

# QUASI-ANALYTICAL SOLUTION FOR PREDICTING THE REDISTRIBUTION OF SURFACE-APPLIED CHEMICALS

M. H. Nachabe, L. R. Ahuja

**ABSTRACT.** We introduce a quasi-analytical solution to predict the redistribution of a surface-applied chemical in the soil profile. The quasi-analytical solution is based on a finite difference scheme of the advection-dispersion transport equation. The solution, however, allows for sorption to the soil matrix and nutrient uptake by the roots. The redistribution of a non-uniform concentration profile is simulated by the method of superposition. Temporal variability of water content, water flux, and dispersion are incorporated into the solution by assuming quasi-steady state flow.

The quasi-analytical solution is accurate and simple. This is attractive for scientists and engineers because the redistribution of a chemical can now be predicted with a hand-held calculator. The quasi-analytical solution can be used to study the redistribution of surface-applied chemicals to (1) analyze the efficiency of fertilizer use, and (2) determine leaching losses from the root zone. **Keywords.** Fertilizer, Application, Transport.

**D**emand for high crop yield has led to surface-applications of large amounts of pesticide and fertilizer in agricultural soils. Poor management of these chemicals has often resulted in both economical losses and deteriorating groundwater quality due to leaching below the root zone. This study will introduce simple and accurate solutions to study the redistribution of surface-applied chemicals in agricultural soils. These solutions will provide tools to assist engineers, agronomists, and soil scientists in their design of chemical applications. The solutions are based on the classical advection-dispersion transport equation which has been widely adopted to predict chemical transport and redistribution in soils (e.g., Smith et al., 1984; Misra and Mishra, 1977; van Genuchten and Wierenga, 1974, among others).

The governing transport equation for a chemical is (van Genuchten and Alves, 1982):

$$\frac{\partial(\theta c + \rho s)}{\partial t} = -\frac{\partial(qc)}{\partial z} + \frac{\partial}{\partial z} \left( D_p \theta \frac{\partial c}{\partial z} \right) + \beta_w \theta c + \beta_s \rho s \quad (1)$$

in liquid and solid phases ( $\text{g/mm}^3/\text{day}$  and  $\text{day}^{-1}$ , respectively). For fertilizers, this decay reflects plants' uptake of the nutrient during its passage in the root zone (e.g., Rose et al., 1982; Smith et al., 1984). The transport equation is linked to the *instantaneous* transient flow field through  $\theta(z,t)$  and  $q(z,t)$  which appear as parameters in equation 1. Solving the transport equation for a transient flow field was achieved lately for the Broadbridge and White and the Green and Ampt infiltration models (Nachabe et al., 1995; Nachabe and Morel-Seytoux, 1995). In this study, however, we seek a solution that is independent of a particular transient water flow model. Indeed, during a period of transient water flow, Wierenga (1977) and De Smedt and Wierenga (1978), among others, suggested that transport can be approximated by a model that assumes an equivalent steady water flux and water content. This allows equation 1 to be written in the simpler form:

$$\frac{\partial(c + \rho s/\theta)}{\partial t} = -\frac{q}{\theta} \frac{\partial(c)}{\partial z} + D_p \frac{\partial^2 c}{\partial z^2} - \beta_w c - \beta_s \rho s/\theta \quad (2)$$

where  $c(z,t)$  is concentration in soil-solution ( $\text{g/mm}^3$ ),  $s(z,t)$  is concentration adsorbed to the solid phase ( $\text{g/g}$ ),  $\theta(z,t)$  is the soil water content ( $\text{mm}^3/\text{mm}^3$ ),  $\rho$  is soil bulk density ( $\text{g/mm}^3$ ),  $q(z,t)$  is flux of soil water ( $\text{mm/day}$ ),  $D_p$  is dispersion coefficient ( $\text{mm}^2/\text{day}$ ),  $z$  is spatial coordinate positive downward (mm), and  $t$  is time (days). The coefficients  $\beta_w$  and  $\beta_s$  are rate constants for first-order decay

