RESEARCH REPORT

NO. 119

NON-EQUILIBRIUM TRANSPORT PARAMETERS FROM MISCIBLE DISPLACEMENT EXPERIMENTS

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FEBRUARY 1981

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SCIENCE AND EDUCATION ADMINISTRATION
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NON-EQUILIBRIUM SOLUTE TRANSPORT PARAMETERS FROM MISCIBLE DISPLACEMENT EXPERIMENTS[1/]

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ABSTRACT

Traditionally, a two-parameter partial differential equation has been used to describe the one-dimensional convective-dispersive transport of chemicals in field soils. The parameters in this equation include the dispersion coefficient and a distribution coefficient, the latter accounting for interactions between the chemical and the solid phase of the soil. For linear equilibrium adsorption the resulting model is relatively easy to use. Recently, however, some inadequacies in this transport model were observed when comparing model predictions with experimental data. More complex conceptual models have therefore been introduced in attempts to better characterize the simulated system. These models are all based on the assumption that, either for physical or chemical reasons, adsorption does not proceed at an equal rate in all parts of the soil medium. The resulting transport equations contain several parameters which must be quantified before actual predictions can be made in the field. Estimates for these parameters can be obtained by analyzing effluent curves from column displacement experiments. Since several parameters have to be estimated simultaneously, elaborate curve-fitting techniques are often needed. This report describes an accurate and

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easy to use least-squares computer program which may be used for that purpose. Depending upon the exact form of the transport model, the program allows up to five different parameters to be estimated simultaneously. A listing of the program is given in an appendix of this report.

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INTRODUCTION

Recent literature shows that much has been learned about the effects of diffusion, dispersion, convection and adsorption on chemical transport in soils. Numerous conceptual-mathematical models have been developed in attempts to describe the one-dimensional transport of chemicals in laboratory columns as well as in field soils. Many others will undoubtedly follow. Such models are important because they continuously increase our understanding of the basic transport mechanisms involved and, consequently, improve our capability to predict the fate in field soils of such diverse chemicals as nitrates, fertilizers, pesticides, heavy metals and radio-active waste materials.

The majority of studies focusing on solute transport in soils have used as a conceptual model the one-dimensional convective-dispersive equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \qquad [1]$$

where

c = solution concentration (ML^{-3}),

D = dispersion coefficient (L^2T^{-1}),

t = time (T),

v = average pore-water velocity (LT^{-1}), and

x = distance (L).

Equation [1] assumes steady-state water flow, a constant soil-water content, and no interactions between the chemical and the solid phase. Its basic properties will not be reviewed here as they have been discussed at length elsewhere (e.g., see Perkins and Johnson, 1963; Biggar and Nielsen, 1967;

Fried and Combarnous, 1971; Kirkham and Powers, 1972; Bear, 1972; Bolt, 1979).

When chemical adsorption is considered, an additional term must be added to Eq. [1] to account for the interaction between the chemical and the solid phase. This is accomplished by redefining [1] as:

$$\frac{\partial c}{\partial t} + \frac{\rho}{\theta}\frac{\partial S}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \qquad [2]$$

where

S = adsorbed concentration (MM^{-1}),
θ = volumetric soil-water content (L^3L^{-3}), and
ρ = bulk density (ML^{-3}).

The solution of Eq. [2] depends on knowledge of the relationship between the adsorbed concentration, S, and the solution concentration, c. Both equilibrium and kinetic non-equilibrium equations are available for this purpose (Boast, 1972; van Genuchten and Cleary, 1979). Most of the early studies on solute transport, especially when applied to pesticide movement, were based on linear equilibrium equations (Kay and Elrick, 1967; Green et al., 1968; Davidson et al., 1968; Davidson and Chang, 1972; Davidson and McDougal, 1973). In nearly all of these studies, serious deviations were observed between calculated and experimental effluent curves. It was often not possible to predict the early arrival of the applied chemical in the effluent as well as the generally skewed or asymmetrical shape of the observed curves. The introduction of experimentally determined nonlinear equilibrium isotherms did, at least in some cases, lead to better predictions, especially when observed hysteresis phemomena in the adsorption-desorption isotherms were taken into account (Swanson and Dutt, 1973; van Genuchten et al., 1974). In general, however, predictions based on equilibrium adsorption models were found to be inadequate.

In attempts to improve the predictions, kinetic non-equilibrium models were intruduced by Lindstrom and Boersma (1972), Hornsby and Davidson (1973) and Mansell et al. (1977). Although this approach resulted in some improvement in predictive capabilities, success with the kinetic non-equilibrium model was generally limited to experiments conducted at relatively low pore-water velocities (Davidson and McDougal, 1973; Hornsby and Davidson, 1973; van Genuchten et al., 1974).

In the last few years, several studies have focused on the description of asymmetrical (skewed) and nonsigmoidal concentration distributions (van Genuchten and Wierenga, 1976b; Rao et al, 1980). The term "tailing" will be used here to indicate the presence of such skewed and nonsigmoidal distributions. At least two groups of models have been proposed to explain and predict tailing. In one group of models, tailing is explained on the basis of physical processes such as the presence of distinct mobile and immobile soil-water regions. Convective solute transport in these models is assumed to occur only in the mobile soil-water phase, while adsorption in a stagnant region of the soil is controlled by diffusion through the immobile (non-moving) fraction of the soil-water phase (Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976b; Leistra, 1977). This situation is primarily a physical problem insofar as the physical make-up of the soil is responsible for the presence of the relatively immobile water. A similar physical non-equilibrium situation can also occur in systems where the chemical is not subject to adsorption, notable in highly aggregated soils or soils that contain many liquid-filled macropores (Nielsen and Biggar, 1961; McMahon and Thomas, 1974; Rao et al., 1980).

In another group of models, tailing in effluent curves is explained on the basis of chemical processes by assuming the presence of a two-site adsorption mechanism. In this approach adsorption on one fraction of the sorption sites is assumed to be instantaneous, while adsorption on the remaining sites is thought to be time-dependent (Selim et al., 1976; Cameron and Klute, 1977).

With the introduction of increasingly complex models, the problem remains of how to measure the different parameters appearing in the governing transport equations. For example, the more involved physical non-equilibrium and two-site adsorption models each contain four independent parameters which must be quantified before the transport equations can be used to simulate solute movement. Unfortunately, presently available experimental techniques are generally inadequate or too complex to measure all four parameters independently (Davidson et al., 1980; Rao et al., 1980). An alternative method is to estimate the different parameters directly from observed effluent curves by fitting the model to the experimental data (van Genuchten and Wierenga, 1976; Gaudet, 1978; De Smedt, 1979). It is the purpose of this report to present a nonlinear least-squares curve-fitting program which may be used for this purpose. The computer program assumes that analytical solutions of the governing transport equations are available. Theoretically one could possibly also use numerical solutions, but this approach is likely to result in a more elaborate and less efficient curve-fitting program. If analytical solutions are to be used, the governing equations must be properly linearized. The transport models discussed in this report are therefore formulated only in terms of linear adsorption. More specifically, the following conceptual models are considered:

Model A: Linear equilibrium adsorption.

Model B: Physical non-equilibrium (van Genuchten and Wierenga, 1976b).

Model C: Physical non-equilibrium in the presence of anion exclusion (Krupp _et al._, 1972).

Model D: Two-site kinetic non-equilibium adsorption (Selim _et al._, 1976).

Model E: One-site kinetic non-equilibium adsorption (Lindstrom and Boersma, 1972).

The anion exclusion model of Krupp _et al_. (1972) is also included since this model can be viewed as a particular application of the physical non-equilibrium model. It will be shown that models B, C, D and E all reduce to the same general equations when properly expressed in dimensionless variables. The advantage of this is that the curve-fitting program can be kept very general, rather than being limited to one single conceptual formulation. The computer program itself is discussed and listed in Appendix B.

A. LINEAR EQUILIBRIUM ADSORPTION

The relation between adsorbed and solution concentrations is described by a linear (or linearized) isotherm of the form

$$S = k\,c \tag{3}$$

where k is an empirical distribution coefficient ($M^{-1}L^3$). Substitution of [3] into [2] gives the transport equation

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \tag{4}$$

where the retardation factor, R, is given by

$$R = 1 + \rho k/\theta \tag{5}$$

If there is no interaction between the chemical and the solid phase, k in Eq. [5] becomes zero and R reduces to one. In some cases R may become less than one, indicating that only a fraction of the liquid phase participates in the transport process. This occurs when the chemical is subject to anion exclusions (e.g., for chloride movement in many fine-textured soils), or when immobile liquid regions are present which do not contribute to convective solute transport (e.g., water inside dense aggregates or away from liquid-filled macro-pores). In the case of anion exclusion (1-R) can be viewed as the relative anion exclusion volume, and (-k) in Eq. [5] as the specific anion exclusion volume (e.g., expressed in cm^3 water per gram of soil).

Analytical solutions of Eq. [4] exist for several sets of initial and boundary conditions. The initial condition for this study is

$$c(x,0) = C_i \tag{6}$$

Two different conditions can be applied to the upper boundary of the soil column (x = 0): a first-type, constant concentration boundary condition of the form

$$c(0,t) = C_o, \tag{7}$$

or a third-type, constant flux boundary condition of the form

$$\left(-D \frac{\partial c}{\partial x} + vc\right)\Big|_{x=0} = v\ C_o \tag{8}$$

where C_o is the concentration of the input solution. It should be mentioned here the Eq. [8] does lead to conservation of mass inside the soil column, while boundary condition [7] will lead to mass balance errors when used for column displacement experiments in which the chemical is applied at a constant rate. These errors can become quite significant for large values of (D/v).

For the lower boundary, the following condition can be applied

$$\frac{\partial c}{\partial x}(\infty,t) = 0. \tag{9}$$

This condition assumes the presence of a semi-infinite soil column. When analytical solutions based on this boundary condition are used to calculate effluent curves from finite columns, some errors may be introduced. An alternative boundary condition, one that is frequently used for column displacement studies, is that of a zero concentration gradient at the lower end of the column:

$$\frac{\partial c}{\partial x}(L,t) = 0 \qquad [10]$$

where L is the column length. This condition, which leads to a continuous concentration distribution at x = L, has been discussed extensively in the literature (Wehner and Wilhelm, 1956; Pearson, 1959; van Genuchten and Wierenga, 1974; Bear, 1979). In our opinion no clear evidence exists that Eq. [10] leads to a better description of the physical processes at and around x = L. In fact, the upper boundary condition [8] does lead to a discontinuous distribution at the inlet position and, as such, seems to contradict the requirement for a continuous distribution at x = L. In this study we will present analytical solutions for both lower boundary conditions (Eq. [9] and [10]). However, only the solutions for a semi-infinite medium will be included in the curve-fitting program. Because of the relatively small influence of the imposed mathematical boundary conditions, the solutions for a semi-infinite system should provide close approximations for those applicable to a physically well-defined finite system, expecially for not too short laboratory soil columns.

For an analysis of effluent data it is convenient to introduce the dimensionless variables

$$T = vt/L \qquad z = x/L \qquad [11]$$

$$P = vL/D \qquad [12]$$

$$c_1 = \frac{c - C_i}{C_o - C_i} \qquad [13]$$

where T is the number of pore volumes and P the column Peclet number. Introducing these variables into [4] gives

$$R\frac{\partial c_1}{\partial T} = \frac{1}{P}\frac{\partial^2 c_1}{\partial z^2} - \frac{\partial c_1}{\partial z} \qquad [14]$$

The dimensionless exit concentration, c_e, is now simply

$$c_e(T) = c_1(1,T). \qquad [15]$$

Table 1 gives analytical expressions for c_e for each of the four possible combinations of upper and lower boundary conditions (Eq. [7] - [10]). Note that the solutions for a finite system (Cases FN-1 and FN-2) are in the form of infinite series. Both series solutions converge slowly for relatively large values of P and/or small values of T. For $P > 5 + 40T/R$ or $P > 100$, the following approximate solutions are recommended: for Case FN-1 (van Genuchten and Alves, 1981),

$$c_e = \frac{1}{2}\,\mathrm{erfc}[(\frac{P}{4RT})^{1/2}(R-T)] - (\frac{PT}{\pi R})^{1/2}\exp[-\frac{P}{4RT}(R-T)^2]$$
$$+ \frac{1}{2}(3 + P + \frac{PT}{R})\exp(P)\,\mathrm{erfc}[(\frac{P}{4RT})^{1/2}(R+T)] \qquad [16]$$

and for Case FN-2 (Brenner, 1962),

$$c_e = \frac{1}{2}\,\mathrm{erfc}[(\frac{P}{4RT})^{1/2}(R-T)]$$
$$+ (\frac{PT}{\pi R})^{1/2}(3 + \frac{P}{2} + \frac{PT}{2R})\exp[-\frac{P}{4RT}(R-T)^2]$$
$$- \frac{1}{2}[1 + 3P + \frac{4PT}{R} + \frac{P^2}{2R^2}(R+T)^2]\exp(P)\,\mathrm{erfc}[(\frac{P}{4RT})^{1/2}(R+T)] \qquad [17]$$

Table 1. **Expressions for the dimensionless exit concentration, c_e, based on analytical solutions of Eq. [14], initial condition [16] and four different sets of boundary conditions.**

CASE	BOUNDARY CONDITIONS		DIMENSIONLESS EXIT CONCENTRATION (c_e)	
SI-1	$c_1(0,T) = 1$	$\frac{\partial c_1}{\partial z}(\infty,t) = 0$	$c_e = \frac{1}{2}\,\mathrm{erfc}[(\frac{P}{4RT})^{1/2}(R-T)] + \frac{1}{2}\exp(P)\,\mathrm{erfc}[(\frac{P}{4RT})^{1/2}(R+T)]$	
SI-2	$(-\frac{1}{P}\frac{\partial c_1}{\partial z} + c_1)\Big\vert_{z=0} = 1$	$\frac{\partial c_1}{\partial z}(\infty,T) = 0$	$c_e = \frac{1}{2}\,\mathrm{erfc}\,[(\frac{P}{4RT})^{1/2}(R-T)] + (\frac{PT}{\pi R})^{1/2}\exp[-\frac{P}{4RT}(R-T)^2]$ $-\frac{1}{2}(1 + P + \frac{PT}{R})\exp(P)\,\mathrm{erfc}[(\frac{P}{4RT})^{1/2}(R+T)]$	
FN-1	$c_1(0,T) = 1$	$\frac{\partial c_1}{\partial z}(1,T) = 0$	$c_e = 1 - \sum_{m=1}^{\infty}\frac{2\,\beta_m\sin(\beta_m)\exp[\frac{P}{2} - \frac{PT}{4R} - \frac{\beta_m^2 T}{PR}]}{\beta_m^2 + \frac{P^2}{4} + \frac{P}{2}}$	$\beta_m\cot(\beta_m) + \frac{P}{2} = 0$
FN-2	$(-\frac{1}{P}\frac{\partial c_1}{\partial z} + c_1)\Big\vert_{z=0} = 1$	$\frac{\partial c_1}{\partial z}(1,T) = 0$	$c_e = 1 - \sum_{m=1}^{\infty}\frac{2\,\beta_m\sin(\beta_m)\exp[\frac{P}{2} - \frac{PT}{4R} - \frac{\beta_m^2 T}{PR}]}{\beta_m^2 + \frac{P^2}{4} + P}$	$P\,\beta_m\cot(\beta_m) + \frac{P^2}{4} = \beta_m^2$

References:
SI-1: Lapidus and Amundson (1952)
SI-2: Lindstrom _et al._ (1967)
FN-1: Cleary and Adrian (1973)
FN-2: Brenner (1962)

The exit concentration given by [16] is exactly twice c_e for Case SI-1 minus c_e for Case SI-2 (Table 1). Because of the approximate nature of [16], this relation does not hold for relatively small values of P.

B. PHYSICAL NON-EQUILIBRIUM

Equations [1] and [4] imply that all soil-water participates freely in the convective transport of chemicals, and that all adsorption sites are equally accessible for the solute if adsorption takes place. Both equations, furthermore, predict effluent curves which are characteristically sigmoidal or symmetrical in shape, at least for not too small values of P. Numerous experiments, both in the laboratory and under field conditions, have shown serious deviations from these type of symmetrical distributions. Experimental curves frequently show a much earlier appearance of the chemical in the effluent than can be accounted for with solutions based on [1] or [4], while at the same time considerably more water is needed before the displacement is complete. Several experimental conditions seem to favor this accelerated transport followed by tailing, notable solute movement in unsaturated soils (Nielsen and Biggar, 1961; Gupta *et al.*, 1973 a, b; Gaudet *et al.*, 1977; De Smedt, 1979), and solute movement through aggregated and undisturbed soils (Biggar and Nielsen, 1962; Green *et al.*, 1972; McMahon and Thomas, 1974; van Genuchten and Wierenga, 1977; Rao *et al.*, 1979). Extreme tailing is also expected when cracked soils, or soils containing macropores, are leached under saturated conditions. Even in uniform, saturated soils, however, tailing may occur, especially when there is a strong interaction between the chemical and the solid phase (van Genuchten and Cleary, 1979).

