NOTATION

C_i = concentration of species i
C_{io} = initial concentration of species i
F = objective function
f_i = normalized reaction rate for i^{th} reaction
H = Hamiltonian function
J = $f_1(\lambda_2 - \lambda_1) + f_2\lambda_2\alpha$
k_1, k_2 = reaction rate constants for arginase and urease, respectively
k = k_1/K_{M1}
K_{M1} = Michaelis constant for arginase
K_{M2} = Michaelis constant for urease
L = reactor length
n = reaction kinetic order
N = $-f_2\lambda_2\alpha$
P = $k_1L/K_{M1}v$
Q = volumetric flow rate
r_i = reaction rate for i^{th} reaction
u = fraction of bed which is arginase catalyst
v = linear superficial velocity
V = total volume of reactor bed
x_i = C_i/C_{Ao}
z = reactor length coordinate

Greek Letters

α = $\dfrac{k_2}{k_1}\dfrac{K_{M1}}{K_{M2}}$
μ_i = C_{Ao}/K_{Mi}
τ = z/L
λ_1, λ_2 = adjoint variables
ϕ = fractional loss of product

Subscripts

s = switching point value
o = optimal value
E = at exit of reactor

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Transport of Nitrate Ion in Unsteady, Unsaturated Flow in Porous Media

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A simplified model of nitrate ion transport (and other nonadsorbing solutes) in unsteady, unsaturated flow in porous media has been developed. The model represents nitrate flow in infiltration and drainage in sand quite well and can be applied to unsaturated flow in other homogeneous media with only minimum extra experimental data needed to describe the medium.

SCOPE

Nitrate contamination of soil and groundwater may originate from the application of agricultural fertilizer, waste treatment facilities, feedlot wastes, irrigation systems, and similar sources of nitrate ion. In spite of extensive work on the transport of solutes in saturated flow, very little literature exists that can predict transport in nonadsorbing media under unsteady state, unsaturated conditions.

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To predict the transport of nitrate ion in soil requires a thorough knowledge of both the unsaturated transport of water and the simultaneous transport of nitrate in the water. Because rigorous transport models do not predict nitrate ion transport in homogeneous porous material, a simplified transport model was developed that is easily implemented in the laboratory and satisfactorily predicts nitrate transport in unsaturated flow (such as occurs in infiltration and drainage).

CONCLUSIONS AND SIGNIFICANCE

Predicted transport based on the mathematical model for unsteady unsaturated water flow was compared with experimental data of nitrate movement in sand columns. Nitrate concentration profiles as a function of time and distance agreed well with the predicted profiles. The nitrate moved through the sand column at the rate of the cumulative interstitial velocity averaged over the depth of the wetted zone and averaged over the accumulated time from the introduction of the step input in the nitrate feed concentration. The depth of the wetted zone for water drainage was the length of the column; for infiltration, it was the depth of the column which would have been saturated had the water that infiltrated up to that time moved through the dry column as a saturated plug.

The nitrate concentration profiles, following the introduction of a step input of nitrate into the feed stream, exhibited typical symmetrical S shaped dispersion fronts observed for the dispersion of a nonadsorbing solute during steady flow through a saturated porous medium. However, for the conditions in this study, both the velocity of the nitrate dispersion front and the dispersion coefficient for nitrate proved to be functions of time as well as flow rate.

A satisfactory correlation between the nitrate dispersion coefficient $\{D_f\}^m$ and the cumulative average seepage velocity $\{\overline{v_s}\}^m$ during unsteady water flow was formulated so that the transport model could be used to predict nitrate transport in porous media other than that used in this work. The major limitation in prediction proved to be the nature of the packing of the media because values of $\{\overline{v}_s\}^m$ were quite sensitive to nonuniformity in the packing, and the prediction of the nitrate ion profile was much more sensitive to variations in $\{\overline{v_s}\}^m$ than to $\{\overline{D_f}\}^m$. For the sand used in this study, the agreement between the values of the nitrate concentration predicted using the transport model developed herein and the experimental values of the concentration was tested by an F test and found to be satisfactory.

Excessive levels of nitrate ion found in groundwater in many parts of the United States have caused concern on the part of many governmental agencies involved in environmental protection and public health. Consequently, a great deal of work is under way to study the primary sources of nitrate in both surface and groundwater, particularly organic nitrate waste from cattle feedlot runoff and the effluent of sewage disposal plants and septic tanks, and inorganic nitrate from chemical fertilizers.

Most of the studies on the leaching of pollutants through soils have been carried out for conditions of steady water flow through fully saturated soils (Boast, 1973; Lindstrom et al., 1967; Michna and Bourodimos, 1973; Preul and Schroepfer, 1968; Tyagi, 1972), a topic that has been thoroughly explored. But a more realistic representation of leaching is an unsteady flow process, one that takes place in an unsaturated medium that becomes more unsaturated as time goes on. Thus, we are concerned here with the transport of nitrate ion during unsteady water flow through unsaturated porous media.

PREVIOUS WORK

A vast literature exists on the transport of solutes during steady and unsteady flow in a saturated porous media. In contrast, relatively little work has been carried out to measure transport in unsaturated porous media. In the exhaustive survey (as of 1972) by Tyagi (1972), about twenty papers refer to models of the transport of solutes in an unsaturated media. But none provide clear-cut prediction techniques for nitrate transport because of uncertainty as to the extent of unsaturation, lack of agreement with experimental results, or differences between experimental conditions and the assumptions underlying the transport model employed. It is clear, though, that solute transport in unsaturated media differs from transport in saturated media.

More recent work is summarized in Table 1. To avoid numerical dispersion (Lantz, 1971; Peaceman and Rachford, 1962; Stone and Brian, 1963) in the finite difference solutions of the solute transport equations, most investigators have used a procedure similar to that of Chaudhari (1971, 1973) and Bresler (1973, 1974) in which higher-order differences are used to approximate first derivatives. Such techniques do not completely suppress numerical dispersion and do require considerable computation time to execute.

Thus, it was deemed desirable to develop a simple but valid mathematical model of unsteady water flow through unsaturated soil that required a minimum of experimental data to evaluate the model coefficients and to obtain what data were needed by using elementary procedures. Both the water and the nitrate transport models were restricted to homogeneous media.

