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CONVECTIVE–DISPERSIVE TRANSPORT OF SOLUTES INVOLVED IN SEQUENTIAL FIRST-ORDER DECAY REACTIONS

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Abstract—Problems of solute transport involving sequential first-order decay reactions frequently occur in soil systems. Examples are the migration of radionuclides, in which the chain members form a first-order decay reaction, and the simultaneous movement of various interacting nitrogen species. This study presents analytical solutions that describe the simultaneous convective–dispersive transport of up to four species involved in such a consecutive chain reaction. Evaluation of the analytical solutions is not straightforward but requires, among other things, the calculation of complex complementary error functions. A FORTRAN IV computer program (CHAIN) that can be used to evaluate the analytical solutions is described. Application of this program to problems of solute transport is illustrated with two examples, one dealing with radionuclide transport and one with nitrification.

Key Words: Convective–dispersive solute transport, First-order decay reactions, Nitrogen transport, Radionuclide transport, Transport modeling.

INTRODUCTION

Problems of solute transport involving sequential first-order decay reactions frequently occur in soil and groundwater systems. One often quoted example is that of the migration of various radionuclides (Lester, Jansen, and Burkholder, 1975; Rogers, 1978; Gureghian and Jansen, 1983). Other examples are concerned with the simultaneous movement of interacting nitrogen species (Cho, 1971; Misra, Nielson, and Biggar, 1974a, b; Wagenet, Biggar, and Nielson, 1976), organic phosphates (Castro and Rolston, 1977), or pesticides (Bromilow and Leistra, 1980). Previous attempts to derive analytical solutions have been limited either to three chain members, using relatively simple boundary conditions (Cho, 1971; Wagenet, Biggar, and Nielson, 1976; Harada and others, 1980), or to transport conditions, where dispersion phenomena could be neglected (Higashi and Pigford, 1980; Harada and others, 1980). This paper presents several analytical solutions that are applicable to sequential first-order decay reactions with up to four chain members. The boundary conditions are formulated in such a way that different sets of input source functions can be included in the formulation. The solutions are evaluated with a FORTRAN IV computer program termed CHAIN.

THEORETICAL

Governing transport equations

This study considers the transport of four species (E_i, $i = 1, 4$) involved in a consecutive first-order decay chain of the form

$$E_1 \rightarrow E_2 \rightarrow E_3 \rightarrow E_4. \qquad (1)$$

The following set of coupled differential equations describes the one-dimensional convective–dispersive transport of the four chain members under transient flow conditions:

$$\frac{\partial}{\partial t}(\theta c_1 + \rho s_1) = \frac{\partial}{\partial x}\left(\theta D \frac{\partial c_1}{\partial x} - q c_1\right) - \mu_{w,1}\theta c_1 - \mu_{s,1}\rho s_1, \qquad (2a)$$

$$\frac{\partial}{\partial t}(\theta c_i + \rho s_i) = \frac{\partial}{\partial x}\left(\theta D \frac{\partial c_i}{\partial x} - q c_i\right) + \mu_{w,i-1}\theta c_{i-1} + \mu_{s,i-1}\rho s_{i-1} - \mu_{w,i}\theta c_i - \mu_{w,i}\rho s_i \quad (i = 2, 3, 4), \qquad (2b)$$

where c is the solution concentration (ML^{-3}), s the adsorbed concentration (MM^{-1}), θ the volumetric water content (L^3L^{-3}), q the volumetric flux (LT^{-1}), D the dispersion coefficient (L^2T^{-1}), ρ the porous medium bulk density (ML^{-3}), x distance (L), and t time (T); the subscript i delineates the ith chain member. The coefficients $\mu_{w,i}$ and $\mu_{s,i}$ are rate constants for first-order decay (T^{-1}) in the liquid and solid phases of the soil, respectively. These two rate coefficients probably will have different values for both chemical and microbiological degradation. However, for radioactive decay we may assume that they are identical:

$$\mu_{w,i} = \mu_{s,i} \ (=\mu_i). \qquad (3)$$

Two assumptions are introduced. First, it is assumed that the soil system is homogeneous and that θ and q are constant in time and space (steady-state flow). Second, we assume that adsorbed concentrations (s_i) can be related to solution concentrations (c_i) by linear (or linearized) and reversible isotherms of the form

$$s_i = k_i c_i \quad (i = 1, 4), \qquad (4)$$

where the k_i are empirical distribution coefficients ($M^{-1}L^3$). Using equations (3) and (4) and the assumptions of steady-state flow and linear equilibrium transport, equations (2a, b) reduce to

$$R_1 \frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial x^2} - v \frac{\partial c_1}{\partial x} - \mu_1 R_1 c_1, \tag{5a}$$

$$R_i \frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x} + \mu_{i-1} R_{i-1} c_{i-1} - \mu_i R_i c_i \quad (i = 2, 3, 4), \tag{5b}$$

where v ($=q/\theta$) is the average pore-water velocity and the retardation factors R_i are given by

$$R_i = 1 + \frac{\rho k_i}{\theta}. \tag{6}$$

Note that equations (5a, b) apply only for the limiting situation when the decay constants $\mu_{w,i}$ and $\mu_{s,i}$ are identical [equation (3)]. If degradation is limited only to the liquid phase ($\mu_{s,i} = 0$), the retardation factors should be dropped from the decay terms in equations (5a, b). Other situations for which $\mu_{s,i} \neq \mu_{w,i}$ can be considered easily by redefining appropriately the general decay coefficient μ_i.

Initial and boundary conditions

In this study we restrict ourselves to analytical solutions that are applicable to semi-infinite systems ($0 \leqslant x < \infty$) using the boundary conditions

$$\frac{\partial c_i}{\partial x}(\infty, t) = 0, \quad t \geqslant 0 \quad (i = 1, 4) \tag{7}$$

and to systems that are initially free of solutes:

$$c_i(x, 0) = 0, \quad x \geqslant 0. \tag{8}$$

The input boundary conditions at $x = 0$ are described by either first-type (or concentration-type) conditions of the form

$$c_i(0, t) = \begin{cases} f_i(t), & 0 < t \leqslant t_0, \\ 0, & t > t_0, \end{cases} \tag{9}$$

or third-type (or flux-type) conditions of the form

$$\left(-D \frac{\partial c_i}{\partial x} + v c_i\right)\Big|_{x=0} = \begin{cases} v f_i(t), & 0 < t \leqslant t_0, \\ 0, & t > t_0, \end{cases} \tag{10}$$

where f_i ($i = 1, 4$) is given by

$$f_1(t) = B_1 e^{-\lambda_1 t}, \tag{11a}$$

$$f_2(t) = B_2 e^{-\lambda_1 t} + B_3 e^{-\lambda_2 t}, \tag{11b}$$

$$f_3(t) = B_4 e^{-\lambda_1 t} + B_5 e^{-\lambda_2 t} + B_6 e^{-\lambda_3 t}, \tag{11c}$$

$$f_4(t) = B_7 e^{-\lambda_1 t} + B_8 e^{-\lambda_2 t} + B_9 e^{-\lambda_3 t} + B_{10} e^{-\lambda_4 t}, \tag{11d}$$

in which the coefficients B_j ($j = 1, 10$) and λ_i ($i = 1, 4$) are all constants. The multiple terms in equations (11a–d) are a consequence of decay reactions in the waste site (e.g., a nuclear waste repository) and also account for a finite rate of release of each chain member from the waste site into the environment. For one particular release mechanism, the constants B_j are related to each other through the Bateman equations (Bateman, 1910). This situation is described briefly.

Consider a waste site that initially for each chain member contains an amount M_i^0 per unit cross-sectional area perpendicular to the direction of flow. It is assumed that the release rate from the repository into the environment for each member is proportional to the amount remaining in the repository. The total amount of each chain member in the waste site as a function of time, $M_i(t)$, then can be calculated by solving the set of equations (Higashi and Pigford, 1980):

$$\frac{dM_1}{dt} = -\mu_1 M_1 - \gamma_1 M_1 \tag{12a}$$

$$\frac{dM_i}{dt} = \mu_{i-1} M_{i-1} - \mu_i M_i - \gamma_i M_i \quad (i = 2, 3, 4), \tag{12b}$$

where the proportionality constant γ_i for each member determines the release rate from the repository. Hence, the first term on the right-hand side of equation (12a) defines the rate of decay of the parent member, and the second term defines the release rate into the environment. Solving equations (12a, b), subject to the initial condition

$$M_i(t) = M_i^0 \quad (t = 0) \tag{13}$$

gives

$$M_1(t) = A_1 e^{-\lambda_1 t}, \tag{14a}$$

$$M_2(t) = A_2 e^{-\lambda_1 t} + A_3 e^{-\lambda_2 t}, \tag{14b}$$

$$M_3(t) = A_4 e^{-\lambda_1 t} + A_5 e^{-\lambda_2 t} + A_6 e^{-\lambda_3 t}, \tag{14c}$$

$$M_4(t) = A_7 e^{-\lambda_1 t} + A_8 e^{-\lambda_2 t} + A_9 e^{-\lambda_3 t} + A_{10} e^{-\lambda_4 t}, \tag{14d}$$

where

$$\lambda_i = \mu_i + \gamma_i; \tag{15}$$

$$A_1 = M_1^0, \quad A_2 = \frac{\mu_1 M_1^0}{\lambda_2 - \lambda_1}, \quad A_3 = M_2^0 - A_2,$$

$$A_4 = \frac{\mu_2 A_2}{\lambda_3 - \lambda_1}, \quad A_5 = \frac{\mu_2 A_3}{\lambda_3 - \lambda_2},$$

$$A_6 = M_3^0 - A_4 - A_5, \tag{16}$$

$$A_7 = \frac{\mu_3 A_4}{\lambda_4 - \lambda_1}, \quad A_8 = \frac{\mu_3 A_5}{\lambda_4 - \lambda_2}, \quad A_9 = \frac{\mu_3 A_6}{\lambda_4 - \lambda_3},$$

$$A_{10} = M_4^0 - A_7 - A_8 - A_9.$$

Equations (14)–(16) are known as the Bateman equations.

Continuity of the solute flux ($q_{s,i}$) for each species across the boundary of the waste site requires

$$q_{s,i} = \gamma_i M_i = \left(-\theta D \frac{\partial c_i}{\partial x} + \theta v c_i\right)\Big|_{x=0} \quad (i = 1, 4), \quad (17)$$

where, as before, the amount of material of each chain member in the waste repository (M_i) is defined per unit cross-sectional area perpendicular to the direction of flow. Combining equations (14) and (17) and dividing by the volumetric water content (θ) leads directly to equations (10) and (11), provided that the coefficients B_j are defined as

$$\begin{aligned} B_1 &= \frac{\gamma_1 A_1}{q}, \quad B_2 = \frac{\gamma_2 A_2}{q}, \quad B_3 = \frac{\gamma_2 A_3}{q}, \\ B_4 &= \frac{\gamma_3 A_4}{q}, \quad B_5 = \frac{\gamma_3 A_5}{q}, \quad B_6 = \frac{\gamma_3 A_6}{q}, \\ B_7 &= \frac{\gamma_4 A_7}{q}, \quad B_8 = \frac{\gamma_4 A_8}{q}, \quad B_9 = \frac{\gamma_4 A_9}{q}, \\ B_{10} &= \frac{\gamma_4 A_{10}}{q}. \end{aligned} \quad (18)$$

Equations (10) and (11) apply to the most general situation of preferential release from the repository; that is, all γ_i's can have different values. Other and more simple boundary conditions can be formulated by forcing appropriate constants (λ_i, B_j) in equations (11) to be zero.