Recently, several attempts have been made to account for the observed asymmetry and tailing. One such approach involves the concept of solute transfer between mobile and immobile soil-water phases (Turner, 1958; Gottschlich, 1963; Coats and Smith, 1964; Skopp and Warrick, 1974; van Genuchten and Wierenga, 1976b). In this approach convective-dispersive solute transport is assumed to be confined only to the mobile water phase. Solute transfer between mobile (dynamic) and immobile (stagnant) soil-water regions, furthermore, is assumed to be diffusion controlled. The model discussed here is essentially that of Coats and Smith, 1964), but using the notation of van Genuchten and Wierenga (1976b) and Gaudet et al. (1977). The governing transport equations for the mobile and immobile water phases, in the absence of solute adsorption, are

$$\theta_m \frac{\partial c_m}{\partial t} + \theta_{im} \frac{\partial c_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial x} \qquad [18]$$

$$\theta_{im} \frac{\partial c_{im}}{\partial t} = \alpha (c_m - c_{im}) \qquad [19]$$

where the subscripts m and im refer to mobile and immobile liquid regions, and where v_m is the average pore-water velocity in the mobile liquid phase:

$$\begin{aligned} v_m &= q/\theta_m \\ &= v/\phi_m \end{aligned} \qquad [20]$$

In Eq. [20], q is the volumetric flux and ϕ_m the fraction mobile water:

$$\phi_m = \theta_m/\theta \qquad (\theta = \theta_m + \theta_{im}) \qquad [21]$$

The mass transfer coefficient, α, in Eq. [19] determines the rate of exchange between the two liquid phases. The transport model assumes that this rate is proportional to the difference in concentration between mobile and immobile soil-water phases.

Equations [18] and [19] assume that no adsorption occurs. van Genuchten and Wierenga (1976) modified the equations to include the effects of chemical adsorption. They suggested the following set of differential equations:

$$\theta_m \frac{\partial c_m}{\partial t} + f\rho \frac{\partial S_m}{\partial t} + \theta_{im} \frac{\partial c_{im}}{\partial t} + (1-f)\rho \frac{\partial S_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial x} \qquad [22]$$

$$\theta_{im} \frac{\partial c_{im}}{\partial t} + (1-f)\rho \frac{\partial S_{im}}{\partial t} = \alpha(c_m - c_{im}) \qquad [23]$$

where S_m and S_{im} are the adsorbed concentrations in the dynamic and stagnant regions of the soil, both expressed per unit mass of soil assigned to these two soil regions, and where f defines the mass fraction of solid phase assigned to the dynamic region. Equations [22] and [23] were derived with the assumption that adsorption around the larger liquid-filled pores is not necessarily the same as adsorption around the micropores in the stagnant region of the soil. When a chemical moves through an unsaturated and/or aggregated soil, only part of the sorption sites may be readily accessible for the chemical in the moving liquid. These sites must be located around the larger pores and in immediate contact with the mobile liquid. When an immobile liquid phase is present, adsorption on the remaining part of the sorption sites can only occur after the chemical has diffused into this immobile liquid. The division of sorption sites into two fractions, one fraction in close contact with the moving liquid, and one fraction away from the larger pores and in contact only with immobile (non-moving) water is characterized by the parameter f. Total adsorption, S, is now given by

$$S = fS_m + (1-f)\ S_{im}. \qquad [24]$$

For equilibrium adsorption and assuming that the same linear equation [3] holds for both the dynamic (S_m) and stagnant (S_{im}) soil regions, we obtain from [22] and [23]:

$$(\theta_m + \rho fk) \frac{\partial c_m}{\partial t} + [\theta_{im} + (1-f)\rho k] \frac{\partial c_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial x} \qquad [25]$$

$$[\theta_{im} + (1-f)\rho k] \frac{\partial c_{im}}{\partial t} = \alpha(c_m - c_{im}). \qquad [26]$$

Equations [25] and [26] will be solved for the same initial and boundary conditions as before (Eq. [6] through [10] with c replaced by c_m), and the additional initial condition

$$c_m(x,0) = c_{im}(x,0) = C_i. \qquad [27]$$

The following dimensionless variable are introduced

$$T = vt/L = v_m t\phi_m/L \qquad z = x/L \qquad [28]$$

$$P = v_m L/D \qquad \omega = \alpha L/q = \alpha L/(\theta_m v_m) \qquad [29]$$

$$\beta = \frac{\theta_m + f\rho k}{\theta + \rho k} = \frac{\phi_m R_m}{R} \qquad [30]$$

$$R_m = 1 + f\rho k/\theta_m \qquad R = 1 + \rho k/\theta \qquad [31]$$

$$c_1 = \frac{c_m - C_i}{C_o - C_i} \qquad c_2 = \frac{c_{im} - C_i}{C_o - C_i} \qquad [32]$$

The variables T, z, R and P are the same as for the previous model A (see Eq. [11] - [13]), except that P here is defined in terms of the average pore-water velocity of the mobile liquid phase ($v_m = v/\phi_m$). The variable R_m, furthermore, is an equivalent retardation factor for the dynamic soil region. With the above definitions, Eq. [25] and [26] reduce to

$$\beta R \frac{\partial c_1}{\partial T} + (1-\beta) R \frac{\partial c_2}{\partial T} = \frac{1}{P} \frac{\partial^2 c_1}{\partial x^2} - \frac{\partial c_1}{\partial x} \qquad [33]$$

$$(1-\beta) R \frac{\partial c_2}{\partial T} = \omega (c_1 - c_2) \qquad [34]$$

Analytical solutions of Eq. [33] and [34], or of mathematically similar equations, have been derived for a variety of initial and boundary conditions (Lapidus and Amudson, 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, 1976; Popovic and Deckwer, 1979). 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 general solution for the exit concentration, c_e, is

$$c_e(T) = G(T) \exp(-\frac{\omega T}{\beta R}) + \frac{\omega}{R} \int_0^T G(\tau) \, H(T,\tau) \, d\tau \qquad [35]$$

where

$$H(T,\tau) = \exp(-a-b) \, [\frac{I_0(\xi)}{\beta} + \frac{\xi I_1(\xi)}{2b(1-\beta)}] \qquad [36]$$

$$a = \frac{\omega \tau}{\beta R} \qquad\qquad b = \frac{\omega(T-\tau)}{(1-\beta)R} \qquad [37]$$

$$\xi = 2(ab)^{1/2} \qquad [38]$$

and where $G(\tau)$ depends on the imposed initial and boundary conditions. Table 2 gives expressions for $G(\tau)$ for an initial dimensionless concentration of zero (see Eq. [27] and [32]) and for the same four sets of boundary conditions

Table 2. **Expressions for G(τ) in Eq. [35] for a dimensionless initial concentration of zero and four sets of boundary conditions.**

CASE	BOUNDARY CONDITIONS		G(τ)	
SI-1	$c_1(0,T) = 1$	$\frac{\partial c_1}{\partial z}(\infty,T) = 0$	$G(\tau) = \frac{1}{2}\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R - \tau)] + \frac{1}{2}\exp(P)\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R - \tau)]$	
SI-2	$(-\frac{1}{P}\frac{\partial c_1}{\partial z} + c_1)\Big\vert_{z=0} = 1$	$\frac{\partial c_1}{\partial z}(\infty,T) = 0$	$G(\tau) = \frac{1}{2}\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R - \tau)] + (\frac{P\tau}{\pi\beta R})^{1/2}\exp[-\frac{P}{4\beta R\tau}(\beta R + \tau)^2]$ $- \frac{1}{2}(1 + P + \frac{P\tau}{\beta R})\exp(P)\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R + \tau)]$	
FN-1	$c_1(0,T) = 1$	$\frac{\partial c_1}{\partial z}(1,T) = 0$	$G(\tau) = 1 - \sum_{m=1}^{\infty}\frac{2\beta_m\sin(\beta_m)\exp[\frac{P}{2} - \frac{P\tau}{4\beta R} - \frac{\beta_m^2\tau}{\beta PR}]}{\beta_m^2 + \frac{P^2}{4} + \frac{P}{2}}$	$\beta_m\cot(\beta_m) + \frac{P}{2} = 0$
FN-2	$(-\frac{1}{P}\frac{\partial c_1}{\partial z} + c_1)\Big\vert_{z=0} = 0$	$\frac{\partial c_1}{\partial z}(1,T) = 0$	$G(\tau) = 1 - \sum_{m=1}^{\infty}\frac{2\beta_m\sin(\beta_m)\exp[\frac{P}{2} - \frac{P\tau}{4\beta R} - \frac{\beta_m^2\tau}{\beta PR}]}{\beta_m^2 + \frac{P^2}{4} + P}$	$P\,\beta_m\cot(\beta_m) + \frac{P^2}{4} = \beta_m^2$

as in Table 1. Note that the expressions for $G(\tau)$ in Table 2 follow from those given in Table 1 by replacing T by τ and R by (βR). This is due to the fact that $G(T)$ is the solution of [33] and [34] for the limiting case when ω is zero (see also Eq. [35]).

An alternative and computationally more convenient form of the general solution is (De Smedt and Wierenga, 1979)

$$c_e(T) = \int_0^T F(\tau)\ J(a,b)\ d\tau \qquad [39]$$

where $F(\tau)$ is the derivative of $G(\tau)$ with respect to τ, i.e.,

$$F(\tau) = \frac{dG(\tau)}{d\tau}, \qquad [40]$$

and where $J(a,b)$ is Goldstein's J-function (Goldstein, 1953):

$$J(a,b) = 1 - e^{-b}\int_0^a e^{-\lambda} I_o[2\sqrt{b\lambda})]\ d\lambda. \qquad [41]$$

Some useful properties and approximations of Goldstein's J-function are given in Appendix A. Table 3 gives expressions for $F(\tau)$ in [39], again for the same four sets of initial and boundary conditions as before. The series solutions for Cases FN-1 and FN-2 in Tables 2 and 3 converge slowly for large values of P and/or small values of T. The following approximations of G and F are recommended for relatively large values of P (see also Eq. [16] and [17]):

Table 3. Expressions for $F(\tau)$ in Eq. [39] for a dimensionless initial concentration of zero and four sets of boundary conditions.

CASE	BOUNDARY CONDITIONS		$F(\tau)$	
SI-1	$c_1(0,T) = 1$	$\frac{\partial c_1}{\partial z}(\infty,T) = 0$	$F(\tau) = \frac{\beta}{\tau}\left(\frac{PR}{4\pi\beta\tau}\right)^{1/2} \exp[-\frac{P}{4\beta R\tau}(\beta R - \tau)^2]$	
SI-2	$(-\frac{1}{P}\frac{\partial c_1}{\partial z} + c_1)\Big\|_{z=0} = 1$	$\frac{\partial c_1}{\partial z}(\infty,T) = 0$	$F(\tau) = \left(\frac{P}{\pi\beta R\tau}\right)^{1/2} \exp[-\frac{P}{4\beta R\tau}(\beta R - \tau)^2]$ $- \frac{P}{2\beta R}\exp(P)\,\mathrm{erfc}[\left(\frac{P}{4\beta R\tau}\right)^{1/2}(\beta R + \tau)]$	
FN-1	$c_1(0,T) = 1$	$\frac{\partial c_1}{\partial z}(1,T) = 0$	$F(\tau) = \sum_{m=1}^{\infty} \frac{\frac{2\beta_m}{\beta PR}(\beta_m^2 + \frac{P^2}{4})\sin(\beta_m)\exp[\frac{P}{2} - \frac{P\tau}{4\beta R} - \frac{\beta_m^2\tau}{\beta PR}]}{\beta_m^2 + \frac{P^2}{4} + \frac{P}{2}}$	$\beta_m \cot(\beta_m) + \frac{P}{2} = 0$
FN-2	$(-\frac{1}{P}\frac{\partial c_1}{\partial z} + c_1)\Big\|_{z=0} = 1$	$\frac{\partial c_1}{\partial z}(1,T) = 0$	$F(\tau) = \sum_{m=1}^{\infty} \frac{\frac{2\beta_m}{\beta PR}(\beta_m^2 + \frac{P^2}{4})\sin(\beta_m)\exp[\frac{P}{2} - \frac{P\tau}{4\beta R} - \frac{\beta_m^2\tau}{\beta PR}]}{\beta_m^2 + \frac{P^2}{4} + P}$	$P\,\beta_m\cot(\beta_m) + \frac{P^2}{4} = \beta_m^2$

for Case FN-1,

$$G(\tau) = \frac{1}{2}\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R - \tau)] - (\frac{P\tau}{\pi\beta R})^{1/2}\exp[-\frac{P}{4\beta R\tau}(\beta R - \tau)^2]$$
$$+ \frac{1}{2}\,(3 + P + \frac{P\tau}{\beta R})\exp(P)\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R + \tau)] \qquad [42]$$

$$F(\tau) = (\frac{\beta R}{\tau} - 1)\,(\frac{P}{\pi\beta R\tau})^{1/2}\exp[-\frac{P}{4\beta R\tau}(\beta R - \tau)^2]$$
$$+ \frac{P}{2\beta R}\exp(P)\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R + \tau)] \qquad [43]$$

and for Case FN-2,

$$G(\tau) = \frac{1}{2}\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R - \tau)]$$
$$+ (\frac{P\tau}{\pi\beta R})^{1/2}(3 + \frac{P}{2} + \frac{P\tau}{2\beta R})\exp[-\frac{P}{4\beta R\tau}(\beta R - \tau)^2]$$
$$- \frac{1}{2}\,[1 + 3P + \frac{4P\tau}{\beta R} + \frac{P^2}{2\beta^2 R^2}(\beta R + \tau)^2]\exp(P)\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R + \tau)] \qquad [44]$$

$$F(\tau) = (2 + \frac{P\tau}{\beta R})\,(\frac{P}{\pi\beta R\tau})^{1/2}\exp[-\frac{P}{4\beta RT}(\beta R - \tau)^2]$$
$$- \frac{P}{2\beta R}(4 + P + \frac{P\tau}{\beta R})\exp(P)\,\mathrm{erfc}[(\frac{P}{4\beta R\tau})^{1/2}(\beta R + \tau)]. \qquad [45]$$

Inspection of Eq. [33] and [34] or the analytical solutions shows that the physical non-equilibrium adsorption model contains four independent parameters: P, R, β and ω. If no adsorption occurs, R equals one and β reduces to ϕ_m. The number of independent parameters is then only three.

C. PHYSICAL NON-EQUILIBRIUM AND ANION EXCLUSION

Instead of being adsorbed, certain anions may also interact with the solid phase of the soil by being excluded from liquid zones adjacent to negatively charged soil particle surfaces (anion exclusion or negative adsorption). The anion exclusion model considered here differs from the physical non-equilibrium model discussed in the previous section in that the effects of anion exclusion rather than chemical adsorption are included in the governing transport equations. The model is conceptually the same as the anion exclusion model of Krupp *et al.* (1972), although the final transport equations are formulated in a slightly different manner.

The soil-water phase is again divided into mobile and immobile zones and anion exclusion is assumed to be restricted to the immobile water phase only i.e., to the smaller-sized pores inside dense aggregates, or to immobile water along pore walls analogous to the situation described by Krupp *et al.* (1972). Double layer theory suggests that the anion concentration within an individual pore increase roughly exponentially with distance from the pore wall, at least for a freely extended diffuse double layer (Babcock, 1963; Bolt and de Haan, 1979). It is assumed here that such a nonlinear concentration distribution can be replaced by an equivalent step function which has a value of zero in the anion excluded part of the liquid phase adjacent to the pore walls, and a value equal to that of the bulk solution near the center of the pore. This assumption leads to an equivalent exclusion distance, d_{ex}, near the pore walls in which the concentration effectively remains zero (Krupp *et al.*, 1972; Bolt and de Haan, 1979). The specific exclusion volume, V_{ex} (in cm^3 water per g of soil), is then simply

$$V_{ex} = d_{ex} A_o \qquad [46]$$

where A_o is the specific surface area (cm^2/g). The anion exclusion volume can also be expressed in terms of an equivalent volumetric soil-water content, θ_{ex}, by multiplying Eq. [46] with the soil bulk density, i.e.:

$$\theta_{ex} = V_{ex}\,\rho. \qquad [47]$$

Assuming that $\theta_{ex} < \theta_{im}$, and that anion exclusion takes place only in the immobile soil-water phase, then the following transport equations can be applied

$$\theta_m \frac{\partial c_m}{\partial t} + \theta_a \frac{\partial c_a}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial x} \qquad [48]$$

$$\theta_a \frac{\partial c_a}{\partial t} = \alpha(c_m - c_a) \qquad [49]$$

where the subscript a refers to that part of the immobile liquid phase that is not affected by anion exclusion:

$$\theta_a = \theta_{im} - \theta_{ex}. \qquad [50]$$

Equations [48] and [49] are very similar to Eq. [18] and [19] for the physical non-equilibrium model without adsorption, except that the immobile sink is reduced from θ_{im} to θ_a.

