THE MOVEMENT AND DESCRIPTION OF FLUOMETURON
IN NORGE LOAM SOIL

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PREFACE

The movement and behavior of fluometuron in Norge loam soil was studied with the objectives: (1) to evaluate the time required for equilibrium adsorption, (2) to evaluate the nature of desorption, (3) to develop and use a miscible displacement technique to evaluate the influence of pore-water velocity on the transient adsorption-desorption characteristics, and (4) to compare the effectiveness of two existing mathematical models for predicting the movement of fluometuron in a soil column.

Sincere appreciation is extended to Dr. James M. Davidson for his interest and encouragement as major adviser. Drs. T. Alan Haliburton, Paul W. Santelmann, and John F. Stone served on the advisory committee and critically reviewed the manuscript. To these men I am indebted for their time and personal interest in my endeavors at the Oklahoma State University.

Special gratitude is due my wife, Kathie, who gave encouragement and understanding for the completion of my graduate studies.

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LIST OF SYMBOLS

Symbol	Description	Units
A	Area	cm^2
C	Concentration of solute	g/cm^3
C_o	Initial concentration of solute	g/cm^3
D	Diffusion coefficient	cm^2/hr
D_o	Dispersion coefficient	cm^2/hr
D'	Scaled dispersion coefficient	cm^2/hr
K	Sorption constant	cm^3/gm
K_d	Equilibrium distribution coefficient	cm^3/gm
n	Constant related to soil-herbicide system	dimensionless
S	Quantity of solute retained per unit wt. of adsorbent	$\mu g/g$
T	Pulse period	hr
t	Elapsed time	hr
U	Solution flux	cm/hr
u_o	Average pore water velocity	cm/hr
u'	Scaled pore water velocity	cm/hr
V	Volume	cm^3
x	Distance along column from inflow plate	cm
α	Sorption constant	hr^{-1}
ρ	Bulk density	g/cm^3
∇	Vector operator	dimensionless
θ	Volumetric water content	cm^3/cm^3

CHAPTER I

INTRODUCTION

Consideration of the manner in which herbicides react with and move through soils is important not only to the effectiveness of the herbicide, but also to the conservation of the quality of the soil and water environment. The adsorption of herbicides is known to vary with the components of the soil. Organic matter, pH, clay content, clay mineral type, and specific surface have all been shown to affect the behavior of herbicides on soil. In addition, the herbicide itself possesses chemical properties which will affect its movement in soils.

Superimposed upon the above effects are others which may affect the movement of herbicides in flowing systems. The water content, bulk density, pore water velocity, and pore size distribution should be considered when evaluating the concentration and location of the herbicide in the soil profile. The adsorption and desorption characteristics of a herbicide are of particular interest in flowing systems since their properties significantly affect the relative herbicide concentration adsorbed and in solution.

Mathematical models have been formulated to describe the behavior of solutes subjected to mass flow, diffusion, and adsorption-desorption processes in soil water systems. However, these models tend to only describe the results when curve fitting procedures are used rather than to describe physically the processes taking place within the soil based on independent measurements.

Fluometuron was used in the study. It is a preemergence herbicide which has wide application in Oklahoma.

The objectives of the investigation reported here are:

(1) To evaluate the time required for equilibrium adsorption between fluometuron and Norge loam.

(2) To evaluate equilibrium desorption of fluometuron from Norge loam.

(3) To develop and use a miscible displacement technique to evaluate the influence of pore water velocity on the transient adsorption-desorption characteristics.

(4) To compare the effectiveness of two existing models in predicting the movement of fluometuron in a soil column using data collected with the miscible displacement method.

CHAPTER II

LITERATURE REVIEW

The influence of soil properties on the behavior of herbicides in soils has been studied by many investigators. In a review of pesticide adsorption and desorption on soil colloids, Bailey and White (1964) state that factors such as soil or colloid type, physico-chemical nature of the pesticide, soil reaction, nature of the saturating cation on the colloid exchange site, soil moisture, nature of formulation, and temperature all directly influence the adsorption of pesticides by soil systems; whereas the soil physical properties exert a more indirect influence. Adsorption phenomena can be separated into two general types, chemical or physical. Chemical adsorption is due to coulombic forces and results from bond formation between adsorbent and adsorbate. Physical adsorption is due to van der Waals forces, that is, orientation or dipole-dipole interactions, dipole-induced dipole interactions, dispersion interactions, and ion-dipole interactions.

The energy of adsorption or tenacity with which the adsorbate is held to the adsorbent may be regarded as the summation of the effects of these forces acting between the adsorbate and adsorbent. Chemical adsorption is in general energetically greater than is physical adsorption.

Upchurch and Pierce (1958), Erickson (1965), and Harris (1966) have shown that the adsorption and movement of Monuron was affected significantly by the amount of organic matter in the soil. The adsorption was greater with higher organic matter contents and as a result herbicide movement was retarded. Organic matter not only provides more exchange sites, but increases the specific surface of the total soil system.

Harris and Sheets (1965), Bailey, White and Rothberg (1968), and Talbert and Fletchall (1965) have studied the role of pH in the adsorption of herbicides by soils. The pH is of particular importance for ionic adsorbates. However, there appears to be such a variability that only a few generalizations can be made regarding pH and adsorption. Harris (1966) found that for some herbicides pH greatly affected adsorption, whereas in others it was not of significance. Bailey and White (1964) concluded that the effect of pH on the adsorption of a particular pesticide is manifested in the degree of dissocation or association of the compound. This may affect the amount that is adsorbed and the strength by which it is held to the adsorbent.

Hance (1967) examined the time required for equilibrium adsorption of herbicides on several adsorbents. He found that for all materials studied, 24 hours was sufficient for equilibrium; however, in some combinations one hour was sufficient. This would indicate that each soil-herbicide combination should be evaluated. Desorption was found to take place at a somewhat slower rate, and in most cases, it was found to be nearly reversible.

Diffusion has been shown to be an important process in the movement of herbicides in soils. Walker and Crawford (1970) studied the relationship between adsorption and diffusion and found an inverse relationship between the two. A log-log graph yielded a linear plot.

Lindstrom, et al. (1967, 1968) have studied the effects of adsorption on the diffusion coefficient and found that organic matter had the greater influence on the diffusion coefficient as compared to clay content, CEC and pH. The effect of greater adsorption was to reduce the diffusion coefficient. Due to relatively low diffusion rates, degradation of some herbicides might occur in surface soils before significant movement could be realized. Water content, pH, organic matter, clay mineral, bulk density, and adsorption have been found to have some effect on herbicide diffusion in soils. In general, the more strongly adsorbed adsorbates are less easily moved by the process of diffusion.

Pesticide movement through soils also may be affected by soil physical properties which influence the microhydrological processes occurring within the soil system. Where water is moving through the soil, pesticides are moved by mass flow and diffusion. The soil properties--water content, bulk density, particle size distribution, aggregate size, and pore water velocity--may significantly affect the manner in which the pesticides move. Kay and Elrick (1967), Elrick, et al. (1966), Green, et al. (1968), Phillips (1964), and Davidson, et al. (1968) have studied many of these relationships using miscible displacement techniques.

Many of the present models used to predict the movement of solutes in porous media have developed from the work of Lapidus and Amundson (1952) who considered the effects of longitudinal diffusion in chromatographic and ion exchange columns. Brenner (1962) presented numerical values for the solution of the diffusion model for miscible displacement of fluids in beds of finite length. He has also discussed the various limiting cases for this treatment. Nielsen and Biggar (1962) have presented a concise treatment of the theory of miscible displacement of solutes in soil systems. They present graphically the effects of such phenomena as longitudinal dispersion, range of velocity distribution, chemical reaction or adsorption, and solute exclusion. Mathematical descriptions of these phenomena are also presented and discussed.

Elrick, et al. (1966) used a miscible displacement technique in the description of the movement and adsorption of atrazine in a silt loam soil. They found it necessary to employ a retardation factor in order to account for the delay in the elution of atrazine from the column due to adsorption. They assumed that the adsorption concentration was linearly related to the solution concentration.

More recently, Kay and Elrick (1967) used this technique to study the movement and adsorption of lindane in soils. They found that the movement of lindane in Honeywood loam under continuous water flow conditions was reasonably well described by a chromatographic model. Divergence between theoretical and measured breakthrough curves was attributed to intra-aggregate diffusion and adsorption.

Green, et al. (1968) studied the transport of atrazine in water saturated and unsaturated latosolic soils. They used a simple chromatographic model which assumed a constant distribution coefficient, instanteneous and reversible adsorption, and laminar fluid flow. The experimental elution curve arrived earlier and had greater spread than that predicted by the model. They concluded that the model could not account for variations in the microscopic flow velocities and nonlinearity of the adsorption isotherm. Davidson and Santelmann (1968) studied the movement of fluometuron and diuron through 250μ glass beads and Norge loam soil. In the nonadsorbing glass beads, fluometuron was found to be as mobile as chloride ion, whereas diuron was slightly less mobile. In the soil system, where more adsorption was evident, they found that the mobility of fluometuron was less than that of the chloride ion. Fluometuron distribution curves were found to be distinctly different at the two solution flow rates imposed during the experiment. Davidson, et al. (1968) further investigated the influence of water flux and porous material on those herbicides. They concluded that fluometuron was sufficiently influenced by the water flux and pore geometry to necessitate a knowledge of these parameters before estimating the movement of a herbicide through a soil. Adsorption isotherms were nearly linear with increased concentration in the range of the experiment. Their data show that fluometuron has a molecular diffusion coefficient near that of the chloride ion in the 250μ glass bead system. Cargill and Davidson (1969) found that the adsorption coefficient for fluometuron in Norge loam was less for a flowing system than that determined from an equilibrium adsorption isotherm procedure.

Panigatti (1970) studied the effect of soil textural stratification on movement of chloride and fluometuron in Norge loam. He found that the most important factor influencing their movement and distribution in a soil profile was the range in pore sizes. The greater the pore size distribution the more dispersion or mixing occurred at the higher soil-water flow rates. At higher flow rates molecular diffusion played a small role as compared to velocity dispersion.

Abernathy and Davidson (1971) evaluated the effect of calcium chloride on adsorption of fluometuron on soils, and concluded that there was not enough effect on the mobility of these herbicides to necessitate a change in current field practices. They also found a difference between transient and equilibrium adsorption isotherms.

Green and Corey (1971) have presented a new method to evaluate adsorption by flow equilibration which is said to be more precise, capable of measuring the reversibility of adsorption, and limits destruction of the soil aggregates.

CHAPTER III

THEORY

The movement of a herbicide through a soil system has been described by various chromatographic models with varying degrees of success. The most frequently used form for simultaneous mixing by molecular diffusion and convective flow is that given by the following partial differential equation:

$$\frac{\partial C}{\partial t} + \nabla U C = D_o \nabla^2 C \qquad [1]$$

where C is the concentration of solute in solution (g/cm^3), t the time (hr.), U the average flux of the solution (cm/hr), and ∇ the three dimensional vector operator $\left(\nabla = \frac{\partial}{\partial x} \vec{i} + \frac{\partial}{\partial y} \vec{j} + \frac{\partial}{\partial z} \vec{k} \right)$. In order to account for pore water velocity and for adsorption within the porous medium, equation [1] has been modified to consider the following one dimensional case:

$$D_o \frac{\partial^2 C}{\partial x^2} - u_o \frac{\partial C}{\partial x} - \left(1 - \frac{\rho K_d}{\theta}\right) \frac{\partial C}{\partial t} = 0 \qquad [2]$$

where u_o is the average pore water velocity (cm/hr), $u_o = U/\theta$ where U is the water flux and θ is the volumetric water content (cm^3/cm^3), ρ the bulk density (gm/cm^3), x the distance from the inflow point (cm), K_d the distribution coefficient, and the other symbols are the same as in equation [1]. The quantity $1 + \frac{\rho K_d}{\theta}$ is called a retardation factor and has the effect of translating the theoretical curve to the right, equivalent to the effect of adsorption. When $K_d = 0$ the retardation factor reduces to one and the last term on the left-hand side of equation [2] reduces to $\partial C/\partial t$. The retardation factor is a function of bulk density, distribution coefficient, and volumetric water content.

Herbicide adsorption in soils had been found to follow the Freundlich adsorption isotherm, Bailey et al. (1964), as given by:

$$S = K_d C^{1/n} \tag{3}$$

where S is the quantity of solute retained per unit weight of adsorbent ($\mu g/g$), 1/n a constant related to the soil-herbicide system in question, and K and C the same as defined above.

For fluometuron in Norge loam the value of 1/n had been found to be nearly 1.0 (Davidson, et al., 1968); therefore the assumption has been to consider a linear relationship between S and C, thus equation [3] is reduced to:

$$S = K_d C \tag{4}$$

The distribution coefficient, K_d, is further assumed to be independent of the concentration C over the range in question. Equilibrium between adsorbed and non-adsorbed phases is assumed to exist at all times and to be reversible.

Solutions of equation [2] with the above assumptions have been obtained for the following boundry conditions:

$$\begin{aligned}
&\text{a)}\quad C_{(x,o)} = 0 \\
&\text{b)}\quad u_oC_o = u_oC - D_o\frac{\partial C}{\partial x} \qquad \text{(for } x=0,\ 0<t<T\text{)} \\
&\text{c)}\quad u_oC_{(0,t)} = 0 \qquad \text{(for } x=0,\ t>T\text{)}
\end{aligned} \qquad [5]$$

where C_o is the concentration of the incoming solution, and T (pulse period) is the time that a solution of concentration C_o was allowed to flow into the column. The solution takes the form:

$$\begin{aligned}
C/_{C_o} = \frac{1}{2}\Bigg\{ &\text{erfc}\left[\frac{x - u't}{\sqrt{4D't}}\right] - \text{erfc}\left[\frac{x - u'(t-T)}{\sqrt{4D'(t-T)}}\right] \\
&+ 2u'\sqrt{\frac{t}{D\pi}}\ \exp\left[\frac{x - u't}{\sqrt{4D't}}\right]^2 - 2u'\sqrt{\frac{t-T}{D'\pi}}\ \exp\left[\frac{x - u'(t-T)}{\sqrt{4D'(t-T)}}\right]^2 \\
&+ \frac{u'}{D'}\left[\frac{D'}{u'} + u'(t-T) + x\right]\exp\left[\frac{xu'}{D'}\right]\text{erfc}\left[\frac{x + u'(t-T)}{\sqrt{4D'(t-T)}}\right]\Bigg\}
\end{aligned} \qquad [6]$$

where

$$D' = \frac{D_o}{1 + (\rho K_d/\theta)} \quad \text{and} \quad u' = \frac{u_o}{1 + (\rho K_d/\theta)} \qquad [7]$$

for times greater than T.

This solution is the one used by Davidson, et al. (1968) and is similar to that used by Elrick, et al. (1966), Kay and Elrick (1967), and Lindstrom, et al. (1967) in that they have attempted to treat the effects of adsorption. Equation [6] is a modification of Brenner's solution to equation [2] subject to conditions [5a] and [5b] for the case of no adsorption. Hashimoto, et al. (1964) solved equation [1] for a finite length column exhibiting adsorption and called the adsorption portion the retardation factor.

Oddson, et al. (1970) have derived basic equations which describe the flow of organic chemicals within a porous system. These equations were solved explicitly under the assumption that the molecular diffusion of organic chemicals within the solution may be neglected. Denoting the concentration of organic solute in solution as $C(x,y,z,t)$ and the concentration of adsorbed organic solute as $S(x,y,z,t)$, both per unit volume of porous media, the total amount of solute within a fixed volume V, at time t will be:

$$\iiint_V (C + \quad) \, d\, V \qquad [8]$$

The rate at which the solute is carried out of this volume through the surface, A, due to mass transport will be given by:

$$\oiint_A C\, u_o \cdot \bar{n} \, d\, A \qquad [9]$$

where $u_o(x,y,z,t)$ denotes the average pore water velocity of the solution. Diffusion of the solute within the solution with a concentration gradient carries solute out of V at the rate:

$$-\oiint D \nabla C \cdot \bar{n} \, d\, A \qquad [10]$$

where $D(x,y,z,t)$ is the diffusion coefficient of the solute.

Conservation of mass requires that

$$\frac{d}{dt} \iiint_V (C + S) \, d\, V = - \oiint_A (Cu_o - D\nabla C) \cdot \bar{n} \, d\, A \qquad [11]$$

which can be rewritten using the divergence theorem in the form:

$$\operatorname{div} (Cu_o) - \operatorname{div} (D\nabla C) + \frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} = 0 \qquad [12]$$

since V is arbitrary.