Table 1. Summary of Recent Solute Transport Models

	Investigator								
Model	Bresler, 1973	Bresler and Laufer, 1974	Bresler, 1975	Davidson et al., 1975	Duguid and Reeves, 1975	Selim et al., 1976	Shah et al., 1975	Walter et al., 1975	Wood and Davidson, 1975
Model characteristics									
Steady water flow		x		x					
Unsteady water flow	x		x	x	x	x	x	x	x
Unsteady mass transport	x	x	x	x	x	x	x	x	x
Saturated flow		x			x		x		
Unsaturated flow	x		x	x	x	x	x	x	x
Two-dimensional flow			x		x				
One-dimensional flow	x	x		x		x	x	x	x
Coefficient in water transport equation	$K(w)$	$D^*(v)$	a	$K(w)$	$K(h)$	$D^*(w)$	$K(S)$	$D(h)$	$K(w)$
Coefficient in solute transport equation	$D(w,v)$	$D(w)$	a	$D(w,Q)$	a	$D(v)$	D	D	D
Adsorption/reaction included in model				x	x	x	x		x
Solution technique									
Water flow: analytical solution								x	
Implicit finite difference	x	x		x			x		
ADI + Newton's method			x						
Finite element					x				
Implicit-explicit						x			x
Solute-transport: Chaudhari	x	x	x	x					x
Analytical solution							x	x	
Finite element					x				
Implicit-explicit						x			

x = classification applied.
a = multiple coefficients.
$^*D = K\dfrac{dh}{dw}$

THEORY

Prediction of the transport of nitrate ion in soils requires a thorough knowledge of the water content of the unsaturated soil as a function of time. Because a higher than one-dimensional model for the transport of nitrate ion is exceptionally time consuming to solve, the experimental apparatus was arranged to represent one-dimensional flow. Two important variables had to be measured for less than saturated flow: the water content of the sand, and the concentration of nitrate ion in the water phase. In saturated flow, only the second need be considered.

Water Content

When Darcy's law is applied to completely saturated flow, that is, flow through a medium in which only one fluid is present, the hydraulic conductivity (or intrinsic permeability) is presumed constant. However, flow of water in soil usually is unsaturated flow because another fluid, air, is present in the medium. If the air present in the medium is assumed to be stagnant, the flow of the moving fluid can still be described by Darcy's equation, but with one important modification. The hydraulic conductivity and permeability are no longer constants but become functions of the water content w or saturation S (the saturation is the fraction of the void volume occupied by the wetting fluid), so that Darcy's law becomes

$$v_d = -K(w)\frac{dH}{dz} \tag{1}$$

where $H = h - z$, or

$$v_d = -k_r(S)\frac{k_o}{\mu}\frac{dP}{dz} \tag{2}$$

In addition, for unsaturated flow, the interstitial velocity $v_s = v_d/w$, so that the flow rate through the column at less than complete saturation depends on the degree of saturation of the bed.

For unsaturated flow, the equation of continuity for the flow of water is

$$\frac{\partial w}{\partial t} = -\frac{\partial v_d}{\partial z} \tag{3}$$

If Darcy's equation is substituted into Equation (3), the final form of the continuity equation for the water content is obtained:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial z}\left\{K(w)\frac{\partial h(w)}{\partial z}\right\} - \frac{\partial K(w)}{\partial z} \tag{4}$$

Transport of Nitrate Ion

The one-dimensional transport of NO_3^- (component A) during flow through a porous medium can be described on a dry bed basis (assuming no adsorption or reaction) as

$$\frac{\partial c_A}{\partial t} + \frac{\partial}{\partial z}(v_s\, c_A) = \frac{\partial}{\partial z}\left\{\rho_b D_{Az}\frac{\partial}{\partial z}\frac{c_A}{\rho_b}\right\} \tag{5}$$

and on the basis of a unit volume of fluid as

$$\frac{\partial(Cw)}{\partial t} + \frac{\partial}{\partial z}(v_s\, Cw) = \frac{\partial}{\partial z}\left(D_f\frac{\partial(Cw)}{\partial z}\right) \tag{6}$$

By introduction of Equation (3) and $v_d = wv_s$, Equation (6) can be simplified to

$$w\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left\{ D_f \frac{\partial (Cw)}{\partial z} \right\} - v_d \frac{\partial C}{\partial z} \tag{7}$$

Equation (7) is the nonlinear nitrate transport differential equation which, when coupled with the water flow Equation (4), describes the movement of the nitrate during unsteady unsaturated flow through a porous medium.

For steady flow, w, v_d, and D_f are constant, so (7) becomes

$$\frac{\partial C}{\partial t} = D_f \frac{\partial^2 C}{\partial z^2} - v_s \frac{\partial C}{\partial z} \tag{8}$$

which is the more familiar form of the dispersion equation. However, Equation (8) is correct only for the case when w and v_s are constant or nearly so. Because D_f is dependent on v_s, D_f cannot be assumed constant unless the velocity is constant.

EXPERIMENTAL APPARATUS AND PROCEDURE

Sand was used as the simulated soil medium in this study in order to minimize the complications arising from such factors as adsorption, bacterial action, and swelling of the medium. A number of investigators (Gupta, 1972; Viets and Hageman, 1971) have reported that nitrate ions are not significantly adsorbed by soil media in general and sand in particular. The range of particle sizes in each sand size category was suggested by the work of others who have studied the dispersion of tracers during steady flow through saturated porous media.

Figure 1 shows the general configuration of a typical experimental column packed with sand. Four size categories of sand were used ranging from 100 to 500 μ (mean particle size diameters of 200, 274, 339, and 400, respectively) and a packing density of 1.53 to 1.59 g/cm^3. Relatively large size sand was used because the literature indicated that for particles of the order of 20 μ, Darcy's law may not hold (Boersma, 1973). Careful analysis indicated that the sand adsorbed at equilibrium only 5×10^{-6} g of potassium nitrate/g of sand (equivalent to 2×10^{-4} mole/l in the water phase), whereas the concentrations of solute in the water phase for the transport experiments was 0.005 to 0.1 mole/l. Hence, the nitrate ion adsorption could indeed be considered negligible.

Two types of runs were carried out, one of infiltration and the other of drainage. Many more drainage runs were made than infiltration runs because the leaching of nitrate in soil takes place principally during drainage of irrigation or rainwater out of the soil root zone. The nitrate was introduced as a step input in the feed at the top of the column in order to simplify both the experimental procedures and the boundary conditions for the mathematical model. Then the column was sectioned (the elements were separated) so that the water content and nitrate concentration in the water phase could be determined at twenty equally spaced points along the length of the column. Specific details of the analysis of the column segments for water content and nitrate concentration are found elsewhere (Hildebrand, 1975). Two or three experimental runs were made for each sand size, and usually the total run times were different for each run for a specific sand size.

