THE INFLUENCE OF SOIL TEXTURAL STRATIFICATION ON CHLORIDE AND FLUOMETURON MOVEMENT

By

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1961

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
May, 1970

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ACKNOWLEDGMENTS

Special gratitude is expressed to my major adviser, Dr. James M. Davidson, for his help during the course of this study. Gratitude is also extended to the other members of the committee, Dr. Paul W. Santelmann and Dr. James E. Garton.

Appreciation is extended to my wife, Amelia, for her encouragement and help in the preparation of this thesis.

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CHAPTER I

INTRODUCTION

The increasing use of agricultural chemicals for pest control has presented a real and pressing possibility of permanent pollution of our natural resources. However, the real danger lies not so much with the use of the chemicals as with the misuse and lack of understanding of the fate of these materials once applied. Although considerable work has been conducted on the behavior of such pesticides as herbicides in plants and soils (9, 11, 27, 43); this work has been primarily confined to studies of their activity in homogeneous and controlled environments. To date, no consideration has been given to the importance of such properties as soil stratification on the movement of soil applied agricultural chemicals.

Because many herbicides are applied directly to the soil, an understanding of their mobility must be established in order to prevent surface or ground water contamination. It has been shown that the movement of these herbicides through uniformly packed soil columns depend upon soil-water flux, pore size, and their reaction within the soil mass. However, because many herbicides move below the plow layer where the soil properties are quite different from those of the topsoils, the movement of the herbicide may be significantly altered by this change in pore geometry. The importance of a textural stratification on herbicide mobility must be known and used for field problems.

The objective of this study was:

1.) Measure the mobility of two herbicides (fluometuron and prometryne) and the chloride ion in Norge loam, Eufaula loamy fine sand and Stratford I and II.

2.) Measure changes in mixing and displacement of chloride and fluometuron resulting from texturally stratified columns of the above soils.

CHAPTER II

LITERATURE REVIEW

Preemergence herbicides are applied to the soil to prevent future weed growth. The chemical's effectiveness is related to the time and concentration of the material in the soil area in which its effects are desired. Sheets and Harris (40) in a review of herbicide residue in the soil concluded that four potential problems can be observed from the application of herbicides: a) accumulation of residues resulting from rates which exceed rates of disappearance b) injury to sensitive plants grown in rotation with the treated crops c) unlawful residues in plants grown in rotation with treated crop and d) modification or inhibition of beneficial soil microorganism activity.

Many factors influence the movement, sorption and disappearance of herbicides in soils. Soil type, chemical properties, climatic conditions, biological population, formulation and methods of application all influence the movement and adsorption of the chemicals (27). Park and Tepe (34) reported that factors which influence herbicide disappearance are: leaching, adsorption, volatility, photodegradation, microbial degradation and chemical degradation. Several workers (6, 18, 21, 22, 42, 43) reported that herbicide phytotoxicity and adsorption and desorption may also be modified by temperature.

Adsorption is one of the most important factors influencing herbicide behavior in the soil (37, 46). Coffey and Warren (8) have shown that herbicides are adsorbed by organic matter, clay mineral, exchange resins, nylon, and activated carbon. A general agreement exists regarding the importance of organic matter and mineral colloids to the adsorption processes (9, 18, 20, 27). Herbicide adsorption has been shown to regulate the extent to which the herbicide will move as a vapor or downward through the soil profile owing to soil-water movement.

Harris (23) has presented evidence that the adsorption of some herbicides are greatly affected by p^H while the adsorption of others remain nearly constant with p^H changes. If herbicide adsorption changes with p^H, lime or sulfur application can introduce a variation in acidity that would modify the adsorption. The herbicide applied to the soil may move deeper into the profile owing to the soil p^H modifications. McGlamery and Slife (30) found an interaction between p^H and temperature in their experiment on adsorption and desorption of atrazine in soils.

Sheets et al. (39) studied and compared the initial and residual toxicities of nine s-triazines in different soils. They reported that lower herbicide dosages were required in Madera silty clay soil than in Yolo silt loam to reduce the fresh weight of oats by 50 percent. The organic matter, clay content, and cation exchange capacity were greatest in the Madera soil. Because of the specific interations mentioned between herbicides and soil constituents and the variation in herbicide behavior, the fact that a herbicide is mobile in a particular soil does not allow the generalization that the same herbicide would be mobile in another soil media. This conclusion can also be extended to other chemicals and how they act in different horizons of a soil profile. Harris (20) states that certain soil constituents present specificity for herbicide attraction i.e. organic matter can present more affinity for one herbicide and montmorillonite clay for another.

Grover (18) found that the addition of organic matter to clay soils reduced the simazine concentration in solution. In soils with a high water content triazine was equally available to plants regardless of the soil clay content. He reported that the adsorption of simazine by clays was not as great as it was by organic matter. Talbert et al. (42) arrived at the same conclusion for the s-triazine group.

Upchurch and Mason (46) show that for 12 soil-incorporated herbicides, the amount of herbicide required for 50 percent growth reduction (GR_{50}) in cotton plants was highly and positively correlated with organic matter, cation exchange capacity, exchangeable calcium, moisture equivalent, free drainage, and total exchangeable bases. As a confirmation of a herbicide phytotoxicity-soil organic matter relation, he also reported that the inclusion of several soil factors in a multiple correlation between soil factors and herbicide phytotoxicity resulted in only a slight improvement in the correlation obtained.

Lailach et al. (26) studied the absorption of pyrimidines, purines and nucleosides by Li-, Na-, Mg- and Ca- Montmorillonite. They concluded that organic absorption was dependent on the p^H of the equilibrating solution, the nature of the organic molecules, particularly the basicity and molecular constitution, and the organic exchangeable cations.

Bailey et al. (3) state that the major factor governing the magnitude of herbicide adsorption by different chemical families was the dissociation constant of the adsorbate. They concluded that the adsorption of a basic compound by a montmorillonite clay system depends more upon the surface acidity than the p^H of the bulk solution. The converse is true for the adsorption of acidic type compounds.

The displacement of water molecules from the clay surface may dominate the adsorption reaction. The bonding forces that may be responsible for the clay-organic molecule adsorption phenomena has been presented by Greenland (17) as follows:

1-Coulombic attractions between
  - Negatively charged surface and positively charged organic compound
  - Positively charged surface, or ion or oligoion* at surface, and organic anion

2-Van der Waals forces, composed of
  - a-Polar: Charge-dipole interactions
    - Dipole-dipole interactions (including H-bonding)
    - Charge-induced dipole interactions
    - Dipole induced dipole interactions
  - b-Non-polar: Dispersion forces

  between
  - Surface and organic compound
  - adsorbed molecules of similar species
  - adsorbed molecules of dissimilar species

* e.g. positively charged hydroxy aluminum oligomers.

Organic compounds with molecular weights larger than 150, whether charged or not, may compete with water molecules for the surfaces and be adsorbed.

Several workers have used biological assay to measure and study herbicide adsorption and movement in soils. Shahied and Andrews (38) studied herbicide leaching in soil columns using different amounts of water. They reported that stunting caused by prometryne was observed at lesser soil depths. Stunting due to fluometuron was found in the deepest portion of the soil columns treated. Another conclusion that could be drawn from this experiment was that the stunting effect that prometryne caused on plants was visualized in samples from the top of the columns which showed a high adsorption of the herbicide not leached. For the same experiment, the fluometuron effect showed a higher mobility of this herbicide compared with prometryne.

Other workers (4, 41) have shown that the s-triazines are primarily adsorbed within the first few inches of soil. Seedlings exhibit more injuries when planted in soil samples from the upper part of the soil columns. Talbert and Fletchall (42) working with five s-triazines found that prometryne was highly adsorbed by soils and less eluted from soils treated with organic solvents.

Bailey and White (2) mention two reasons why herbicides are not biologically effective at low moisture contents. One is a difference in herbicide solubility at low soil-water contents. If a unit of water dissolved a unit of herbicide in an absorbent media and the unit of water decreases, the herbicide concentration will increase. At a certain level of water content, the solubility product of the pesticide will be exceeded and precipitation will occur. The other reason is the competition water-organic molecules for the adsorption places at different soil water contents. Water molecules, as dipoles, are strongly adsorbed by colloids. If the soil water content decreases, the number of dipoles present to compete for adsorption sites become less. As a result of this situation fewer polar organic molecules can compete favorably for the adsorption sites at different moisture levels. Soil-water content appears to have a significant effect on both degree of adsorption and bioactivity of pesticides present in aqueous and vapor phase within the soil profile.

A herbicide can move from a point of application, where it is highly concentrated to another point were less or nil herbicide is present, under the influence of natural or artificially applied water. Harris (19) emphasized that diffusion will produce a reduction in herbicide concentration; but for those chemicals with low water solubility, adsorption is more important in reducing the concentration. He found that adsorption gave a better approximation of herbicide movement in soils than did their solubilities. As an example, he compared prometryne which soluble to 48 ppm, 10 times more soluble than simazine, and then shows prometryne less mobile in the soils. Lavy (28) has shown that both mass flow and diffusion of C^{14} ring-labeled s-triazines occurred in three Nebraska soils. Mass flow is described as the means by which water-soluble compounds are transported in the soil solution.

In the water percolating process, a herbicide is dissolved and displaced by the flowing solution. In the process the herbicide equilibrates with the soil colloid, where it is strongly adsorbed, the total amount and the rate at which the chemical is leached decreases. Freed et al. (14) state that when the water percolation is fast, the herbicide movement is in the same direction of water flow. As the water flow rate is reduced, diffusion becomes more significant in determining the final distribution of the herbicide in the soil profile. They also concluded that the amount of herbicide carried by the soil-water was proportional to the amount of water available to dissolve the chemical and carry it into the soil. The pore size and pore size distribution of a soil are determined and characterized to a great extent by soil structure. Both parameters influence the flow rate through the soil. The larger the flow rate, the greater the water volume that will pass a given point for a given soil-water pressure difference per unit of time. This may influence the degree of equilibrium between pesticides and soil colloids, particularly at high flow rates.

Burnside and Behrens (6) tested herbicide dissipation in soils whose textures varied between sandy loam and silty clay loam at different locations (Nebraska). They reported that soil texture differences had a greater influence on herbicide residue carry over than did climatic differences. Harris and Sheets (21) state that variations in soil-water holding capacity can produce different herbicide concentrations in the soil solution even though the total amount of herbicide applied is the same.

It has been shown in several studies (10, 11, 27, 45) that the principal factors that influence herbicide movement in the soil are water flux, molecular diffusion of the chemical, adsorption properties of the medium, pore size, soil-water content, herbicide solubility, and degradation.

It is well established that herbicide dissipation from the soil may be due to biological (45) and nonbiological (7) means. Upchurch (45) reports that as subsurface soil horizons vary in oxygen and carbon dioxide tension, temperature, nutrients, p^H, etc., the herbicide might reach an unfavorable media for microbial activity.

The literature presents extensive information on herbicide adsorption in soil and other media. There is, however, a lack of information on chemical adsorption and movement through texturally stratified soils. The objective of this investigation was to study textural stratifications as an influential factor in herbicide movement.

CHAPTER III

MATERIALS AND METHODS

The soils used in this study were Norge loam and Eufaula loamy fine sand from the Perkins Experimental Station at Perkins, Oklahoma, and Stratford I and Stratford II from the Oklahoma Peanut Research Station at Stratford, Oklahoma.

The samples were taken only from the upper 15 cm, air dried and screened through a 1 mm sieve for Norge soil and 2 mm sieve for all other soils. Soil samples were initially treated with calcium solutions until completely calcium saturated. This procedure consisted of mixing the soil with 0.5 N calcium acetate in 1:1 proportions (by volume). After one hour the liquid portion was removed with a Buchner funnel and vacuum and washed again with 0.5 N calcium acetate. Three washings with 0.01 N $CaSO_4$ followed the calcium acetate treatments after which the soils were air dried and screened again as described above.

The air dried calcium saturated soils were packed in a glass cylinder to a specific soil bulk density for each soil: Norge 1.60 g/cm^3, Eufaula 1.83 g/cm^3, Stratford I 1.89 g/cm^3, and Stratford II 1.82 g/cm^3.

The stratified soil columns were packed in 30 cm long glass cylinders, of which 15 cm was Norge and the remaining 15 cm one of the above soils. This procedure provided an abrupt change between the two soils.

The apparatus used in this study was similar to that described by Davidson and Santelmann (11) (Figure 1). The diameter of the glass column was 7.5 cm and their lengths 15 or 30 cm.

The soil packed in the columns was held between two fritted glass bead plates sealed in glass. A reservoir existed behind the fritted glass plates whose capacity varied from 10 to 25 ml. The porous plate was of a larger diameter than the glass cylinder and had a medium porosity[1]. They were sealed to the cylinder with paraffine and epoxy to avoid leaks during the experiments. A small hole in the cylinder permitted air to escape from the soil during the initial soil-water saturation process with 0.01 N $CaSO_4$.