The following dimensionless variables are now introduced:

$$T = vt/L = v_m t \phi_m / L \qquad z = x/L \qquad [51]$$

$$P = v_m L/D \qquad R = 1 - \phi_{ex} \qquad [52]$$

$$\beta = \frac{\phi_m}{1 - \phi_{ex}} \qquad \omega = \alpha L/q \qquad [53]$$

$$\phi_m = \theta_m/\theta \qquad \phi_{ex} = \theta_{ex}/\theta \qquad [54]$$

$$c_1 = \frac{c_m - C_i}{C_o - C_i} \qquad c_2 = \frac{c_a - C_i}{C_o - C_i} \qquad [55]$$

Of these variable, only R, β and c_2 are different from those given for Model B (see Eq. [28] - [32]). In fact, the dimensionless variables of the previous case reduce to those given here by making the substitution

$$k = - V_{ex} \qquad f = 0 \qquad c_{im} = c_a \qquad [56]$$

Substitution of Eq. [51] - [55] into [48 and [49] leads therefor to the same dimensionless transport equations as in the previous section (Eq. [33] and [34]. Because the dimensionless initial and boundary condition for this and the previous case are also the same, the analytical solutions of Model B should also be applicable to the present model.

The anion exclusion model described above is slightly different from the one given by Krupp et al. (1972). Using our notation, the model of Krupp et al. can be formulated as follows

$$\theta_m \frac{\partial c_m}{\partial t} + \theta_{im} \frac{\partial c_{im}}{\partial t} = \theta_m D \frac{\partial^2 c_m}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial t} \qquad [57]$$

$$\frac{\partial c_{im}}{\partial t} = k_r (c_m - \gamma c_{im}) \qquad [58]$$

where k_r is a rate constant similar to α in Eq. [49], and where

$$\gamma = \theta_{im}/\theta_a \qquad [59]$$

The difference between Eq. [48] and [49] and Eq. [57] and [58] is due to the fact that in the latter equations the concentration c_{im} is applied to the entire immobile liquid phase, although still corrected for anion exclusion through the introduction of the parameter γ. By making the substitutions

$$k_r = \alpha/\theta_{im} \qquad [60]$$

and

$$c_{im} = c_a/\gamma \qquad [61]$$

in Eq. [58] and [59], the equations of Krupp et al. (1972) reduce to Eq. [48] and [49]. The same dimensionless transport equations and the same analytical solutions as before hence apply also to the model of Krupp et al. (1972).

The anion exclusion models given in this section assume that θ_{ex} is always smaller than θ_{im}, and that anion exclusion is restricted to the immobile liquid phase. Because convective transport takes place only in the mobile liquid phase which, at least in the present example, is not affected by anion exclusion, it follows that the mobile concentration, c_m, in the soil will never exceed the input concentration, C_o. This situation, however, becomes different when θ_{ex} also includes part of the mobile liquid. In that case the concentration of the non-excluded part of the liquid phase, whether it is mobile or immobile water, is likely to exceed at times C_o inside the column, but not in the effluent. This situation, which is considerably more complex than the one discussed above, will not be considered here.

D. TWO-SITE KINETIC NON-EQUILIBRIUM ADSORPTION

The two-site kinetic adsorption model described below is the same model as discussed by Selim et al. (1976) and by Cameron and Klute (1977). The model was later also used by Rao et al. (1979), De Camargo et al. (1979) and by Hoffman and Rolston (1980). 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, aluminum and iron-oxides), and that a chemical is likely to react with these different constituents at different rates and with different intensities. The two-site model assumes that the 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. At equilibrium, adsorption on both types of sorption sites is described by linear equations:

$$\begin{aligned} S_1 &= k_1 c \\ &= Fkc \end{aligned} \qquad [62]$$

$$\begin{aligned} S_2 &= k_2 c \\ &= (1-F)kc \end{aligned} \qquad [63]$$

where the subscripts 1 and 2 refer to type-1 and type-2 sites, respectively, and where F is the fraction of sites occupied by type-1 sorption sites. Total adsorption, S, is simply

$$S = S_1 + S_2 \qquad [64]$$

which at equilibrium reduces to

$$S = kc. \quad [65]$$

Because type-1 sites are always at equilibrium, it follows from [62] that

$$\frac{\partial S_1}{\partial t} = Fk \frac{\partial c}{\partial t} . \quad [66]$$

The adsoption rate for the kinetic non-equilibrium (type-2) sites is given by a linear, reversible, first-order rate equation of the form

$$\frac{\partial S_2}{\partial t} = \alpha(k_2 c - S_2) \quad [67]$$

where α is a first-order rate coefficient. Combining Eq. [2] with the equations above leads to the following transport model

$$(1 + \frac{F\rho k}{\theta}) \frac{\partial c}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad [68]$$

$$\frac{\partial S_2}{\partial t} = \alpha[(1-F)kc - S_2] \quad [69]$$

Equations [68] and [69] will again be solved for the same initial and boundary conditions as before (Eq. [6] - [10]), but augmented by the additional condition

$$S_2(x,0) = (1-F)kC_i \quad [68]$$

The dimensionless variables for this case are

$$T = vt/L \qquad z = x/L \quad [69]$$

$$P = vL/D \qquad \beta = \frac{\theta + F\rho k}{\theta + \rho k} = \frac{R_m}{R} \qquad [70]$$

$$R_m = 1 + F\rho k/\theta \qquad R = 1 + \rho k/\theta \qquad [71]$$

$$\omega = \alpha(1-\beta)RL/v$$

$$c_1 = \frac{c - C_i}{C_o - C_i} \qquad c_2 = \frac{S_2 - (1-F)kC_i}{(1-F)k(C_o - C_i)} \qquad [72]$$

Substitution of these variables into [68] and [69] leads to the same dimensionless transport equations as for the physical non-equilibrium model (Eq. [33] and [34]). Because the dimensionless boundary conditions are also the same, the analytical solutions of Model B are also applicable to the two-site non-equilibrium adsorption model.

E. ONE-SITE KINETIC NON-EQUILIBRIUM ADSOPTION

The one-site kinetic non-equilibrium adsorption model is a special case of the two-site adsorption model in that now all sorption sites are assumed to be time-dependent (type-2) sites. The parameter F in the previous section is hence zero and the transport equations reduce to

$$\frac{\partial c}{\partial t} + \frac{\rho}{\theta}\frac{\partial S}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \qquad [73]$$

$$\frac{\partial S}{\partial t} = \alpha(kc - S) \qquad [74]$$

The dimensionless variables are the same as for the previous case, with the following exceptions

$$\beta = 1/R \qquad \omega = \alpha(R-1)L/v \qquad [75]$$

$$c_2 = \frac{S_2 - kC_i}{k(C_o - C_i)} \qquad [76]$$

The dimensionless transport equations remain therefor the same as before, and the same analytical solutions for the exit concentration can again be used. Note that these solutions could have been simplified by using $\beta R = 1$ in the different expressions of Tables 2 and 3. This simplificaton is not carried out here, so that the analytical expressions remain the same for models B, C, D and E.

DETERMINING THE PARAMETERS FROM AN EFFLUENT CURVE

The analytical expressions for the exit concentration, c_e, given thus far are only applicable to column displacement experiments in which the chemical is applied continuously at the inlet position (continuous tracer application). For pulse-type applications, the different expressions (see Models A and B), must be replaced by

$$c_e^*(T) = \begin{cases} c_e(T) & 0 < T \leqslant T_1 \\ c_e(T) - c_e(T-T_1) & T > T_1 \end{cases} \qquad [77]$$

where $c_e^*(T)$ is the effluent concentration for a pulse-type application, and where

$$T_1 = vt_1/L \qquad [78]$$

with t_1 representing the length of time during which the tracer was present in the feed solution. Equation [77] assumes that the input concentration for times greater than t_1 is again the same as the initial concentration, C_i.

A computer program was written which may be used to fit any of the analytical expressions for c_e of c_e^* to observed effluent data. The program is actually a simplification of the nonlinear least-squares curve-fitting program of Meeter (1964). The applied curve-fitting technique uses the maximum neighborhood method of Marquardt (1963), which is based on an optimum interpolation between the Taylor series expansion and the method of steepest descent. A more detailed description of the method is given by Daniel and Wood (1973).

In the case of a continuous tracer application (i.e., for c_e), only two parameters (P and R) need to be determined if Model A is used, four parameters (P, R, β and ω) if Models B, C or D are used, and three parameters (P, R and ω is Model E is used. For a pulse-type effluent curve, information is also needed about the dimensionless pulse time, T_1. Although T_1 is usually available from the experimental conditions, it may sometimes be necessary to also estimate this parameter directly from the experimental curve. The curve-fitting program is therefor written in such a way that also T_1 can be estimated from the observed curve. This means that, at least for Models B, C and D, up to five parameters have to be estimated simultaneously.

APPLICATIONS

Several examples are given below to demonstrate the accuracy and flexibility of the curve-fitting program. The soil-physical data of each example are given in Table 4. Of the six displacement experiments, only four are based on actual column experiments. The two remaining examples (Exp. No. 1 and 6) are based on hypothetical data, and were used to check the accuracy of the computer program. Table 5 summarizes the curve-fitting results, listing for each example the type of model used, the type of boundary conditions applied (SI-1 or SI-2; see Table 1), the number of data points used in the curve-fitting program, and the fitted values of the unknown coefficients. The coefficient values shown in parenthesis were obtained independently, and hence were kept constant during the least-squares calculations.

The accuracy of the program was first tested by fitting the coefficients P, R, β and ω to an hypothetical effluent curve with known values of these four coefficients. The analytical solution of Model B, Case SI-2 was used to generate this curve. Figure 1 shows the location of the 20 "observed" data points used in the program. The data points were obtained with the following parameter value: $P = 40$, $R = 2.5$, $\beta = 0.5$ and $\omega = 0.5$. As expected, the correct parameter values were duplicated exactly when the analytical solution of Case SI-2 was used in the curve-fitting program (see Table 5). The fitted values for Case SI-1, however, deviate slightly from the correct values because of the different boundary condition. The differences in fitted values between the two analytical solutions are relatively small in this particular example, but are likely to increase significantly when P becomes much smaller (e.g., less than 10 - 15). The solid line in Fig. 1 represents the fitted curve for Case SI-2. The fitted curve for SI-1 was found to be nearly identical to the curve for SI-2, even though the estimated parameters for the two

Table 4. Soil-physical data for six column displacement experiments.

Exp. No.	ρ (g/cm^3)	θ (cm^3/cm^3)	q (cm/day)	L (cm)	t_1 (days)	T_1 (--)	tracer
1*	1.200	0.400	10.00	30.0	--	--	--
2	1.126	0.401	16.58	30.0	1.508	2.080	^3H_2O
3	1.309	0.456	16.81	30.0	--	--	2,4,5-T
4	1.222	0.445	17.12	30.0	5.060	6.488	Boron
5	--	0.463	8.92	30.0	--	--	Chloride
6*	1.400	0.400	16.00	100.0	--	--	--

*) hypothetical values.

Table 5. Curve-fitted parameter values for the six examples discussed in this report. The values in parenthesis were known beforehand and were kept constant during the least-squares calculations.

Example	Model	Case	Number of Data Points	P	R	β	ω	T_1
1A	B	SI-1	20	40.40	2.563	0.500	0.512	--
1B	B	SI-1	10	40.38	2.563	0.500	0.512	--
1C	B	SI-2	20	39.99	2.500	0.500	0.500	--
1D	B	SI-2	10	39.97	2.500	0.500	0.500	--
2A	B	SI-1	29	30.69	1.048	0.719	0.534	2.103
2B	B	SI-1	15	29.80	1.053	0.720	0.515	2.105
2C	B	SI-2	29	30.37	1.014	0.718	0.519	2.103
2D	B	SI-2	15	29.47	1.018	0.720	0.500	2.104
2E	A	SI-1	29	9.43	0.974	--	--	2.079
2F	A	SI-1	15	9.38	0.976	--	--	2.077
2G	A	SI-2	29	9.13	0.875	--	--	2.078
2H	A	SI-2	15	9.09	0.877	--	--	2.076
3A	B	SI-1	26	25.85	(2.223)	0.605	0.495	--
3B	B	SI-2	26	21.90	(2.223)	0.596	0.407	--
4A	B	SI-1	30	38.64	3.891	0.624	0.655	6.183
4B	B	SI-1	30	23.94	4.297	0.600	0.424	(6.490)
4C	B	SI-2	30	38.72	3.788	0.623	0.646	6.182
4D	B	SI-2	30	23.55	4.120	0.600	0.408	(6.490)
5A	C	SI-1	23	90.60	0.656	0.852	0.605	--
5B	C	SI-2	23	90.18	0.649	0.852	0.599	--
6A	D	SI-1	13	133.25	(1.700)	--	0.875	--
6B	D	SI-2	13	123.36	(1.700)	--	0.836	--

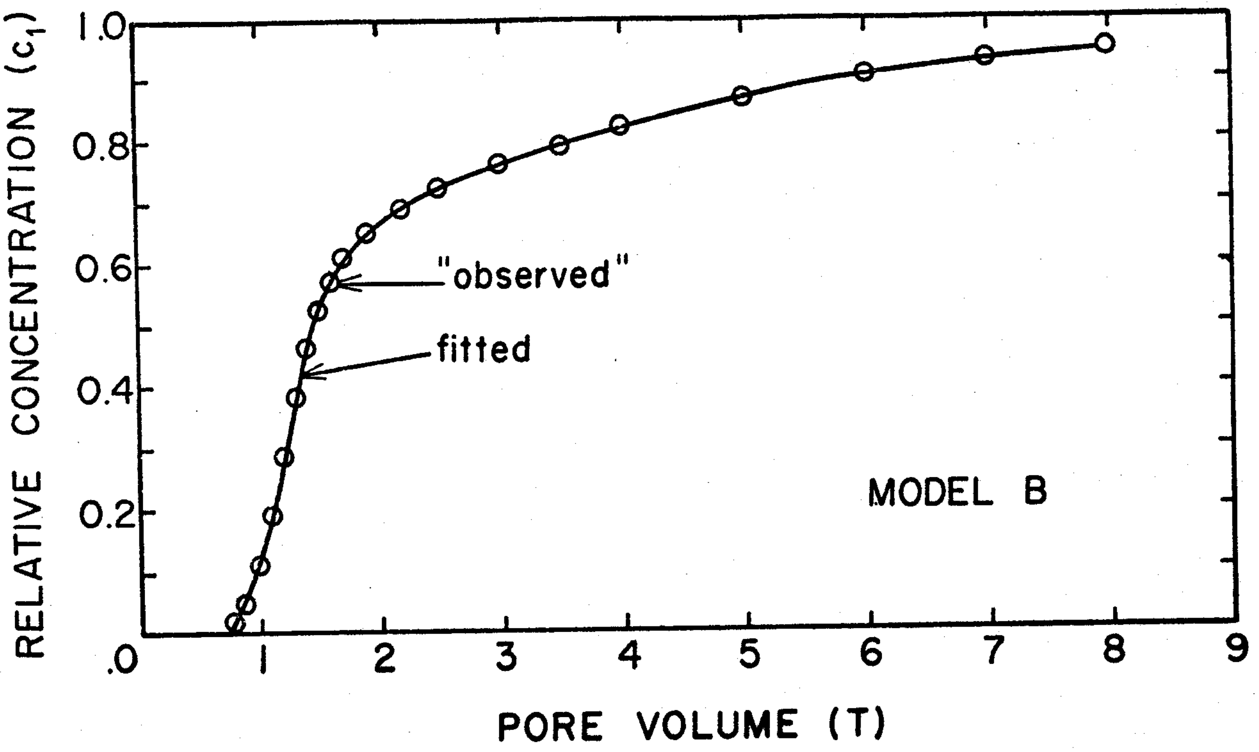

Figure 1. "Observed" and fitted effluent curves for example 1. The data points were generated with the analytical solution of Model B, Case SI-2.

cases are somewhat different.