Analytical solutions

Standard Laplace transform techniques were used for the derivation of the analytical solutions presented here (van Genuchten, 1981a; van Genuchten and Alves, 1982). Details of the derivation are omitted.

The solution of equations (5), (7), and (8) for the flux-type boundary condition [equations (10) and (11)] is

$$c_i(x, t) = \begin{cases} c_i^*(x, t), & 0 < t \leq t_0, \\ c_i^*(x, t) - \exp(-\lambda_i t_0) c_i^*(x, t - t_0), & t > t_0, \end{cases} \quad (19)$$

where $c_i^*(x, t)$ is given in Appendix 1. The analytical solution for the concentration-type boundary condition [equations (9) and (11)] is identical to this solution, except that the term F_{ijk} in Appendix 1 must be replaced by

$$F_{ijk} = \exp(-a_{ijk}t)\left\{\frac{1}{2}\exp\left[\frac{(v - w)x}{2D}\right]\operatorname{erfc}\left[\frac{R_i x - wt}{2(DR_i t)^{1/2}}\right] + \frac{1}{2}\exp\left[\frac{(v + w)x}{2D}\right]\operatorname{erfc}\left[\frac{R_i x + wt}{2(DR_i t)^{1/2}}\right]\right\}. \quad (20)$$

PROGRAM CHAIN

A FORTRAN IV computer program termed CHAIN was written to evaluate the two analytical solutions derived here; the program is listed in Appendix 2. Much of the notation used in CHAIN is identical to the notation of the theoretical section. The most significant program variables are defined in Appendix 3, and Appendix 4 gives instructions for setting up the input data file.

The program consists of a main program (MAIN), two functions (F and EXF), and one subroutine (CEXF). Most of the calculations are carried out in MAIN, including input and output instructions and the calculation of various constants. The function F evaluates the variables F_{ijk} or S_{ij} according to (see also Appendix 1)

$$\mathrm{F}(I, JJ) = \begin{cases} F_{ij0} & \text{if } JJ \leq 0 \quad (I = i, JJ = -j), \\ S_{ij} & \text{if } JJ > 0 \quad (I = i, JJ = j). \end{cases} \quad (21)$$

The function EXF(A, B) defines the product of the exponential function (exp) and the complementary error function (erfc) as follows:

$$\mathrm{EXF}(A, B) = \exp(A)\operatorname{erfc}(B), \quad (22)$$

where

$$\operatorname{erfc}(B) = \frac{2}{\sqrt{\pi}}\int_B^\infty \exp(-\tau^2)\, d\tau. \quad (23)$$

Two different approximations are used for EXF(A, B). For $0 \leq B \leq 2.5$ [see also equation (7.1.26) of Gautschi, 1964]:

$$\mathrm{EXF}(A, B) \simeq \exp(A - B^2)(a_1\tau + a_2\tau^2 + a_3\tau^3 + a_4\tau^4 + a_5\tau^5), \quad (24)$$

where

$$\tau = \frac{1}{1 + 0.3275911B}; \quad (25)$$

$$\begin{aligned} a_1 &= 0.254829592, \quad a_2 = -0.284496736, \\ a_3 &= 1.421413741, \quad a_4 = -1.453152027, \\ a_5 &= 1.061405429; \end{aligned} \quad (26)$$

and, for $B > 2.5$ [see also equation (7.1.14) of Gautschi, 1964];

$$\mathrm{EXF}(A, B) \simeq \frac{1}{\sqrt{\pi}} \frac{\exp(A - B^2)}{(B + 0.5/(B + 1/(B + 1.5/(B + 2/(B + 2.5/(B + 1))))))}. \quad (27)$$

For negative values of B, the following additional relation is needed:

$$\mathrm{EXF}(A, B) = 2\exp(A) - \mathrm{EXF}(A, -B). \quad (28)$$

The function EXF(A, B) cannot be used for small or large values of its arguments A, B. The function returns zero for the following two conditions:

$$\begin{cases} |A| > M, \\ B \leq 0, \end{cases} \quad \text{or} \quad \begin{cases} |A - B^2| > M, \\ B > 0, \end{cases} \quad (M = 170). \quad (29)$$

Subroutine CEXF(A, B, Z, U, V) is used to evaluate the complementary error function for complex arguments:

$$U + iV = \exp(Z)\,\mathrm{erfc}\,(A + iB). \quad (30)$$

Complex erfc functions occur in the formulation whenever w^2 (see last equation of Appendix 1) becomes negative.

For $(A + B) > 6$ with $A \geq 0$ and $B \geq 0$, equation (30) is evaluated as follows [see also equations (7.13, 7.14, 7.4.13, and 7.1.14) of Gautschi, 1970]:

$$U = \frac{1}{\pi}\exp(Z + B^2 - A^2)[T\cos(2AB) - W\sin(2AB)], \quad (31)$$

$$V = \frac{1}{\pi}\exp(Z + B^2 - A^2)[-T\sin(2AB) - W\cos(2AB)], \quad (32)$$

$$T = \int_{-\infty}^{\infty} \frac{A\exp(-\tau^2)}{(B + \tau)^2 + A^2}\,d\tau, \quad (33)$$

$$W = \int_{-\infty}^{\infty} \frac{(B + \tau)\exp(-\tau^2)}{(B + \tau)^2 + A^2}\,d\tau, \quad (34)$$

where T and W are evaluated with a Hermitian quadrature scheme of the form

$$\int_{-\infty}^{\infty} \exp(-\tau^2)g(\tau)\,d\tau = \sum_{i=1}^{n} w_i g(\tau_i). \quad (35)$$

Values for the weighting factors w_i and the associated abscissas τ_i were obtained from Table 25.10 of Davis and Polonsky (1964). The program uses 20 quadrature points ($n = 20$).

For $0 < A + B < 6$ with $A > 0$, $B \geq 0$, equation (30) is evaluated with equation (7.1.29) of Gautschi (1970). Specifically, the following set of equations is used:

$$U = \exp(Z)\,\mathrm{erfc}\,(A) - \exp(Z - A^2) \times \left[\frac{1 - C}{2\pi A} + \sum_{n=1}^{\infty} \alpha(2A - b_1 C + b_2 S)\right], \quad (36)$$

$$V = \exp(Z - A^2)\left[\frac{S}{2\pi A} + \sum_{n=1}^{\infty} \alpha(b_1 S + b_2 C)\right], \quad (37)$$

where

$$\alpha = \frac{2\exp(-n^2/4)}{\pi(n^2 + 4A^2)}; \quad (38a)$$

$$C = \cos(2AB), \qquad S = \sin(2AB); \quad (38b)$$

$$b_1 = 2A\cosh(nB), \qquad b_2 = n\sinh(nB). \quad (38c)$$

This method gives an accuracy of at least six significant digits if the number of terms in the series expansions of equations (36) and (37) equals or exceeds m, where m is the integer closest to $(12 + 2B)$.

The two methods for evaluating the complex erfc-function hold for nonnegative values of A and B. Given equation (30) for positive A and B, the two methods can be extended to negative values by making use of the relationships

$$2\exp(Z) - U - iV = \exp(Z)\,\mathrm{erfc}\,(-A - iB), \quad (39a)$$

$$2\exp(Z) - U + iV = \exp(Z)\,\mathrm{erfc}\,(-A + iB), \quad (39b)$$

$$U - iV = \exp(Z)\,\mathrm{erfc}\,(A - iB). \quad (39c)$$

Initially, serious round-off errors were observed when the approximations for erfc were used directly in the equations for F_{ijk}, especially for the solution of the flux-type boundary condition (Appendix 1). Such round-off errors become immediately apparent when the expressions for F_{ijk} are evaluated for relatively large values of R, x, and/or t. Fortunately, round-off errors could be limited greatly by first substituting the appropriate erfc approximations into the F_{ijk} terms and subsequently combining and simplifying various terms in the resulting series expansions. Although straightforward in principle, this manipulation and simplification of the various terms in F_{ijk} required extensive bookkeeping. Details are omitted here; if needed, they can be retrieved from the function F(I, JJ) in Appendix 2.

Finally, the program also contains the statement

$$\mathrm{CALL\ ERRSET\ (208, 0, -1, 1),} \quad (40)$$

which suppresses all underflow error messages during execution. If this subroutine is not available, underflow problems in most situations can be avoided by using $M = 100$ in equation (29), rather than the present value of 170 (these changes are made easily at selected places in the program).

EXAMPLES

Two examples are presented here to illustrate typical results that can be obtained with the program. Appendix 5 lists the input data for the examples; the associated output file is given in Appendix 6. The first example applies to the three-species nitrification chain

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \quad (41)$$

and is the same as described earlier by Cho (1971),

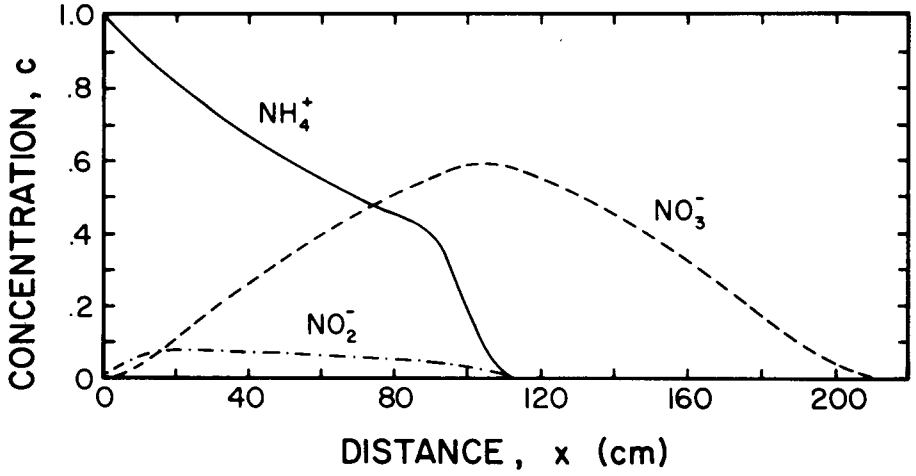

Figure 1. Calculated distributions for nitrogen decay chain $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ at t = 200 h.

except that the constant concentration boundary condition for Cho's solution is replaced here by a constant flux condition, that is, by equations (10) and (11) with $B_1 = 1$, $B_j = 0$ ($j = 2, 10$), and $\lambda_1 = 0$. Other parameter values for the example are

$$v = 1 \text{ cm h}^{-1}, \quad D = 0.18 \text{ cm}^2 \text{ h}^{-1},$$
$$R_1 = 2 \quad R_2 = R_3 = 1, \tag{42}$$
$$\mu_1 R_1 = 0.01 \text{ h}^{-1}, \quad \mu_2 = 0.1 \text{ h}^{-1}, \quad \mu_3 = 0.$$

Calculated concentration distributions for the three species at t = 200 h are shown in Figure 1. The distributions are nearly identical to those given by Cho (1971), thus showing that the effect of a different boundary condition is small for the parameter values of this example.