In agricultural applications, the water content and flux are assumed constant averages over certain time period,  $T_p$ . When changes in water content and flux are important for long-term prediction, different water content and flux are used for subsequent time periods; thus variability in soil moisture and water flux are incorporated using this quasi-steady-state approach. In general, the choice of  $T_p$  depends on the degree of temporal variability and the frequency of measurements of  $q$  and  $\theta$ . This quasi-steady approach is realistic and practical because (1) changes in water content and flux are rarely monitored *continuously* for long durations in agricultural soils, and (2) the redistribution of the chemical is predicted using average water flow conditions. Solving equation 2 requires a relation between the adsorbed concentration,  $s(z,t)$ , and the concentration in

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solution,  $c(z,t)$ . If single ion-equilibrium described by the linear isotherm:

$$s = k c \quad (3)$$

is used in equation 2, one obtains:

$$\frac{\partial(Rc)}{\partial t} = -\frac{\partial(vc)}{\partial z} + D_p \frac{\partial^2 c}{\partial z^2} - \beta c \quad (4)$$

where  $v = q/\theta$ , the constant interstitial pore water velocity,  $R = 1 + \rho k/\theta$ , a retardation factor, and  $\beta = \beta_w + \beta_s \rho k/\theta$ , a combined decay rate coefficient.

The objective of this study is to introduce a quasi-analytical solution for chemical redistribution which (1) includes dispersion, chemical decay, and linear sorption, (2) accounts for variability in water content, water flux, and dispersion by assuming quasi steady-state flow, and (3) allows one to manage the application of chemicals to control their concentration redistribution in the root zone. This quasi-analytical solution shall provide a simple management tool to balance chemical needs for crops and their applied mass.

## METHODS

The quasi-analytical solution presented here solves equation 4 with a mixing cell scheme (e.g., Bajracharya and Barry, 1994). In the mixing cell scheme, the second-order dispersion term on the right side of equation 4 is dropped and the convective part of the transport equation is discretized using finite difference. Here, we use a time-forward and backward space fully implicit finite difference scheme to discretize equation 4. A similar scheme was adopted for the model GPFARM, Great Plains Framework for Agricultural Resources Management (Nachabe and Ahuja, 1995). The resulting algebraic equation is:

$$R \frac{c(i, j+1) - c(i, j)}{\Delta t} = -v \frac{c(i, j+1) - c(i-1, j+1)}{\Delta z} - \beta c(i, j+1) \quad (5)$$

where  $c(z,t) = (i\Delta z, j\Delta t) = c(i,j)$ . For simplicity,  $\Delta z$ , the space step, is assumed uniform through the profile. Similarly,  $\Delta t$ , the time step, is assumed constant with time. Equation 5 can be rearranged to obtain:

$$c(i, j+1) = A c(i-1, j+1) + B c(i, j) \quad (6)$$

where A and B are the constant coefficients:

$$A = \frac{v\Delta t}{R\Delta z + v\Delta t + \beta\Delta t\Delta z} = \frac{q\Delta t}{\theta(\Delta z + \beta_w\Delta z\Delta t) + \rho k(\Delta z + \beta_s\Delta z\Delta t) + q\Delta t} \quad (7)$$

$$B = \frac{R\Delta z}{R\Delta z + v\Delta t + \beta\Delta t\Delta z} = \frac{\Delta z\theta + \rho k\Delta z}{\theta(\Delta z + \beta_w\Delta z\Delta t) + \rho k(\Delta z + \beta_s\Delta z\Delta t) + q\Delta t} \quad (8)$$

Note that  $A + B = 1$ , if  $\beta$ , the decay rate, is zero. This guarantees that the numerical scheme preserves the mass of the chemical in the profile at all times.

