Simulation of One-Dimensional Solute Transfer in Porous Media
SUMMARY

A S/360 CSMP (Continuous System Modeling Program) simulation model was developed to analyze one-dimensional transfer of a solute in a porous medium of constant water content. The CSMP model, which was shown to be equivalent to a finite difference approximation of the one-dimensional convection diffusion equation, contained considerable numerical dispersion, caused primarily by a first order numerical approximation of the convection term.

Results comparable to existing analytical solutions were obtained when corrections were made for this numerical dispersion. Stability conditions were derived for the rectangular integration method and equations were developed which allowed a proper selection of layer thickness and time step. The use of higher order integration methods was discussed (Runge-Kutta, Milne). Substantially more computer time was needed with these methods of integration, while the accuracy was similar or even less compared with the (corrected) rectangular method. The importance of using correct boundary conditions, especially for short laboratory columns, was emphasized.

The proposed simulation model is rather simple and requires less programming experience than often is needed for other numerical techniques. Computer programs written in CSMP also tend to be short and compact, which is an additional advantage. These factors may become important when describing more complex distributive systems. Three examples are discussed briefly, showing how the basic program can be adapted to other problems.

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Simulation of One-Dimensional Solute Transfer in Porous Media

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In recent years, many models have been proposed to describe solute movement in soils. Most frequently the one-dimensional convection diffusion equation has been used to investigate theoretically or experimentally the movement of non-interactive solutes. Under steady flow conditions this equation may be written as:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v_0 \frac{\partial C}{\partial x}
\]

(1)

where \( C \) is the solute concentration (meq/cm\(^3\)), \( v_0 \) the average pore water velocity (cm/day), \( D \) the dispersion coefficient (cm\(^2\)/day), \( x \) the distance (cm), and \( t \) the time (days). The value for \( D \) includes both diffusion and dispersion processes and is referred to as the dispersion coefficient. Exact solutions of equation (1) are available only for specific initial and boundary conditions [Lapidus and Amundson (1952), Danckwerts (1953), Brenner (1962), and Cleary and Adrian (1973)]. Although these solutions are useful, especially for laboratory investigations, they are less suitable for field studies, where spatial variations in \( D \) and \( v_0 \) may occur. Many investigators, therefore, use numerical techniques, which also provide greater flexibility in the selection of boundary conditions. Phenomena such as cation exchange, adsorption, and/or decay along with non-homogeneous soils may be included in numerical models without appreciable difficulties.

A special numerical technique is provided by the S/360 CSMP simulation language. This programming language was recently used in several studies of transport processes in soils, e.g. unsaturated water movement [Van Keuleen and Van Beek (1971), Bhuiyan et al. (1971)], solute movement [Frissel et al. (1970)], pesticide movement (van Genuchten et al., 1974), and heat transfer [Wierenga and De Wit (1970)]. General discussions of the simulation of transport processes in soils were presented by De Wit and Van Keuleen (1972) and by Beck and Frissel (1973). Simulation of these transport processes involves dividing the soil into a number of layers or compartments of a given thickness. For each time step, the flow of water, heat, or solute is calculated over the
compartamental boundaries by means of well-known mass transfer equations. Upon computing these flow rates, the computer updates (integrates) for each time step the net gain of material in each layer, using one of the available integration subroutines.

With solutes, however, it was found that the calculated salt front exhibited more dispersion than could be accounted for by the dispersion coefficient used in the program. This phenomenon, called numerical dispersion, has been experienced frequently in the past when numerical approximations were made of the one- or two-dimensional convective diffusion equation [Peaceman and Rachford (1962), Gardner et al (1964), Stone and Brian (1963), Finner and Cooper (1970), Lai and Juttun (1970), Breier (1973), and Goudriaan (1974)].

In this paper a S/360 CSMP solution of equation (1) is discussed. Special attention is given to the problem of numerical dispersion, to the stability of the solution, and to the boundary conditions. Three examples are presented to demonstrate the usefulness of the model.

DESCRIPTION OF THE PHYSICAL SYSTEM

The physical system to be simulated here is defined in the region \(0 < x < \infty\). Solute is allowed to flow from a large reservoir at \(x < 0\) into an initially solute-free column at a rate of \(v_0\), \(C_0\), where \(v_0\) is the average pore-water velocity (cm/day), \(\theta\) the volumetric water content (cm\(^3\)/cm\(^3\)) and \(C_0\) the concentration of the influent (meg/cm\(^3\)). The solute is allowed to diffuse and disperse in the region \(x > 0\). Based on the law of conservation of mass, the upper boundary condition (\(x = 0\)) is:

\[
v_0C_0 = \lim_{x\to 0^+} (v_0 \cdot C - D \frac{\partial C}{\partial x})
\]

where \(\lim_{x\to 0^+}\) indicates that the right-hand side of equation (2a) is evaluated when \(x\) approaches 0 from the positive side. The initial condition of the system is:

\[
C = 0 \quad x > 0 \quad t = 0
\]

When a finite column is considered, a relation similar to equation (2a) can be applied to the lower boundary (\(x = L\)):

\[
\lim_{x\to L^+} (v_0 \cdot C - D \frac{\partial C}{\partial x}) = \lim_{x\to L^-} (v_0 \cdot C)
\]

However, the system then becomes undetermined, unless the region \(x > L\) also is considered. To avoid this difficulty, many authors used the condition:

\[
\frac{\partial C}{\partial x} = 0
\]
\[ \lim_{x \to \infty} \frac{\partial C}{\partial x} = 0 \] (2d)

The solution of equation (1), subject to conditions (2a), (2b), and (2d), was presented by Brenner (1962) both in the form of an infinite summation and as an asymptotic expansion.

A different solution is obtained when a semi-infinite column is considered. In this case, the lower boundary condition becomes:

\[ \lim_{x \to -\infty} C(x,t) = 0 \] (2c)

The solution of equation (1) subject to conditions (2a), (2b), and (2e) has been given by Lindstrom et al (1967) as:

\[ \frac{C(x,t)}{C_0} = \frac{1}{2} \left[ L(x,t) \cdot M(x,t) + N(x,t) \right] \] (3)

where:

\[ L(x,t) = \text{erfc} \left( \frac{x - v_0 t}{\sqrt{4Dt}} \right) \]

\[ M(x,t) = \frac{x}{v_0} \left[ \text{erfc} \left( \frac{x + v_0 t}{\sqrt{4Dt}} \right) \cdot \exp \left( \frac{v_0 x}{D} \right) \right] \]

\[ N(x,t) = v_0 \left[ \frac{x}{v_0} \exp \left( \frac{v_0 x}{D} \right) \right] \cdot \left( \frac{x + v_0 t}{\sqrt{4Dt}} \right) \]

When a pulse of solute is added to the semi-infinite column, the upper boundary condition becomes:

\[ \lim_{x \to 0^+} \left( v_0 C - \frac{\partial C}{\partial x} \right) = v_0 C_0 \quad t < T \]

\[ \lim_{x \to 0^+} \left( v_0 C - \frac{\partial C}{\partial x} \right) = 0 \quad t > T \] (2f)

where \( T \) is the pulse period (days). The solution of equation (1) subject to conditions (2b), (2c), and (2f) is:

\[ \frac{C(x,t)}{C_0} = \frac{1}{2} \left[ L(x,t) \cdot L(x,t-T) \cdot M(x,t) + M(x,t-T) + N(x,t) - N(x,t-T) \right] \] (4)

**DESCRIPTION OF THE SIMULATION MODEL**

Detailed descriptions of CSMP programs for one-dimensional transfer problems can be found in the literature cited above. Only the central equations in the dynamic part of the model will be presented here. A
schematic representation of the dynamic part is given in figure 1, while a listing of the program is given in table 1. The following statements form the central part of the model:

The flow of salt (SFLW) into a soil layer of thickness ΔX (TCOM), is the sum of diffusive and convective transport, according to:

\[
SFLW_i = D \cdot \frac{C_{i+1} - C_i}{\Delta X} + v_0 C_{i-1}
\]  

Fig. 1. Schematic representation of the CSMP-model for solute movement
Table 1. CSMP program for simulation of one-dimensional solute transfer in soil. Output from the listed program was used for constructing Fig. 1 and Table 2 (column 3).