A second curve-fitting was also carried out with only ten of the twenty data ponts shown in Fig. 1. Every other data point on the curve was deleted for that purpose. Table 5 show that the fitted values of the four parameters are the same for both number of data points. The same values were also obtained when different initial estimates of the coefficients were inputted into the curve-fitting program. By making a judicious choice of the unknown coefficients, the number of iterations required to reach convergence can be reduced considerably. This, in turn, will lead to less computer time. Serious convergence problems, however, are only expected when unreasonable initial estimates are inputted into the program, for example when the initial estimates of R or T_1 are many times larger or smaller than the correct values. The iterative least-squares technique could, in such cases, even converge to the wrong solution. No convergence problems were encountered in all examples discussed here, even though in some cases the initial estimates in the program were quite different than the correct values. The initial estimates for the first example were: $P = 25$, $R = 2$, $\beta = 0.6$ and $\omega = 0.2$. Note that these values deviate considerably from the correct values (Table 5), but that the program nevertheless converged to the correct solution.

The second example considers the movement of tritiated water through Glendale clay loam (Exp. 5-2 of van Genuchten and Wierenga, 1977). Figure 2 compares the observed and fitted effluent curves (Model B, Case SI-2). The fitted curve for Case SI-1 was again essentially the same as for Case SI-2. In this case, all five coefficients were fitted to the data (Table 5, examples 2A and 2C). Note that 29 data points were used for these two examples. The final results were again not significantly affected by deleting every other data point, and hence by decreasing the total number of points from 29 to

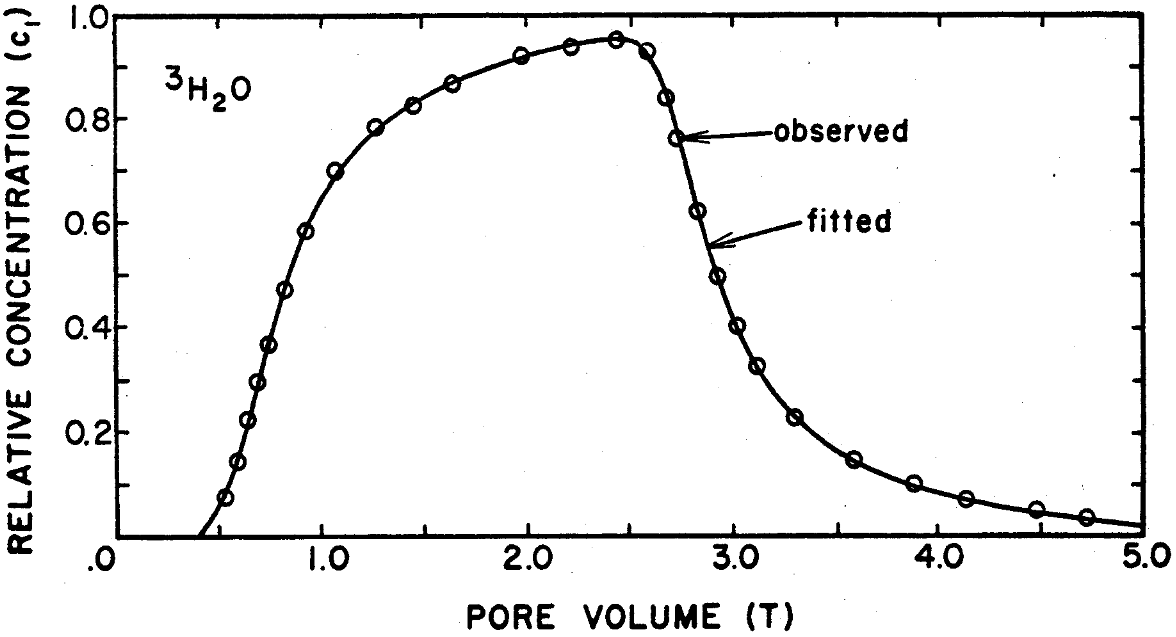

Figure 2. Observed and fitted effluent curves for tritiated water movement through Glendale clay loam (Example 2D).

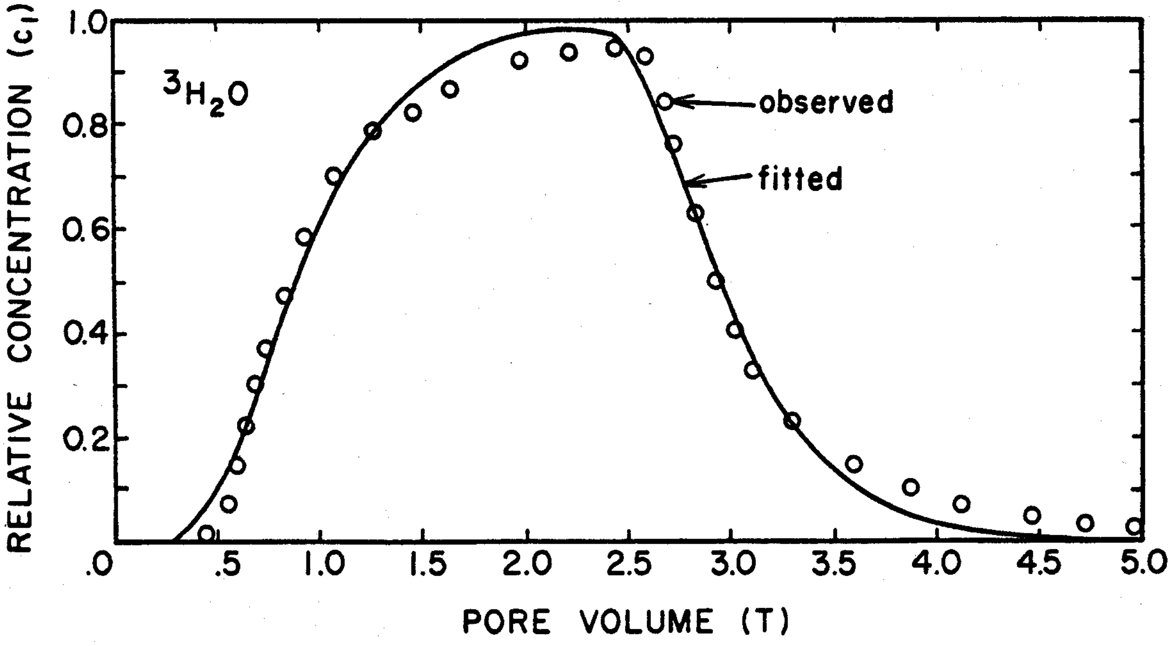

Figure 3. Observed and fitted effluent curves for tritiated water movement through Glendale clay loam (Example 2G).

15. Table 5 shows that the fitted values of R are slightly larger than one: R~1.050 for Case SI-1 and 1.015 for Case SI-2. This indicates that some adsorption or exchange of ^3H_2O takes place. The extent of this adsorption, however, is so small that it could have been neglected easily. In fact, as shown by the differences in R-values between Cases SI-1 and SI-2, the adsorption effects are completely overshadowed by the effects of the boundary conditions on the fitted values.

Table 5 also lists results obtained when Model A was fitted to the same effluent data, again using both 29 and 15 data points. In this case only three parameters (P, R, T_1) needed to be estimated. Figure 3 compares the observed and fitted curves. The fitted curves for SI-1 and SI-2 were again nearly identical. The fitted parameter values, however, are quite different for the two analytical solutions, especially the retardation factor: R ~ 0.98 for Case SI-1 and 0.88 for Case SI-2. These large differences are directly related to the small values of P obtained with Model A (P is about 9). At such low values of P, the analytical solutions for Cases SI-1 and SI-2 are known to diverge from each other. Consequently, if both solutions are fitted to the same curve, different parameter values can be expected (see also van Genuchten, 1980). Low values of P are also known to cause considerable asymmetry in pulse-type effluent curves based on Model A. Figure 3, however, shows that the obtained asymmetry is not enough to produce an accurate description of the experimental data. The observed tailing and asymmetry could have been described somewhat better by forcing P to be smaller than the fitted value of 9. This would at the same time, however, caused more deviations between observed and calculated curves during the initial breakthrough of the chemical at the lower pore volumes. The calculated curve here would have become still more dispersed than the observed one. Lower values of P, furthermore, would have lead at to even lower values for R, especially for Case SI-2. An R-value of less than one suggests the presence of an anion exclusion phenomenon. This does not seem realistic for tritiated water, at least not of the magnitude observed here.

For demonstration purposes, also the dimensionless pulse time, T_1, was fitted to the data of example 2. The experimentally derived value for T_1 was 2.08 (van Genuchten and Wierenga, 1977), which agrees well with the fitted values given in Table 5. In general it is not recommended to fit also T_1 to the data unless the experimental value is suspect, for example because of measurement errors or lack of reliable data. Including T_1 as an unknown parameter in the program can, in some cases, increase the computer expenses considerably, except possibly when the much simpler Model A is used.

Table 5 gives only estimates of the dimensionless parameters P, R, β and ω. To obtain estimates of the original variables (D, k, θ_m, f, etc.) in each transport model, it is necessary to express these original variables in terms of the dimensionless ones. Table 6 gives expressions for the different dimensionless variable as they apply to each transport model. Similar expressions for the original variable in terms of the dimensionless ones are given in Table 7. This table can be used to obtain estimates for the original variables, once the dimensionless parameters have been quantified. It is thereby assumed that independent measurements are available for the column length, L, the volumetric water content, θ, the volumetric flux, q, and bulk density, ρ. In some cases, independent estimates may also be available for the distribution coefficient, k (e.g., from batch equilibrium studies) or the dispersion coefficient, D (e.g., from another displacement experiment).

For example 2, it follows from the expressions in Table 7 (Model B), the soil-physical data in Table 4 (Exp. No. 2), and the fitted values of R

Table 6. Expressions for the dimensionless parameters as they apply to each transport model.

MODEL A	$P = \frac{vL}{D}$	$R = 1 + \frac{\rho k}{\theta}$	--	--
MODEL B	$P = \frac{v_m L}{D}$	$R = 1 + \frac{\rho k}{\theta}$	$\beta = \frac{\theta_m + f\rho k}{\theta + \rho k}$	$\omega = \frac{\alpha L}{q}$
MODEL C	$P = \frac{v_m L}{D}$	$R = 1 - \frac{\theta_{ex}}{\theta}$	$\beta = \frac{\theta_m}{\theta - \theta_{ex}}$	$\omega = \frac{\alpha L}{q}$ $\omega = \frac{k_r \theta_{im} L}{q}$
MODEL D	$P = \frac{vL}{D}$	$R = 1 + \frac{\rho k}{\theta}$	$\beta = \frac{\theta + F\rho k}{\theta + \rho k}$	$\omega = \frac{\alpha(1-F)\rho kL}{q}$
MODEL E	$P = \frac{vL}{D}$	$R = 1 + \frac{\rho k}{\theta}$	$\beta = \frac{1}{R}$	$\omega = \frac{\alpha\rho kL}{q}$

Table 7. Expressions for the original coefficients in each transport model as they relate to the dimensionless parameters P, R, β and ω.

MODEL A	$D = \frac{vL}{P}$	$k = \frac{\theta(R-1)}{\rho}$	--	--
MODEL B	$D = \frac{qL}{\theta_m P}$	$k = \frac{\theta(R-1}{\rho}$	$\theta_m = \theta\beta + (\beta-f)\rho k$ $f = \beta + \frac{\theta\beta - \theta_m}{\rho k}$	$\alpha = \frac{\omega q}{L}$
MODEL C	$D = \frac{qL}{\theta_m P}$	$\theta_{ex} = \theta(1-R)$	$\theta_m = \beta(\theta - \theta_{ex})$	$\alpha = \frac{\omega q}{L}$ $k_r = \frac{\omega q}{(\theta-\theta_m)L}$
MODEL D	$D = \frac{vL}{P}$	$k = \frac{\theta(R-1)}{\rho}$	$F = \beta - \frac{\theta(1-\beta)}{\rho k}$	$\alpha = \frac{\omega q}{(1-F)\rho kL}$
MODEL E	$D = \frac{vL}{P}$	$k = \frac{\theta(R-1)}{\rho}$	--	$\alpha = \frac{\omega q}{\rho kL}$

and ω in Table 5 (Example 2D), that $k = 0.006$ (g/cm^3) and $\alpha = 0.287$ (day $^{-1}$). Similar estimates for θ_m and f, unfortunately, cannot be obtained from the present experiment alone. This is because both parameters appear in only one dimensionless variable (β). Consequently, either θ_m or f needs to be know before the other parameter can be estimated. Using the soil-physical data for this example and the fitted value of β, the following relation between θ_m and f can be derived

$$\theta_m = 0.293 - 0.0072\ f \qquad [79]$$

This relation shows that the influence of f on the final value for θ_m is extremely small. This is due to the fact that k is very small. A good first approximation for θ_m may be obtained by assuming that f is equal or slightly lower than β. Taking $f = \beta$ (=0.72), the mobile water content, θ_m, equals 0.289. The fraction mobile water, ϕ_m, is then also equal to β. Once θ_m is known, the dispersion coefficient can also be calculated: $D = 22.8$ (cm^2/day).

The third example considers the movement of the pesticide 2,4,5-T (2,4,5-Trichlorophenoxyacetic acid) through Glendale clay loam (Exp. 4-1 of van Genuchten _et al._, 1977). Observed and fitted effluent curves are shown in Fig. 4. Because of chemical hysteresis only the breakthrough side of the curve was considered. Only three parameters (P, β and ω) were fitted to the data, thereby assuming that the retardation factor, R, is know. The adsorption isotherm for 2,4,5-T was described well with the nonlinear Freundlich isotherm (van Genuchten _et al._, 1977):

$$S = K\ c^N. \qquad [80]$$

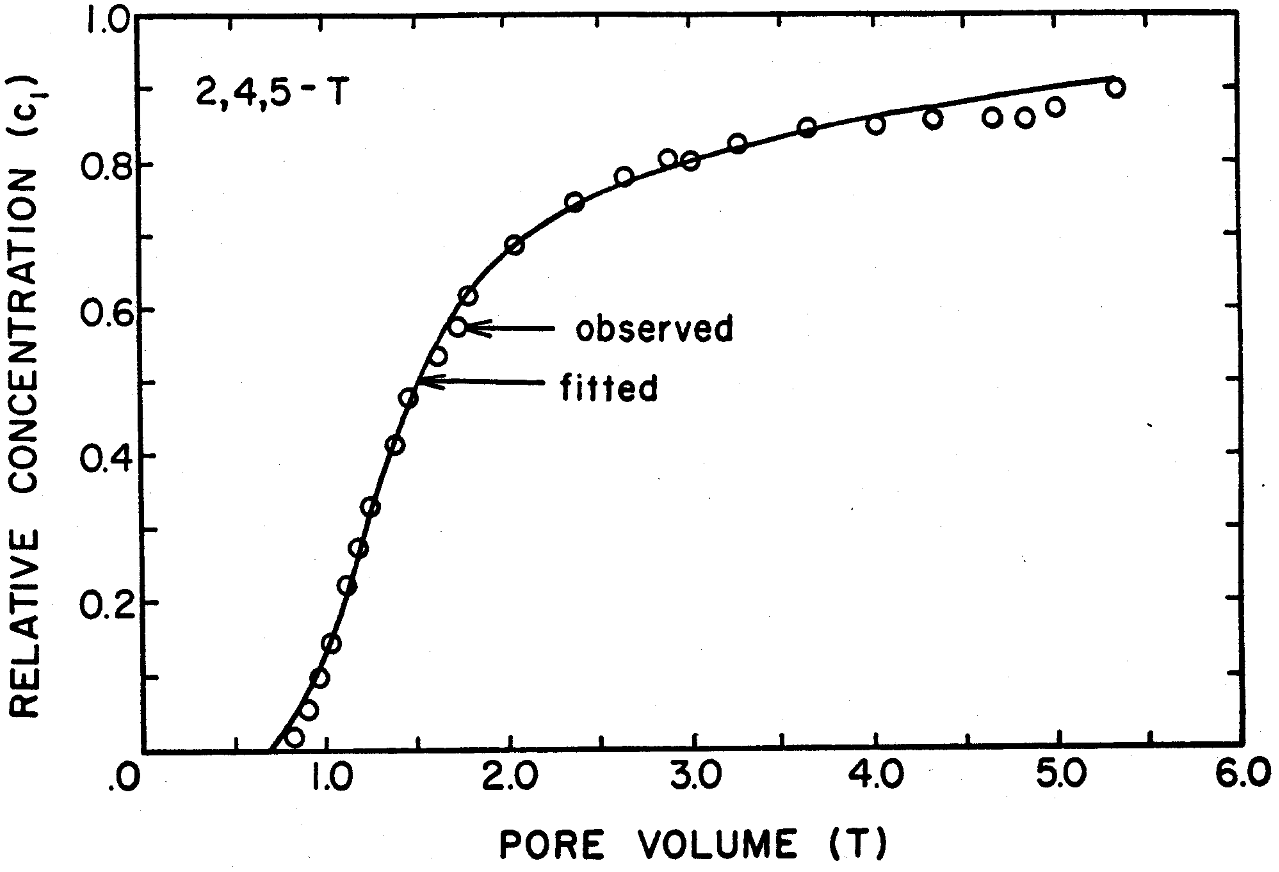

Figure 4. Observed and fitted effluent curves for 2,4,5-T movement through Glendale clay loam (Example 3B).

