A REVIEW OF PHYSICAL AND CHEMICAL PROCESSES PERTAINING TO SOLUTE TRANSPORT

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I. INTRODUCTION

Solute transport in soils has received considerable attention during the past decades. Agriculturalists are interested in the behavior and effectiveness of applied fertilizers and pesticides. Leaching of salts (solutes) through the soil profile, which depends on exchange, exclusion, dissolution and precipitation, volatilization, chemical and biological transformations, and other processes, affects both the chemical and physical condition of a soil. Other areas of interest are miscible displacement, such as the mixing of fresh ground water with salt sea water and the secondary recovery of oil.

The main reason for the increased interest in the transport of solutes is the concern about contamination of the soil, in particular the movement of contaminants to the ground water. A wide variety of substances is involved, including agricultural chemicals, industrial compounds, radio-active materials, and domestic waste.

Solute transport through porous media has been studied by workers from many disciplines: chemical, civil, and petroleum engineering; hydrology, hydrogeology, and geochemistry; and soil science and agronomy. Because of this diversity, research areas include mathematical approaches to solve flow and transport equations, experimental work concerning homogeneous media under laboratory conditions, and field experiments with inherent heterogeneity. Laboratory work has focused on exchange chromatography, the influence of biological, hydrodynamic, and geochemical processes, and the transport during unsaturated flow conditions.

This literature review covers, in very general terms, what has been done to date in the area of solute transport in soils. In particular, it examines both chemical and physical processes and explores transport during saturated as well as unsaturated flow conditions.

II. FORMULATION OF THE TRANSPORT EQUATION

Non-reactive Solutes

As a starting point we will consider the transport of a chemical species in an isotropic porous medium, which is homogeneous with respect to the relevant transport and flow parameters. The porous medium consists of a rigid solid phase, of which the pores are filled with liquid. It is assumed that the species does not react or interact with the medium and that the solute is completely miscible with the solvent. At the macroscopic level, the equation of conservation of mass, assuming no source/sink terms, leads to:

$$\frac{\partial \theta C}{\partial t} = -\nabla\cdot\left[J_D + J_V C\right] = -\nabla\cdot J_s \tag{2-1}$$

where θ is the volumetric water content $[L^3L^{-3}]$, C is the concentration of the solute expressed in mass of solute per volume solution phase $[ML^{-3}]$, t is time [T], J_D is the diffusive-dispersive mass flux $[ML^{-2}T^{-1}]$, J_V is the volumetric flux of the carrier $[L^3L^{-2}T^{-1}]$, J_s is the total solute mass flux $[ML^{-2}T^{-1}]$ and $\nabla\cdot$ denotes the divergence $[L^{-1}]$.

The autonomous flux J_D is generally expressed as a Fick-type equation:

$$J_D = -\theta D\,\frac{\partial C}{\partial x} \tag{2-2}$$

where D is the coefficient of hydrodynamic dispersion $[L^2T^{-1}]$ and x is distance [L]. D represents the random effects due to molecular diffusion and mechanical dispersion, which occur during transport or flow. Many references exist with regard to this topic *(15, 53)*. Although the mechanisms behind these two processes are quite different, they behave similarly and Fick's law for diffusion can be used to describe both effects. Therefore, the coefficient of mechanical dispersion, D_{dis} $[L^2T^{-1}]$, and the effective coefficient of molecular diffusion, D_e $[L^2T^{-1}]$, are added to give an effective coefficient of dispersion:

$$D = D_{dis} + D_e \qquad (2\text{-}3)$$

D depends, among other things, on water content and pore-water velocity. Because of the intimate relation between microscopic variation of the water velocity and solute spreading, D is also called coefficient of hydrodynamic dispersion *(15)*. One might argue that this is somewhat ambiguous because only D_{dis} depends on the pore-water velocity. The use of one coefficient is especially convenient when solving the transport equation analytically. Sometimes a third mechanism, which contributes to dispersion, is included; the diffusive transfer of solute between mobile and immobile regions of the liquid phase *(135)*.

Substituting Eq.(2-2) into Eq.(2-1) and using the relation between the Darcy flux and the pore-water velocity ($J_V=v\theta$), we obtain for one-dimensional transport:

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial x}\left[\theta D(v,\theta)\ \frac{\partial C}{\partial x} - v\theta C\right] \qquad (2\text{-}4)$$

where v is the average pore-water velocity $[LT^{-1}]$. Assuming v and θ and to be uniform with respect to x and assuming steady-state flow, Eq.(2-4) leads to:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \qquad (2\text{-}5)$$

which is a special form of the Fokker-Planck equation for one variable, namely with v and D independent of x and t *(157)*. It is a linear second-order partial differential equation of parabolic type, which will be referred to as the advection-dispersion equation (ADE); it is also known as convection-dispersion or convection-diffusion equation. It has been widely used in miscible displacement studies *(e.g., 121)*. For multidimensional, anisotropic flow, Eq.(2-5) needs to be rewritten *(cf. 165)* as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left[\mathbf{D}_{ij} \frac{\partial C}{\partial x_j}\right] - \frac{\partial v_i C}{\partial x_i} \qquad (2\text{-}6)$$

where $\mathbf{D}_{ij}$ is the dispersion tensor and i,j are indices denoting directions.

For laboratory conditions the ADE is very useful for modeling solute movement. The equation can be adjusted to include phenomena such as cation-exchange *(107)*, adsorption-desorption of pesticides *(198)*, anion exclusion *(29)*, precipitation-dissolution *(159)*, nutrient uptake by plants *(47)*, microbial induced transformations *(41)* and radioactive decay *(154)*.

For field conditions, Eq.(2-5) is less useful to describe transport, because most soils are macroscopically heterogeneous due to factors such as structural development, heterogeneity of the soil profile, swelling and shrinking, and biological activity.

Reactive Solutes

Solutes and porous media often interact with each other. Many soils, due to the presence of negatively charged clay minerals, variably charged organic matter, hydrous oxides and mineral edges, exhibit adsorption and exclusion phenomena. These generally cause the solute and the carrier to travel at a different speed.

It is assumed that the chemical species is present only in the liquid and the sorbed phase, and that there is only one liquid phase. The process of adsorption/desorption can be included into Eq.(2-1) to yield:

$$\frac{\partial}{\partial t}\left[\theta C + q\right] = -\nabla\cdot\left[J_D + J_V C\right] \qquad (2\text{-}7)$$

where q is the concentration in the sorbed phase expressed in mass of solute per volume of soil $[ML^{-3}]$. Sorbed refers to adsorption and precipitation, although the latter process will be ignored. Actually q can be regarded as a source/sink term. It should be noted that, under unsaturated flow conditions, the vapor phase needs to be considered if volatile solutes are present. For one-dimensional transport, Eq.(2-7) leads to:

$$\frac{\partial}{\partial t}\left[\theta C + q\right] = \frac{\partial}{\partial x}\left[D\theta \frac{\partial C}{\partial x}\right] - \frac{\partial v\theta C}{\partial x} \qquad (2\text{-}8)$$

If an exchange isotherm is known, which relates the concentration of the species in the adsorbed phase to the concentration of all species in the liquid phase, the dependent variable q can be expressed in terms of C. However, this is only justified in case of a single valued relationship between q and C, implying that the exchange reaction reaches instantaneous equilibrium and that no hysteresis exists. The importance of hysteresis in the q(C) relationship was illustrated by van Genuchten and Cleary *(198)*. In case of a binary system, S_k, the adsorbed mass of species k per mass of soil $[MM^{-1}]$, can be expressed as:

$$S_k = f(C_T, C_k) \tag{2-9}$$

where C_T is the total electrolyte concentration and C_k is the concentration of species k in solution $[ML^{-3}]$; both C_T and C_k are expressed per volume of solution phase. To express the adsorbed concentration on the basis of volume of soil, the following relationship is used:

$$q_k = S_k \rho_b \tag{2-10}$$

where ρ_b is the soil bulk density $[ML^{-3}]$.

For conditions similar to those stated for the derivation of Eq.(2-5), Eq.(2-8) can be written as:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta}\frac{\partial S}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{2-11}$$

where C and S refer to the concentrations of solute species k in a binary system. Applying the chain rule and assuming a constant total electrolyte level with respect to time, i.e., $S_k = f(C_k)$, yields:

$$\frac{\partial S}{\partial t} = \frac{dS}{dC}\frac{\partial C}{\partial t} \tag{2-12}$$

where dS/dC is the slope of the exchange isotherm, which is constant in case of linear adsorption or exchange and which is usually referred to as the distribution coefficient K_d $[L^3M^{-1}]$. This quantity indicates how the species is distributed between the liquid and adsorbed phase:

$$S = K_dC \tag{2-13}$$

Using Eq.(2-12), Eq.(2-11) can be rewritten in terms of one dependent variable:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{2-14}$$

where the dimensionless retardation factor R is defined as follows:

$$R = 1 + \frac{\rho_b}{\theta} \frac{dS}{dC} \tag{2-15}$$

Depending on the assumed adsorption mechanism, different transport equations were given by Gupta and Greenkorn *(75)*:

1. Linear adsorption isotherm: $q = k_1C$

$$\left[1 + \frac{k_1}{\theta}\right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{2-16}$$

2. Freundlich adsorption isotherm: $q=k_2C^n$

$$\left[1 + \frac{nk_2}{\theta} C^{n-1}\right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{2-17}$$

3. Langmuir equilibrium adsorption: $q = aC/(1 + bC)$

$$\left[1 + \frac{a}{\theta(1+bC)^2}\right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{2-18}$$

In the above three examples k, n, a and b are empirical constants.

Dividing Eq.(2-14) by the retardation factor leads again to the ADE, as for the non-reactive case:

$$\frac{\partial C}{\partial t} = D^{*}\frac{\partial^{2} C}{\partial x^{2}} - v^{*}\frac{\partial C}{\partial x} \tag{2-19}$$

with $D^{*}=D/R$ and $v^{*}=v/R$. In case of non-linear exchange ($R=f(C_i)$), Eq.(2-19) is a non-linear partial differential equation for which analytical solutions are difficult to obtain.

A more general equation should include sink/source terms to account for phenomena such as radioactive decay, precipitation, dissolution and chemical reactions. Parker and van Genuchten *(130)* presented the following, more general expression:

$$\frac{\rho_b}{\theta}\frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D\frac{\partial^{2} C}{\partial x^{2}} - v\frac{\partial C}{\partial x} - \mu_w C - \frac{\mu_s \rho_b}{\theta} S + \gamma_w + \frac{\gamma_s \rho_b}{\theta} \tag{2-20}$$

where μ_w and μ_s are rate constants for first-order decay in liquid and solid phase $[T^{-1}]$, respectively, and γ_w $[ML^{-3}T^{-1}]$ and $\gamma_s[T^{-1}]$ are rate constants for zero-order production in liquid and solid phase, respectively.

Solutions of the Transport Equation

Before presenting some analytical solutions for Eq.(2-19), it is worthwhile to mention the different types of concentrations that can be considered and to pay attention to the appropriate boundary and initial conditions *(131, 200)*.

Concentrations

The time average of C is defined *(60)* as:

$$\overline{C}_t(x,y,z,t_o) = \frac{1}{\Delta t}\int_{t_o-\frac{\Delta t}{2}}^{t_o+\frac{\Delta t}{2}} C(x,y,z,t)\ dt \tag{2-21}$$

A spatial or volume average of c, a microscopic variable in this case, at a position (x_o,y_o,z_o) is defined as

$$\overline{C}_V(x_o,y_o,z_o,t) = \lim_{\Delta V\rightarrow\delta V} \frac{\int_{\Delta V_\ell} c\ dV}{\int_{\Delta V_\ell} dV} \tag{2-22}$$

where the volume ΔV and ΔV_ℓ represent a "large" chunk of the porous medium and the liquid phase, respectively, and dV and δV correspond to a microscopic differential volume element and the Representative Elementary Volume *(16)*, respectively. All volumes are expressed in L^3. Furthermore, x_o, y_o and z_o are fixed positions (the center of a physical or material point). It should be noted that the macroscopic concentration, C, is generally taken as the volume-averaged concentration, $\overline{C}_V$.

At a certain position, the flux-averaged concentration, $\overline{C}_f$, is given as the ratio of the transport and flow term:

$$\overline{C}_f(t) = J_s/J_V \tag{2-23}$$

$\overline{C}_f(t)$ represents the mass of solute per unit volume of fluid passing through a given cross section during an arbitrary time interval *(102)*. As was stated by Parker and van Genuchten *(131)*, solute flux distributions are in many cases of more interest than pore fluid concentrations. The relationship between flux-averaged concentration, $\overline{C}_f$, and volume-averaged concentration, $\overline{C}_V$, the two types of concentrations pertinent to many displacement experiments, can be derived from Eq.(2-23):

$$\overline{C}_f = \overline{C}_V - \frac{D}{v}\frac{\partial \overline{C}_V}{\partial x} \qquad (2\text{-}24)$$

Parker and van Genuchten *(131)* discussed the importance of distinguishing between both concentration modes in conjunction with the way an experiment is performed and the results are analyzed *(cf. 34, 102)*. Unless stated otherwise, we will assume, as was done previously, that all concentrations are volume averaged, i.e., $C=\overline{C}_V$.

Boundary and Initial Conditions

In order to solve Eq.(2-5), or for that matter (2-19), specific boundary and initial conditions are needed. Following van Genuchten and Alves *(197)*, the initial condition is:

$$C(x,t) = f(x) \qquad x>0\ ,\ t=0 \qquad (2\text{-}25)$$

where f(x) is an arbitrary function.

For the boundary condition at x=0, the first- or concentration-type boundary condition, the Dirichlet problem, is given by:

$$C(x,t) = g(t) \qquad x{\downarrow}0\ ,\ t>0 \qquad (2\text{-}26)$$

and the third- or flux-type boundary condition is given by:

$$\left.\left(-D\frac{\partial C}{\partial x} + vC\right)\right|_{x{\downarrow}0} = vg(t) \qquad t>0 \qquad (2\text{-}27)$$

where g(t) is an arbitrary function describing the concentration of the incoming solution. The exit boundary condition can be defined for a semi-infinite or for a finite soil column. For a semi-infinite column the appropriate boundary condition is:

$$\frac{\partial C}{\partial x}(x,t) = 0 \qquad x \to \infty\ ,\ t>0 \qquad (2\text{-}28)$$

In case of a finite system the following continuity condition at the exit boundary needs to be satisfied:

$$\left(-D\frac{\partial C}{\partial x} + vC\right)\bigg|_{x\uparrow L} = vC_{ex} \qquad t>0 \qquad (2\text{-}29)$$

where C_{ex} is the exit concentration, which is assumed to be equal to $C|_{x\uparrow L}$. Hence:

$$\frac{\partial C}{\partial x}(x,t) = 0 \qquad x\uparrow L,\ t>0 \qquad (2\text{-}30)$$

Analytical solutions of Eq.(2-5) for conditions (2-28) and (2-30) are approximately equal.

For the inlet boundary, a third-type condition is generally preferred, because the mathematical solution for this condition leads to conservation of mass. Eq.(2-26) implies equal concentrations in the feed solution and in the porous medium at the boundary. However, in reality it takes some time to attain the same concentration. First, the input solution might not be well mixed resulting in a boundary layer outside the porous medium *(24)*. More important, because at the microscopic level the concentration varies gradually, a transition zone should be taken into account. Obviously a volume averaged concentration of a representative elementary volume (REV) will not immediately be equal to the concentration of the feed solution. In other words, since a (tracer) solution can only be injected at a certain rate, a prescribed concentration will not be established instantaneously. For displacement experiments, involving a step change in concentration ($g(t<0)=0$ and $g(t>0)=C_o$), a third-type condition should therefore be used:

$$\left(-D \frac{\partial C}{\partial x} + vC\right)\Bigg|_{x\downarrow 0} = vC_o \tag{2-31}$$

where C_o is the concentration of the feed solution. The discontinuity in the concentration across the inlet boundary increases with increasing D/v. Van Genuchten and Parker *(200)* showed that solutions of the ADE, subject to a first-type boundary condition, lead to flux average concentrations, whereas solutions for a third-type boundary condition lead to volume average concentrations. One is also referred to the work by Parlange and Starr *(133, 134)*, Parlange et al. *(132)*, and Pandey and Gupta *(128)*.

Analytical Solutions

In case of an infinite system ($-\infty<x<\infty$), a solution of Eq.(2-5) can be obtained by making the following transformation of coordinates:

$$\begin{aligned} \xi &= x-vt \\ \tau &= t \end{aligned} \tag{2-32}$$

which transforms Eq.(2-5) to:

$$\frac{\partial C}{\partial \tau} = D \frac{\partial^2 C}{\partial \xi^2} \tag{2-33}$$

The original boundary and initial conditions

$$\begin{aligned} C &= C_i \qquad x>0 \quad t<0, \; x\to\infty \quad t>0 \\ C &= C_o \qquad x<0 \quad t<0, \; x\to-\infty \quad t>0 \end{aligned} \tag{2-34}$$

need to be transformed as well. Note that C_i is the initial concentration in the soil. The solution of Eq.(2-33) can be found in the areas of heat flow *(37)* and diffusion *(45)*.

Using an alternative transformation:

$$\xi = \frac{x-vt}{\sqrt{4Dt}} \tag{2-35}$$

results in an ordinary differential equation:

$$\frac{d^2C}{d\xi^2} + 2\xi \frac{dC}{d\xi} = 0 \tag{2-36}$$

With the transformed initial and boundary concentrations described by:

$$\begin{aligned} C &= C_i \qquad && \xi \to \infty \\ C &= C_o \qquad && \xi \to -\infty \end{aligned} \tag{2-37}$$

the solution of Eq.(2-36) is:

$$\bar{C} = (C-C_i)/(C_o-C_i) = \frac{1}{2} \operatorname{erfc} \xi \tag{2-38}$$

where $\bar{C}$ is the dimensionless concentration and erfc is the complementary error function. For other boundary conditions, involving semi-infinite or finite media, a coordinate transformation cannot be employed or is inconvenient. Carslaw and Jaeger *(37, p. 388)* showed how Laplace transforms can be used to solve Eq.(2-5). Van Genuchten and Alves *(197)* provided a compendium of available analytical solutions to Eq.(2-14), many of them obtained with the help of Laplace transforms. The solutions for four combinations of inlet and exit conditions are listed in table 1.

Table 1. Analytical Solutions of Eq.(2-14) for Various Boundary Conditions with Constant R, after van Genuchten and Wierenga *(204)*

Case	Inlet boundary condition	Exit boundary condition	Analytical solution
A-1	$C(0, t) = C_o$	$\frac{\partial C}{\partial x}(\infty, t) = 0$	$c = \frac{1}{2} \operatorname{erfc}\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right] + \frac{1}{2} \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right]$
A-2	$\left(-D\frac{\partial C}{\partial x} + vC\right)\Big\vert_{x=0} = vC_o$	$\frac{\partial C}{\partial x}(\infty, t) = 0$	$c = \frac{1}{2} \operatorname{erfc}\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right] + \left(\frac{v^2 t}{\pi DR}\right)^{1/2} \exp\left[-\frac{(Rx - vt)^2}{4DRt}\right]$ $- \frac{1}{2}\left(1 + \frac{vx}{D} + \frac{v^2 t}{DR}\right) \exp\left(\frac{vx}{D}\right) \operatorname{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right]$
A-3	$C(0, t) = C_o$	$\frac{\partial C}{\partial x}(L, t) = 0$	$c = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin\left(\frac{\beta_m x}{L}\right) \exp\left[\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\beta_m^2 Dt}{L^2 R}\right]}{\left[\beta_m^2 + \left(\frac{vL}{2D}\right)^2 + \frac{vL}{2D}\right]}$ $\beta_m \cot(\beta_m) + \frac{vL}{2D} = 0$
A-4	$\left(-D\frac{\partial C}{\partial x} + vC\right)\Big\vert_{x=0} = vC_o$	$\frac{\partial C}{\partial x}(L, t) = 0$	$c = 1 - \sum_{m=1}^{\infty} \frac{\frac{2vL}{D} \beta_m \left[\beta_m \cos\left(\frac{\beta_m x}{L}\right) + \frac{vL}{2D} \sin\left(\frac{\beta_m x}{L}\right)\right] \exp\left[\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\beta_m^2 Dt}{L^2 R}\right]}{\left[\beta_m^2 + \left(\frac{vL}{2D}\right)^2 + \frac{vL}{D}\right]\left[\beta_m^2 + \left(\frac{vL}{2D}\right)^2\right]}$ $\beta_m \cot(\beta_m) - \frac{\beta_m^2 D}{vL} + \frac{vL}{4D} = 0$

References: A-1: *(109)*, A-2: *(113)*, A-3: *(42)*, A-4: *(27)*

By using the following dimensionless variables

$$T = vt/L \tag{2-39}$$

$$Z = x/L \tag{2-40}$$

$$P = vL/D \tag{2-41}$$

$$\bar{C} = (C-C_i)/(C_o-C_i) \tag{2-42}$$

Eq.(2-14) can be rewritten as

$$R\,\frac{\partial \bar{C}}{\partial T} = \frac{1}{P}\,\frac{\partial^2 \bar{C}}{\partial Z^2} - \frac{\partial \bar{C}}{\partial Z} \tag{2-43}$$

where T is the number of pore volumes, L is the column length [L], Z is the dimensionless distance and P is usually referred to as the Peclet number. Analytical expressions for $\bar{C}\vert_{Z=1}=C_e$, the dimensionless exit concentration, are provided in table 2 for different boundary

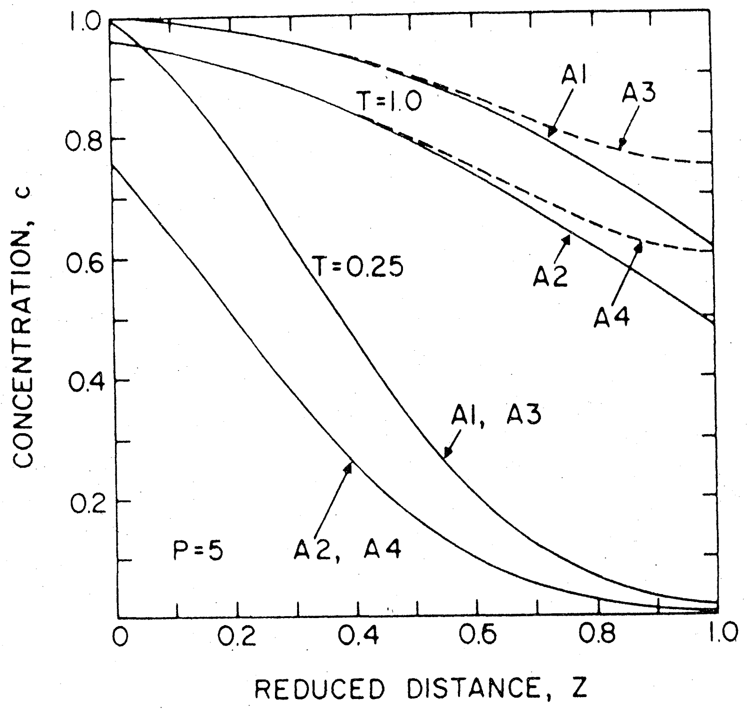
Table 2. Expressions for the Relative Effluent Concentration, $C_e(T)$, in Terms of the Column Peclet Number (P) and Pore Volume (T) for the Four Analytical Solutions Listed in table 1, after van Genuchten and Wierenga *(204)*

Case	Relative effluent concentration	
A-1	$c_e(T) = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R - T) \right] + \frac{1}{2} \exp(P) \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R + T) \right]$	
A-2	$c_e(T) = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R - T) \right] + \left(\frac{PT}{\pi R} \right)^{1/2} \exp \left[- \frac{P}{4RT} (R - T)^2 \right] - \frac{1}{2} \left(1 + P + \frac{PT}{R} \right) \operatorname{erfc} \left[\left(\frac{P}{4RT} \right)^{1/2} (R + T) \right]$	
A-3	$c_e(T) = 1 - \sum_{m=1}^{\infty} \frac{2 \beta_m \sin(\beta_m) \exp \left[\frac{P}{2} - \frac{PT}{4R} - \frac{\beta_m^2 T}{PR} \right]}{\beta_m^2 + \frac{P^2}{4} + \frac{P}{2}}$	$\beta_m \cot(\beta_m) + \frac{P}{2} = 0$
A-4	$c_e(T) = 1 - \sum_{m=1}^{\infty} \frac{2 \beta_m \sin(\beta_m) \exp \left[\frac{P}{2} - \frac{PT}{4R} - \frac{\beta_m^2 T}{PR} \right]}{\beta_m^2 + \frac{P^2}{4} + P}$	$P\beta_m \cot(\beta_m) - \beta_m^2 + \frac{P^2}{4} = 0$

conditions. The influence of the different boundary conditions on the concentration profiles is graphically illustrated in figure 1. At small times, the use of the first-type inlet condition results in a considerable error.

