THE EFFECT OF CALCIUM CHLORIDE CONCENTRATION ON

PROMETRYNE AND FLUOMETURON ADSORPTION

AND MOVEMENT IN SOIL

By

JOHN RAY ABERNATHY

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Oklahoma State University

Stillwater, Oklahoma

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Thesis Approved:

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Thesis Adviser

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Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Herbicides are widely used in agriculture and industry for weed control. Experience has shown that many climatic and edaphic factors influence their activity. In the soil, such factors as soil type, organic matter content, clay type, and pH have been shown to influence the activity of herbicides. The herbicide's activity and persistence is also influenced by the way in which the herbicide disappears from the soil. Such modes of disappearance as vaporization from the soil surface, photodecomposition, codisstillation from the soil surface, chemical degredation, microbial detoxification, removal from the soil by resistent crops, leaching of the herbicide into drainage waters, or adsorption on soil colloids may be important.

Adsorption by the soil colloidal complex is one of the major factors influencing the loss of herbicide activity. The amount of herbicide adsorption is dependent upon such factors as: chemical structure of the herbicide, pH of the soil colloidal surface, organic matter content of the soil, clay content of the soil, temperature of the soil, and perhaps salt content of the irrigation water source. Much of the irrigation water used in Oklahoma and throughout the world for agronomic crops contain high salt concentrations. However, little research has been done on the influence of cations in the soil or soil water on herbicide activity.

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Laboratory studies were initiated using two commonly used post-emergence cotton herbicides to determine the effect $CaCl_2$ concentrations would have on herbicide mobility and specifically on whether or not the salt concentration would effect the amount of herbicide adsorbed by the soil complex. Thus, the objectives of this study were: (1) determine if a difference in the amount of herbicide adsorbed at low and high $CaCl_2$ concentrations were equal and (2) study two chemical herbicide families in two contrasting soils to see if these adsorptive effects were the same for the different soil types and salt concentrations, and (3) compare the flowing or transient adsorption measurements with those obtained from equilbrium adsorption conditions.

CHAPTER II

LITERATURE REVIEW

Today herbicides are being used in ever increasing amounts to expand agricultural production. There are many known factors which influence the way in which various herbicides operate to control weeds. One phase of herbicide research is centered in the soil and how its' vast complex of reactions accepts a foreign chemical such as a herbicide.

The purely physical processes of molecular diffusion and mass transport by soil water are necessary to move the non-incorporated herbicides into the soil. These processes are weather-dependent and the herbicide dosage necessary for a biological response is as much dependent on weather and soil properties as on the rate of field application. Despite the variability in performance of soil applied herbicides they are used in increasing amounts each year. It is therefore very important that we understand the factors involved in the activity of herbicides in the soil as fully as possible. Limited control of these factors may be possible, particularly in irrigated agriculture, and a fuller understanding can lead to a better choice of the proper herbicide with less danger to the crop involved.

There are three major means of transport for a surface-applied herbicide in the soil; (1) diffusion in the soil water, (2) diffusion as a vapor in the unsaturated soil, and (3) transport in the flowing water. Diffusion can be defined here as molecular diffusion, i.e. the process

of random thermal movement of molecules. It has been calculated (Hartley, 1961) that several years would be necessary for as little as 1% of a surface-applied herbicide to migrate by diffusion in a moist soil to a depth of two feet. This assumes no adsorption or chemical destruction of the herbicide. Diffusion is, however, a very important means of molecular transport over distances of up to 1 mm from the surface of a solid and may be of particular importance when coupled with mass transport.

It is generally accepted that the tortuosity of the soil pore sequences do not vary greatly between soils. Also, it is approximately the same whether air or water is the diffusion substance, assuming one or the other liquid (gas or water) completely fills the spaces between the particles. In fertile soils, water occupies only part of the volume between the particles, the rest being air-filled. In an un-saturated soil the water is contained only in the small pores and is isolated in concave-sided elements about the points of contact of solids. The tortuosity factor may be much greater for water in an aerated soil than for soil air in an aerated soil or for water in a waterlogged soil.

Although most herbicides are compounds of low volitility, the significance of air diffusion cannot be lightly dismissed. Little reliable data exists for both vapour pressure and water solubility of herbicides, from which the partition coefficient water/air could be calculated. Hartley (1961) estimates values of about 20,000 for phenol and 30,000 for benzoic acid. Phenol would probably therefore diffuse faster into the air than the water component of most soils. Benzoic acid would not diffuse into the air faster than the water component

for the reason that soil water is always buffered at a sufficiently high pH for most of the acid to exist in ionized, involatile, form.

Water flow through a very simple non-adsorbent soil might be expected to transfer a completely soluble surface-applied herbicide downwards in proportion to the total flow. However, as the band of herbicide moves downward with the water, it will become more diffuse owing to the various pore sizes and water velocity distribution in the soil. Disperison during flow arises from the fact that the flow of a liquid in any vessel cannot be uniform through a cross-section of the general direction of flow. This is true even in a simple tube where, at low flow rates, the velocity is greatest at the center and at high rates the flow is turbulent. In either case, some mixing results from the flow itself. In a porous soil, the mixing is greater because the flow is constantly dividing into separate pore sequences and reuniting, some of which are flowing at different rates (Hartley, 1964). Since the alternative paths are in general unequal, the times of passage from each junction will be different. A sharp solute concent-ration boundary located initally at one place therefore tends to become diffuse owing to the different pore-water velocities. The result is mass transport with mixing.

Scheidegger (1955) called this non-uniform mixing "dispersion" and worked out a generalized theory of its behavior for a simplified porous bed systems. A more empirical descriptive theory of leaching is presented by Gardner and Brooks (1957) who introduced two controlling parameters of the soil column without discussing their relationship to static measures of soil structure. The form of the variation of concentration with effluent volume and depth of column involves no

quantities containing a time dimension, and assumes mixing was purely dynamic and proportional to flow rate. Their experimental results on a leaching of inorganic salts gave curves of the predicted form. In sand columns subjected to different rates of water flow, the variation of concentration with effluent volume was essentially the same. Gardner and Brooks (1957) point out that leaching is less efficient in natural soils than in the columns or re-packed soil, which in the interests of reproducibility have been used in laboratory studies.

During leaching of a soluble substance through a soil there exists a complex flow behavior which tends to create an inequality in concentration at a given level; diffusion tends to reduce these inequalities. A similar complexity exists in packed fractional distillation and chromatographic columns (Keulmans and Verver, 1957). It is possible that a much greater variation in flow rates exist in well cultivated agricultural soils as compared to the fine undisturbed clay which Van der Molen (1956) used. A soil is not only a mosaic of solid particles, water, and air, but the soild matrix has a fine and coarse crumb structure. Migration of water at a soil water content below saturation is generally slow. By contrast, the movement of water when above the unsaturated condition can be very high (Nielsen et.al., 1959). Certainly much of the rapid flow in the saturated case is occuring in channels not occupied by water in the unsaturated soil but the scale of the mosaic pattern of rapidly flowing and nearly stagnated water is little known and probably quite variable.

If herbicides are applied during a rain, deeper penetration is more likely to be achieved than if rain falls after spraying. For this reason the content of soluble granules may sometimes penetrate better.

Leaching from a soil surface can still be efficient after complete drying. Under heavy rain, disintegrated clods or dusty soil impede infiltration and give rise to run-off, causing uneven herbicidal action.

There is little experimental work recorded on leaching under realistic conditions in natural soils. Most herbicide workers have used laboratory columns filled with soil rendered more homogeneous than it would be in the field and have applied water at unrealistically high rates. A partial exception is the work of Upchurch and Pierce (1957), who used artifical rain in short bursts with dry intervals between. The same amounts of water were therefore applied over widely varied periods, but the actual intensity of rain when falling was very high and not widely varied. They found no great difference between treatments unless the dry periods were long enough for the soil to dry out in the surface layers.