The composition of the solution entering the soil was changed by flushing the glass tubing and reservoir behind the inflow porous plate. This was done by flushing 8-10 times the plate reservoir capacity through this section of the apparatus. Due to the fact that the cylinder outlet was closed (D in Figure 1) and that the soil was saturated, no significant amount of new solution could enter the porous plate during the change from one solution to another. After a change in solutions, the previously establish flow rate was continued. A constant volume pump[2] was used to control and maintain the flow rate. The cylinder outlet was opened following the change in inflow solution and samples collected with an automatic fraction collector.

The herbicides used in this study were 3-(m-trifluoromethylphenyl)-1, 1-dimethylurea (fluometuron) and 2,4 bis (isopropylamino)-6-methylmercapto-s-triazine (prometryne). Both were labelled with C^{14}.

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[1] Corning Glass Works, Corning, New York.

[2] Sigmamotor, Inc., Middleport, New York, Model A1-2-E.

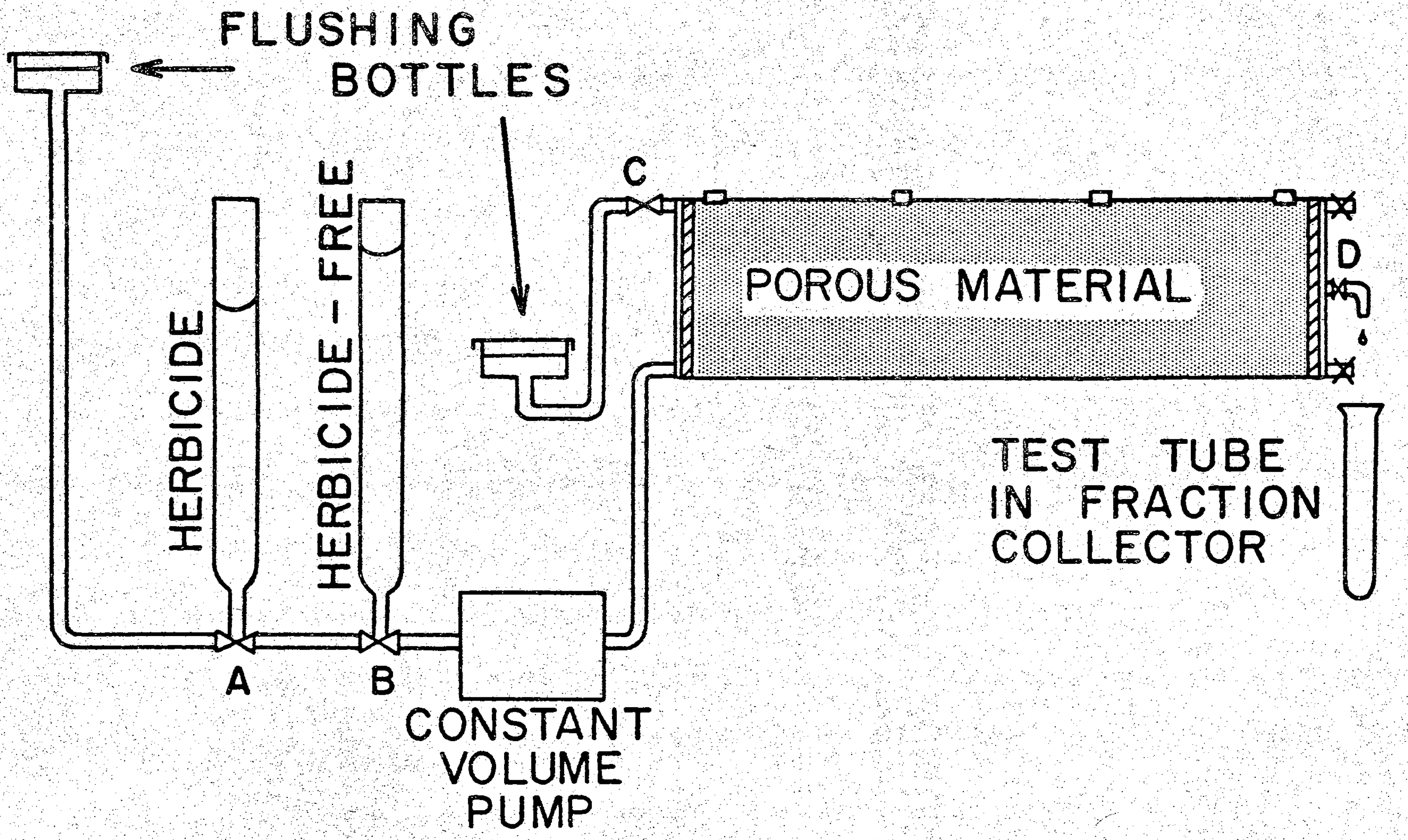

Figure I. Schematic Diagram of Experimental Apparatus Used to Study Herbicide and Chloride Displacement Through Soils.

The radioactive herbicides and the commercial wettable powder form (80% for fluometuron and 81.3% for prometryne) of each herbicide were dissolved in 0.01 N $CaCL_2$ to obtain solutions with 5 microcuries per liter and a total herbicide concentration of 29 parts per millon of each herbicide.

A 200 ml slug of each herbicide solution were used. After each 200 ml slug had been placed in the soil, the solution behind the inflow plate was changed to 0.01 N $CaSO_4$ and the displacement of the herbicide solution at the established flow rate continued until the end of the experiment. The solution used to saturate the soil column and also to displace the herbicide from the medium was 0.01 N $CaSO_4$. The calcium solutions were used to prevent physical changes in the soil during the treatments.

All effluent samples collected were analyzed for chloride by titration with silver nitrate. The amount of herbicide was determined as follows: 0.5 ml was removed from the effluent samples and mixed with 15 ml of liquid scintillation solution and placed in a counter[3] to determine the radioactivity in counts per minutes. The liquid scintillation solution's (36) composition was 4 g of 2.5-Diphenyloxazole (PPO), 50 mg of 1,4-bis-[2-(5-Phenyloxazolyl)] - Benzene (POPOP) and 120 g of naphtalene dissolved in a liter of p-dioxane.

This study was conducted in a constant temperature laboratory (24 ± 1°C). All materials were stored in the room for at least 24 hours prior to use in order to avoid difference from temperature gradients.

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[3] Beckman L S - 100 Liquid Scintillation System, Beckman Instruments, Inc., California.

Some physical and chemical properties of the soil were evaluated after the calcium saturation treatment. The results are shown in Table I. Mechanical analysis was determined by the hydrometer method (5). Organic matter was determined by the potassium dichromate wet-oxidation method (44), and CEC was determined by the sodium acetate saturation (44) method. The soil p^H was measured in a 1:1 mixture of soil and distilled water. Readings were taken on a model H2 Beckman pH meter.

Herbicide adsorption was determined by shaking 20 grams of soil with 20 ml of various herbicide concentrations for 5 hours. After centrifugation, 0.5 ml of the supernatant solution was mixed with the scintillation solution to determine the herbicide concentration. At the same time blanks were prepared from 0.01 N $Ca^{CL}{}_2$ and herbicide solutions. The difference between blanks and soil extracts was considered to be the amount of herbicide adsorbed by the soil. All samples were duplicated.

Pore volume or total volume of solution held by the soil was determined by oven drying the soil at 100-105° C for at least 48 hours, following every experiment. Also, the volume of solution in both plates and in the effluent reservoir were measured and substracted from the total volume that had passed through the column. The amount of solution passing through the soil in a given time was read directly from burettes containing the solutions. The volume of solution in both porous plates and effluent reservoir were substracted from the total amount of solution applied to obtain the amount of solution that had passed through the soil.

The number of pore volumes displaced through each column was calculated as the ratio of total amount of effluent over the measured

TABLE I

CHARACTERISTICS OF SOILS USED IN STUDY

Particle Size Distribution		Norge	Eufaula	Stratford I	Stratford II
Course sand	(>500μ)	0.33	0.36	6.22	6.00
Sand	(>50μ)	70.2	90.00	87.3	84.4
Course slit	(20μ-50μ)	9.8	4.5	6.3	5.1
Fine slit	(2μ-20μ)	7.7	2.0	3.3	4.3
Clay	(<2μ)	12.3	3.3	3.1	5.2
Percent Organic Matter		1.28	0.36	0.39	0.56
Cation Exchange Capacity (m.e. per 100 grams)		7.1	2.7	2.2	2.3
pH		6.5	6.6	6.4	6.3

pore volume.

Textural stratifications were obtained using Norge soil with either the Eufaula or Stratford soils in the same column. The soils were packed in a 30 cm long glass column using the same technique used for the non-stratified case. Two stratified soil columns were prepared for each combination in order to study the influence of the direction of flow on herbicide movement.

Two water flow rates selected for the study were: 1.78 cm/hr and 0.112 cm/hr, the latter is 16 times slower than the former. The average pore water velocity was obtained for each column by dividing the soil-water flux by the soil-water content by volume.

CHAPTER IV

RESULTS AND DISCUSSION

The amount of fluometuron and prometryne absorbed by each of the four soils is shown in Figures 2 and 3. For all the soil and herbicide combinations, the amount of herbicide adsorbed increased linearly with subsequent increases in the supernatant concentration. The slope of the lines in Figure 3 illustrates the greater amount of prometryne adsorbed as compared to fluometuron for the same soils. Norge loam exhibited with the greater adsorption for both herbicides, this was expected owing to the larger organic matter and clay content and CEC. Eufaula adsorbed the least amount of prometryne and fluometuron, probably due to its lower organic matter and clay content.

The 200 ml volume of 0.01 N $CaCl_2$ that containes the herbicides fluometuron or prometryne was equivalent to applying 13.4 kg/ha (12 lb/A) to the soil surface. This is similar to a field situation where the herbicide is being dissolved and displaced through a saturated soil at a constant flow rate. Chloride and fluometuron concentration distributions in 15 cm long columns of Eufaula loamy fine sand and Norge loam are presented in Figures 4 and 5, respectively. The chloride concentration curves show similar shapes for both soils with the distribution (near piston displacement) displaced to the left of the bulls eye. This displacement to the left results from some pore spaces not contributing to the transport process; therefore, the pore volume

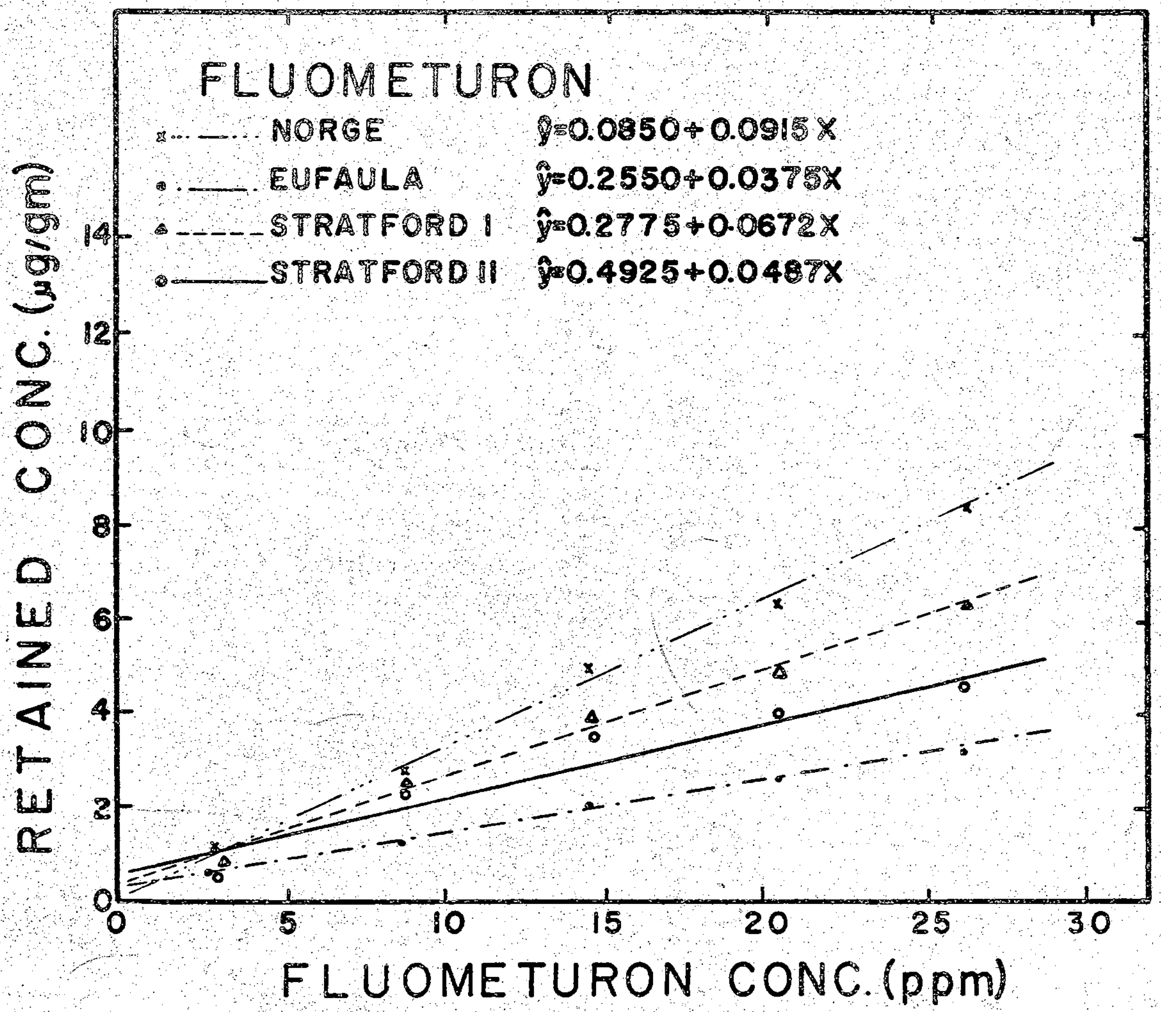

Figure 2. Adsorption of Fluometuron on Calcium-saturated Norge, Eufaula, Stratford I and Stratford II Soils.

