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DETERMINING TRANSPORT PARAMETERS FROM
SOLUTE DISPLACEMENT EXPERIMENTS

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DETERMINING TRANSPORT PARAMETERS FROM SOLUTE DISPLACEMENT EXPERIMENTS^{1/}

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ABSTRACT

Predictions of solute transport in the field are generally based upon convective-dispersive type transport equations. The one-dimensional form of this equation contains two parameters which must be determined beforehand. They are the dispersion coefficient and a distribution coefficient, the latter accounting for adsorption or exchange between liquid and solid phases. Both coefficients can be obtained by fitting an analytical solution of the one-dimensional convective-dispersive transport equation to observed column effluent data. This paper describes a non-linear least-squares curve-fitting computer model which may be used for that purpose. A listing of the program is given in an appendix.

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INTRODUCTION

Predictions of solute transport in the field are often obtained by solving convective-dispersive type transport equations. For a one-dimensional system at constant water content and steady-state flow, the appropriate equation is

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

where

c = solute concentration,
D = dispersion coefficient,
R = retardation factor
t = time,
v = average pore-water velocity,
x = distance.

The parameter R in Eq. [1] accounts for possible interactions between the chemical and the solid phase of the soil. For the special case of chemical adsorption or exchange, the retardation factor is given by (van Genuchten et al., 1974)

$$R = 1 + \frac{\rho k}{\theta} \quad [2]$$

where

k = distribution coefficient,
 θ = volumetric water content,
 ρ = soil bulk density.

Equation [2] assumes that the adsorption or exchange reactions are always instantaneous (equilibrium adsorption). If there is no interaction between the chemical and the solid phase, k in Eq. [2] 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 tracer is subject to anion

exclusion (e.g., for chloride movement in fine-textured soils), or when immobile liquid regions are present which do not contribute to convective solute transport (water in dead-end pores or inside dense aggregates). In the case of anion exclusion, $(1-R)$ can be viewed as the relative anion exclusion volume, and $(-k)$ as the specific anion exclusion volume (e.g., expressed in cm^3 water per gram of soil).

Equation [1] contains two parameters (R and D) which need to be quantified before the equation can be used for actual prediction purposes. Estimates for these two parameters are often obtained by analyzing experimental column effluent curves. Several methods of analysis are available for that purpose. Rifai et al. (1956), for example, proposed a method for calculating D from the slope of a breakthrough curve. Rose and Passioura (1971) and Passioura et al. (1970) discuss a procedure which allows D and R to be determined from a plot of $\ln(t)$ versus c on probability paper. Agneessens et al. (1978) used the method of moments to obtain D from pulse-type effluent curves. Another method, probably the most accurate one, is based upon a least-squares analysis of the effluent data (Elprince and Day, 1977; Laudelout and Dufey, 1977; Agneessens et al., 1978; Le Renard, 1979). For that purpose an appropriate analytical solution of Eq. [1] is fitted to the effluent data, thereby allowing D and R to be estimated simultaneously from the experimental data. This method is further discussed in this paper.

REVIEW OF ANALYTICAL SOLUTIONS

Several analytical solutions of Eq. [1] exist, each one based upon a different set of initial and boundary conditions. Appendix A lists five analytical solutions which are the most useful for the purpose of analyzing effluent data. It is noted here that each set of boundary conditions involves different assumptions regarding the physics of the column displacement experiment. This paper does not deal with the advantages and disadvantages of each boundary condition, but rather will use each analytical solution as a basis for estimating R and D from observed effluent data.

The different analytical solutions in Appendix A are expressed in terms of the original variables (x , t , R , v , D). For an analysis of the

effluent data it is more convenient to introduce the dimensionless variable

$$T = vt/L, \quad [3]$$

and the dimensionless group

$$P = vL/D, \quad [4]$$

where T is the number of pore volumes, P is the column Peclet number, and L is the column length. The effluent concentrations at $x=L$, $c_e(T)$, can then be represented by much simpler equations. Appendix B gives expressions for the effluent concentration for each of the five analytical solutions given in Appendix A.

The analytical solutions in Appendices A and B are applicable only to column experiments where the tracer is applied continuously at the inlet position (continuous tracer application). For pulse-type applications, the expressions must be replaced by

$$c^*(x,t) = \begin{cases} c(x,t) & 0 < t \leq t_1 \\ c(x,t) - c(x,t-t_1) & t > t_1 \end{cases} \quad [5]$$

$$c_e^*(T) = \begin{cases} c_e(T) & 0 < T \leq T_1 \\ c_e(T) - c_e(T-T_1) & T > T_1 \end{cases} \quad [6]$$

where

t_1 = time length of tracer pulse added to column,

T_1 = vt_1/L ,

$c^*(x,t)$ = concentration for pulse-type application.

$c_e^*(T)$ = effluent concentration for pulse-type application.

DETERMINING P AND R FROM THE EFFLUENT CURVE

A computer program was written which allows one to fit any of the five analytical solutions for c_e (or c_e^*) to observed effluent data. The program is a simplification of the multi-purpose, non-linear, least-squares program of Meeter (1964). The curve-fitting technique uses the maximum neighborhood method of Marquardt (1963), which is based upon an optimum interpolation between Taylor series expansions and the method of steepest descent. A detailed description of this particular technique is given in 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. When a pulse-type tracer effluent curve is present (c_e^*), information is also needed about the dimensionless pulse length, T_1 . Although T_1 is often available from the experimental conditions, it is often more convenient (and accurate) to also estimate this parameter from the experimental curve. The computer program therefore allows both a two-parameter (P and R, P and T_1 , or R and T_1) or a three-parameter (P, R, and T_1) curve-fitting to be carried out. Appendix C gives a short description and listing of the program.

APPLICATIONS

The accuracy of the curve-fitting program was first tested by fitting P and R to three hypothetical effluent curves with known values of P and R. The analytical solution of Case SI-1 in Appendix B (Eq. [B2]) was used to generate these "observed" curves. Calculated curves were obtained for $P = 10, 40, \text{ and } 400$, and $R = 1$. The datapoints in each case were distributed in equal intervals along the T-axis, and located between relative concentrations of 0.05 and 0.95 (34 datapoints for $P=10$, 19 points for $P=40$, and 12 points for $P=400$). Table 1 gives the curve-fitted values of P and R for all five analytical solutions. As expected, the input values of P and R were duplicated exactly when the analytical solution of Case SI-1 was fitted to the "observed" effluent curve. The curve-fitted values of P and R for the other analytical solutions, however, deviate from the input values. This, of course,

Table 1. Curve-fitted values of P and R for the five analytical solutions in Appendix B. The "observed" effluent curves were based on Eq. [B2], with $R=1$, and $P = 10, 40$, and 400 , respectively.