The recursive relationship in equation 6 shall be solved sequentially for the concentration  $c(i, j+1)$  in cell  $i$  at time  $(j+1)\Delta t$  using  $c(i, j)$ , the concentration at the previous time step in cell  $i$ , and  $c(i-1, j+1)$ , the concentration in the preceding cell at time  $(j+1)\Delta t$ . This approach is demonstrated in the following section. Three observations have practical implications concerning the transport equation 2 and its finite difference form in equation 6. First, although the second-order physical dispersion term is dropped from equation 2 in the finite difference procedure, numerical dispersion will incur by using equation 6. This numerical dispersion is attributed to mixing or spatial and temporal averaging of concentrations values in a cell. In Appendix I, we show that the numerical dispersion coefficient  $D_n$  resulting from this mixing can be expressed as a function of  $\Delta t$  and  $\Delta z$  as:

$$D_n = (\Delta z + v\Delta t / R)v/2 \quad (9)$$

Therefore, one accounts for dispersion in the finite difference (mixing cell) scheme, by choosing  $\Delta t$  (or  $\Delta z$ ) so that  $D_n$  matches  $D_p$ , the physical dispersion coefficient. Secondly, because the space derivative is evaluated at the advanced time step, the finite difference scheme is fully implicit and thus unconditionally stable. Finally, because the parameters of the flow field,  $q$  and  $\theta$  are constants, equation 2 is space and time invariant. This allows superposition of solution in the space and time domains. In the following section, we use equation 6 to develop a non-recursive transport solution for a chemical located initially in the surface cell. The case of non-uniform concentration distribution will then be determined by superposition.

## SIMPLE SOLUTION

At time zero, concentration  $c_1$  is in the first or surface cell. Zero concentration is in the rest of the profile. Equation 6 solves recursively for the transport of this chemical into other cells. For example,

**In Cell 1— end of 1st time step**

$$c(1,1) = B \times c_1$$

**2nd time step**

$$c(1,2) = B \times c(1,1) = B^2 \times c_1$$

**3rd time step**

$$c(1,3) = B \times c(1,1) = B^3 \times c_1$$

⋮

**In Cell 2**— end of 1st time step

$$c(2,1) = A c(1,1) = AB c_1$$

2nd time step

$$c(2,2) = A \times c(1,2) + B \times c(2,1) = 2A B^2 c_1$$

3rd time step

$$c(2,3) = A \times c(1,3) + B \times c(2,2) = 3A B^3 c_1$$

**In Cell 3**— end of 1st time step

$$c(3,1) = A^2 B c_1$$

2nd time step

$$c(2,2) = 3A^2 B^2 c_1$$

3rd time step

$$c(2,3) = 6A^2 B^3 c_1$$

Therefore, if we continue these computations, we find by induction that the concentration distribution is:

$$c(i, j) = \frac{(i + j - 2)!}{(i - 1)! (j - 1)!} A^{i-1} B^j c_1 \quad (10)$$

Equation 10 is an explicit solution that permits the calculation of the concentration in any cell  $i$  at time step  $j$ . Equation 10 requires no recursive computations for other cells. The factorial of a number is available on most calculators. A good approximation of  $n!$  is (Kreyszig, 1988):

$$n! \cong \sqrt{(2\pi n)} \left(\frac{n}{e}\right)^n \quad (11)$$

For  $n > 4$ , the relative error is less than 1.5%. Also, we note that the solution in equation 10 can be expressed in terms of the binomial function which is tabulated in many references (e.g., Kreyszig, 1988).

Given an arbitrary initial concentration distribution  $c_1, c_2, c_3, \dots, c_i$  in cells 1 through  $i$  of the soil profile, the concentration redistribution with time is:

$$c(i, j) = \sum_{m=1}^i \frac{(i + j - m - 1)!}{(i - m)! (j - 1)!} A^{i-m} B^j c_m \quad (12)$$

Equation 12, which is simply the superposition of solutions for different cells, predicts the redistribution of any arbitrary non-uniform concentration profile.

#### MASS OF CHEMICAL LEACHED

The mass of chemical in the portion of the profile between  $Z_1 = u \times \Delta z$  and  $Z_2 = w \times \Delta z$  can be determined with the formula:

$$M_z(j) = \sum_{i=u}^w c(i, j) \times \Delta z \times \theta \quad (13)$$

where  $M_z$  is the total mass between  $Z_1$  and  $Z_2$  at time  $j \times \Delta t$ . Obviously, by choosing appropriate indices  $u$  and  $w$ , equation 13 can be used to determine the mass of the chemical in any portion of the root zone, or the mass leached below the root zone.