A difference in the solutions for the semi-infinite and the finite cases occurs once the solute concentration starts to increase at the exit. Just as for the inlet, the concentration at the exit is not likely to be continuous. Unless backmixing occurs from the effluent solution to the soil, the semi-infinite solution is to be preferred. These solutions are useful to predict the solute concentration in homogeneous media and to determine transport parameters in conjunction with an experimentally determined concentration distribution.

It should be noted that much more work on the analytical solution of the ADE has been published *(e.g., 65, 112, 127)*.



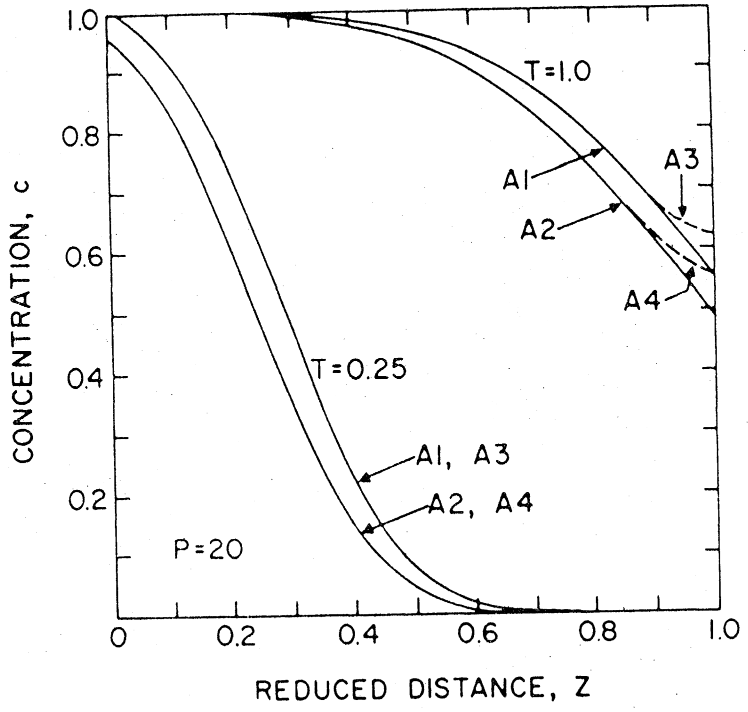


FIG. 1. Calculated concentration distribution for R=1 and P-values of 5 and 20, respectively. The curves were obtained with the analytical solutions listed in table 2, after van Genuchten and Alves *(197)*.

Non-equilibrium Conditions

So far, it has been assumed that instantaneous local equilibrium exists between the solute in the liquid and the adsorbed phase, the distribution of ions in both phases being determined by the exchange isotherm. However, instantaneous equilibrium might not always be achieved. Two different kinds of non-equilibrium exist: physical and chemical.

Physical Non-equilibrium

Physical non-equilibrium is of particular importance for aggregated media, where flow occurs predominantly between aggregates, and for unsaturated media, where the liquid phase in effect might be discontinuous. During miscible displacement the solute in the feed solution cannot reach all sorption sites immediately and no instantaneous exchange equilibrium can be achieved. This situation is generally classified as physical non-equilibrium. Conceptually, advective flow occurs only in the so called mobile region of the fluid phase. The concentration in the immobile region, both in the liquid and the adsorbed phase, will therefore lag behind the concentration in the mobile region. A large part of the sorption sites are usually only accessible via the immobile or stagnant region of the liquid. Transfer of solute from the mobile to the immobile region, and vice versa, occurs via a diffusion controlled process. For physical non-equilibrium, the transport equation was reformulated by van Genuchten and Wierenga *(202)* following Coats and Smith *(43)*:

$$\theta_{mo}\frac{\partial C_{mo}}{\partial t}+\theta_{im}\frac{\partial C_{im}}{\partial t}+\rho_b f\frac{\partial S_{mo}}{\partial t}+\rho_b(1-f)\frac{\partial S_{im}}{\partial t}=\theta_{mo}D\frac{\partial^2 C_{mo}}{\partial x^2}-\theta_{mo}v_{mo}\frac{\partial C_{mo}}{\partial x} \tag{2-44}$$

where the medium is supposed to be homogeneous with respect to θ_{mo}, θ_{im} and v_{mo} and the flow is steady. The fraction of sorption sites in direct contact with the mobile region of the liquid is given by f. Transfer of the species between mobile (mo) and immobile (im) regions of the liquid phase was given by:

$$\theta_{im}\frac{\partial C_{im}}{\partial t} + \rho_b(1-f)\frac{\partial S_{im}}{\partial t} = \alpha\ (C_{mo}-C_{im}) \tag{2-45}$$

where α is the mass transfer coefficient $[T^{-1}]$.

Anion exclusion *(29, 103)* can be viewed as a situation of physical non-equilibrium, where the exclusion volume roughly corresponds to the immobile region. Eq.(2-44) and (2-45) can be readily adapted *(207)* to describe the transport of anions which are excluded from certain regions of the liquid phase. A further discussion on the concept of mobile and immobile regions of the liquid phase will be given in the section on mobile and stagnant regions in Chapter V.

Chemical Non-equilibrium

Chemical non-equilibrium occurs when the adsorption/exchange process requires some time to be completed. No instantaneous equilibrium between the solute concentration in the liquid and the adsorbed phase will occur. To account for chemical non-equilibrium exchange, a kinetic approach can be taken by combining the transport equation with the appropriate rate equation for adsorption of the species by the medium *(7, 8, 109)*.

Because of the variety of adsorption sites (clay minerals, organic matter, oxydes) models with two kinds of adsorption sites have been introduced *(168)*. Adsorption occurs almost instantaneously for "type-1" sites, whereas for "type-2" sites adsorption is time-dependent. Using somewhat arbitrary first-order kinetics, the general sorption rates were given by Selim et al. *(168)* as:

$$\frac{\partial S_1}{\partial t} = \frac{\theta}{\rho_b} k_1C - k_2S_1 \qquad (2\text{-}46)$$

$$\frac{\partial S_2}{\partial t} = \frac{\theta}{\rho_b} k_3C - k_4S_2 \qquad (2\text{-}47)$$

where S_1 and S_2 are the concentrations of solute sorbed to sites 1 and 2, respectively. Furthermore, k_1 and k_3 are forward and k_2 and k_4 are backward reaction rate coefficients $[T^{-1}]$, respectively. It should be noted that the same assumptions and restrictions apply as were made for the derivation of Eqs.(2-5) and (2-11). At equilibrium, the sorbed concentrations are given by the following linear isotherms:

$$S_1 = \frac{\theta}{\rho_b} \frac{k_1}{k_2} C = K_1C \qquad (2\text{-}48)$$

$$S_2 = \frac{\theta}{\rho_b} \frac{k_3}{k_4} C = K_2C \qquad (2\text{-}49)$$

The sorbed concentration for all sites, at equilibrium, is given by:

$$S = S_1 + S_2 = (K_1 + K_2)C = KC \qquad (2\text{-}50)$$

A fraction F of the total sites belongs to "type-1" (i.e., $F=S_1/S=K_1/K$). Since "type-1" sites are always at equilibrium, it follows from Eq.(2-48) that:

$$\frac{\partial S_1}{\partial t} = FK \frac{\partial C}{\partial t} \tag{2-51}$$

For "type-2" sites, the sorption rate may be given by a linear, reversible first-order rate equation *(cf. 109)*. The sorbed concentration for these sites follows from the rate expression given by:

$$\frac{\partial S_2}{\partial t} = \alpha\ (K_2C - S_2) \tag{2-52}$$

where α is a first-order rate coefficient $[T^{-1}]$, as before, which is in this case equal to k_4. Eq.(2-51) and (2-52) can be substituted into Eq.(2-11) resulting in the following pair of equations to be solved:

$$(1+ \frac{KF\rho_b}{\theta}) \frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S_2}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{2-53}$$

$$\frac{\partial S_2}{\partial t} = \alpha \Big[(1-F)KC-S_2\Big] \tag{2-54}$$

Various authors *(124, 168, 196)* were able to describe the breakthrough curves fairly well with a numerical solution of Eq.(2-53) in conjunction with Eq.(2-54).

The "one-site" kinetic non-equilibrium model follows from the previous model. In this case, F=0 and Eq.(2-53) and (2-54) transform to:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{2-55}$$

$$\frac{\partial S}{\partial t} = \alpha\ (KC - S) \tag{2-56}$$

where S still refers to the adsorbed concentration of a particular species.

Apparent Non-equilibrium

Cameron and Klute *(36)*, in effect, combined the physical and chemical non-equilibrium models. The transition from a chemical reaction at one site (the microscopic viewpoint) to the average observed for a large number of pores (the macroscopic viewpoint) is very complicated because macroscopically uniform soils are generally not microscopically uniform. This involves both the physical and chemical processes pertaining to sorption. In the section on physical non-equilibrium the limited supply of the solute, due to immobile water, was discussed. In fact, a whole range of supply rates exists. The same holds for the actual sorption process; many rate equations might be needed to describe sorption depending on the various soil constituents and the solute. Furthermore, a distinction between physical and chemical non-equilibrium is generally not possible. Therefore, Cameron and Klute *(36)* proposed a "black box" approach to describe the sorption process. They differentiated between two types of sites, those which appear to react rapidly with the solute and those which appear to react more slowly. Sorption at the latter type is described with a kinetic type of reaction which is used to take into account both chemical and physical non-equilibrium.

The sorption sites are divided, as in the section on chemical non-equilibrium, into two fractions: S_1 (equilibrium) and S_2 (kinetic). Exchange between ions in the adsorbed and liquid phase occurs via a linear Freundlich (S_1) and a kinetic (S_2) type of process, respectively:

$$\frac{\partial S}{\partial t} = K_1 \frac{\theta}{\rho_b} \frac{\partial C}{\partial t} + k_3 \frac{\theta}{\rho_b} C - k_4 S_2 \qquad (2\text{-}57)$$

where K_1 $(=k_1/k_2)$, k_3 and k_4 are the equilibrium constant and the adsorption and desorption rate, respectively. $S=S_1+S_2$ is the adsorbed concentration and C is the liquid concentration, expressed in mass per volume of solution. The transport equation for combined kinetic and equilibrium adsorption is:

$$\frac{\rho_b}{\theta} \frac{\partial S_2}{\partial t} + (1 + K_1) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \qquad (2\text{-}58)$$

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\theta}{\rho_b} C - k_4 S_2 \qquad (2\text{-}59)$$

Cameron and Klute *(36)* expressed these equations in dimensionless form and obtained a solution via Laplace transforms. Application of the model to transport of atrazine, phosphorus, and silver was successful; a purely equilibrium or kinetic model did not fit the data accurately.

Nkedi-Kizza et al. *(124)* fitted two non-equilibrium models, a diffusion controlled and a first-order reversible kinetic model, through experimental breakthrough curves. How fast equilibrium is attained in the ion exchange process, merely a redistribution of ions rather than a typical chemical reaction, is determined by two mechanisms: the supply of solute through the liquid phase to the liquid/solid interface and the nature of the exchange reaction at that interface. The actual ion exchange reaction is generally not the rate limiting factor in most instances *(84)*. Rather, the diffusion of ions from solution to exchange sites, and vice versa, seems to be the rate limiting step even if no immobile water is present and we deal with chemical non-equilibrium. Presumably, both chemical and physical non-equilibrium models might be used to represent non-equilibrium exchange.

In summary, both models can be considered to have two types of adsorption sites. The physical non-equilibrium model has "mobile" sites with instantaneous equilibrium, while for the "immobile" sites exchange is diffusion controlled. This model is described with Eq.(2-44) and (2-45). The chemical non-equilibrium model is described with Eq.(2-53) and (2-54). For "type-2" sites, instantaneous equilibrium is not achieved because of the kinetic nature of the exchange process. When expressed in dimensionless variables it can be shown that the transport models for both models are identical and have equivalent breakthrough curves. Both models can be used when describing ion exchange during transport through aggregated sorbing media. Based on breakthrough curves, obtained via curve fitting, Nkedi-Kizza et al. *(124)*, however, did not want to draw the conclusion that the two models were conceptually similar.

Judgment whether local equilibrium exists can be based on exchange data and the physical properties of the medium *(cf. 24)*. Valocchi *(191)* presented criteria for the validity of the local equilibrium assumption. Presently, much work is being done in the area of transport through structured soils. As far as physical non-equilibrium is concerned, sometimes an effective dispersion coefficient can be used for soils containing aggregates of a particular size and shape. In this way, the sink/source term describing mass transfer from mobile to stagnant regions of the liquid phase can be omitted *(cf. 57, 135, 150)*. On the other hand, a distinction can be made between the inter-aggregate pore space (macropores), containing the mobile liquid, and the intra-aggregate pore space (micropores), containing the immobile liquid. In the intra-aggregate porespace the predominant transport mechanism consists of diffusion. Generally it is assumed that inside the aggregate instantaneous equilibrium is achieved between the species in the adsorbed and liquid phase. A number of analytical solutions have been published *(cf. 153, 186, 201)*. Some of these solutions will be discussed in Chapter V.

III. DISPERSION AND DIFFUSION

When a feed solution containing a given solute displaces a resident solution containing another solute or the same solute at a different concentration, a transition zone will develop in which a variation of solute concentration will occur. During displacement experiments, the solute concentration of the effluent is generally monitored to obtain a breakthrough curve. The curve is indicative of the amount of mixing between the two solutions. For a non-reactive solute, the spreading is caused by dispersion and diffusion. In order to describe solute transport, one generally needs to quantify both processes. Solutes can also be useful in hydrological studies, where they are used as tracers to study flow phenomena in porous media. Many references exist about diffusion and dispersion *(15, 23, 24, 60, 61, 165)*.

Following Fried and Combarnous *(61)*, two mechanisms of dispersion will be distinguished:

1. Mechanical dispersion. When adopting a microscopic viewpoint, nonuniform velocity profiles exist in a porous medium because of the following reasons:

- The velocity of the soil solution is zero at the solid surfaces. Slip flow does not occur because of the relatively high viscosity of water and the small mean free path length *(165)*.

- The pore dimensions vary, so different maximum velocities occur along the axes of the pores.
- Streamlines fluctuate with respect to the mean direction of flow.

2. Physico-chemical dispersion: diffusion. This type of dispersion is due to concentration gradients, actually gradients in chemical potential. The following phenomena take place:

- If inside a streamtube a concentration gradient occurs, then diffusion tries to annihilate the gradient.
- If concentration gradients exist between two adjacent streamtubes, mass transfer between the streamtubes occurs by diffusion.

For both types of dispersion a longitudinal and transverse component can be distinguished. Mechanical dispersion (dispersion) and physico-chemical dispersion (diffusion) are closely related. Diffusion occurs at the molecular level and dispersion at the pore level. Usually it is not possible to distinguish between these levels. Because of their similar nature, diffusion and dispersion are conveniently described together by the coefficient of hydrodynamic dispersion.

Molecular Diffusion

The process of molecular diffusion is of interest for at least two reasons. First, at low pore-water velocities transport of solutes is dominated by the diffusion process, and second, an analogy exists between molecular diffusion and mechanical dispersion. Because of this analogy, knowledge of the diffusion process is helpful in understanding dispersion. Let us first consider molecular diffusion in a (free) solution, next diffusion in porous media, and conclude with a discussion of mechanical dispersion.

The solute molecules in the solution possess random thermal motion which causes an exchange of molecules between adjacent volume elements. If isothermal and isobaric conditions exist, a net transfer of molecules of some species k occurs when the concentration of k in the adjacent volume elements differs. More particles of k move from elements of higher to elements of lower concentrations than vice versa. Such a net transfer under the influence of a concentration gradient is termed molecular diffusion. The process of molecular diffusion is described by Fick's first law. In the case of one-dimensional diffusion in a free liquid, it can be expressed as:

$$J_D = -D_o \frac{\partial C}{\partial x} \tag{3-1}$$

where J_D is the solute mass flux due to diffusion $[ML^{-2}T^{-1}]$ and D_o is the coefficient of molecular diffusion $[L^2T^{-1}]$.

Thermodynamically, it is the gradient in the chemical potential that is the driving force for the diffusion process. The chemical potential is defined as:

$$\mu_k = \left(\frac{\partial G}{\partial n_i}\right)_{\mathcal{T},\mathcal{P},n_{j\neq k}} \tag{3-2}$$

where μ_k is the chemical potential of species k $[J\ mol^{-1}]$, n_k is the number of moles of species k, G is the free enthalpy or Gibbs free energy $[J\ mol^{-1}]$, and $\mathcal{T}$ and $\mathcal{P}$ are temperature and pressure, respectively.

For mixtures with ideal behavior (i.e., non-interacting), such as certain gases, μ_k can be expressed in terms of its mole fraction:

$$\mu_k = \mu_k^o + \mathcal{R}\mathcal{T} \ln C_{Mk}^* \tag{3-3}$$

where μ_k^o is the chemical potential of species i in a chosen standard state and the mole fraction $C_{Mk}^* = C_{Mk}/C_M$, the ratio of the molar concentration of species k to the total molar concentration. Hence, for an ideal thermodynamic solution, the gradient of the chemical potential is proportional to the gradient of the natural logarithm of the concentration:

$$\left[\frac{\partial \mu_k}{\partial x}\right]_{ideal} = \mathcal{R}\mathcal{T} \frac{\partial \ln C_{Mk}^*}{\partial x} \tag{3-4}$$

However, most solutions do not exhibit ideal mixing behavior. In transport studies, the non-ideality of the solute needs to be addressed for diffusion dominated transport if, for example, the total solute concentration is "high" (sea water) or for the thermodynamic description of ion exchange. For non-ideal systems, Eq.(3-3) is generally rewritten as:

$$\mu_k = \mu_k^o + \mathcal{R}\mathcal{T} \ln a_k \tag{3-5}$$

where a_k is the chemical activity of component k, which is related to the concentration by the activity coefficient:

$$a_k = \gamma_k C_{Mk}^* \tag{3-6}$$

The value of the activity coefficient, γ_k, depends on the nature of the microscopic interactions. Activity coefficients for ions can be estimated with the Debye-Hückel equation for solutions with ionic strength less than 0.1 *M (e.g., 125)*. The 'Davies' extension of the Debye-Hückel equation can be used to approximate γ_k for systems containing mainly small ions at ionic strengths less than 0.5 *M*. For non-ideal solutions, the gradient of the chemical potential is:

$$\left[\frac{\partial \mu_k}{\partial x}\right]_{\text{non-ideal}} = \mathcal{R}\mathcal{T}\,\frac{\partial \ln a_k}{\partial x} \qquad (3\text{-}7)$$

The diffusion flux for ideal solutions is given by Fick's first law for a constant total molar concentration C_M:

$$N_k = -C_M D_o \frac{dC^*_{Mk}}{dx} \qquad (3\text{-}8)$$

where N_k is the molar flux density of species k due to diffusion $[ML^{-2}T^{-1}]$. The diffusion flux for non-ideal solutions is obtained by inserting the ratio of the non-ideal to the ideal chemical potential gradients in Eq.(3-8):

$$N_k = -C_M D_o \frac{\partial \ln a_k}{\partial \ln C^*_{Mk}} \frac{dC^*_{Mk}}{dx} \qquad (3\text{-}9)$$

The contribution of molecular diffusion to the total molar flux can be shown by substituting Eq.(3-9) into the continuity equation, Eq.(2-1). The result is:

$$\frac{\partial C_{Mk}}{\partial t} = \frac{\partial}{\partial x}\left[C_M D_o \frac{\partial \ln a_k}{\partial \ln C^*_{Mk}} \frac{dC^*_{Mk}}{dx}\right] - \frac{\partial J_V C_{Mk}}{\partial x} \qquad (3\text{-}10)$$

Assuming an ideal system with a liquid velocity of zero and D_o independent of position and concentration, the well known diffusion equation, Fick's second law, is obtained:

$$\frac{\partial C}{\partial t} = D_o \frac{\partial^2 C}{\partial x^2} \qquad (3\text{-}11)$$

where the subscript notation for C_{Mk} has been dropped.

It can be shown by differentiation that *(45)*:

$$C(x,t) = \frac{A}{\sqrt{t}} \exp\left[-\frac{x^2}{4D_o t}\right] \tag{3-12}$$

is a solution of Eq.(3-11), where A is an arbitrary constant. The total amount of substance, m_0, diffusing in an infinitely long cylinder with unit cross section, is given by:

$$m_0 = \int_{-\infty}^{\infty} C\,dx \tag{3-13}$$

With an initial condition $C(x,0) = m_0\delta(x)$, $\delta(x)$ being the Dirac delta function (i.e. a spike of solute in an otherwise solute free medium), the concentration distribution becomes *(60)*:

$$C(x,t) = \frac{m_0}{\sqrt{4\pi D_o t}} \exp\left[-\frac{x^2}{4D_o t}\right] \tag{3-14}$$

Substituting $\sigma = \sqrt{2D_o t}$, yields a Gaussian or normal distribution:

$$C(x,t) = \frac{m_0}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] \tag{3-15}$$

where σ is the standard deviation of the solute concentration distribution.

The process of molecular diffusion in porous media is similar to that in a free solution, except that we must now define the mean flow path for diffusion in terms of the structure of the medium. Let us assume that diffusion in other phases than the liquid phase can be ignored. If necessary, the additional contribution to molecular diffusion from exchangeable ions can be accounted for *(126)*. The coefficient of molecular diffusion in soils can be expressed as *(24)*:

$$D_e = D_o/\lambda \tag{3-16}$$

where λ is the tortuosity factor. In simple terms, tortuosity can be viewed as the ratio of the "true" (i.e., circuitous) and straight line flow path distances between two points in a porous medium. Theoretically, its value should only depend on the geometry of the medium. Tortuosity can also be characterized with the so called formation factor, which is frequently used in petroleum engineering. This factor is the ratio of the electrical conductivity of the pure liquid phase to that of the porous medium *(cf. 46)*. It depends on the volume fraction of liquid and the tortuosity of the medium:

$$D_e/D_o = 1/(\Phi\theta) \tag{3-17}$$

where D_e is considered an effective coefficient of molecular diffusion $[L^2T^{-1}]$ and Φ is the formation factor. It should be noted that the validity and usefulness of this concept of tortuosity has been questioned *(165)*.

In media with a very low hydraulic conductivity, diffusion is the main mechanism of solute transport. Therefore, the determination of diffusion coefficients for low-permeability media has recently received a considerable amount of interest *(e.g., 173)*. For a concentration profile following a Gaussian distribution, i.e., Fickian diffusion, the coefficient of molecular diffusion of a stagnant liquid in a porous medium can be determined from:

$$\frac{d\sigma^2}{dt} = 2D_e \tag{3-18}$$

where D_e has been substituted for D_o. This relationship is frequently used to obtain the diffusion coefficient from the standard deviation of the concentration distribution as a function of position. In porous media, spreading is caused by various mechanisms. Integration of Eq.(3-18) shows that the variance increases linearly with time for constant diffusion coefficient. Thus, Eq.(3-17) can be used to evaluate whether these mechanisms exhibit Fickian behavior.

An approach which is not restricted to profiles following a Gaussian distribution is the method of moments. The moments of a concentration distribution, resulting from a pulse type of solute input, can be used to determine the mean and variance from the observed or calculated distribution *(9, 10)*. No assumption about the distribution of the solute concentration needs to be made in order to determine these moments. The p-th moment of a concentration distribution with respect to x, m_p, is defined as:

$$m_p = \int_{-\infty}^{\infty} x^p \, C(x,t) \, dx \tag{3-19}$$

This operator m_p can be applied to each term of the advection-dispersion equation. Aris *(10)* showed how these moments can be determined without evaluating the integrals, which is convenient if the distribution of C(x,t) cannot be described by a mathematical relationship. Some properties which can be determined with these moments are the mean, μ or μ_x, and the variance, σ^2 or σ_x^2, of the concentration distribution, where

$$\mu = m_1/m_0 \tag{3-20}$$

$$\sigma^2 = (m_2/m_0) - \mu^2 \tag{3-21}$$

Aris' moment method is also an important tool in obtaining solutions for the diffusion/dispersion equation in stratified media *(80, 81, 115)*.