The second example is concerned with the radionuclide decay chain

$$^{238}\text{Pu} \rightarrow {}^{234}\text{U} \rightarrow {}^{230}\text{Th} \rightarrow {}^{226}\text{Ra}. \tag{43}$$

This decay chain was recently used by Higashi and Pigford (1980) as an example in predictive modeling of subsurface radionuclide transport. Of the four species in equation (43), ^{226}Ra presumably is the more crucial chain member, partly because of the high biological hazard associated with this species, and partly because the relatively low R value of ^{226}Ra leads to a higher mobility in the system than is the situation with the other chain members. Values of the various input parameters, listed in Appendices 5 (input file) and 6 (output file), are the same as those used in the original study by Higashi and Pigford

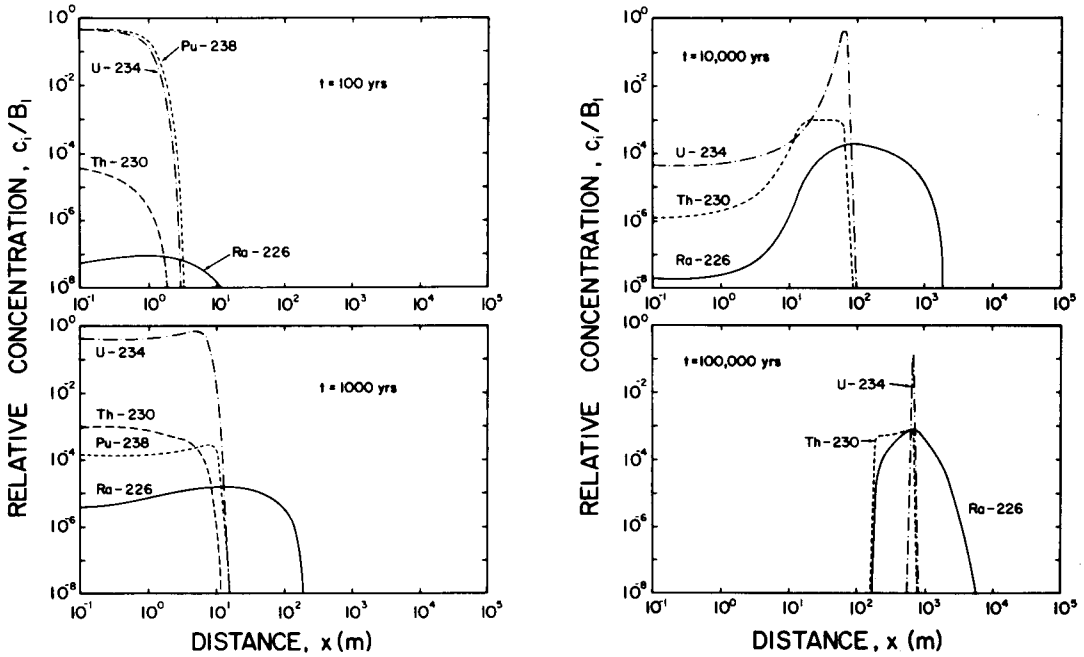

Figure 2. Calculated distributions for radionuclide decay chain $^{238}\text{Pu} \rightarrow {}^{234}\text{U} \rightarrow {}^{230}\text{Th} \rightarrow {}^{226}\text{Ra}$ at four different times.

(1980). An arbitrary value of $10m^2$/year was assigned to the dispersion coefficient D (Higashi and Pigford neglected dispersion phenomena in their analysis). The reader is referred to the original paper of Higashi and Pigford (1980) for a more detailed discussion of the physical problem.

Figure 2 shows relative concentration distribution at four different times; concentrations are expressed as fractions of the input concentration (B_1) of ^{238}Pu at $x = 0$ [see equation (18)]. A careful comparison of the plotted results with figure 3 of Higashi and Pigford (1980) shows that the shapes of the distributions are nearly identical. Hence, the effects of dispersion are relatively small in this example, although it should be realized that these effects are not clearly visible in graphic form because of the logarithmic scale of the figures.

CONCLUSION

This study presents a FORTRAN IV computer program (CHAIN) that can be used to evaluate the convective–dispersive transport of up to four chain members that are involved in consecutive first-order decay reactions. The analytical solutions for this problem, especially those for the fourth chain member, are complicated and require special programming care if serious round-off errors are to be avoided. Examples concerned with nitrogen and radionuclide transport illustrate the type of problems that can be considered with the program. Compared with numerical transport models, the analytical formulation presented here may prove to be useful in several situations. First, the program can be used to obtain initial and approximate estimates for solute transport for a number of simplified field situations (notably for steady-state flow in one dimension). For example, the long-term vertical transport of chemicals through the unsaturated zone may be described accurately with appropriate analytical solutions (Wierenga, 1977). Second, analytical solutions of the type given here are important tools for estimating transport parameters from observed laboratory or field data, notably with respect to dispersion coefficients, retardation factors, or decay coefficients (see Misra, Nielsen, and Biggar, 1974b, and van Genuchten, 1981b, for examples). Finally, the analytical model may be used for verification of appropriate numerical multi-ion chain solutions.

REFERENCES

Bateman, H., 1910, The solution of a system of differential equations occurring in the theory of radioactive transformations: Proc. Cambridge Philos. Soc., v. 15, pt V, p. 423–427.

Bromilow, R. H., and Leistra, M., 1980, Measured and simulated behaviour of aldicarb and its oxidation products in fallow soils: Pestic. Sci., v. 11, no. 4, p. 389–395.

Castro, C. L., and Rolston, D. E., 1977, Organic phosphate transport and hydrolysis in soil: theoretical and experimental evaluation: Soil Sci. Soc. America Jour., v. 41, no. 6, p. 1085–1092.

Cho, C. M., 1971, Convective transport of ammonium with nitrification in soil, Can. Jour. Soil Sci., v. 51, no. 3, p. 339–350.

Davis, P. J., and Polonsky, I., 1964, Numerical interpolation, differentiation and integration, *in* Abramowitz, M., and Stegun, I. A., eds., Handbook of mathematical functions: U.S. Government Printing Office, Washington D.C., p. 875–924.

Gautschi, W., 1964, Error function and Fresnel integrals, *in*, Abramowitz, M., and Stegun, I. A., eds., Handbook of mathematical functions: U.S. Government Printing Office, Washington D.C., p. 295–329.

Gureghian, A. B., and Jansen, G., 1983, LAYFLO: A one-dimensional semianalytical model for the migration of a three-member decay chain in a multilayered geologic medium: Tech. Rep. ONWI-466, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 83 p.

Harada, M., Chambre, P. L., Foglia, M., Higashi, K., Iwamoto, F., Leung, D., Pigford, T. H., and Ting, D., 1980, Migration of radionuclides through sorbing media, analytical solutions—I: Rep. no. LBL-10500 (UC-11), Lawrence Berkeley Laboratory, Univ. California, Berkeley, 245 p.

Higashi, K., and Pigford, T. H., 1980, Analytical models for migration of radionuclides in geologic sorbing media: Jour. Nucl. Sci. and Techn., v. 17, no. 9, p. 700–709.

Lester, D. H., Jansen, G., and Burkholder, H. C., 1975, Migration of radionuclide chains through an adsorbing medium, *in* Adsorption and ion exchange: Am. Inst. Chem. Eng., Symp. Series no. 152, v. 71, p. 202–213.

Misra, C., Nielsen, D. R., and Biggar, J. W., 1974a, Nitrogen transformations in soil during leaching: I. Theoretical considerations: Soil Sci. Soc. America Proc., v. 38, no. 2, p. 289–293.

Misra, C., Nielsen, D. R., and Biggar, J. W., 1974b, Nitrogen transformations in soil during leaching: II. Steady state nitrification and nitrate reduction: Soil Sci. Soc. America Proc., v. 38, no. 2, p. 294–299.

Rogers, V. C., 1978, Migration of radionuclide chains in groundwater: Nucl. Techn., v. 40, no. 3, p. 315–320.

van Genuchten, M. Th., 1981a, Analytical solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay: Jour. Hydrol., v. 49, no. 3–4, p. 213–233.

van Genuchten, M. Th., 1981b, Non-equilibrium transport parameters from miscible displacement experiments: Research Rep. no. 119, U.S. Salinity Laboratory, Riverside, California, 88 p.

van Genuchten, M. Th., and Alves, W. J., 1982, Analytical solutions of the one-dimensional convective-dispersive solute transport equation: Tech. Bull., no. 1661, U.S. Dep. of Agriculture, 151 p.

Wagenet, R. J., Biggar, J. W., and Nielsen, D. R., 1976, Analytical solutions of miscible displacement equations describing the sequential microbiological transformations of urea, ammonium and nitrate: Research Rep. no. 6001, Dep. of Water Science and Engineering, Univ. California, Davis, 53 p.

Wierenga, P. J., 1977, Solute distribution profiles computed with steady-state and transient water movement models, Soil Sci. Soc. America Jour., v. 41, no. 6, p. 1050–1055.

APPENDIX 1

Expressions for $c_i^*(x, t)$ in equation (19) *for the analytical solution of equations* (5), (7), (8), (10) *and* (11)

$$c_1^* = B_1F_{110},$$

$$c_2^* = B_2F_{210} + B_3F_{220} + \frac{\mu_1R_1B_1(S_{12} - F_{210} + F_{110})}{R_{12}\lambda_1 - \mu_{12}},$$

$$c_3^* = B_4F_{310} + B_5F_{320} + B_6F_{330} + \frac{\mu_2R_2B_2(S_{23} - F_{310} + F_{210})}{R_{23}\lambda_1 - \mu_{23}} + \frac{\mu_2R_2B_3(S_{23} - F_{320} + F_{220})}{R_{23}\lambda_2 - \mu_{23}} + \frac{A_1B_1R_{12}(F_{210} - F_{110} - S_{12})}{R_{12}\lambda_1 - \mu_{12}} + \frac{A_1B_1R_{13}(S_{13} - F_{310} + F_{110})}{R_{13}\lambda_1 - \mu_{13}} + \frac{A_1B_1R_{23}(F_{310} - F_{210} - S_{23})}{R_{23}\lambda_1 - \mu_{23}},$$

