

An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement Through Porous Media¹

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ABSTRACT

Miscible displacement techniques were used to study the movement of picloram (4-amino-3,5,6-trichloropicolinic acid) through a water-saturated Norge loam soil. The equilibrium adsorption and desorption isotherms for picloram and Norge loam soil were not single-valued relations. Picloram mobility was reduced significantly when the average pore-water velocity was decreased from 145 to 14.2 cm/day. Observed and predicted effluent concentration distributions were compared. Predictions were made with a S/360 CSMP simulation model, using two kinetic rate equations and an equilibrium Freundlich equation. The two kinetic models and the equilibrium model each satisfactorily described the observed effluent concentration distributions at low pore-water velocities provided the non-single-valued character of the adsorption-desorption process was included in the calculations. At high pore-water velocities, the kinetic adsorption models were found inadequate to predict the picloram movement. An empirical model was then developed, based on the assumption that equilibrium existed during displacement and that only a fraction of the soil participated in the adsorption process. This fraction was found to be a function of the average pore-water velocity. With the empirical model, a reasonable fit between data and calculated effluent curves was obtained for all pore-water velocities.

Additional Index Words: herbicide movement, adsorption, molecular diffusion, miscible displacement, computer simulation, S/360 CSMP.

RECENTLY, several mathematical models have been proposed to describe the movement of chemicals through

adsorbing porous media (7, 12, 13, 14). One of the earliest solutions for equilibrium adsorption between the solution and adsorbed phases was presented by Lapidus and Amundson (10). Hashimoto et al. (7) obtained a similar solution which included the longitudinal mixing process as well as equilibrium and linear adsorption during one-dimensional flow. Their solution, including the "retardation factor," was later used by Kay and Elrick (9). Lindstrom et al. (13) and Davidson and Chang (2) used a similar solution to describe the movement of several organic chemicals through porous media. These solutions assumed instantaneous adsorption and a linear and single-valued adsorption-desorption relation. These assumptions may not be valid for all conditions that occur in a soil-water system.

Kay and Elrick (9) and Davidson and Chang (2) showed considerable deviation between the mathematical model based on the assumption of equilibrium adsorption (7) and experimental data, especially at the high flow velocities. The two studies suggested that for high pore-water velocities, the use of a kinetic rate equation to describe the adsorption process may be necessary. Lapidus and Amundson (10), Oddson et al. (14) and Lindstrom et al. (12) each presented solutions that included a rate equation in a convective type transport equation to describe the displacement of a chemical in a sorbing porous medium. Oddson et al. (14) and Lapidus and Amundson (10) used a first-order rate equation, but assumed that the diffusion and dispersion processes were negligible in the transport equation in order to obtain an analytical solution. Lindstrom et al. (12) used an adsorption rate equation as well as a "sticking probability" factor.

The presence of a non-single-valued (hysteretic) adsorption-desorption relation has received little attention in earlier studies. Swanson and Dutt (16), studied the movement of 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine) through different soils and encountered such a non-single-valued adsorption-desorption relationship. They found that both the adsorption and desorption isotherms were of the Freundlich form, but that the coefficients for adsorption were not equal to those for desorption. These same authors were able to predict the movement of atra-

¹Contribution from the Departments of Agronomy at New Mexico State University, Las Cruces and Oklahoma State University, Stillwater. The work upon which this report was based was supported in part by funds obtained from the U. S. Department of the Interior, Office of Water Resources Research, as authorized under the Water Resources Research Act of 1964, and by E. P. A. Research Grant no. R-800364 at Oklahoma State University. Journal Article no. 463, Agr. Exp. Sta., New Mexico State Univ., Las Cruces, New Mexico, 88003. Received April 3, 1973. Approved September 5, 1973.

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zine reasonably well with a computer model that assumed instantaneous adsorption and desorption.

The purpose of this study was to use some of the available adsorption models in a transport equation to describe experimental laboratory data. A S/360 CSMP (Continuous System Modeling Program) computer program (8) was developed for three different adsorption models, based on equations presented by Lindstrom et al. (12), Oddson et al. (14), and an equilibrium Freundlich adsorption relationship, respectively. Computer results were then compared with experimentally determined picloram effluent concentration distributions from a water-saturated Norge loam soil.

ADSORPTION EQUATIONS

The movement of adsorbed chemicals through a porous medium under steady state soil-water conditions was assumed to obey the following differential equation:

$$\frac{\rho \partial S}{\theta \partial t} + \frac{\partial C}{\partial t} = D_o \frac{\partial^2 C}{\partial x^2} - v_o \frac{\partial C}{\partial x} \quad [1]$$

where C is the concentration of the chemical in solution ($\mu\text{g}/\text{cm}^3$), S is the amount of chemical adsorbed per gram of soil ($\mu\text{g}/\text{g}$), D_o is the dispersion coefficient (cm^2/day), v_o is the average pore-water velocity (cm/day), ρ is the bulk density (g/cm^3), θ is the saturated water content (cm^3/cm^3), x is the linear distance in the direction of flow (cm), and t is time (days).