The relationship between adsorbed and solution concentration must be ascertained to solve the above equation. For equilibrium conditions, the Freundlich equation as given in equation [3] was considered to hold and that the value of 1/n is near unity, thus a linear relationship between the adsorbed and solution concentration. For non-equilibrium conditions, the rate of adsorption is assumed to be proportional to the difference between the amount which has already been adsorbed and the equilibrium value as expressed below:

$$\frac{\partial S}{\partial t} = \alpha\ (K\ C - S) \qquad [13]$$

where K and α are constants depending upon the soil and organic chemical.

By assuming that diffusion can be neglected and for $t > 0$, the wetting front will be at $x = ut$. Using equation [13], $C(x,t)$ can be eliminated such that equation [12] can be expressed as the second order partial differential equation:

$$u_o \frac{\partial^2 S}{\partial x \partial t} + \frac{\partial^2 S}{\partial t^2} + \alpha\ u_o \frac{\partial S}{\partial x} + \alpha\ (K + 1) \frac{\partial S}{\partial t} = 0 \qquad [14]$$

For the case where a solution has been added for a finite time T and thereafter the column is flushed with water containing no chemical we have that:

a) $C_o(t) \equiv C_o \qquad 0 \leq t \leq T$
and
b) $C_o(t) = 0 \qquad t > T$ [15]
and
c) $S(x) \equiv 0 \qquad x \geq 0 \qquad$ for $t = 0$

Solving equation [14] using the conditions above, the following solution for adsorbed concentration is obtained:

$$S(x,t) = \begin{cases} 0 \text{ for } 0 \leq t \leq x/u_o \\ KC_o \exp(-\alpha K\ x/u_o) \displaystyle\int_o^{\alpha(t-x/u_o)} \exp(-\tau)\ I_o\left(2\sqrt{\frac{\alpha K x \tau}{u_o}}\right) d\tau \\ \qquad \text{for } x/u_o \leq t \leq x/u_o + T \\ KC_o \exp\ (-\alpha K\ x/u_o) \displaystyle\int_{\alpha(t-x/u_o-T)}^{\alpha(t-x/u_o)} \exp(-\tau)\ I_o\left(2\sqrt{\frac{\alpha K x \tau}{u_o}}\right) d\tau \\ \qquad \text{for } t \geq x/u_o + T \end{cases} \qquad [16]$$

and for solution concentration:

$$C(x,t) = \begin{cases} 0 \text{ for } 0 \leq t \leq x/u_o \\ \dfrac{S(x,t)}{K} + C_o \exp\left[(-\alpha Kx/u_o) - \alpha(t-x/u_o)\right] I_o\left(2\sqrt{\dfrac{\alpha^2 Kx(t-x/u_o)}{u_o}}\right) \\ \qquad \text{for } x/u < t < x/u + T \\ \dfrac{S(x,t)}{K} + C_o \exp\left[(-\alpha Kx/u_o) - \alpha(t-x/u_o)\right] \left\{ I_o\left(2\sqrt{\dfrac{\alpha^2 Kx(t-x/u_o)}{u_o}}\right) \right. \\ \quad \left. - \exp\ (\alpha T)\ I_o\left(2\sqrt{\dfrac{\alpha^2 Kx(t-x/u_o\ -\ T)}{u_o}}\right) \right\} \\ \qquad \text{for } t > x/u_o + T \end{cases} \qquad [17]$$

Equations [16] and [17] can be shown to be equivalent to that considered by Lapidus and Amundson (1952) in their equation [7] with diffusion neglected.

Experimental data obtained in this investigation will be used to test the validity of equation [2] and equation [14] in predicting the location and concentration of fluometuron in Norge loam.

CHAPTER IV

MATERIALS AND METHODS

Soil Treatment

Calcium Saturation

The Norge loam soil material used in this study was obtained from the Agronomy Research Station near Perkins, Oklahoma. The soil was taken from the surface six inch depth, allowed to air dry, and then sieved to pass through an 8.00 mm sieve. Calcium saturation of the soil exchange complex was accomplished in the following manner. Ten-gallon plastic containers were half filled with soil and a 0.5 N calcium acetate solution was applied to the surface of the soil and allowed to percolate through the soil until fifteen gallons had passed through. Following the acetate solution, a 0.01N $CaSO_4$ solution was allowed to percolate through the soil until no acetate could be detected in the outflow solution. The soil was dried and passed through a 2.0 mm sieve. Gravimetric moisture determinations showed a 1.45% water content by weight.

Aggregate Stabilization

To obtain stabilized soil aggregates, calcium saturated soil was treated with a 2.0% solution by weight of Krilium[1] soil conditioner, "loamaker formula," by spraying the aqueous solution onto thin layers of soil and manually mixing. After air drying, the stabilized soil was sieved into the desired aggregate sizes. The aggregate sizes separated were: whole soil < 2.0mm, 2.0-1.0mm, 1.0-0.5mm, and 0.5-0.25mm. The physical and chemical characteristics of the soil are given in Table I.

Column Packing

Lucite columns 30.0 cm in length and 7.65 cm in inside diameter with a fritted glass end plate sealed with epoxy cement were packed with soil. The desired soil bulk density was achieved by successive additions of approximately 45 grams of soil followed by stirring the added layer into the top of the previous layer using a 1/8 inch diameter brass rod and tapping the column wall lightly with a rubber faced mallet. The bulk density of the packed column was determined by weighing the added soil, correcting the soil water content, and dividing by the column volume. The remaining end plate was then sealed with epoxy cement.

Herbicide Solution

The substituted urea herbicide fluometuron (1,1-dimethyl-3-(a,a,a-trifluo-m-tolyl) urea), Figure 1, was mixed with either 0.01 N $CaSO_4$ or 0.01 N $CaCl_2$ aqueous solutions. A fluometuron concentration of 2.549 μg/ml was obtained by combining 80% wettable powder and carbon-14 labeled fluometuron (100μc/9.74mg) to yield a ^{14}C activity

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[1] A product of Monsanto Chemical Company.

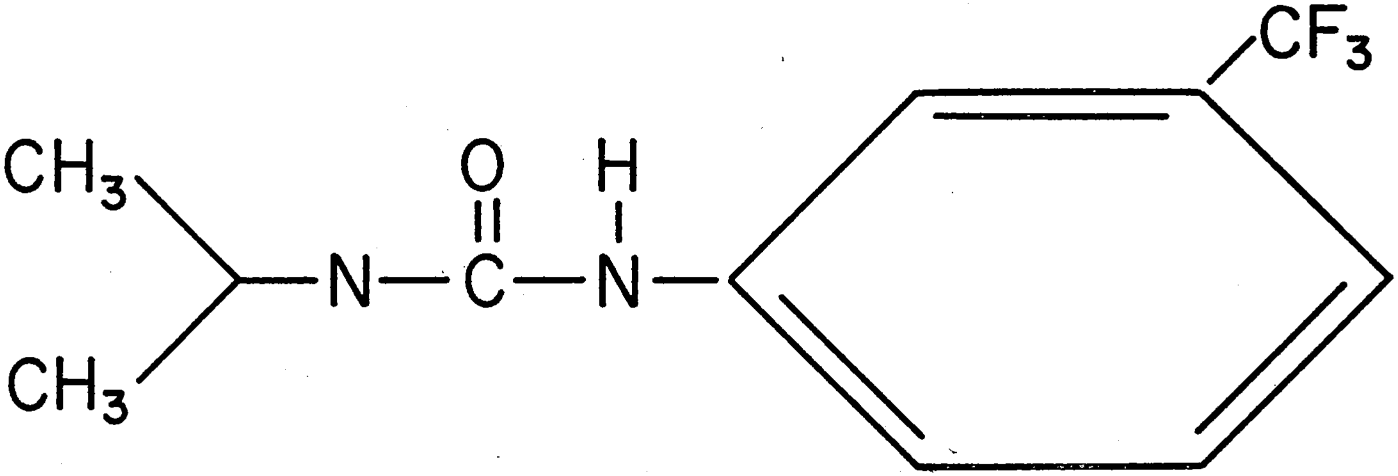
of 5.0 microcuries per liter of solution. The ^{14}C label was on the trifluomethyl radical.

TABLE I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF NORGE LOAM SOIL TAKEN FROM THE 0-6" DEPTH

Soil Treatment	Aggregate Size Fraction mm	pH	C.E.C. meq/100g	Exchangable Ca meq/100g	Organic Matter (°/o)
Norge loam, calcium saturated	< 2.0	6.6	9.2	7.06	1.7
Norge loam, calcium saturated, Krilium treated	< 2.0 > 1.0	6.6	10.1	7.50	1.7
Norge loam, calcium saturated, Krilium treated	< 1.0 > 0.5	6.5	8.1	7.38	1.6
Norge loam, calcium saturated, Krilium treated	< 0.5 > 0.25	6.5	9.3	6.88	0.9
Norge loam, calcium saturated, Krilium treated	< 2.0	6.5	6.8	5.00	1.1

Mechanical Analysis: 46.0% sand, 37.6% silt, 16.4% clay



FLUOMETURON

Figure 1. Chemical Structure of Fluometuron

Miscible Displacement Technique

The displacement of the herbicide solution through the soil columns was accomplished using an apparatus similar to that described by Davidson and Santelmann (1968). The column was constructed of extruded acrylic plastic tubing approximately 7.65cm inside diameter and 30.0cm in length. The column was modified to permit soil sampling at 2.0cm intervals along the length of the column, Figure 2. Neoprene rubber stoppers were used to confine the soil in the column. The end plates were constructed of medium porosity fritted glass discs with the volume behind the disc kept to a minimum. The end plates were sealed to the columns with epoxy cement. A constant volume pump was used to regulate the flow rate of the herbicide and the herbicide free solutions through the soil column.

The procedure for displacement of herbicide through the soil was as follows: the soil was saturated by gravity flow upwards with 0.01N $CaSO_4$ solution, and the flow rate adjusted to the desired value using the constant volume pump. When the amount of solution leaving the column was the same as the amount entering the column per unit time, equilibrium flow was assumed. At this time the inflow plate was flushed with the herbicide solution and a 200 ml pulse of herbicide solution was introduced into the column. Following the herbicide pulse, the inflow endplate was flushed with the displacing solution (0.01N $CaSO_4$), and the displacement of the herbicide solution through the column with the $CaSO_4$ solution continued until termination of the experiment.

For those experiments where the herbicide was displaced from the column, a fraction collector was used to collect the effluent solution

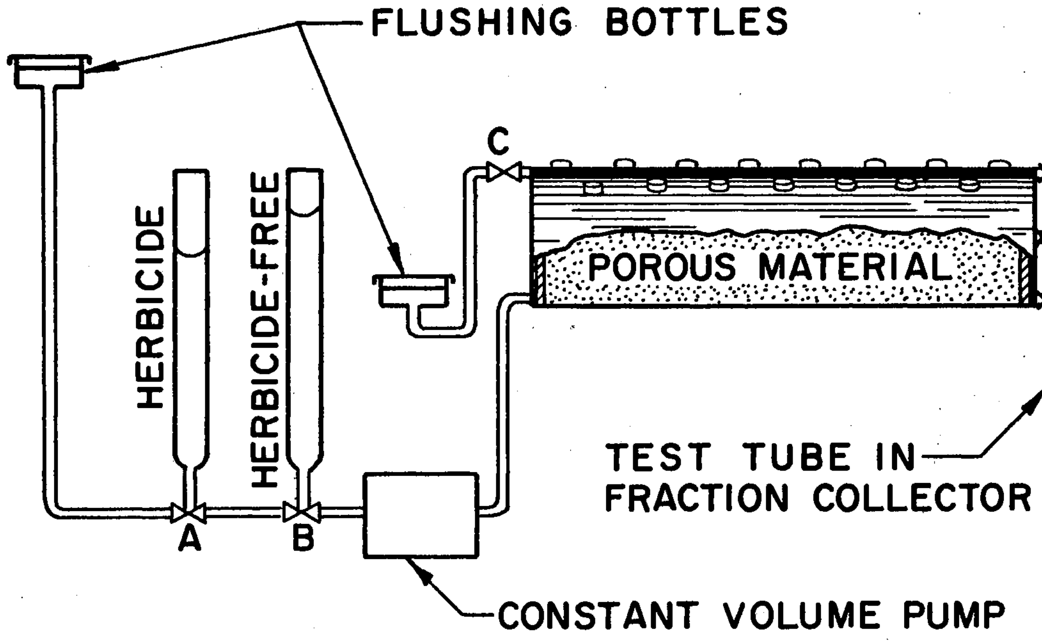


Figure 2. Apparatus Used in Miscible
Displacement Study

at the outflow endplate. For all experiments, the soil was sampled at 2.0 cm intervals to determine the concentration of herbicide in solution and the concentration of herbicide adsorbed on the soil.

Sampling the Soil Column

After weighing the saturated soil to determine the pore volume, the column was sampled at two-centimeter intervals beginning one centimeter from the inflow endplate. Soil samples were taken by removing the neoprene stopper from the opening in the lucite column, inserting a #9 cork borer through the wall of the column to delineate the sample, then removing the soil plug using a curved scoopula. The samples were quickly transferred to a fritted glass filter extraction apparatus, Figure 3, and stoppered to prevent loss of water by evaporation. The samples in fritted filters were then centrifuged at 8000x gravity to obtain a soil solution sample. After centrifugation, the samples were weighed for subsequent determination of residual soil water content. After weighing, the samples were leached with three successive five ml increments of absolute ethanol. The samples were centrifuged after each increment to remove the remaining herbicide. Following leaching, the soil and fritted filter were oven-dried to a constant weight in order to determine the oven-dry soil weight and water content following the initial centrifugation.

Preliminary experiments indicated that three five ml increments of absolute ethanol were sufficient to remove the remaining herbicide present on the soil. It was also established that water and ethanol follow the same quenching curve for ^{14}C analysis over the range of concentrations used in this experiment.

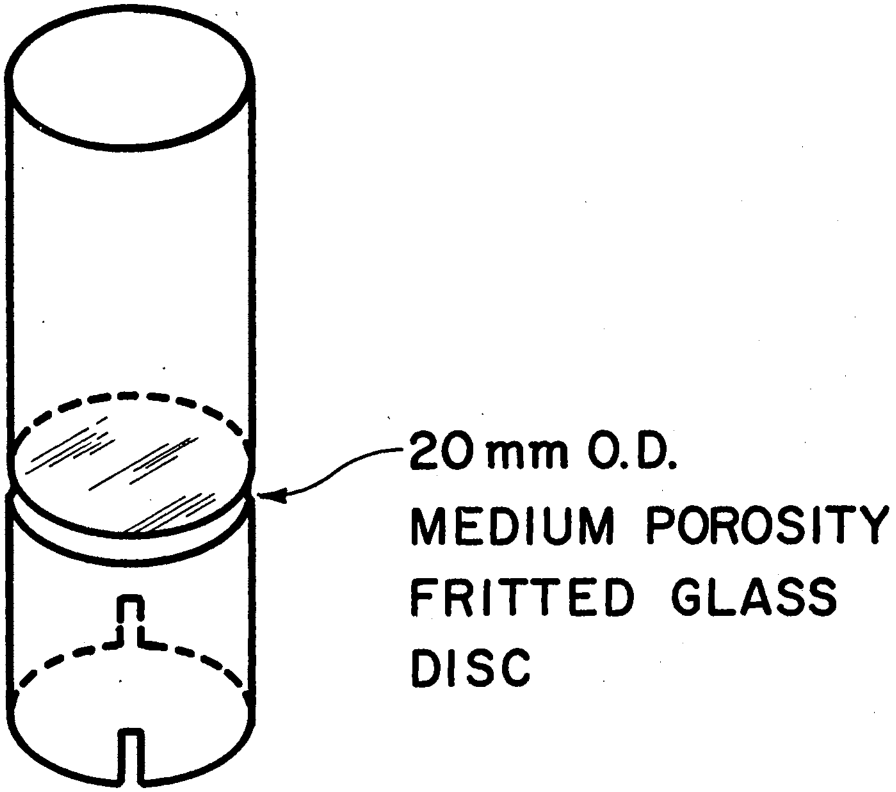


Figure 3. Apparatus Used To Separate Adsorbed and Nonadsorbed Fluometuron Phases

Liquid Scintillation Technique

Carbon-14 activity in the effluent and extract samples was determined by liquid scintillation counting[2]. Duplicate 0.5 ml aliquots were pipetted into counting vials containing 15 ml scintillation cocktail solution. The solution consisted of 50 mg of 1,4-bis-2-(5-Phenyloxazolyl) - Benzene (POPOP), 4 gm of 2,5-Diphenyloxazole (PPO), and 120 gm of naphthalene made to one liter volume with p-dioxane.

Chloride ion concentration in effluent samples was determined by titration with silver nitrate using K_2CrO_4 as an indicator.

