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*Movement and Adsorption of
Pesticides in Sterilized Soil
Columns*

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**MOVEMENT AND ADSORPTION OF PESTICIDES IN STERILIZED
SOIL COLUMNS**

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ABSTRACT

MOVEMENT AND ADSORPTION OF PESTICIDES IN STERILIZED SOIL COLUMNS

Rapid transport of systemic and soil sterilant herbicides in soil during periods of net water flow may decrease the effectiveness of the chemicals to control unwanted vegetation and produce undesirable pollution of the ground water. An investigation of the influence of physical-chemical soil properties upon the transport of 2,4-D and paraquat in columns of organic and sandy soils was therefore performed. These herbicides are water soluble organic chemicals which are used extensively in agriculture. The toxicant portions of 2,4-D and paraquat behave as anion and cation, respectively. Miscible displacement of aqueous solutions of these herbicides through columns of Everglades mucky peat resulted in most of the 2,4-D and all of the paraquat being removed from solution by adsorption. Limited transport of 2,4-D was observed for the same fine sands. Very small quantities of organic matter in the fine sands effectively removed paraquat from the flowing soil solution. The presence of large concentrations of KCl in the soil solution was observed to decrease the quantity of paraquat sorbed. Mathematical transfer function theory was used in connection with statistical hydrodynamics to develop a technique for analysis and prediction of herbicide elution from soil columns during miscible displacement experiments.

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water pollution/ ground water.

SUMMARY

Chemicals applied to crops or soils for the purpose of killing weeds may be classified as contact, systemic or soil sterilant herbicides. Contact materials require direct application to foliage of the target plants; whereas, systemic chemicals may be applied directly to foliage or indirectly to the soil. Systemic herbicides may be absorbed through leaves or roots and may be translocated through the entire plant system. Soil sterilants prevent plant growth when present in the soil. Thus, most herbicides used in agriculture reach the soil, whether by direct application or indirectly as residual loss from spray applications to the plant leaves. During periods of rainfall or irrigation these chemicals may move with water downward through the soil. If an herbicide moves through the soil profile to the water-saturated zone beneath the water table, the groundwater may become contaminated. The objective of this research project was to evaluate the influence of specific physical-chemical properties of the soil environment upon movement and consequent adsorption of 2,4-D and paraquat herbicides in agricultural sands. Properties investigated were water flow velocity, initial soil water and soil organic matter content.

Paraquat and 2,4-D chemicals were selected for this research because of their extensive use as contact, systemic and soil sterilant herbicides. Both are highly water-soluble; therefore, they are suspects for leaching and movement through soils. In aqueous solution, however, paraquat and 2,4-D molecules respectively, form organic cations and anions, which are highly toxic to plants. As these ions move in water through the interconnected pores of soils, retention may occur as physical and chemical sorption to the pore walls. For soils high in clay mineral or organic matter content the divalent cation of paraquat is very strongly adsorbed. Adsorption of the 2,4-D anion is much less than for paraquat.

A technique based upon statistical hydrodynamics and Laplace transfer function theory was developed to mathematically describe the movement of herbicides or other solutes through columns of soil. For miscible displacement of herbicide solutions, through columns, experimentally determined breakthrough curves (concentration of herbicide in the effluent as a function of time) may be used to calculate a transfer function for a known influent application function. The transfer function is characteristic of the specific soil flow system, and it indicates how the influent concentration function is modified to give the effluent concentration function during displacement through the soil. From the transfer function the value of the coefficient of hydrodynamic dispersion (includes effects of convection, diffusion, and retention mechanisms such as adsorption) may easily be calculated. The

transfer function technique also provides a means to predict breakthrough curves (or effluent concentration functions) of a given herbicide for a given soil when the dispersion coefficient, the flow velocity, the column length, and the soil transfer function are known.

Movement of 2,4-D in columns of moist fine sand was found to be influenced by water-repellancy of the sand. Displacement of a volume "slug" of 2,4-D solution through columns gave maximum recovery in the effluent from water-repellant Blanton fine sand, less recovery in ignited Blanton, and even less for naturally water-wettable Blanton. The larger recovery of 2,4-D in the effluent from the water-repellant sand was attributed to incomplete and non-uniform water-saturation of the packed column. When this column was dismantled at the end of the experiment small zones of dry soil were observed within the moist soil. Thus the water-filled porosity was less in the water-repellant soil and thus adsorption of 2,4-D should be less. Ignition removed the soil organic matter; therefore, 2,4-D adsorption should be low. Increasing the liquid flow velocity resulted in greater herbicide recoveries in the effluents from all the porous materials.

Miscible displacement experiments showed 2,4-D to move readily with water through initially dry columns of glass beads, Lakeland fine sand, and Fellowship sandy clay. Most of the chemical was recovered within two pore volumes of effluent in these soils. Movement of 2,4-D greatly lagged water movement in columns of Everglades mucky peat. More than five pore volumes were required to recover only 60% of soil-applied 2,4-D. Adsorption of 2,4-D appeared to be reversible in the mineral soils but not so in the organic peat.

Intact columns of dry Oldsmar fine sand were sterilized by fumigation with methyl bromide gas and by irradiation with an intense field of gamma rays. Both treatments gave complete sterilization and provide convenient means for evaluating the influence of specific physical-chemical soil properties upon miscible displacement of herbicides through soil columns.

Displacement of three successive "slugs" or paraquat and tritiated water through water-saturated columns of irradiated, fumigated and non-treated Oldsmar fine sand gave unexpected breakthrough curves for the tritiated water. The successive curves for the sterilized soil gave almost complete recovery, but for the untreated soil recovery decreased with each "slug" applied. The phenomenon was attributed to rapid growth of microorganisms in the non-sterile soil. The breakthrough curves for tritiated water behaved similarly when Cl-36 and tritiated water were applied as three successive "slugs" to another non-sterile column. A definite separation was observed for Cl-36 and tritium curves. Tritium lagged the chloride anion in the effluent, as might be expected.

The concentration of KCl in the soil solution was found to influence movement and sorption of the paraquat cation in columns of soils. Application of a dilute KCl solution to water-saturated columns of Wabasso fine sand resulted in elution of small quantities of adsorbed paraquat and diquat. Desorption of both chemicals was greater from Wabasso fine sand taken from 33-76 cm profile depth than for sand taken from 0-10 cm depth. The organic matter content in the surface soil is approximately 10 times greater than in the material taken from 33-76 cm.

Increasing concentrations of KCl over the range from 0 to 9000 ppm in aqueous solutions of paraquat resulted in decreasing adsorption of paraquat by Pomello, Wabasso and Blanton fine sands. Initial solution concentrations of 17 and 51 ppm paraquat were used. The KCl concentration had little effect upon paraquat adsorption in Everglades mucky peat, ignited Pomello fine sand, and ignited Blanton fine sand. With no KCl present in the solution adsorption isotherms were linear for the organic peat over the range of 0 to 500 ppm paraquat in the initial solution phase. Linear sorption of paraquat by the fine sands was limited to narrower solution concentration ranges. The assumption of linear adsorption is therefore valid for these soils for the recommended application rates of paraquat for herbicidal purposes. The presence of large concentrations of KCl or other salts in the soil solution following fertilizer applications to agricultural sands may stimulate limited profile movement of adsorbed paraquat.

An inexpensive flow cell method is described for continuously recording the concentration of chloride in effluents from soil columns. The method was potential for miscible displacement studies which involve chloride as a "tracer" for herbicide movement in soils.

In conclusion, movement of 2,4-D and paraquat with water in sandy soils investigated indicate that both chemicals undergo retention due to sorption by small amounts of soil organic matter. Paraquat was completely sorbed in most cases; whereas 2,4-D did move through soil columns under most conditions. At the very low concentrations of 2,4-D normally applied to these soils, significant amounts of the chemical would not be expected to traverse field profiles to contaminate ground water.

INTRODUCTION AND REVIEW OF LITERATURE

Movement of 2,4-D and Paraquat Herbicides in Soils

Organic pesticides applied directly or indirectly to

surface soil may move with water downward through the profile to ultimately contaminate ground water. The pollution potential of an individual pesticide is a complex function of properties of the soil-water system which contribute to solute transport and properties of both the pesticide and the soil-water system which contribute to attenuation. Movement of one of these chemicals into and through porous media occurs primarily by mass flow (convection) coupled with molecular diffusion. These two mechanisms also cause a chemical to undergo dispersion (mixing) with water in the soil pores. Mixing of a solute during flow of a liquid through porous media is referred to as hydrodynamic dispersion (Bear, *et al.*, 1968). As the pesticide moves through the soil pores, adsorption, fixation, precipitation, degradation, and other attenuating mechanisms tend to remove the chemical from the flowing stream of soil solution. Those materials which interact strongly with the soil and which also resist decomposition are commonly called persistent pesticides (Van Middlelem, 1966). The capacity of a soil to adsorb chemical molecules has been cited (Shaw, 1966) as one of the most important inactivating mechanisms in man's total environment. Properties of a specific pesticide such as solubility in water, ionic charge, etc., also determine the extent of attenuation during movement through the soil-water environment.

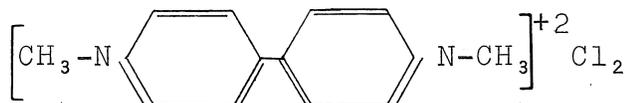
Van Middlelem (1966) states that herbicides present a special problem of pesticide movement in soils since many are applied directly to the soil as selective pre-emergence sprays and as nonselective soil sterilants. Intensive rainfall and sandy soils in Florida create a favorable environment for contamination of ground water with soil-applied herbicides. This research investigation was performed to determine the influence of specific physical-chemical properties of soil-water environments upon the movement of 2,4-D and paraquat herbicides through columns of sandy soil.

Chemical Properties of Paraquat and 2,4-D Herbicides

Chemical properties have been used by Goring (Kirkham, 1964) to classify pesticides into three broad categories as far as movement in soil by water is concerned. The first category includes chemicals with a reasonably high water solubility, which are nonionic or the toxicant portion is anionic. Movement of these materials in soil should be somewhat similar to that of the inorganic anions, nitrate and chloride. An example of the latter is 2,4-D herbicide. Soluble organic salts where the toxicant portion is an organic cation form a second category. Movement of these chemicals in soils should be similar to that of potassium or calcium cations except that organic cations are usually more strongly sorbed than inorganic cations. The quaternary bipyridylum herbicides, paraquat and diquat, occur within that classification. The third category is composed of highly water insoluble nonionic chemicals.

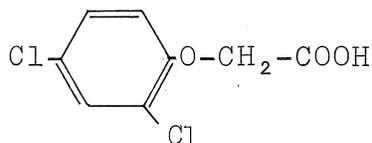
Movement of these materials in soils is particularly complicated because they dissolve in both soil water and soil organic matter. Triazine herbicide is an example of this category.

The dichloride salt of paraquat is a quaternary dipyridylium herbicide which has the structural formula (Herbicide Handbook, pages 137-141, 1967)



The toxicant portion of the molecule is an organic cation with an electrical charge of +2 and a molecular weight of 186.2 g/mole. Paraquat is used effectively as a pre-emergence herbicide, general contact herbicide, direct post-emergence herbicide, crop desiccant, and as a crop defoliant. It is normally applied in water as a spray at a rate of 0.5 to 1.0 lb of cation per acre (Calderbank, 1961) for general weed control. The nonvolatile salt is a strong electrolyte and largely dissociates in aqueous solution. Paraquat has the distinction of being an almost completely water-soluble (70% at 20°C, Akhavein and Linscott, 1968) organic cation which becomes very strongly adsorbed to materials with cation-exchange properties. It undergoes very rapid adsorption (Boon, 1965) with clay and organic matter constituents of soils. Adsorption is primarily physical and is not dependent upon pH, temperature, or exposure time (Akhavein and Linscott, 1968). Paraquat has a very long persistence (Herbicide Handbook, 1967) in soils which is only limited by microbial breakdown of the strongly sorbed chemical. Chemical properties of paraquat have been published by Crafts (1961), Funderburk (1969), Boon (1965), Calderbank (1968), and Akhavein and Linscott (1968).

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is a phenoxyacetic acid with the structural formula (Herbicide Handbook, 1967)



The molecular weight is 221 g/mole and the vapor pressure at 160°C is 0.4 mm Hg. Solubility in water ranges from 6 to 7% (Herbicide Handbook, 1967) over the temperature range 20 to 23°C. Water, diesel oil or oil-water emulsion are common carriers for 2,4-D application. At low dosage rates of 0.25 to 1 lb/acre (Herbicide Handbook, 1967) 2,4-D is used for pre-emergence control of weeds in crops, and at high dosage rates of 3 to 4 lb/acre it is used in non-cropped areas as a

temporary soil sterilant against perennial weeds. It behaves as an organic anion in aqueous solution. Adsorption occurs with clay and organic matter constituents, but in sandy soils it may be (Herbicide Handbook, 1967) readily leached. Low dosage rates of 2,4-D undergo microbial breakdown in warm, moist soil. Average persistence in soils is 1-4 weeks. Further chemical properties of 2,4-D have been reported by Crafts (1957 and 1961).

Physical-Chemical Properties of Soil-Water Systems that Influence the Movement and Adsorption of Herbicides in Soils

A nonvolatile chemical applied to the surface of a soil may move with water into the soil pore space. Because recommended application rates to soils are generally low, most organic herbicides dissolve at least partially in the soil water. Therefore herbicides will be referred to here as solutes. Mass flow (convection) and molecular diffusion are physical processes (Kirkham, 1964) which move a given solute through the soil pores. The behavior of a given herbicide as it moves through the environment of a specific soil determines (Freed, 1966) the effectiveness of the chemical as a weed-controlling agent and predicts the capacity of that chemical to contaminate ground water. The soil environment depends upon temperature, water content, pore size distribution, ionic exchange capacity of the soil, pH of soil solution, salt content of soil solution, organic matter content of soil, clay content of soil, microbial activity, and many other variables. As the solute moves along tortuous pathways through the soil, interactions such as adsorption to pore walls, chemical precipitation, and biological degradation tend to remove the herbicide from the moving solution. If the sorption is reversible, the herbicide may be slowly released with time into the mobile soil solution and the soil may be thought of as a reservoir (Freed, 1966) for the chemical.

The flow velocity of the soil solution is important from the standpoints of influencing the convection flow rate of the solute and of determining the average detention time of a solute molecule within the soil environment. Slower liquid flow velocities give longer detention times which are favorable to sorption and other deactivating mechanisms. Tortuous pathways of movement for a solute molecule also increase the detention time. In water-saturated soil the pore size distributions control the degree of tortuosity. In sandy soils, decreasing the water content below saturation rapidly increases tortuosity, which in turn gives increased solute detention times and decreased liquid flow velocities (because of decrease in percentage of pore space filled with water). The probability for adsorption also increases with a decrease in water content because the solute is forced to move in a film of water in intimate contact with the electrically charged pore wall surfaces.

Hartley (1964), Freed (1966), and LeGrand (1966) have published on the behaviour of herbicide movement and retention in soil.

EXPERIMENTAL MATERIALS, METHODS AND PROCEDURES

Herbicides

Carbon-14 labeled quantities of 2,4-D acid and paraquat chloride were purchased as standard catalog items from commercial suppliers of radioisotopes. The carboxyl carbon atom of the 2,4-Dichlorophenoxy acetic acid molecule was labeled with C-14, and the specific activity of the aqueous solution purchased was 3.03 m Ci per mM (221 mg/mM). The methyl carbon atom of the paraquat chloride was labeled with C-14 and was supplied as a freeze-dried solid under a nitrogen atmosphere in glass ampoules. Specific activity of the solid was 14.5 m Ci per mM (257 mg/mM). Analytical standards of non-labeled paraquat chloride was provided free of charge from the Ortho Division of Chevron Chemical Company, 940 Hensley Street, Richmond, California 94804. Reagent grade non-labeled 2,4-D acid was purchased from a chemical supplier.

Tritiated water and chloride-36 labeled NaCl were also used as inorganic tracers for the movement of the organic herbicides through soil columns. Herbicides were applied individually in aqueous solutions to the surface of columns of soil, and for several of these investigations either H³-labeled water or NaCl³⁶ was included with each influent herbicide solution. Both of the radioactive tracers have been widely used as tracers of water flow in soils. Because of the relatively small physical-chemical reaction of H³ and Cl³⁶ during movement through moist soil, these materials were selected as "non-reactive herbicides."

Soils

Soil materials used in this study were one organic soil, a soil high in clay content, and several sands. Samples of these materials were collected from various field locations in Florida, air-dried, passed through a 2 mm sieve, and then stored for future use. Samples of Lakeland fine sand and Fellowship sandy clay were collected from near Gainesville, Everglades mucky peat was collected near Zellwood, Wabasso and Oldsmar fine sands were collected near Ft. Pierce, and Pomello and Blanton fine sands were collected from Orange County. These soils are typical of large land areas in the state. In addition to soil materials, glass beads with diameter range from 105-210 μ M (Cataphote Corporation, Jackson, Mississippi) were used. Glass beads were selected as a "non-

reactive soil" because of the low adsorption properties of the beads for many organic materials. Movement of an herbicide through glass beads provides a valuable indication of the influence of the mean pore size upon hydrodynamic dispersion under conditions of minimal herbicide sorption to the pore walls. Each porous media was hand-packed into cylindrical columns before each miscible displacement of herbicide.

Miscible Displacement Technique for Studying Herbicide Movement in Soil Columns

Miscible displacement in porous media refers to the displacement of one fluid by a second fluid when the two fluids are mutually soluble (Collins, 1961, page 207). When the fluids used are aqueous solutions where the displacing solution contains solute ions or molecules of interest, we may speak of miscible displacement of solutes. During displacement, the moving front undergoes spreading as a result of mixing of the two solutions by molecular diffusion and convection (mass flow). Gradients in solute concentration in the vicinity of the advancing front or within individual pores drive the diffusion, and convection occurs as a consequence of the distribution of microscopic flow velocities within the porous medium. If the solute or aqueous solution interacts with the porous medium, miscible displacement can be complicated by the processes of ionic exchange, anion repulsion, adsorption, biological degradation, etc. Since the total surface area exposed and the retention time for a solute in porous medium increase with increasing length of the porous medium, the amount of mixing which occurs during displacement of a solution through a column of porous medium will be greater for longer columns.

Miscible displacement experiments in soil are generally accomplished by applying a displacing solution of a chemical to one end of a soil column. Flow velocities and water contents through the soil are controlled. Small aliquots of liquid effluent from the column are collected and analyzed to determine the concentration of the displacing solute. The solute concentration in the effluent plotted versus the volume of effluent collected give plots that have been termed "breakthrough curves." Solute concentration is normally expressed as a dimensionless ratio, C/C_0 , of the solute concentration in the effluent, and the initial solute concentration in the displacing solution. A dimensionless ratio, V/V_0 , referred to as "pore volume" is sometimes used to express the accumulative volume of effluent. Pore volume is obtained by dividing the effluent volume by the volume of water in the soil column under the conditions of the experiment.

A laboratory technique developed by Nielsen and Biggar (1961, 1962, 1963) gives a convenient procedure for study of

miscible displacement of water and herbicide solutions applied to soil columns. Movement of different chemical solutes may be studied under controlled environmental conditions, such as flow velocity or water content, with this procedure. In this method, a solution containing a chemical of interest is applied to one end of a soil column. Effluent from the column is collected in small volume increments and each aliquot is then analyzed to determine the concentration of solute. If the displacing solution is applied as a pulse or volume "slug" the curve will increase from $C/C_0=0$ to a maximum or peak and then decrease until $C/C_0=0$ is again reached.

In a discussion of theoretical considerations for miscible displacement in porous media, Nielsen and Biggar (1962) discussed the types of breakthrough curves predicted from existing theories of dispersion. For the extremely ideal situation where no mixing due to diffusion or convection occurs, the tracer front proceeds by piston flow. For piston flow the breakthrough curve is a vertical line passing through the point at one pore volume of effluent. This type of transport process would be expected for a single capillary tube of constant radius, and cannot be expected to occur in soils. But the model gives insight into the occurrence of mixing in soil by establishment of the vertical line at one pore volume as a point of reference for comparison with more realistic types of breakthrough curves. If mixing results entirely from convection (mass flow) in a nonreactive soil having rather large microscopic flow velocities narrow in their distribution, a skewed sigmoid breakthrough curve will pass through $C/C_0=0.5$ at one pore volume. Coupling of molecular diffusion with the convection during miscible displacement results in translation of the curve to the left at the smaller flow velocities as well as a slight clockwise rotation. Another type of breakthrough curve occurs for miscible displacement in nonreactive porous media having an extremely wide range in velocity distribution. Assuming dispersion results from both diffusion and convection, this type of curve is concave to the right. For each type of breakthrough curve in nonreactive media, the area enclosed beneath the curve and to the left of a vertical line passing through one pore volume is equivalent to the area enclosed above the curve but to the right of that line.