Exact solutions to Eq. [1] for specific initial and boundary conditions are only available when assumptions are made concerning the mechanisms of adsorption or diffusion and dispersion (7, 10, 13, and 14). Although it would be desirable, as indicated by Lapidus and Amundson (10), to use a general relation for adsorption-desorption of the form:

$$\partial S / \partial t = f(C, S) \quad [2]$$

only three special cases of [2] will be considered in this manuscript.

Adsorption Model I

A rate expression for the adsorption process which considers both the forward and backward kinetic rate coefficients as well as the sticking probability of the chemical on the surface of the adsorbent has been derived by Lindstrom et al. (12). This adsorption equation allows the energies of activation for adsorption and desorption to change with surface coverage. This special case of Eq. [2] is

$$\frac{\partial S}{\partial t} = \left\{ k_2 \exp [bS] \right\} \left\{ \frac{k_1}{k_2} \exp [-2bS] \frac{\theta C}{\rho} - S \right\} \quad [3]$$

where k_1 and k_2 are the forward and backward kinetic rate coefficients (day^{-1}), respectively, b is similar to the surface stress coefficient ($\text{g}/\mu\text{g}$) described by Fava and Eyring (6), and S , C , θ , and ρ are as defined previously for Eq. [1]. Note that in Eq. [3], the backward rate coefficient, k_2 , and the partition coefficient, k_1/k_2 , are independent of concentration. For equilibrium adsorption ($\partial S/\partial t = 0$), Eq. [3] reduces to the following:

$$S = (\theta k_1 C / \rho k_2) \exp (-2bS). \quad [4]$$

The parameters b and $\theta k_1 / \rho k_2$ may be obtained from the slope and intercept of the curve $\ln (S/C)$ vs. S for various equilibrium concentrations.

The values of k_1 , k_2 , and b may not be the same for adsorption and desorption if these processes are not single-valued, and hence may change with the sign of the adsorption rate, e.g.:

$$b = \begin{cases} b_{\text{ads}} & \text{when } \partial S / \partial t > 0 \\ b_{\text{des}} & \text{when } \partial S / \partial t < 0 \end{cases} \quad [5]$$

where b_{ads} and b_{des} represent the values of b used to describe the adsorption and desorption of the chemical, respectively.

Adsorption Model II

The second form of Eq. [2] considered is:

$$\frac{\partial S}{\partial t} = k'_2 \left[\frac{k'_1 \theta}{k'_2 \rho} C^N - S \right]. \quad [6]$$

Equation [6] is a first-order kinetic rate equation, with first-order forward, k'_1 , and backward, k'_2 , kinetic rate coefficients (day^{-1}). Lapidus and Amundson (10) and Oddson et al. (14) used this adsorption relation (for $N = 1.0$) to obtain an exact solution to Eq. [1]. Their solution assumed the dispersion coefficient D_o to be equal to zero. For equilibrium adsorption ($\partial S/\partial t = 0$), Eq. [6] reduces to

$$S = (k'_1 \theta / k'_2 \rho) C^N = KC^N \quad [7]$$

where K is a distribution coefficient.

Adsorption Model III

The Freundlich equation has been shown to describe for several organic pesticides (3, 9) the relationship, at equilibrium, between the amount in solution (C) and the amount adsorbed (S). The Freundlich equation is as follows:

$$S = KC^N. \quad [8]$$

Differentiating Eq. [8] with respect to time gives

$$\frac{\partial S}{\partial t} = KNC^{N-1} \frac{\partial C}{\partial t}. \quad [9]$$

Equation [9] substituted into Eq. [1] allows this equation to be expressed in terms of one dependent variable, C . The solution to Eq. [1] and [9] with $N = 1.0$ for single-valued adsorption and desorption has been used by Davidson and Chang (2) and Kay and Elrick (9).

SOLUTION PROCEDURE

A procedure similar to that used to describe water movement [De Wit and van Keulen (5); van Keulen and van Beek (17); Bhuiyan et al. (1)] and heat transfer in soils [Wierenga and De Wit (18)] was used to find a solution for Eq. [1]. The differential equation was solved by dividing the soil column into N layers of thickness Δx . The mass flow across each boundary was calculated and the mass balance equation for each layer employed. A schematic representation of the procedure is given in Fig. 1, together with some of the variables associated with each layer. The flow of herbicide (HFLW, $\mu\text{g}/\text{day}$) in and out of each layer per unit time was calculated with the following equation:

$$\text{HFLW}_i = \left[D_o * \frac{C_{i-1} - C_i}{\Delta x} + v_o * \frac{C_i + C_{i-1}}{2} \right] * \theta * \text{AREA} \quad [11]$$

where C_i is the concentration in each layer or compartment at time t , i is the index for depth ($i = 1, 2, \dots, n$) and AREA is the cross-sectional area of the column most conveniently set at unity, as was done in this study. The net flux of herbicide into each compartment is given by Eq. [12].

