 0 < t \leq t_o \\ \\ \frac{\gamma}{\mu} + (C_i - \frac{\gamma}{\mu})\ A(x,t) + (C_o - \frac{\gamma}{\mu})\ B(x,t) - C_o B(x,t-t_o) & t > t_o \end{cases}$$

where

$$A(x,t) = \exp(-\frac{\mu t}{R})\ \{1 - \frac{1}{2}\ \mathrm{erfc}[\frac{Rx - vt}{2(DRt)^{1/2}}] - \frac{1}{2}\ \exp(\frac{vx}{D})\ \mathrm{erfc}[\frac{Rx + vt}{2(DRt)^{1/2}}]\ \}$$

$$B(x,t) = \frac{1}{2}\ \exp[\frac{(v-u)x}{2D}]\ \mathrm{erfc}[\frac{Rx - ut}{2(DRt)^{1/2}}] + \frac{1}{2}\ \exp[\frac{(v+u)x}{2D}]\ \mathrm{erfc}[\frac{Rx + ut}{2(DRt)^{1/2}}]$$

and

$$u = (v^2 + 4\mu D)^{1/2}\ .$$

3.4 Solution for c_f with $\mu = 0$.

The solution is (case B5 of van Genuchten and Alves, 1982)

$$c(x,t) = \begin{cases} C_i + (C_o - C_i)\ A(x,t) + B(x,t) & 0 < t \leq t_o \\ \\ C_i + (C_o - C_i)\ A(x,t) + B(x,t) - C_o A(x,t-t_o) & t > t_o \end{cases}$$

where

$$A(x,t) = \frac{1}{2}\ \mathrm{erfc}[\frac{Rx - vt}{2(DRt)^{1/2}}] + \frac{1}{2}\ \exp(\frac{vx}{D})\ \mathrm{erfc}[\frac{Rx + vt}{2(DRt)^{1/2}}]$$

$$B(x,t) = \frac{\gamma}{R}\left\{t + \frac{(Rx-vt)}{2v}\,\mathrm{erfc}\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right]\right.$$

$$\left. - \frac{(Rx+vt)}{2v}\,\exp\left(\frac{vx}{D}\right)\,\mathrm{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right]\right\}.$$

4. TWO-SITE/TWO-REGION NON-EQUILIBRIUM MODELS

We now consider the case where the adsorption term in [1] consists of two components, one governed by equilibrium adsorption and one by first-order kinetic non-equilibrium adsorption. This type of "two-site" adsorption model has been discussed by Selim et al. (1976), Cameron and Klute (1977), Rao et al. (1979), De Camargo et al. (1979), Hoffman and Rolston (1980) and by Fluhler and Jury (1983). Basic to the two-site adsorption model is the idea that the solid phase of the soil is made up of different constituents (soil minerals, organic matter, iron and aluminum oxides), and that a chemical is likely to react with these different constituents at different rates and with different intensities. The model assumes that sorption sites can be divided into two fractions; adsorption on one fraction ("type-1" sites) is assumed to be instantaneous, while adsorption on the other fraction ("type-2" sites) is thought to be time-dependent. As was the case in the earlier report (van Genuchten, 1981), we will ignore any production or decay processes for the non-equilibrium models.

At equilibrium, adsorption on both the equilibrium and kinetic sites is described by linear equations:

$$s_1 = k_1 c_r$$

$$= Fkc_r \qquad [25]$$

$$s_2 = k_2 c_r$$

$$= (1-F)kc_r \qquad [26]$$

where the subscripts 1 and 2 refer to type-1 (equilibrium) and type-2 (kinetic) sites, respectively, and where F is the fraction of all sites occupied by type-1 sorption sites. Total adsorption at equilibrium is simply

$$s = s_1 + s_2 = kc_r \qquad [27]$$

Because type-1 sites are always at equilibrium, it follows from [25] that

$$\frac{\partial s_1}{\partial t} = Fk \frac{\partial c_r}{\partial t} \qquad [28]$$

The adsorption rate for the type-2 kinetic non-equilibrium sites is given by a linear and reversible rate equation of the form

$$\frac{\partial s_2}{\partial t} = \alpha(k_2 c_r - s_2) \qquad [29]$$

where α is a first-order rate coefficient (T^{-1}). Ignoring the production and decay terms in Eq. (1) and combining this equation with the adsorption expressions above leads to the following transport model:

$$(1 + \frac{F\rho k}{\theta}) \frac{\partial c_r}{\partial t} + \frac{\rho}{\theta} \frac{\partial s_2}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v \frac{\partial c_r}{\partial x} \qquad [30]$$

$$\frac{\partial s_2}{\partial t} = \alpha[(1-F)kc_r - s_2] \qquad [31]$$

As in previous cases, Eqs. [30] and [31] will be solved for a uniform initial concentration (Eq. 2) and for a pulse-type injection (Eq. 15) into a semi-infinite medium. For s_2 an additional initial condition is required:

$$s_2(x,0) = (1-F)kC_i. \qquad [32]$$

The following dimensionless variables are introduced:

$$T = vt/L \qquad [33]$$

$$z = x/L \qquad [34]$$

$$P = vL/D \qquad [35]$$

$$R = 1 + \rho k/\theta \qquad [36]$$

$$\beta = \frac{\theta + F\rho k}{\theta + \rho k} \qquad [37]$$

$$\omega = \alpha(1-\beta)RL/v \qquad [38]$$

$$c_1 = \frac{c_r - C_i}{C_o - C_i} \qquad [39]$$

$$c_2 = \frac{s_2 - (1-F)kC_i}{(1-F)k(C_o - C_i)} \qquad [40]$$

where L is an arbitrary positive distance from the origin. Substituting these variables into [30] and [31] yields

$$\beta R \frac{\partial c_1}{\partial T} + (1-\beta)R \frac{\partial c_2}{\partial T} = \frac{1}{P}\frac{\partial^2 c_1}{\partial z^2} - \frac{\partial c_1}{\partial z} \qquad [41]$$

$$(1-\beta)R \frac{\partial c_2}{\partial T} = \omega(c_1 - c_2). \qquad [42]$$

As pointed out by van Genuchten (1981), a mathematical problem identical to that of the two-site kinetic model is obtained when apparent non-equilibrium conditions in the system are attributed to large heterogeneities in microscopic pore-water velocities. This approach assumes that the liquid phase can be partitioned into "mobile" (dynamic or macro-porosity) and "immobile" (stagnant or micro-porosity) regions. Convective and dispersive transport is restricted to the mobile water phase, while transfer of solutes into and out of the immobile (nonmoving) liquid phase is assumed to be diffusion-limited. The governing equations for this two-region model are

$$(\theta_m + f\rho k) \frac{\partial c_m}{\partial t} + [\theta_{im} + (1-f)\rho k] \frac{\partial c_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - q \frac{\partial c_m}{\partial x} \qquad [43]$$

$$[\theta_{im} + (1-f)\rho k] \frac{\partial c_{im}}{\partial t} = \alpha^*(c_m - c_{im}) \qquad [44]$$

where c_m and c_{im} are the resident concentrations of the mobile and immobile liquid phases, respectively; θ_m and θ_{im} are the mobile and immobile volumetric water contents such that $\theta = \theta_m + \theta_{im}$, D_m is the dispersion coefficient for the mobile region, f represents the fraction of the sorption sites that equilibrates with the mobile liquid phase, and α^* is a first-order rate constant that governs the rate of solute exchange between the mobile and immobile regions.

The dimensionless form of the two-site model is identically preserved when [43] and [44] are expressed in terms of T, z and R (Eqs. [33], [34] and [36]), and the following reduced variables:

$$P = v_m L/D_m \qquad [45]$$

$$\beta = \frac{\theta_m + f\rho k}{\theta + \rho k} \qquad [46]$$

$$\omega = \alpha^* L/q \qquad [47]$$

$$c_1 = \frac{c_m - C_i}{C_o - C_i} \qquad [48]$$

$$c_2 = \frac{c_{im} - C_i}{C_o - C_i} \qquad [49]$$

where $v_m = q/\theta_m$. Note that [45] is the same as [35] if we define D for the two-region model as $D = D_m\theta_m/\theta$. Because the dimensionless transport equations and their initial and boundary conditions are identical, parameters obtained by fitting data to the two-site adsorption model may be interpreted also in terms of a two-region physical non-equilibrium model (and vice-versa) if deemed appropriate.

4.1. Solution for c_r.

Analytical solutions of Eqs. [41] and [42], or of mathematically similar equations, have been derived for a variety of initial and boundary conditions (Lapidus and Amundson, 1952; Coats and Smith, 1964; Villermaux and van Swaay, 1969; Bennet and Goodridge, 1970; Lindstrom and Narasimhan, 1973; Lindstrom and Stone, 1974; van Genuchten, 1974; Lindstrom and Boersma, 1975; Lindstrom, 1976; Cameron and Klute, 1977; Popovic and Deckwer, 1976). As shown by De Smedt and Wierenga (1979), these solutions can all be expressed in the same general format. For the initial and boundary conditions of this study, the solution for the volume-averaged concentration (c_r) in terms of the reduced variables given in the previous section is (see also van Genuchten, 1981):

$$c_r(z,T) = \begin{cases} C_i + (C_o - C_i)\, A(z,T) & 0 < T < T_o \\ \\ C_i + (C_o - C_i)\, A(z,T) - C_o A(z,T-T_o) & T > T_o \end{cases} \qquad [50]$$

where

$$A(z,T) = \int_0^T g(z,\tau)\, J(a,b)\, d\tau \qquad [51]$$

$$g(z,\tau) = \left(\frac{P}{\pi\beta R\tau}\right)^{1/2} \exp\left[-\frac{P(\beta Rz - \tau)^2}{4\beta R\tau}\right]$$

$$- \frac{P}{2\beta R} \exp(Pz)\, \mathrm{erfc}\left[\left(\frac{P}{4\beta R\tau}\right)^{1/2} (\beta Rz + \tau)\right] \qquad [52]$$

$$J(a,b) = 1 - e^{-b} \int_0^a e^{-\lambda} I_o[2\sqrt{b\lambda}]\, d\lambda \qquad [53]$$

$$a = \frac{\omega\tau}{\beta R} \qquad [54]$$

and

$$b = \frac{\omega(T-\tau)}{(1-\beta)R}. \qquad [55]$$

The function J(a,b) above is often referred to as Goldstein's J-function (Goldstein, 1953); I_o in this function represents a zero-order Bessel function. Some properties and computational approximations of the J-function are summarized elsewhere (van Genuchten, 1981). We emphasize here that the analytical solution for c_r above represents the volume-average concentration of the entire liquid phase if applied to the two-site model, while for the two-region model the solution represents the volume-averaged concentration of the "mobile" liquid phase only.

4.2. Solution for c_f.

The analytical solution for the flux-averaged concentration (c_f) follows immediately if one applies transformation [9] to the analytical solution for c_r given in the previous section. The solution is exactly the same as before, except that [52] is replaced by

$$g(z,\tau) = \frac{z}{\tau}\left(\frac{P\beta R}{4\pi\tau}\right)^{1/2} \exp\left[-\frac{P(\beta Rz - \tau)^2}{4\beta R\tau}\right]. \qquad [56]$$

One may verify that the solution for c_f thus obtained is the analytical solution of Eqs. [41] and [42] for a semi-infinite medium subject to a first-type input boundary condition of the same form as given by Eq. [24] of section 3.3.

5. REGIONAL TRANSPORT MODELS

Growing evidence in the literature indicates that deterministic solutions of the convection-dispersion equation may not adequately describe solute transport in natural porous media at the field-scale (Gelhar et al., 1979; Bresler and Dagan, 1981; Pickens and Grisak, 1981; Amoozegar-Fard et al., 1982; Simmons, 1982; Tang et al., 1982). At least in part, this inadequacy is caused by medium heterogeneities which often increase significantly with the scale of observation. The two-region model discussed in the preceding section represents an attempt to accommodate pore structure variability at a scale intermediate between the usual laboratory measurements and the larger field scale. To evaluate the effects of field-scale heterogeneities, the stochastic nature of the transport process must be explicitly dealt with. The model formulated below is similar to the one-dimensional stochastic transport models of Bresler and Dagan (1981) and Amoozegar-Fard et al. (1982). Conceptually, we regard the transport region as being composed of numerous parallel porous columns (which we denote as the "local scale"), each having specific properties and being subject to specific local boundary conditions. We further assume that transport within each column can be described by the one-dimensional convection-dispersion equation (Eq. 11) with deterministic coefficients. Lateral flow, transverse dispersion, and vertical inhomogeneities are thus regarded to be negligible.

Variations in local pore water velocities are considered to be log-normally distributed. Because the flow region is assumed implicitly to be fixed, a unique realization of the stochastic variables will be obtained and the actual spatial pattern of the velocity distribution is of no concern. The probability density function for an idealized log-normal distribution of v is

$$\rho(v) = \frac{1}{v\sigma_{\ln}(2\pi)^{1/2}} \exp\{-\frac{[\ln(v) - \mu_{\ln}]^2}{2\sigma_{\ln}^2}\} \qquad [57]$$

where $\mu_{\ln}$ and $\sigma_{\ln}$ are the mean and standard deviation of ln(v). The density function is normalized so as to yield unity for the integral of $\rho(v)$ from $v = 0$ to ∞. The first moment, $\langle v\rangle$, of this density funtion gives the expected value of v:

$$\langle v\rangle = \frac{\int_0^\infty v\ \rho(v)\ dv}{\int_0^\infty \rho(v)\ dv} \qquad [58]$$

which yields

$$\langle v\rangle = \exp(\mu_{\ln} + \frac{1}{2}\sigma_{\ln}^2). \qquad [59]$$

Hence, $\langle v\rangle$ represents the mean field value of v.

Dispersion coefficients measured at the scale of single solution sampling devices have also been found to vary log-normally (Biggar and Nielsen, 1976). These variations, however, are not independent of the observed pore water velocity variations and may, to a first approximation, be described by the relation

$$D = \varepsilon v \qquad [60]$$

where ε is the local-scale dispersivity (L). We assume ε to be deterministic and constant within the flow region. This assumption effectively means that $\rho(D)$ is defined completely in terms of $\rho(v)$ and ε. Sensitivity analyses suggest that variations in D beyond those linked directly to v through [60] are insignificant compared to the effects of areal velocity variations on local convective transport (Amoozegar-Fard et al., 1982).

We further assume that water contents, adsorption coefficients and the zero- and first-order reaction constants are all deterministic variables. Thus the medium properties are completely defined by the deterministic coefficients R, μ, γ and ε and the stochastic probability density function $\rho(v)$, characterized by the coefficients μ_{ln} and σ_{ln}. We now consider solutions for field-scale resident and flux concentrations pertinent to specified field-scale initial and boundary conditions.

5.1. Solution for $\hat{c}_r$.

The field-scale resident concentration $\hat{c}_r$ represents the mean concentration value occurring over any plane perpendicular to the velocity field and parallel to the injection boundary:

$$\hat{c}_r = \frac{\int_{(A)} c_r \, dA}{\int_{(A)} dA} \qquad [61]$$

where c_r is the local-scale concentration and A is the areal domain of interest. Since velocity is the only stochastic variable over the areal domain, [61] may be written as

$$\hat{c}_r = \frac{\int_0^\infty c_r \rho(v) \, dv}{\int_0^\infty \rho(v) \, dv} \qquad [62]$$

where $\hat{c}_r = \hat{c}_r(x,t)$ and $c_r = c_r(x,t,v)$. By definition of the normalized density function, the denominator in [62] is unity. Equation

[62] indicates that $\hat{c}_r$ represents the expected value of the random variable c_r (denoted as $\langle c_r \rangle$).

To solve [62], we must evaluate the local value of c_r, which is assumed to be described by analytical solutions of section 3.1 and 3.2 for a uniform initial condition and a pulse-type injection at the local scale. The initial and input concentrations (C_i and C_o) in these solutions are assumed to be deterministic. The field-scale injection boundary condition can be formulated in one of two ways. To stipulate these conditions, let us first introduce the cumulative local inlet solute flux M (ML^{-2}):

$$M(t) = \int_0^t J_o(\tau)\, d\tau \qquad [63]$$

where J_o is the local mass flux density at the inlet boundary. For a pulse-type injection, [63] yields

$$M(t) = \begin{cases} v\theta C_o t & 0 < t < t_o \\ v\theta C_o t_o & t > t_o \end{cases} \qquad [64]$$

We also define $M_o \equiv M(t \to \infty) = v\theta C_o t_o$ which represents the total amount of material to be added to the profile. The two field-scale boundary conditions for which we will obtain solutions are determined by the following situations:

(1) Deterministic t_o, θ, C_o; Stochastic M_o, v.
(2) Deterministic M_o, θ, C_o; Stochastic t_o, v.

Thus either the pulse duration (t_o) or the asymptotic value of the cumulative influx (M_o) may be taken as constant.

By fixing t_o, it is implied that M and M_o vary locally in direct proportion to v. The mean value $\langle M \rangle$ of M at the field scale is then

$$\langle M\rangle(t) = \begin{cases} \langle v\rangle \theta C_o t & 0 < t < t_o \\ \\ \langle v\rangle \theta C_o t_o & t > t_o \end{cases} \quad [65]$$

As before, let $\langle M_o\rangle \equiv \langle v\rangle\theta C_o t_o$. Equation [65] should be used when a tracer solution is applied uniformly over the flow region for a fixed time period.

A second field-scale boundary condition can be formulated by stipulating a uniform local cumulative flux $M_o = M(t\to\infty)$, thus indicating that t_o varies inversely with v in accordance with [64]. This condition is appropriate when chemicals are added uniformly over an area in solid form and subsequently leached continuously with a solute-free solution. In that case, C_o may be viewed as being governed by the chemical solubility. The temporally integrated areal mean mass flux is now given by

$$\langle M\rangle(t) = \int_0^t \int_0^{v_o} \theta C_o \rho(v)\, dv\, d\tau \qquad (v_o = \frac{M_o}{\tau\theta C_o}) \quad [66]$$

which in the limit when $t \to \infty$ yields $\langle M\rangle(\infty) = \langle M_o\rangle = M_o$.

The initial and boundary conditions for the regional transport models are completely defined by the constants C_i, C_o and t_o or by C_i, C_o, M_o and θ. When in addition ε and the reaction constants R, μ and γ are known, the solutions for $c_r(x,t,v)$ of sections 3.1 and 3.2 can be applied. Further specification of μ_{ln} and σ_{ln} defines $\rho(v)$, thus allowing $\hat{c}_r$ to be evaluated by numerical quadrature of [62].

For purposes of field calibration involving a large number (n) of random observations for c_r at fixed x and t over the areal extent of the flow region, we may take $\rho(v) = 1/n$ in [62] for each observation c_{ri}. This discrete case gives

$$\hat{c}_r = \frac{1}{n} \sum_{i=1}^{n} c_{ri} \quad [67]$$

which is simply the arithmetic average of the observed local resident concentrations. When observations are not available at fixed x and t, it may be feasible to interpolate between given x and t graphically or by means of smoothing functions prior to averaging.