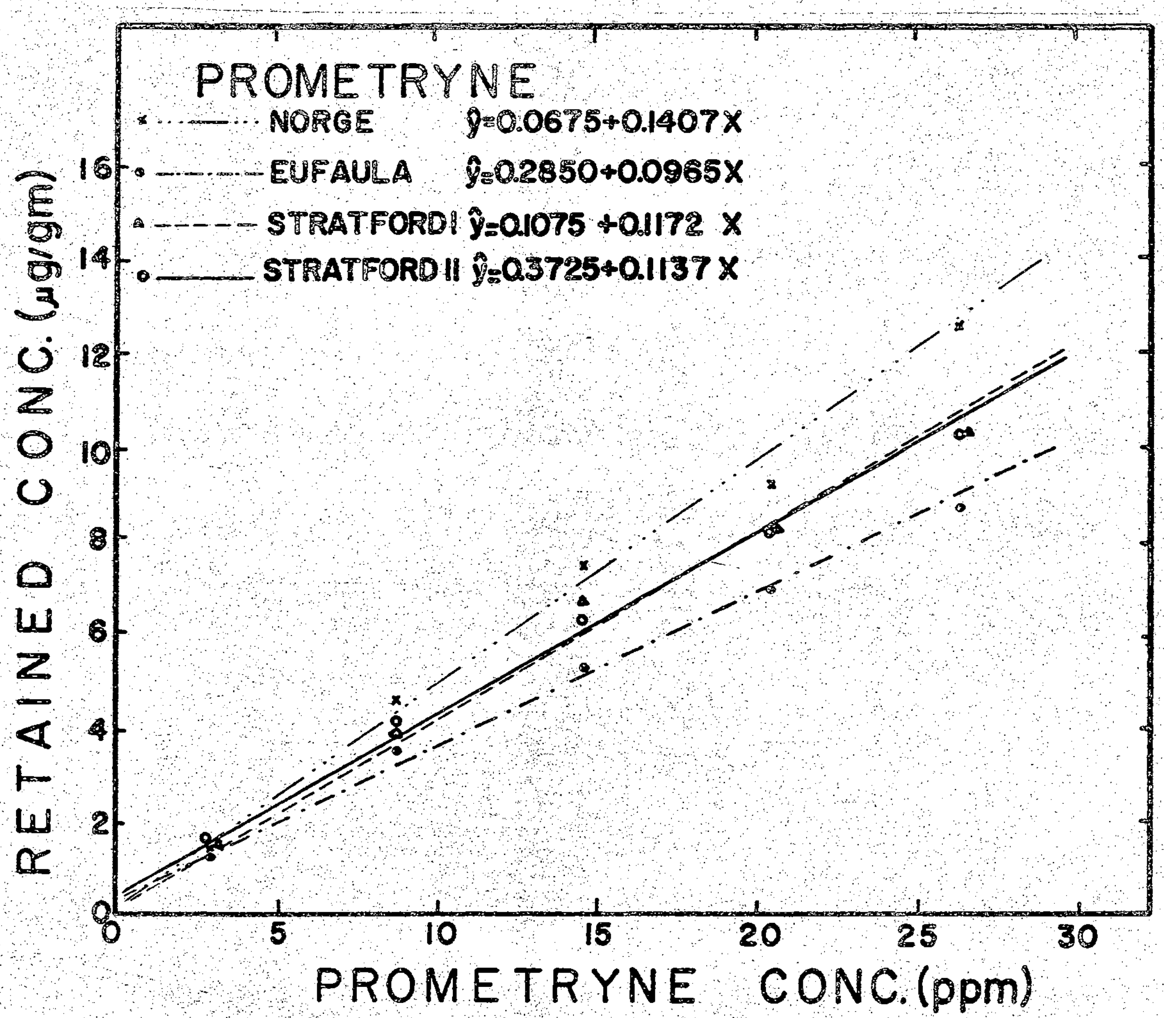

Figure 3. Adsorption of Prometryne on Calcium-Saturated Norge, Eufaula, Stratford I and Stratford II Soils.

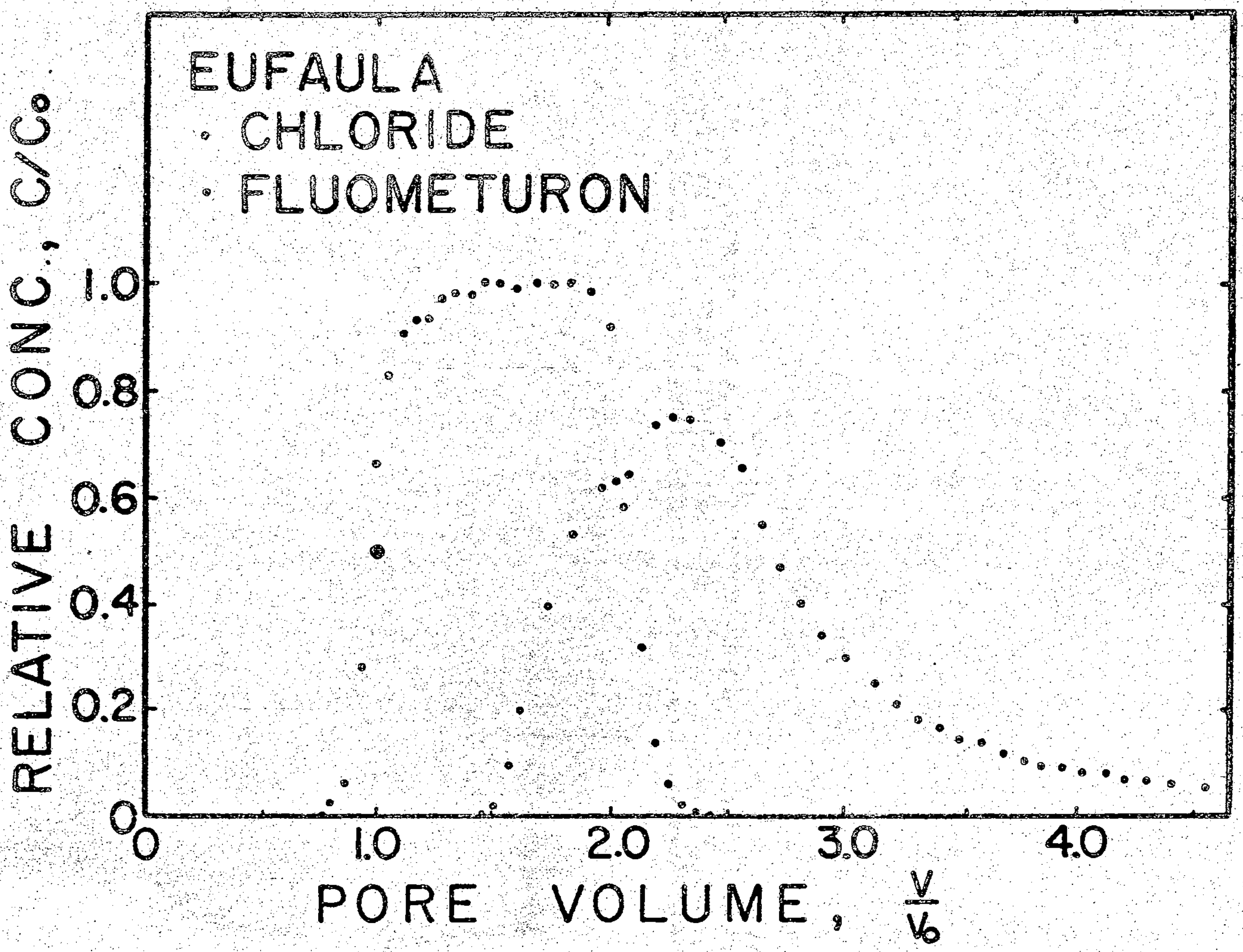

Figure 4. Relative Chloride and Fluometuron Concentration Distributions from 15 cm Long Saturated Eufaula Loamy Fine Sand Soil with a Water Flux of 1.78 cm/hr.

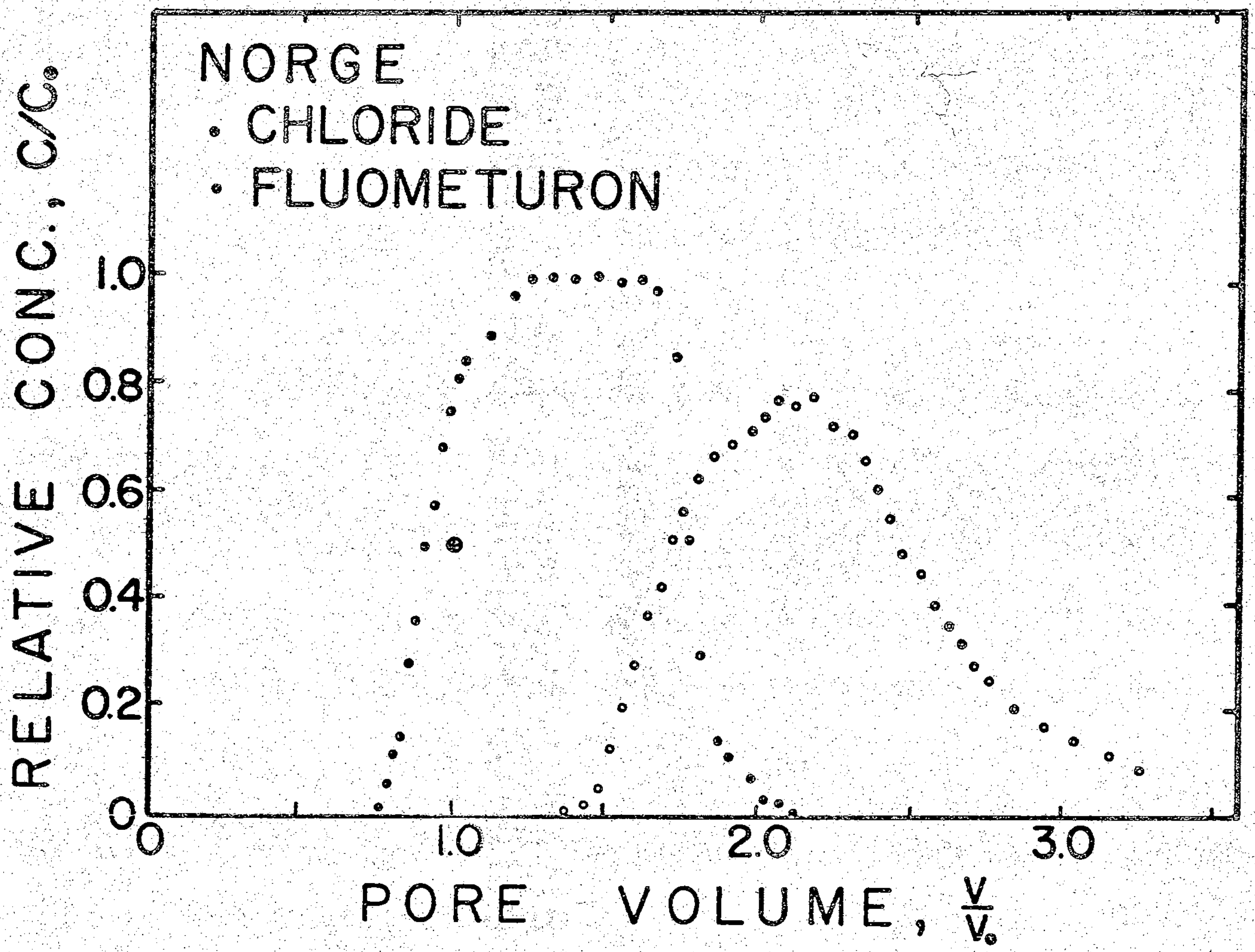

Figure 5. Relative Chloride and Fluometuron Concentration Distributions from 15 cm Long Saturated Norge Loam Soil with a Water Flux of 1.78 cm/hr.

measured by oven drying is not the true pore volume of the flowing system. This displacement to the left is not attributed to molecular diffusion (32) due to the fact that the pore water velocity was greater than 5 cm/hr for both soils.

Relative fluometuron concentration distributions for both soils are also presented in Figures 4 and 5. These results show a similar shape for both soils and are displaced to the right indicating herbicide retention or adsorption by the soil. The 0.8 relative concentration was obtained after 2.3 pore volumes had been displaced through the soil columns.

The mixing and retention of fluometuron in 30 cm long columns of Norge and Eufaula soils are presented in Figures 6 and 7, respectively. Chloride concentration distributions are displaced to the left of the bulls eye in both cases with a larger displacement occurring in the Norge soil. As the length of the column doubled, the curve displacement from the bulls eye appears to double. There is no significant differences in the shape of the two chloride curves when the two soil lengths are compared.