$$\text{NHFLW}_i = \text{HFLW}_i - \text{HFLW}_{i+1} - \text{ADSR}_i \cdot \text{VOLL} \cdot \text{RHO} \quad [12]$$

where ADSR_i is the adsorption rate, calculated with the available variables (C, S, \dots) at time t , VOLL is the volume of each layer ($\Delta x \cdot \text{AREA}$), and RHO is the bulk density. ADSR is expressed in $\mu\text{g/g}$ of soil per day, and is calculated as follows:

$$\text{ADSR}_i = \partial S / \partial t \quad [13]$$

where $\partial S / \partial t$ is the adsorption rate, calculated from Eq. [3], [6] or [9]. The net flow of herbicide per unit time into each layer (NHFLW_i) gives the change in the amount of herbicide in solution in each layer, AMSOL_i . Using the rectangular integration method, we may now calculate the amount of herbicide at time $t + \Delta t$ in layer i with the following equation:

$$\text{AMSOL}_i^{t + \Delta t} = \text{AMSOL}_i^t + \text{NHFLW}_i \cdot \Delta t. \quad [14]$$

The amount of herbicide adsorbed in every layer (AMADS_i) was calculated in the same way

$$\text{AMADS}_i^{t + \Delta t} = \text{AMADS}_i^t + \text{ADSR}_i \cdot \text{VOLL} \cdot \text{RHO} \cdot \Delta t. \quad [15]$$

The adsorbed, S_i ($\mu\text{g/g}$ soil), and solution, C_i ($\mu\text{g}/\text{cm}^3$ soil solution), concentrations in each layer were calculated with the equations

$$S_i = \frac{\text{AMADS}_i}{\text{VOLL} \cdot \text{RHO}} \quad C_i = \frac{\text{AMSOL}_i}{\text{VOLW}} \quad [16]$$

where VOLW equals the volume of water in each layer, $\text{VOLW} = \text{VOLL} \cdot \theta$.

MATERIALS AND METHODS

The procedure described by Davidson and Santelmann (4) was used to study the movement of 4-amino-3,5,6-trichloropicolinic acid (picloram) through Norge loam. The carboxyl group on the picloram was ^{14}C -labeled and had a specific activity of $4.1 \mu\text{Ci}/\text{mg}$. The displacement rate of the picloram through the soil was varied with a constant volume pump. The pore-water velocities used to displace the herbicide ranged between 145 and 14.2 cm/day . The soil-water flux was divided by the water content θ , determined after each displacement, to give the average pore-water velocity v_o . Five-milliliter effluent water samples were collected sequentially with a fraction collector and analyzed for picloram and chloride. The picloram concentration in each 5-ml effluent sample was determined from ^{14}C activity using a liquid scintillation counter. The relative concentration (C/C_o) was calculated from the picloram concentration in the effluent (C) and the initial concentration (C_o) of the picloram at the inflow location. The study was conducted in a temperature-controlled room at $25 \pm 0.5\text{C}$.

The soil, initially calcium saturated, was air-dried and the complete sample forced through a 2-mm sieve. The soil was packed into a glass cylinder to an average bulk density of $1.54 \text{ g}/\text{cm}^3$. The cross-sectional area and length of the soil columns were 45 cm^2 and 30 cm , respectively. The soil was saturated with $0.01N \text{ CaSO}_4$ and the desired soil-water velocity was estab-

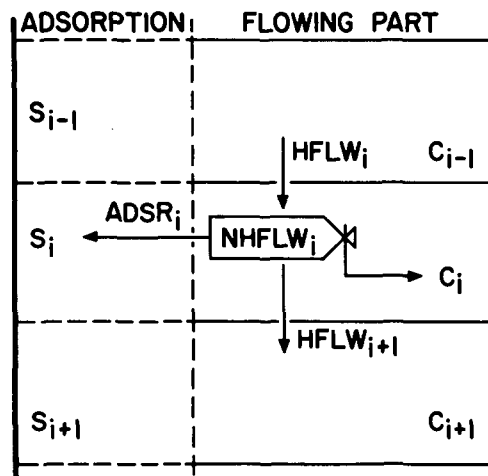


Fig. 1—Schematic representation of the CSMP-model for pesticide movement in soil.

lished. The number of pore volumes (V/V_o) displaced through the soil was calculated by dividing the volume of effluent (V) by the volumetric water capacity (V_o) of the soil. The pH, cation exchange capacity, and organic matter content of the Norge loam soil were 6.6, $9.2 \text{ meq}/100 \text{ g}$, and 1.7% , respectively. The soil had 46% sand, 38% silt, and 16% clay.