The constant K and N in this equation were obtained from batch equilibrium studies: K = 0.616 and N = 0.792. To obtain an estimate for k, the nonlinear isotherm must first be linearized. At least two linearization methods may be used for that purpose. One approach is to assume that the area under the linearized isotherm (S = kc) is the same as the area under the nonlinear isotherm over the range of concentration values used in the displacement experiment, i.e.

$$\int_{C_i}^{C_o} kc\ dc = \int_{C_i}^{C_o} Kc^N dc. \qquad [81]$$

For an initial concentration, C_i, of zero, [81] becomes

$$k = \frac{2KC_o^{N-1}}{N+1} . \qquad [82]$$

Another linearization method assumes that k can be approximated by the average slope of the nonlinear isotherm:

$$k = \frac{1}{C_o - C_i} \int_{C_i}^{C_o} \frac{dS}{dc}\ dc \qquad [83]$$

which, for an initial concentration of zero, reduces to

$$k = K\ C_o^{N-1}. \qquad [84]$$

In the present experiment (Example 3), the column was leached with a 2,4,5-T solution of 10 meq/l. Using C_o = 10, K = 0.616 and N = 0.792, it follows that k equals 0.426 if based on Eq. [82], and 0.382 if based on Eq. [84]. The equivalent retardation factors are 2.223 and 2.097, respectively. Only the value of 2.223 for R was used in the present example.

One may again calculate the original variables from the curve-fitted parameters in Table 5 and the soil-physical data in Table 4. If Model B is assumed to be the governing transport model, it is again necessary to have an independent estimate of either θ_m or f (Table 7). From separate experiments with tritiated water, it was earlier concluded that the fraction mobile water, ϕ_m, must be about 0.85 (van Genuchten et al., 1977). The mobile water content is hence 0.388 (cm^3/cm^3). With this information, it is now possible to calculate the remaining parameters: $f = 0.39$, $D = 59.4$ (cm^2/day) and $\alpha = 0.288$ (1/day). The estimated value of f suggests that about 40% of the sorption sites are in equilibrium with the mobile liquid, while the remaining 60% are in contact with immobile water. This, of course, assumes that the physical non-equilibrium model (Model B) applies. If, on the other hand, the two-site kinetic non-equilibrium model (Model D) is taken as the governing transport model, different parameter values will be calculated. From the expressions in Table 7 and the fitted values in Table 5 (Example 3B), one may calculate the following values: $D = 50.5$ (cm^2/day), $F = 0.27$ and $\alpha = 0.557$ (1/day). Hence, about 27% of the sorption sites are type-1 (equilibrium) sites, and about 73% are type-2 (kinetic) sites if the two-site adsorption model is the correct transport model.

The fourth example considers the movement of boron (H_3BO_4) through Glendale clay loam (Exp. 3-1 of van Genuchten, 1974). Figure 5 compares the observed data with the fitted curve based on Model B, Case SI-2 (Example 4D in Table 5). The fitted curve for Case SI-1 deviated only slightly from the curve of Case SI-2. In this case all parameters except T_1 were fitted to the data. Including also T_1 as an unkown coefficient resulted in quite different curve-fitted values (Example 4A, C in Table 5). These large deviations are

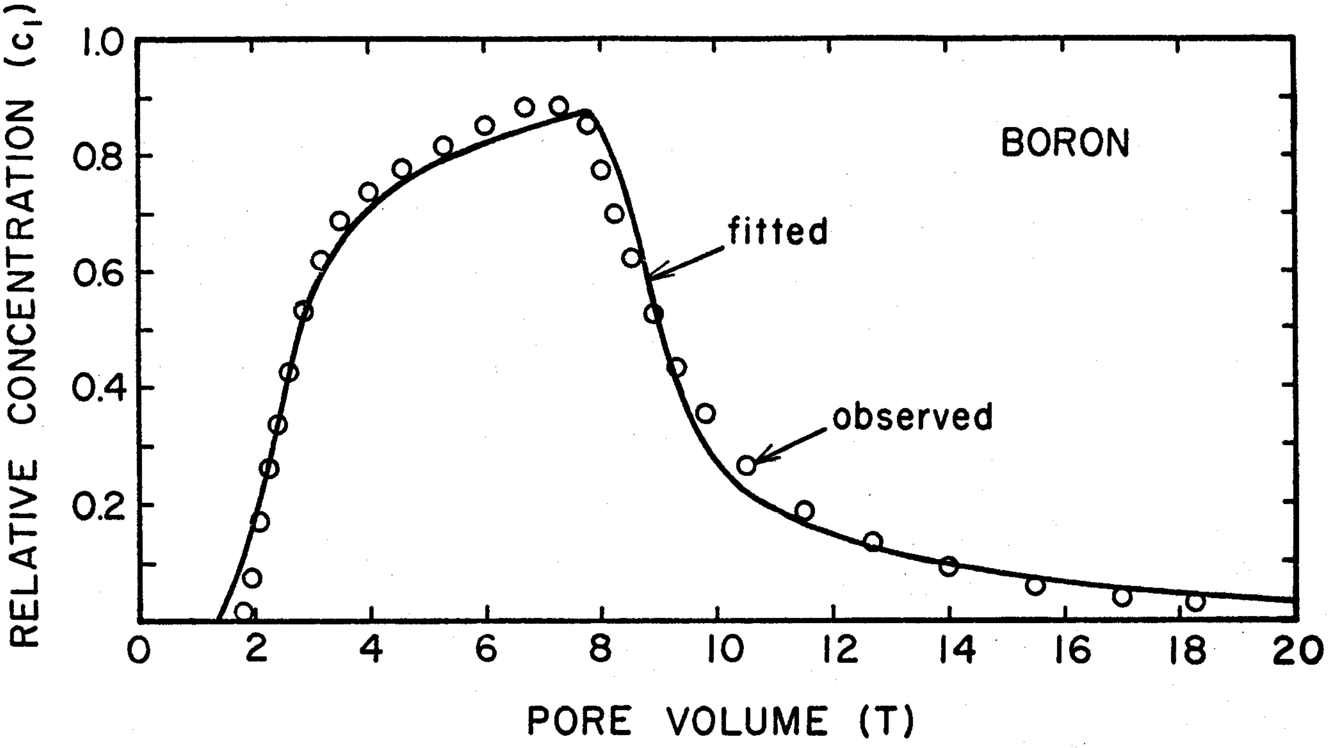

Figure 5. Observed and fitted effluent curves for Boron movement through Glendale clay loam (Example 4D).

most likely caused by the rather severe nonlinearity of the present problem. The coefficients K and N in Eq. [80], as determined with batch equilibrium studies, were found to be 2.77 and 0.672, respectively (van Genuchten, 1974). Application of Eq. [82] and [84] with C_o = 20 (meq/l) leads to linearized k-values of 1.24 and 1.04, respectively. By comparison, the values of k obtained from the fitted R-values in Table 5 are 1.05, 1.20, 1.02 and 1.14 for examples 4A through 4D, respectively. From these values, it is difficult to conclude which linearization technique is better. In fact, both linearized k-values would have produced fitted curves (P, β and ω) which, in accuracy, are comparable to the one shown in Fig. 5. While the fitted values in Table 5 are not expected to be very accurate because of the observed nonlinearity, they nevertheless will give a good first approximation for the various parameters. Assuming that the physical non-equilibrium model is applicable, and using a value of 0.852 for ϕ_m (van Genuchten, 1974), one may calculate the following values for the original variables: $f = 0.52$, $D = 57.5$, and $\alpha = 0.233$. These estimates are based on the fitted values of Example 4D. Similar values for the two-site adsorption model (Model D) are: $F = 0.47$, $D = 49.0$ and $\alpha = 0.320$.

It should be mentioned here that the dimensionless variables for the Boron experiment were obtained with only 30 data points as shown in Fig. 5. In reality, 105 data points were measured during the leaching experiment. The 30 points were selected from a smooth, eye-fitted curve, carefully drawn through all measured data points. Using all 105 data points in the curve-fitting program would have increased the required computer time many-fold. This is due to the fact that not only 75 more points need to be calculated during each iteration in the least-squares program, but that often also more iterations are required before convergence is reached when more points are present. This is expecially the case when the original data exhibit considerable scatter. Of course, considerable care is necessary when many data points are deleted. By doing so, an additional source of error is easily introduced into the data set.

Figure 6 gives a plot of all 105 measured data points of the boron curve. The solid line in this figure was obtained with a numerical solution (van Genuchten and Wierenga, 1976a) of the physical non-equilibrium nonlinear transport model, i.e., of Eq. [22], [23], [24] and [80]. The parameters in the numerical solution were exactly the same as those given earlier for the linearized solution (see also Fig. 5), except that in the present case the experimentally determined nonlinear isotherm was used in the calculations (Eq. [80] with $K = 2.77$ and $N = 0.672$). The excellent fit of the observed data in Fig. 6 shows that the linearized model can be used to obtain estimates of the various transport parameters, even if the adsorption isotherm is highly nonlinear. Part of the good fit in Fig. 6 is due to the fact that the linearized solution in Fig. 5 was fitted to the entire curve, rather than being limited to only the front (breakthrough) part.

The next example considers the movement of chloride through Glendale clay loam (unpublished data of Wierenga, 1971). Figure 7 shows both the observed and fitted effluent curves. In this case all 23 measured data points were used in the curve-fitting program. The fitted values of the four unknown coefficients (P, R, β and ω) are nearly identical for both analytical solutions (Model B, Cases SI-1 and SI-2). Because the value of R is less than one, the anion exclusion model (Model C) can be applied. Using the estimated values of Case SI-2 in Table 5, the following values for the original variables in Model C can be calculated (see also Table 7): $D = 11.6$ (cm^2/day), $\theta_{ex} = 0.163$, $\theta_m = 0.256$, $\theta_a = 0.044$ and $\alpha = 0.178$ (1/day). It follows, in

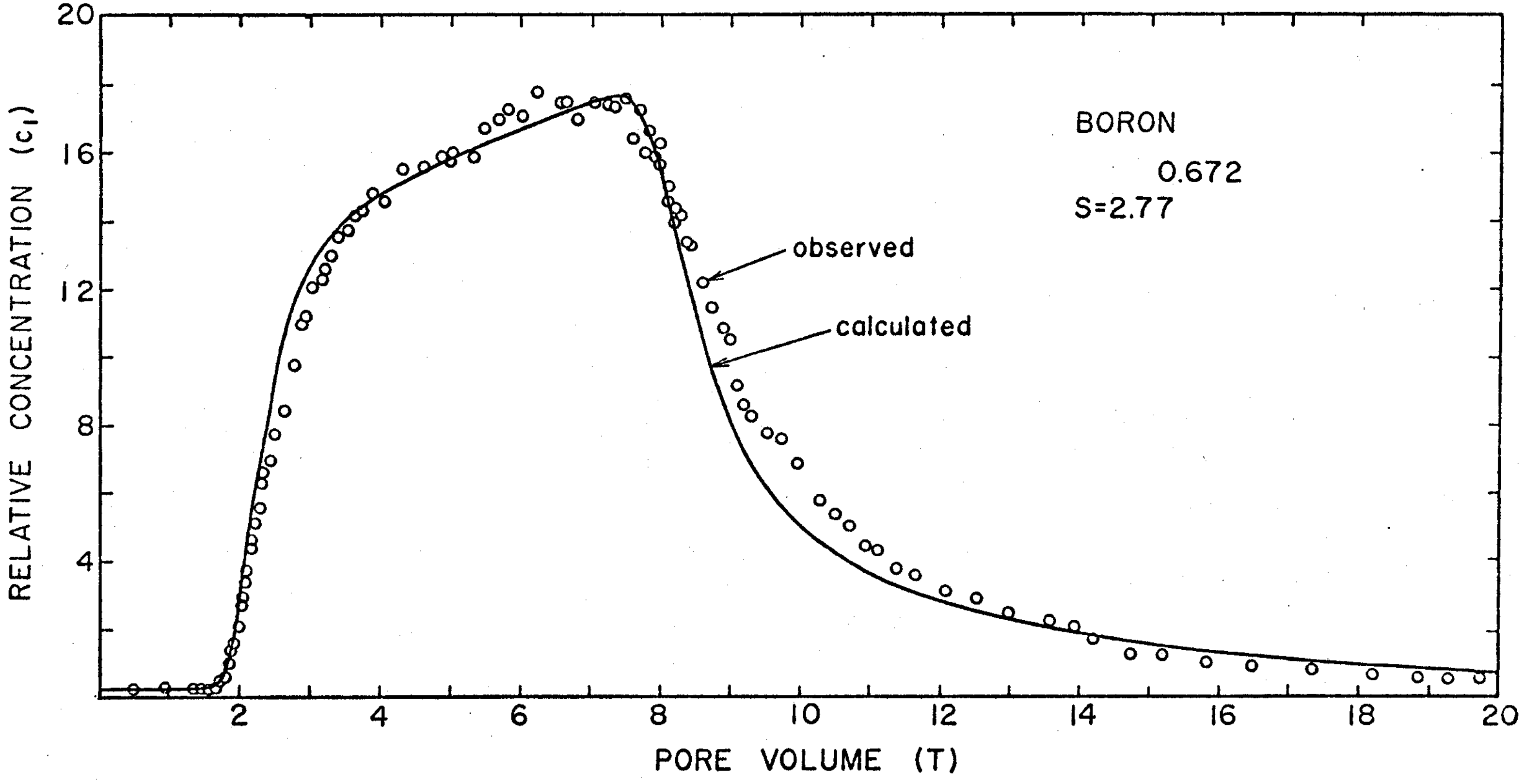

Figure 6. Observed and calculated effluent curves for Boron movement through Glendale clay loam.

addition, that k_r = 0.869 (1/day) and γ = 0.70 if the model of Krupp et al. (1972) is used (see section C).

The last example was used to check the accuracy of the curve-fitting model in conjuction with the one-site kinetic adsorption model (Model E). Figure 8 compares the "observed" and fitted effluent curves for this case. The observed points were generated with the analytical solution of Model E, Case SI-1, using the following parameter values: P = 133.33, R = 1.70 and ω = 0.875. As expected, the fitted values for Case SI-1 (Example 6A in Table 5) are essentially the same as the correct values. The fitted values for Case SI-2 deviate somewhat from the correct values because of the different analytical solution used in the fitting program. Note that only two parameters (P and ω) were fitted to the data, thereby assuming that R could have been derived from batch adsorption studies.