S/360 CSMP VERSION 1.3

TITLE SIMULATION OF ONE-DIMENSIONAL SOLUTE TRANSFER IN SOIL
/ REAL AMSLT(60),SFLW(61),C(60),NSFLW(60)
/ EQUIVALENCE (AMSLT(1),AMSLT(11),INSFLW,NSFLW(1))
INITIAL FIXED 1, NL, TT
PARAM D=30.,FLRW=40.,T=8.,WC=0.4,CO=10.,NL=30,T=COM+3.
DEPTI=NL*TCOM
VOLW=TCOM*WC
TT=T/DELT
T1=TT**DELT
APDI=F-0.5*FLRW*(T=COM-FLRW**DELT)

DYNAMIC NOSORT
CIW=FCNSWITIME-T1,CO,(TT-1)**CO/DELT,0.1
DO 11 I=1,NL
11 CI(I)=AMSLT(I)/VOLW
SFLW(I)=FLRW*CIW
DO 12 I=2,NL
12 SFLW(I)=FLRW*C(I-1)+APDF*C(I-1)-C(I))/T=COM
SFLWNL+1)=FLRW*C(NL)-APDF*[2.*C(NL)-3.*C(NL-1)+C(NL-2)]/T=COM
DO 13 I=1,NL
13 NSFLW(I)=(SFLW(I)-SFLW(I+1))**WC
AMSLT(I+1)=INTGLD(0.,NSFLW(I),30)
A=IMPULS(0.,PRDEL)
IF(A*KEEPLT,1.0) GO TO 15
WRITE(6,14) (CI(I),I=1,NL)
14 FORMAT(1H,29H(I)), PRINTED FOR EVERY LAYER/(10E12.4I)
15 VVO=FLRW**TIME/DEPTH
CCO=SFLWNL(I)/FLRW**CCO

METHOD RECT
TIMER FINTIM=6.,DELT=0.0375,PRDEL=0.3,OUTDEL=0.075
PRINT D,APDF,VOLW,CCO,VVO,T=COM,DEPTW,WC,FLRW,DELT
FINISH VVO=2.
PRINT CO(0,1),VVO
END
STOP
ENDJOB
where \( i \) is the index for depth \((i = 2, 3, \ldots, \text{NL})\), \( \text{NL} \) the number of layers, 
\( C \), the average concentration in the \( i \)th layer, and \( D \) the dispersion coefficient as defined in equation (1). The net flow of salt into each layer \((\text{NSFLW}_i)\) is:
\[
\text{NSFLW}_i = (\text{SFLW}_i - \text{SFLW}_{i+1}) \times \text{WC} \times \text{AREA} \tag{6}
\]
where \( \text{WC} \) is the volumetric water content \((\text{cm}^3/\text{cm}^2)\) and \( \text{AREA} \) the cross-sectional area of the soil column \((\text{cm}^2)\), most conveniently set to unity. The net salt flow into each layer \((\text{NSFLW}_i)\) \((\text{mg/day})\) causes a change in the amount of solute in each layer \((\text{AMSLT}_i)\). This amount is updated every time increment \((\Delta t)\) by integrating the rate of change of \(\text{AMSLT}_i\):
\[
\text{AMSLT}_i = \frac{\text{AMSLT}_{i}}{\text{INTGRL}(\text{AMSLT}_i, \text{NSFLW}_i, \text{NL})} \tag{7}
\]
where \(\text{AMSLT}_i\) represents the updated array of the amount of salt in all layers \((\text{AMSLT}(1, \ldots, \text{NL}))\), \(\text{AMSLT}_1\) represents the array \(\text{AMSLT}_i\) at time zero, and \(\text{NSFLW}_1\) represents the array \(\text{NSFLW}(1, \ldots, \text{NL})\). The third argument of the \text{INTGRL} statement gives the number of integrations to be performed per time increment and is equal to the number of layers \((\text{NL})\). Several integration methods are available to perform the integration of equation (7), ranging from a simple rectangular method (METHOD RECT) to the fifth-order predictor-corrector-modifier method of Milne (METHOD MILNE). A list of the available integration methods is given in the \text{CSMP} manual (IBM, 1972). When the rectangular method is used, equation (7) is synonymous with:
\[
\frac{\text{AMSLT}_i}{\text{AMSLT}_i^{+\Delta t}} + \frac{\text{NSFLW}_i^{+\Delta t}}{\text{NSFLW}_i} = \text{INTGRL}_{\text{AMSLT}_i, \text{NSFLW}_i, \text{NL}} \tag{8}
\]
Finally, the concentration at time \((t+\Delta t)\) is given by:
\[
\frac{\text{AMSLT}_i^{+\Delta t}}{\text{VOLW}} \times \frac{\text{AMSLT}_i^{+\Delta t}}{\text{AMSLT}_i^{+\Delta t}} \times \frac{\text{NSFLW}_i^{+\Delta t}}{\text{NSFLW}_i} \tag{9}
\]
where \(\text{VOLW}\) is the amount of water in each layer: \(\text{VOLW} = \text{AREA} \times \Delta x \times \text{WC}\)
Calculations were made for a finite soil column with the following initial and boundary conditions:
\[
C(x,t) = 0 \quad x > 0 \quad t = 0 \tag{10a}
\]
\[
\text{SFLW}_i = \text{v}_o C_o \quad 1 \leq T \leq T \tag{10b}
\]
\[
\text{SFLW}_{i+1} = \text{v}_o C_{o NL} \cdot \text{D} \cdot \left(2 \cdot C_{o NL} \cdot 3 \cdot C_{o NL-1} + C_{o NL-2}\right) / \Delta x \tag{10c}
\]
The condition for the lower boundary (equation 10c) was derived from equation (2c), i.e.:
\[
\text{SFLW}_{i+1} = \text{v}_o C_{o NL} \cdot D \times \left[ \frac{\partial C}{\partial x} \right]_{NL+\frac{1}{2}} \tag{11}
\]
where \( \frac{\partial C}{\partial x} \bigg|_{x=L+\Delta L/2} \) is the concentration gradient within the column when \( x \) approaches \( L \) (+\( NL + \Delta x \)). The limiting value of this gradient can be estimated upon extrapolation, using the first two terms of the Taylor series expansion:

\[
\frac{\partial C}{\partial x} \bigg|_{x=L+\Delta L/2} \approx \frac{3}{2} \frac{\partial^2 C}{\partial x^2} \bigg|_{x=L-1} + \ldots
\]

(12)

With central differences this becomes:

\[
\frac{\partial C}{\partial x} \bigg|_{x=L+\Delta L/2} \approx \frac{C_{NL+1} - C_{NL-2}}{2 \Delta x} + \frac{3}{2} \frac{\partial^2 C}{\partial x^2} \bigg|_{x=L-1}
\]

\[
= \frac{2 C_{NL} - 3 C_{NL-1} + C_{NL-2}}{\Delta x^2}
\]

(13)

**COMPARISON OF SIMULATION AND ANALYTICAL SOLUTION**

**Rectangular Integration**

Figure 2 gives the relative concentration \( (C/C_0) \) versus depth in a soil column for both the CSMP solution (dashed line) and the analytical solution of equation (4) (solid line). The numerical result is obtained with the rectangular integration method (method RECT). The deviation between the two solutions is substantial and a direct result of replacing the original differential equation [equation (1)] by a difference equation with finite time steps \( (\Delta t) \) and layers of finite thickness \( (\Delta x) \). When equations (5), (6), (8), and (9) are combined, the dynamic part of the model is equivalent to the following difference equation:

\[
\frac{C_t^{n+1} - C_t^n}{\Delta t} = D \left( \frac{C_{t+1} - 2C_t^n + C_{t-1}}{\Delta x^2} \right) - \frac{1}{\Delta x} \left( v_0 + \frac{C_t^n - C_{t-1}}{\Delta x} \right)
\]

(14)

The numerical dispersion introduced in this difference approximation of equation (1) was first quantified by Chaudhari (1971). Also Lantz (1971) discussed equation (14) quite extensively and obtained basically the same results. The derivation of the amount of numerical dispersion as given by Chaudhari is expanded herein, since some other equally useful relations can be obtained, which may be employed for the definition of an "optimal" grid system \( (\Delta t, \Delta x) \) for the CSMP model.

The derivation of Chaudhari (1971) starts by considering the following Taylor series expansion of \( C_t^{n+1} \):

\[
C_t^{n+1} = C_t^n + \frac{\partial C}{\partial t} \Delta t + \frac{\partial^2 C}{\partial t^2} \Delta t^2 \Delta x^2 + \frac{\partial^3 C}{\partial t^3} \Delta t^3 + \ldots
\]

(15)
Fig. 2. Comparison of analytically and numerically computed concentration-distance curves after 1.5 days for a pulse of 0.8 days. Numerical calculations were based on rectangular integration. The results of the analytical and numerical (D corrected) calculations are also presented in table 2, columns 2 and 3, respectively. The computer program is listed in table 1.