| Input value of P (SI-1) | ----- FITTED VALUE OF P ----- | | | | |
|-------------------------------|-------------------------------|--------------|--------------|--------------|--------------|
| | Case INF | Case SI-1 | Case SI-2 | Case FN-1 | Case FN-2 |
| 10.00 | 10.46 | 10.00 | 9.58 | 9.11 | 8.92 |
| 40.00 | 40.49 | 40.00 | 39.52 | 39.40 | 38.96 |
| 400.00 | 400.45 | 399.96 | 399.46 | 399.45 | 400.00 |

| Input value of P (SI-1) | ----- FITTED VALUE OF R ----- | | | | |
|-------------------------------|-------------------------------|--------------|--------------|--------------|--------------|
| | Case INF | Case SI-1 | Case SI-2 | Case FN-1 | Case FN-2 |
| 10.00 | 0.911 | 1.000 | 0.904 | 1.124 | 0.999 |
| 40.00 | 0.976 | 1.000 | 0.975 | 1.026 | 1.000 |
| 400.00 | 0.998 | 1.000 | 0.998 | 1.003 | 0.999 |

is to be expected since each analytical solution is based upon different boundary conditions. Differences between fitted and input values are greatest when P is small, i.e., for short soil columns (Table 1).

A second example considers the movement of Chromium through sand (Wierenga, 1980; unpublished data). Observed effluent data from the 5-cm long soil column are shown in Fig. 1. The analytical solutions of Cases SI-2 and FN-2 were fitted to these data. Results of the two-parameter curve-fittings are given in Table 2. The solid line in Fig. 1 represents the fitted analytical solution for Case SI-2. The fitted curve for FN-2 was found to be essentially the same as for SI-2, even though the estimated parameters P and R are different (Table 2). By making use of Eq. [4] and [2], it is possible to obtain also estimates for the dispersion coefficient (D) and the distribution constant (k). Table 2 shows that the values of D and k are somewhat different for the two analytical models. The differences between the estimated values could have been made smaller if a longer soil column were used for the displacement experiment (see also Table 1).

A third example considers the movement of a pulse of Chloride through Norge Loam (Davidson, 1973; unpublished data). Figure 2 com-

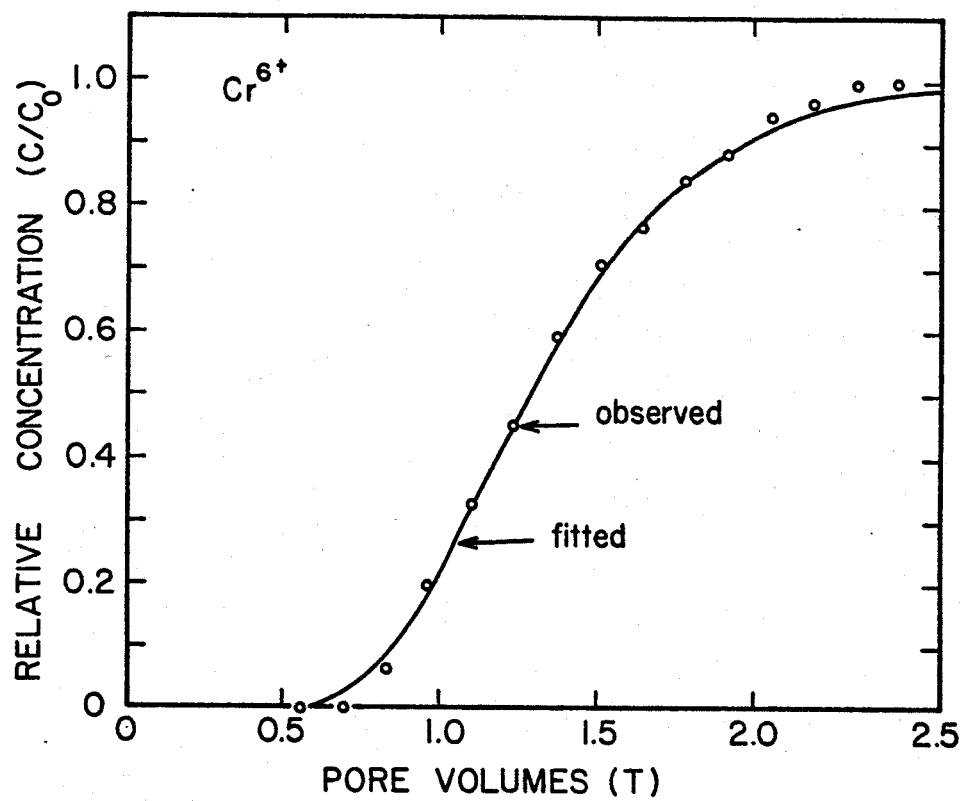


Fig. 1. Observed and curve-fitted breakthrough curves for Chromium movement through sand (example 2).

compares the observed and fitted effluent curves (Case SI-2). The fitted curve for Case SI-1 was again essentially the same as for Case FN-2. In this case all three parameters (P , R , and T_1) were fitted to the data (Table 2). Note that the estimated values of P are much higher than for the previous experiment. The value of R is less than 1, indicating some anion exclusion. The specific anion exclusion volume ($-k$) is about 0.02 cm^3 water per gram of soil (Table 2).

Table 2. Measured and curve-fitted parameters for two column displacement experiments.

| Experiment | 2A | 2B | 3A | 3B |
|-------------------------------------|------------------|------------------|---------------|---------------|
| Tracer | Cr^{6+} | Cr^{6+} | Cl^- | Cl^- |
| Model | SI-2 | FN-2 | SI-2 | FN-2 |
| $\theta \text{ (cm}^3/\text{cm}^3)$ | 0.184 | 0.184 | 0.3626 | 0.3626 |
| $\rho \text{ (g/cm}^3)$ | 1.679 | 1.679 | 1.527 | 1.527 |
| $v \text{ (cm/day)}$ | 19.64 | 19.64 | 14.23 | 14.23 |
| $L \text{ (cm)}$ | 5.0 | 5.0 | 30.0 | 30.0 |
| $P \text{ (fitted)}$ | 19.19 | 18.59 | 287.4 | 287.4 |
| $R \text{ (fitted)}$ | 1.281 | 1.349 | 0.918 | 0.918 |
| $T_1 \text{ (fitted)}$ | - | - | 0.408 | 0.408 |
| $T_1 \text{ (measured)}$ | - | - | 0.425 | 0.425 |
| $D \text{ (cm}^2/\text{day)}$ | 5.12 | 5.28 | 1.49 | 1.49 |
| $k \text{ (cm}^3/\text{g)}$ | 0.031 | 0.038 | -0.019 | -0.019 |

