

# Mass Transfer Studies in Sorbing Porous Media: II. Experimental Evaluation with Tritium ( $^3\text{H}_2\text{O}$ )<sup>1</sup>

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## ABSTRACT

A comparison is made between observed tritium effluent concentration distributions and those calculated with a previously published analytical solution for the movement of chemicals through unsaturated, aggregated sorbing media. In the analytical model the liquid phase of the soil is divided into mobile and immobile regions, with transfer between the two regions diffusion controlled. Effluent data obtained from several displacements of tritium through 30-cm long columns of Glendale clay loam were used to determine the different parameters in the analytical solution by curve fitting. The data indicate some adsorption or isotopic exchange of tritium during its flow through the soil columns. The amount of immobile water increases with decreasing flow velocity and increasing aggregate size, and varies between 6 and 45% of the total volume of water in the columns. The analytical solution provides an excellent description of the experimental effluent data, and shows that tailing can be explained satisfactorily by diffusional exchange of tritium between mobile and immobile regions of the soil.

**Additional Index Words:** intra-aggregate diffusion, immobile water, miscible displacement

IN PART I OF THIS STUDY (van Genuchten and Wierenga, 1976), a mathematical model was developed to describe the movement of chemicals through unsaturated, aggregated sorbing porous media. The medium was thereby analyzed by dividing the liquid phase into mobile and immobile regions. Transfer between the two liquid regions, presumably a diffusion process, was assumed to be proportional to the concentration difference between the mobile and immobile liquid phases. Sorption processes in both the stagnant and dynamic regions of the medium were further assumed to be instantaneous. The resulting differential equations were solved analytically assuming a linear equilibrium adsorption isotherm.

The experiments to be discussed in this study were carried out to evaluate the model of van Genuchten and Wierenga (1976), and to obtain estimates of the different parameters in the adsorption model. The effects of flow velocity, bulk density, and aggregate size on the amount of immobile water (and hence, on the amount of tailing and asymmetry) were also studied. In a subsequent paper (van Genuchten et al., 1977) the theoretical model will be used to describe the movement of 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) through the same soil columns.

## MATHEMATICAL DESCRIPTION

We refer to the original paper of van Genuchten and Wierenga (1976) for a more extensive discussion of the physical system. The following general system of equations describes the mobile ( $C_m$ )

and immobile ( $C_{im}$ ) concentration distributions in a semi-infinite column, resulting from a pulse input of solute.

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

$$[\theta_{im} + (1-f)\rho KNC_{im}^{N-1}] \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) \quad [2]$$

$$\lim_{z \rightarrow 0^+} \left[ v_m C_m - D \frac{\partial C_m}{\partial z} \right] = \begin{cases} v_m C_0 & 0 \leq t < t_1 \\ 0 & t \geq t_1 \end{cases} \quad [3]$$

$$\lim_{z \rightarrow \infty} [C_m(z, t)] = 0 \quad [4]$$

$$C_m(z, 0) = C_{im}(z, 0) = 0. \quad [5]$$

The variables in these and the following equations are defined in the Appendix.

Assuming a linear adsorption isotherm ( $N=1$ ), the following analytical solutions were derived for the relative concentrations in the mobile and immobile liquids:

$$c_m(x, T) = \begin{cases} c_1(x, T) & 0 \leq T < T_1 \\ c_1(x, T) - c_1(x, T - T_1) & T \geq T_1 \end{cases} \quad [6]$$

$$c_{im}(x, T) = \begin{cases} c_2(x, T) & 0 \leq T < T_1 \\ c_2(x, T) - c_2(x, T - T_1) & T \geq T_1 \end{cases} \quad [7]$$

$$c_1(x, T) = G(x, T) \exp(-\alpha T/\beta R) + \frac{\alpha}{R} \int_0^T G(x, \tau) H_1(T, \tau) d\tau \quad [8]$$

$$c_2(x, T) = \alpha \int_0^T G(x, \tau) H_2(T, \tau) d\tau \quad [9]$$

$$G(x, T) = \frac{1}{2} \operatorname{erfc} \left\{ (P/4\beta RT)^{1/2} (\beta R x - T) \right\} - \frac{1}{2} (1 + Px + PT/\beta R) \exp(Px) \operatorname{erfc} \left\{ (P/4\beta RT)^{1/2} (\beta R x + T) \right\} + (PT/\pi\beta R)^{1/2} \exp\{-P(\beta R x - T)^2/4\beta RT\} \quad [10]$$

$$H_1(T, \tau) = \exp(-u - v) \left\{ I_0(\xi)/\beta + I_1(\xi)(u/v)^{1/2}/(1 - \beta) \right\} \quad [11]$$

$$H_2(T, \tau) = \exp(-u - v) \left\{ I_0(\xi)/(1 - \beta) + I_1(\xi)(v/u)^{1/2}/\beta \right\} \quad [12]$$

$$u = \alpha\tau/\beta R \quad v = \alpha(T - \tau)/(1 - \beta)R \quad \xi = 2(uv)^{1/2} \quad [13]$$

