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Mass Transfer Studies in Sorbing Porous Media I. Analytical Solutions[1]

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ABSTRACT

An analytical solution is presented for the movement of chemicals through a sorbing porous medium with lateral or intra-aggregate diffusion. The liquid phase in the porous medium is divided into mobile and immobile regions. Diffusional transfer between the two liquid regions is assumed to be proportional to the concentration difference between the mobile and immobile liquids. Sorption processes in both the dynamic and stagnant regions of the medium are assumed to be instantaneous and the adsorption isotherm is assumed to be linear. The analytical model derived here describes the extensive tailing observed during flow through an unsaturated, aggregated sorbing medium and explains the often observed early breakthrough of chemicals in the effluent.

Additional Index Words: **intra-aggregate diffusion, adsorption, analytical solution, immobile water, and miscible displacement.**

DISPLACEMENT STUDIES have become important tools in soil physics, particularly for predicting the movement of pesticides, nitrates, heavy metals, and other solutes through soil. These studies can provide valuable information about both the behavior of a chemical in a porous medium (diffusion, dispersion, anion exclusion, adsorption, or exchange processes), and about the medium itself (pore size distribution, aggregation). Much of the work which has been done to date can be found in reviews by Biggar and Nielsen (1967), Fried and Combarnous (1971), and by Bear (1972). Attempts to formulate displacement processes quantitatively have been based generally on the convective-dispersive equation (Lapidus and Amundson, 1952)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v_o\frac{\partial C}{\partial z} \qquad [1]$$

where C is the concentration (meq/cm^3), D is the dispersion coefficient (cm^2/day), v_o is the pore-water velocity (flux divided by the volumetric water content θ; cm/day), z is the distance (cm), and t is time (days). Except for small values of v_o/D, all solutions of Eq. [1] predict nearly sigmoid or symmetrical concentration distributions (Coats and Smith, 1964; Gershon and Nir, 1969). However, several experimental studies have shown strongly nonsigmoid and asymmetrical distributions, either vs. depth (Aylmore and Karim, 1970) or as effluent curves (Kay and Elrick, 1967; Green et al., 1972). Following others (cf. Giddings, 1963), we will use furtheron the word "tailing" to indicate the appearance of such highly asymmetrical or nonsigmoid concentration profiles. Tailing has been observed under several experimental conditions:

1) *Unsaturated Flow*—Nielsen and Biggar (1961) noted considerable tailing with decreasing water content at approximately the same flow velocity. They argued that under unsaturated conditions the larger pores are eliminated for transport and that the proportion of water which does not readily move within the soil is increased. This water has been identified as dead, stagnant or immobile water (Turner, 1958; Coats and Smith, 1964; Deans, 1963). A decrease in water content increases the fraction of air-filled macro-pores, resulting in the creation of additional dead-end or blind pores which rely on diffusion processes to attain equilibrium with the displacing solution (Gupta et al., 1973).

2) *Aggregated Media*—Soils are composed of slowly and rapidly conducting pore sequences. Aggregates have many micropores in which displacement is dependent upon diffusion, since convection in these smaller pores is usually negligible. This results in slow and incomplete mixing and hence tailing, even under saturated conditions. In large aggregates the amount of immobile water increases while the diffusion pathway becomes longer, resulting in

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breakthrough curves with more and longer tailing. (Biggar and Nielsen, 1962; Green et al., 1972; McMahon and Thomas, 1974).

3) Pore-water Velocity—Several experimental studies indicate that tailing becomes more pronounced as the pore-water velocity decreases (Biggar and Nielsen, 1962; Villermaux and van Swaay, 1969; Skopp and Warrick, 1974).

From the discussions above it is evident that solutions of Eq [1] may not always give an accurate description of the physical processes which occur in aggregated and/or unsaturated soils. Several attempts have been made recently to account for the observed tailing. Deans (1963) modified eq. [1] to include transfer by diffusion from dynamic flowing regions to stagnant zones, but neglected longitudinal dispersion. He used a first-order mass transfer equation to describe this diffusional exchange. Similar concepts were proposed by Turner (1958), Gottschlich (1963), and more recently by Skopp and Warrick (1974), who each described the diffusional transfer of material from dynamic to stagnant fluid by the diffusion equation. Of immediate interest in our study is the model described by Coats and Smith (1964), who expanded Deans' (1963) model to include longitudinal dispersion. Their model uses the following equations:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial z^2} - v_m \theta_m \frac{\partial C_m}{\partial z} \quad [2]$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) \quad [3]$$

where θ_m and θ_{im} are the fractions of the soil filled with mobile and stagnant water, respectively (cm^3/cm^3); C_m and C_{im} are the concentrations (meq/cm^3) in both the mobile and stagnant regions; v_m is the average pore-water velocity in the mobile liquid; and α is a mass transfer coefficient (day^{-1}). Equation [2] is the same as Eq. [2] of Passioura (1971). Solutions of Eq. [2] and [3] for a semi-infinite column were obtained by Coats and Smith (1964) and by Villermaux and Swaay (1969), the latter authors using a tracer pulse input, approximated by the Dirac δ-function. Bennet and Goodridge (1970) obtained the solutions for a finite column. The last three studies mentioned here each obtained excellent descriptions of experimental concentration-time curves.