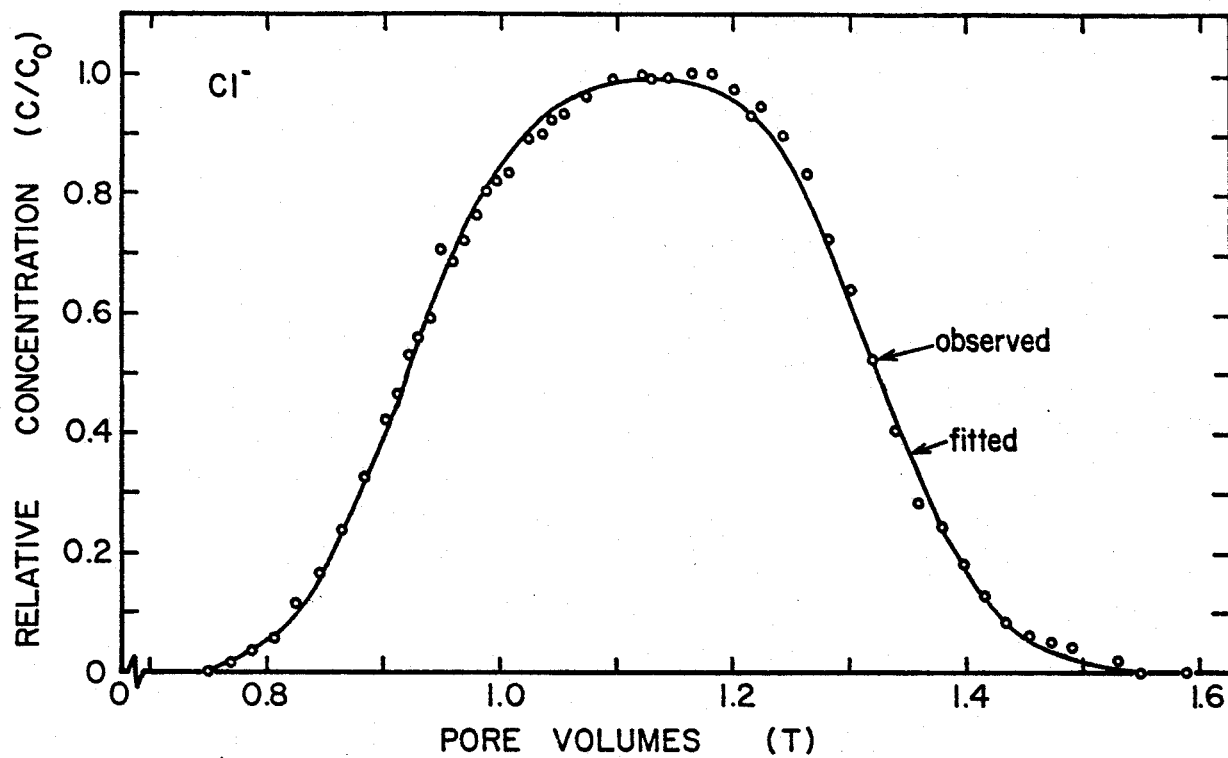


Fig. 2. Observed and curve-fitted effluent curves for Chloride movement through Norge loam (example 3).

CONCLUSIONS

The least-squares computer model discussed in this report provides an easy to use, efficient and accurate means of fitting various transport parameters to observed column effluent data. The unknown parameters include the column Peclet number, P , the retardation factor, R , and the dimensionless pulse time, T_1 . The three examples, furthermore, demonstrate that the use of different analytical solutions can lead to large differences between the curve-fitted P - and R -values. These differences are most significant when P is small, i.e., for relatively short soil columns.

REFERENCES

- Agneessens, J.-P., P. Dreze, and L. Sine. 1978. Modélisation de la migration d'éléments dans les sols. II. Détermination du coefficient de dispersion et de la porosité efficace. *Pedologie*, 27: 373-388.
- Brenner, H. 1962. The diffusion model of longitudinal mixing in beds of finite length. Numerical values. *Chem. Eng. Sci.* 17: 229-243.
- Cleary, R. W., and D. D. Adrian. 1973. Analytical solution of the convective dispersive equation for cation adsorption in soils. *Soil Sci. Soc. Am. Proc.* 37: 197-199.
- Danckwerts, P. V. 1953. Continuous flow systems. *Chem. Eng. Sci.* 2: 1-13.
- Daniel, C., and F. S. Wood. 1973. *Fitting Equations to Data*. Wiley-Interscience, New York. 350 p.
- Elprince, A. M., and P. R. Day. 1977. Fitting solute breakthrough equations to data using two adjustable parameters. *Soil Sci. Soc. Am. J.* 41: 39-41.
- Laudelout, H., and J. E. Duffy. 1977. Analyse numérique des expériences de lixiviation en sol homogène. *Ann. Agron.* 28: 65-73.
- Lapidus, L., and N. R. Amundson. 1952. Mathematics of adsorption in beds. IV. The effect of longitudinal diffusion in ion exchange chromatographic columns. *J. Phys. Chem.* 56: 984-988.
- Le Renard, J. 1979. Description d'une méthode de détermination du coefficient de dispersion hydrodynamique longitudinal en milieu poreux homogène saturé en eau. II. Utilisation d'un modèle mathématique à trois paramètres dont un phénoménologique. *Ann. Agron.* 30: 109-119.
- Lindstrom, F. T., R. Haque, V. H. Freed, and L. Boersma. 1967. Theory on the movement of some herbicides in soils: linear diffusion and convection of chemicals in soils. *Environ. Sci. Technol.* 1: 561-565.
- Marquardt, D. W. 1963. An algorithm for least-squares estimation of non-linear parameters. *J. Soc. Ind. Appl. Math.* 11: 431-441.
- Meeter, D. A. 1964. Non-linear least-squares (Gaushaus). Univ. of Wisconsin Computing Center. Program revised 1966.

- Passioura, J. B., D. A. Rose, and K. Haszler. 1970. Lognorm: a program for analysing experiments on hydrodynamic dispersion. Technical Memorandum 70/6, CSIRO, Div. of Land Res., Canberra.
- Rifai, M. N. E., W. J. Kaufman, and D. K. Todd. 1956. Dispersion phenomena in laminar flow through porous media. Sanitary Eng. Res. Lab., Univ. of Calif., Berkeley. Inst. of Eng. Res. Ser. No. 93(2).
- Rose, D. A., and J. B. Passioura. 1971. The analysis of experiments on hydrodynamic dispersion. Soil Sci. 111: 252-257.
- van Genuchten, M.Th., J.M. Davidson, and P.J. Wierenga. 1974. An evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media. Soil Sci. Soc. Am. Proc. 38: 29-35.
- van Genuchten, M. Th., and W. J. Alves. 1980. A compendium of available analytical solutions of the one-dimensional convective-dispersive transport equation. U. S. Salinity Laboratory, Riverside, California.