## MATERIALS AND METHODS

Table 1 summarizes some physical and chemical properties of the Glendale clay loam soil used in this study. This soil is a subsample of the calcareous Glendale series, a fine silty mixed ther-

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**Table 1—Physical and chemical properties of the Glendale clay loam soil.**

Analysis	Amount
Sand, %	38.8
Silt, %	29.8
Clay, %	31.4
CEC, meq/100 g	31.1
Exchangeable ions (meq/100 g)	
Ca	22.0
Mg	3.6
Na	0.8
K	1.5
NH <sub>4</sub>	1.2
EC × 10 <sup>3</sup> (saturation extract)	3.3
pH (saturation extract)	7.5
pH (saturated paste)	7.7
CaCO <sub>3</sub> equivalent, %	7.0
Organic matter, %	0.8
Gypsum, %	0.0

mic typic torrifuvent. The soil was air dried and passed through either a 6.3 or 2.0 mm screen.

A solution of 0.01N CaCl<sub>2</sub> in tritiated water was used for the displacement studies. Ten millicuries of tritium were added to each liter of water resulting in a final tritium activity of approximately 23,000 cpm/ml solution. Activities of tritium were determined on a Packard Tricarb Model 3310 liquid scintillation counter, using Aquasol (New England Nuclear, Boston, Mass.) as the counting medium.

Soil columns, 30 cm long, were prepared by carefully packing air-dried Glendale clay loam soil into plexiglass cylinders of 5.4-cm inside diameter (ID). A fine fritted glass porous plate was attached to the outflow end of each cylinder. The column was positioned vertically on top of, and connected to, a vacuum chamber enclosing an automatic fraction collector (Instrumentation Specialties Co., Lincoln, Nebraska). Through the use of the vacuum chamber and fritted glass porous plate, a constant vacuum could be maintained at the lower end of the soil column, using a vacuum regulator (Moore Products Co., Springhouse, Pennsylvania). The leaching solution was applied to the top of the soil column using a modified syringe pump described by Wierenga et al. (1973). A constant inflow could be maintained with the pump over long periods of time. The columns were first leached extensively with 0.01N CaCl<sub>2</sub>. After steady state flow conditions were established, the 0.01N CaCl<sub>2</sub> solution was replaced with the tritiated CaCl<sub>2</sub> solution. The number of pore volumes (*T*) displaced through the soil was calculated by dividing the volume of effluent by the volumetric water capacity of the soil column. The relative effluent concentration (*c<sub>m</sub>*) was calculated from the tritium activity in the effluent and the initial activity of the tritium at the inflow location. The average water content of the soil during a displacement was determined by weighing the column before leaching and several times during the displacement experiment. Water contents of the columns were regulated within a narrow range by adjusting the pressure in the vacuum chamber. However, to assure uniform water content distributions with depth, only suctions between 20 and 75 cm H<sub>2</sub>O were applied. Gravimetrically measured water contents at the end of the leaching studies showed < 0.02 cm<sup>3</sup>/cm<sup>3</sup> difference between the upper and lower parts of the columns, the average water contents being identical to those determined by weighing the columns. As was shown by Cassel et al. (1975), variations in water contents of this magnitude have very little effect on effluent concentration distributions. A total of 15 runs were made with five columns, using soil of two different aggregate sizes, and employing soil water fluxes (*q*), ranging from 1.3 to 34 cm/day. The experimental data for the different displacement studies are given in Table 2 where the experiments are numbered by column and flux.

## RESULTS AND DISCUSSION

The data from the various displacement experiments were used to determine for each run the values of the different un-

**Table 2—Soil-physical data for tritium displacements through Glendale clay loam.**

Exp. no.	Bulk density, $\rho$ g/cm <sup>3</sup>	Water content, $\theta$ cm <sup>3</sup> /cm <sup>3</sup>	Flux, $q$ cm/day	Pulse period		Largest aggregate size mm
				$T_1$	$t_1$	
1-1	1.360	0.460	5.09	2.334	6.331	2.0
1-2	1.360	0.460	5.09	0.512	1.389	2.0
1-5	1.360	0.460	2.55	1.990	10.76	2.0
2-1	1.361	0.464	4.55	2.361	7.215	2.0
2-2	1.361	0.468	4.57	0.452	1.389	2.0
2-5	1.361	0.467	2.29	1.762	10.77	2.0
3-2	1.222	0.454	17.0	3.102	2.475	6.3
3-4	1.222	0.445	4.20	1.909	6.076	6.3
3-6	1.222	0.434	1.32	1.788	9.653	6.3
4-2	1.309	0.433	4.04	1.871	6.021	6.3
5-1	1.126	0.421	33.9	3.145	1.172	6.3
5-2	1.126	0.401	16.6	2.080	1.508	6.3
5-3	1.126	0.395	8.22	2.763	3.987	6.3
5-4	1.126	0.399	5.54	3.160	6.822	6.3
5-5	1.126	0.393	2.29	2.419	12.45	6.3