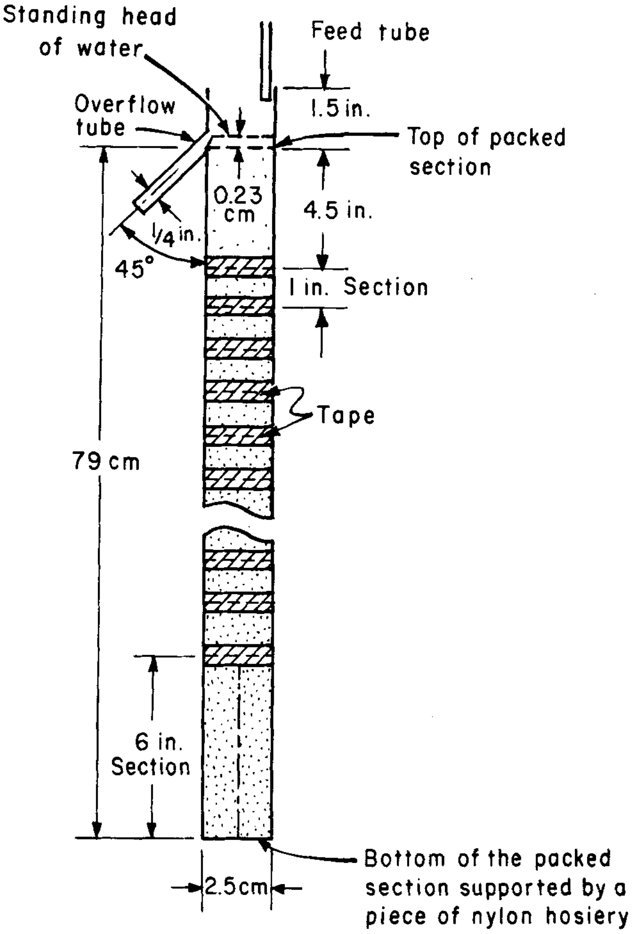

Fig. 1. The experimental column.

CALCULATION OF WATER CONTENT

Equation (4) can be solved for either w or h if the function $w(h)$ is known. Most investigators have followed the lead of Hanks and Bowers (1962) and set up the finite difference representation of the water flow equation in terms of the capillary pressure head h:

$$B(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left\{ K(h) \frac{\partial h}{\partial z} \right\} - \frac{\partial K(h)}{\partial z} \tag{9}$$

where

$B(h) = \partial w / \partial h =$ the water capacity

However, the use of Equation (9) presents the investigator with some severe problems in the design of experiments and collection of data.

In order to use Equation (9), the moisture characteristic $w(h)$ and the hydraulic conductivity-hydraulic head relationship $K(h)$ for the soil being studied must be known for any value of h. One way of obtaining accurate $K(h)$ and $B(h)$ relationships is to fit the experimental data from the instantaneous profile method (Watson, 1967; Giesel et al., 1973). But the validity of applying the $K(h)$ and $B(h)$ relationships obtained from one column to another column is doubtful because both functions vary significantly with the packing of the bed. Furthermore, hysteresis exists in the $K(h)$ and $w(h)$ functions so that they are not unique functions.

Consequently, although computation of the $K(h)$ and $w(h)$ functions from water content and hydraulic head profiles may superficially seem to be a good idea, use of a cheaper and simpler procedure is desirable. The method used in this study consisted of obtaining $K(w)$ and $h(w)$ functions from the water content profile only. $K(w)$ exhibits much less hysteresis than $K(h)$. In fact, for sands and glass bead media, the observed hysteresis in $K(w)$ is of the same magnitude as the experimental error (Rogers and Klute, 1971; Topp and Miller, 1966; Vachaud and Thony, 1971; Watson, 1967) so that the $K(w)$ function could be taken as a unique curve. Thus, the procedure used in this study did not require the measurement of the hydraulic head profile data $h(z, t)$.

Instead, in Equation (4), $\partial h / \partial z$, was expressed as

$$\frac{\partial h}{\partial z} = \left(\frac{\partial h}{\partial w}\right)\left(\frac{\partial w}{\partial z}\right) \tag{10}$$

The $h(w)$ relationship was determined as follows. First, a suitable functional relationship between h and w had to be assumed. We chose the combination of hyperbola and a straight line shown in Figure 2 as the best simple fit of the existing data in the literature (Bresler et al., 1969; Rogers and Klute, 1971; Vachaud and Thony, 1971; Watson, 1967). The combined functions contained only three coefficients.

Because $h(w)$ was determined by a least-squares fit, $K(w)$ had to be determined independently because of the interaction [multiplication of $K(w)$ and the derivative of $h(w)$] in the first term on the right-hand side of Equation (4). The relative permeability vs. saturation data for sand reported in Muscat (1949) was accepted as representative for an air-sand-water system. The value of any $K(w)$ for w less than w_{sat} could be calculated relative to K_{sat} from an equation of the following form

$$K(w) = K_{sat}\,(w/w_{sat})^{3.482} \tag{11}$$

where w_{sat} was the average water content (obtained by experiment) of the porous medium in the saturated portion of the column at steady flow with air entrapment, and K_{sat} was computed from a single measurement of the steady outflow rate prior to drainage. For steady flow, Equation (4) becomes

$$v_{sat} = -K_{sat}\,(h_{st}/L - 1) \tag{12}$$

Since the discharge velocity v_{sat}, the standing head of water h_{st}, and the column length L could all be measured, Equation (12) could be solved for K_{sat}. The precision of the value of K_{sat} was approximately ± 0.75% of the value of K_{sat}.

Thus, using $K(w)$ from Equation (11) and $h(w)$ from the approximating relation shown in Figure 2, we can predict water content profiles $w(z,t)$ for other similarly packed columns of the same material with a degree of accuracy equivalent to that attained by using $K(w)$ and $h(w)$ determined by the instantaneous profile method.

In order to predict solute movement during unsteady flow through an unsaturated medium, the water velocity profile had to be computed as a function of time and depth. A finite difference model was set up to calculate not only $w(z,t)$ but also $v_d(z,t)$ explicitly. The scheme of calculation and boundary conditions used in connection with the nonlinear difference equations to predict water movement during drainage and infiltration were variations on the scheme of calculation and boundary conditions published by Hornberger and Remson (1970) for linear equations. Details are shown in Hildebrand (1975). Hornberger and Remson's scheme of calculation and boundary conditions assumed that a discontinuity existed in the soil moisture characteristic $h(w)$. This assumption has been verified by Luthin and Miller (1953), who reported a sudden change in the hydraulic head at the surface when drainage first begins, that is, after the standing head of water disappears.