The picloram solution was prepared using $0.01N \text{ CaCl}_2$ and $10.6 \mu\text{Ci}/\text{liter}$ of ^{14}C -labeled picloram. Two hundred ml (approximately 0.41 pore volume) of picloram solution were added to the initially water-saturated soil at the desired soil-water flow rate and displaced through the soil with $0.01N \text{ CaSO}_4$ using the same flow rate. The picloram application was equivalent to $1.11 \text{ kg}/\text{ha}$ ($1.0 \text{ lb}/\text{acre}$). The time, T (pulse period), required to introduce the 200-ml of picloram solution at each flow rate is given in Table 2.

The equilibrium adsorption isotherm for picloram was determined using duplicate 1:1 mixtures of 5 g of soil in 5 ml of various picloram concentrations in $0.01N \text{ CaCl}_2$. Each sample was shaken for 5 hours and then centrifuged at 1,250 times the force of gravity for 15 min. Earlier tests had shown that the 5 hours of shaking exceeded that required for equilibrium adsorption. One-half ml samples of the clear supernatant were analyzed for ^{14}C activity and the count ratios converted to herbicide concentration. The difference between the original picloram concentration and that in the supernatant was assumed to be the result of adsorption.

Equilibrium desorption isotherms for picloram were obtained using the duplicate 1:1 soil-to-herbicide solution mixtures prepared for the adsorption study. A known volume of solution was extracted from each mixture following the initial adsorption and replaced with herbicide free $0.01N \text{ CaCl}_2$. The concentration of picloram in the extract was measured and the micrograms of picloram removed from the system by the extraction calculated. After each extraction, the samples were shaken for 5 hours, centrifuged, and another extraction and analysis of the supernatant made. The 5-hour shaking period was experimentally determined to be sufficient time to obtain equilibrium between the solution and adsorbed phases. This procedure was followed for each successive desorption step.

RESULTS AND DISCUSSION

The equilibrium adsorption and desorption data for picloram and Norge loam soil are given in Fig. 2. It is obvious from the data that these two processes, adsorption and desorption, cannot be described by one equation and hence are not single-valued. Also, note that the adsorbed concentration does not appear to approach zero as the solution

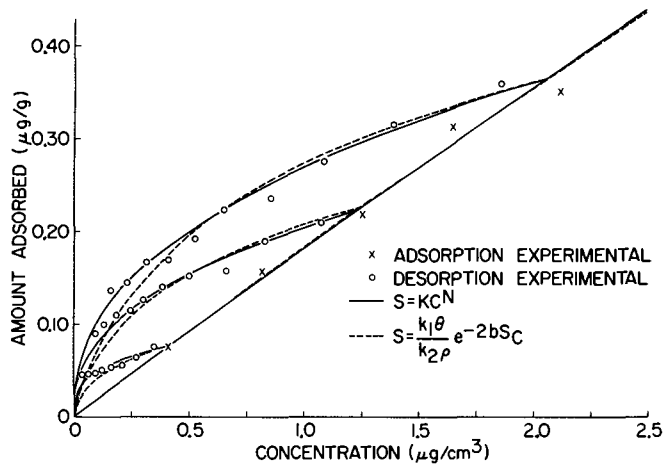


Fig. 2—Equilibrium adsorption and desorption data for picloram in Norge loam.

concentration, C , goes to zero during desorption. The solid lines in Fig. 2 were calculated using the Freundlich equation (Eq. 8), and the dashed lines were calculated using the adsorption equation (Eq. [4]) proposed by Lindstrom et al. (12). The parameters for desorption are a function of the maximum adsorbed concentration prior to the initiation of desorption. These parameters are defined below and were substituted into Eq. [4] and [8] to calculate the desorption curves.

Writing Eq. [4] for adsorption and desorption and equating the two relations gives

$$\frac{(k_1\theta/k_2\rho)_{\text{ads}} \exp[-2b_{\text{ads}} S_{\text{max}}] C_{\text{max}}}{(k_1\theta/k_2\rho)_{\text{des}} \exp[-2b_{\text{des}} S_{\text{max}}] C_{\text{max}}} = [17]$$

where ads and des refer to adsorption and desorption and S_{max} and C_{max} represent the adsorbed and solution concentrations prior to the initiation of desorption. Solving Eq. [17] for b_{des} gives:

$$b_{\text{des}} = b_{\text{ads}} + \frac{1}{2S_{\text{max}}} \ln \left[\frac{(k_1/k_2)_{\text{des}}}{(k_1/k_2)_{\text{ads}}} \right]. \quad [18]$$

The values of $(k_2)_{\text{ads}}$ and $(k_2)_{\text{des}}$ in Eq. [4] used for calculating the adsorption rate were selected on the basis of data fit. The other parameters for Eq. [4] are given in Table 1.