METHOD RECT

\[ D = 30 \text{ cm}^2/\text{day} \]
\[ v_0 = 40 \text{ cm/day} \]
\[ \Delta x = 3 \text{ cm} \]
\[ \Delta t = 0.0375 \text{ days} \]
Substitution of equation (1) into equation (15) and rearrangement results in:

$$\frac{\Delta C}{\Delta t} = \left( D \frac{\partial^2 C}{\partial x^2} - \nu_0 \frac{\partial C}{\partial x} \right) + \frac{\Delta t}{2} \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} - \nu_0 \frac{\partial C}{\partial x} \right)$$

$$+ \frac{\partial^2}{\partial x^2} \left( \frac{\partial C}{\partial x} \right) + \ldots .$$

(16)

If we reverse the order of differentiation and repeatedly use equation (1), equation (16) simplifies to:

$$\frac{\Delta C}{\Delta t} = \nu_0 \frac{\partial C}{\partial x} + \left( D + \nu_0^2 \Delta t \right) \frac{\partial^2 C}{\partial x^2} - \nu_0 \frac{\partial}{\partial x} \left( \nu_0 D \Delta t + \frac{\nu_0^2 \Delta t^2}{6} \right) \frac{\partial^2 C}{\partial x^2}$$

$$+ \ldots .$$

(17)

Consider further the following central difference quotients for $\Delta C/\Delta x$ and $\Delta^2 C/\Delta x^2$, both based on Taylor series:

$$\frac{\Delta C}{\Delta x} = \frac{C_{i+1} - C_{i-1}}{2\Delta x} = \frac{\Delta C}{\Delta x} + \frac{\Delta^2 C}{\Delta x^2} + \ldots .$$

(18)

$$\frac{\Delta^2 C}{\Delta x^2} = \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta x^2} = \frac{\Delta^2 C}{\Delta x^2} + \frac{\Delta^3 C}{\Delta x^3} + \ldots .$$

(19)

When the first and second derivatives of $C$ with respect to $x$, as given by equations (18) and (19), are substituted into equation (17), this equation finally becomes:

$$\frac{\Delta C}{\Delta t} = \nu_0 \frac{\partial C}{\partial x} + \left( D + \nu_0^2 \Delta t \right) \frac{\Delta^2 C}{\Delta x^2} - \nu_0 \frac{\partial}{\partial x} \left( \nu_0 D \Delta t + \frac{\nu_0^2 \Delta t^2}{6} \right) \frac{\Delta^2 C}{\Delta x^2}$$

$$+ \nu_0 \frac{\partial^2 C}{\partial x^2} \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} - \nu_0 \frac{\partial C}{\partial x} \right)$$

$$+ \nu_0^2 \Delta t^2 + \frac{\nu_0^2 \Delta t^2}{12} - \nu_0 \frac{\partial}{\partial x} \frac{\partial C}{\partial x} \Delta^2 \frac{\partial C}{\partial x}$$

$$+ \ldots .$$

(20)

Equation (20), being based on central differences, suggests that an accurate approximation of equation (1) may be obtained when the appropriate difference equation uses an "apparent" dispersion coefficient ($D^*$) of the form:

$$D^* = D + \frac{\nu_0^2 \Delta t}{12}$$

(21)
Still higher accuracy is realized when time increment (Δt) and layer thickness (Δx) are chosen such that the coefficient of \( \partial^2 C / \partial x^2 \) is small, i.e., when:

\[
\Delta x^2 = 6 \Delta t \Delta x + \frac{\partial C}{\partial x} \Delta t^2 \tag{22}
\]

The CSMP model as discussed above uses backward differences (equation 14) rather than central differences for \( \frac{\partial C}{\partial x} \). When backward differences are used equation (20) needs to be modified. It is easily shown that:

\[
\frac{\Delta C}{\Delta x} \frac{c_{i+1}^t - c_{i}^t}{2 \Delta x} = \frac{c_{i}^t \cdot c_{i+1}^t}{\Delta x} + \frac{c_{i+1}^t \cdot c_{i+1}^t + 2c_{i}^t \cdot c_{i+1}^t}{\Delta x^2} \tag{23}
\]

The first 3 terms of equation (20) now become (all other terms remain the same):

\[
\frac{c_{i+1}^t - c_{i}^t}{\Delta t} = \nu \frac{c_{i}^t \cdot c_{i+1}^t}{\Delta x} + \left[ D \cdot \nu \frac{c_{i+1}^t \cdot c_{i+1}^t}{\Delta x} - 2c_{i}^t \cdot c_{i+1}^t \right] \frac{c_{i+1}^t - 2c_{i}^t + c_{i-1}^t}{\Delta x^2} \tag{24}
\]

Comparing equations (14) and (24), we see that an accurate CSMP model should use the following corrected dispersion coefficient:

\[
D^* = D - D_n \tag{25}
\]

with the numerical dispersion \( (D_n) \) given by

\[
D_n = \frac{\nu}{\Delta x} \left( \frac{\Delta x}{\Delta t} - \nu \right) \tag{26}
\]

This is the result of Chaudhuri (1971). The success of the use of equations (25) and (26) is demonstrated in figure 2 and table 2. Figure 2 shows graphically the excellent comparison of analytical and simulation solutions. Table 2 compares some numerical results obtained with different time steps and layer thicknesses. More accurate results were generally obtained with the smaller values of \( \Delta x \) and \( \Delta t \). The third column in table 2 used values for \( \Delta x \) (3 cm) and \( \Delta t \) (0.0375 days) such that equation (22) was satisfied. The accuracy in this case is the same (or better) than when \( \Delta x \) was 1.5 cm (fourth column) and \( \Delta t = 0.02 \). Hence equation (22) provides a means to increase the layer thickness without losing accuracy in the numerical calculations. Also important here is that for the latter case the computer time was decreased sharply compared with other grid systems.

Another useful result can be obtained from the derivation above. If we assume that the coefficient \( D \) is zero, equation (1) reduces to:

\[
\frac{\partial C}{\partial t} = \nabla \cdot \frac{\partial C}{\partial x} \tag{27}
\]
Table 2. Comparison of analytical and numerical results at TIME = 1.5 days for rectangular integration using different values of $\Delta x$ and $\Delta t$ and a pulse of 0.8 days (see Fig. 2)

<table>
<thead>
<tr>
<th>Depth</th>
<th>Analytical $\Delta x=3$</th>
<th>$\Delta x=1.5$</th>
<th>$\Delta x=1.0$</th>
<th>$\Delta x=0.005$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta t=0.0375$</td>
<td>$\Delta t=0.02$</td>
<td>$\Delta t=0.01$</td>
<td>$\Delta t=0.005$</td>
</tr>
<tr>
<td>10.5</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>11.25</td>
<td>0.004</td>
<td>0.006</td>
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</tr>
<tr>
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<td>0.037</td>
<td>0.038</td>
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</tr>
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</table>
If further $\Delta x$ and $\Delta t$ are chosen such that

$$\Delta x = v_0 \Delta t$$  \hspace{1cm} (28)

the difference approximation (20) can be shown to reduce to:

$$c_{i+1}^{n+1} = c_{i+1}^n$$  \hspace{1cm} (29)

Equation (29) merely states that the concentration after a certain time step in the $i^{th}$ layer is simply the concentration of the $(i+1)^{st}$ layer at the previous time, i.e.: the salt content of a given layer is simply moved into the next layer upon integration. The solution of equation (27) by finite difference techniques imposes generally great difficulty with respect to both accuracy and stability [see for example the discussion by Stone and Baren (1959)]. Equation (29) might serve a purpose here. Figure 2 shows the output of the CSMP model (table 1), with D=0 and with $\Delta x=2$ and $\Delta t=0.05$. (Hence: $\Delta x=v_0 \Delta t$ and $\Delta t^*$, named APDIF in table 1, becomes zero). The results are plotted in the form of an effluent curve for a pulse of five days. The square wave characteristic of equation (27), is clearly maintained in the plot. It should be mentioned here, that for very small values of D the oscillations in the calculations are small when choosing $\Delta x$ and $\Delta t$ according to equation (28).

