

THE EFFECT OF SOIL-WATER REDISTRIBUTION ON
FLUOMETURON MOVEMENT IN SOIL

By

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PREFACE

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CHAPTER I

INTRODUCTION

Herbicides are an integral part of modern agriculture. Without effective weed control procedures higher yields cannot be achieved. Herbicides can play an important part in attaining effective weed control. However, care must be exercised to prevent the accumulation of harmful herbicide residues in the soil. Knowledge of the exact fate of a herbicide once it reaches the soil surface is necessary to insure that harmful residues do not occur.

Many environmental and edaphic factors influence the mobility and degradation of a herbicide in the soil. Soil factors such as pH, organic matter content, type of clay colloids, adsorptive and desorptive processes, soil temperature, and molecular structure of the compound all influence herbicide phytotoxicity, persistence and movement.

Soil water is also of primary importance to herbicidal activity, since the amount of water present in the soil regulates to some extent many of the factors mentioned above.

Laboratory experiments were conducted with the herbicide 1,1-dimethyl-3-(a,a,a,-trifluoro-m-tolyl)urea (fluometuron) to determine the degree of herbicide movement after the cessation of infiltration in the presence and absence of evaporation. The objectives of this study were: (1) measure the effect of soil

water redistribution on fluometuron movement, (2) determine what affect evaporation from the soil surface has on fluometuron movement in the soil, and (3) determine the effect of a dry and wet soil on fluometuron mobility.

CHAPTER II

LITERATURE REVIEW

There are many factors which influence the adsorption, desorption and movement of herbicides in soil. Bailey and White (1) state that the factors which appear to affect overall pesticide movement are (1) adsorption, (2) physical properties of the soil, and (3) climatic conditions. Lambert et al. (12) also have listed the factors which affect herbicide movement in soil. They include only two of those given by Bailey and White. The five categories listed by Lambert et al. are: (1) type of soil, (2) type of herbicide, (3) climatic conditions, (4) biological population, and (5) method of application. The experiments conducted by these researchers consisted of adding water to the top of cylinders of soil in order to study the movement of various herbicides. The amount of herbicide movement was then measured utilizing a bioassay procedure.

One of the most important environmental factors which affects herbicide behavior in the soil is water. Both intensity and frequency of rainfall or irrigation appear to have an effect on herbicide mobility in soil. The water content of the soil system appears to have great affect on both the degree of adsorption and the bioactivity of herbicides present in both the aqueous and vapor phase (1).

For a complete understanding of herbicide movement in the soil, one must first have an understanding of the movement of water in the soil. The redistribution of soil water after the cessation of infiltration may influence the depth that a herbicide moves in the soil. Youngs (19) conducted an experiment using slate dust and glass beads to determine soil water distribution after redistribution. His results indicate that the amount of soil water redistribution depended upon the initial depth of infiltration; the greater the depth, the more rapid the redistribution.

Biswas et al., (3) have an informative discussion on the redistribution of soil water. They found that the rate of redistribution within the soil profile depended upon the initial depth of wetting and the soil-water content versus capillary conductivity relations. At the cessation of infiltration, they assumed that the soil was saturated to the wetting front. During the initial stages of redistribution in a sand, water drains from near the soil surface and passes through a zone of constant soil water content.

To determine the influence of soil water content on herbicidal response, Lambert (11) used previously published material to describe a quantitative treatment of the influence of soil water on herbicidal activity. This was based upon the use of the distribution coefficient, an application of chromatographic theory to the movement and sorption of herbicides in soil. He concluded that the phytotoxicity of 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) was a function of the water content of the soil only insofar as the concentration of diuron in the soil water phase is a function of the distribution coefficient.

Green and Obrien (8) found that the effect of a change in soil water content on herbicide concentration in solution is clearly dependent on the magnitude of adsorption. They state that soil drying results in an increased concentration of herbicide in solution on soils with less herbicide adsorption. An increased concentration in solution, however, does not mean that a herbicide will be more phytotoxic under dry conditions. Other factors of the plant-soil-water-herbicide system operate in such a way that the opposite effect of soil water content is expected. That is, herbicides are generally more phytotoxic at relatively high water contents.

Herbicidal transport through the soil takes place by mass flow and molecular diffusion. The rate of soil water movement decreases with a reduction in water content for a constant driving force because of the relationship between soil-water content and capillary conductivity (2). Also, the shape of the adsorption isotherm may change as the soil dries if the herbicide molecule competes for the solid surface more effectively when less water is present (8).

Upchurch (15) measured the response of cotton to diuron under varying soil moisture regimes. Results of his experiments show that soil-water content has only a slight influence on the response of cotton to diuron. Also, it was shown that diuron is more toxic under moist soil conditions than under dry soil conditions.

Columns of soil were utilized by Harris (10) to study the movement of several herbicides in soil. In this study, upward water movement was used to determine the mobility factors of the various herbicides. Two soil types were used in these studies and, in general, results were comparable. He found that the

aromatic acid herbicides were the most mobile, and the insoluble toluidines least mobile, with the other classes of herbicides in between.

Geissbuhler et al. (7) describe the adsorption and leaching characteristics of 3-(p-chlorophenoxy)phenyl)-1,1-dimethylurea (chloroxuron) as well as giving a generalized description of several other substituted urea herbicides. They show that the adsorption of substituted ureas was positively correlated with organic matter content, the percentage of clay, and cation exchange capacity, with soil pH being of minor importance. Also, they reported that adsorption increased with decreasing water solubility of the compounds. In order of decreasing adsorption, they listed 1-butyl-3-(3,4-dichlorophenyl)-1-methylurea (neburon), diuron, 3-(p-chlorophenyl)-1,1-dimethylurea (monuron) and 1,1-dimethyl-3-phenylurea (fenuron). Conclusions from their experiments indicate that the leaching of chloroxuron is practically nonexistent. Also, they found that chloroxuron was strongly adsorbed indicating that its adsorption to the soil particles had a definite effect on the amount of movement the herbicide would exhibit, regardless of the water content of the soil. Wiese and Davis (18) conducted laboratory experiments to determine the effect of simulated flood irrigation on the leaching of herbicides. The substituted urea herbicides, monuron and diuron, were used in the study. The amount and frequency of water applied to the soil was varied to determine what affect it would have on the depth to which the herbicides were leached. They found that when the herbicide was applied to a column of wet soil, there was a general tendency for the herbicide to move deeper than when applied

to dry soil. When the herbicides were applied in 500 cm³ of water to a wet soil, and later flushed with 1000 cm³ of water, detectable amounts of all herbicides except monuron and the ester formulation of 2,4,5-trichlorophenoxyacetic acid were leached out of the 24 inch soil columns. They concluded that herbicide leaching with simulated flood irrigation varied with the herbicide, method of herbicide application and amount of water in the soil system.

The influence of the frequency and intensity of simulated rainfall on herbicide movement was thoroughly investigated by Upchurch and Pierce (16). Results of their work showed that more frequent applications of simulated rainfall resulted in more removal of monuron from the upper soil horizons than did less frequent applications. This was explained by the fact that less frequent application allowed moisture to evaporate from the soil surface, thereby making less moisture available to percolate through the soil. They further state that interpreting these results was facilitated by assuming that the leaching process involves at least two steps; the entrance of herbicide into solution and the adsorption of herbicide on the soil from the percolating solution. The frequency of rainfall affects both of these steps, but the intensity affects the latter only.