Two types of curves are given for cases where the solute and the soil interact. If the reaction is a chemical process, a precipitation or an exchange, the sigmoid curve is displaced to the right with only a small portion of the curve extending to the left of one pore volume. Exclusion of the solute by a solute-solid interaction or a velocity distribution with velocities near zero results in a sigmoid breakthrough curve with a large displacement to the left of one pore volume.

A useful quantity referred to as "holdback" has been

defined as the area beneath the portion of the breakthrough curve displaced to the left of the vertical line for piston flow which occurs at one pore volume. For soils, holdback is a measure of the volume of original soil solution not displaced but remaining within the sample. Values for holdback vary from zero for piston flow to values less than 100% for other cases. Nielsen and Biggar (1961) have shown that the magnitude of holdback for water-unsaturated soils greatly exceeds that for saturated soils. A slow approach to a maximum $C/C_0=1$ also occurs and the skewness of breakthrough curves increase upon desaturation. They attributed part of this to the extremely wide range in microscopic pore velocity and a changing cross-sectional area between displacing and displaced solutions for miscible displacement through unsaturated soil. The influence of molecular diffusion upon dispersion is greater for displacement through unsaturated soil than for saturated soil.

Radioassay Procedure for Measurement of Herbicide Concentration in Soil Effluent

Chemical assays for 2,4-D and paraquat are frequently time-consuming and require elaborate equipment. Radioassay rather than chemical assay was used in this study for measurement of herbicide concentrations. That method offers advantages of being simple, being rapid, providing precise measurement of very small quantities of herbicide, and requiring access only to liquid scintillation counting equipment.

One ml aliquots of aqueous effluent from soil columns were added to counting vials containing 15 ml of Bray's scintillation solution (Bray, 1960). Both plastic and glass vials were used. The vials were placed in a Packard Tri Carb Liquid Scintillation Counter to determine the radioactivity. Count rates (cpm) for soil effluent were corrected for background and were divided by the corrected count rate for the initial influent herbicide solution. This relative concentration, C/C_0 , was then plotted versus accumulative volume of soil effluent to provide breakthrough curves for each herbicide.

INVESTIGATIONS

Theoretical Analysis of the Movement of Solutes in Soils: An Application of Transfer Functions

Introduction

Most recent efforts to provide an analytic description of solute movement with water media have been directed at solving the hydrodynamic dispersion equation as a boundary

value problem, with the boundary values determining the particular solution. An alternative approach is the method of Laplace transfer function theory. This alternative approach has been used with considerable success in other fields which deal with diffusion-like problems. Basically, this theory treats the problem of miscible displacement statistically, and properties of the Laplace transform provide an analytic form to the solute content of effluent from a soil column. This treatment should provide additional understanding of those processes which influence solute transport through porous media.

Simple analytic examples illustrate the diverse utility of the theory when applied to miscible displacement. In contrast to the boundary value solution, the transfer function theory can be applied to cases of complex influent functions with considerable ease. When applied to experimental data, the transfer function theory gives results identical with the boundary value solution; however, the transfer function method requires considerably less effort, illustrating the power of the method.

In this paper, the soil is treated as a continuous medium in order to ascribe to it the average macroscopic properties of the soil system. The statistical nature of the macroscopic viewpoint obscures the actions or mechanics of individual pores on the macroscopic scale.

Probability Density

The statistical approach to the analysis of the flow of solutes through porous media as performed by Day (1956), Scheidegger (1957 and 1964) and Bear et al. (1968), provides the probability density function for steady one-dimensional flow.

This approach assumes that Darcy's Law holds for liquid flow and that it follows from the central limit theorem, which says that irregardless of the probability distribution of each step in the process, after a sufficiently large number of steps, the probability distribution tends to be Gaussian. This leads to the probability density distribution of a solute "particle" to be

$$\psi(x,t) = (4\pi Dt)^{-1/2} \exp[-(x-vt)^2/4Dt] \quad 1.$$

where $\psi(x,t)$ = probability density distribution as a function of x and t .

x = spatial variable with its zero at the entrance to the column and proceeding in the direction of flow.

t = temporal variable with its zero at the time that the solute "pulse" enters the column at x = 0.

D = coefficient of hydrodynamic dispersion (not the coefficient of molecular diffusion).

v = average liquid pore velocity or the rate of advance of the center of the "pulse".

It is convenient to transform equation 1 to a set of coordinates traveling with the "pulse" center. The distribution function is changed only to the extent that in the new system, the observer travels with the peak of the "pulse." Using the center of mass coordinate, $z = x - vt$, equation 1 transforms to the form

$$\psi(z,t) = (4\pi Dt)^{-1/2} \exp[-z^2/4Dt] \quad 2.$$

A quantity of immediate interest is the concentration $C(z,t)$ of solute in the soil solution, expressed as g per cm^3 . Since ψ is the fraction of the total solute mass per unit pore volume (total volume of solution present in soil column) of the soil solution

$$C(z,t) = \psi(z,t) \frac{m}{LA\theta} \quad 3.$$

m = total mass of solute.

L = length of soil column.

A = cross-sectional area of soil column.

θ = volumetric water content of soil.

The concentration of a volume "slug" of solution applied to the soil surface at time $t = 0$ is simply

$$c(0,0) = \frac{m}{LA\theta} \quad 4.$$

Therefore the probability density is just the relative concentration of the solute or the concentration ratio $c(z,t) = C(z,t)/C(0,0)$. The concentration ratio is therefore a normal Gaussian distribution

$$c(z,t) = \psi(z,t) = (4\pi Dt)^{-1/2} \exp[-z^2/4Dt] \quad 5.$$

with zero mean ($x = vt$) and variance $2Dt$.

Impulse Response and Transfer Functions

It is often useful when dealing with the transmission of aqueous solutions through porous media, to mentally visualize a flow system which in effect neglects the microscopic aspects of the medium and regards only macroscopic quantities such as distance (in the one dimensional case), average liquid flow velocity, concentration of solute, and some characteristic quantity or quality of the system as a whole. The Laplace transform, the impulse response function, and transfer function have been applied here to the problem of solute transport in porous media for the purpose of giving a workable macroscopic model. This method has been applied successfully in electronic circuit design and analysis, and mechanics, and it is related to the Fourier transform used in obtaining the point spread function and the modulation transfer function of optics, radar, sonar and other wave phenomena. The Laplace transform method is an extension of the Laplace transform equations used in solving boundary value problems of diffusion and heat flow.

Consider the case of one-dimensional flow through a porous medium. Assume that no information is given about the microscopic nature of the porous medium, as this does not aid us in determining the gross behavior. Let the solute be applied in solution to a column of porous media with the liquid flow velocity maintained constant with time. The solute concentration of the influent will be taken as a function of time, $c_o(t)$ and will be referred to as the influent function. Let $c_o(t)$ be properly behaved such as to possess a Laplace transform which will be referred to as the influent amplitude where

$$h_o(s) = \int_0^{\infty} c_o(t) e^{-st} dt \quad 6.$$

and its inverse is defined by

$$c_o(t) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} h_o(s) e^{st} ds \quad 7.$$

$$c_o(t) = \text{influent function.}$$

$$h_o(s) = \text{influent amplitude.}$$

$$s = \text{complex variable} = \sigma + iw \text{ where } \sigma \text{ and } w \text{ are real variables.}$$

$$t = \text{time variable.}$$

$$i = \sqrt{-1}$$

The constant a is chosen to be to the right of any singularity of $h_o(s)$ and the integration path is sometimes known as a

Bromwich contour. The response function of the system is the concentration of solute in the effluent and will be referred to as the effluent function, $c_1(t)$. It will also possess a Laplace transform which will be called the effluent amplitude

$$h_1(s) = \int_0^{\infty} c_1(t) e^{-st} dt \quad 8.$$

and the inverse,

$$c_1(t) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} h_1(s) e^{st} ds \quad 9.$$

The effluent amplitude, $h_1(s)$, is related to the influent amplitude, $h_0(s)$, by the transfer function, $H(s)$, i.e.

$$h_1(s) = H(s)h_0(s) \quad 10.$$

The transfer function has the property of a spectral filter inasmuch as it modifies the spectrum (Laplace transform) of the influent function to produce the spectrum of the effluent function. Once the transfer function is known for a specific flow system of a given porous medium, no other information is necessary in order to predict the effluent function for a known influent function. Note that so far these are generalized functions with the only restricting condition being that each possess a Laplace transform.

The usefulness of the transfer function will be illustrated by showing how it can be found for select cases of influent functions.

Consider an initially solute-free medium into which is introduced a pulse of solute whose width may vary with time but is small in time. The magnitude of the pulse is subject to the condition

$$\int_0^T \delta_T(t) dt = 1 \quad 11.$$

where $\delta_T(t)$ is defined as

$$\delta_T(t) = \begin{cases} 1/T & 0 < t < T \\ 0 & t > T \end{cases} \quad 12.$$

$\delta_T(t)$ might represent a very short "slug" of solute whose concentration is very high. The magnitude of $\delta_T(t)$ is inversely proportional to its duration which is small in comparison to some quantity which characterizes the duration of the efflu-

ent function (breakthrough curve). Thus the solute transport may be described by

$$c_0(t) = \delta_T(t) \quad 13.$$

and

$$h_0(s) = \frac{1}{sT}(1 - e^{-sT}) \quad 14.$$

For a pulse of this nature, T is very small so that when the right hand side of equation 14 is expanded in a series and the limit taken as T approaches zero we have

$$h_0(s) \cong 1 \quad 15.$$

Then the transfer function becomes

$$H(s) = \lim_{T \rightarrow 0} h_1(s) \quad 16.$$

or is equal to the effluent amplitude when $c_0(t)$ is a very short pulse. This method provides an excellent procedure for determining the transfer function for a specific flow system as will be seen later. Under these specific conditions the effluent function is simply the inverse Laplace transformation of the transfer function, thus

$$c_1(t) = L^{-1}[H(s)] \quad 17.$$

where $L^{-1}[\]$ is the inverse Laplace transformation and $L[\]$ is the Laplace transform. In general, the effluent function will be

$$c_1(t) = L^{-1}[H(s)L[c_0(t)]] = L^{-1}[H(s)h_0(s)] \quad 18.$$

$$\text{If for example } c_0(t) = \begin{cases} 0 & t < 0 \\ 1 & t > 0 \end{cases} \quad 19.$$

then from tables of Laplace transforms or by applying equation 6 directly we obtain

$$h_0(s) = \frac{1}{s} \quad 20.$$

Hence the effluent function becomes

$$c_1(t) = L^{-1}\left[H(s)\frac{1}{s}\right] = \int_0^t g(t)dt \quad 21.$$

where $g(t)$ is the inverse Laplace transform of $H(s)$ and is the impulse response function. If $c_0(t)$ is a long pulse,

that is, long in duration compared with the duration of $g(t)$, then

$$c_o(t) = \begin{cases} 1/t_o & 0 < t < t_o \\ 0 & t_o < t \end{cases} \quad 22.$$

and by equation 14

$$h_o(s) = \frac{1 - e^{-st_o}}{t_o s} \quad 23.$$

Thus the effluent function is

$$c_1(t) = L^{-1} \left[H(s) \frac{(1 - e^{-st_o})}{t_o s} \right] \quad 24.$$

which gives

$$c_1(t) = \frac{1}{t_o} \left[\int_0^t g(t) dt - \int_0^{t-t_o} g(t-t_o) dt \right] \quad 25.$$

The last two examples suggest a second practical method of obtaining the transfer function, $H(s)$, or its inverse transform, $g(t)$, the impulse response function. From equation 21 we see that

$$g(t) = \frac{d}{dt} [c_1(t)] \quad 26.$$

when $c_o(t)$ is a step function. By substitution for $g(t)$ in the definition of $H(s)$ we obtain

$$H(s) = L[g(t)] = L \left[\frac{d}{dt} [c_1(t)] \right] \quad 27.$$

Thus one may easily apply solute in solution as a step function to the surface of a porous medium, differentiate the resulting effluent function and perform the Laplace transformation. The result then is the characteristic transfer function for the flow system.

Evaluation of inverse Laplace transforms can sometimes be difficult with or without the use of tables of transforms, so that an alternative method would be useful in evaluating the effluent function from a known impulse response function and influent function. The convolution integral provides a convenient method. Equation 10 gives the product of two transforms and its inverse transformation is given by

$$c_1(t) = L^{-1} [H(s)h_o(s)] = \int_0^t g(t-\tau) c_o(\tau) d\tau = g(t) * c_o(t) \quad 28.$$

when $*$ is the notation for the convolution. The relationships

between the influent function, influent amplitude, effluent function, effluent amplitude, impulse response function and transfer function are presented in the schematic diagram in Figure 1. Horizontal arrows indicate Laplace transforms and are reversible when the inverse Laplace transform is taken. Vertical arrows represent the convolution integral on the left (not generally reversible) and multiplication by the transfer function (reversible) is given on the right. Thus there are two pathways from a known influent function to a desired effluent function when an impulse response function is known. One way involves direct use of the convolution and the second way involves a Laplace transformation, a multiplication and an inverse Laplace transformation.

Applications to Miscible Displacement

A practical application of the transfer function theory to solute transport in soils is miscible displacement of herbicides and fertilizer nutrients in soils. Potentially, this field promises to be one of its most important uses.

Consider the effluent function, $c_1(t)$, given by equation 5 when $z = L-vt$ where L is the column length. This is the effluent function $c_1(z,t)$ for a case when the influent function is an infinitesimal thickness pulse, so that equation 12 applies. $c_1(z,t)$ is the impulse response function of a system whose length is L and the system characteristic is the coefficient of hydrodynamic dispersion, D . Thus

$$g(z,t) = (4\pi Dt)^{-1/2} \exp\left[-(L-vt)^2/4Dt\right] \quad 29.$$

and the Laplace transform of $g(z,t)$ is the transfer function

$$H(s) = H(z,s) = 2(Ds)^{-1/2} \exp\left[-z(s/D)^{1/2}\right] \quad 30.$$

In practice it will sometimes be easier to obtain the effluent functions by the convolution integral

$$c_1(z,t) = \int_0^t (4\pi D\tau)^{-1/2} \exp\left[-\tau^2/4D\tau\right] c_0(t-\tau) d\tau \quad 31.$$

The integral cannot be evaluated until the form of $c_0(t)$ is known due to the convolution. However, for a specified $c_0(t)$, $c_1(z,t)$ can be evaluated by analytical or numerical methods. If $c_0(t)$ is a step function as described by equation 19, $c_1(z,t)$ is given by

$$c_1(z,t) = \left(\frac{t}{\pi D}\right)^{1/2} \exp\left[-\frac{(L-vt)^2}{4Dt}\right] - \frac{(L-vt)}{2D} \operatorname{erfc}\left[\frac{L-vt}{\sqrt{4Dt}}\right] \quad 32.$$

If $c_0(t)$ takes the form of equation 22, then $c_1(z,t)$ takes

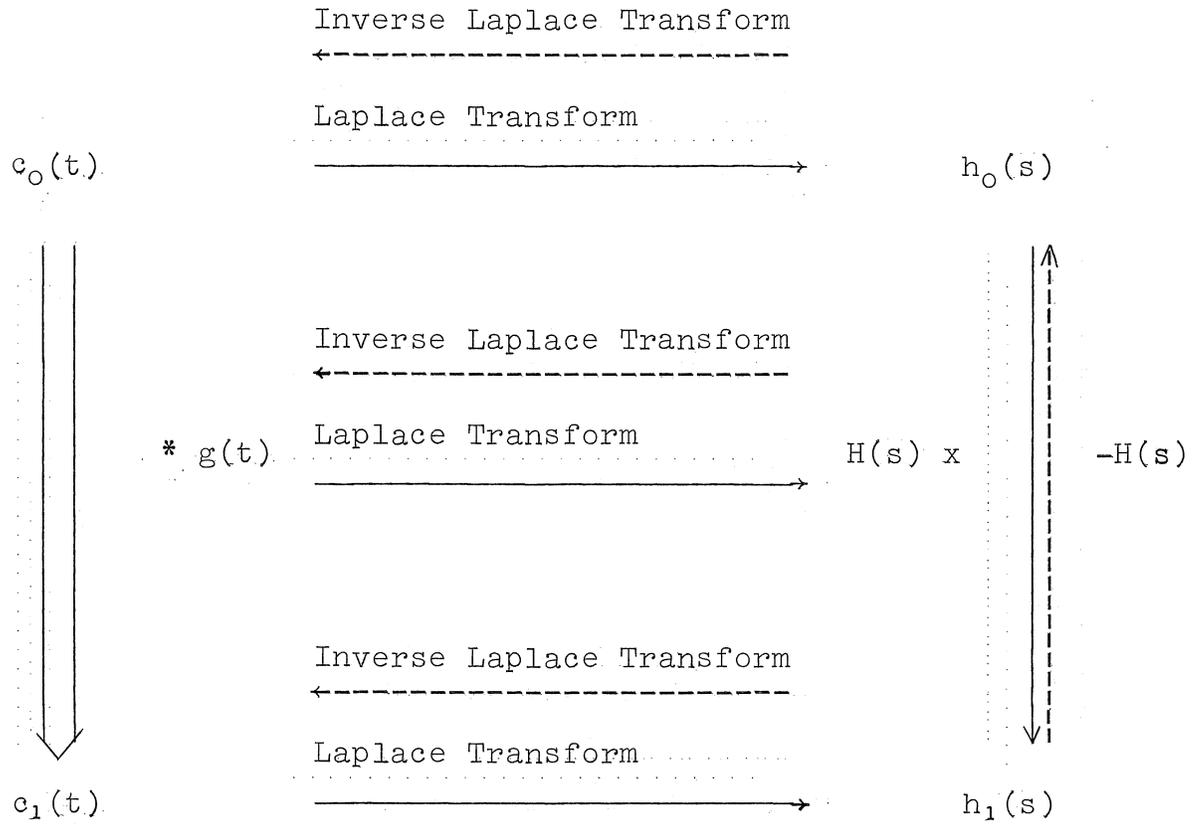


Figure 1. Relationships Between $c_0(t)$, $h_0(s)$, $c_1(t)$, $h_1(s)$, $g(t)$, and $H(s)$

The symbol * stands for convolution.

the form of equation 25 and using $g(z,t)$ from above we get

$$c_1(z,t) = \frac{1}{t_0} \left[\left(\frac{t}{\pi D} \right)^{1/2} \exp\left(-\frac{(L-vt)^2}{4Dt}\right) - \frac{(L-vt)}{2D} \operatorname{erfc}\left(\frac{L-vt}{\sqrt{4Dt}}\right) \right. \\ \left. - \left(\frac{(t-t_0)}{\pi D} \right)^{1/2} \exp\left(-\frac{(L-v(t-t_0))^2}{4D(t-t_0)}\right) + \frac{L-v(t-t_0)}{2D} \operatorname{erfc}\left(\frac{L-v(t-t_0)}{\sqrt{4D(t-t_0)}}\right) \right] \quad 33.$$

If $c_0(t)$ is periodic and of the form of equation 22 with period, $2t_0$, it can be written as

$$c_0(t) = 1/t_0 \sum_{k=0}^{\infty} \frac{(-1)^k S(t)}{kt_0} \quad k = 0,1,2,3\dots$$

where

$$S(t) = \begin{cases} 0 & 0 < t < kt_0 \\ 1 & t > kt_0 \end{cases} \quad 34.$$

In this case, it is more convenient to determine $c_1(z,t)$ by the transform method. By that method,

$$h_0(s) = \frac{1}{st_0} \sum_{k=0}^{\infty} (-1)^k e^{-ks} \quad 35.$$

and

$$h_1(z,s) = \frac{2}{t_0 \sqrt{Ds^3}} \exp \left[-z(s/D)^{1/2} \right] \sum_{k=0}^{\infty} (-1)^k e^{-ks} \quad 36.$$

The resulting effluent function is

$$c_1(z,t) = \frac{1}{t_0} \left[\left(\frac{t}{\pi D} \right)^{1/2} \exp\left(-\frac{(L-vt)^2}{4Dt}\right) - \frac{(L-vt)}{2D} \operatorname{erfc}\left(\frac{L-vt}{\sqrt{4Dt}}\right) \right] \sum_{k=0}^{\infty} (-1)^k S_k t_0(t) \quad 37.$$

Note that equation 37 is equivalent to equation 33 when $k = 0,1$.

Results and Discussion

In order to have any practical value, soil transfer function theory must predict the concentration of solute in the effluent from a soil column when characteristic parameters of the specific flow system are given and the solute concentration in the liquid influent is given as a function of time.