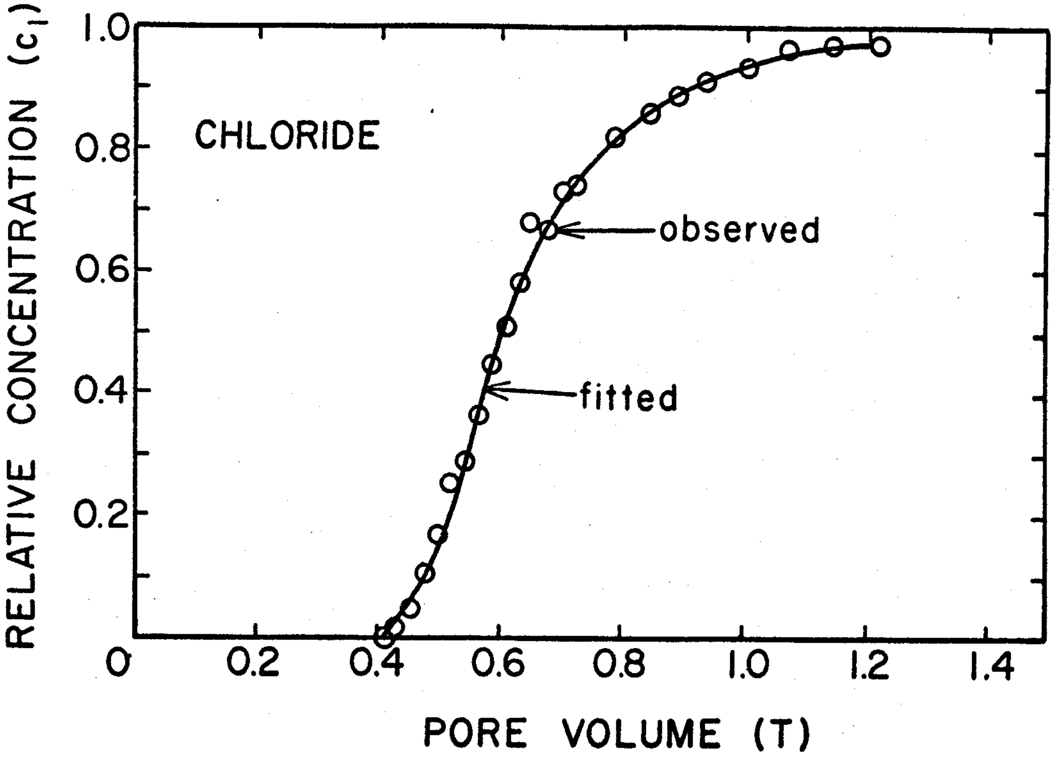

Figure 7. Observed and fitted effluent curves for Chloride movement through Glendale clay loam (Example 5B).

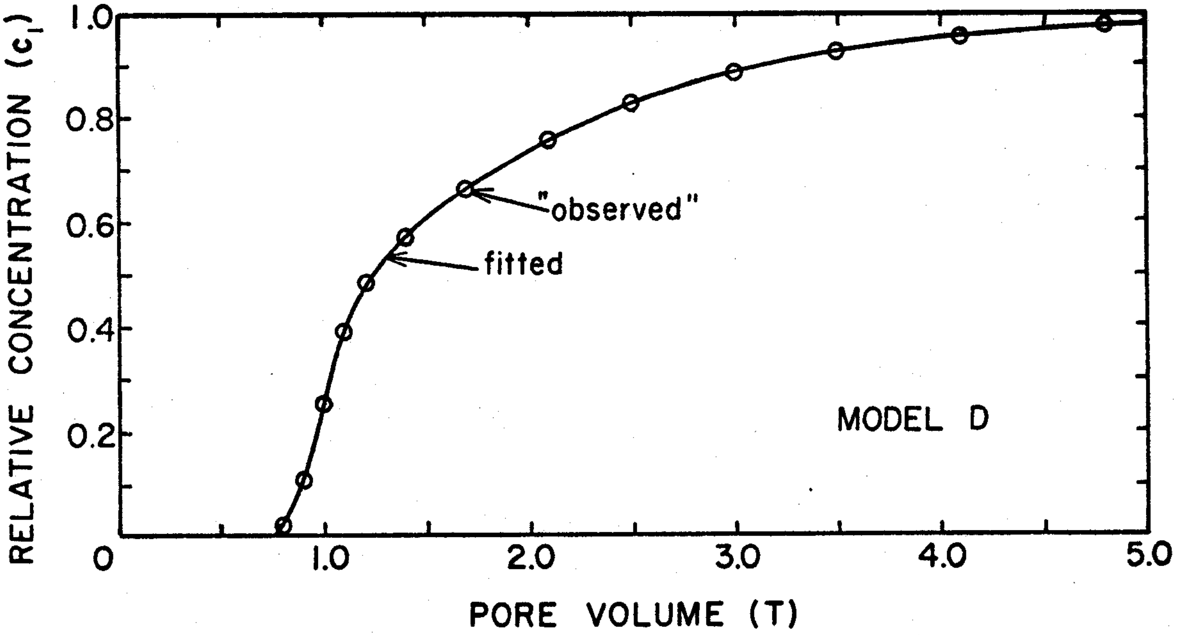

Figure 8. "Observed" and fitted effluent curves for example 6. The data points were generated with the analytical solution of Model E, Case SI-1.

SUMMARY AND CONCLUSIONS

The least-squares computer model discussed in this report provides a convenient, efficient and accurate means of fitting various transport parameters to column effluent data. Both equilibrium and non-equilibrium type transport models can be used alternatively in the curve-fitting program. The conceptually more complex non-equilibrium models may contain up to four unknown parameters if only the break-through side of the effluent curve is considered. In some cases, one may also obtain estimates for the dimensionless pulse time from the observed curve, leading to an additional unknown parameter. Several examples are given which demonstrate the versatility of the program. Although the computer program is dimensioned for up to 90 data points, it is recommended that only a limited number of points be used in the program, e.g., about 10 to 20 for those experiments in which the tracer is applied continuously, and about 15-30 points for a pulse-type effluent curve. The use of considerably more data points will generally not increase the accuracy of the fitted parameters, but rather will lead to an increase in computer time. Computer expenses can become especially high when many data points are used which, at the same time, show considerable scatter. The examples also show that one may expect some differences between the curve-fitted parameters values when different analytical solutions are used, especially for relatively small values of the column Peclet number, P. In this report, only solutions for a semi-infinite medium are considered in the computer program.

NOTATION

Symbol	Definition
a	Dimensionless constant defined by Eq. [37].
A_o	Specific surface area.
b	Dimensionless constant defined by Eq. [37].
c	Solution concentration.
c_1, c_2	Dimensionless concentrations.
c_a	Concentration in immobile, non-excluded liquid (Model C).
c_e	Dimensionless effluent concentration.
c_m, c_{im}	Concentrations in mobile and immobile liquid regions (Model B).
C_i	Initial concentration.
C_o	Input concentration.
d_{ex}	Equivalent exclusion distance (Model C).
D	Dispersion coefficient.
f	Mass fraction of solid phase in direct contact with mobile liquid (Model B).
F	Fraction of sorption sites occupied by type-1 equilibrium sites (Model D).
I_o, I_1	Modified Bessel functions.
J	Goldstein's J-function (see Appendix A).
k	Distribution coefficient between solid and liquid phases.
k_1, k_2	Distribution constants defined by Eq. [62] and [63], respectively.
k_r	Rate coefficient defined by Eq. [60].
K	Constant in Freundlich isotherm.
L	Column length.
N	Exponent in nonlinear Freundlich isotherm.
P	Column Peclet number (Table 6).
q	Volumetric flux.

NOTATION (cont'd)

Symbol	Definition
R	Retardation factor (Table 6).
R_m	Retardation factor for dynamic region (Eq. [31]).
S	Adsorbed concentration.
S_1, S_2	Adsorbed concentrations for equilibrium (type-1) and kinetic (type-2) sites (Model D).
S_m, S_{im}	Adsorbed concentrations in dynamic and stagnant soil regions (Model B).
t	Time.
t_1	Pulse time.
T	Pore volume: $T = vt/L$
T_1	Dimensionless pulse time: $T_1 = vt_1/L$.
v	Average pore-water velocity.
v_m	Average pore-water velocity in mobile liquid (Model B).
V_{ex}	Specific exclusion volume (Model C).
x	Distance.
z	Dimensionless distance: $z = x/L$
α	First-order rate coefficient.
β	Dimensionless variable (Table 6).
β_m	Eigenvalue (Tables 1,2,3).
γ	Constant defined by Eq. [59] (Model C).
θ	Volumetric soil-water content.
θ_a	Equivalent volumetric water content of the immobile, non-excluded liquid phase (Model C).
θ_{ex}	Equivalent volumetric water content of the anion excluded part of the liquid phase (Model C).
θ_m, θ_{im}	Volumetric water contents of the mobile and immobile liquid phases respectively (Models B, C).
λ	Dummy integration variable (Eq. [41]).

NOTATION (cont'd)

Symbol	Definition
ξ	Dimensionless constant defined by Eq. [38] (Model C).
ρ	Soil bulk density.
τ	Dummy integration variable (Eq. [35]).
ϕ_{ex}	Fraction of liquid phase subject to anion exclusion (Model C).
ϕ_m	Fraction of liquid phase assumed to be mobile (Models B, C).
ω	Dimensionless rate constant (Table 6).

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APPENDIX A. Properties of Goldstein's J-function (Goldstein, 1953)

$$J(x,y) = 1 - e^{-y}\int_0^x e^{-\tau} I_o(2\sqrt{y\tau})\, d\tau \qquad (x,y>0) \qquad [A1]$$

$$J(x,y) = e^{-y}\int_x^\infty e^{-\tau} I_o(2\sqrt{y\tau})\, d\tau \qquad [A2]$$

$$J(x,y) + J(y,x) = 1 + \exp(-x-y)\ I_o(2\sqrt{xy}) \qquad [A3]$$

$$J(x,0) = e^{-x} \qquad J(x,\infty) = 1 \qquad [A4]$$

$$J(0,y) = 1 \qquad J(\infty,y) = 0 \qquad [A5]$$

$$\frac{\partial J}{\partial x} = -\exp(-x-y)\ I_o(2\sqrt{xy}) \qquad [A6]$$

$$\frac{\partial J}{\partial y} = \exp(-x-y)\ \left(\frac{x}{y}\right)^{1/2} I_1(2\sqrt{xy}) \qquad [A7]$$

Approximation 1 ($xy < 3.5$; $|E| < 2.10^{-9}$)

$$J(x,y) = 1 - (1+b_5 y)e^{-y} + \exp(-x-y)\ [1 + b_5(1+x)y + \frac{(xy)^2}{2} b_4$$

$$+ \frac{(xy)^3}{6} b_3 + \frac{(xy)^4}{24} b_2 + \frac{(xy)^5}{120} b_1 + \frac{(xy)^6}{720} a_6] + E \qquad [A8]$$

where

$b_1 = a_5 + a_6\ y$ $\qquad$ $b_2 = a_4 + b_1\ y$

$b_3 = a_3 + b_2\ y$ $\qquad$ $b_4 = a_2 + b_3\ y$

$b_5 = a_1 + b_4\ y$

and

a_1 = .999 999 403 a_2 = .500 006 087

a_3 = .166 632 856 a_4 = .041 786 784

a_5 = .008 061 141 a_6 = .001 747 052

Approximation 2 (Lindstrom and Stone, 1974)

$$J(x,y) = \exp(-x-y) \sum_{n=0}^{\infty} (\frac{y}{x})^{n/2} I_n(2\sqrt{xy}) \qquad (x \geqslant y) \qquad [A9]$$

$$J(x,y) = 1 - \exp(-x-y) \sum_{n=1}^{\infty} (\frac{x}{y})^{n/2} I_n(2\sqrt{xy}) \qquad (x < y) \qquad [A10]$$

where I_n are modified Bessel functions of order n. These Bessel functions are easily evaluated by noting that for n>1

$$I_{n+1}(a) = I_{n-1}(a) - \frac{2n}{a} I_n(a) \qquad [A11]$$

Approximation 3 (De Smedt and Wierenga, 1979)

$$J(x,y) = \exp(-x-y) \sum_{n=0}^{k} \frac{y^n}{n!} \sum_{m=0}^{n} \frac{x^m}{m!} + E \qquad (x \geqslant y) \qquad [A12]$$

where

$$|E| < \frac{y^{k+1}}{(k+1)!} \qquad [A13]$$

$$J(x,y) = 1 - \exp(-x-y) \sum_{n=1}^{k} \frac{x^n}{n!} \sum_{m=0}^{n-1} \frac{y^m}{m!} + E \qquad (x < y) \qquad [A14]$$

where

$$|E| < \frac{x^k}{k!}$$

Approximation 4 (Klinkenberg, 1948) $(x+y > 10, |E| < 8.10^{-4})$

$$J(x,y) = \frac{1}{2} \operatorname{erfc}\left(\sqrt{x} - \sqrt{y} - \frac{1}{8\sqrt{x}} - \frac{1}{8\sqrt{y}}\right) + E \qquad [A15]$$

Approximation 5 (Goldstein, 1953).

$$J(x,y) = \begin{cases} A + B & (x \geqslant y) \\ 1 - A + B & (x < y) \end{cases} \qquad [A16]$$

where

$$A = \frac{\sqrt{x} + \sqrt{y}}{\sqrt{8\xi}} \operatorname{erfc}(\sqrt{z}) \qquad [A17]$$

$$B = \frac{1}{2} \exp(-x-y)\, I_o(\xi) + \frac{(x-y)e^{-z}}{\sqrt{8\pi\xi}} \sum_{m=1}^{\infty} \frac{\alpha_m S_m(z)}{(2\xi)^m} \qquad [A18]$$

$$\alpha_m = \frac{\Gamma(m + \frac{1}{2})}{\Gamma(\frac{1}{2})\, m!} \qquad [A19]$$

$$S_{m+1}(z) = \frac{\Gamma(m + \frac{1}{2})}{\Gamma(\frac{1}{2})} - z\, S_m(z) \qquad [A20]$$

$$S_1(z) = 1 - \sqrt{\pi z}\, e^z \operatorname{erfc}(\sqrt{z}) \qquad [A21]$$

$$z = (\sqrt{x} - \sqrt{y})^2 \qquad [A22]$$

$$\xi = 2\sqrt{xy} \qquad [A23]$$

APPENDIX B. CFITIM, a computer program for calculating non-equilibrium transport parameters from observed column effluent curves.

This appendix gives a brief description and listing of CFITIM, a computer program which may be used to calculate several parameters appearing in both equilibrium and non-equilibrium type transport models. The parameters are obtained by means of a least-squares fit of the appropriate analytical solution (see sections A and B) to column effluent data. The analytical solutions hold only for a semi-infinite system and two types of boundary conditions at the column entrance: Case SI-1 for a first-type, constant concentration boundary condition, and Case SI-2 for a third-type, constant flux boundary condition.

The program consists of a main program (MAIN), two subroutines (MODEL and MATINV), and three functions (CCO, EXF and GOLD). Most of the calculations for the least-squares analysis are carried out in MAIN, including input and output instructions, calculation of a correlation matrix between the unknown coefficients, and calculation of a 95% confidence interval for each unknown coefficient. Subroutine MODEL calculates the exit concentration for each transport model. The choice of the transport model is governed by the input variable MODE:

MODE = 1 for Model A, Case SI-1

MODE = 2 for Model A, Case SI-2,

MODE = 3 for Model B, C or D, Case SI-1,

MODE = 4 for Model B, C or D, Case SI-2,

MODE = 5 for Model E, Case SI-1, and

MODE = 6 for Model E, Case SI-2.

Subroutine MATINV describes a matrix inversion scheme which is needed for the least-squares analysis in MAIN. The function CCO is used to calculate the argument under the integral sign of Eq. [39]. The integral of this equation is evaluated with a 20-point Gaussian quadrature scheme. This scheme was found to be slightly more efficient than a Romberg integration scheme used in earlier versions of this program (see also van Genuchten and Wierenga, 1976; and De Smedt, 1979). Equation [39] also contains Goldstein's J-function. This function is evaluated in GOLD. Appendix A gives several approximate relations for J(x,y). The function GOLD uses approximation 3 for small values of x and y, and approximation 5 for relatively large values. The function EXF, finally, is used to calculate the complementary error function (erfc), the exponential function (exp), or the product of exp and erfc.

Table B1 gives a list of the most significant variables of CFITIM. Table B2 gives instructons regarding set-up of the data cards. An example of the the input data is given in Table B3, in this case for Cases 1D, 2D and 2H of Table 5. Table B4 shows the output obtained for these examples. The program itself is listed in Table B5.

An extra comment is needed about the vector B(I) in Table B1. This vector contains the initial estimates of the unknown coefficients. For Model A, B(I) contains the estimated values of P, R and T_1 (in that order). For models B,C, D and E, B(I) contains estimates for P, R, β, ω and T_1, again in that order. If a coefficient is known, the measured values of that coefficient should be entered on the fifth data card (see Tables B2 and B3). At the same time the input value for INDEX(I), associated with the known B(I)-values, should be set to zero. The vector INDEX(I) specifies if the I-th coefficient, B(I), is an unknown parameter in the program and needs to be fitted to the data [INDEX(I) = 1], or if that coefficient is known beforehand

and should be kept constant in the program [INDEX(I) = 0]. For a continuous tracer application (no pulse of solute), a large dummy variable should be assigned to T_1. This value should exceed all measured pore volumes, Y(I), entered into the program. At the same time INDEX(3) must be zero if Model A is used, while INDEX(5) must be zero for the other models; this is necessary to indicate that T_1 is a known parameter.