Sorption Studies

Equilibrium adsorption of fluometuron on Norge loam was evaluated using 1:1 ratios by weight of soil to volume of herbicide solution at $23 \pm 1^{\circ}$ C. Five grams of soil and 5 ml of the desired concentration of herbicide solution was combined in a 20 ml screw cap glass test tube, shaken for a specified length of time, centrifuged at approximately 8000g to settle the soil, and duplicate 0.5 ml samples removed to determine the ^{14}C activity in the supernatant solution. A blank was run with 0.5 ml herbicide solution for each concentration and each time interval. The difference between the amount of herbicide measured in the blank and in the 1:1 mixtures was taken to be the amount adsorbed on the soil. The time required for equilibrium adsorption was examined by using exposure time intervals of 10, 20, 40, 60 and 120 minutes.

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[2] Beckman LS-100 Liquid Scintillation System, Beckman Instruments, Inc.

Equilibrium desorption of fluometuron from Norge loam was examined also from 1:1 soil-herbicide ratios at 23 ± 1° C. Five grams of soil and 5 ml of herbicide solution was combined in a 20 ml screw cap glass test tube and shaken for 120 minutes. The amount adsorbed was determined as in the adsorption experiment. Then 1.0 ml of 0.01N $CaSO_4$ was added to each test tube to replace the two 0.5 ml aliquots removed for analysis. The samples were again shaken 120 minutes, centrifuged, and analyzed for ^{14}C activity to determine the amount of herbicide desorbed. This procedure was repeated for successive dilutions of the herbicide in solution. The amount of herbicide desorbed was determined by taking the difference between the amount of herbicide in solution and that calculated by dilution of the blank.

CHAPTER V

RESULTS AND DISCUSSION

Equilibrium Sorption Studies

Adsorption of fluometuron by Norge loam is characterized by the equilibrium adsorption isotherms given in Figure 4. The rate of adsorption equilibrium was found to be very rapid with better than 85 per cent of adsorption occurring within ten minutes. For all concentrations studied, 60 minutes was sufficient to reach an equilibrium value. Employing a log-log plot for the Freundlich adsorption isotherm equation:

$$S = K_d C^{1/n}$$

the values of K_d and 1/n for the 10 minute reaction time were 0.34 and 0.918 respectively. For the 120 minute reaction time the values were 0.40 and 0.976 respectively. Since the value 0.976 is nearly 1.0, the adsorption of fluometuron on Norge loam may be considered linearly related to the solution concentration. The data for the time dependency of adsorption is given in Table III in the Appendix.

Adsorption of fluometuron on Norge loam treated with the Krilium soil conditioner was found not to be significantly different from that of the untreated Norge loam.

Desorption of fluometuron from Norge loam is characterized by the equilibrium desorption isotherms given in Figure 5. The adsorption

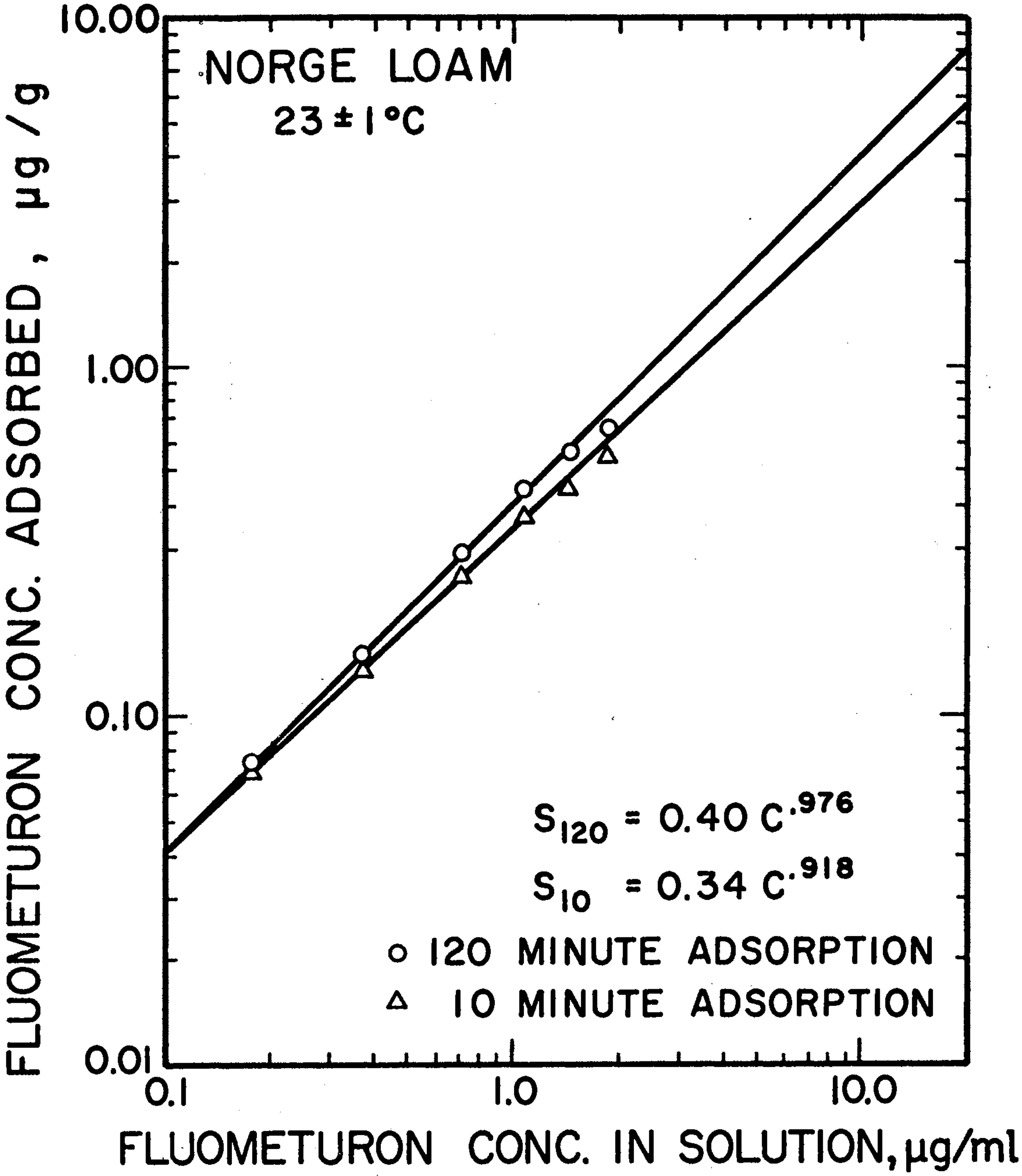

Figure 4. Adsorption Isotherms for Fluometuron on Norge Loam Soil (5 gm Soil: 5 ml Fluometuron Solution) Following 10 and 120 Minute Reaction Period

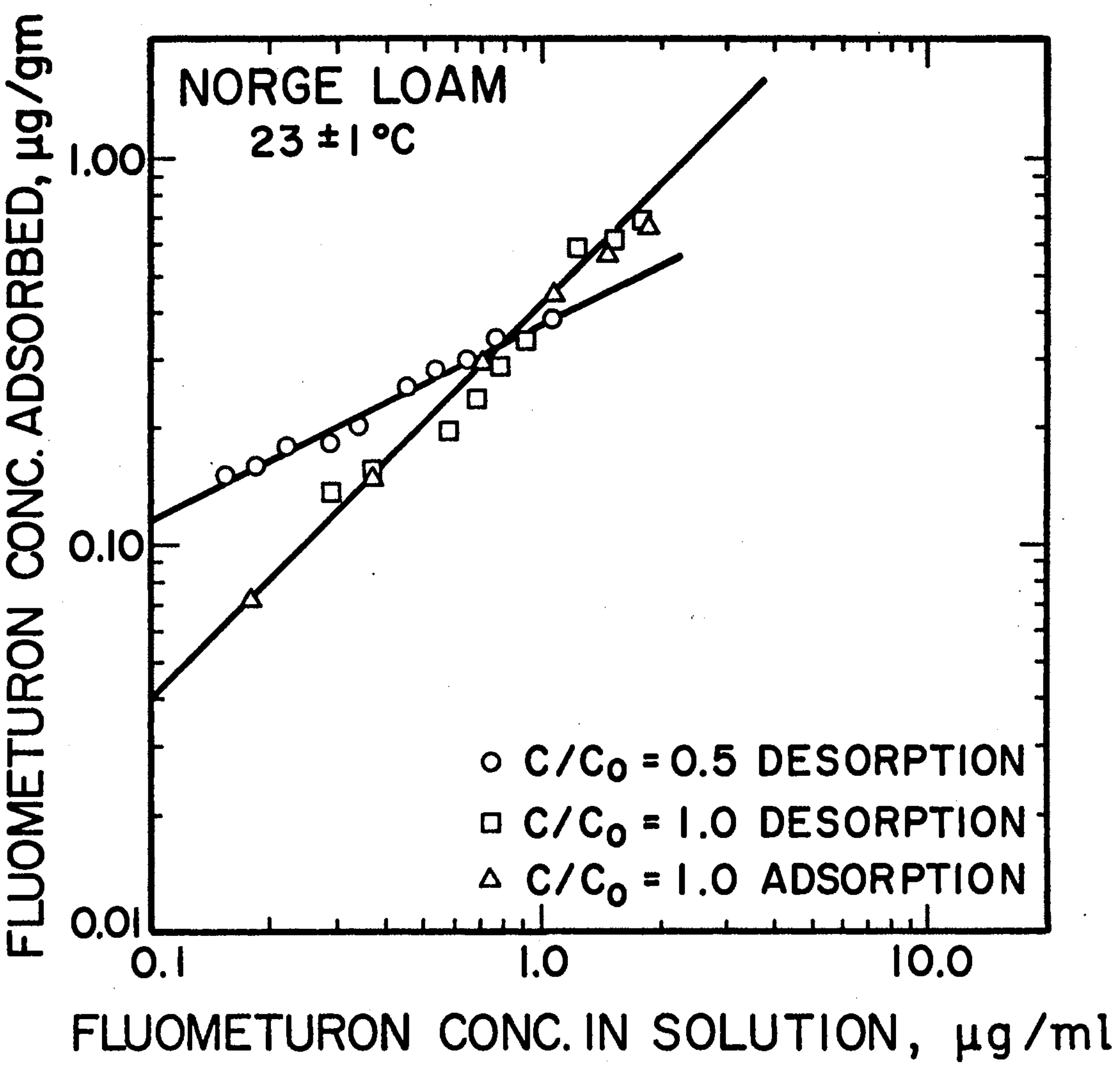

Figure 5. Desorption Isotherms for Fluometuron on Norge Loam Soil (5 gm Soil: 5 ml Fluometuron Solution) for 120 Minute Reaction Periods at Two Initial Adsorbed Fluometuron Concentrations. 120 Minute Adsorption Isotherm Given for Reference.

isotherm is included for reference. From this study it was found that desorption was dependent upon the maximum amount adsorbed before desorption was initiated. When less was adsorbed, the desorption was not reversible. Scott and Lutz (1971) have shown that the amount of herbicide released was a function of soil-water content and was dependent upon the amount initially adsorbed, however, in the reverse order from that found above. The data for the desorption studies are given in Table IV in the Appendix.

Transient Sorption Studies

Adsorption-desorption envelopes are presented in Figures 6 and 7. These results were obtained from the fast and slow herbicide displacement columns. These data were obtained from the soil samples removed from the columns after a specified amount of displacing solution had been applied. A "best-fit" line was calculated from a least squares regression analysis of the data. For an average pore water velocity of 5.51 cm/hr the slope of the linear regression line was 0.854 (K_d=0.335) indicating that the processes of adsorption and desorption were not quite at equilibrium as compared to the slope of 0.976 (K_d=0.40) for equilibrium adsorption plotted on a linear scale. In general, as the herbicide moved farther along the column the sorption envelopes closed about the regression line.

In the case of an average pore water velocity of 0.59 cm/hr the envelopes were more symmetrically arranged about the regression line. As the herbicide moved farther along the column, the linear regression line agreed more closely with the sorption envelopes than for the fast flow rate envelopes. The slope of the regression line was 0.944

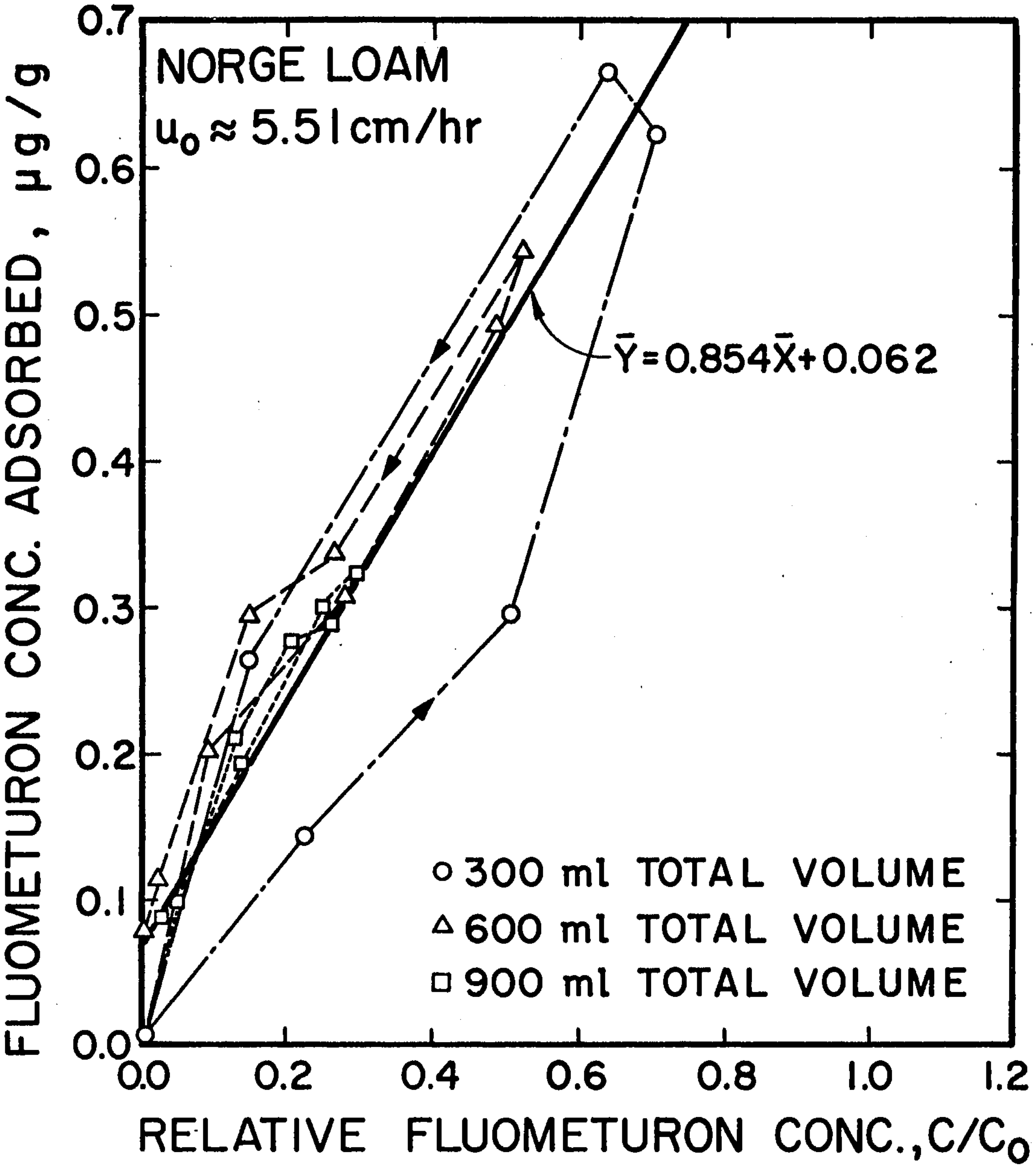

Figure 6. Transient Adsorption-Desorption Behavior of Fluometuron in Norge Loam Soil Columns With an Average Pore-Water Velocity of 5.51 cm/hr.