When a sorbing porous medium is considered, an additional term must be added to the left-hand side of Eq. [1] to account for the interaction between the chemical and the medium. If the sorbed concentration is denoted by S (μg/g soil), the general transport equation can be written in the following form:

$$\frac{\rho}{\theta} \frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v_o \frac{\partial C}{\partial z} \quad [4]$$

where ρ is the bulk density (g/cm^3). Equation [4] is an extension of Eq. [1] in that only a sorption term is added. Because of this, the limitations of Eq. [4] in describing the movement of a chemical through an unsaturated, aggregated sorbing medium should be similar to those found for Eq. [1] in a nonsorbing medium.

Solutions of Eq. [4] can be obtained by specifying the rate of adsorption ($\partial S/\partial t$). When equilibrium is assumed between adsorbed and solution concentration, the Freundlich isotherm may be used. This equation is as follows:

$$S = KC^N \quad [5]$$

where K and N are constants. Substitution of Eq. [5] into Eq. [4] yields a transport equation in terms of one dependent variable, C:

$$\frac{\partial C}{\partial t} = \frac{1}{R}\left(D \frac{\partial^2 C}{\partial z^2} - v_o \frac{\partial C}{\partial z}\right) \quad [6]$$

where the retardation factor R is defined as (Hashimoto et al, 1964)

$$R = 1 + \rho K N C^{N-1}/\theta. \quad [7]$$

Instead of equilibrium, several authors have assumed a kinetic approach towards equilibrium. A widely quoted model stems from Lapidus and Amundson (1952), who proposed the following rate expression:

$$\frac{\partial S}{\partial t} = \alpha(KC - S). \quad [8]$$

Solutions of Eq. [4] and [8] for a semi-infinite medium were obtained by Lapidus and Amundson, using a step input in concentration, and by Lindstrom and Narasimhan (1973) for an initially distributed chemical. Note that Eq. [4] and [8] are mathematically similar to Eq. [2] and [3].

Kinetic models derive their rationale from the assumption that the rate of adsorption is slow compared to the rate at which the chemical moves through the soil. In an earlier study (van Genuchten et al, 1974), experimental data were compared with predictions based on Eq. [4], using both the equilibrium and the kinetic models (Eq. [5] and [8], respec-

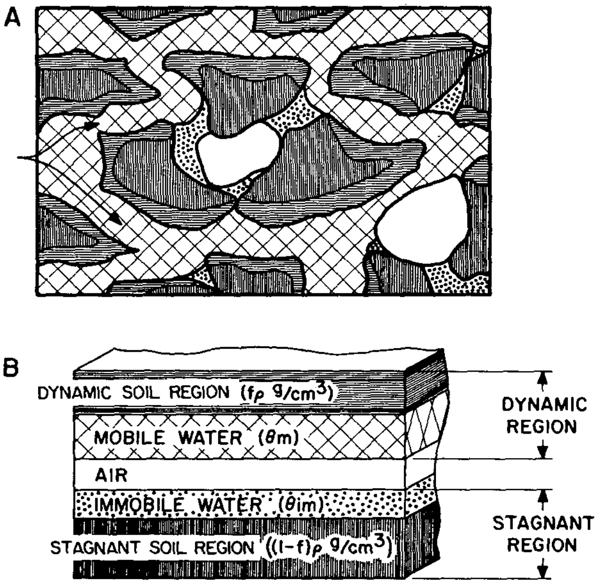

Fig. 1—Schematic diagram of unsaturated aggregated porous medium. *(A)* Actual model. *(B)* Simplified model. The shading patterns in *A* and *B* represent the same regions.

tively). Both models were found to describe the effluent data reasonably well at low pore-water velocities, but were inadequate in describing the data at higher velocities. Because of the poor predictions, we suggested that only a certain fraction of the sorption sites, i.e. those located around the larger pores, participated actively in the adsorption process. This would have the same effect as a reduction in the adsorption constant, leading to a relatively faster movement of the chemical and resulting in an earlier breakthrough. At the same time a considerable portion of the chemical must diffuse to the remaining sites, located inside aggregates and along dead pores. This slow diffusion process would continuously remove material from the larger water-saturated pores, resulting in extensive tailing. Basically the same reasoning was used in other studies to account for the deviations between the predictions based on Eq. [4] and experimental data (Kay and Elrick, 1967; Green et al, 1972). It is the purpose of this paper to further expand the model proposed by van Genuchten et al. (1974). Transfer equations are derived which include diffusion controlled adsorption, and an analytical solution is presented for the case when the adsorption isotherm is linear.

THEORETICAL

Consider the movement of a chemical through an unsaturated, aggregated sorbing porous medium. Figure 1 represents schematically such a medium. Five different regions can be identified:

1) Air spaces.

2) Mobile (or dynamic) water, located inside the larger (inter-aggregate) pores. The flow of fluid in the medium is assumed to occur in this region only. Solute transfer occurs by both convection and longitudinal diffusion.