Alternatively, if the impulse response is known for the flow system then the characteristic parameters -L, v, and D- can be recovered by a Least Squares curve fitting routine. Of course, it is easier to work with a situation where the influent function is known and the parameters of L, v, and D have been measured. This case may be illustrated using the data from Davidson *et al.* (1968) where fluometron pesticide and chloride were infiltrated through a 30 cm long column of 250 μ m diameter glass beads. Figure 2 shows the calculated impulse response function using the parameters of the experimental flow system. This is the theoretical effluent function which would be obtained if the influent had been a very narrow solute "pulse" of unit area. This has been calculated from equation 29 and normalized to unity. Using the same parameters, the effluent function was calculated for a 200 ml "slug" from equation 33 and this is shown in Figure 3 along with experimental curves for fluometron and chloride. The curve which Davidson calculated by solving the diffusion equation is also given. Note that both theoretical curves fall to the right of the data indicating perhaps an occluded volume, as Davidson has suggested.

It might be noted that this work uses time, t, as the independent variable and that it was necessary to use the following relation in order to calculate the abscissa, pore volume, V_p , for Figure 3.

$$V_p = \frac{vt}{L} \quad 38.$$

Also it might be noted that when the impulse response function is used, the maximum value of the effluent function occurs when

$$t_{\max} = \frac{L}{v} \quad 39.$$

and thus for a unit area pulse, the amplitude of the peak on the breakthrough curve is given by

$$c_1(o, t_{\max}) = (4\pi Dt_{\max})^{-1/2} \quad 40.$$

from which the value of the dispersion coefficient, D, can be recovered.

Conclusions

Given values of length, L, and dispersion coefficient, D, for the specific soil and solute under observation and the average flow velocity, v, of the fluid, transfer function theory can be used to calculate breakthrough curves (plots of relative solute concentration versus pore volume of effluent) for elution of herbicides or fertilizer solutes from

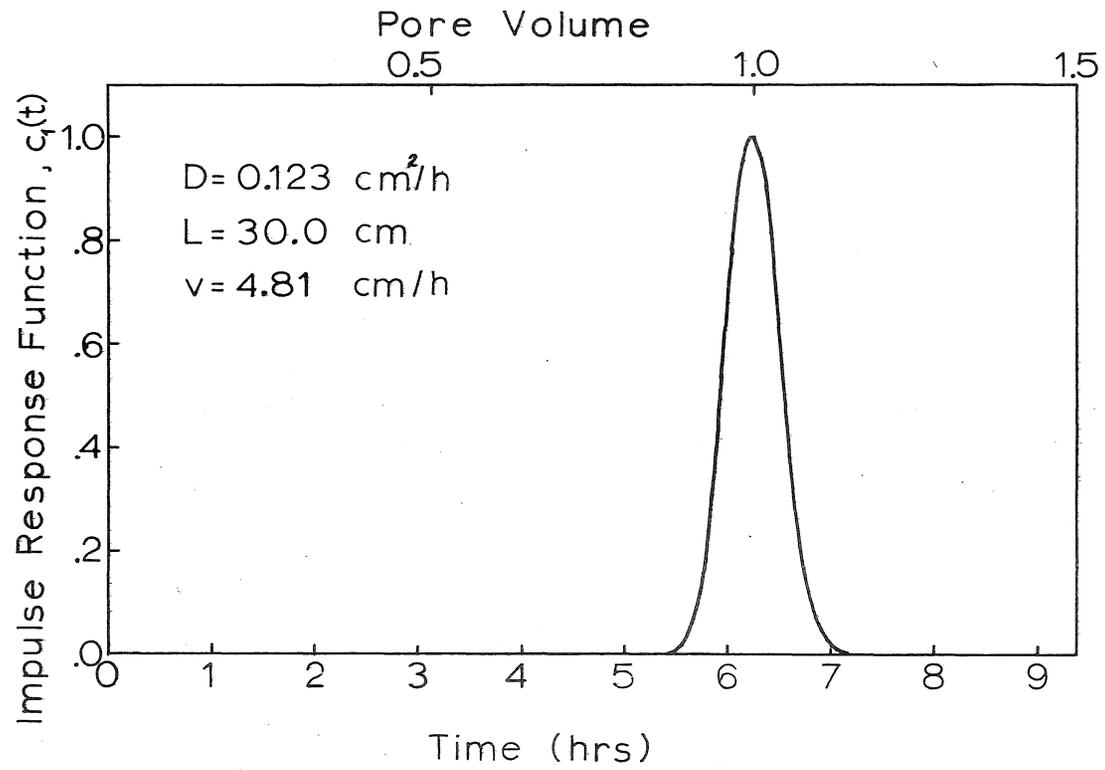


Figure 2. Impulse Response Function

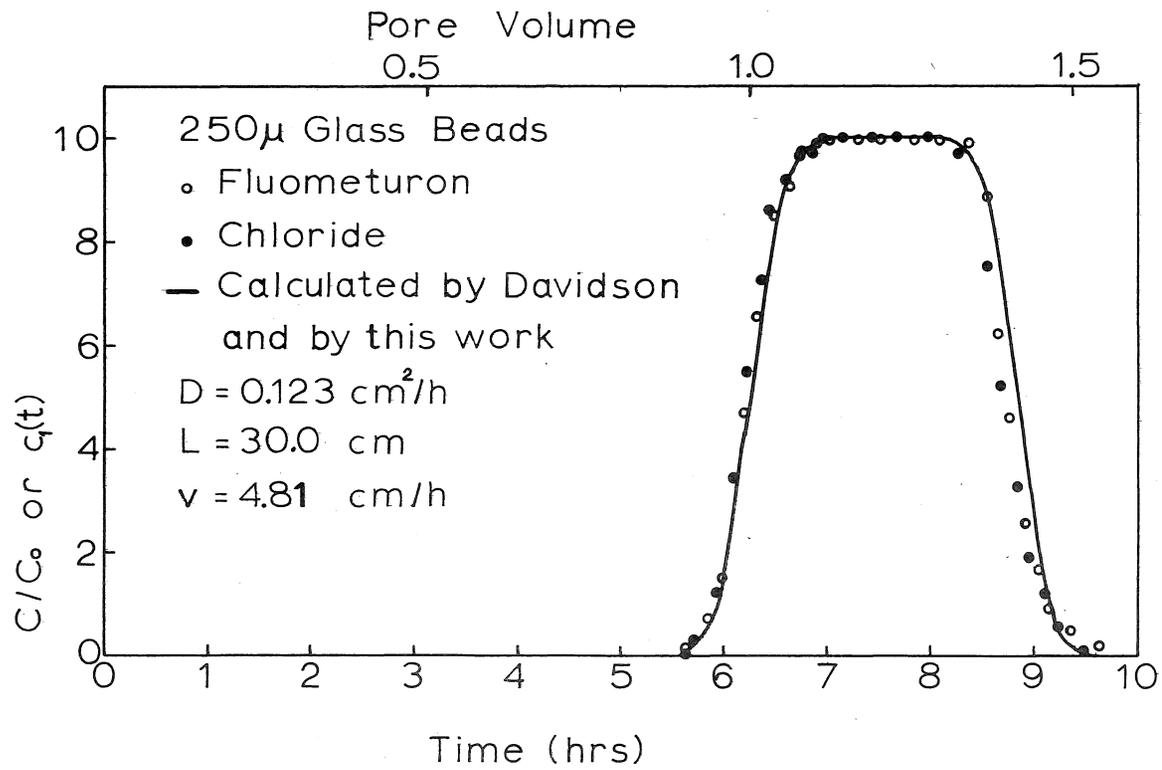


Figure 3. Effluent Function

columns of soil. The function describing the solute concentration in the effluent can be calculated with excellent accuracy if the mathematical form of the solute concentration of the influent is known. This method provides a means to predict the effluent without actually performing the experiment in the field, when such experiments are not practical. It is based solely on statistical hydrodynamics and transfer function theory and is not directly subject to the boundary and initial conditions as are solutions to the differential equations.

Miscible Displacement of 2,4-D Herbicide Through Water-Repellant Soils

Many agricultural sands of Florida exhibit resistance to wetting with liquid water. Soils with this property are referred to as being water-repellant. With time water will move through most water-repellant sands, although wetting often proceeds along channels leaving pockets of dry soil in between the channels. Since water is the principal carrier for the transport of non-volatile herbicides through soils, water-repellancy should alter the movement and consequent adsorption of a soil-applied herbicide. Aqueous solutions of dilute 2,4-D herbicide plus tritiated water were applied as influent slugs to water-saturated columns of water-wettable, water-repellant, ignited (water-repellant sand was ignited at 600°C for 12 hours), and ignited plus silicone (R-20 Silicone, Union Carbide Corporation, 270 Park Avenue, New York 17, New York) coated Blanton fine sand. Movement and adsorption were evaluated by means of breakthrough curves of 2,4-D and tritiated water in the column effluents.

The dry soil materials were hand-packed into a glass column of 2.54 cm inside diameter and 25 cm length. Average bulk densities of 1.47, 1.52, 1.57, and 1.56 g/cm³, respectively, were obtained for columns of the wettable, water-repellant, ignited and silicone coated materials. The columns were then wet with distilled water. Long time periods were required to wet the water-repellant and silicone coated porous materials. A variable-flow pump was used to establish constant liquid flow velocities of 2.04 and 4.08 cm/h through the columns. The column influent was initially water, but at a time we shall call zero a 10 ppm solution of C¹⁴ labeled 2,4-D was introduced to the column. After a 25 ml "slug" of the 2,4-D solution had entered the column, the influent was changed to water.

Breakthrough curves of 2,4-D are presented only for wettable and water-repellant Pomello fine sands (Figures 4 and 5) for liquid flow velocities of 2.04 and 4.08 cm/h. Recoveries of the applied 2,4-D in the effluents for columns of all four porous media are given in Table 1. Increasing the flow velocities from 2.04 to 4.08 cm/h resulted in increased

WETTABLE POMELLO

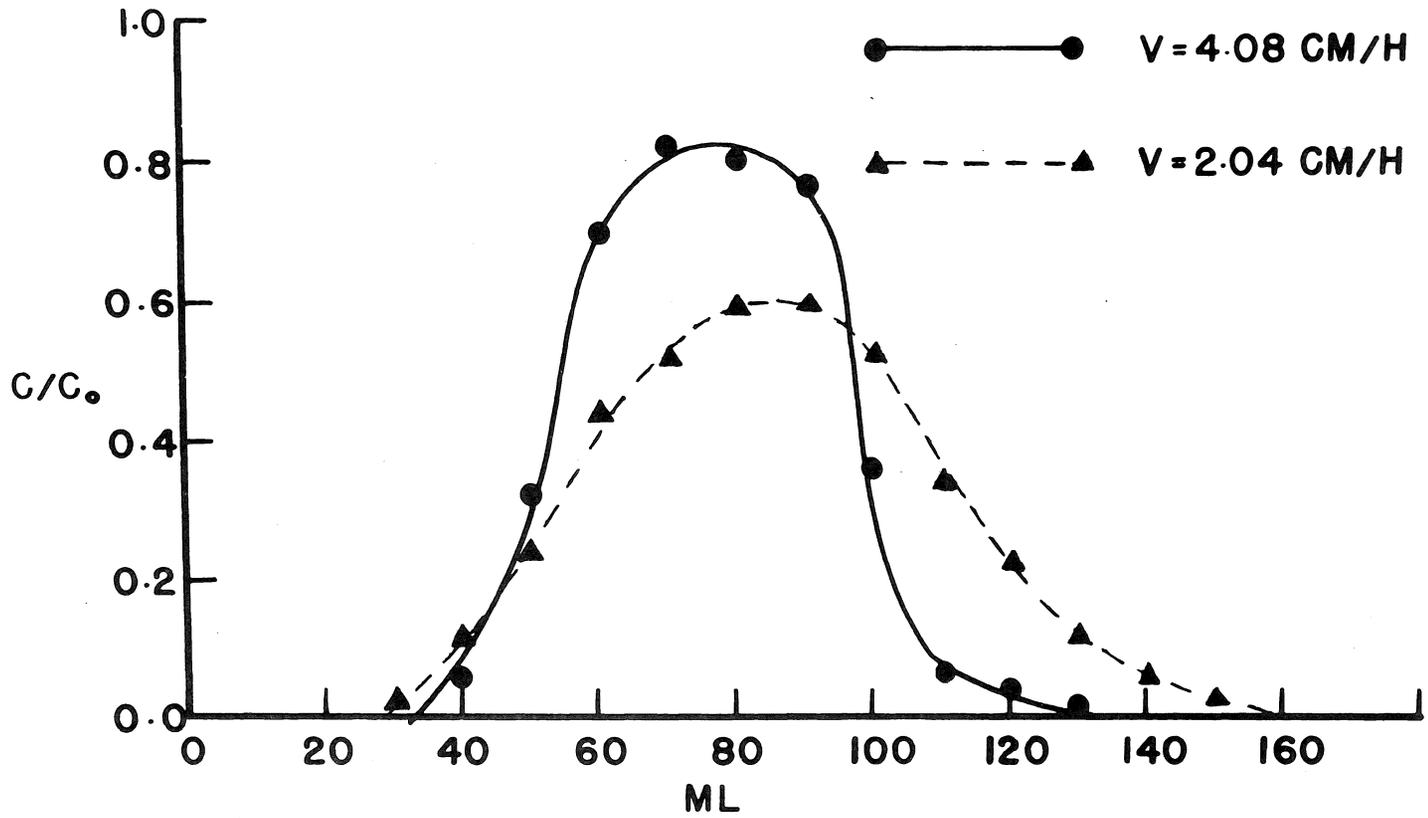


Figure 4. Breakthrough Curves of 2,4-D Corresponding to 2 Liquid Flow Velocities in Water-Wettable Pomello Fine Sand

WATER REPELLANT POMELLO

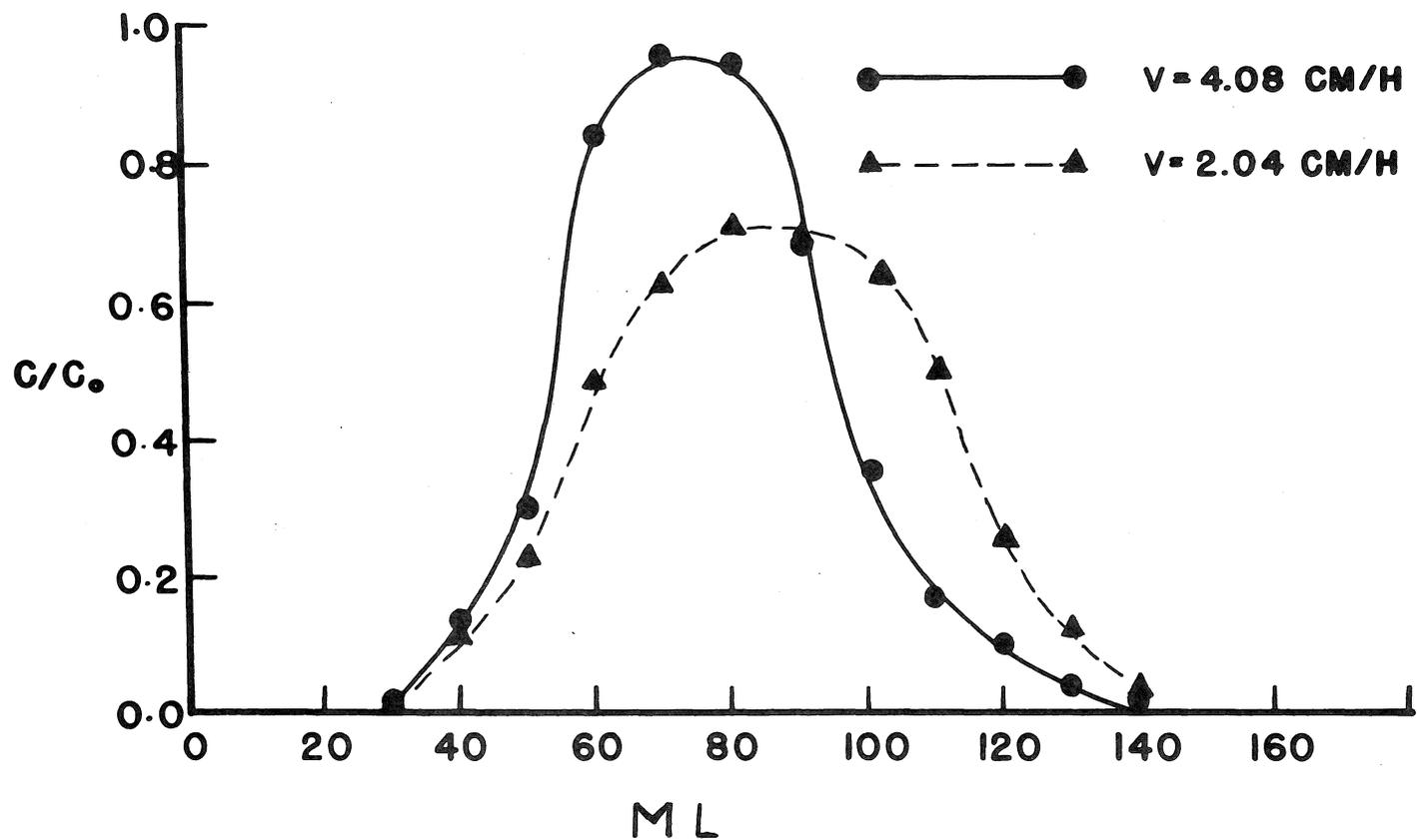


Figure 5. Breakthrough Curves of 2,4-D Corresponding to 2 Liquid Flow Velocities in Water-Repellant Pomello Fine Sand

Table 1. Tabulation of Recoveries of Applied 2,4-D
in the Effluent From Columns of Water-Repellant,
Water-Wettable, Ignited, and Ignited
Plus Silicone Coated Samples of Pomello Fine Sand

Recovery of 2,4-D

Soil	% 2,4-D Recd.	
	2.04 cm/h	4.08 cm/h
Water Repellant	82.0	85.5
Wettable	76.0	83.2
Ignited	86.3	95.0
Silicone Coated	98.5	99.8

2,4-D recoveries for all columns. At the slower velocity, recoveries of 2,4-D were 76.0, 82.0, 86.3, and 98.5%, respectively, for wettable, water-repellant, ignited, and silicone-coated Blanton fine sand. Thus the recovery of 2,4-D was almost complete for the silicone-coated sand regardless of the liquid flow velocity. The 2,4-D recovery from displacement through naturally water-repellant sand was less than that for the ignited sand but greater than for the water repellent sand. Ignition of the sand removed the organic matter, and thus soil adsorption of 2,4-D was therefore decreased during movement. The lower 2,4-D recovery in the effluent from the wettable soil as compared to that for the water-repellant soil was attributed to incomplete and non-uniform water-saturation. After termination of the experiments, small zones of dry soil were observed within the water-repellant column. The incomplete wetting should give a smaller volume of soil pores participating in transport of water and 2,4-D. The quantity of 2,4-D adsorbed during water flow through the wettable soil was therefore greater than for the water-repellant soil.

Solutions of 10 ppm 2,4-D and tritiated water were also displaced through columns of wettable, water-repellant, and ignited plus silicone-coated Pomello fine sand. Breakthrough curves of 2,4-D and tritiated water for the water-repellant and silicone-coated columns are presented in Figures 6 and 7. Elution of the 2 chemicals were similar for the silicone-coated sand, but elution of tritiated water and 2,4-D from the water-repellant sand column gave separate breakthrough curves. Tritiated water appeared in the effluent before the 2,4-D and the greater spread for the 2,4-D curve indicates adsorption by the soil. Behaviour of 2,4-D and tritiated water curves for wettable sand (not shown) were similar to the curves in Figure 3.

Work performed on the study indicates that water-repellancy in water-saturated sands influences the movement of 2,4-D. Further studies are needed to evaluate movement of herbicide solutions into initially dry water-repellant soils.

Miscible Displacement of 2,4-D Herbicide During Constant Liquid Flow Velocity Through Initially Dry Soils

A theoretical model was developed to predict the movement of organic chemicals through porous materials packed in columns of finite length. Movement due to diffusion was assumed to be negligible. The model assumes that transport of the chemical is mainly due to the liquid flow velocity and that at equilibrium adsorption is linear. The model also considers the rate at which equilibrium between the dissolved and the adsorbed phases progresses with time.