known parameters ( $P$ ,  $R$ ,  $\bar{\alpha}$ , and  $\beta$ ) in the linear adsorption model (Eq. [6]–[13]). The values of these parameters were obtained by means of fitting Eq. [8] to the experimental effluent data. Because four dimensionless parameters had to be evaluated for each effluent curve, a nonlinear curve-fitting technique was used for this determination rather than a trial and error procedure. The program used in this study is the nonlinear least-squares (GAUSHAUS) curve-fitting program, originally written by Meeter (1964). This program<sup>4</sup> is based on the maximum neighborhood method of Marquardt (1963), which combines the Gauss (Taylor series) method and the method of steepest descent. A detailed treatment of this technique is given by Daniel and Wood (1973).

Figure 1 shows the results obtained when the curve-fitting program is applied to the experimental data of experiment 5-3 (Table 2). The open circles in the figure represent the observed data points, symbolically given by the data set  $\{T, c_m(1, T)\}$ . Recall that the effluent concentration distribution  $c_m(1, T)$  is given by Eq. [6], with  $x = 1$  ( $z = L$ ). Hence

$$c_m(1, T) = \begin{cases} c_1(1, T) & 0 \leq T < T_1 \\ c_1(1, T) - c_1(1, T - T_1) & T \geq T_1 \end{cases} \quad [14]$$

For  $T > 3.1$ ,  $c_1(1, T)$  in Eq. [14] is very close to one (Fig. 1), and we may approximate the effluent concentration by ( $T > 3.1$ ):

$$c_m(1, T) = 1 - c_1(1, T - T_1) \quad T > 3.1 \quad [15]$$

or

$$c_1(1, T) = 1 - c_m(1, T + T_1) \quad T + T_1 > 3.1. \quad [16]$$

Equation [16] states that when the linear model is used with a large enough pulse  $T_1$ , the break-through part of the effluent concentration curve, i.e. where  $dc_m/dt > 0$ , can be represented also by the data set  $\{T, 1 - c_m(1, T + T_1)\}$ , obtained from the elution side of the curve, i.e., where  $dc_m/dt < 0$ . Both data sets  $\{T, c_m(1, T)\}$  and  $\{T, 1 - c_m(1, T + T_1)\}$  are plotted in Fig. 1, and define approximately the same curve. Some discrepancies occur at the lower concentrations but

<sup>4</sup>Available upon request.

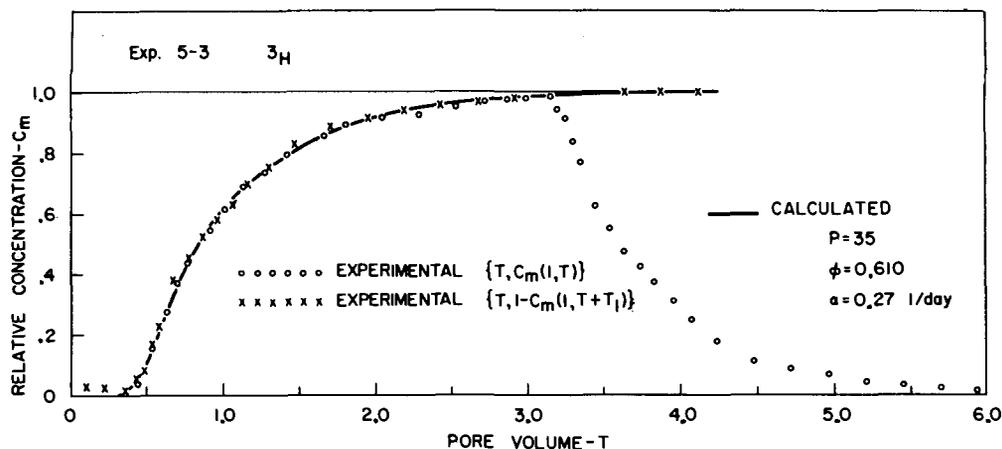


Fig. 1—Example of curve fitting with the non-linear least squares GAUSHAUS curve fitting program, using the effluent data of experiment 5-3.

are primarily caused by the assumption of Eq. [16] that  $c_1(1, T) = 1$  for  $T > 3.1$ . By using Eq. [16] an accurate description of the break-through and elution sides of the curve is obtained. Also the tailing at the higher concentrations can be extended towards higher pore volumes, as shown in Fig. 1. The latter procedure is useful since the experimental errors during scintillation counting of the tritium are usually quite large at the higher concentrations.