Table 1—Parameters used in Eq. [4] and [8] to describe the adsorption and desorption isotherm data (Fig. 2). S_{max} is the adsorbed concentration ($\mu\text{g/g}$) when desorption is initiated

Process	b	$k_1\theta/k_2\rho$	K	N_{ads}^*	N_{des}^*
	g/ μg	cm^3/g			
Adsorption	0.094	0.188	0.180	0.94	--
Desorption	2.34	0.967	0.268	--	0.424
$S_{\text{max}} = 0.365 \mu\text{g/g}$					
Desorption	3.73	0.967	0.204	--	0.402
$S_{\text{max}} = 0.223 \mu\text{g/g}$					
Desorption	10.7	0.967	0.101	--	0.315
$S_{\text{max}} = 0.0767 \mu\text{g/g}$					

* ads and des refers to adsorption and desorption, respectively.

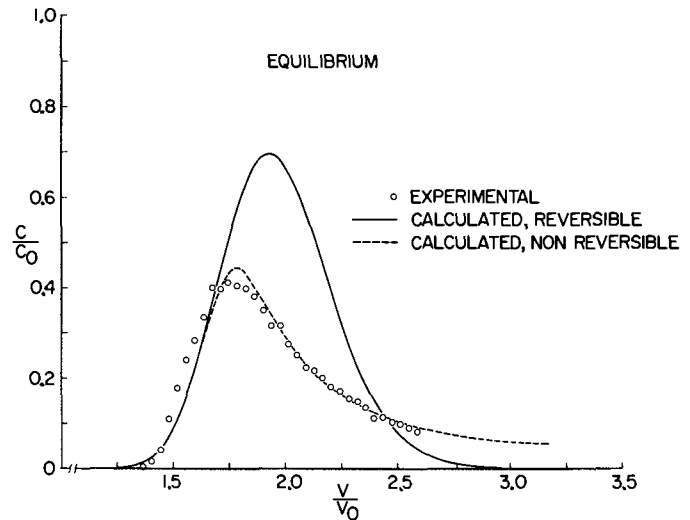


Fig. 3—Observed and computed relative effluent curves for picloram movement through Norge loam. Calculations were made assuming equilibrium during adsorption and desorption.

The desorption parameters for the Freundlich relationship (Eq. [8]) were determined in a similar manner to those in Eq. [17] and [18].

$$S_{\text{max}} = K_{\text{ads}} \times (C_{\text{max}})^{N_{\text{ads}}} = K_{\text{des}} \times (C_{\text{max}})^{N_{\text{des}}} \quad [19]$$

where

$$K_{\text{des}} = K_{\text{ads}}^{N_{\text{des}}/N_{\text{ads}}} \times S_{\text{max}}^{(1-N_{\text{des}}/N_{\text{ads}})}. \quad [20]$$

The ratio $N_{\text{ads}}/N_{\text{des}}$ was found to be a function of the maximum adsorbed concentration

$$N_{\text{ads}}/N_{\text{des}} = 2.105 + 0.062 S_{\text{max}}^{-1.076}. \quad [21]$$

The $N_{\text{ads}}/N_{\text{des}}$ values for the three picloram desorption curves ranged from 2.3 to 3.1 (Table 1). Swanson and Dutt (16) found that an average $N_{\text{ads}}/N_{\text{des}}$ value of 2.3 satisfactorily described atrazine adsorption and desorption in several soils.

Equations [4] and [8] fit the adsorption data reasonably well. However, the two equations differ in their ability to describe the desorption data at low picloram solution concentrations. The Freundlich relation appears to fit the lower desorption data somewhat better. The physical parameters associated with each picloram displacement are presented in Table 2. The dispersion coefficients (D_o) for chloride and picloram were determined using a procedure similar to the one proposed by Rose and Passioura (15).

Table 2—Soil physical data for various picloram displacement experiments through Norge loam soil

Experiment no.	Average Pore-water velocity, v_o	Soil-water content, θ	Bulk density, ρ	Dispersion coefficient, D_o		Pulse period T
				Chloride	Picloram	
	cm/day	cm^3/cm^3	g/cm^3	cm^2/day		day
1	14.2	0.3626	1.53	1.5	2.8	0.896
2	31.2	0.3698	1.54	--	4.5	0.372
3	66.5	0.3649	1.53	--	6.0	0.181
4	132	0.3634	1.55	11.6	9.5	0.091
5	145	0.3508	1.63	8.8	10.8	0.088

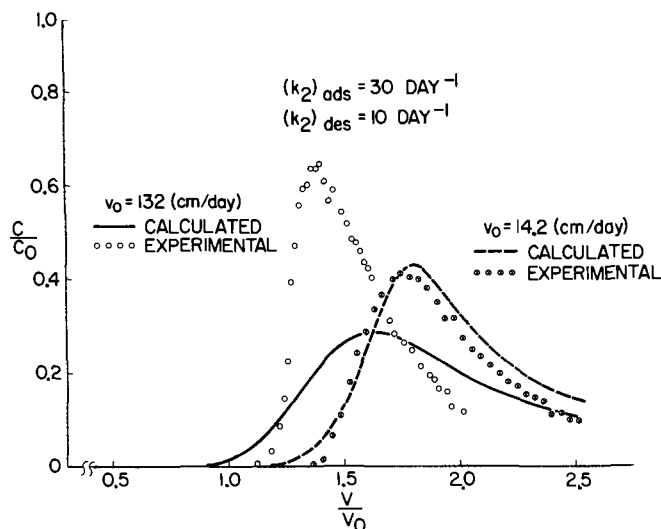


Fig. 4—Observed and computed relative effluent curves for picloram movement through Norge loam at two pore-water velocities. Calculations were based on the kinetic rate equation (Eq. [3]).