$$\begin{aligned} c_4^* = {} & B_7F_{410} + B_8F_{420} + B_9F_{430} + B_{10}F_{440} + \frac{\mu_3R_3B_4(S_{34} - F_{410} + F_{310})}{R_{34}\lambda_1 - \mu_{34}} + \frac{\mu_3R_3B_5(S_{34} - F_{420} + F_{320})}{R_{34}\lambda_2 - \mu_{34}} + \frac{\mu_3R_3B_6(S_{34} - F_{430} + F_{330})}{R_{34}\lambda_3 - \mu_{34}} \\ & + \frac{A_2B_2R_{34}(F_{410} - F_{310} - S_{34})}{R_{34}\lambda_1 - \mu_{34}} + \frac{A_2B_2R_{23}(F_{310} - F_{210} - S_{23})}{R_{23}\lambda_1 - \mu_{23}} \\ & + \frac{A_2B_2R_{24}(S_{24} - F_{410} + F_{210})}{R_{24}\lambda_1 - \mu_{24}} + \frac{A_2B_3R_{34}(F_{420} - F_{320} - S_{34})}{R_{34}\lambda_2 - \mu_{34}} \\ & + \frac{A_2B_3R_{23}(F_{320} - F_{220} - S_{23})}{R_{23}\lambda_2 - \mu_{23}} + \frac{A_2B_3R_{24}(S_{24} - F_{420} + F_{220})}{R_{24}\lambda_2 - \mu_{24}} \\ & + \frac{A_3B_1R_{14}^2(S_{14} - F_{410} + F_{110})}{G_{134}G_{124}(R_{14}\lambda_1 - \mu_{14})} + \frac{A_3B_1R_{24}^2(F_{410} - F_{210} - S_{24})}{G_{124}G_{234}(R_{24}\lambda_1 - \mu_{24})} \\ & + \frac{A_3B_1R_{34}^2(S_{34} - F_{410} + F_{310})}{G_{134}G_{234}(R_{34}\lambda_1 - \mu_{34})} + \frac{A_3B_1R_{13}^2(F_{310} - F_{110} - S_{13})}{G_{123}G_{134}(R_{13}\lambda_1 - \mu_{13})} \\ & + \frac{A_3B_1R_{23}^2(S_{23} - F_{310} + F_{210})}{G_{123}G_{234}(R_{23}\lambda_1 - \mu_{23})} + \frac{A_3B_1R_{12}^2(S_{12} - F_{210} + F_{110})}{G_{123}G_{124}(R_{12}\lambda_1 - \mu_{12})}; \end{aligned}$$

$$A_1 = \frac{\mu_1\mu_2R_1R_2}{G_{123}}, \qquad A_2 = \frac{\mu_2\mu_3R_2R_3}{G_{234}}, \qquad A_3 = \mu_1\mu_2\mu_3R_1R_2R_3;$$

$$G_{ijk} = \mu_iR_iR_{kj} + \mu_jR_jR_{ik} + \mu_kR_kR_{ji}; \qquad S_{ij} = F_{jji} - F_{iji};$$

$$R_{ij} = R_i - R_j; \qquad \mu_{ij} = \mu_iR_i - \mu_jR_j;$$

$$F_{ijk} = \exp(-a_{ijk}t)\left\{\frac{v}{v+w}\exp\left[\frac{(v-w)x}{2D}\right]\operatorname{erfc}\left[\frac{R_ix - wt}{2(DR_it)^{1/2}}\right] + \frac{v}{v-w}\exp\left[\frac{(v+w)x}{2D}\right]\operatorname{erfc}\left[\frac{R_ix + wt}{2(DR_it)^{1/2}}\right]\right\} + \frac{2v^2}{w^2 - v^2}\exp\left(\frac{vx}{D} - \mu_it\right)\operatorname{erfc}\left[\frac{R_ix + vt}{2(DR_it)^{1/2}}\right] \qquad (\mu_i \neq a_{ijk}),$$

$$F_{ijk} = \exp(-a_{ijk}t)\left\{\frac{1}{2}\operatorname{erfc}\left[\frac{R_ix - vt}{2(DR_it)^{1/2}}\right] + \left(\frac{v^2t}{\pi DR_i}\right)^{1/2}\exp\left[-\frac{(R_ix - vt)^2}{4DR_it}\right] - \frac{1}{2}\left(1 + \frac{vx}{D} + \frac{v^2t}{DR_i}\right)\exp\left(\frac{vx}{D}\right)\operatorname{erfc}\left[\frac{R_ix + vt}{2(DR_it)^{1/2}}\right]\right\} \qquad (\mu_i = a_{ijk});$$

$$a_{ijk} = \begin{cases} \lambda_j, & k = 0, \\ \dfrac{\mu_{ij}}{R_{ij}}, & k > 0; \end{cases}$$