**Higher Order Integration Methods**

The problem of the numerical dispersion becomes simpler when higher order integration methods are used, especially those where the computer selects its own time step (methods MILNE and RKS). Here the evaluation of the integrals is essentially continuous in time and the numerical dispersion is caused only by using a backward instead of a central difference quotient for $\frac{\partial c}{\partial x}$. From equation (23) it follows immediately that the numerical dispersion $D_n$ becomes:

$$D_n = \frac{3}{2} v_0 \Delta x$$  \hspace{1cm} (30)

This is shown in figure 4 and table 3. Figure 4 compares the analytical solution (equation 4) with results of the CSMP model when using a fourth order integration method with variable time step (Method RKS), with and without correcting for numerical dispersion (equation 30). Table 3 lists some numerical results for different integration methods. Although the results are basically the same as the analytical solution, method RKS provides no improvement over the use of the rectangular integration method provided layer thickness and time step are chosen according to
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Fig. 4. Comparison of analytically and numerically computed concentration-distance curves after 1.5 days for a pulse of 0.8 days. Numerical calculations were based on Runge-Kutta integration with variable time steps. The results of the analytical and numerical (D corrected) calculations are also presented in table 3, columns 2 and 6, respectively.

METHOD RKS
- $D = 30 \text{ cm}^2/\text{day}$
- $v_0 = 40 \text{ cm/day}$
- $\Delta x = 1.5 \text{ cm}$
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<th>Analytical</th>
<th>ADAMS</th>
<th>SIMP</th>
<th>TRAPZ</th>
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ADAMS: Adams second order integration
SIMP: Simpson’s rule
TRAPZ: Trapezoidal rule
RK5: Fourth order Runge-Kutta (variable-step integration)
RKSFX: Fourth order Runge-Kutta (Fixed-step integration)

1Methods RK5 and MILNE (Milne’s fifth order predictor-corrector method) gave identical results.
equation (22), resulting in a third order accurate difference approximation of equation (1). The lack of improvement results from the approximation of the convection term, being of second order accuracy only when using the Runge-Kutta integration method. Hence, there is little advantage in using an integration method which is fourth or fifth order in its integration, while the discreteness of the differential equation into layers is only of the second order. The required computer time needed for the methods RKS and MILNE is much greater than for the rectangular method (RECT), usually two to four times greater. The methods RKS and MILNE are best used in those cases where a proper selection of time step is difficult, e.g., for more complex systems where sources or sinks are present.

A summary of the corrections to be made in the CSMP program to the dispersion coefficient for two formulations of the convection term for both the rectangular and the Runge-Kutta integration methods is presented in Table 4.

<table>
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<th>Convection term written as:</th>
<th>Corrected form of the dispersion coefficient</th>
</tr>
</thead>
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<tr>
<td>FLRW*CI(i-1)</td>
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</tr>
<tr>
<td>FLRW*CI(i-1)+</td>
<td>APDIF = D - 0.5<em>DELT</em>FLRW**2</td>
</tr>
<tr>
<td>CI(i)/2.</td>
<td></td>
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</table>

**STABILITY**

To be able to formulate stability criteria for the CSMP model listed in Table 1, we first consider the following difference approximation of equation (1):

$$c_i^{n+1} - c_i^n = \frac{c_{i+1}^n - 2c_i^n + c_{i-1}^n}{\Delta x^2} \cdot \frac{x_i}{\Delta x}$$

(31)

The stability of this and related difference equations has been discussed extensively in previous work (e.g., Richtmeyer (1967), Fried
Combarneus (1968). For a central difference approximation of \( \frac{\partial C}{\partial x} \) (equation 31), the stability criteria are:

\[
\nu_0 \Delta x < D < \frac{\nu_0^2 \Delta x^2}{\Delta t} \quad \text{(central)}
\]

(32)

For backward differences (equation 14) the criteria become:

\[
0 < D < \frac{\nu_0^2 \Delta x^2}{\Delta t} \quad \text{(backward)}
\]

(33)

Finally, when corrections are made for the numerical dispersion, as was done with the program listed in table 1, the stability conditions become:

\[
\frac{\nu_0}{%} \Delta x - \frac{\nu_0}{%} \Delta t < D < \frac{\nu_0^2}{%} \Delta x - \frac{\nu_0}{%} \Delta t \quad \text{(corrected)}
\]

(34)

The left-hand inequality of equation (34) merely states that \( D^* \) must be nonnegative, where \( D^* \) is given by equations (25) and (26). This observation may be used to define an “optimal grid system”, i.e. a grid system which uses a layer thickness as large as possible without becoming unstable, while still maintaining a high degree of accuracy. Equating the left-hand inequality of equation (34) and using equation (22) we obtain the following relations:

\[
\Delta x = \frac{4D}{\nu_0} \quad \text{and} \quad \Delta t = \frac{2D}{\nu_0^2}
\]

(35)

These equations were used in the selection of time step (DELT) and layer thickness (TCOM) for the program in table 1 and explain the relative high degree of accuracy of the results appearing in the third column of table 2. At the same time, the required computer time was reduced considerably, especially compared with the Runge-Kutta method.

The CSMP model (table 1) responded immediately with severe oscillations when the right-hand stability condition of equation (34) was not met. However, the oscillations caused by not satisfying the left-hand condition were small or even negligible for small but negative values of \( D^* \). When these latter oscillations are ignored, an important increase in layer thickness can be achieved. This may be especially important when simulating the movement of chemicals through deep profiles where the required computer time can become an important consideration. An example of such a problem is shown in figure 5 where two different values of \( \Delta x \) were used to construct concentration-distance curves. The program used to obtain the numerical results was the same as the one listed in table 1, with the exception that \( \Delta x \) (TCOM) was not defined by means of a PARAMETER-input card, but by the following statement in the INITIAL segment (see equation (22)):

\[
TCOM = \text{SORT} \ (6 \cdot D \cdot \text{DELT} + (\text{FLRW} \cdot \text{DELT})^{*2})
\]

(36)
Fig. 6. Comparison of analytically and numerically calculated concentration-distance curves after 5.0 days for a pulse of 3.0 days. Δt and Δx were based on equation (36).

- **ANALYTICAL**
  - Δx = 10 cm
  - Δt = 0.2 days
  - D* = 40 cm²/day

- **NUMERICAL**
  - Δx = 23.14 cm
  - Δt = 0.5 days
  - D* = 12.72 cm²/day

**METHOD RECT**

- D = 30 cm²/day
- v = 40 cm/day
Figure 5 shows that a considerable increase in TCDM was possible without appreciably reducing the accuracy of the results. Oscillations became more severe at a layer thickness of 22.14 cm. It will depend on the problem under investigation whether such oscillations are allowed. The required computer time for the numerical calculations shown in figure 5 was reduced to a few seconds.

The above discussions hold for rectangular integration. When higher order integration methods are used, the stability conditions become more obscure and are difficult to derive. However, it is our experience that for all integration methods other than rectangular, D* still must be non-negative, where D* now is given by equations (25) and (30). Comparing equation (26) and equation (30), we see that in order to have a non-negative D* the rectangular method may use a larger ∆x without causing instability. In terms of the values of D and v0 used previously for the construction of figures 7 and 4 and tables 2 and 3, this amounted to a ∆x twice as large for the rectangular (3 cm) compared to the maximum ∆x which could be used with the Runge-Kutta integration method (1.5 cm).

**BOUNDARY CONDITIONS**

Difficulties were encountered in the formulation of the conditions at the lower boundary used in the CSMP program. Although differences in the boundary condition here are relatively unimportant for large columns (Gershon and Nir, 1967), they may cause deviating results when small columns are considered (i.e. for small values of the Peclet number v0 L/D).

The problem of the lower boundary was extensively discussed by Wehner and Wilhelm (1956) and by Pearson (1959). Both concluded that boundary condition (2e) should be replaced by condition (2d). Danckwerts (1955) reasoned that ∂C/∂x should be zero at the lower boundary to avoid a discontinuous concentration: When ∂C/∂x < 0 at x = L, C(L) will be greater than C(L'), the opposite being true when ∂C/∂x is positive. This problem was studied with the CSMP model on a very short column 1 cm in length. Results are shown in figures 6 and 7. The simulation solution in figure 6 is based on boundary condition (2e) (see equation 10c). The effluent concentration therefore is:

\[ C_{eff} = SFLW_{NL+1}/v_0 \]  

(37)

where SF = LNL+1 is given by equation (10c), and \( C_{eff} = C(L') \). Both the reservoir of solute at x = 0 and the effluent tube at x > L were given the same cross-sectional area as the soil column (figures 6 and 7). The concentration distribution in the effluent was calculated with:

\[ C(L+x,t) = C(L'), 1 \cdot \frac{x}{v_0 R} \]
The discontinuity of the concentration at $x = L$ is clear and a direct result of the non-zero $\partial C / \partial x$ inside the column, together with the assumption of zero $D$ in the effluent (the same applies in fact for the upper boundary). The numerical solution follows equation (3) for the semi-infinite column rather closely, indicating that the error made by treating the semi-infinite column as a finite column in the computer model is relatively small. The data plotted in figure 7 were calculated using equation (37) with the following relation for $SFLW_{NL+1}$:

$$SFLW_{NL+1} = v_0 C_{NL}$$  \hspace{1cm} (38)
Fig. 7. Comparison of analytically and numerically calculated concentration-distance curves for a 1 cm column. The CSMP-program was based on boundary condition (2R).