Dispersion

The description of dispersion as a diffusion type process has been shown plausible in the classical paper by Taylor *(189)*. Taylor's analysis, concerning flow in a circular tube, is often discussed in the literature *(e.g., 60, 61, 73, 121)*. Because dispersion in a free solution provides a qualitative explanation of dispersion in a porous medium, a brief treatment of Taylor's paper will be presented.

Taylor *(189)* considered laminar flow in a circular tube with radius a, having the following parabolic velocity profile:

$$u(r) = u_o \left[1 - \frac{r^2}{a^2}\right] \tag{3-22}$$

where u_o is the maximum velocity at the axis [LT^{-1}] and r is the radial distance from the axis [L]. It can be seen that the mean velocity over a cross section of the tube, u_m, is equal to $u_o/2$.

First, transport of a solute by advection only will be considered. When a solute is introduced into the tube, the concentration profile develops similarly to the velocity profile, since no transport in the radial direction occurs. Taylor *(189)* discussed three cases for which the initial conditions and the mean concentrations at time t are shown in figure 2. The mean concentration over a cross section of the tube is defined as

$$C_m = \frac{2}{a^2} \int_0^a Cr \, dr \tag{3-23}$$

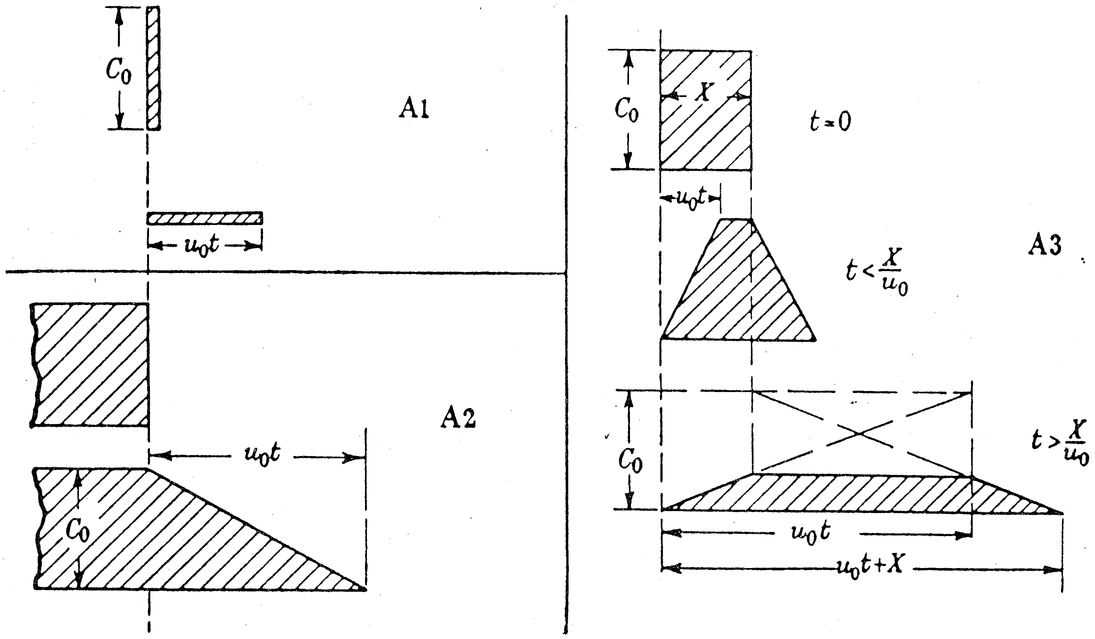


FIG. 2. Distribution of mean concentration in three cases in absence of molecular diffusion, after Taylor *(189)*.

In the first case, A1, the solute is originally only present in a short segment of the tube, with width *X* and concentration C_o. The solute will be distorted into a parabola with its shape depending on u(r). The mean concentration over a cross-section is now given by:

$$\begin{aligned} C_m &= C_o X/(u_o t) \qquad && 0<x<u_o t \qquad t>0 \\ C_m &= 0 && x>u_o t \qquad t>0 \end{aligned} \tag{3-24}$$

In the second case, A2, a solute with concentration C_o enters the tube. This case can be solved by assuming that the constant initial concentration for x<0 consists of a number of thin sections as discussed before, leading to the following mean concentration:

$$C_m = C_o \qquad x<0$$
$$C_m = C_o(1-x/(u_o t)) \qquad 0<x<u_o t \qquad t>0 \tag{3-25}$$
$$C_m = 0 \qquad x>u_o t$$

The third case, A3, deals with a solute which is initially confined to a greater distance *X* than for the first case *(189)*.

In all three cases, the concentration profiles are determined merely by advection, i.e., by the shape of the velocity profile. However, at low velocities the concentration is determined by molecular diffusion as well. Subsequently, the second step is to include molecular diffusion in the transport equation.

Taylor assumed that diffusion was significant for radial transport and negligible for longitudinal transport. Therefore, the following respective restrictions were imposed:

$$\sqrt{2D_o\Delta t} \geq 2a \qquad \text{or} \qquad \Delta t \geq \frac{2a^2}{D_o} \tag{3-26-a}$$

$$\sqrt{2D_o\Delta t} \leq L \qquad \text{or} \qquad \Delta t \leq \frac{L^2}{2D_o} \tag{3-26-b}$$

where Δt is the time required for a particle to travel through a tube with length L.

For a circular tube, solute transport via diffusion and advection is given by:

$$\frac{\partial C}{\partial t} = D_o\left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x^2}\right] - u_o\left[1 - \frac{r^2}{a^2}\right]\frac{\partial C}{\partial x} \tag{3-27}$$

where D_o is assumed to be independent of concentration. To derive an expression for the dispersion coefficient, as a result of the combined action of diffusion and advection, we follow the treatment by Fischer et al. *(60)*. Deviations from the mean velocity and concentration were described by:

$$u' = u(r) - u_m \tag{3-28-a}$$

$$C' = C(r) - C_m \tag{3-28-b}$$

where u' and C' are deviations from the cross-sectional means u_m and C_m, respectively. Substitution of Eq.(3-28) in (3-27) results in:

$$\frac{\partial}{\partial t}(C_m+C') = D_o\left[\frac{\partial^2}{\partial r^2}(C_m+C') + \frac{1}{r}\frac{\partial}{\partial r}(C_m+C') + \frac{\partial^2}{\partial x^2}(C_m+C')\right] + \\ - (u_m+u')\frac{\partial(C_m+C')}{\partial x} \tag{3-29}$$

This equation can be simplified. First, the contribution of molecular diffusion to transport in the longitudinal direction can be assumed to be negligible. Second, note that $\frac{\partial C_m}{\partial r} = 0$. Furthermore, it is convenient to apply the following transformation of coordinates:

$$\begin{aligned} \xi &= x - u_m t \\ \tau &= t \\ Z &= r/a \end{aligned} \tag{3-30}$$

Eq.(3-29) can now be rewritten as:

$$\frac{\partial C_m}{\partial \tau} + \frac{\partial C'}{\partial \tau} = \frac{D_o}{a^2}\left[\frac{\partial^2 C'}{\partial Z^2} + \frac{1}{Z}\frac{\partial C'}{\partial Z}\right] - u'\left(\frac{\partial C_m}{\partial \xi} + \frac{\partial C'}{\partial \xi}\right) \tag{3-31}$$

If we apply the operator $\frac{1}{A}\int_A [\quad]\, dA$, i.e., the mean over a cross section A, to Eq.(3-31) we obtain:

$$\frac{\partial C_m}{\partial \tau} + \overline{u'\frac{\partial C'}{\partial \xi}} = 0 \tag{3-32}$$

where the cross-sectional mean is denoted with an overbar. Subtraction of Eq.(3-32) from (3-31) results in:

$$\frac{\partial C'}{\partial \tau} = \frac{D_o}{a^2}\left[\frac{\partial^2 C'}{\partial Z^2} + \frac{1}{Z}\frac{\partial C'}{\partial Z}\right] - u'\left(\frac{\partial \bar{C}}{\partial \xi} + \frac{\partial C'}{\partial \xi}\right) + \overline{u'\frac{\partial C'}{\partial \xi}} \tag{3-33}$$

It is reasonable to assume that $\overline{u'\frac{\partial C'}{\partial \xi}} \approx u'\,\frac{\partial C'}{\partial \xi}$, hence Eq.(3-33) can be rewritten as:

$$\frac{\partial C'}{\partial \tau} = \frac{D_o}{a^2}\left[\frac{\partial^2 C'}{\partial Z^2} + \frac{1}{Z}\frac{\partial C'}{\partial Z}\right] - u'\,\frac{\partial \bar{C}}{\partial \xi} \tag{3-34}$$

Because $\overline{u'}=0$, the net addition of solute is zero for the system, which moves at velocity u_m. After sufficient time has elapsed, a steady concentration profile will have developed: the advective and the dispersive flux balance each other.

We now want to solve the steady concentration profile (i.e., $\frac{\partial C'}{\partial \tau} = 0$. Using Eq.(3-22) and $u_m=u_o/2$, we can rewrite Eq.(3-34) as:

$$\frac{\partial^2 C'}{\partial Z^2} + \frac{1}{Z}\frac{\partial C'}{\partial Z} = \frac{a^2 u_o}{D_o}\frac{\partial \bar{C}}{\partial \xi}\left[\frac{1}{2} - Z^2\right] \tag{3-35}$$

After multiplication with Z, integration with respect to Z yields:

$$Z\,\frac{\partial C'}{\partial Z} = \frac{a^2 u_o}{D_o}\frac{\partial \bar{C}}{\partial \xi}\left[\frac{Z^2}{4} - \frac{Z^4}{4}\right] + \alpha_1 \tag{3-36}$$

where α_1 is an integration constant. Division by Z and a second integration result in:

$$C' = \frac{a^2 u_o}{D_o}\frac{\partial \bar{C}}{\partial \xi}\left[\frac{Z^2}{8} - \frac{Z^4}{16}\right] + \alpha_1 \ln Z + \alpha_2 \tag{3-37}$$

where α_2 is a second integration constant. Because no solute transfer occurs across the wall of the tube, we have $\frac{\partial C'}{\partial Z}=0$ at Z=1 and hence $\alpha_1=0$. Note that $\alpha_2=C'(0)$.

The dispersive flux, i.e., the mass transport relative to the moving coordinate axis, is given by:

$$J_D = \frac{1}{A} \int_A u' C' \; dA \tag{3-38}$$

which can also be expressed according to Fick's law (Eq.(2-2)):

$$J_D = -D \frac{\partial C_m}{\partial \xi} \tag{3-39}$$

and hence:

$$D = - \left[A \frac{\partial C_m}{\partial \xi} \right]^{-1} \int_A u' C' \; dA \tag{3-40}$$

Substitution of Eq.(3-37), using $\alpha_2=0$, in Eq.(3-40) and subsequent integration results in:

$$D = \frac{a^2 u_o}{192 D_o} \tag{3-41}$$

which is generally referred to as the dispersion coefficient rather than diffusivity coefficient since it quantifies the spreading of a solute due to the combined effects of advection and (transverse) diffusion. Note that the dispersion coefficient D is inversely proportional to the coefficient of molecular diffusion, D_o. Using the continuity equation along with Eq.(3-32) and (3-33), the equation governing longitudinal dispersion becomes:

$$\frac{\partial C_m}{\partial \tau} = D \frac{\partial^2 C_m}{\partial \xi^2} \tag{3-42}$$

Solving this equation, for appropriate boundary and initial conditions, results in concentration distributions which are assumed to be caused bydispersion only. Aris *(9)* extended the theory, by using different velocity profiles and a concentration dependent D_o. In many situations in the field, it might take a long time to obtain steady state conditions and initially no Fickian diffusion will occur.

The Concept of Dispersion in Porous Media

Unfortunately, the dispersion process in a porous medium does not lend itself very well to a theoretical description like the one given by Taylor. Since the geometrical boundaries in a porous medium are generally not known, it is impossible to describe transport at the microscopic level in an exact mathematical way. In most cases it is assumed that Fick's law, originally used to describe diffusion in free liquids, can be applied. This law provides merely an operational definition of the diffusion/dispersion coefficient in soils *(126)*.

Most of the dispersion in a porous medium is caused by the presence of solids (meandering, changing pore sizes) with their concomitant microscopic velocity profiles in the liquid. To study dispersion phenomena at the microscopic level requires detailed knowledge of the pore structure. Since such knowledge is only available for simplified cases, porous media models or statistical mechanics must be employed. A variety of geometrical models has been suggested. Klinkenberg *(98)*, using a straight, non-interconnected, capillary pore model, showed that pore size distributions obtained via displacement studies, were quite different for different displacement methods. The model does not seem to be very satisfactory. Random capillary models, consisting of a network of randomly oriented and distributed pores, have been presented by de Josselin de Jong *(54)*, Saffman *(164)* and Bear and Bachmat *(17)*.

De Josselin de Jong *(54)* considered a 3-D medium which consisted of a network of interconnected straight equal channels of length L, oriented at random. The overall flow occurred in one direction. The movement of a solute particle in each channel depends on the deviation of the channel from the overall direction of flow. At the junction of various channels, the probability that a particle chooses a particular channel is proportional to the ratio of the discharge to that channel to the total discharge at the junction. De Josselin de Jong *(54)* then determined the probability of a particle arriving at a given point for a particular time after a large number of displacements. He came up with a normal distribution in three dimensions to formulate expressions for the longitudinal and transverse dispersion coefficient.

Saffman *(164)* used a very similar model, but he included molecular diffusion. The movement of the particle by advection was studied using the Lagrangian approach, i.e., the movement of the particle is described with respect to its initial position, whereas the movement by diffusion was described with Euler's method, i.e., the movement of all particles was observed from a fixed position.

It can be argued that only a completely statistical approach will predict the phenomenon of dispersion *(165)*. One can attempt to predict the path of a solute particle by using probability theory. This path is determined by physical processes, but we are unable to describe these processes at a microscopic level. The pathline for a solute particle is considered as a vectorsum of elementary displacements. The elementary displacement in a time interval Δt, for a certain position, depends on the statistical model, for instance a random walk model or a probability density function as a function of time and position. After many intervals Δt, the total displacement of that particle obeys a Gaussian distribution according to the Central Limit Theorem. This can be extended to a large number of particles at that particular position to predict a spatial distribution of the particles at a certain time (i.e., a concentration profile).

Scheidegger *(165)* derived the following probability that a specific molecule is at a certain position at time t:

$$\psi(x,t) = (4\pi Dt)^{-3/2} \exp\left[-\frac{\xi^2}{4Dt}\right] \tag{3-43}$$

where ψ is the probability and $\xi = x - \bar{x}$ is the position with respect to the time averaged position, $\bar{x}$, of the molecule. Scheidegger developed longitudinal and transverse dispersivity constants from statistical concepts, ignoring molecular diffusion. He obtained a linear relationship between pore-water velocity and longitudinal and transverse dispersion coefficients. This serves as a justification for the well known empirical expressions used for the longitudinal and transverse dispersion coefficients *(14)*, namely:

$$D_L = D_e + \alpha_L v^n \tag{3-44}$$

$$D_T = D_e + \alpha_T v^n \tag{3-45}$$

where α_L and α_T are the longitudinal and transverse dispersivity, respectively, [L], D_L and D_T are the coefficient of longitudinal and transverse dispersion, respectively, $[L^2T^{-1}]$, v is the pore-water velocity $[LT^{-1}]$ and n is an empirical coefficient, frequently taken equal to 1. D_e, the part of dispersion which is independent of the velocity, is equal to the effective coefficient of molecular diffusion, viz. D_o/λ [L^2T^{-1}].

The significance of the space-time scale at which dispersion occurs has been discussed theoretically by Bhattacharya and Gupta *(19)*, who distinguished three scales: a kinetic or molecular, a microscopic, and a macroscopic or Darcy scale. Transitions from one scale to the next higher scale can be made through application of the Central Limit Theorem. Transformation to field scales could be attempted as well to study the so called macrodispersivity.

Plumb and Whitaker *(145)* used two length scales to study the effect of the heterogeneity of the porous medium on solute transport. First, they used local volume averages, with the ADE developed by combining "point" equations within a homogeneous layer and interfacial boundary conditions. Second they used large-scale averaging, i.e., a length scale was used that is large compared to the scale of the heterogeneity. The resulting ADE for the latter approach contained additional terms involving the time derivative. The theory was applied to predict dispersion in stratified and 2-D spatially periodic media *(146)*. The dispersion coefficient determined with the large-scale model for such media compared favorably with experimental observations. The value of the dispersion coefficients was several orders of magnitude larger than the value predicted for a medium which was assumed to be homogeneous.

Finally, the concept of multiple length scales should be mentioned. The resulting transport problem can then be solved with the use of fractals *(213, 215)*.

Physical Non-equilibrium and Dispersion

The existence of physical non-equilibrium, which enhances spreading, is an important factor when describing solute transport. This is particularly true for structured soils, which will be discussed in Chapter V. In order to retain the 'simple' form of transport equations such as Eq.(2-5), attempts have been made to include the effects of physical non-equilibrium in the effective dispersion coefficient. This can be done by lumping together the dispersion processes already discussed, namely mechanical dispersion and molecular diffusion, and non-equilibrium spreading *(cf. 53, 135)*. Following Bolt *(24)*, a general approach will be presented here, which describes molecular diffusion, mechanical dispersion and apparent (physical) non-equilibrium in terms of their respective diffusion lengths. This practice is quite common in the theory of chromatography *(66)*. Summation of these lengths allows the use of one apparent coefficient of dispersion.

According to Bolt *(24)*, the diffusion length, L_{diff} [L], is given by:

$$L_{diff} = \theta D_e / J_V \tag{3-46}$$

This length can be associated with the distance in a column to which a solute front has advanced such that the concentration gradient at the column entrance is zero. At larger times, the effect of spreading due to diffusion can usually be ignored, in particular for small values of L_{diff}.

Next, a similar expression for the dispersion length needs to be found. It is assumed that the flow is laminar, i.e., streamlines coincide with pathlines. For a typical porous medium, where the pore space consists of an inter-capillary and an intra-capillary part, the coefficient of mechanical dispersion should contain terms accounting for transverse diffusion into the intra-capillary pore space, the microscopic velocity distribution (i.e., advective dispersion), and mixing in the inter-capillary pore space. The latter process was referred to by Bear *(15)* as intensive mixing. It takes place at positions where fluid streams from different channels are interconnected. This provides an opportunity to mix via diffusion or by the (partial) combination of fluid streams. Mixing counteracts advective dispersion, which occurs because of differences in the mean pore velocity for the various tubes. Differences in solute concentration due to physical non-equilibrium, which in effect leads to longitudinal dispersion, are reduced by transverse diffusion. Because mixing and transverse diffusion limit dispersion, they will be examined in more detail.

Assuming that liquid flow in a porous medium occurs in semi-infinite, circular tubes with non-limited advective dispersion, i.e., the velocity profile causes all dispersion, Bolt presented:

$$D_{dis} = (\sigma')^2 \langle v \rangle^2 \, \Delta t \qquad (3\text{-}47)$$

where Δt is the mean residence time of a solute particle in a tube. The relative spread of velocities, $(\sigma')^2$, is given by $\langle \Delta v \rangle^2 / \langle v \rangle^2$, which is a constant for a particular medium with average velocity $\langle v \rangle$ and variations about that velocity of $\Delta v = |v - \langle v \rangle|$. This part of the dispersion in porous media was first developed by Taylor *(189)*. By reversing the direction of flow, this type of dispersion can be annihilated *(cf. 167)*.

Obviously, dispersion in a porous medium is much more complex because pore channels are interconnected and not straight. This situation can be modeled by using so called mixing compartments, figure 3, where complete mixing occurs at points x=0, x=L, x=2L, etc. The effective dispersion coefficient has a value of zero at x=0 and reaches a maximum at x=L. With the mean residence time of a solute particle in a tube between two mixing points being $\Delta t = L/\langle v \rangle$, an average dispersion coefficient can be used:

$$D_{dis} = (\sigma')^2 \langle v \rangle L/2 \tag{3-48}$$

Figure 3 illustrates the effect of mixing, at regular intervals L, on the coefficient of mechanical dispersion according to Eq.(3-48). As can be seen, 'unlimited' spreading occurs only over a finite distance, L, between mixing points. An effective, average dispersion coefficient for such a distance is used for computational purposes.

If transport in separate channels is the main mechanism behind dispersion, this dispersion will be limited by mixing at intervals with length L. Then the mechanical dispersion coefficient is presumably of the form:

$$D_{dis} = L_{dis} \langle v \rangle \tag{3-49}$$

where L_{dis} can be approximated from Eq.(3-48), i.e., from $(\sigma')^2 L/2$. Bolt *(24)* suggested that a value equal to the grain diameter be used.

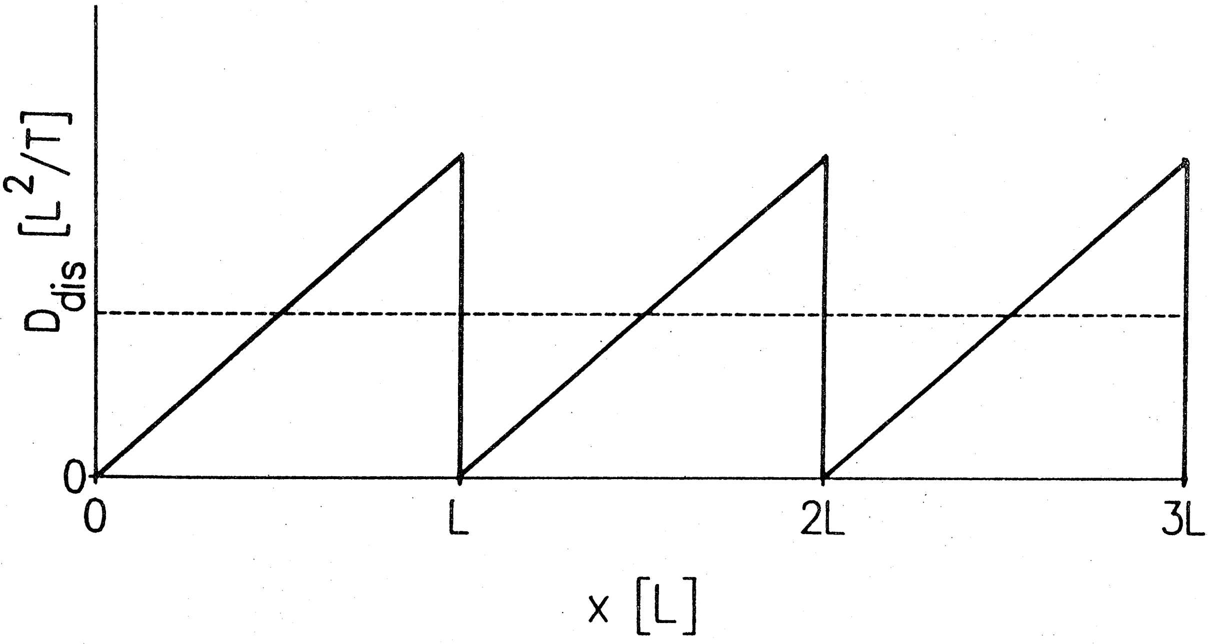


FIG. 3. The value for D_{dis} determined by mixing and the averaged value for D_{dis} according to Eq.(3-48) (dashed line).

Usually, however, L_{dis} has to be quantified by experimental procedures. Theoretically, if the flow were to be reversed along the same steamlines as before the reversal, only the contribution of molecular diffusion to mixing would not vanish. In reality, a larger part of this mixing is not reversible.

In addition to mixing, advective spreading is limited by transverse diffusion. This mechanism becomes important if flow occurs in a single tube or if no mixing occurs because of the absence of inter-capillary pore space, as inside the aggregate. It is still assumed that the porous medium consists of simple tubes for which Taylor's *(189)* results can be used. An expression for D_{dis} was obtained by combining Eq.(3-47) and an appropriate expression for the diffusion time needed to traverse the width R over which the velocity profile is spread. Bolt proposed:

$$D_{dis} = (\sigma')^2 \langle v \rangle^2 gR^2 / D_e \tag{3-50}$$

where g is a geometry factor. This expression is similar to Taylor's result for a circular tube (Eq.(3-41)). The dispersion length becomes:

$$L_{dis} = (\sigma')^2 \langle v \rangle gR^2 / D_e \tag{3-51}$$

In porous media, mixing and transverse diffusion (i.e., in a single tube) occur simultaneously. The question then arises as to which of the two prevails. This can be estimated by evaluating Eq.(3-48) and (3-50). Since both processes counteract spreading, it can be assumed that the process which results in the smallest value for D_{dis} dominates.