$$w = [v^2 + 4DR_i(\mu_i - a_{ijk})]^{1/2}.$$

APPENDIX 2

Listing of program CHAIN

```
001  C     ********************************************************************
002  C     *                                                                  *
003  C     *      MULTI-ION SOLUTE TRANSPORT                    CHAIN         *
004  C     *                                                                  *
005  C     *      FOUR SPECIES                                                *
006  C     *      PREFERENTIAL RELEASE                                        *
007  C     *                                                                  *
008  C     *      MAY,1982                                                    *
009  C     *                                                                  *
010  C     ********************************************************************
011  C
012        IMPLICIT REAL*8 (A-H,O-Z)
013        COMMON R(4),DONE(4),RLAM(4),D,V,X,T,KSURF
014        DIMENSION ZERO(4),GAMMA(4),TITLE(20),A(10),B(10)
015        CALL ERRSET(208,0,-1,1)
016  C
017  C     ----- READ NUMBER OF CASES CONSIDERED ----
018        READ(5,1000) NC
019        DO 14 NCASE=1,NC
020        READ(5,1001) TITLE
021  C
022  C     ----- READ INPUT PARAMETERS
023        READ(5,1000) NS,NR,NB,KSURF,KDB,KPR,V,D,WC,TP
024        READ(5,1002) (R(I),I=1,4),(DONE(I),I=1,4)
025        READ(5,1002) (ZERO(I),I=1,4),(GAMMA(I),I=1,4)
026        READ(5,1002) XI,DX,XM,TI,DT,TM
027  C
028  C     ---------
029        DO 1 I=1,4
030        ZERO(I)=NB*ZERO(I)
031      1 RLAM(I)=NB*DONE(I)+GAMMA(I)
032        IF(NB.EQ.0) GO TO 3
033  C
034  C     ----- CALCULATE BATEMAN EQUATIONS IF NB=1 ----
035        Q=V*WC
036        A(1)=ZERO(1)
037        A(2)=DONE(1)*A(1)/(RLAM(2)-RLAM(1))
038        A(3)=ZERO(2)-A(2)
039        A(4)=DONE(2)*A(2)/(RLAM(3)-RLAM(1))
040        A(5)=DONE(2)*A(3)/(RLAM(3)-RLAM(2))
041        A(6)=ZERO(3)-A(4)-A(5)
042        A(7)=DONE(3)*A(4)/(RLAM(4)-RLAM(1))
043        A(8)=DONE(3)*A(5)/(RLAM(4)-RLAM(2))
044        A(9)=DONE(3)*A(6)/(RLAM(4)-RLAM(3))
045        A(10)=ZERO(4)-A(7)-A(8)-A(9)
046        K=0
047        DO 2 I=1,4
048        DO 2 J=1,I
049        K=K+1
050      2 B(K)=A(K)*GAMMA(I)/Q
051        GO TO 4
052      3 READ(5,1002) (B(I),I=1,10)
053  C
054  C     ----- WRITE INPUT PARAMETERS ----
055      4 IF(NS.LT.0) GO TO 14
056        WRITE(6,1003)
057        IF(KSURF.EQ.0) WRITE(6,1004)
058        IF(KSURF.NE.0) WRITE(6,1005)
059        WRITE(6,1006) TITLE
060        WRITE(6,1007) NS,V,D,NR,WC,TP,NB
061        WRITE(6,1008) (I,ZERO(I),R(I),DONE(I),GAMMA(I),RLAM(I),I=1,NS)
062        WRITE(6,1009) (I,B(I),I=1,10)
063  C
064  C     ----- MULTIPLY DONE WITH R IF NR=1 ----
065        IF(NR.EQ.0) GO TO 6
066        DO 5 I=1,4
067      5 DONE(I)=R(I)*DONE(I)
068  C
069  C     ----- CALCULATE VARIOUS CONSTANTS ----
070      6 D12=DONE(1)-DONE(2)
071        D13=DONE(1)-DONE(3)
072        D23=DONE(2)-DONE(3)
073        D14=DONE(1)-DONE(4)
074        D24=DONE(2)-DONE(4)
```

```
075         D34=DONE(3)-DONE(4)
076         R12=R(1)-R(2)
077         R13=R(1)-R(3)
078         R23=R(2)-R(3)
079         R14=R(1)-R(4)
080         R24=R(2)-R(4)
081         R34=R(3)-R(4)
082         B123=-DONE(1)*R23+DONE(2)*R13-DONE(3)*R12
083         B124=-DONE(1)*R24+DONE(2)*R14-DONE(4)*R12
084         B134=-DONE(1)*R34+DONE(3)*R14-DONE(4)*R13
085         B234=-DONE(2)*R34+DONE(3)*R24-DONE(4)*R23
086         DD=DONE(1)*DONE(2)
087         DP=DONE(2)*DONE(3)
088         DDD=DD*DONE(3)
089         C21=DONE(1)*B(1)/(D12-R12*RLAM(1))
090         C31=DONE(2)*B(2)/(D23-R23*RLAM(1))
091         C32=DONE(2)*B(3)/(D23-R23*RLAM(2))
092         C331=DD*B(1)*R12/(B123*(R12*RLAM(1)-D12))
093         C332=DD*B(1)*R13/(B123*(R13*RLAM(1)-D13))
094         C333=DD*B(1)*R23/(B123*(R23*RLAM(1)-D23))
095         C41=DONE(3)*B(4)/(D34-R34*RLAM(1))
096         C42=DONE(3)*B(5)/(D34-R34*RLAM(2))
097         C43=DONE(3)*B(6)/(D34-R34*RLAM(3))
098         C441=DP*B(2)*R34/(B234*(R34*RLAM(1)-D34))
099         C442=DP*B(2)*R23/(B234*(R23*RLAM(1)-D23))
100         C443=DP*B(2)*R24/(B234*(R24*RLAM(1)-D24))
101         C451=DP*B(3)*R34/(B234*(R34*RLAM(2)-D34))
102         C452=DP*B(3)*R23/(B234*(R23*RLAM(2)-D23))
103         C453=DP*B(3)*R24/(B234*(R24*RLAM(2)-D24))
104         C461=DDD*B(1)*R14**2/(B134*B124*(R14*RLAM(1)-D14))
105         C462=DDD*B(1)*R24**2/(B124*B234*(R24*RLAM(1)-D24))
106         C463=DDD*B(1)*R34**2/(B134*B234*(R34*RLAM(1)-D34))
107         C464=DDD*B(1)*R13**2/(B123*B134*(R13*RLAM(1)-D13))
108         C465=DDD*B(1)*R23**2/(B123*B234*(R23*RLAM(1)-D23))
109         C466=DDD*B(1)*R12**2/(B123*B124*(R12*RLAM(1)-D12))
110   C
111   C     ----- PRINT COEFFICIENTS IF KDB.GT.0 ----
112         IF(KDB.GT.0) WRITE(6,1010) C21,C31,C32,C331,C332,C333,C41,C42,C43
113        1,C441,C442,C443,C451,C452,C453,C461,C462,C463,C464,C465,C466
114         F12=0.
115         F13=0.
116         F23=0.
117         F32=0.
118         F14=0.
119         F24=0.
120         F42=0.
121         F34=0.
122         F43=0.
123         F44=0.
124         E=0.
125         P12=DABS(1000.*R12/R(1))
126         P13=DABS(1000.*R13/R(1))
127         P23=DABS(1000.*R23/R(2))
128         P14=DABS(1000.*R14/R(1))
129         P24=DABS(1000.*R24/R(2))
130         P34=DABS(1000.*R34/R(3))
131         IF(DX.EQ.0.) DX=1.0
132         IF(DT.EQ.0.) DT=1.0
133         IMAX=(XM+DX-XI)/DX
134         JMAX=(TM+DT-TI)/DT
135   C
136   C     ----- DYNAMIC PART OF PROGRAM -----
137         DO 12 JJ=1,JMAX
138         IF(IMAX.GE.JJ) WRITE(6,1011)
139         TIME=TI+(JJ-1)*DT
140         DO 12 II=1,IMAX
141         X=XI+(II-1)*DX
142         VVO=0.0
143         IF(X.EQ.0.) GO TO 7
144         VVO=V*TIME/X
145       7 DO 10 KK=1,2
146         C1=0.0
147         C2=0.0
148         C3=0.0
149         C4=0.0
150         E1=1.0
151         E2=1.0
152         E3=1.0
153         E4=1.0
```

```
      T=TIME+(1-KK)*TP
      IF(T.LE.0.) GO TO 10
      IF(KK.EQ.1) GO TO 8
      E1=EXF(-RLAM(1)*TP,E)
      E2=EXF(-RLAM(2)*TP,E)
      E3=EXF(-RLAM(3)*TP,E)
      E4=EXF(-RLAM(4)*TP,E)
    8 F110=F(1,0)*E1
C
C     ----- FIRST TRACER ----
      C1=B(1)*F110
      IF(NS.EQ.1) GO TO 9
C
C     ----- SECOND TRACER ----
      F220=F(2,0)*E2
      F210=F(2,-1)*E1
      IF(P12.GT.1.) F12=F(1,2)*E1
      C2=B(2)*F210+B(3)*F220+C21*(F210-F110-F12)
      IF(NS.EQ.2) GO TO 9
C
C     ----- THIRD TRACER ----
      F310=F(3,-1)*E1
      F320=F(3,-2)*E2
      F330=F(3,0)*E3
      IF(P13.GT.1.) F13=F(1,3)*E1
      IF(P23.GT.1.) F23=F(2,3)
      F32=F23*E2
      F23=F23*E1
      IF(KDB.EQ.2) WRITE(6,1012) F110,F210,F220,F12,F310,F320,F330,F13,F
     123,F32
      C3=B(4)*F310+B(5)*F320+B(6)*F330+C31*(F310-F210-F23)+C32*(F320-F22
     10-F32)+C331*(F210-F110-F12)+C332*(F13-F310+F110)+C333*(F310-F210-F
     223)
      IF(NS.EQ.3) GO TO 9
C
C     ----- FOURTH TRACER ----
      F410=F(4,-1)*E1
      F420=F(4,-2)*E2
      F430=F(4,-3)*E3
      F440=F(4,0)*E4
      IF(P14.GT.1.) F14=F(1,4)*E1
      IF(P24.GT.1.) F24=F(2,4)
      IF(P34.GT.1.) F34=F(3,4)
      F42=F24*E2
      F24=F24*E1
      F43=F34*E3
      F44=F34*E2
      F34=F34*E1
      IF(KDB.EQ.2) WRITE(6,1013) F410,F420,F430,F440,F14,F24,F42,F34,F4
     1,F44
      C4=B(7)*F410+B(8)*F420+B(9)*F430+B(10)*F440+C41*(F410-F310-F34)+C4
     12*(F420-F320-F44)+C43*(F430-F330-F43)+C441*(F410-F310-F34)+C442*(F
     2310-F210-F23)+C443*(F24-F410+F210)+C451*(F420-F320-F44)+C452*(F320
     3-F220-F32)+C453*(F42-F420+F220)+C461*(F110-F410+F14)+C462*(F410-F2
     410-F24)+C463*(F34-F410+F310)+C464*(F310-F110-F13)+C465*(F23-F310+F
     5210)+C466*(F12-F210+F110)
    9 IF(KK.EQ.2) GO TO 10
      CONC1=C1
      CONC2=C2
      CONC3=C3
      CONC4=C4
   10 CONTINUE
      CONC1=CONC1-C1
      CONC2=CONC2-C2
      CONC3=CONC3-C3
      CONC4=CONC4-C4
      IF(KPR.EQ.0) WRITE(6,1014) X,TIME,VVO,CONC1,CONC2,CONC3,CONC4
   12 IF(KPR.EQ.1) WRITE(6,1015) X,TIME,VVO,CONC1,CONC2,CONC3,CONC4
   14 CONTINUE
C
C     ---------
 1000 FORMAT(6I5,5F10.0)
 1001 FORMAT(20A4)
 1002 FORMAT(8F10.0)
 1003 FORMAT(1H1,10X,82(1H*)/11X,1H*,80X,1H*/11X,1H*,9X,'MULTI-ION SOLUT
     1E TRANSPORT',30X,'CHAIN',10X,1H*/11X,1H*,80X,1H*/11X,1H*,9X,'FOUR
     2SPECIES',59X,1H*/11X,1H*,9X,'PREFERENTIAL RELEASE',51X,1H*/11X,1H*
     3,80X,1H*)
```

```
 1004 FORMAT(11X,1H*,9X,'FIRST-TYPE BOUNDARY CONDITION',42X,1H*)
 1005 FORMAT(11X,1H*,9X,'THIRD-TYPE BOUNDARY CONDITION',42X,1H*)
 1006 FORMAT(11X,1H*,80X,1H*/11X,1H*,20A4,1H*/11X,1H*,80X,1H*/11X,82(1H*
     1))
 1007 FORMAT(//11X,'INPUT PARAMETERS'/11X,16(1H=)//11X,'NS =',I5,10X,'V
     1=',F12.4,10X,'D =',F12.4/11X,'NR =',I5,10X,'WC =',F11.4,10X,'TP ='
     2,F11.4/11X,'NB =',I5)
 1008 FORMAT(///9X,'TRACER',7X,'ZERO',13X,'R',11X,'DONE',11X,'GAMMA',11X
     1,'RLAM'//(11X,I2,D16.5,F14.3,3F15.8))
 1009 FORMAT(///11X,'B(I)-COEFFICIENTS'/11X,17(1H=)//11X,4('I',9X,'B(I)'
     1,9X)/(10X,4(I2,D15.6,6X)))
 1010 FORMAT(//9X,'C21= ',D13.5,6X,'C31= ',D13.5,6X,'C32= ',D13.5/9X,
     1'C331= ',D12.5,6X,'C332= ',D12.5,6X,'C333= ',D12.5/9X,'C41= ',