3) Immobile (dead or stagnant) water, located inside aggregates and at the contact points of aggregates and/or particles. In saturated media this region is mainly confined to intra-aggregate pores. Note that air-bubbles and unsaturated conditions may increase the proportion of dead water by creating more dead-end pores.

4) A dynamic soil region, located sufficiently close to the mobile water phase for equilibrium (assumed) between the solute in the mobile liquid and that sorbed by this part of the soil mass.

5) A stagnant soil region, that part of the soil matrix where sorption is diffusion limited. This part of the soil is located mainly around the micro-pores inside the aggregates, or along dead-end water pockets. Sorption occurs here only after the chemical has diffused through the liquid barrier of the immobile liquid phase.

We will characterize the division of the soil matrix into the two regions, dynamic and stagnant, by the parameter f. Equivalently f may be defined as that fraction of the sorption sites which is in direct contact with the mobile liquid. On the basis of the equation of continuity we may now state the following general transport equation:

$$\frac{\partial}{\partial t}(\theta_m C_m) + \frac{\partial}{\partial t}(\theta_{im} C_{im}) + \frac{\partial}{\partial t}(f\rho S_m) + \frac{\partial}{\partial t}(1-f)\rho S_{im} = \frac{\partial}{\partial z}\left(\theta_m D \frac{\partial C_m}{\partial z}\right) - \frac{\partial}{\partial z}(qC_m) \qquad [9]$$

where the subscripts m and im refer to mobile and immobile regions, respectively. This study assumes a constant water flux (q); hence D, θ_m, θ_{im}, f and v_m ($= q/\theta_m$) are constants and Eq. [9] simplifies to

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im}\frac{\partial C_{im}}{\partial t} + f\rho\frac{\partial S_m}{\partial t} + (1-f)\rho\frac{\partial S_{im}}{\partial t} = \theta_m D\frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z}. \qquad [10]$$

We further assume that adsorption is instantaneous and that the relation between adsorption and solution concentration can be described by the Freundlich relationship (Eq. [5]). Hence

$$\frac{\partial S}{\partial t} = KNC^{N-1}\frac{\partial C}{\partial t}. \qquad [11]$$

Substitution of Eq. [11] in Eq. [10] results in

$$(\theta_m + f\rho KNC_m^{N-1})\frac{\partial C_m}{\partial t} + [\theta_{im} + (1-f)\rho KNC_{im}^{N-1}]\frac{\partial C_{im}}{\partial t} = \theta_m D\frac{\partial^2 C_m}{\partial z^2} - v_m\theta_m\frac{\partial C_m}{\partial z}. \qquad [12]$$

A relationship between the concentrations of solute in the mobile and immobile liquids has to be established in order to complete the description of the transport mechanism. Diffusional transfer between these two liquid regions is defined here by a relation similar to Eq. [3]. Since a sorbing medium is considered and since adsorption takes place from the immobile liquid to the immobile part of the porous medium a sorption term must be added to the left-hand side of Eq. [3]. The resulting transfer equation is

$$\theta_{im}\frac{\partial C_{im}}{\partial t} + (1-f)\rho\frac{\partial S_{im}}{\partial t} = \alpha(C_m - C_{im}). \qquad [13]$$

Substitution of Eq. [11] in Eq. [13] leads finally to

$$[\theta_{im} + (1-f)\rho KNC_{im}^{N-1}]\frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}). \qquad [14]$$

Linear adsorption

For linear adsorption ($N = 1$) Eq. [12] and [14] reduce to:

$$(\theta_m + f\rho K)\frac{\partial C_m}{\partial t} + [\theta_{im} + (1-f)\rho K]\frac{\partial C_{im}}{\partial t} = \theta_m D\frac{\partial^2 C_m}{\partial z^2} - v_m\theta_m\frac{\partial C_m}{\partial z} \qquad [15]$$

$$[\theta_{im} + (1-f)\rho K]\frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}). \qquad [16]$$

For a semi-infinite column and a pulse input of solute, the boundary and initial conditions are

$$\lim_{z\to 0^+}\left(v_m C_m - D\frac{\partial C_m}{\partial z}\right) = \begin{cases} v_m C_o & 0 \le t < t_1 \\ 0 & t \ge t_1 \end{cases} \qquad [17]$$

$$\lim_{z\to\infty}[C_m(z,t)] = 0 \qquad [18]$$

$$C_m(z,0) = C_{im}(z,0) = 0. \qquad [19]$$

To obtain a more amenable system of equations, the following dimensionless variables are introduced:

$$T = v_o t/L = v_m t\phi/L \qquad [20]$$

$$x = z/L \qquad [21]$$

$$\phi = \theta_m/\theta = \theta_m/(\theta_m + \theta_{im}) \qquad [22]$$

$$c_m = C_m/C_o, \qquad c_{im} = C_{im}/C_o \qquad [23]$$

$$P = v_m L/D \qquad [24]$$

$$\bar{\alpha} = \alpha L/(v_m \theta_m) = \alpha L/q. \qquad [25]$$

Equations [15] and [16] can now be written in the following form:

$$\phi R_m \frac{\partial c_m}{\partial T} + (1 - \phi) R_{im} \frac{\partial c_{im}}{\partial T} = \frac{1}{P}\frac{\partial^2 c_m}{\partial x^2} - \frac{\partial c_m}{\partial x} \qquad [26]$$

$$(1 - \phi) R_{im} \frac{\partial c_{im}}{\partial T} = \bar{\alpha}(c_m - c_{im}) \qquad [27]$$

where R_m and R_{im} are retardation factors based on the dynamic and stagnant regions, respectively (Fig. 1):

$$R_m = 1 + \frac{\rho f K}{\theta_m} \qquad [28]$$

$$R_{im} = 1 + \frac{(1 - f)\rho K}{\theta_{im}} \qquad [29]$$

The average retardation factor R for linear adsorption is (Eq. [7]):

$$R = 1 + (\rho K/\theta). \qquad [30]$$

Define further the dimensionless parameter, β, as

$$\beta = \frac{\theta_m + \rho f K}{\theta + \rho K} = \frac{\theta_m}{\theta}\frac{R_m}{R}. \qquad [31]$$

With these definitions of R and β, the transport equations finally become

$$\beta R \frac{\partial c_m}{\partial T} + (1 - \beta) R \frac{\partial c_{im}}{\partial T} = \frac{1}{P}\frac{\partial^2 c_{im}}{\partial x^2} - \frac{\partial c_m}{\partial x} \qquad [32]$$

$$(1 - \beta) R \frac{\partial c_{im}}{\partial T} = \bar{\alpha}(c_m - c_{im}). \qquad [33]$$

The initial and boundary conditions in dimensionless form are

$$\lim_{x \to 0+}\left(c_m - \frac{1}{P}\frac{\partial c_m}{\partial x}\right) = \begin{cases} 1 & 0 \le T < T_1 \\ 0 & T \ge T_1 \end{cases} \qquad [34]$$

$$\lim_{x \to \infty}[c_m(x,T)] = 0 \qquad [35]$$

$$c_m(x,0) = c_{im}(x,0) = 0 \qquad [36]$$

One technique for solving Eq. [32]–[36] is to apply the Laplace transform and then to treat the transformed equations as ordinary differential equations. Lindstrom and Narasimhan (1973) have applied this technique to a similar mathematical problem and obtained the solutions of Eq. [4] and [8] for an initially distributed chemical. With straight-forward, albeit lengthy, transformations of their solutions, it can be shown that the solutions of Eq. [32]–[36] become (van Genuchten, 1974,[4] Appendix C):

$$c_m(x,T) = \begin{cases} c_1(x,T) & 0 \le T < T_1 \\ c_1(x,T) - c_1(x,T - T_1) & T \ge T_1 \end{cases} \qquad [37]$$

$$c_{im}(x,T) = \begin{cases} c_2(x,T) & 0 \le T < T_1 \\ c_2(x,T) - c_2(x,T - T_1) & T \ge T_1 \end{cases} \qquad [38]$$

$$c_1(x,T) = G(x,T)\exp(-\bar{\alpha}T/\beta R) + \frac{\bar{\alpha}}{R}\int_0^T G(x,\tau)H_1(T,\tau)\,d\tau \qquad [39]$$

$$c_2(x,T) = \bar{\alpha}\int_0^T G(x,\tau)H_2(T,\tau)\,d\tau \qquad [40]$$

$$G(x,T) = \frac{1}{2}\,erfc\{(P/4\beta RT)^{1/2}(\beta Rx - T)\}$$

$$- \frac{1}{2}(1 + Px + PT/\beta R)\exp(Px)\,erfc\{(P/4\beta RT)^{1/2}(\beta Rx + T)\}$$

$$+ (PT/\pi\beta R)^{1/2}\exp\{-P(\beta Rx - T)^2/4\beta RT\} \qquad [41]$$

$$H_1(T,\tau) = \exp(-u - v)\,\{I_0(\xi)/\beta + I_1(\xi)(u/v)^{1/2}/(1 - \beta)\} \qquad [42]$$

$$H_2(T,\tau) = \exp(-u - v)\{I_0(\xi)/(1 - \beta) + I_1(\xi)(v/u)^{1/2}/\beta\} \qquad [43]$$

$$u = \bar{\alpha}\tau/\beta R \qquad v = \bar{\alpha}(T - \tau)/(1 - \beta)R \qquad \xi = 2(uv)^{1/2} \qquad [44]$$

DISCUSSION

Equations [37]–[44], representing the solute concentrations in both mobile and immobile regions of the soil, depend on four dimensionless parameters: R, β, $\bar{\alpha}$ and P. Both R and β (Eq. [30] and [31], respectively) depend on the adsorption constant K, and hence are determined by both the chemical and the porous medium. The mass transfer coefficient $\bar{\alpha}$ will also depend on the chemical and the medium, because this parameter involves the diffusion coefficient of the chemical, the length over which the average concentration difference is considered and the cross-sectional area through which the lateral diffusion process takes place (Coats and Smith, 1964). The column Peclet number P, however, will depend solely on the medium, provided the contribution of longitudinal diffusion to the dispersion coefficient is negligibly small (only mechanical dispersion).