The following procedure was used to obtain values of the four dimensionless variables  $\beta$ ,  $P$ ,  $R$ , and  $\bar{\alpha}$ .

1) Approximately 15 points were chosen from the two data sets given above, and fitted to Eq. [8]. In this way initial estimates were obtained for the variable  $\beta$ , the retardation factor  $R$ , the mass transfer coefficient  $\bar{\alpha}$  and the Peclet number  $P$ . Estimates of these parameters were obtained for all tritium experiments.

2) The initial estimates of the retardation factor  $R$  for the different experiments were used to estimate the adsorption constant  $K$  for tritium by using the definition of  $R$  and the values of the water contents ( $\theta$ ) and bulk densities ( $\rho$ ) listed in Table 2.  $R$  values found ranged from 1.007 to 1.043, while the estimates of  $K$  ranged from 0.003 to 0.017, the average being 0.009. The impact of these low values of  $K$  on the displacements is small; the retardation is only about 0.025 pore volumes. Attempts were made to also measure the adsorption constant independently by equi-

brating increasing concentrations of tritium with soil over a 10-day period. No significant adsorption could be detected. The batch equilibration technique is apparently not sensitive enough to measure small values of  $K$ . In this study, the value of 0.009 for  $K$  will be used for all experiments, resulting in the retardation factors as given in Table 3. Other studies have also revealed some retardation of tritium (Nielsen and Biggar, 1962; Heemstra et al., 1961; Mansell et al., 1973; Wierenga et al., 1975). The retardation may be caused by some isotopic exchange of tritium with crystal-lattice hydroxyls of the soil clay fraction and/or by the replacement of some exchangeable cations by  $^3\text{H}^+$ .

3) An average Peclet number  $P$  was assumed for each column, and was obtained by taking the arithmetic average of the  $P$ -values of the different experiments of the same column. For example, for the five experiments involving column 5, the initial estimates were 48, 27, 29, 40, and 32, respectively, resulting in an average Peclet number of approximately 35. The use of a constant  $P$  for each column is consistent with the assumption that the dispersion coefficient  $D$  varies approximately linearly with the flow velocity in the mobile liquid, provided longitudinal diffusion has a negligible influence on the dispersion coefficient. Earlier studies have shown that this assumption is correct as long as the water content does not vary appreciably among the different experiments (Raimondi et al., 1959; Harleman et al., 1963; Villiermaux and van Sway, 1969; Bear, 1972). Simpson (1969) concluded that the dispersion coefficient ( $D$ ) changed approximately linearly with flow velocity and that deviations from this assumption were probably not much larger than the experimental error in the work of a single investigator.

4) In order to obtain final values for the two remaining parameters  $\beta$  and  $\bar{\alpha}$ , a second 2-parameter curve fitting was carried out, using the previously determined values of  $P$  and  $R$  as known variables in the fitting program. We believe that by carrying out a second curve fitting, more exact estimates of  $\beta$  and  $\bar{\alpha}$  are obtained than by using the initial estimates. Changes in the value of  $P$ , for example, are directly reflected in the value of  $\bar{\alpha}$ , while experimental or fitting errors in  $R$  are carried over into  $\beta$ .

When the four parameters  $P$ ,  $R$ ,  $\beta$ , and  $\bar{\alpha}$ , obtained with the two curve fittings, are substituted in Eq. [8], the solid line in Fig. 1 results. In Fig. 2, a comparison is shown be-

Table 3—Summary of various tritium ( $^3\text{H}_2\text{O}$ ) displacements through Glendale clay loam.

Exp. no.	Flux, $q$ cm/day	$\beta$	$R$	$P$	$\bar{\alpha}$	$\phi$	$D$ cm <sup>2</sup> /day	$\alpha$ 1/day
1-1	5.09	0.926	1.027	95	1.47	0.940	3.7	0.25
1-2	5.09	0.926	1.027	95	1.47	0.940	3.7	0.25
1-5	2.55	0.928	1.027	95	0.56	0.942	1.9	0.048
2-1	4.55	0.850	1.026	45	1.50	0.862	7.6	0.23
2-2	4.57	0.887	1.026	45	1.31	0.900	7.2	0.20
2-5	2.29	0.830	1.026	45	1.05	0.841	3.9	0.080
3-2	17.0	0.841	1.024	56	0.39	0.852	24.0	0.22
3-4	4.20	0.872	1.025	56	0.72	0.884	5.7	0.10
3-6	1.32	0.717	1.025	56	1.96	0.725	2.2	0.086
4-2	4.04	0.788	1.027	57	0.93	0.798	6.2	0.12
5-1	33.9	0.723	1.024	35	0.33	0.731	94.0	0.37
5-2	16.6	0.704	1.025	35	0.55	0.711	50.0	0.31
5-3	8.22	0.605	1.026	35	1.00	0.610	29.0	0.27
5-4	5.54	0.531	1.025	35	1.54	0.534	22.0	0.28
5-5	2.29	0.694	1.026	35	1.46	0.702	7.1	0.11