For equation (38) to be valid, the dispersion coefficient should vanish at the lower end of the column. This is generally true with respect to mechanical dispersion. However, the dispersion coefficient includes diffusion as well as dispersion. When mechanical dispersion is negligible and diffusion is the dominant mechanism, D is neither zero inside the column, at the boundary, nor in the effluent and equation (38) is invalid. However, when dispersion is dominant and diffusion is negligible, the assumption of zero dispersion at the boundary is realistic because no dispersive flow across the lower boundary occurs. Hence equation (2c) (with D=0) reduces to equation (2d), i.e. the zero slope condition. In
figure 7, Brenner's solution is compared with the numerical solution based on equation (38). Both solutions gave essentially identical results.

Comparing the results in figures 6 and 7, we see that for small columns proper formulation of the boundary conditions is important. In order to simulate the salt distribution in a semi-infinite column a finite numerical model, together with boundary condition (10c), may be used. For the 90 cm-long columns, as used in the calculations for the data in figures 2 and 4, it was found that the CSMP program, Brenner's solution for finite columns, and equation (4) for semi-infinite columns gave the same results up to a depth of about 87 cm. Deviations occurred, however, at the lower boundary (90 cm) depending whether boundary condition (10c) or boundary condition (38) was used. These differences amounted to approximately 0.01 C/CO units at one pore volume. In light of the above discussion, the best boundary condition for the semi-infinite column (field investigations) seems to be equation (10c), since it gave the same results (up to $x = L$) as the semi-infinite solution (equation 4). For small columns, especially when breakthrough curves are to be determined, equation (38) seems to be more appropriate.

SOME APPLICATIONS

The basic program as listed in table 1 is easily adapted to describe other phenomena. Of the following three examples, two are taken from the work of Van Genuchten et al. (1974) and describe the movement of adsorbed chemicals through soils. One of these considers equilibrium adsorption and a non-singular (hysteresis) adsorption-desorption isotherm, and the other a rate expression for the adsorption process. A third example, taken from Cassel et al. (1974) considers nitrification during NO$_3$ movement through large soil columns.

Pesticide Movement, Equilibrium Adsorption

The movement of adsorbed chemicals through a porous medium under steady state soil-water conditions is assumed to obey the following differential equation:

$$\frac{\partial S}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2} - \frac{BC}{C}$$

(39)

where $C$ is the concentration of the chemical in solution ($\mu g/cm^3$), $S$ is the amount of chemical adsorbed per gram of soil ($\mu g/g$), and $a$ the bulk density ($g/cm^3$). Further it is assumed that the relationship, at equilibrium, between adsorbed ($S$) and solution ($C$) concentrations can be described
by the Freundlich equation:

\[ S = KC^N \]  

(40)

Differentiating equation (40) with respect to time gives

\[ \frac{\partial S}{\partial t} = KNC^{N-1} \frac{\partial C}{\partial t} \]  

(41)

Equation 41 substituted into equation (1) allows this equation to be expressed in terms of one dependent variable, C:

\[ \frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial x^2} + v_1 \frac{\partial C}{\partial x} \]  

(42)

where

\[ D_1 = D / R_f \]  

(43)

\[ R_f = 1 + pKNC^{N-1} \beta \]  

(44)

\( R_f \) is often called the retardation factor. Initial and boundary conditions are the same as used previously. Lindstrom et al. (1967) solved this problem, assuming the exponent N in equation (40) to be unity. Their solution is given by equation (4), when using \( v_f \) and \( D_1 \) instead of \( v_0 \) and \( D \), respectively.

The equations above are only valid when adsorption and desorption of the herbicide are described by the same equilibrium equation [equation (40)]. There are, however, some indications in the literature that this assumption may not be true. Swanson and Dutt (1973) observed that both the adsorption and desorption isotherms for the adsorption of atrazine on different soils were of the Freundlich form, but that the coefficients for adsorption and desorption were not the same. Similar observations were later made by van Genuchten et al. (1974) for the adsorption of picloram on Norge loam, and by Hornsby and Davidson (1973) for the adsorption of fluometuron on Norge loam. Hence the coefficients \( K \) and \( N \) in equation (40) may depend on the adsorption direction, i.e., whether \( \partial S/\partial t \) is positive (adsorption) or negative (desorption). Denoting these coefficients by \( K_{ads} \) and \( N_{ads} \) during adsorption and by \( K_{des} \) and \( N_{des} \) during desorption, we may establish the following relation (Van Genuchten et al. 1974):

\[ S_{max} = K_{ads} C_{N_{ads}} = K_{des} C_{N_{des}} \]  

(45)

or:

\[ K_{des} = K_{ads} \frac{N_{des} N_{ads}}{S_{max}^{N_{des} N_{ads}}} \]  

(46)
where $S_{\text{MAX}}$ and $C_{\text{MAX}}$ represent the adsorbed and solution concentrations where the sorption direction is reversed from adsorption to desorption. ($\delta S/\delta t = 0$). Although the ratio $N_{\text{ads}}/N_{\text{des}}$ may depend on the maximum adsorbed concentration ($S_{\text{MAX}}$), it seems that a value of 2.5 provides a good average for the pesticides and soils referred to above. Hence, equation (46) determines the coefficient $K_{\text{des}}$ during desorption, and we have for adsorption and desorption, respectively:

$$S = K_{\text{ads}} C^{N_{\text{ads}}} \quad (\text{adsorption}) \quad \delta S/\delta t > 0 \quad (47)$$

$$S = K_{\text{des}} C^{N_{\text{ads}}/2.5} \quad (\text{desorption}) \quad \delta S/\delta t < 0 \quad (48)$$

When adsorption and desorption do not follow the same equilibrium relation, or when the adsorption isotherm is not linear ($N \neq 1$), no analytical solution exists and numerical techniques have to be used. The CSFP program for solving this case is listed in Table 5. Figure 8 shows some results of this program. The solid line in Figure 8 represents the analytical solution ($N=1, AB=N_{\text{ads}}/N_{\text{des}}=1$, see Table 5). The dashed curve gives the solution for $N=1$ and $AB=2.5$, and exhibits considerable tailing, indicating that a non-singularity in the adsorption-desorption process cannot be ignored.

The CSFP solution of Table 5 requires some comments. The equivalent difference equation is:

$$\frac{c_i^{n+1} - c_i^n}{\Delta t} = \frac{1}{R_f} \left[ D \cdot \frac{c_i^{n+1} - 2c_i^n + c_i^{n-1}}{\Delta x^2} - \frac{c_i^n - c_i^{n-1}}{\Delta x} \right] \quad (49)$$

It is easily shown that the numerical dispersion of this difference approximation can be corrected in a way similar to equations (25) and (26). The corrected dispersion coefficient becomes:

$$D^* = D \cdot \left[ \frac{1}{2} \frac{\Delta x}{R_f} \frac{\Delta t}{\Delta x} \right] \quad (50)$$

The retardation factor $R_f$ is constant during adsorption ($N = 1$); during desorption however, $R_f$ will change with the concentration according to equation (44). This dependency on $C$ makes it necessary that the retardation factor be evaluated at some point between $t$ and $t+\Delta t$. An alternative way, however, is to take a weighed average of the following form:

$$e_i^n + \beta \Delta t - \beta c_i^n + (1-\beta) c_i^{n-1} \quad 0 < \beta < 1 \quad (51)$$

$$R_f = 1 + \rho KN (|E|^N - 1) \beta \quad (52)$$

24
Table 5. CSMP program for simulation of one-dimensional transfer of an adsorbing chemical, assuming equilibrium between adsorbed and solution concentrations. Output from the listed program was used to construct Fig. 8.