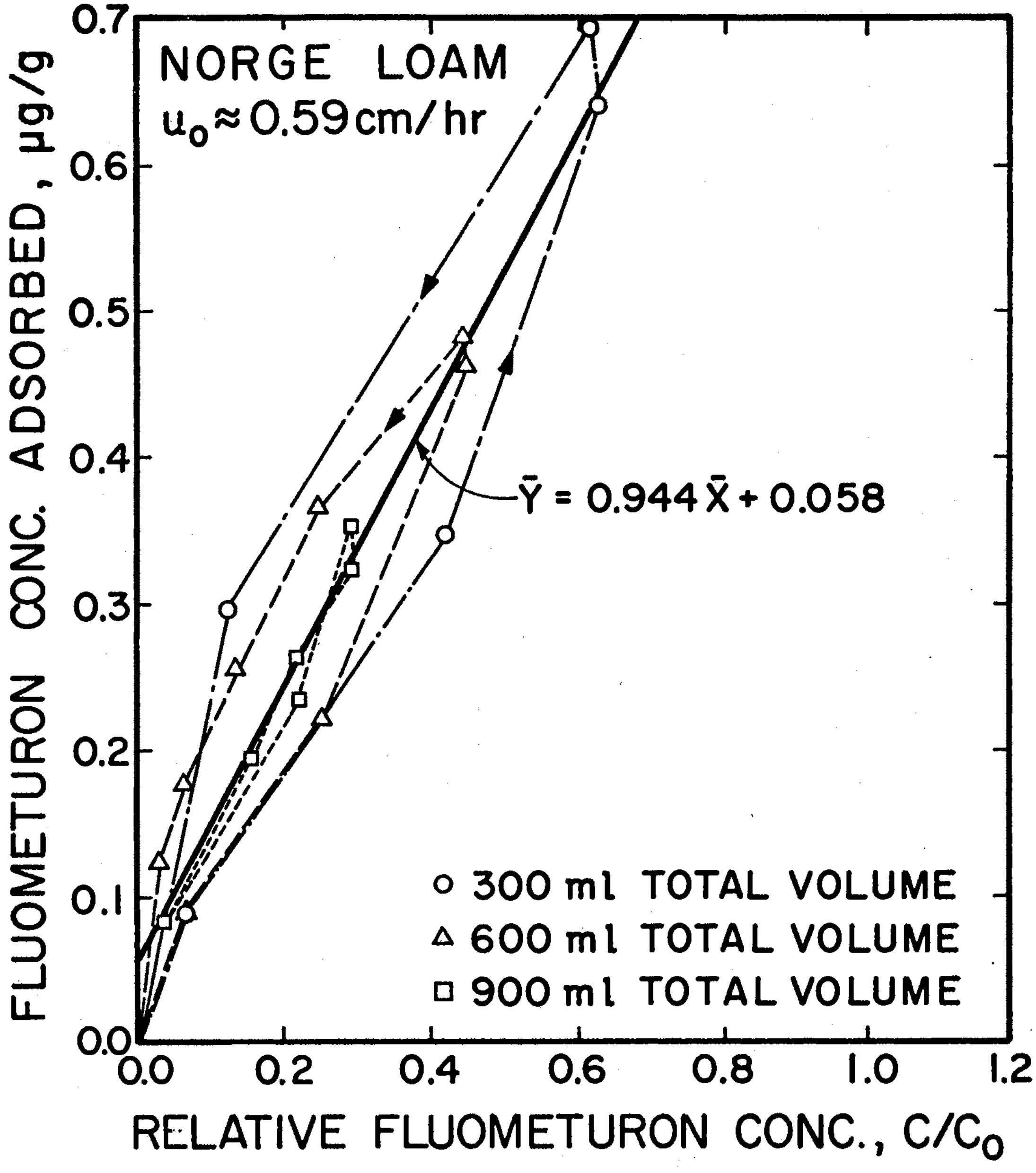

Figure 7. Transient Adsorption-Desorption Behavior of Fluometuron in Norge Loam Soil Columns With an Average Pore-Water Velocity of 0.59 cm/hr.

(K_d=0.370) indicating near equilibrium conditions were in existence, especially as the herbicide had moved farther down the column.

Distribution of Herbicide Within the Column

A 200 ml pulse of herbicide solution was allowed to move into the water saturated columns and this was followed by either 100, 400 or 700 ml of 0.01N calcium sulfate to displace the pulse along the column. The 200 ml pulse was equivalent to a 1.12 kg/ha application of fluometuron to the soil surface. At the above designated throughput volumes the columns were sectioned and the distribution of fluometuron in the solution phase and adsorbed phase determined. The experimental parameters imposed on each of the columns are given in Table II. The fluometuron concentration distributions in Norge loam for pore water velocities of 5.30, 5.49, and 5.73 cm/hr are given in Figure 8, and for pore water velocities of 0.632, 0.571, and 0.577 cm/hr given in Figure 9. These velocities will hereafter be referred to as "fast" and "slow" velocities, and have been chosen to be approximately a factor of ten different. The reduced concentrations is given by C/C_o where C is the instantaneous concentration of solute at distance x, and C_o is the initial concentration of solute in the end plate at t=0.

The distributions for both the fast and slow velocity columns tend to become reduced in peak height and increased in base width as the pulse proceeds along the column. This is a result of mixing by velocity dispersion and the effect of adsorption of the herbicide by the soil material. Comparisons of Figure 8 and 9 show that, in general, the pulse heights of the slower velocity columns are lower and to the left of those obtained from the faster velocity columns. This

TABLE II

EXPERIMENTAL PARAMETERS IMPOSED ON SOIL COLUMNS

Column I.D.	Total Volume cm^3	Bulk Density g/cm^3	Water Content cm^3/cm^3	Solution Flux cm/hr	Pore Water Velocity cm/hr	Pulse Time hr	Total Time hr	Pore Volume cm^3	Distribution Coefficient cm^3/g
0301	300	1.501	0.396	2.10	5.30	2.12	3.15	538.7	0.266 *
0102	600	1.503	0.383	2.10	5.49	2.11	6.30	520.2	0.275 *
0203	900	1.500	0.373	2.14	5.73	2.08	9.30	506.9	0.291 *
0103	1200	1.505	0.389	2.12	5.47	2.07	12.48	529.0	
0206	2400	1.494	0.387	2.12	5.49	2.07	24.85	525.9	0.280 *
0104	300	1.499	0.347	0.219	0.632	19.80	30.13	510.5	0.434 **
0105	600	1.511	0.382	0.218	0.571	20.33	60.67	520.0	0.403 **
0302	900	1.520	0.378	0.218	0.577	20.42	91.00	514.1	0.404 **
0204	2400	1.501	0.387	0.221	0.569	20.83	239.95	526.9	0.409 **
0205	2400	1.063	0.563	1.65	3.88	2.07	24.27	765.4	
0106	2400	1.069	0.555	1.63	3.88	2.05	24.57	755.0	
0304	2400	1.224	0.494	2.01	4.08	2.22	26.28	671.3	

* Based on u' = 2.64 cm/hr

** Based on u' = 0.22 cm/hr

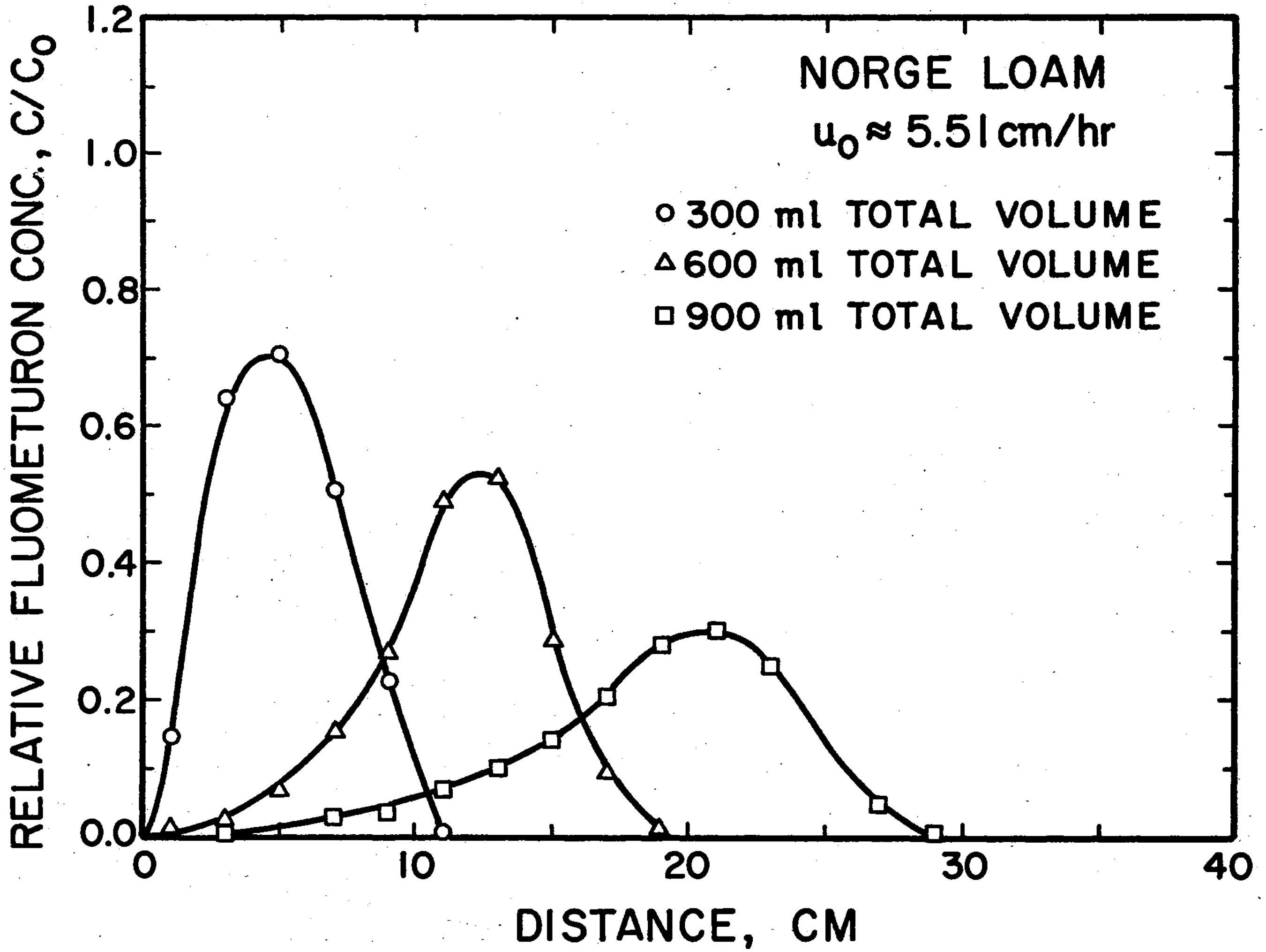

Figure 8. Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Columns for an Average Pore-Water Velocity of 5.51 cm/hr.

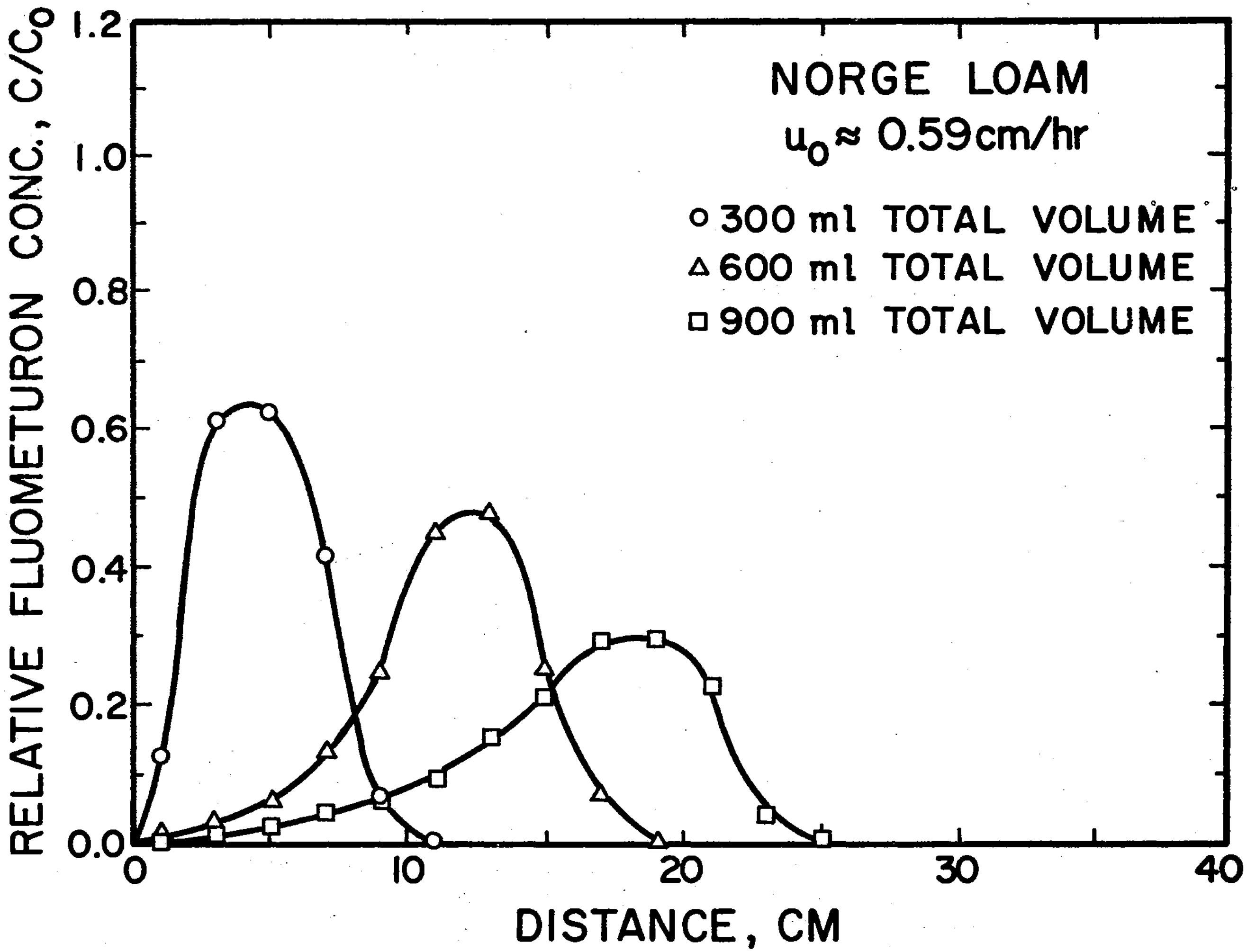

Figure 9. Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Columns for an Average Pore-Water Velocity of 0.59 cm/hr.

phenomenon occurs owing to the greater time for adsorption and diffusion at the slower velocity. At the faster velocity the solution may not reach equilibrium adsorption and the velocity component overshadows the effects of molecular diffusion. These effects tend to translate the distribution curves in opposite directions for the fast and slow velocities. These effects are not as evident for the middle distribution curves, and it has been concluded that experimental uncertainties such as changes in pore distribution and pore water velocities for these two columns have masked the effects. At the faster velocity, approximately 95 ml of solution passes through a one cm section of soil each hour. Thus, the "residence time" for the solution in the soil section may not be adequate for adsorption since most of the contact between the soil particle and herbicide solution takes place in the larger pores. These pores conduct the bulk of the solution. If the convective flow is great compared to diffusion, then equilibrium between solution concentration in the larger pores and that in the smaller pores or dead end pores cannot be achieved. Inspection of Figures 6 and 7 bears out the lack of equilibrium at the faster velocity and the nearer approach to equilibrium for the slower velocity.

The magnitude of the effects of flow velocity on the adsorption of the herbicide in the column can be more easily observed when compared with the no adsorption case. The leading edge of the pulse with no adsorption or velocity dispersion would be approximately 17 cm for the 300 ml total volume curve, and completely out of the column with equivalent distances of 34 and 51 cm for the 600 and 900 ml total volume. These predicted leading edges would be the same for both fast and slow velocities. An integral part of this investigation was to compare the effectiveness of existing models for predicting the concentration distribution within the soil column as the pulse progressed through the soil. For purposes of comparison, two different solutions to Equation [1] have been selected. The first is that used by Davidson, et al. (1968) as given in Equation [6] for the expressed assumptions and boundry conditions, and the second is that used by Oddson, et al. (1970) as given in Equation [17] with its respective assumptions and boundry conditions.

Computer programs were written in Fortran IV language for the solutions given in Equation [6] and Equations [16] and [17] and were processed on an IBM System 360 Model 65 computer. Since these solutions did not produce concentration distributions which would exactly represent the experimental data, criterion of "fit" were established. The location of the maximum (peak) solution concentration and the edge of the leading front (right side for within column distributions and left side for effluent distributions) were used to establish a "fit".

Figures 10 and 11 show the experimental data "fitted" for Equation [6] for both fast and slow pore-water velocities. A good fit was obtained for all curves except the 600 ml fast velocity and the 900 ml slow velocity. These two have been noted to contain small experimental uncertainties. For the fast velocity, a fit was obtained using a value of 2.64 cm/hr for u' and a value of 0.33 cm^2/hr for D'. The distribution coefficient, K_d = 0.28 cm^3/hr, was calculated using the experimental and fitted values in Equation [7]. This value is lower than the 0.40 value found for equilibrium adsorption indicating that equilibrium was not achieved at this flow velocity.