In the case of infiltration, the entire column was initially dry, with a water content w_{dry}, a capillary pressure head $h_{dry} = h(w_{dry})$, and no flow. When the water first entered the column, there was no head of ponded water at the surface, and the top layer of the column was only partially saturated. In the initial period of infiltration, the column soaked up all of the water supplied to it until the top layer became saturated. At this stage, the column can be divided into three zones: the top saturated zone, the center unsaturated zone around the wetting front, and the bottom dry zone. Once the top layer of the column was saturated, a standing head of water started to build up at the surface. The velocity in the saturated zone was equal to v_{sat}, which was less than $v_{d_{in}}$, the input flow rate, so the excess incoming flow caused the head of ponded water at the surface to build up to h_{st}, the maximum head of standing water permitted by the overflow tube.

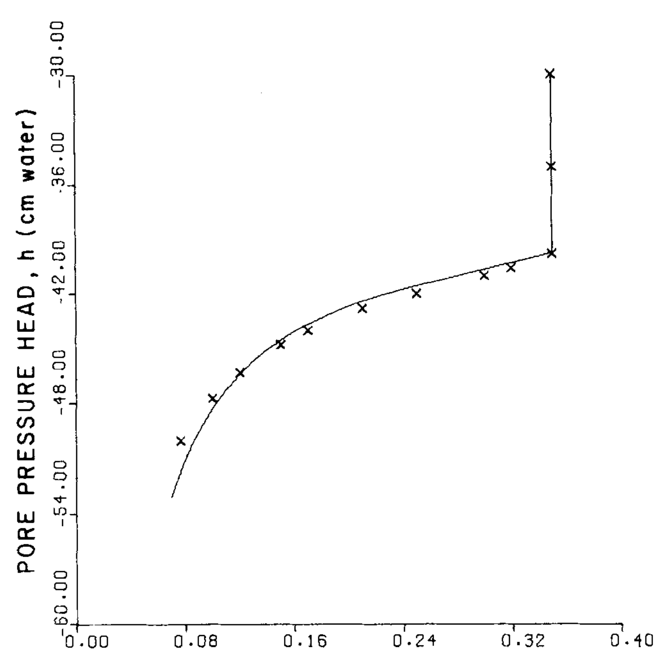

Fig. 2. Comparison between Watson's $h(w)$ data (points) for drainage and the $h(w)$ function (solid line) obtained using a least-squares fit. The intersection of the hyperbola and straight line has the coordinates $(w_{sat}, h_{sat}) = (0.35, -39.8)$.

In the case of drainage, the entire column was initially saturated to some water content w_{sat}. A standing head of water existed at the surface h_{st}, and the hydraulic head at the bottom of the column was equal to zero, since the pore pressure at the bottom of the column had to equal to atmospheric pressure in order for outflow to take place. The gradient $\partial h/\partial z$ of the hydraulic head within the column was linear, and the discharge velocity was assumed constant throughout. Drainage began when the water supply to the top of the column was shut off. In the initial period of drainage, the top layer remained saturated as the standing head was drained away. At the instant the standing head of water was reduced to zero, the hydraulic head at the top of the column dropped to $h_{sat} = h(w_{sat}) < 0$, and desaturation of the column began. For the purpose of calculation, the column was divided into two zones: the top unsaturated zone and the bottom saturated zone. Drainage continued until such time as the height of the saturated zone above the bottom of the column was equal to the absolute value of h_{sat}, when all flow ceased.

COMPUTATION OF NITRATE TRANSPORT

A great deal of work has been done on developing finite difference approximations for Equation (7) to reduce the magnitude of the truncation error and the resulting numerical dispersion (Chaudhari, 1971, 1973; Garder et al., 1964; Laliberte et al., 1968; Lapidus and Amundson, 1952; Stone and Brian, 1963). For the movement of a nonadsorbing solute through a sandy medium in this work, D_f/v_s was on the order of 0.15 cm. Therefore, $Pe_\zeta = \zeta/(D_f/v_s)$ had already reached the threshold value of 100 at a characteristic depth of 15 cm. A review of the references listed in Table 1 indicates that no one has been completely successful in reducing the truncation error in finite difference approximations of Equation (7) for unsteady flow because of the presence of w inside the second differential in the dispersion term and the functional dependence of D_f on time and depth.

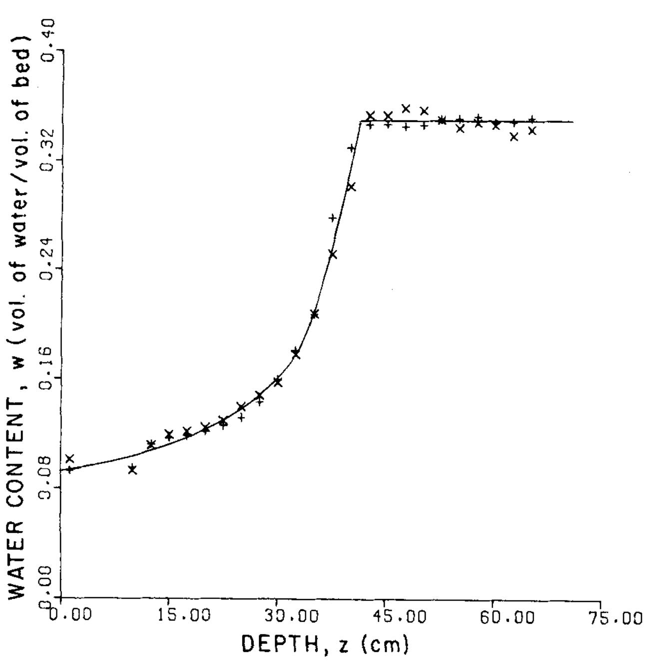

Fig. 3. Water content data $w(z)$ from two similarly packed columns of sand of mean particle size of 274 μ after 14 min of drainage, data from the first column indicated with + marks, data from the second column indicated with x marks. Solid line is line of best fit by least squares using the nonlinear water flow model.