The theory was tested by studying the movement of C¹⁴ labeled 2,4-D herbicide through glass beads (105-210 μm),

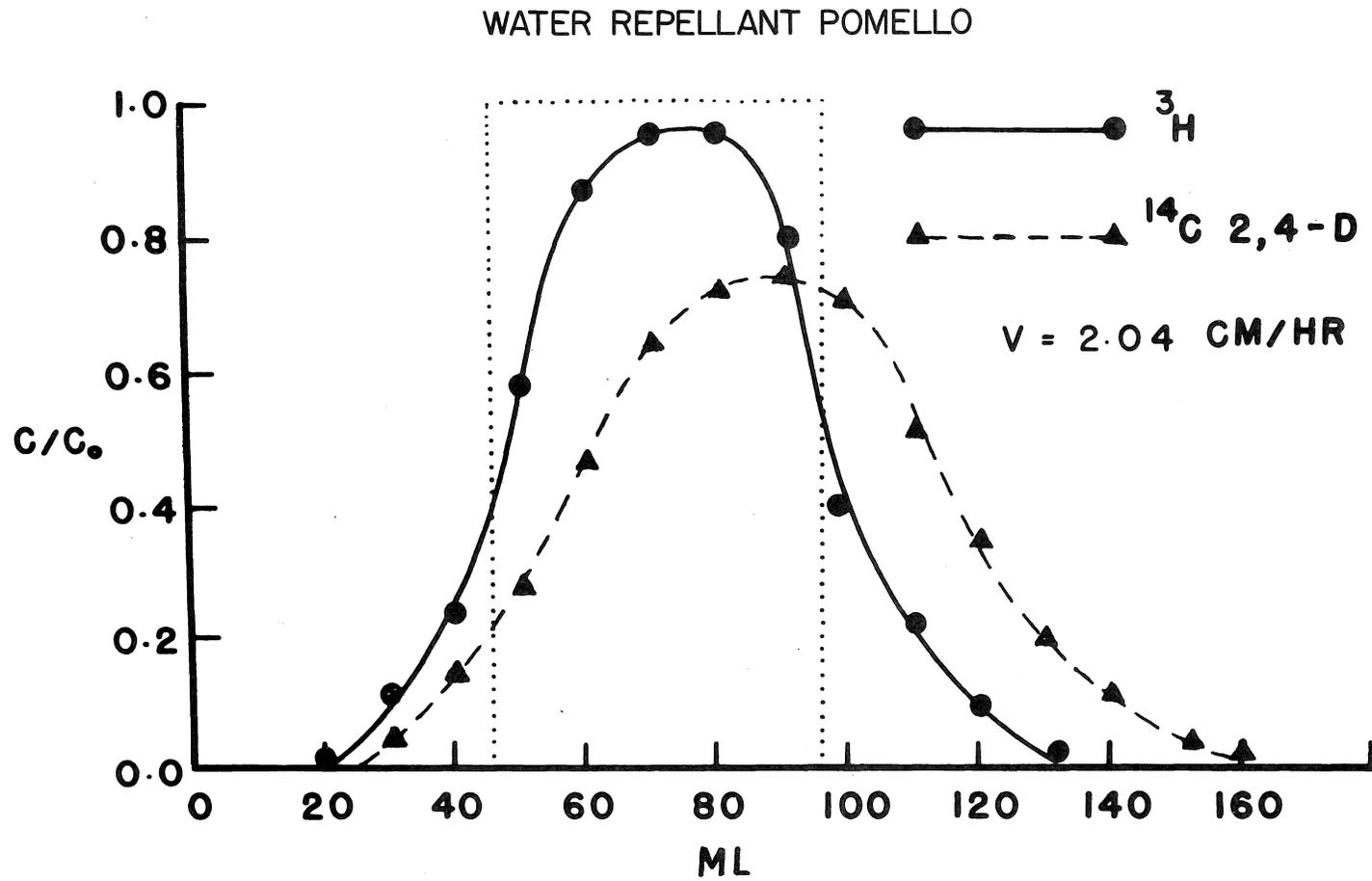


Figure 6. Breakthrough Curves of 2,4-D and Tritiated Water in Water-Repellant Pomello Fine Sand

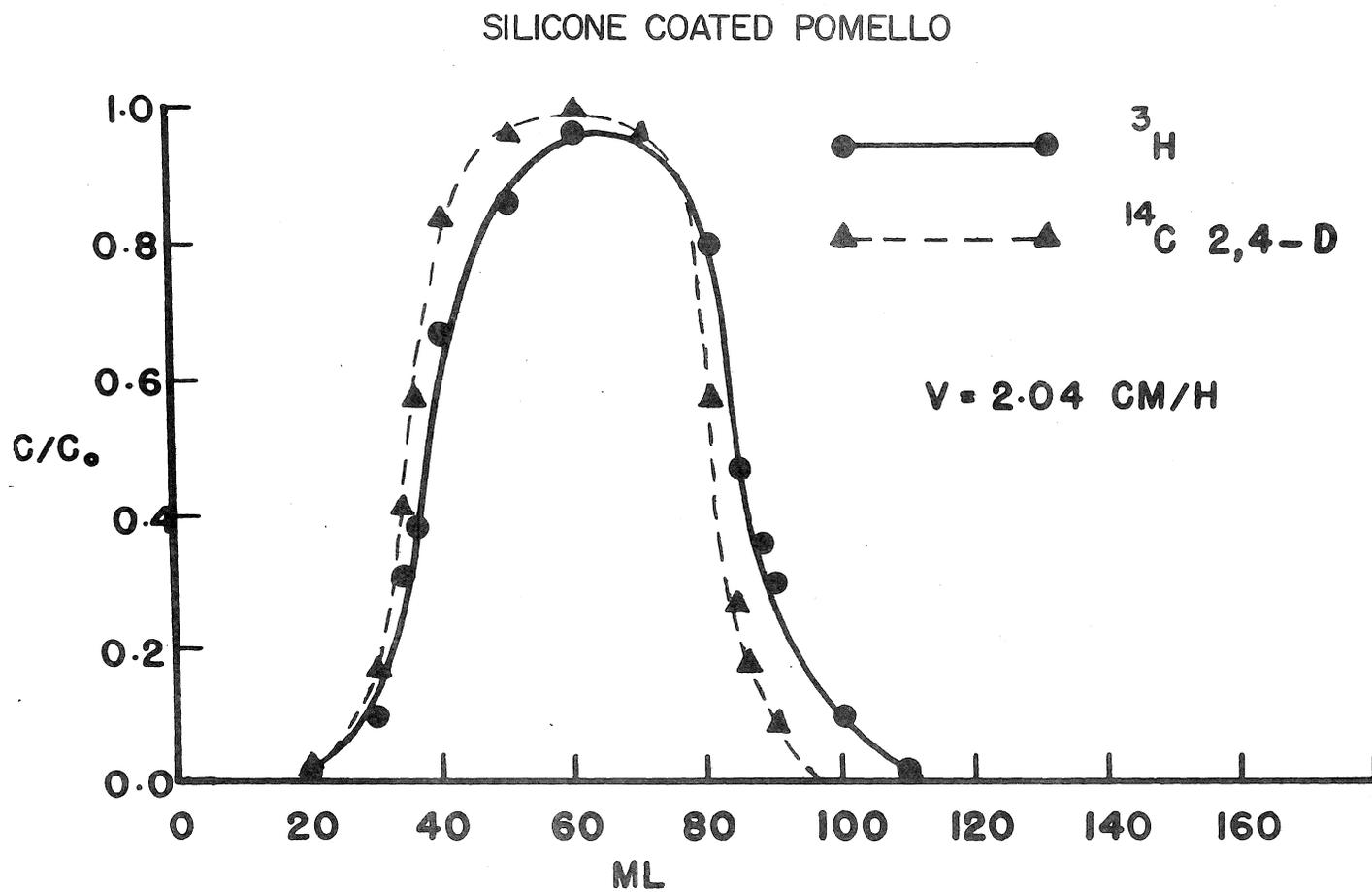


Figure 7. Breakthrough curves of 2,4-D and Tritiated Water in Ignited and Silicone Coated Pomello Fine Sand

Lakeland fine sand, Fellowship sandy clay and Everglades mucky peat, under constant flow velocities. Air dry soils were packed uniformly in a column of 7.5 cm inside diameter and 30 cm length which was held vertical during the studies. A photograph of one of the soil columns is shown in Figure 8. A dilute solution (10 mg/l) of 2,4-D was introduced at the bottom of the column with constant liquid flux maintained at 50 ml/h with a positive displacement pump. The same flux was continued until 200 ml of solution had entered the soil, at which time the solution was immediately replaced by pure water containing 0.5% phenol. Thus, a "volume slug" of herbicide solution was displaced upward in the column by water at the same flow rate. Studies were also made at a liquid flux of 100 ml/h. Effluent was collected in equal volume aliquots for analyses. Soil solution was extracted at the midway point (15 cm elevation) with a specially constructed sampling device using a porous plate and partial vacuum. The extract was collected periodically in amounts of 25 microliters. Effluent samples and the extracts were analyzed for 2,4-D content with a liquid scintillation counting system. Random effluent samples were subjected to additional analyses for 2,4-D to determine if the herbicide was degraded in the soil columns. The analyses were done by thin layer chromatography. The thin layer chromatographic studies revealed that the herbicide did not disintegrate during transport through the soil.

Experimental breakthrough curves of 2,4-D applied as a 500 ml "slug" of aqueous solution to columns of glass beads and Lakeland fine sand are shown in Figures 9 and 10. The almost rectangular shape of the curve for elution from glass beads indicates that the herbicide underwent only limited retention and the herbicide movement closely paralleled the water movement. The breakthrough curve for displacement through Lakeland fine sand is very wide which indicates interaction of 2,4-D with the porous medium. The low value of C/C_0 (approximately 0.2) for the first aliquot of column effluent indicates that the movement of 2,4-D lagged behind that for the water. The herbicide also lingered in the soil effluent for longer periods than for the glass beads. These two curves were included in this report as being representative of data reported in the Ph.D. dissertation of V. Jyothi (1971).

Theoretical and experimental breakthrough curves of herbicide concentration were expressed as functions of accumulative volume of solution introduced at the bottom of the columns. These elution curves were plotted for effluent and soil extracts at both liquid flow velocities. It was observed that the theoretical curves compared fairly well with experimental results. However, some discrepancy was observed between calculated and experimental curves during the initial time periods. Calculated concentrations were higher than the observed concentrations in the effluent. This indicated that there was

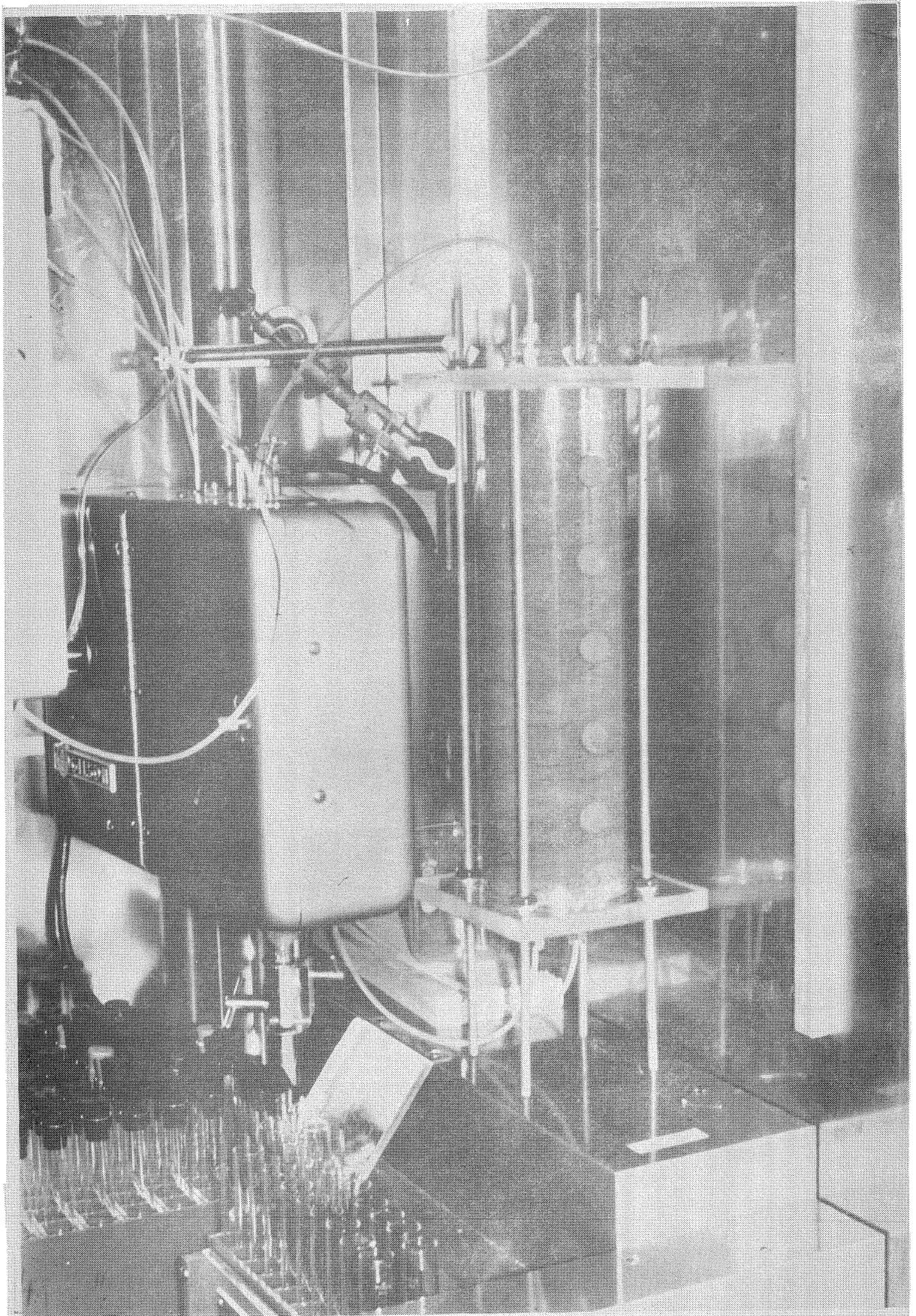


Figure 8. Photograph of a soil column in a constant temperature chamber. A linear fraction collector is also shown.

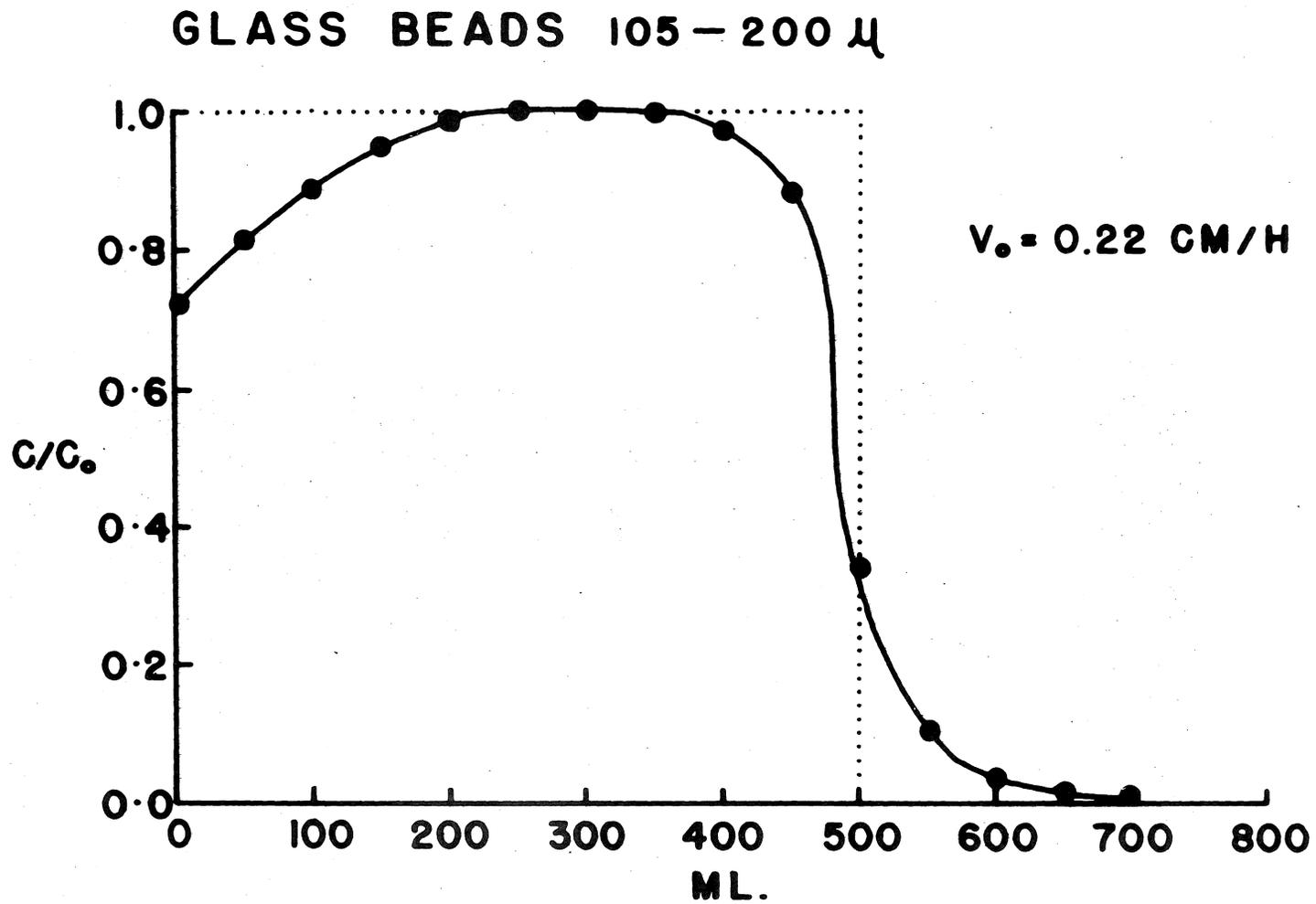


Figure 9. Experimentally Determined Breakthrough Curve for a 500 ml "Slug" of 2,4-D Applied as Influent to a Column of Initially Dry Glass Beads at a Liquid Flow Velocity of 0.22 cm/h.

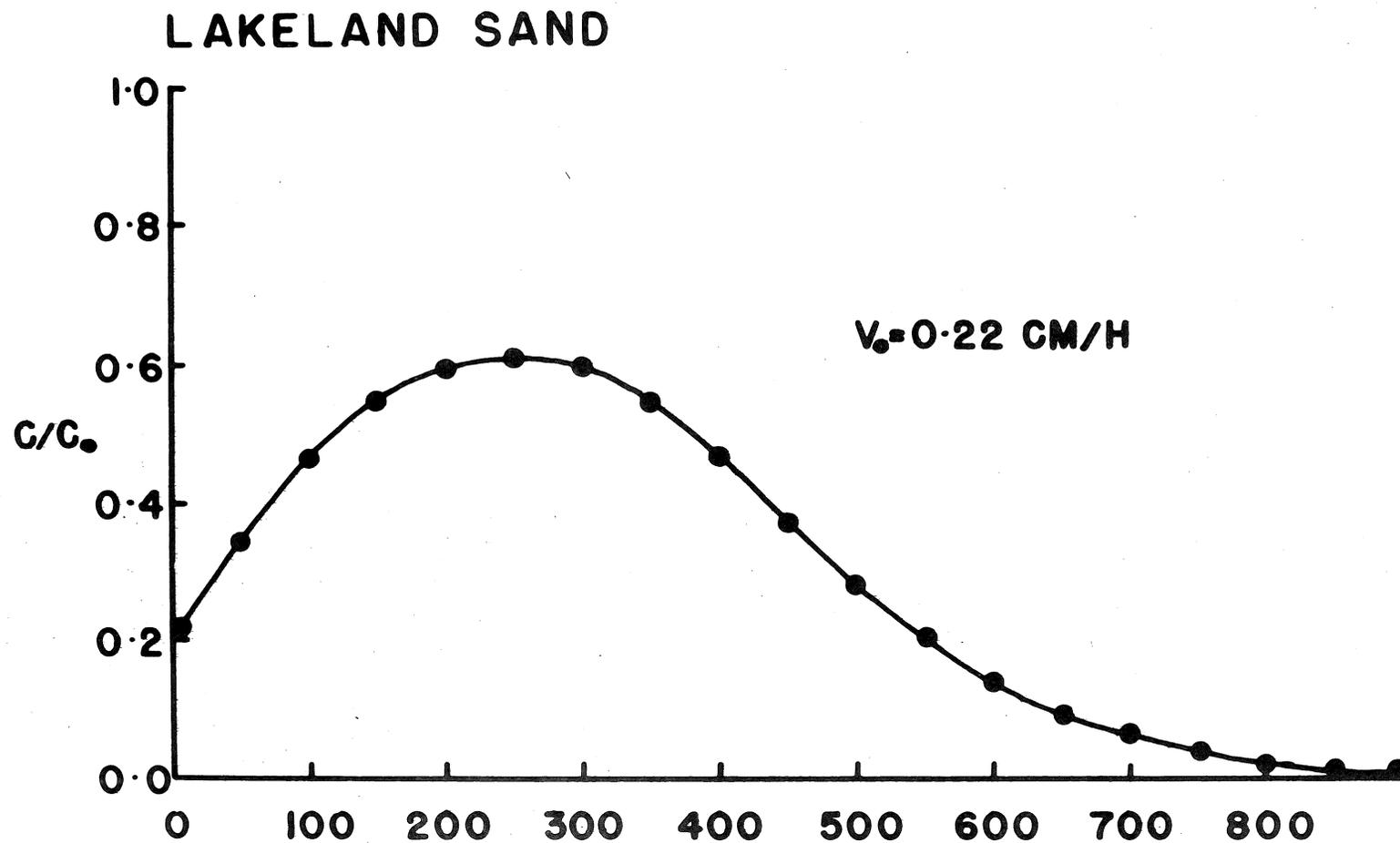


Figure 10. Experimentally Determined Breakthrough Curve for a 500 ml "Slug" of 2,4-D Applied as Influent to a Column of Initially Dry Lakeland Fine Sand at a Liquid Flow Velocity of 0.22 cm/h

higher adsorption on the porous material during the wetting stage since all the surface area was readily available for adsorption.

