

## Mass Transfer Studies in Sorbing Porous Media: III. Experimental Evaluation with 2,4,5-T

M. TH. VAN GENUCHTEN,<sup>2</sup> P. J. WIERENGA,<sup>3</sup> AND G. A. O'CONNOR<sup>3</sup>

### ABSTRACT

Comparisons are made between observed and calculated effluent concentration distributions for the movement of 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) through 30-cm long unsaturated soil columns. The comparisons are made using both analytical and numerical solutions of a previously published model, which included the effects of intra-aggregate diffusion and adsorption. The results in this study indicate that intra-aggregate diffusion and adsorption/desorption are the main mechanisms responsible for effluent tailing. An estimated 60% of the adsorption was found to occur in the stagnant region of the soil. When intra-aggregate diffusion was included in the model, the observed adsorption/desorption hysteresis phenomenon found to be significant in several earlier studies, was shown to be much less important in describing the observed concentration distributions.

*Additional Index Words:* intra-aggregate diffusion, adsorption-desorption, hysteresis, miscible displacement, 2,4,5-T.

**I**N PART I OF THIS STUDY (van Genuchten and Wierenga, 1976a), a theoretical model was developed to describe the movement of chemicals through unsaturated, aggregated, sorbing porous media. Analytical solutions were derived for both the mobile and immobile liquid regions of the medium,

assuming the presence of a linear equilibrium isotherm. These solutions were subsequently used in part II (van Genuchten and Wierenga, 1977; this issue) to describe tritium movement through unsaturated, aggregated Glendale clay loam. In this paper, part III of the study, the theoretical model will be used to describe experimental data on the movement of the herbicide 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) through the same Glendale soil. As was mentioned in Part I, no analytical solutions exist when either the adsorption isotherm is nonlinear, or when the adsorption-desorption process is not single-valued (hysteretic). For these conditions numerical techniques must be used. The numerical solutions used in this analysis were programmed in IBM S/360 CSMP as described by van Genuchten and Wierenga (1974; 1976b).

<sup>1</sup>Journal article no. 568, Agric. Exp. Stn., New Mexico State Univ., Las Cruces, NM 88003. The work upon which this report was based was supported in part by funds obtained from the U.S. Dep. of the Interior, Office of Water Resources Research, as authorized under the Water Resources Act of 1964. Received 8 March 1976. Approved 9 Nov. 1976.

<sup>2</sup>Formerly Graduate Student, Dep. of Agronomy, New Mexico State Univ.; presently Research Associate, Dep. of Civil Engineering, Princeton Univ., Princeton, NJ 08540.

<sup>3</sup>Associate Professor, Dep. of Agronomy, New Mexico State Univ., Las Cruces, NM 88003.

**Table 1—Soil-physical data for data for various displacements through Glendale clay loam.**

Exp. no.	Tracer	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
					$T_1$	$t_1$	
Experiment 1							
1-1	<sup>3</sup> H	1.360	0.460	5.09	2.334	6.331	2.0
1-2	<sup>3</sup> H	1.360	0.460	5.09	0.512	1.389	2.0
1-4	2,4,5-T	1.360	0.473	5.11	2.761	7.672	2.0
1-5	<sup>3</sup> H	1.360	0.460	2.55	1.990	10.76	2.0
Experiment 2							
2-1	<sup>3</sup> H	1.361	0.464	4.55	2.361	7.215	2.0
2-2	<sup>3</sup> H	1.361	0.468	4.57	0.452	1.389	2.0
2-4	2,4,5-T	1.361	0.479	4.59	2.460	7.708	2.0
2-5	<sup>3</sup> H	1.361	0.467	2.29	1.762	10.77	2.0
Experiment 3							
3-2	<sup>3</sup> H	1.222	0.454	17.0	3.102	2.475	6.3
3-3	2,4,5-T	1.222	0.475	17.0	3.994	3.212	6.3
3-4	<sup>3</sup> H	1.222	0.445	4.20	1.909	6.076	6.3
3-6	<sup>3</sup> H	1.222	0.434	1.32	1.788	9.653	6.3
Experiment 4							
4-1	2,4,5-T	1.309	0.456	16.8	4.948	4.028	6.3
4-2	<sup>3</sup> H	1.309	0.433	4.04	1.871	6.021	6.3