Physical non-equilibrium occurs when flow in the intra-capillary pore space is negligible. The stagnant phase of the liquid in the intra-capillary pores does not participate in any (turbulent) mixing. Rather, mixing between mobile and immobile phases of the liquid occurs via transverse diffusion only. A description of dispersion in the stagnant phase can be obtained by adapting Eq.(3-50) to account for the limited accessibility of the liquid in the immobile phase. This was done using a functional relationship between mobile and stagnant liquid concentrations. This relationship can be presented, assuming a linear increase of the surface concentration of the aggregate with time, $C_{mo}=kt$, as *(45, 135)*:

$$C_{mo}-\langle C_{im}\rangle = kg(R_a)^2/D_e \tag{3-52}$$

where C_{mo} is the concentration in the mobile phase [ML^{-3}], $\langle C_{im}\rangle$ is the average concentration in the immobile or stagnant phase [ML^{-3}], k is a rate coefficient [$ML^{-3}T^{-1}$] and R_a is the radius of the aggregate [L]. The geometry factor of the aggregate, g, varies between 1/8 for infinitely extended cylinders to 1/15 for a sphere. By using the solute flux over the entire liquid phase, Passioura (1971) obtained the following dispersion coefficient, as caused by the stagnant phase effect:

$$D_{dis} = g\theta_{im}R_a^2\langle v\rangle^2/\theta D_e \tag{3-53}$$

with accompanying dispersion length:

$$L_r = g\theta_{im}R_a^2\langle v\rangle/\theta D_e \tag{3-54}$$

The effects of longitudinal diffusion, advective dispersion (microscopic variation in the velocity profile in combination with mixing and/or transverse diffusion) and the presence of a stagnant phase can presumably be added since they act more or less independently. It should be noted, however, that this last assumption deserves more investigation *(123)*. In the case of autonomous effects, the diffusion/dispersion flux can be written as:

$$J_D = -J_V L_D \frac{\partial C}{\partial x} \tag{3-55}$$

where L_D is given by:

$$L_D = L_{diff}+L_{dis}+L_r = (\theta D_e/J_V) + L_{dis} + (\frac{\theta_{im}}{\theta} R_a^2 J_v)/15\theta D_e \tag{3-56}$$

It appears that, in many instances, mixing is the major counteracting factor of advective dispersion. L_{dis} can therefore be assumed to be constant ($\approx 2R_a$). L_{dif} is only important at small fluxes, while L_r (dispersion length due to stagnant phase) becomes significant for larger values of J_V and increasing aggregate size R_a. An increasing aggregate size also causes the breakthrough curve to lose its sigmoidal shape *(22)*. Because of the relative importance of the larger (inter-capillary) pores for transport, the tracer will appear sooner in the effluent with larger aggregate sizes.

It should be noted that L_{diff} is inversely proportional to J_V (Eq.(3-46)), and assuming that mixing prevails (Eq.(3-48)), L_{dis} is approximately equal to the aggregate diameter, i.e., independent of the flow, and L_r is proportional to J_V (Eq.(3-54)). Despite the fact that a number of simplifications and assumptions were made, the correspondence between the experimental and theoretical behavior of L_D was fairly good, figure 9.8 *(24)*. In terms of the Pe-number, defined as $Pe=vL/D_e$ ($L=2R_a$), diffusion is the dominant term for $Pe<1$ and the stagnant phase effect becomes dominant for $Pe>120$.

Experimental Determination of Dispersion Coefficients

To describe the dispersion process and to solve the ADE, a numerical value for the longitudinal, and sometimes for the transverse, dispersion coefficient needs to be determined. For one-dimensional flow in a homogeneous medium with two-dimensional transport, the ADE can be written as:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} + D_T \frac{\partial^2 C}{\partial y^2} \qquad (3\text{-}57)$$

D_L and D_T can be obtained by relating experimental results of the concentration profile with explicit expressions for C. For this purpose, displacement experiments are carried out, either in the laboratory or in the field. For the determination of D_L, these experiments often involve a laboratory column filled with a packed soil. The solute concentration of the resident solution in the column is known, and a feed solution, with generally the same concentration of a different solute, is leached through the column. In most cases the effluent concentration is determined as a function of time, although the concentration in the soil solution, at different locations along the direction of flow, can be determined as well. A variety of methods, used to obtain dispersion coefficients from these experimental data, will be presented here. A review of some of these methods can also be found in van Genuchten and Wierenga *(203)*.

Because macroscopic variations in water content and pore water velocity result in additional spreading, the column should be packed in such a way that the soil is homogeneous with respect to the advection term. Although this situation will never be reached totally, a constant 'effective' pore water velocity can be used for many practical purposes. Deviations from this velocity during the experiment obviously lead to incorrect results.

Mixing due to viscosity and density differences between resident and feed solution are not to be included in the coefficient of hydrodynamic dispersion. Therefore, many studies involve the so called tracer case *(e.g., 20)*. The low concentration of a non-reactive solute (i.e., a tracer) does not affect the density and the viscosity of the solvent. Displacing and displaced fluids have the same density and viscosity. Differences in viscosity and density lead to instabilities (fingering). Biggar and Nielsen *(21)* showed that unstable flow dominates for a density difference of 3.4×10^{-3} g cm^{-3} and a difference in viscosity of 0.003 cP, obscuring the effect of molecular diffusion. Rose and Passioura *(161)* demonstrated that, during horizontal displacement experiments, small differences in density of the displaced and displacing fluids lead to quite different dispersion coefficients. The displacing liquids consisted of water, 0.1, 0.2, and 0.4 *M* NaCl solutions with densities of 0.99707, 1.00116, 1.00523, and 1.0133 g cm^{-3}, respectively. The amount of gravity segregation could be characterized with a gravity segregation factor β:

$$\beta = gkh\Delta\rho/(\bar{\eta}vL) \tag{3-58}$$

where g is the acceleration due to gravity $[LT^{-2}]$, k is the permeability $[L^2]$, h the height of the porous medium in the transverse direction of flow, [L], $\Delta\rho$ is the difference in liquid density $[ML^{-3}]$, $\bar{\eta}$ is the mean of the viscosities of the resident and feed solution $[ML^{-1}T^{-1}]$, v is the mean pore-water velocity $[LT^{-1}]$ and L is the length of the porous medium in the direction of flow, [L]. Since k decreases rapidly during desaturation, gravity segregation is not much of a factor during unsaturated flow. An increase in D by a factor 2 was reported by these authors for their experiments, with $\Delta\rho=8.2\times10^{-4}$ g

cm^{-3} compared to $\Delta\rho=0$. Gravity segregation might also be important when contaminated salt water intrudes horizontally into a fresh water aquifer. Because of the stratified flow and the subsequent mixing by diffusion at the interface, contamination will extend further into the fresh water than expected on the basis of the conventional hydrodynamic dispersion process. Further discussions on viscosity and density effects can be found in Krupp and Elrick *(105)*, Bachmat *(12)*, and Scheidegger *(165)*. Due to the temperature dependence of these parameters, displacement experiments need to be carried out at constant temperature.

One should also be aware of apparatus-induced dispersion *(87)*, which is especially important for short-column experiments and for unsaturated media. These authors studied a conceptual porous medium consisting of two different layers: the soil and the apparatus. Apparatus-induced dispersion was assessed by carrying out displacement experiments in the absence of the porous medium. The dispersion coefficient of the porous medium was obtained by solving the advection-dispersion equation for a two-layer system. The value of this dispersion coefficient was as much as 40% less than obtained with the one layer equation, where mixing was assumed to occur in the medium only. The so called dead-volume, inside the apparatus but outside the porous medium, should therefore always be kept to a minimum.

Rather than relying on effluent concentrations, in situ determinations of the solute concentration can also be made. Harleman and Rumer *(82)* measured electrical resistance with a conductivity probe to determine NaCl-concentrations. Gupta et al. *(76)* used an Ag-AgCl electrode to measure Cl concentrations in an unsaturated glass bead medium. Electrical potential, in contrast with electrical resistance, is not greatly affected by the water content of the medium. Kirda et al. *(95)* used labeled Cl in the feed solution, of which the concentration was measured in situ with a Geiger-Muller tube. Grismer et al. *(70)* used a dual-source gamma-attenuation system to determine salt and water content. In an error analysis, thse authors showed that the accuracy of solute concentrations determined at low water contents was limited. Grismer *(69)* used the same technique to determine $SrCl_2$ and NaI concentrations in a displacement study during horizontal transient unsaturated flow. Initially, no salt was present and the feed solutions had a molality of 0.205 and 0.1 m, respectively. No mention was made of density or viscosity effects.

Following Fried and Combarnous *(61)*, some methods to determine D_L and D_T will be discussed. The solute (tracer) concentration can be determined as a function of position at a certain time or for various times at a certain position, as with breakthrough experiments. For both cases, analytical solutions exist. For a uniform medium and steady flow (v and θ are constant), the 1-D ADE was given as:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \qquad (3\text{-}59)$$

subject to the following initial and boundary conditions

$$\begin{array}{lll} C(x,t) = C_o & x=0 & t>0 \\ C(x,t) = 0 & x\to\infty & t>0 \\ C(x,t) = 0 & x>0 & t=0 \end{array} \qquad (3\text{-}60)$$

Utilizing the definition of the complementary error function, the solution of Eq.(3-59) may be written as (i.e., an approximation of the solution by Lapidus and Amundson *(109)*):

$$C/C_o = \frac{1}{2} \operatorname{erfc} \left[\frac{x - vt}{\sqrt{4D_L t}} \right] \tag{3-61}$$

For a given time, the solution follows a normal distribution $1-N[(x-\mu)/\sigma]$ with mean displacement $\mu=vt$ and standard deviation $\sigma = \sqrt{2D_L t}$. N[ ] is the probability density function for a normal distribution with values N[-1]=0.16 and N[1]=0.84. The width of the transition zone, 2σ, can be determined by plotting C/Co versus x, with:

$$2\sigma = x_{0.16} - x_{0.84} = \sqrt{8D_L t} \tag{3-62}$$

where $x_{0.16}$ and $x_{0.84}$ denote positions for which C/C_o is equal to 0.16 and 0.84, respectively. The value of the longitudinal dispersion coefficient follows from:

$$D_L = (x_{0.84} - x_{0.16})^2 / 8t \tag{3-63}$$

If the concentration is observed at a certain position as a function of time, the following expression for D_L can be used:

$$D_L = \frac{1}{8} \left[\frac{x-vt_{0.16}}{\sqrt{t_{0.16}}} - \frac{x-vt_{0.84}}{\sqrt{t_{0.84}}} \right]^2 \tag{3-64}$$

After the discussion of the determination of the longitudinal dispersion coefficient, D_L, Fried and Combarnous *(61)* continue with the determination of the transverse dispersion coefficient, D_T. It should be noted that relatively little in-depth work has been done in the area of transverse dispersion, because of the increased experimental difficulties and the much smaller effect of transverse dispersion in comparison with longitudinal dispersion *(e.g., 82)*.

For the determination of D_T in a semi-infinite 2-D system consisting of a uniform soil, it is assumed that 1-D steady state flow conditions exist and that steady solute transport is established (C=C(x,y)), in which case the longitudinal dispersive flux is usually negligible. Under these circumstances the transport equation becomes:

$$v \frac{\partial C}{\partial x} = D_T \frac{\partial^2 C}{\partial y^2} \qquad (3\text{-}65)$$

where y is the distance in the direction transverse of the flow [L]. For the following boundary conditions:

$$\begin{aligned} &\frac{\partial C}{\partial y} = 0 && x>0 \,, \quad y \to \pm\infty \\ &C(0,y) = C_o && x=0 \,, \quad 0<y<\infty \qquad (3\text{-}66) \\ &C(0,y) = 0 && x=0 \,, \quad -\infty<y<0 \end{aligned}$$

the analytical solution is:

$$C/C_o = \frac{1}{2}\left[1 + \text{erf}\left(\frac{y}{((4xD_T)/v)^{1/2}}\right)\right] \qquad (3\text{-}67)$$

The transverse dispersion coefficient determined from this solution is:

$$D_T = \frac{v}{2x}\,\sigma^2 \qquad (3\text{-}68)$$

where the standard deviation at an arbitrary point $x=x_o$ is given by:

$$\sigma = \frac{1}{2}\left[\, y(x_o, C/C_o=0.84) - y(x_o, C/C_o=0.16)\right] \qquad (3\text{-}69)$$

Because relatively little work has been devoted to transverse dispersion, it is assumed in this review that we deal with longitudinal dispersion, i.e., $D=D_L$, unless stated otherwise.

Rose and Passioura *(160)*, making use of the solution of Brenner *(27)*, determined D by plotting $C_e=(C-C_i)/(C_o-C_i)$ versus ℓn T on probability paper. C_e is the dimensionless exit concentration and T is the number of pore volumes (T=vt/L). Almost straight lines for particular values of the Brenner number were obtained. The Brenner number is defined as:

$$B = vL/D \tag{3-70}$$

where L is the column length [L]. Because of this linear relationship, the following expression seems plausible:

$$\text{inverfc}\ (2C_e-1) = -\alpha\ \ell n\ T - \beta \tag{3-71}$$

where inverfc denotes the inverse of the complementary error function, and α and β are slope and intercept, respectively. For 16<B<640, the following empirical relationship was proposed by Rose and Passioura *(160)*:

$$\begin{aligned} \log B = {} & 0.1139\ (\log \alpha)^3 - 0.3504\ (\log \alpha)^2 + \\ & 2.3623\ \log \alpha + 0.4732 \end{aligned} \tag{3-72}$$

By plotting $-\ell n$ T versus inverfc $(2C_e-1)$ the slope α and the intercept β can be obtained. The Brenner number follows then from Eq.(3-72) and D can be calculated from Eq.(3-70). Van Genuchten and Wierenga *(204)* presented various improvements of this method, viz. an inversion formula for inverfc, a simplified expression of Eq.(3-72), and approximations for various boundary conditions.

A popular technique to obtain dispersion coefficients is via curve fitting. Parker and van Genuchten *(130)* provided a curve fitting program, using a non-linear, least-squares inversion method, to determine various transport parameters including dispersion coefficients. The curve fitting program can be used for experiments involving concentrations at a fixed location at different times or for a certain time at different locations; other parameters to be determined are retardation factors and degradation constants. The program can also deal with physical and chemical non-equilibrium transport models as discussed in the section on non-equilibrium conditions, and a stochastic model of transport under log-normally distributed flow conditions. An independent validation of the physical model cannot be achieved by curve fitting *(36, 149)*.

Amoozegar-Fard et al. *(6)* used the solution given by Eq.(3-61). By taking the inverse complementary error function and applying an error minimization technique, D and R were determined. Some other methods, such as the point calculation, finding the variance, and the slope method, are discussed in Levenspiel and Smith *(114)*.

Smiles et al. *(179)* used Matano's method to study the hydrodynamic dispersion during absorption of water by soil. This method uses the Boltzmann transformation to transform a partial differential equation into an ordinary differential equation *(cf. 35, 45)*. Because of the relatively low velocity, the small value of the Peclet number and the rapidly changing water content during infiltration, the dispersion coefficient is assumed to be only dependent on water content. By using the relations $D_s(\theta)=\theta D(\theta)$, the product of water content and the coefficient of hydrodynamic dispersion, and $J_V=v\theta$, the volumetric water flux, the one-dimensional transport equation (Eq.(2-4)), can be rewritten as:

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial x}\left[D_s(\theta) \frac{\partial C}{\partial x} \right] - \frac{\partial J_V C}{\partial x} \qquad (3\text{-}73)$$

with the following boundary and initial conditions:

$$\begin{array}{lll} C = C_i & x>0 & t=0 \\ C = C_o & x=0 & t\geq 0 \\ C = C_i & x\to\infty & t\geq 0 \end{array} \qquad (3\text{-}74)$$

where $D_s(\theta)$ is an alternative expression for the dispersion coefficient. It is assumed that the medium is semi-infinite; the initial and exit boundary conditions transform to the same condition.

For a homogeneous soil with horizontal, non-hysteretic flow we have:

$$J_V = -D_w(\theta) \frac{\partial \theta}{\partial x} \qquad (3\text{-}75)$$

therefore Eq.(2-132) was rewritten as:

$$\theta \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D_s(\theta) \frac{\partial C}{\partial x} \right] + D_w(\theta) \frac{\partial \theta}{\partial x} \frac{\partial C}{\partial x} \qquad (3\text{-}76)$$

where D_w is the soil water diffusivity $[L^2T^{-1}]$. Using the Boltzmann transformation ($\omega = x/\sqrt{t}$), Eq.(3-76) becomes

$$\frac{d}{d\omega}\left[D_s(\theta) \frac{dC}{d\omega} \right] + \frac{g}{2} \frac{dC}{d\omega} = 0 \qquad (3\text{-}77)$$

while the boundary and initial conditions, Eq.(3-73), become

$$\begin{array}{ll} C = C_i & \omega\to\infty \\ C = C_o & \omega=0 \end{array} \qquad (3\text{-}78)$$

The function g is defined as:

$$g = \theta\omega + 2D_w(\theta) \frac{d\theta}{d\omega} = \theta\omega - \int_{\theta_i}^{\theta} \omega \, d\theta \qquad (3\text{-}79)$$

The dispersion coefficient can then be obtained from

$$D_s(\theta) = -\frac{1}{2}\frac{d\omega}{dC}\int_{C_i}^{C} g\, dC \qquad (3\text{-}80)$$

in a way as described by Bruce and Klute *(35)* for D_w. $D_s(\theta)$ may be determined by carrying out experiments using segmented soil columns. For each segment, average values for θ, C, and g can be determined as a function of ω. Laryea et al. *(110)* determined dispersion coefficients for both cations and anions during horizontal infiltration. Elrick et al. *(59)* extended the above analysis to vertical flow. A power series solution similar to that of Philip *(139)* was used to express the solutions of flow and transport equations.

The dispersion process depends on viscosity, density, velocity, water content, molecular diffusion, and permeability. In order to assess the influence of velocity and particle size, experimental results are commonly analyzed by plotting D_L/D_o versus the Peclet number ($Pe=vd/D_o$) on a log-log scale graph. In this case, d is a characteristic pore or particle size dimension. Bear *(16)* distinguished the following dispersion regimes *(61)* based on values of the Peclet number:

- Molecular diffusion is dominant for $Pe<0.4$.
- Molecular diffusion and mechanical dispersion are of the same order for $0.4<Pe<5$. Both effects can be added up.
- Major mechanical dispersion with some molecular diffusion occurs in the range $5<Pe<1000$. These effects interfere and cannot be added up.

- Dominant mechanical dispersion for $1000<Pe<1.5\times10^5$ with negligible molecular diffusion.
- Mechanical dispersion for the flow regime being out of the domain of Darcy's law for $Pe>1.5\times10^5$.

Several authors have provided graphical relationships between velocity or the Peclet number and the dispersion coefficient *(e.g., 22, 24, 61, 138, 160)*.

Finally, the so-called numerical dispersion should be mentioned. When the transport equation is solved by numerical methods, using experimental values of the dispersion coefficient, the solute front exhibits additional spreading. Especially at high values of the Peclet number, 'smearing' of the numerical solution occurs around the front. This is an artifact due to the numerical procedure *(26)*. A number of approaches can be taken to reduce this phenomenon *(cf. 1, 29, 39, 195)*.

IV. ION EXCHANGE

Equilibrium transport of linearly exchanging solutes can be described in a straightforward way with Eq.(2-19). However, for transport of non-linearly exchanging solutes, the situation is somewhat more complicated.

First, the influence of exchange on the solute front without dispersion/diffusion is reviewed. Second, the effect of dispersion is included. Several approximate analytical techniques can be used to study transport under these conditions, which illustrate the effect of non-linear exchange. In a majority of the studies, however, the transport problem is solved numerically by using experimentally determined exchange isotherms. Some of these studies will be discussed.

Equilibrium Chromatography

Following Reiniger and Bolt *(156)* and Bolt *(24)*, the qualitative influence of the exchange isotherm on the concentration front will be studied for a relatively simple case. It is assumed that only two different cation species are present during miscible displacement under steady flow conditions. This provides a fairly representative picture for many soil-water systems. The adsorbed concentration q of a solute species depends on the liquid concentration of that species, C, and the total concentration of all solute species, C_T. It is convenient to express q in $mol_c\ m^{-3}$, i.e., moles of charge per volume of porous medium, and C in $\mathrm{mol_c\ m^{-3}}$, i.e., moles of charge per volume of solution. The total concentration is constant during ion exchange. When diffusion and dispersion are neglected, a step change in concentration occurs at the "concentration front" located around $J_V t/\theta$, the penetration depth. If C_T is assumed to be constant across this concentration front, q depends only on C. For a particular species Eq.(2-7) then becomes:

$$(q' + \theta)\,\frac{\partial C}{\partial t} = -\,J_V\,\frac{\partial C}{\partial x} \tag{4-1}$$

where q'(=dq/dC) is the differential capacity of the exchanger for the exchanging species, J_V is the Darcy flux which is assumed to be positive, and x is the (positive) distance from the inlet. In order to solve Eq.(4-1), and to justify neglecting the dispersive flux, $\partial C/\partial x$ needs to be finite. With the chain rule for partial derivatives, $\left(\frac{\partial C}{\partial t}\right)_x\left(\frac{\partial x}{\partial C}\right)_t\left(\frac{\partial t}{\partial x}\right)_C = -1$, Eq.(4-1) can be rewritten as

$$\left(\frac{\partial x}{\partial t}\right)_C = \frac{J_V}{q' + \theta} \tag{4-2}$$

If the condition that $\frac{\partial C}{\partial x}$ be finite is violated, i.e., if the concentration profile exhibits jumps, the conservation of mass (Eq.(4-1)) needs to be expressed in an alternative way:

$$(\Delta q + \theta\Delta C)\,dx = \Delta C\,dV \tag{4-3}$$

where V is the input volume per unit area of the column. The rate of propagation, given by Eq.(4-2), then needs to be rewritten as:

$$\left(\frac{dx}{dt}\right)_{\Delta C} = \frac{J_V}{\frac{\Delta q}{\Delta C} + \theta} \tag{4-4}$$

The position of a particular solute concentration (for $\frac{\partial C}{\partial x}$ finite) follows from integration of Eq.(4-2). For a soil with q and θ homogeneous with respect to position and $dV=J_V dt$, the position for a particular concentration is given by:

$$x_C = \int_0^t \frac{J_V}{q'+\theta}\, dt = \frac{V-V_o(C)}{q'+\theta} \qquad (4\text{-}5)$$

where the feed solution, with concentration C_o, enters a column having an initial concentration C_i; $V_o(C)$ is an inverse feed function, which is the volume of solution applied to the column at the moment that the concentration at x=0 reaches C (for step type displacement $V_o \equiv 0$). The average depth of the concentration fronts in the adsorbed and liquid phase is given by:

$$x_p = \int_{C_i}^{C_o} x_C\, (q'+\theta)\, dC \Big/ \int_{C_i}^{C_o} (q'+\theta)\, dC \qquad (4\text{-}6)$$

The rate of propagation of the solute in the liquid phase follows from Eq.(4-2). Equilibrium chromatography enables us to determine the propagation in the adsorbed phase as well by using the exchange isotherm.

To study the shape of the solute front, Eq.(4-5) is differentiated (V_o=0):

$$\left(\frac{\partial x}{\partial C}\right)_V = -\frac{Vq''}{(q'+\theta)^2} \qquad (4\text{-}7)$$

At this point, a distinction needs to be made among favorable, unfavorable, and linear exchange. If the incoming cation has a convex isotherm, $q''=d^2q/dC^2<0$, we deal with so-called favorable exchange, while the exchange is said to be unfavorable if $q''>0$ and linear if $q''=0$.

In case of favorable exchange there is a dilemma. According to Eq.(4-1), the slope of the solute front is negative ($\partial C/\partial x<0$), but using Eq.(4-7) we find that $\partial C/\partial x>0$. The latter implies that the solute travels faster at higher concentrations than at lower concentrations. This is physically not possible for a step front and, as already mentioned, the rate of propagation should then be determined based on Eq.(4-4). For cases other than a step change in the concentration of the eluent, a "self sharpening" effect will occur until a step front has been established.