5.2. Solution for $\hat{c}_f$.

Let us define a field-scale flux concentration $\hat{c}_f$ in the same fashion as introduced earlier (Eq. 6) at the "local" level:

$$\hat{c}_f = \frac{\langle J\rangle}{\langle q\rangle} \qquad [68]$$

where $\langle J\rangle$ and $\langle q\rangle$ respectively represent the time-dependent solute mass flux and volumetric fluid flux across a plane perpendicular to the velocity field. From the definition of c_f at the local continuum level (Eq. 6), we may replace J by qc_f. With the assumption that θ is deterministic, [68] becomes then

$$\hat{c}_f = \frac{\langle vc_f\rangle}{\langle v\rangle} \qquad [69]$$

which in turn may be expanded to give

$$\hat{c}_f = \frac{\int_0^\infty vc_f\rho(v)\,dv}{\int_0^\infty v\rho(v)\,dv} \qquad [70]$$

The denominator in [70] can be obtained analytically for the log-normal distribution function as indicated by [58] and [59]. The numerator can be evaluated numerically for given $\rho(v)$ and c_f, with the latter obtained analytically from the solutions in sections 3.3 and 3.4. Field-scale initial and boundary conditions for $\hat{c}_f$ are analogous to those imposed on $\hat{c}_r$.

From Eq. [70], it follows that $\hat{c}_f$ differs from the expected value $\langle c_f\rangle$, which for deterministic θ is given by

$$\langle c_f \rangle = \frac{\int_0^\infty c_f \rho(v)\, dv}{\int_0^\infty \rho(v)\, dv}. \qquad [71]$$

This behavior is in contrast to that for $\hat{c}_r = \langle c_r \rangle$ and has important implications to model calibration via measurements of local c_f-values. For the general case of variable water content θ, random sampling leads to the discrete form for $\hat{c}_f$:

$$\hat{c}_f = \frac{\sum_{i=1}^{n} (qc_f)_i}{\sum_{i=1}^{n} q_i}. \qquad [72]$$

Because local values for q are not easily obtained experimentally, evaluation of the field-scale flux-weighted average concentration (Eq. 72) is extremely difficult. In general it is therefore advisable to use resident concentration measurements for calibration of regional transport models. The main advantage of the solution for c_f lies in the fact that it leads directly to an estimate for the field-scale solute flux $\langle J \rangle(x,t)$ for given $\langle q \rangle$.

6. COMPUTER PROGRAM DESCRIPTION

A FORTRAN IV computer program (CXTFIT) was written that permits one to fit any of the previously discussed analytical solutions for c_r, c_f, $\hat{c}_r$ or $\hat{c}_f$ to observed concentration distributions as a function of time and/or distance. The curve-fitting method uses the maximum neighborhood method of Marquardt (1963) to minimize the sums of squares of the residuals between observed and calculated concentrations. A detailed description of the method is given by Daniel and Wood (1973). Two previous versions of this same curve-fitting program were used by van Genuchten (1980, 1981) to analyze breakthrough curves in time. Program CXTFIT can be applied also to spatial concentration distributions (e.g., as obtained from sectioned soil columns or from field core data) as well as to simultaneous spatial and temporal distributions (e.g., as obtained from replicated cores sectioned at different times). The basic format of the earlier programs, including notation and set-up of the input data file, has been maintained as much as possible. Aside from the least-squares regression analysis, the program can be used also to predict spatial and temporal concentration profiles for given coefficient values using one of the analytical solutions listed in this report. The least-squares inversion part of the program will be bypassed in that case. A listing of CXTFIT is given in Appendix E.

A list of the most important parameters of CXTFIT is presented in Appendix A. Appendix B gives instructions for setting up data input files, while Appendix C lists selected input files used for various examples to be discussed later. The computer output file for these examples is given in Appendix D.

The computer model itself consists of a MAIN section, six subroutines (LIMIT, MATINV, MODEL, MOD12, MOD34 and ROMB) and four functions (CAVG, CCO, EXF and GOLD). Input and output instructions and most of the parameter optimization calculations are carried out in MAIN. Of the four functions, EXF evaluates the product of the exponential function (exp) and the complementary error function (erfc). The function CAVG calculates the arguments of the integrals in [62] and [70] for the regional transport model. The function CCO calculates the argument of the integral in [51] for the two site/two-region model, while GOLD evaluates Goldstein's J-function that appears in that same equation.

Of the six subroutines, MATINV performs a matrix inversion needed for the least-squares analysis. Subroutine MODEL performs coefficient assignments and routes execution to the appropriate subroutine for evaluation of one of the analytical solutions. Subroutine MOD12 evaluates all analytical solutions for deterministic models involving linear equilibrium adsorption while MOD34 similarly evaluates the analytical solutions for the two-site/two-region non-equilibrium models. The stochastic models also call on subroutine MOD12 to evaluate local concentration distributions.

Numerical integrations required for the two-site/two-region and stochastic models are carried out in subroutine ROMB which performs an eighth-order Romberg quadrature on a log-transformed interval. A relative error (STOPER) of 5×10^{-5} is currently used in ROMB. For most of our problems, convergence was reached with only 16-32 quadrature points. This high degree of efficiency was achieved in part by using a logarithmic transformation and in part by judiciously limiting the integration interval to a small region within which the argument of the integral is not negligible. This approach concentrates the quadrature points in the region of greatest sensitivity.

The modified lower (T1) and upper (T2) integration limits employed for the two-site/two-region models are (see also Eq. [51])

$$T1 = MAX(0.,A) \qquad [73]$$

$$T2 = MIN(TT,B) \qquad [74]$$

where

$$A = \beta Rz + \frac{40\beta R}{P}\left[1 - \left(1 + \frac{Pz}{20}\right)^{1/2}\right] \qquad [75]$$

$$B = \beta Rz + \frac{40\beta R}{P}\left[1 + \left(1 + \frac{Pz}{20}\right)^{1/2}\right]. \qquad [76]$$

This modified integration interval was obtained by limiting integration to that region where the exponential function in [56] exceeds exp(-20). In instances where a zero lower limit remains, a five point Gaussian quadrature is carried out in MOD34 on the interval from 0 to $T2\times10^{-4}$ before passing to ROMB. This procedure was found to be more accurate and efficient than a fixed 40-point Gaussian quadrature scheme previously applied to the untransformed interval (van Genuchten, 1981).

To increase computational efficiency, we also narrowed the integration limits for the stochastic transport model. Computation of these limits in subroutine LIMIT involves incremental searching with convergence by the Newton-Raphson method. Reasonable initial estimates for the narrowed limits, derived from known properties of the probability density function and also using the relationship between initial breakthrough and the local Peclet number $Pz=x/\varepsilon$, facilitated rapid convergence to suitable limits. For most problems that we investigated, subroutine LIMIT required only 10-20 solutions for local concentration values, while subsequent numerical integration in subroutine ROMB required 16-32 quadrature points.

Table 1 lists salient features of the eight models, each distinguished by a different value for the input parameter MODE. Model parameters listed in the table represent the variable coefficients for each model, i.e., coefficients that potentially can be fitted to observed data. The deterministic equilibrium models (MODE = 1,2) and the two-site/two-region non-equilibrium models (MODE = 3,4) each contain six parameters, while the stochastic models (MODE = 5,6,7 or 8) contain seven parameters. Note that t_o is a fixed input parameter for Models 5 and 6, while for Models 7 and 8 the ratio M_o/θ must be entered. Also note that for the stochastic models the probability distribution function for v is described by $\langle v \rangle$ and σ_{ln} rather than by μ_{ln} and σ_{ln}. This mode of input was deemed more useful because it is much more likely that one has an estimate for the mean field velocity $\langle v \rangle$ rather than μ_{ln}, the latter quantity corresponding to the median of the untransformed velocity distribution. For example, $\langle v \rangle$ can at least in principle be estimated from a simple water balance. Due to the log-transformation, σ_{ln} represents a dimensionless index of the dispersion of the velocity distribution.

Of the six coefficients in Models 1-4, at most five are mutually independent. Thus, for those models a maximum of only five parameters can be fitted simultaneously to the observed data. This

Table 1. Characteristics of models designated in program CXTFIT

Model number (MODE)	Model Type	Concentration detection mode	Model parameters	Report section
1	Deterministic linear equilibrium adsorption	Resident	$v, D, R, t_o, \mu, \gamma$	3.1
2	Same as 1	Flux	Same as 1	3.2
3	Two-site/two-region	Resident	$v, D, R, t_o, \beta, \omega$	4.1
4	Same as 3	Flux	Same as 3	4.2
5	Stochastic linear equilibrium adsorption with constant t_o	Resident	$\langle v \rangle, \varepsilon, R, t_o,$ μ, γ, σ_{ln}	5.1
6	Same as 5	Flux	Same as 5	5.2
7	Stochastic linear equilibrium adsorption with constant M_o	Resident	$\langle v \rangle, \varepsilon, R, M_o/\theta,$ μ, γ, σ_{ln}	5.1
8	Same as 7	Flux	Same as 7	5.2

dependency of at least one of the coefficients follows immediately by considering one of the transport equations, for example Eq. [11] for the linear equilibrium adsorption model. It is apparent that dividing this equation through by a constant permits one of the coefficients to be eliminated. Consequently, at least one of the coefficients v, D, R, μ or γ in [11] must be known independently. Because the values of D, μ and γ generally are not easily measured independently, in practice either v or R (or both) must be known beforehand. For non-adsorbing chemicals, $R = 1$, and the pore-water velocity v can be fitted to the data if so desired--a useful procedure when poor estimates for v are available, e.g., because of uncertainty about the effective water content in the system owing to negative adsorption (assuming the flux q to be known), or because of experimental problems. For adsorbing chemicals, R can at least in principle be estimated using batch-equilibration techniques, thus allowing v to be estimated from tracer experiments. On the other hand, R is often obtained also by directly fitting this coefficient to experimental data. In that case it is imperative that an accurate independent estimate for v be obtained first.

In addition to the mutual dependeny of v and R, we also observed in some cases significant interactions between the coefficients μ, γ and t_o (see examples 1 and 2 of section 7). This behavior is not surprising since these three parameters, together with R, determine the total amount of solute that will be found in the porous medium (or in the effluent). Similar interactions also occur for Models 5-8, in particular between $\langle v \rangle$ and R and between μ, γ and t_o (Models 5, 6) or μ, γ and M_o/θ (Models 7, 8). To avoid these type of uniqueness problems, we recommend to limit as much as possible the number of coefficients that will be fitted to observed data. Limiting the number of unknown coefficients is particularly important when experimental and medium variabilities create uncertainty in the data.

Appendix B gives instructions for setting up the data input file. The first card specifies the number of examples that will be executed. The second card specifies the model number (MODE) as indicated in Table 1 and a data input code (NDATA) specifying whether the next example uses the same c(x,t) data as in the previous example (but for a different model number), or whether new data are to be read in. This second card also gives the input values for NREDU (a code specifying whether or not the input concentrations and times are in dimensionless form), MIT (maximum number of iterations allowed during execution), NOB (number of observed data points), NSKIP (a code indicating whether the following example in the input data file is to be executed or skipped--a convenient feature to reduce editing of large input files), and NPRT (a code that allows one to omit input concentration data from the computer printout). After two information cards (cards 3 and 4), the input file needs a list of names for the six coefficients, BI(I), on card 5. Initial estimates for these coefficients are given on card 6. Table 1 specifies the exact sequence of the names and estimates that must be provided. Card 7 lists 6 indices, INDEX(I), that stipulate whether a certain coefficient is to be held constant (INDEX = 0) or fitted to the data (INDEX = 1). If a coefficient is assumed to be known, the initial estimate of this coefficient on card 6 will remain unchanged during the least-squares analysis. Card 8 lists CI (the initial concentration) and CO (the inlet pulse concentration). Finally, the remaining cards are used to enter the observed tracer concentration data as a function of observed distances, x, and times, t (see Appendix B for required formats).

Experimental results from laboratory soil columns are often presented in reduced form as a function of the number of pore volumes T (=vt/L) leached through the column. Dimensionless effluent concentrations, $\bar{c}$, for pulse-type injections are usually expressed in the form

$$\bar{c}(z,T) = \frac{c(z,T) - C_i}{C_o - C_i} \qquad [77]$$

where c(z,T) is the observed concentration. For effluent data, c in [77] represents a flux concentration. A similar reduction into dimensionless concentrations may be carried out also for resident concentration values when appropriate. As mentioned before, an option in the program allows reduced data to be accepted as input. By setting input code NREDU = 1, all concentrations are read in as reduced values but times are still considered to be actual values. Setting NREDU = 2 stipulates the input of reduced concentrations ($\bar{c}$) as well as reduced times (T). For Models 1-4, the value of t_o in the input file must then be replaced by its reduced counterpart T_o =

vt_o/L. Finally, when NREDU = 2, the program does not allow v to be fitted to the data, which means that the value of v must be specified on input. For the stochastic models (MODE = 5-8), time reduction may be achieved by substituting $\langle v \rangle$ for v, provided $\langle v \rangle$ is then also fixed on input.

The value of L used in defining several dimensionless variables, in particular ω for Models 3 and 4, is defined internally in the program as the maximum value in the x-array. Because of the scaled form of [41] and [42], it is apparent from the definitions of the dimensionless variables that if values for z, T and T_o are entered in lieu of x, t and t_o, and provided v is fixed at unity, then the coefficient that occupies the D-field is in actuality 1/P, while the other coefficients (β and R) retain their original meaning. The same implicit reduction can be applied also to Models 1 and 2 to obtain 1/P in lieu of D. More generally, any one of the coefficients v, D, R, μ or γ in Models 1-4 can be arbitrarily fixed at unity on input while the other coefficients are entered as usual. Because of the linearity of [11] and [21], the input or fitted parameters then take on the meaning v/a, D/a, R/a, μ/a or γ/a where a is the actual value of the fixed coefficient. These reductions of the input data can be imposed irrespective of the value of NREDU and add more flexibility when applying the computer code to different types of data sets.

7. APPLICATIONS

Several examples have been run with CXTFIT to demonstrate its accuracy and versatility. These include a number of hypothetical examples used primarily to test the inversion method as well as several experimental data sets, thus illustrating practical applications of the program.

The first example (1a) simply calculates hypothetical concentration distributions for a reactive solute exhibiting linear equilibrium adsorption, zero-order production, and first-order decay. The analysis is deterministic with medium coefficients $v=25$ cm day^{-1}, $D=100$ cm^2 day^{-1}, $R = 2.5$, $\mu=0.25$ day^{-1} and $\gamma=0.5$ μg cm^{-3} day^{-1}. The initially solute-free medium ($C_i=0$) is subjected to a pulse input of $C_o=100$ μg cm^{-3} for a duration t_o of 5 days. The predicted resident concentrations for depths 0-100 cm at t=5 and 10 days were calculated by setting MIT=0 in the input file. The input and output files are shown in Appendices C and D, respectively. Results for example 1a are plotted in Figure 1.

In example 1b, the $c_r(x,t)$ data from example 1a for both t=5 and 10 days were used as input to the nonlinear regression program, thus providing a test of the parameter estimation method. The parameters D, R, μ and γ were estimated from initial input estimates of 1.0 for all coefficients. The pore water velocity v was assumed to be known independently (at least one non-zero coefficient must be known). The fitted parameter values were essentially equal to the true values (Table 2), with residuals of the concentrations all being less than the roundoff level of the input data (Appendix D). Results of nearly the same accuracy were obtained when the inversion was restricted to only the t=5 days data (example 1c, Table 2). Attempts to estimate t_o in addition to the other four parameters indicated a large plateau in the response surface. No convergence was obtained with a stop criterion (STOPCR) of 0.0005 and with a maximum number of trials with no residual decrease within each iteration (MAXTRY) set at 50. A larger value for MAXTRY probably

Table 2. Comparison of fitted transport parameters for example 1.*

Example		D	R	μ	γ
1a	True values for c_r	100.000	2.5000	.2500	.5000
1b	22 point fit to c_r	100.062	2.4990	.2499	.4999
1c	11 point fit to c_r	100.280	2.5006	.2496	.4971
1d	11 point fit to c_f	85.6	2.52	.34	.76
1e	11 point fit to c_f	161.7	3.00	(.25)	(.50)

*D in cm^2 day^{-1}, μ in day^{-1}, γ in μg cm^{-3} day^{-1}; values in parenthesis were fixed on input.

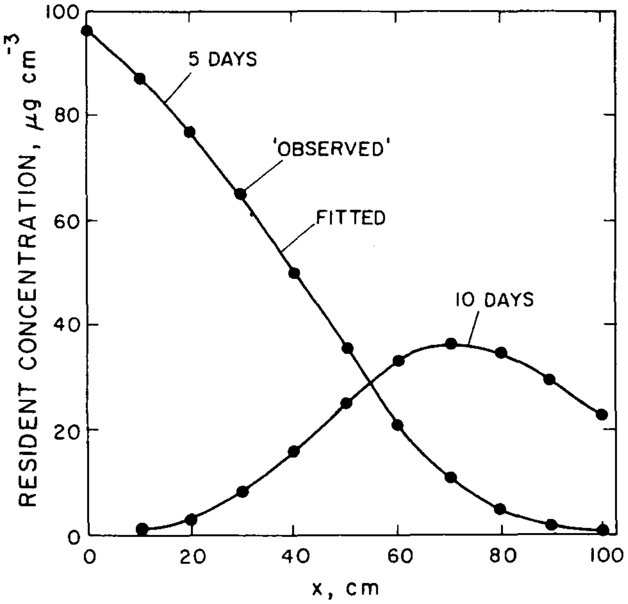

Figure 1. Hypothetical and fitted resident concentration distributions for deterministic linear equilibrium adsorption (example 1 using Model 1).

would have facilitated estimation of t_o also. However, in most cases t_o will be known, rendering its estimation unnecessary.

Boundary conditions appropriate for the analysis of flux concentrations have frequently been used to interpret data assumed to represent resident concentrations. To evaluate the effect of fitting the flux concentration solution to observed resident concentration data, the parameters in Model 2 for c_f were fitted to the t=5 data for c_r. As shown by example 1d in Table 2, the fitted coefficient values in this case do not compare well with the "true" values. With μ and γ fixed at their correct values, a two-parameter fit greatly overestimated D and R (example 1e, Table 2). This overestimation is a characteristic occurrence when resident concentrations are misintepreted as flux concentrations (Parker and van Genuchten, 1984). The converse will be found when flux concentrations are interpreted as resident concentrations.

Example 2a predicts hypothetical flux concentrations for the two-site/two-region non-equilibrium model (Model 4) using as parameter values $v=10$ cm day^{-1}, $D=1.5$ cm^2 day^{-1}, $R=3.0$, $\beta=0.3$ and $\omega=2.5$ (based on $L=40$ cm). A 2.5 day (t_o) long pulse of concentration $C_o=500$ µg cm^{-3} is applied to an initially solute-free medium ($C_i=0$). Predicted concentrations at x=20 and 40 cm from 0 to 12 days are shown in Figure 2. In example 2b, these predicted concentrations are used in the inversion program to estimate D, R, t_o, β and ω, using as starting values for these coefficients 10 cm^2 day^{-1}, 5.0, 1.0, 0.5 and 1.0, respectively. In 10 iterations the program converged to the correct values within a relative error of 0.0001 (see Appendix D). Using the concentration data for only one of the depths, the program failed to converge to the correct parameter values when all five parameters were fitted. However, the program converged correctly when t_o was fixed and the remaining four parameters were estimated from the smaller data sets.