In order to evaluate the different parameters and their sensitivity, effluent curves were calculated for a 30-cm long soil column (L = 30), leached with 3 pore volumes of a chemical ($T_1 = 3$) at a constant flux (q) of 10 cm/day. Ignoring exit effects and assuming that only mobile liquid leaves the basal plane of the column, the effluent concentrations can be calculated with Eq. [37], with $x = 1$. Results are shown in Fig. 2–5.

Figure 2 shows the influence of the fraction mobile water (ϕ) on the shape of the effluent concentration distribution. Values of the different parameters used in the calculations are given in the figure. When the amount of immobile liquid increases (i.e. ϕ decreases), convective transfer is increasingly confined to a smaller cross-sectional area of the column, resulting in a higher solute velocity in the mobile liquid ($v_m = q/\theta_m$) and hence leading to an earlier break through of the chemical in the effluent. Also, the slope of the effluent curve at the higher concentrations is affected by a change in ϕ. When $\phi = 1$, no immobile water is present, i.e. no intra-aggregate diffusion takes place, and the curve becomes more or less symmetrical (curve not included in Fig. 2). Equations [15] and [16] then reduce to Eq. [6] and [7] with $N = 1$ and ρ replaced by $f\rho$. In that case f becomes identical to the variable FREQ ("fraction near equilibri-

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[4] M. Th. van Genuchten. 1974, Mass transfer studies in sorbing porous media. Ph.D. Thesis. New Mexico State Univ, Las Cruces.

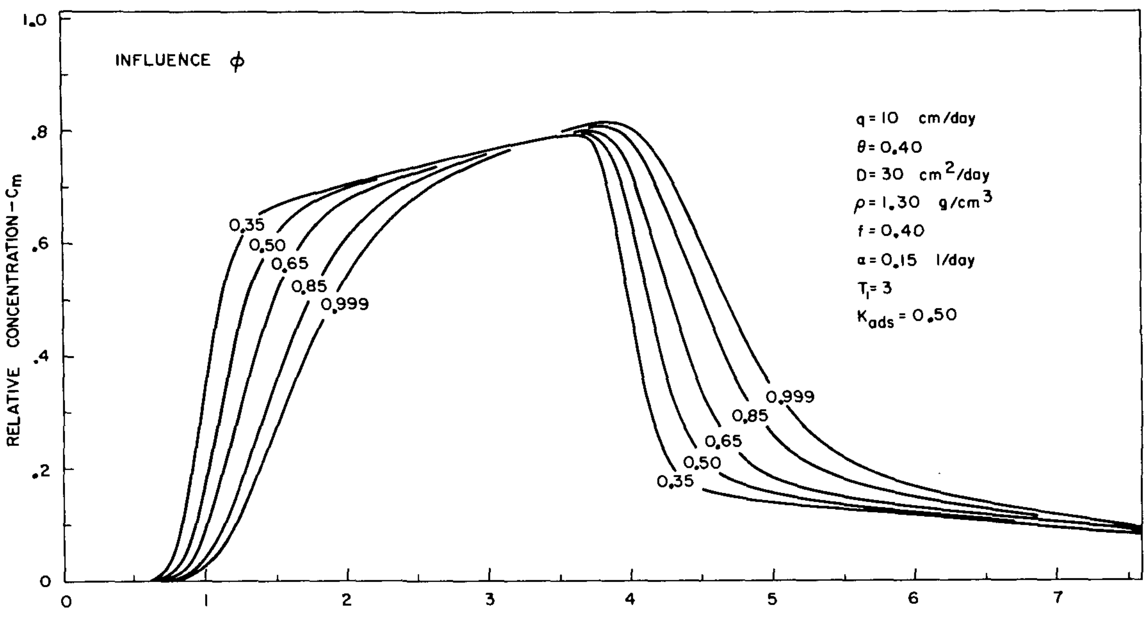

Fig. 2—Calculated effluent curves for a sorbing medium, as influenced by the fraction mobile liquid. (ϕ).

um") which van Genuchten et al. (1974) used in their calculations to account for the early arrival of picloram in the effluent. FREQ is hence that fraction of the sorption sites which participates actively in the adsorption process, the remaining fraction being inaccessible for the displacing fluid. However, as long as some immobile liquid is present ($\phi = 0.999$ or <1.) extensive tailing will occur, since approximately 60% of the chemical ($f = 0.40$) has to diffuse into the stagnant region of the soil, i.e. to those sorption sites which are in equilibrium with the immobile liquid.

Approximately the same set of curves as shown in Fig. 2 is obtained when the parameter f is allowed to vary (Fig. 3). This parameter describes the amount of adsorption taking place inside the dynamic region of the soil, as a fraction of the total adsorption. When f increases, i.e. when relatively more adsorption occurs in the dynamic region and relatively less inside the aggregates, the total adsorption remaining the same, the chemical will appear later in the effluent. When $f = 1$, adsorption takes place only in the dynamic region of the soil. Some solute may then still diffuse into the stagnant region; however, no adsorption occurs here and the chemical can only be stored in the immobile liquid.