Consequently, a simpler model of the dispersion of a a solute during unsteady, unsaturated fluid flow was sought in this work, one that imitated Equation (8) but appropriately averaged for the column the seepage velocity and the dispersion coefficient (both being functions of time and depth):

$$\frac{\partial C}{\partial t} = \overline{D_f}(Z_w, t)\,\frac{\partial^2 C}{\partial z^2} - \overline{v_s}(Z_w, t)\,\frac{\partial C}{\partial z} \qquad (13)$$

where

$\overline{v_s}(Z_w, t)$ = a seepage velocity averaged over the depth of the wetted zone Z_w and the time t, length/time

$\overline{D_f}(Z_w, t)$ = a dispersion coefficient averaged over the depth of the wetted zone Z_w and the time t, length^2/time

The wetted zone Z_w is that portion of the length of the column which is involved in the flow. In the case of drainage, because the whole length of the column is involved in the flow over the total elapsed time, the wetted zone equals L, the length of the column. In the case of infiltration, the portion of the length of the column which is involved in the flow changes with time, some portions experiencing flow only during the later stages of infiltration. The Z_w for infiltration, therefore, is defined as that portion of the length of the column which would have been wetted to saturation had the volume of water infiltrated at time t moved through the column as a saturated plug:

$$Z_w(t) = \frac{Q_{\text{in}}(t)}{(w_{\text{sat}} - w_{\text{dry}})\,(A)} \qquad (14)$$

Because Z_w is either constant, as for drainage, or a function of time t, but not distance z, as for infiltration, at any specific time $t = \{t\}^m$

$$\{\overline{v_s}\}^m = \overline{v_s}(Z_w, \{t\}^m) = \overline{v_s}(Z_w, t) \qquad (15)$$

and

$$\{\overline{D_f}\}^m = \overline{D_f}(Z_w, \{t\}^m) = \overline{D_f}(Z_w, t) \qquad (16)$$

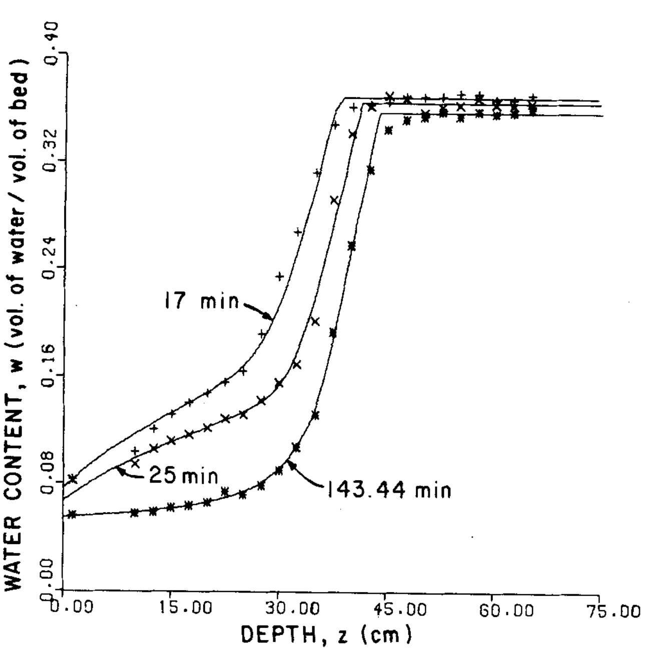

Fig. 4. Experimental and computed $w(z, t)$ profiles for drainage in sand with mean particle size of 240 μ, run 1 experimental values indicated with + marks, run 2 data with x marks, and run 3 data with * marks. Solid lines indicate $w(z, t)$ profiles computed using estimated parameter values determined from 274 μ sand illustrated in Figure 3.

may be considered constant, and Equation (13) becomes Equation (17)

$$\frac{\partial C^*}{\partial t^*} = \frac{1}{Pe_\zeta}\,\frac{\partial^2 C^*}{\partial z^{*2}} - \frac{\partial C^*}{\partial z^*} \qquad (17)$$

in which

$$C^* = (C - C_o)/(C_{\text{in}} - C_o)$$

$$t^* = t/\{t\}^m$$

$$z^* = z/(\{\overline{v_s}\}^m\{t\}^m)$$

$$Pe_\zeta = \{\overline{v_s}\}^m\zeta/\{\overline{D_f}\}^m \qquad (17a)$$

Equation (17) has well-known analytical solutions for various types of initial and boundary conditions. Values of $v_s(Z_w, t) = \{v_s\}^m$ *at* $t = \{t\}^m$ can be calculated from the velocity and water content profiles, $v_d(z, t)$ and $w(z, t)$, which in turn are obtained from the nonlinear water flow model equation.

Because Equation (17) has an analytical solution, the estimation of Pe_ζ from experimental data is relatively simple. $\{\overline{D_f}\}^m$ can be obtained from the nitrate profile. If a suitable correlation between the experimental values of $\{v_s\}^m$ and $\{\overline{D_f}\}^m$ can be found, then $\overline{D_f}(Z_w, t)$ can be predicted for any value of $\overline{v_s}(Z_w, t)$. How well this approach works out is described in the next section.

RESULTS AND DISCUSSION

Water Flow—Drainage

The nonlinear water flow model was found to yield an $h(w)$ function that fit the data taken by Watson (1967) (via in situ gamma attenuation and transducer tensiometers) quite well. Examine Figure 2.

Figure 3 shows two typical replicate runs obtained in this work for sand with an average particle diameter of 274μ packed similarly. Both columns had K_{sat} equal to 0.0340 cm/s and W_{sat} of 0.351 cm^3 water/cm^3 sand bed. Bartlett's test was carried out to determine if the individual variances of the two replicate $w(z)$ data points corre-

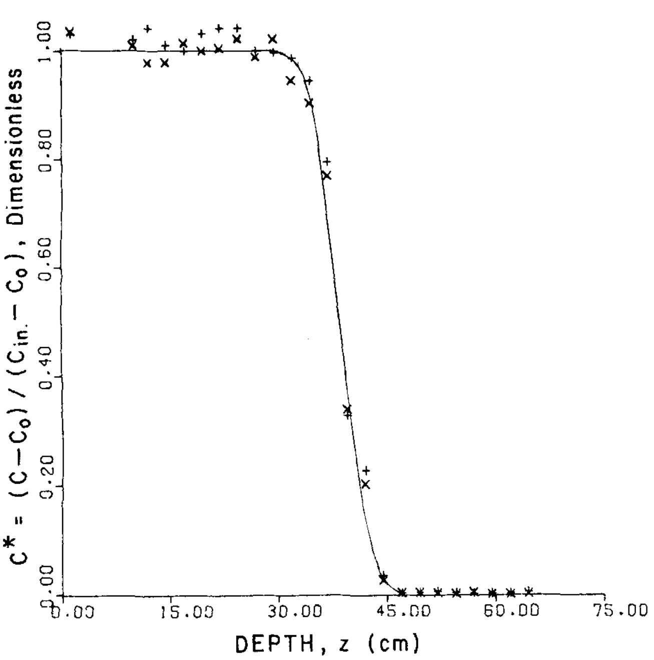

Fig. 5. Experimental $C^*(z, \{t\}^m)$ data for two columns of sand of mean particle size of 274 μ following 3 min of steady flow input of high concentration of nitrate solution and 14 min of drainage. Data from the first column are indicated with + marks; data from the second column are indicated with x marks. The solid line represents the least-squares fit based on the proposed transport model.