In another experiment, Upchurch and Pierce (17) examined the effect of soil moisture content on the rate of leaching of monuron. Monuron was applied to columns containing air dry soil and moist soil. Results indicated that moisture content had little or no influence on the leaching of monuron.

The depth to which a herbicide is moved also depends on the molecular structure of the herbicide. Experiments have shown that individual herbicides from the same herbicide family will leach to different depths. Primarily, this is due to greater adsorption to the soil particles. In a comparison of the leaching of four herbicides, Shahied and Andrews (14) found that fluometuron was leached to a greater depth in several soils than was linuron. Davidson et al. (6) found that diuron was retained by the soil to a greater extent than was fluometuron in horizontal columns under a constant flow rate. Fluometuron also has been shown to have a molecular diffusion coefficient similar to that of the chloride ion (4). This gives an indication of the potential movement of fluometuron in soil.

Although considerable research has been conducted with the leaching of herbicides, only a small portion has been concerned with the effect of soil moisture and the redistribution of soil water on herbicide movement.

CHAPTER III

MATERIALS AND METHODS

The soil used in this study was a Cobb sand obtained from the Caddo County Research Station near Ft. Cobb. Selected chemical and physical properties are given in Table I.

TABLE I

SELECTED CHEMICAL AND PHYSICAL SOIL PROPERTIES

<u>Soil</u>	<u>pH</u>	<u>O.M.</u>	<u>% Sand</u>	<u>% Silt</u>	<u>% Clay</u>	<u>C.E.C.</u>
Cobb sand	7.8	1.2%	93	4	3	5.4 m.e.

To study the movement of fluometuron in a confined volume of soil, rectangular columns of acrylic plastic were constructed. Air dry soil was packed uniformly into the columns and the average bulk density determined. The cross sectional area and length of each plastic column was 169 cm² and 100 cm, respectively. To achieve uniform packing, small amounts of soil were added to the column and the four sides of the column were tapped with a rubber mallet an equal number of times. One side of the container could be removed to facilitate soil sampling.

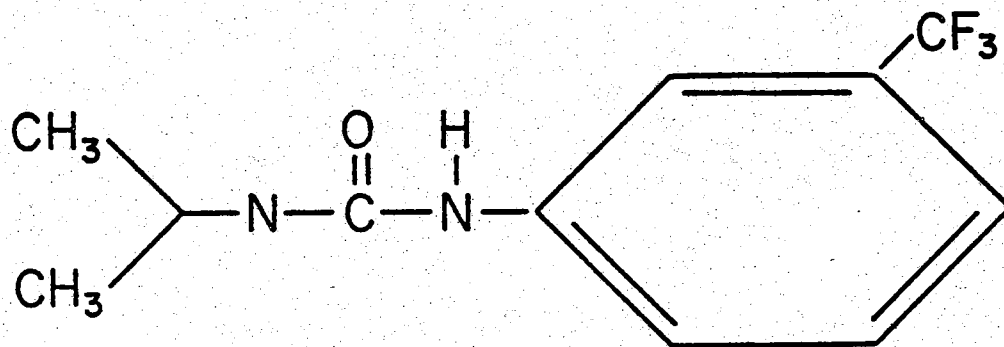
Fluometuron (Figure 1) was applied as a dry powder at a rate of 30 μ g of fluometuron per gram soil. The herbicide was mixed with the surface 200 grams of soil before leaching.

Some columns of soil were wet before fluometuron was applied. A 0.01 N CaSO_4 solution was used as the wetting agent. Also, the same CaSO_4 solution was used to leach the herbicide through the soil in both dry and wet soil columns. A 0.01 N CaSO_4 solution was used to prevent dispersion of the soil particles. The initial wetting procedure consisted of wetting the soil to a depth of 15 cm and allowing redistribution for 30 days before fluometuron was added. A list of treatment combinations are given in Table II.

Where fluometuron was applied to the air dry soil, the columns were wet to a depth of 15 cm with the 0.01 N CaSO_4 solution immediately after herbicide application. At the cessation of infiltration, fluometuron and water content were determined at each two centimeter increment below the soil surface. Soils treated in the same manner were sampled at 5, 10, and 20 days after the cessation of infiltration. The tops of the columns were covered to prevent evaporation.

To determine the effect of soil surface evaporation on fluometuron redistribution in the soil, a set of columns were left uncovered. These columns were treated the same as the ones where fluometuron was applied to air dry soil and immediately leached. The only difference being that these were left uncovered after the water application. Also, a fan blowing across the uncovered tops was used to facilitate evaporation.

To study the movement of fluometuron under continuous infiltration, four columns were filled with air dry soil and were then wet



FLUOMETURON

Figure 1. Chemical Structure of the Substituted Urea Fluometuron

TABLE II

WATER CONTENT AND SAMPLING DATE COMBINATIONS USED IN THIS STUDY

Soil Moisture Content ¹	Time of Sampling ²
Air Dry (covered)	0
"	5
"	10
"	20
Wet (covered)	0
"	5
"	10
Air Dry (covered)	0
"	5
"	10
"	20

¹Water content of the soil at the time of fluometuron application. Those indicated were covered to prevent evaporation.

²Days after the cessation of infiltration that the columns were sampled.

with 0.01 CaSO₄ solution to depths of 15, 30, 45 and 60 cm. The time required for the wetting front to move each centimeter was recorded. These experiments were conducted at 25°C ± 0.5°C.

Samples were taken after removing one side of the column. A number ten cork cutter was used to remove the soil sample. One sample was taken for fluometuron determination and one for soil-water content at 2 cm intervals. A gravimetric procedure was used to determine soil water content of the samples.

Fluometuron concentration was determined using an extraction procedure similar to that of Davidson et al. (5). The fluometuron was extracted from the soil using spectro-quality n-pentane and analyzed on an ultra-violet spectrophotometer at a wavelength of 238 mμ. To extract the fluometuron from the soil, twenty grams of soil were placed in an Erlenmyer flask. Ten milliliters of distilled water and twenty milliliters of n-pentane were added to the soil. The flask was then placed on a wrist action shaker for thirty minutes. The pentane containing the fluometuron was decanted and read on the spectrophotometer.

To convert the optical density reading of the spectrophotometer to μg of fluometuron per gram of soil, a standard curve was utilized. This was obtained by extracting known concentrations of fluometuron from soil samples and plotting optical density values versus fluometuron concentration in μg per gram of soil.

CHAPTER IV

RESULTS AND DISCUSSION

In a preliminary experiment, it was determined that n-pentane extracted fluometuron that was adsorbed and that in solution. It was also found that when a given amount of fluometuron was present, no difference in the amount of fluometuron extracted with the n-pentane was observed with soil-water content.

The soil water content for continuous infiltration to depths of 15, 30, 45 and 60 centimeters is shown in Figure 2. This shows that the water content behind the wetting front is approximately the same for each column. The depth of fluometuron movement under continuous infiltration is shown in Figure 3. If the movement of fluometuron is in proportion to the mass transport of water, then a constant ratio between the depth of the wetted front and the depth of fluometuron concentration front should exist. In Figure 4 the depth to which the water and fluometuron front has moved is plotted versus time in minutes. The wetted front line is an average of the four infiltration depths (0, 15, 30, 60 cm.). Excluding the first 12 minutes, the rate of advance of the water and fluometuron is constant. Thus after 12 minutes a constant infiltration rate was achieved.