The third example is used to analyze a column tracer experiment reported by Parker (1984). The experiment was conducted

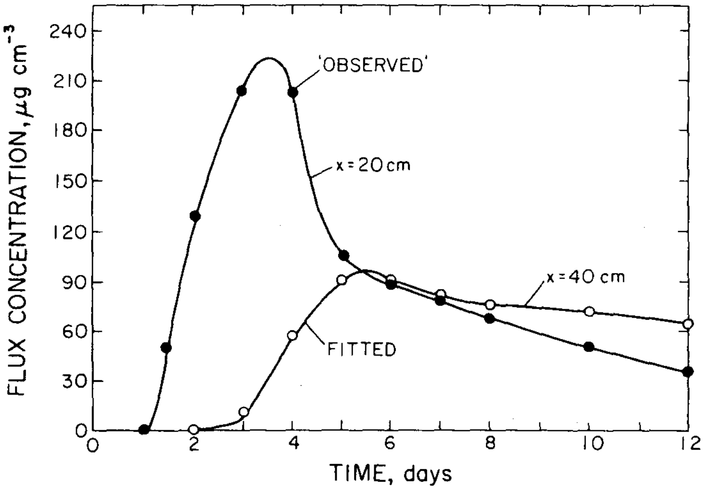

Figure 2. Hypothetical and fitted flux concentration distributions for deterministic two-region/two-site nonequilibrium model (example 2 using Model 4).

on a cylindrical column 52 mm in diameter, 190 mm long, filled with a mixture of sand and a small amount of cement as a binding agent. The column contained a straight 1.7 mm diameter "wormhole" passing axially through the center of the medium. Effluent from the column, subjected to steady saturated flow, was collected subsequent to the addition of 0.65 pore volumes of a bromide tracer to an initially Br-free pore solution. In total about 1.8 pore volumes of effluent were collected. A similar experiment was performed on a replicate column, but in this case the column was sectioned into 19 mm depth intervals immediately following the addition of the bromide pulse. The column sections were extracted to determine the Br resident concentration distribution at the time of sectioning.

The bromide effluent curve (Fig. 3) is plotted in terms of reduced concentrations versus reduced times or pore volumes. The

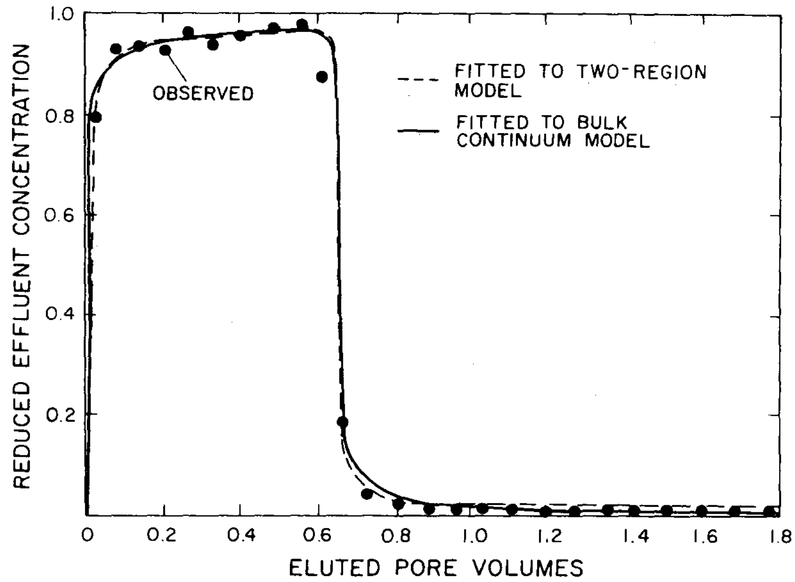

Figure 3. Experimental bromide effluent curve for packed sand with "wormhole", and fitted curves for bulk continuum model (Model 2) and two-region model (Model 4).

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mean pore water velocity v determined from the measured hydraulic flux (39.7 m day^{-1}) and water content (0.371 cm^3 cm^{-3}) was 107 m day^{-1}. Assuming no bromide adsorption (positive or negative), R was taken to be unity. Effluent concentrations and corresponding times were entered in the program as reduced values $\bar{c}(T)$, while also a reduced pulse duration T_o was used in lieu of t_o (NREDU=2). Finally, because reduced variables are used and because $\gamma=\mu=0$, we may simply set $C_i=0$ and $C_o=1$.

If the porous medium is viewed as a simple continuum, then Model 2 for c_f should be used to analyze the effluent data. In our example only D is unknown. The fitted value for D (see example 3a, Appendix D) was found to be 8745 m^2 day^{-1}. Alternatively, one may view the bromide experiment as a two-region transport problem, in which case Model 4 should be applied. With R=1, the values of

D, β and ω in this model were found to be 300 m^2 day^{-1}, 0.043 and 0.103, respectively. Figure 3 shows that Models 2 and 4 describe the experimental data with comparable accuracy. Hence, there is in this case little advantage in adopting the two-region model with three parameters instead of the much simpler bulk continuum model with only one adjustable parameter.

The importance of distinguishing between resident and flux concentrations may be evaluated by using the fitted value for D, based on Model 2 for c_f, to predict with Model 1 the resident concentration distribution (c_r) at the time the second column was sectioned. These predicted values are compared in Figure 4 with the

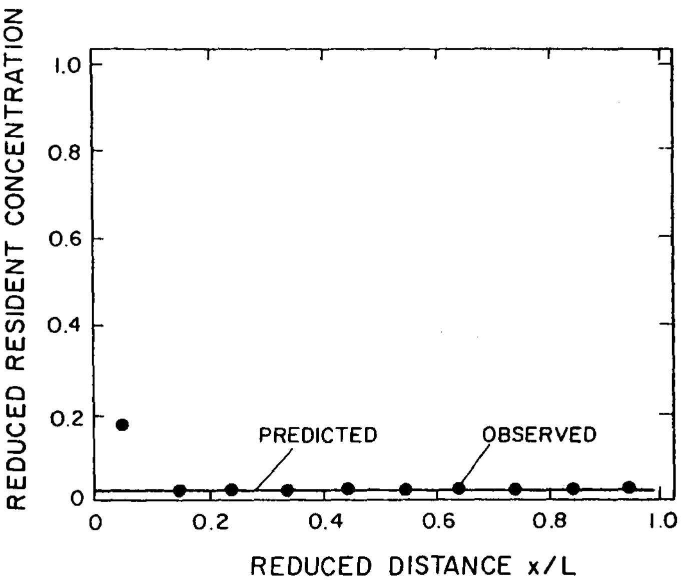


Figure 4. Experimental resident concentration distribution in "wormhole" column and predicted distribution from Model 1 using D fitted to the effluent data of Figure 3 with Model 2.

measured resident values representing mean concentrations in each 19 mm section. The correspondence is very close except in the uppermost section in immediate contact wth the influent solution. The discepency here may be expected owing to assumptions implicit in the macroscopic description of the boundary region at or near x=0 (Parker, 1984). In any case, this example emphasizes the importance of distinguishing between resident and flux concentrations. The data show that the reduced flux-averaged effluent concentration was about 0.98 at the time the column was sectioned, while the resident concentration in the column near the exit was only 0.02. Failure to realize that the effluent concentration is not equal to the resident concentration at the exit would make it impossible to fit D with Model 1 to the effluent data using the measured value for the pore water velocity. A two-parameter fit of Model 1 with variable v and D would actually lead to an estimate for the pore-water velocity that is about 1000 times greater than the measured value, thus suggesting that a large fraction of the pore space was effectively excluding the bromide tracer. This conclusion is unwarranted and unnecessary when the transport model is chosen to correspond to the proper solute detection mode.

Example 4 considers the movement of boron through Glendale clay loam (Exp. 3-1 of van Genuchten, 1974). A boron tracer pulse of duration t_o=5.06 days and having a concentration of C_o=20 μg cm^{-3} was leached through an initially solute-free 30 cm long column. The measured pore water velocity was 38.5 cm day^{-1}. Reduced concentration and times were used (NREDU=2); hence, $T_o=vt_o/L$ was entered in lieu of t_o as a known input parameter for the pulse duration. Assuming non-equilibrium adsorption and noting that flux concentrations must be used to describe effluent data, we employed Model 4 to fit the coefficients D, R, β and ω. The final parameter estimates and the sum of squared residuals (SSQ) of the observed versus fitted concentrations for two different sets of initial estimates (examples 4a,b) are shown in Table 3. Results of example 4a, which yielded the lowest SSQ, are compared with the experimental data in Figure 5. Note that the initial estimates for example 4b yielded fitted coefficient values with a higher SSQ using the currently set stop criteria (STOPCR and MAXTRY). Clearly, the program can converge to local minima with erroneous final estimates. Critical to correct and relatively rapid convergence is a good initial estimate of the product βR. For negligible dispersion (D=0), this product is equivalent to the number of pore volumes T at which the tracer initially appears in the effluent (van Genuchten and Cleary, 1979). From the experimental data in Figure 5, we may estimate the product βR to be about 2.0 (initial boron breakthrough) to 3.0 (the value of T at a reduced concentration of approximately 0.5). For not too wild initial guesses for D and ω, we always obtained convergence to the final estimates of example 4a in Table 3 when the initial estimates for β and R were such that $1.5 < \beta R < 4$. For other estimates, the program sometimes converged to the same estimates, sometimes converged to estimates with higher SSQ-values, or sometimes diverged. Consequently, a reasonable initial guess for the product βR is essential when applying the two-site/two-region

Table 3. Fitted parameter values and associated residual SSQ's for example 4 for two sets of initial estimates.*

	Example	D	R	β	ω	SSQ
4a.	Initial values	2.00	10.00	.200	.200	
	Final values	47.7	4.30	.600	.424	.053
4b.	Initial values	1.0	1.00	.500	.200	
	Final values	216.	3.58	.564	14.2	.142

*D in $cm^2 \, day^{-1}$; other parameters are dimensionless.

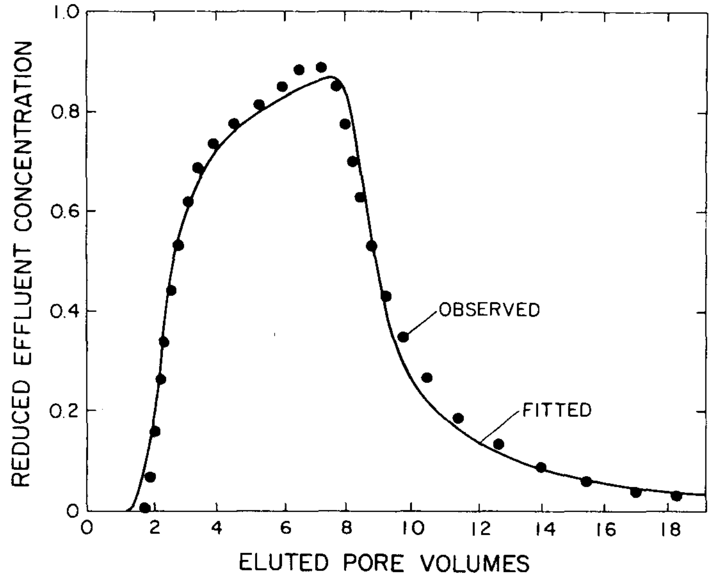


Figure 5. Experimental and fitted boron effluent curves for Glendale clay loam (example 4 using Model 4).

non-equilibrium model. We finally note that the fitted parameter values of example 4a (Table 3) obtained here with a Romberg integration scheme are the same as those obtained previously with a 40-point Gaussian quadrature scheme (van Genuchten, 1981).

Example 5 involves again a hypothetical case and deals with the stochastic regional transport model applied to a field subject to a mean velocity <v> of 25 cm day^{-1} with a standard deviation for the logarithmic probability density distribution (σ_{ln}) of 1.37. The initially solute-free medium (C_i=0) is subjected to a uniform dose of solute (M_o) of 10,000 μg cm^{-2}, which for θ=0.5 yields the input parameter SOLOAD $\equiv M_o/\theta$ = 20,000 μg cm^{-2}. We assume the inlet solute concentration (C_o) to be 1,000 μg cm^{-3} and take ε=10 cm, R=5.0 and μ=γ=0.0. Figure 6 shows calculated concentration profiles

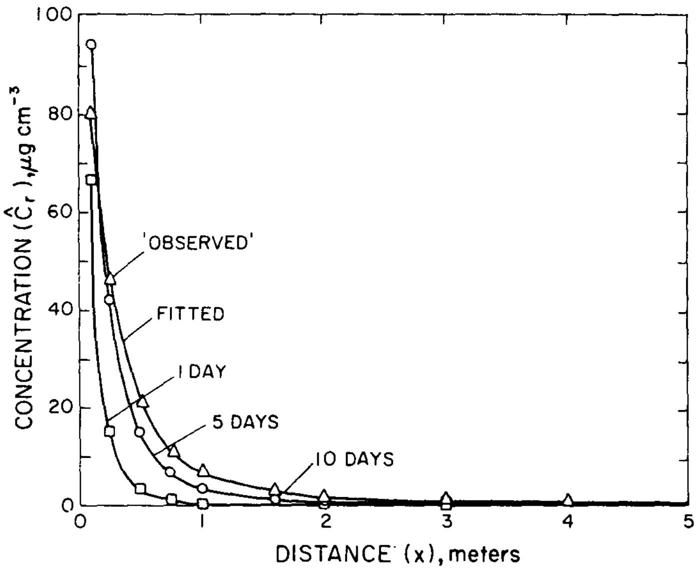


Figure 6. Hypothetical and fitted resident concentration distributions for stochastic transport model (example 5 using Model 7).

(Model 4; MIT=0) from 0 to 500 cm and for t=1, 5 and 10 days (example 5a). Using 30 input data points for the combined times and initial guesses of 10 cm day^{-1} for <v> and unity for the other parameters, the inversion program yielded estimates for <v>, ε, R and σ_{ln} with a maximum error of 0.0001 from the correct values (example 5b, Appendix D). The program converged to incorrect parameter values when in addition M_o/θ was fitted to the data. Execution terminated with parameter values fixed on a very flat response surface with SSQ still large. In such cases it is sometimes possible to move off the plateau in the response surface by decreasing STOPCR and increasing MAXTRY. In less troublesome circumstances, greater computational efficiency will be obtained, however, when STOPCR is relatively large and MAXTRY relatively small (see also our comments on uniqueness problems in the previous section).

The final example considers a case of field-scale stochastic transport. Unfortunately, field measurements suitable for testing and calibrating stochastic transport models are scarce. Jury et al. (1982) reported areally-averaged concentrations over a 0.64 ha field subjected to a bromide pulse of fixed duration and subsequently leached under transient hydraulic conditions. The stochastic model presented here does not strictly apply to transient conditions. However, by invoking some approximate transformations of temporal variables, the model can be extended in an approximate manner also to transient conditions.

Let us define a time-averaged flux $\langle q\rangle^*$, a time-averaged water content $\langle\theta\rangle^*$, and a time-averaged pore water velocity $\langle v\rangle^*$ as follows:

$$\langle q\rangle^* = \frac{1}{t_m} \int_0^{t_m} \langle q\rangle(\tau)\, d\tau \qquad [78]$$

$$\langle\theta\rangle^* = \frac{1}{t_m} \int_0^{t_m} \langle\theta\rangle(\tau)\, d\tau \qquad [79]$$

$$\langle v\rangle^* = \frac{\langle q\rangle^*}{\langle\theta\rangle^*} \qquad [80]$$

where $\langle q\rangle$ and $\langle\theta\rangle$ respectively represent the actual time-dependent areally-averaged fluxes and water contents over the time interval $t=0$ to t_m of interest. We assume $\langle q\rangle^*$ and $\langle\theta\rangle^*$ to be independent of x. For $\langle q\rangle^*$ this assumption implies that there are no fluid sources or sinks in the flow region, while t_m must be relatively large. For $\langle\theta\rangle^*$, the additional constraint of medium homogeneity in the x direction is implied. If these assumptions are not appropriate and information regarding the variation of $\langle q\rangle$ and $\langle\theta\rangle$ with x is available, an approximate transformation of the space coordinate may be imposed in the manner of Bresler and Dagan (1981):

$$x^* = \frac{\langle\langle v\rangle^*(x)\rangle}{\langle v\rangle^*(x)}\, x \qquad [81]$$

where $\langle v\rangle^*(x)$ is the temporally- and areally-averaged velocity at distance x, while $\langle\langle v\rangle^*(x)\rangle$ represents the mean of $\langle v\rangle^*$ over all x. We will not impose the latter transformation but instead take $\langle v\rangle^*$ as constant and calculate $\langle q\rangle^*$ by means of a water balance at x=0. Transformation of the time variable itself is accomplished with

$$t^* = \frac{\int_0^t \langle q\rangle(\tau)\, d\tau}{\langle q\rangle^*} \qquad [82]$$

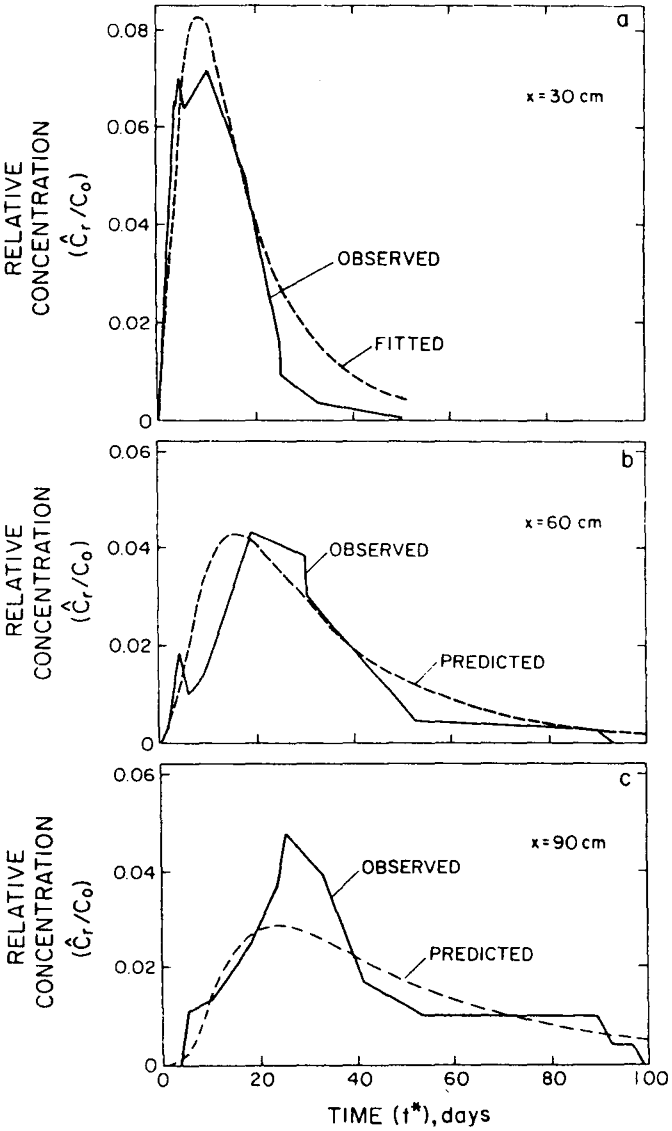
where the numerator represents the cumulative flux until time t. To implement this model for temporally transformed data, we need to estimate t* and $\langle v\rangle^*$ instead of t and $\langle v\rangle$. Averaging the data of Jury et al. (1982) over a period of 100 days yields $\langle q\rangle^*=5.9$ mm day^{-1}. From $\langle q\rangle^*$ and the reported values of the cumulative net amount of applied water versus areally-averaged concentrations, we may calculate the times t* that correspond to these measured concentrations. Since $\langle\theta\rangle^*$ is not known, $\langle v\rangle^*$ cannot be calculated directly. However, a reasonable first guess of $\langle v\rangle^*$ for the inversion program can be obtained by using $\langle\theta\rangle^*=0.2$. Application of the tracer was accomplished by means of a uniform 10-mm irrigation over the entire field. By regarding the measured concentrations as resident values, we may use Model 5 to analyze the data. The input value of t_o for that purpose was replaced by the transformed pulse time t_o^*, which according to [82] equals $10/\langle q\rangle^*=1.69$ days. We further assume R=1.0 and $\mu=\gamma=0.0$ for bromide transport. The program can now be used to calculate $\langle v\rangle^*$, ε and σ_{ln}.