#### APPLICATION AND COMPARISON WITH ANALYTICAL SOLUTION

The solutions in equations 10 and 12 are easy to apply and require trivial computations. To verify the accuracy of equation 10 we compare it with an analytical solution. For the particular case of  $\beta = 0$  (no nutrient uptake),  $R = 1$  (no retardation), and uniform initial concentration  $c_1$  from the surface to depth  $z_1$ , the analytical solution for  $c(z, t)$  is:

$$c(z, t) = \frac{c_1}{2} \left\{ \operatorname{erf} \left[ \frac{(z - z_1) - vt}{2(Dt)^{1/2}} \right] + e^{vz/D} \operatorname{erf} \left[ \frac{(z + z_1) + vt}{2(Dt)^{1/2}} \right] - \operatorname{erf} \left[ \frac{z - vt}{2(Dt)^{1/2}} \right] - e^{vz/D} \operatorname{erf} \left[ \frac{z + vt}{2(Dt)^{1/2}} \right] \right\} \quad (14)$$

We choose a reference simulation with parameters  $q = 5$  mm/day,  $\theta = 0.167$  mm<sup>3</sup>/mm<sup>3</sup>,  $D_p = 150$  mm<sup>2</sup>/day,  $R = 1$ , and  $\beta = 0$ . Initially, the chemical is in the top 5 mm of the surface. Therefore, there is concentration  $c_1$  in the surface cell, i.e.,  $c(z < 5 \text{ mm}, t = 0) = c_1$ , and zero concentration in the rest of the profile, i.e.,  $c(z > 5 \text{ mm}, t = 0) = 0$ . For the quasi-analytical solution, we choose  $\Delta z = 5$  mm and  $\Delta t = 0.167$  day. This choice of  $\Delta z$  and  $\Delta t$  guarantees that  $D_n$ , calculated using equation 9, equals 150 mm<sup>2</sup>/day, the physical dispersion coefficient in the analytical solution. Figure 1 shows the concentration distribution by the two solutions for seven days. The analytical and quasi-analytical solutions are essentially the

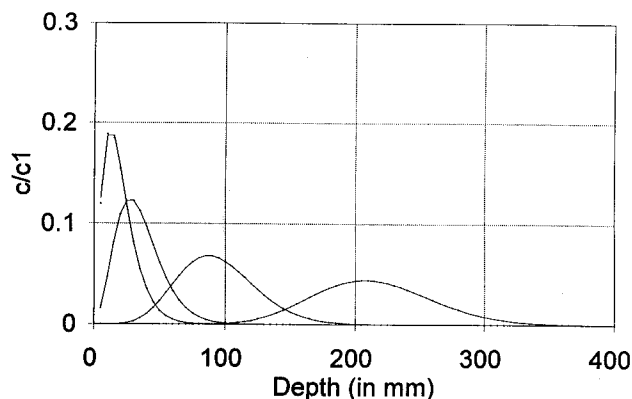


Figure 1—Quasi-analytical (solid line) and Analytical (+) solutions for the concentration distribution at 0.5, 1, 3, and 7 days.

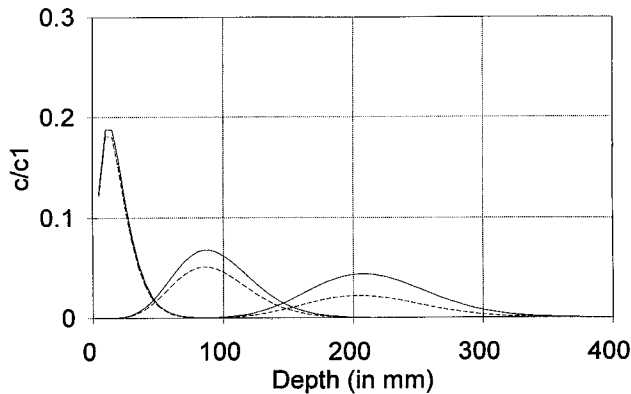


Figure 2—Concentration distribution with first order decay (dashed line) and without decay (solid line) at 0.5, 3, and 7 days.