## MATERIALS AND METHODS

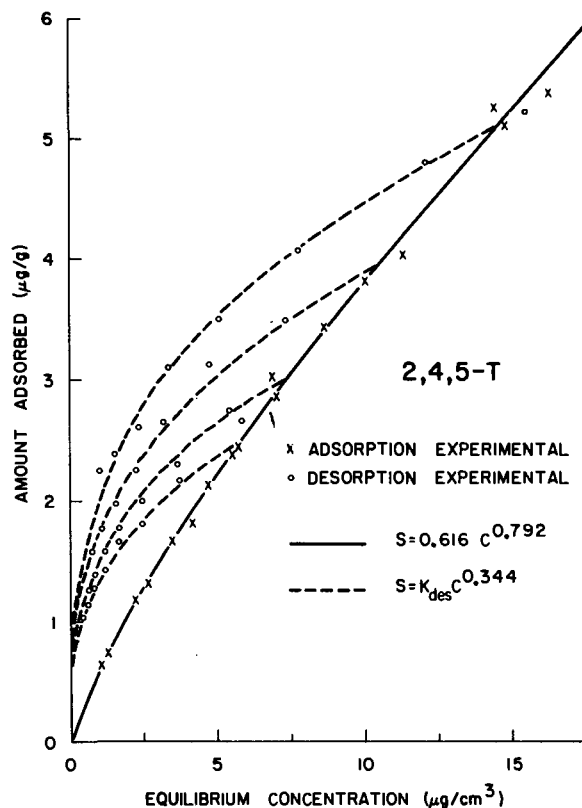
The same experimental setup as discussed in part II (van Genuchten and Wierenga, 1977) was used to study the movement of 2,4,5-T through 30-cm long soil columns uniformly packed with the same aggregated (Glendale clay loam soil as was used for the tritium experiments. Concentrations of 10 ppm of 2,4,5-T were used for the leaching studies. Radioactive 2,4,5-T with a specific activity of 4.93  $\mu\text{Ci}/\text{mg}$ , and labeled at the carboxyl position was added to unlabeled herbicide solution. Activities of the 2,4,5-T-<sup>14</sup>C were determined on a Packard TriCarb Model 3310 liquid scintillation counter, using Aquasol (New England Nuclear, Boston, Mass.) as the counting medium. Relative effluent concentrations ( $C_m$ ) were obtained by dividing the herbicide concentrations in the effluent ( $C_m$ ) by the concentration of the herbicide pulse ( $C_0$ ) applied to the columns.

A total of five runs were made with four columns, using Glendale clay loam of two different aggregate sizes and employing soil water fluxes ( $q$ ), ranging from 4.0 to 17.0 cm/day. The experimental data for the various 2,4,5-T displacements are given in Table 1. Included in this table are the soil physical data of several tritium displacements at similar water contents and flow velocities through the same columns. The experiments in Table 1 are numbered by column and flux ( $q$ ).

The equilibrium adsorption isotherm for 2,4,5-T and the Glendale clay loam was determined using duplicate 1:1 mixtures of 25 g of soil and 25 ml of various herbicide concentrations in 0.01N CaCl<sub>2</sub>. Each sample was shaken for 24 hours and then centrifuged at 1,500 rpm for 15 min. The 24-hour shaking period was experimentally determined to be more than sufficient time to obtain equilibrium between sorbed and solution concentrations (G. A. O'Connor, 1972)<sup>4</sup>. Ten milliliters of the supernatant was removed and analyzed for <sup>14</sup>C activity and the count rates were converted to herbicide concentrations. The difference between the original herbicide concentration and that in the supernatant was assumed to be the result of adsorption.

Equilibrium desorption isotherms were obtained using the same duplicate 1:1 soil-to-herbicide solution mixtures used for the adsorption study. The 10-ml supernatant sample removed from the centrifuged samples to determine the initial adsorption was replaced by 10 ml of 2,4,5-T-free 0.01N CaCl<sub>2</sub>. The soil was loosened from the tubes by vigorous hand shaking. The samples were then shaken mechanically for 24 hours to establish a new

<sup>4</sup>G. A. O'Connor. 1972. Soil adsorption and desorption of 2,4,5-T. Agron. Abstr. p. 92.



**Fig. 1—Equilibrium adsorption and desorption data for 2,4,5-T sorption on Glendale clay loam.**

equilibrium, centrifuged, and another 10-ml extraction and analysis of the supernatant was made. This procedure was followed for each successive desorption step. In total, seven data points were determined for each of four desorption curves.

The adsorption studies for 2,4,5-T were repeated using two different soil solution ratios: 20 g of soil mixed with 30 ml of herbicide solution, and 30 g of soil with 20 ml of herbicide solution. No differences in adsorption were found. The adsorption points obtained with these two additional adsorption studies were used, together with the earlier results to construct the equilibrium adsorption isotherm.

## RESULTS AND DISCUSSION

The equilibrium adsorption and desorption data for 2,4,5-T and Glendale clay loam are given in Fig. 1. The data show that adsorption and desorption cannot be described by the same relation, and hence, are nonsingle valued (hysteretic). Both the adsorption and desorption isotherms could be described by Freundlich-type equations of the form:

$$S = KC^N \quad [1]$$

The coefficients  $K$  and  $N$  in Eq. [1] are different for adsorption and desorption. Values for  $K$  and  $N$  are listed in Table 2; they were obtained following the procedures outlined by Hornsby and Davidson (1973) and van Genuchten et al. (1974). In this study a value of 2.3 for the ratio  $N_{\text{ads}}/N_{\text{des}}$  was obtained, as shown by the data in Table 2. This value was found to be independent of the maximum concentration ( $C_{\text{max}}$ ) before desorption is initiated. Similar values were reported in several earlier studies on the adsorption and desorption of several pesticides from different soils (Swan-

**Table 2**—Parameters used in Eq. [1] to describe the adsorption and desorption of 2,4,5-T on Glendale clay loam.  $C_{max}$  is the solution concentration before desorption is initiated. The subscripts "ads" and "des" indicate adsorption and desorption, respectively.