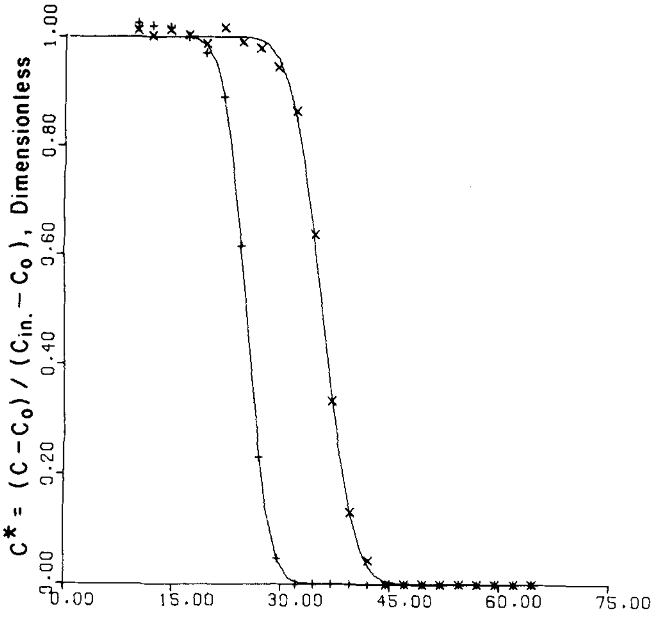

Fig. 6. Computed and experimental $C^*(z, \{t\}^m)$ profiles for infiltration through a sand with a mean particle size of 274 μ. Experimental points indicated with + marks correspond to the $\{t\}^m = 3.5$ min run and x marks correspond to the $\{t\}^m = 5.5$ min run.

sponding to each of the twenty-four monitored depths could be considered the same or different, and the hypothesis that $\sigma_1^2 = \sigma_2^2 = \ldots = \sigma_{24}^2$ was accepted, yielding a pooled variance for the experimental error of $s_B^2 = 2.92 \times 10^{-5}$ with 24 deg of freedom.

In order to test whether the nonlinear water flow model represented the experimental data satisfactorily, a hypothesis test for variability (F test) was performed to determine if σ_A^2, the ensemble variance of the fit of the nonlinear water flow model was equal to σ_B^2, the ensemble variance of the error of the water content data, $w(z, t)$, at $t = 14$ min of drainage. For the case illustrated in Figure 3, the sample variance of the fit was $s_A^2 = 2.93 \times 10^{-5}$, with $\nu_A = 21$ deg of freedom so that variance ratio had to satisfy the inequality

$$\frac{s_A^2}{s_B^2} = \frac{2.93 \times 10^{-5}}{2.92 \times 10^{-5}} = 1.003 \leq F_{0.975}(21, 24) = 2.3$$

for $\alpha = 0.05$. Clearly, the inequality was satisfied; hence, it was concluded that the nonlinear water flow model was a satisfactory model to represent the flow of water during drainage.

It was observed that the larger the sand particle diameters, the more prone the column was to flow irregularities, such as channeling. The experimental water content profiles for the larger sands exhibited more irregularity in the sense of $w(z)$ not increasing consistently with increasing depth than in columns with the smaller particle size sands, as can be seen by comparing the experimental data in Figure 3 and 4, but the water content model was still acceptable. As indicated in Figure 4 by the solid line, the nonlinear water flow model was not highly sensitive to the values of the three regression coefficients in the $h(w)$ relation (Figure 2). The values of the parameters could vary quite a bit, on the order of 30 to 40%, between runs of the same material and still give good predictions of the $w(z, t)$ profiles when interchanged between runs. On the other hand, common values of K_{sat} and w_{sat} could not be used. As can be seen from Figure 4, the values of w_{sat} (indicated by the region where the three solid lines become horizontal at around $z = 45$ cm) differed for each of the runs; hence, for best accuracy in prediction, K_{sat} and w_{sat} would have to be determined in each column separately by experiment.

Water Flow—Infiltration

During the infiltration runs, it was noted that the steepness (in the sense of approaching plug flow) of the wetting front increased with the speed with which the column was sectioned, which meant that speed in sectioning was essential to eliminate excessive error. Another characteristic noted during the infiltration runs was that the water content $w(z, t)$ in the saturated zone (which, for the purposes of the nonlinear water flow model, was assumed to be of constant value w_{sat} at any time and depth) actually tended to increase with time. As the infiltration progressed, the air entrapped in the saturated zone by the rapidly advancing wetting front slowly diffused up and out through the top of the column, allowing more water to fill the void spaces. Consequently, the values for the variances s_B^2 for the infiltration runs were higher than those for drainage through columns of similar size sands. Nevertheless, the nonlinear water flow model for infiltration predicted both the location and the shape of the wetting front reasonably well for each of the infiltration runs.

Transport of Nitrate Ion in Drainage

As for the case of the nonlinear water flow model, an analysis of variance was carried out using replicate $C(z, \{t\}^m)$ data to test the validity of the transport model for nitrate ion. Figure 5 is a plot of the experimental $C^*(z, \{t\}^m)$ values vs. z for a step input for the same sands previously shown in Figure 3. The concentration profile data and results for the unsteady runs are plotted as $C^*(z, \{t\}^m)$ vs. z, rather than z^*, so that the concentration profiles may be more easily compared with the water content profiles for the same runs. As can be seen in Figure 5, for the bottom eight points, $C^*(z, \{t\}^m)$ equaled 0; that is, the step input of the (higher) concentration of potassium nitrate solution, $C = C_{in}$ or $C^* = 1$, had not yet penetrated the column below 47 cm. Therefore, only the first sixteen $C(z, \{t\}^m)$ values for the two drainage runs were used in the analysis of variance.

As with the tests for water flow, it was determined that the sample variances could be pooled, and the F test was

$$\frac{s_A^2}{s_B^2} = 2.17 < F_{0.975}(14, 16) = 2.79$$

so that the transport model for nitrate, Equation (17), was accepted as a satisfactory model for the dispersion of a step input of nitrate during unsteady water flow. Greater deviations in the fit of the transport model were observed for the sands having less uniformity than the type of sand illustrated in Figure 5.