Table B1. List of the most significant variables in CFITIM.

VARIABLE	DEFINITION
B(I)	Vector containing estimates of the various coefficients: P, R and T_1 for Model A; P, R, β, ω and T_1 (in that order) for Models B through E.
BI(I)	Vector of coefficient names.
EXF(A,B)	Function to calculate exp(A) erfc(B).
INDEX(I)	Index for each coefficient. If INDEX(I) = 0, the coefficient B(I) is known and kept constant in the program. If INDEX(I) = 1, the coefficient is assumed to be unknown and fitted to the data. At least two coefficient need to be unknown.
MIT	Maximum number of iterations allowed in the least-squares analysis.
MODE	Model number specifying the type of transport model and boundary conditions to be used (see text).
NC	Number of cases considered.
NDATA	Data input code. If NDATA = 1, new data are read in for that particular case. If NDATA = 0, the data of the previous case (or part of them) are used for the new problem. This code allows one to fit the same data to different models.
NIT	Iteration number during least-squares analysis.
NOB	Number of observations (cannot exceed 90 with presently dimensioned arrays).
SSQ,SUMB	Residual sum of squares.
STOPCR	Stop criterion. The iterative curve-fitting process stops when the relative change in the ratio of all coefficients becomes less than STOPCR.
TITLE	Vector containing information of title card (input label).
X(I), Y(I)	Observed effluent data: pore volume and concentration, respectively.

Table B2. Data input instructions.

CARD	COLUMNS	FORMAT	VARIABLE	COMMENTS
1	1-5	I5	NC	Number of cases considered. The remaining cards are read in for each case. If NDATA = 0 on card 2, data cards 7, etc. are not needed for that particular case.
2	1-5	I5	MODE	Model number.
2	6-10	I5	NDATA	Data input code.
2	11-15	I5	MIT	Maximum number of iterations.
2	16-20	I5	NOB	Number of observations.
3	1-80	20A4	TITLE	Information card.
4	1-6	A4,A2	BI(1)	Coefficient name for P.
4	11-16	A4,A2	BI(2)	Coefficient name for R.
4	21-26	A4,A2	BI(3)	Coefficient name for B(3).
4	31-36	A4,A2	BI(3)	Coefficient name for B(4).
4	41-46	A4,A2	BI(4)	Coefficient name for B(5).
5	1-10	F10.0	B(1)	Initial value of P.
5	11-20	F10.0	B(2)	Initial value of R.
5	21-30	F10.0	B(3)	Initial value of B(3).
5	31-40	F10.0	B(4)	Initial value of B(4).
5	41-50	F10.0	B(5)	Initial value of B(5).
6	1-5	I5	INDEX(1)	Index for each coefficient. See text for explanation.
6	6-10	I5	INDEX(2)	
6	11-15	I5	INDEX(3)	
6	16-20	I5	INDEX(4)	
6	21-25	I5	INDEX(5)	
7, etc.	1-10	F10.0	X(I)	Value of observed pore volume.
7, etc.	11-20	F10.0	Y(I)	Value of observed concentration. Card 7 is repeated NOB times.

Table B3. Input data for Examples 1D, 2D and 2H.

```
           0         1         2         3         4         5
Column:    12345678901234567890123456789012345678901234567890
Card
 1             3
 2             4    1   20   10
 3                    EXAMPLE 1D  P=40
 4         PECLET      RF       BETA     OMEGA     PULSE
 5               25.0       2.0       0.6       0.2     100.0
 6             1    1    1    1    0
 7                 .8     .0155
 8                1.0     .1100
 9                1.2     .2896
10                1.4     .4620
11                1.6     .5740
12                1.9     .6548
13                2.5     .7218
14                3.5     .7952
15                5.0     .8710
16                7.0     .9308
17             4    1   20   15
18                    EXAMPLE 2D  TRITIATED WATER (EXP. 5-2)
19         PECLET      RF       BETA     OMEGA     PULSE
20               50.0       1.0       0.6       0.5       2.0
21             1    1    1    1    1
22               .449      .007
23               .593      .148
24               .688      .301
25               .832      .476
26              1.072      .703
27              1.455      .825
28              1.981      .922
29              2.442      .949
30              2.682      .843
31              2.825      .630
32              3.017      .404
33              3.304      .233
34              3.879      .103
35              4.477      .052
36              4.956      .028
37             2    0   40   15
38                    EXAMPLE 2H  TRITIATED WATER (EXP. 5-2)
39         PECLET      RF      PULSE
40               50.0       1.0       2.0
41             1    1    1
```

Table B4. Output for examples 1D, 2D and 2H.

```
**********************************************************************************
*                                                                                *
*          NON-LINEAR LEAST SQUARES ANALYSIS                                     *
*                                                                                *
*          NON-EQUILIBRIUM TRANSPORT (MODEL B)                                   *
*          THIRD-TYPE BOUNDARY CONDITION                                         *
*          EXAMPLE 1D  P=40                                                      *
*                                                                                *
**********************************************************************************

INITIAL VALUES OF COEFFICIENTS
==============================
 NO       NAME         INITIAL VALUE
  1      PECLET          25.000
  2        RF             2.000
  3       BETA            0.600
  4      OMEGA            0.200
  5      PULSE          100.000

OBSERVED DATA
=============
OBS. NO.     PORE VOLUME     CONCENTRATION
    1           0.8000          0.0155
    2           1.0000          0.1100
    3           1.2000          0.2896
    4           1.4000          0.4620
    5           1.6000          0.5740
    6           1.9000          0.6548
    7           2.5000          0.7218
    8           3.5000          0.7952
    9           5.0000          0.8710
   10           7.0000          0.9308

ITERATION      SSQ           PECLET         RF         BETA        OMEGA
    0       0.1226629      25.00000      2.00000     0.60000     0.20000
    1       0.0065263      32.62142      2.35200     0.52071     0.44918
    2       0.0000438      38.42969      2.49917     0.49943     0.49621
    3       0.0000000      39.93600      2.50020     0.49999     0.49980
    4       0.0000000      39.97443      2.50014     0.50000     0.49985
    5       0.0000000      39.97469      2.50014     0.50000     0.49985
```

```
CORRELATION MATRIX
==================
         1           2           3           4
 1   1.0000
 2  -0.0998      1.0000
 3  -0.2188     -0.8752      1.0000
 4   0.6886     -0.3901     -0.0304      1.0000


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

                                                                95% CONFIDENCE LIMITS
VARIABLE     NAME         VALUE         S.E.COEFF.    T-VALUE    LOWER          UPPER
    1       PECLET      39.97469          0.0087      4578.35   39.9533        39.9961
    2         RF         2.50014          0.0001     23701.32    2.4999         2.5004
    3        BETA        0.50000          0.0000     24186.01    0.4999         0.5000
    4       OMEGA        0.49985          0.0001      8878.93    0.4997         0.5000

---------ORDERED BY COMPUTER INPUT----------       ------------ORDERED BY RESIDUALS-----------
         PORE       CONCENTRATION        RESI-                  PORE      CONCENTRATION       RESI-
NO      VOLUME      OBS.     FITTED       DUAL        NO      VOLUME      OBS.     FITTED      DUAL
 1       0.800      0.016     0.016     -0.000         2      1.000      0.110     0.110      0.000
 2       1.000      0.110     0.110      0.000         8      3.500      0.795     0.795      0.000
 3       1.200      0.290     0.290     -0.000         9      5.000      0.871     0.871      0.000
 4       1.400      0.462     0.462     -0.000         6      1.900      0.655     0.655      0.000
 5       1.600      0.574     0.574     -0.000         4      1.400      0.462     0.462     -0.000
 6       1.900      0.655     0.655      0.000         3      1.200      0.290     0.290     -0.000
 7       2.500      0.722     0.722     -0.000         5      1.600      0.574     0.574     -0.000
 8       3.500      0.795     0.795      0.000         7      2.500      0.722     0.722     -0.000
 9       5.000      0.871     0.871      0.000        10      7.000      0.931     0.931     -0.000
10       7.000      0.931     0.931     -0.000         1      0.800      0.016     0.016     -0.000


END OF PROBLEM
==============
```

```
**************************************************************************
*                                                                        *
*         NON-LINEAR LEAST SQUARES ANALYSIS                              *
*                                                                        *
*         NON-EQUILIBRIUM TRANSPORT (MODEL B)                            *
*         THIRD-TYPE BOUNDARY CONDITION                                  *
*         EXAMPLE 2D  TRITIATED WATER (EXP. 5-2)                         *
*                                                                        *
**************************************************************************

INITIAL VALUES OF COEFFICIENTS
==============================
 NO       NAME          INITIAL VALUE
  1      PECLET            50.000
  2        RF               1.000
  3       BETA              0.600
  4      OMEGA              0.500
  5      PULSE              2.000

OBSERVED DATA
=============
OBS. NO.      PORE VOLUME     CONCENTRATION
    1            0.4490           0.0070
    2            0.5930           0.1480
    3            0.6880           0.3010
    4            0.8320           0.4760
    5            1.0720           0.7030
    6            1.4550           0.8250
    7            1.9810           0.9220
    8            2.4420           0.9490
    9            2.6820           0.8430
   10            2.8250           0.6300
   11            3.0170           0.4040
   12            3.3040           0.2330
   13            3.8790           0.1030
   14            4.4770           0.0520
   15            4.9560           0.0280

ITERATION     SSQ          PECLET        RF          BETA        OMEGA        PULSE
    0      0.4027378     50.00000     1.00000     0.60000     0.50000     2.00000
    1      0.0555833     14.48690     0.95559     0.67835     0.82089     2.06764
    2      0.0024006     20.92183     1.00686     0.77344     0.34140     2.09776
    3      0.0011066     26.77567     1.01423     0.72304     0.49048     2.10374
    4      0.0008358     29.52979     1.01858     0.71883     0.50203     2.10446
    5      0.0008351     29.47266     1.01802     0.71966     0.49997     2.10448
    6      0.0008351     29.46003     1.01800     0.71972     0.49980     2.10448
```

```
 CORRELATION MATRIX
 =================
          1          2          3          4          5
  1   1.0000
  2   0.2258     1.0000
  3  -0.8353    -0.5069     1.0000
  4   0.8271    -0.0434    -0.7777     1.0000
  5  -0.2288     0.0925     0.0127    -0.3353     1.0000


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

                                                                95% CONFIDENCE LIMITS
 VARIABLE     NAME        VALUE       S.E.COEFF.   T-VALUE     LOWER          UPPER
     1       PECLET     29.46003        3.2101        9.18    22.3076        36.6125
     2         RF        1.01800        0.0099      102.50     0.9959         1.0401
     3        BETA       0.71972        0.0132       54.51     0.6903         0.7491
     4       OMEGA       0.49980        0.0577        8.66     0.3712         0.6284
     5       PULSE       2.10448        0.0062      338.68     2.0906         2.1183

---------ORDERED BY COMPUTER INPUT----------      ------------ORDERED BY RESIDUALS-----------
       PORE      CONCENTRATION        RESI-                PORE     CONCENTRATION        RESI-
NO    VOLUME     OBS.      FITTED      DUAL         NO    VOLUME     OBS.      FITTED     DUAL
 1     0.449     0.007      0.021    -0.014          3     0.688     0.301      0.288     0.013
 2     0.593     0.148      0.149    -0.001          5     1.072     0.703      0.695     0.008
 3     0.688     0.301      0.288     0.013          7     1.981     0.922      0.915     0.007
 4     0.832     0.476      0.491    -0.015         14     4.477     0.052      0.047     0.005
 5     1.072     0.703      0.695     0.008          9     2.682     0.843      0.839     0.004
 6     1.455     0.825      0.829    -0.004         15     4.956     0.028      0.025     0.003
 7     1.981     0.922      0.915     0.007         11     3.017     0.404      0.401     0.003
 8     2.442     0.949      0.954    -0.005         12     3.304     0.233      0.233     0.000
 9     2.682     0.843      0.839     0.004          2     0.593     0.148      0.149    -0.001
10     2.825     0.630      0.635    -0.005         13     3.879     0.103      0.105    -0.002
11     3.017     0.404      0.401     0.003          6     1.455     0.825      0.829    -0.004
12     3.304     0.233      0.233     C.000          8     2.442     0.949      0.954    -0.005
13     3.879     0.103      0.105    -0.002         10     2.825     0.630      0.635    -0.005
14     4.477     0.052      0.047     0.005          1     0.449     0.007      0.021    -0.014
15     4.956     0.028      0.025     0.003          4     0.832     0.476      0.491    -0.015


 END OF PROBLEM
 ==============
```

```
*************************************************************************
*                                                                       *
*          NON-LINEAR LEAST SQUARES ANALYSIS                            *
*                                                                       *
*          EQUILIBRIUM TRANSPORT (MODEL A)                              *
*          THIRD-TYPE BOUNDARY CONDITION                                *
*          EXAMPLE 2H  TRITIATED WATER (EXP. 5-2)                       *
*                                                                       *
*************************************************************************

INITIAL VALUES OF COEFFICIENTS
==============================
 NO      NAME          INITIAL VALUE
  1     PECLET            50.000
  2       RF               1.000
  3     PULSE              2.000

OBSERVED DATA
=============
OBS. NO.      PORE VOLUME     CONCENTRATION
    1            0.4490          0.0070
    2            0.5930          0.1480
    3            0.6880          0.3010
    4            0.8320          0.4760
    5            1.0720          0.7030
    6            1.4550          0.8250
    7            1.9810          0.9220
    8            2.4420          0.9490
    9            2.6820          0.8430
   10            2.8250          0.6300
   11            3.0170          0.4040
   12            3.3040          0.2330
   13            3.8790          0.1030
   14            4.4770          0.0520
   15            4.9560          0.0280

ITERATION       SSQ            PECLET          RF           PULSE
    0        0.3173597        50.00000      1.00000       2.00000
    1        0.0542867        10.95283      0.96905       2.00986
    2        0.0212378         8.04071      0.87710       2.07660
    3        0.0204228         8.73193      0.87711       2.07649
    4        0.0202247         8.94261      0.87660       2.07660
    5        0.0201638         9.39116      0.87934       2.07573
    6        0.0200267         9.10190      0.87632       2.07637
    7        0.0200257         9.09707      0.87683       2.07610
    8        0.0200256         9.09217      0.87683       2.07611
    9        0.0200256         9.09145      0.87684       2.07611
```

```
CORRELATION MATRIX
==================
        1          2          3
 1   1.0000
 2   0.1357     1.0000
 3  -0.2286    -0.6565     1.0000


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

                                                              95% CONFIDENCE LIMITS
VARIABLE     NAME        VALUE        S.E.COEFF.    T-VALUE    LOWER         UPPER
    1       PECLET      9.09145        1.2686         7.17     6.3274       11.8555
    2         RF        0.87684        0.0213        41.23     0.8305        0.9232
    3        PULSE      2.07611        0.0289        71.89     2.0132        2.1390

---------ORDERED BY COMPUTER INPUT----------        ------------ORDERED BY RESIDUALS------------
          PORE      CONCENTRATION      RESI-                    PORE      CONCENTRATION       RESI-
NO       VOLUME     OBS.      FITTED    DUAL             NO    VOLUME     OBS.      FITTED     DUAL
 1       0.449     0.007     0.062    -0.055             13     3.879     0.103     0.052     0.051
 2       0.593     0.148     0.185    -0.037              9     2.682     0.843     0.797     0.046
 3       0.688     0.301     0.287     0.014             14     4.477     0.052     0.010     0.042
 4       0.832     0.476     0.446     0.030              5     1.072     0.703     0.666     0.037
 5       1.072     0.703     0.666     0.037              4     0.832     0.476     0.446     0.030
 6       1.455     0.825     0.869    -0.044             15     4.956     0.028     0.003     0.025
 7       1.981     0.922     0.968    -0.046              3     0.688     0.301     0.287     0.014
 8       2.442     0.949     0.970    -0.021             12     3.304     0.233     0.230     0.003
 9       2.682     0.843     0.797     0.046             10     2.825     0.630     0.642    -0.012
10       2.825     0.630     0.642    -0.012              8     2.442     0.949     0.970    -0.021
11       3.017     0.404     0.443    -0.039              2     0.593     0.148     0.185    -0.037
12       3.304     0.233     0.230     0.003             11     3.017     0.404     0.443    -0.039
13       3.879     0.103     0.052     0.051              6     1.455     0.825     0.869    -0.044
14       4.477     0.052     0.010     0.042              7     1.981     0.922     0.968    -0.046
15       4.956     0.028     0.003     0.025              1     0.449     0.007     0.062    -0.055


END OF PROBLEM
==============
```

<u>Table B5</u>. Fortran listing of CFITIM.