The extensive investigations of Upchurch and Pierce (1958) on leaching of monuron into a sandy lakeland soil are particularly informative on the subject of adsorption. These authors examined, in closely controlled laboratory columns, the desent of surface-applied monuron at different rates. They concluded that some factor other than low water solubility was holding back the herbicide, and that the solubility of the herbicide in the soil is apparently much greater than it was in the water alone. This fact is now known as the adsorptive influence resulting from the enormous surface area provided by the soil matrix.

Bioassay results (Weber, 1966) has shown that the clay content of the soil is an important factor in adsorption. Upchurch (1963) showed that herbicide adsorption was influenced by the soil pH and organic

matter content. A report by Frissel (1961) put the adsorption of herbicides by clays on a much sounder basis both in theory and experiment. Frissel worked with suspensions of a less than 2 micron fraction of three different clay minerals (illite, montmorillonite, and kaolinite). He measured herbicide concentrations in the water before introduction of the clay and after its removal by centrifugation. He examined several herbicides including the neutral substituted phenyl ureas and the s-triazines. Salt concentration and pH were additional variables considered. His primary conclusions were that all herbicides were adsorbed in larger quantities under acid conditions, but this effect is only slight for the unionized herbicides in the normal soil pH range. The adsorption falls drastically for the acid herbicides as the pH goes above six or seven. If a soil consisted entirely of the mineral fractions examined, less than 5% of the neutral herbicides would be freely dissolved.

To explain the greater adsorption of triazines at lower pH's, Frissel postulated that as the pH was lowered more hydrogen ions associate with the triazine molecules to give them cationic characteristics which would lead to more adsorption.

Yuen and Hilton (1962) studied the adsorption of monuron and diuron on Hawaiian soils and reported that soil pH, presence or absence of soluble sulfate or phosphate anions, soluble monovalent cation (K), and inorganic acids or bases had little or no effect on the observed results. Soil adsorption could be increased by adding carbon and could be decreased by surface active agents implying molecular adsorptive forces of the Van der Waals type.

The effect of time and temperature on the adsorption of the

s-triazines by Marshall silty clay loam was investigated by Talbert and Fetchall (1965). The results show adsorption equilbrium was established after one hour. An increase in temperature resulted in a decrease in the adsorption of simazine and atrazine. Frissel and Bolt (1962) determined adsorption isotherms for a series of herbicides on clays and found adsorption to be highly dependent on pH and electrolyte concentration. Based on these findings they made several assumptions and calculated the amounts of herbicides adsorbed at specific pH's for a soil containing either kaolinite, illite, or montmorillonite.

Weaver (1947) found that hydrogen saturated exchangers adsorbed more 2,4-D and its salts, but not always in equal amounts. Sodium or calcium saturated exchangers adsorbed little or no 2,4-D or its salts. Nearpass (1966) reported the adsorption of simazine and atrazine by Bayboro clay soil decreased with increasing degree of base saturation. This occured whether the predominating basic cation was Ca, Mg, K, or Na. He attributed the decrease in adsorption to the occupation of adsorptive sites by the cation, rather than a specific effect of cation species on the adsorption of the herbicides.

Considerable work has been done on the movement and adsorption of herbicides in soil, and more recently consideration has been given to the influence of salts and their effects on herbicide adsorption, however, these studies all fall short of explaining the true effect of salt versus herbicide adsorption. In an effort to more completely describe the issue, all possible interactions were eliminated in order to focus directly on the effect that $CaCl_2$ concentration has on the adsorption and movement of prometryne and fluometuron.

CHAPTER III

PROCEDURE

The two soils used in the study were: (1) Eufaula loamy fine sand obtained from the east portion of the Oklahoma State University Agronomy Research Station located near Perkins, and (2) Norge loam from the north part of the same experiment station. Table I presents some selected soil properties for each soil.

TABLE I

PROPERTIES OF SOILS USED IN THE STUDY

	pH	% sand	% silt	% clay	% organic matter
Eufaula loamy fine sand	6.40	84.0	11.0	5.0	0.68
Norge loam	6.35	57.5	25.0	17.5	2.49

Both soils were pretreated to insure complete calcium saturation of the soil exchange capacity. This procedure consisted of mixing 1000 grams of soil with 1000 ml of 0.5 N calcium acetate and allowing it to stand for one hour before the liquid portion was filtered off using a Buchner funnel. A second washing with 0.5 N calcium acetate followed. After the calcium acetate washings, two washings with 0.01 N $CaSO_4$ were

followed with a fifth and final washing with distilled water. After

the soils were calcium saturated, the soil was air dried and screened

through a 2 mm sieve. The entire amount of each soil series was then

mixed and used in the herbicide movement and adsorption studies.

The herbicides (Fig. 1 and Fig. 2) fluometuron (3-(m-trifluomethyl-

phenyl)-1,1-dimethyl urea) or prometryne (2,4-bis(isopropylamino)-

6-methylmercapto-s-triazine) were mixed with either 0.01 N $CaCl_2$ or 0.5

N $CaCl_2$. The concentration of the herbicide present was measured by

the C^{14}-labeled compound. Ten microcurries of the radioactive C^{14}-

labeled herbicide was added per 1000 ml of each $CaCl_2$ solution. Enough

commercial herbicide was then added to the mixtures to bring the total

active ingredient concentration up to 29 ppm.

The transient displacement of each herbicide and salt solution

through the saturated soil was accomplished using the apparatus

described by Davidson and Santelmann (1968) and shown in Figure 3.

The soil was packed in the glass column and saturated initially with

0.01 N $CaSO_4$ and flushed through the column at a rate of 1.70 cm per

hour, until an equilibrium soil-water contact condition existed.

Following the wetting and equilbration procedures, 400 ml of the

appropriate herbicide and $CaCl_2$ combination shown in Table II were

introduced at one end of the soil column.
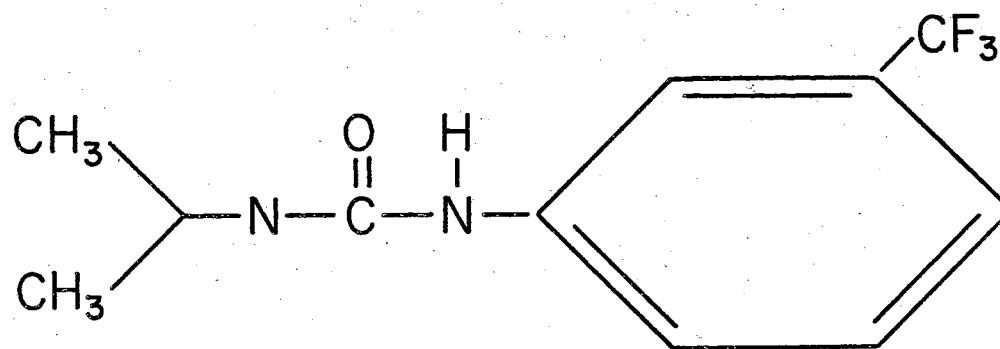
FLUOMETURON