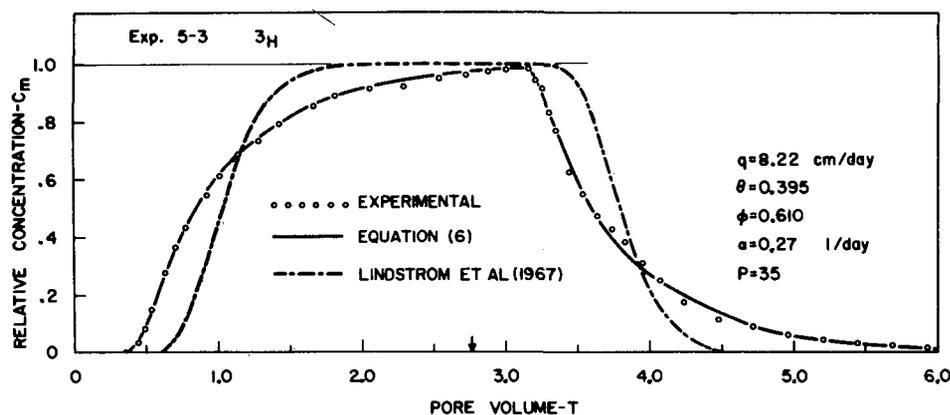


Fig. 2—Observed and calculated tritium effluent curves for experiment 5-3.

tween the entire effluent concentration distribution of experiment 5-3, and the calculated curve using Eq. [6] for the pulse. The figure shows an excellent agreement between calculated and observed results. The dashed line in Fig. 2 represents the solution of the convective-dispersive equation obtained by Lindstrom et al. (1967) for the same initial and boundary conditions as adopted here (including the observed tritium retardation). This solution requires all the water in the column to be mobile ( $\phi=1, f=1$ ). No satisfactory description of the effluent data could be obtained, even by allowing the value of  $P$  to deviate from 35. Somewhat better results were obtained with the solutions of Brenner (1962) and Lapidus and Amundson (1952). However, for these latter solutions Peclet numbers in the order of 3 or 4 had to be used, leading to dispersion coefficients of about  $175 \text{ cm}^2/\text{day}$ .

We emphasize here that the linear adsorption model (Eq. [6] – [13]) depends on four dimensionless variables ( $\beta, R, P, \bar{\alpha}$ ), while the original model in dimensionalized form contains five parameters ( $\phi, f, K, D, \alpha$ ). This difference in the number of parameters is due to the fact that the dimensionless variable  $\beta$  contains both the parameter  $\phi$  (fraction mobile liquid) and the parameter  $f$  (fraction of the adsorption sites in the dynamic region of the soil). Both  $\phi$  and  $f$  have similar effects on the displacements; a decrease in either parameter results in an increased mobility of the chemical during the displacements as was shown earlier (van Genuchten and Wierenga, 1976). Although an estimate of  $\beta$  suffices to complete the mathematical description, the physical picture of the soil is clarified when also an estimate of the fraction mobile water is available. The following procedure was used to obtain an estimate of  $\phi$  from the curve fitted value of  $\beta$ . From the definition of  $\beta$  (Appendix) we have

$$\beta R = \phi R_m = \phi + f(R - 1) \quad [17]$$

or

$$\phi = \beta R - f(R - 1). \quad [18]$$

When we use the fitted values of  $\beta$  and  $R$  from experiment 5-3 (Table 3), Eq. [18] reduces to:

$$\phi = 0.620 - 0.0256f. \quad [19]$$

Because the retardation factors for tritium are very close to unity, it is clear from Eq. [19] that fairly imprecise estimates of  $f$  will still yield accurate values of  $\phi$ . A value of

0.4 for  $f$  was used in Eq. [18], obtained from data on the movement of 2,4,5-T through the same soil (van Genuchten et al., 1977). This value of  $f$  is obviously only an estimate since the adsorption mechanism for 2,4,5-T and tritium are not necessarily the same.