Observed concentrations were slightly higher than the calculated values near the tail end of the curve. This prolonged skewness was attributed to diffusion which is likely to show in a run of longer time period but the simplified model does not account for diffusion. In addition, hysteresis may exist in the partition coefficient during adsorption and desorption. Calculated and observed peaks of maximum herbicide concentration appear at almost the same time. This mainly depended upon the partition coefficient determined in the adsorption isotherms. The rate of adsorption increased the spreading of the breakthrough curves.

The herbicide moved readily through glass beads, Lakeland fine sand and Fellowship sandy clay. Most of the herbicide was recovered within two pore volumes of effluent in these soils. Movement was very much hindered in Everglades mucky peat. It took more than 5 pore volumes to recover only 60% of applied 2,4-D. Adsorption of 2,4-D appeared to be irreversible in the organic soils but not in the mineral soils.

Sterilization of Intact Soil Columns Using Exposure to Gamma Radiation and Methyl Bromide Fumigation

Sterilization of intact soil columns permits a convenient means for eliminating microbiological effects during miscible displacement of herbicide solutions through soil columns. The influence of specific physical and chemical variables upon herbicide movement may therefore be easily evaluated in sterilized columns of soil.

Two methods commonly employed for sterilization of soil are radiation with gamma rays and fumigation with methyl bromide gas. Eno and Popenoe (1964) observed that a radiation dose in excess of 10^6 rads (one rad is the dose of any ionizing radiation which produces the energy adsorption of 100 ergs per gram of soil) is required for sterility. Corey et al. (1967) used gamma radiation to sterilize intact columns of Webster-silica sand soil. Solutions of chloride and nitrate anions were then miscibly displaced through both sterilized and non-sterile soil columns. Recoveries of applied nitrate were 100 and 66%, respectively, for sterile and non-sterile columns. Steam, methyl bromide fumigation, and gamma radiation methods were experimentally compared by Eno and Popenoe (1964) on disturbed soil samples.

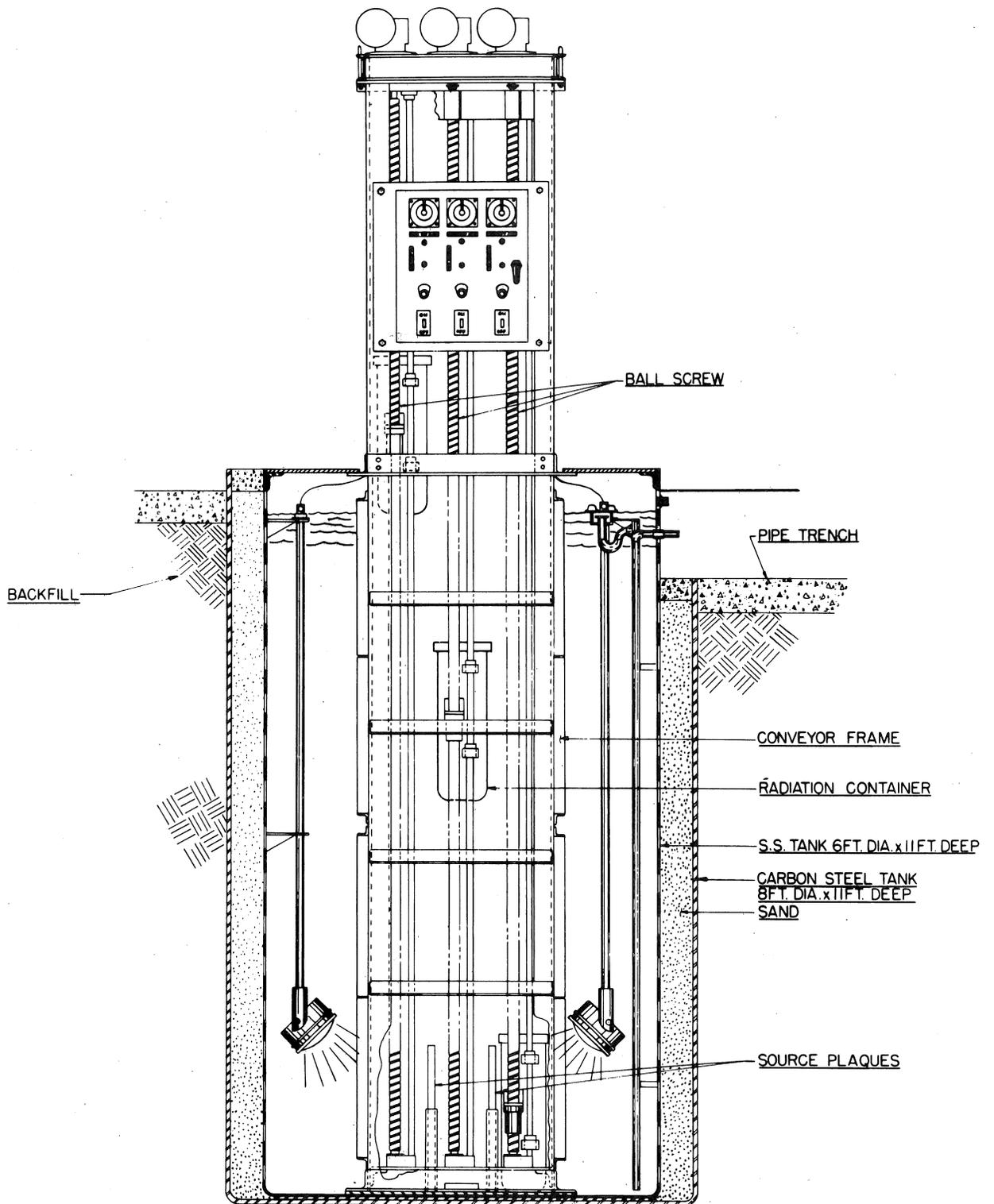
The effectiveness of methyl bromide fumigation and gamma radiation sterilization methods were evaluated in this study for intact columns of Oldsmar fine sand.

Experimental Methods and Procedure

Air-dry samples of Oldsmar fine sand (taken from 0.10 cm depth in the field profile) were hand packed into glass columns of 2.54 cm internal diameter and 30 cm length. Sections of silicon rubber tubing were attached to each end of the columns. The columns were hermetically sealed by attaching a rubber septum to the end of each section of tubing. Two of the air-tight columns were placed in the sample container of the Research Food Irradiator, Food Science Department. The radiation source in the facility was 10^5 Ci of cesium-137 which gives a dosage rate of 2×10^5 rads per hour in the center of the stainless steel sample container (15 cm x 30 x 45 cm). A diagram of the irradiator is presented in Figure 11. The soil columns were exposed to the radiation field for a period of 20 hours to give a calculated total dose of 4×10^6 rads. After sterilization these columns were stored for later incubation analysis.

Two other soil columns were fumigated with methyl bromide gas in a laboratory hood. A pressurized can of the gas was purchased from a garden store for this purpose. Thick-walled tygon tubing was used to connect a valve which was connected to the outflow from the methyl bromide container to a 40 liter glass carboy and the carboy was connected by tygon tubing to a glass Y-tube. Both forks of the tube were connected to large syringe needles which were inserted into the rubber septums at the ends of the two columns. Needles attached to separate sections of tygon tubing were also inserted into the septums at the gas outflow end of the columns. The outflow ends of each piece of tubing were placed at about 1 cm depth in a beaker of water. Visually monitoring the relative flow rate of gas bubbles in the water permitted a rapid determination of the approximate gas flow rate in the columns. The flow system was first tested with air flow to test for leaks; however, the test revealed the system functioned properly. The valve was then opened on the methyl bromide container and allowed to move into the soil columns, initially flushing air from the pores. Rubber gloves, a long-sleeved lab coat, and protective eye goggles were worn during the fumigation as safety precautions. Also the glass door of the hood separated the experimenter from the experiment. The columns were left exposed to methyl bromide for a 24-hour period, after which the needles were removed from the septums and the sealed columns were stored for later incubation analyses.

Samples of radiated, fumigated and control soils were incubated in several growth media to determine the growth of microorganisms. Seven media were specific for the growth of aerobic organisms and one medium was specific for the growth of anaerobic organisms. Tryptic soy agar, Bacillus medium, sporulation agar, mycological agar, peptone yeast - trypticose agar, mannitol agar, and gelatin agar were the culture media



RESEARCH FOOD IRRADIATOR

Figure 11. Schematic Diagram of University of Florida Research Food Irradiator

for aerobes. The culture media and procedure for anaerobes was that described by Smith (1964). Approximately one gram of radiated, fumigated or non-treated soil was placed upon the growth media in each petri dish. Incubation was allowed to proceed for seven days at 28°C. For a control, 1 ml of steam sterilized distilled water was placed on the growth media in petri dishes. The steam sterilized media were initially poured into steam sterilized petri dishes in a transfer chamber equipped to provide a positive outflow of sterilized air. At the end of the incubation period the presence or absence of growth was recorded for each petri dish. Observations were visually determined under a microscope at 2X magnification. The binomial data was reported as ratios, R, of the number of petri dishes with growth to the total number of dishes. The ratios were transformed by the relation $X = \arcsin \sqrt{R}$ before statistical analysis of the data.

Results and Discussion

Data for the study is shown in Table 2 and statistical analysis is presented in Tables 3 and 4. Both the methyl bromide fumigation and the gamma irradiation treatments of the soil columns were shown to be highly effective means for sterilization.

The two treatments were observed to be equally effective methods of sterilization for both aerobes and anaerobes.

Miscible Displacement of Paraquat Herbicide, C^{14} , and Tritiated Water Through Sterile and Nonsterile Soil Columns

Steam sterilized aqueous solutions of 10 ppm C^{14} labeled paraquat herbicide and tritiated water were displaced through 3 columns each of methyl bromide fumigated, gamma irradiated and unsterilized Oldsmar fine sand (0-10 cm depth). Air dry soil was packed in glass columns of 2.54 cm inside diameter and 30 cm length to give a soil bulk density of 1.00 g per cm^3 . Each column was water-saturated one day before displacement was to begin and water was then pumped through the column at a velocity of 5.2 cm per h for 24 hours. The purpose of the study was to determine if sterilization influenced the retention of the paraquat or tritiated water during movement through the soil. Soil columns were sterilized by placing each intact column of air-dry soil within a high intensity field of gamma radiation (Cs^{137}) or by flushing gaseous methyl bromide through the intact columns. Sterilization procedures are described previously in this report. Three successive applications of paraquat and tritiated water solution were applied to water-saturated soil columns. As expected for this soil, which had 8% organic matter, no paraquat was recovered in the liquid effluent from radiation sterilized, methyl bromide sterilized, or unsterilized columns due to strong adsorption by the soil particles. However, tritiated

Table 2. Growth of Microorganisms in Samples of Fumigated, Irradiated, and Non-treated Oldsmar Fine Sand Incubated with Seven Culture Media for Aerobes and Anaerobes

The data are reported as values of R, ratio of number of samples with growth observed to the total number of samples.

<u>Culture Media</u>	<u>Replicate No. 1</u>			<u>Replicate No. 2</u>		
	<u>Fumi- gated Soil</u>	<u>Irradi- ated Soil</u>	<u>Non- treated Soil</u>	<u>Fumi- gated Soil</u>	<u>Irradi- ated Soil</u>	<u>Non- treated Soil</u>
specific for aerobes:						
1. tryptic soy agar	12.92	12.92	69.30	12.92	12.92	69.30
2. Bacillus medium	12.92	12.92	69.30	12.92	26.56	69.30
3. sporulation agar	12.92	12.92	69.30	12.92	12.92	69.30
4. mycological agar	26.56	12.92	69.30	12.92	12.92	69.30
5. peptone yeast - trypticose agar	12.92	12.92	69.30	26.56	12.92	69.30
6. mannitol agar	12.92	12.92	69.30	12.92	12.92	69.30
7. gelatin agar	26.56	12.92	69.30	26.56	12.92	69.30
specific for anaerobes:	12.50	12.92	69.30	12.50	12.50	91.7

Table 3. Analysis of Variance for Growth of Aerobic Microorganisms in Sterilized and Non-treated Oldsmar Fine Sand During Incubation with Seven Growth Media.

The data were transformed with the relation $X = \arcsin \sqrt{R}$.

	<u>Degrees of Freedom</u>	<u>Mean Squares</u>	<u>F-value</u>
Replicates	1	4.45	0.23
Media	6	16.21	0.85
Treatments	2	13,608.00	721.50**
Error	32	18.86	
Total	41		

** Indicates significance at 1% level of probability.

Table 4. Analysis of Variance for Growth of Anaerobic Microorganisms in Sterilized and Non-treated Oldsmar Fine Sand During Incubation with a Single Growth Media

The data were transformed with the relation $X = \text{arc sin } \sqrt{R}$.

	<u>Degrees of Freedom</u>	<u>Mean Squares</u>	<u>F-Value</u>
Replicates	1	0	
Treatment	2	3683.40	∞
Error	2		
Total	<u>5</u>		

water recovery was pronounced as three successive breakthrough curves (one for each application) in the effluent from all soil columns. Percentage recovery of tritiated water was very nearly the same for each of the three successive curves (Figures 12 and 13) for the sterilized columns, but recovery progressively decreased with the 3 successive curves (Figure 14) from the unsterilized soil column. Recovery of tritiated water in the effluent from the unsterilized column was 92.5, 86.1, and 81.2%, respectively. Although data reported in Figures 1, 2 and 3 represent average values from 3 replicate soil columns, a fourth column of unsterilized soil was prepared as a check. This column was water-saturated and three successive 5 ml "slugs" of an aqueous solution of NaCl^{36} and tritiated water were applied as influent to the column. A constant liquid flow velocity was maintained through the soil, and water was applied as influent prior to and following each slug. Breakthrough curves of Cl^{36} and tritiated water in the column effluent are given in Figure 15. Note that the Cl^{36} recovery was 99.2, 98.1, and 98.0%, respectively, for the successive "slugs;" whereas the tritiated water recovery was 95.2, 92.2, and 86.1%, respectively. The chloride anion recovery was constant and almost complete, but the recovery of tritiated water decreased for the successive "slugs." For a given "slug" the breakthrough curves indicate that the chloride appeared in the effluent prior to the tritiated water. The tritiated water also lingered in the effluent after elution of chloride has ceased. Corey et al. (1963) also observed separation of chloride and tritiated water breakthrough curves for single displacements through water-saturated columns of sandstone. They observed that separation was greater for lower than for higher liquid flow velocities due to molecular diffusion effects.

The decrease in recovery of tritiated water with successive "slug" applications as influent to columns of unsterilized Oldsmar fine sand was definitely related in some way to microbiological activity. Since microorganisms multiply at very rapid rates (population may double within one-half hour under correct conditions) the population of soil microbes probably increased considerably during the 2 to 3 days required to displace three successive "slugs" through each unsterilized soil column. We therefore postulate that the observed decrease in recovery of tritiated water was due to increased microbial retention in the unsterilized soil with increasing time. Skewness of breakthrough curves for tritiated water in Figures 3 and 4 imply that retention by some mechanism did occur. Comparison of symmetry for these curves to those in Figures 1 and 2 show that minimal retention of tritiated water occurred in the fumigated or irradiated soil columns.

Displacement of Paraquat and Diquat Herbicides by KCl Solution from Water-Saturated Columns of Soil

The toxicant portions of paraquat and diquat herbicides

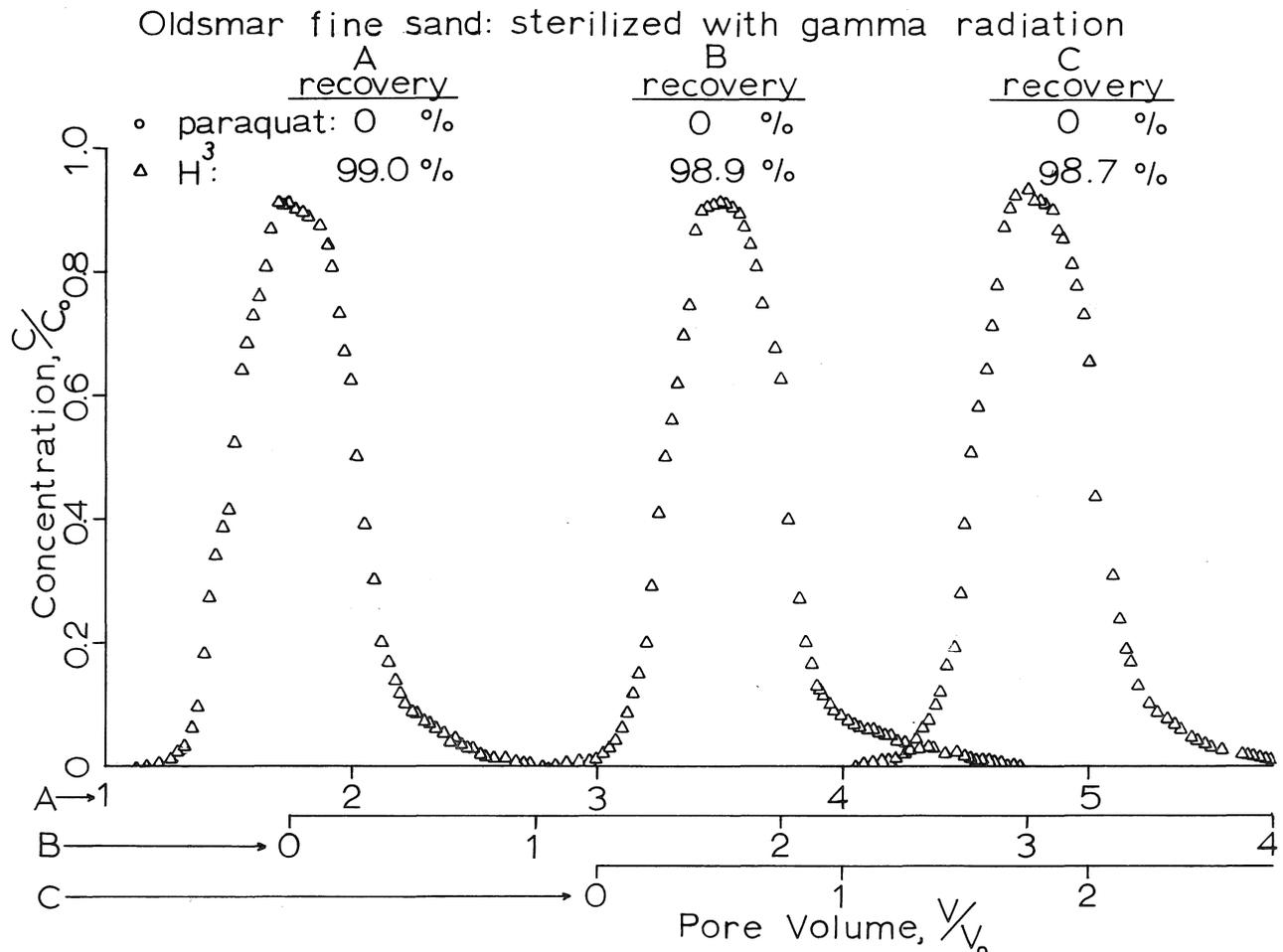


Figure 12. Breakthrough Curves for C^{14} Labeled Paraquat and Tritiated Water in the Effluent From a Column (Average of Data From Three Replicates) of Gamma Irradiated Oldsmar Fine Sand After Three Successive Influent Applications of "Slugs"