Process	Chemical	$K_{ads}$	$N_{ads}$	$K_{des}$	$N_{des}$
Adsorption	2,4,5-T	0.616	0.792	--	--
Desorption	2,4,5-T	--	--	1.36	0.344
	$C_{max} = 5.87 \mu\text{g}/\text{cm}^3$	--	--	1.51	0.344
	$C_{max} = 7.41 \mu\text{g}/\text{cm}^3$	--	--	1.75	0.344
	$C_{max} = 10.30 \mu\text{g}/\text{cm}^3$	--	--	2.03	0.344
	$C_{max} = 14.35 \mu\text{g}/\text{cm}^3$	--	--	--	--

son and Dutt, 1973; Hornsby and Davidson, 1973; van Genuchten et al., 1974). Somewhat smaller values (closer to one) however, were obtained by Farmer and Aochi (1974) and Wood and Davidson (1975).

Observed and calculated 2,4,5-T effluent curves for column experiment number 2-4 are shown in Fig. 2. The solid line represents the analytical solution for the concentration in the mobile liquid ( $c_m$ ). Since this solution requires a linear adsorption isotherm (see van Genuchten and Wierenga, 1976a), it was necessary to approximate the nonlinear adsorption isotherm in Fig. 1 by a straight line. The following procedure was used to linearize the equilibrium isotherm. We denote the linearized isotherm by  $S = K^1_{ads}C$  and require that the areas under the isotherms over the range 0-10 ppm (all columns were leached with 10-ppm solutions) for both the linearized and the nonlinear Freundlich equations be the same (Fig. 1). Thus

$$\int_0^{10} K_{ads} C dC = \int_0^{10} 0.616 C^{0.792} dC \quad [2]$$

where  $K^1_{ads}$  ( $=0.426$ ) is referred to as the linearized adsorption constant. From the value of 0.426 a retardation factor  $R$  (for notation see the appendix) of 2.210 was calculated. A three-parameter curve fitting was then carried out with the previously described GAUSHAUS nonlinear curve fitting program (van Genuchten and Wierenga, 1977) to obtain estimates for the dimensionless parameters  $\beta$ ,  $P$ , and  $\bar{\alpha}$  which appear in the analytical solution. Results obtained for four

2,4,5-T displacements are given in Table 3. Included in the table are data obtained from several tritium displacements through the same columns. The fraction of the adsorption sites located in the dynamic region of the soil ( $f$ ), was subsequently calculated for each 2,4,5-T displacement using Eq. [17] of van Genuchten and Wierenga (1977) i.e.

$$\beta R = \phi + f(R - 1) \quad [3]$$

or

$$f = \frac{\beta R - \phi}{R - 1} \quad [4]$$

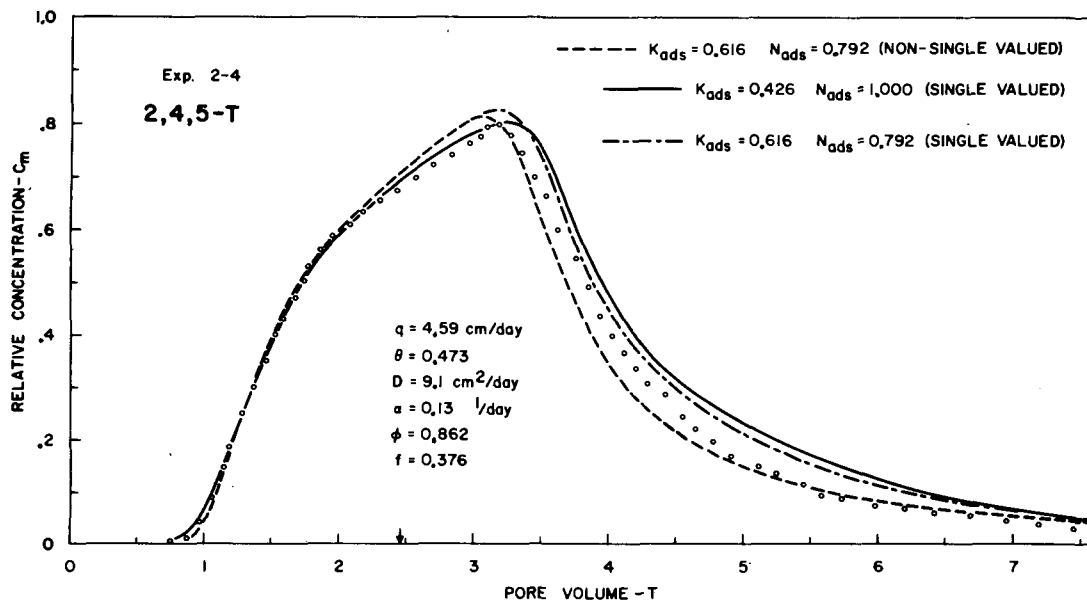
For the data of experiment no. 2-4, one obtains

$$f = \frac{(0.596)(2.21) - (0.862)}{(1.21)} = 0.376. \quad [5]$$

The solid line in Fig. 2 was calculated with the analytical solution and shows a fairly good agreement with the experimental data. The dashed-dotted line was obtained with the numerical solution of van Genuchten and Wierenga (1976b), using the value of  $f$  as calculated above and including the nonlinearity of the adsorption isotherm. The differences between the nonlinear (numerical) model and the linear (analytical) model are rather small. The breakthrough part of the curve becomes somewhat steeper and the peak concentration decreases when the nonlinearity is taken into account. These two effects of the nonlinear isotherm on the calculated curves are easily explained by considering the retardation factor  $R_m$  of the dynamic region (van Genuchten and Wierenga, 1976a)

$$R_m = 1 + f\rho KNC_m^{N-1}/\theta_m. \quad [6]$$

Since  $N < 1$ ,  $R_m$  will decrease with increasing concentration  $C_m$ . Retardation of the chemical will be more extensive at the lower and less extensive at the higher concentrations as compared to the linear case. The net result will be a steeper



**Fig. 2**—Observed and calculated 2,4,5-T effluent curves for experiment 2-4. The open circles represent observed data points.