For linear exchange ($q''=0$), we can see from Eq.(4-7) that $\partial x/\partial C=0$ for any applied volume. The initial profile will therefore not be altered during passage through the porous medium. If the initial profile contains jumps, Eq.(4-3) needs to be used, otherwise Eq.(4-1) suffices.

For unfavorable exchange we can conclude from Eq.(4-7) that for a particular value of C, the front flattens with increasing *V*. Unfavorable exchange induces solute spreading (i.e., decreases the concentration gradient).

The Combined Effect of Ion Exchange and Dispersion

Bolt *(24)* examined the combined effect of exchange and diffusion/dispersion using analytical techniques. Having expressed all (physical) dispersion effects in one dispersion length, L_D, he attempted to include exchange as well. The ADE in terms of the dispersion length is obtained with Eq.(2-7) and (3-55):

$$(q' + \theta)\,\frac{\partial C}{\partial t} + J_V \left[\frac{\partial C}{\partial x} - \frac{\partial}{\partial x}(L_D\,\frac{\partial C}{\partial x}) \right] = 0 \tag{4-8}$$

Although the 'effective' value of L_D varies through the soil column, Frissel et al. *(62)* showed that a column averaged value might be used. For a constant L_D, Eq.(4-8) might be written as Eq.(2-14). If, in addition, dq/dC=constant (linear exchange), the same analytical solutions as for Eq.(2-19) can be used.

In case of favorable exchange, the solute front in the adsorbed phase is generally located ahead of the solute front in the liquid phase. In terms of the effective retarded velocity, v^*, the "high" concentrations will travel at a velocity greater than v^* and the "low" concentrations will travel at a velocity less than v^*. In contrast, diffusion/dispersion causes just the opposite effect. Eventually, a steady front will develop with respect to the moving coordinate $x-v^*t$ and all concentrations will travel at a velocity equal to v^*. For a constant L_D, Eq.(4-8) can be rewritten to obtain a general expression for the propragation of the solute front:

$$(\frac{\partial x}{\partial t})_C = \frac{J_V}{q' + \theta} \left[1 - L_D\,\frac{\partial(\partial C/\partial x)}{\partial C} \right] \tag{4-9}$$

Once steady state has been established, we obtain:

$$v^* = (\frac{\partial x}{\partial t})_C = \frac{J_V}{\frac{\Delta q}{\Delta C} + \theta} \tag{4-10}$$

Based on these two expressions, Bolt *(24)* presented a method to analytically determine adsorbed and liquid concentrations.

In case of unfavorable exchange, no steady front will develop with respect to the moving coordinate, because dispersion/diffusion and exchange both cause the "low" concentrations to travel faster than the "high" concentrations. The ADE must now be solved numerically to get an accurate picture of the solute front in the adsorbed and liquid phase *(Cf. 106, 107)*. For estimation purposes, one can add the two effects by first solving the front position as determined by Eq.(4-5) (exchange only) and then adding the effect of diffusion/dispersion. The latter effect causes the solute front to spread around $x_p=v^*t$. With Eq.(2-38), we can estimate this spreading according to:

$$x-x_p = 2\sqrt{D^*t}\ \mathrm{inverfc}(2\bar{C}) \qquad (4\text{-}11)$$

where $\bar{C}$ is the dimensionless concentration defined in Eq.(2-38). This term can be treated as a perturbation term to be added to the front position according to Eq.(4-3). In this way, a conservative estimate was obtained for the maximum amount of spreading.

Finally, the occurrence of non-equilibrium during ion exchange should be mentioned. In aggregated soils, the deviation from local equilibrium is most likely to be caused by physical non-equilibrium, i.e. the limited accessibility of exchange or adsorption sites. Bolt *(24)* assumed that all adsorption takes place in the stagnant region of the liquid. Examples of adsorption in both mobile and stagnant region were treated by van Genuchten and Wierenga *(202)*, Tang et al. *(186)* and Selim et al. *(170)*. Transport from the mobile to the stagnant region occurs via a diffusion process (Eq.(2-44)), which was described by Bolt *(24)* with:

$$\frac{\partial(q_{im}+\theta_{im}C_{im})}{\partial t} = k_a\theta_{mo}(C_{mo}-C_{im}) \qquad (4\text{-}12)$$

where q_{im} is the concentration in the adsorbed phase (immobile sites only), k_a is a rate constant for diffusion inside the aggregate, and instantaneous chemical equilibrium is assumed inside the aggregate. A distribution ratio between mobile and immobile phase, defined as:

$$K_D^{mi} = \left(\frac{\Delta q}{\Delta C} + \theta_{im}\right)/\ \theta_{mo} \qquad (4\text{-}13)$$

can be used to rewrite Eq.(4-12) as

$$\frac{\partial C_{im}}{\partial t} = \frac{k_a}{K_D^{mi}}\,(C_{mo} - C_{im}) \qquad (4\text{-}14)$$

Without longitudinal diffusion/dispersion the transport equation becomes (Eq.(4-1)):

$$\theta_{mo}K_D^{mi}\,\frac{\partial C_{im}}{\partial t} + \theta_{mo}\,\frac{\partial C_{mo}}{\partial t} + J_V\,\frac{\partial C_{mo}}{\partial x} = 0 \qquad (4\text{-}15)$$

Equations.(4-14) and (4-15) can be solved by introducing a position dependent time and by using a transformation in order to obtain scaled variables. The solution is expressed in the so called Goldstein J-function *(cf. 56, 196)*.

Instead of using the above approach, the stagnant phase effect can be described by an equivalent length parameter L_r. For spherical aggregates with radius R_a, the expression of Crank *(45)* is adapted for a situation where exchange occurs:

$$\frac{\partial(q_{im}+\theta_{im}C_{im})}{\partial t} = \frac{15}{R_a^2}\,\theta_{im}D\,(C_{mo}-C_{im}) \qquad (4\text{-}16)$$

Combination of Eqs.(4-12) and (2-16) results in the following expression for k_a:

$$k_a = \frac{15D}{R_a^2} \frac{\theta_{im}}{\theta_{mo}} \tag{4-17}$$

With the use of Eq.(3-46), L_r can now be expressed in terms of k_a. Two different expressions were given by Bolt *(24)*, depending on whether adsorption/exchange takes place. The advantage of this approach is, as was mentioned in the section on physical non-equilibrium and dispersion, that all effects are accounted for by one effective value of the dispersion length. Consequently, analytical solutions can be used to solve the advection-dispersion equation.

Numerical Solutions of Transport Involving Equilibrium Exchange

The two preceding sections, discussed some of the fundamentals of transport of exchanging solutes with and without dispersion. This was done in a way so that explicit expressions for the position of the solute front were obtained, and that (approximate) analytical solutions were available. However, because of the non-linearity of the (measured) exchange isotherms, numerical techniques are usually needed to solve the transport equation. For that reason, this section focuses on the (numerical) simulation of exchanging solutes.

One of the earlier works on transport of reactive solutes was reported by Kay and Elrick *(94)*. These authors determined adsorption isotherms of lindane for various soils and soil fractions. Linear adsorption was observed; the lindane was particularly strong adsorbed by organic matter. A chromatographic model developed by Hashimoto et al. *(83)* was used to predict the movement of lindane through the soil. A reasonably good agreement between predicted and experimental breakthrough curves was obtained. At higher pore water velocities, the prediction was somewhat poorer, perhaps because of physical non-equilibrium. Displacement of the lindane (elution curve) was described poorly, possibly because of inadequate knowledge of the desorption curve.

Lai and Jurinak (*106, 107)* solved the transport equation for non-linear adsorption with an explicit finite difference method. These authors considered homovalent exchange in a binary system for one-dimensional steady flow. The dimensionless variables $X_k=C_k/C_T$ and $Y_k=S_k/S_T$ were introduced for the solute concentration in the liquid and adsorbed phase, respectively. The following equation was obtained, using a similar relation as Eq.(2-12):

$$\frac{\partial X_k}{\partial t} = D(X_k)\,\frac{\partial^2 X_k}{\partial x^2} - v(X_k)\,\frac{\partial X_k}{\partial x} \tag{4-18}$$

where the dispersion coefficient and velocity were adapted according to:

$$D(X_k) = \frac{D}{1 + (\rho_b S_T/\theta C_T)\; f'(X_k)} \tag{4-19}$$

$$v(X_k) = \frac{v}{1 + (\rho_b S_T/\theta C_T)\; f'(X_k)} \tag{4-20}$$

with $f'(X_k)=dY_k/dX_k$. The denominator of the latter two terms can be recognized as the retardation factor; its value depends on X_k because of non-linear exchange. Following Helfferich *(84)*, various adsorption functions $Y_k=f(X_k)$ were used. For a number of isotherms (linear, concave and convex), numerical solutions were obtained for Eq.(4-18) subject to specified boundary and initial conditions. Column studies were carried out involving Ca and Mg, which exhibit a slightly non-linear exchange isotherm. The comparison between experimental and numerical results was good.

Rubin and James *(163)* presented a comprehensive analysis of multi-component equilibrium exchange during one-dimensional steady flow in layered and homogeneous profiles with a variable C_T. The equations to describe exchange and transport were solved numerically with the Galerkin method. These authors showed some interesting features, such as multiple fronts and plateau zones during multi-species transport with a varying C_T. It was also demonstrated how ion exchange and hydrodynamic dispersion influence solute transport.

Along the same lines, Valocchi et al. *(192)* presented an analytical framework for transport of various species of ion exchanging solutes, based upon the theory of chromatography. In contrast with some previous work in this area, the effect of hydrodynamic dispersion was included and the total electrolyte level was not assumed to be constant. The development of the transport equations is quite similar to that presented by Rubin and James *(163)*. In case of n exchanging ions, the governing set of equations is:

$$\theta \frac{\partial C_k}{\partial t} + \rho_b \frac{\partial S_k}{\partial t} = \theta D \frac{\partial^2 C_k}{\partial x^2} - J_V \frac{\partial C_k}{\partial x} \qquad k=1,2,\ldots,n \tag{4-21}$$

$$C_T = \sum_{k=1}^{n} C_k \tag{4-22}$$

$$S_T = \sum_{k=1}^{n} S_k \tag{4-23}$$

C_T is the variable total solute concentration in the liquid phase and S_T is the constant, total solute concentration in the adsorbed phase or the cation exchange capacity. In case an adsorbed species k, with valence υ_k, is exchanged for species j, with valence υ_j, the exchange coefficient can be defined as:

$$K_{jk} = (Y_j/X_j)^{\upsilon_k} (X_k/Y_k)^{\upsilon_j} \tag{4-24}$$

where Y and X again denote dimensionless concentrations. It should be noted that a more accurate solution might be obtained by using chemical activities. Furthermore, the assumption that K_{jk} is constant is strictly not correct.

To solve the transport equations, we need to reduce the number of dependent variables, by expressing S_k in terms of C_k. This can be done by using the n-1 independent equilibrium expressions, and by using Eq.(4-23). The multi-component exchange isotherm for a species k is given as:

$$S_k = F_k(C_1, C_2, \ldots, C_n) \qquad k=1,2,\ldots,n \tag{4-25}$$

Eq.(4-25) can be substituted into Eq.(4-21), which leads to a set of n transport equations of the following form:

$$\theta \frac{\partial C_k}{\partial t} + \rho_b \sum_{k=1}^{n} f_{jk} \frac{\partial C_j}{\partial t} = D\theta \frac{\partial^2 C_k}{\partial x^2} - J_V \frac{\partial C_k}{\partial x} \tag{4-26}$$

where $f_{jk} = \frac{\partial F_k}{\partial C_j} = \frac{\partial S_k}{\partial C_j}$. This system has been solved for binary and ternary exchange using the Galerkin finite element method *(e.g., 163)*.

As was mentioned earlier, the value of K_{jk} is important as it affects the shape of the front. For a concave isotherm, $K_{jk} < 1$, the X_k-profile travels at a speed proportional to t instead of $t^{1/2}$, as for Fickian dispersion. For a convex isotherm, $K_{jk} > 1$, the X_k-profile becomes steeper when the front travels through the medium. Although the situation with a varying C_T is somewhat more complex, one can assume that each particular concentration travels in a constant C_T environment.

A qualitatively good comparison of theoretically predicted concentrations, using multi-component exchange, with experimental results, involving the monitoring of Ca and Mg in a ground water aquifer, was reported by Valocchi et al. *(192)*. Finally, these authors reported that dispersion induced exchange, a phenomenon reported by Lake and Helfferich *(108)*, which occurs as a result of dispersive mixing across the solute front in case C_T varies and which leads to changes in the adsorbed phase, was of minor importance.

Selim et al. *(169)* examined the concentration of 2,4-D during infiltration and redistribution. This was one of the first studies concerning reactive solute movement during transient, unsaturated flow. Numerical solutions were obtained with an explicit-implicit finite difference technique. The dispersion coefficient was obtained as a function of pore-water velocity and the retardation factor was described similarly as by Lai and Jurinak *(106, 107)*. The concentration profiles obtained from a field experiment, involving the application of 2 cm of an aqueous solution containing 50 μg/ml of 2,4-D, were in good agreement with the simulated profiles.

Although the retardation factor, R, is not constant for non-linear exchange, one may want to use an effective, constant value for R which can be used over the whole concentration range. Valocchi *(190)* introduced an effective distribution coefficient, K_d, as the ratio of the step change in aqueous phase concentration and the step change in sorbed phase concentration. The effective velocity of the solute front can be given by (Eq.(4-2)):

$$v^* = v/R = dx_p/dt \tag{4-27}$$

which provides a way to determine a (constant) value for R. The use of a constant value for R is plausible for a number of cases. For "trace" quantities of the species (i.e., $C_i << C_T$), as for certain pollution problems, we can safely assume linear exchange. Valocchi *(190)* claimed that for many situations involving non-linear exchange and multi-species systems, a constant R can be used for predictive purposes provided that dispersion is negligible. Valocchi *(190)* applied a mass balance across the step change in concentrations to come up with:

$$v^*/v = R^{-1} = (1 + \frac{\rho_b}{\theta} \frac{\Delta S}{\Delta C})^{-1} \tag{4-28}$$

where $C=C_o-C_i$ and $S=S_o-S_i$, i.e., the difference between final and initial concentrations, can be used to define an effective K_d. It seems, however, that the dependence of K_d on the initial and final concentration values limits its applicability to specific cases.

Robbins et al. *(159)* used a model by Childs and Hanks *(40)* to simulate water movement and solute transport. Transport was simulated for a variety of cases: non-reactive solute transport, precipitation and dissolution of lime and gypsum during transport, and multi-cation exchange. The numerical model to simulate transport involving exchange accounted for ion pair formation and it used activities rather than concentrations. During concomitant lysimeter studies, soil solution samples were obtained at various depths using porous cups attached to sampling tubes. Solute concentration and electrical conductivity could only be predicted satisfactorily by including precipitation/dissolution and cation exchange. The adsorbed concentrations of Ca, Mg, Na, and K followed from the CEC, the cation exchange capacity, and the selectivity coefficients characterizing equilibrium exchange for various pairs of cations. These relationships were *(158)*:

$$CEC = S_{Ca} + S_{Mg} + S_{Na} + S_K \tag{4-29}$$

$$K_1 = \frac{C_{Ca}^{1/2} S_{Mg}}{C_{Mg}^{1/2} S_{Ca}} \qquad K_3 = \frac{C_K\, S_{Ca}}{C_{Ca}^{1/2} S_K} \qquad K_5 = \frac{C_{Na}\, S_{Mg}}{C_{Mg}^{1/2} S_{Na}}$$

$$K_2 = \frac{C_{Na}\, S_{Ca}}{C_{Ca}^{1/2} S_{Na}} \qquad K_4 = \frac{C_K\, S_{Mg}}{C_{Mg}^{1/2} S_K} \qquad K_6 = \frac{C_{Na}\, S_K}{C_K\, S_{Na}} \tag{4-30}$$

where C is the concentration in the liquid phase [mol m^{-3}] and S is the adsorbed concentration [$cmol_c\, kg^{-1}$]. By combining the above expressions one can determine, for example, the amount of adsorbed Ca as:

$$S_{Ca} = CEC \Big/ \left[\frac{C_{Mg}^{1/2} K_1}{C_{Ca}^{1/2}} + \frac{C_{Na}}{C_{Ca}^{1/2} K_2} + \frac{C_K}{C_{Ca}^{1/2} K_3} + 1 \right] \tag{4-31}$$

In contrast with Eq.(4-25), a straightforward explicit expression is now obtained.

The approach by Robbins et al. *(159)* to calculate complexation, precipitation/dissolution, and cation exchange in separate subroutines seems to be quite popular. The calculations are facilitated by the availability of computer packages which can be used to simulate the equilibrium chemistry involving many components and reactions. A drawback is that convergence problems are reported to be common when the transport equation and the model describing the equilibrium chemistry (exchange, complexation, protonation etc.) are combined. Jennings et al. *(88)* suggested, therefore, that the technique of direct insertion into the main transport equation be used rather than solving a number of equations simultaneously. This is basically the approach discussed so far, i.e., the inclusion of a retardation factor in the transport equation. The dependency of the solid phase concentration on various quantities was expressed by Jennings et al. *(88)* as follows:

$$S = \int(C, S_T, t, x, \partial C/\partial t) \qquad (4\text{-}32)$$

A solution of the problem was accomplished by a Galerkin finite element method *(cf. 144)*. Kirkner et al. *(97)* elaborated on this technique.

It should be noted that the type of chemical reaction needs to be considered when chosing the technique of numerical solution. Rubin *(162)* distinguished six broad classes of chemical reactions during transport, each with its own mathematical formulation. One is also referred to the review article by Abriola *(1)*, which discusses recent work on the modeling of contaminant transport, including geochemical and sorption models.

The exchange of K by Na, governed by the Gapon equation *(63)* was studied by van Eykeren and Loch *(194)* for soil systems with a mobile and an immobile liquid phase. Experimental results obtained with a cation exchanger column compared reasonably well with numerical solutions. Selim et al. *(170)* obtained breakthrough curves for aggregated soils by also considering a mobile and immobile region of the liquid phase. Experimentally determined exchange isotherms were used to quantify the exchange reaction.

V. TRANSPORT IN STRUCTURED AND LAYERED SOILS

The structure of a soil, i.e., the spatial arrangement or clustering of primary soil particles into secondary units called aggregates, can have a great impact on the transport of solutes through that soil. The REV, i.e., the smallest volume for which macroscopic uniformity exists, is much larger for an aggregated soil than for a non-aggregated soil. The dispersion in aggregated media is caused by molecular diffusion, mechanical dispersion, and the previously discussed "stagnant phase" effect. Spreading in a medium which consists of homogeneous layers exhibits some additional characteristics in comparison with non-layered soils where dispersion can be described with a Fickian process. For aggregated and layered media, the medium can conceptually be divided into homogeneous zones (mobile and immobile regions, individual layers). In this way the transport problem lends itself to an exact description.

First, the concept of mobile and immobile regions of the liquid phase will be reviewed in more detail than previously, along with a discussion of the velocity dependency of the dispersion coeffcient. Next, some cases of transport through media with a particular structure will be cited followed by some remarks about transport in layered media. The discussion is quite general and merely concerns transport in well defined systems. Much work is still needed to explain and predict transport on a field scale, which will be discussed in the next Chapter.

Mobile and Stagnant Regions

In order to describe the appearance of asymmetrical breakthrough curves (tailing), van Genuchten and Wierenga *(202)* used the concept of mobile and immobile regions of the liquid with diffusional transfer between the two (see section on physical non-equilibrium). This concept had been previously applied by Coats and Smith *(43)* and Villermaux and van Swaay *(206)*. A sensitivity analysis was carried out by van Genuchten and Wierenga *(206)* with an analytical model, which indicated that the tailing observed during unsaturated flow in an aggregated medium was succesfully predicted. In two subsequent papers, the experimental determination of breakthrough curves for aggregated, unsaturated media was described *(203, 205)*. Columns were packed with a clay loam, aggregate size 2.0 or 6.3 mm, to study breakthrough curves. The outlets of the columns were connected to a vacuum chamber containing an automatic fraction collector. The solution was applied with a syringe pump to maintain a constant flux. The solutes used in these studies were ^3H_2O *(203)* and 2,4,5-T *(205)*. It appeared that the amount of immobile water increased with decreasing velocity and with increasing aggregate size. A fairly good prediction of experimentally determined breakthrough curves was obtained.

Since then, the concept of mobile and immobile regions of the liquid phase has widely been used to describe physical non-equilibrium dispersion. This concept, however, applies not only to structured soils according to de Smedt and Wierenga *(55, 57)*. These authors showed that, for unsaturated conditions in a non-structured medium (glass beads), the effluent concentration could only be described by taking into account an immobile water fraction as well. If no distinction was made between those fractions, a very large value for the dispersion coefficient was needed to fit the data with the advection-dispersion equation.

On the other hand, it has been reported that no basis exists for a subdivision into mobile and immobile regions of the liquid phase. Philip *(140, 141)* performed a theoretical study of diffusion in a semi-infinite porous medium containing dead-end pores filled with immobile water. The cumulative diffusive fluxes in the mobile and immobile region of the medium, J_{mo} and J_{im}, were defined as:

$$J_{mo} = \int_0^{\infty} \left\{ C_{mo}(x,t) - C_{mo}(x,0) \right\} dx \tag{5-1-a}$$

$$J_{im} = \int_0^{\infty} \left\{ C_{im}(x,t) - C_{im}(x,0) \right\} dx \tag{5-1-b}$$

where the concentrations are based on unit volume of porous medium. These concentrations were solved analytically.

Philip *(140)* found that transient diffusion is only different for mobile and immobile regions during the initial stage of the diffusion process, when the relationship between time of infiltration and the dimensionless cumulative diffusive flux obeys a $(\text{time})^{1/2}$ law, whereas it obeys a $(\text{time})^{3/2}$ law in the stagnant region. Shortly after the initiation of the diffusion process, however, the dimensionless cumulative diffusive flux in both kind of pores obeys a $(\text{time})^{1/2}$ law. Philip *(141)* argued that the effect of dead-end-porosity is insignificant and the distinction of two regions of the liquid phase seems unwarranted.

Philip's arguments were supported by Smiles and Philip *(178)* and Smiles et al. *(179)* who observed a pistonlike displacement during infiltration of a KCl solution in relatively dry soil. Their medium contained 30% kaolinite in a matrix of fine sand. Work by Warrick et al. *(209)* and Kirda et al. *(95, 96)* also seemed to support the observation that, at least in non-aggregated media, no basis exists for a subdivision into mobile and immobile regions. Awad *(11)*, who did similar displacement experiments as de Smedt and Wierenga *(57)* in a sand, also concluded that no distinction between mobile and immobile regions could be made.

Somewhat related to this issue is the dependence of the dispersion coefficient, D, on the pore water velocity, v. Smiles et al. *(179)* found no dependence of D on v during infiltration of a KCl-solution into the dry kaolinite/sand medium. As was pointed out by these authors, different results can be expected for coarse textured soils. Smiles et al. *(179*) observed, that for the low Pe-numbers encountered during infiltration into a dry soil, the water and solute profiles preserved similarity in terms of ω $(=x/\sqrt{t})$ (see section on experimental determination of dispersiuon coefficients). This implies that D is velocity-independent. Saffman *(164)* and Pfannkuch *(138)* also reported that D is independent of v, but Saffman *(164)* used Pe<1 as a condition for D to be independent of v ($Pe=vd/D_e$, where d is the average grain diameter). Values for v can be found by using Philip's theory of infiltration, while d can be estimated with the Kozeny-Carman relation. It appeared that for t>1.1 s, D was independent of velocity under the conditions stated by Smiles and Philip *(178)*. Groenevelt et al. *(72)* studied dispersion in a dispersed clay paste, using a slit model to represent the flow between clay platelets. The dispersion coefficient was found to be virtually velocity independent and could be equated to the coefficient of molecular diffusion. It should be noted that in their case the Peclet number ($Pe=wv/D_o$, where w is half the width of the slit), was also very small (<1) because of the absence of large pores.

Findings by Watson and Jones *(212)*, who conducted similar experiments as Smiles et al. *(179)*, seem to indicate that hydrodynamic dispersion is velocity dependent. In the literature, a linear dependence of D on v has often been reported for (steady) flow at higher values of the Pe-number. Yule and Gardner *(219)*, for example, reported a longitudinal dispersion coefficient for a Plainfield sand which was linearly related to v. At large Pe-numbers (e.g. Pe>35) it is plausible to assume a linear relationship between v and D *(cf. 15, 82, 206)*.