In Figures 5 and 6 the results of applying fluometuron to an air dry Cobb sand soil and allowing the 0.01 N CaSO_4 to redistribute

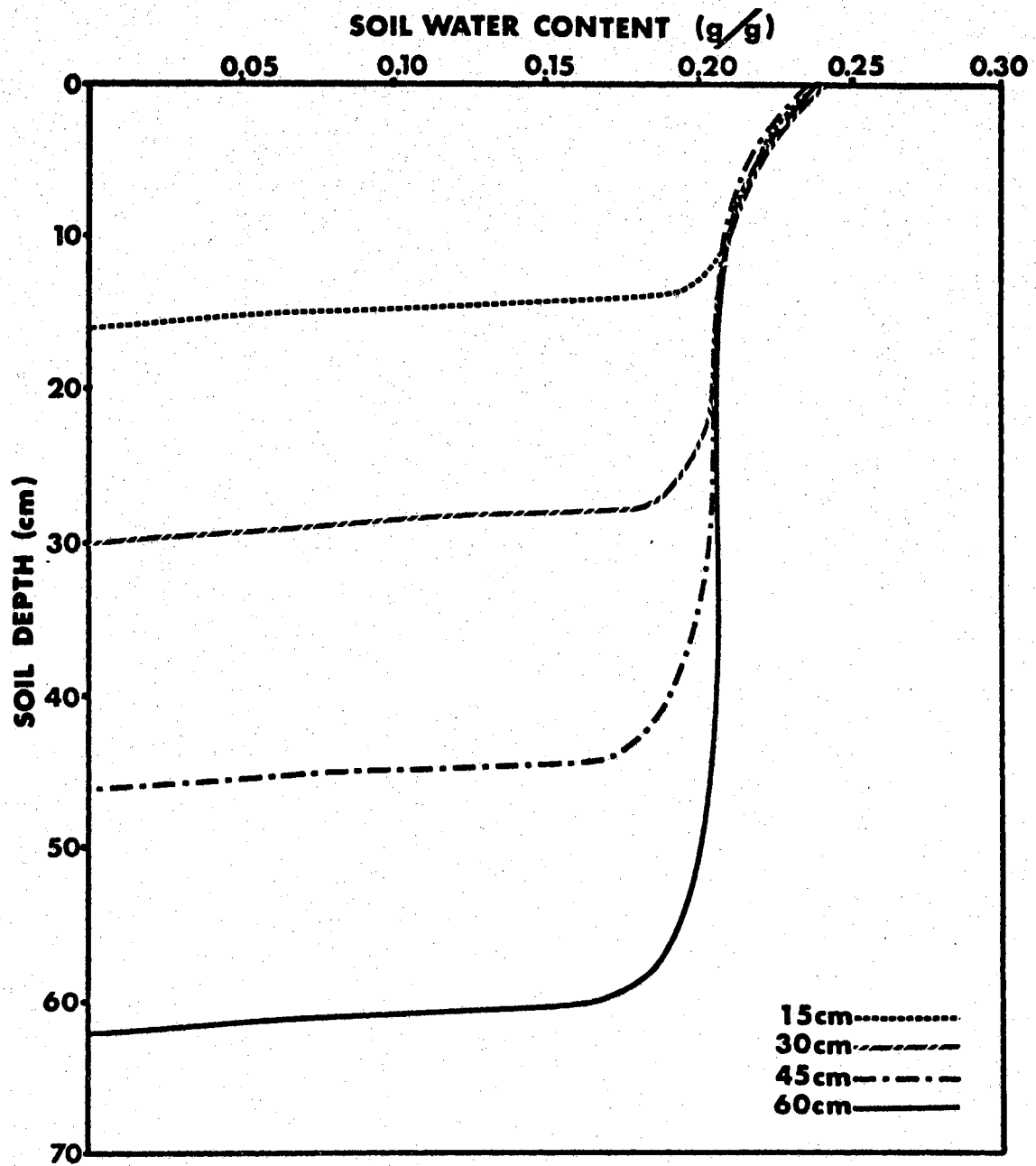


Figure 2. Distribution of Soil Water Content When Infiltrated to 4 Depths

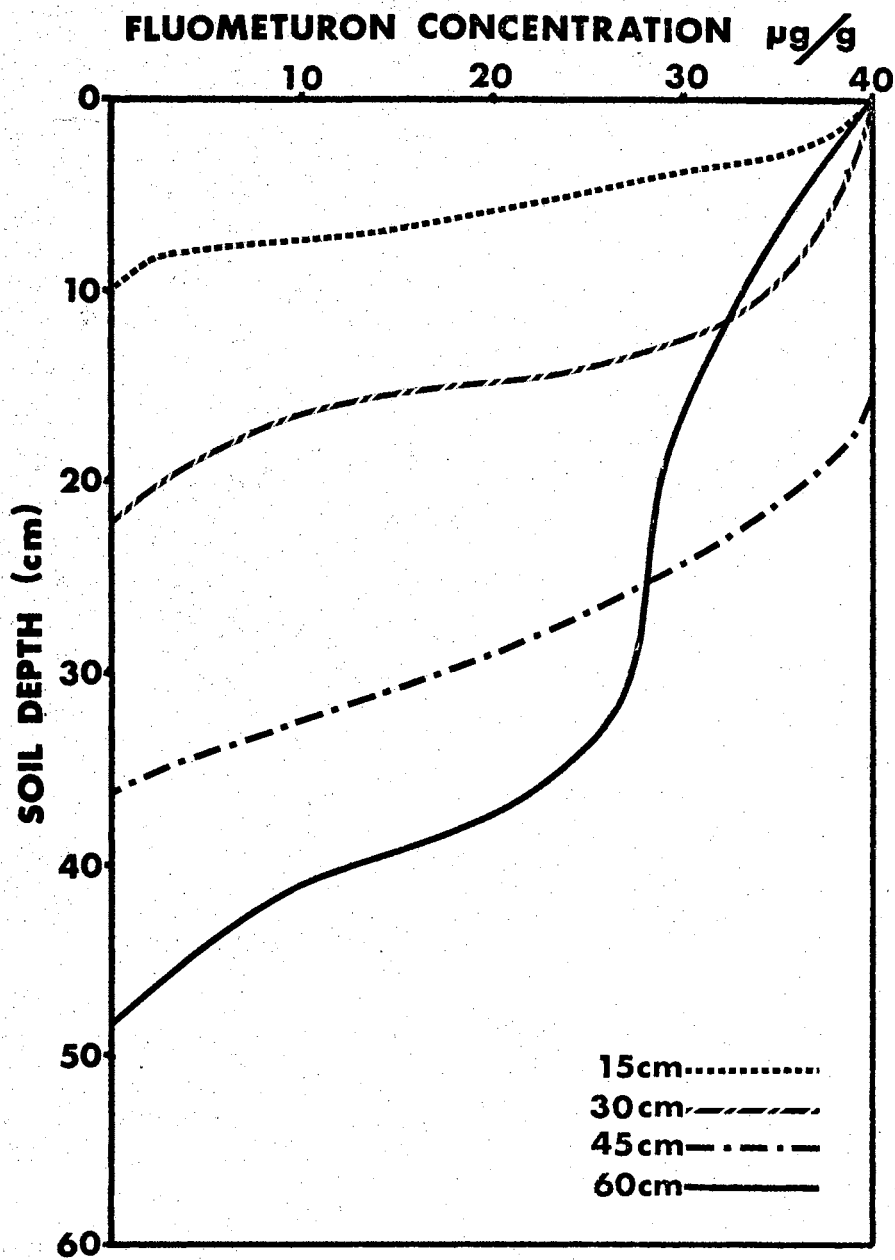


Figure 3. Fluometuron Concentration at 4 Depths of Infiltration

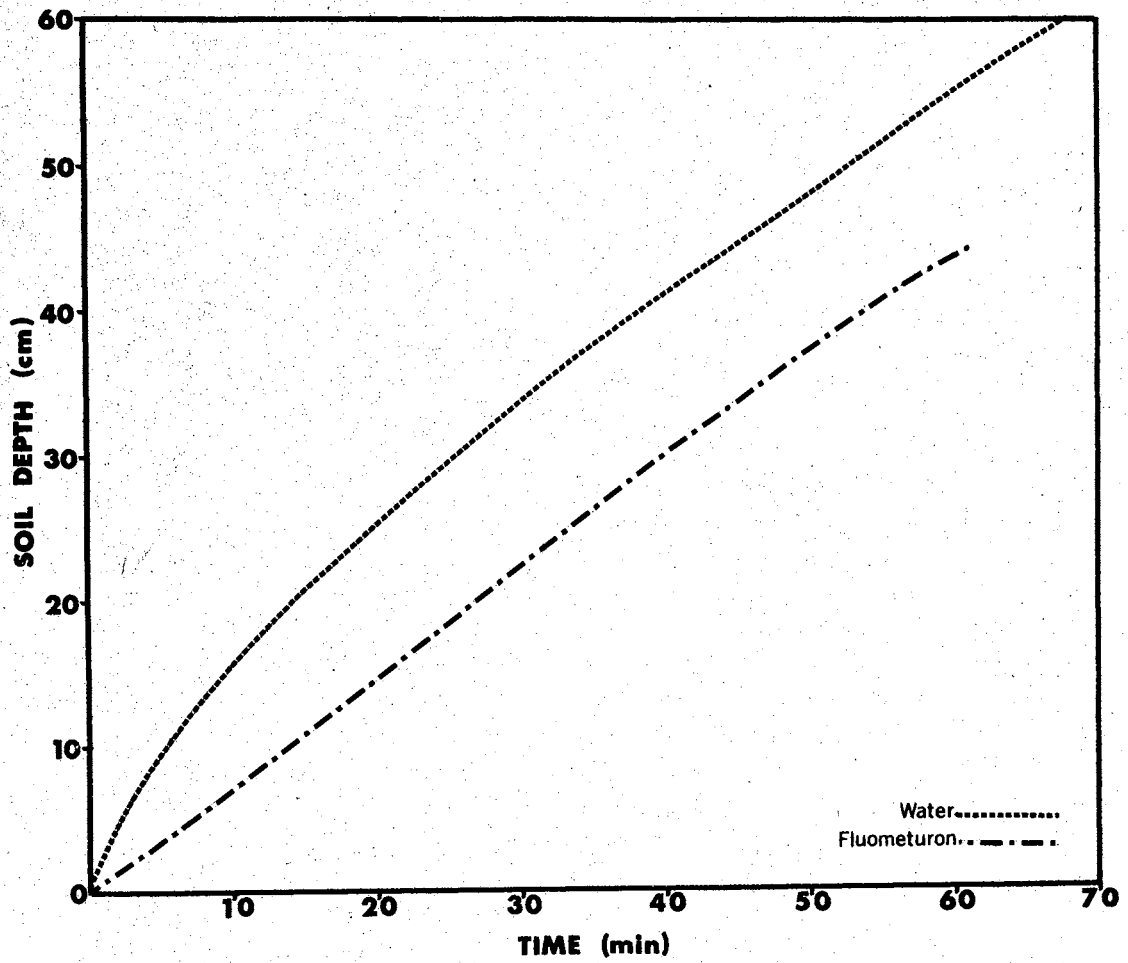


Figure 4. Relationship of Water Content and Fluometuron Concentration with Time

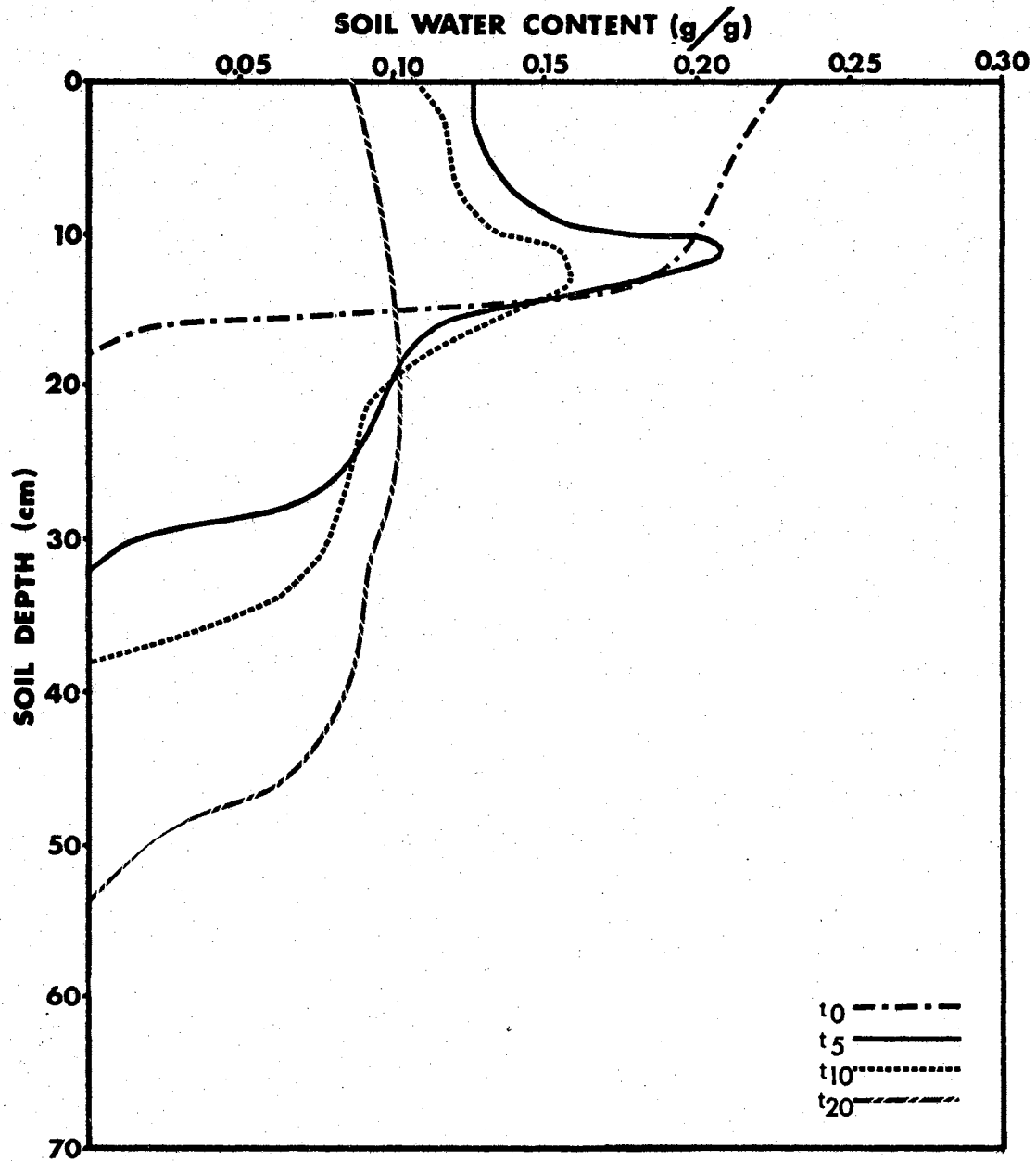


Figure 5. Distribution in Soil Water Content in Cobb Sand When Sampling Occurred at 0, 5, 10 and 20 Days After the Cessation of Infiltration

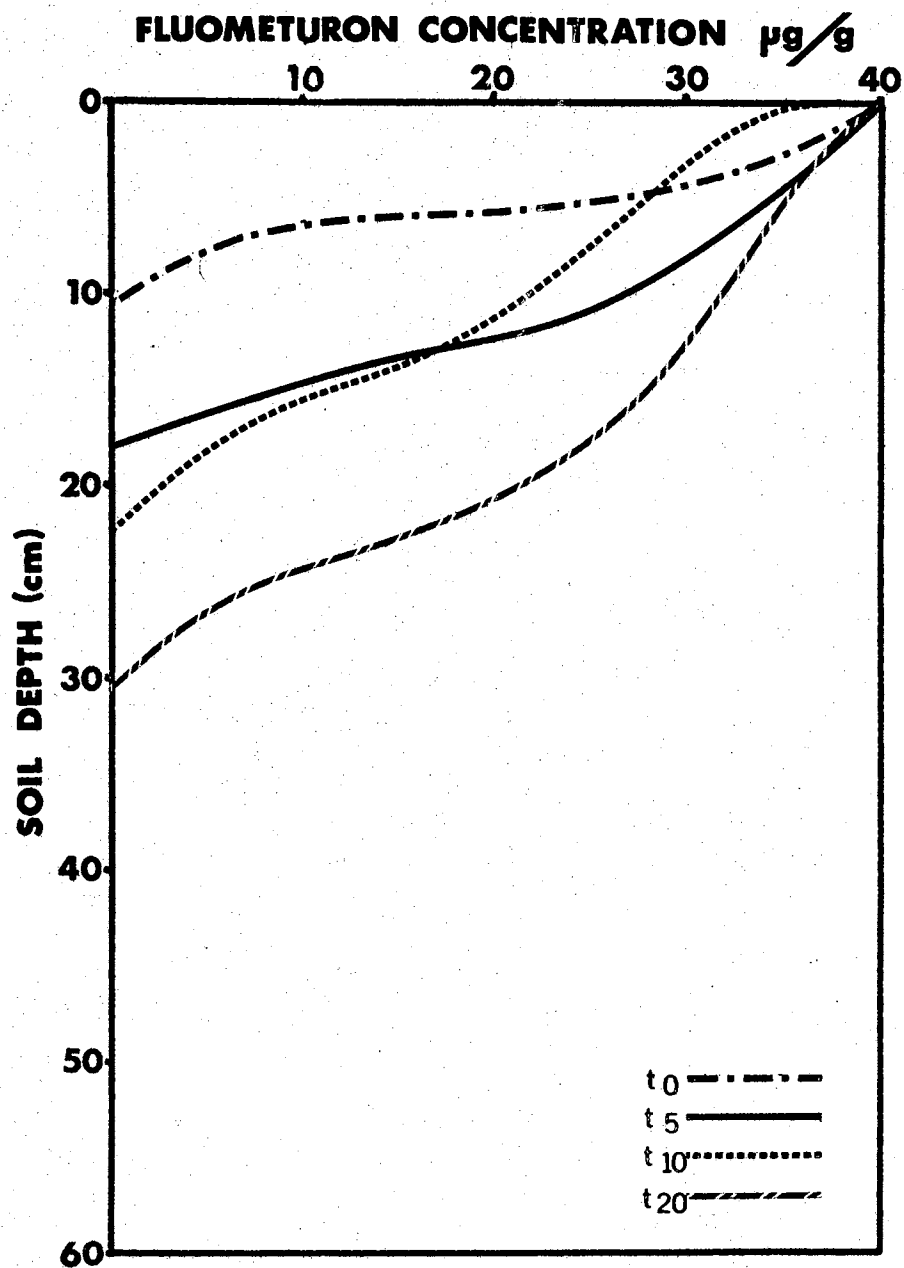


Figure 6. Distribution of Fluometuron in Cobb Sand Which was Air Dry at the Time of Herbicide Application

are shown. Figure 5 shows the soil-water content in columns where evaporation was absent. Owing to the small bulk density differences between soil columns, a different quantity of 0.01 N CaSO_4 solution was required to wet the soil to the desired depth. However, the