The effluent concentration distributions for column experiments 5-1, 5-2, and 5-4 are shown in Fig. 3, 4, and 5, respectively, and are compared with the analytical solution (Eq. [6]). The agreement between data and the curves calculated with Eq. [6] are good in each case. Similar agreement was found for all other tritium displacements (figures not presented). The solution of Lindstrom et al. (1967) again fails to accurately describe the experimental data of Fig. 3, 4, and 5. No significant improvements could be obtained by adjusting the value of  $P$  in the solution of Lindstrom et al. However, with the solutions of Lapidus and Amundson (1952) and Brenner (1962), choosing values for  $P$  of approximately 2-5 (resulting in dispersion coefficients of  $150\text{-}500 \text{ cm}^2/\text{day}$ ), differences between calculated and experimental curves could be made quite small.

The following observations can be made when examining Fig. 2-5 and the data presented in Table 3.

1) The amount of immobile water generally increases with decreasing flow velocity. This effect is clearly shown by the displacements through column 5, except for experiment 5-5 (Table 3). Between experiments 5-4 and 5-5, the column was allowed to dry for several days, which may have had an effect on the amount of immobile liquid. For column 5 the amount of immobile water increases from about 25% of the total amount of water in the column at a flux of  $33.9 \text{ cm}/\text{day}$ , to approximately 45% at a flux of  $5.5 \text{ cm}/\text{day}$ . Similar effects of flow velocity on the amount of immobile water have also been observed by Nielsen and Biggar (1962); Coats and Smith (1964); Villermaux and van Swaay (1969); and by Bennet and Goodridge (1970).

2) The mass transfer coefficient  $\alpha$  decreases with flow velocity, indicating a slower mixing between the two liquid regions with decreasing velocity. Bennet and Goodridge (1970) and Coats and Smith (1964) noted similar effects. The decrease in  $\alpha$  with decreasing flow velocity may be caused by an increase in the amount of immobile water, and hence by an increase in the diffusion length for the chemical from the mobile liquid to the center of the immobile liquid. In addition, convective mixing may have occurred inside the immobile liquid at higher flow velocities. Such a mixing

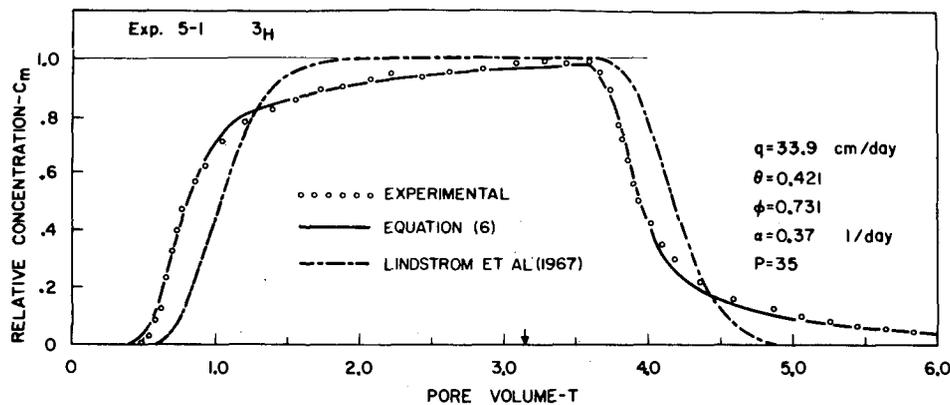


Fig. 3—Observed and calculated tritium effluent curves for experiment 5-1.

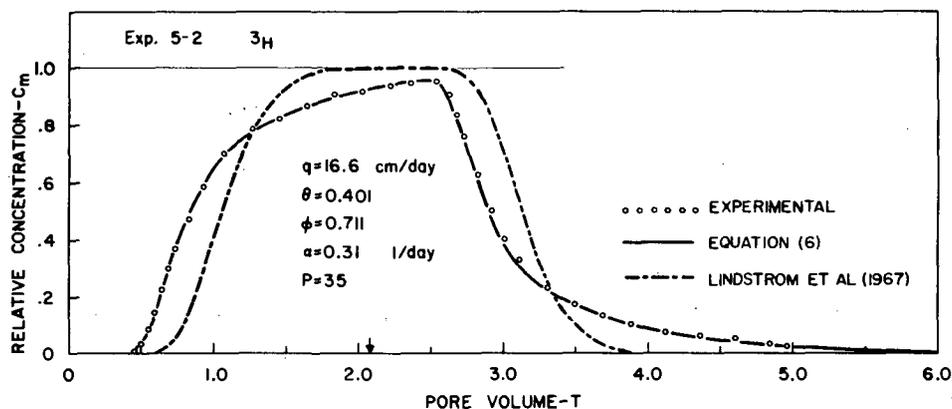


Fig. 4—Observed and calculated tritium effluent curves for experiment 5-2.

