Predicting Anion Movement in Disturbed and Undisturbed Soils

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ABSTRACT

Prediction of anion displacement in soils has proven difficult owing to anion exclusion and the occurrence of anion sources or sinks within the soil system. In addition, variations in bulk density and texture with depth cause mean pore water velocity and soil water content to be functions of depth. In this paper a numerical solution of a modified convective diffusion equation, which accounts for apparent anion exclusion and variations in soil water content and mean pore water velocity as functions of depth, is discussed. Moreover, a zero-order rate term is incorporated to account for nitrification occurring in the upper portion of the soil profile.

The model was tested using previously published NO$_3$ and $^{36}$Cl displacement data for disturbed and undisturbed cores of Aberdeen loam. The model predicted $^{36}$Cl displacement well. Incorporation of the source term improved prediction of the nitrate breakthrough curve, but agreement of the predicted curve with observed data was only fair. When average values for water content and bulk density were used throughout the entire column, instead of depth dependent values, the description of anion movement was not as good. It is suggested, however, that the improvement in accuracy of prediction of anion displacement may be less than the variation in solute movement observed among replicate soil cores.

Additional Index Words: miscible displacement, anion exclusion, disturbed soils.

Many models have been proposed for predicting or describing solute movement in soils. Nielsen and Biggar (1962) discussed several analytical models for predicting the concentration of solute in the effluent when water containing solute displaces water in a porous medium initially free of solute. They included the diffusion equation and the convective-diffusion equation. Experimental results show that these models seldom, if ever, predict the observed solute behavior accurately, partly because the soils are assumed to be nonreactive porous media. Most agriculturally-important soils, however, react with the solute in a variety of ways.

Adsorption and exchange processes associated with cations and some pesticides tend to delay the transport of these solutes through soils [Biggar and Nielsen (1963), Lai and Jurinak (1971)]. Furthermore, some solute may be gained or lost from the soil system due to microbiological or chemical processes [Mansell et al. (1968), Corey et al. (1967), Erh et al. (1967), Misra et al. (1974), Starr et al. (1974)]. For negatively charged ions, anion exclusion phenomena may cause the solute to appear in the effluent earlier than predicted [Thomas and Swoboda (1970)]. Solute such as pesticides and fertilizers which are applied to soils react with the soil in one or more of the manners described above.

Corey et al. (1963) used an analytical solution of the diffusion equation to describe pulse or slug flow of $^{36}$Cl and tritiated water through sandstone. They observed that tritium appeared in the effluent later than predicted while the reverse was true for $^{36}$Cl. The delayed appearance of tritium in the effluent was attributed to the surface activity of the sandstone, while the $^{36}$Cl behavior was associated with anion exclusion. Experiments of this nature indicate that the models commonly used, whether solved analytically or by numerical techniques, rarely predict anion movement adequately. This is true even for simple homogeneous systems, e.g., Krupp et al. (1972); Thomas and Swoboda (1970); Bresler (1973). One of the more important limitations imposed by the present models is the requirement that the porous medium or soil be uniform. This requirement leads to further assumptions that bulk density, initial microbial populations, etc., are also uniform with depth. Soils very rarely exist in this manner.

The purposes of this study were three-fold: The first was
The one dimensional convective-diffusion equation at variable water content may be written as:

$$\frac{∂θ}{∂t} = \frac{∂}{∂x} \left( D'(x) \frac{∂θ}{∂x} + v'(x) θ \right)$$

where $θ$ is the volumetric water content (cm$^3$/cm$^3$), $C$ the solute concentration in the soil (meq/cm$^3$ soil solution) at soil depth $x$ (cm) and time $t$ (days), $D'$ the apparent dispersion coefficient (cm$^2$/day), and $v'$ the pore water velocity (cm/day). Initial and boundary conditions for solving Eq. [1] for a pulse of solute entering the surface of a semi-infinite profile are:

$$C(x, 0) = 0$$

$$\lim_{x \to 0^+} \left( \frac{∂θ}{∂x} + v_0 θ \right) = v_0 C_0, \quad 0 < t \leq t_o$$

$$= 0, \quad t > t_o$$

Under conditions of constant water content ($θ = \bar{θ}$), $θ$ can be eliminated from Eq. [1] and [2], $v_0$ assumed constant, and the equations solved analytically [Lindstrom et al. (1967)].