S/380 CSMP VERSION 1.3
TITLE  HERBICIDE MOVEMENT (EQUILIBRIUM)
/ REAL C(60),AMSLT(60),ADMX(60),AD(60),SFLW(60),NSFLW(60)
/ REAL P(60),KD(60),NA(60),RF(60),E(60)
/ EQUIVALENCE (AMSLT1,AMSLT(1)),(NSFLW1,NSFLW(1))
FIXED I,N,L,T
INITIAL
NOSORT
PARAMETERS RHO=1.4,D=30, N=1, CO=1, AB=1, BET=0.18, ISALT C=1, E=10
PARAMETER TCOM=2, FLRW=40, T=1, WC=4, KADS=2, NL=4G
DEPTH=NL*TCOM
VOLW=TCOM*WC
DO I =1,NL
P(I)=1.0
KD(I)=KADS
NA(I)=N
RF(I)=1+RHO*KADS*N*CO**(N-1)/WC
ADS(I)=KADS*ISALT*C**N*RHO
1
ADMX(I)=ADS(I)
T=T/DELT
T1=T**DELT
DYNAMIC
NOSORT
CIW = FCNSW(TIME,T1,CO,(T-T1)*CO/DELT,0)
DO 11 I = 1,NL
11 CI(I)=AMAX1(1,ISALT,C,AMSLT(I)/VOLW)
E(I)=BET*CIW+1.8*E(T-C(I))
SFLW(I) = CIW*FLRW
DO 12 I = 1,NL
APDF(I)=0.5*FLRW*(TCOM-FLRW/RF(I)**DELT)
E(I)=E(I)+BET*(CI(I)-1)/2.8*E(C(I))
12 SFLW(NL+I)=SFLW(NL)-APDF(I)**2*(SFLW(CNL-I)-SFLW(CNL-2))/TCOM
DO 15 I = 1,NL
ADMX(I) = AMAX1(ADS(I),ADMX(I))
IF(TIME.LE.(T-DELT)) GO TO 14
IF(F(P(I)) 14,13,13

25
Table 5. Continued

13 IF(SFLW(I)-SFLW(I+1)+0.001,GT,0.) GO TO 14
  P(I) = 1.0
  NA(I) = N/AB
  KD(I) = KAD5**(1./AB)*(ADMX(I)/RHO)**(1.1./AB)
14 RF(I) = 1./RHO*KD(I)*NA(I)**E(I)**(NA(I)-1.)/WC
  ADS(I) = RHO*KD(I)**(C(I)**NA(I))
15 NSFLW(I) = SFLW(I)-SFLW(I+1)*WC/RF(I)
  AMSL(I) = INTGRDL(SFLW(I+1),45)

*************** PRINT OUT - MATERIAL BALANCE ***************

A = IMPULS(0,PRDEI)
IF(A**KEEP,LT,1.) GO TO 19
WRITE(6,16)TIME
16 FORMAT(H11,,H/420.***CONCENTRATION VERSUS DEPTH, PRINTED FOR EVERY
  SLAYER**,H/420.***MICROGRAM PER CC SOIL SOLUTION AT**,H/420.***DAYS**)
  WRITE(6,17) (C(I), I=1,NL)
17 FORMAT(H11,,H/450.***DAYS**)
  WRITE(6,18)TIME
18 FORMAT(1H,T15,'AMOUNT ADSORBED (MICROGRAM PER CC SOIL VOLUME) AT
  $,H/420.***DAYS**)
  WRITE(6,17) (ADS(I)**(1+1,NL)
19 CO=SFRLW(NL+1)/(FLRW*CO)
  TSLPRF = 0.0
  DO 20 I=1,NL
20 TSLPRF = TSLPRF + C(I)**VOLW +ADS(I)**TCOM
  VVO = FLRW**TIME/DEPTH
  TSLTN = INTGRDL(0,SFRLW(I)**WC)
  TSLOUT = INTGRDL(0,FLRLW(NL+1)**WC)
  NETTO = TSLTN-TSLOUT-TSLPRF
  RFNL = RF(NL)

METHOD RECT
TIME FINISH=R0,DEL0=0.03,PRDEI=0.6,OUTDEL=0.12
PRINT VVO,CO,AB,T,COM,DELT,TSLIN,TSLOUT,TSLPRF,DEPTH,RFNL
FINISH VVO=4.0

PRFNL CO(0.,..,VVO,RFNL,NETTO)
END
PARAMETER AB=2.5
END
STOP
ENDJOB
Fig. 8. Comparison of analytically and numerically computed concentration-distance curves after 3.0 days for a pulse of 1 day. The dashed line shows the effect of using a non-single valued adsorption-desorption isotherm (AB=2.5). Numerical calculations were based on the program listed in table 5.

**METHOD RECT**

- $D = 30 \text{ cm}^2/\text{day}$
- $v_o = 40 \text{ cm/day}$
- $\Delta x = 2 \text{ cm}$
- $\Delta t = 0.03 \text{ days}$
An adequate estimate of the coefficient \( \beta \) in equation (51) can be obtained in the following way:

\[
E_i = \% \left( C_I^* + C_I^+ \Delta t \right)
\]

(53)

Solving equation (49) for \( C_I^+ \Delta t \), assuming \( D^* \to \) be zero and substitution in equation (53) gives:

\[
E_i = \% \left[ C_I^* + C_I^+ \frac{\Delta t}{R_I} \left( C_{I-1} - C_I^* \right) \right]
\]

(54)

Comparing equations (51) and (54), we see that our estimate becomes:

\[
\beta = \% \frac{\Delta t}{R_I} \frac{C_I^*}{\Delta x}
\]

(55)

From equation (55) it is obvious that the corrections of equations (51) and (52) are negligible for small pore-water velocities, time increments and/or large compartments. In other cases, however, these corrections are necessary to avoid inconsistencies in the material balance of the profile under consideration. A check on the material balance was carried out in the program (table 5). Deviations in the balance were stored in the variable NETTO, being defined as:

\[
\text{NETTO} = \text{TSLIN} \times \text{TSLOW} \times \sum_{i=1}^{NL} \left[ \text{C}(i)^* + \text{ADS}(i) \right] \times \text{TCOM}
\]

(56)

where TSLIN is the amount of herbicide added to the soil and TSLLOW the total amount of salt collected at a depth \( NL \times \text{TCOM} \). NETTO ranged from about 3% of TSLIN for \( \beta = 0 \) (no corrections) to less than 0.5% of TSLIN when \( \beta = 0.18 \).

A constant value of \( \beta \) was used in the program. However, since \( \beta \) is a function of \( R_I \), it would probably be better to evaluate this variable (BET) each time step for each layer during desorption. This can be achieved by including the following statement in the DYNAMIC section:

\[
\text{BET}(i) = 0.5 \times \text{FLRW} \times \text{DELT} / \left( \text{TCOM} \times \text{RF}(i) \right)
\]

(57)

The stability conditions of the program follow directly from equation (34) and by comparing equations (14) and (49):

\[
\% K_v \left( \Delta x \times \Delta t \right) \ll D \ll \% R_I \frac{\Delta x^2}{\Delta t} \ll \% \frac{\Delta x^2}{R_I} \Delta t
\]

(58a)

28
or in terms of the corrected dispersion coefficient $D^*$ (equation (50))

$$0 < D^* < \frac{\alpha}{R_f \frac{\Delta x^2}{\Delta t} - \frac{\alpha}{v_0 \Delta x}}$$

(58b)

**Pesticide Movement, Kinetic Adsorption**

Again, the movement of adsorbed chemicals through a porous medium under steady state soil water conditions is assumed to obey the differential equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} \cdot v_0$$

(59)

However, instead of assuming equilibrium between adsorbed and solution concentrations, a first order rate equation is used for the adsorption rate,

$$\frac{\partial S}{\partial t} = \alpha (KC - S)$$

(60)

with the following initial and boundary conditions:

$$C = 0 \quad x > 0 \quad t = 0$$

(61)

$$\lim_{x \to 0^+} \left( \frac{\partial C}{\partial x} + v_0 C \right) = v_0 C_0$$

(62)

$$\lim_{x \to \infty} C(x, t) = 0$$

(63)

The solution of equations (59) and (60) with (61), (62), and (63) is:

$$\frac{C_t(x, t)}{C_0} = G(x, t) e^{-\frac{\alpha \phi K t}{\theta}} + \int_0^t G(x, r) \left[ I_0(\xi) \frac{\sqrt{2 \pi}}{\gamma^2 R_f} e^{-\xi^2} \right] \, dr$$

(64)

with

$$\frac{\alpha \phi K r}{\theta} \quad \theta = 2 \sqrt{uv}$$

(65)

and with $G(x, t)$ given by the right-hand side of equation (3) (van Genuchten, 1974). Note that $G(x, t)$ is the solution for the case $\alpha = 0$.