total water in a particular column can be calculated. In Table III the time of sampling after the cessation of infiltration, the amount of water added, the amount of water measured in the columns, and the per cent of water not accounted for are listed.

TABLE III
AMOUNT OF WATER PRESENT IN THE SOIL

Soil Moisture Content	Sampling Time (Days)	Cm^3 of Water Added	Cm^3 of Water Calculated	Per Cent Lost
Air dry (covered)	0	1000	976	-2.4
	5	1000	930	-7.0
	10	1000	994	-0.6
	20	1124	1124	-0.4
Pre-wetted	0	1600	1555	-2.8
	5	1800	1671	-7.2
	10	1700	1757	3.4
Air dry (uncovered)	0	1000	960	-4.0
	5	1050	562	46.5
	10	1179	592	49.8
	20	1179	521	55.7

In the columns which were uncovered to allow evaporation, there is a large difference owing to losses in water by evaporation. Nearly

50 per cent of the water which was added originally was lost from the soil column due to evaporation.

Also of interest is the quantity of the herbicide that was moved deeper into the soil profile as the redistribution continued for 0, 5, 10 and 20 days after the cessation of infiltration. The column was sampled immediately after infiltration, when the wetted front was located at 14 centimeters. The soil above this depth is at a soil-water content approaching saturation. However, after 5 and 10 days of redistribution, it can be seen that the water has moved further in the soil. Water is moving through a zone of constant water content into the dry soil below. Twenty days after the cessation of infiltration, there is only a 3 per cent difference in water content between the surface and 46 centimeters. In Figure 6, the depth to which the fluometuron moved in the soil column is presented. It is evident that there is a large concentration of fluometuron in the first few centimeters of soil. The depth to which the herbicide moved increased with water redistribution. In the column that was wetted to 15 centimeters and sampled immediately after infiltration, the fluometuron had moved to approximately 10 centimeters. However, after 20 days the fluometuron had reached approximately 30 centimeters, with the 5 and 10 day sampling dates being intermediate.