     2D13.5,6X,'C42= ',D13.5,6X,'C43= ',D13.5/9X,'C441= ',D12.5,6X,
     3'C442= ',D12.5,6X,'C443= ',D12.5/9X,'C451= ',D12.5,6X,'C452= ',
     4D12.5,6X,'C453= ',D12.5/9X,'C461= ',D12.5,6X,'C462= ',D12.5,6X,
     5'C463= ',D12.5/9X,'C464= ',D12.5,6X,'C465= ',D12.5,6X,'C466= ',
     6D12.5)
 1011 FORMAT(///8X,'DISTANCE',6X,'TIME',7X,'PORE VOLUME',4X,19(1H-),'CON
     1CENTRATION',19(1H-)/11X,'(X)',8X,'(T)',9X,'(VVO)',11X,'(1)',11X,'(
     22)',11X,'(3)',11X,'(4)')
 1012 FORMAT(//9X,'F110= ',D12.5,4X,'F210= ',D12.5,4X,'F220= ',D12.5/9X,
     1'F12= ',D13.5,4X,'F310= ',D12.5,4X,'F320= ',D12.5/9X,'F330= ',D12.
     25,4X,'F13= ',D13.5,4X,'F23= ',D13.5/9X,'F32= ',D13.5)
 1013 FORMAT(//9X,'F410= ',D12.5,4X,'F420= ',D12.5,4X,'F430= ',D12.5/9X,
     1'F440= ',D12.5,4X,'F14= ',D13.5,4X,'F24= ',D13.5/9X,'F42= ',D13.5,
     24X,'F34= ',D13.5,4X,'F43= ',D13.5/9X,'F44= ',D13.5)
 1014 FORMAT(2X,3F13.3,2X,4F14.5)
 1015 FORMAT(2X,3F13.3,2X,4D14.5)
      STOP
      END


      FUNCTION F(I,JJ)
C
C     PURPOSE: TO CALCULATE FIJK-TERMS
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON R(4),DONE(4),RLAM(4),D,V,X,T,KSURF
C
C     ---------
      J=IABS(JJ)
      IF(JJ.LT.0) A=RLAM(J)
      IF(JJ.EQ.0) A=RLAM(I)
      IF(JJ.GT.0) A=(DONE(I)-DONE(J))/(R(I)-R(J))
      U2=V*V+4.*D*(DONE(I)-A*R(I))
      S1=2.*DSQRT(D*R(I)*T)
      U=DSQRT(DABS(U2))
      VT=V*T
      UT=U*T
      E=0.0
C
C     ----- CASE FOR POSITIVE VALUES OF U2 ----
      IF(U2.LT.0.) GO TO 28
      AM=0.5*(V-U)*X/D-A*T
      BM1=(R(I)*X-UT)/S1
      BP1=(R(I)*X+UT)/S1
      AP=0.5*(U+V)*X/D-A*T
      IF(KSURF.EQ.0) GO TO 20
C
C     ----- CASE FOR THIRD-TYPE BOUNDARY CONDITION ----
      CP1=(R(I)*X+VT)/S1
      ALP=.3275911
      CM1=(R(I)*X-VT)/S1
      DUV=DABS(1.-U/V)
      IF((BP1.GT.4.).AND.(CP1.GT.4.)) GO TO 4
      IF((BP1.LT.2.5).AND.(CP1.LT.2.5)) GO TO 2
      IF(DUV.GT.0.1) GO TO 1
      IF(CP1.GT.3.) GO TO 4
      GO TO 2
    1 E1=2./((U/V)**2-1.)
      G1=V*X/D-DONE(I)*T/R(I)
      F1=V/(U-V)*EXF(AP,BP1)-E1*EXF(G1,CP1)
      GO TO 6
    2 D1=-CM1**2-DONE(I)*T/R(I)
      BETA=ALP*V*DSQRT(T/(D*R(I)))
      T1=1./(1.+ALP*BP1)
      T2=1./(1.+ALP*CP1)
```

```
      C1=T1*T2*(1.+ALP*CM1)
      C2=T1*(C1-BETA*T2**2)
      C3=T1*(C2-BETA*T2**3)
      C4=T1*(C3-BETA*T2**4)
      C5=T1*(C4-BETA*T2**5)
      F1=V*(.2548296*C1-.2844967*C2+1.421414*C3-1.453152*C4+1.061405*C5)
     1*EXF(D1,E)/(V+U)
      GO TO 6
    4 B=DONE(I)*T/R(I)+CM1**2
      H=1./(BP1*(R(I)*X+VT))
      WT=H*VT
      HT=H*UT
      B1=WT+2.*HT
      B2=WT*B1+2.*HT**2
      B3=WT*B2+2.*HT**3
      B4=WT*B3+2.*HT**4
      B5=WT*B4+2.*HT**5
      B6=WT*B5+2.*HT**6
      B7=WT*B6+2.*HT**7
      B8=WT*B7+2.*HT**8
      Z1=H*R(I)*X
      Z2=Z1**2
      Z3=Z1*Z2
      Z4=Z1*Z3
      Z5=Z1*Z4
      Z6=Z1*Z5
      Z7=Z1*Z6
      Z8=Z1*Z7
      Z9=Z1*Z8
      A1=Z1-WT
      A2=Z3-WT*(B2+3.*(B1*Z1+Z2))
      A3=Z5-WT*(B4+5.*(B3*Z1+Z4)+10.*(B2*Z2+B1*Z3))
      A4=Z7-WT*(B6+7.*(B5*Z1+Z6)+21.*(B4*Z2+B1*Z5)+35.*(B3*Z3+B2*Z4))
      A5=Z9-WT*(B8+9.*(B7*Z1+Z8)+36.*(B6*Z2+B1*Z7)+84.*(B5*Z3+B2*Z6)+126
     1.*(B4*Z4+B3*Z5))
      F1=.5641896*V*EXF(-B,E)*(A1-.5*A2+.75*A3-1.875*A4+6.5625*A5)/(U+V)
    6 IF(JJ.GT.0) GO TO 8
      F=V/(V+U)*EXF(AM,BM1)-F1
      RETURN
    8 S2=2.*DSQRT(D*R(J)*T)
      BM2=(R(J)*X-UT)/S2
      BP2=(R(J)*X+UT)/S2
      CP2=(R(J)*X+VT)/S2
      CM2=(R(J)*X-VT)/S2
      IF((BP2.GT.4.).AND.(CP2.GT.4.)) GO TO 14
      IF((BP2.LT.2.5).AND.(CP2.LT.2.5)) GO TO 10
      IF(DUV.GT.0.1) GO TO 9
      IF(CP2.GT.3.) GO TO 14
      GO TO 10
    9 E2=2./((U/V)**2-1.)
      G2=V*X/D-DONE(J)*T/R(J)
      AP=0.5*(V+U)*X/D-A*T
      F2=V/(U-V)*EXF(AP,BP2)-E2*EXF(G2,CP2)
      GO TO 18
   10 D2=-CM2**2-DONE(J)*T/R(J)
      BETA=ALP*V*DSQRT(T/(D*R(J)))
      T1=1./(1.+ALP*BP2)
      T2=1./(1.+ALP*CP2)
      C1=T1*T2*(1.+ALP*CM2)
      C2=T1*(C1-BETA*T2**2)
      C3=T1*(C2-BETA*T2**3)
      C4=T1*(C3-BETA*T2**4)
      C5=T1*(C4-BETA*T2**5)
      F2=V*(.2548296*C1-.2844967*C2+1.421414*C3-1.453152*C4+1.061405*C5)
     1*EXF(D2,E)/(V+U)
      GO TO 16
   14 B=DONE(J)*T/R(J)+CM2**2
      H=1./(BP2*(R(J)*X+VT))
      WT=H*VT
      HT=H*UT
      B1=WT+2.*HT
      B2=WT*B1+2.*HT**2
      B3=WT*B2+2.*HT**3
      B4=WT*B3+2.*HT**4
      B5=WT*B4+2.*HT**5
      B6=WT*B5+2.*HT**6
      B7=WT*B6+2.*HT**7
      B8=WT*B7+2.*HT**8
```

```
      Z1=H*R(J)*X
      Z2=Z1**2
      Z3=Z1*Z2
      Z4=Z1*Z3
      Z5=Z1*Z4
      Z6=Z1*Z5
      Z7=Z1*Z6
      Z8=Z1*Z7
      Z9=Z1*Z8
      A1=Z1-WT
      A2=Z3-WT*(B2+3.*(B1*Z1+Z2))
      A3=Z5-WT*(B4+5.*(B3*Z1+Z4)+10.*(B2*Z2+B1*Z3))
      A4=Z7-WT*(B6+7.*(B5*Z1+Z6)+21.*(B4*Z2+B1*Z5)+35.*(B3*Z3+B2*Z4))
      A5=Z9-WT*(B8+9.*(B7*Z1+Z8)+36.*(B6*Z2+B1*Z7)+84.*(B5*Z3+B2*Z6)+126
     1.*(B4*Z4+B3*Z5))
      F2=.5641896*V*EXF(-B,E)*(A1-.5*A2+.75*A3-1.875*A4+6.5625*A5)/(U+V)
   16 IF((BM1.GT.0.).OR.(BM2.GT.0.)) GO TO 18
      Q=-BM2
      BM2=-BM1
      BM1=Q
   18 F=V/(V+U)*(EXF(AM,BM2)-EXF(AM,BM1))+F1-F2
      RETURN
C
C     ----- CASE FOR FIRST-TYPE BOUNDARY CONDITION ----
   20 IF(JJ.GT.0) GO TO 22
      F=0.5*(EXF(AM,BM1)+EXF(AP,BP1))
      RETURN
   22 S2=2.*DSQRT(D*R(J)*T)
      BM2=(R(J)*X-UT)/S2
      BP2=(R(J)*X+UT)/S2
      IF((BM1.GT.0.).OR.(BM2.GT.0.)) GO TO 24
      Q=-BM2
      BM2=-BM1
      BM1=Q
   24 F=0.5*(EXF(AM,BM2)-EXF(AM,BM1)+EXF(AP,BP2)-EXF(AP,BP1))
      RETURN
C
C     ----- CASE FOR NEGATIVE VALUES OF U2 ----
   28 AM=0.5*V*X/D-A*T
      ARG=0.5*U*X/D
      CS=DCOS(ARG)
      SN=DSIN(ARG)
      A1=R(I)*X/S1
      A2=UT/S1
      CALL CEXF(A1,A2,AM,X1,Y1)
      IF(KSURF.EQ.0) GO TO 32
      CP1=(R(I)*X+VT)/S1
      CM1=V*X/D-DONE(I)*T/R(I)
      C1=2.*V/(V*V-U2)
      C2=0.5*V*V/(D*(DONE(I)-A*R(I)))
      IF(JJ.GT.0) GO TO 30
      F=C1*(CS*(X1*V-Y1*U)-SN*(X1*U+Y1*V))+C2*EXF(CM1,CP1)
      RETURN
   30 CONTINUE
      S2=2.*DSQRT(D*R(J)*T)
      CM2=V*X/D-DONE(J)*T/R(J)
      C3=0.5*V*V/(D*(DONE(J)-A*R(J)))
      CP2=(R(J)*X+VT)/S2
      A1=R(J)*X/S2
      A2=UT/S2
      CALL CEXF(A1,A2,AM,X2,Y2)
      F=C1*(CS*(V*(X2-X1)-U*(Y2-Y1))-SN*(U*(X2-X1)+V*(Y2-Y1)))+C3*EXF(CM
     12,CP2)-C2*EXF(CM1,CP1)
      RETURN
   32 IF(JJ.GT.0) GO TO 34
      F=CS*X1-SN*Y1
      RETURN
   34 S2=2.*DSQRT(D*R(J)*T)
      A1=R(J)*X/S2
      A2=UT/S2
      CALL CEXF(A1,A2,AM,X2,Y2)
      F=CS*(X2-X1)-SN*(Y2-Y1)
      RETURN
      END


      FUNCTION EXF(A,B)
C
```

```
462  C     PURPOSE: TO CALCULATE EXP(A) ERFC(B)
463  C
464         IMPLICIT REAL*8 (A-H,O-Z)
465         EXF=0.0
466         IF((DABS(A).GT.170.).AND.(B.LE.0.)) RETURN
467         IF(B.NE.0.0) GO TO 1
468         EXF=DEXP(A)
469         RETURN
470       1 C=A-B*B
471         IF((DABS(C).GT.170.).AND.(B.GT.0.)) RETURN
472         IF(C.LT.-170.) GO TO 4
473         X=DABS(B)
474         IF(X.GT.2.5) GO TO 2
475         T=1./(1.+.3275911*X)
476         Y=T*(.2548296-T*(.2844967-T*(1.421414-T*(1.453152-1.061405*T))))
477         GO TO 3
478       2 Y=.5641896/(X+.5/(X+1./(X+1.5/(X+2./(X+2.5/(X+3./(X+1.)))))))
479       3 EXF=Y*DEXP(C)
480       4 IF(B.LT.0.0) EXF=2.*DEXP(A)-EXF
481         RETURN
482         END


483         SUBROUTINE CEXF(A,B,Z,U,V)
484  C
485  C      COMPLEX ERFC-FUNCTION: U+IV=EXP(Z)ERFC(A+IB)
486  C
487         IMPLICIT REAL*8 (A-H,O-Z)
488         DIMENSION W(10),H(10)
489         DATA W/.4622437,.2866755,.1090172,.02481052,.3243773D-2,
490        1.2283386D-3,.7802556D-5,.1086069D-6,.4399341D-9,.2229394D-12/,
491        2H/.2453407,.7374737,1.234076,1.738538,2.254974,
492        32.788806,3.347855,3.944764,4.603682,5.387481/
493  C
494  C      ----------
495         X=DABS(A)
496         Y=DABS(B)
497         U=0.0
498         V=0.0
499         E=0.0
500         XYZ=Y*Y+Z-X*X
501         IF(DABS(XYZ).GT.170.)RETURN
502         COS=DCOS(2.*X*Y)
503         SIN=DSIN(2.*X*Y)
504         IF((X+Y).LT.6.) GO TO 2
505         T=0.0
506         DO 1 K=1,10
507         T=T+W(K)*((X/((Y-H(K))**2+X*X))+(X/((Y+H(K))**2+X*X)))
508       1 V=V+W(K)*((Y-H(K))/((Y-H(K))**2+X*X)+(Y+H(K))/((Y+H(K))**2+X*X))
509         U=.3183099*DEXP(XYZ)*(T*COS-V*SIN)
510         V=.3183099*DEXP(XYZ)*(-T*SIN-V*COS)
511         IF(X.EQ.0.)U=DEXP(DMIN1(Z,1.7D2))
512         GO TO 8
513       2 IF(X.GT.2.5) GO TO 3
514         T=1./(1.+.3275911*X)
515         U=T*(.2548296-T*(.2844967-T*(1.421414-T*(1.453152-1.06145*T))))
516         GO TO 4
517       3 U=.5641896/(X+.5/(X+1./(X+1.5/(X+2./(X+2.5/(X+3./(X+1.)))))))
518       4 IF(Y.EQ.0.) GO TO 7
519         IF(X.EQ.0.) V=-.3183099*Y
520         IF(X.EQ.0.) GO TO 5
521         U=U-.1591549*(1.D0-COS)/X
522         V=V-.1591549*SIN/X
523       5 NT=12.+2.*Y
524         DO 6 I=1,NT
525         P=I
526         ARG=P*Y
527         F1=X*(DEXP(ARG)+DEXP(-ARG))
528         F2=0.5*P*(DEXP(ARG)-DEXP(-ARG))
529         EX=.6366198*DEXP(-0.25*P*P)/(4.*X*X+P*P)
530         U=U-EX*(2.*X-F1*COS+F2*SIN)
531       6 V=V-EX*(F1*SIN+F2*COS)
532         V=V*DEXP(Z-X*X)
533       7 U=U*DEXP(Z-X*X)
534       8 IF(B.LT.0.) V=-V
535         IF(A.LT.0.) U=2.*EXF(Z,E)-U
536         RETURN
537         END
```