When a pulse of solute is added, boundary condition (62) should be replaced by equation (2f). Due to the linearity of the problem, the solution for this case becomes:

$$\frac{C(x, t)}{C_0} = C_t(x, t) \cdot \frac{C_t(x, t+T)}{C_0}$$

(66)

where $C_t(x, t)$ is given by equation (64).
The CSMP solution of the problem described by equation (59 to 63) is listed in table 6. Instead of equation (60) for the adsorption rate, it uses the more general equation:

\[
\frac{\partial S}{\partial t} = - \alpha (K \cdot C_N \cdot S) \tag{67}
\]

The program in table 6 is rather simple and straightforward. More detail is given in van Genuchten et al (1974). The integration was performed with the Runge-Kutta method (METHOD RKS) and central differences were used for SFIW(1), eliminating numerical dispersion. In figure 9, the CSMP solution is compared with the analytical solution (equation 66) for a 90-cm column. The integral in equation (64) was evaluated by using a Romberg integration scheme with a tolerance of \(10^{-4}\). (Gerald, 1973, program 2, page 74.)

**Nitrate Movement with Nitrification**

The movement of a non-interacting chemical through a porous medium which acts at the same time as a source (or sink) of the chemical can be described by the following partial differential equation:

\[
\frac{\partial C}{\partial t} + D \frac{\partial^2 C}{\partial x^2} - v_0 \frac{\partial C}{\partial x} = \sigma_0 \frac{\partial C}{\partial x} + \sigma_0 \tag{68}
\]

where all symbols are as defined before and \(\sigma_0\) is the source term (meq/cm² per day). Assume a semi-infinite column and the following initial and boundary conditions:

\[
C(x, t) = \alpha x \quad t = 0 \quad x > 0 \tag{69}
\]

\[
C(x, t) = C_0 \quad t > 0 \quad x = 0 \tag{70}
\]

where \(\alpha\) is a constant. The solution of equations (68 to 70) for a semi-infinite column is given by Carlaw and Jaeger (1959, p. 388).

\[
C(x, t) = \alpha x + \sigma_0 t - \sigma_0 t + \frac{\sigma_0}{2v_0} \left[ \text{erfc} \left( \frac{x - v_0 t}{\sqrt{4Dt}} \right) - \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right) \right]
\]

\[
+ \frac{1}{2v_0} (\sigma_0 - \alpha) \left[ \left( x + v_0 t \right) \text{erfc} \left( \frac{x - v_0 t}{\sqrt{4Dt}} \right) - \left( x - v_0 t \right) \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right) \right] \tag{71}
\]
Fig. 9. Comparison of analytically and numerically computed concentration-distance curves after 3.0 days for a pulse of 1.0 day. The dashed line shows the effect of using a non-singular adsorption-desorption isotherm \((AB=2.5)\). Numerical calculations were based on the program listed in Table 6.

**METHOD RKS**

- \(D = 30 \text{ cm}^2/\text{day}\)
- \(v_0 = 40 \text{ cm/day}\)
- \(\alpha = 3 \text{ 1/day}\)
- \(\Delta x = 1.5 \text{ cm}\)
Table 6. CSMP program for simulation of one-dimensional transfer of an adsorbing chemical, with adsorption described by a first order rate equation. Output from the program was used to construct Fig. 9.

S/360 CSMP VERSION 1,3

TITLE ADSORPTION RATE = ALP*(RHO*K*C**N - S)
/ REAL F(60), KD(60), NA(60), SFLW(61), ADMX(60), CI(60), ADS(60)
/ REAL ADSR(60), NSFLW(60), AMA(60), AMSOL(60), ALP(60)
/ EQUIVALENCE (AMSOL(1),AMSOL(11),,ADSR(-1),ADSR(11))
/ EQUIVALENCE (NSFLW(1),NSFLW(11),AMA(1),AMA(11))
FIXED 1,NL,TT
INITIAL
NOSORT
PARAMETERS CO=1.0, T=1.00, KADS=0.20, AADS= 5., ADES= 5., FLRW=40.
PARAMETERS NL=60, TCOM=1.50, D=30., N=1., WC=40., AB=1., RHO=1.4
APDIF=0.5*FLRW**TCOM
DEPTH=NL**TCOM
DO 2 I=1,NL
NA(I)=N
KD(I)=KADS
ALP(I)=AADS
ADMX(I)=0.
2 P(I)= 1.0
VOLW=WC**TCOM
DYNAMIC
NOSORT
TT = T/DELT
T1=T/DELT
CIW = FCNSWTIME - T1,CO,(T - T1)**CO/DELT,0.)
DO 11 I=1,NL
CI(I)=AMAX11(E-08,AMSOL(I)/VOLW)
11 ADSR(I) = AMA(SR)(I)**TCOM
SFLW(I) = CIW*FLRW
DO 12 I=2,NL
12 SFLW(I) = CI(I)**(1)*FLRW + APDIF*(CI(I)-CI(I-1))**TCOM
SFLW(NL+I)=(NL)*FLRW-APDIF*(T2,*(CNL-3)**(NL-1)+CNL-2))**TCOM
DO 15 I=1,NL
ADSR(I)=ALP***(RHO*KD(I)**(Ci)**NA(I)**ADS(I))**TCOM
ADMX(I) = AMAX11(ADMX(I),ADS(I))
IF(TIME.LT.(T-DELT)) GO TO 15
IF((I)(I,15,13,13)

32
Table 6. Continued

13 IF((ADSR(I)+1.0/4.0,GT.0,I) GO TO 15
   ALP(I)+=ADES
   PI(I)+=1.0
   KDI(I)=KADS***(1.0/AB)***(ADMX(I)/RHO)***(II-1.0/AB)
   NA(I)=N/AB
   ADSR(I)=ALP(I)*RHO*KDI(I)*CIII*NA(I)*ADSRI(TCOM)
   NSFLWI(I)=NSFLWI(I)+1.0
   NC=ADSRI(TCOM)
   AMSOL1=INTGRSL(0.0,ADSRI,60)
   AMADS1=INTGRSL(0.0,ADSRI,60)

*************** PRINT OUT  ***************
   A = IMPULSE(0.0,90.0)
   IF(A*KEEP.LT.1.) GO TO 21
   WRITE(8,18)TIME
   18 FORMAT(1X,2F10.8,'UNI UN VERSUS DEPTH, PRINTED FOR EVERY
   SLAYER',/T20, 'MICROGRAM PER CC SOIL SOLUTION AT',F5.2,T6.1, 'DAYS')
   WRITE (6,19) (CIII,J=1,NL)
   19 FORMAT(1H, ,15F8.4)
   WRITE(8,20)TIME
   20 FORMAT(1H/T15, 'AMOUNT ADSORBED (MICROGRAM PER CC SOIL VOLUME) A *
       S',F5.2,T7.0,'DAYS')
   WRITE (6,19) (ADSRI(I),J=1,NL)
   21 CC0=SLFW1(I+1)/FLRW*C0)
   TSLPRF = 0.0
   DO 22 I=1,NL
   22 TSLPRF = TSLPRF + ADSRI(I)*TSHI
   V0 = FLRW/TME/DEPT
   TSLN=INTGRSL(0.0,SLFW1(I)*WC)
   TSLOUT = INTGRSL(0.0,SLFW1(NL+1)*WC)
   NETTO=TSLN-TSLOUT-TSLPRF

METHOD RKS

TIMER FINISH=0.30,OUTDEL=0.15,PRDEL=0.30
PRINT COO,V0,DELT,DEPT,TSLPRF,TSLN,TSLOUT,AB,NETTO
PRPTLT CC0(I),V0,NETTO)
END
PARAMETER A=2.5
END
The equilibrium concentration distribution in the profile \((t=\infty, C_0=0)\) follows directly from equation (71) and has the form:

\[
\lim_{t \to \infty} C(x,t) = a_0 x / V_0 \tag{72}
\]

Cassel et al. (1974) compared calculated and observed nitrate distributions in 87 cm deep lysimeters. They assumed that nitration occurred in the upper part of the columns and could be described by a zero order rate term \(a_0\) (equation 68). Before adding fertilizer nitrate, the lysimeters were leached for several weeks with nitrate-free irrigation water. Since the assumption is made here that nitration takes place over the whole profile, we see that the equilibrium solution at time \(t = 0\) is given by equation (72). Hence by comparing equations (69) and (72) we find that \(a = a_0 / V_0\) and equation (71) simplified to:

\[
C(x,t) = a_0 x / x_0 + \frac{1}{4} C_0 \left[ \text{erf} \left( \frac{k - x_0 t}{2(4Dt)^{1/2}} \right) + \frac{x_0}{D} \text{erfc} \left( \frac{k + x_0 t}{2(4Dt)^{1/2}} \right) \right] \tag{73}
\]

The CSMP program for this problem is listed in table 7. A comparison of the analytical and the numerical solutions is presented in figure 10, where nitrate concentrations are given as a function of depth for various times after leaching with irrigation water containing nitrate. Initial and final equilibrium concentrations are also presented. Excellent agreement was obtained between the two solutions.