Figure 7 illustrates the distribution of soil water in columns that were wet previously. Samples for water and fluometuron were taken at 0, 5, and 10 days after an application of water to the wet soil. In these columns, apparently less time was required for the wet as compared to the dry column for a constant soil-water content to be attained during redistribution of the column. Although the

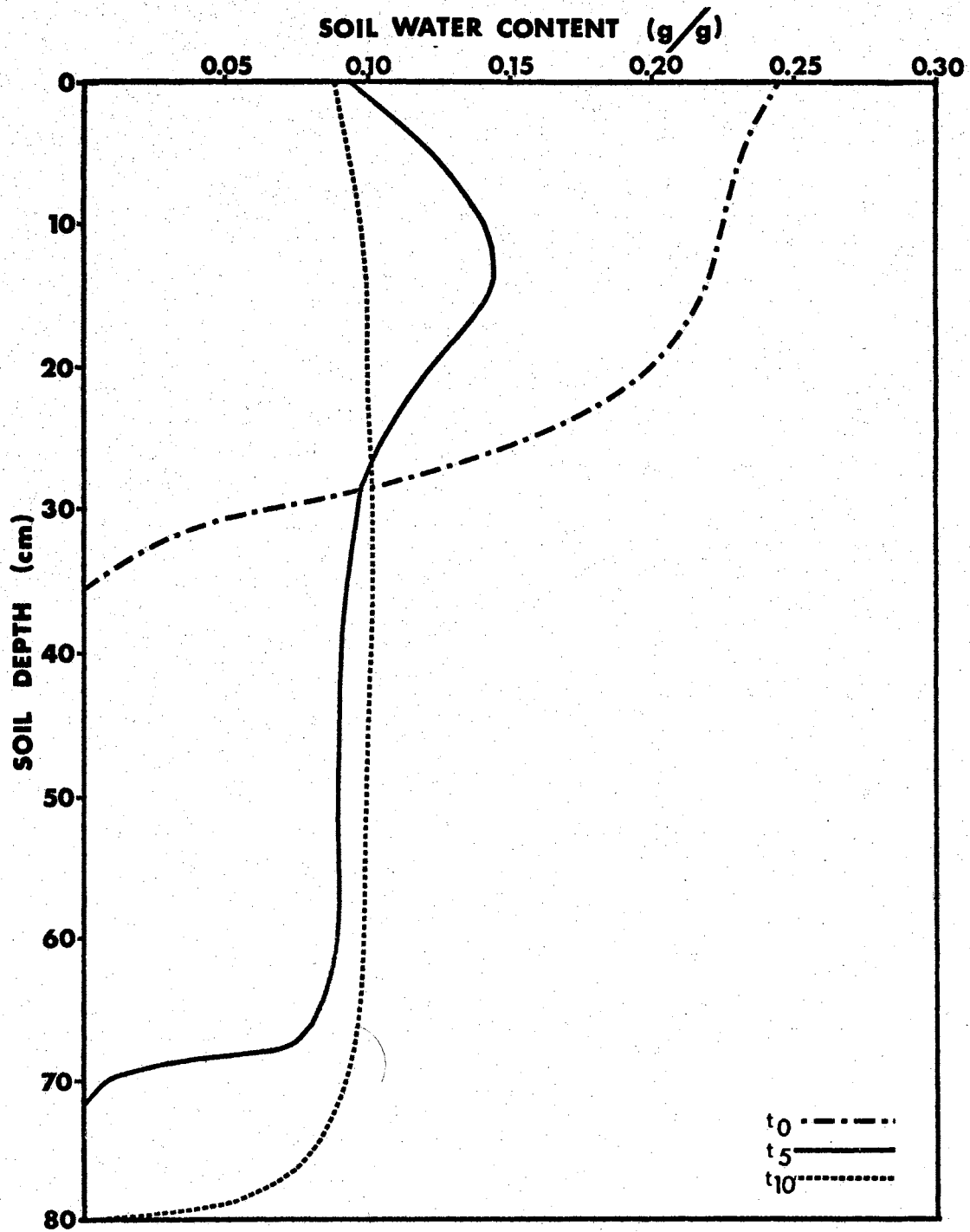


Figure 7. Soil Water Content Distribution in Cobb Sand Which Was Wet to 15 cm., Allowed to Redistribute for 30 Days and Re-wet

depth to which redistribution extended was considerably more in soils which were wet previously, there was not as great a difference in the depth to which the fluometuron moved (Figures 6 and 8). Five and ten days after the cessation of infiltration in the pre-wetted soil, fluometuron moved to approximately 30 centimeters, which was ten centimeters more than in the air dry soil.

Allowing evaporation to occur from the soil surface had a drastic effect on the soil-water content in the surface of the soil (Figure 9). Five days after the cessation of infiltration, water had reached a depth of 30 centimeters in the column allowed to evaporate and the one which was covered. However, there is a considerable difference in the shapes of the two curves. In the soil column allowed to evaporate, there is not the characteristic curve indicating a zone of saturation during redistribution. This is also true for the column sampled 10 days after the cessation of infiltration. There is only a slight difference in the curves for the columns allowed to evaporate for 5 and 10 days after infiltration (Figure 9).

The difference in the depth of fluometuron movement between the covered and uncovered soil columns were small (Figures 6 and 10). At 0 time the fluometuron in both cases had moved to 10 centimeters. After 5 and 10 days of redistribution, in both cases, the depth of the fluometuron was approximately 20 centimeters. As seen in Figure 10, the difference of fluometuron after 5 and 10 days is slight.

According to Biswas et al. (3), the amount of water leaving the saturated surface soil must be equal to the amount entering the dry