APPENDIX A. Analytical solutions of the one-dimensional convective-dispersive transport equation (Eq. [1] for different initial and boundary conditions.

Case INF (Infinite System).

The solution of Eq. [1], subject to

$$c(x,0) = \begin{cases} 1 & x < 0 \\ 1/2 & x = 0 \\ 0 & x > 0 \end{cases} \quad [A1]$$

$$c(-\infty, t) = c_o \quad [A2]$$

$$c(\infty, t) = 0 \quad [A3]$$

is (Danckwerts, 1953)

$$c/c_o = \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right] \quad [A4]$$

where erfc is the complementary error function.

Case SI-1 (Semi-infinite system, first-type boundary condition).

The solution of Eq. [1], subject to

$$c(x,0) = 0 \quad (x > 0) \quad [A5]$$

$$c(0,t) = c_o \quad [A6]$$

$$\frac{\partial c}{\partial x}(\infty, t) = 0 \quad [A7]$$

is (Lapidus and Amundson, 1952)

$$c/c_o = \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right] + \frac{1}{2} \exp(vx/D) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{1/2}} \right] \quad [A8]$$

Case SI-2 (Semi-infinite system, third-type boundary condition).

The solution of Eq. [1], subject to

$$c(x,0) = 0 \quad (x > 0) \quad [A9]$$

$$\left(-D \frac{\partial c}{\partial x} - vc \right) \Big|_{x=0} = vc_o \quad [A10]$$

$$\frac{\partial c}{\partial x} (\infty, t) = 0 \quad [A11]$$

is (Lindstrom et al., 1967)

$$\begin{aligned} c/c_o = & \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right] + \left(\frac{v^2 t}{\pi DR} \right)^{1/2} \exp \left[- \frac{(Rx - vt)^2}{4DRt} \right] \\ & - \frac{1}{2} \left(1 + \frac{vx}{D} + \frac{v^2 t}{DR} \right) \exp(vx/D) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{1/2}} \right]. \end{aligned} \quad [A12]$$

Case FN-1 (Finite profile, first-type boundary condition).

The solution of Eq. [1], subject to

$$c(x,0) = 0 \quad (x > 0) \quad [A13]$$

$$c(0,t) = c_o \quad [A14]$$

$$\frac{\partial c}{\partial x} (L,t) = 0 \quad [A15]$$

is (Cleary and Adrian, 1973)

$$c/c_o = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin(\frac{\beta_m x}{L}) \exp \left[\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\beta_m^2 Dt}{L^2 R} \right]}{\beta_m^2 + \left(\frac{vL}{2D} \right)^2 + \frac{vL}{2D}} \quad [A16]$$

where the eigenvalues β_m are the positive roots of

$$\beta_m \cot(\beta_m) + \frac{vL}{2D} = 0. \quad [A17]$$

The series solution converges very slowly for large values of (vL/D) and/or small values of (vt/RL) . For

$$\frac{vL}{D} > 5 + 40 \frac{vt}{RL} \quad [A18]$$

or

$$\frac{vL}{D} > 100 \quad [A19]$$

the following approximation gives very accurate answers (van Genuchten and Alves, 1980)

$$\begin{aligned} c/c_o = & \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{1/2}} \right] + \frac{1}{2} \exp(vx/D) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{1/2}} \right] \\ & + \frac{1}{2} \left[2 + \frac{v(2L - x)}{D} + \frac{v^2 t}{DR} \right] \exp(vL/D) \operatorname{erfc} \left[\frac{R(2L-x) + vt}{2(DRt)^{1/2}} \right] \\ & - \left(\frac{v^2 t}{\pi DR} \right)^{1/2} \exp \left[\frac{vL}{D} - \frac{R}{4Dt} \left(2L-x + \frac{vt}{R} \right)^2 \right]. \end{aligned} \quad [A20]$$

Case FN-2 (Finite profile, third-type boundary condition).

The solution of Eq. [1], subject to

$$c(x,0) = 0 \quad (x > 0) \quad [A21]$$

$$\left(-D \frac{\partial c}{\partial x} + vc \right) \Big|_{x=0} = vc_0 \quad [A22]$$

$$\frac{\partial c}{\partial x} (L,t) = 0 \quad [A23]$$

is (Brenner, 1962)

$$c/c_0 = 1 - \sum_{m=1}^{\infty} \frac{\frac{2vL}{D} \beta_m \left[\beta_m \cos\left(\frac{\beta_m x}{L}\right) + \frac{vL}{2D} \sin\left(\frac{\beta_m x}{L}\right) \exp\left[\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\beta_m^2 Dt}{L^2 R}\right] \right]}{\left[\beta_m^2 + \left(\frac{vL}{2D}\right)^2 + \frac{vL}{D} \right] \left[\beta_m^2 + \left(\frac{vL}{2D}\right)^2 \right]} \quad [A24]$$

where the eigenvalues of β_m are the positive roots of

$$\beta_m \cot(\beta_m) - \frac{\beta_m^2 D}{vL} + \frac{vL}{4D} = 0 \quad [A25]$$

Also this series solution converges slowly for large values of (vL/D) and/or small values of (vt/RL) . For conditions [A18,19] the following approximate solution provides accurate answers (Brenner, 1962):

$$\begin{aligned} c/c_0 = & \frac{1}{2} \operatorname{erfc}\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right] + \left(\frac{v^2 t}{\pi DR}\right)^{1/2} \exp\left[-\frac{(Rx - vt)^2}{4DRt}\right] \\ & - \frac{1}{2} \left(1 + \frac{vx}{D} + \frac{v^2 t}{DR}\right) \exp(vx/D) \operatorname{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right] \\ & + \left(\frac{4v^2 t}{\pi DR}\right)^{1/2} \left[1 + \frac{v}{4D} \left(2L - x + \frac{vt}{R}\right)\right] \exp\left[\frac{vL}{D} - \frac{R}{4Dt} \left(2L - x + \frac{vt}{R}\right)^2\right] \\ & - \frac{v}{D} \left[2L - x + \frac{3vt}{2R} + \frac{v}{4D} \left(2L - x + \frac{vt}{R}\right)^2\right] \exp(vL/D) \operatorname{erfc}\left[\frac{R(2L - x) + vt}{2(DRt)^{1/2}}\right] \end{aligned} \quad [A26]$$

APPENDIX B. Effluent concentration, $c_e(T)$, for each of the five analytical solutions given in Appendix A.