Using 10 values for $\hat{c}_r$ that were estimated from observations at x=30 cm from t*=0 to 50 days, the fitted coefficient values were found to be <v>*=30.5 mm day^{-1}, ε=1.0 mm and σ_{ln}=0.800 (example 6a, Table 4). The results indicate that the estimated value of ε includes zero within the 95% confidence limits. To further investigate the implications of this uncertainty in the estimation of local dispersivity, we fitted <v>* and σ_{ln} to the data while fixing ε at various values. The results (examples 6b–6e, Table 4) show that the fitted values of <v>* and σ_{ln} are little affected by variations in ε between 0.1 and 10.0 mm. Much larger values of ε, however, cause SSQ to increase while σ_{ln} decreases to compensate for the high local dispersion. It is apparent that local-scale dispersion is small compared to the effects of areal velocity variations on resultant field-scale distributions. Noting that the program requires ε>0, it is therefore justifiable to fix ε in this instance at some small value. If the stochastic model is forced to degenerate to the deterministic monocontinuum model by fixing σ_{ln}=0 (example 6f, Table 4), the best fit for ε is 123 mm, yielding a markedly higher SSQ than when $\sigma_{ln} \neq 0$.

Table 4. Fitted model parameters for example 6.*

Example	ε	<v>*	σ_{ln}	SSQ
6a	1.0 ± 227.	30.5 ±21.0	.800 ± .943	.0005177
6b	(.1)	30.5 ± 1.8	.803 ± .060	.0005182
6c	(1.)	30.5 ± 1.8	.800 ± .060	.0005177
6d	(10.)	29.7 ± 1.7	.763 ± .063	.0005182
6e	(100.)	24.7 ± 1.6	.370 ± .143	.00056
6f	123. ± 22.	23.6 ± 1.4	(0.0)	.00061

values ± the standard error; units of ε in mm and <v> in mm day^{-1}; values in parenthesis were fixed on input.


a
x = 30 cm
RELATIVE CONCENTRATION ($\hat{C}_r/C_0$)
0.08
0.06
0.04
0.02
0
OBSERVED
FITTED
b
x = 60 cm
RELATIVE CONCENTRATION ($\hat{C}_r/C_0$)
0.06
0.04
0.02
0
OBSERVED
PREDICTED
c
x = 90 cm
RELATIVE CONCENTRATION ($\hat{C}_r/C_0$)
0.06
0.04
0.02
0
OBSERVED
PREDICTED
0
20
40
60
80
100
TIME (t^*), days

Observed and fitted concentration-time curves for the 30 cm depth are plotted in Figure 7a. Using the coefficient values fitted to the 30 cm depth data (example 6a), $\hat{C}_r(t^*)$ distributions were calculated for depths of 60 cm and 90 cm. Figures 7b and 7c compare these predicted concentrations with the measured values. The tendency for the predicted time of maximum concentration to lag somewhat behind the measured peak time may be due to a variation in $\langle\theta\rangle$ and hence in $\langle v\rangle$ with depth in contrast to the homogeneity assumption invoked in our analysis. Implementation of a coordinate transformation, as previously mentioned, may alleviate this problem. On the other hand, the shift in peak concentration could be attributable also to uncertainties in the measured $\hat{C}_r$-values. Owing to the rather small sampling size of 14 for each concentration value, Jury et al. (1982) indicated experimental errors in $\hat{C}_r$ of about 0.05 C_0 units at the 95% confidence level. A more stringent test of this or any other stochastic transport model will require a considerably greater sampling density within the transport region.

←

Figure 7. Experimental areally-averaged concentrations $\hat{C}_r$ at three depths as a function of transformed time t* for bromide transport in a field soil. (a) Data for 30 cm depth and fitted curve using Model 5; (b) data for 60 cm depth and predicted curve using parameter values fitted to the 30 cm depth data; (c) same as b for the 90 cm depth data.

8. SUMMARY AND CONCLUSIONS

The least-squares inversion method discussed in this report provides a convenient, efficient and accurate means of fitting various transport parameters to observed spatial and/or temporal concentration distributions. Both equilibrium and two-site/two-region type non-equilibrium transport models can be implemented in the program. The linear equilibrium adsorption model also includes terms accounting for zero-order production and/or first-order decay. In addition, a stochastic model is described that can be applied to field-scale problems involving log-normally distributed pore water velocity distributions. This model also includes provisions for zero- and first-order production/decay processes. All models are formulated in terms of both flux-averaged concentrations (applicable to column effluent curves) and volume-averaged concentrations (applicable to in situ or resident concentrations). Several example problems illustrating practical applications of the inversion program are discussed in detail.

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10. APPENDIX A. List of the most significant variables in CXTFIT (units in brackets, L^o is dimensionless).

Variable	Definition
BETA	Dimensionless coefficient β for Models 3 and 4 $[L^o]$.
BETR	Value of β/R in Models 3 and 4 $[L^o]$.
B(I)	Vector containing estimates of the coefficients: v, D, R, t_o, μ and γ for Models 1 and 2, v, D, R, t_o, β and ω for Models 3 and 4, $\langle v\rangle, \varepsilon, R, t_o, \mu, \gamma$ and σ_{ln} for Models 5 and 6, or $\langle v\rangle, \varepsilon, R, M_o/\theta, \mu, \gamma$ and σ_{ln} for Models 7 and 8.
BI(I)	Vector of coefficient names.
C(I)	Concentration for I-th observation corresponding to X(I) and T(I) $[ML^{-3}]$.
CI	Uniform initial concentration, C_i $[ML^{-3}]$.
CO	Concentration of the inlet solution, C_o $[ML^{-3}]$.
D	Dispersion coefficient $[L^2T^{-1}]$.
DISP	Dispersivity ε for Models 5-8 $[L]$.
DR	Value of D/R $[L^2T^{-1}]$.
INDEX(I)	Index for each coefficient. If INDEX(I) = 0, the coefficient B(I) is known and kept constant; if INDEX(I) = 1, the coefficient is assumed to be unknown and fitted to the data.
MAXTRY	Maximum number of trials allowed within an iteration to find new parameter values that decrease SSQ (currently set at 50 in the program).

MIT	Maximum number of iterations allowed in the least-squares analysis. If MIT=0, the least-squares inversion part is bypassed and the program calculates and prints concentrations for given input values of x, t and the different parameters; dummy values of C(I) and INDEX(I) are then still read in but not used in the program.
MODE	Model number specifying type of transport model and boundary conditions to be used (see Table 1 in text).
NC	Number of cases considered.
NDATA	Data input code. If NDATA=1, new cards are read in for that case, if NDATA=0, all or part of the data from the previous example are used for the new problem.
NIT	Iteration number in least-squares analysis.
NOB	Number of observations (cannot exceed 90 with currently dimensioned arrays).
NP	Number of variable parameters to be fitted to the data.
NPRNT	Output print code. If NPRNT=1, the input c(x,t) array is printed out; NPRNT=0 suppresses this printing.
NREDU	Data input code. If NREDU=0, input concentrations and times are not reduced. If NREDU=1, only the input concentrations are reduced. If NREDU=2, input concentrations and times are both assumed to be dimensionless.
NSKIP	Input file execution code. If NSKIP=0, the problem is executed; if NSKIP≠0, the problem is read in but not executed.
OMEGA	Dimensionless coefficient ω for Models 3 and 4 $[L^0]$.
R	Retardation factor $[L^0]$.
RX0	Zero-order rate constant, γ (positive for production, negative for decay) $[ML^{-3}T^{-1}]$.
RX0R	Value of γ/R $[ML^{-3}T^{-1}]$.
RX1	First-order decay constant, μ $[T^{-1}]$.
RX1R	Value of μ/R $[T^{-1}]$.
SDLN	Value of $\sigma_{\ln}$ in Models 5-8.

SOLOAD	Value of M_o/θ in Models 7 and 8 $[ML^{-2}]$.
STOPCR	Stop criterion. The curve-fitting process stops when the relative change in the ratio of all coefficients becomes less than STOPCR (currently set to .0005 in the program).
T(I)	Time corresponding to the I-th observed concentration value [T].
TITLE	Vector containing information of title cards.
TO	Pulse duration for Models 1-6.
V	Pore water velocity, v $[LT^{-1}]$.
VLNM	Value of μ_{1n} in Models 5-8.
VR	Value of v/R $[LT^{-1}]$
X(I)	Distance from source corresponding to the I-th observed concentration value [L].
XL	Maximum value L of X(I) array [L].
Z	Dimensionless distance, x/L $[L^o]$.

11. APPENDIX B. Data input instructions.

Card	Columns	Format	Variable	Comments
1	1-10	I10	NC	Number of cases considered. The remaining cards are read in for each case. If NDATA=0 on card 2, data cards 9, etc. are not needed for that particular case.
2	1-10	I10	MODE	Model number. See Table 1 of text for explanation.
2	11-20	I10	NDATA	New data input code. See Appendix A for explanation.
2	21-30	I10	NREDU	Reduced data input code. See Appendix A for explanation.
2	31-40	I10	MIT	Maximum number of iterations. See Appendix A for explanation.
2	41-50	I10	NOB	Number of observations. See Appendix A for explanation.
2	51-60	I10	NSKIP	Input execution code. See Appendix A for explanation.
2	61-70	I10	NPRNT	Output print code. See Appendix A for explanation.
3	1-80	20A4	TITLE	Information card 1.
4	1-80	20A4	TITLE	Information card 2.
5	5-10	A4,A2	BI(1)	Name of each coefficient B(I). Coefficient 7 applies only for Models 5-8. See Appendix A and Table 1 of text for additional explanation.
5	15-20	A4,A2	BI(2)	
5	25-30	A4-A2	BI(3)	
5	35-40	A4,A2	BI(4)	
5	45-50	A4,A2	BI(5)	
5	55-60	A4,A2	BI(6)	
5	65-70	A4,A2	BI(7)	

6	1-10	F10.0	B(1)	Initial value for each coefficient. See Table 1 of text.
6	11-20	F10.0	B(2)	
6	21-30	F10.0	B(3)	
6	31-40	F10.0	B(4)	
6	41-50	F10.0	B(5)	
6	51-60	F10.0	B(6)	
6	61-70	F10.0	B(7)	
7	1-10	I10	INDEX(1)	Index for each coefficient. See Appendix A and text for explanation.
7	11-20	I10	INDEX(2)	
7	21-30	I10	INDEX(3)	
7	31-40	I10	INDEX(4)	
7	41-50	I10	INDEX(5)	
7	51-60	I10	INDEX(6)	
7	61-70	I10	INDEX(7)	
8	1-10	F10.0	CI	Initial concentration.
8	11-20	F10.0	CO	Influent concentration.
9	1-10	F10.0	C(I)	Value of the Ith observed concentration (blank for MIT=0).
9	11-20	F10.0	X(I)	Distance from source for observation I.
9	21-30	F10.0	T(I)	Elapsed time for observation I.
				Card 9 is repeated NOB times.

12. APPENDIX C.

Input files for selected examples discussed in text.

```
         1         2         3         4         5         6         7
1234567890123456789012345678901234567890123456789012345678901234567890

         7
         1         1         0         0        22         0         0
          EX.1A: HYPOTHETICAL CASE OF EQUILIBRIUM ADSORPTION
          (UNITS: CENTIMETERS, DAYS, MICROGRAMS)
    V.....    D.....    R.....    TO....    RX1...    RXO...
      25.0     100.0       2.5       5.0      0.25       0.5
         0         0         0         0         0         0
       0.0     100.0
                 0.0       5.0
                10.0       5.0
                20.0       5.0
                30.0       5.0
                40.0       5.0
                50.0       5.0
                60.0       5.0
                70.0       5.0
                80.0       5.0
                90.0       5.0
                25.0       5.0
                 0.0      10.0
                10.0      10.0
                20.0      10.0
                30.0      10.0
                40.0      10.0
                50.0      10.0
                60.0      10.0
                70.0      10.0
                80.0      10.0
                90.0      10.0
               100.0      10.0
         1         1         0        30        11         0         0
          EX.1C: HYPOTHETICAL CASE OF EQUILIBRIUM ADSORPTION
          FIT TO EX.1A DATA (UNITS: CENTIMETERS, DAYS, MICROGRAMS)
    V.....    D.....    R.....    TO....    RX1...    RXO...
      25.0       1.0       1.0       5.0       1.0       1.0
         0         1         1         0         1         1
       0.0     100.0
     96.23       0.0       5.0
     86.84      10.0       5.0
     76.73      20.0       5.0
     64.66      30.0       5.0
     50.24      40.0       5.0
     34.71      50.0       5.0
     20.75      60.0       5.0
     10.63      70.0       5.0
      4.75      80.0       5.0
      2.08      90.0       5.0
      1.13     100.0       5.0
         4         1         0        30        30         0         0
          EX.2B: HYPOTHETICAL CASE OF NONEQUILIBRIUM TRANSPORT
          (UNITS: CENTIMETERS, DAYS, MICROGRAMS)
```

```
    V.....    D.....    R.....    PULSE.    BETA..    OMEGA.
      10.0       1.0       1.0       1.0       0.5       1.0
         0         1         1         1         1         1
       0.0     500.0
      0.0       20.0       0.2
      0.0       20.0       0.4
      0.00      20.0       0.6
      0.04      20.0       0.8
      1.36      20.0       1.0
     49.95      20.0       1.5
    134.25      20.0       2.0
    206.49      20.0       3.0
    198.76      20.0       4.0
    105.25      20.0       5.0
     89.12      20.0       6.0
     77.63      20.0       7.0
     67.25      20.0       8.0
     49.70      20.0      10.0
     36.12      20.0      12.0
      0.0       40.0       0.2
      0.0       40.0       0.4
      0.0       40.0       0.6
      0.0       40.0       0.8
      0.0       40.0       1.0
      0.00      40.0       1.5
      0.01      40.0       2.0
     11.64      40.0       3.0
     56.57      40.0       4.0
     90.53      40.0       5.0
     90.09      40.0       6.0
     80.44      40.0       7.0
     78.75      40.0       8.0
     73.38      40.0      10.0
     65.08      40.0      12.0
         2         1         2        30        14         0         0
          EX.3A: BROMIDE EFFLUENT FROM 'WORMHOLE' COLUMN
          (UNITS: METERS, DAYS, ARBITRARY MASS UNITS)
    V.....    D.....    R.....    PULSE.    RX1...    RX0...
     107.0      10.0       1.0      0.65       0.0       0.0
         0         1         0         0         0         0
       0.0       1.0
    0.8060      0.19     0.030
    0.9420      0.19     0.147
    0.9650      0.19     0.272
    0.9600      0.19     0.410
    0.9800      0.19     0.558
    0.8820      0.19     0.613
    0.1850      0.19     0.662
    0.0226      0.19     0.798
    0.0101      0.19     0.949
    0.0077      0.19     1.093
    0.0064      0.19     1.244
    0.0057      0.19     1.409
    0.0054      0.19     1.578
    0.0050      0.19     1.751
```

```
     4         1         2        30        30         0         0
      EX.4A: BORON EFFLUENT FROM GLENDALE CLAY LOAM
      (UNITS: CENTIMETERS, DAYS, MICROGRAMS)
V.....    D.....    R.....    PULSE.    BETA..    OMEGA.
  38.5       2.0      10.0      6.49       0.2       0.2
     0         1         1         0         1         1
   0.0      20.0
 0.015      30.0      1.80
 0.075      30.0      1.95
 0.170      30.0      2.10
 0.265      30.0      2.25
 0.340      30.0      2.40
 0.430      30.0      2.60
 0.535      30.0      2.85
 0.620      30.0      3.15
 0.687      30.0      3.50
 0.738      30.0      4.00
 0.777      30.0      4.60
 0.819      30.0      5.30
 0.852      30.0      6.00
 0.880      30.0      6.70
 0.882      30.0      7.30
 0.852      30.0      7.75
 0.776      30.0      8.00
 0.699      30.0      8.25
 0.621      30.0      8.55
 0.527      30.0      8.90
 0.433      30.0      9.30
 0.357      30.0      9.80
 0.269      30.0     10.50
 0.186      30.0     11.50
 0.133      30.0     12.70
 0.090      30.0     14.00
 0.054      30.0     15.50
 0.040      30.0     17.00
 0.029      30.0     18.50
 0.025      30.0     20.00
     7         1         0        30        30         0         0
      EX.5B: HYPOTHETICAL REGIONAL TRANSPORT PROBLEM
      FIT TO EX.5A (UNITS: CENTIMETERS, DAYS, MICROGRAMS)
<V>...    DISP..    R.....    SOLOAD    RX1...    RX0...    SDLN..
  10.0       1.0       1.0   20000.0       0.0       0.0       1.0
     1         1         1         0         0         0         1
   0.0    1000.0
 68.14     10.00      1.00
 15.26     25.00      1.00
  2.84     50.00      1.00
  0.87     75.00      1.00
  0.35    100.00      1.00
  0.09    150.00      1.00
  0.03    200.00      1.00
  0.01    300.00      1.00
  0.00    400.00      1.00
  0.00    500.00      1.00
 94.94     10.00      5.00
```

```
 41.89     25.00      5.00
 14.91     50.00      5.00
  6.85     75.00      5.00
  3.67    100.00      5.00
  1.39    150.00      5.00
  0.65    200.00      5.00
  0.21    300.00      5.00
  0.09    400.00      5.00
  0.04    500.00      5.00
 79.38     10.00     10.00
 45.49     25.00     10.00
 20.94     50.00     10.00
 11.34     75.00     10.00
  6.86    100.00     10.00
  3.07    150.00     10.00
  1.63    200.00     10.00
  0.62    300.00     10.00
  0.29    400.00     10.00
  0.16    500.00     10.00
     5         1         1        30        10         0         0
      EX.6A: FIELD-SCALE BROMIDE MOVEMENT (JURY ET AL.,1982)
     (UNITS: MILIMETERS, DAYS, ARBITRARY MASS--REDUCED C)
<V>*..    DISP..    R.....    PULSE.    RX1...    RX0...    SDLN..
  25.0     100.0       1.0      1.69       0.0       0.0       1.0
     1         1         0         0         0         0         1
   0.0       1.0
 0.062     300.0       5.0
 0.076     300.0      10.0
 0.059     300.0      15.0
 0.038     300.0      20.0
 0.014     300.0      25.0
 0.007     300.0      30.0
 0.004     300.0      35.0
 0.003     300.0      40.0
 0.001     300.0      45.0
 0.000     300.0      50.0
```