Both f (fraction adsorption sites in dynamic region) and ϕ (fraction mobile water) have the same effect on the shape of the effluent curves. This is not surprising since both parameters are included in the dimensionless variable β (Eq. 31) which determines the fraction of the retardation occurring in the dynamic region of the soil.

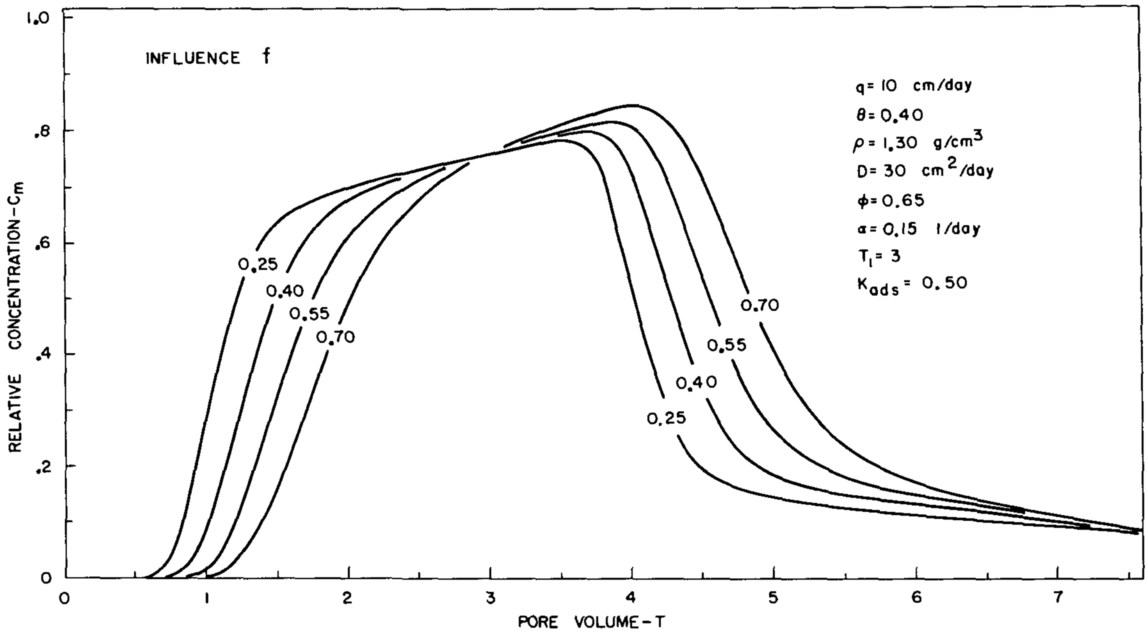

Fig. 3—Calculated effluent curves for a sorbing medium, as influenced by the fraction of the adsorption sites in the dynamic region (f).

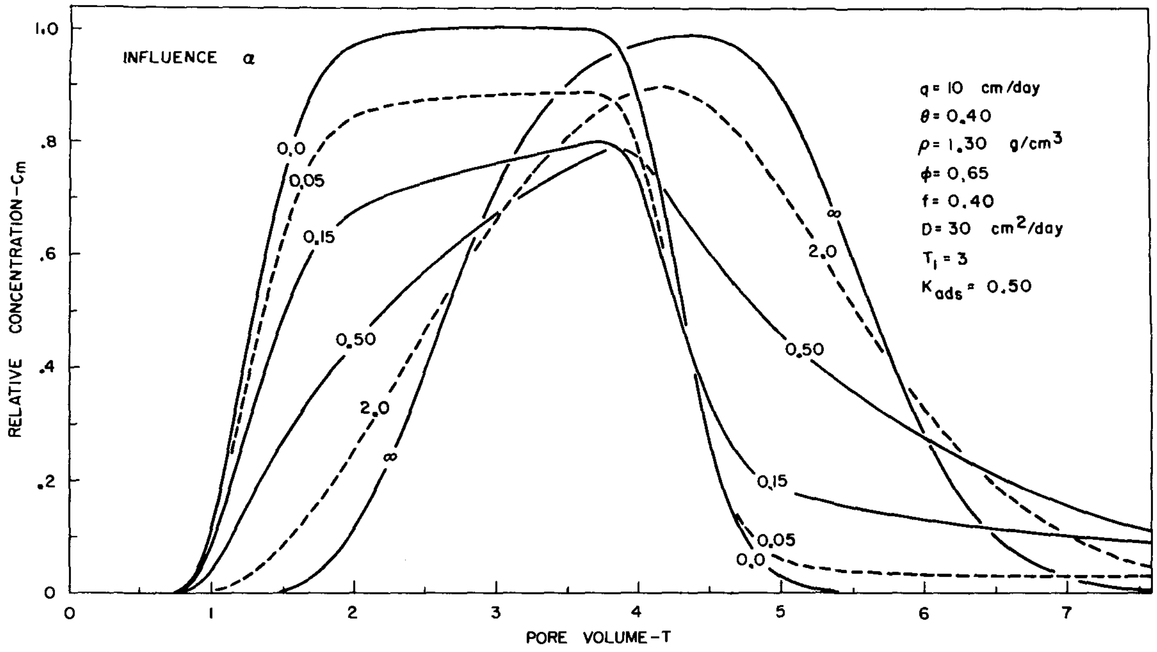

Fig. 4—Calculated effluent curves for a sorbing medium, as influenced by the mass transfer coefficient (α).