Figure 1. Chemical Structure of the Substituted Urea Fluometuron
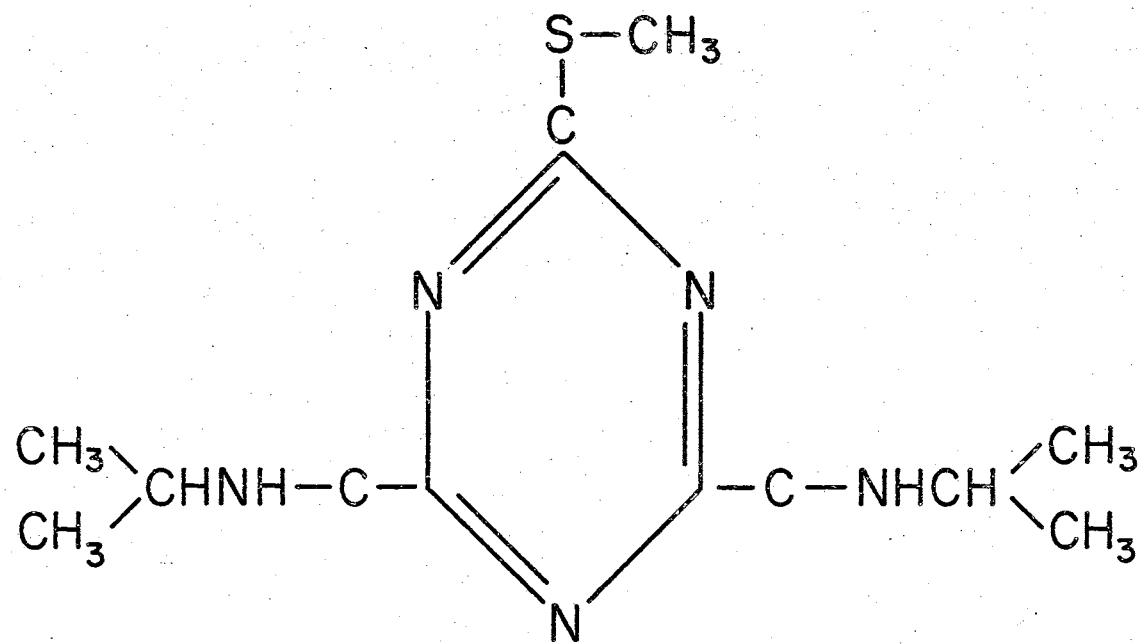
PROMETRYNE

Figure 2. Chemical Structure of the s-triazine Prometryne

TABLE II

HERBICIDE-CaCl$_2$-SOIL COMBINATIONS USED IN THE STUDY

Prometryne- - - - - -0.01 N CaCl$_2$- - - - - -Norge Loam

Prometryne- - - - - -0.5 N CaCL$_2$- - - - - -Norge loam

Prometryne- - - - - -0.01 N CaCl$_2$- - - - - -Eufaula loamy fine sand

Prometryne- - - - - -0.5 N CaCl$_2$- - - - - -Eufaula loamy fine sand

Fluometuron - - - - -0.01 N CaCl$_2$- - - - - -Norge loam

Fluometuron - - - - -0.5 N CaCl$_2$- - - - - -Norge loam

Fluometuron - - - - -0.01 N CaCl$_2$- - - - - -Eufaula loamy fine sand

Fluometuron - - - - -0.5 N CaCl$_2$- - - - - -Eufaula loamy fine sand

After the 400 ml slug of herbicide solution had been introduced into the column, the solution flowing into the soil was switched to 0.01 N CaSO$_4$ and the herbicide displacement through the soil continued at the same flow rate. Effluent samples were collected in a fraction collector every five minutes. From the effluent samples, one-half ml alloquates were removed and placed into a liquid scintillation counting solution. The counting solution consisted of 120 gm of naphthalene, 4 gm of PPO, and 50 mg of POPOP in 1000 ml of p-dioxane. The herbicide concentration was established by measuring the C^{14} activity on a Nuclear Chicago liquid scintillation counter.

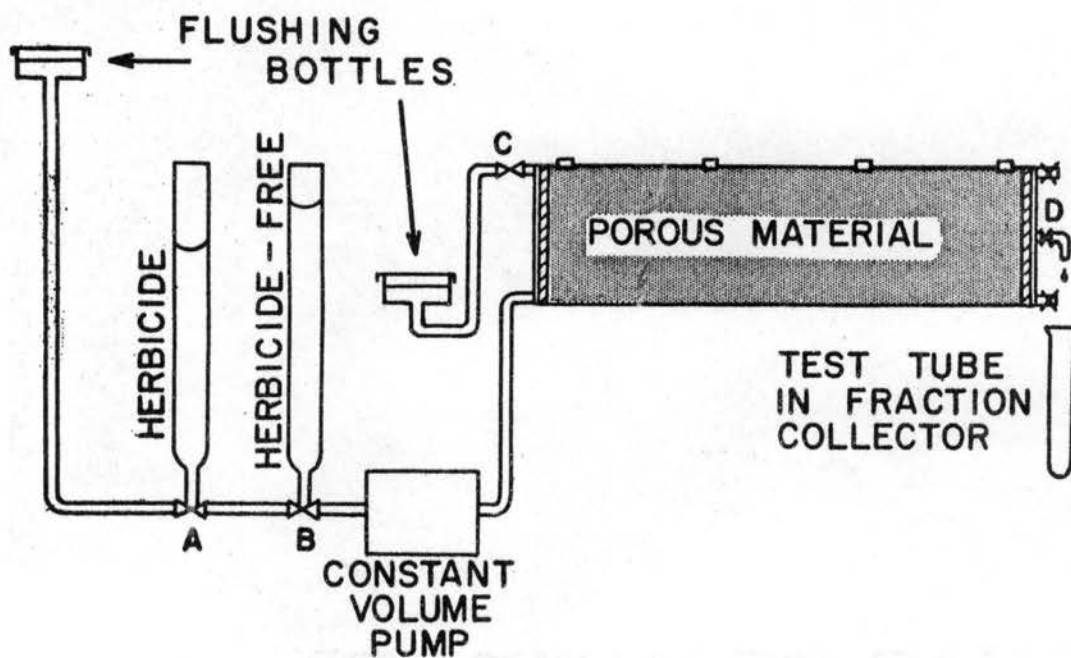Adsorption isotherms for each herbicide and salt concentration

Figure 3. Apparatus Used in the Soil Column Adsorption and Movement Study

were measured in duplicate using 10 gm of calcium saturated soil and 10
ml of the proper herbicide and salt concentration in a pyrex test tube.
The 1:1 mixture was mixed for one minute on a vortex mixer and the
solution allowed to stand for 30 minutes. Then the mixture was again
stirred for 15 seconds and allowed to stand. A total time of $1\frac{1}{2}$ hours
for each tube was allowed for equilbrium. After the appropriate time
interval, the tube was centrifuged at 1200 rpm for 5 minutes and two
$\frac{1}{2}$ ml alloquates of the supernatant solution analyzed in the liquid
scintillation counter.

The herbicide concentration in the supernatant solution was
determined, and this concentration was subtracted from the concentration
of the original herbicide solution added to obtain the amount of
herbicide adsorbed. A regression analysis was made of the adsorbed
herbicide concentration versus herbicide concentration in the supernatant
solution and a best fit line by least squares was drawn through the data.
The data was plotted with the herbicide concentration in the supernatant
solution on the absissa and the amount of herbicide adsorbed (μg/mg)
on the ordinate.

The entire experiment was conducted in a constant temperature
room at a temperature of $23\pm1^{\circ}C$, thus removing the effects of temper-
ature on herbicide adsorption. Also the time interval for any one
column run or isotherm study was assumed short enough to prevent
measurable bacterial activity. If there was any microbial activity,
then it would have consisted of anaerobic strains because each system
was conducted under completely saturated conditions.

In this study there was no attempt made to control the soil or salt
solution pH. The pH determinations for the $CaCl_2$ concentrations, soil

plus distilled water, and soil plus $CaCl_2$ are given in Table III. No
more than a 0.2 difference in pH readings was noted for any of the soil
plus contrasting $CaCl_2$ mixtures.

TABLE III

pH READINGS OF $CaCl_2$ -SOIL MIXTURES USED IN THE STUDY

	pH		pH
0.01 N $CaCl_2$	6.7	0.5 N $CaCl_2$	6.65
0.01 N $CaCl_2$ + Eufaula	6.2	0.5 N $CaCl_2$ + Eufaula	6.4
0.01 N $CaCl_2$ + Norge	6.12	0.5 N $CaCl_2$ + Norge	5.92
Distilled H_2O + Eufaula	6.40		
Distilled H_2O + Norge	6.35		

The possibility of prometryne being precipitated at high $CaCl_2$
concentrations was studied. Sufficient $CaCl_2$ was added to prometryne
solutions to obtain the following salt concentrations: 0.01, 0.125,
0.25, 0.5 and 1.0 N $CaCl_2$. After the addition of the $CaCl_2$, samples
were extracted from each solution at 12 hour intervals and analyzed
for reduction in herbicide activity in the solution.