same. To illustrate the influence of nutrient uptake or chemical decay, we use the same parameters in the reference simulation but assume  $\beta = 0.1$ . Figure 2 compares the two quasi-analytical solutions with and without nutrient uptake. For  $\beta = 0$ , the mass of the chemical is conserved and the areas under the concentration profiles remain the same at all times. This area, however, decreases with time due to nutrient uptake when  $\beta = 0.1$ . To demonstrate the influence of sorption of the chemical to the soil matrix, figure 3 compares the concentration profiles for the reference simulation ( $\beta = 0, R = 1$ ) with the concentration profiles for a simulation with  $\beta = 0.1$  and  $R = 1.5$ . Sorption delays the movement of the chemical by reducing dispersion and advection. At time 0.6 day, the peak of the concentration profile is larger than the peak of the profile for the reference simulation because of the reduction in dispersion. However, after seven days, the peak of the concentration profile becomes smaller than the peak for the reference simulation because of chemical decay.

#### REDISTRIBUTION OF AN ARBITRARY CONCENTRATION PROFILE

Equation 12 solves for the concentration redistribution given an arbitrary initial concentration profile. This is particularly useful for simulating variable water content, water flux, or dispersion by assuming quasi steady flow between time periods. As mentioned earlier for quasi

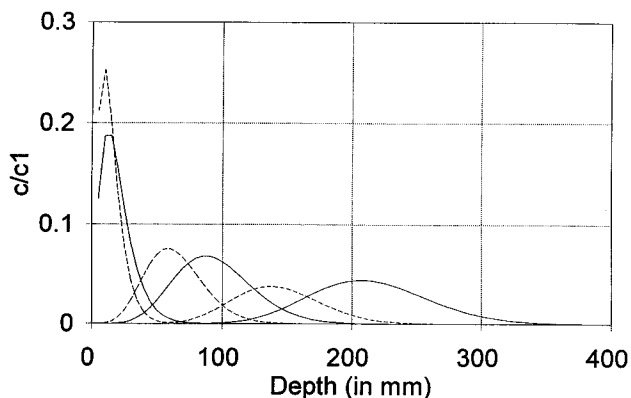


Figure 3—Concentration distribution with first-order decay and linear sorption (dashed line) and without decay and sorption (solid line).

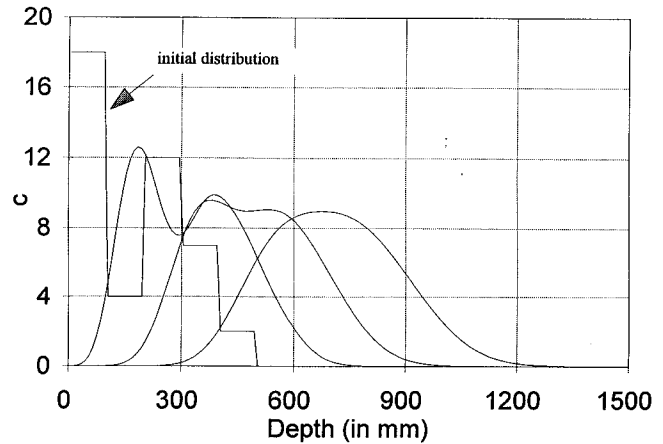


Figure 4—Concentration distribution given a non-uniform initial concentration profile and quasi steady flow.

Table 1. Parameters for quasi steady-state flow

Time Period	q (mm/day)	$D_p$ (mm <sup>2</sup> /day)
1	3.34	100
2	4.18	218
3	5.0	300

steady flow, average water content and flux are constant within a time period, but different for subsequent time periods. The concentration profile at the beginning of a time period,  $T_p$ , is determined from the non-uniform concentration profile at the end of the previous time period. To illustrate this procedure, figure 4 shows an initial non-uniform profile and its redistribution after one, two, and three weeks using the variable parameters in table 1. For this example, the time period is one week, and the profile at the end of one time period becomes the initial condition for the following period.