Figure 3 presents observed and computed relative effluent concentration distributions for experiment 1 (Table 2) assuming equilibrium conditions during the movement ($v_0 = 14.2$ cm/day). The figure illustrates the importance of using both adsorption and desorption characteristics. The solid line was calculated using the adsorption parameters for both adsorption and desorption. The dashed line was calculated using the same equilibrium Freundlich relation (Eq. [8]), but with equations [20] and [21] in Eq. [8] for desorption. The data and dashed line are in agreement, both in shape and position. The maximum effluent concentration occurs earlier and is reduced in magnitude compared to the single-valued adsorption-desorption case (solid line). Also, the area under the dashed line between 0 and 2.5 pore volumes is less than that under the solid line. The difference in area under the two curves represents the quantity of picloram remaining in the soil after 2.5 pore volumes as a result of the nonsingular relationship between adsorption and desorption. The assumption that the adsorption and desorption processes were at equilibrium when the average pore-water velocity was 14.2 cm/day appears justified based upon the agreement between the calculated dashed line and data.

In Fig. 4 the effluent data of experiment 1 are compared with effluent data of experiment 4. Increasing the average pore-water velocity from 14.2 to 132 cm/day significantly changed the position and shape of the picloram concentration distribution. The shift to the left of the effluent curve relative to V/V_0 was also observed by Kay and Elrick (9) for 1, 2, 3, 4, 5, 6-hexachlorocyclohexane (lindane). Such a shift is not expected under equilibrium conditions. Changes in pore-water velocity may affect the slope of the front portion of the effluent curve but should not displace the curve if equilibrium conditions exist. Apparently, the assumption of equilibrium adsorption-desorption is invalid at a pore water velocity of 132 cm/day.

Figure 4 also presents calculated effluent curves for pi-

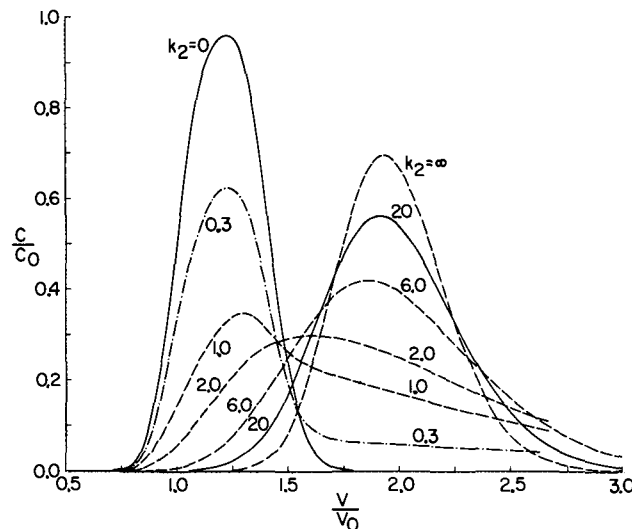


Fig. 5—Computed relative effluent curves for picloram movement through Norge loam using a kinetic rate coefficient k_2 , (Eq. [3]), which varied from zero to infinity.

cloram. The calculations were based on the kinetic adsorption-desorption model (Eq. [3]). The rate coefficients described in Eq. [3] were estimated from the shape of the effluent curve of experiment 1. The values obtained were 30 and 10 day⁻¹ for $(k_2)_{ads}$ and $(k_2)_{des}$, respectively. Because of the difficulty in measuring such values, they should be considered estimates.

The relative picloram concentration of the effluent in experiment 1 ($v_0 = 14.2$ cm/day) is adequately described using the kinetic adsorption-desorption model (Fig. 4). However, the calculated line does not fit the data as well as when the equilibrium Freundlich adsorption-desorption relation was assumed (Fig. 3). The calculated effluent curve for the fast displacement of experiment 4 ($v_0 = 132$ cm/day) deviates substantially from the data, and has a shape typical to that generally found for nonequilibrium systems [Davidson and McDougal (3)]. In calculating the latter curve, the same rate coefficients were used (30 and 10 day⁻¹, respectively) as those used for the slow displacement since rate coefficients are considered to be independent of the pore-water velocity. When rate coefficients were selected to fit the fast displacement in Fig. 4 (3 and 1 day⁻¹ for $(k_2)_{ads}$ and $(k_2)_{des}$, respectively), the prediction of the effluent curve for the slow displacement failed. It thus appears impossible to adequately predict picloram effluent curves in this soil with Eq. [3] using rate coefficients that are independent of pore-water velocity.