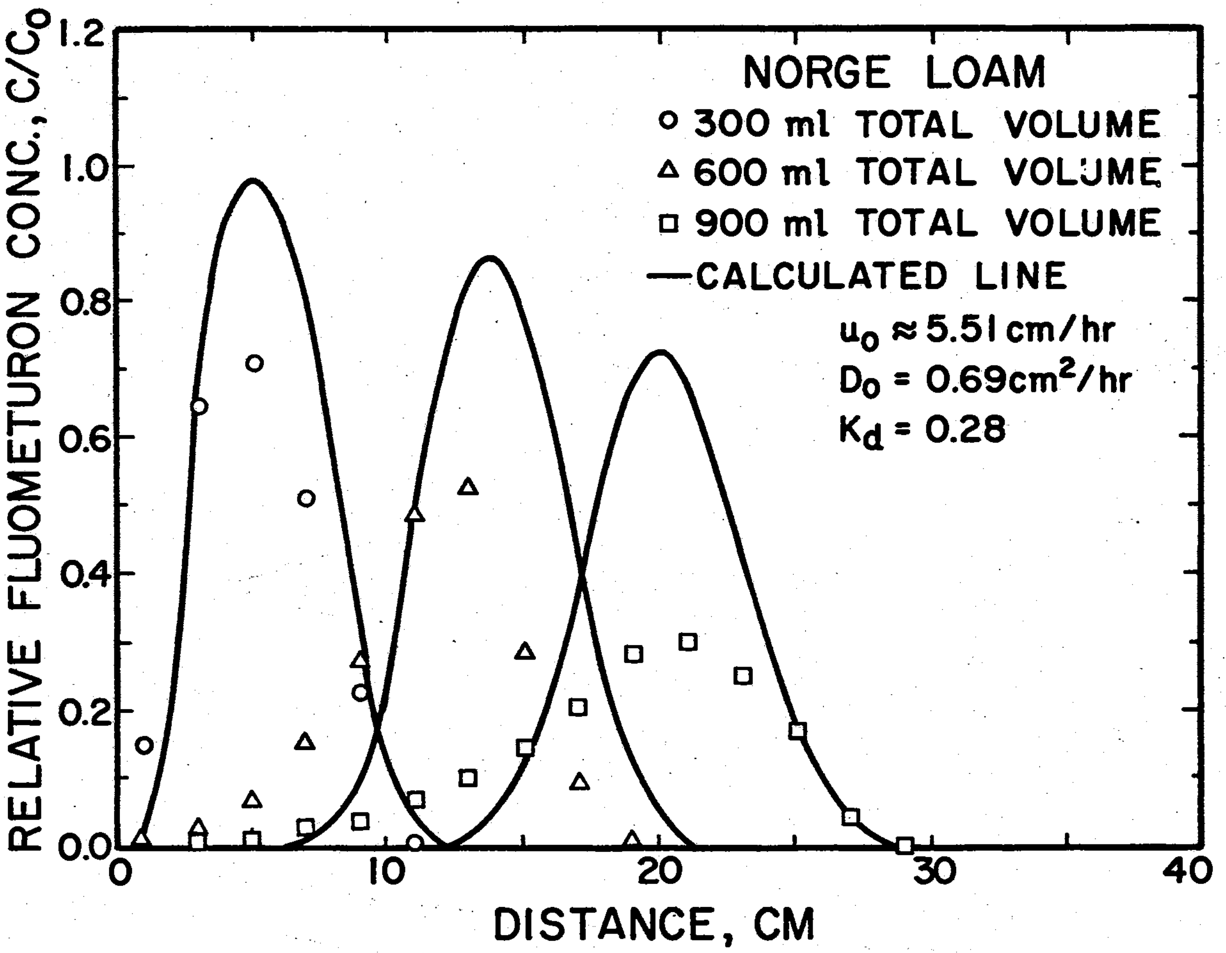

Figure 10. Experimental and Calculated Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Columns. Experimental Average Pore-Water Velocity Was 5.51 cm/hr. Solid Lines Were Calculated Using Equation [6] (Davidson et al.) for $u_o = 5.51$ cm/hr, $D_o = .069$ cm^2/hr, and $K_d = 0.28$ cm^3/gm.

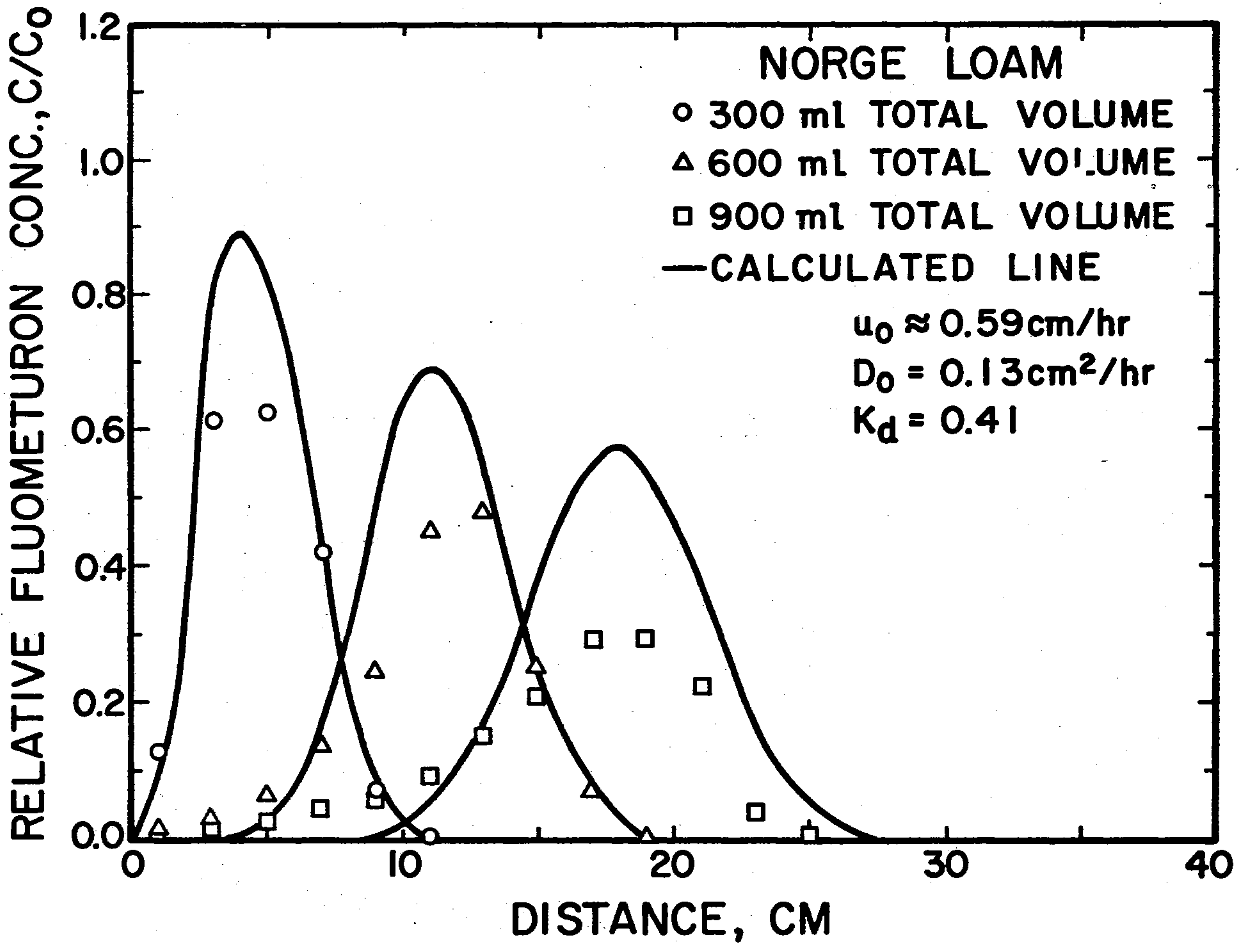

Figure 11. Experimental and Calculated Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Columns. Experimental Average Pore-Water Velocity Was 0.59 cm/hr. Solid Lines Were Calculated Using Equation [6] (Davidson et al.) for u_o = 0.59 cm/hr, D_o = 0.13 cm^2/hr, and K_d = 0.41 cm^3/gm.

For the slow velocity columns a value of 0.22 cm/hr for u' and a value of 0.05 cm^2/hr for D' gave the best fit. Calculation of K_d from these values resulted in a value of 0.41 which is very close to the equilibrium K_d value of 0.40 indicating that adsorption was near equilibrium. In all cases the concentration at the peak maximum was over estimated by 25 to 100 per cent.

Figures 12 and 13 show the experimental data fitted with Equation [17]. A good fit was obtained for both fast and slow velocities by varying both α and K, however, by varying α we have introduced a variable rate constant for the sake of fitting the data. If Equation [13] is valid, then α should be unique in the soil-herbicide system in the range of the experiment. For the fast velocity a fit was obtained for $\alpha = 8.0\ hr^{-1}$ and K = 1.55 cm^3/gm. Again the theoretical curves over predicted the solution concentration at the peak maximum by 25 to 300 per cent with the best fit for the 300 ml total volume.

To make direct comparisons of the applicability of these solutions, one experimental curve was chosen at each velocity and theoretical curves were computed as follows:

A. Equation [6] with a fitted K_d value,

B. Equation [6] with equilibrium K_d value,

and C. Equation [17] with equilibrium K value.

The K term used in Equation [17] is different from the K_d value used in Equation [6]. They are related by the relationship:

$$K = \frac{\rho K_d}{\theta}$$

where ρ, 0, and K_d have been previously defined. An equilibrium K value would be the value resulting from use of the equilibrium K_d value

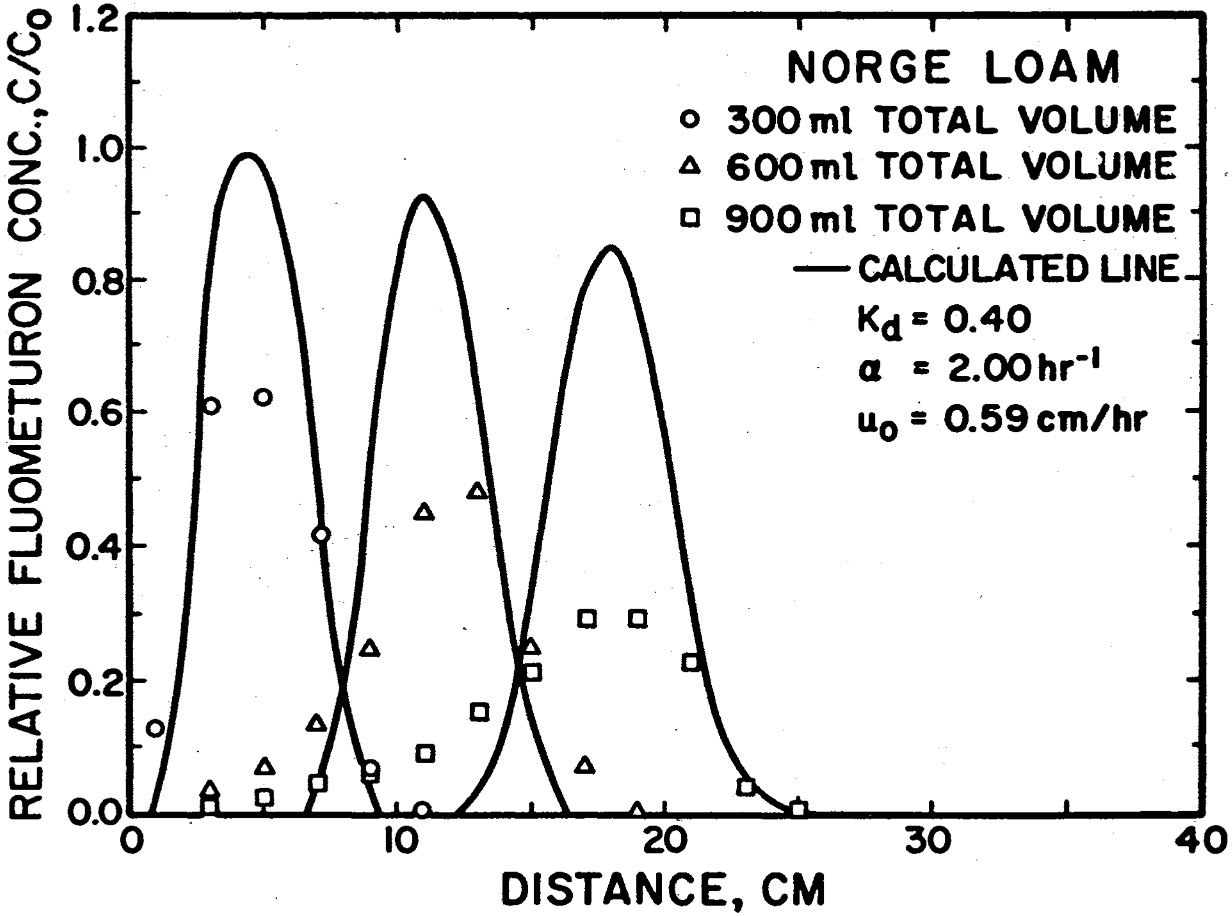

Figure 12. Experimental and Calculated Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Columns. Experimental Average Pore-Water Velocity Was 0.59 cm/hr. Solid Lines Were Calculated Using Equation [17] (Oddson et al.) for u_o = 0.59 cm/hr, K_d = 0.40 cm^3/hr, and α = 2.0 hr^{-1}.

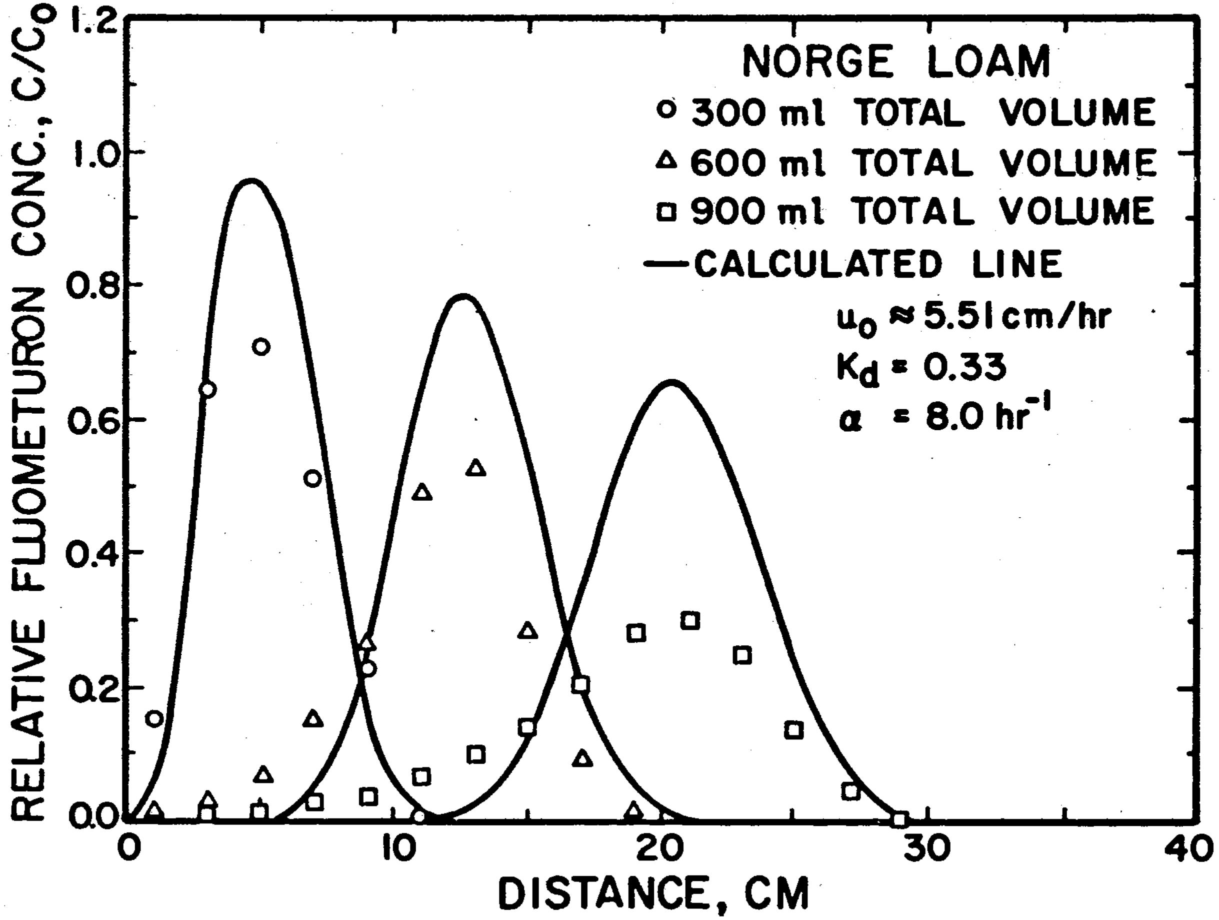

Figure 13. Experimental and Calculated Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Columns. Experimental Average Pore-Water Velocity Was 5.51 cm/hr. Solid Lines Were Calculated Using Equation [17] (Oddson et al.) for u_o = 5.51 cm/hr, K_d = 0.33 cm^3/hr, and α = 8.0 hr^{-1}.

in the above formula. Since Equation [17] assumes diffusion can be neglected, the value of 8.0 hr^{-1} for α was chosen to be a best estimate of the rate constant and used for further comparisons, however, Oddson, et al. (1970) have suggested that 0.6 was a reasonable value and used it for their calculations. These results are presented in Figures 14 and 15 for the fast and slow velocities respectively. For the fast velocity a fitted K_d value of 0.28 and an equilibrium K_d value of 0.40 was used. Curve A produced a fairly good fit with the correct peak location and only a slight overprediction of the location of the leading edge. Curves B and C were a poor fit with neither the peak location nor leading edge accurately determined. Since this curve is based on an equilibrium K_d value it was expected that the peak and leading edge of the curve would be to the left of the actual data since adsorption has been previously shown not to be at equilibrium for the fast velocity.