13. APPENDIX D

Output files for selected examples
discussed in text.

```
*********************************************************************************
*                                                                               *
*          ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION                   *
*                                                                               *
*          DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR PULSE INJECTION      *
*          WITH FIRST- AND ZERO-ORDER PRODUCTION AND DECAY                      *
*          SOLUTION FOR RESIDENT CONCENTRATIONS                                 *
*                                                                               *
*          EX.1A: HYPOTHETICAL CASE OF EQUILIBRIUM ADSORPTION                   *
*          (UNITS: CENTIMETERS, DAYS, MICROGRAMS)                               *
*                                                                               *
*********************************************************************************

INITIAL VALUES OF COEFFICIENTS
==============================
 NAME              INITIAL VALUE
V.........    25.0000
D.........   100.0000
R.........     2.5000
T0........     5.0000
RX1.......     0.2500
RX0.......     0.5000
CI........     0.0
CO........   100.0000

---------RESULTS FOR INITIAL COEFFICIENT VALUES---------
NO          DISTANCE          TIME         CONCENTRATION
 1            0.0            5.0000           96.2355
 2           10.0000         5.0000           86.8428
 3           20.0000         5.0000           76.7266
 4           30.0000         5.0000           64.6646
 5           40.0000         5.0000           50.2391
 6           50.0000         5.0000           34.7099
 7           60.0000         5.0000           20.7448
 8           70.0000         5.0000           10.6034
 9           80.0000         5.0000            4.7493
10           90.0000         5.0000            2.0823
11           25.0000         5.0000           70.9998
12            0.0           10.0000            0.2022
13           10.0000        10.0000            1.0973
14           20.0000        10.0000            3.4644
15           30.0000        10.0000            8.3961
16           40.0000        10.0000           16.1408
17           50.0000        10.0000           25.2015
18           60.0000        10.0000           32.6311
19           70.0000        10.0000           35.9173
20           80.0000        10.0000           34.4879
21           90.0000        10.0000           29.5869
22          100.0000        10.0000           23.1039
```

```
********************************************************************************
                                                                               *
          ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION                   *
          NON-LINEAR LEAST-SQUARES ANALYSIS                                    *
                                                                               *
          DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR PULSE INJECTION      *
          WITH FIRST- AND ZERO-ORDER PRODUCTION AND DECAY                      *
          SOLUTION FOR RESIDENT CONCENTRATIONS                                 *
                                                                               *
          EX.1C: HYPOTHETICAL CASE OF EQUILIBRIUM ADSORPTION                   *
          FIT TO EX.1A DATA (UNITS: CENTIMETERS, DAYS, MICROGRAMS)             *
                                                                               *
********************************************************************************


NITIAL VALUES OF COEFFICIENTS
=============================
NAME              INITIAL VALUE
.........         25.0000
.........          1.0000
.........          1.0000
0........          5.0000
X1.......          1.0000
X0.......          1.0000
I........          0.0
0........        100.0000


TERATION      SSQ            D.....        R.....        RX1...        RX0...
   0      3917.13832        1.00000       1.00000       1.00000       1.00000
   1      3912.71790        1.00000       1.49210       1.00000       1.00000
   2       458.36066        9.82327       1.94834       0.39060       2.85959
   3        90.39628       25.50612       2.04880       0.41171       1.09147
   4        16.03210       59.46360       2.24656       0.34172       0.54057
   5         0.81370       89.70647       2.43398       0.27487       0.48151
   6         0.00828       99.49115       2.49552       0.25169       0.49078
   7         0.00039      100.25669       2.50052       0.24964       0.49666
   8         0.00038      100.27995       2.50062       0.24960       0.49705
   9         0.00038      100.28036       2.50062       0.24960       0.49706


ORRELATION MATRIX
=================
        1          2          3          4
 1   1.0000
 2   0.8601     1.0000
 3  -0.9592    -0.8974     1.0000
 4  -0.6091    -0.2490     0.6051     1.0000

SQUARE FOR REGRESSION OF OBSERVED VS PREDICTED=0.99999997
```

```
NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
================================================

                                                                  95% CONFIDENCE LIMITS
VARIABLE     NAME        VALUE          S.E.COEFF.    T-VALUE      LOWER          UPPER
    1        D.....   100.28036          0.15469      648.29      99.91460      100.64612
    2        R.....     2.50062          0.00066     3768.48       2.49905        2.50219
    3        RX1...     0.24960          0.00030      840.28       0.24890        0.25031
    4        RX0...     0.49706          0.00413      120.34       0.48730        0.50683

-----------------------ORDERED BY COMPUTER INPUT-----------------------
                                      CONCENTRATION            RESI-
NO     DISTANCE        TIME        OBS         FITTED          DUAL
1        0.0          5.0000     96.2300      96.2293          0.0007
2       10.0000       5.0000     86.8400      86.8437         -0.0037
3       20.0000       5.0000     76.7300      76.7272          0.0028
4       30.0000       5.0000     64.6600      64.6615         -0.0015
5       40.0000       5.0000     50.2400      50.2360          0.0040
6       50.0000       5.0000     34.7100      34.7133         -0.0033
7       60.0000       5.0000     20.7500      20.7558         -0.0058
8       70.0000       5.0000     10.6300      10.6163          0.0137
9       80.0000       5.0000      4.7500       4.7578         -0.0078
10      90.0000       5.0000      2.0800       2.0848         -0.0048
11     100.0000       5.0000      1.1300       1.1250          0.0050

---------------------------ORDERED BY RESIDUAL---------------------------
                                      CONCENTRATION            RESI-
NO     DISTANCE        TIME        OBS         FITTED          DUAL
8       70.0000       5.0000     10.6300      10.6163          0.0137
11     100.0000       5.0000      1.1300       1.1250          0.0050
5       40.0000       5.0000     50.2400      50.2360          0.0040
3       20.0000       5.0000     76.7300      76.7272          0.0028
1        0.0          5.0000     96.2300      96.2293          0.0007
4       30.0000       5.0000     64.6600      64.6615         -0.0015
6       50.0000       5.0000     34.7100      34.7133         -0.0033
2       10.0000       5.0000     86.8400      86.8437         -0.0037
10      90.0000       5.0000      2.0800       2.0848         -0.0048
7       60.0000       5.0000     20.7500      20.7558         -0.0058
9       80.0000       5.0000      4.7500       4.7578         -0.0078
```

```
********************************************************************************
*                                                                              *
*          ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION                  *
*          NON-LINEAR LEAST-SQUARES ANALYSIS                                   *
*                                                                              *
*          DETERMINISTIC TWO-SITE/TWO-REGION NONEQUILIBRIUM MODEL FOR          *
*          PULSE-TYPE INJECTION WITH NO PRODUCTION OR DECAY                    *
*          SOLUTION FOR FLUX CONCENTRATIONS                                    *
*                                                                              *
*          EX.2B: HYPOTHETICAL CASE OF NONEQUILIBRIUM TRANSPORT                *
*          (UNITS: CENTIMETERS, DAYS, MICROGRAMS)                              *
*                                                                              *
********************************************************************************


INITIAL VALUES OF COEFFICIENTS
==============================
 NAME          INITIAL VALUE
V.........    10.0000
D.........     1.0000
R.........     1.0000
PULSE.....     1.0000
BETA......     0.5000
OMEGA.....     1.0000
CI........     0.0
CO........   500.0000


ITERATION     SSQ             D.....        R.....        PULSE.        BETA..        OMEGA.
    0    246022.36623        1.00000       1.00000       1.00000       0.50000       1.00000
    1    128996.36620        0.81180       1.63115       1.03430       0.16113       3.35233
    2     58793.65999        8.05817       2.45991       1.71952       0.00106       6.80566
    3     30511.23505        6.56908       2.33221       2.21464       0.21050       7.77231
    4     22294.31832       20.03290       2.42207       2.03889       0.26845       8.38396
    5     10681.56125       19.39181       2.32613       2.15505       0.27720       5.79992
    6      6515.38259       11.36916       2.39445       2.15037       0.45088       1.61625
    7      4065.76046        7.47247       3.05962       2.50670       0.26818       2.42405
    8        81.72203        7.03156       3.02647       2.51254       0.30288       2.49950
    9         3.40572        4.65404       2.99762       2.49972       0.29603       2.51777
   10         0.58235        4.95646       2.99820       2.49870       0.29739       2.51109
   11         0.57551        4.97379       2.99812       2.49853       0.29749       2.51090
   12         0.57547        4.97406       2.99811       2.49853       0.29749       2.51088
```

```
CORRELATION MATRIX
==================
        1         2         3         4         5
  1   1.0000
  2   0.3155    1.0000
  3   0.2718    0.7586    1.0000
  4   0.4293   -0.6260   -0.6191    1.0000
  5  -0.6169   -0.2879   -0.0743   -0.3728    1.0000

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED=0.99999404

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
================================================

                                                          95% CONFIDENCE LIMITS
VARIABLE    NAME        VALUE        S.E.COEFF.   T-VALUE    LOWER          UPPER
    1       D.....      4.97406        0.03742     132.92     4.89698        5.05113
    2       R.....      2.99811        0.00270    1111.47     2.99256        3.00367
    3       PULSE.      2.49853        0.00138    1806.39     2.49568        2.50138
    4       BETA..      0.29749        0.00034     884.54     0.29680        0.29819
    5       OMEGA.      2.51088        0.00223    1124.95     2.50628        2.51548


----------------------ORDERED BY COMPUTER INPUT-----------------------
                                          CONCENTRATION            RESI-
NO     DISTANCE        TIME          OBS           FITTED          DUAL
 1     20.0000        0.2000       0.0           0.0             0.0
 2     20.0000        0.4000       0.0           0.0             0.0
 3     20.0000        0.6000       0.0           0.0001         -0.0001
 4     20.0000        0.8000       0.0400        0.0441         -0.0041
 5     20.0000        1.0000       1.3600        1.4077         -0.0477
 6     20.0000        1.5000      49.9500       49.7093          0.2407
 7     20.0000        2.0000     134.2500      134.4251         -0.1751
 8     20.0000        3.0000     206.4900      206.3964          0.0936
 9     20.0000        4.0000     198.7600      198.7150          0.0450
10     20.0000        5.0000     105.2500      105.7654         -0.5154
11     20.0000        6.0000      89.1200       89.0365          0.0835
12     20.0000        7.0000      77.6300       77.5696          0.0604
13     20.0000        8.0000      67.2500       67.2064          0.0436
14     20.0000       10.0000      49.7000       49.6825          0.0175
15     20.0000       12.0000      36.1200       36.1054          0.0146
16     40.0000        0.2000       0.0           0.0             0.0
17     40.0000        0.4000       0.0           0.0             0.0
18     40.0000        0.6000       0.0           0.0             0.0
19     40.0000        0.8000       0.0           0.0             0.0
```

```
20       40.0000         1.0000        0.0          0.0           0.0
21       40.0000         1.5000        0.0          0.0000       -0.0000
22       40.0000         2.0000        0.0100       0.0164       -0.0064
23       40.0000         3.0000       11.6400      11.8712       -0.2312
24       40.0000         4.0000       56.5700      56.4797        0.0903
25       40.0000         5.0000       90.5300      90.7646       -0.2346
26       40.0000         6.0000       90.0900      89.9546        0.1354
27       40.0000         7.0000       80.4400      80.4107        0.0293
28       40.0000         8.0000       78.7500      78.5777        0.1723
29       40.0000        10.0000       73.3800      73.2438        0.1362
30       40.0000        12.0000       65.0800      64.9753        0.1047

 --------------------------ORDERED BY RESIDUAL---------------------------
                                         CONCENTRATION           RESI-
 NO     DISTANCE          TIME         OBS          FITTED       DUAL
  6      20.0000         1.5000       49.9500      49.7093       0.2407
28       40.0000         8.0000       78.7500      78.5777       0.1723
29       40.0000        10.0000       73.3800      73.2438       0.1362
26       40.0000         6.0000       90.0900      89.9546       0.1354
30       40.0000        12.0000       65.0800      64.9753       0.1047
 8       20.0000         3.0000      206.4900     206.3964       0.0936
24       40.0000         4.0000       56.5700      56.4797       0.0903
11       20.0000         6.0000       89.1200      89.0365       0.0835
12       20.0000         7.0000       77.6300      77.5696       0.0604
 9       20.0000         4.0000      198.7600     198.7150       0.0450
13       20.0000         8.0000       67.2500      67.2064       0.0436
27       40.0000         7.0000       80.4400      80.4107       0.0293
14       20.0000        10.0000       49.7000      49.6825       0.0175
15       20.0000        12.0000       36.1200      36.1054       0.0146
 1       20.0000         0.2000        0.0          0.0           0.0
 2       20.0000         0.4000        0.0          0.0           0.0
16       40.0000         0.2000        0.0          0.0           0.0
17       40.0000         0.4000        0.0          0.0           0.0
18       40.0000         0.6000        0.0          0.0           0.0
19       40.0000         0.8000        0.0          0.0           0.0
20       40.0000         1.0000        0.0          0.0           0.0
21       40.0000         1.5000        0.0          0.0000       -0.0000
 3       20.0000         0.6000        0.0          0.0001       -0.0001
 4       20.0000         0.8000        0.0400       0.0441       -0.0041
22       40.0000         2.0000        0.0100       0.0164       -0.0064
 5       20.0000         1.0000        1.3600       1.4077       -0.0477
 7       20.0000         2.0000      134.2500     134.4251       -0.1751
23       40.0000         3.0000       11.6400      11.8712       -0.2312
25       40.0000         5.0000       90.5300      90.7646       -0.2346
10       20.0000         5.0000      105.2500     105.7654       -0.5154
```

```
***********************************************************************************
*                                                                                 *
*          ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION                     *
*          NON-LINEAR LEAST-SQUARES ANALYSIS                                      *
*                                                                                 *
*          DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FOR PULSE INJECTION        *
*          WITH FIRST- AND ZERO-ORDER PRODUCTION AND DECAY                        *
*          SOLUTION FOR FLUX CONCENTRATIONS                                       *
*          REDUCED CONCENTRATION AND TIME DATA                                    *
*                                                                                 *
*          EX.3A: BROMIDE EFFLUENT FROM 'WORMHOLE' COLUMN                         *
*          (UNITS: METERS, DAYS, ARBITRARY MASS UNITS)                            *
*                                                                                 *
***********************************************************************************


INITIAL VALUES OF COEFFICIENTS
==============================
 NAME            INITIAL VALUE
V.........     107.0000
D.........      10.0000
R.........       1.0000
PULSE.....       0.6500
RX1.......       0.0
RX0.......       0.0
CI........       0.0
CO........       1.0000


ITERATION       SSQ           D.....
    0         4.10659       10.00000
    1         2.46778       37.23245
    2         1.41558      123.82341
    3         0.64858      400.18590
    4         0.19115     1229.76741
    5         0.04893     2937.47280
    6         0.01575     5485.46972
    7         0.01076     7779.78289
    8         0.01048     8660.86768
    9         0.01048     8744.04483
   10         0.01048     8745.07988

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED=0.99683340
```

```
NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
================================================

                                                              95% CONFIDENCE LIMITS
VARIABLE    NAME       VALUE          S.E.COEFF.               LOWER          UPPER
   1        D.....    8745.07988      1786.53980              4885.38692     12604.77285

-----------------------ORDERED BY COMPUTER INPUT------------------------
                                           CONCENTRATION            RESI-
NO     DISTANCE          TIME           OBS          FITTED          DUAL
1        0.1900          0.0300         0.8060        0.8449        -0.0389
2        0.1900          0.1470         0.9420        0.9302         0.0118
3        0.1900          0.2720         0.9650        0.9490         0.0160
4        0.1900          0.4100         0.9600        0.9586         0.0014
5        0.1900          0.5580         0.9800        0.9647         0.0153
6        0.1900          0.6130         0.8820        0.9664        -0.0844
7        0.1900          0.6620         0.1850        0.2112        -0.0262
8        0.1900          0.7980         0.0226        0.0402        -0.0176
9        0.1900          0.9490         0.0101        0.0218        -0.0117
10       0.1900          1.0930         0.0077        0.0148        -0.0071
11       0.1900          1.2440         0.0064        0.0109        -0.0045
12       0.1900          1.4090         0.0057        0.0083        -0.0026
13       0.1900          1.5780         0.0054        0.0066        -0.0012
14       0.1900          1.7510         0.0050        0.0054        -0.0004

---------------------------ORDERED BY RESIDUAL---------------------------
                                           CONCENTRATION            RESI-
NO     DISTANCE          TIME           OBS          FITTED          DUAL
3        0.1900          0.2720         0.9650        0.9490         0.0160
5        0.1900          0.5580         0.9800        0.9647         0.0153
2        0.1900          0.1470         0.9420        0.9302         0.0118
4        0.1900          0.4100         0.9600        0.9586         0.0014
14       0.1900          1.7510         0.0050        0.0054        -0.0004
13       0.1900          1.5780         0.0054        0.0066        -0.0012
12       0.1900          1.4090         0.0057        0.0083        -0.0026
11       0.1900          1.2440         0.0064        0.0109        -0.0045
10       0.1900          1.0930         0.0077        0.0148        -0.0071
9        0.1900          0.9490         0.0101        0.0218        -0.0117
8        0.1900          0.7980         0.0226        0.0402        -0.0176
7        0.1900          0.6620         0.1850        0.2112        -0.0262
1        0.1900          0.0300         0.8060        0.8449        -0.0389
6        0.1900          0.6130         0.8820        0.9664        -0.0844
```

```