CHAPTER IV

RESULTS AND DISCUSSION

Adsorption by Eufaula Loamy Fine Sand

The adsorption isotherms for both prometryne and fluometuron and

their CaCl$_2$ combinations in Eufaula loamy fine sand are shown in

Figure 4. More fluometuron adsorption occurred in the presence of 0.01

N CaCl$_2$ than when 0.5 N CaCl$_2$ was used. In Figure 4, the line with

the largest angle or slope, indicates the greatest amount of adsorption.

The results from the system in which the herbicide moved through the

soil as shown in Figure 5, however indicates no significant difference

in adsorption of fluometuron when 0.01 N CaCl$_2$ was included in the

solution than if 0.5 N CaCl$_2$ was used. The left leg of the curve where

fluometuron was used with 0.01 N CaCl$_2$ as indicated in Figure 5 is

shifted very slightly to the right of the 0.5 N CaCl$_2$ curve, thus

showing slightly more herbicide adsorption; however this slight

difference is not great enough to say that there was any significant

difference shown by these two curves. Also, the curve in Figure 5

with the lowered peak (0.01 N CaCl$_2$) is indicative of a lesser

concentration of herbicide in the effluent thus indicating the

possibility of greater adsorption of the herbicide onto the soil

colloid surface. The results of the adsorptive isotherm for

fluometuron as shown in Figure 4 indicates considerably more adsorption

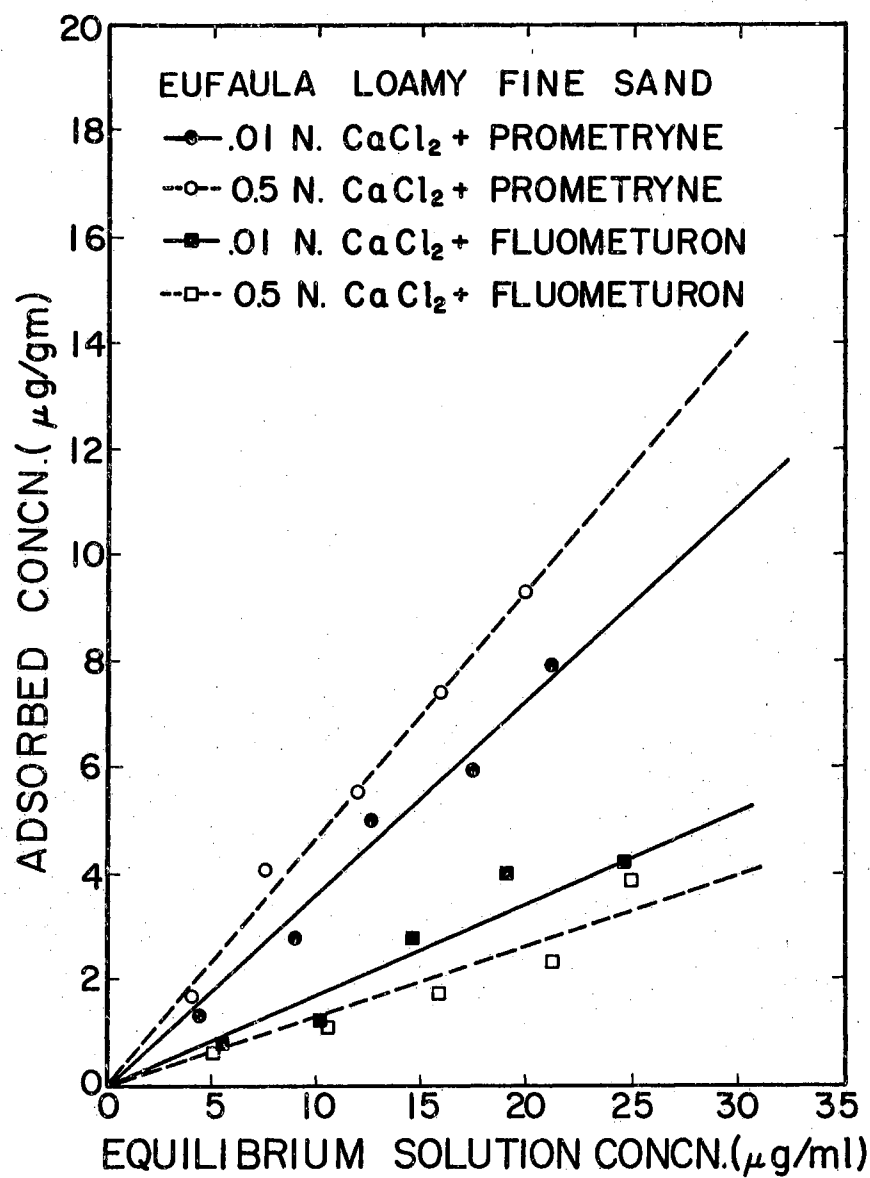differences where the two CaCl$_2$ concentrations were used than does the

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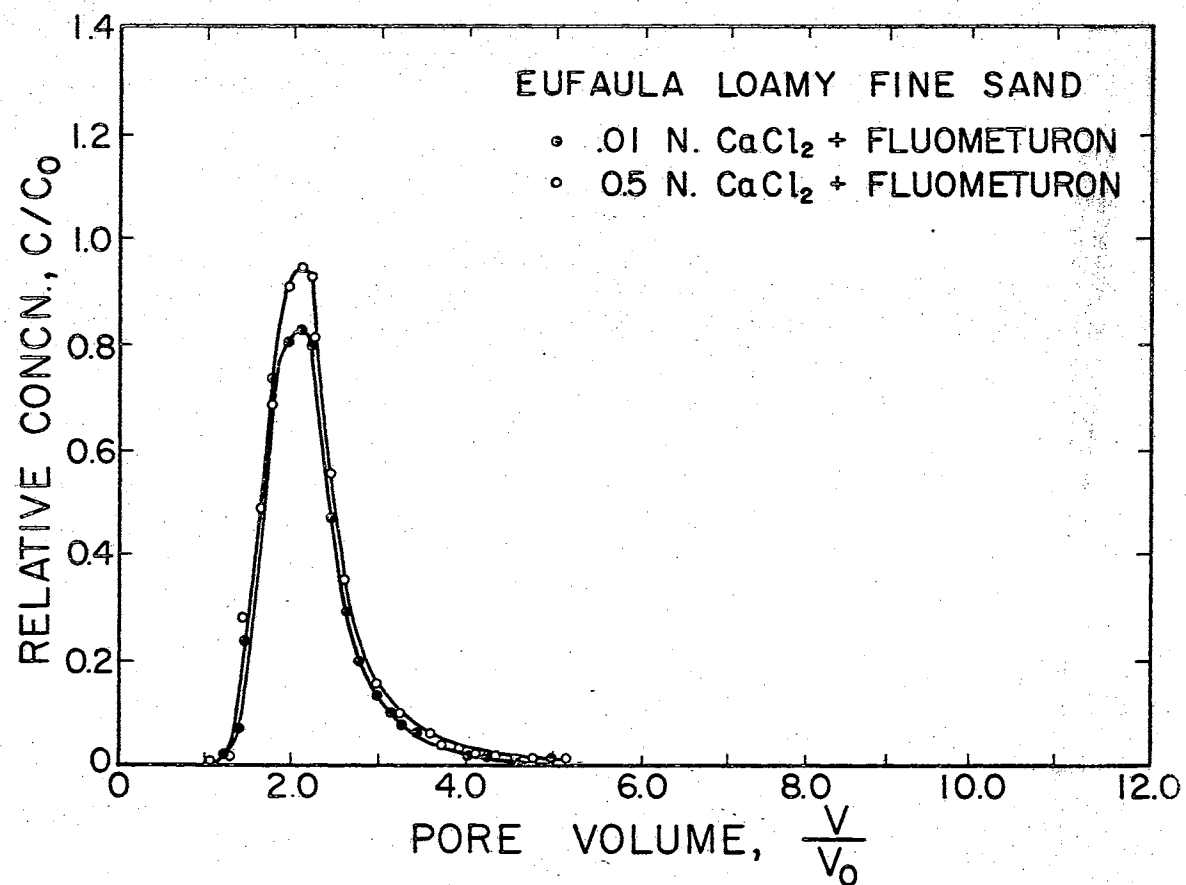Figure 4. Adsorption of Prometryne and Fluometuron by
Eufaula Loamy Fine Sand