Solving Eq. [1] by numerical methods allows several improvements over the analytical solution. In order to clarify these differences consider the generalized soil property data plotted as a function of soil depth for a nonuniform soil (Fig. 1). Rarely does bulk density ($D_b$) remain constant with depth, even for artificially, "uniformly packed" soil systems. Variations in bulk density in the Ap soil horizon occur throughout the year as a result of tillage practices. In addition, $D_b$ varies with depth in a given profile due to variations in texture, structure, and horizontation. Figure 1a shows one possible variation of $D_b$ with depth. For a tilled, agricultural soil, the greater density around 20 cm might result from a plow pan. As a consequence of this $D_b$-depth variation, the water content $θ$ is also expected to vary with depth (Fig. 1b). Other possible causes of variation of $θ$ with depth may be attributed to changes in soil texture or structure as they affect the soil water characteristics. The presence of zones or horizons that restrict water movement may also give rise to temporary changes in soil water content with depth. In general, the increase or decrease of $θ$ with depth will not be monotonic. The broken vertical line in Fig. 1b represents the mean soil water content ($θ$) for the entire soil profile; also shown in Fig. 1b is $θ_{ex}$ the apparent exclusion volume or that volume fraction of water which apparently repels anions. $θ_{ex}$ may vary with depth due to changes in soil texture, mineralogy, and organic matter content [Bower and Goertzen (1955)].

If we assume a steady-state soil water flux $q$ (cm/day) through the soil, the average pore water velocity ($v_0$, Fig. 1c) varies with depth in a manner inversely proportional to the soil water content $θ$ at that depth and is given by

$$v_0(x) = q/θ(x).$$

If $θ_{ex}$ can be evaluated, the apparent pore water velocity for anion transport $v'_0(x)$ is given by

$$v'_0(x) = v_0(x)θ(x)/θ'(x)$$

where $θ'(x)$ is defined as

$$θ'(x) = θ(x) - θ_{ex}(x)$$

$$= θ(x) [1-θ_{ex}(x)/θ(x)] = β(x)θ(x), \quad 0 < β(x) < 1.$$
is a function of $x$ since $\beta$ and $D$ are both functions of $x$; $D$ is a function of depth because $v_\alpha$ and $\theta$ are depth-dependent.

Using these relations, Eq. [1] in terms of $\theta^*$, $v_\alpha^*$, $D^*$, and $C^*$ and $t'$ becomes now, including a zero-order reaction term $\alpha$ (meq/cm$^3$/day):

$$ \frac{\partial(\theta^*C^*)}{\partial t'} = \frac{\partial^2}{\partial x^2} (\theta^* D^* C^*) - \frac{\partial}{\partial x} (\theta^* v_\alpha^* C^*) + a\theta^* $$

[6]

with the following initial and boundary conditions for a semi-infinite profile:

$$ C(x, 0) = 0 $$

[7a]

$$ \lim_{x \to 0^+} \left( \frac{\partial \theta^* D^* C^*}{\partial x} + v_\alpha^* \theta^* C^* + a\theta^* \right) = v_\alpha^* \theta_0 C_o \quad 0 < t' < t_o $$

$$ = 0 \quad t' \geq t_o $$

[7b]

The $\alpha$ term in Eq. [6] may represent a source (+) or a sink (-) for the anion under consideration; $\alpha$ may, or may not, be a function of depth in a given soil profile. In this study, $\alpha$ was assumed to be zero for Cl-movement and positive for NO$_3$-, varying with depth in a manner similar to that shown in Fig. 1d. In soils experiencing net denitrification, $\alpha$ is negative. Ideally, an independent measurement of $\alpha$ as a function of soil depth is desirable.

In the desire to obtain a model which has some degree of utility an attempt was made to keep that portion of the numerical model dealing with the source term $\alpha$ as simple as possible. Experimental data for displacement of nitrate and chloride through the soils involved were analyzed and a value of $\alpha$ obtained by curve fitting. A zero-order term was found to obtain an acceptable fit. Zero-order reactions are applicable to transformations when substrate is plentiful, due to the 5 to 6 weight percent organic matter in the A horizon, there apparently was sufficient substrate for nitrification of organic matter initially present. It is not the purpose of this paper to dwell on the proper order of rate reaction: this will depend upon the soil phenomena as discussed above, and allowing $v$, $\alpha$, and $\theta$ to vary with depth.