Case INF (Infinite system)

$$c_e/c_o = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R-T) \right] \quad [B1]$$

Case SI-1 (Semi-infinite system, first-type boundary condition).

$$c_e/c_o = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R-T) \right] + \frac{1}{2} \exp(P) \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R+T) \right] \quad [B2]$$

Case SI-2 (Semi-infinite system, third-type boundary condition).

$$c_e/c_o = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R-T) \right] + \left(\frac{PT}{\pi R} \right)^{1/2} \exp \left[- \frac{P}{4RT} (R-T)^2 \right] \\ - \frac{1}{2} \left(1 + P + \frac{PT}{R} \right) \exp(P) \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R+T) \right] \quad [B3]$$

Case FN-1 (Finite system, first-type boundary condition).

$$c_e/c_o = 1 - \sum_{m=1}^{\infty} \frac{2 \beta_m \sin(\beta_m) \exp \left[\frac{P}{2} - \frac{PT}{4R} - \frac{\beta_m^2 T}{PR} \right]}{\beta_m^2 + \frac{P^2}{4} + \frac{P}{2}} \quad [B4]$$

where the eigenvalues β_m are the positive roots of

$$\beta_m \cot(\beta_m) + \frac{P}{2} = 0 \quad [B5]$$

For $P > 5 + 40 T$ or $P > 100$, the following approximation is used

$$c_e/c_o = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R-T) \right] - \left(\frac{PT}{\pi R} \right)^{1/2} \exp \left[- \frac{P}{4RT} (R-T)^2 \right]$$

$$+ \frac{1}{2} \left(3 + P + \frac{PT}{R} \right) \exp(P) \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R+T) \right] \quad [B6]$$

Case FN-2 (Finite system, third-type boundary condition).

$$c_e/c_o = 1 - \sum_{m=1}^{\infty} \frac{2 \beta_m \sin(\beta_m) \exp \left[\frac{P}{2} - \frac{PT}{4R} - \frac{\beta_m^2 T}{PR} \right]}{\beta_m^2 + \frac{P^2}{4} + P} \quad [B7]$$

where the eigenvalues β_m are the positive roots of

$$P \beta_m \cot(\beta_m) - \beta_m^2 + \frac{P^2}{4} = 0 \quad [B8]$$

The approximate solution for $P > 5 + 40T$ or $P > 100$ is

$$\begin{aligned} c_e/c_o = & \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R-T) \right] \\ & + \left(\frac{PT}{\pi R} \right)^{1/2} \left(3 + \frac{P}{2} + \frac{PT}{2R} \right) \exp \left[- \frac{P}{4RT} (R-T)^2 \right] \\ & - \frac{1}{2} \left[1 + 3P + \frac{4PT}{R} + \frac{P^2}{2R^2} (R+T)^2 \right] \exp(P) \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R+T) \right] \end{aligned} \quad [B9]$$

APPENDIX C. CFITM, a computer program for calculating transport parameters from observed solute effluent curves.

This appendix gives a brief description and listing of CFITM, a computer program for calculating the Peclet number (P), the retardation factor (R) and, if needed, the dimensionless pulse time (T_1) from observed effluent data. The program does this by means of a least-squares fit of any of the five analytical expressions in Appendix B to observed effluent data.

The program consists of a main program (MAIN), four subroutines (MODEL, CONC, EIGEN, and MATINV), and one function (EXF). Most of the calculations for the least-squares analysis are carried out in MAIN, including input and output instructions, calculation of a correlation matrix for the different coefficients, and calculation of a 95% confidence interval for each coefficient. Subroutine MODEL calculates the exit concentration for each of the five models given in Appendix B. The choice of the model is governed by the variable MODE: MODE = 0 for Case INF, 1 for SI-1, 2 for SI-2, 3 for FN-1, and 4 for Case FN-2. The analytical solution for Cases FN-1 and FN-2 (MODE = 3,4) requires the evaluation of series (see Appendix B). These calculations are carried out in subroutine CONC. The approximate solutions for FN-1 and FN-2 are also evaluated in CONC. The eigenvalues, β_m , needed for the series solutions, are calculated in subroutine EIGEN. Subroutine MATINV gives a matrix inversion scheme needed for the least-squares analysis in MAIN. The function EXF, finally, is used to calculate the complementary error function (erfc), the exponential function (exp), or the product of erfc and exp.

Table C1 gives a list of the most significant program variables. Table C2 gives instructions regarding set-up of the data cards. The actual input data for example 2 (Chromium transport through sand) are shown in Table 3. The computer output for Example 2 is given in Table C4, while the listing of the program is given in Table C5.

An extra comment is needed for the vector B(I) in Table C1. This vector contains the estimated values of the three coefficients P, R, and T_1 (in that order). If a coefficient is known and a two-parameter curve-fitting is carried out, the measured value of that coefficient

should be entered on the fifth data card (see Tables C2 and C3). For a continuous tracer application (no pulse of solute), a large dummy value should be assigned to T_1 . This value must exceed all measured pore volumes, $Y(I)$. For Example 2 a dummy value of 100 was assigned to T_1 (card 5 in Table C3). Actually, any value higher than 2.463 could have been used (see card 21 in Table C3).

Table C1. List of the most significant variables in CFITM.

| <u>VARIABLE</u> | <u>DEFINITION</u> |
|-----------------|--|
| B(I) | Vector containing estimates of the coefficients (P, R, T_1). |
| BI(I) | Vector of coefficient names (P, R, T_1). |
| EXF(A,B) | Function to calculate $\exp(A) \operatorname{erfc}(B)$. |
| G(I) | Eigenvalues (β_m) for Cases FN-1 and FN-2 (MODE = 3,4). |
| INDEX(I) | Index for each coefficient. If INDEX(I) = 0, the coefficient is known. If INDEX(I) = 1, the coefficient is assumed to be unknown and fitted to the data. For example, if INDEX(1) = 1, INDEX(2) = 0, and INDEX(3) = 1, the coefficients P and T_1 are fitted to the data, while R is assumed to be known (for example from batch equilibrium studies). At least two coefficients need to be unknown. |
| MIT | Maximum number of iterations in least-squares analysis. |
| MODE | Model number for the five analytical solutions: MODE = 0 for case INF (infinite system, MODE = 1 for Case SI-1 (semi-finite system, first-type surface boundary condition), MODE = 2 for Case SI-2 (semi-infinite system, third-type boundary conditions), MODE = 3 for Case FN-1 (finite system, first-type boundary condition), and MODE = 4 for Case FN-2 (finite system, third-type boundary condition). |
| NC | Number of cases considered. |
| NDATA | Data input code: if NDATA = 1, new data are read in, if NDATA = 0, the same data (or a part of them) are used for the new case. This code allows one to fit the same data to two different models (see Tables C3 and C4). |
| NIT | Iteration number during least-squares analysis. |
| NOB | Number of observations (must not 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 C2. Data input instructions.