For the slow velocity columns a fitted K_d value of 0.41, and equilibrium K_d value of 0.40 and a value of 8.0 for α were used. Curves A and B gave a good fit for the concentration distribution, whereas Curve C grossly over predicted the maximum concentration at the peak. Comparison of the theoretical curves in Figures 14 and 15 shows that there is a decrease in area under the slow velocity curves from those for the fast velocity. This agrees with the data which show greater adsorption should occur at the slower velocity.

From the above comparisons it is evident that neither equation predicts accurately the distribution of solution concentration within the soil. The most obvious failure is in predicting the concentration at the point of maximum concentration. Poor fit is obtained on the

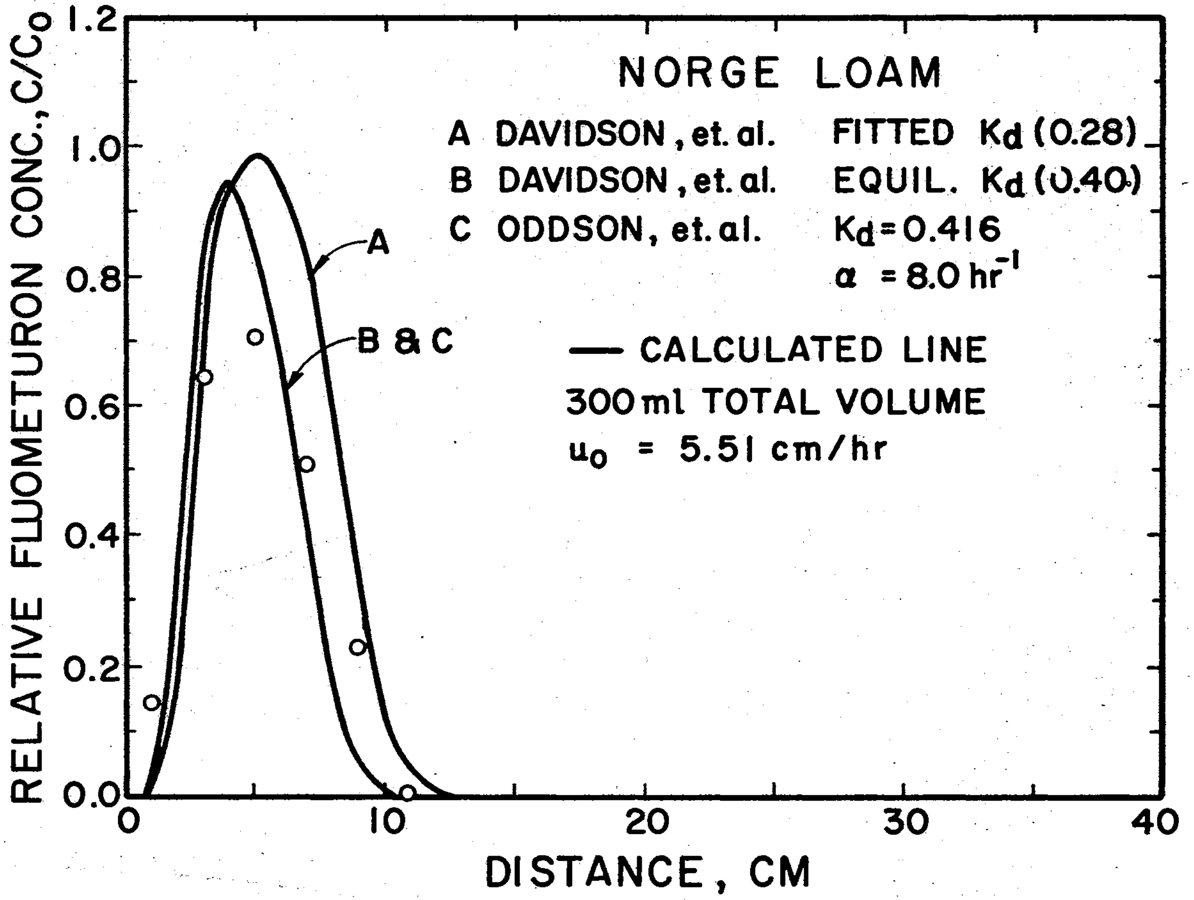

Figure 14. Experimental and Calculated Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Column for 300 ml Total Pulse Volume With Average Pore-Water Velocity of 5.51 cm/hr. Solid Lines Were Calculated Using Equation [6] (Davidson et al., Curve A for $D_o = 0.69$ cm^2/hr, $K_d = 0.28$ cm^3/hr; Curve B for $D_o = 0.69$ cm^2/hr, $K_d = 0.40$ cm^3/hr), and Equation [17] (Oddson et al., Curve C $K_d = 0.41$ cm^3/hr, $\alpha = 8.0$ hr^{-1}).

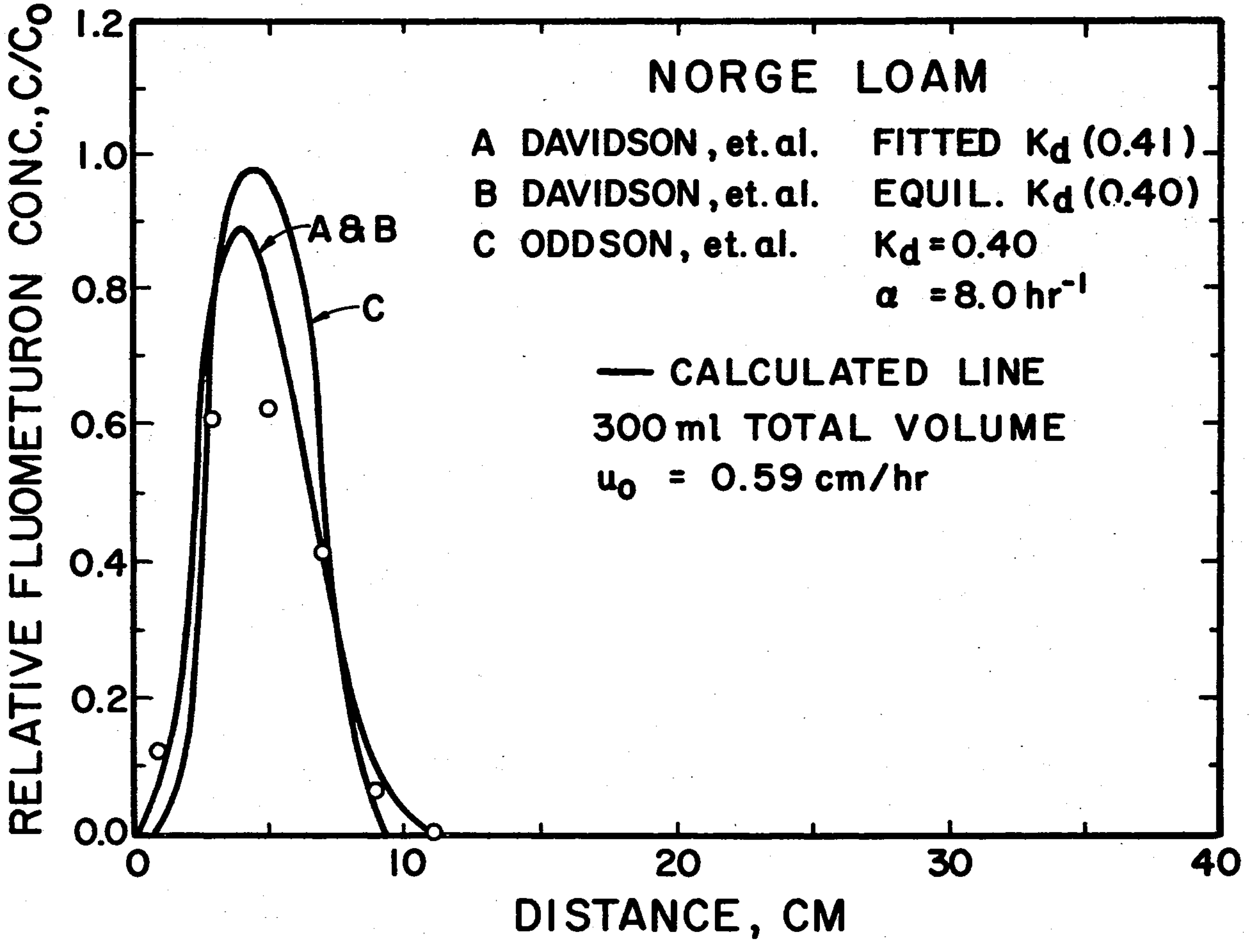

Figure 15. Experimental and Calculated Relative Fluometuron Solution Concentration Distributions in Norge Loam Soil Column for 300 ml Total Pulse Volume With Average Pore-Water Velocity of 0.59 cm/hr. Solid Lines Were Calculated Using Equation [6] (Davidson et al., Curve A for D_o = 0.13 cm^2/hr, K_d = 0.41 cm^3/hr; Curve B for D_o = 0.13 cm^2hr, K_d = 0.40 cm^3/hr), and Equation [17] (Oddson et al., Curve C for K_d = 0.41 cm^3/hr, α = 2.0 hr^{-1}).

trailing edge of the pulse, especially as the pulse progresses down the column. When the velocity is slow enough to allow near equilibrium adsorption, Equation [6] gives a good fit, whereas Equation [17] gives a poor fit. This would indicate that diffusion should not be assumed negligible under these conditions. At present, both equations have limitations and are not generally acceptable in predicting the concentration distribution in this soil-herbicide system. The apparent lack of fit does not indicate that the models are invalid, but rather suggests that all the variables in the system are not considered or the physical constants used were not adequately determined.

Elution of Herbicide From the Column

Comparison of the relative retention at the two flow velocities can also be made for the elution curves given in Figure 16. The faster velocity elutes from the column earlier by about 0.3 pore volumes and its maximum concentration is greater than that for the slower velocity. This relationship is due to a greater adsorption at the slower velocity, thus reducing the concentration of the herbicide in the soil solution. These curves are in agreement with the results obtained within the columns.

Theoretical curves have been calculated using Equation [6] for the values of u' and D' used for the column data, that is, the equilibrium value of $K_d = 0.40$ and fitted value of $K_d = 0.41$. These curves are shown in Figures 17 and 18 with the experimental data also plotted. As was the case for the within column data, the theoretical curves over predicted the concentration at the maximum for both equilibrium and fitted K_d values. The equilibrium K_d calculated curve predicts that

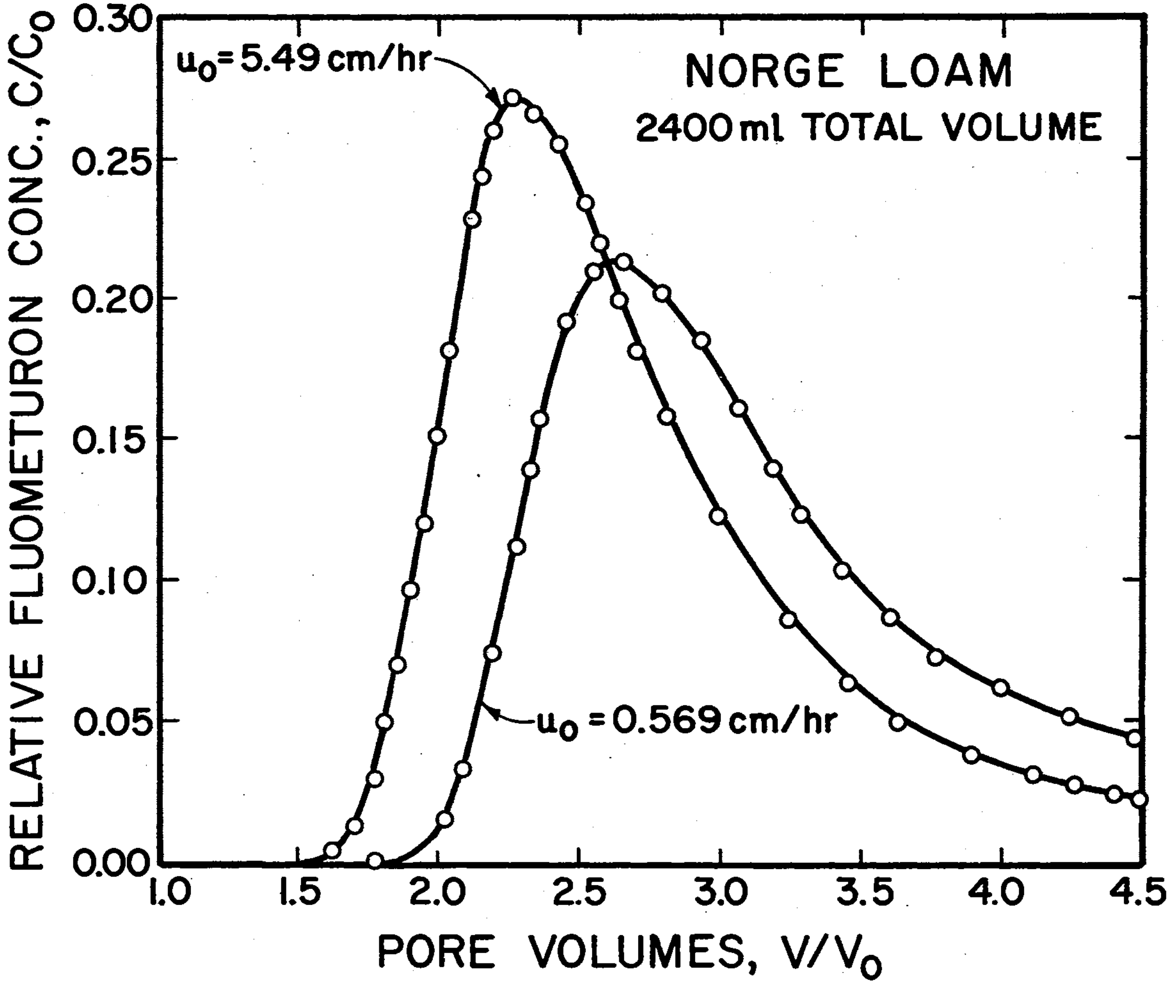

Figure 16. Relative Fluometuron Effluent Solution Concentration Distribution Curves for 2400 ml Total Throughput Volumes at Average Pore-Water Velocities of 5.49 cm/hr and 0.569 cm/hr.