Aggregated Media

The study of transport in aggregated media has received considerable in recent years. Agronomists seek to optimally use irrigation water and applied chemicals, which might be easily lost in aggregated soils because of "bypass" flow. Chemical properties, such as pe, pH, and pO_2, might be quite different for inter- than for intra-aggregate pores, leading to more complex sink/source terms. The performance of ion exchange columns is the topic of many studies in the chemical engineering literature *(e.g., 155)*. Transport in these columns is usually described in terms of a transport equation containing a sink/source term which describes the exchange inside the solid particles of the column. This section will examine how the transport equation is formulated for aggregated media.

Passioura *(135)* distinguished between micropores, inside the soil aggregates where solute movement occurs only via diffusion, and in macropores, located between the aggregates where transport occurs via viscous (advective) flow. The latter type of transport can be completely dominant, and considerable work has been devoted towards a better understanding of flow in macropores *(e.g., 18)*. The liquid present in the micropores is supposed to be immobile or stagnant, whereas the liquid in the macropores is said to be mobile. Passioura *(135)* used the following equation to describe transport in an aggregated medium (cf. Eq.(2-44)):

$$\frac{\theta_{im}}{\theta_{mo}} \frac{\partial C_{im}}{\partial t} + \frac{\partial C_{mo}}{\partial t} = D_{mo} \frac{\partial^2 C_{mo}}{\partial x^2} - v_{mo} \frac{\partial C_{mo}}{\partial x} \tag{5-2}$$

where D_{mo} is the dispersion coefficient of the mobile liquid phase and where the immobile phase, inside the aggregate, is treated as a distributed sink. In general, C_{mo} and C_{im} are not known and one has to resort to a simpler model (Eq.(2-5)) and use an effective value for D. An expression for D should combine the advective dispersion in the mobile region with the stagnant phase effect in the immobile region.

Therefore, Passioura *(135)* adapted the expression of Aris *(9)* for a dispersion coefficient in a tube, to obtain the following expression for "overall" dispersion in an aggregated porous medium:

$$D = D_{mo}\theta_{mo}/\theta_T + gv^2a^2/D_{eim} \tag{5-3}$$

where a is the radius of the aggregate [L], g is a coefficient characterizing shape, θ_T is the total (liquid) volume fraction available for the solute, θ_{mo} is the volume fraction of the mobile liquid phase, and D_{eim} is the coefficient of molecular diffusion in the immobile liquid phase $[L^2T^{-1}]$.

Following Taylor *(189)*, one can introduce a moving coordinate ξ=x-vt. For large t, steady-state transport will occur so that $C_{mo}-C_{im}$= constant. As advective dispersion can be neglected for a plane moving at velocity v (ξ=constant), the solute flux across such a plane is:

$$J_{dif} = -\frac{\theta_{im}}{\theta_T}\frac{v^2a^2}{15D_{eim}}\frac{\partial C_{mo}}{\partial x} \tag{5-4}$$

where Passioura *(135)* erroneously omitted the negative sign, and the expression of Crank *(45)* was used for the concentration inside the spherical aggregates. Because the steady-state assumption implies that $\partial C_{mo}/\partial x=\partial C/\partial x$, the following expression for the effective dispersion coefficient inside the aggregate was suggested by Passioura *(135)*:

$$D_{im} = \frac{\theta_{im}}{\theta_T}\frac{v^2a^2}{15D_{eim}} \tag{5-5}$$

The effective dispersion coefficient for the liquid in the macropores, which characterizes advective dispersion, was described with (cf. Eq.(3-44)):

$$D_{mo} = D_{emo} + v_{mo}a \qquad (5\text{-}6)$$

where D_{emo} is the coefficient of molecular diffusion in the mobile phase $[L^2T^{-1}]$ and v_{mo} the velocity in the mobile phase ($=v\theta_T/\theta_{mo}$). This leads to the following overall dispersion coefficient:

$$D = D_{mo}\theta_{mo}/\theta_T + D_{im} \qquad (5\text{-}7)$$

Passioura and Rose *(136)* performed experiments to evaluate D according to Eq.(5-7). Water retention data were used to estimate θ_{im}, which is approximately the volumetric water content at a suction of 75 cm of water. Pores which drained at suctions less than 75 cm were considered to be macropores. D was obtained via the technique described by Rose and Passioura *(160)*. Values for D_{eim} between 4×10^{-6} and 6×10^{-6} cm^2s^{-1} were used, depending on the porous material. It is of interest to examine the Brenner number (B) as a function of va. For low values of va, the main contribution to B will be from advective dispersion, whereas at higher values of va the stagnant phase effect becomes more important. Therefore, we will have somewhere an absolute maximum for B. This maximum will occur when $va=(15D_{eim}D_{emo}\theta_{mo}/\theta_{im})^{1/2}$. Displacement is likely to be most efficient, i.e., closest to piston flow, for this value of va.

The study of transport during flow of other fluids than water might provide independent ways to characterize soil structure. Millington and Shearer *(118)* discussed the effect of aggregation in porous media on gas diffusion. These authors distinguished between a solid phase and an intra- and inter-aggregate porespace filled with water or gas. Various expressions for D_e/D_o were derived, where D_e and D_o are diffusivities of the fluid in presence and absence of the porous medium, respectively. Millington and Shearer *(118)* illustrated the contrasting behavior of diffusion in the gas phase and ion diffusion in the liquid phase. The ratio D_e/D_o was found to be higher for non-aggregated than for aggregated media as far as diffusion in the liquid phase is concerned, while the opposite seemed to hold for gas diffusion, except during very dry conditions.

Scotter *(166)*, studying the preferential solute movement through larger soil voids *(cf. 174)*, considered two pore geometries: cylindrical channels and planar voids. Theoretical breakthrough curves for a non-reactive solute showed that a substantial amount of the solute appeared in the effluent before one pore volume had leached through, especially for large channel diameters. Van Genuchten et al. *(201)* used the development by Scotter *(166)* to solve transport through cylindrical macropores analytically. The cylindrical pore is supposed to contain the mobile region of the liquid phase, while the surrounding porous medium contains small pores in which the immobile region resides. The adsorption sites were divided into a fraction in close contact with the mobile liquid phase, and a fraction in contact with the immobile region. A separate retardation factor was used for both fractions. A set of equations similar to Eq.(2-44) and (2-45) was obtained, which was expressed in dimensionless form and solved with help of Laplace transforms. It was found that, at early times, the soil surrounding a macropore might be considered to be semi-infinite;

furthermore, dispersion in the macropore can usually be ignored without loss of accuracy.

The approach taken by van Genuchten et al. *(201)* seems to be generally accepted to describe solute transport in aggregated porous media. The overall transport equation contains both the concentration in the mobile and immobile phase. The geometry of the aggregates influences the diffusive transport between the two regions as well as the average solute concentration inside the aggregates.

Valocchi *(191)* studied the validity of the assumption of local physical and chemical equilibrium by comparing solutions of the non-equilibrium and equilibrium type transport equations for aggregated media. Two cases of physical non-equilibrium were considered, namely diffusion in spherical aggregates and first order transport between mobile and immobile regions of the liquid phase. The general equation for reactive solute transport, assuming linear adsorption in both mobile and immobile region, can be written as:

$$\theta_{mo} R_{mo} \frac{\partial C_{mo}}{\partial t} + \theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \theta_{mo} D \frac{\partial^2 C_{mo}}{\partial x^2} - \theta_{mo} v \frac{\partial C_{mo}}{\partial x} \qquad (5\text{-}8)$$

For spherical aggregates the physical non-equilibrium diffusion model is:

$$C_{im} = \frac{3}{a^3} \int_0^a C_a(x,r,t)\, r^2\, dr \qquad (5\text{-}9)$$

$$C_a(x,r,t)\Big|_{r=a} = C_{mo}(x,t) \qquad (5\text{-}10)$$

$$R_{im} \frac{\partial C_a}{\partial t} = D_{eim} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_a}{\partial r}\right) \qquad (5\text{-}11)$$

where a is the aggregate radius and C_a is the local concentration inside the aggregate. In case the transfer of solute between mobile and immobile zones can be described as a first order process we get:

$$\theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \alpha(C_{mo} - C_{im}) \tag{5-12}$$

The transport problem is thus posed by Eq.(5-8) in combination with Eq.(5-9) to (5-19) or in combination with Eq.(5-12). One case of chemical non-equilibrium, involving first order kinetics, was studied by Valocchi *(191)*. The ADE was described as

$$\theta \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \theta D \frac{\partial^2 C}{\partial x^2} - \theta v \frac{\partial C}{\partial x} \tag{5-13}$$

where S is governed by the first-order linear kinetic expression

$$\frac{\partial S}{\partial t} = k_1 C - k_2 S \tag{5-14}$$

with k_1 and k_2 as the forward and reverse rate coefficient, respectively. This is referred to as the linear chemical non-equilibrium model.

These models are well documented *(150, 151)*. They were written in dimensionless form and solved in the Laplace domain by Valocchi *(191)*. In order to quantify deviations from local equilibrium, a time moment analysis was carried out. Aris *(10)* showed how absolute time moments, m_p, which are defined analagous to moments for position dependent concentrations (Eq.(3-18)), can be determined with the solution in the Laplace domain:

$$m_p = (-1)^n \lim_{s \to 0} \left[\frac{d^p}{ds^p} \bar{C}(X,s) \right] \tag{5-15}$$

where X is the dimensionless position and $\bar{C}(X,s)$ is the Laplace transform of C(X,t) with s as the transformation variable. The advantage of this approach is that the solution in the Laplace domain is fairly easy to obtain. Based on these moments, Valocchi *(191)* obtained expressions for the first normalized moment and the second and third central moment for the equilibrium and the three non-equilibrium models for a Dirac-type input. In this way, mean breakthrough time, spreading, and tailing could be characterized.

It was found that sorption rate limitations (non-equilibrium) caused enhanced spreading and tailing. Non-equilibrium, however, does not influence the mean breakthrough time. At large values for the dimensionless rate parameter, $F=k_2L/v$, where L is the column length, the non-equilibrium and equilibrium results are similar. By comparing the equilibrium solution with the more realistic non-equilibrium solution, the error, which is made by using the local equilibrium solution, can be established. This error increases linearly with incresing Pe/F and decreases with increasing retardation factor. Following Passioura *(135)*, Rao et al. *(151)*, and de Smedt and Wierenga *(57)*, Valocchi *(191)* obtained effective dispersion coefficients for the non-equilibrium situations.

Before discussing transport in fractured media, which is very similar to transport in aggregated media, a few other studies should be mentioned. Rasmuson and Neretnieks *(153)* obtained an analytical solution for the ADE in a porous medium consisting of spherical particles. Rasmuson *(152)* extended this analytical solution to a case where two-dimensional dispersion occurred. Other solutions involving spherical particles were given by Skopp and Warrick *(175)* and Tang et al. *(186)*, while Sudicky and Frind *(184)* provided solutions for porous media with rectangular voids. One of the first attempts to combine analytical and experimental work was reported by Rao et al. *(150)*, who studied transport in a medium consisting of spherical aggregates.

Fractured Media

Because of interest in the disposal of hazardous wastes in fractured bedrock, geologists and engineers have lately been studying transport in fractured media. Fractures are important for the advective transport of contaminants because of their relatively high water conductance (bypass). Formulation of the transport problem is very similar to that for aggregated media, i.e., the two components are advective transport in the fissure (the mobile region) and diffusion into the rock (the immobile region). For a number of cases, analytical solutions are available. In other instances, numerical methods need to be used. The finite element method is particularly convenient to obtain numerical solutions for transport in fractured media *(86)*.

Tang et al. *(186)* presented an analytical solution for contaminant transport in a single fracture. They considered a radio-active contaminant with a finite migration distance because of decay. Diffusion of the contaminant into the porous rock matrix slows down its transport and increases the opportunity for decay within a given travel distance. Processes to be distinguished were (1) advective transport along the fracture, (2) longitudinal mechanical dispersion in the fracture, (3) molecular diffusion within the fracture, in the direction of the fracture axis, (4) molecular diffusion from the fracture into the porous matrix, (5) adsorption onto the face of the matrix, (6) adsorption within the matrix, and (7) radio-active decay. For solute transport in the fracture, the following equation was used:

$$\frac{\partial C_{mo}}{\partial t} = \frac{D}{R_{mo}} \frac{\partial^2 C_{mo}}{\partial z^2} - \mu_w C_{mo} + \frac{\theta D_{eim}}{bR_{mo}} \left.\frac{\partial C_{im}}{\partial x}\right|_{x=w} - \frac{v}{R_{mo}} \frac{\partial C_{mo}}{\partial z} \tag{5-16}$$

where 2w is the fracture width [L], μ_w is a decay constant $[T^{-1}]$, $R_{mo}=1 + \frac{\rho_b}{\theta} K_{dmo}$ is a face retardation factor, and K_{dmo} is the distribution coefficient in the fracture. For transport inside the matrix the equation was:

$$\frac{\partial C_{im}}{\partial t} = \frac{D_{eim}}{R_{im}} \frac{\partial^2 C_{im}}{\partial x^2} - \mu_w C_{im} \tag{5-17}$$

where D_{eim} is the effective diffusion coefficient in the matrix, $R_{im}= 1 + \frac{\rho_b}{\theta} K_{dim}$ is the matrix retardation factor, and K_{dim} is the distribution coefficient in the porous matrix. In both cases the adsorption was assumed to follow a linear adsorption isotherm.

Equations (5-16) and (5-17) were solved analytically by Tang et al. *(186)* for specified initial and boundary conditions with the help of Laplace transforms. Some numerical examples were given as well. It was found that the effect of dispersion cannot be ignored. If D=0 m^2s^{-1}, the solution lags substantially behind the general solution, which used an expression for D as Eq.(3-36). This is in agreement with the findings of Rasmuson and Neretnieks *(154)* who also investigated the migration of decaying radionuclides in fissured rocks. They found that advective dispersion in the fissures results in larger travel distances for the radionuclides, therefore decreasing diffusion into the matrix and subsequent decay inside the rock matrix. Agreement between the analytical solution by Tang et al. *(186)* and a finite element method solution by Grisak and Pickens *(68)* was generally good, except for the transient case. The results demonstrated that matrix diffusion can prevent severe contamination of underlying aquifers with the (decaying) radioactive substances.

Neretnieks *(119)* treated dispersion in fissured rock, idealizing the medium by assuming flow through parallel channels of different size. The fissure width, w, is given by a distribution function f(w). A pulse with concentration C_o, introduced at the inlet, travels a distance x in time t_i in fissures with width w_i. Therefore, w can be expressed in terms of t. If the residence time for a fissure is less than a certain time t, it delivers tracer. At the outlet, mixing among solutions exiting from all fissures occurs, resulting in the following dimensionless exit concentration:

$$C(t)/C_o = \frac{\int_{w(t)}^{\infty} f(w)J_V(w)\ dw}{\int_{0}^{\infty} f(w)J_V(w)\ dw} = J_V(t)/J_V \tag{5-18}$$

The flow of water containing tracer, $J_V(t)$, from fissures with widths $w(t)<w<\infty$ is diluted by the total flow of water, J_V, from all fissures. An analytical expression for the mean residence time for a response curve C(t) was obtained. The spreading was quantified with σ_t^2, obtained with the second moment of the time dependent concentration. The dispersion coefficient depended strongly on the fissure width distribution.

Neretnieks *(119)* referred to his approach as stratified flow, i.e., the flow in each fissure depends on the size fissure just like the flow in a stratified medium depends on the permeability of each layer. In case of stratified flow, the width of the dispersion zone, σ, is proportional to the traveled distance x *(117)* instead of $x^{1/2}$ as for Fickian dispersion. Therefore, an increase in the observation distance will yield a larger value for D if the ADE is used to describe the transport process in stratified media *(cf. 49)*. As stated by Neretnieks *(119)*, the implications of using the wrong mechanism (for instance Fickian) when using a model for extrapolation to large distances may have grave consequences in some applications.

Besides the mixing due to the advection term, mixing occurs due to matrix diffusion. Diffusion of the tracer from the fissure into the matrix of the rock is accompanied by sorption. Neretnieks *(119)* could not obtain a mean and variance of the residence time with the moment method because they appear to be unbounded (i.e., the curve exhibits considerable tailing) even if the penetration depth in the rock is small compared to the distance between fissures. The dispersion process could be evaluated by comparing experimental data with theoretically calculated response curves. By solving the analytical model, Neretnieks *(119)* demonstrated that, for larger distances (larger residence times), the effects of stratification and matrix diffusion become major factors in comparison with the effect of hydrodynamic dispersion.

Layered Media

Solute transport in layered media has drawn a considerable amount of attention *(81, 116, 117, 142, 182, 185, 188)*. Almost all studies concern stratified aquifers with flow parallel to the stratification. Besides different soil-physical properties for each layer, differences in transport parameters occur. Consequently, a different transport and flow behavior might be expected, both perpendicular to and parallel to the stratification, compared to a uniform medium.

Tanji *(188)* studied the leaching of boron in a soil column consisting of homogeneous layers, the stratification was perpendicular to the direction of flow. Each layer had particular adsorption and moisture characteristics. A scaled down field profile was used to determine the amount of leaching experimentally. Calculated results for the stratified columns were in good agreement with the measurements.

As mentioned earlier, layered media tend to enhance the dispersion effect. Due to transverse diffusion from layers with a significant advective transport to layers with minimal advective transport, spreading of the solute front will occur in case of flow parallel to the stratification *(67)*. When using the conventional ADE, a large value for the dispersion coefficient will be found. It was argued by Gillham et al. *(67)* that under such heterogeneous conditions, no Fickian dispersion will occur. The dispersion coefficient is time dependent due to the transverse diffusion *(64, 116)*. Gupta and Bhattacharya *(74)* and Güven and Molz *(80)*, on the other hand, pointed out that Fickian dispersion will occur at large times for nonuniform velocity fields.

Sudicky et al. *(185)* and Starr et al. *(182)* discussed the migration of a reactive and a non-reactive solute in a layered porous medium. A system consisting of a thin sand layer between two silt layers was used to study the movement of a Cl solution applied to the sand layer for horizontal flow parallel to the stratification. The important processes were advection in the sand layer, transverse diffusion from sand to silt layers, and molecular diffusion (transverse to the flow direction) in the silt layers. The medium was water saturated. For the sand, where complete mixing was supposed to occur, the following transport equation applied:

$$\frac{\partial C_{mo}}{\partial t} = D_T \frac{\partial^2 C_{mo}}{\partial y^2} - v \frac{\partial C_{mo}}{\partial x} \qquad (5\text{-}19)$$

where the diffusive flux between sand and silt layers is represented as transverse dispersion, C_{mo} is the concentration in the sand layer, and v is the pore water velocity, in the sand layer, in the x direction parallel to the stratification. Transport in the silt layers, which is supposed to be purely diffusive, is described with:

$$\frac{\partial C_{im}}{\partial t} = D_e \frac{\partial^2 C_{im}}{\partial y^2} \qquad (5\text{-}20)$$

where C_{im} is the concentration in the silt layers and D_e is the effective diffusion coefficient.

Solutions of these equations for appropriate boundary and initial conditions, under the assumptions that the thickness of the sand layer can be ignored, were given by Tang et al. *(186)*. As the sand layer becomes thicker, a transverse concentration profile develops in the sand layer. The analytical solution for the "thick" sand layer is more complicated *(185)*.

The exit concentration was determined as an average over the sand layer with a fraction collector. The solute arrival time for the system, with transverse diffusion from the sand into the silt layers, was later than for pure plug flow. Strong dispersion seemed to occur due to interlayer solute transfer. The experimental breakthrough curve was poorly fitted when transverse transport was ignored.

Starr et al. *(182)* studied the same problem for a reactive solute, ^{85}Sr. Since the Sr-concentration was low, the exchange-isotherm was assumed to be linear and non-hysteretic, hence a constant K_d could be used. Application of the conventional ADE gave poor results for the reactive case, especially at higher velocities. Neglecting longitudinal dispersion, transport in the sand layer was described by:

$$\frac{\partial C_{mo}}{\partial t} = \frac{\theta_{im}}{\theta_{mo}} \frac{D_e}{R_{mo} w} \left. \frac{\partial C_{im}}{\partial y} \right|_{y=w} - \frac{v}{R_{mo}} \frac{\partial C_{mo}}{\partial x} - \mu C_{mo} \qquad (5\text{-}21)$$

where R_{mo} is the retardation factor in the sand layer, which has a width 2w, and μ is the radio-active decay constant $[T^{-1}]$. Transport in the silt layers was described by:

$$\frac{\partial C_{im}}{\partial t} = \frac{D_e}{R_{im}} \frac{\partial^2 C_{im}}{\partial y^2} - \mu C_{im} \qquad (5\text{-}22)$$

A diffusion coefficient for Sr in dilute solutions of 1.33×10^{-9} $m^2\ s^{-1}$ was used. Since a correct value for the retardation factor is essential for the prediction of the breakthrough curve, this factor was determined in two independent ways for the silt material. The first method determined K_d by the batch procedure, which resulted in values of 1.65 mL/g for the sand and 12.5 mL/g for the silt. R could be determined with Eq.(2-15), resulting in $R_{mo}=10$ and $R_{im}=60$. The second method was via diffusion. Two diffusion half cells, one of them containing a solution with ^{85}Sr and the other free of ^{85}Sr, were brought in contact with each other. After 35 days the columns were sliced in increments of 0.5 cm. The concentration in each segment was determined and, via curve fitting of the analytical solution, an effective diffusion coefficient was obtained. The ratio of the effective diffusion coefficient and the diffusion coefficient in water provides 1/R. A value of 70 was found for R_{im}. The agreement between the values obtained with the two methods was considered to be good. The experimental breakthrough curve could, however, not be as well predicted as for the non-reactive case. Better results were obtained if the values of R were varied with v. However, no physical basis exists for such an adjustment.

In the study of transport parallel to the stratification, frequent use is made of the moment method of Aris *(10)*, already discussed previously. By using depth averaged moments, one can account for the heterogeneity due to the stratification *(115)*. Therefore, this method, following Fischer et al. *(60)*, will be discussed briefly. These authors considered transport in a medium with depth h, bounded by horizontal impermeable layers at y=0 and y=h. The magnitude of the flow, in the x-direction, depends on y. For a moving coordinate system the transport equation is:

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial \xi^2} + \frac{\partial^2 C}{\partial y^2}\right] - v'\frac{\partial C}{\partial \xi} \tag{5-23}$$

where $v'=v-\bar{v}$ and $\xi=x-\bar{v}t$. Having the overbar notation indicate a depth averaged value:

$$\bar{v} = \frac{1}{d}\int_0^h v\,dy \tag{5-24}$$

Spatial moments can be defined according to (cf. Eq.(3-19)):

$$m_p = \int_{-\infty}^{\infty} \xi^p\, C(\xi,y,t)\, d\xi \tag{5-25}$$

The operator defined by Eq.(5-25) can be applied to the individual terms of Eq.(5-23). Assuming that C=0 and $\frac{\partial C}{\partial \xi} = 0$ for $\xi \to \pm\infty$, we can find:

$$\frac{\partial m_p}{\partial t} = D\left[\,p(p-1)\,m_{p-2} + \frac{\partial^2 m_p}{\partial y^2}\right] + v' p m_{p-1} \tag{5-26}$$

This equation can be averaged over depth, according to Eq.(5-24), and the resulting equation is:

$$\frac{\partial \overline{m_p}}{\partial t} = Dp(p-1)\overline{m_{p-2}} + \overline{pv'm_{p-1}} \tag{5-27}$$

We can now solve $\overline{m_p}$ sequentially for p=0,1,2,... Using the theory of statistical moments we can characterize the concentration distribution by determining the mean, variance, skewness, kurtosis, etc. *(81)*.

Fried and Combarnous *(61)* described the work by Marle et al. *(115)* which showed how the moment method can be applied to a multi-layered medium with flow in the horizontal x-direction and for which the transport properties depend on y. The mathematical formulation of the problem is:

$$\theta(y)\frac{\partial C}{\partial t} = \theta(y)D_L(y)\frac{\partial^2 C}{\partial x^2} + \frac{\partial}{\partial y}\left[D_T(y)\theta(y)\frac{\partial C}{\partial y}\right] - \theta(y)v\frac{\partial C}{\partial x} \qquad (5\text{-}28)$$

$$\frac{\partial C}{\partial y} = 0 \qquad y = y_1 \quad \text{and} \quad y = y_2 \qquad (5\text{-}29)$$

where it is assumed that v is independent of x. The boundaries of the stratified medium are at $y=y_1$ and $y=y_2$. The problem can be solved in a similar manner as described before, using depth averaged moments. Fried and Combarnous *(61)* also described how an equivalent dispersion coefficient can be used to represent dispersion in a layered medium.