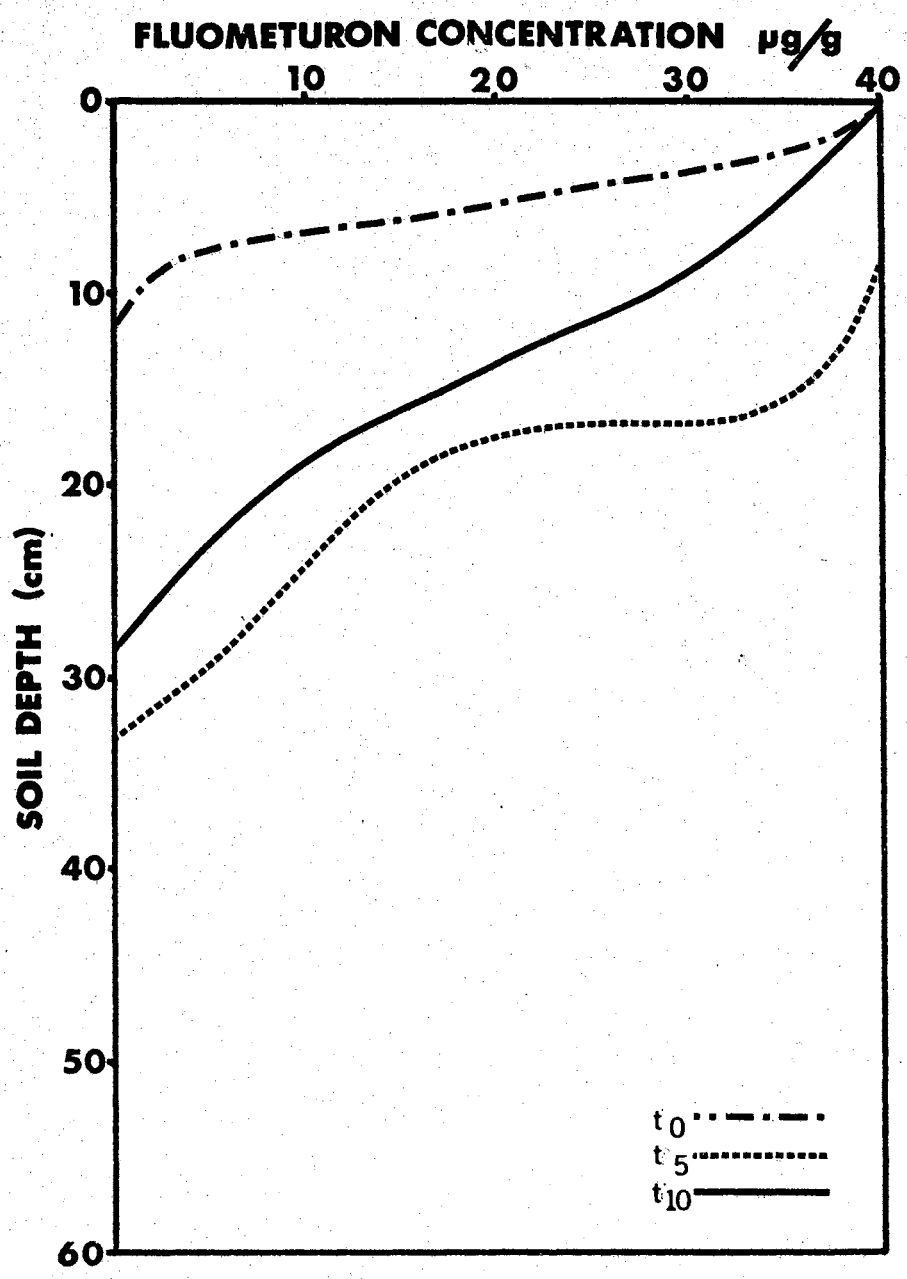


Figure 8. Fluometuron Distribution in Cobb Sand Which Had Been Wetted Before Herbicide Application

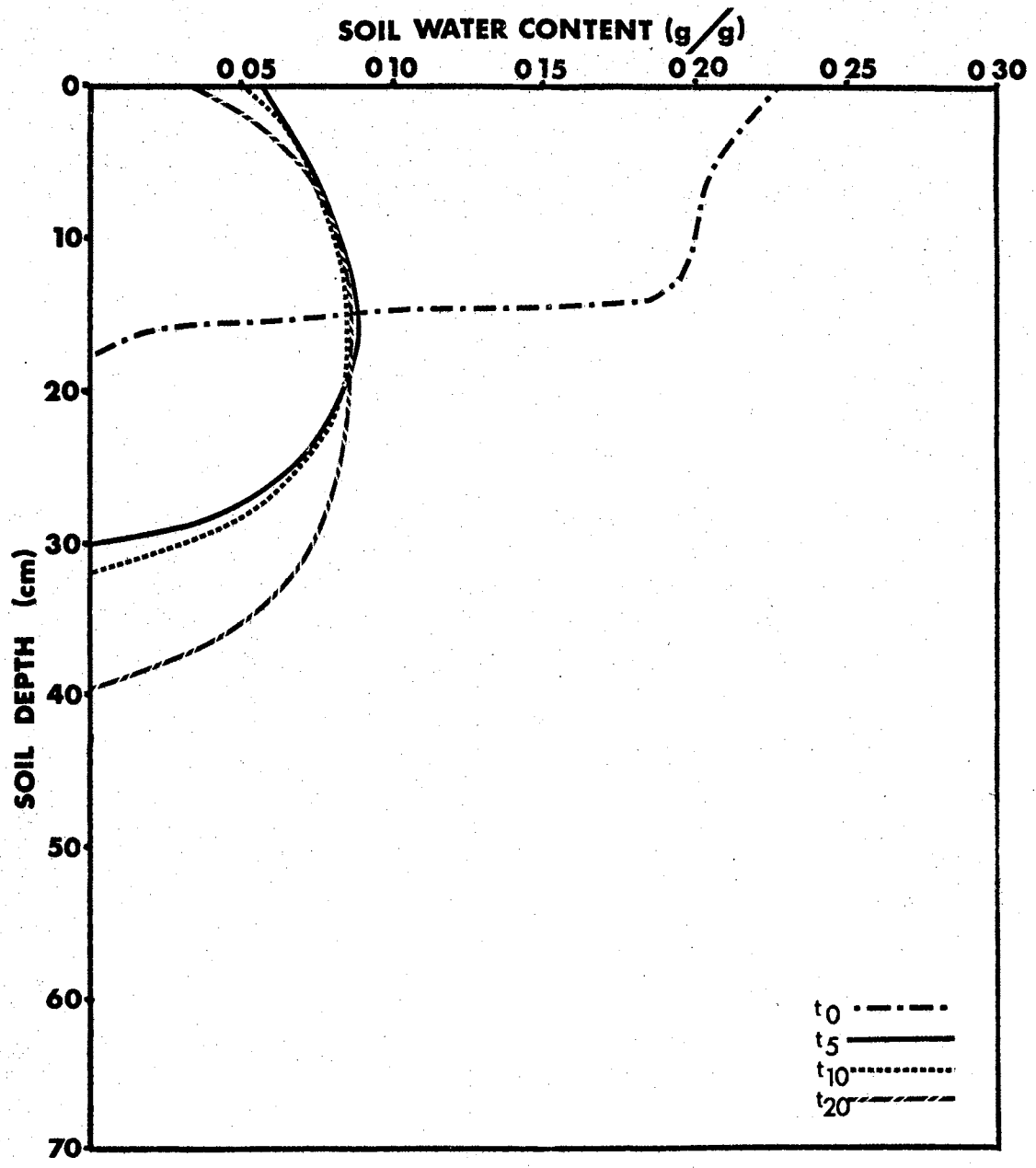


Figure 9. Soil Water Content Distribution in Cobb Sand When Evaporation Occurred at the Soil Surface