Figure 5. Effluent Concentration Distribution of Fluometuron in 0.01 N CaCl$_2$
and 0.5 N CaCl$_2$ After Displacement Through Eufaula Loamy fine sand

transient system in Figure 5. This variation was probably due to there

being more soil surface area exposed to the herbicide in the equilbrium

1:1 system than in the transient soil column system. This will be

pointed out better when the movement of fluometuron is discussed.

The adsorptive isotherm for prometryne in Figure 4 shows more

adsorption of the prometryne when it was combined with the 0.5 N $CaCl_2$

than when in combination with the 0.01 N $CaCl_2$. This is shown by the

dotted prometryne line which has the greatest slope in Figure 4.

However, a comparison of the two curves of the transient soil column

system in Figure 6 shows only a small difference between the effects of

the two $CaCl_2$ concentrations on prometryne adsorption. The 0.01

N $CaCl_2$ curve in Figure 6 is slightly shifted to the right and the peak

is somewhat lower, but this amount is not significant enough to indicate

that one $CaCl_2$ concentration influenced the prometryne adsorption more

than the other concentration in the transient system. These results

for prometryne in the transient system are similar to the results of

the transient fluometuron adsorption shown in Figure 5 in that there

is no significant difference in the two fluometuron of two prometryne

curves due to $CaCl_2$ concentration.

The greater adsorption of prometryne indicated in the adsorptive

isotherm as shown in Figure 4 in the presence of 0.5 N $CaCl_2$ was

questionable as to whether or not this was actually true adsorption,

but rather a precipitation of the herbicide oweing to the high salt

concentration; however results of the precipitation study showed no

difference in prometryne precipitation due to different $CaCl_2$

concentrations. Another factor which could have been influenced by the

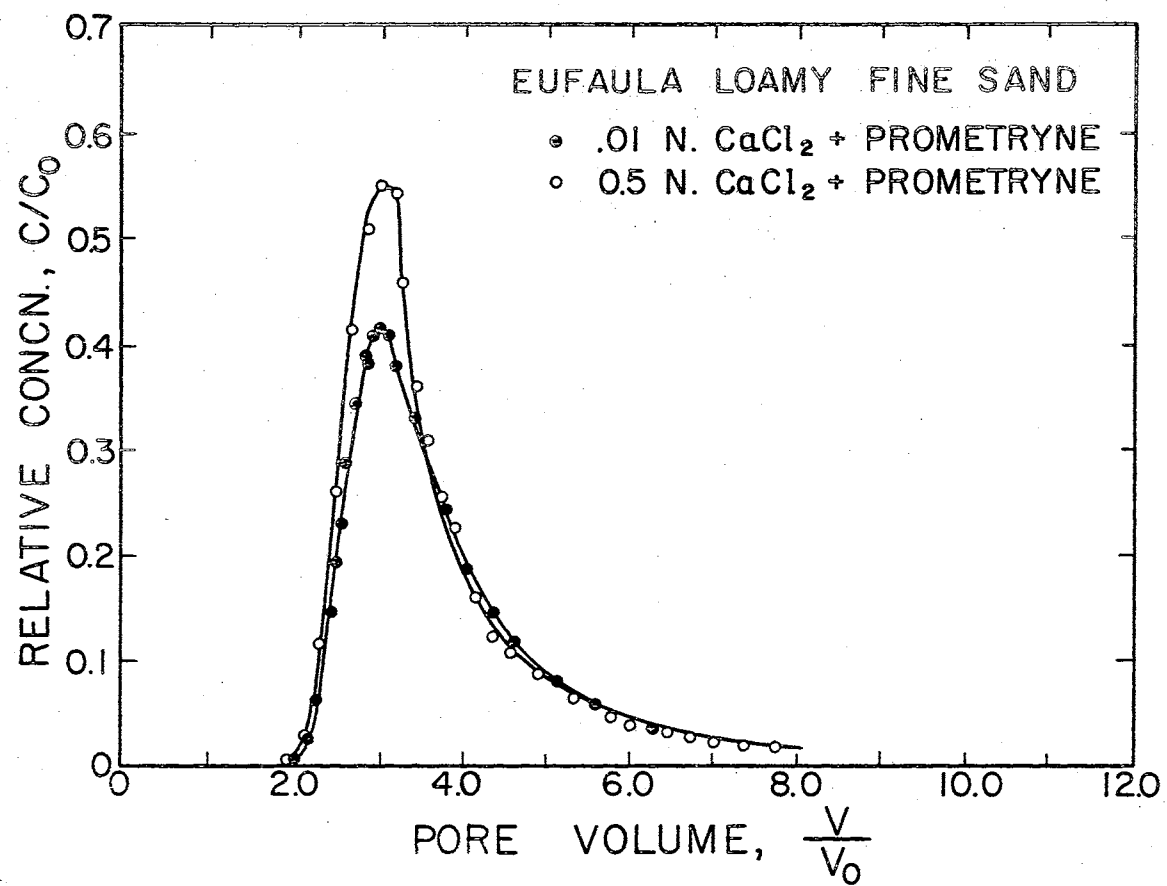two $CaCl_2$ concentrations was pH at the soil surface. If the higher

Figure 6. Eufflent Concentration Distribution of Prometryne in 0.01 N $CaCl_2$ and 0.5 N $CaCl_2$ After Displacement Through Eufaula Loamy Fine Sand

$CaCl_2$ concentration could have caused a lowering of the soil surface pH versus the less influence of the lower $CaCl_2$ concentration on the pH of the soil surface, then the effect of $CaCl_2$ concentration could have caused more prometryne adsorption at the 0.5 N $CaCl_2$ level than at the 0.01 N $CaCl_2$ concentration. Weber (1968) and Bailey and White (1968) clearly point out that prometryne is protonated and thus a lower pH at the high salt concentration may result in more adsorption. However, this same phenomenom is not present to as great an extent in the flowing system indicated in Figure 6, thus the higher soil surface activity in the adsorptive isotherm system may have changed the salt's ability to influence pH more than the lower soil surface activity of the flowing soil column system.

Even for the sandy soil, the adsorption isotherms show that the prometryne is adsorbed in greater amounts than fluometuron. Also, in comparing the two herbicides in the two transient systems, the fluometuron effluent appears shortly after one pore volume has passed through the soil column as in Figure 5, while more than two pore volumes must pass through the column before prometryne appears in the effluent sample as indicated in Figure 6; thus indicating much more retention or adsorption of the prometryne by the Eufaula loamy fine sand.

Movement in Eufaula Loamy Fine Sand

The movement of fluometuron and prometryne in the Eufaula loamy sand was studied using the inches of water necessary to move the solution containing the highest concentration of the original herbicide added to the soil column, through the 30 cm. column represented in

Table IV. This type of measurement is very applicable to actual field

applications of herbicides. Also, the amount of water required for

movement of the herbicide through the soil column was theorically

calculated using the adsorptive isotherm data and transposing it to the

soil column situation by the use of the formula:

$$\frac{(K \rho b}{(\theta} \cdot \frac{V_o)}{A_o)}$$

where K equals the slope of the isotherm line, ρb equals the bulk

density of the soil, θ equals the soil water content, V_o equals the

pore volume of the soil water system, and A_o equals the cross sectional

area of the soil column.