Figure 4 shows the influence of the mass transfer coefficient α (day^{-1}). When $\alpha = 0$, there is no diffusion of material into the immobile liquid, and the solution for the mobile concentration (c_m) reduces to

$$c_m(x,T) = \begin{cases} G(x,T) \\ G(x,T-T_1) \end{cases} \quad [45]$$

with $G(x, T)$ given by Eq. [41]. Note that the effluent curve acquires a more or less symmetrical shape. When α is small, a slow exchange of material between mobile and immobile regions takes place, causing a significant decrease in peak concentration and considerable tailing. With increasing values of the mass transfer coefficient, the rate of exchange between the two regions increases, eventually leading to a new "equilibrium," where the concentrations in both mobile and immobile liquid are identical: $c_m = c_{im}$. The linear adsorption model (Eq. [15] and [16]) then reduces to a single equation ($\alpha \rightarrow \infty$):

$$(\theta + \rho K)\frac{\partial C}{\partial t} = \theta_m D \frac{\partial^2 C}{\partial z^2} - v_m \theta_m \frac{\partial C}{\partial z} \quad [46]$$

The curve $\alpha \rightarrow \infty$ represents the solution of Eq. [46] for identical initial and boundary conditions as used before.

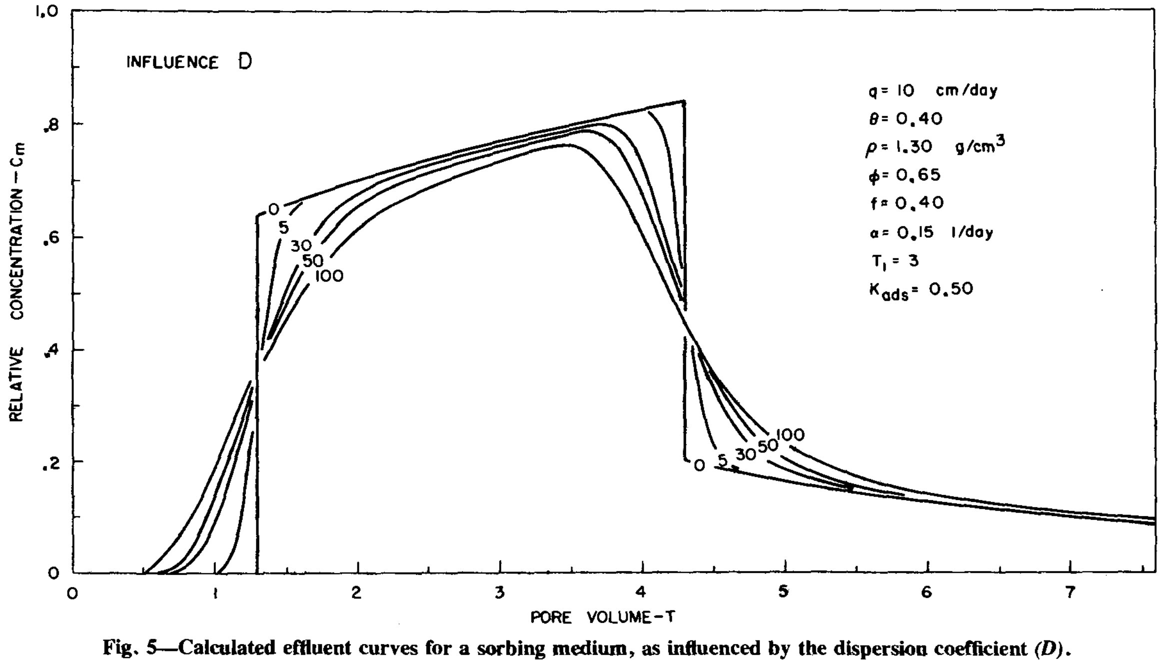

Fig. 5—Calculated effluent curves for a sorbing medium, as influenced by the dispersion coefficient (D).