**EXPERIMENTAL**

Aberdeen loam, a soil belonging to the fine, montmorillonite family of the Glossic Udic Natriborolls, was used. The 22-cm deep Ap horizon is underlain by a clay loam B2 having strong medium prismatic structure. Undisturbed Aberdeen soil cores 30 cm in diameter and 80 cm long were collected from the field (Cassel et al., 1974). Disturbed Aberdeen soil cores, 87 cm long, were packed horizon by horizon to reconstruct the original morphological horizonation. After prewetting and preleaching the core, a 2.54 cm pulse of water containing 71.4 meq/liter NO$_3$-N and tagged with $^{36}$Cl was applied to the soil surface. The relative concentrations of NO$_3$ and $^{36}$Cl in the effluent were analyzed and plotted versus pore volumes of column effluent. The number of pore volumes ($T$) displaced through the soil was calculated by dividing the volume of effluent by $P_o$. The volumetric water capacity is defined by

$$ V = P \frac{L}{A} $$

[9]

where $P$ is the total volume of effluent collected at the moment when the relative $^{36}$Cl concentration in the effluent is equal to 0.50. The apparent anion exclusion volume $V_{ex}$ is then calculated by

$$ V_{ex} = (P_o - P)/P_o $$

[10]

**RESULTS AND DISCUSSION**

**Disturbed Aberdeen Loam**

Figure 2 presents data for the displacement of a pulse of $^{36}$Cl through disturbed Aberdeen soil (Cassel et al., 1974). Three separate disturbed soil cores were used for this experiment. The vertical lines indicate the range of $^{36}$Cl measured for the three replicates. The seemingly large range in relative $^{36}$Cl concentrations may be explained by the variation in the total amount of water held in each core: $P_o$ ranged from 19.8 to 23.3 liters even though gamma radiation attenuation data showed that the three cores had nearly identical bulk density distributions (Fig. 3). In Fig. 2, the abscissa refers to the mean pore volume for the three cores. Chloride appeared earlier in the effluent of the core having the smallest pore volume since the soil water flux was identical for all cores, being 0.383 cm$^3$/day.

The solid curve in Fig. 2 was obtained by solution of Eq. [6] with $\beta = 0.815$, $\alpha = 0$, and an apparent dispersion co-
Fig. 3—Mean and range of bulk density and soil water content distributions for disturbed cores of Aberdeen loam.

Fig. 4—Relative $^{36}$Cl concentration versus pore volume for disturbed Aberdeen loam. The solid line is the numerical solution of Eq. [6]. Anion exclusion was ignored for the dashed curve. The dashed-dotted curve is the analytical solution of Eq. [6], assuming a constant soil water content.

Fig. 5—Mean and range of relative concentration versus pore volume for displacement of nitrate through disturbed Aberdeen loam. The curve is the numerical solution of Eq. [6] using $\alpha = 0.0001 \text{ meq/cm}^3$ per day.

Fig. 6—Mean relative concentration data for displacement of nitrate and $^{36}$Cl through undisturbed cores of Aberdeen loam. The curves are numerical solutions of Eq. [6] with $\beta = 0.815$, $D' = 7.6 \text{ cm}^2$/day.

The effect of ignoring anion exclusion and variation of water content with depth is shown in Fig. 4. Curve 1 is identical to the curve shown in Fig. 2. Curve 2 was obtained using an average water content $\bar{\theta}$ of 0.383. Curve 3 represents results obtained when ignoring the anion exclusion. Comparison of Curve 1 and Curve 2 indicates little advantage in using the actual water content distribution as opposed to the mean water content for this soil under the conditions of this experiment. It should be mentioned that curves 2 and 3 could have been obtained with an analytical solution as mentioned in the theoretical part of this paper. Curves 2 and 3 could also have been obtained with an analytical solution of Eq. [6] [Lindstrom et al. (1967), and van der Ploeg and Benecke, (1974)].

Data similar to that for $^{36}$Cl in Fig. 2 are shown for NO$_3$ in Fig. 5. Once again considerable variation between the three replicate disturbed Aberdeen soil cores was observed. The solid line represents the numerical solution with the following parameters: $\alpha = 0.0007 \text{ meq NO}_3$/cm$^3$ per week, $D' = 5.6 \text{ cm}^2$/day, $v_\theta = f(x)$. The source term was included to account for a net increase in NO$_3$ resulting from microbial nitrification: $\alpha$ was obtained by curve fitting and was found to have a value of approximately $10^{-4}$ meq/cm$^3$ per day in the A horizon or the upper 22 cm of the soil profile; $\alpha$ was assumed to be zero below 22 cm, a choice based partially upon Dancer and Peterson’s (1974) conclusion that nitrification is largely confined to the Ap horizon. Moreover, organic matter content decreases rapidly at this depth. Although the calculated curve does not accurately describe the observed nitrate concentration distribu-
tion in the effluent, it better approximates the data than for the case where $a = 0$ throughout the profile (see Fig. 4). A more exact manner of accounting for nitrification within the soil profile in a steady-state flow system has been proposed by McLaren (1969a, 1969b). McLaren's model treats each step in the nitrification process and employs specific rate constants for each reaction. Starr et al. (1974) have verified experimentally a portion of McLaren's nitrogen transformation model using uniformly packed columns of Yolo loam. In order to use this model, however, appropriate rate constants for each reaction must be measured for each soil and possibly each horizon in a given soil. Hence such a model is limited in use at the field level whereas the simpler approach used in this paper might serve to provide a realistic estimate of the nitrate produced.