Table IV shows that in the Eufaula loamy fine sand, 10.3 inches

of water were required for prometryne movement through the soil column

for both the 0.01 N $CaCl_2$ and 0.5 N $CaCl_2$ combinations, however the

isotherm calculations predicted 23.2 inches of water would be required

for the 0.01 N $CaCl_2$ - prometryne and 27.9 inches for the 0.5

N $CaCl_2$ - prometryne to have been moved through the column. This

suggests that for the transient soil column system, there was much less

soil surface actually exposed to the herbicide for adsorption. For

the iostherm system, where the soil surface has much more area exposed,

there were many more reactive sites available and thus almost twice as

much water was indicated as being required for equal movement.

TABLE IV

INCHES OF WATER REQUIRED FOR HERBICIDE MOVEMENT

	Eufaula Loamy Fine Sand		Norge Loam	
	Isotherm	Column	Isotherm	Column
Prometryne +0.01 N CaCl$_2$	23.2	10.3	40.9	15.1
Prometryne +0.5 N CaCl$_2$	27.9	10.3	57.6	16.5
Fluometuron +0.01 N CaCl$_2$	14.6	6.9	20.2	9.8
Fluometuron +0.5 N CaCl$_2$	11.9	6.9	16.4	9.0

The soil column movement of fluometuron at the two CaCl$_2$ combinations required 6.9 inches of water (Table IV), however, again a greater amount of water was indicated to be required for the herbicide movement when based on the isotherm data. Also, the isotherm calculations show more water was required to move fluometuron when combined with 0.01 N CaCl$_2$ (14.6 inches) than when combined with 0.5 N CaCl$_2$ (11.9 inches), however in the soil column the same amount of water was required for both of the two CaCl$_2$ - fluometuron combinations (6.9 inches). Again, here as with the prometryne, the differences can be attributed to more soil surface area being exposed in the adsorptive isotherm experiment than in the transient soil column systems.

Another comparison of interest in the Eufaula loamy fine sand was the difference in amounts of water required for the two different herbicides (Table IV). The substituted urea, fluometuron, which is more easily leached under actual field conditions required less water for its movement than the s-triazine prometryne which is quite persistent under actual field conditions.

Adsorption by Norge Loam

The adsorption isotherms for prometryne and fluometuron and their contrasting $CaCl_2$ combinations are shown in Figure 7. Comparing the two herbicides in Figure 7, it is apparent that the prometryne was adsorbed in greater quantities by the Norge loam soil than was the fluometuron. This is in agreement with the results obtained for the Eufaula loamy fine sand. However, the adsorption of both herbicides in the Norge loam is greater than in the fine sand due to the higher clay and organic matter content of the Norge soil (Table I). As with the fine sand, when the transient soil column systems are compared, the prometryne appears in the effluent (Figure 9) much later than does the fluometuron (Figure 8), again indicating greater retention or adsorption of the prometryne. These results agree with the adsorptive results of the Eufaula loamy fine sand.

Figure 7 shows the adsorption of fluometuron in the adsorptive isotherm system to be greater when in the presence of 0.01 N $CaCl_2$ than when combined with 0.5 N $CaCl_2$. This is in agreement with the results of the isotherm studies in the Eufaula loamy fine sand. In Figure 8, there is a definite shift of the entire 0.01 N $CaCl_2$ curve to the right, thus indicating that the effluent from the fluometuron
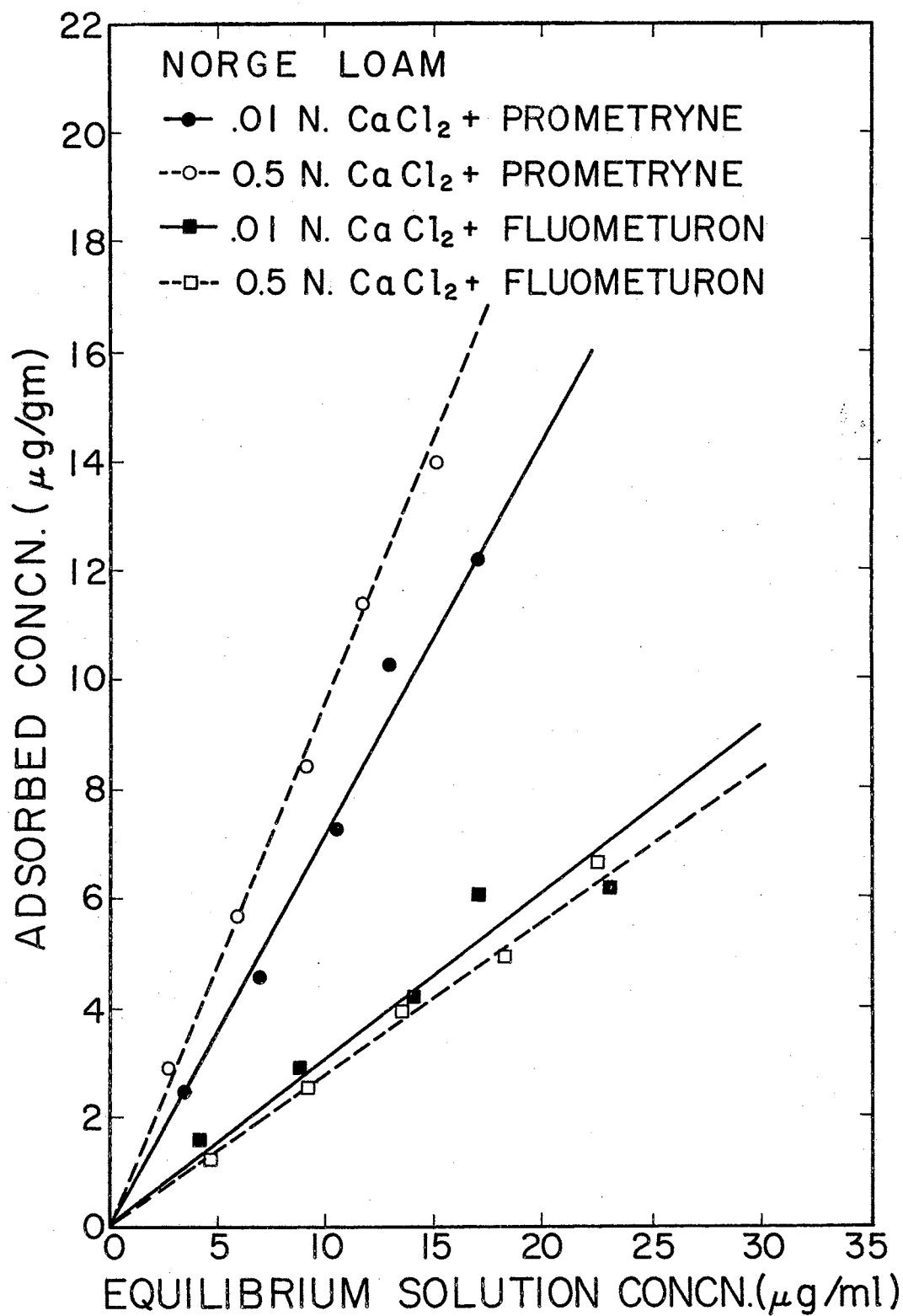
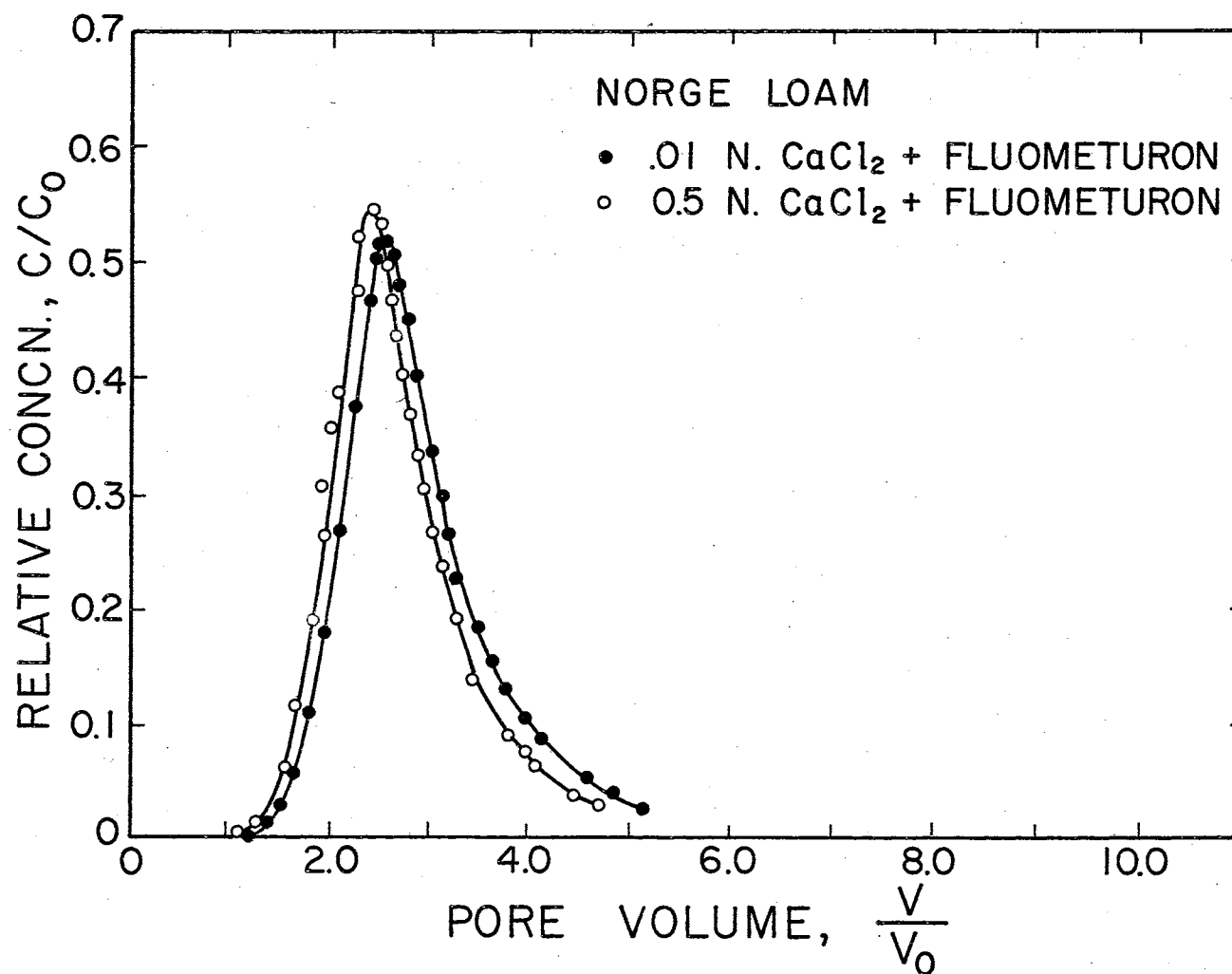Figure 7. Adsorption of Prometryne and Fluometuron by Norge Loam