#### CHEMICAL APPLICATION WITH TIME

Surface-applied chemicals, especially fertilizers, can be applied at different times to control the concentration distribution of the nutrients and optimize their uptake in the root zone. Equation 12 can be used to determine the redistribution for any sequence of chemical application with time. At the time of application, the concentration at the surface cell is adjusted to reflect the increase in mass. Figure 5 shows the redistribution for the first four weeks given the two examples of nitrogen application in table 2. The resulting distributions of the chemical are very different for the two examples. For these examples, the same total mass of the chemical was applied at different times. After four weeks, 4.2 kg/ha of nitrate leached below 60 cm for example 1 versus 12.2 kg/ha for example 2. Thus equations 12 and 13 provide a tool to design the mass and time of the chemical application in order to control its concentration redistribution in the profile. Engineers can try different scenarios of application to balance the requirement of plants' nutrients and the chemicals applied in order to (1) improve the efficiency of use of the fertilizer, and to (2) reduce leaching from the root zone.

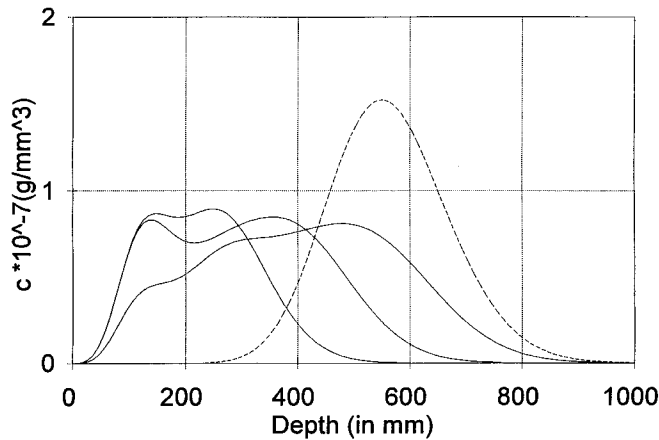


Figure 5—Concentration for the two examples of chemical application in table 2. The concentration distribution for the first example (solid line) is shown after two, three, and four weeks. For the second example (dashed line), only the concentration distribution after four weeks is shown.

Table 2. Nitrate mass\*

Time of Application from Beginning of Simulation (in days)	Example 1	Example 2
1	15	40
8	10	0
15	10	0
22	5	0

\* kg/ha ( $q = 2 \text{ mm/day}$ ;  $q = 0.1 \text{ mm}^3/\text{mm}^3$ ;  $D_p = 200 \text{ mm}^2/\text{day}$ )

## CONCLUSION

We introduced a quasi-analytical solution to predict the redistribution of a surface-applied chemical. The quasi-analytical solution accounts for chemical decay and linear sorption to the soil matrix. Dispersion is incorporated numerically by choosing appropriate space and time steps. The simplicity of application of the quasi-analytical solution shall attract soil scientists, engineers, and agronomists because predictions can now be achieved with hand-held calculator.

The solution in equation 12 accounts for temporal variability in water flow by assuming quasi steady state: average flow parameters are constant within a time period, but different for subsequent time periods. This approach will prove practical for long-term prediction in agricultural soils because average water flow conditions are easier to obtain in the field. In the absence of field measurements, average water flow conditions can be more easily derived from a water balance of the field.

Equation 12 allows us to determine the chemical redistribution in the profile for any sequence of chemical application. We recommend the use of equations 12 and 13 to study different scenarios of application to generate a chemical distribution that balances nutrients' needs by crops and the mass of chemical applied. This will improve the efficiency of use of fertilizers and minimize leaching losses.