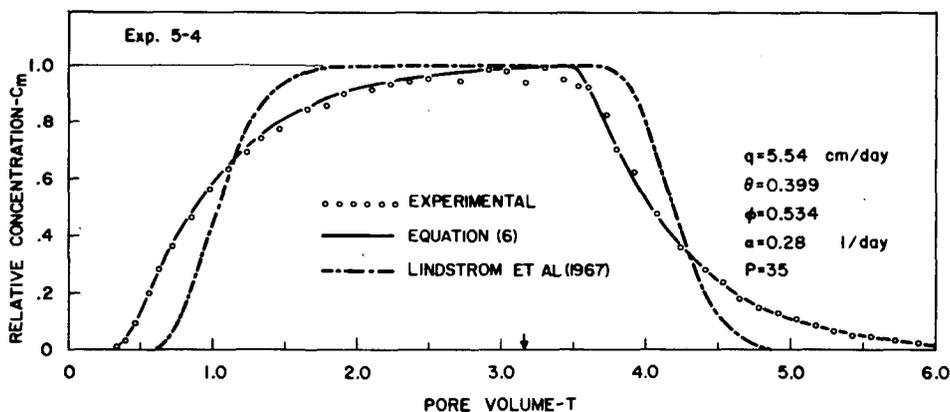


Fig. 5—Observed and calculated tritium effluent curves for experiment 5-4.

process would effectively increase the value of  $\alpha$ , because the present model assumes that solute exchange between mobile and immobile liquid regions occurs only by diffusion and not by convection.

3) A decrease in the size of the aggregates decreases the amount of dead water in the column. An analysis of the effluent data of column 1 showed that only 6% of the water in the column was immobile (Table 3). This column was uniformly packed with aggregates of  $< 2$  mm. Column 2 showed a slightly higher immobile water content than column 1, although both were packed with the same aggregate-sized material and at the same bulk density. It is important to note here that the effluent data of columns 1 and 2,

packed with aggregates  $< 2$  mm, could be described equally well with the two-parameter model of Lindstrom et al. (1967) as with the four-parameter model discussed in this paper. The solution of Lindstrom et al. gave inaccurate descriptions of the data only when large percentages of immobile water were present, such as is the case with column 5, and to a lesser degree with columns 3 and 4.

4) A reduction in bulk density appears to increase the amount of immobile water, as shown by the data in Table 2 and 3. Soil column 5 had the lowest bulk density, but showed the most dead water and hence the most tailing. An increase in bulk density is likely to cause a compaction of the soil, resulting in a narrower pore-size distribution. The

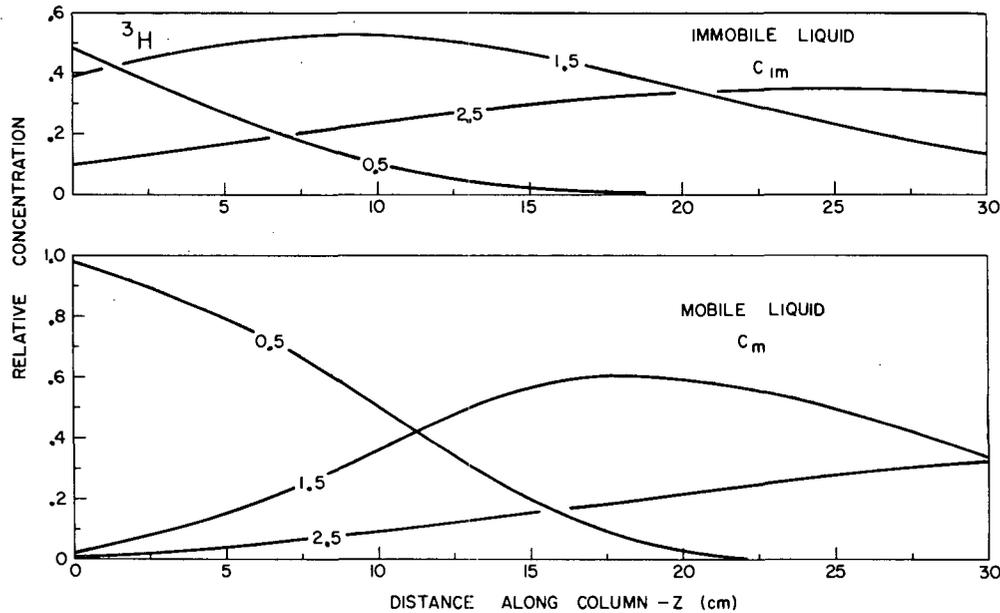


Fig. 6—Concentration profiles inside a 30-cm long soil column at different times during leaching with a short pulse ( $t_1 = 1$  day) of tritiated water. Values of the parameters used to construct the curves are given in Fig. 5. Numbers on the curves indicate times (days) after leaching was initiated.

narrower the pore-size distribution, the narrower is the pore-water velocity distribution, resulting in relatively less immobile water.