| <u>CARD</u> | <u>COLUMNS</u> | <u>FORMAT</u> | <u>VARIABLE</u> | <u>COMMENTS</u> |
|-------------|----------------|---------------|-----------------|---|
| 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 4 through 7 are not needed for that particular case. |
| 2 | 1-5 | I5 | MODE | Model number. |
| 2 | 5-10 | 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 T_1 . |
| 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 T_1 . |
| 6 | 1-5 | I5 | INDEX(1) | Index for each coefficient. |
| 6 | 6-10 | I5 | INDEX(2) | See Table C1 for explanation. |
| 6 | 11-15 | I5 | INDEX(3) | |
| 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 C3. Data input for example 2.

| | | | | | | |
|---------|------------|------------|------------|------------|------------|------------|
| | 0 | 1 | 2 | 3 | 4 | 5 |
| Column: | 1234567890 | 1234567890 | 1234567890 | 1234567890 | 1234567890 | 1234567890 |
| Card | | | | | | |

| | | | | |
|----|--------|-------|--|----|
| 1 | 2 | | | |
| 2 | 2 | 1 | 15 | 15 |
| 3 | | | EXAMPLE 2A: CHROMIUM (COLUMN NUMBER 4) | |
| 4 | PECLET | RF | PULSE | |
| 5 | 20.0 | 1.30 | 100.0 | |
| 6 | 1 | 1 | 0 | |
| 7 | 0.558 | 0.000 | | |
| 8 | 0.695 | 0.006 | | |
| 9 | 0.831 | 0.061 | | |
| 10 | 0.967 | 0.198 | | |
| 11 | 1.103 | 0.325 | | |
| 12 | 1.239 | 0.450 | | |
| 13 | 1.375 | 0.592 | | |
| 14 | 1.511 | 0.705 | | |
| 15 | 1.647 | 0.768 | | |
| 16 | 1.783 | 0.841 | | |
| 17 | 1.919 | 0.881 | | |
| 18 | 2.055 | 0.944 | | |
| 19 | 2.191 | 0.966 | | |
| 20 | 2.327 | 0.994 | | |
| 21 | 2.463 | 0.999 | | |
| 22 | 4 | 0 | 15 | 15 |
| 23 | | | EXAMPLE 2B: CHROMIUM (COLUMN NUMBER 4) | |

Table C4. Output for example 2.

```
*****
*
*      NON-LINEAR LEAST SQUARES ANALYSIS
*
*      SEMI-INFINITE PROFILE, 3-TYPE BC
*      EXAMPLE 2A CHROMIUM (COLUMN NUMBER 4)
*
*****
```

```
INITIAL VALUES OF COEFFICIENTS
=====
NO   NAME      INITIAL VALUE
1   PECLET     20.000
2   RF         1.300
3   PULSE      100.000
```

```
OBSERVED DATA
=====
OBS. NO.   PORE VOLUME   CONCENTRATION
1          0.5580        0.0
2          0.6950        0.0060
3          0.8310        0.0610
4          0.9670        0.1980
5          1.1030        0.3250
6          1.2390        0.4500
7          1.3750        0.5920
8          1.5110        0.7050
9          1.6470        0.7680
10         1.7830        0.8410
11         1.9190        0.8810
12         2.0550        0.9440
13         2.1910        0.9660
14         2.3270        0.9940
15         2.4630        0.9990
```

```
ITERATION   SSQ          PECLET      RF
0           0.0047356    20.00000    1.30000
1           0.0029914    19.03803    1.28139
2           0.0029844    19.19318    1.28138
3           0.0029844    19.18872    1.28137
```

```
CORRELATION MATRIX
=====
1 1.0000
2 0.2612 1.0000
```

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

| VARIABLE | NAME | VALUE | S.E. COEFF. | T-VALUE | 95% CONFIDENCE LIMITS | |
|----------|--------|----------|-------------|---------|-----------------------|---------|
| | PECLET | | | | LOWER | UPPER |
| 1 | | 19.18872 | 0.9535 | 20.12 | 17.1287 | 21.2488 |
| 2 | RF | 1.28137 | 0.0068 | 187.38 | 1.2666 | 1.2961 |

| -----ORDERED BY COMPUTER INPUT----- | | | | | | | | | |
|-------------------------------------|-------------|--------------------|--------|-----------|--------------------------------|-------------|--------------------|--------|-----------|
| NO | PORE VOLUME | CONCENTRATION OBS. | FITTED | RESI-DUAL | -----ORDERED BY RESIDUALS----- | | | | |
| | | | | | NO | PORE VOLUME | CONCENTRATION OBS. | FITTED | RESI-DUAL |
| 1 | 0.558 | 0.0 | 0.003 | -0.003 | 14 | 2.327 | 0.994 | 0.972 | 0.022 |
| 2 | 0.695 | 0.006 | 0.024 | -0.018 | 15 | 2.463 | 0.999 | 0.982 | 0.017 |
| 3 | 0.831 | 0.061 | 0.082 | -0.021 | 4 | 0.967 | 0.198 | 0.183 | 0.015 |
| 4 | 0.967 | 0.198 | 0.183 | 0.015 | 5 | 1.103 | 0.325 | 0.314 | 0.011 |
| 5 | 1.103 | 0.325 | 0.314 | 0.011 | 12 | 2.055 | 0.944 | 0.934 | 0.010 |
| 6 | 1.239 | 0.450 | 0.455 | -0.005 | 13 | 2.191 | 0.966 | 0.957 | 0.009 |
| 7 | 1.375 | 0.592 | 0.586 | 0.006 | 8 | 1.511 | 0.705 | 0.697 | 0.008 |
| 8 | 1.511 | 0.705 | 0.697 | 0.008 | 7 | 1.375 | 0.592 | 0.586 | 0.006 |
| 9 | 1.647 | 0.768 | 0.786 | -0.018 | 1 | 0.558 | 0.0 | 0.003 | -0.003 |
| 10 | 1.783 | 0.841 | 0.852 | -0.011 | 6 | 1.239 | 0.450 | 0.455 | -0.005 |
| 11 | 1.919 | 0.881 | 0.900 | -0.019 | 10 | 1.783 | 0.841 | 0.852 | -0.011 |
| 12 | 2.055 | 0.944 | 0.934 | 0.010 | 9 | 1.647 | 0.768 | 0.786 | -0.018 |
| 13 | 2.191 | 0.966 | 0.957 | 0.009 | 2 | 0.695 | 0.006 | 0.024 | -0.018 |
| 14 | 2.327 | 0.994 | 0.972 | 0.022 | 11 | 1.919 | 0.881 | 0.900 | -0.019 |
| 15 | 2.463 | 0.999 | 0.982 | 0.017 | 3 | 0.831 | 0.061 | 0.082 | -0.021 |

END OF PROBLEM
=====

```

*****
*
*      NCN-LINEAR LEAST SQUARES ANALYSIS
*
*      FINITE PROFILE, 3-TYPE BC
*      EXAMPLE 28 CHROMIUM (COLUMN NUMBER 4)
*
*****