*****************************************************************************************
*                                                                                       *
*          ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION                           *
*          NON-LINEAR LEAST-SQUARES ANALYSIS                                            *
*                                                                                       *
*          DETERMINISTIC TWO-SITE/TWO-REGION NONEQUILIBRIUM MODEL FOR                   *
*          PULSE-TYPE INJECTION WITH NO PRODUCTION OR DECAY                             *
*          SOLUTION FOR FLUX CONCENTRATIONS                                             *
*          REDUCED CONCENTRATION AND TIME DATA                                          *
*                                                                                       *
*          EX.4A: BORON EFFLUENT FROM GLENDALE CLAY LOAM                                *
*          (UNITS: CENTIMETERS, DAYS, MICROGRAMS)                                       *
*                                                                                       *
*****************************************************************************************


INITIAL VALUES OF COEFFICIENTS
==============================
 NAME           INITIAL VALUE
V.........     38.5000
D.........      2.0000
R.........     10.0000
PULSE.....      6.4900
BETA......      0.2000
OMEGA.....      0.2000
CI........      0.0
CO........     20.0000


ITERATION       SSQ          D.....        R.....        BETA..        OMEGA.
    0         1.86497        2.00000      10.00000       0.20000       0.20000
    1         0.89540        5.55891       8.09839       0.24822       0.44224
    2         0.41722       15.45646       7.03675       0.30592       0.51867
    3         0.20896       33.01378       5.60759       0.40860       0.44036
    4         0.19442       48.25238       3.91843       0.57399       0.41148
    5         0.05591       60.59524       4.26294       0.60434       0.40417
    6         0.05290       48.80769       4.28093       0.59715       0.41627

NO FURTHER DECREASE IN SSQ OBTAINED AFTER 50 TRIALS
```

```
CORRELATION MATRIX
==================
         1          2          3          4
 1    1.0000
 2    0.0834     1.0000
 3    0.5889    -0.6561     1.0000
 4   -0.7262    -0.3436    -0.4080     1.0000

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED=0.98139377


NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
================================================

                                                               95% CONFIDENCE LIMITS
VARIABLE     NAME         VALUE        S.E.COEFF.   T-VALUE     LOWER          UPPER
    1       D.....      48.80769       13.39505      3.64      21.27210       76.34327
    2       R.....       4.28093        0.22611     18.93       3.81611        4.74574
    3       BETA..       0.59715        0.03308     18.05       0.52914        0.66516
    4       OMEGA.       0.41627        0.09013      4.62       0.23099        0.60156

-----------------------ORDERED BY COMPUTER INPUT-----------------------
                                         CONCENTRATION           RESI-
NO     DISTANCE         TIME          OBS          FITTED        DUAL
1       30.0000        1.8000       0.0150        0.1035       -0.0885
2       30.0000        1.9500       0.0750        0.1558       -0.0808
3       30.0000        2.1000       0.1700        0.2152       -0.0452
4       30.0000        2.2500       0.2650        0.2779       -0.0129
5       30.0000        2.4000       0.3400        0.3406       -0.0006
6       30.0000        2.6000       0.4300        0.4195        0.0105
7       30.0000        2.8500       0.5350        0.5053        0.0297
8       30.0000        3.1500       0.6200        0.5862        0.0338
9       30.0000        3.5000       0.6870        0.6536        0.0334
10      30.0000        4.0000       0.7380        0.7115        0.0265
11      30.0000        4.6000       0.7770        0.7574        0.0196
12      30.0000        5.3000       0.8190        0.7927        0.0263
13      30.0000        6.0000       0.8520        0.8198        0.0322
14      30.0000        6.7000       0.8800        0.8427        0.0373
15      30.0000        7.3000       0.8820        0.8599        0.0221
16      30.0000        7.7500       0.8520        0.8644       -0.0124
17      30.0000        8.0000       0.7760        0.8445       -0.0685
18      30.0000        8.2500       0.6990        0.7922       -0.0932
19      30.0000        8.5500       0.6210        0.6911       -0.0701
20      30.0000        8.9000       0.5270        0.5524       -0.0254
```

```
21       30.0000        9.3000       0.4330       0.4121       0.0209
22       30.0000        9.8000       0.3570       0.2934       0.0636
23       30.0000       10.5000       0.2690       0.2121       0.0569
24       30.0000       11.5000       0.1860       0.1584       0.0276
25       30.0000       12.7000       0.1330       0.1238       0.0092
26       30.0000       14.0000       0.0900       0.0964      -0.0064
27       30.0000       15.5000       0.0540       0.0723      -0.0183
28       30.0000       17.0000       0.0400       0.0541      -0.0141
29       30.0000       18.5000       0.0290       0.0405      -0.0115
30       30.0000       20.0000       0.0250       0.0303      -0.0053

 --------------------------ORDERED BY RESIDUAL---------------------------
                                          CONCENTRATION            RESI-
 NO     DISTANCE         TIME           OBS          FITTED        DUAL
22       30.0000        9.8000       0.3570       0.2934       0.0636
23       30.0000       10.5000       0.2690       0.2121       0.0569
14       30.0000        6.7000       0.8800       0.8427       0.0373
 8       30.0000        3.1500       0.6200       0.5862       0.0338
 9       30.0000        3.5000       0.6870       0.6536       0.0334
13       30.0000        6.0000       0.8520       0.8198       0.0322
 7       30.0000        2.8500       0.5350       0.5053       0.0297
24       30.0000       11.5000       0.1860       0.1584       0.0276
10       30.0000        4.0000       0.7380       0.7115       0.0265
12       30.0000        5.3000       0.8190       0.7927       0.0263
15       30.0000        7.3000       0.8820       0.8599       0.0221
21       30.0000        9.3000       0.4330       0.4121       0.0209
11       30.0000        4.6000       0.7770       0.7574       0.0196
 6       30.0000        2.6000       0.4300       0.4195       0.0105
25       30.0000       12.7000       0.1330       0.1238       0.0092
 5       30.0000        2.4000       0.3400       0.3406      -0.0006
30       30.0000       20.0000       0.0250       0.0303      -0.0053
26       30.0000       14.0000       0.0900       0.0964      -0.0064
29       30.0000       18.5000       0.0290       0.0405      -0.0115
16       30.0000        7.7500       0.8520       0.8644      -0.0124
 4       30.0000        2.2500       0.2650       0.2779      -0.0129
28       30.0000       17.0000       0.0400       0.0541      -0.0141
27       30.0000       15.5000       0.0540       0.0723      -0.0183
20       30.0000        8.9000       0.5270       0.5524      -0.0254
 3       30.0000        2.1000       0.1700       0.2152      -0.0452
17       30.0000        8.0000       0.7760       0.8445      -0.0685
19       30.0000        8.5500       0.6210       0.6911      -0.0701
 2       30.0000        1.9500       0.0750       0.1558      -0.0808
 1       30.0000        1.8000       0.0150       0.1035      -0.0885
18       30.0000        8.2500       0.6990       0.7922      -0.0932
```

```
********************************************************************************
*                                                                              *
*          ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION                  *
*          NON-LINEAR LEAST-SQUARES ANALYSIS                                   *
*                                                                              *
*          STOCHASTIC TRANSPORT MODEL WITH EQUILIBRIUM ADSORPTION              *
*          ZERO-ORDER PRODUCTION AND FIRST-ORDER DECAY FOR UNIFORM SOLUTE LOAD *
*          SOLUTION FOR RESIDENT CONCENTRATIONS                                *
*                                                                              *
*          EX.5B: HYPOTHETICAL REGIONAL TRANSPORT PROBLEM                      *
*          FIT TO EX.5A (UNITS: CENTIMETERS, DAYS, MICROGRAMS)                 *
*                                                                              *
********************************************************************************

INITIAL VALUES OF COEFFICIENTS
==============================
 NAME          INITIAL VALUE
<V>.......    10.0000
DISP......     1.0000
R.........     1.0000
SOLOAD.... 20000.0000
RX1.......     0.0
RX0.......     0.0
SDLN......     1.0000
CI........     0.0
CO........  1000.0000

ITERATION      SSQ             <V>...       DISP..       R.....       SDLN..
    0    212138.759151       10.00000      1.00000      1.00000      1.00000
    1     41671.379895       18.41775      0.18538      2.12304      0.99829
    2      5685.699634       27.95026      0.47473      3.49626      1.12868
    3       290.163378       36.19773      0.71330      4.58340      1.29284
    4        14.092663       35.68894      1.91076      4.90676      1.39359
    5        10.146888       32.36309      3.55284      4.95535      1.40809
    6         9.219075       27.73219      6.60219      5.00988      1.40006
    7         0.623445       25.04830      9.65937      5.00271      1.37347
    8         0.002403       25.00682     10.01930      4.99709      1.37003
    9         0.002053       24.99640     10.03234      4.99673      1.36991
   10         0.002045       25.00137     10.02680      4.99668      1.36996
   11         0.002045       25.00148     10.02672      4.99668      1.36996
```

```
CORRELATION MATRIX
==================
        1           2           3           4
  1   1.0000
  2  -0.9193      1.0000
  3  -0.2474     -0.0124      1.0000
  4   0.6063     -0.3364     -0.8575      1.0000

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED=0.99999992


NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
================================================

                                                                 95% CONFIDENCE LIMITS
VARIABLE     NAME         VALUE          S.E.COEFF.   T-VALUE     LOWER          UPPER
    1        <V>...      25.00148         0.01785    1400.87     24.96480       25.03817
    2        DISP..      10.02672         0.01919     522.54      9.98727       10.06616
    3        R.....       4.99668         0.00087    5739.96      4.99489        4.99847
    4        SDLN..       1.36996         0.00034    3981.22      1.36925        1.37067


-----------------------ORDERED BY COMPUTER INPUT-----------------------
                                           CONCENTRATION             RESI-
NO      DISTANCE          TIME           OBS           FITTED         DUAL
1        10.0000         1.0000        68.1400        68.1516        -0.0116
2        25.0000         1.0000        15.2600        15.2561         0.0039
3        50.0000         1.0000         2.8400         2.8408        -0.0008
4        75.0000         1.0000         0.8700         0.8653         0.0047
5       100.0000         1.0000         0.3500         0.3310         0.0190
6       150.0000         1.0000         0.0900         0.0800         0.0100
7       200.0000         1.0000         0.0300         0.0263         0.0037
8       300.0000         1.0000         0.0100         0.0            0.0100
9       400.0000         1.0000         0.0            0.0            0.0
10      500.0000         1.0000         0.0            0.0            0.0
11       10.0000         5.0000        94.9400        94.9317         0.0083
12       25.0000         5.0000        41.8900        41.8875         0.0025
13       50.0000         5.0000        14.9100        14.9128        -0.0028
14       75.0000         5.0000         6.8500         6.8512        -0.0012
15      100.0000         5.0000         3.6700         3.6538         0.0162
16      150.0000         5.0000         1.3900         1.3846         0.0054
17      200.0000         5.0000         0.6500         0.6486         0.0014
18      300.0000         5.0000         0.2100         0.2016         0.0084
19      400.0000         5.0000         0.0900         0.0841         0.0059
```

```
20     500.0000        5.0000        0.0400        0.0410       -0.0010
21      10.0000       10.0000       79.3800       79.3887       -0.0087
22      25.0000       10.0000       45.4900       45.4854        0.0046
23      50.0000       10.0000       20.9400       20.9485       -0.0085
24      75.0000       10.0000       11.3400       11.3201        0.0199
25     100.0000       10.0000        6.8600        6.8567        0.0033
26     150.0000       10.0000        3.0700        3.0740       -0.0040
27     200.0000       10.0000        1.6300        1.6167        0.0133
28     300.0000       10.0000        0.6200        0.6138        0.0062
29     400.0000       10.0000        0.2900        0.2919       -0.0019
30     500.0000       10.0000        0.1600        0.1590        0.0010

 ---------------------------ORDERED BY RESIDUAL----------------------------
                                        CONCENTRATION            RESI-
 NO     DISTANCE          TIME          OBS         FITTED         DUAL
24      75.0000       10.0000       11.3400       11.3201        0.0199
 5     100.0000        1.0000        0.3500        0.3310        0.0190
15     100.0000        5.0000        3.6700        3.6538        0.0162
27     200.0000       10.0000        1.6300        1.6167        0.0133
 8     300.0000        1.0000        0.0100        0.0           0.0100
 6     150.0000        1.0000        0.0900        0.0800        0.0100
18     300.0000        5.0000        0.2100        0.2016        0.0084
11      10.0000        5.0000       94.9400       94.9317        0.0083
28     300.0000       10.0000        0.6200        0.6138        0.0062
19     400.0000        5.0000        0.0900        0.0841        0.0059
16     150.0000        5.0000        1.3900        1.3846        0.0054
 4      75.0000        1.0000        0.8700        0.8653        0.0047
22      25.0000       10.0000       45.4900       45.4854        0.0046
 2      25.0000        1.0000       15.2600       15.2561        0.0039
 7     200.0000        1.0000        0.0300        0.0263        0.0037
25     100.0000       10.0000        6.8600        6.8567        0.0033
12      25.0000        5.0000       41.8900       41.8875        0.0025
17     200.0000        5.0000        0.6500        0.6486        0.0014
30     500.0000       10.0000        0.1600        0.1590        0.0010
 9     400.0000        1.0000        0.0           0.0           0.0
10     500.0000        1.0000        0.0           0.0           0.0
 3      50.0000        1.0000        2.8400        2.8408       -0.0008
20     500.0000        5.0000        0.0400        0.0410       -0.0010
14      75.0000        5.0000        6.8500        6.8512       -0.0012
29     400.0000       10.0000        0.2900        0.2919       -0.0019
13      50.0000        5.0000       14.9100       14.9128       -0.0028
26     150.0000       10.0000        3.0700        3.0740       -0.0040
23      50.0000       10.0000       20.9400       20.9485       -0.0085
21      10.0000       10.0000       79.3800       79.3887       -0.0087
 1      10.0000        1.0000       68.1400       68.1516       -0.0116
```

```
*****************************************************************************
*                                                                           *
*         ONE-DIMENSIONAL CONVECTION-DISPERSION EQ. SOLUTION                *
*         NON-LINEAR LEAST-SQUARES ANALYSIS                                 *
*                                                                           *
*         STOCHASTIC TRANSPORT MODEL WITH EQUILIBRIUM ADSORPTION            *
*         ZERO-ORDER PRODUCTION AND FIRST-ORDER DECAY FOR UNIFORM PULSE INPUT *
*         SOLUTION FOR RESIDENT CONCENTRATIONS                              *
*         REDUCED CONCENTRATION DATA                                        *
*                                                                           *
*         EX.6A: FIELD-SCALE BROMIDE MOVEMENT (JURY ET AL.,1982)            *
*         (UNITS: MILIMETERS, DAYS, ARBITRARY MASS--REDUCED C)              *
*                                                                           *
*****************************************************************************


INITIAL VALUES OF COEFFICIENTS
==============================
 NAME              INITIAL VALUE
<V>*......      25.0000
DISP......     100.0000
R.........       1.0000
PULSE.....       1.6900
RX1.......       0.0
RX0.......       0.0
SDLN......       1.0000
CI........       0.0
CO........       1.0000


ITERATION      SSQ            <V>*..         DISP..        SDLN..
    0        0.001957        25.00000      100.00000      1.00000
    1        0.001062        27.41737       38.93184      0.91028
    2        0.000620        25.72053       77.91321      0.60558
    3        0.000545        28.47699       11.22351      0.76138
    4        0.000518        29.69033        9.38482      0.76866
    5        0.000518        30.44372        0.38794      0.80010
    6        0.000518        30.44455        0.38133      0.80012
    7        0.000518        30.45577        0.86023      0.79995
    8        0.000518        30.45479        0.98181      0.79984
    9        0.000518        30.45601        0.97338      0.79984
   10        0.000518        30.45886        1.00424      0.79974
   11        0.000518        30.46018        0.96600      0.79977
   12        0.000518        30.46087        0.99540      0.79974
   13        0.000518        30.46136        0.98188      0.79976
   14        0.000518        30.46136        0.98188      0.79976
```

```
CORRELATION MATRIX
==================
          1            2             3
  1    1.0000
  2  -0.9956       1.0000
  3   0.9954      -0.9977       1.0000

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED=0.98518064



NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
================================================

                                                                   95% CONFIDENCE LIMITS
VARIABLE      NAME          VALUE          S.E.COEFF.    T-VALUE      LOWER            UPPER
    1        <V>*..        30.46136         21.01538        1.45     -19.22989         80.15261
    2        DISP..         0.98188        227.53307        0.00    -537.02429        538.98805
    3        SDLN..         0.79976          0.94273        0.85      -1.42936          3.02887

-----------------------ORDERED BY COMPUTER INPUT------------------------
                                           CONCENTRATION              RESI-
NO      DISTANCE          TIME          OBS           FITTED          DUAL
1       300.0000          5.0000       0.0620         0.0676        -0.0056
2       300.0000         10.0000       0.0760         0.0812        -0.0052
3       300.0000         15.0000       0.0590         0.0592        -0.0002
4       300.0000         20.0000       0.0380         0.0400        -0.0020
5       300.0000         25.0000       0.0140         0.0268        -0.0128
6       300.0000         30.0000       0.0070         0.0183        -0.0113
7       300.0000         35.0000       0.0040         0.0127        -0.0087
8       300.0000         40.0000       0.0030         0.0090        -0.0060
9       300.0000         45.0000       0.0010         0.0065        -0.0055
10      300.0000         50.0000       0.0            0.0047        -0.0047
```

```
---------------------------ORDERED BY RESIDUAL----------------------------
                                                CONCENTRATION             RESI-
NO      DISTANCE          TIME            OBS            FITTED          DUAL
 3      300.0000         15.0000         0.0590         0.0592         -0.0002
 4      300.0000         20.0000         0.0380         0.0400         -0.0020
10      300.0000         50.0000         0.0            0.0047         -0.0047
 2      300.0000         10.0000         0.0760         0.0812         -0.0052
 9      300.0000         45.0000         0.0010         0.0065         -0.0055
 1      300.0000          5.0000         0.0620         0.0676         -0.0056
 8      300.0000         40.0000         0.0030         0.0090         -0.0060
 7      300.0000         35.0000         0.0040         0.0127         -0.0087
 6      300.0000         30.0000         0.0070         0.0183         -0.0113
 5      300.0000         25.0000         0.0140         0.0268         -0.0128
```