Fluometuron concentration curves are displaced to the right of the bulls eye having a peak relative concentration rear 0.6. The curve displacement and lowered peak for the fluometuron, when compared with the 15 cm columns, indicates the greater number of adsorption sites for herbicide in the longer column. If the two curves were displaced to the right until the chloride concentration distribution passed through the bulls eye in Figures 4, 5, 6, and 7, the maximum fluometuron concentration would occur between 2.0 and 2.1 pore volumes for Norge and Eufaula. This suggests that for the flowing system there was no

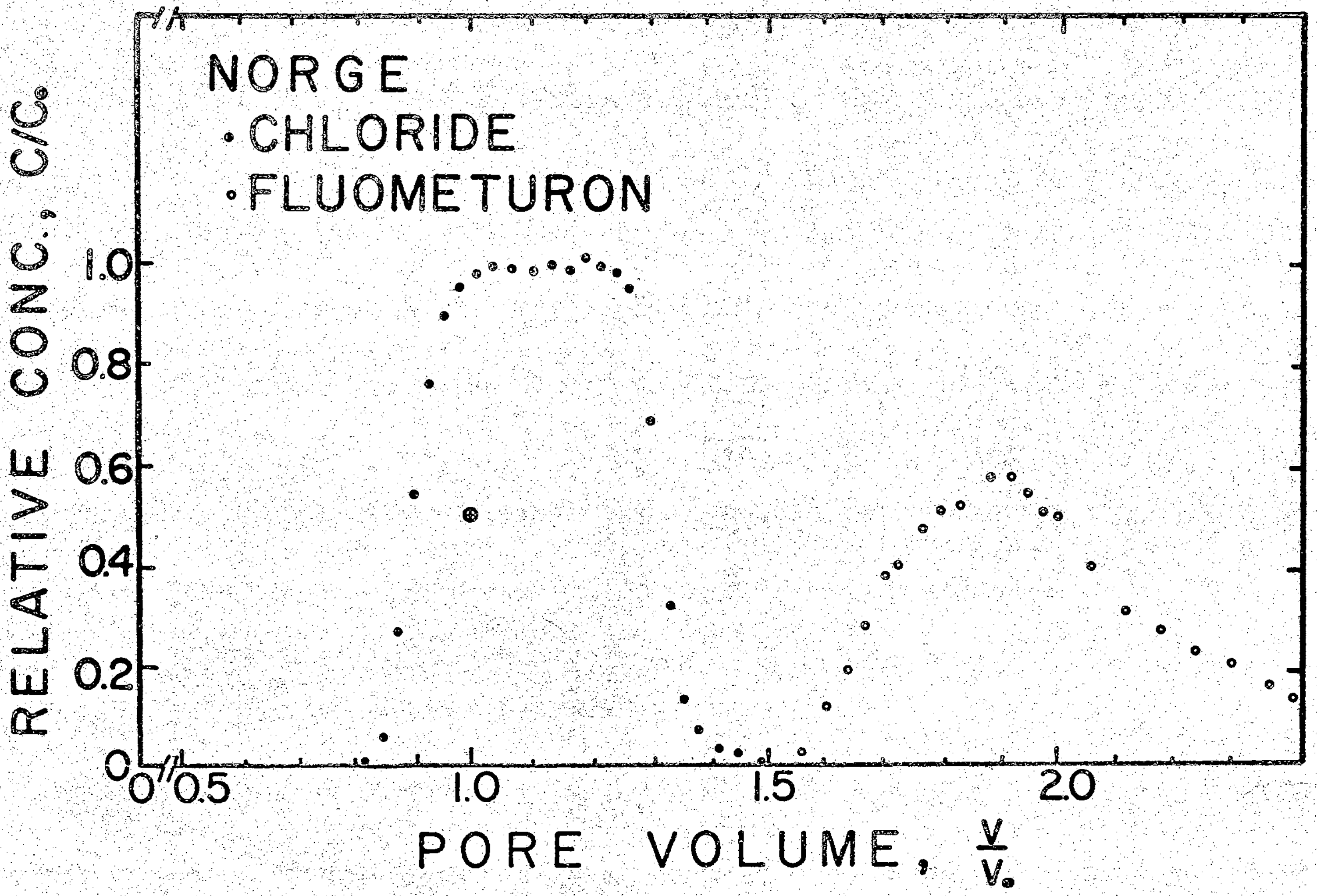

Figure 6. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Norge Loam Soil with a Water Flux of 1.78 cm/hr.

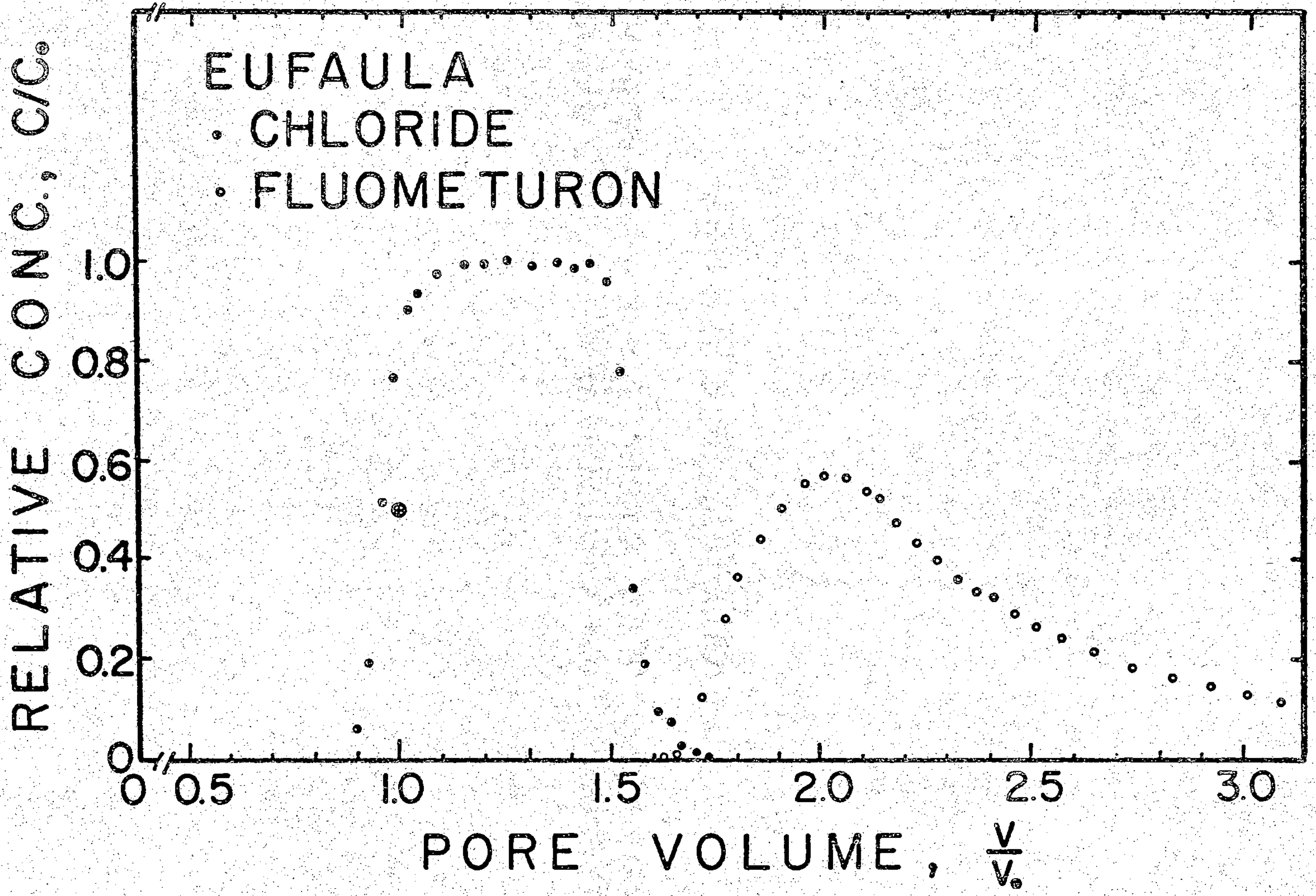

Figure 7. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Eufaula Loamy Fine Sand Soil with a Water Flux of 1.78 cm/hr.

significant differences in the amount of herbicide adsorption.

A comparison of the relative chloride and fluometuron concentration distributions for Stratford I and Stratford II is shown in Figures 8 and 9, respectively. In Figure 2 the fluometuron isotherm results show less adsorption for Stratford II than that for Stratford I. The lower relative concentration of fluometuron in Stratford II (Figures 9) compared with Stratford I (Figure 8) is not the result of a higher retention or adsorption, but of the dispersion phenomena. The lower peak and earlier arrival of chloride and fluometuron in Stratford II is caused by the more complex pore geometry of this soil. Visually Stratford II has a larger aggregation than Stratford I; therefore, a greater possibility existed for a wide range of pore sizes in the packed column. When a herbicide in a 0.01 N $CaCl_2$ solution was displaced by 0.01 N $CaSO_4$, the interface between the two solution was gradually and continually changing due to the fluids mixing in the porous media. The mixing process in a soil is due to a continuous variation in pore-water velocities and the tortuous path through which the solute moves. This allows some molecules (or solvent) to arrive at the effluent point earlier than others moving through smaller pores and more tortuous paths. The transitional front that is formed between herbicide solution and $CaSO_4$ in the Stratford II soil column results in a flatter chloride and herbicide relative concentration distribution with an early arrival initially and a tailing off after the maximun concentration has been reached.

In those soils that present wider differences in particle sizes and aggregation, a possibility exists for a wider range of pore water velocities. When the solution flows into this system (i.e., Stratford

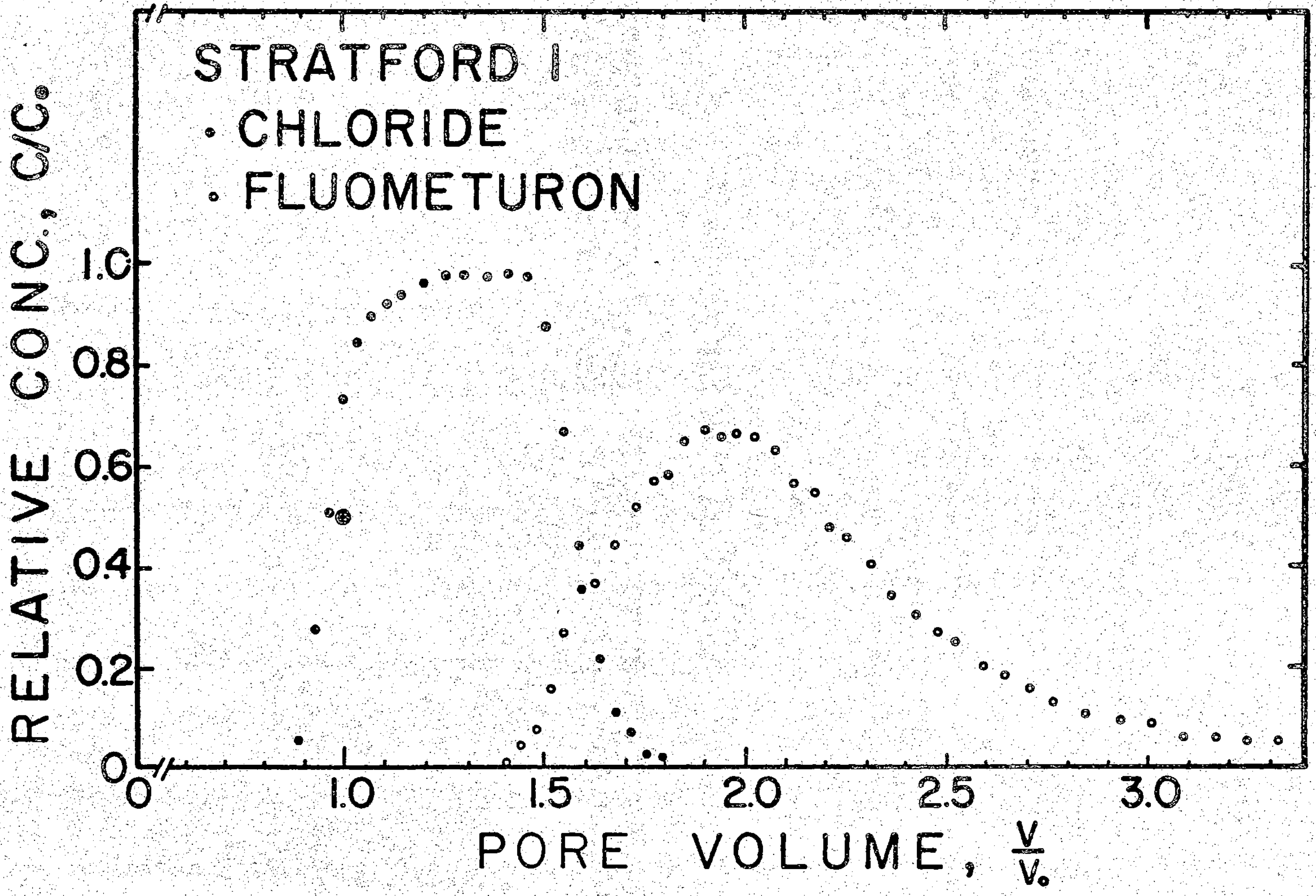

Figure 8. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Stratford I Soil with a Water Flux of 1.78 cm/hr.