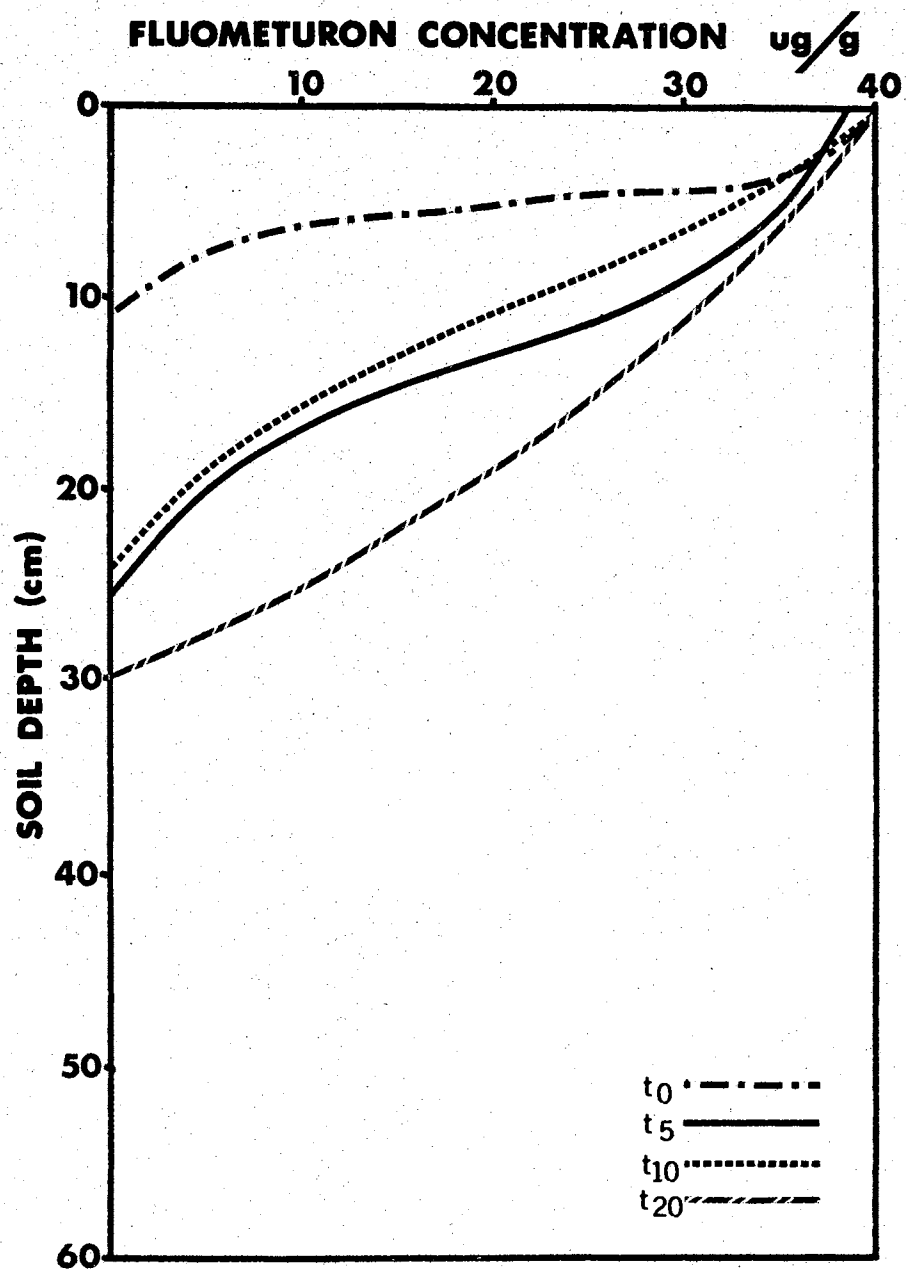


Figure 10. Fluometuron Distribution in Cobb Sand After Evaporation From the Soil Surface

soil below when no evaporation exists. Thus the area under the soil water redistribution curves should be equal for any group of soil contents. The amount of fluometuron present in each two centimeters layer was determined. Therefore the amount which was moved downward can be determined by the following formula:

$$\sum_{1}^n C \times \rho_b \times V$$

where C is the concentration in micrograms of fluometuron per gram of soil, ρ_b the bulk density of the soil and V the volume of each 2 centimeter layer of soil.

The percentage of fluometuron recovered from the various soil columns is presented in Table IV. When the columns were sampled immediately after the cessation of infiltration, only 7.4 per cent of the fluometuron was recovered. This was true for all three experiments. As time after the cessation of infiltration increased, the amount of fluometuron recovered also increased. More fluometuron was released in the pre-wetted soils than the air dry soil. This is apparently because fluometuron in the surface soil is still going into solution. Thus, where there is more water present there is more fluometuron movement downward because of more herbicide in solution.

In Table V, the amount of water moved deeper than the initial wetting front with time is listed. Also given is the amount of fluometuron which moved with the corresponding quantity of water. This gives an indication of the amount of fluometuron which moved with the water during redistribution.

TABLE IV
 AMOUNT OF FLUOMETURON ADDED AND RECOVERED

Soil Moisture Content	Sampling Time (Days)	Fluometuron Added (g.)	Fluometuron Recovered (g.)	Per Cent Recovered
Air dry (covered)	0	0.9021	0.0669	7.42
	5	0.8856	0.0932	10.52
	10	0.8984	0.1151	12.81
	20	0.8798	0.2112	24.01
Pre-wetted	0	0.8921	0.0659	7.39
	5	0.8978	0.1962	24.29
	10	0.8048	0.1372	17.05
Air dry (uncovered)	0	0.9021	0.0668	7.42
	5	0.8971	0.1422	15.85
	10	0.8931	0.1246	13.95
	20	0.7996	0.1696	21.21

TABLE V

AMOUNT OF WATER AND FLUOMETURON MOVED BELOW INITIAL WETTED DEPTH

Soil Moisture Content	Sampling Time (Days)	Water Moved Below Initial Wetted Depth ¹	Fluometuron Moved Below Initial Wetted Depth ²
Air dry (covered)	0		
	5	328	0.0263
	10	480	0.0482
	20	896	0.1443
Pre-wetted	5	814	0.1303
	10	1129	0.0717
Air dry (uncovered)	5	255	0.0754
	10	294	0.0578
	20	380	0.1028

¹Milliliters of water

²Micrograms of fluometuron

The depth to which the fluometuron moved in the air dry soils, in which evaporation occurred in one case but not in the other, is approximately the same for the 5 and 10 days sampling dates (Figures 6 and 10). In the columns which were covered, the fluometuron apparently was moved to this depth with the initial amount of water added. The same appears to be true for the soils which were allowed to evaporate because the fluometuron moved the same distance. Therefore, it appears that evaporation from the soil surface has a great effect on soil-water redistribution, but apparently no effect on the depth to which the fluometuron moved.

CHAPTER V

SUMMARY AND CONCLUSION

Laboratory experiments were conducted to (1) determine the effect of a dry and moist soil on the mobility of fluometuron, (2) find the effect of soil water redistribution on fluometuron movement, and (3) determine the effect of soil surface evaporation on fluometuron movement in the soil.

Results of these experiments indicate that when a 0.01 N CaSO_4 solution is applied to the soil surface of an air dry soil, and allowed to redistribute that there is a zone of saturation in the upper portions of the soil profile, and as time increases water moves out to this zone into the dry soil below. As time increases, the depth to which fluometuron moves also increases.

When fluometuron is applied to a soil which has previously been wetted, then the depth to which the fluometuron moves increases over that of air dry soil.

Evaporation from the soil surface had a marked effect on the redistribution of soil water, particularly in the upper portions of the soil columns. However, only a slight effect on the depth of fluometuron movement was noted with evaporation from the soil surface. This indicates that the fluometuron is moved downward in a short period of time with the initial quantity of water.

The amount of fluometuron recovered from the soil surface increased with time. Also, more fluometuron was recovered from soils which were wetted before fluometuron was added to the soil. This was probably caused by the fluometuron going into solution with the soil water as it redistributed through the soil.

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