14. APPENDIX E.

Listing of program CXTFIT for the analysis of transport parameters from measured resident or flux concentration data

```
C     ****************************************************************
C     *                                                              *
C     *   CXTFIT:  NON-LINEAR LEAST-SQUARES ANALYSIS OF C(X,T) DATA  *
C     *   FOR  ONE-DIMENSIONAL  DETERMINISTIC OR STOCHASTIC  SOLUTE  *
C     *   TRANSPORT  WITH  DETECTION  IN  RESIDENT  OR  FLUX  MODES  *
C     *                                                              *
C     ****************************************************************
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION C(90),F(90),R(90),DELZ(90,7),B(14),E(7),TH(14),P(7),
     1PHI(7),Q(7),LSORT(90),TB(14),A(7,7),BI(14),TITLE(20),D(7,7)
      COMMON/MODAT1/X(90),T(90),INDEX(7),NOB,NREDU,NVAR
      COMMON/MODAT2/CI,CO,DM1,XL,DM2,DM3,DM4,DM5,DM6,DM7,DM8,DM9,DM10,
     1DM11,DM12,MODE,MODT
      DATA STOPCR/0.0005/
      DATA MAXTRY/50/
C
C     ----- READ NUMBER OF CASES -----
      READ(5,1006) NC
      DO 150 NCASE=1,NC
C
C
C     ----- READ INPUT PARAMETERS -----
      READ(5,1006) MODE,NDATA,NREDU,MIT,NOB,NSKIP,NPRNT
      IF(NSKIP.NE.0) GO TO 2
      WRITE(6,1000)
      IF(MIT.NE.0) WRITE(6,1035)
      WRITE(6,1036)
      M=(MODE-1)/2
      IF(M.EQ.0) WRITE(6,1021)
      IF(M.EQ.1) WRITE(6,1022)
      IF(M.EQ.2) WRITE(6,1023)
      IF(M.EQ.3) WRITE(6,1039)
      N=MODE-2*M
      IF(N.EQ.1) WRITE(6,1024)
      IF(N.EQ.2) WRITE(6,1025)
      IF(NREDU.EQ.1) WRITE(6,1037)
      IF(NREDU.EQ.2) WRITE(6,1040)
      WRITE(6,1036)
    2 NVAR=6
      IF(MODE.GE.5) NVAR=7
      NU1=NVAR+1
      NU2=2*NVAR
      DO 4 I=1,2
      READ(5,1001) TITLE
    4 IF(NSKIP.EQ.0) WRITE(6,1002) TITLE
      IF(NSKIP.EQ.0) WRITE(6,1003)
C
C     ----- READ COEFFICIENTS NAMES -----
      READ(5,1004) (BI(I),I=1,NU2)
C
C     ----- READ INITIAL ESTIMATES -----
      READ(5,1005) (B(I),I=NU1,NU2)
C
C     ----- READ INDICES -----
      READ(5,1006) (INDEX(I),I=1,NVAR)
      IF(NSKIP.NE.0) GO TO 8
      WRITE(6,1007)
      DO 6  I=1,NVAR
      J=2*I-1
    6 WRITE(6,1008) BI(J),BI(J+1),B(I+NVAR)
    8 CONTINUE
```

```
C
C     ----- READ INITIAL AND INLET CONCENTRATIONS -----
      READ(5,1005) CI,CO
      IF(NSKIP.EQ.0) WRITE(6,1026) CI,CO
      IF(NDATA.NE.1) GO TO 11
C
C     ----- READ AND WRITE EXPERIMENTAL DATA -----
      XL=0.0
      DO 10 I=1,NOB
      READ(5,1005) C(I),X(I),T(I)
   10 XL=DMAX1(XL,X(I))
   11 IF(NREDU.EQ.2) INDEX(1)=0
      IF(NSKIP.NE.0) GO TO 150
      IF(MIT.EQ.0) GO TO 18
      IF(NPRNT.NE.1) GO TO 15
      WRITE(6,1009)
      DO 14 I=1,NOB
   14 WRITE(6,1010) I,C(I),X(I),T(I)
C
C     -----CHECK FOR INPUT ERROR-----
   15 NZC=0
      NFC=0
      DO 17 I=1,NVAR
      IF((B(I+NVAR).EQ.0.0).AND.(I.LE.3)) GO TO 129
      IF((B(I+NVAR).EQ.0.0).AND.(INDEX(I).EQ.1)) GO TO 130
      IF((I.EQ.4).OR.(MODE.GE.5)) GO TO 17
      IF(INDEX(I).EQ.1) NFC=NFC+1
      IF(B(I+NVAR).NE.0.0) NZC=NZC+1
   17 CONTINUE
      IF(MODE.GE.5) GO TO 18
      IF(NZC.LE.NFC) GO TO 120
C
C     ----- REARRANGE VARIABLE ARRAYS -----
   18 NP=0
      DO 20 I=NU1,NU2
      TB(I)=B(I)
      IF(INDEX(I-NVAR).EQ.0) GO TO 20
      NP=NP+1
      K=2*NP-1
      J=2*(I-NVAR)-1
      BI(K)=BI(J)
      BI(K+1)=BI(J+1)
      B(NP)=B(I)
      TB(NP)=B(I)
      TH(NP)=B(NP)
   20 TH(I)=B(I)
C
C     ----------
      GA=0.02
      NIT=0
      NP2=2*NP
      CALL MODEL(TH,F)
      IF (MIT.EQ.0) GO TO 140
      SSQ=0.
      DO 32 I=1,NOB
      R(I)=C(I)-F(I)
   32 SSQ=SSQ+R(I)*R(I)
      WRITE(6,1011) (BI(J),BI(J+1),J=1,NP2,2)
      WRITE(6,1012) NIT,SSQ,(B(I),I=1,NP)
```

```
C
C     ----- BEGIN ITERATION -----
   34 NIT=NIT+1
      NTRIAL=0
      GA=0.1*GA
      DO 38 J=1,NP
      TEMP=TH(J)
      TH(J)=1.01*TH(J)
      Q(J)=0.
      CALL MODEL(TH,DELZ(1,J))
      DO 36 I=1,NOB
      DELZ(I,J)=DELZ(I,J)-F(I)
   36 Q(J)=Q(J)+DELZ(I,J)*R(I)
      Q(J)=100.*Q(J)/TH(J)
C
C     ----- Q=XT*R (STEEPEST DESCENT) -----
   38 TH(J)=TEMP
      DO 44 I=1,NP
      DO 42 J=1,I
      SUM=0.
      DO 40 K=1,NOB
   40 SUM=SUM+DELZ(K,I)*DELZ(K,J)
      D(I,J)=10000.*SUM/(TH(I)*TH(J))
   42 D(J,I)=D(I,J)
      E(I)=DSQRT(D(I,I))
   44 IF(E(I).EQ.0.) E(I)=1.E-30
   50 DO 52 I=1,NP
      DO 52 J=1,NP
   52 A(I,J)=D(I,J)/(E(I)*E(J))
C
C     ----- A IS THE SCALED MOMENT MATRIX -----
      DO 54 I=1,NP
      P(I)=Q(I)/E(I)
      PHI(I)=P(I)
   54 A(I,I)=A(I,I)+GA
      CALL MATINV(A,NP,P)
C
C     ----- P/E IS THE CORRECTION VECTOR -----
      STEP=1.0
   56 DO 58 I=1,NP
   58 TB(I)=P(I)*STEP/E(I)+TH(I)
      DO 62 I=1,NP
      IF(TH(I)*TB(I))66,66,62
   62 CONTINUE
      SUMB=0.0
      CALL MODEL(TB,F)
      DO 64 I=1,NOB
      R(I)=C(I)-F(I)
   64 SUMB=SUMB+R(I)*R(I)
   66 SUM1=0.0
      SUM2=0.0
      SUM3=0.0
      DO 68 I=1,NP
      SUM1=SUM1+P(I)*PHI(I)
      SUM2=SUM2+P(I)*P(I)
   68 SUM3=SUM3+PHI(I)*PHI(I)
      ARG=SUM1/DSQRT(SUM2*SUM3)
      ARG1=0.0
      IF(NP.GT.1) ARG1=DSQRT(1.-ARG*ARG)
      ANGLE=57.29578*DATAN2(ARG1,ARG)
```

```
C
C     ----------
      DO 72 I=1,NP
      IF(TH(I)*TB(I))74,74,72
   72 CONTINUE
      NTRIAL=NTRIAL+1
      IF(NTRIAL.GT.MAXTRY) GO TO 95
      IF(SUMB/SSQ-1.0) 80,80,74
   74 IF(ANGLE-30.0)76,76,78
   76 STEP=0.5*STEP
      GO TO 56
   78 GA=10.*GA
      GO TO 50
C
C     ----- PRINT COEFFICIENTS AFTER EACH ITERATION -----
   80 CONTINUE
      DO 82 I=1,NP
   82 TH(I)=TB(I)
      WRITE (6,1012) NIT,SUMB,(TH(I),I=1,NP)
      DO 86 I=1,NP
      IF(DABS(P(I)*STEP/E(I))/(1.0D-20+DABS(TH(I)))-STOPCR) 86,86,94
   86 CONTINUE
      GO TO 96
   94 SSQ=SUMB
      IF(NIT.LT.MIT) GO TO 34
      IF(NIT.EQ.MIT) WRITE(6,1034) MIT
      GO TO 96
   95 WRITE(6,1038) MAXTRY
C
C     ----- END OF ITERATION LOOP -----
   96 CONTINUE
      CALL MATINV(D,NP,P)
C
C     ----- WRITE CORRELATION MATRIX -----
      DO 98 I=1,NP
      E(I)=DSQRT(D(I,I))
   98 IF(E(I).EQ.0.) E(I)=1.E-30
      IF(NP.EQ.1) GO TO 104
      WRITE(6,1013) (I,I=1,NP)
      DO 102 I=1,NP
      DO 100 J=1,I
  100 A(J,I)=D(J,I)/(E(I)*E(J))
  102 WRITE(6,1014) I,(A(J,I),J=1,I)
  104 SUMC=0.0
      SUMF=0.0
      SUMC2=0.0
      SUMF2=0.0
      SUMCF=0.0
      DO 106 I=1,NOB
      SUMC=SUMC+C(I)
      SUMF=SUMF+F(I)
      SUMC2=SUMC2+C(I)*C(I)
      SUMF2=SUMF2+F(I)*F(I)
  106 SUMCF=SUMCF+C(I)*F(I)
      RSQ=(SUMCF-SUMC*SUMF/NOB)**2/((SUMC2-SUMC*SUMC/NOB)*(SUMF2-SUMF*
     1SUMF/NOB))
      WRITE(6,1041) RSQ
```

```
C
C     ----- CALCULATE 95% CONFIDENCE INTERVAL -----
      Z=1./FLOAT(NOB-NP)
      SDEV=DSQRT(Z*SUMB)
      TVAR=1.96+Z*(2.3779+Z*(2.7135+Z*(3.187936+2.466666*Z**2)))
      WRITE(6,1015)
      DO 108 I=1,NP
      SECOEF=E(I)*SDEV
      TVALUE=TH(I)/SECOEF
      TSEC=TVAR*SECOEF
      TMCOE=TH(I)-TSEC
      TPCOE=TH(I)+TSEC
      J=2*I-1
      IF(NP.EQ.1)
     1WRITE(6,1043) I,BI(J),BI(J+1),TH(I),SECOEF,TMCOE,TPCOE
      IF(NP.GT.1)
     1WRITE(6,1016) I,BI(J),BI(J+1),TH(I),SECOEF,TVALUE,TMCOE,TPCOE
  108 CONTINUE
C
C     ----- PREPARE FINAL OUTPUT -----
  110 LSORT(1)=1
      DO 116 J=2,NOB
      TEMP=R(J)
      K=J-1
      DO 111 L=1,K
      LL=LSORT(L)
      IF(TEMP-R(LL)) 112,112,111
  111 CONTINUE
      LSORT(J)=J
      GO TO 116
  112 KK=J
  113 KK=KK-1
      LSORT(KK+1)=LSORT(KK)
      IF(KK-L) 115,115,113
  115 LSORT(L)=J
  116 CONTINUE
      WRITE(6,1017)
      DO 117 I=1,NOB
  117 WRITE(6,1018) I,X(I),T(I),C(I),F(I),R(I)
      WRITE(6,1019)
      DO 118 I=1,NOB
      J=LSORT(NOB+1-I)
  118 WRITE(6,1018) J,X(J),T(J),C(J),F(J),R(J)
      GO TO 150
  120 WRITE(6,1028)
      DO 125 I=1,NVAR
      J=2*I-1
      IF(I.EQ.4) GO TO 125
      IF((INDEX(I).EQ.1).AND.(B(I+6).NE.0.0)) WRITE(6,1029)BI(J),BI(J+1)
  125 CONTINUE
      GO TO 150
  129 WRITE(6,1032)
      GO TO 150
  130 WRITE(6,1031)
      GO TO 150
  140 WRITE(6,1030)
      DO 145 I=1,NOB
  145 WRITE(6,1033)I,X(I),T(I),F(I)
  150 CONTINUE
C
C     ----- END OF PROBLEM -----
```

```
 999 FORMAT(2F10.4,I5)
1000 FORMAT(1H1,10X,82(1H*)/11X,1H*,80X,1H*/11X,1H*,10X,'ONE-DIMENSIONA
    1L CONVECTION-DISPERSION EQ. SOLUTION',20X,1H*)
1001 FORMAT(20A4)
1002 FORMAT(11X,1H*,20A4,1H*)
1003 FORMAT(11X,1H*,80X,1H*/11X,82(1H*))
1004 FORMAT(7(4X,A4,A2))
1005 FORMAT(7F10.0)
1006 FORMAT(7I10)
1007 FORMAT(//11X,'INITIAL VALUES OF COEFFICIENTS'/11X,30(1H=)/12X,
    1'NAME',11X,'INITIAL VALUE')
1008 FORMAT(11X,A4,A2,4(1H.),F12.4)
1009 FORMAT(//11X,'OBSERVED DATA',/11X,13(1H=)/11X,'OBS. NO.',5X,'CONCE
    1NTRATION',6X,'DISTANCE',9X,'TIME')
1010 FORMAT(11X,I5,6X,F12.4,4X,F12.4,4X,F12.4)
1011 FORMAT(//11X,'ITERATION',6X,'SSQ',4X,5(7X,A4,A2))
1012 FORMAT(11X,I5,3X,F13.5,2X,5(F13.5))
1013 FORMAT(///,11X,'CORRELATION MATRIX'/11X,18(1H=)/14X,10(4X,I2,5X))
1014 FORMAT(11X,I3,10(2X,F7.4,2X))
1015 FORMAT(1H1,10X,'NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS'
    1/11X,48(1H=)//72X,'95% CONFIDENCE LIMITS'/11X,'VARIABLE',4X,'NAME'
    2,8X,'VALUE',8X,'S.E.COEFF.',3X,'T-VALUE',5X,'LOWER',10X,'UPPER')
1016 FORMAT(14X,I2,6X,A4,A2,1X,F13.5,3X,F13.5,2X,F8.2,1X,F13.5,
    12X,F13.5)
1017 FORMAT(//11X,23(1H-),'ORDERED BY COMPUTER INPUT',24(1H-)/
    150X,'CONCENTRATION',12X,'RESI-'/11X,'NO',4X,'DISTANCE',9X,'TIME',
    210X,'OBS',9X,'FITTED',9X,'DUAL')
1018 FORMAT(10X,I2,1X,F12.4,4(2X,F12.4))
1019 FORMAT(//11X,27(1H-),'ORDERED BY RESIDUAL',28(1H-)/
    150X,'CONCENTRATION',12X,'RESI-'/11X,'NO',4X,'DISTANCE',9X,'TIME',
    210X,'OBS',9X,'FITTED',9X,'DUAL')
1020 FORMAT(///11X,'END OF PROBLEM'/11X,14(1H=))
1021 FORMAT(11X,1H*,10X,'DETERMINISTIC LINEAR EQUILIBRIUM ADSORPTION FO
    1R PULSE INJECTION',7X,1H*/11X,1H*,10X,'WITH FIRST- AND ZERO-ORDER
    2PRODUCTION AND DECAY',23X,1H*)
1022 FORMAT(11X,1H*,10X,'DETERMINISTIC TWO-SITE/TWO-REGION NONEQUILIBRI
    1UM MODEL FOR    ',8X,1H*/11X,1H*,10X,'PULSE-TYPE INJECTION WITH NO
    2 PRODUCTION OR DECAY',22X,1H*)
1023 FORMAT(11X,1H*,10X,'STOCHASTIC TRANSPORT MODEL WITH EQUILIBRIUM AD
    1SORPTION',16X,1H*/11X,1H*,10X,'ZERO-ORDER PRODUCTION AND FIRST-ORD
    2ER DECAY FOR UNIFORM PULSE INPUT',3X,1H*)
1024 FORMAT(11X,1H*,10X,'SOLUTION FOR RESIDENT CONCENTRATIONS',34X,1H*)
1025 FORMAT(11X,1H*,10X,'SOLUTION FOR FLUX CONCENTRATIONS',38X,1H*)
1026 FORMAT(11X,'CI',8(1H.),F12.4/11X,'CO',8(1H.),F12.4)
1028 FORMAT(//11X,'INPUT ERROR-- TOO MANY UNKNOWNS! '/11X,'ONE OF THE F
    1OLLOWING COEFFICIENTS MUST BE FIXED:')
1029 FORMAT(60X,A4,A2)
1030 FORMAT(//11X,9(1H-),'RESULTS FOR INITIAL COEFFICIENT VALUES',9(1H-
    1)/11X,'NO',8X,'DISTANCE',8X,'TIME',7X,'CONCENTRATION')
1031 FORMAT(//11X,'INPUT ERROR: NONZERO INITIAL VALUES OF VARIABLE COEF
    1FICIENTS MUST BE SPECIFIED!'/11X,'FOR REACTION CONSTANTS BE SURE S
    2IGN OF COEFFICIENT IS CORRECT AS'/11X,'FITTING PROCEDURE WILL NOT
    3CHANGE SIGNS')
1032 FORMAT(//11X,'INPUT ERROR: V,D AND R MUST BE GREATER THAN ZERO!')
1033 FORMAT(11X,I2,3(3X,F12.4))
1034 FORMAT(/11X,'CONVERGENCE CRITERIA NOT MET IN',I3,' ITERATIONS')
1035 FORMAT(11X,1H*,10X,'NON-LINEAR LEAST-SQUARES ANALYSIS',37X,1H*)
1036 FORMAT(11X,1H*,80X,1H*)
1037 FORMAT(11X,1H*,10X,'REDUCED CONCENTRATION DATA',44X,1H*)
1038 FORMAT(/11X,'NO FURTHER DECREASE IN SSQ OBTAINED AFTER ',I2,' TRIA
    1LS')
1039 FORMAT(11X,1H*,10X,'STOCHASTIC TRANSPORT MODEL WITH EQUILIBRIUM AD
    1SORPTION',16X,1H*/11X,1H*,10X,'ZERO-ORDER PRODUCTION AND FIRST-ORD
    2ER DECAY FOR UNIFORM SOLUTE LOAD',3X,1H*)
1040 FORMAT(11X,1H*,10X,'REDUCED CONCENTRATION AND TIME DATA',35X,1H*)
1041 FORMAT(/11X,'RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED=',
    1F10.8/)
```

```
 1042 FORMAT(1H1,10X,'NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS'
     1/11X,48(1H=)//64X,'95% CONFIDENCE LIMITS'/11X,'VARIABLE',4X,'NAME'
     2,8X,'VALUE',8X,'S.E.COEFF.',7X,'LOWER',10X,'UPPER')
 1043 FORMAT(14X,I2,6X,A4,A2,1X,F13.5,3X,F13.5,1X,F13.5,2X,F13.5)
      STOP
      END
C
      SUBROUTINE MATINV(A,NP,B)
C
C     PURPOSE: PERFORM MATRIX INVERSION FOR PARAMETER ESTIMATION
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(7,7),B(14),INDEX(7,2)