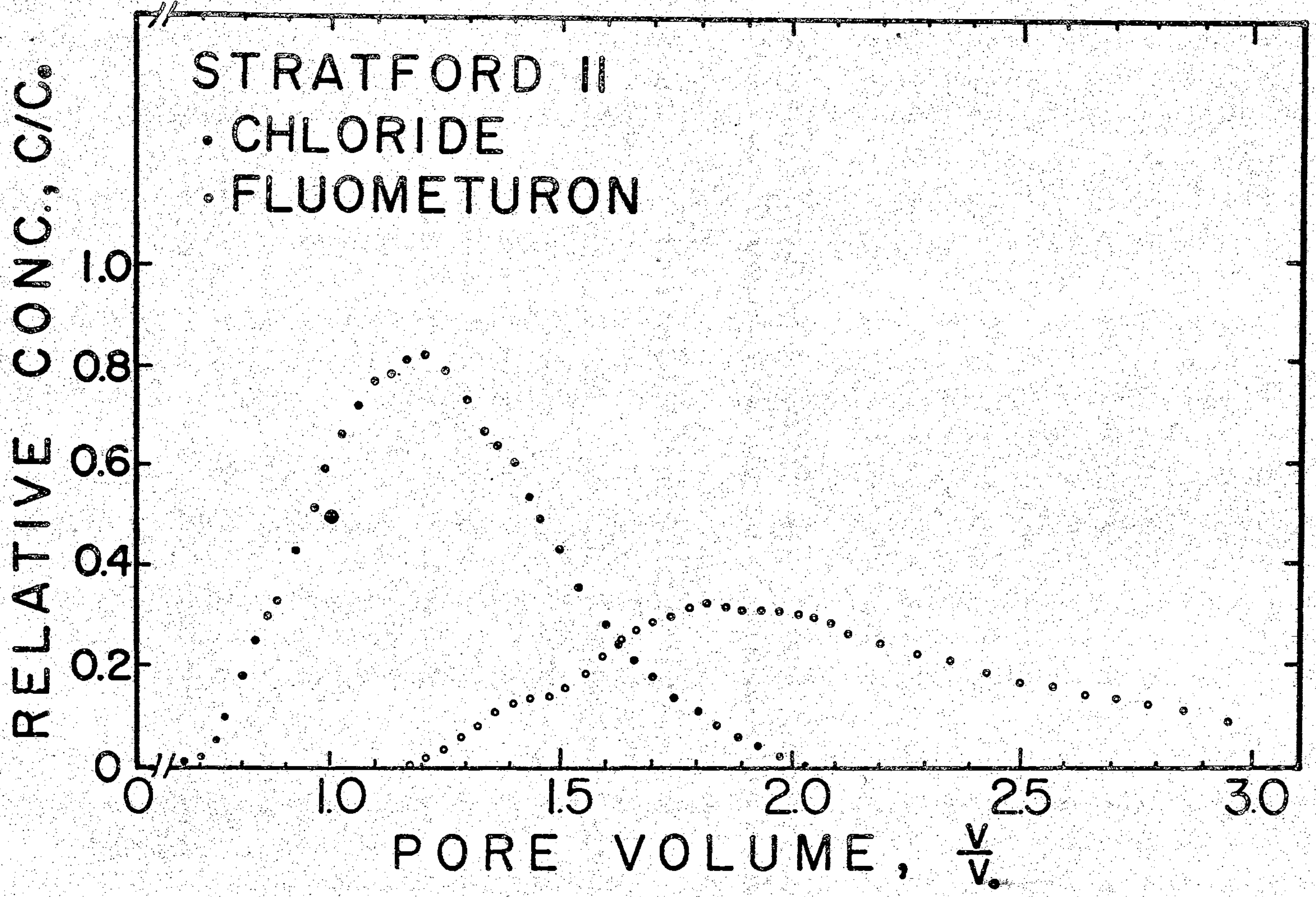

Figure 9. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Stratford II Soil with a Water Flux of 1.78 cm/hr.

II) the pore velocities are quite differente, with higher values in larger pores and non-tortuous paths as compared with lower pore velocity in small pores and tortuous paths.

Relative chloride concentration curves for all soils used in this study were displaced to the left of the bulls eye, indicating a portion of the porosity not available for solution displacement. The amount of space occluded to water movement was larger for Norge soil; 11.2% of the total porosity. Available mathematical models, derived from chromatography theory, do not describe solute movement through such soil columns (10).

Relative fluometuron and chloride ion concentration distributions for a stratified soil column composed of Norge loam and Eufaula fine sandy loam are illustrated in Figure 10. Figure 11 shows similar curves for the reverse arrangement of the two materials. It can be seen that the amount of porous material not available for solution displacement is about an average of the values found with Norge and Eufaula independently. The distribution curves have similar shapes with the left leg of the fluometuron curve, in Norge-Eufaula stratification having a greater slope and arriving at a higher peak; however this difference is not sufficient to say conclusively that there was any significant difference. It should be noted that Norge has a 34.5% water content by volume and 5.14 cm/hr average pore water velocity. The values for Eufaula soil were 26.1% and 6.81 cm/hr. If we consider only the pores where the solution is flowing, in the Norge soil, the values are 31.0% and 5.74 cm/hr for water content and average pore water velocity, respectively. These new values show less differences compared with those obtained for the Eufaula soil. This assists in explaining

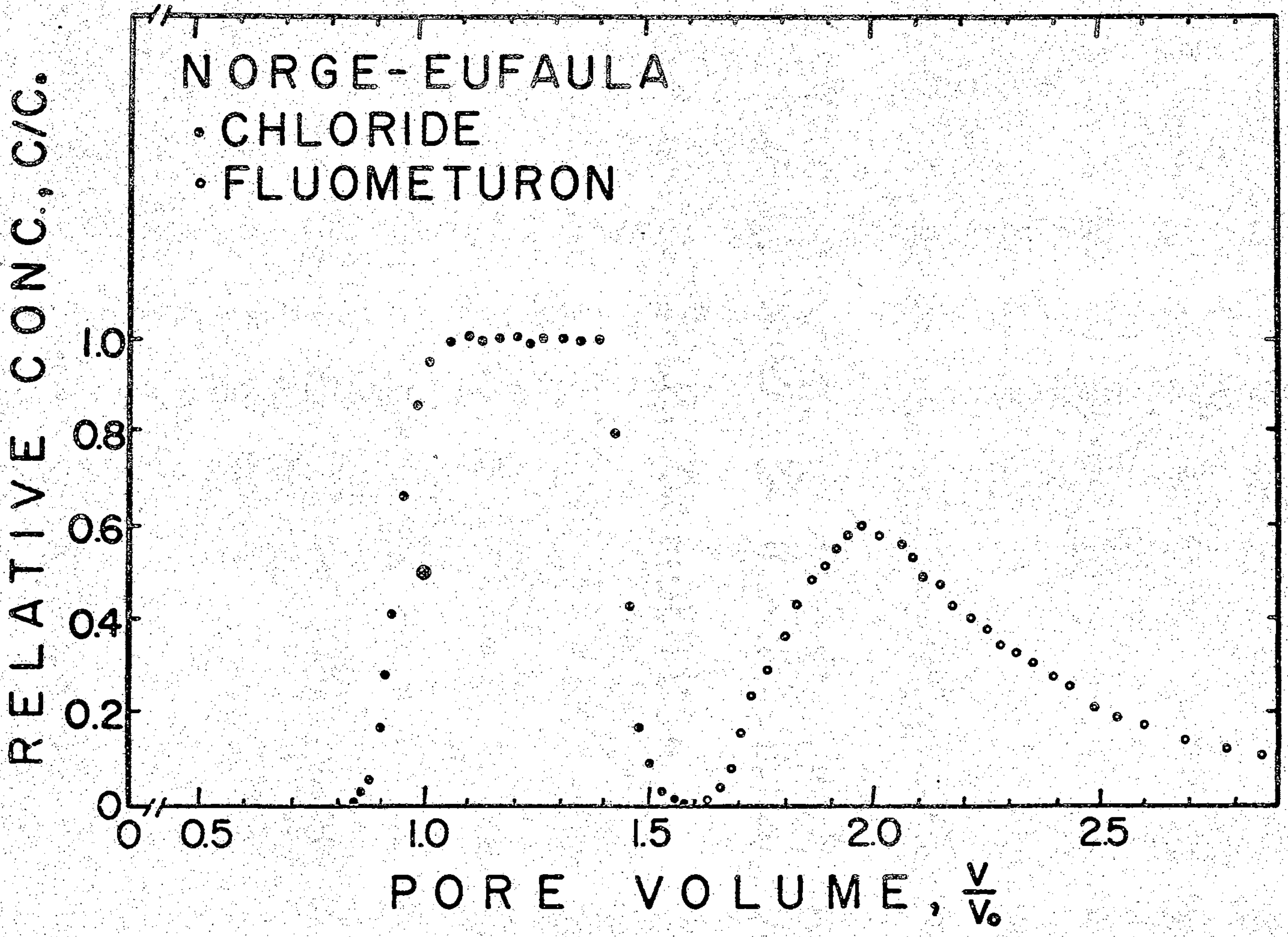

Figure 10. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Norge-Eufaula Stratified Soil with a Water Flux of 1.78 cm/hr.

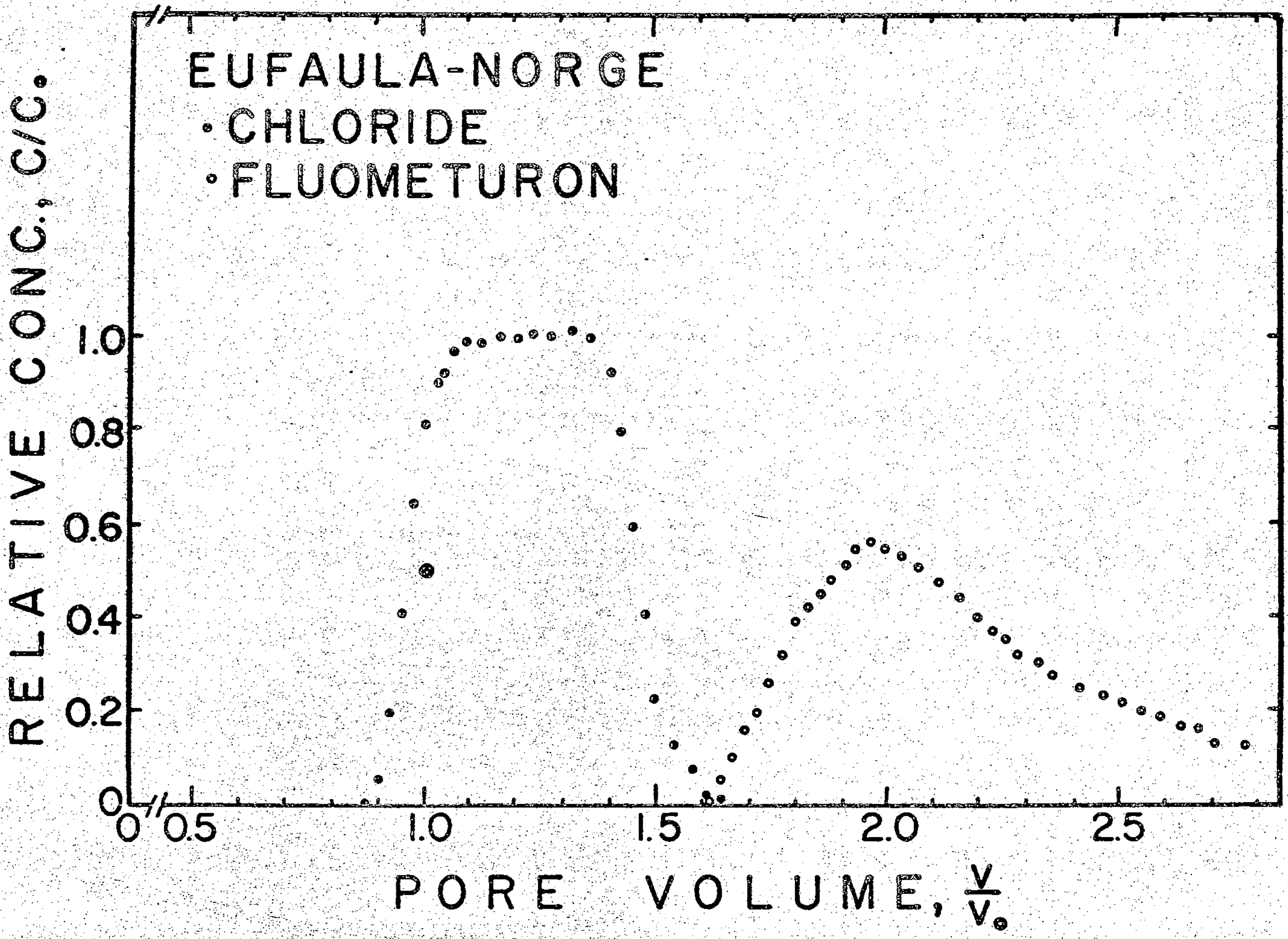

Figure 11. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Eufaula-Norge Stratified Soil with a Water Flux of 1.78 cm/hr.

in part the similar shape that the two distribution curves presented.