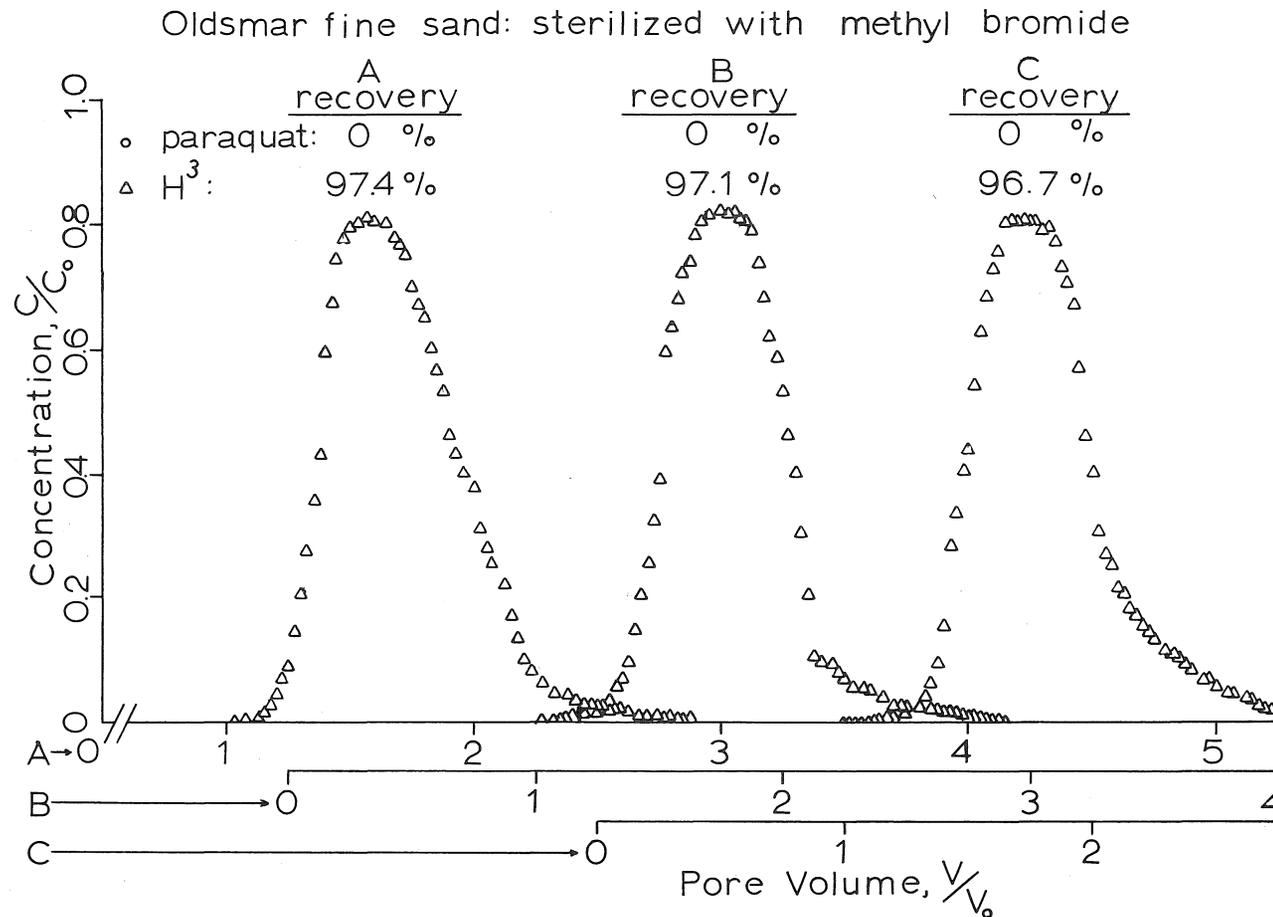


Figure 13. Breakthrough Curves for C¹⁴ Labeled Paraquat and Tritiated Water in the Effluent From a Column (Average of Data from Three Replicates) of Methyl Bromide Fumigated Oldsmar Fine Sand After Three Successive Influent Applications of "Slugs"

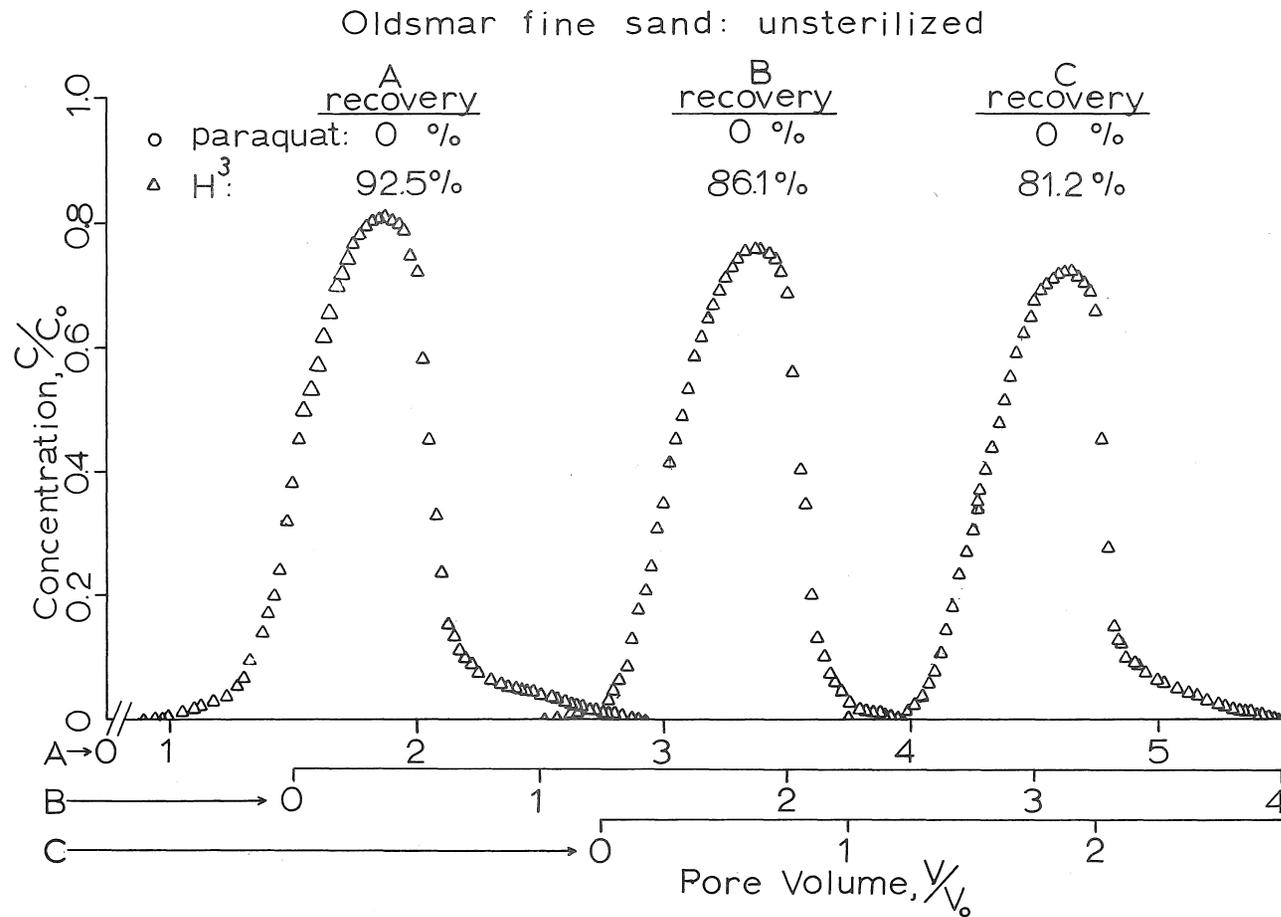


Figure 14. Breakthrough Curves for C^{14} Labeled Paraquat and Tritiated Water in the Effluent From a Column (Average Data from Three Replicates) of Non-Sterilized Oldsmar Fine Sand After Three Successive Influent Applications of "Slugs"

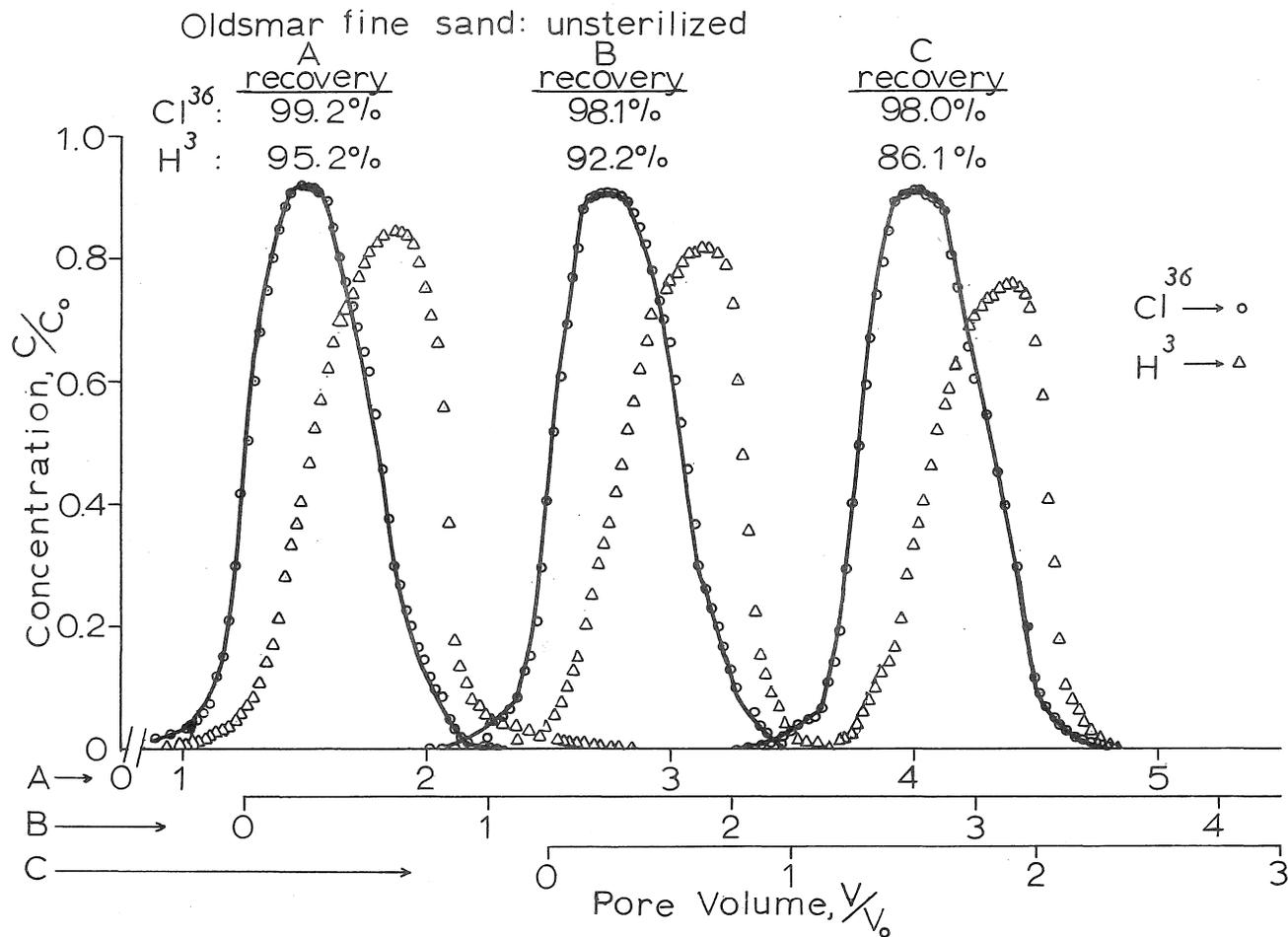


Figure 15. Breakthrough Curves for Cl^{36} and Tritiated Water in the Effluent From a Column of Non-Sterilized Oldsmar Fine Sand After Three Successive Influent Applications of "Slugs"

are divalent organic cations which undergo rapid physical adsorption with soil components (Weber *et al.*, 1965; Weber and Weed, 1968; Tucker *et al.*, 1967; Coats and Funderburk, 1966; and Knight and Tomlinson, 1967). A short study was performed to determine if these chemicals could be desorbed from soil columns by aqueous solutions of KCl.

Air-dry Wabasso fine sand taken from 0-10 and 33-76 cm profile depths were packed into glass columns of 2.54 cm inside diameter and 30 cm length. The organic matter contents of these two soil materials were determined to be 1.3 and 0.1%, respectively, both composed of greater than 97% sand. The average bulk density for the two columns was 1.32 g per cm³. The columns were saturated with distilled water and a variable-flow pump was used to maintain a fluid flow velocity of 6 cm per hour. After one day of flow, the influent was changed from water to an aqueous solution of 10 ppm paraquat for one column and diquat for the other. Both chemicals were labeled with C¹⁴. After one hundred ml of herbicide solution entered the columns, the influent was switched to water. Water was allowed to displace the herbicides into the column until 5 pore volumes of column effluent had been collected by an automatic fraction collector. At that time the influent was switched to a 746 ppm aqueous solution of KCl.

Breakthrough curves for paraquat and diquat in the effluents of columns of 0-10 and 33-76 cm soil materials are presented in Figures 16 and 17. Between 0 and 5 pore volumes neither of the chemicals appeared in the effluent for either soil material. The paraquat and diquat were thus assumed to be completely adsorbed in the soil columns. After 5 pore volumes, paraquat occurred in the effluent from the 0-10 cm soil but the recovery was very small. None of the diquat appeared in the effluent. For the 33-76 cm soil both herbicides appeared in the effluent with a sharp breakthrough; however, the amount of paraquat exceeded that of diquat. Small quantities of the chemicals remained in the effluent even after 20 pore volumes of liquid flow.

Paraquat and diquat, to a lesser extent, were observed to be desorbed from Wabasso fine sand by KCl solution. Thus, it would appear that applications of fertilizer to this soil could influence the desorption and consequent movement of paraquat and diquat in the soil solution.

Soil Adsorption of Paraquat Herbicide

Equilibrium adsorption isotherms of paraquat were performed for Everglades mucky peat, water-repellant and ignited (600°C for 12 hours) Blanton fine sand, and Wabasso fine sand. Five grams (oven dry basis) of soil were placed with 25 ml of C¹⁴ labeled aqueous solutions of known concentration of paraquat into centrifuge tubes. The tubes were placed on a mechani-

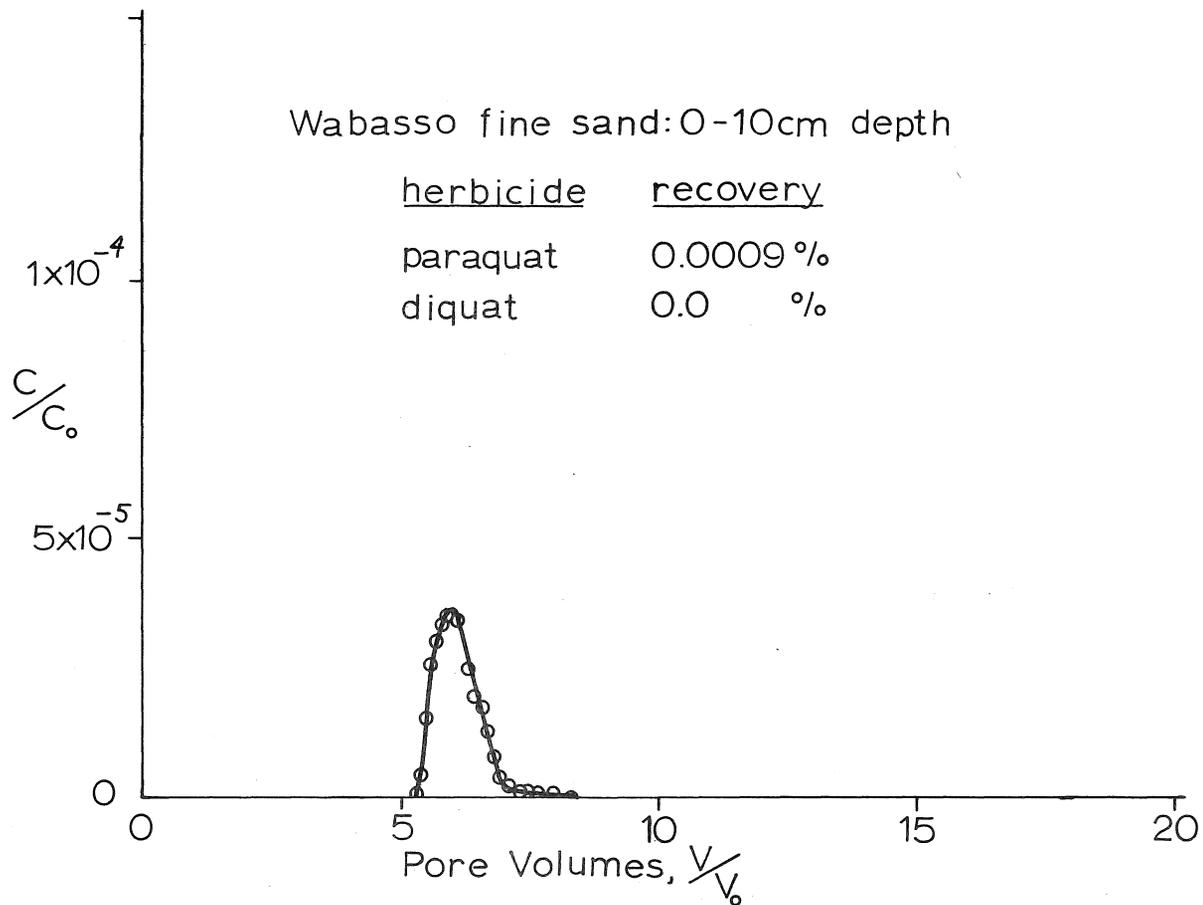


Figure 16. Displacement of Paraquat and Diquat Herbicides by KCl
From a Column of Wabasso Fine Sand, 0-10 cm Profile Depth

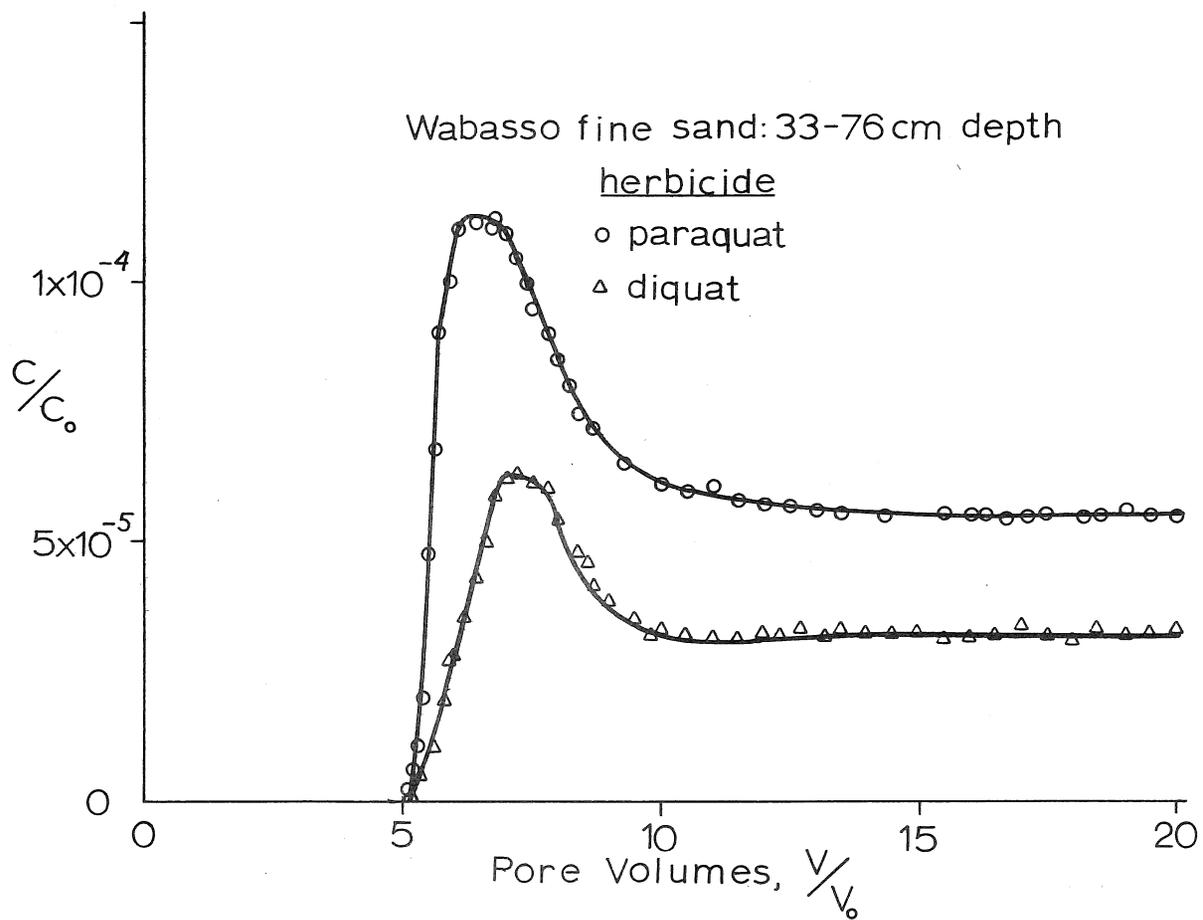


Figure 17. Displacement of Paraquat and Diquat Herbicides by KCl From A Column of Wabasso Fine Sand, 33-76 cm Profile Depth

cal shaker for one hour and centrifuged for 15 minutes. The concentration of paraquat in the supernatant liquid was determined by placing one ml in 15 ml of Bray's counting solution and counting the radioactivity with a liquid scintillation counter. The concentrations of paraquat in the initial solutions ranged from zero to 500 ppm ($\mu\text{g}/\text{ml}$).