Undisturbed Aberdeen Loam

Finally, Fig. 6 compares observed and calculated curves of $\text{NO}_3^{-}$ and $^{36}\text{Cl}$ from undisturbed cores of Aberdeen loam. The $^{36}\text{Cl}$ effluent curves are described well; prediction of the effluent is not good but is slightly better than the prediction of $\text{NO}_3^{-}$ for the disturbed Aberdeen loam cores (Fig. 5). Notice that $a$ is greater for the undisturbed than for the disturbed Aberdeen cores indicating a greater net nitrification than for the disturbed soil. This behavior is further evidence that the use of disturbed soils in experiments can lead to results very dissimilar from identical experiments performed using natural soil cores. In addition, the apparent dispersion coefficient is greater for undisturbed Aberdeen being 7.6 cm$^2$/day compared with 5.6 cm$^2$/day for disturbed Aberdeen.

Throughout this paper we have dealt with an apparent anion exclusion volume which varied with depth. No attempt was made to separate the "double layer" type anion exclusion from exclusion arising from incomplete intra-aggregate mixing, sometimes referred to as "dead end" pores. Saxena et al. (1974) have recently questioned the concept of "dead pores."

Immediately after adding a 2.5-cm pulse of water to the soil surface, the water moves downward through the soil and flows at a slower rate as time and depth increase, i.e., the process is transient. Nearly all water will have passed the 5-cm depth, for example, after 1 hour, but it takes 6 to 7 days for this same quantity of water to flow past the lower end of the core. Hence the deeper in the soil core, the more time there is available for diffusion of anions out of dead end pores to occur. In the upper portion less time for diffusion is available as water moves relatively rapidly. For this reason the ratio of "double layer" to "dead end" pore type anion exclusion, if indeed, both types are manifested, will change with depth. Therefore, separation of these two processes in a model designed for field application in nonuniform soils is academic. We conclude that a useful anion displacement model, capable of working in the field situation, needs only an apparent anion exclusion volume or coefficient.

LITERATURE CITED

Predicting Anion Movement in Disturbed and Undisturbed Soils


Several confusing errors occurred in publication of the above article in the November-December 1975 issue of the SSSA Proceedings.

1) The first paragraph of the 'Theoretical' section should read:
The one dimensional convective-diffusion equation at variable water content may be written as

\[ \frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial x} \left( \theta D \frac{\partial C}{\partial x} \right) - \frac{\partial (\theta v_0 C)}{\partial x} \]  \[ 1 \]

where \( \theta \) is the volumetric water content (cm\(^3\)/cm\(^3\)), \( C \) the solute concentration (meq/cm\(^3\) soil solution) at soil depth \( x \) (cm) and time \( t \) (days), \( D \) the dispersion coefficient (cm\(^2\)/day), and \( v_0 \) the pore-water velocity (cm/day). Boundary and initial conditions for solving Eq. [1] for a pulse of solute entering the surface of a semi-infinite profile are

\[ C(x,0) = 0 \quad x > 0 \]  \[ 2a \]

\[ \lim_{x \to 0^+} \left( - \theta D \frac{\partial C}{\partial x} + v_0 \theta C \right) = v_0 \theta C_o \quad 0 \leq t < t_o \]

\[ = 0 \quad t \geq t_o \]  \[ 2b \]

where \( C_o \) is the concentration of the incoming solution (meq/cm\(^3\) solution) and \( t_o \) is the pulse period.

2) The first paragraph of page 1017 should read:

Using these relations, Eq. [1] in terms of \( \theta', v_o', D', C' \), and \( t' \) now becomes, including a zero-order reaction term \( \alpha' \) (meq/cm\(^3\)/day) equal to \( \alpha/\beta \) where \( \beta \) is constant with depth:

\[ \frac{\partial \theta' C'}{\partial t'} = \frac{\partial}{\partial x} \left( \theta' D' \frac{\partial C'}{\partial x} \right) - \frac{\partial (\theta' v_0 C')}{\partial x} + \alpha' \]  \[ 6 \]