Transport of Nitrate Ion in Infiltration

The results of the two infiltration runs for the sand with a mean particle size of 274μ are shown in Figure 6. Surprisingly, the values of the minimum sum of the squares, for the fit of the model, were even lower than those obtained for the step input of a solute during steady water flow in the same sand and less than those found for all the sands in the drainage experiments.

In view of the less precise agreement between experimental values of $w(z, \{t\}^m)$ and those computed using the nonlinear water flow model for the infiltration runs mentioned previously, the excellent agreement between experimental and computed values of $C^*(z, \{t\}^m)$ for infiltration was somewhat unexpected. However, the lack of agreement between experimental and computed values of $w(z, \{t\}^m)$ for infiltration was primarily due to the inadequacy of the nonlinear water flow model and not due to departure from the ideal water flow pattern for homogeneous media. Consequently, the principal assumption of the transport model, that of homogeneous water flow through the medium, was met, and the lack of agreement between experimental and computed $w(z, \{t\}^m)$ values was evaded because the transport model did not involve the direct use of either the computed or the experimental values of $w(z, t)$.

PREDICTION OF NITRATE TRANSPORT

To be useful, the nitrate transport model should have the capability of predicting transport in nonadsorbing porous media other than those used in this work. How the model can be so employed (with the assistance of a minimum of experimentation) is described in this section.

In order to apply the solution of Equation (17) to other porous media, values of Pe_ζ must be determined for the media. Direct fitting of a linear relation between the logarithms of the Peclet number and the Reynolds number

$$Pe_d = \frac{d_p\{\overline{v}_s\}^m}{\{\overline{D}_f\}^m} \quad \text{vs.} \quad R_d = \frac{d_p\{\overline{v}_s\}^m}{\nu}$$

while yielding a nice equation introduces too much spurious correlation because the numerators of the two dimensionless quantities are identical.

A quite satisfactory correlation was established for $\{\overline{D}_f\}^m$ vs. R_d as shown in Figure 7:

$$\{\overline{D}_f\}^m/\nu = 4.60\ R_d^{0.847} \tag{18}$$

[Keep in mind that the sum of squares in fitting Equation (18) is relatively insensitive to deviations in $\{\overline{D}_f\}^m$ as shown in Figure 8.] When the deviations about the correlation Equation (18) are compared to the deviations about corresponding correlations for steady flow through saturated porous media (Ebach and White, 1958; Greenkorn, 1970; Harleman et al., 1963), the scatter of the data about Equation (18) is found to be comparable. Unfortunately, values of $\{\overline{D}_f\}^m$ for the dispersion of nitrate during unsteady flow through unsaturated media cannot be predicted using the D_f vs. v_s correlations for steady flow through saturated porous media.

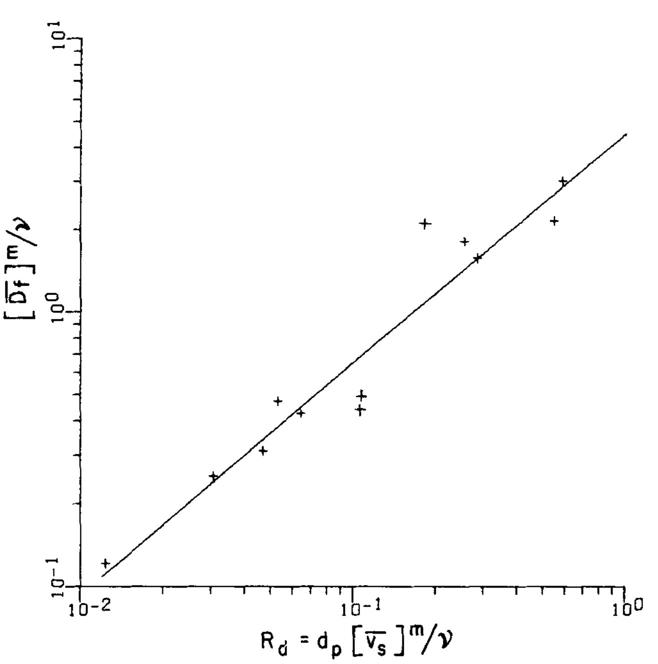

Fig. 7. Correlation of the dimensionless dispersion coefficient $\{\overline{D}_f\}^m/\nu$ vs. the Reynolds number based on the particle size R_d is the solid line. Plus signs designate the experimentally determined values of $\{\overline{v}_s\}^m$ and $\{\overline{D}_f\}^m$ for the unsteady water flow runs.

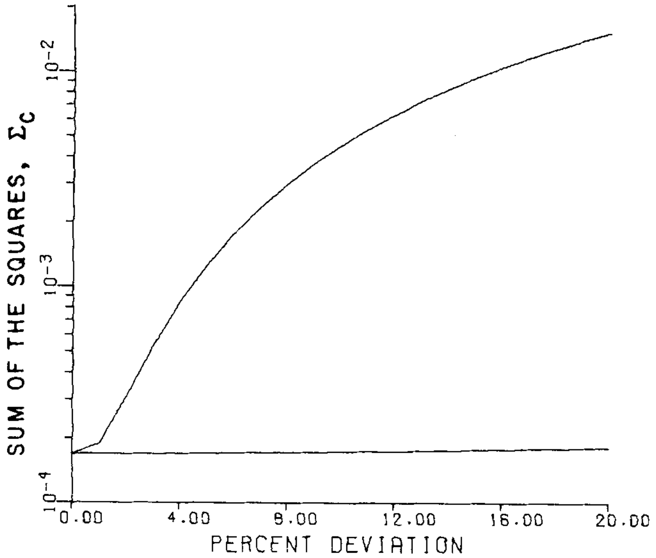

Fig. 8. Sensitivity in the value of the sum of squares for fit for the sand of mean particle size of 274 μ with increasing deviation in $\{\overline{D}_f\}^m$ and $\{\overline{v}_s\}^m$. The lower line represents the percent difference in the value of $\{\overline{D}_f\}^m$ used in Equation (17) from the value of $\{\overline{D}_f\}^m$ that yielded the best fit, while the upper line represents the percent difference in the value of $\{\overline{v}_s\}^m$ used in the same equation and that for the best fit.