Güven et al. *(81)* applied Aris' moment method to describe dispersion of a tracer in a horizontally stratified aquifer of finite thickness and infinite length and with vertical variations in the hydraulic conductivity. Several idealized hydraulic conductivity profiles were used. The experimentally and theoretically determined macro-dispersivities were of the same order of magnitude. These authors stressed the importance of detailed measurements of the hydraulic conductivity profile at various positions along the aquifer. In a later paper, Güven and Molz *(80)* extended this work to an unbounded aquifer with flow components parallel and perpendicular to the stratification.

The variation of the hydraulic conductivity, indicative of the heterogeneity of the medium, strongly influences D_L via variations in v *(79, 183)*. Unfortunately, porous media generally do not consist of homogeneous layers with distinct transport and flow parameters; v(y) is not known in sufficient detail to predict the concentration profile with the moment method. An even more complicated case arises if v varies in both the longitudinal and the transverse direction.

A simplified approach for vertical transport might be to consider only one-dimensional flow. Heterogeneity in the direction of flow is most easily modeled by assuming that the soil consists of homogeneous layers, i.e., horizontal layers *(cf. 171)*. Bresler and Dagan *(30)* used the approach of representing a field as an ensemble of individual columns, i.e., vertical layers, restricting the transport and flow problem to one dimension.

Simmons *(172)* described dispersion during one-dimensional solute transport in an arbitrary medium in terms of stochastic-advective transport. He contributed the spreading in laboratory soils largely to local variations in the hydraulic conductivity, which was incorrectly interpreted as hydrodynamic dispersion. In the field, the heterogeneity of the soil will be even larger, and the use of laboratory-measured hydrodynamic dispersion coefficients is inappropriate. The stochastic flow velocity depends on time and position, i.e., v(x,t). In contrast with Bresler and Dagan *(30)*, who used an ensemble of columns, the description of the transport is truly one-dimensional. Simmons *(172)* also questioned the validity of deterministic descriptions of transport during transient (unsaturated) flow conditions because of the time dependence of the dispersivity.

It has been suggested that for large distances or times, Fickian behavior could be assumed (asymptotical approach of diffusive type of transport). However, Matheron and de Marsily *(116)* showed that this assumption does not always hold, even for a Gaussian covariance function of the velocity. This was attributed to the lack of transverse mixing. These authors studied horizontal transport in a medium with horizontal layers. In case of a small constant vertical velocity, i.e., the flow vector is somewhat inclined with respect to the horizontal stratification, transverse mixing is enhanced and diffusive behavior is approached much faster.

Among other studies, dealing with stochastic modeling of transport in heterogeneous media, the work by Gelhar *(64)* can be mentioned. However, a further discussion of the topic is beyond the scope of this review.

VI. PREDICTION OF SOLUTE TRANSPORT UNDER FIELD CONDITIONS

Prediction of solute movement under field conditions is the primary objective of many workers in the area of solute transport. The application of the conventional advection-dispersion equation, ADE, has proven to be quite successful for laboratory experiments (see section on experimental determination of dispersion coefficients), where in general macroscopically homogeneous conditions exist. Once the relevant transport and flow parameters are known, the ADE is solved, generally numerically, and a unique concentration distribution can be determined. This is referred to as the deterministic approach. If necessary, the structuredness of the soil can be taken into account by using various non-equilibrium models (Chapter V).

Some of the earlier work involving the prediction of solute transport under field conditions made use of the ADE, while the corresponding transport parameters were measured in the laboratory. This approach, also referred to as deterministic, leads to a uniquely defined outcome for a given set of events. However, the description of solute movement in the field, using this deterministic approach, was often not very succesful. Three reasons were pointed out by van Genuchten and Jury *(199)*: (1) inaccurate or incomplete description of the chemistry affecting transport of reactive solutes, (2) preferential movement of water and solutes through macropores, and (3) spatial and temporal variability of field scale flow and transport properties. In order to deal with some of these problems, a variety of approaches has been taken to model solute flow in the field. The variability on a field scale has recently been investigated *(48, 181)*.

Deterministic Models

An example of the use of experimentally determined data to numerically predict solute profiles under different conditions is the work by Bresler *(28)*. Bresler used data from Warrick et al. *(209)*, who applied a pulse of 0.2 N $CaCl_2$ during infiltration on a 6.1 by 6.1 m plot. The chloride concentrations in a 1 by 1 m square in the center of the plot were monitored at depths of 30, 60, 90, 120, and 150 cm, using duplicate ceramic cups. The dispersion coefficient was obtained by fitting the experimentally and analytically determined profiles. Bresler used these data to validate a numerical model to predict solute profiles. The model used an implicit method, which minimized the effect of numerical dispersion. After validation, the model was used to predict solute concentrations during infiltration, redistribution, and evaporation. In a later paper, Bresler *(29)* discussed anion movement under transient conditions. He included ionic diffusion, anion exclusion, mechanical dispersion, and osmosis.

Selim et al. *(169)* determined the redistribution of 2,4-D and water both numerically and experimentally in a field study. The solute concentration was monitored, at various depths, for an area of 1 m^2 using ceramic solution samplers connected to a vacuum pump. The water retention curve, $h(\theta)$, and the functional relationship between volumetric water content and unsaturated hydraulic conductivity, $K(\theta)$, were determined in the laboratory on undisturbed soil cores. The adsorption isotherm and the $D(v)$ relationship were determined as well in the laboratory. The water distribution was predicted fairly well, whereas agreement between measured and predicted distributions of the 2,4-D was only fair. These authors were able to show that the cumulative amount of irrigation water, and not the intensity of application, determined the penetration depth of the herbicide.

The above examples concern rather small studies for which homogeneous conditions might be expected. In larger field studies, this is not likely to be true. The macroscopic heterogeneity ofthe advection and dispersion terms, was illustrated in a large field study by Biggar and Nielsen *(22)*. They used an analytical solution of the advection-dispersion equation to fit the experimental data. In their field study, 20 plots were ponded with water containing Cl and NO_3. Solution samples were taken via extraction through porous ceramic cups. They observed a large variation in v and D for the various plots with both variables following a log-normal distribution.

Researchers who applied the conventional ADE under field conditions found significantly higher values for the dispersivity than for column experiments in the laboratory. Gillham et al. *(67)* gave values for α_L in the range of 10^{-4} to 10^{-2} m for laboratory experiments, while for heterogeneous sand or gravel aquifers, a value for the macrodispersivity of 1 to 100 m was found when the ADE was used to fit the field data. Biggar and Nielsen *(22)* obtained a value of 2.93

cm for α_L via regression of D versus v for 359 measurements at different depths and plots in case of vertical transport.

The concept of dispersion, as outlined in the introduction to Chapter III, does not account for macroscopic non-uniformities in the advection term, which is a major cause of mixing in the field. If one wants to proceed with the deterministic approach, a detailed knowledge of basic soil physical properties as $K(\theta)$ and $h(\theta)$ is needed. However, in view of the field heterogeneity of these soil properties, a considerable experimental effort is needed.

Stochastic Models

To circumvent the problem of a detailed quantification of the flow term, several researchers have chosen for a different approach by using stochastic models. These assume that the outcome of a series of events is uncertain. Due to the uncertainty of the mechanisms and the values of the parameters involved, a concentration distribution is described in terms of probability. These stochastic models can be of a mechanistic nature *(49, 137)* or a non-mechanistic nature *(90)*. In the first case, an attempt is made to describe the fundamental processes contributing to transport, whereas in the latter case no assumption is made for the mechanism behind the flow and transport processes.

Mechanistic models

Dagan and Bresler *(49)* assumed that the heterogeneity of the relevant soil properties could be described with random variables to predict the average solute concentration over an entire field as a result of a step input of a solute. The statistically homogeneous field, i.e., stationarity exists as discussed by Journel and Huijbregts *(89)*, represents an ensemble of columns, each with uniform soil properties. A generic notation of soil parameters, α_i, was used to describe the soil properties in the field, e.g., $\theta=\theta)z,t,\alpha_1,\alpha_2\ldots,\alpha_n)$. In order to describe the distribution of particular soil properties, a multivariate probability density function, $f=f(\alpha_1,\alpha_2,\ldots,\alpha_n)$, was used. The joint probability that $\alpha_1<A_1$, $\alpha_2<A_2,\ldots,\alpha_n<A_n$ at position x is given by:

$$P(A_1,A_2,\ldots,A_n,x)=\int^{A_1}\int^{A_2}..\int^{A_n} f(\alpha_1,\alpha_2..\alpha_n)d\alpha_1 d\alpha_2..d\alpha_n \qquad (6\text{-}1)$$

Because the medium is assumed to be statistically homogeneous, f does not depend on x. Since dispersion is supposed to be an insignificant factor for spreading compared to the heterogeneity of the advective term, transport in the vertical direction is governed by $v(z,t,\alpha_i)$ and $\theta(z,t,\alpha_i)$. The independent variables z and t are of a deterministic nature and α_i represents random hydraulic parameters that characterize $h(\theta)$ and $K(\theta)$. It should be noted that the condition of no interaction between different columns might be too stringent. In order to describe the hydraulic conductivity in terms of α_i, the scaling approach of Warrick et al. *(210)* was followed.

Because of the random nature of v and θ, the solute concentration is also a random variable. The dependency in the horizontal x,y-plane is also given in terms of $f(\alpha_i)$. The probability that $C<A$, in a plane with depth z and at time t, is:

$$P(z,t,A) = \int^{A} f(z,t,C)\, dA \qquad (6\text{-}2)$$

The concentration over the whole field can be described in terms of the frequency function, $f(\alpha_1,\alpha_2,..,\alpha_n)$, as well. The probability that $A<C(x,y,z,t)<A+dA$ is determined by the frequency function $f(z,t,C)$ where C varies between 0 and 1. This function is generally not known, but can be characterized by its moments:

$$\langle C(z,t)\rangle = \int_0^1 C\, f(z,t,C)\, dC \qquad (6\text{-}3)$$

$$\sigma_C^2\,(z,t) = \int_0^1 (C-\langle C\rangle)^2\, f(z,t,C)\, dC \qquad (6\text{-}4)$$

where <C> is the average concentration over the entire field in a given x,y-plane. The randomness of the flow term at the input boundary (rainfall, irrigation) was taken into account by introducing a random leaching rate, which is linked to the random behavior of the hydraulic conductivity to give a probability distribution, $P(v)$, for the pore water velocity.

Because dispersion/diffusion effects are neglected, the concentration profile obeys a step function ($C(z,t)=0$ or 1 for $z>vt$ and $z<vt$, respectively). The concentration over the field is the average of all individual column values:

$$\langle C(z,t)\rangle = 1 - P(z/t) = 1 - P(v) \qquad (6\text{-}5)$$

where $P(v)$ is expressed in terms of variables α_i. The field scale dispersion, caused by random changes in θ and v across the field, exceeds the mechanical dispersion at the pore scale. If desirable, the pore scale dispersion could be taken into account by introducing an 'effective' dispersion coefficient to make up for vertical heterogeneity. Dagan and Bresler *(49)* argued that the large transition zone, $(0< \langle C\rangle <1)$, which is commonly encountered under field conditions, can now be described correctly. When using the advection-dispersion equation an unrealistically high value for the dispersion coefficient would be needed.

Bresler and Dagan *(30)* compared the solute spreading effect, due to heterogeneity of soil properties, with Taylor's *(189)* theory of dispersion during flow in a capillary tube. The analogy is that (transverse) diffusion initially cannot annihilate the longitudinal concentration gradient caused by the advective term. However, for larger times, diffusion becomes the dominant process. For conditions normally encountered during infiltration, they concluded that only the advection term is needed to describe the transport process, but that for very large travel distances, e.g. 100 m, dispersion should be included. The model derived by Dagan and Bresler *(49)* was used by Bresler and Dagan *(30)* to predict solute concentrations for various rates of infiltration using data of Warrick et al. *(210)*. For a travel distance of 1 m, an effective dispersivity between 16.1 and 334.2 cm was found. If one had used the ADE, assuming Fickian dispersion, the transition zone (the width of the solute front) would grow proportional with $t^{1/2}$. However, Bresler and Dagan *(30)* found this zone to grow linearly with t. It should be noted that the work by these authors did not include an independent field study to validate the model by comparing measured and calculated solute distributions.

Bresler and Dagan *(31)* added pore scale dispersion, as measured in the laboratory, or the much larger average field value for dispersion, which reflects mainly heterogeneity of the profile, to the previously mentioned mechanisms of spreading (horizontal heterogeneity of soil properties and a variable infiltration rate). They concluded that the use of the conventional ADE, with constant coefficients, poorly predicted <C(z,t)> in a heterogeneous field. To model transport, one should focus on the variability of the hydraulic conductivity, the average rate of recharge, and the value for the (average) field dispersion. The influence of laboratory-measured pore scale dispersion is negligible, and the variability of recharge on the soil surface, provided that it is of modest value, had little influence on the predicted solute profiles.

In a subsequent series of papers, a more general approach was given for the stochastic modeling of unsteady flow and transport. Dagan and Bresler *(50)* derived a model for infiltration and redistribution in a heterogeneous field, which was applied to two spatially variable soils *(32)*. Bresler and Dagan *(33)* derived a model to predict solute transport using the results of their work on water flow modeling. Expected solute concentrations were calculated by using either an accurate numerical scheme or a simplified model, or by representing the variable field by an equivalent uniform field. The simplified model seemed to give quite accurate results in comparison with the "accurate" numerical model. Therefore, the authors concluded that improvement of numerical modeling, or the use of sophisticated theories for the hydrodynamic dispersion process, do not seem to have an appreciable improvement upon prediction of statistical moments in spatially variable fields. Using an equivalent uniform medium resulted in a much larger error. In the simplified model, the solute concentration was predicted with statistical moments rather than deterministic values. The advantage of this procedure is that, although it might not accurately predict concentrations at specific positions, the averaging procedure resulted in reasonably accurate concentrations for an entire field. This is often of more interest than specific values at given locations.

Non-mechanistic Models

A recent approach to model solute transport in the field ignores the actual mechanism of flow and transport and merely focuses on the solute concentration as a result of these unknown processes. In this "black box" approach, the transport and flow processes are represented by a transfer function, which characterizes systems whose internal mechanisms are unknown or unknowable *(90)*. This approach has been used for some time by hydrologists and engineers *(51)*.

Raats *(147)* applied the concept of transfer functions to describe advective solute transport during steady flow in soils. He described the movement of a certain water parcel in the course of time by focusing on the travel time, usually of primary interest in contamination studies. The position, $\vec{x}$, that a parcel, $\mathcal{X}$, occupies at time t can be given by:

$$\vec{x} = \vec{x}\,(\mathcal{X}, t) \tag{6-6}$$

with the velocity for $\mathcal{X}$:

$$\vec{v} = \left.\frac{\partial \vec{x}}{\partial t}\right|_{\mathcal{X}} \tag{6-7}$$

Denoting s as the arc-length along the streamline [L], Raats *(147)* characterized $\vec{v}$ by its magnitude, v, and unit tangent vector, $\vec{\tau}$:

$$v = \left.\frac{\partial s}{\partial t}\right|_{\mathcal{X}} \tag{6-8-a}$$

$$\vec{\tau} = \vec{v}/v \tag{6-8-b}$$

The travel time between two points on the streamline was given by:

$$t-t_o = \int_{s_o}^{s} \frac{1}{v}\, ds \tag{6-9}$$

where s and s_o are an arbitrary and a reference position, respectively. For steady flow without sinks and sources, Raats *(147)* obtained the following alternative expression for the travel time, making use of Eq.(6-8-b):

$$t-t_o = \frac{1}{(\theta v)_o} \int_{s_o}^{s} \theta \exp\left[\int_{s_o}^{s} \nabla\cdot\vec{\tau}\, ds\right] ds \tag{6-10}$$

where $(\theta v)_o$ is the flux at s_o. Raats *(147)* noted that the divergence of the unit tangent vector field, $\nabla\cdot\vec{\tau}$, is a characteristic of the flow pattern and a measure of the divergence or convergence of infinitesimal stream tubes. For such a stream tube, Raats *(147)* obtained:

$$A(s) = A_o \exp\left[\int_{s_o}^{s} \nabla\cdot\vec{\tau}\, ds\right] \tag{6-11}$$

where A is the area of the stream tube $[L^2]$. With $\theta vA=(\theta v)_o A_o$, he derived:

$$t-t_o = \frac{1}{(\theta v)_o A_o} \int_{s_o}^{s} \theta A \, ds \qquad (6\text{-}12)$$

The integral on the right-hand side corresponds to the total amount of water in the stream tube between s_o and s, whereas $(\theta v)_o A_o$ is the steady input flux. Eq.(6-12) gives the ratio of these quantities, being the travel time between s and s_o. Having established a link between the exact analytical expression for the travel time in terms of $\vec{\tau}$, and an expression for approximate graphical analyes, viz. Eq.(6-12), Raats *(147)* proceeded by considering more specific flow problems.

After evaluating the travel time for one parcel, the movement of collections of particles forming a surface was studied. This is useful to examine the effect of solute application as a pulse or step front. In order to predict whether the solute passes a certain point, e.g., the outlet of a soil column, the time needed to pass the column (transit time) and the time the solute resides in the column (residence time) need to be known. Therefore, Raats *(147)* used expressions for the transit time, τ, for each streamline and the residence time for a parcel in the system. In order to study the effect of a solute application, one can follow a collection of particles which enter the system simultaneously, forming an isochrone.

Obviously, the frequency distribution of transit times in the medium, consisting of various tubes, is of importance. It is also important to determine the contribution of each tube to the total transport. This can be done by monitoring the output concentration as a function of time. The cumulative transit time distribution function, q, is defined as the fraction of the streamtubes with transit times smaller than τ. At any time, a fraction q of the output will be "younger" than τ and a fraction (1-q) will be "older" than τ. The transit time density distribution function is equal to $d\tau/dq$, i.e., the frequency distribution of the volume of the streamtubes. It takes into account the rate of solute movement in a particular tube and the contribution of that tube to the total solute transport. Finally, the transfer function is the product of the input and transit time density distribution function. Raats *(148)* applied the theory to a number of flow patterns.

Jury *(90)* determined the solute concentration at various depths in the soil by means of an output function, which was the result of a solute flux applied at the soil surface, i.e., an input function. These two functions were related by using a transfer function, which could be determined by using measurements of the solute concentration at a particular depth. The concentration at other depths could be predicted with the transfer function. A brief derivation of the transfer function follows.

Instead of using time as the independent variable, Jury *(90)* used the cumulative amount of surface-applied water, I, as the independent random variable for solute transport at a particular location *(214)*. The probability that a tracer injected at the surface will reach a depth L after an amount of water I has been applied, is

$$P_L(I) = \int_0^I f_L(I')\, dI' \tag{6-13}$$

I' is a dummy integration variable and $f_L(I)$ is the probability density function, denoting that the injected tracer will arrive at depth L upon application of an amount of water between I and I+dI, i.e., a distribution of travel times. The inlet concentration is given by $C_{in}=C_o=\delta(I)$, a narrow pulse injected at I=0 at the soil surface. The average concentration, at z=L, for arbitrary variations in C_{in} and spatially uniform water input is given by:

$$C_L(I) = \int_0^{\infty} C_{in}(I-I')\, f_L(I')\, dI' \qquad (6\text{-}14)$$

where $f_L(I')$ is the probability of the solute reaching z=L between 'time' I' and I'+dI', i.e., the cumulative infiltration, and $C_{in}(I-I')$ is the concentration discharging at depth L if for a 'breakthrough time' I'. Note that this concentration remains equal to the inlet concentration, because front spreading is ignored.

The rate of water input is not uniformly distributed over the field, therefore a second probability density function, g(i), is needed to describe the variabilty of input rate for various locations. The relation between time and cumulative infiltration follows from i=dI/dt. The probability that a unit area of soil will receive a water input flux between i and i+di is ig(i). The probability that the solute reaches a depth z=L between t and t+dt depends on the soil properties (via $f_L(I)$) and on the input rate (via g(i)). This probability is given by the travel time density function, $h_L(t)$, which is the joint probability function:

$$h_L(t) = \int_0^\infty ig(i)f_L(it)\,di \tag{6-15}$$

The average concentration at a given depth L, for a spatially uniform input concentration $C_{in}(t)$, follows from:

$$C_{out}(t) = \int_0^\infty C_{in}(t-t')\;h_L(t')\;dt' \tag{6-16}$$

where t' is a dummy integration variable. Jury *(90)* assumed that the distribution of physical processes contributing to the density function, $f_L(I)$, between z=0 and z=L is equal for all depths. In that case, the probability that a tracer will reach a given depth z, after a cumulative infiltration $I=I_1$, is equal to the probability of reaching a reference depth z=L after a cumulative infiltration of $I=I_1L/z$:

$$P_z(I) = P_L(IL/z) = \int_0^{IL/z} f_L(I')\;dI' \tag{6-17}$$

and by combining Eq.(6-15) and (6-16), the concentration for a spatially variable water application is given by:

$$C(z,t) = \int_0^\infty C_{in}(t-t') \int_0^\infty \frac{L}{Z}\;ig(i)f_L(it')\;di\;dt' \tag{6-18}$$

for a water application I=it. To obtain f_L, a calibration at one depth is necessary. For this purpose, Jury et al. *(93)* obtained soil solution samples by vacuum extraction at a depth of 30 cm at 14 locations. Usually a lognormal distribution seemed to fit $f_L(I)$, but other functional relationships could be used as well. Once $f_L(I)$ was obtained, the performance of the model was tested by comparing predicted values of $C_{out}(z,I)$ with measured values at other depths than for which the model was calibrated. Good agreement was found between results obtained by using the transfer function and experimental values. It is not clear how well the model works for stratified soils. The model also used for unsaturated conditions *(92)*.

Concluding Remarks

A review of some modeling approaches was presented by Addiscott and Wagenet *(4)*, who concluded that among the many models available, few have been exhaustively tested under field conditions. Tests by others than the original authors, under different circumstances, have been rare.

Most analytical and numerical models are deterministic and mechanistic by nature. Because of the spatial variability of soil properties in the field, stochastic models seem to be more attractive. One such stochastic model, involving transport of a reactive solute, was presented by van der Zee and van Riemsdijk *(193)*. For fundamental laboratory studies, the mechanistic deterministic model is the most appropriate. Combination of the deterministic ADE with a stochastic flow model could be a useful approach in future field studies.

Of course, many more efforts have been made to model water flow for field conditions. Some involved scaling *(180)*, others incorporated geostatistics or the theory of stochastic processes *(99, 100, 114, 208, 216, 217, 218)*. Charbeneau *(38)* applied the kinematic theory, i.e., a functional relationship between flux and water content. A similar theory was developed for solute transport. The kinematic waves can be distinguished in self sharpening, during infiltration, and self spreading, during drainage.

Although much of the material already discussed includes transport during unsaturated flow, some specific work appearing in the soil science literature is discussed in this section. In particular, some of the laboratory experiments are reviewed. A distinction is made between steady state and transient flow conditions. A few approaches to control the flow and/or water content for steady state conditions will be mentioned as well.

Steady Flow

One of the first results on miscible displacement during unsaturated flow was reported by Nielsen and Biggar *(120).* They observed that the magnitude of water not readily displaced, the hold back, increased with desaturation. The inclusion of dispersion phenomena in the transport equation seems more appropriate for unsaturated than for saturated flow conditions. Biggar and Nielsen *(20)* emphasized the role of diffusion, pointing out that, although mechanical dispersion will decrease at lower velocities, the process of molecular diffusion tends to enhance spreading.

Krupp and Elrick *(104)* explained tailing during unsaturated steady flow with the 'stagnant liquid concept'. According to these authors, the dispersion coefficient is not related to θ in a simple manner. Variation in the sequences of fully filled and partially filled pores and transport in the surface films contribute to spreading. Elrick et al. *(58)* observed that the apparent dispersion coefficient increased with decreasing pore-water velocities in a saturated glass bead medium at low flow velocities. Eq.(3-44) did not seem to describe the dispersion coefficient accurately in this case. Also, at very low water contents, the variance in pore-water velocity is likely to vanish since there is no pore sequence for liquid flow. Thus, the amount of spreading is reduced *(104)*.