The resulting adsorption isotherms are presented in Figures 18 and 19. For linear isotherms, the slope gives the value R, the distribution coefficient. Sorption was clearly linear over the range of 0 to 500 $\mu\text{g}/\text{ml}$ of paraquat in solution and had an R value of 6 ml/g. The water-repellant Blanton soil was linear over the range of 0-100 $\mu\text{g}/\text{ml}$ with an R of 4.8 ml/g, but the ignited Blanton was linear over approximately 0 to 50 $\mu\text{g}/\text{ml}$ with an R of about 3 ml/g. Over the narrow range of 0-10 $\mu\text{g}/\text{ml}$ paraquat adsorption was linear for Wabasso fine sand with an R of 3 ml/g. Thus adsorption by the peat soil was clearly greater than for either of the sand soils used. Ignition of the Blanton fine sand removed all soil organic matter and greatly decreased the adsorption of paraquat. The assumption of linear adsorption for dilute solutions of paraquat is valid for the organic soil and the two sands used.

Adsorption experiments were also performed with solutions of 17 and 51 $\mu\text{g}/\text{ml}$ paraquat when various concentrations of KCl were present in the paraquat solutions. The influence of 0-9000 ppm KCl concentrations upon paraquat adsorption in Everglades mucky peat, water-repellant and ignited Pomello fine sand, Wabasso fine sand, and water-repellant and ignited Blanton fine sand is presented by curves in Figures 20 and 21. The level of KCl concentration in the initial solution clearly had no effect upon adsorption of paraquat in the mucky peat at either level of paraquat concentration. This was expected because of the tremendous affinity of soil organic matter for paraquat. At the 51 ppm level of paraquat, adsorption decreased sharply and curvilinearly with increased level of KCl for Wabasso fine sand. At the 17 ppm paraquat concentration, adsorption decreased only slightly but linearly as the KCl concentration was increased from 0 to 9000 ppm for Wabasso soil. Paraquat adsorptions by ignited samples of Pomello and Blanton fine sands were much less than for the unignited counterparts. However, it is important to note that destruction of the organic matter did not eliminate all adsorption of paraquat. Although Pomello and Blanton soils are classified as sands, small quantities of clay and silt are present in the sand. An increase in KCl concentration in the 51 ppm paraquat solution gave a small linear decrease in adsorption and a more abrupt curvilinear adsorption decrease for unignited Pomello and Blanton fine sands, respectively. Thus for high levels of KCl concentration present in the soil solution, paraquat adsorption in sands may be less than if no salts were in the soil water. This observation has important implications to movement of paraquat in sandy

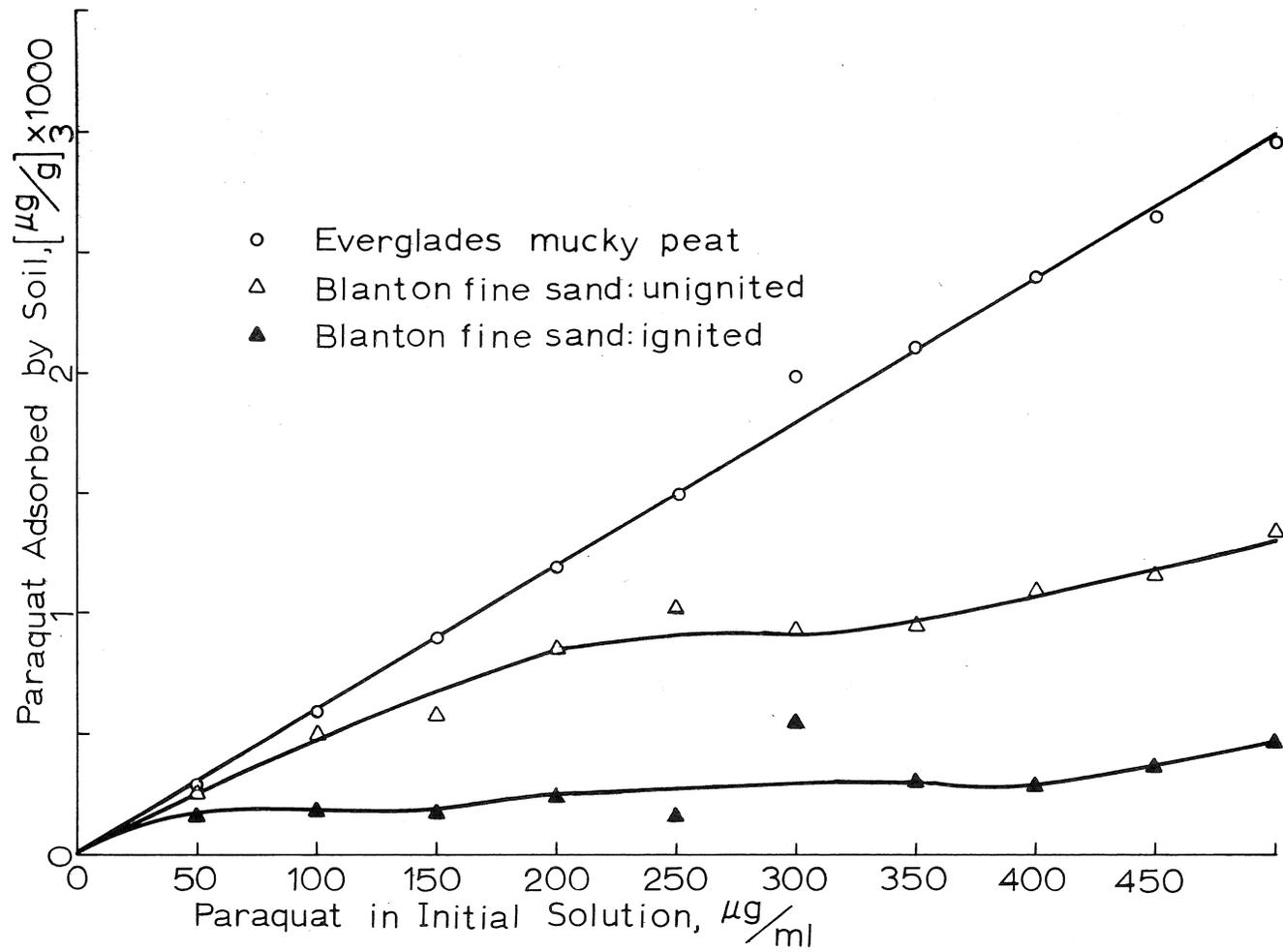


Figure 18. Adsorption Isotherms of Paraquat for Everglades Mucky Peat, Water-Repellant Blanton Fine Sand, and Ignited Blanton Fine Sand

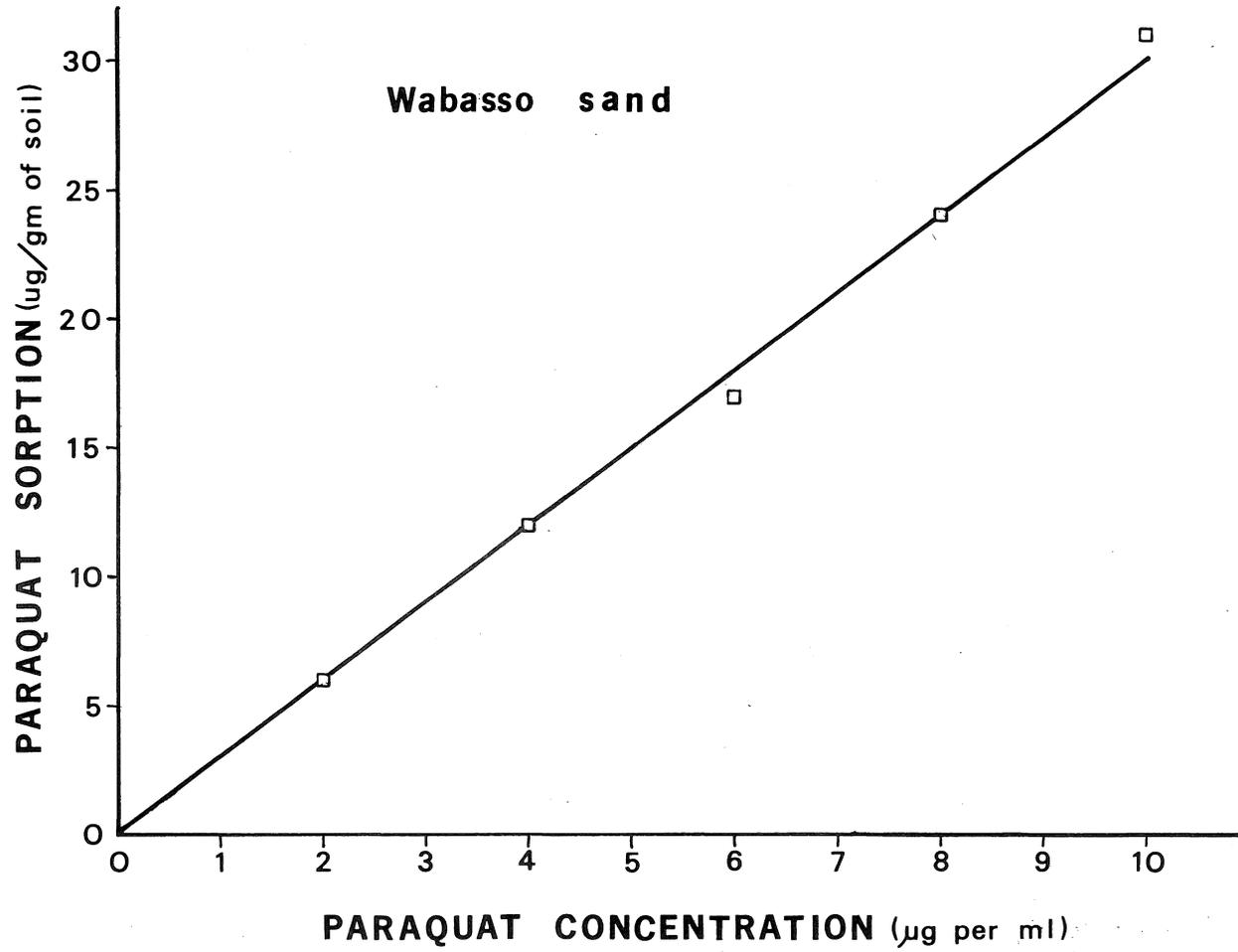


Figure 19. Adsorption Isotherm of Paraquat for Wabasso Fine Sand

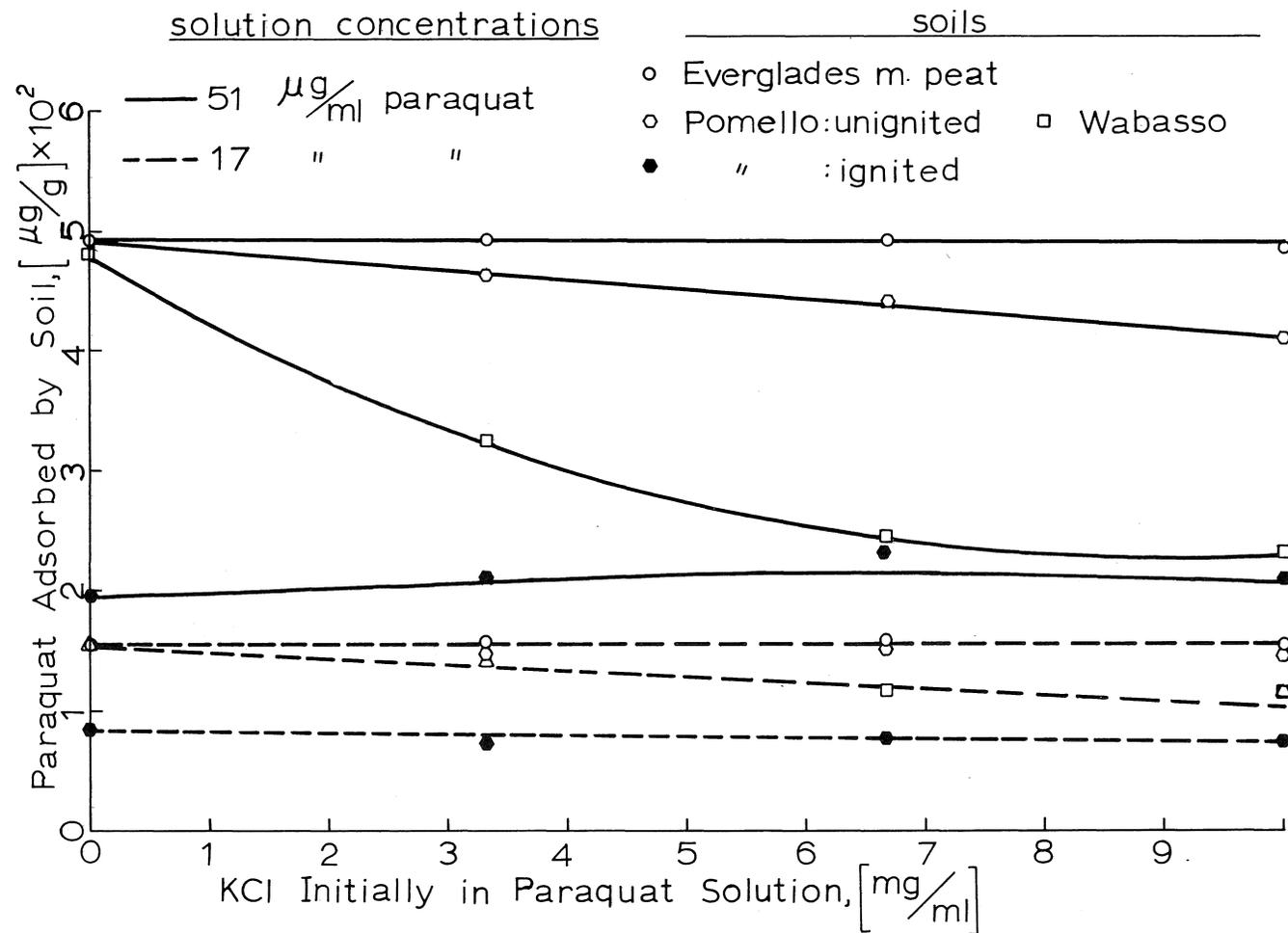


Figure 20. Influence of KCl in Solution Upon Adsorption of Paraquat in Everglades Mucky Peat, Water-Repellant and Ignited Pomello Fine Sand, and Wabasso Fine Sand

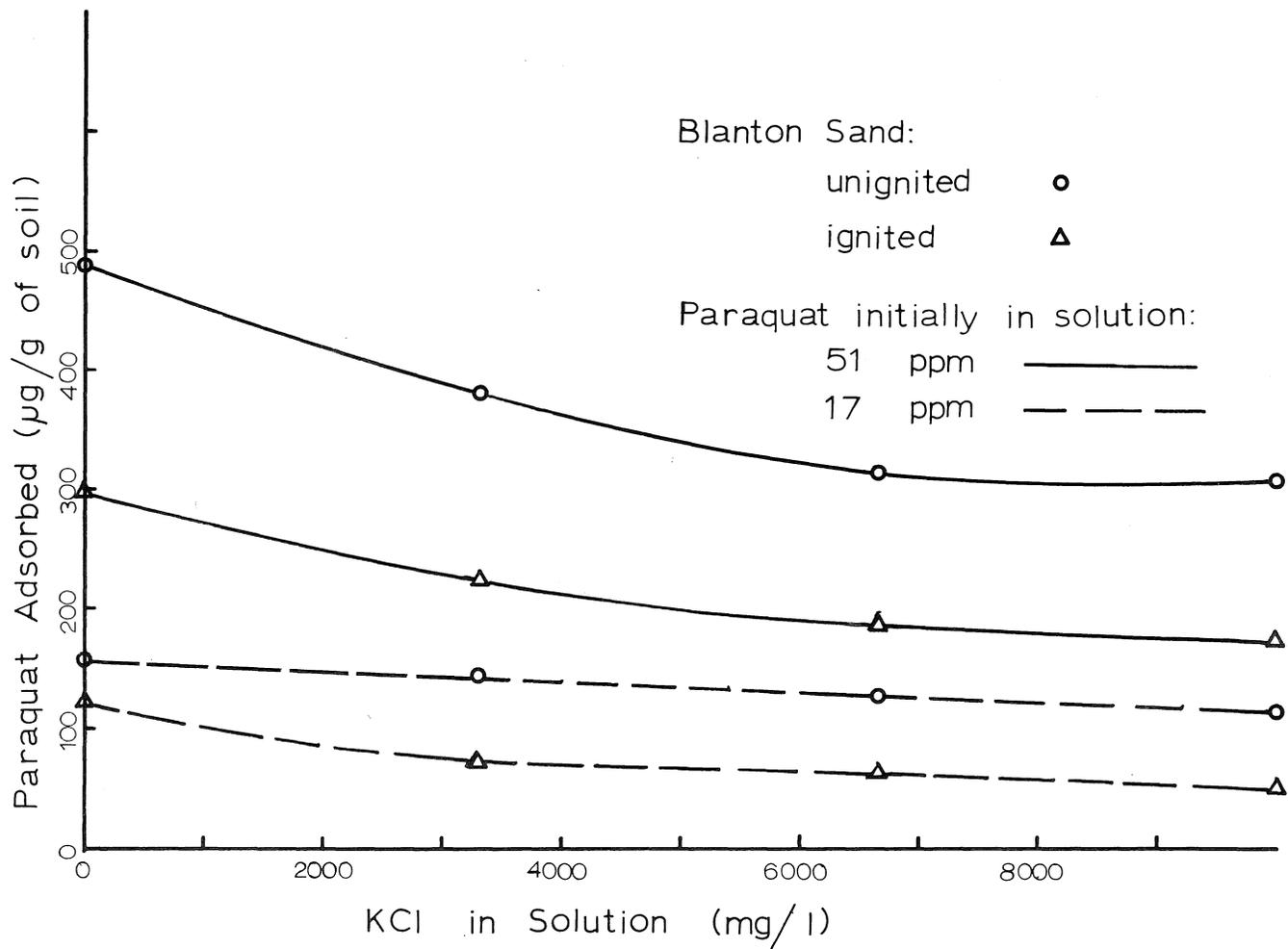


Figure 21. Influence of KCl in Solution Upon Adsorption of Paraquat in Water-Repellant and Ignited Blanton Fine Sand

soils. For example, under conditions of intense fertilizer application, paraquat may move further down the profile than otherwise expected.