**Table 3**—Summary of various 2,4,5-T and tritium displacements through Glendale clay loam. The tritium data were obtained from van Genuchten and Wierenga (1977). The superscripts l and f indicate linearization and fitted, respectively.

Exp. no.	Tracer	$R$	$\beta$	$P$	$\bar{\alpha}$	$f$	$\phi$	$D$ cm <sup>2</sup> /day	$\alpha$ 1/day	$R^f$	$K_{ads}^f$	$K_{ads}^f/K_{ads}^l$
1-1	<sup>3</sup> H	1.027	0.926	95	1.47	0.400†	0.940	3.7	0.25	--	0.009	--
1-2	<sup>3</sup> H	1.027	0.926	95	1.47	0.400†	0.940	3.7	0.25	--	0.009	--
1-4	2,4,5-T	2.225	0.661	41	0.55	0.433	0.940	8.4	0.09	2.301	0.453	1.06
1-5	<sup>3</sup> H	1.027	0.928	95	0.56	0.400†	0.942	1.9	0.048	--	0.009	--
2-1	<sup>3</sup> H	1.026	0.850	45	1.50	0.400†	0.862	7.6	0.23	--	0.009	--
2-2	<sup>3</sup> H	1.026	0.887	45	1.31	0.400†	0.900	7.2	0.20	--	0.009	--
2-4	2,4,5-T	2.210	0.596	37	0.88	0.376	0.862	9.1	0.13	2.279	0.450	1.06
2-5	<sup>3</sup> H	1.026	0.830	45	1.05	0.400†	0.841	3.9	0.080	--	0.009	--
3-2	<sup>3</sup> H	1.024	0.841	56	0.39	0.400†	0.852	24.0	0.22	--	0.009	--
3-3	2,4,5-T	2.139	0.616	19	0.21	0.409	0.852	68.0	0.12	1.855	0.338	0.79
3-4	<sup>3</sup> H	1.025	0.872	56	0.72	0.400†	0.884	5.7	0.10	--	0.009	--
3-6	<sup>3</sup> H	1.025	0.717	56	1.96	0.400†	0.725	2.2	0.086	--	0.009	--
4-1	2,4,5-T	2.223	0.602	20	0.39	0.399	0.850	64.0	0.22	2.476	0.489	1.15
4-2	<sup>3</sup> H	1.027	0.788	57	0.93	0.400†	0.798	6.2	0.12	--	0.009	--

† Assumed to be 0.400.

front and a higher peak concentration for the curve based on the nonlinear model.

Figure 2 also shows the effect of the observed hysteresis on the numerical results. The break-through side of the effluent curve is not affected by the hysteresis, but the relative concentration during elution decreases much faster and more prolonged tailing occurs at the higher pore volumes if hysteresis is taken into account. From Fig. 2 one may conclude that both the nonlinearity of the adsorption isotherm, as well as the observed hysteresis do not affect the shape and position of the effluent curve to any great extent. All three calculated curves describe the experimental data reasonably well. Note that an  $f$ -value of 0.376 was obtained from the data presented in Fig. 2. This indicates that more than 60% of the adsorption occurs in the stagnant region of the soil.

The dispersion coefficient  $D$  used to construct the three curves in Fig. 2 is higher than the dispersion coefficient used to describe tritium displacement through the same column at the same velocity. Table 3 shows that the Peclet numbers based on the 2,4,5-T displacements are smaller than those determined from the tritium data. Theoretically, only one value of the Peclet number should hold for all displacements through the same column, independent of the tracer used, provided the flow velocities are sufficiently high that longitudinal diffusion is negligible compared to mechanical dispersion (Perkins and Johnson, 1963). The discrepancies between the Peclet numbers for 2,4,5-T and tritium are in our opinion due to the existence of kinetic phenomena during adsorption of the herbicide. This study assumes equilibrium adsorption, a condition which may not have been met during the leaching experiments. In a study of the equilibrium times for 2,4,5-T and Glendale clay loam, G. A. O'Connor (1972)<sup>4</sup> showed that although the initial adsorption rate was very fast, complete adsorption could be obtained only after herbicide and soil were shaken for several hours. When a kinetic adsorption mechanism is present, the front portion of the effluent curve will be less steep, as shown in previous studies (van Genuchten et al., 1974; van Genuchten and Wierenga, 1974). By neglecting the kinetic effects and using an equilibrium instead of a kinetic model, a higher dispersion coefficient will hence be necessary in order to obtain the same description of the front

portion of the curve. It should be mentioned that in addition to the occurrence of kinetic phenomena, the curve-fitted value of the Peclet number will be influenced also by the fact that a linearized adsorption relation is used in the model, instead of the nonlinear one observed. However, this effect is small as shown by the differences between the solid and dashed lines in Fig. 2. It should be further noted that a slightly different value of  $D$  will somewhat affect the value of the mass transfer coefficient  $\alpha$  that is obtained; however, it will not influence the value of  $f$  obtained with the curve-fitting procedure.