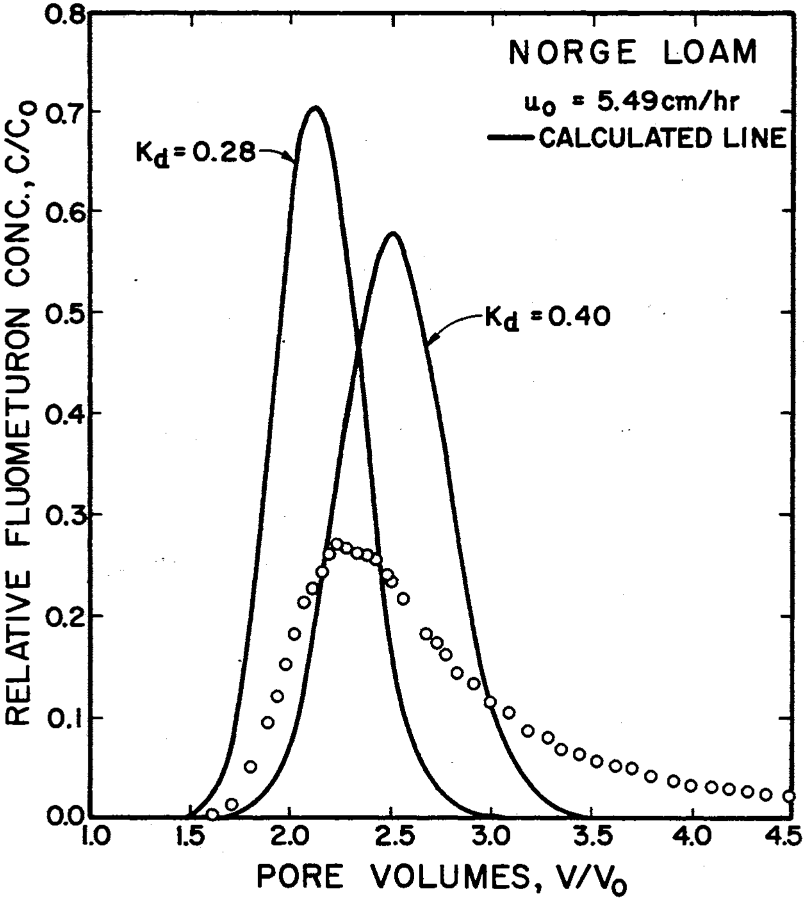

Figure 17. Experimental and Calculated Relative Fluometuron Effluent Solution Concentration Distributions for 2400 ml Total Throughput Volume at an Average Pore-Water Velocity of 5.49 cm/hr. Solid Lines Calculated Using Equation [6] (Davidson et al.) with D_o = 0.69 cm^2/hr and K_d = 0.28 cm^3/hr, and D_o = 0.69 cm^2/hr, and K_d = 0.40 cm^3/hr.

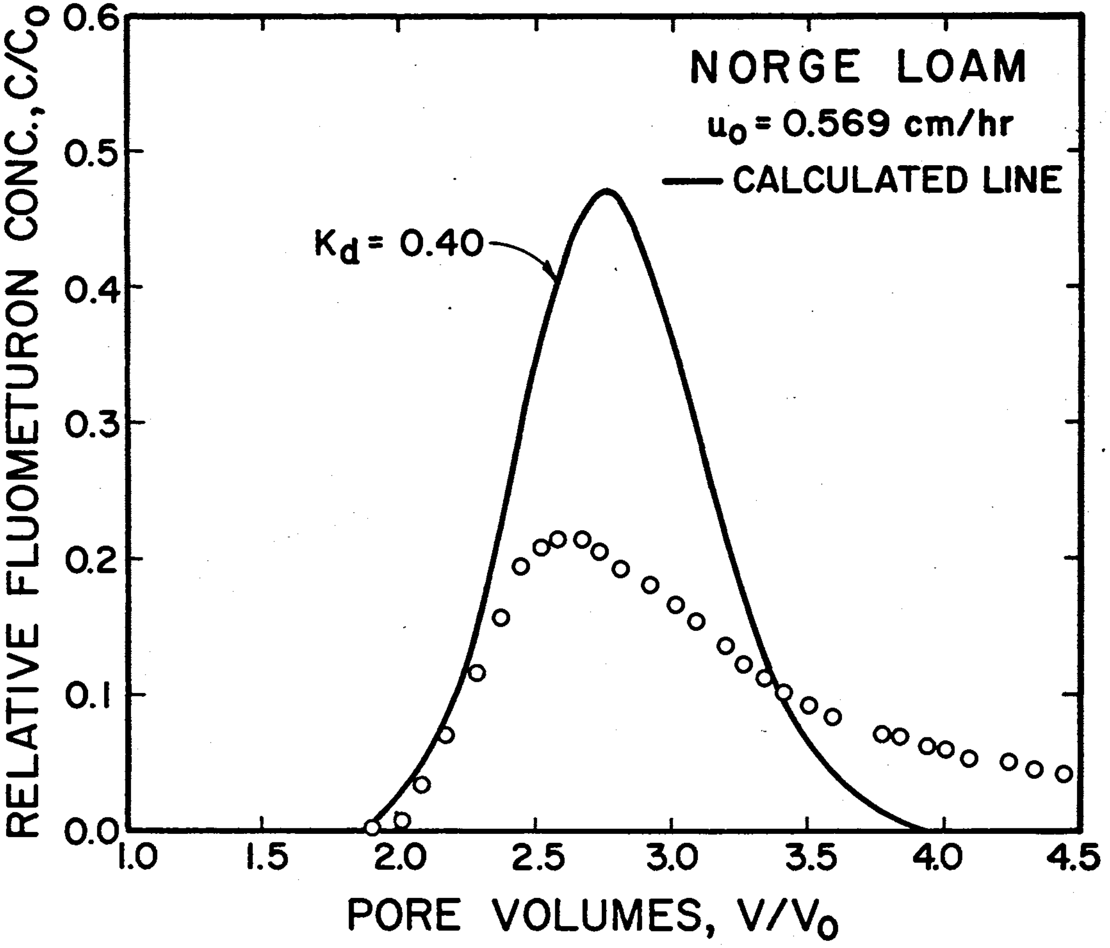

Figure 18. Experimental and Calculated Relative Fluometuron Effluent Solution Concentration Distributions for 2400 ml Total Throughput Volume at an Average Pore-Water Velocity of 0.569 cm/hr. Solid Lines Calculated Using Equation [6] (Davidson et al.) With D_o = 0.13 cm^2/hr and K_d = 0.40 cm^3/hr.

the herbicide would elute at a later volume than the data show for the faster flow velocity (Figure 17). Again this is attributed to the non-equilibrium conditions which exist in this case. For the slow velocity, a good fit was obtained between the theoretical curve and the experimental data (Figure 18) with the elution of herbicide accurately predicted with respect to location of the leading edge and occurrence of the peak maximum.

Stabilized Aggregate Study

Norge loam soil aggregates stabilized with Krilium soil conditioner were used to study the effect of aggregate size on the movement of fluometuron in soil. The ranges of aggregate sizes studied were 2.0 to 1.0, 1.0 to 0.5, and 0.5 to 0.25 mm. The elution curves for fluometuron from the above size aggregates are presented in Figure 19. Columns A and B were packed to the same bulk density. Column C was slightly more dense since the small size aggregates could not be packed to the same low density that exists for the larger aggregates. The solution flux was adjusted to keep the pore water velocity nearly equal for all three columns. The concentration of the chloride ion in the effluent was monitored to determine the variation in mixing due to flow in the various pore space. A plot of relative concentration, C/C_o, versus pore volume, V/V_o, is given in Figure 20. The pore volume is given by V/V_o, where V is the volume of effluent at time t and V_o is the pore volume (volume of water contained in the column at time t). For idealized piston flow, the chloride ion distribution curve would be vertical at $V/V_o = 1.0$. Dispersion due to mixing causes the distribution to become sigmoid in shape, however, the curve should pass through

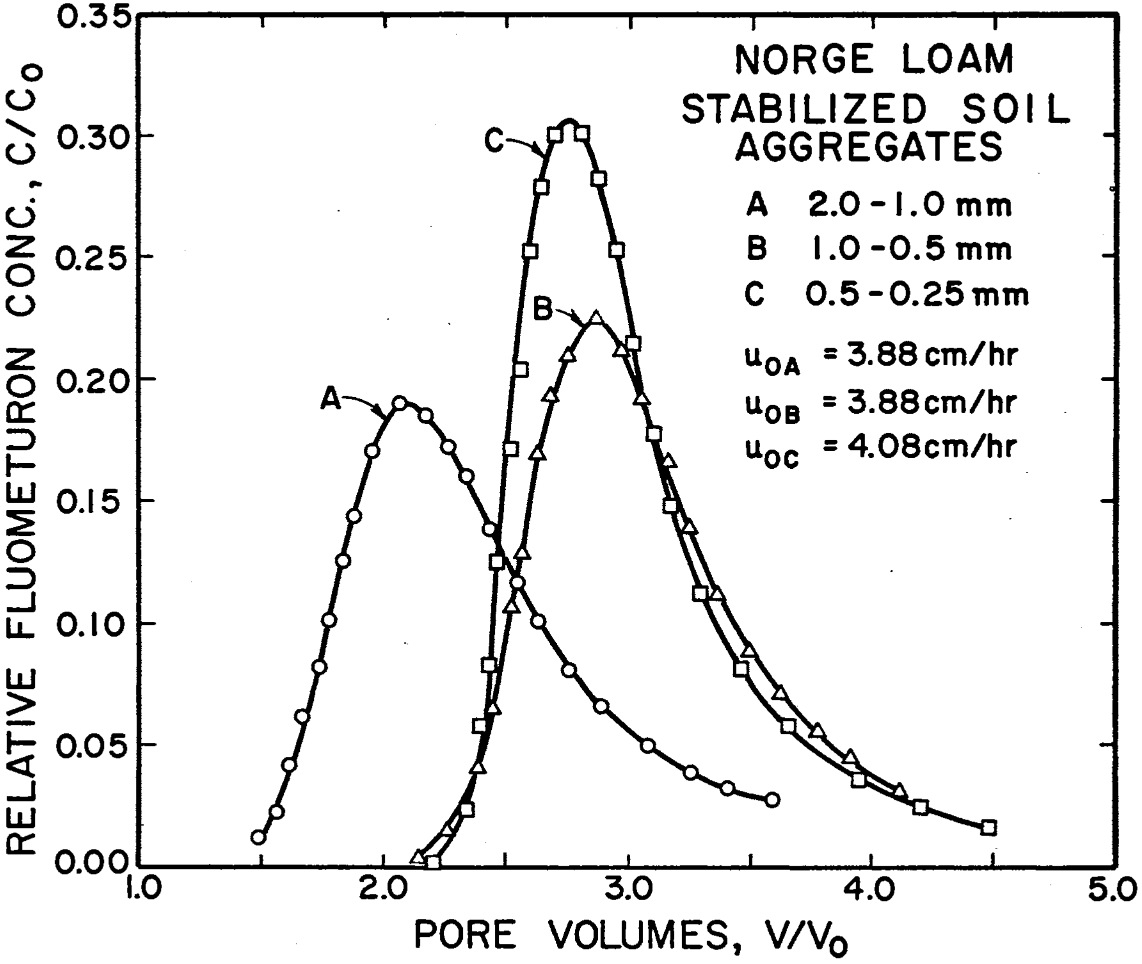

Figure 19. Relative Fluometuron Effluent Solution Concentration Distributions for 2.0 to 1.0, 1.0 to 0.5, and 0.5 to 0.25 mm Size Stabilized Aggregates at 3.88, 3.88, and 4.08 cm/hr Average Pore-Water Velocities Respectively.

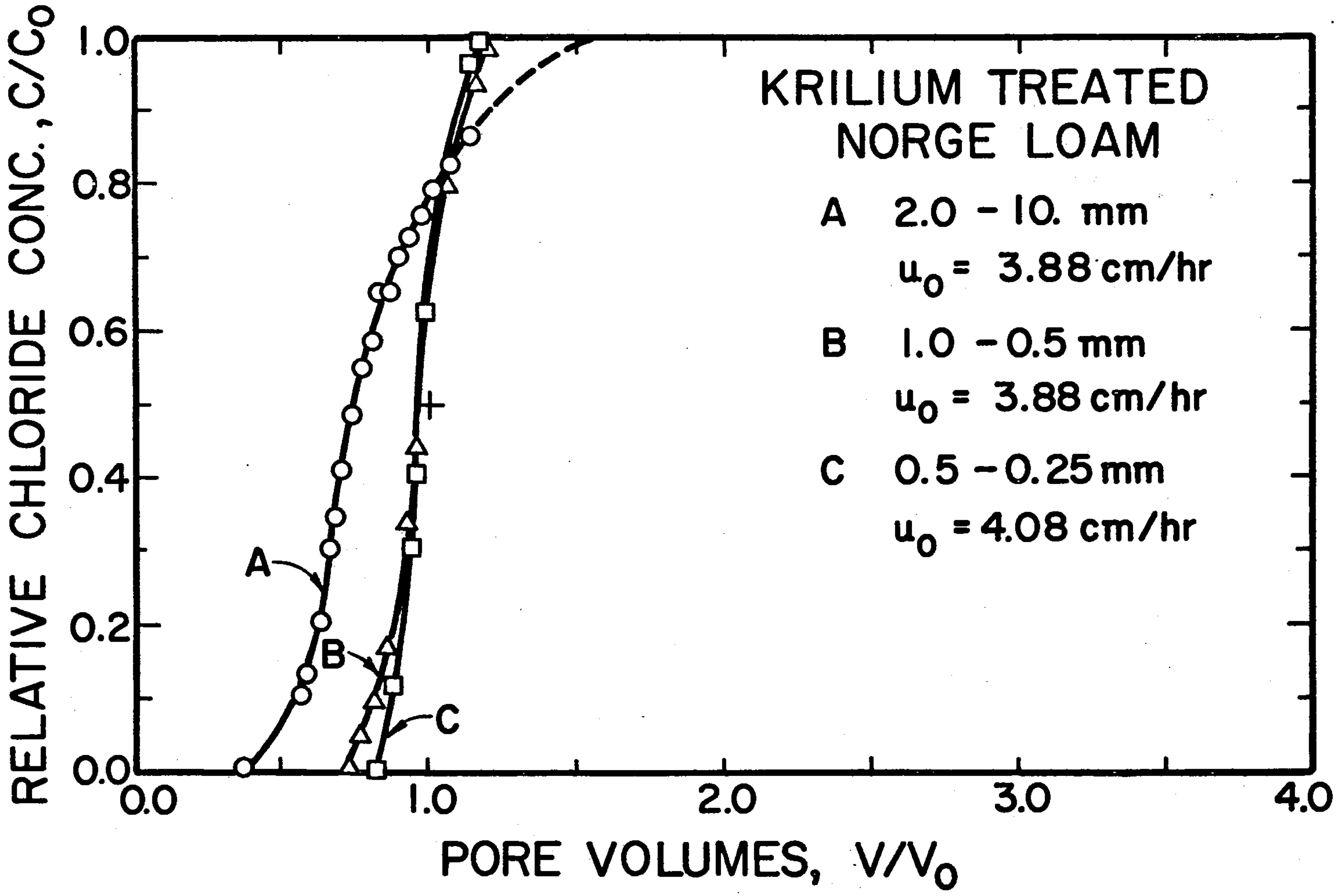

Figure 20. Relative Chloride Ion Concentration Distributions for 2.0 to 1.0, 1.0 to 0.5, and 0.5 to 0.25 mm Size Stabilized Aggregates at 3.88, 3.88, and 4.08 cm/hr Average Pore-Water Velocities Respectively.

$C/C_o = 0.5$ when $V/V_o = 1.0$. For a nonreacting solute, such as the chloride ion, a distribution of the chloride ion left of $V/V_o = 1.0$ (early) at $C/C_o = 0.5$ indicates that flow is not occurring in all the pore spaces available and incomplete mixing is achieved. For Curve A (Figure 20) the chloride ion arrived 0.25 pore volumes early. For Curves B and C the chloride ion arrived 0.04 pore volumes early (Figure 20). Curves A, B, and C as plotted in Figure 19 have been adjusted for the early arrival by using the smaller pore volume, thus the effect of non-contributing pore space has been eliminated.

Curve A (Figure 19) represents the concentration distribution for the 2.0 to 1.0 mm size aggregates, Curve B for the 1.0 to 0.5 mm size aggregates, and Curve C for the 0.5 to 0.25 mm size aggregates. Curve A is to the left of the other curves owing to incomplete mixing in the smaller pores within the aggregates. Since most of the flow takes place in the larger pores, the herbicide does not move readily into the smaller pores to be adsorbed. Curve B is displaced to the right of Curve A due to the increased adsorption and more complete mixing. The range in aggregate size has been reduced by one half, therefore the range of pore water velocities has decreased. The peak height is higher than for Curve A due to the reduced range of pore distribution. Davidson and Chang (1972) noted greater adsorption in soil columns containing small aggregates (< 0.42 mm) as compared with columns containing large aggregates (< 2.0 mm) in a study using Norge loam soil and picloram.

Curve C (Figure 19) has a much greater peak height than either Curve A or B. It is not translated to the right of B since it was necessarily packed to a greater density. The increased peak height is a result of the decreased pore size distribution which is one-fourth that of A and one-half that of C.