When Eq. [6] rather than Eq. [3] was used with values of 30 and 15 (day⁻¹) for $(k_2)_{ads}$ and $(k_2)_{des}$, respectively, approximately the same results were obtained. This indicates that Eq. [3] may have little advantage over Eq. [6] in describing picloram displacement. The adsorption model described by Eq. [6] is the same as that used by Lapidus and Amundson (10) and Oddson et al. (14), except for the dispersion term and the nonsingular adsorption-desorption characteristics which the latter did not include.

Figure 5 shows the relative effluent concentration distributions obtained for various kinetic rate coefficients at an

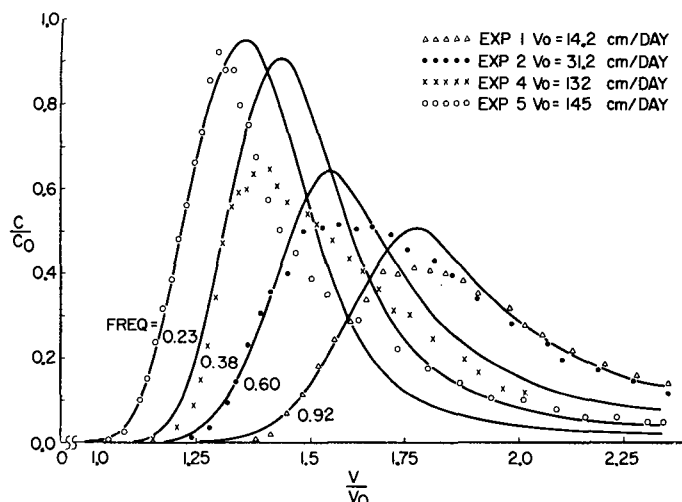


Fig. 6—Observed and computed relative effluent curves for picloram movement through soil at four pore-water velocities. Calculations were made by assuming equilibrium in the FREQ part of the soil, and using the nonsingular, adsorption-desorption equilibrium model.

average pore-water velocity of 14.2 cm/day. The distribution coefficient, $k_1\theta/k_2\rho$ (Eq. [3]), is 0.188 cm³/g for both adsorption and desorption (assumed here to be single-valued); the other parameters necessary for the calculations are the same as those associated with experiment 1 (Table 2). The line calculated with $k_2 = \infty$ represents equilibrium adsorption. Note that as the rate coefficients decrease to 2.0 day⁻¹, the peak concentration is reduced and the shape of the curve is flattened. Further decreases in k_2 resulted in the distributions moving to the left and in an increase in the maximum concentration. When $k_2 = 0$, the distribution is the same as that for a non-adsorbed material. Similar results to those shown in Fig. 5 would be obtained if the rate coefficient were held constant and the average pore-water velocity were varied from very large ($v_o \rightarrow \infty$) to very small values ($v_o \rightarrow 0$). Lindstrom et al. (12) calculated the chemical distribution inside a soil column along the vertical axis. Their results, when plotted as effluent concentration versus pore volume, look very similar to those in Fig. 5, including the low peak concentrations at intermediate kinetic rate coefficients. However, when comparing observed and computed effluent data in Fig. 4 and the shapes and positions of the observed effluent curves in Fig. 6 (e.g., the absence of a lower peak concentration at intermediate pore-water velocities and a gradual increase in peak concentration with increasing velocity), it becomes evident that the kinetic models alone are unable to predict the effluent curves for all pore-water velocities.

The data in Fig. 4 and 6 show that an increase in the pore-water velocity causes the chemical to appear at lower V/V_o values in the effluent. This would suggest that the time for adsorption at higher velocities is too short, and that a kinetic rate model needs to be employed. It has been shown above that this was not the case. A more likely reason is that at high pore-water velocities less herbicide will reach the adsorbing sites inside the aggregates. The residence time of the herbicide in the soil is too short to allow

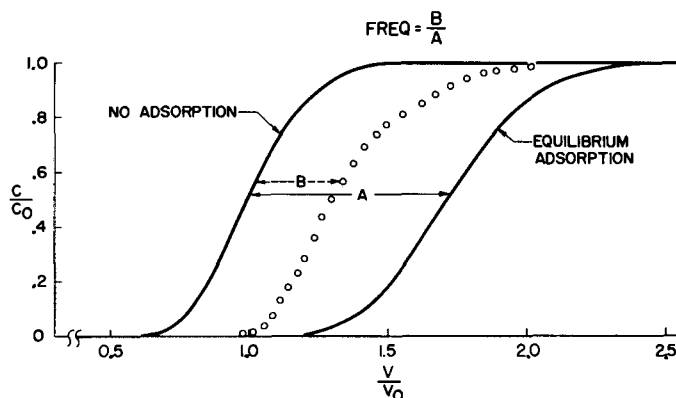


Fig. 7—Computed relative effluent curves for movement of an adsorbing chemical through soil. The ratio of B over A is defined as the fraction near equilibrium (FREQ).

diffusion to all adsorbing sites. Therefore, only a fraction of the adsorbing sites of the soil is in direct contact with the displacing solution. The movement of picloram to the smaller pores (e.g., interparticle and intraparticle) is primarily by diffusion from the larger pores. This agrees with Leenheer and Ahlrichs (11), who concluded that the rate limiting step in the adsorption of *O,O*-Diethyl-*o-p*-nitrophenylphosphorothioate (parathion) on soil was the diffusion of the insecticide molecule into the interior of the adsorbing material. At low pore-water velocities, the time available for diffusion is greater than at high velocities, and as a result, a greater portion of the adsorbing sites can be reached by the pesticide.