Yule and Gardner *(219)* studied both longitudinal and transverse dispersion under unsaturated conditions. Transverse dispersion, i.e., diffusion, gains importance during unsaturated flow due to the lower pore water velocity. The value for the transverse dispersion coefficient was found to be nearly independent of pore water velocity.

Van Genuchten and Wierenga *(202)* noted that more tailing is to be expected in unsaturated sorbing media. Not only will the relative amount of stagnant water increase, the fraction of sorption sites located in the stagnant region will increase as well. Among others, they used the concept of a mobile and immobile region of the liquid phase to formulate the transport equations for unsaturated soils. De Smedt and Wierenga *(57)* observed early breakthrough and prolonged tailing during unsaturated conditions. Dispersion coefficients obtained from saturated displacement experiments, with the same pore-water velocity, could be used to fit the results from unsaturated experiments if the transport equation accounted for mobile and immobile water. When this distinction was not made, dispersion coefficients many times larger than for saturated conditions were needed to fit the experimental results.

Gupta et al. *(77)* measured Cl concentrations within an unsaturated glass bead medium. The occurrence of stagnant water qualitatively explained the asymmetry of the experimental concentration profile. By varying the velocity and water content independently, using different gravitational heads, Gupta et al. *(78)* found that D increased with v and generally decreased with increasing θ. However, no functional relationship was derived.

Awad *(11)* examined dispersion phenomena in a medium fine sand. He found that the hydrodynamic dispersion coefficient appeared to increase with decreasing water content, but found no basis for the presence of a mobile and stagnant region of the liquid phase. A theoretical investigation of the relationship between the hydrodynamic dispersion coefficient and water content was pursued, but not established.

Transient Flow

This section briefly reviews transport during infiltration, the development of leaching strategies and the exploration of the dependence of D on v. Wierenga *(214)* showed that transient flow could be represented by an effective steady state flow to describe solute transport. This simplifies considerably the task of obtaining a correct flow term to predict solute movement considerably *(38)*.

Kirda et al. *(95, 96)* determined the displacement of chloride during infiltration with chloride-free water in soil columns, both experimentally and theoretically. For a given amount of cumulative infiltration, the Cl salt was leached more efficiently (i.e., with less dispersion, and to a relatively greater depth) for lower initial and surface water contents than for higher water contents. Frequent small quantities of irrigation water seem to be more effective in displacing the salt than larger, less frequent water applications. Warrick et al. *(209)* observed that the water content at the soil surface determines the propagation of the solute present in the irrigation water, while the influence of the initial water content in the remainder of the soil profile was shown to be small. For equal quantities of water infiltrated, the depth of the maximum solute concentration increases with decreasing surface water content.

Smiles et al. *(179)* investigated the absorption of a KCl solution by initially rather dry soils. They observed that for a low Peclet-number, the dispersion coefficient, D_s, was virtually velocity-independent and that piston displacement of the solute occurred. Smiles and Philip *(178)*, using low initial salt and water contents, noticed that the Cl concentration profile was somewhat asymmetrical due to changes in the advection-term across the front. However, the prediction of the solute front was relatively insensitive to changes in D_s. Quantitatively, diffusion and dispersion are identical. Smiles et al. *(177)* transformed the transport equation to describe (transient) absorption by using a constant surface flux v_o. The solution, expressed in terms of position, v_ox, and time, v_o^2t, was unique, suggesting that D_s is velocity-independent. Smiles and Gardiner *(176)* also observed close to piston displacement of the solute in a clay soil. Thin films of water on the clay surface were not accessible to the invading solute. The Cl front was located ahead of the piston front, which was attributed to anion exclusion. Bond *(25)* analytically solved transport of a solute, applied as a pulse, during unsteady flow.

He used a velocity dependent D. Experimentally and analytically determined curves matched fairly well for ^3H_2O but not for Cl. No explanation could be offered for the poor prediction of the Cl profile. The initial volumetric water content was 0.176.

Finally, Grismer *(69)* studied the absorption of water containing NaI or $SrCl_2$ by a silt loam. The dispersion coefficients, determined according to Smiles et al. *(179)*, depended on θ in a way similar to the diffusion coefficient. Complete displacement of the initial water was observed, although for the initial water content of 0.124, a higher flux was required than for an initial water content of 0.035 to achieve complete displacement.

Apparently, solute transport during steady flow differs from transport during transient flow, at least for infiltration processes. In the latter case, the dispersion coefficient is reported to be virtually independent of the velocity and a complete displacement of the resident solution occurs (piston displacement). Since the solute acts as a tracer of relative water movement, it is assumed that the same holds for the flow process in general.

Experimental Considerations

A major task when obtaining breakthrough curves for steady, unsaturated flow conditions is the independent control of water content and pore water velocity. Because both factors influence dispersion, it would be desirable to vary them independently during displacement studies.

The driving force for water flow is a hydraulic head gradient, ∇H, with H given by:

$$H = h + z \tag{7-1}$$

where h is the pressure head [L] and z the gravitational head [L]. The osmotic head is ignored in this expression. The flow of water is given by Darcy's law:

$$J_V = -K(\theta)\ \nabla H \tag{7-2}$$

where $K(\theta)$ is the hydraulic conductivity $[LT^{-1}]$. It follows from Eq.(7-1) and (7-2) that the water flow can be manipulated directly by adjusting h or z, or indirectly via the water content which influences K and h.

Nielsen and Biggar *(120)* used hanging water columns and a negative air pressure at the outlet to obtain a constant average water content and flowrate. The glass bead medium required a change in head of only 3 cm of water to obtain identical flowrates at full and approximately half of the saturated water content. Fritted glass plates, which have a negligible exchange capacity, a large capillary conductivity, and a narrow pore size distribution, were used to maintain unsaturated conditions.

Elrick et al. *(58)* and Krupp and Elrick *(104)* regulated the water content by placing a perforated sample holder in a pressure chamber, while the desired flowrate was obtained, with a constant volume pump and a head tube. Both ends of the sample were in close contact with a cellulose acetate membrane filter, supported by a porous screen and a stainless steel end cap containing three plastic nipples. The sample and pressure chamber were placed on a balance to allow continuous monitoring of the sample weight and hence water content. A driving head, equal to the sample length, was established by increasing the air pressure in the chamber(unit gradient). The gradient in pressure head was equal to zero; a constant water content was obtained throughout the sample. This meant that only one flowrate was possible for each water content.

Yule and Gardner *(219)* stated that variations in the hydraulic gradient can only be achieved by variations in water content. This is not quite true, as will be discussed shortly, but it accurately points out the problem. Their experimental setup consisted of a rectangular plexiglasss soil container with an inflow and outflow control section. Each section consisted of 11 one-bar porous ceramic tubes. At the inlet, the inflow in each tube was controlled by a Mariotte bottle and at the outlet, the outflow from each tube was collected in a plastic vial maintained under suction controlled with a bubbling tower. A unit gradient (gravitational head) was established to obtain a uniform moisture content throughout the column.

Gupta et al. *(77)* used tilted soil columns to study dispersion phenomena in an unsaturated glass bead medium. Solutions with different KCl concentrations were applied with a pump. The water flow could be adjusted, via changes in z, without affecting the water content, over a range of velocities between 0.0168 and 0.14 cm min^{-1}. However, their approach does not seem to be very practical.

Awad *(11)* used a two phase steady-state flow system to obtain independent control of the volumetric water content and pore water velocity. A horizontal system was used. Awad *(11)* proposed to use changes in the pneumatic head to vary the flowrate. The pressure head is given by:

$$h = h_m + h_a \tag{7-3}$$

where h_m is the matric pressure head, which governs the volumetric water content, and h_a is the pneumatic head which does not influence the water content *(101)*. Hence, by manipulating h_a, the flow can be regulated (with a pump) without affecting the water content. A flow cell was constructed with fritted glass plates. The pneumatic head was regulated by maintaining a gradient in air pressure in the medium between the plates. A constant flowrate of water was established with a pump. Water content and bulk density were measured with a gamma attenuation system. The hydraulic head was obtained by using tensiometers connected to pressure transducers. The method could not be used at very low water contents, due to the occurence of a high resistance boundary layer between plates and medium.

VIII. MULTI-PHASE TRANSPORT

A logical extension of the previously discussed unsaturated transport is the study of transport of immiscible fluids. Multiphase transport involves vapor and liquid phase or various liquid phases. There is a need to study these processes in order to predict movement of (volatile) substances such as pesticides, oil products, and other (organic) compounds. First, pesticide movement in liquid and vapor phase will be discussed based on the work by Jury et al. *(91)*, followed by a brief mention of research in the area of immiscible liquid transport.

Transport in Vapor and Liquid Phase

Jury et al. *(91)* determined the loss of pesticide via volatilization and diffusion in the vapor phase and via advection and diffusion in the liquid phase. Their investigation involved the movement of triallate in soil samples placed in a volatilization chamber at relative humidities of 50 and 100%. The vaporized triallate was collected on polyurethane plugs.

The total concentration of the solute in the soil was given by:

$$C_t = \rho_b S + \theta_\ell C_\ell + \theta_g C_g \qquad (8\text{-}1)$$

where C_t is the total concentration expresses as mass of solute per volume of soil $[ML^{-3}]$, S is the adsorbed concentration, expressed as mass of solute per mass of soil [MM^{-1}], C_ℓ and C_g are liquid and gas concentration, respectively, expressed as mass of solute per volume of fluid [ML^{-3}], and θ_ℓ and θ_g are the liquid and gas content, respectively, expressed as volume of fluid per volume of soil [L^3L^{-3}] . The solute flux was expressed as

$$J_s = -D_g \frac{\partial C_g}{\partial x} - D_\ell \frac{\partial C_\ell}{\partial x} - J_V C_\ell \tag{8-2}$$

where J_s is the solute flux, D_g is the gas diffusion coefficient [L^2T^{-1}], D_ℓ is the liquid diffusion coefficient [L^2T^{-1}] and J_V is the volumetric water flux [$L^3L^{-2}T^{-1}$]. It should be noted that advective transport in the vapor phase was considered to be negligible. Under some circumstances, such as non-isothermal flow, this might not be justified. The continuity equation for one-dimensional transport in the absence of a sink/source term is:

$$\frac{\partial C_t}{\partial t} + \frac{\partial J_s}{\partial x} = 0 \tag{8-3}$$

Eq.(8-1) and (8-2) can be substituted in Eq.(8-3) to describe mass transport. In order to solve the resulting equation, it should contain only one dependent variable, viz. a concentration in a particular phase. The following relationships are useful for this purpose:

1) Gas and liquid concentration are related by Henry's law

$$C_\ell = K_H C_g \tag{8-4}$$

where K_H is the partition coefficient. Eq.(8-4) is only valid for dilute solutions.

2) The adsorption isotherm is linear, which seems reasonable for the trace amounts of solute encountered:

$$q = aC_\ell + b \tag{8-5}$$

Some additional assumptions were made by Jury et al. *(91)* to rewrite Eq.(8-3) in terms of C_g:

$$\varepsilon \frac{\partial C_g}{\partial t} = D_e \frac{\partial^2 C_g}{\partial x^2} + v_e \frac{\partial C_g}{\partial x} \tag{8-6}$$

where $\varepsilon = \rho_b aK_H+\theta_\ell K_H+\theta_g$, $D_e=D_g+K_HD_\ell$ and $v_e=J_VK_H$. For appropriate boundary and initial conditions, Eq.(8-6) can be solved analytically for C_g. Of course, due to hysteresis and non-equilibrium, Eq.(8-4) and (8-5) might not be representative. This would subsequently influence the accuracy of the solutions of Eq.(8-6).

Jury et al. *(91)* considered two cases, viz. transport by diffusion only (J_V=0) and transport by advection-diffusion (J_V≠0), which obviously led to different solutions for C_g. An expression for the solute flux at the surface, $J_s(0,t)$, was found by using Eq.(8-2), in conjunction with the solution for C_g and Eq.(2-4). The cumulative loss was then obtained via integration of the flux over time. The experimentally measured cumulative loss was used to determine the effective diffusion coefficient, D_e. Knowledge of this D_e enables one to make theoretical predictions of the mass flow. It was shown that advection (evaporation) caused the vapor loss to increase slightly. Loss of the pesticide was mainly due to depletion from the upper soil layer. Because of the increase in the concentration gradient, diffusion becomes more important close to the soil surface.

Transport in Immiscible Liquid Phases

Recently, an increasing amount of research has been initiated in the area of non-aqueous phase liquids, NAPL *(2, 129)*. The situation is slightly different for this type of flow than for flow in systems containing a single liquid phase. Advective transport plays a role in all phases, and knowledge of the flow properties for each phase is needed. Multiple phase flow is, among others, discussed by Scheidegger *(165)*. Once the flow problem has been solved, an attempt can be made to describe transport. The distribution coefficients of the solute between the various phases, as well as in some cases the exchange and adsorption parameters, need to be known. In some instances, the immiscible fluids may consist of multiple components with distinct coefficients describing the distribution between the various fluids *(44)*. Baehr and Corapcioglu *(13)* studied transport of the various components of gasoline for which they predicted quite different travel times. Numerical solutions for multiphase flow and transport can be found in Huyakorn and Pinder *(86)*.

Abriola and Pinder *(2, 3)* treated the simultaneous transport of organic compounds in three phases: the non-aqueous, aqueous, and vapor phases. These authors derived a system of three non-linear partial differential equations with five independent variables (i.e., two capillary pressures and three mass fractions). The capillary pressures occur as a result of interfacial tension. The mass balance equation for a particular species within a certain phase contains a storage term, an advective and autonomous flux, a sink or source term, and exchange resulting from a phase change or interphase diffusion. The mass balance needs to be derived for all species in each phase. Often a number of terms can be neglected, like the advective transport in the gasphase as mentioned before. These authors did not consider the (ad)sorption of the solute to the solid phase. An implicit numerical model was used to solve the resulting system of non-linear equations with Newton-Raphson iteration. The study was restricted to one-dimensional tranport. The primary mechanism by which the volatile component was transported through the medium was via gas diffusion. Since it was assumed that local equilibrium existed between gas and liquid phases at all times, the concentration in the liquid phases changed accordingly.

IX. EPILOGUE

It is hoped that this review demonstrated that the problem of solute transport is a very broad one with many interesting aspects. Combined with the urgency of ground water pollution, it is therefore not surprising that a great deal of work has been done in this area. Obviously, it was impossible to cover all aspects of transport modeling and to discuss fundamental processes in great detail in a review like this. Instead, it was restricted to a discussion of some basic processes which affect transport. These processes are of a chemical, physical, and biological nature, which explains why often an interdisciplinary approach is needed (Chapter I). It should be noted that, because of thisinterdisciplinary nature, the terminology and the focus of the research vary widely. Some useful references were provided in the discussions on the basic transport equation (Chapter II and III). The reader is encouraged to consult the more advanced and comprehensive discussions in the literature.

The principles of transport, i.e. using the principle of conservation of mass, can be applied to transport under "complicating" conditions: with non-linear exchange (Chapter IV), in structured and layered media (Chapter V), during unsaturated flow (Chapter VII), and for multi-phase systems (Chapter VIII). Although the fundamental processes are essentially the same, these (and other) conditions offer challenges for additional research. As our understanding of transport progresses, new questions will undoubtedly arise. Because this report's objective was to formulate transport problems, or at least refer to it, relatively little attention was paid to the mathematical, in particular the numerical, solution of transport problems. Many good references exist on the mathematical tools which are available to solve transport problems.

The ultimate goal of much of the reasearch is geared towards a better understanding of solute transport in natural porous media. Some of the basic research might be helpful to solve "real problems," some might not. Chapter VI pointed out that many of the traditional deterministic models are of limited value. It is clear that modeling should be accompanied by measurements, which makes such studies very challenging for researchers because of the amount of effort involved (time, money, expertise). Furthermore, some of the research findings are not applicable under different conditions.

To put research efforts in the area of solute transport in perspective, it is noted that many social and economical aspects are involved as well. Some pollutants can safely be dispersed in large water bodies, whereas others need to be contained. For some materials (e.g., radioactive waste), one might argue that nonproduction and nonuse is the only sensible approach. The short term economic benefits of, for instance, agricultural chemicals, do not warrant their use in view of possible adverse effects in the long term. Transport modelers can provide part of the information needed to make a rational decision. Finally, in light of all the difficulties associated with transport modeling, it seems only logical to improve management practices in dealing with dangerous chemicals and to educate potential developers, producers, and users. This requires input from researchers in the area of solute transport as well.

NOTATION

This section contains the description and units of most of the symbols used in this review. Because the notation in the literature is not uniform, occasionally some unusual symbols were used or symbols were used twice.

Symbol	Description	Units
a	(aggregate) radius	L
a_k	chemical activity of species k	
B	Brenner number (column Peclet number)	
C	concentration of solute in liquid phase	ML^{-3}
$\bar{C}$	dimensionless concentration	
$\bar{C}(x,s)$	concentration in Laplace domain	ML^{-3}
C_a	local concentration inside aggregate	ML^{-3}
C_e	dimensionless exit concentration	
C_{ex}	exit concentration	ML^{-3}
$\bar{C}_f$	flux-averaged concentration	ML^{-3}
C_g	concentration of solute in gas phase	ML^{-3}
C_i	initial concentration	ML^{-3}
C_{in}	inlet concentration	ML^{-3}
C_ℓ	concentration of solute in liquid phase (=C)	ML^{-3}
C_m	mean concentration	ML^{-3}
C_{im}, C_{mo}	C for immobile and mobile region	ML^{-3}
C_M	molar concentration of species	ML^{-3}
C_M^*	mole fraction of species k (C_{Mk}/C_M)	
C_o	concentration of feed solution (eluent)	ML^{-3}
C_{out}	outlet concentration	ML^{-3}
C_t	total mass of solute per bulk volume	ML^{-3}

Symbol	Description	Units
$\bar{C}_t$	time average of C	ML^{-3}
C_T	total concentration in liquid phase	ML^{-3}
$\bar{C}_V$	volume averaged concentration	ML^{-3}
d	depth or characteristic particle size	L
D, **D**	coefficient of (hydrodynamic) dispersion	L^2T^{-1}
D^*	effective (retarded) value for D (=D/R)	L^2T^{-1}
D_{dis}	coefficient of mechanical dispersion	L^2T^{-1}
D_e	(effective) coefficient of molecular diffusion	L^2T^{-1}
D_{eim}	D_e for immobile region	L^2T^{-1}
D_{emo}	D_e for mobile region	L^2T^{-1}
D_g	gas diffusion coefficient	L^2T^{-1}
D_ℓ	liquid diffusion coefficient	L^2T^{-1}
D_L	coefficient of longitudinal dispersion	L^2T^{-1}
D_{im}, D_{mo}	D for immobile and mobile region	L^2T^{-1}
D_o	coefficient of molecular diffusion in the free liquid	L^2T^{-1}
$D_s(\theta)$	dispersion coefficient (=$\theta D(\theta)$)	L^2T^{-1}
D_T	coefficient of transverse dispersion	L^2T^{-1}
$D_w(\theta)$	soil water diffusivity	L^2T^{-1}
f	probability density function	
$f_L(I)$	probability density function for movement in a soil as	
f	fraction of sorption sites in direct contact with the mobile region	
f'	slope of exchange isotherm (dS/dC or dY/dX)	
F	fraction of adsorption sites belonging to "type-1" (=S_1/S)	
F	dimensionless rate parameter (k_2L/v)	
g	acceleration due to gravity	L^2T^{-1}
g	geometry factor	
g(i)	probability density function for infiltration	
G	Gibbs free energy	J mol^{-1}

Symbol	Description	Units
$h(\theta)$	soil water retention function	
h	pressure head or height	L
h_a	pneumatic head	L
$h_L(t)$	travel time density function	
h_m	matric head	L
H	hydraulic head	L
i	infiltration rate	LT^{-1}
I	cumulative infiltration	L
J_D	diffusive/dispersive mass flux	$ML^{-2}T^{-1}$
J_{im}, J_{mo}	cumulative diffusive flux in immobile and mobile region	ML^{-2}
J_s	total solute mass flux	$ML^{-2}T^{-1}$
J_V	volumetric water flux (Darcy flux)	LT^{-1}
k	rate coefficient	T^{-1}
k	permeability	L^2
k_a	rate constant in the aggregate	T^{-1}
$K(\theta)$	hydraulic conductivity	LT^{-1}
K	equilibrium constant	
K_d	distribution coefficient	L^3M^{-1}
K_{dim}	K_d for immobile region	L^3M^{-1}
K_{dmo}	K_d for mobile region	L^3M^{-1}
K_D^{mi}	distribution ratio of ions between mobile and immobile region	
K_H	partition coefficient in Henry's law	
K_{jk}	exchange coefficient	
L	column or mixing length	L
L_D	effective diffusion/dispersion length	L
L_{dif}	diffusion length	L
L_{dis}	dispersion length	L
L_r	dispersion length due to stagnant phase effect	L
m_0	total mass of solute per area of column	ML^{-2}
m_p	p-th moment of temporal or spatial distribution	

Symbol	Description	Units
$\overline{m}_p$	depth-averaged moment	
n	number of moles	
N[ ]	normal distribution function	
N_i	diffusive molar flux	$ML^{-2}T^{-1}$
P	probability	
$\mathcal{P}$	pressure	$ML^{-1}T^{-2}$
P or Pe	Peclet number (vd/D_e, vL/D)	
q	concentration of solute in adsorbed phase	ML^{-3}
q'	differential capacity of exchanger ($=dq/dC$)	
q_{im}	q for immobile sites	ML^{-3}
r	radial distance	L
$\mathcal{R}$	gas constant	J mol^{-1}K^{-1}
R	retardation factor	
R_{im}, R_{mo}	R for immobile and mobile region	
R_a	aggregate radius	L
s	position along a streamline	L
S	concentration of solute in adsorbed phase on a mass basis	MM^{-3}
S_{im}, S_{mo}	S for immobile and mobile region	MM^{-3}
S_T	total solute concentration in adsorbed phase	MM^{-3}
t	time	T
$\mathcal{T}$	temperature	K
T	number of pore volumes (vt/L)	
u	velocity in a free liquid	LT^{-1}
u_o	maximum value for u	LT^{-1}
v	pore-water velocity	LT^{-1}
v^*	effective (retarded) velocity (v/R)	LT^{-1}
V	volume	L^3
V	volume per unit cross sectional area	L^3L^{-2}
v_{mo}	pore-water velocity in mobile region ($v\theta_T/\theta_{mo}$)	LT^{-1}
v_m	mean	
w	width	L

Symbol	Description	Units
x	Cartesian coordinate in direction of flow	L
X	width	L
x_C	position at which a particular concentration resides	L
X_k	dimensionless concentration in liquid phase for species k ($=C_k/C_T$)	
x_p	equivalent depth of penetration of a solute front	L
y	space coordinate	L
Y_k	dimensionless concentration in adsorbed phase for species k ($=S_k/S_T$)	
z	space coordinate	L
z	gravitational head	L
Z	dimensionless distance (r/a, x/L)	
α	mass transfer coefficient	T^{-1}
α_i	random hydraulic parameter	
α_L	longitudinal dispersivity	L
α_T	transversal dispersivity	L
β	gravity segregation factor	
γ	activity coefficient	
γ_w, γ_s	rate constant for production in liquid and adsorbed phase	$ML^{-3}T^{-1}$ T^{-1}
δ	Dirac delta function	
η	viscosity	$ML^{-1}T^{-1}$
θ	volumetric water content or volume fraction	L^3L^{-3}
θ_{im}, θ_{mo}	θ for immobile and mobile region	L^3L^{-3}
θ_ℓ, θ_g	volume fraction in liquid and gas phase	L^3L^{-3}
θ_T	total volume fraction	L^3L^{-3}
λ	tortuosity factor	
μ_k	chemical potential of species k	J mol^{-1}
μ_k^o	μ_k in a chosen standard state	J mol^{-1}
μ	mean of spatial (μ_x) or temporal (μ_t) distribution	L or T

Symbol	Description	Units
μ_w, μ_s	rate constant for first order decay in liquid and adsorbed phase	T^{-1}
ν_k	valence of species k	
ξ	Cartesian coordinate in a moving system	L
ρ	density	ML^{-3}
ρ_b	dry bulk density	ML^{-3}
σ	standard deviation of spatial (σ_x) or temporal (σ_t) distribution	L or T
σ'	relative spread in velocities	
τ	(transit) time	T
$\vec{\tau}$	unit vector field ($\vec{v}/v$)	
Φ	formation factor	
ψ	probability function	
ω	Boltzmann variable ($x/\sqrt{t}$)	$LT^{-1/2}$

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