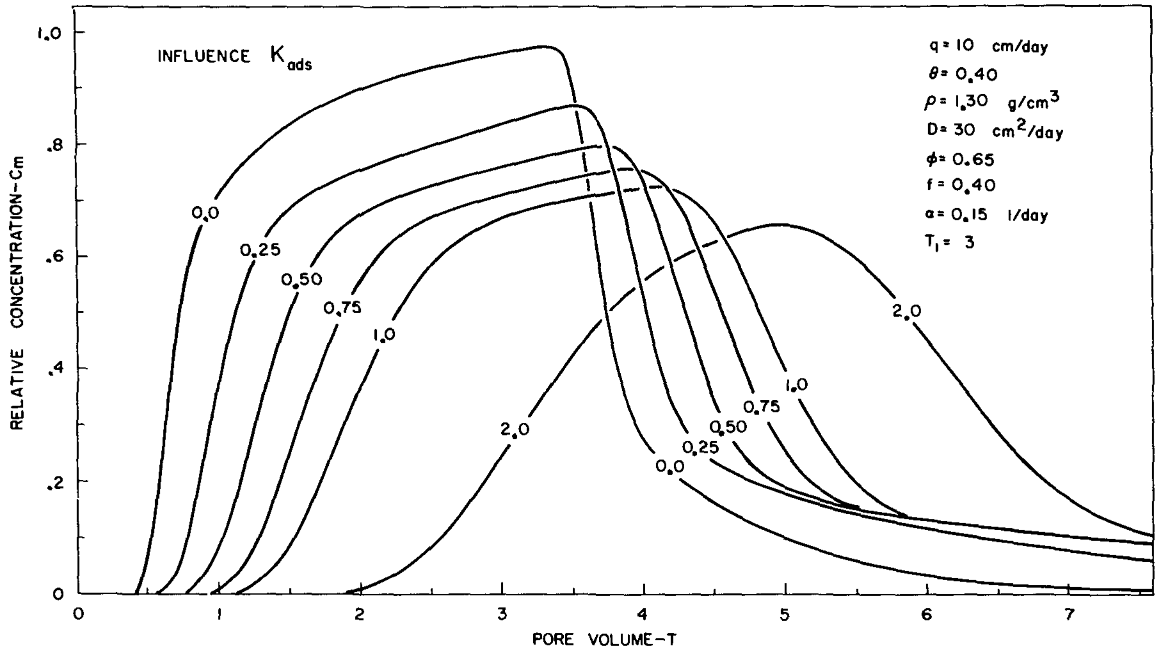

Fig. 6—Calculated effluent curves for a sorbing medium, as influenced by the adsorption constant (K_{ads}).

The influence of the dispersion coefficient D (cm^2/day) on the effluent curves is shown in Fig. 5. The influence of D on the shape of the calculated curves is not very large. Note the discontinuities at both 1.3 and 4.3 pore volumes for the limiting case when D becomes zero. From Fig. 5 we may conclude that for the purpose of predicting effluent concentration distributions an estimated value of the dispersion coefficient may often be adequate.

Figure 6 finally shows the influence of the adsorption constant K on the shape and position of the effluent concentration distributions. The curve $K = 0$ represents the solution for a nonsorbing medium, given by Eq. [33]–[40] with $R = 1$. Note that the curves are highly asymmetrical, even for the nonsorbing medium. When K increases, the chemical appears later in the effluent, while the peak concentration decreases somewhat. Also the tailing becomes more pronounced with increasing values of K. This is to be expected since more and more solute is allowed to diffuse into and be adsorbed by the stagnant region of the soil. After passage of the solute pulse the chemical slowly diffuses back into the mobile liquid, resulting in extensive tailing.

In conclusion, the calculated effluent curves in Fig. 2–5 clearly show the very significant effects of adsorption, immobile water and lateral diffusion on the position and shape of effluent concentration distributions. In two following papers (van Genuchten and Wierenga, 1976; van Genuchten et al., 1976) the solutions presented here will be used to describe observed effluent data from soil columns leached with tritium (^3H_2O) and 2,4,5-T (2,4,5-Trichlorophenoxyacetic acid), respectively.

APPENDIX—NOTATION

C_o = influent concentration (μg/cm^3)
C_1 = concentration breakthrough side effluent curve (μg/cm^3)
C_m, C_{im} = concentration of mobile and immobile liquid, respectively (μg/cm^3)
c_m, c_{im} = relative concentrations (C_m/C_o; C_{im}/C_o, respectively)
D = dispersion coefficient (cm^2/day)
f = fraction adsorption sites in dynamic region
I_o, I_1 = modified Bessel functions
K, N = constants in Freundlich isotherm: $S = KC^N$
L = length of column (cm)
P = Peclet number of column: $P = v_m L/D$
q = volumetric flow velocity (cm/day)
R = average retardation factor: $R = 1 + \rho K/\theta$
R_m = retardation factor of dynamic region: $R_m = 1 + f\rho K/\theta_m$
R_{im} = retardation factor of stagnant region: $R_{im} = 1 + (1 - f)\rho K/\theta_{im}$
S_m, S_{im} = adsorption in dynamic and stagnant region, respectively (μg/g)
t = time (days)
t_1 = pulse period (days)
T = pore volume: $T = v_o t/L = v_m t\phi/L$
T_1 = dimensionless pulse period: $T_1 = v_o t_1/L$
v_o = average pore-water velocity (cm/day): $v_o = q/\theta$
v_m = average pore-water velocity in dynamic region (cm/day): $v_m = q/\theta_m$
x = dimensionless distance: $x = z/L$
z = distance (cm)
α = mass transfer coefficient (day^{-1})
$\bar{\alpha}$ = dimensionless mass transfer coefficient: $\bar{\alpha} = \alpha L/q$
β = $\phi R_m/R$
ϕ = fraction mobile water: $\phi = \theta_m/\theta$
ρ = bulk density (g/cm^3)
θ = water content: $\theta = \theta_m + \theta_{im}$(cm^3/cm^3)
θ_m = mobile water content (cm^3/cm^3)
θ_{im} = immobile water content (cm^3/cm^3)

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