Continuous Measurement of Chloride in Effluent Flowing from a Soil Column

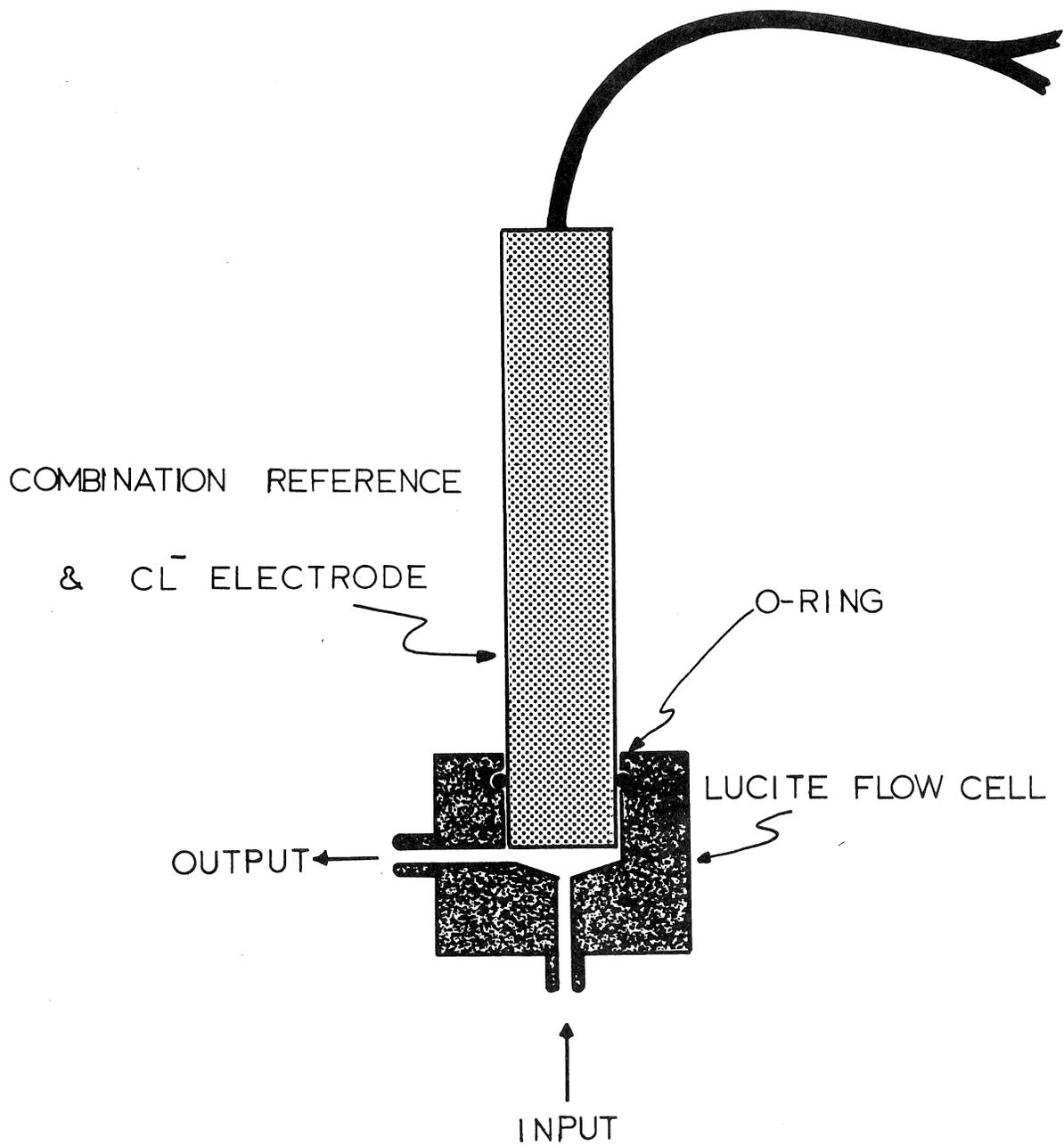
Miscible displacement of chloride solutions through a soil column normally requires the use of a fraction collector to collect aliquots of effluent and some means for measurement of the Cl^- concentration in each aliquot. Yoo and Kirkham (1971) described a liquid scintillation flow cell for continuously recording Cl^{36} concentration in soil effluent. Their method has advantages of eliminating the need for fraction collectors, provides instantaneous concentration measurements without need for sample storage and provides a continuous recording of concentration; however, the method has the inherent disadvantage of requiring that the chloride be radioactive. An inexpensive flow cell method is described in this study which does not require that the chloride be radioactive.

Experimental Apparatus

An Orion Model 96-17 Combination reference and chloride electrode provides the transducer for the method. The concentration range of the electrode is 1 to $5 \times 10^{-5}\text{M}$ chloride and the minimum sample size is 10^{-2} ml. The outer sleeve of the electrode is constructed of unbreakable plastic which is resistant to most solvents and is resistant to mechanical shock or stress. The reference portion of the combination electrode produces a stable, drift-free reference potential and low stirring and junction potentials.

A flow cell was constructed from a cylindrical section of lucite plastic. A schematic of the flow cell and the combination electrode is presented in Figure 22. A water-tight seal around the sleeve of the electrode was insured by the use of silicon rubber sealant rather than the rubber O-ring as shown in the schematic. The O-ring has the advantage of providing easy removal of the electrode from the flow cell for cleaning purposes.

The electrical voltage from the combination electrode was measured by a pH meter and the output from the meter was connected to a strip chart recorder. The transducer was calibrated by measuring the voltage for a range of chloride solutions of known concentration. The resulting calibration curve is shown in Figure 23. Calibration was performed in the flow cell except that the solutions were stationary during voltage measurements. Selected points from a strip chart recording of the transducer voltage can thus be converted to activities of chloride through the calibration curve.



FLOW CELL FOR Cl^- MEASUREMENT

Figure 22. Schematic Diagram Showing Combination Reference and Chloride Electrode in a Lucite Flow Cell

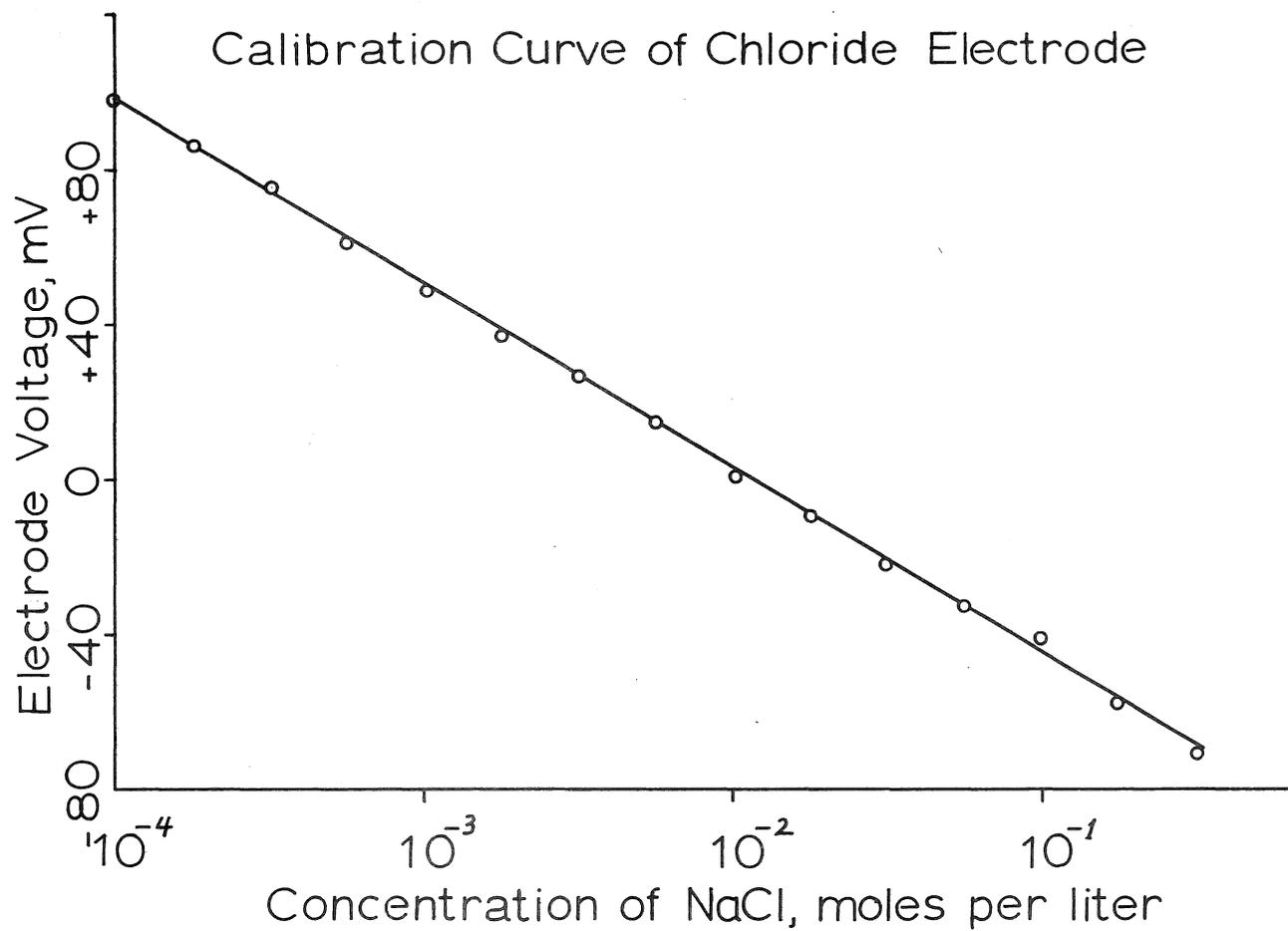


Figure 23. Calibration Curve for the Combination Reference and Chloride Electrode

To test the transient response of the flow cell and transducer system a concentrated aqueous solution of NaCl was displaced through a column of glass beads. A glass chromatography column with 2.54 cm internal diameter and 30 cm internal length was packed with 105-210 μm glass beads. The bulk density of the packed column was 1.57 g/cm^3 . The column was saturated with 5 ppm NaCl solution, and a variable flow pump was used to maintain a flow velocity of 7.0 cm/h of the dilute chloride solution through the porous media. After one day the 5 ppm influent solution was replaced by a 5005 ppm solution. A 2 ml "slug" of the concentrated NaCl solution was allowed to enter the column before switching back to the original dilute chloride influent. During the miscible displacement of the concentrated slug of chloride through the column the electrode voltage was recorded on the strip chart recorder. The chart speed was maintained at 31.17 cm/h . Column effluent flowing from the flow cell was collected in 2 ml aliquots in glass tubes on a fraction collector. Samples from the aliquots were later titrated with AgNO_3 to obtain the concentration of chloride in solution. The titration measurement provided a means for checking the concentrations obtained by the electrode method.

Results and Discussion

The breakthrough curve (relative concentration of chloride versus the number of pore volumes of column effluent) for concentrated chloride slug displaced through the column of glass beads is presented in Figure 24. Zero pore volume corresponds to the time at which the slug was first introduced as influent to the column. Circles on the graph correspond to concentrations determined by titration of effluent aliquots, and the smooth curve was provided by connecting concentrations determined by the transducer. Very close agreement between the two methods is clearly shown. Although the breakthrough curve is skewed, the aliquot concentrations also indicate a similar skewness. Integration of the curve by Simpson's rule indicated 96.0% recovery of the chloride slug. This large recovery percentage is only 4% less than the expected value of 100% and thus is an indication that the electrode method gave realistic concentrations of chloride.

Conclusion

An inexpensive flow cell and combination chloride electrode system is described for continuously recording the chloride concentration in effluent flowing from a column of soil. A breakthrough curve for chloride solution displaced through a column of glass beads was in close agreement with a corresponding breakthrough curve obtained by titration of aliquots of the same effluent.

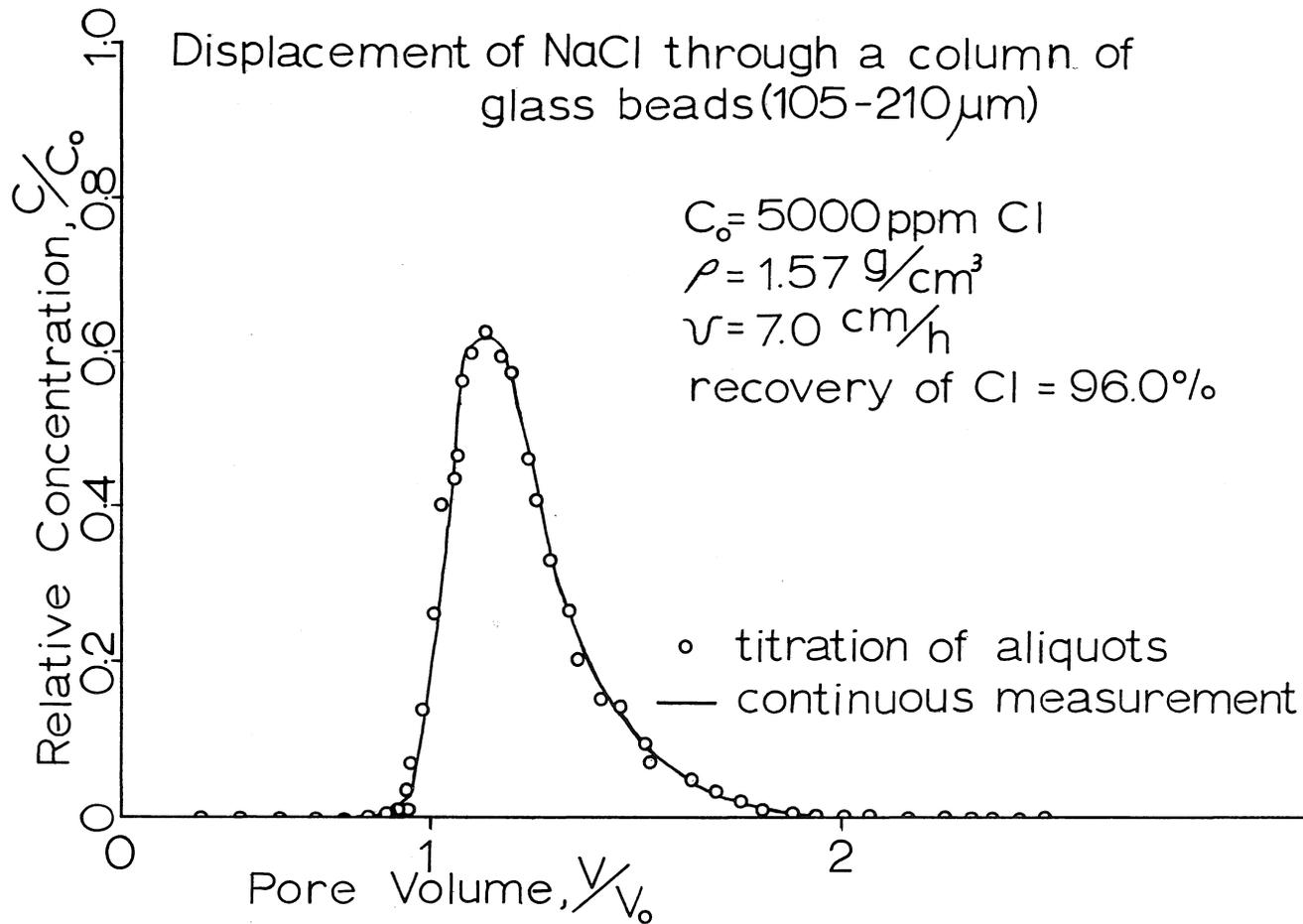


Figure 24. Breakthrough Curve of Chloride in Effluent from Column of Glass Beads

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LITERATURE CITED

1. Akhavein, A. A. and D. L. Linscott. 1968. The dipyridylum herbicides, paraquat and diquat. Residue Reviews, Vol. 23:97-145.
2. Bear, J., D. Zaslavsky, and S. Irmay. 1968. Hydrodynamic dispersion. Physical Principles of Water Percolation and Seepage, Publication 29 of Arid Zone Research Series, UNESCO, Paris, pages 307-349.
3. Boon, W. R., 1965. Diquat and paraquat - new agricultural tools. Chemistry and Industry, May 8, 1965, pages 782-788.
4. Bray, G. A., 1960. A simple efficient liquid scintillator for counting aqueous solutions in a liquid scintillation counter. Anal. Biochem. 1:279-285.
5. Calderbank, A., 1968. The bipyridylum herbicides. Advances in Pest Control Research, Vol. 8:127-235.
6. Coats, G. E., H. H. Funderburk, Jr., J. M. Lawrence, and D. E. Davis. 1966. Factors affecting persistence and inactivation of diquat and paraquat. Weed Res. 6:58-66.
7. Collins, R. E., 1961. Flow of Fluids Through Porous Materials. Reinhold Publishing Corporation, New York, N.Y.
8. Corey, J. C., D. R. Nielsen, and J. W. Biggar. 1963. Miscible displacement in saturated and unsaturated sandstone. Soil Sci. Soc., Amer. Proc. 27:258-262.
9. Corey, J. C., D. R. Nielsen, J. C. Picken, Jr., and Don Kirkham. 1967. Miscible displacement through gamma radiation - sterilized soil columns. Environmental Science and Technology, Vol. 1:144-147.
10. Crafts, A. S., 1957. The chemistry and mode of action of herbicides. Advances in Pest Control Research, Vol. 1:39-79.
11. Crafts, A. S., 1961. The chemistry and mode of action of herbicides. Interscience Publishers, New York. 269 pages.
12. Davidson, J. M., C. E. Rieck, and P. W. Santelman. 1968. Influence of water flux and porous material on the movement of selected herbicides. Soil. Sci. Soc., Amer. Proc. 32:629-633.

13. Davidson, J. M., and P. W. Santelman. 1968. Displacement of Fluometuron and Diuron through saturated glass beads and soil. *Weed Science* 16:544-548.
14. Day, Paul R., 1956. Dispersion of a moving salt-water boundary advancing through saturated sand. *Transactions, American Geophysical Union*, Vol. 37:595-601.
15. Eno, C. F., and Hugh Popenoe. 1964. Gamma radiation compared with steam and methyl bromide as a soil sterilizing agent. *Soil Sci. Soc. Amer. Proc.* 28:533-535.
16. Freed, V. H., 1966. Chemistry of herbicides. *Pesticides and Their Effects on Soils and Water*, American Society of Agronomy, Special Publication Number 8, pages 25-43.
17. Funderburk, H. H., Jr. 1969. Diquat and paraquat. *Degradation of Herbicides*, Marcel Dekker, Inc., New York, N.Y., pages 283-298.
18. Hartley, G. S., 1964. Herbicide behaviour in the soil. *The Physiology and Biochemistry of Herbicides*. Academic Press, New York, pages 111-161.
19. *Herbicide Handbook of the Weed Society of America*. 1967. W. F. Humphrey Press, Inc., Geneva, New York.
20. Jyothi, V., 1971. Miscible displacement of 2,4-D herbicide during constant liquid flow velocity into initially dry soils. Unpublished Ph.D. dissertation, Soil Science Department, University of Florida, Gainesville.
21. Kirkham, Don. 1964. Some physical processes causing movement of ions and other matter through soil. *Overdruk Uit De Mededelingen Van De Landbouwhogeschool En De Opzoekingsstations Van De Staat Te Gent*. DEEL XXIX; paper presented at 15th Annual Phytopharmacy Symposium, May 6, 1963, Ghent, Belgium.
22. Knight, B. A. G., and T. E. Tomlinson. 1967. The interaction of paraquat (1:1'-dimethyl 4:4'-dipyridylum dichloride) with mineral soils. *J. Soil Sci.* 18:233-243.
23. LeGrand, H. E., 1966. Movement of pesticides in the Soil. *Pesticides and Their Effects on Soils and Water*, American Society of Agronomy, Special Publication Number 8, pages 71-77.
24. Nielsen, D. R., and J. W. Biggar. 1961. Miscible displacement in soils. I. Experimental information. *Soil Sci. Soc. Amer. Proc.* 25:1-5.
25. Nielsen, D. R., and J. W. Biggar. 1962. Miscible displacement in soils. II. Theoretical considerations. *Soil Sci. Soc. Amer. Proc.* 26:216-221.

26. Nielsen, D. R., and J. W. Biggar. 1963. Miscible displacement in soils. III. Mixing in glass beads. Soil Sci. Soc. Amer. Proc. 27:10-13.
27. Scheidegger, A. E., 1957. Physics of Flow Through Porous Media. The MacMillan Co., New York, N.Y., pages 31-35 and 197-202.
28. Scheidegger, A. E., 1964. Statistical hydrodynamics in porous media. Advances in Hydroscience, Vol. 1:161-181.
29. Smith, P. H., 1964. Pure culture studies of methanogenic bacteria. Proceedings, 20th Industrial Waste Conference, Purdue University, Lafayette, Indiana.
30. Tucker, B. V., D. E. Pack, and J. N. Ospenson. 1967. Adsorption of bipyridylum herbicides in soil. J. Agr. Food Chem. 15:1005-1008.
31. Weber, J. B. and S. B. Weed. 1968. Adsorption and desorption of diquat, paraquat, and prometone by montmorillonitic and kaolinitic clay minerals. Soil Sci. Soc. Amer. Proc. 32:485-487.
32. Weber, J. B., P. W. Perry, and R. P. Upchurch. 1965. The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D, and prometone by clays, charcoal, and anion exchange resin. Soil Sci. Soc. Amer. Proc. 29:678-688.
33. Yoo, Sun-Ho and Don Kirkham. 1971. Flow Cell System for Miscible Displacement Experiments. Water Resources Research. 7:211-213.