The solid line in Fig. 2 was obtained with the linear adsorption model, using a value of 0.426 for the (linearized) adsorption constant, obtained from the batch equilibrium studies. This coefficient may also be estimated directly from the effluent curve, using a four-parameter rather than a three-parameter curve fit. Results for experiment No. 1-4 are shown in Fig. 3, where the solid line was calculated with a fitted adsorption constant of 0.453, while the dashed line was obtained with the linearized adsorption constant of 0.426. Both calculated curves are essentially the same. Note that the values of the parameters  $D$ ,  $\alpha$ , and  $f$  obtained with the four-parameter curve fitting are also very close to those determined with the three-parameter fitting. Values of the fitted adsorption constant ( $K_{ads}^f$ ) for the four 2,4,5-T displacements are listed in Table 3. The values of  $K_{ads}^f$  agree reasonably well with the linearized adsorption constant  $K_{ads}^l$ , the average  $K_{ads}^f$  being nearly identical to  $K_{ads}^l$ . This suggests that, when assuming a linear adsorption isotherm, the adsorption constant can be estimated with reasonable accuracy from the effluent data. However, Green et al. (1972) in a study on the movement of picloram through two aggregated soils obtained much higher values for  $K_{ads}^f$  than could be accounted for by means of equilibrium measurements. It appears that additional experimental verification, using different pesticides and soils is necessary before definite conclusions can be reached.

Figure 4 compares observed and calculated 2,4,5-T effluent curves for experiment no. 4-1. The largest aggregate size used for this experiment was 6.3 mm, compared to 2.0 mm for the data shown in Fig. 2 and 3. The solid line in Fig. 4 again represents the analytical solution using the linearized adsorption constant. A reasonable description of the

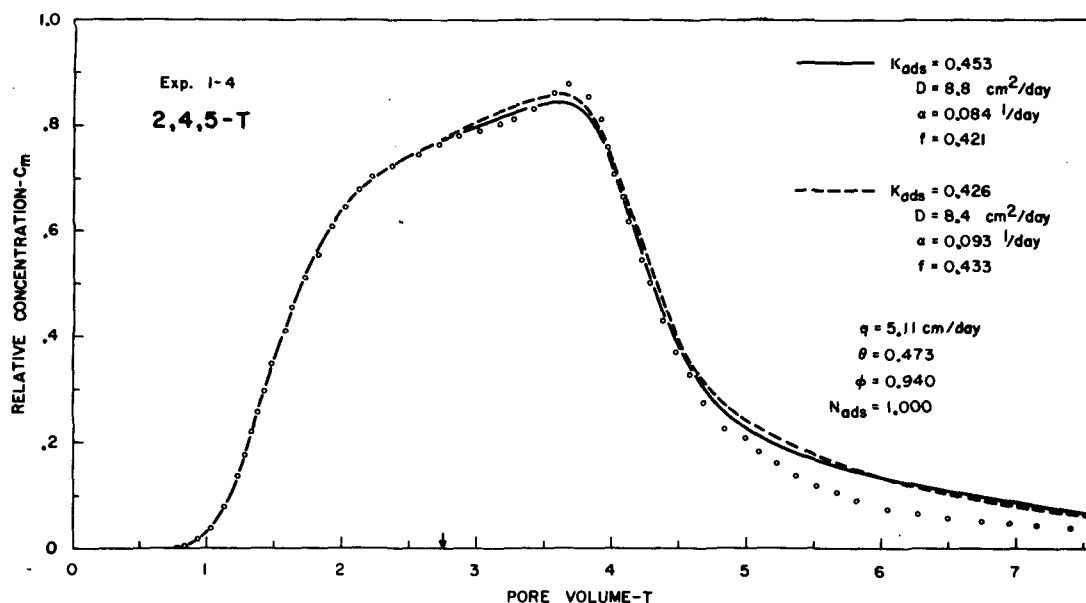


Fig. 3—Observed and calculated 2,4,5-T effluent curves for experiment 1-4. Calculations were based on the linear adsorption model, with and without fitting the adsorption constant  $K_{ads}$  to the effluent data. The open circles represent observed data points.