It is evident from these curves that range in aggregate size and thus range in pore velocity distribution is important in the movement of fluometuron in Norge loam, and serves to illustrate the importance of defining the aggregate size and range used in studies of herbicide movement in soils as well as the pore size distribution.

CHAPTER VI

SUMMARY AND CONCLUSIONS

A miscible displacement technique was used to evaluate the movement and adsorption of fluometuron in Norge loam. A procedure was developed to permit sampling of the solution and adsorbed phases within the column at designated soil positions. Transient adsorption-desorption isotherms were obtained from the miscible displacement experiment. Equilibrium adsorption-desorption isotherms were obtained using the batch method.

The concentration distributions of a fluometuron pulse were established for various throughput volumes at two average pore water velocities, and for different ranges of aggregate sizes. Two computer solutions to Equation [1] were compared for their effectiveness in predicting the concentration distributions of fluometuron within soil columns.

It was concluded that for the velocities studied, the faster soil-water flux resulted in the movement of the herbicide further along the column for the same throughput volume. Since most of the flow was in the larger pores, less adsorption and incomplete mixing occurred. Molecular diffusion was negligible compared to convective flow at the fast velocity.

For the slower velocity, the herbicide was nearly in equilibrium as the pulse moved along the soil column since there was adequate time for the adsorption and desorption, diffusion, and mixing processes to take place. The equilibrium K_d value was found to be 0.40.

The two mathematical models studied were found to be inadequate to accurately describe the concentration distributions within the column. However, they can be useful in predicting the location of the maximum concentration and edge of the leading front. This was accomplished by curve fitting to obtain the correct distribution coefficient K_d. Equation [6] was found to be of greater applicability. Neither program accounts for the amount of adsorption within the column in a manner which is consistent with the physical processes taking place within the column.

The time required for equilibrium adsorption of fluometuron on Norge loam was found to be very short, with 85 per cent of the reaction complete within 10 minutes. One hour was found sufficient for equilibrium adsorption. Desorption was found to be dependent upon the maximum adsorption level before desorption was initiated.

These studies have shown the importance of evaluating the effects of pore water velocity, adsorption, desorption, and aggregate size on the movement of a herbicide through a soil.

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APPENDIX

TABLE III

ADSORPTION OF FLUOMETURON BY NORGE LOAM SOIL AFTER 10, 20, 40, 60, AND 120 MINUTE REACTION PERIODS AT 23 ± 1° C

	Fluometuron Adsorbed Per Gram of Soil, Microgram					Fluometuron in Solution	
	Time in Minutes						
	10	20	40	60	120	µg/ml	C/C_o
	0.056	0.068	0.070	0.077	0.074		
	0.066	0.078	0.076	0.079	0.072		
avg	0.061	0.073	0.073	0.078	0.073	0.180	0.072
	0.133	0.142	0.138	0.151	0.151		
	0.136	0.142	0.138	0.147	0.148		
avg	0.134	0.142	0.138	0.149	0.149	0.369	0.145
	0.260	0.289	0.290	0.303	0.295		
	0.248	0.287	0.281	0.303	0.300		
avg	0.254	0.288	0.286	0.303	0.297	0.718	0.282
	0.367	0.390	0.381	0.418	0.444		
	0.365	0.387	0.378	0.420	0.440		
avg	0.366	0.389	0.379	0.419	0.442	1.096	0.430
	0.447	0.503	0.511	0.561	0.549		
	0.459	0.550	0.543	0.551	0.568		
avg	0.453	0.526	0.527	0.555	0.558	1.489	0.584
	0.526	0.646	0.654	0.650	0.651		
	0.592	0.646	0.660	0.699	0.668		
avg	0.559	0.646	0.657	0.675	0.659	1.884	0.739

TABLE IV

DESORPTION OF FLUOMETURON FROM NORGE LOAM SOIL AFTER 120 MINUTE REACTION PERIODS AT 23 ± 1° C

Fluometuron Concentration in the Supernatant	$C/C_o = 0.5$		$C/C_o = 1.0$	
	Amount Desorbed	Total Remaining in Soil	Amount Desorbed	Total Remaining in Soil
μg/ml	μg/g	μg/g	μg/g	μg/g
1.850	--	--	--	0.699
1.551	--	--	0.075	0.624
1.275	--	--	0.032	0.592
1.083	--	--	0.200	0.392
0.921	--	--	0.050	0.342
0.912	--	0.359	--	--
0.794	--	--	0.053	0.289
0.766	0.019	0.340	--	--
0.682	--	--	0.051	0.238
0.648	0.041	0.299	--	--
0.584	--	--	0.043	0.195
0.537	0.012	0.288	--	--
0.457	0.029	0.258	--	--
0.436	--	--	0.010	0.184
0.396	0.031	0.227	--	--
0.372	--	--	0.028	0.157
0.347	0.027	0.200	--	--
0.317	--	--	0.019	0.138
0.292	0.018	0.182	--	--
0.221	0.005	0.177	--	--
0.187	0.016	0.161	--	--
0.160	0.009	0.152	--	--

TABLE V

EXPERIMENTAL DATA FROM SOIL COLUMN STUDIES

Column 0301 - 300 ml Volume - Fast Flow

C ZERO = 11503.6 DPM BKG = 24.9 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/gm	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.149	0.262	13.64	35.70
3	0.642	0.667	58.76	90.77
5	0.708	0.626	64.80	85.17
7	0.512	0.294	46.84	40.21
9	0.229	0.141	20.99	19.20
11	0.003	0.002	0.27	0.32
13	0.002	**	0.16	0.04
15	0.002	**	0.16	0.02
17	0.001	**	0.10	0.04
19	**	**	0.05	0.09
21	**	**	0.07	***
23	**	**	0.06	***
25	**	**	0.02	***
27	**	**	***	***
29	**	**	***	***

Total Herbicide in Soil = 271.73 µg

Total Herbicide in Water = 206.02 µg

Total Herbicide in Column = 477.75 µg

** Less than 0.001

*** Less than 0.01

TABLE V (Continued)

Column 0102 - 600 ml Volume - Fast Flow

C ZERO = 11371.3 BKG = 24.9 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/gm	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.011	0.082	0.94	11.18
3	0.027	0.116	2.36	15.78
5	0.066	0.178	5.85	24.19
7	0.155	0.292	13.69	39.72
9	0.266	0.338	23.50	46.01
11	0.488	0.494	43.17	67.29
13	0.522	0.545	46.14	74.20
15	0.285	0.312	25.16	42.57
17	0.097	0.209	8.57	28.42
19	0.012	0.009	1.08	1.25
21	0.004	0.020	0.39	2.65
23	0.001	0.001	0.11	0.12
25	0.001	0.003	0.09	0.41
27	0.001	0.004	0.14	0.48
29	0.001	0.002	0.12	0.31

Total Herbicide in Soil = 354.59 µg

Total Herbicide in Water = 171.30 µg

Total Herbicide in Column = 525.89 µg

TABLE V (Continued)

Column 0203 - 900 ml Volume - Fast Flow

C ZERO = 11216.7　　BKG = 23.8　　EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/gm	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.004	0.044	0.33	5.92
3	0.009	0.056	0.78	7.55
5	0.017	0.070	1.47	9.55
7	0.030	0.089	2.61	12.06
9	0.037	0.104	3.16	14.19
11	0.068	0.137	5.89	18.56
13	0.102	0.138	8.76	18.73
15	0.141	0.221	12.13	30.01
17	0.204	0.278	17.54	37.85
19	0.283	0.295	24.33	40.11
21	0.303	0.323	26.14	43.93
23	0.256	0.307	22.02	41.74
25	0.253	0.179	21.78	24.36
27	0.054	0.104	4.69	14.07
29	0.008	0.030	0.66	4.11

Total Herbicide in Soil = 322.73 µg

Total Herbicide in Water = 152.28 µg

Total Herbicide in Column = 475.01 µg

TABLE V (Continued)

Column 0103 - 1200 ml Volume - Fast Flow

C ZERO = 11579.3 DPM BKG = 24.9 DPM EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil μg/g	Total Herb. in Water μg	Total Herb. in Soil μg
1	0.002	0.046	0.17	6.32
3	0.005	0.040	0.45	5.40
5	0.008	0.044	0.74	5.99
7	0.012	0.050	1.10	6.80
9	0.019	0.049	1.68	6.64
11	0.027	0.093	2.43	12.74
13	0.036	0.082	3.20	11.19
15	0.501	0.107	4.50	14.65
17	0.073	0.114	6.60	15.54
19	0.104	0.130	9.38	17.75
21	0.130	0.226	11.71	30.80
23	0.183	0.271	16.43	37.02
25	0.214	0.321	19.20	43.82
27	0.258	0.271	23.23	37.01
29	0.267	0.242	24.02	33.00

Total Herbicide in Soil = 284.68 μg

Total Herbicide in Water = 124.84 μg

Total Herbicide in Column = 409.52 μg

TABLE V (Continued)

Column 0206 - 2400 ml Volume - Fast Flow

C ZERO = 11679.0 DPM BKGND = 23.0 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil μg/g	Total Herb. in Water μg	Total Herb. in Soil μg
1	**	0.014	0.05	1.93
3	0.001	0.016	0.09	2.15
5	0.001	0.017	0.09	2.27
7	0.003	0.019	0.23	2.58
9	0.003	0.018	0.23	2.37
11	0.004	0.023	0.32	3.08
13	0.004	0.019	0.39	2.62
15	0.006	0.025	0.52	3.35
17	0.007	0.024	0.65	3.22
19	0.010	0.028	0.90	3.85
21	0.011	0.033	0.95	4.45
23	0.013	0.032	1.20	4.37
25	0.015	0.036	1.34	4.86
27	0.018	0.039	1.60	5.25
29	0.023	0.050	2.04	6.74

Total Herbicide in Soil = 53.10 μg

Total Herbicide in Water = 10.59 μg

Total Herbicide in Column = 63.69 μg

** Less than 0.001

TABLE V (Continued)

Column 0104 - 300 ml Volume - Slow Flow

C ZERO = 11520.6 DPM BKGND = 23.5 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/g	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.126	0.297	10.14	40.41
3	0.616	0.690	49.48	93.78
5	0.628	0.642	50.40	87.26
7	0.420	0.347	33.70	47.10
9	0.068	0.093	5.43	12.62
11	0.003	0.001	0.20	0.02
13	0.002	0.001	0.12	0.15
15	0.001	**	0.07	0.09
17	0.001	**	0.09	***
19	**	**	0.06	***
21	**	**	0.01	***
23	**	**	0.01	***
25	**	**	***	***
27	**	**	***	***
29	**	**	***	***

Total Herbicide in Soil = 281.71 µg

Total Herbicide in Water = 149.76 µg

Total Herbicide in Column = 431.47 µg

** Less than 0.001

*** Less than 0.01

TABLE V (Continued)

Column 0105 - 600 ml Volume - Slow Flow

C ZERO = 11458.7 DPM BKGND = 21.6 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/g	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.014	0.081	1.20	11.05
3	0.036	0.126	3.19	17.20
5	0.064	0.175	5.78	24.03
7	0.137	0.254	12.10	34.83
9	0.247	0.366	21.84	50.14
11	0.452	0.482	39.92	66.02
13	0.480	0.464	42.39	63.55
15	0.258	0.220	22.83	30.09
17	0.072	0.091	6.42	12.41
19	0.003	0.005	0.27	0.67
21	0.003	0.005	0.27	0.65
23	0.003	0.003	0.23	0.47
25	0.003	0.004	0.29	0.57
27	0.003	0.004	0.26	0.59
29	0.003	0.002	0.28	0.34

Total Herbicide in Soil = 312.63 µg

Total Herbicide in Water = 157.27 µg

Total Herbicide in Column = 469.90 µg

TABLE V (Continued)

Column 0302 - 900 ml Volume - Slow Flow

C ZERO = 11588.2 DPM BKGND = 23.8 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil μg/g	Total Herb. in Water μg	Total Herb. in Soil μg
1	0.010	0.054	0.89	7.44
3	0.017	0.061	1.50	8.35
5	0.026	0.083	2.29	11.44
7	0.043	0.104	3.75	14.26
9	0.056	0.118	4.87	16.32
11	0.096	0.139	8.39	19.16
13	0.158	0.197	13.81	27.12
15	0.210	0.264	18.31	36.40
17	0.292	0.329	25.46	45.30
19	0.292	0.356	25.50	49.12
21	0.224	0.237	19.54	32.65
23	0.041	0.085	3.54	11.74
25	0.013	0.046	1.12	6.32
27	**	0.001	0.03	0.07
29	**	**	0.07	0.02

Total Herbicide in Soil = 285.71 μg

Total Herbicide in Water = 129.09 μg

Total Herbicide in Column = 414.80 μg

** Less than 0.001

TABLE V (Continued)

Column 0204 - 2400 ml Volume - Slow Flow

C ZERO = 11061.0 DPM BKGND = 21.9 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/g	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.002	0.022	0.21	2.97
3	0.003	0.018	0.28	2.46
5	0.004	0.018	0.32	2.50
7	0.004	0.021	0.38	2.90
9	0.005	0.023	0.41	3.19
11	0.008	0.028	0.67	3.81
13	0.010	0.025	0.86	3.45
15	0.012	0.033	1.06	4.45
17	0.012	0.039	1.06	5.36
19	0.015	0.038	1.30	3.14
21	0.017	0.042	1.49	5.72
23	0.022	0.043	1.93	5.83
25	0.027	0.048	2.42	6.59
27	0.033	0.053	2.92	7.20
29	0.034	0.070	3.01	9.56

Total Herbicide in Soil = 71.12 µg

Total Herbicide in Water = 18.34 µg

Total Herbicide in Column = 89.46 µg

TABLE V (Continued)

Column 0205 - 2400 ml Volume - 2.0-1.0 mm

C ZERO = 11269.1 DPM BKGND = 23.0 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil μg/g	Total Herb. in Water μg	Total Herb. in Soil μg
1	0.002	0.028	0.22	2.68
3	0.002	0.030	0.23	2.88
5	0.002	0.035	0.21	3.41
7	0.006	0.036	0.71	3.43
9	0.004	0.036	0.46	3.50
11	0.010	0.044	1.37	4.26
13	0.006	0.040	0.71	3.82
15	0.019	0.049	2.42	4.67
17	0.007	0.044	0.91	4.21
19	0.012	0.044	1.56	4.27
21	0.009	0.050	1.16	4.83
23	0.021	0.057	2.73	5.46
25	0.012	0.054	1.61	5.17
27	0.023	0.060	2.98	5.80
29	0.019	0.063	2.47	6.05

Total Herbicide in Soil = 64.44 μg

Total Herbicide in Water = 19.74 μg

Total Herbicide in Column = 84.18 μg

TABLE V (Continued)

Column 0106 - 2400 ml Volume - 1.0-0.5 mm

C ZERO = 11292.3 DPM BKGND = 23.0 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/g	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.001	0.025	0.17	2.46
3	0.002	0.026	0.19	2.51
5	0.003	0.028	0.36	2.69
7	0.002	0.027	0.27	2.63
9	0.004	0.026	0.51	2.49
11	0.005	0.036	0.69	3.46
13	0.006	0.034	0.79	3.32
15	0.009	0.030	1.10	2.87
17	0.010	0.038	1.32	3.65
19	0.012	0.041	1.59	3.98
21	0.016	0.048	2.05	4.64
23	0.018	0.049	2.38	4.74
25	0.024	0.055	3.05	5.29
27	0.031	0.056	4.01	5.44
29	0.035	0.069	4.45	6.67

Total Herbicide in Soil = 56.82 µg

Total Herbicide in Water = 22.92 µg

Total Herbicide in Column = 79.75 µg

TABLE V (Continued)

Column 0304 - 2400 ml Volume - 0.5-0.25 mm

C ZERO = 11636.4 DPM BKGND = 23.0 EFFCY = 0.906

Column Location cm	Relative Conc. in H_2O	Conc. in Soil µg/g	Total Herb. in Water µg	Total Herb. in Soil µg
1	0.001	0.016	0.08	1.80
3	0.001	0.012	0.12	1.29
5	0.001	0.016	0.16	1.77
7	0.002	0.016	0.22	1.73
9	0.003	0.018	0.35	1.98
11	0.003	0.020	0.38	2.25
13	0.004	0.022	0.50	2.44
15	0.006	0.021	0.71	2.35
17	0.007	0.021	0.75	2.33
19	0.008	0.025	0.93	2.71
21	0.010	0.026	1.15	2.82
23	0.012	0.028	1.34	3.07
25	0.014	0.029	1.56	3.19
27	0.015	0.036	1.67	3.95
29	0.019	0.034	2.11	3.80

Total Herbicide in Soil = 37.50 µg
Total Herbicide in Water = 12.04 µg
Total Herbicide in Column = 49.54 µg

VITA

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