Pleshek (35) studying dispersion in linear heterogeneous porous media concluded that there was a significant effect of pore arrangement on dispersion. However, he noted no significant effect upon dispersion when one arrangement and its reverse were considered. The same conclusion was obtained for the stratified column with Norge-Eufaula and it's reverse.

Figures 12 and 13 show the relative concentration distributions for the chloride ion and fluometuron in a Norge-Stratford I stratified column and its reverse respectively. When the sequence of soil was Norge-Stratford I, there could be detected a peak of fluometuron curve, at 1.9 pore volume, higher than that found in the reverse arrangement, but this difference is not large enough to be considered significant. The porosity change was 34.5% in Norge to 24.3% in Stratford I and the average pore water velocity 5.14 cm/hr to 7.32 cm/hr, respectively.

The left leg of the chloride and fluometuron curves for Stratford I and Norge, as indicated in Figures 12 and 13, are shifted to the left of those curves obtained from the Eufaula and Norge stratifications. This is not due exclusively to the retention process, as dispersion has a significant role owing to the more complex pore geometry that exists in Stratford I. This result could not be anticipated from the fluometuron isotherms, where Stratford I present a greater slope than Eufaula. For Figures 7 and 8 the fluometuron concentration in the effluent for Stratford I was detected more than 0.2 pore volumes earlier than fluometuron in Eufaula soil column. A more square chloride concentration distribution was obtained in the stratified columns of Norge-Eufaula than when Norge-Stratford I combination was used.

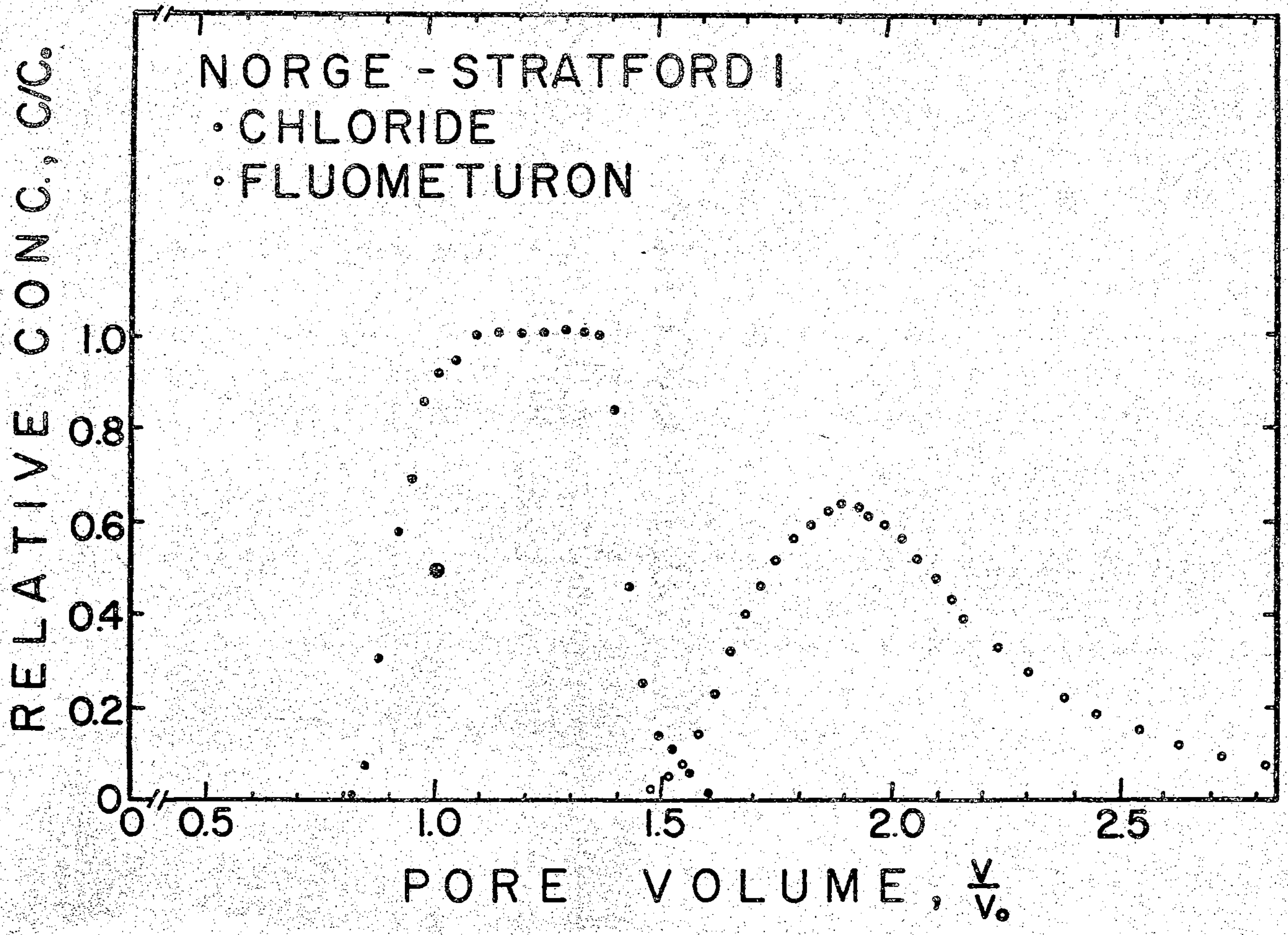

Figure 12. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Norge-Stratford I Stratified Soil with a Water Flux of 1.78 cm/hr.

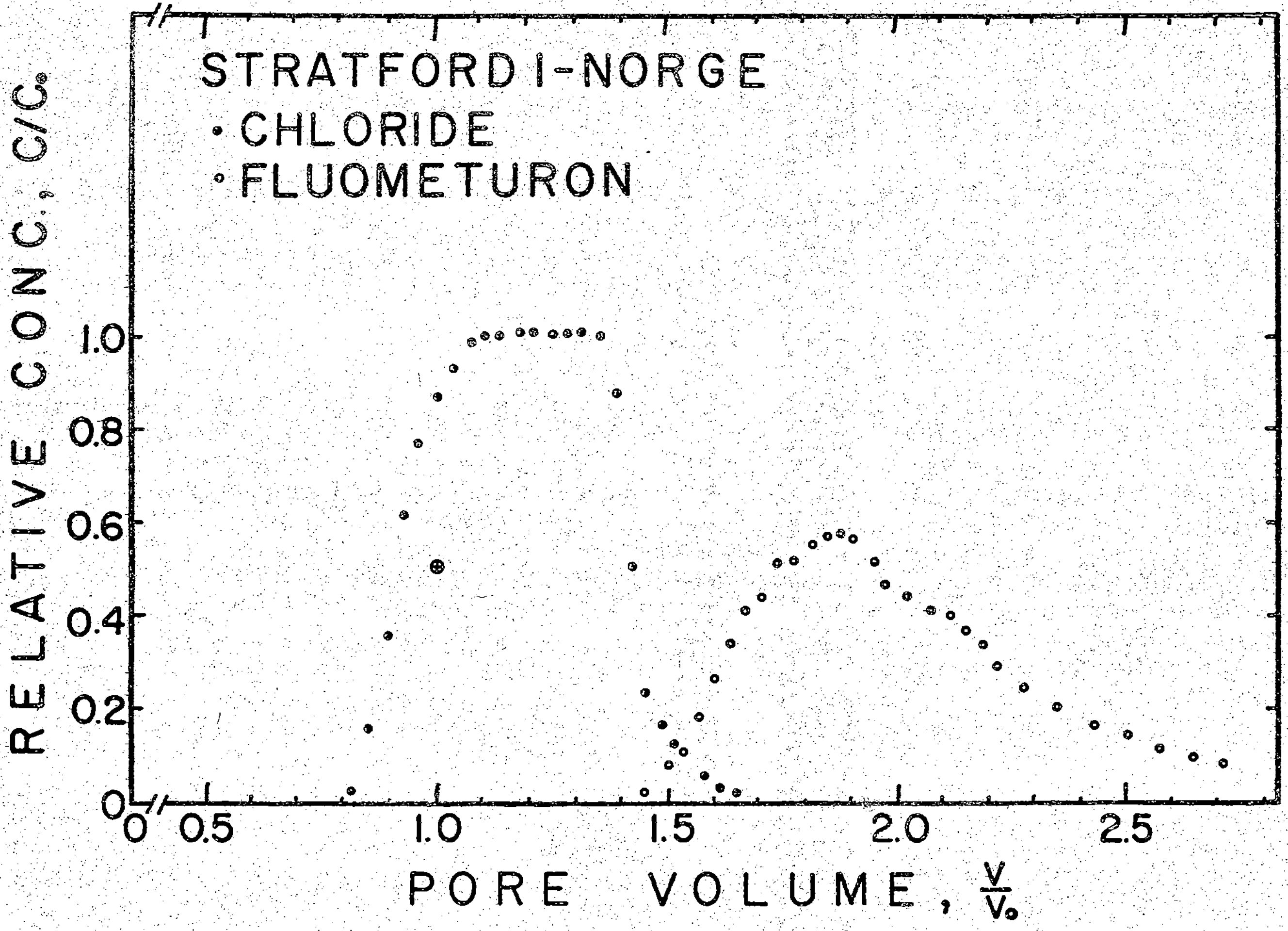

Figure 13. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Stratford I-Norge Stratified Soil with a Water Flux of 1.78 cm/hr.

The effluent concentration distribution obtained for chloride and fluometuron for the Norge-Stratford II stratification and it's reverse are shown in Figures 14 and 15. The differences shown by these curves imply that the order of stratification is of importance to ion and herbicide movement.

Niemann (33) studied dispersion during flow in non-uniform heterogeneous porous media constructed of different size glass beads and concluded that there was a significant effect due to the packing technique used in the constructing of the porous media. He also stated that the dispersion coefficient for a given stratification and its reverse are approximately equal.

Lenth (29) studied permeability in an octogonal model layered with difference size glass beads. This procedure allowed the solution to be introduced into the porous media from the different sides alternatively. He concluded that when a solution entered the system such that the face contained only one bead size no path choice existed, and therefore, the permeability was the same. However, when water entered the system such that more than one bead size was present on the face a choice in path existed and the permeability changed and the dispersion coefficient increased in the direction of decreasing permeability. A lower dispersion was obtained when the permeability was high.

The porosity and average pore water felocity were 34.5% and 5.14 cm/hr, respectively, for Norge and 27.3% and 6.52 cm/hr respectively for Stratford II. These amounts show that the difference between Norge loam and Stratford II are less than Norge compared to Eufaula or Stratford I. The porosity of Norge is 30% higher than Stratford I and 20.9 % higher than Stratford II. Since the order of stratification is

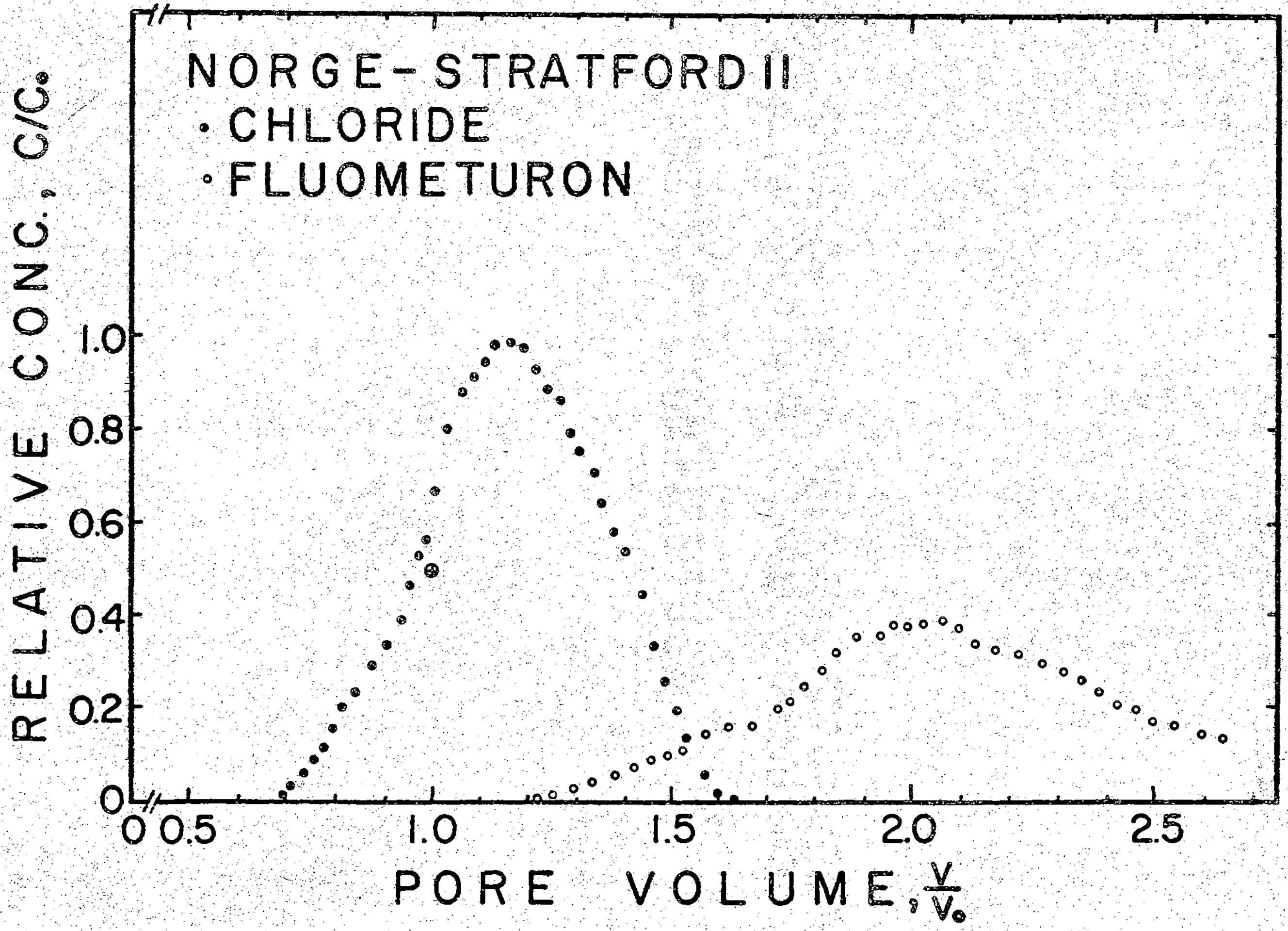

Figure 14. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Norge-Stratford II Stratified Soil with a Water Flux of 1.78 cm/hr.