Figure 8. Effluent Concentration Distribution of Fluometuron in 0.01 N $CaCl_2$ and 0.5 N $CaCl_2$ After Displacement Through Norge Loam

plus the 0.01 N $CaCl_2$ mixture was slower in passing through the soil column than the 0.5 N $CaCl_2$ - fluometuron mixture. The slower appearance of the 0.01 N $CaCl_2$ - fluometuron mixture in the effluent reflects the fact that more adsorption has taken place. In the Norge loam soil there was a definite effect of the $CaCl_2$ concentration shown, probably due to the increased soil colloidal surface. The Eufaula loamy fine sand showed no significant effects of the salt concentration on fluometuron adsorption in the transient system (Figure 5).

Adsorptive isotherms shows increased prometryne adsorption when the 0.5 N $CaCl_2$ herbicide combination was used as compared with the 0.01 N $CaCl_2$ combination (Figure 7). This difference in prometryne adsorption is of considerable magnitude as indicated in Figure 7 by the distance separating the two prometryne adsorptive lines. This greater adsorption of prometryne in the presence of the 0.5 N $CaCl_2$ combination occurred also in the transient soil column system (Figure 9). The significant shift of the 0.5 N $CaCl_2$ curve to the right of the 0.01 N $CaCl_2$ curve indicates a greater adsorption of the prometryne in the 0.5 N $CaCl_2$ mixture in the Norge loam soil. Again this increased absorption of prometryne at the high salt concentration may have been an indirect effect resulting from a change of the soil surface pH by the different $CaCl_2$ concentrations.

It can be seen from Figures 4 through 9, that there is an opposite effect of the two $CaCl_2$ concentrations on the adsorption of the herbicides representatives of two separate structural classifications. This point is especially clear in the Norge loam soil (Figures 7, 8, and 9) which contains about three times as much clay and three and one-half times as much organic matter as the Eufaula loamy fine sand (Table I).
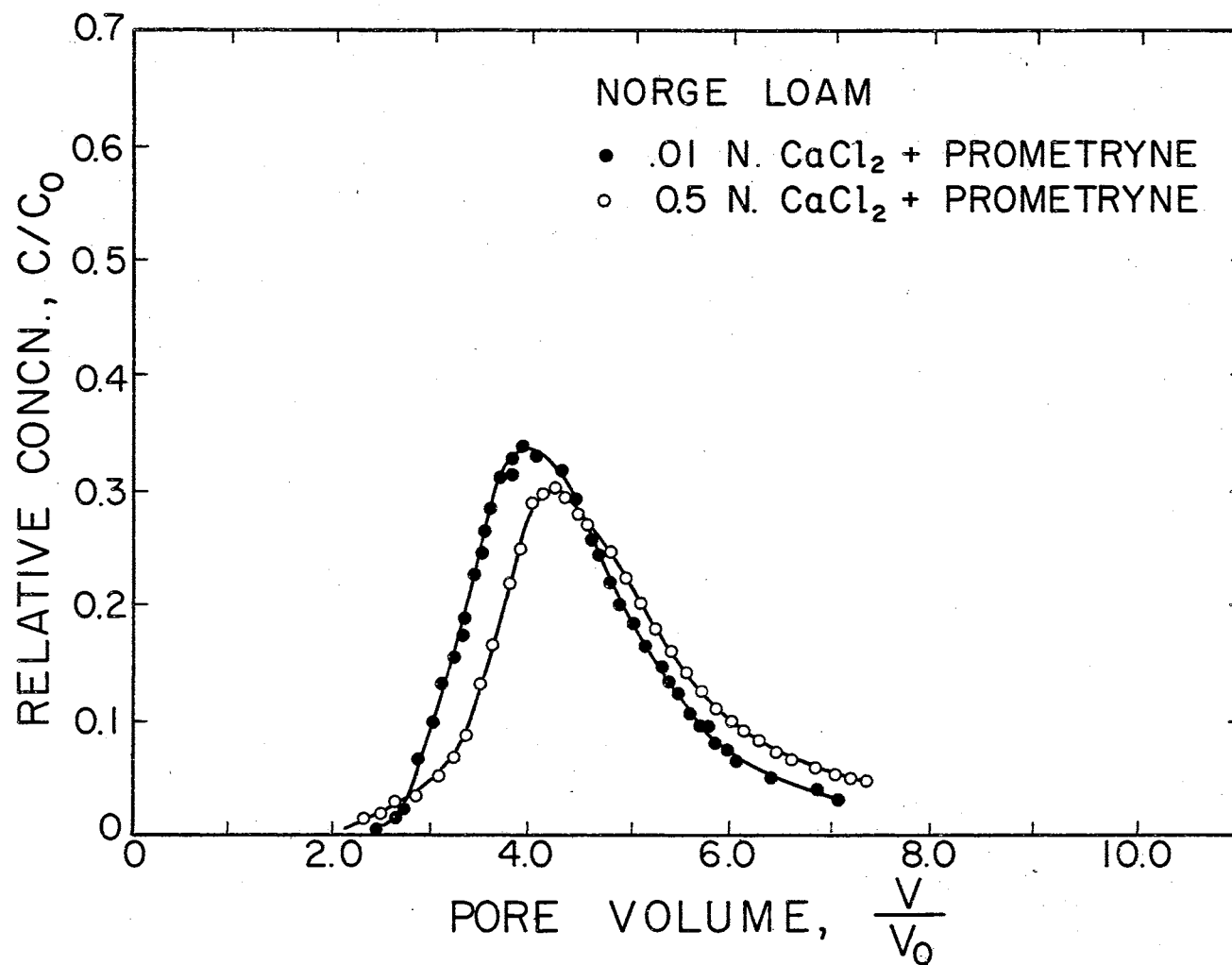
Figure 9. Effluent Concentration Distribution of Prometryne in 0.01 N CaCl$_2$ and 0.5 N CaCl$_2$ After Displacement Through Norge Loam