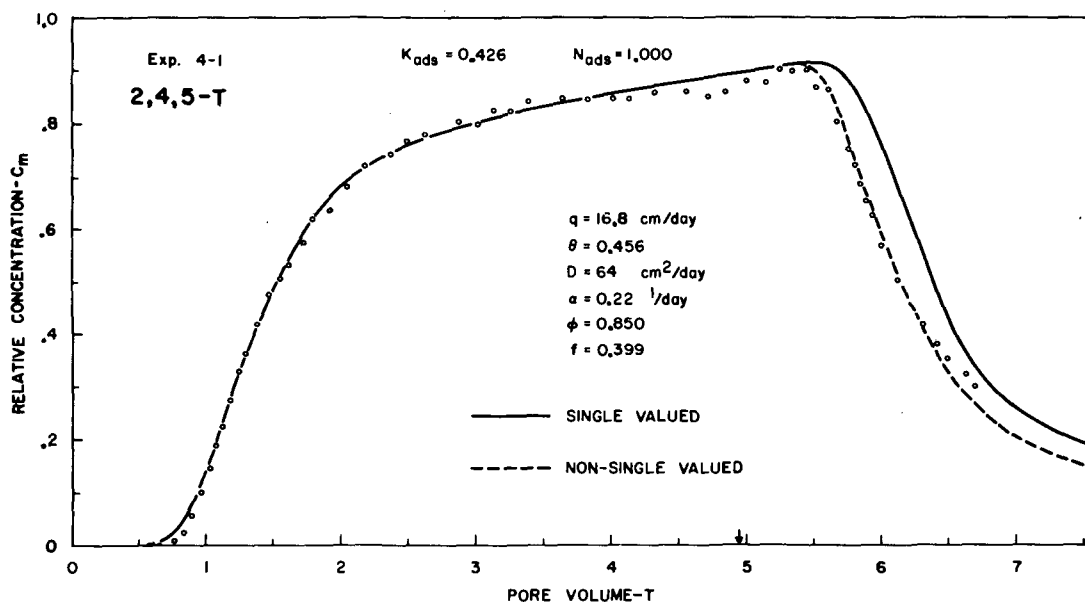


Fig. 4—Observed and calculated 2,4,5-T effluent curves for experiment 4-1. The adsorption constant  $K^1$  was obtained by linearization of the equilibrium adsorption isotherm. The open circles represent observed data points.

experimental data is obtained, even though in this case the fitted adsorption constant was found to be 15% higher than the linearized value (Table 3). Note that an  $f$ -value of approximately 0.40 was obtained from the data in Fig. 4. Hence 40% of the adsorption occurred in the dynamic and 60% in the stagnant region of the soil. Similar values for  $f$  were obtained for the other displacements (Table 3), suggesting that the relative location of the sorption sites is not influenced significantly by either aggregate size or bulk density.

Table 3 further shows that the values of the mass transfer coefficient,  $\alpha$ , obtained from the 2,4,5-T displacements are lower than those obtained from the tritium displacements at similar flow velocities. This may be expected since the mass

transfer coefficient is proportional to the diffusion coefficient (Coats and Smith, 1964), and the diffusion coefficient of tritium is very large compared to those of most organic chemicals (Wang et al., 1953; International Critical Tables, 1929). The data in Table 3, except for the displacements in column 4, show that the ratio of the mass transfer coefficients of 2,4,5-T and tritium is approximately 0.5 ( $\pm 0.15$ ) at similar flow rates. A comparison of experiments 4-1 and 4-2 is meaningless, since the displacements of 2,4,5-T and tritium in this column were carried out at different velocities ( $\alpha$  is a function of the average pore-water velocity).

The inclusion of hysteresis in the model does not appreciably affect the calculated curves (Fig. 2 and 4). Thus, for the conditions of this study, intra-aggregate exchange of

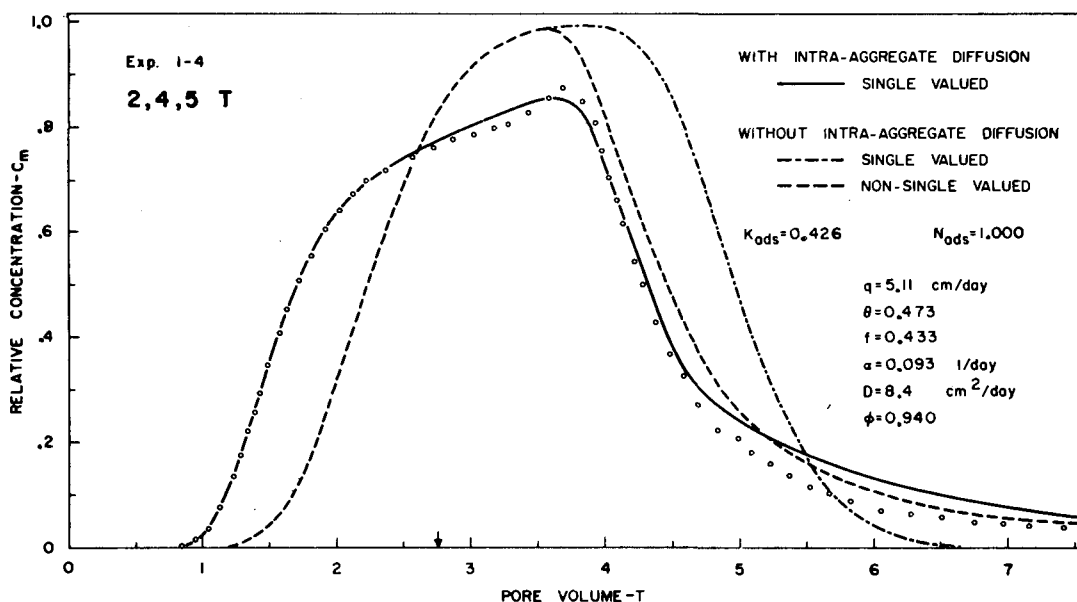


Fig. 5—Observed and calculated 2,4,5-T effluent curves for experiment 1-4, with and without including intra-aggregate diffusion. The open circles represent observed data points.