```

```

OBSERVED DATA
=====
OBS. NO.      PORE VOLUME      CONCENTRATION
1             0.5580            0.0
2             0.6950            0.0060
3             0.8310            0.0610
4             0.9670            0.1980
5             1.1030            0.3250
6             1.2390            0.4500
7             1.3750            0.5920
8             1.5110            0.7050
9             1.6470            0.7680
10            1.7830            0.8410
11            1.9190            0.8910
12            2.0550            0.9440
13            2.1910            0.9660
14            2.3270            0.9940
15            2.4630            0.9990

```

```

ITERATION      SSQ      PECLET      RF
0             0.0141245    20.00000    1.30000
1             0.0030266    18.28417    1.34697
2             0.0029795    18.60950    1.34848
3             0.0029795    18.58894    1.34851
4             0.0029795    18.59020    1.34851

```

```

CORRELATION MATRIX
=====
1             1
2      1.0000    1.0000
      -0.2061

```

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

| VARIABLE | NAME | VALUE | S.E. COEFF. | T-VALUE | 95% CONFIDENCE LIMITS | |
|----------|--------|----------|-------------|---------|-----------------------|---------|
| 1 | PECLET | 18.59020 | 0.9509 | 19.55 | LOWER | UPPER |
| 2 | RF | 1.34851 | 0.0071 | 190.08 | 16.5359 | 20.6445 |
| | | | | | 1.3332 | 1.3638 |

| -----ORDERED BY COMPUTER INPUT----- | | | | | | | | | |
|-------------------------------------|-------------|--------------------|--------|-----------|----|-------------|--------------------|--------|-----------|
| NO | PORE VOLUME | CONCENTRATION OBS. | FITTED | RESI-DUAL | NO | PORE VOLUME | CONCENTRATION OBS. | FITTED | RESI-DUAL |
| 1 | 0.558 | 0.0 | 0.003 | -0.003 | 14 | 2.327 | 0.994 | 0.972 | 0.022 |
| 2 | 0.695 | 0.006 | 0.024 | -0.018 | 15 | 2.463 | 0.999 | 0.982 | 0.017 |
| 3 | 0.831 | 0.061 | 0.082 | -0.021 | 4 | 0.967 | 0.198 | 0.183 | 0.015 |
| 4 | 0.967 | 0.198 | 0.183 | 0.015 | 12 | 2.055 | 0.944 | 0.933 | 0.011 |
| 5 | 1.103 | 0.325 | 0.315 | 0.010 | 5 | 1.103 | 0.325 | 0.315 | 0.010 |
| 6 | 1.239 | 0.450 | 0.455 | -0.005 | 13 | 2.191 | 0.966 | 0.956 | 0.010 |
| 7 | 1.375 | 0.592 | 0.586 | 0.006 | 8 | 1.511 | 0.705 | 0.697 | 0.008 |
| 8 | 1.511 | 0.705 | 0.697 | 0.008 | 7 | 1.375 | 0.592 | 0.586 | 0.006 |
| 9 | 1.647 | 0.768 | 0.786 | -0.018 | 1 | 0.558 | 0.0 | 0.003 | -0.003 |
| 10 | 1.783 | 0.841 | 0.852 | -0.011 | 6 | 1.239 | 0.450 | 0.455 | -0.005 |
| 11 | 1.919 | 0.881 | 0.900 | -0.019 | 10 | 1.783 | 0.841 | 0.852 | -0.011 |
| 12 | 2.055 | 0.944 | 0.933 | 0.011 | 9 | 1.647 | 0.768 | 0.786 | -0.018 |
| 13 | 2.191 | 0.966 | 0.956 | 0.010 | 2 | 0.695 | 0.006 | 0.024 | -0.018 |
| 14 | 2.327 | 0.994 | 0.972 | 0.022 | 11 | 1.919 | 0.881 | 0.900 | -0.019 |
| 15 | 2.463 | 0.999 | 0.982 | 0.017 | 3 | 0.831 | 0.061 | 0.082 | -0.021 |

END OF PROBLEM

TABLE C5. Fortran listing of CFITM.

MAIN

```

C
C
C *****
C *
C *      NON-LINEAR LEAST-SQUARES ANALYSIS      CFITM
C *
C *      ----- INPUT INFORMATION -----
C *
C *      CARD 1: NUMBER OF CASES CONSIDERED: NC (15)
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) (415)
C *      CARD 3: INFORMATION CARD (20A4)
C *
C *      THE NEXT CARDS ARE READ IN ONLY IF NDATA=1
C *
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(15)
C *              =0 IF COEFFICIENT IS KNOWN (CONSTANT)
C *              =1 IF COEFFICIENT IS UNKNOWN
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)
C      DIMENSION Y(90),X(90),F(90),R(90),DELZ(90,5),B(10),E(5),TH(10),
C      IP(5),PHI(5),Q(5),LSORT(90),TB(10),A(5,5),BI(10),TITLE(20),D(5,5),
C      ZINDEX(5)
C      DATA STOPCR/0.0005/
C
C      ----- READ NUMBER OF CASES -----
C      READ(5,1006) NC
C      DO 120 NCASE=1,NC
C
C      WRITE(6,1000)
C
C      ----- READ INPUT PARAMETERS -----
C      READ(5,1006) MODE,NDATA,MIT,NOB
C      IF(MODE.EQ.0) WRITE(6,1021)
C      IF(MODE.EQ.1) WRITE(6,1022)
C      IF(MODE.EQ.2) WRITE(6,1023)
C      IF(MODE.EQ.3) WRITE(6,1024)
C      IF(MODE.EQ.4) WRITE(6,1025)
C      READ(5,1001) TITLE
C      WRITE(6,1002) TITLE
C      IF(NDATA.EQ.0) GO TO 10

```

MAIN

```

C      ----- READ COEFFICIENTS NAMES -----
C      READ(5,10C4) (BI(I),I=1,6)
C
C      ----- READ INITIAL ESTIMATES -----
C      READ(5,10C5) (B(I),I=4,6)
C
C      ----- READ INDICES -----
C      READ(5,10C6) (INDEX(I),I=1,3)
      WRITE(6,1007)
      DO 4 I=1,3
        J=2*I-1
4      WRITE(6,1008) I,BI(J),BI(J+1),B(I+3)
C
C      ----- READ AND WRITE EXPERIMENTAL DATA -----
C      DO 6 I=1,NOB
6      READ(5,10C5) X(I),Y(I)
10     WRITE(6,1009)
      DO 12 I=1,NCB
12     WRITE(6,1010) I,X(I),Y(I)
C
C      -----
      NP=0
      DO 14 I=4,6
        TB(I)=B(I)
        IF(INDEX(I-3).EQ.0) GO TO 14
        NP=NP+1
        K=2*NP-1
        J=2*I-7
        BI(K)=BI(J)
        BI(K+1)=BI(J+1)
        B(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
        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