APPENDIX 3

Definition of the most significant variables

Variable	Definition
A(10)	Vector containing the values of the coefficients A_1 – A_{10}.
B(10)	Vector containing the values of the coefficients B_1 – B_{10}.
C1,...,C4	Dummy variables for the concentration of the four species.
CONC1,...,CONC4	Calculated concentrations of the four chain members.
D	Dispersion coefficient.
DONE(4)	Values of μ_i for the four chain members.
DT	t-increment for printout.
DX	x-increment for printout.
F12	Value of the term S_{12}; more general:
FIJ	Value of the term S_{ij}.
F110	Value of the term F_{110}; more general:
FIJK	Value of the term F_{ijk}.
GAMMA(4)	Values of γ_i for the four chain members.
KDB	Debugging code. If KDB > 0, various coefficients will be printed during execution. In addition, values of all terms F_{ijk} and S_{ij} will be printed during execution when KDB = 2.
KPR	Format code for printout. If KPR = 0, concentrations are printed in regular F14.5 format; if KPR = 1, concentrations are printed in the exponential D14.5 format.
KSURF	Code specifying the input boundary condition. If KSURF = 0, the solution for a first-type boundary condition will be given; if KSURF ≠ 0, the solution for a third-type boundary conditions is given.
NB	Boundary code that specifies if the Bateman equations must be used for the input boundary conditions. If NB = 1, the parameters A_i and B_i are calculated in the program. If NB = 0, the Bateman equations are not used; values of the parameters B_i are then read in.
NC	Number of examples to be executed.
NR	Code specifying the form of the decay terms. If NR = 0, the retardation factors R_i are dropped from the decay terms in the transport equations; if NR = 1, the decay terms are not altered.
NS	Number of chain members considered (NS ≤ 4).
Q	Volumetric flux density.
R(4)	Values of R_i for the four chain members.
RLAM(4)	Values of λ_i for the four chain members.
T	Dummy variable for time.
TI	Smallest t-value for which concentrations are calculated.
TIME	Time, t.
TITLE(20)	Title (input label).
TM	Maximum value of t for which concentrations are calculated.
TP	Pulse time, t_o.
V	Average pore-water velocity, v.
VVO	Local value of the amount of pore volumes (VVO = vt/x).
WC	Volumetric water content, θ (dummy variable if NB = 0).

X	Distance, x.
XI	Smallest value of x for which concentrations are calculated.
XM	Maximum value of x for which concentrations are calculated.
ZERO(4)	Values of M_i^o for the four chain members; not needed if NB=0.

APPENDIX 4

Input data instructions

Line	Variables	Format	Comments
1	NC	I5	Number of problems to be considered. The remaining lines are read in for each case (hence, they are repeated NC times).
2	TITLE	20(A4)	Title.
3	NS,NR,NB,KSURF, KDB,KPR,V,D,WC, TP	6I5,4F10.0	Value for WC is not needed if NB = 0.
4	(ZERO(I) (GAMMA(I), I=1,4)	8F10.0	Use dummy values for ZERO(I) = M_i^o if NB = 0.
5	XI,DX,XM TI,DT,TM	8F10.0	These parameters define the x and t-values for which concentrations are calculated.
6,7	(B(I),I=1,10)	8F10.0	These two lines are needed only if NB = 0.

APPENDIX 5

Input data for the two examples considered in this study

```
2
     EXAMPLE 1: NITRIFICATION  (CHO,1971)
3    0    0    1    0    0       1.0      0.18      1.00      200.0
   2.00      1.00      1.00       5.0      0.01      0.10        0.0       0.95
    1.0       0.0       0.0       0.0       0.0       0.0        0.0        0.0
    0.0       5.0     200.0     200.0       0.0     200.0
    1.0       0.0       0.0       0.0       0.0       0.0        0.0        0.0
    0.0       0.0
     EXAMPLE 2: RADIONUCLIDE TRANSPORT
4    1    1    1    0    1     100.00      10.0       0.4     10000.
10000.0   14000.0   50000.0     500.0     .0079 0.0000028 0.0000087   0.00043
 50000.       0.0        .0       0.0      .001      .001      .001       .001
    0.0       5.0     250.0    1000.0    9000.0   10000.0
```

APPENDIX 6

Output file for the data of Appendix 5

```
*******************************************************************************
*                                                                             *
*        MULTI-ION SOLUTE TRANSPORT                                  CHAIN    *
*                                                                             *
*        FOUR SPECIES                                                         *
*        PREFERENTIAL RELEASE                                                 *
*                                                                             *
*        THIRD-TYPE BOUNDARY CONDITION                                        *
*                                                                             *
*        EXAMPLE 1: NITRIFICATION  (CHO,1971)                                 *
*                                                                             *
*******************************************************************************
```

INPUT PARAMETERS
==========

NS =	3	V =	1.0000	D =	0.1800
NR =	0	WC =	1.0000	TP =	200.0000
NB =	0				

TRACER	ZERO	R	DONE	GAMMA	RLAM
1	0.00000D+00	2.000	0.01000000	0.00000000	0.00000000
2	0.00000D+00	1.000	0.10000000	0.00000000	0.00000000
3	0.00000D+00	1.000	0.00000000	0.00000000	0.00000000

B(I)-COEFFICIENTS
==========

I	B(I)	I	B(I)	I	B(I)	I	B(I)
1	0.100000D+01	2	0.000000D+00	3	0.000000D+00	4	0.000000D+00
5	0.000000D+00	6	0.000000D+00	7	0.000000D+00	8	0.000000D+00
9	0.000000D+00	10	0.000000D+00				

DISTANCE (X)	TIME (T)	PORE VOLUME (VVO)	CONCENTRATION (1)	(2)	(3)	(4)
0.000	200.000	0.000	0.99821	0.00173	0.00006	0.00000
5.000	200.000	40.000	0.94961	0.03871	0.01168	0.00000
10.000	200.000	20.000	0.90338	0.05951	0.03712	0.00000
15.000	200.000	13.333	0.85940	0.07048	0.07012	0.00000
20.000	200.000	10.000	0.81756	0.07554	0.10690	0.00000
25.000	200.000	8.000	0.77775	0.07706	0.14519	0.00000
30.000	200.000	6.667	0.73989	0.07648	0.18363	0.00000
35.000	200.000	5.714	0.70387	0.07470	0.22143	0.00000
40.000	200.000	5.000	0.66960	0.07226	0.25815	0.00000
45.000	200.000	4.444	0.63700	0.06947	0.29354	0.00000
50.000	200.000	4.000	0.60599	0.06653	0.32748	0.00000
55.000	200.000	3.636	0.57648	0.06356	0.35995	0.00000
60.000	200.000	3.333	0.54842	0.06063	0.39095	0.00000
65.000	200.000	3.077	0.52172	0.05778	0.42050	0.00000
70.000	200.000	2.857	0.49632	0.05503	0.44865	0.00000
75.000	200.000	2.667	0.47215	0.05239	0.47545	0.00000
80.000	200.000	2.500	0.44901	0.04986	0.50097	0.00000
85.000	200.000	2.353	0.42508	0.04738	0.52522	0.00000
90.000	200.000	2.222	0.38943	0.04453	0.54804	0.00000
95.000	200.000	2.105	0.31490	0.03979	0.56824	0.00000
100.000	200.000	2.000	0.19272	0.03122	0.58260	0.00000
105.000	200.000	1.905	0.07679	0.01995	0.58714	0.00000
110.000	200.000	1.818	0.01794	0.01024	0.58083	0.00000
115.000	200.000	1.739	0.00231	0.00449	0.56635	0.00000
120.000	200.000	1.667	0.00016	0.00183	0.54705	0.00000
125.000	200.000	1.600	0.00001	0.00073	0.52498	0.00000
130.000	200.000	1.538	0.00000	0.00029	0.50106	0.00000
135.000	200.000	1.481	0.00000	0.00012	0.47562	0.00000
140.000	200.000	1.429	0.00000	0.00005	0.44876	0.00000
145.000	200.000	1.379	0.00000	0.00002	0.42047	0.00000
150.000	200.000	1.333	0.00000	0.00001	0.39072	0.00000
155.000	200.000	1.290	0.00000	0.00000	0.35943	0.00000
160.000	200.000	1.250	0.00000	0.00000	0.32652	0.00000
165.000	200.000	1.212	0.00000	0.00000	0.29193	0.00000
170.000	200.000	1.176	0.00000	0.00000	0.25557	0.00000
175.000	200.000	1.143	0.00000	0.00000	0.21736	0.00000
180.000	200.000	1.111	0.00000	0.00000	0.17741	0.00000
185.000	200.000	1.081	0.00000	0.00000	0.13628	0.00000
190.000	200.000	1.053	0.00000	0.00000	0.09581	0.00000
195.000	200.000	1.026	0.00000	0.00000	0.05947	0.00000
200.000	200.000	1.000	0.00000	0.00000	0.03134	0.00000

```
*******************************************************************************
*                                                                             *
*         MULTI-ION SOLUTE TRANSPORT                                CHAIN     *
*                                                                             *
*         FOUR SPECIES                                                        *
*         PREFERENTIAL RELEASE                                                *
*                                                                             *
*         THIRD-TYPE BOUNDARY CONDITION                                       *
*                                                                             *
*         EXAMPLE 2: RADIONUCLIDE TRANSPORT                                   *
*                                                                             *
*******************************************************************************
```

INPUT PARAMETERS

NS = 4 V = 100.0000 D = 10.0000
NR = 1 WC = 0.4000 TP = 10000.0000
NB = 1

TRACER	ZERO	R	DONE	GAMMA	RLAM
1	0.50000D+05	10000.000	0.00790000	0.00100000	0.00890000
2	0.00000D+00	14000.000	0.00000280	0.00100000	0.00100280
3	0.00000D+00	50000.000	0.00000870	0.00100000	0.00100870
4	0.00000D+00	500.000	0.00043000	0.00100000	0.00143000

B(I)-COEFFICIENTS

I	B(I)	I	B(I)	I	B(I)	I	B(I)
1	0.125000D+01	2	-0.125044D+01	3	0.125044D+01	4	0.443684D-03
5	0.593431D+00	6	-0.593874D+00	7	-0.516740D-06	8	0.120853D-01
9	-0.122637D-01	10	0.178925D-03				