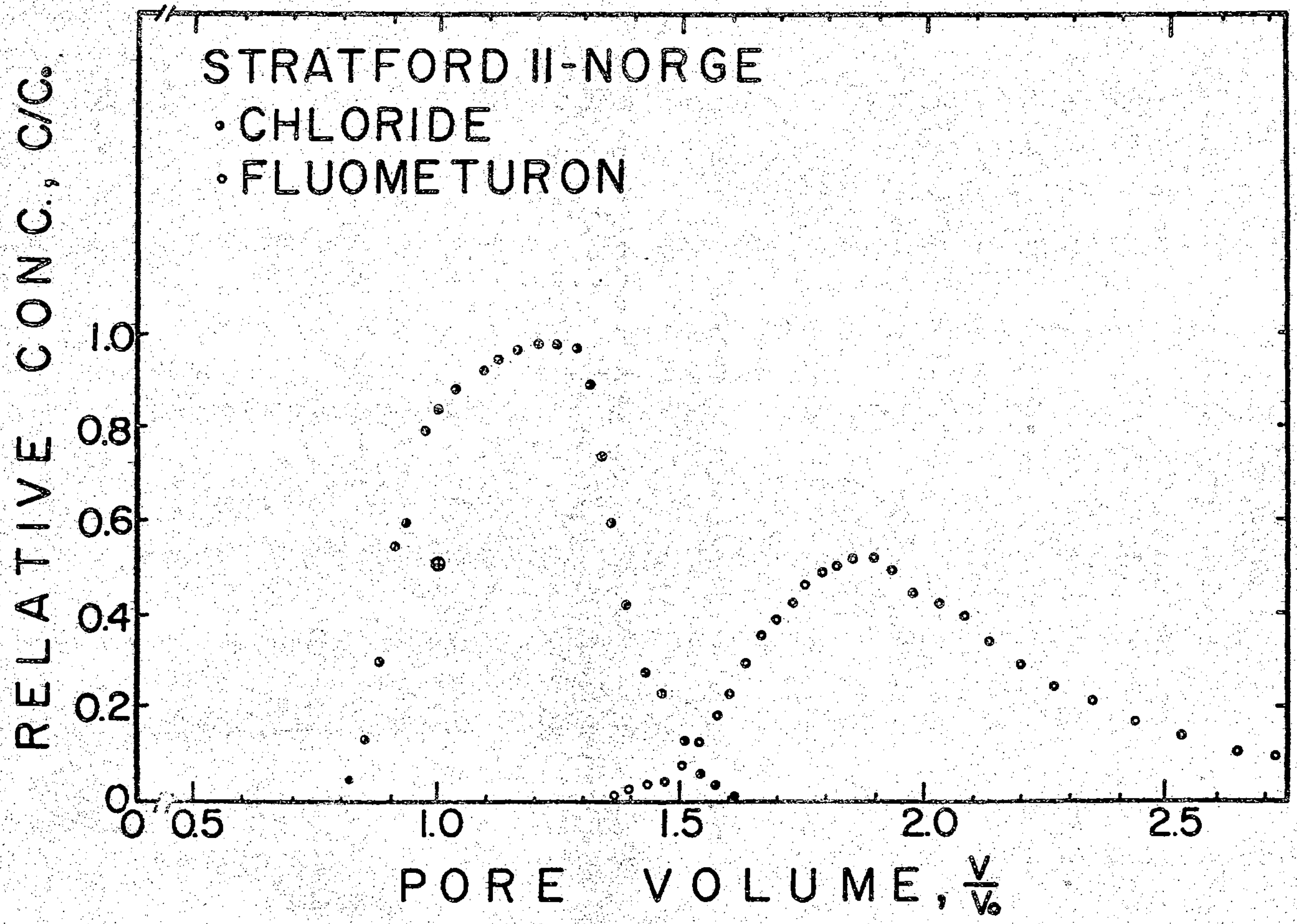

Figure 15. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Stratford II-Norge Stratified Soil with a Water Flux of 1.78 cm/hr.

important for Stratford II and Norge, but no significant difference was observed for Stratford I and Norge, it was concluded that the effluent concentration was independent of the differences in porosity of the two materials present. The Stratford I has a more homogeneous pore size distribution, and constant pore-water velocity, which results in less dispersion in this soil (Figure 8) as compared to that obtained with Stratford II (Figure 9).

Of all the soils studied, Stratford II showed the greatest dispersion. Pleshek (35) points out that the displacement of one solution by another fluid filling the voids in a porous media does not result in a sharp plane of a given concentration. Some molecules show up earlier because they traveled at a greater pore velocity than the average velocity and a less tortuous path or a combination of both. Some particles show up late due to an inverse behavior in a porous media.

For all experiments considered, the water flux was constant, 1.78 cm/hr, and at the high soil water flux the molecular diffusion of chloride ions and fluometuron molecules was considered negligible. The differences in effluent concentration distribution for these two materials in different soils were attributed partially to the retention processes; however, of greater importance is the variation in the complex pore geometry that the soils present which influences the dispersion process. This spreading is influenced by the physical characteristics of the media, the flow velocity, and the distance traveled.

Figure 16 shows the relative concentration distribution for the chloride ion and fluometuron in a Norge-Stratford II stratified column at a soil-water flux of 0.112 cm/hr. Figure 17 shows the same for the

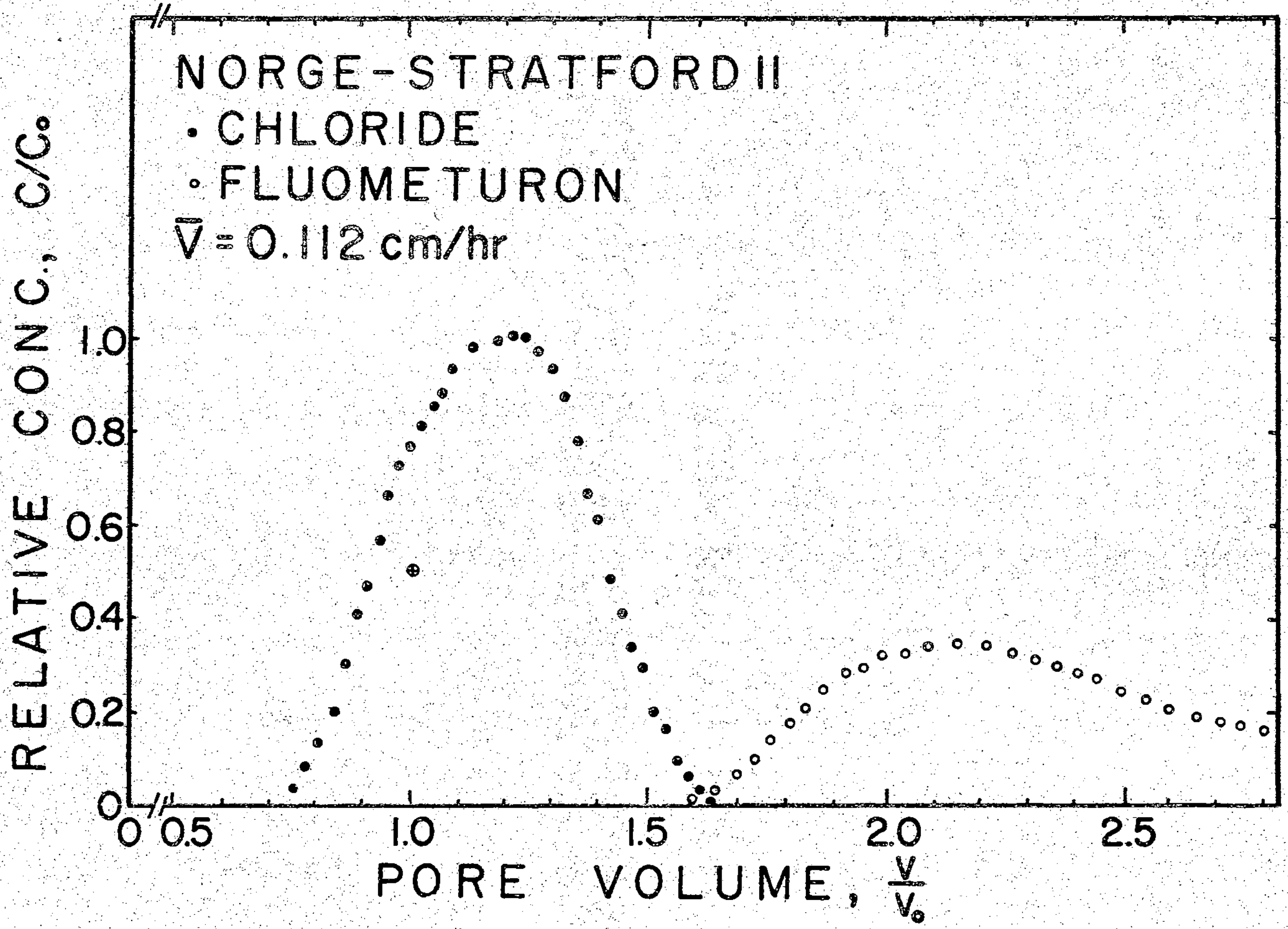

Figure 16. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Norge-Stratford II Stratified Soil with a Water Flux of 0.112 cm/hr.

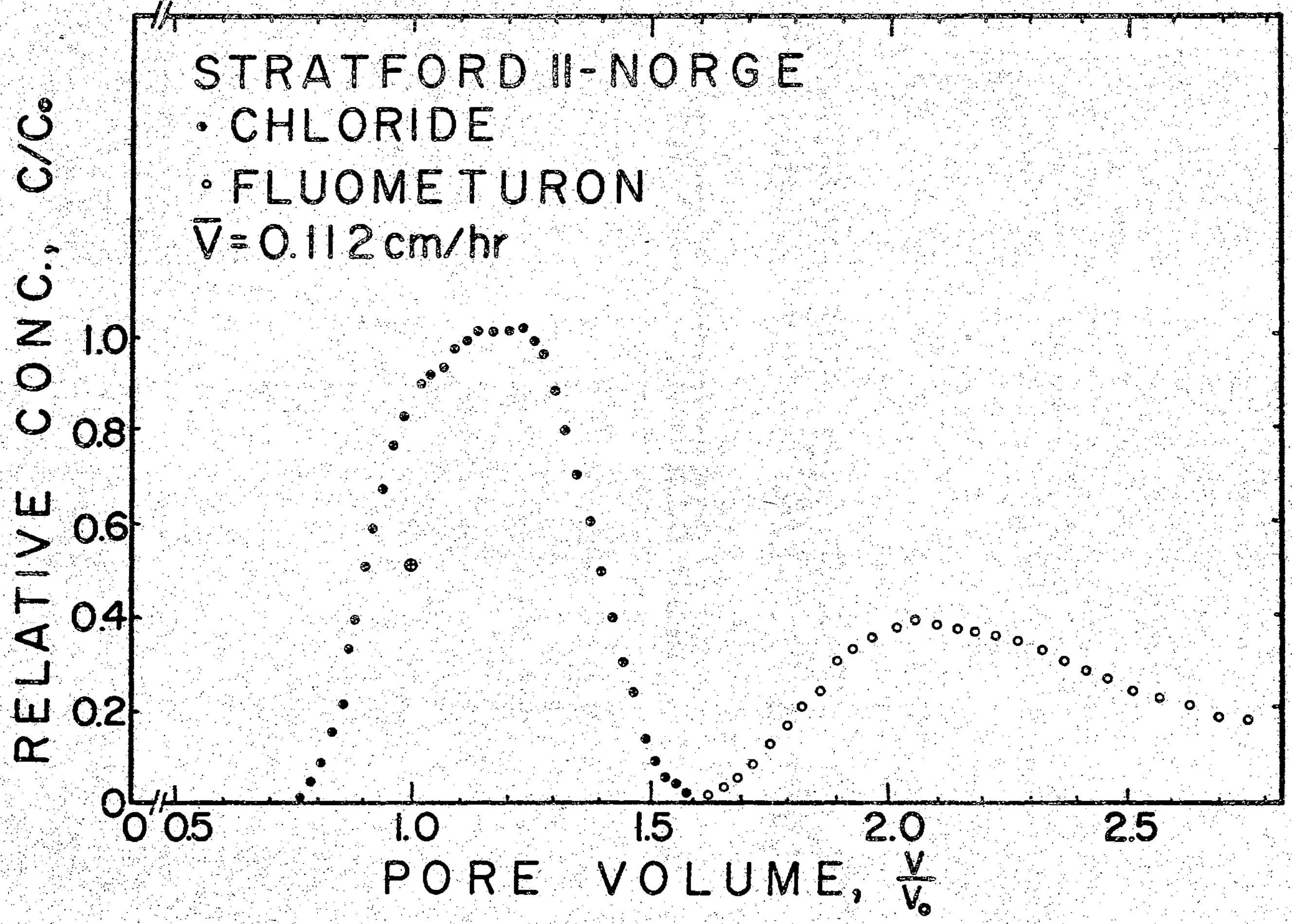

Figure 17. Relative Chloride and Fluometuron Concentration Distributions from 30 cm Long Saturated Stratford II-Norge Stratified Soil with a Water Flux of 0.112 cm/hr.

reverse stratification. As the water flux was reduced 16 times, molecular diffusion should be an important factor in the effluent concentration distribution for the two materials studied in these experiments. A comparison of these curves with those at the higher water flux illustrate significant differences, in fluometuron particularly.