2,4,5-T between mobile and immobile regions was far more important than the hysteresis in the adsorption-desorption process. The effects of hysteresis, however, become more pronounced when intra-aggregate diffusion is neglected, as was suggested in several earlier studies (e.g., Swanson and Dutt, 1973; van Genuchten et al., 1974). This is clearly demonstrated in Fig. 5, where the experimental data of experiment no. 1-4 are compared with calculated curves, which include (solid line) or neglect intra-aggregate diffusion (dashed and dashed-dotted lines). The dashed line includes the effect of hysteresis and was obtained with the numerical program of van Genuchten and Wierenga (1974, example 1). The dashed-dotted line assumes no hysteresis. The linear adsorption model without intra-aggregate diffusion ( $\alpha=0$ ,  $\beta=1$ ) reduces then to the solution of Lindstrom et al. (1967). The more or less symmetrical curve obtained with this solution fails to describe the data in Fig. 5. When hysteresis is included in the calculations, the observed tailing during elution of the chemical is fairly well described. However, hysteresis has no effect on the breakthrough side of the curve, and hence, cannot explain the early appearance of the chemical in the effluent nor the tailing at the higher concentrations. Tailing during breakthrough will remain largely unnoticed when relatively short pulses are used. This may have influenced earlier conclusions about the importance of hysteresis on solute movement in soils (Swanson and Dutt, 1973; van Genuchten et al., 1974).

The break in the effluent concentration distributions during breakthrough of the chemical, and its subsequent tailing off, has been observed also by Kay and Elrick (1967) for the movement of lindane through Honeywood silt loam, and by J. M. Davidson (unpublished data, 1973) for the movement of picloram through Norge loam. Kay and Elrick (1967) attributed the tailing to intra-aggregate diffusion and adsorption, a phenomena which is substantiated by both experimental and theoretical descriptions of 2,4,5-T effluent curves in this study.

In Fig. 4 a comparison was made between the linear adsorption model and the observed data from experiment No. 4-1. An accurate description of the data was obtained, especially during break-through of the chemical. The parameter values presented in Fig. 4 were also used to calculate concentration profiles inside the column for both the mobile ( $c_m$ ) and the immobile liquids ( $c_{im}$ ). The results are given in Fig. 6. The differences in concentration between the two liquid regions are significant. For example, the relative concentration in the mobile region at a depth of 20 cm reaches a value of 0.5 after only 0.8 days, while it takes about 2.3 days for the concentration in the immobile region to reach this same value. Previously, (van Genuchten and Wierenga, 1977) similar distributions for tritium were shown. Although still considerable, the differences between  $c_m$  and  $c_{im}$  for tritium were less than those shown in Fig. 6. This may be expected, since tritium adsorption is very small ( $K = 0.009$ ), and material which diffuses into the stagnant region of the soil can be stored only in the (immobile) liquid.

The fraction of the chemical diffusing into the stagnant region which will remain in solution may be calculated by considering the transport equation which describes the diffusional exchange between dynamic and stagnant regions. Assuming linear adsorption, this equation is given by (van Genuchten and Wierenga, 1976a, Eq. [16])

$$[\theta_{im} + (1-f)\rho K] (\partial C_{im} / \partial t) = \alpha (C_m - C_{im}). \quad [7]$$

The first term on the left represents the material stored in the immobile liquid, while the second term gives the material adsorbed by the stagnant region. The fraction remaining in solution hence is given by

$$\theta_{im} / [\theta_{im} + (1-f)\rho K].$$

Using the data from experiment no. 4-1, one may calculate that only 17% of 2,4,5-T will remain in solution, while the remaining 83% will be adsorbed (for tritium nearly 100%

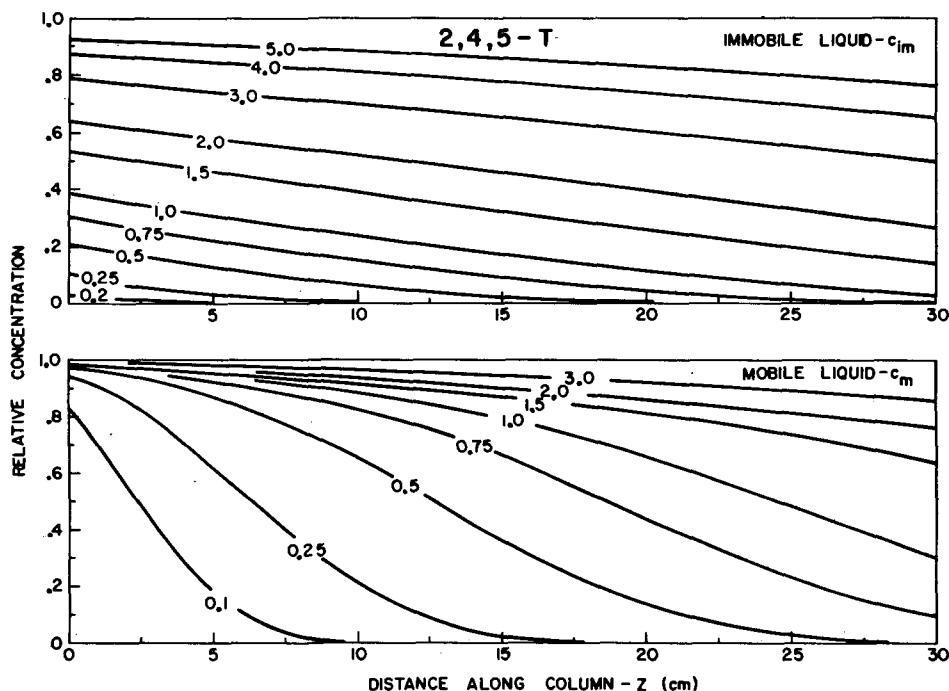


Fig. 6—Concentration profiles inside column 4, at different times during leaching with 2,4,5-T. Values of the parameters used to construct the curves are given in Fig. 4. Numbers on the curves indicate time (days) after leaching was initiated.