We now turn to prediction of $\{\overline{v}_s\}^m = \overline{v}_s(Z_w, t)$ for $t = \{t\}^m$. During unsteady water flow through the sand column, the potassium nitrate dispersion front moved at the effective rate of $\overline{v}_s(Z_w, t)$, the cumulative seepage velocity averaged over the depth of the wetted zone Z_w, and over the total time from the introduction of the step input into the feed stream. The dispersion front exhibited a typical S shaped symmetrical pattern commonly observed for steady fluid flow through saturated porous media.

The ability of any model to predict water movement in one column based on data, that is, w_{sat} and K_{sat}, from another column, is limited by the differences in packing between the columns, even when filled by the same technique with the same material, as noted by the ± 5.1% error in measured K_{sat} values in carefully packed laboratory sand columns in this work and the ± 20% error between values of K_o measured from disturbed soil samples and in situ experiments in the field. For the type of sand media used in this study, if one were to determine values of w_{sat} and K_{sat}, and an experimental $w(z, t)$ profile for a representative sand column during unsteady flow, and make use of the nonlinear water flow model, one could predict the depth of the midpoint of the nitrate front at any time during unsteady water flow through that same column within a centimeter or less. One could also describe the shape of the dispersion front with quite reasonable accuracy at any time during unsteady flow through that column.

If the prediction procedure were extended to similar columns of the same material, using the values of w_{sat}, K_{sat}, and regression coefficients for the $h(w)$ function evaluated from the initial test column, the accuracy of the predictions could still be good, but it would be limited by the error resulting from the variability of packing between the columns. Nevertheless, one could certainly estimate the depth of the midpoint of the dispersion front following a period of infiltration or drainage through similar columns of the same material to within 3 to 5 cm and describe the shape of the dispersed potassium nitrate concentration front quite satisfactorily.

Finally, some limitations of the transport model must be reemphasized. The nonlinear water flow model and the model of nitrate transport during unsteady flow are limited to one-dimensional transport of a nonadsorbing ion in a homogeneous medium. The model of unsteady water flow is limited to either drainage or infiltration alone, not a combination of the two, as would be the case when the upper wetted part of a column is draining ino a drier lower portion, so that the lower part of the column is undergoing infiltration. Furthermore, the drainage or infiltration must be unimodal; that is, the column cannot be rewetted during drainage, nor can the infiltration be interrupted for some period of time so that the column can undergo a short period of drainage before the infiltration is resumed. Any combination of infiltration and drainage requires the use of an $h(w)$ function which takes hysteresis into account, a feature not included in this work.

NOTATION

$B(h)$ = water capacity, $\partial w/\partial h$, length^{-1}

c_A = concentration of solute A per volume of dry soil, mass/volume

C = concentration of a solute per volume of water, mass/volume

C^* = dimensionless concentration, $(C - C_o)/(C_{in} - C_o)$

C_{in} = input concentration to the column, mass/volume

C_o = original background concentration of solute in the column, mass/volume

d_p = representative average particle size, length

D_{Az} = general time averaged longitudinal diffusion coefficient, length^2/time

D_f = longitudinal dispersion coefficient, length^2/time

$(\overline{D_f})^m$ = longitudinal dispersion coefficient averaged over the depth of the wetted zone Z_w and the total time, $t = \{t\}^m$

$\overline{D_f}(Z_w, t) = \{\overline{D_f}\}^m$, length^2/time

$D(v)$ = dispersion coefficient that is a function of fluid velocity

$D(w)$ = dispersion coefficient that is a function of water content $= K(w)dh/dw$

F = F test parameter

g = acceleration of gravity, length/time^2

h = hydraulic, capillary, or pore pressure head, length

h_{dry} = hydraulic head of the column prior to infiltration, length

h_{st} = imposed depth of ponded water at the surface, length

h_{sat} = hydraulic head of the medium at saturation with air entrapment, length

H = total hydraulic head $= h - z$, length

k_o = permeability at complete saturation, length^2

k_r = relative permeability, dimensionless

K = hydraulic conductivity, length/time

K_{sat} = hydraulic conductivity at saturation with air entrapment, $w = w_{sat}$, length/time

L = length of the column

p = hydraulic, pore, or capillary pressure relative to atmospheric, mass/(length)(time^2)

P = total hydraulic pressure $= p - \rho gz$, mass/(length) (time^2) or force/area

Pe_d = Peclet number based on the particle size, $v_s d_p/D_f$, dimensionless

Pe_ζ = Peclet number based on the characteristic depth, $v_s\zeta/D_f$, dimensionless

Q = volumetric discharge rate, volume/time

R_d = Reynolds number based on the particle size, $\rho v_s d_p/\mu$, dimensionless

$s_B{}^2$ = sample variance for experimental error

$s_A{}^2$ = sample variance for fit to model

S = saturation, volume of water per volume of pores $= w/\phi$, dimensionless

t = time

t^* = dimensionless time, $t/\{t\}^m$

$\{t\}^m$ = time at which the experimental profile is determined

v_d = discharge of superficial velocity, length/time

v_{in} = input discharge velocity to the column, length/time

v_s = seepage or interstitial velocity $= v_d/w$, length/time

$\{\overline{v_s}\}^m$ = interstitial or seepage velocity averaged over the depth of the wetted zone Z_w and the total time, $t = \{t\}^m$

$\overline{v_s}(Z_w, t) = \{\overline{v_s}\}^m$, length/time

V_o = total pore volume

w = water content, volume of water per volume of bed

w_{dry} = initial water content prior to infiltration

w_{sat} = water content at saturation with air entrapment

z = depth, positive down, length

z^* = dimensionless depth, $z/\zeta = z/(v_s\, t)$

Z_w = depth of the wetted zone over which $\{\overline{v_s}\}^m$ is averaged, length

Greek Letters

α = significance level

ζ = characteristic depth, $(v_s\, t)$, length

μ = viscosity, mass/(length time)

ν = kinematic viscosity, μ/ρ, length^2/time

ν = number of degrees of freedom

μ = density of the wetting fluid, usually water, mass/volume

ρ_b = density of the dry bed, mass/volume

σ^2 = population variance

Σ_C = sum of the squares of the differences between experimental and computed values of $C(z, t)$, (mass/volume)^2

ϕ = total porosity, volume of voids per volume of bed

Subscripts

A = solute A

b = dry bed

d = discharge

in = input condition

o = total saturation condition

s = seepage

sat = saturation with air entrapment condition

Superscripts

m = $j = m$ when $t = \{t\}^m$

Overlays

— = averaged over the depth of the wetted zone, Z_w, and the total time

Other

{ } = a variable evaluated at the time and/or depth node indicated in superscript and/or subscript to the right of brackets

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