## REFERENCES

- Bajracharya, K. and D. A. Barry. 1994. Note on common mixing cell models. *J. of Hydrol.* 153:189-214.
- De Smedt, F. and P. J. Wierenga. 1978. Solute transport through soil with non-uniform water content. *Soil Sci. Soc. Am. J.* 42:7-10.
- Kreyszig, E. 1988. *Advanced Engineering Mathematics*. New York, N.Y.: Wiley & Sons, Inc.
- Misra, C. and B. K. Mishra. 1977. Miscible displacement of nitrate and chloride under field conditions. *Soil Sci. Soc. Am. J.* 41:496-499.
- Nachabe, M. H., A. Islas and T. H. Illangasekare. 1995. Analytical solutions for water flow and solute transport in the unsaturated zone. *Ground Water* 33:304-310
- Nachabe, M. H. and H. J. Morel-Seytoux. 1995. Modeling the displacement of resident soluble salts during infiltration. *Soil Science* 160:243-249.
- Nachabe, M. H. and L. R. Ahuja. 1995. A water balance and chemical transport module for GPFARM. Document in preparation.
- Rose, C. W., F. W. Chichester, J. R. Williams and J. T. Ritchie. 1982. Application of an approximate analytical method for computing solute profiles with dispersion in soils. *J. Environ. Qual.* 11:151-155.
- Smith, S. J., L. R. Ahuja and J. D. Ross. 1984. Leaching of a soluble chemical under field crop condition. *Soil Sci. Soc. Am. J.* 48:252-258.
- Van Genuchten, M. T. and W. J. Alves. 1982. Analytical solutions for the one-dimensional convective-dispersive solute transport equation. U.S. Dept. of Agriculture, Technical Bulletin No. 1661, 151p. Washington, D.C.: U.S. GPO.
- Van Genuchten, M. T. and P. J. Wierenga. 1974. Simulation of one dimensional solute transfer in porous media. New Mexico Agricultural Experiment Station Bulletin No. 628, Las Cruces.
- Wierenga, P. J. 1977. Solute distribution profiles computed with steady-state and transient water movement models. *Soil Sci. Soc. Am. J.* 41:1050-1055.

## APPENDIX I. NUMERICAL DISPERSION COEFFICIENT

Numerical dispersion incurs by finite differencing the equation:

$$R \frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial z} \quad (\text{A-1})$$

Taylor series expansion of  $c(z,t)$  around cell  $c(z = i\Delta z, t = j\Delta t) = c(i,j)$  at time  $(j + 1)\Delta t$  yields:

$$c(i, j + 1) \cong c(i, j) + \left. \frac{\partial c}{\partial t} \right|_{i,j} \Delta t + \left. \frac{\partial^2 c}{\partial t^2} \right|_{i,j} \frac{(\Delta t)^2}{2!} + O(\Delta t^3) \quad (\text{A-2})$$

After noting that  $\partial^2 c / \partial t^2 = (v^2 / R^2) \partial^2 c / \partial z^2$ , equation A-2 is rearranged to obtain the approximation for the left term in A-1:

$$R \frac{\partial c}{\partial t} \Big|_{i,j} \cong R \frac{c(i, j+1) - c(i, j)}{\Delta t} - \frac{v^2}{R} \frac{\partial^2 c}{\partial z^2} \frac{\Delta t}{2} \quad (\text{A-3})$$

Similarly, Taylor series expansion of  $c(i, j)$  at location  $i - 1$  yields:

$$c(i-1, j+1) = c(i, j+1) - \frac{\partial c}{\partial z} \Big|_{i,j+1} \Delta z - \frac{\partial^2 c}{\partial z^2} \frac{(\Delta z)^2}{2!} - O(\Delta z^3) \quad (\text{A-4})$$

Equation A-4 is rearranged to obtain the approximation for the right term in A-1:

$$-v \frac{\partial c}{\partial z} \Big|_{i,j+1} \cong -v \frac{c(i, j+1) - c(i-1, j+1)}{\Delta z} + v \frac{\partial^2 c}{\partial z^2} \frac{\Delta z}{2} \quad (\text{A-5})$$

Substituting equations A-3 and A-5 in A-1 yields:

$$R \frac{c(i, j+1) - c(i, j)}{\Delta t} = -v \frac{c(i, j+1) - c(i-1, j+1)}{\Delta z} + \left( \frac{v^2}{R} \frac{\Delta t}{2} + v \frac{\Delta z}{2} \right) \frac{\partial^2 c}{\partial z^2} \quad (\text{A-6})$$

Therefore, the finite difference (mixing cell) scheme results in the numerical dispersion coefficient:

$$D_n = \frac{v}{2} \left( \frac{v \Delta t}{R} + \Delta z \right) \quad (\text{A-7})$$