DISTANCE	TIME	PORE VOLUME	CONCENTRATION			
(X)	(T)	(VVO)	(1)	(2)	(3)	(4)
0.000	1000.000	0.000	0.17223D-03	0.46515D+00	0.11223D-02	0.43196D-05
5.000	1000.000	20000.000	0.28532D-03	0.86173D+00	0.32843D-03	0.18007D-04
10.000	1000.000	10000.000	0.20949D-03	0.23503D-01	0.15595D-05	0.19105D-04
15.000	1000.000	6666.667	0.87774D-07	0.13240D-06	0.38435D-11	0.18089D-04
20.000	1000.000	5000.000	0.31171D-15	0.11647D-15	0.15561D-20	0.17095D-04
25.000	1000.000	4000.000	0.52002D-29	0.95033D-30	0.72587D-35	0.16128D-04
30.000	1000.000	3333.333	0.36043D-48	0.40354D-49	0.20127D-54	0.15188D-04
35.000	1000.000	2857.143	0.99318D-73	0.76193D-74	0.00000D+00	0.14274D-04
40.000	1000.000	2500.000	0.00000D+00	0.00000D+00	0.00000D+00	0.13386D-04
45.000	1000.000	2222.222	0.00000D+00	0.00000D+00	0.00000D+00	0.12525D-04
50.000	1000.000	2000.000	0.00000D+00	0.00000D+00	0.00000D+00	0.11690D-04
55.000	1000.000	1818.182	0.00000D+00	0.00000D+00	0.00000D+00	0.10883D-04
60.000	1000.000	1666.667	0.00000D+00	0.00000D+00	0.00000D+00	0.10102D-04
65.000	1000.000	1538.462	0.00000D+00	0.00000D+00	0.00000D+00	0.93487D-05
70.000	1000.000	1428.571	0.00000D+00	0.00000D+00	0.00000D+00	0.86226D-05
75.000	1000.000	1333.333	0.00000D+00	0.00000D+00	0.00000D+00	0.79242D-05
80.000	1000.000	1250.000	0.00000D+00	0.00000D+00	0.00000D+00	0.72536D-05
85.000	1000.000	1176.471	0.00000D+00	0.00000D+00	0.00000D+00	0.66110D-05
90.000	1000.000	1111.111	0.00000D+00	0.00000D+00	0.00000D+00	0.59969D-05
95.000	1000.000	1052.632	0.00000D+00	0.00000D+00	0.00000D+00	0.54114D-05
100.000	1000.000	1000.000	0.00000D+00	0.00000D+00	0.00000D+00	0.48548D-05
105.000	1000.000	952.381	0.00000D+00	0.00000D+00	0.00000D+00	0.43276D-05
110.000	1000.000	909.091	0.00000D+00	0.00000D+00	0.00000D+00	0.38300D-05
115.000	1000.000	869.565	0.00000D+00	0.00000D+00	0.00000D+00	0.33624D-05
120.000	1000.000	833.333	0.00000D+00	0.00000D+00	0.00000D+00	0.29251D-05
125.000	1000.000	800.000	0.00000D+00	0.00000D+00	0.00000D+00	0.25185D-05
130.000	1000.000	769.231	0.00000D+00	0.00000D+00	0.00000D+00	0.21429D-05
135.000	1000.000	740.741	0.00000D+00	0.00000D+00	0.00000D+00	0.17985D-05
140.000	1000.000	714.286	0.00000D+00	0.00000D+00	0.00000D+00	0.14857D-05
145.000	1000.000	689.655	0.00000D+00	0.00000D+00	0.00000D+00	0.12045D-05
150.000	1000.000	666.667	0.00000D+00	0.00000D+00	0.00000D+00	0.95504D-06
155.000	1000.000	645.161	0.00000D+00	0.00000D+00	0.00000D+00	0.73722D-06
160.000	1000.000	625.000	0.00000D+00	0.00000D+00	0.00000D+00	0.55073D-06
165.000	1000.000	606.061	0.00000D+00	0.00000D+00	0.00000D+00	0.39497D-06
170.000	1000.000	588.235	0.00000D+00	0.00000D+00	0.00000D+00	0.26898D-06

175.000	1000.000	571.429	0.00000D+00	0.00000D+00	0.00000D+00	0.17130D-06
180.000	1000.000	555.556	0.00000D+00	0.00000D+00	0.00000D+00	0.99831D-07
185.000	1000.000	540.541	0.00000D+00	0.00000D+00	0.00000D+00	0.51629D-07
190.000	1000.000	526.316	0.00000D+00	0.00000D+00	0.00000D+00	0.22713D-07
195.000	1000.000	512.821	0.00000D+00	0.00000D+00	0.00000D+00	0.80500D-08
200.000	1000.000	500.000	0.00000D+00	0.00000D+00	0.00000D+00	0.21611D-08
205.000	1000.000	487.805	0.00000D+00	0.00000D+00	0.00000D+00	0.41075D-09
210.000	1000.000	476.190	0.00000D+00	0.00000D+00	0.00000D+00	0.52264D-10
215.000	1000.000	465.116	0.00000D+00	0.00000D+00	0.00000D+00	0.42319D-11
220.000	1000.000	454.545	0.00000D+00	0.00000D+00	0.00000D+00	0.21017D-12
225.000	1000.000	444.444	0.00000D+00	0.00000D+00	0.00000D+00	0.62278D-14
230.000	1000.000	434.783	0.00000D+00	0.00000D+00	0.00000D+00	0.10719D-15
235.000	1000.000	425.532	0.00000D+00	0.00000D+00	0.00000D+00	0.10562D-17
240.000	1000.000	416.667	0.00000D+00	0.00000D+00	0.00000D+00	0.58848D-20
245.000	1000.000	408.163	0.00000D+00	0.00000D+00	0.00000D+00	0.18361D-22
250.000	1000.000	400.000	0.00000D+00	0.00000D+00	0.00000D+00	0.31844D-25

DISTANCE	TIME	PORE VOLUME	CONCENTRATION			
(X)	(T)	(VVO)	(1)	(2)	(3)	(4)
0.000	10000.000	0.000	0.28126D-38	0.55998D-04	0.15580D-05	0.23970D-07
5.000	10000.000	200000.000	0.46609D-38	0.11391D-03	0.16208D-04	0.16912D-06
10.000	10000.000	100000.000	0.77239D-38	0.23171D-03	0.14107D-03	0.15111D-05
15.000	10000.000	66666.667	0.12800D-37	0.47133D-03	0.79188D-03	0.10577D-04
20.000	10000.000	50000.000	0.21211D-37	0.95877D-03	0.12984D-02	0.35898D-04
25.000	10000.000	40000.000	0.35150D-37	0.19503D-02	0.12595D-02	0.63125D-04
30.000	10000.000	33333.333	0.58249D-37	0.39672D-02	0.12686D-02	0.90103D-04
35.000	10000.000	28571.429	0.96528D-37	0.80700D-02	0.12715D-02	0.11690D-03
40.000	10000.000	25000.000	0.15996D-36	0.16416D-01	0.12697D-02	0.14343D-03
45.000	10000.000	22222.222	0.26508D-36	0.33392D-01	0.12585D-02	0.16954D-03
50.000	10000.000	20000.000	0.43928D-36	0.67925D-01	0.12280D-02	0.19491D-03
55.000	10000.000	18181.818	0.72796D-36	0.13815D+00	0.11584D-02	0.21892D-03
60.000	10000.000	16666.667	0.12063D-35	0.27885D+00	0.10095D-02	0.24029D-03
65.000	10000.000	15384.615	0.19991D-35	0.49784D+00	0.71635D-03	0.25653D-03
70.000	10000.000	14285.714	0.33128D-35	0.50542D+00	0.30805D-03	0.26436D-03
75.000	10000.000	13333.333	0.54898D-35	0.16927D+00	0.53143D-04	0.26424D-03
80.000	10000.000	12500.000	0.90973D-35	0.13664D-01	0.26364D-05	0.26109D-03
85.000	10000.000	11764.706	0.15048D-34	0.23341D-03	0.31209D-07	0.25760D-03
90.000	10000.000	11111.111	0.24057D-34	0.80838D-06	0.81080D-10	0.25414D-03
95.000	10000.000	10526.316	0.30950D-34	0.57275D-09	0.45632D-13	0.25073D-03
100.000	10000.000	10000.000	0.22346D-34	0.89203D-13	0.59308D-17	0.24736D-03
105.000	10000.000	9523.810	0.66130D-35	0.37366D-17	0.21940D-21	0.24404D-03
110.000	10000.000	9090.909	0.67537D-36	0.65890D-22	0.36646D-26	0.24075D-03
115.000	10000.000	8695.652	0.21927D-37	0.86333D-27	0.47609D-31	0.23751D-03
120.000	10000.000	8333.333	0.21735D-39	0.10942D-31	0.60324D-36	0.23432D-03
125.000	10000.000	8000.000	0.64370D-42	0.13856D-36	0.76390D-41	0.23116D-03
130.000	10000.000	7692.308	0.56249D-45	0.17537D-41	0.96611D-46	0.22804D-03
135.000	10000.000	7407.407	0.14390D-48	0.21856D-46	0.11916D-50	0.22497D-03
140.000	10000.000	7142.857	0.10722D-52	0.23819D-51	0.12357D-55	0.22193D-03
145.000	10000.000	6896.552	0.23189D-57	0.16519D-56	0.77441D-61	0.21893D-03
150.000	10000.000	6666.667	0.14520D-62	0.51493D-62	0.21249D-66	0.21598D-03
155.000	10000.000	6451.613	0.26271D-68	0.58278D-68	0.21085D-72	0.21306D-03
160.000	10000.000	6250.000	0.13717D-74	0.21571D-74	0.00000D+00	0.21018D-03
165.000	10000.000	6060.606	0.00000D+00	0.00000D+00	0.00000D+00	0.20733D-03
170.000	10000.000	5882.353	0.00000D+00	0.00000D+00	0.00000D+00	0.20453D-03
175.000	10000.000	5714.286	0.00000D+00	0.00000D+00	0.00000D+00	0.20176D-03
180.000	10000.000	5555.556	0.00000D+00	0.00000D+00	0.00000D+00	0.19902D-03
185.000	10000.000	5405.405	0.00000D+00	0.00000D+00	0.00000D+00	0.19632D-03
190.000	10000.000	5263.158	0.00000D+00	0.00000D+00	0.00000D+00	0.19366D-03
195.000	10000.000	5128.205	0.00000D+00	0.00000D+00	0.00000D+00	0.19103D-03
200.000	10000.000	5000.000	0.00000D+00	0.00000D+00	0.00000D+00	0.18843D-03
205.000	10000.000	4878.049	0.00000D+00	0.00000D+00	0.00000D+00	0.18587D-03
210.000	10000.000	4761.905	0.00000D+00	0.00000D+00	0.00000D+00	0.18334D-03
215.000	10000.000	4651.163	0.00000D+00	0.00000D+00	0.00000D+00	0.18085D-03
220.000	10000.000	4545.455	0.00000D+00	0.00000D+00	0.00000D+00	0.17839D-03
225.000	10000.000	4444.444	0.00000D+00	0.00000D+00	0.00000D+00	0.17596D-03
230.000	10000.000	4347.826	0.00000D+00	0.00000D+00	0.00000D+00	0.17356D-03
235.000	10000.000	4255.319	0.00000D+00	0.00000D+00	0.00000D+00	0.17119D-03
240.000	10000.000	4166.667	0.00000D+00	0.00000D+00	0.00000D+00	0.16885D-03
245.000	10000.000	4081.633	0.00000D+00	0.00000D+00	0.00000D+00	0.16655D-03
250.000	10000.000	4000.000	0.00000D+00	0.00000D+00	0.00000D+00	0.16427D-03