MAIN

```
C
C     ************************************************************
C     *                                                          *
C     *     NON-LINEAR LEAST-SQUARES ANALYSIS          CFITIM    *
C     *                                                          *
C     *     --------------- INPUT INFORMATION ---------------    *
C     *                                                          *
C     *     CARD 1: NUMBER OF CASES CONSIDERED: NC (I5)          *
C     *                                                          *
C     *           THE NEXT CARDS ARE REPEATED NC TIMES           *
C     *                                                          *
C     *     CARD 2: MODEL  NUMBER (MODE), DATA INPUT CODE (NDATA),*
C     *             MAXIMUM NUMBER OF ITERATIONS (MIT) AND NUMBER*
C     *             OF OBSERVATIONS (NOB)  (4I5)                 *
C     *             MODE=1,2: EQUILIBRIUM TRANSPORT (MODEL A)    *
C     *                 =3,4: NON-EQUILIBRIUM TRANSPORT (MODEL B)*
C     *                 =5,6: ONE-SITE KINETIC ADSORPTION (MODEL D)*
C     *                 =1,3,5: FIRST-TYPE BOUNDARY CONDITION    *
C     *                 =2,4,6: THIRD-TYPE BOUNDARY CONDITION    *
C     *             NDATA=0: SAME DATA AS PREVIOUS CASE          *
C     *                  =1: NEW DATA                            *
C     *     CARD 3: INFORMATION CARD  (20A4)                     *
C     *     CARD 4: NAMES OF THE COEFFICIENTS  3(A4,A2,4X)       *
C     *     CARD 5: INITIAL ESTIMATES OF COEFFICIENTS (3F10.0)   *
C     *     CARD 6: INDEX FOR EACH COEFFICIENT  5(I5)            *
C     *             =0  IF COEFFICIENT IS KNOWN (CONSTANT)       *
C     *             =1  IF COEFFICIENT IS UNKNOWN                *
C     *                                                          *
C     *             THE NEXT CARDS ARE READ IN ONLY IF NDATA=1   *
C     *                                                          *
C     *     CARD 7,ETC.: EXPERIMENTAL DATA: PORE VOLUME AND      *
C     *           CONCENTRATION (NOB CARDS)  (2F10.0)            *
C     *                                                          *
C     ************************************************************
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(90),X(90),F(90),R(90),DELZ(90,5),B(10),E(5),TH(10),
     1P(5),PHI(5),Q(5),LSORT(90),TB(10),A(5,5),BI(10),TITLE(20),D(5,5),
     2INDEX(5)
      DATA STOPCR/0.0005/
C
C     ----- READ NUMBER OF CASES -----
      READ(5,1006) NC
      DO 120 NCASE=1,NC
      WRITE(6,1000)
C
C     ----- READ INPUT PARAMETERS -----
      READ(5,1006) MODE,NDATA,MIT,NOB
      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)
      N=MODE-2*M
```

MAIN

```
      IF(N.EQ.1) WRITE(6,1024)
      IF(N.EQ.2) WRITE(6,1025)
      NU=3
      IF(MODE.GT.2) NU=5
      NU1=NU+1
      NU2=2*NU
      READ(5,1001) TITLE
      WRITE(6,1002) TITLE
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)
      IF(M.EQ.2) B(8)=1./B(7)
C
C     ----- READ INDICES -----
      READ(5,1006) (INDEX(I),I=1,NU)
      IF(M.EQ.2) INDEX(3)=0
      WRITE(6,1007)
      DO 4  I=1,NU
      J=2*I-1
    4 WRITE(6,1008) I,BI(J),BI(J+1),B(I+NU)
      IF(NDATA.EQ.0) GO TO 10
C
C     ----- READ AND WRITE EXPERIMENTAL DATA -----
      DO 6 I=1,NOB
    6 READ(5,1005) X(I),Y(I)
   10 WRITE(6,1009)
      DO 12 I=1,NOB
   12 WRITE(6,1010) I,X(I),Y(I)
C
C     ----------
      NP=0
      DO 14 I=NU1,NU2
      TB(I)=B(I)
      IF(INDEX(I-NU).EQ.0) GO TO 14
      NP=NP+1
      K=2*NP-1
      J=2*(I-NU)-1
      BI(K)=BI(J)
      BI(K+1)=BI(J+1)
      B(NP)=B(I)
      TB(NP)=B(I)
      TH(NP)=B(NP)
   14 TH(I)=B(I)
C
C     ----------
      GA=0.02
      NIT=0
      NP2=2*NP
      CALL MODEL(TH,F,NOB,X,INDEX,MODE)
      SSQ=0.
      DO 32 I=1,NOB
```

MAIN

```
      R(I)=Y(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 OF ITERATION -----
   34 NIT=NIT+1
      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),NOB,X,INDEX,MODE)
      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)
   44 E(I)=DSQRT(D(I,I))
   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
      CALL MODEL(TB,F,NOB,X,INDEX,MODE)
      DO 64 I=1,NOB
      R(I)=Y(I)-F(I)
   64 SUMB=SUMB+R(I)*R(I)
   66 SUM1=0.0
      SUM2=0.0
      SUM3=0.0
```

MAIN

```
      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)
      ANGLE=57.29578*DATAN2(DSQRT(1.-ARG*ARG),ARG)
C
C     ----------
      DO 72 I=1,NP
      IF(TH(I)*TB(I))74,74,72
   72 CONTINUE
      IF((SUMB-SSQ).LT.1.D-08)GO TO 80
   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.LE.MIT) GO TO 34
C
C     ----- END OF ITERATION LOOP -----
   96 CONTINUE
      CALL MATINV(D,NP,P)
C
C     ----- WRITE CORRELATION MATRIX -----
      DO 98 I=1,NP
   98 E(I)=DSQRT(DMAX1(D(I,I),1.D-20))
      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)
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
```

```
  108 WRITE(6,1016) I,BI(J),BI(J+1),TH(I),SECOEF,TVALUE,TMCOE,TPCOE
C
C     ----- PREPARE FINAL OUTPUT -----
      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 118 I=1,NOB
      J=LSORT(NOB+1-I)
  118 WRITE(6,1018) I,X(I),Y(I),F(I),R(I),J,X(J),Y(J),F(J),R(J)
      WRITE(6,1020)
  120 CONTINUE
C
C     ----- END OF PROBLEM -----
 1000 FORMAT(1H1,10X,82(1H*)/11X,1H*,80X,1H*/11X,1H*,10X,'NON-LINEAR LEA
     1ST SQUARES ANALYSIS',37X,1H*/11X,1H*,80X,1H*)
 1001 FORMAT(20A4)
 1002 FORMAT(11X,1H*,20A4,1H*/11X,1H*,80X,1H*/11X,82(1H*))
 1004 FORMAT(5(A4,A2,4X))
 1005 FORMAT(5F10.0)
 1006 FORMAT(5I5)
 1007 FORMAT(//11X,'INITIAL VALUES OF COEFFICIENTS'/11X,30(1H=)/12X,'NO'
     1,6X,'NAME',9X,'INITIAL VALUE')
 1008 FORMAT(11X,I3,5X,A4,A2,4X,F12.3)
 1009 FORMAT(//11X,'OBSERVED DATA',/11X,13(1H=)/11X,'OBS. NO.',5X,'PORE
     1VOLUME',5X,'CONCENTRATION')
 1010 FORMAT(11X,I5,5X,F12.4,4X,F12.4)
 1011 FORMAT(//11X,'ITERATION',6X,'SSQ',4X,5(7X,A4,A2))
 1012 FORMAT(11X,I5,5X,F11.7,2X,5F13.5)
 1013 FORMAT(1H1,10X,'CORRELATION MATRIX'/11X,18(1H=)/14X,10(4X,I2,5X))
 1014 FORMAT(11X,I3,10(2X,F7.4,2X))
 1015 FORMAT(///,11X,'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,A2,2X,F12.5,5X,F9.4,4X,F8.2,2X,F9.4,6X,F9.4)
 1017 FORMAT(//10X,9(1H-),'ORDERED BY COMPUTER INPUT',10(1H-), 7X,12(1H-
     1),'ORDERED BY RESIDUALS',12(1H-)/18X,'PORE',6X,'CONCENTRATION',
     26X,'RESI-',18X,'PORE',6X,'CONCENTRATION',6X,'RESI-'/10X,'NO',4X,
     3'VOLUME',6X,'OBS.',4X,'FITTED',6X,'DUAL',10X,'NO',4X,'VOLUME',6X,
     4'OBS.',4X,'FITTED',6X,'DUAL')
 1018 FORMAT(10X,I2,4F10.3,10X,I2,4F10.3)
```

```
1020 FORMAT(///11X,'END OF PROBLEM'/11X,14(1H=))
1021 FORMAT(11X,1H*,10X,'EQUILIBRIUM TRANSPORT (MODEL A)',39X,1H*)
1022 FORMAT(11X,1H*,10X,'NON-EQUILIBRIUM TRANSPORT (MODEL B)',35X,1H*)
1023 FORMAT(11X,1H*,10X,'ONE-SITE KINETIC ADSORPTION (MODEL D)',33X,1H*
    1)
1024 FORMAT(11X,1H*,10X,'FIRST-TYPE BOUNDARY CONDITION',41X,1H*)
1025 FORMAT(11X,1H*,10X,'THIRD-TYPE BOUNDARY CONDITION',41X,1H*)
     STOP
     END
```

MODEL

```
      SUBROUTINE MODEL(B,Y,NOB,X,INDEX,MODE)
C
C     PURPOSE: TO CALCULATE CONCENTRATIONS FOR GIVEN PORE VOLUME
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION B(10),Y(90),X(90),INDEX(5),XG(20),W(20)
      DATA XG/.03877242,.1160841,.1926976,.2681522,.3419941,.4137792,
     1.4830758,.5494671,.6125539,.6719567,.7273183,.7783057,.8246122,
     2.8659595,.9020988,.9328128,.9579168,.9772599,.9907262,.9982377/
      DATA w/.07750595,.07703982,.07611037,.07472317,.07288658,.07061165
     1,.06791204,.06480401,.06130624,.05743977,.05322785,.04869581,.0438
     27091,.03878217,.03346019,.02793701,.02224585,.01642106,.01049828,.
     300452128/
C
C     ---------------
      K=0
      IF(MODE.LE.2) GO TO 12
C
C     ----- SOLUTION FOR NON-EQUILIBRIUM TRANSPORT (MODEL B) -----
      DO 2 I=6,10
      IF(INDEX(I-5).EQ.0) GO TO 2
      K=K+1
      B(I)=B(K)
    2 CONTINUE
      P=B(6)
      R=B(7)
      IF(MODE.GE.5) B(8)=1./R
      BETA=DMIN1(B(8),.9999D00)
      OMEGA=B(9)
      DO 10 J=1,NOB
      DO 8 M=1,2
      C=0.0
      T=X(J)+(1-M)*B(10)
      IF(T.LE.0.) GO TO 6
      A=DSQRT(1.+.05*P)
      T2=DMIN1(T,BETA*R*(1.+40.*(1.+A)/P))
      T1=DMAX1(0.D00,BETA*R*(1.+40.*(1.-A)/P))
      IF(T2.LE.T1) GO TO 6
      DO 4 I=1,20
      TAU=0.5*(T1+T2+(T2-T1)*XG(I))
      C=C+W(I)*CCO(P,R,BETA,OMEGA,T,TAU,MODE)
      TAU=0.5*(T1+T2+(T1-T2)*XG(I))
    4 C=C+W(I)*CCO(P,R,BETA,OMEGA,T,TAU,MODE)
      C=0.5*(T2-T1)*C
    6 IF(M.EQ.2) GO TO 8
      Y(J)=C
    8 CONTINUE
   10 Y(J)=Y(J)-C
      RETURN
C
C     ----- SOLUTION FOR EQUILIBRIUM TRANSPORT (MODEL A) -----
   12 DO 14 I=4,6
      IF(INDEX(I-3).EQ.0) GO TO 14
      K=K+1
```

MODEL

```
      B(I)=B(K)
   14 CONTINUE
      E=0.0
      P=B(4)
      R=B(5)
      DO 18 J=1,NOB
      DO 16 M=1,2
      C=0.0
      T=X(J)+(1-M)*B(6)
      IF(T.LE.0.) GO TO 18
      CM=0.5*(R-T)*DSQRT(P/(R*T))
      CP=0.5*(R+T)*DSQRT(P/(R*T))
      C=0.5*EXF(E,CM)+0.5*EXF(P,CP)
      IF(MODE.EQ.2) C=C+DSQRT(.3183099*P*T/R)*EXF(-CM*CM,E)-0.5*(2.+P+P*
     1T/R)*EXF(P,CP)
      IF(M.EQ.2) GO TO 18
      Y(J)=C
   16 CONTINUE
   18 Y(J)=Y(J)-C
      RETURN
      END
```

CCO

```
      FUNCTION CCO(P,R,BETA,OMEGA,T,TAU,MODE)
C
C     PURPOSE: TO CALCULATE THE ARGUMENT UNDER THE INTEGRAL SIGN
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CCO=0.0
      BER=BETA*R
      CM=P*(BER-TAU)**2/(4.*BER*TAU)
      C=.2820948*DSQRT(P*BER/TAU**3)*DEXP(-CM)
      IF((MODE.EQ.3).OR.(MODE.EQ.5)) GO TO 2
      CP=(BER+TAU)*DSQRT(P/(4.*BER*TAU))
      C=2.*C*TAU/BER-0.5*P*EXF(P,CP)/BER
    2 IF(C.LT.1.D-07) RETURN
      EPSI=OMEGA*TAU/BER
      ETHA=OMEGA*(T-TAU)/(R-BER)
      CCO=C*GOLD(EPSI,ETHA)
      RETURN
      END
```

GOLD

```
      FUNCTION GOLD(X,Y)
C
C     PURPOSE: TO CALCULATE J(X,Y)
C
      IMPLICIT REAL*8(A-H,O-Z)
      GOLD=0.0
      BF=0.0
      E=2.*DSQRT(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.)
      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
    4 GXY=GXY+GY*GZ
      GOLD=GXY*DEXP(-X-Y)
      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*DEXP(-Z)
      P=1./(1.+.3275911*(DA-DB))
      ERF=P*(.2548296-P*(.2844967-P*(1.421414-P*(1.453152-P*1.061405))))
      P=0.25/E
      CO=1.-1.772454*(DA-DB)*ERF
      C1=0.5-Z*CO
      C2=0.75-Z*C1
      C3=1.875-Z*C2
      C4=6.5625-Z*C3
      SUM=.1994711*(A-B)*P*(CO+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
```

EXF

```
      FUNCTION EXF(A,B)
C
C     PURPOSE: TO CALCULATE EXP(A) ERFC(B)
C
      IMPLICIT REAL*8 (A-H,O-Z)
      EXF=0.0
      IF((DABS(A).GT.170.).AND.(B.LE.0.)) RETURN
      IF(B.NE.0.0) GO TO 1
      EXF=DEXP(A)
      RETURN
    1 C=A-B*B
      IF((DABS(C).GT.170.).AND.(B.GT.0.)) RETURN
      IF(C.LT.-170.) GO TO 4
      X=DABS(B)
      IF(X.GT.3.0) GO TO 2
      T=1./(1.+.3275911*X)
      Y=T*(.2548296-T*(.2844967-T*(1.421414-T*(1.453152-1.061405*T))))
      GO TO 3
    2 Y=.5641896/(X+.5/(X+1./(X+1.5/(X+2./(X+2.5/(X+1.))))))
    3 EXF=Y*DEXP(C)
    4 IF(B.LT.0.0) EXF=2.*DEXP(A)-EXF
      RETURN
      END
```

MATINV

```
      SUBROUTINE MATINV(A,NP,B)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(5,5),B(10),INDEX(5,2)
      DO 2 J=1,5
    2 INDEX(J,1)=0
      I=0
    4 AMAX=-1.0
      DO 12 J=1,NP
      IF(INDEX(J,1)) 12,6,12
    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
   12 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
```