The main difference between the CSMP programs in tables 1 and 7, except for the source term, lies in the programming of the upper boundary condition [Equation (2a) versus equation (70)]. Boundary condition (70) becomes (see figure 1):

\[
SF LW(1) = \frac{\partial C}{\partial x} \bigg|_{x=0} \tag{74}
\]

The dispersion term in this equation can be approximated with:

\[
-D \frac{\partial C}{\partial x} = D C_{dx} - \frac{\partial C(1)}{\partial x} \tag{75}
\]

or more accurately:

\[
-D \frac{\partial C}{\partial x} = D C_{dx} - \frac{\partial C(1) + C(2)}{\partial x} \tag{76}
\]

Stability criteria for the program listed in table 1 were given in the section on stability. These criteria could be applied to all layers since both the upper and lower boundary conditions did not interfere with the general criteria. Boundary condition (70), however, is not smooth for the
Fig. 10. Comparison of analytically and numerically calculated concentration-distance curves during nitrification in a 87-cm lysimeter. Numerical values at the different curves indicate the times after irrigating with nitrate containing leaching water. Numerical calculations were based on the program in Table 7.

**Graph Details**
- **Analytical**
- **Numerical**: $\Delta x = 3$ cm, $\Delta t = 0.5$ days
- **Method Rect**
- $D = 4.6$ cm$^2$/day
- $v_0 = 0.95$ cm/day
- $\theta = 0.385$
- $C_0 = 0.01$ meq/cm$^3$ day

**Axes**
- **Y-axis**: Concentration - meq/cm$^3$
- **X-axis**: Distance - cm
Table 7. CSMP program for simulation of one-dimensional transfer of a non-interacting chemical with a source term. Output from the program was used to construct Fig. 10.

S/360 CSMP VERSION 1.3
TITLE NITRIFICATION IN LARGE SOIL COLUMNS
/ REAL SFNW(BB),C(BB),ASFLNW(BB),AMSLT(TBB),AMSLLT(BB),X(BB),SC(BB)
/ EQUIVALENCE (NSFLNW1,NSFLNW1(TBB)),(AMSLLT1,AMSLLT(TBB)),(AMSLL1,AMSLL(TBB))
FIXED 1,NL,TT
INITIAL
NOSORT
PARAMETERS CO=19,FLRW=0.96,NL>29,TCOM=3.3,T=4.6,ALPHA=0.01,WC=0.383,T=7
DEPTH=NL*TCOM
VOLW=WC*TCOM
SOURCE=ALPHA*TCOM*WC
WRITE(6,1)
1 FORMAT(H,T20,'INITIAL CONCENTRATION OF NO3 VERSUS DEPTH',/T25,
$DEPTH (CM),T44,C (MEQ/CM3)')
DO 2 =1,NL
X(I)=10.5*TCOM
2 SC(I)=ALPHA/FLRW*X(I)
WRITE(6,3) (X(I),SC(I)),I=1,NL
3 FORMAT(H,8x,2F9.3)
DO 4 =1,NL
4 AMSLL(I)=SC(I)*VOLW
TT = T/DELT
T1=TT*DELT
APDF =0.5*FLRW*(TCOM-FLRW*DELT)
APDF=D-0.5*FLRW*2.*DELT
DYNAMIC
NOSORT
CIW = FCNWTI(TIME · T1,CO,(T-T1)*CO/DELT,0.1)
DO 11 =1,NL
11 CI(W)=AMSLL(TI)/VOLW
SFNW(I)=FLRW*CIW+APDF*8.*CIW/(9.*CI(W)+CI(W-1)+CI(W+1)+2.*TCOM)
DO 12 =2,NL
12 SFNW(I)=FLRW*(CI(I-1)+CI(I)+CI(I+1))/6+APDF*6.*CI(W)/TCOM
SFNW(NL+1)=FLRW*C(NL-2)+APDF*12.*C(NL-3)+C(NL-2))/TCOM
DO 13 =1,NL
13 NSFLNW1(I)=NSFLNW1(I)+NSFLNW(I)*WC/SOURCE
AMSLLT1=INTGR(GL(JAMSLL1),NSFLNW1,29)

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| Table 7. Continued |

| PRINT OUT |

A = (IMPULS0, PRODEL)
IFIA*KEEP,LT,1.11 GO TO 16
WRITE(8,144) TIME
14 FORMAT(1H,1//,720, 'CONCENTRATION NO3 VERSUS DEPTH AT TIME=',T61,
$F5.1,T68,'DAYS')
WRITE(6,151) C[1],[1],NL
15 FORMAT(1H,1$F8.4)
16 CNL=C(NL)
METHOD RECT
TIMER FINTR=200.,DELT=50.,PRODEL=5.,OUTDEL=5.
PRPTLT CNL.
END
STOP
ENDJOB

grid system adopted in this study (figure 1), and the stability of the first layer has to be considered in addition to the general criteria stated earlier.

By combining appropriate statements of table 7, the following difference equation can be shown to hold for the first layer:

\[
C^1_{i+1} = \left( a_0 + 8 b_0 / 3! \right) C^1_i + \left( 1 / \nu a_0 + 4b_0 / 3 \right) C^1_i + \left( 4b_0 / 3 - 3 a_0 \right) C^1_i + a_0 \tag{77}
\]

where

\[
a_0 = \frac{\Delta t}{\Delta x}, \quad b_0 = \frac{(D + h^2 \Delta t \Delta t)}{\Delta x^2}
\]

Ignoring the influence of \( \phi \), and by requiring that the coefficients of \( C^1_{i+1} \), \( C^1_i \), and \( C^1_{i-1} \) be positive, we find the following additional conditions for the stability of the numerical program of table 7:

\[
\frac{1}{3} a_0 + 4b_0 < 1 \tag{78}
\]

\[
\frac{8}{3} b_0 > 2 a_0 \tag{79}
\]

The original program described by Cassel et al (1974) uses a source function \( a_0 \) as a function of depth, i.e., \( a_0 = a_0(\phi) \). Changes like these are relatively easy to make in the program.
CONCLUSION

It is clear from the foregoing that a computer language such as CSMP is a powerful tool for solving partial differential equations. This is demonstrated with CSMP solutions for the one-dimensional transport of a chemical in a sorbing medium, where either the adsorption equilibrium equation is nonlinear and the coefficients for adsorption and desorption are different, or where a rate equation is used for the adsorption process.

The approach used in this paper for solving partial differential equations is essentially similar to the method of lines (Carver, 1974), whereby the partial derivatives in space are replaced by a set of coupled ordinary differential equations. In CSMP, this is done by compartmentalization i.e. representation of the one-dimensional medium by a number of thin layers, each of which is homogeneous with respect to the dependent variable (concentration). The integration of the ordinary differential equation for each layer is performed in CSMP with one of five available integration methods. For two of these methods, the simple rectangular method and the fourth order Runge-Kutta method, stability criteria and corrections for numerical dispersion were discussed.

Beside CSMP, several other continuous systems simulation languages (CSSL's) are available for different computer systems. Several of these have a structure which is similar to CSMP. They are all user and application oriented and are designed for the primary purpose of solving differential equations.

It is also possible to use the method of lines or the compartmentalization approach with existing Fortran based integration systems. A good example is LEANS. The Fortran based LEANS is a user-oriented system for solving partial differential equations with the method of lines.

The solutions presented in this paper should be readily adaptable to such other computer systems, whether one uses a special-purpose language, such as CSMP, or a Fortran-based system.
LITERATURE CITED


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