In order to model the latter system, the soil may, as a first approach, be divided in two fractions, i.e. the fraction of the soil or the adsorbing sites that is readily adsorbing picloram and that is in equilibrium with the displacing solution, and the fraction of the soil where adsorption is diffusion controlled.

The first fraction, which is near equilibrium (FREQ), may be determined from the position of the picloram effluent concentration distribution. This is illustrated in Fig. 7, where the left hand curve was obtained by assuming no adsorption (FREQ = 0), and the right hand curve was obtained for equilibrium adsorption (FREQ = 1.0). The FREQ term is defined as the ratio of the retardation distances B and A, and is a function of the average pore-water velocity. With increasing pore-water velocities, the residence time of the herbicide in the soil decreases resulting in less soil in direct contact with the pesticide. Therefore the values of FREQ decrease with increasing pore-water velocity. Using the breakthrough data from experiments 1-5 (Table 2), the relation between FREQ and flow rate was established. FREQ values varied between 0.92 ($v_o = 14.2$ cm/day) and 0.23 ($v_o = 145$ cm/day). Using these calculated FREQ values and the data in Tables 1 and 2, four picloram effluent concentration distributions were calculated with the computer model based on Eq. [1] and [9] (Fig. 6). The computer model was identical to the one used for calculating the solid line in Fig. 3, except that for Fig. 6 the value of the bulk density, which is the mass of soil per unit volume, was multiplied by the appropriate FREQ

value. It was assumed that the fraction of the adsorbing sites in equilibrium with the picloram was proportional to the mass of the soil in equilibrium with the picloram. No effort was made to calculate the amount of picloram diffusing into, and out of the smaller pores and aggregates. This may be the reason why the prediction of the effluent curves during desorption was not good.

The calculated lines and experimental data in Fig. 6 agree reasonably well. The predicted curves certainly are much closer to the data than for the fast displacement in Fig. 4. The calculated peak concentration is too high in some instances, but can be considered reasonable. Also, the left hand (breakthrough) portion of each curve agrees, in general, surprisingly well with the data, indicating conditions near equilibrium during adsorption, even at the high flow rates. The largest deviation between the calculated line and data occurs during desorption. This deviation also may be caused by desorption not being an equilibrium process as was assumed in the model.

The success of the *FREQ* approach to describe picloram displacements raises some doubts about the usefulness of the kinetic rate models in describing picloram movement through soil. The accurate description of the adsorption side of the effluent curves suggests that conditions near equilibrium exist, even at high flow velocities (132 cm/day). It may also indicate that the rate coefficients used in this study for adsorption were underestimated. The difficulty of measuring these coefficients is a serious problem in studying the kinetics of adsorption-desorption.

Because of the complexity of the soil-water system, the procedure of defining a function that relates the surface area readily available for adsorption to pore-water velocity may be a reasonable approach to the problem at the present time. In the model described here, the soil was divided into two fractions. A better approach may be to divide the soil into three fractions, e.g. a fraction at equilibrium, a fraction with a slow adsorption rate, and a fraction where adsorption is diffusion controlled. With the approach used in this paper it is not difficult to model such a system. The main difficulty is in obtaining the necessary soil parameters.

CONCLUSIONS

1) The adsorption and desorption of picloram by Norge loam soil is not a single-valued function. Excluding this nonsingularity of the adsorption and desorption process in calculating effluent concentration distributions resulted in a serious disagreement between the calculated and observed distributions.

2) Kinetic adsorption-desorption models were evaluated and found inadequate when predicting picloram mobility for high average pore-water velocities. These models, however, agreed with the equilibrium adsorption model when used to describe the picloram effluent concentration distribution at low pore-water velocities.

3) An empirical model was developed that could describe the movement of picloram at high flow rates. The procedure defines a fraction of the adsorbing sites (along large pores) that is in equilibrium with the picloram during displacement. This fraction is a function of the average

pore-water velocity. The procedure provided a reasonable fit between data and calculated effluent concentration distributions for four pore-water velocities. The adsorption in the remaining part of the adsorbing sites is slow and controlled by physical processes (diffusion, intra-aggregate transport).

4) The simulation program (*CSMP*) is constructed in such a way that other processes influencing the movement of picloram can be included (unsaturated flow, decay).

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