will remain in solution). Thus, when sorption increases, relatively more material can diffuse into the stagnant region of the soil. Since this diffusion is very slow compared to the rate at which the bulk of the chemical moves through the soil, the differences between the concentrations  $c_m$  and  $c_{im}$  are expected to increase progressively as sorption increases.

$\beta$	= $\phi R_m/R$
$\theta$	= 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 ( $\text{g}/\text{cm}^3$ )

#### APPENDIX-NOTATION

$C_0$	= influent concentration ( $\mu\text{g}/\text{cm}^3$ )
$C_1$	= concentration break-through side effluent curve
$C_m, C_{im}$	= concentration in 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 sorption isotherm: $S = KC^N$
$L$	= length of column (cm)
$P$	= Peclet number of column: $P = v_m L/D$
$q$	= flux
$R$	= total 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 regions, respectively ( $\mu\text{g}/\text{g}$ )
$t$	= 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 ( $\text{cm}/\text{day}$ ): $v_o = q/\theta$
$v_m$	= average pore-water velocity in dynamic region: $v_m = q/\theta_m$ ( $\text{cm}/\text{day}$ )
$x$	= dimensionless distance: $x = z/L$
$z$	= distance (cm)
$\alpha$	= mass transfer coefficient ( $1/\text{day}$ )
$\bar{\alpha}$	= dimensionless mass transfer coefficient: $\bar{\alpha} = \alpha L/q$

#### LITERATURE CITED

- Coats, K. R., and B. D. Smith. 1964. Dead-end pore volume and dispersion in porous media. *Soc. Pet. Eng. J.* 4:73-84.
- Farmer, W. J., and Y. Aochi. 1974. Picloram sorption by soils. *Soil Sci. Soc. Am. Proc.* 38:418-423.
- Green, R. E., P. S. C. Rao, and J. C. Corey. 1972. Solute transport in aggregated soil: tracer zone shape in relation to pore-velocity distribution and adsorption. *In Proc. 2nd Symp. Fundamentals of transport phenomena in porous media. IAHR-ISSS. (Guelph, Canada) August 7-11, 1972. Vol. 2:732-752.*
- Hornsby, A. G., and J. M. Davidson. 1973. Solution and adsorbed fluometuron concentration distribution in a water-saturated soil: experimental and predicted evaluation. *Soil Sci. Soc. Am. Proc.* 37:823-828.
- International Critical Tables. 1929. McGraw-Hill Book Co., Inc., New York. Vol. V.
- Kay, B. D., and D. E. Elrick. 1967. Adsorption and movement of lindane in soils. *Soil Sci.* 104:314-322.
- Lindstrom, F. T., R. Hague, V. H. Freed, and L. Boersma. 1967. Theory on the movement of some herbicides in soils. *Environ. Sci. Technol.* 1:561-565.
- Perkins, T. K., and O. C. Johnson. 1963. A review of diffusion in porous media. *Soc. Pet. Eng. J.* 19:70-84.
- Swanson, R. A., and G. R. Dutt. 1973. Chemical and physical processes that affect atrazine movement and distribution in soil systems. *Soil Sci. Soc. Am. Proc.* 37:872-876.
- van Genuchten, M. Th., and P. J. Wierenga. 1974. Simulation of one-dimensional solute transfer in porous media. *N. Mex. Agric. Exp. Stn. Bull.* 628. 40 p.
- van Genuchten, M. Th., J. M. Davidson, and P. J. Wierenga. 1974. An evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media. *Soil Sci. Soc. Am. Proc.* 38:29-35.
- van Genuchten, M. Th., and P. J. Wierenga. 1976a. Mass transfer studies in sorbing porous media: I. Analytical solutions. *Soil Sci.*

- Soc. Am. Proc. 40:473-480.
13. van Genuchten, M. Th., and P. J. Wierenga. 1976b. Numerical solution for convective dispersion with intra-aggregate diffusion and non-linear adsorption. p. 275-292. *In* G. C. van Steenkiste (ed) *System Simulation in Water Resources* North Holland Publ. Co., Amsterdam.
  14. van Genuchten, M. Th., and P. J. Wierenga. 1977. Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium ( $^3\text{H}_2\text{O}$ ). *Soil Sci. Soc. Am. J.* 41:272-278 (this issue).
  15. Wang, J. H., C. V. Robinson, and I. S. Edelman. 1953. Self-diffusion and structure of liquid water: III. Measurement of the self-diffusion of liquid water with  $\text{H}^2$ ,  $\text{H}^3$  and  $\text{O}^{18}$  as tracers. *J. Am. Chem. Soc.* 75:466-470.
  16. Wood, A. L., and J. M. Davidson. 1975. Fluometuron and water content distributions during infiltration: measured and calculated. *Soil Sci. Soc. Am. Proc.* 39:820-825.