Chloride curves are "more square" for the lower water flow rates than for the higher flow rates. The later arrival of fluometuron in the effluent (Figure 16 and 17) also illustrate the lower dispersion produced at lower water flux. The molecular diffusion was expected to be more important at 0.112 cm/hr water flux, than at 1.78 cm/hr water flux. The greater shift of the chloride curves to the left of the bulls eye may, however, be the result of molecular diffusion.

When Figures 16 and 17 are compared, an earlier arrival of the chloride ion and fluometuron molecule in the effluent is detected for the Norge-Stratford II stratification as compared to the reverse case. Thus, the slower soil-water flux case gives similar results to those obtained for the higher water flux. These differences are reduced, however, when the water flux was decreased 16 times.

A quantitative comparison of the retention and movement of fluometuron and prometryne in Norge is shown in Figure 18. Two independent experiments were conducted using similar soil columns. The chloride concentration distribution (Figure 18) were almost identical. Herbicide curves show a highly significant differences in adsorption and displacement, confirming the fact that prometryne is adsorbed to a greater extent than fluometuron as shown by the adsorption isotherm results presented in Figures 2 and 3. Because the prometryne concen-

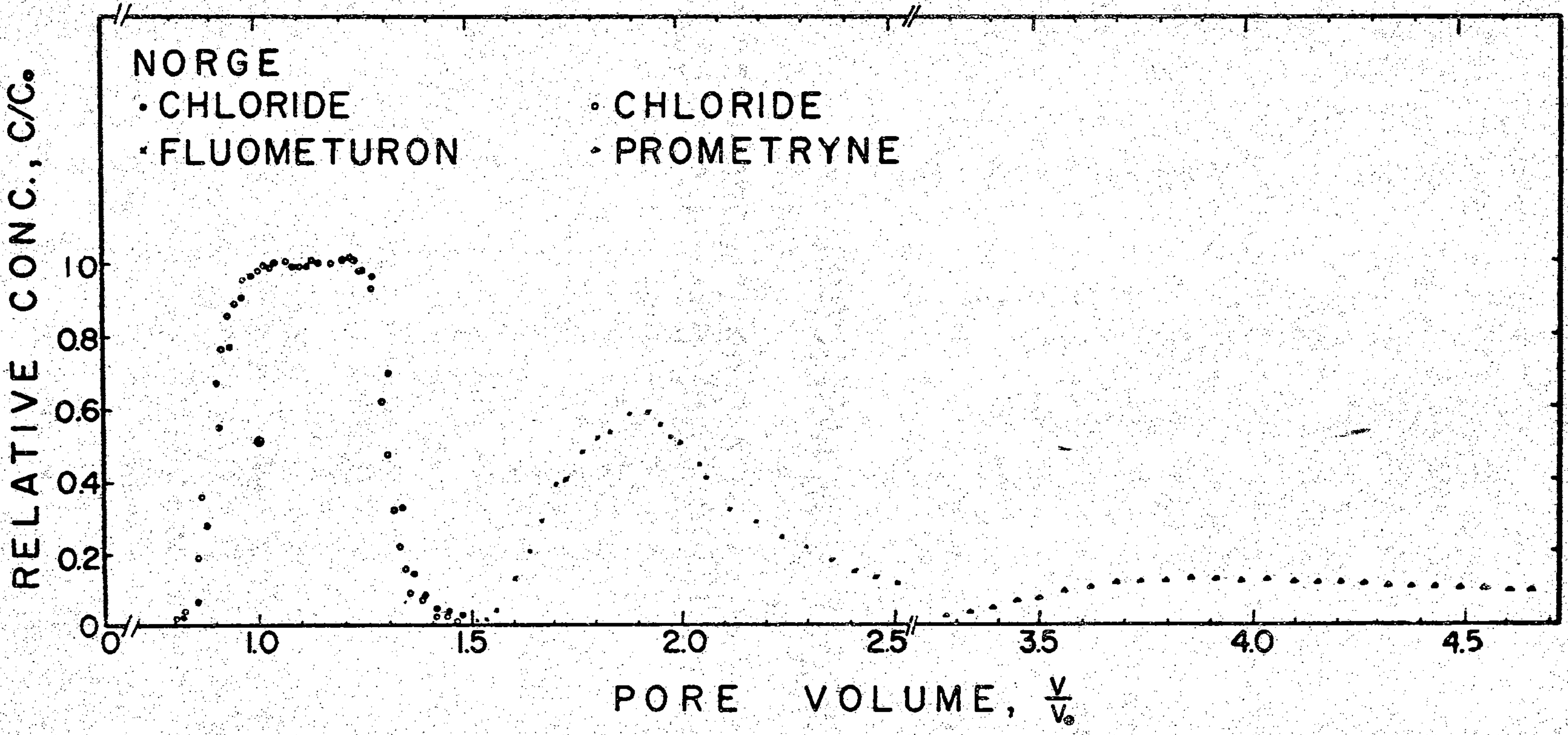

Figure 18. Relative Chlorides, Fluometuron and Prometryne Concentration Distributions from 30 cm Long Saturated Norge Loam Soil with a Water Flux of 1.78 cm/hr.

tration distribution curve is so flat, giving a peak relative concentration of about 0.1 after several pore volumes, this herbicide was not used in the soil stratification study.

The adsorption isotherms for prometryne in Stratford I and Stratford II are shown in Figure 3. Practically the same adsorption of prometryne can be considered for the two Stratford soils for the herbicide concentrations studied. As was emphasized earlier, when discussing Figures 8 and 9, chloride and fluometuron movement through these two soils are considerably different. These differences point out the importance of pore size distribution on the shape and position of the curves. This same difference can be observed for prometryne in Figure 19. In Figure 19 the lower peak and earlier arrival of the chloride ion in the effluent of Stratford II illustrates the larger dispersion mentioned before. A more significant difference is shown by the relative concentration distribution of prometryne. The herbicide was detected in the effluents of Stratford II 1.4 pore volumes in advance that prometryne in Stratford I with a 1.78 cm/hr water flux used in both experiments.

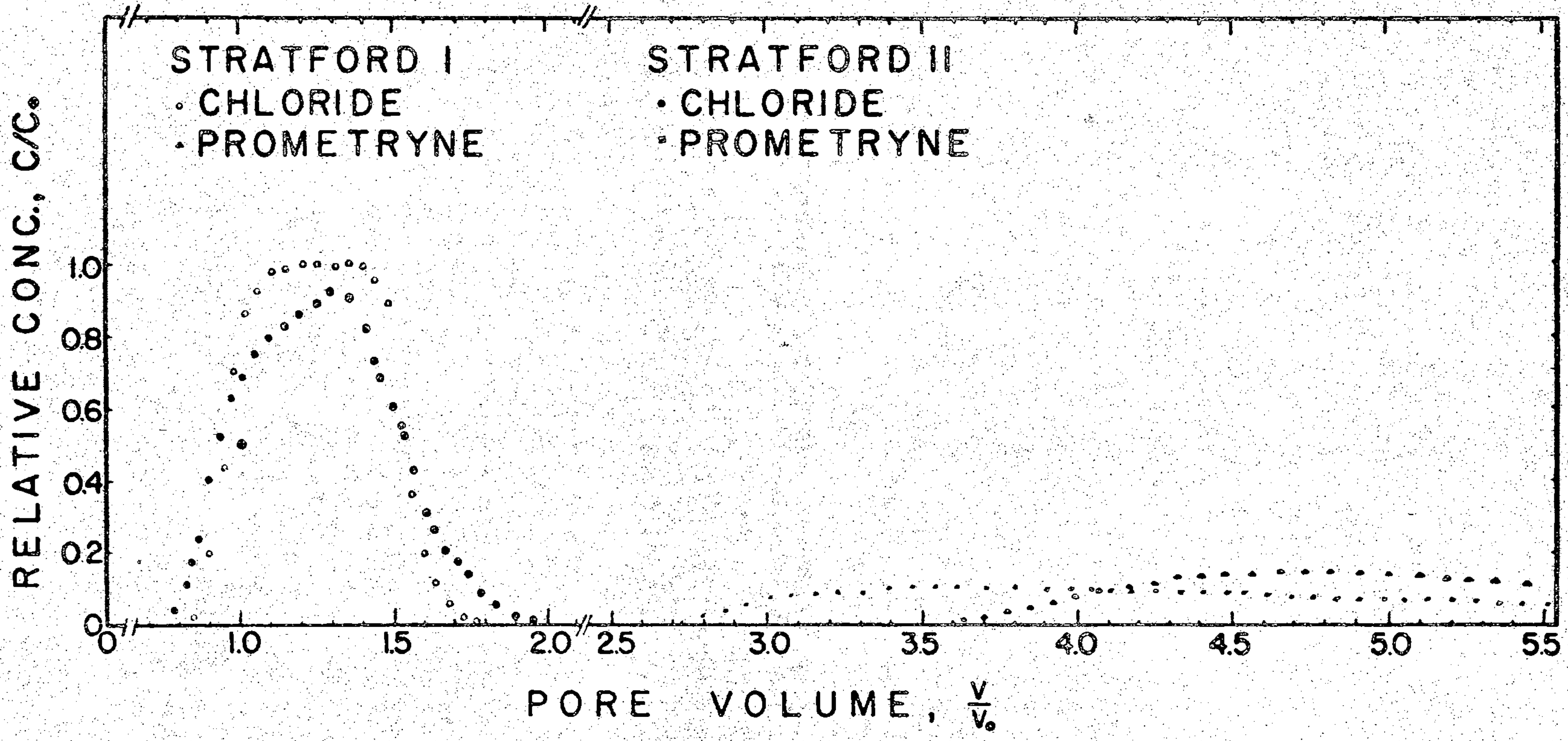

Figure 19. Relative Chlorides and Prometrynes Concentration Distributions from 30 cm Long Saturated Stratford I and Stratford II Soil with a Water Flux of 1.78 cm/hr.

CHAPTER V

SUMMARY AND CONCLUSIONS

The importance of a soil textural stratification on the movement and adsorption of chloride and fluometuron was studied. Also studied were: (1) mobility of two herbicides (fluometuron and prometryne), and (2) the influence of soil textural stratification at two soil-water flow rates.

The major conclusions drawn from the above study are:

1. Prometryne was adsorbed in greater quantities than fluometuron by each of the four soils studied. This was true in both the equilibrium and transient experiments.

2. The relative effluent concentration distributions of chloride and fluometuron from the Norge-Eufaula, and Norge-Stratford I soil stratifications and their reverses do not show differences owing to the direction of flow through the stratification.

3. The relative effluent concentration distributions from the Norge-Stratford II and its reverse stratification are different and dependent on the order of stratification.

4. The most important factor influencing chloride and herbicide movement and their distribution within the soil profile is the range in pore sizes. The greater the pore size distribution the more dispersion or mixing that occurred at the higher soil-water flow rates.

5. Differences in soil porosity of 20 to 30% between soils

apparently had no influence on the chloride and fluometuron relative effluent concentration distribution. However, the pore size distributions for these soils were narrow and produced a minimum amount of dispersion owing to the mass flow process.

6. The two soil-water flow rates illustrated that chloride and herbicide movement are controlled primarily by dispersion at high flow rates. Ion and molecular diffusion played only a small role in the effluent concentration distribution or spreading obtained at the higher flow rates.

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VITA

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