```

MAIN

```

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
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-1.0)80,80,74
74 IF(ANGLE-30.0)76,76,78

```


MAIN

```
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(D(I,I))
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(NCB-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,NCB
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
```

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```

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(NCB+1-I)
118 WRITE(6,1018) I,X(I),Y(I),F(I),R(I),J,X(J),Y(J),F(J),R(J)
120 WRITE(6,1020)

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,I3(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(/11X,'CORRELATION MATRIX'/11X,18(1H=)/14X,10(4X,I2,5X))
1014 FORMAT(11X,I3,1C(2X,F7.4,2X))
1015 FORMAT(1H1,10X,'NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS'
1/11X,48(1H=)/72X,'95% CONFIDENCE LIMITS'/11X,'VARIABLE',4X,'NAME'
2,8X,'VALUE',8X,'S.E. COEFF.',3X,'T-VALUE',5X,'LOWER',10X,'UPPER')
1016 FORMAT(14X,I2,6X,A4,A2,2X,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,'INFINITE PROFILE',54X,1H*)
1022 FORMAT(11X,1H*,10X,'SEMI-INFINITE PROFILE, 1-TYPE BC',38X,1H*)
1023 FORMAT(11X,1H*,10X,'SEMI-INFINITE PROFILE, 3-TYPE BC',38X,1H*)
1024 FORMAT(11X,1H*,10X,'FINITE PROFILE, 1-TYPE BC',45X,1H*)
1025 FORMAT(11X,1H*,10X,'FINITE PROFILE, 3-TYPE BC',45X,1H*)
STOP
END

```

EIGEN

SUBROUTINE EIGEN(G,P,MODE)

C
C
C

PURPOSE: TO CALCULATE THE EIGENVALUES

IMPLICIT REAL*8 (A-H,O-Z)

DIMENSION G(20)

BETA=0.1

S=0.0

IF(MODE.EQ.4) S=1.0

DO 4 I=1,20

J=0

1 J=J+1

IF(J.GT.15) GO TO 3

DELTA=-0.2*(-0.5)**J

2 BET2=BETA

BETA=BETA+DELTA

A=BET2*DCCS(BET2)+(0.25*(2.-S)*P-S*BET2**2/P)*DSIN(BET2)

B=BETA*DCCS(BETA)+(0.25*(2.-S)*P-S*BETA**2/P)*DSIN(BETA)

IF(A*B)1,3,2

3 G(I)=(BET2*B-BETA*A)/(B-A)

4 BETA=BETA+0.2

RETURN

END

CONC

SUBROUTINE CONC(C,G,P,T,MODE)

C
C
C

PURPOSE: TO CALCULATE CONCENTRATION C FOR MODE=3,4

IMPLICIT REAL*8 (A-H,O-Z)

DIMENSION G(20)

E=0.0

TOL=.00001

S=DMIN1(1.D02,5.+40.*T)

IF(P.GE.S) GO TO 4

S=1

IF(MODE.EQ.3) S=0.5

C
C

-----SERIES SOLUTION-----

EX=0.5*P-C.25*P*T

SUM=0.0

DO 2 J=1,10

DSUM=0.0

DO 1 K=1,2

I=2*J+K-2

A=G(I)*DSIN(G(I))

IF(DABS(A).LT.1.D-04) A=0.0

EXP=EX-G(I)**2*T/P

1 DSUM=DSUM+A*EXF(EXP,E)/(G(I)**2+0.25*P*P+S*P)

SUM=SUM+DSUM

IF(DABS(DSUM/SUM).LT.TOL) GO TO 3

2 CONTINUE

GO TO 4

3 C=1.-2.*SUM

RETURN

4 AM=0.5*(1.-T)*DSQRT(P/T)

AP=0.5*(1.+T)*DSQRT(P/T)

A=0.5*EXF(E,AM)

B=0.5*EXF(P,AP)

D=DSQRT(.3183095*P*T)*EXF(-AM*AM,E)

IF(MODE.EQ.3) C=A+(3.+P*P*T)*B-D

IF(MODE.EQ.4) C=A+(3.+5*P+.5*P*T)*D-(1.+3.*P*P*T*(4.+2.*AP**2))*B

RETURN

END

EXF

FUNCTION EXF(A,B)

C
C
C

PURPOSE: TO CALCULATE EXP(A) ERFC(B)

IMPLICIT REAL*8 (A-H,O-Z)

EXF=0.0

IF((DABS(A).GT.170.).AND.(B.LE.0.)) RETURN

C=A-B*B

IF((DABS(C).GT.170.).AND.(B.GE.0.)) RETURN

IF(C.LT.-170.) GO TO 3

X=DABS(B)

IF(X.GT.3.0) GO TO 1

T=1./(1.+0.3275911*X)

Y=T*(.2548296-T*(.2844967-T*(1.421414-T*(1.453152-1.061405*T))))

GO TO 2

1 Y=.5641896/(X+.5/(X+1.5/(X+2.5/(X+2.5/X+1.))))

2 EXF=Y*DEXP(C)

3 IF(B.LT.0.0) EXF=2.*DEXP(A)-EXF

RETURN

END

MATINV

```
SUBROUTINE MATINV(A,NP,8)
  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
```

MODEL

SUBROUTINE MODEL(B,Y,NOB,X,INDEX,MODE)

C
C
C

PURPOSE: TO CALCULATE CONCENTRATIONS FOR GIVEN PORE VOLUME

```
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION B(10),Y(90),X(90),INDEX(5),G(20)
E=0.
K=0
DO 2 I=4,6
  IF(INDEX(I-3).EQ.0) GO TO 2
  K=K+1
  B(I)=B(K)
2 CONTINUE
P=B(4)
R=B(5)
IF((P.LE.100.).AND.(MODE.GE.3)) CALL EIGEN (G,P,MODE)
DO 6 J=1,NOB
  DO 4 M=1,2
    C=0.0
    T=(X(J)+(1-M)*B(6))/R
    IF(T.LE.C) GO TO 6
    AM=0.5*(1.-T)*DSQRT(P/T)
    AP=0.5*(1.+T)*DSQRT(P/T)
    IF(MODE.EQ.0) C=0.5*EXF(E,AM)
    IF(MODE.EQ.1) C=0.5*EXF(E,AM)+0.5*EXF(P,AP)
    IF(MODE.EQ.2) C=0.5*EXF(E,AM)+DSQRT(.3183099*P*T)*EXF(-AM*AM,E)-
10.5*(1.+P+P*T)*EXF(P,AP)
    IF(MODE.GE.3) CALL CCNC(C,G,P,T,MODE)
    IF(M.EQ.2) GO TO 6
    Y(J)=C
  4 CONTINUE
  6 Y(J)=Y(J)-C
  RETURN
END
```