The increased clay and organic matter content provides a greater surface activity for the prometryne and fluometuron adsorption and thus provides a better medium for testing the effects of salt concentrations on the adsorption of these herbicides.

For fluometuron, there was slightly more adsorption of the herbicide at the 0.01 N $CaCl_2$ level (particularly in the Norge loam), which expected considering that all the sites on the adsorptive clay complex were available to the calcium and fluometuron molecules and thus the $CaCl_2$ concentration interfered with fluometuron adsorption.

With prometryne, more adsorption was also expected at the lower salt concentration; however, the opposite appears to be the case. Bailey and White (1967) have postulated that the s-triazines are adsorbed as the protonated hydroxy analog of the original herbicide compound. If prometryne is a protonated compound when in contact with the colloidal clay surface, then there is a very good possibility that the higher $CaCl_2$ concentration caused a lowering of the soil surface pH and thus resulted in more prometryne adsorption. Bailey (1968) suggests that the pH of the soil colloidal surface may be 3 to 4 pH units below the pH of the soil solution. This evidence is undoubtedly a very important consideration in adsorption and may also explain some of the adsorptive results from the prometryne-$CaCl_2$ combinations.

Movement in Norge Loam

In the Norge loam soil again the actual amount of water used in moving the herbicide through the soil column was compared to the amount of water calculated to be required by use of the adsorption isotherm data and the formula described earlier. With the Norge loam soil which

has a much higher clay and organic matter content (Table I) there were
many more reactive sites available in the soil surface, thus much more
water was required to move the herbicides through the actual soil
column and also more water was calculated to be required than was used
to move herbicides through the Eufaula loamy fine sand.

A comparison of the actual amount of water used for movement of
the prometryne shows more water was necessary for herbicide movement
when prometryne was combined with 0.5 N $CaCl_2$ (16.5 inches) than when
with 0.01 N $CaCl_2$ (15.1 inches) as shown in Table IV. Also the water
required for prometryne movement based on the isotherm data shows more
water was required with the 0.5 N $CaCl_2$ - prometryne mixture (57.6
inches) as compared with the 0.01 N $CaCl_2$ - prometryne mixture (40.9
inches). Here again as the prometryne in the Eufaula loamy fine
sand, the isotherm data indicates more water required for herbicide
movement than actually was used in movement of prometryne through
the soil column. Also this significant difference is indicative of
many more reactive soil sites actually available and participating in
the equilibrium isotherm system versus the soil column system.

The actual amount of water required to move fluometuron through
the transient soil column was greater when fluometuron was mixed with
0.01 N $CaCl_2$ (9.8 inches) than when in a mixture with 0.5 N $CaCl_2$
(9.0 inches). The actual water requirement for fluometuron agrees
proportionally to the indicated water requirement as calculated from
the adsorptive isotherm data where 0.01 N $CaCl_2$ - fluometuron required
20.2 inches versus 16.4 inches for the 0.5 N $CaCl_2$-fluometuron
combination. Again the higher water requirement indicated from the
adsorptive isotherm data as compared to the actual water used for the

movement of fluometuron through the soil columns suggests that more
soil surface area was exposed and a greater number of reactive sites
were available in the equilbrum isotherm system than in the
corresponding soil column.

CHAPTER V

SUMMARY AND CONCLUSION

From the results of this study, $CaCl_2$ concentrations appear to
have a definite effect on the adsorption of the s-triazine prometryne by
increasing the amount of adsorption when in the presence of the high
level of $CaCl_2$. The results of the fluometuron adsorption studies
indicated that the substituted urea, fluometuron was only slightly
affected, but this effect was opposite to those observed with
prometryne. More fluometuron was adsorbed at the lower salt concen-
tration, thus indicating that the higher $CaCl_2$ concentration competed
more for the adsorptive sites in the soil.

Also, it was noted by the adsorptive isotherms results and the
transient adsorptive studies that more prometryne was always adsorbed
in a given soil than fluometuron. The magnitude of difference was
noted as being almost two-fold, thus indicating the higher reactive
nature of the s-triazine prometryne over the substituted urea
fluometuron.

Also, after having looked at the amount of water required for
each of the herbicides to move through the two soil types, it is quite
apparent that more water is required to move the more highly adsorbed
herbicide (prometryne) through the soil, regardless of the soil type
involved. Thus, the water required for herbicide movement is
correlated directly to herbicide adsorption, i.e. the more herbicide

that is adsorbed, the more water that will be required for the
herbicide (either prometryne or fluometuron) movement through the soil.

The water needed to move a herbicide through soil has also shown
that if adsorptive isotherm results are used to determine the water
requirement, then an over estimation of water requirement will occur
and this error will become greater for soils having higher clay and
organic matter contents. Even though the transient soil columns are
an artificial system, it still appears to relate more closely to actual
field conditions than the adsorptive isotherm.

For this laboratory study, 0.5 N $CaCl_2$ concentration was an
extreme and this type of $CaCl_2$ concentration would not be used as an
irrigation water source. Although the results show a definite effect
of $CaCl_2$ solutions on herbicide adsorption and mobility, it would appear
that various sources of irrigation water would not significantly
influence the mobility or adsorption of fluometuron and prometryne
under actual field conditions. The high rate of $CaCl_2$ (0.5 N)
would be equivalent to 28000 ppm, while 0.01 N $CaCl_2$ would equal 500
ppm which is classified as good water for irrigation purposes.

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VITA ν

John Ray Abernathy

Candidate for the Degree of

Master of Science

Thesis: THE EFFECT OF CALCIUM CHLORIDE CONCENTRATION ON PROMETRYNE AND FLUOMETURON ADSORPTION AND MOVEMENT IN SOIL

Major Field: Agronomy

Biographical:

Personal Data: Born in Altus, Oklahoma, January 4, 1945, the son of Raymond and Tommy Abernathy.

Education: Graduated from Altus Senior High School, Altus, Oklahoma, in May, 1963; received the Bachelor of Science degree from Oklahoma State University with a major in Agronomy in May, 1967; graduate study at Oklahoma State University, June, 1967 to August, 1969.

Experience: Reared and worked on a farm near Altus, Oklahoma until after high school graduation; employed by Pioneer Farm Center of Altus, Oklahoma, as a herbicide and insecticide consultant during summers of 1965 and 1966; half-time research assistant, Department of Agronomy, Oklahoma State University, 1967-1969.

Member: Weed Science Society of America, and Sigma Xi.