5) The dispersion coefficient  $D$  appears to increase somewhat with increasing aggregate size and decreasing bulk density (Tables 2 and 3). Further experiments, however, are necessary to clearly separate the effects of these two soil-physical properties on the magnitude of the dispersion coefficient.

An important feature of the model is that the solute concentrations in both the mobile and immobile regions of the soil can be calculated. Figure 6 shows concentration distributions inside a 30-cm long soil column for both the mobile and immobile liquid at different times during leaching with a 1-day pulse of tritium. Values of the different parameters used to construct the curves were obtained from experiment 5-4 (see Tables 2 and 3). The effluent curve of this experiment was described accurately with the linear adsorption model (Eq. [6]), as shown by Fig. 5. Hence some confidence in the accuracy of the calculations seems justified. The concentrations in the mobile and immobile liquids were calculated with Eq. [6] and [7], respectively. Figure 6 shows considerable differences between the concentrations in both liquid regions. Due to the slow exchange by diffusion between mobile into the immobile liquids, the immobile concentration lags behind the mobile concentration. The average concentration  $c_{av}$  at any point in the column is given by

$$c_{av} = \phi c_m + (1 - \phi) c_{im}. \quad [20]$$

Since the fraction mobile liquid ( $\phi$ ) was 0.534 for experiment 5-4, it follows that the average concentration is roughly the average of  $c_m$  and  $c_{im}$ . It may be argued that the soil solution withdrawn through porous cups or similar devices represents mainly mobile liquid, since it is this liquid which most readily moves within the soil. Definite state-

ments about whether this is true however, are difficult to verify. In fact, the ratio of mobile vs. immobile water extracted and thus the concentration of the extract will depend on the applied vacuum, the duration of the applied vacuum and the way in which the porous cups is installed. Solute distributions such as those shown in figure 6 may be helpful in interpreting soil solution extracts, as they define upper and lower limits of the solute concentrations in the soil.

From the discussions above it appears that the linear adsorption model may provide a physically realistic description of the tailing phenomena in unsaturated soils. The model may prove to be useful in describing the removal by leaching of various chemicals from field soils. This leaching is often accomplished under unsaturated conditions, when large percentages of immobile water may be present.

#### APPENDIX - NOTATION

- $C_0$  = influent concentration ( $\mu\text{g}/\text{cm}^3$ )
- $C_1$  = concentration breakthrough side effluent curve
- $C_m, C_{im}$  = concentration of mobile and immobile liquid, respectively, ( $\mu\text{g}/\text{cm}^3$ )
- $c_m, c_{im}$  = relative concentrations ( $C_m/C_0, C_{im}/C_0$ , respectively).
- $D$  = dispersion coefficient ( $\text{cm}^2/\text{day}$ )
- $f$  = fraction adsorption sites in dynamic region
- $I_0, I_1$  = modified Bessel functions
- $K, N$  = constants in Freundlich isotherm:  $S = K C^N$
- $L$  = length of column (cm)
- $P$  = pecllet number of column:  $P = v_m L/D$
- $q$  = volumetric flux (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 ( $\mu\text{g}/\text{g}$ )
- $t$  = time (days)
- $t_1$  = pulse period (days)
- $T$  = pore volume:  $T = v_0 t/L = v_m t\phi/L$
- $T_1$  = dimensionless pulse period:  $T_1 = v_0 t_1/L$
- $v_0$  = average pore-water velocity (cm/day):  $v_0 = q/\theta$

$v_m$	= average pore-water velocity in dynamic region (cm/day): $v_m = q/\theta_m$
$x$	= dimensionless distance: $x = z/L$
$z$	= distance (cm)
$\alpha$	= mass transfer coefficient (1/day)
$\bar{\alpha}$	= dimensionless mass transfer coefficient: $\bar{\alpha} = \alpha L/q$
$\beta$	= $\phi R_m/R$
$\theta$	= water content: $\theta = \theta_m + \theta_{im}(\text{cm}^3/\text{cm}^3)$
$\theta_m$	= mobile water content ( $\text{cm}^3/\text{cm}^3$ )
$\theta_{im}$	= immobile water content ( $\text{cm}^3/\text{cm}^3$ )
$\phi$	= fraction mobile water: $\phi = \theta_m/\theta$
$\rho$	= bulk density ( $\text{g}/\text{cm}^3$ )

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