      DO 2 J=1,7
    2 INDEX(J,1)=0
      I=0
    4 AMAX=-1.0
      DO 10 J=1,NP
      IF(INDEX(J,1)) 10,6,10
    6 DO 10 K=1,NP
      IF(INDEX(K,1)) 10,8,10
    8 P=DABS(A(J,K))
      IF(P.LE.AMAX) GO TO 10
      IR=J
      IC=K
      AMAX=P
   10 CONTINUE
      IF(AMAX) 30,30,14
   14 INDEX(IC,1)=IR
      IF(IR.EQ.IC) GO TO 18
      DO 16 L=1,NP
      P=A(IR,L)
      A(IR,L)=A(IC,L)
   16 A(IC,L)=P
      P=B(IR)
      B(IR)=B(IC)
      B(IC)=P
      I=I+1
      INDEX(I,2)=IC
   18 P=1./A(IC,IC)
      A(IC,IC)=1.0
      DO 20 L=1,NP
   20 A(IC,L)=A(IC,L)*P
      B(IC)=B(IC)*P
      DO 24 K=1,NP
      IF(K.EQ.IC) GO TO 24
      P=A(K,IC)
      A(K,IC)=0.0
      DO 22 L=1,NP
   22 A(K,L)=A(K,L)-A(IC,L)*P
      B(K)=B(K)-B(IC)*P
   24 CONTINUE
      GO TO 4
   26 IC=INDEX(I,2)
      IR=INDEX(IC,1)
      DO 28 K=1,NP
      P=A(K,IR)
      A(K,IR)=A(K,IC)
   28 A(K,IC)=P
      I=I-1
   30 IF(I) 26,32,26
   32 RETURN
      END
```

```
C
      SUBROUTINE MODEL(BN,CXT)
C
C     PURPOSE: ASSIGN COEFFICIENTS AND ROUTE EXECUTION FOR MODELS
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION BN(14),CXT(90)
      COMMON/MODAT1/X(90),T(90),INDEX(7),NOB,NREDU,NVAR
      COMMON/MODAT2/CI,CO,SOLOAD,XL,F1,F2,F3,F4,F5,R,VLNM,SDLN,DISP,XJ,
     1TJ,MODE,MODT
      EXTERNAL CAVG
C
C     ----UPDATE COEFFICIENT ARRAY----
      K=0
      NU1=NVAR+1
      NU2=NVAR*2
      DO 2 I=NU1,NU2
      IF(INDEX(I-NVAR).EQ.0) GO TO 2
      K=K+1
      BN(I)=BN(K)
    2 CONTINUE
C
C     ----- ASSIGN PARAMETERS AND CHANGE FROM REDUCED TO ACTUAL TIMES
      V=BN(NU1)
      R=BN(NVAR+3)
      REDT=1.0
      IF(NREDU.NE.2) GO TO 8
      REDT=XL/V
      DO 4 I=1,NOB
    4 T(I)=T(I)*REDT
    8 IF(MODE.LE.6) F3=REDT*BN(NVAR+4)
      IF(MODE.GE.5) GO TO 150
      IF(MODE.GE.3) GO TO 100
      F1=V/R
      F2=BN(8)/R
      F4=BN(11)/R
      F5=BN(12)/R
C
C     ----SOLVE FOR MODELS 1 AND 2
   50 DO 75 J=1,NOB
      CALL MOD12(CXT(J),X(J),T(J))
   75 CONTINUE
      GO TO 350
C
C     ----SOLVE FOR MODELS 3 AND 4
  100 F1=V
      F2=V*XL/BN(8)
      F4=DMIN1(BN(11),0.9999D00)*R
      F5=BN(12)
      DO 125 J=1,NOB
      CALL MOD34(CXT(J),X(J),T(J))
  125 CONTINUE
      GO TO 350
C
C     ----SOLVE FOR MODELS 5 THRU 8
  150 F4=BN(12)/R
      F5=BN(13)/R
      SDLN=BN(14)
      VLNM=DLOG(V)-0.5*SDLN*SDLN
      DISP=BN(9)
      IF(MODE.GE.7) SOLOAD=BN(11)/CO
```

```
      VMIN1=DEXP(VLNM-3.9*SDLN)
      VMAX1=DEXP(VLNM+3.9*SDLN)
      CMIN=DABS(CO-CI)*1.D-06
      MODT=MODE
      IF((MODT.EQ.5).OR.(MODT.EQ.7)) MODE=1
      IF((MODT.EQ.6).OR.(MODT.EQ.8)) MODE=2
      DO 175 J=1,NOB
      XJ=X(J)
      TJ=T(J)
      PL=DMAX1(XJ/DISP,1.D-10)
      VMIN=DMAX1(VMIN1,DMIN1(0.14*DLOG(PL)*XJ/TJ-.05,0.9*XJ/TJ)*R)
      CALL LIMIT(VMIN,VMAX,VMAX1,CMIN)
      CALL ROMB(CAVG,CXT(J),VMIN,VMAX)
      IF(MODE.EQ.2) CXT(J)=CXT(J)/V
  175 CONTINUE
      MODE=MODT
  350 CONTINUE
      IF(NREDU.EQ.0) GO TO 360
      DO 355 I=1,NOB
      T(I)=T(I)/REDT
  355 CXT(I)=(CXT(I)-CI)/(CO-CI)
  360 CONTINUE
      RETURN
      END
C
      SUBROUTINE MOD12(CXT,X,TIME)
C
C     PURPOSE: TO CALCULATE C(X,T) FOR MODE=1
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/MODAT2/CI,CO,DM1,XL,VR,DR,TO,RX1R,RXOR,R,DM2,DM3,DM4,DM5,
     1DM6,MODE,MDMY
      IF(RX1R.NE.0.0) GO TO 50
C
C     ------CALCULATE C(X,T) FOR RX1R=0
      DO 20 M=1,2
      A=0.0
      B=0.0
      T=TIME+(1-M)*TO
      IF(T.LE.0.0) GO TO 20
      S2=(X-VR*T)/DSQRT(4.*DR*T)
      S6=VR*X/DR
      S7=(X+VR*T)/DSQRT(4.*DR*T)
      E1=EXF(0.0D00,S2)
      E2=EXF(S6,S7)
      IF(MODE.EQ.2) GO TO 2
      S3=VR*DSQRT(T/(DR*3.141593))
      S4=(X-VR*T)*(VR*T-X)/(4*DR*T)
      S5=-0.5*(1.+VR*X/DR+VR*VR*T/DR)
      E3=EXF(S4,0.0D00)
      GO TO 3
    2 S3=0.0
      S5=0.5
      E3=0.0
    3 A=0.5*E1+S3*E3+S5*E2
      IF(M.EQ.2) GO TO 30
      IF(RXOR.EQ.0.0) GO TO 10
      IF(MODE.EQ.2) GO TO 5
      S8=(X-VR*T+DR/VR)/(2*VR)
      S9=DSQRT(T*0.079577/DR)*(X+VR*T+2.*DR/VR)
```

```
      S10=T/2.-DR/(2.*VR*VR)+(X+VR*T)**2./(4*DR)
      GO TO 7
    5 S8=(X-VR*T)/(2.*VR)
      S9=0.0
      S10=-(X+VR*T)/(2.*VR)
    7 B=RXOR*(T+S8*E1-S9*E3+S10*E2)
   10 CXT=CI+(CO-CI)*A+B
   20 CONTINUE
   30 CXT=CXT-CO*A
      RETURN
C
C     ------CALCULATE RX1R.NE.0. CASE
   50 RAT=RXOR/RX1R
      DO 70 M=1,2
      A=0.0
      B=0.0
      T=TIME+(1-M)*TO
      IF(T.LE.0.0) GO TO 70
      S7=(X+VR*T)/DSQRT(4.*DR*T)
      IF(M.EQ.2) GO TO 55
      S1=-RX1R*T
      S2=(X-VR*T)/DSQRT(4.*DR*T)
      S6=VR*X/DR
      E1=EXF(0.0D00,S2)
      E2=EXF(S6,S7)
      IF(MODE.EQ.2) GO TO 52
      S3=VR*DSQRT(T/(DR*3.141593))
      S4=(X-VR*T)*(VR*T-X)/(4*DR*T)
      S5=-0.5*(1.+VR*X/DR+VR*VR*T/DR)
      E3=EXF(S4,0.0D00)
      GO TO 53
   52 S3=0.0
      S5=0.5
      E3=0.0
   53 A=EXF(S1,0.D00)*(1.-0.5*E1-S3*E3-S5*E2)
   55 CONTINUE
      U=DSQRT(VR*VR+4.*RX1R*DR)
      S9=(VR-U)*X/(2.*DR)
      S10=(X-U*T)/DSQRT(4.*DR*T)
      S12=(VR+U)*X/(2.*DR)
      S13=(X+U*T)/DSQRT(4.*DR*T)
      IF(MODE.EQ.2) GO TO 57
      S8=VR/(VR+U)
      S11=VR/(VR-U)
      S14=VR*VR/(2.*RX1R*DR)
      S15=VR*X/DR-RX1R*T
      S16=S14*EXF(S15,S7)
      GO TO 59
   57 S8=0.5
      S11=0.5
      S16=0.0
   59 B=S8*EXF(S9,S10)+S11*EXF(S12,S13)+S16
   60 IF(M.EQ.2) GO TO 80
      CXT=(CI-RAT)*A+(CO-RAT)*B+RAT
   70 CONTINUE
   80 CXT=CXT-CO*B
      RETURN
      END
```

```
C
      SUBROUTINE MOD34(CXT,X,T)
C
C     PURPOSE: CALCULATE C(X,T) FOR MODELS 3 AND 4
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/MODAT2/CI,CO,DM1,XL,V,P,TO,BETR,OMEGA,R,DM2,DM3,DM4,Z,TT,
     1MODE,MDMY
      DIMENSION WG(5),XG(5)
      DATA XG/.04691008,.23076534,.50000000,.76923466,.95308992/
      DATA WG/.1184634,.2393143,.2844444,.2393143,.1184634/
      EXTERNAL CCO
      TRO=V*TO/XL
      TR=V*T/XL
      Z=X/XL
      IF(Z.GT.0.0) GO TO 5
      Z=1.D-10
      IF(MODE.EQ.3) GO TO 5
      CXT=0.0
      IF(T.LE.TO) CXT=CO
      RETURN
    5 DO 20 M=1,2
      A=0.0
      TT=TR+(1-M)*TRO
      IF(TT.LE.0.) GO TO 20
      AP=DSQRT(1.+.05*P*Z)
      TMAX=DMIN1(TT,BETR*(Z+40.*(1.+AP)/P))
      TMIN=DMAX1(0.D00,BETR*(Z+40.*(1.-AP)/P))
      IF(TMAX.LE.TMIN) GO TO 15
      A1=0.0
      IF(TMIN.GT.0.) GO TO 10
      TMAX2=TMAX*1.D-4
      DO 8 I=1,5
      TAU=TMIN+(TMAX2-TMIN)*XG(I)
    8 A1=A1+WG(I)*CCO(TAU)
      A1=A1*(TMAX2-TMIN)
      TMIN=TMAX2
   10 CONTINUE
      CALL ROMB(CCO,A2,TMIN,TMAX)
      A=A1+A2
   15 IF(M.EQ.2) GO TO 30
      CXT=CI+(CO-CI)*A
   20 CONTINUE
   30 CXT=CXT-CO*A
      RETURN
      END
```

```
C
      SUBROUTINE LIMIT(VMIN,VMAX,VMAX1,CMIN)
C
C     PURPOSE:  TO CALCULATE INTEGRATION LIMITS FOR MODELS 5-8
C
      IMPLICIT REAL*8 (A-H,O-Z)
C
C     ----- CALCULATE VMIN -----
      IF(VMIN.GE.VMAX1)RETURN
      F=(VMAX1/VMIN)**0.1
      DO 8 J=1,3
      DO 4 I=1,11
      CLST=CAVG(VMIN)
      IF(CLST.GT.CMIN/100.) GO TO 6
    4 VMIN=VMIN*F
      VMAX=VMIN
      RETURN
    6 SLOPE=(CAVG(VMIN*1.001)-CLST)/(0.001*VMIN)
      IF(SLOPE.GT.0.) GO TO 10
      VMIN=VMIN/F
    8 F=F**0.1
      GO TO 20
   10 IF(CLST.LT.CMIN) GO TO 20
      DO 12 I=1,5
      VMIN=VMIN-CLST/SLOPE
      IF(VMIN.LE.0.0)GO TO 15
      IF(CLST.LT.CMIN) GO TO 20
      CLST=CAVG(VMIN)
      SLOPE=(CAVG(VMIN*1.001)-CLST)/(0.001*VMIN)
      IF(SLOPE.LE.0.) GO TO 20
   12 CONTINUE
      GO TO 20
   15 VMIN=VMIN+CLST/SLOPE
C
C     ----- CALCULATE VMAX -----
   20 F=(VMAX1/VMIN)**0.1
      VMAX=VMAX1
      DO 28 J=1,3
      DO 24 I=1,11
      CLST=CAVG(VMAX)
      IF(CLST.GT.CMIN/100.) GO TO 26
   24 VMAX=VMAX/F
   26 SLOPE=(CAVG(VMAX*1.01)-CLST)/(0.01*VMAX)
      IF(SLOPE.LT.0.) GO TO 30
      VMAX=VMAX*F
   28 F=F**0.1
      RETURN
   30 IF(CLST.LT.CMIN) RETURN
      DO 32 I=1,5
      VMAX=VMAX-CLST/SLOPE
      IF(CLST.LT.CMIN) RETURN
      CLST=CAVG(VMAX)
      SLOPE=(CAVG(VMAX*1.01)-CLST)/(0.01*VMAX)
      IF(SLOPE.EQ.0.) RETURN
   32 CONTINUE
      RETURN
      END
```

```
C
      SUBROUTINE ROMB(FUNC,AREA,XMIN,XMAX)
C
C     PURPOSE: PERFORM ROMBERG INTEGRATION ON LOG-TRANSFORMED INTERVAL
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION R(9,9)
      AREA=0.0
      IF(XMIN.GE.XMAX)RETURN
      LEVEL=9
      STOPER=0.00005
      XLN1=DLOG(XMIN)
      XLN2=DLOG(XMAX)
      DX1=XLN2-XLN1
      SUM=0.5*XMIN*FUNC(XMIN)
      AREA=SUM*DX1
      R(1,1)=AREA
      DX2=DX1/2.
      INC=1
      DO 20 I=2,LEVEL
      XLN=XLN1+DX2
      DO 4 M=1,INC
      XE=DEXP(XLN)
      SUM=SUM+XE*FUNC(XE)
    4 XLN=XLN+DX1
      AREA=SUM*DX2
      R(1,I)=AREA
      DO 17 J=2,I
      K=I+1-J
   17 R(J,K)=(4.**(J-1)*R(J-1,K+1)-R(J-1,K))/(4.**(J-1)-1)
      IF(R(I,1).GT.0.0) GO TO 18
      IF(I.GT.4) RETURN
      GO TO 19
   18 ERROR=DABS((R(I,1)-R(I-1,2))/R(I,1))
      IF((ERROR.LT.STOPER).AND.(I.GT.4)) RETURN
   19 DX1=DX1/2.
      DX2=DX2/2.
   20 INC=INC*2
      RETURN
      END
C
      FUNCTION CCO(TAU)
C
C     PURPOSE: CALCULATE ARGUMENT IN INTEGRAL FOR MODELS 3 AND 4
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/MODAT2/DM1,DM2,DM3,DM4,DM5,P,DM6,BETR,OMEGA,R,DM7,DM8,DM9,
     1Z,T,MODE,MDMY
      CCO=0.0
      G1=EXF(P*(BETR*Z-TAU)*(TAU-BETR*Z)/(4.*BETR*TAU),0.D00)
      IF(MODE.EQ.4) GO TO 5
      G2=DSQRT(P/(BETR*TAU))
      G=0.56419*G2*G1-P/(2.*BETR)*EXF(P*Z,G2/2.*(BETR*Z+TAU))
      GO TO 10
    5 G=(Z/TAU)*DSQRT(P*BETR/(12.5664*TAU))*G1
   10 IF(G.LT.1.D-07) RETURN
      A=OMEGA*TAU/BETR
      B=OMEGA*(T-TAU)/(R-BETR)
      CCO=G*GOLD(A,B)
      RETURN
      END
```

```
C
      FUNCTION CAVG(V)
C
C     PURPOSE: CALCULATE ARGUMENT IN INTEGRAL FOR MODELS 5-8
C
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/MODAT2/CI,CO,SOLOAD,XL,VR,DR,TO,RX1R,RXOR,R,VLNM,SDLN,DISP,
     1X,T,MODE,MODT
      VLN=DLOG(V)
      VR=V/R
      DR=VR*DISP
      IF(MODT.GE.7) TO=SOLOAD/V
      CALL MOD12(C,X,T)
      ARG=DMIN1(1.D02,(VLN-VLNM)*(VLN-VLNM)/(2.*SDLN*SDLN))
      PROB=DEXP(-ARG)/(2.50663*SDLN*V)
      IF(C.LT.1.D-70)C=0.D00
      IF(MODE.EQ.1) CAVG=PROB*C
      IF(MODE.EQ.2) CAVG=PROB*C*V
      RETURN
      END
C
      FUNCTION EXF(A,B)
C
C     PURPOSE:  TO CALCULATE EXP(A) ERFC(B)
C
      IMPLICIT REAL*8(A-H,O-Z)
      EXF=0.D00
      IF((DABS(A).GT.100.).AND.(B.LE.0.)) RETURN
      C=A-B*B
      IF((DABS(C).GT.100.).AND.(B.GE.0.)) RETURN
      IF(C.LT.-100.) GO TO 3
      X=DABS(B)
      IF(X.GT.3.0) GO TO 1
      T=1./(1.+.3275911*X)
      Y=T*(.2548296-T*(.2844967-T*(1.421414-T*(1.453152-1.061405*T))))
      GO TO 2
    1 Y=.5641896/(X+.5/(X+1./(X+1.5/(X+2./(X+2.5/X+1.)))))
    2 EXF=Y*DEXP(C)
    3 IF(B.LT.0.0) EXF=2.*DEXP(A)-EXF
      RETURN
      END
```

```
C
      FUNCTION GOLD(X,Y)
C
C     PURPOSE: TO CALCULATE GOLDSTEIN'S J-FUNCTION J(X,Y)
C
      IMPLICIT REAL*8(A-H,O-Z)
      GOLD=0.0
      BF=0.0
      E=2.*DSQRT(DMAX1(0.D0,X*Y))
      Z=X+Y-E
      IF(Z.GT.17.) GO TO 8
      IF(E.NE.0.) GO TO 2
      GOLD=DEXP(-X)
      RETURN
    2 A=DMAX1(X,Y)
      B=DMIN1(X,Y)
      NT=11.+2.*B+0.3*A
      IF(NT.GT.25) GO TO 6
      I=0
      IF(X.LT.Y) I=1
      GXY=1.+I*(B-1.)
      GXYO=GXY
      GX=1.0
      GY=GXY
      GZ=1.0
      DO 4 K=1,NT
      GX=GX*A/K
      GY=GY*B/(K+I)
      GZ=GZ+GX
      GXY=GXY+GY*GZ
      IF((GXY-GXYO)/GXY.LT.1.D-08) GO TO 5
    4 GXYO=GXY
    5 GOLD=GXY*EXF(-X-Y,0.0D00)
      GO TO 8
    6 DA=DSQRT(A)
      DB=DSQRT(B)
      P=3.75/E
      BO=(.3989423+P*(.01328592+P*(.00225319-P*(.00157565-P*(.00916281-P
     1*(.02057706-P*(.02635537-P*(.01647633-.00392377*P))))))))/DSQRT(E)
      BF=BO*EXF(-Z,0.0D00)
      P=1./(1.+.3275911*(DA-DB))
      ERF=P*(.2548296-P*(.2844967-P*(1.421414-P*(1.453152-P*1.061405))))
      P=0.25/E
      C0=1.-1.772454*(DA-DB)*ERF
      C1=0.5-Z*C0
      C2=0.75-Z*C1
      C3=1.875-Z*C2
      C4=6.5625-Z*C3
      SUM=.1994711*(A-B)*P*(C0+1.5*P*(C1+1.666667*P*(C2+1.75*P*(C3+P*(C4
     1*(1.8-3.3*P*Z)+97.45313*P)))))
      GOLD=0.5*BF+(.3535534*(DA+DB)*ERF+SUM)*BF/(BO*DSQRT(E))
    8 IF(X.LT.Y) GOLD=1.+BF-GOLD
      RETURN
      END
```

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