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Capillary-Diffusion and Self-Diffusion of Liquid Water in Unsaturated Soils


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Ronald E. Phillips
University of Kentucky

V.L. Quisenberry Jr.
University of Kentucky

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CAPILLARY-DIFFUSION AND SELF-DIFFUSION OF
LIQUID WATER IN UNSATURATED SOILS

Ronald E. Phillips
Principal Investigator

Graduate Student Assistant: V. L. Quisenberry, Jr.

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ABSTRACT

CAPILLARY-DIFFUSION AND SELF-DIFFUSION OF LIQUID WATER IN UNSATURATED SOILS

Capillary-diffusion coefficients were measured by use of inflow and outflow methods. With both methods the capillary-diffusion coefficients decreased very rapidly with decreasing water content. The lighter textured soils were found to have the higher diffusion coefficients over the entire moisture content range studied, 0 to 1 bar tension.

Self-diffusion coefficients were measured over a moisture content range from air dryness to saturation using ^3H as a tracer of water. Each of the soils gave the same diffusion characteristics when the self-diffusion coefficients were expressed as a function of either water content or average number of water layers on the external surface of each mineral. As the water content decreased from saturation to near field capacity, the self-diffusion coefficients decreased very rapidly.

An attempt was made to separate the self-diffusion coefficients into a liquid and a vapor component by use of ^{36}Cl as a tracer of liquid water. The results showed ^{36}Cl not to be a good tracer of liquid water movement in soil.

The results suggest that a functional relationship exists between capillary-diffusion and self-diffusion; however, before this relationship can be firmly established, the liquid and vapor components of water movement must be separated.

KEYWORDS: * Unsaturated Water Movement
* Capillary-Diffusion
* Self-Diffusion, Soil

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OBJECTIVES

1. To evaluate the effect of soil water content, clay type, and clay content upon the capillary-diffusion and self-diffusion of liquid water in unsaturated soil.
2. To attempt to establish a functional relationship between capillary-diffusion and self-diffusion of liquid water in unsaturated soil.

At the present time, the usable water supply in the world is becoming critical. Therefore, it is essential that the hydrologic cycle be understood. The segment of the cycle which involves the movement of water within the soil and from the soil to the plant is one of the more important portions of the hydrologic cycle. An adequate supply of water for the production of food and fiber is an important indirect contribution of this segment of the hydrologic cycle.

The top meter of soil acts as a giant reservoir for the storage of water. However, the water held within the soil is ever in a dynamic state. Water moves from soil pores to plant roots and moves through the pores downward, laterally, or to the soil surface. The water may later be lost from the soil due to transpiration and evaporation or by drainage into underground aquifers.

Movement of much of the soil water occurs under low tension (0 to 1 bar) even though water held at tensions up to 15 bars is potentially available for subsequent plant use or evaporation. The rate at which these processes occur is primarily a function of the rate of water movement with the soil mass, the evaporative potential of the soil surface, and the leaf area of the growing plants. The amount of water held and the rates of water movement vary greatly among soils. The rates at which soils transmit water is known qualitatively, but little is known quantitatively, especially under field conditions. A complete description of soil water movement is a prerequisite to understanding the processes of evaporation, transpiration, or drainage which in turn are prerequisites to an

understanding of the conservation and efficient use of both soil water and irrigation water.

A description of soil water movement will enable workers in other areas of soil science to explain various problems that are related to water and its movement. The areas of soil chemistry, soil fertility, soil microbiology, soil genesis, and soil mineralogy will all benefit from an understanding of the dynamic soil water processes. Today the citizenry is concerned about environmental pollutants, many of which supposedly come from agriculture: nitrates, phosphates, herbicides, insecticides, and soil sediment. Before we can describe and control these areas of concern, we must describe the media in which they move: soil water is perhaps the most important medium of transport.

The flux of water in soil is the product of two quantities, the potential gradient and the diffusivity term which may be dependent upon the soil water content. Consequently, to predict the flux of water in soil it is imperative that work be done to measure these diffusion coefficients in the laboratory under controlled conditions. Later, these values can be used in the field so that a quantitative description of soil water movement can be obtained.

RESEARCH PROCEDURES

Six Kentucky soils: Maury, Pembroke, Eden, Burgin, Henry, and Huntington; and one California soil, Yolo, were used in this study to measure the capillary-diffusion and self-diffusion coefficients of soil water. Table I shows the soil type, location sampled, the particle size distribution, the dominant clay mineral, and the total and external surface areas of each of these soils. All soils were sampled in the A_p horizon with the exception of the Henry which was sampled in the B₂.

Capillary-Diffusion (Outflow Method)

The procedures used to measure the soil water diffusivity coefficients by the outflow method is that described by Doering (1965). Subsamples of Maury, Huntington, Eden, Burgin, Pembroke, and Yolo were passed through a 40-mesh sieve and carefully packed in pressure cells which were equipped with

TABLE I. Some Physical and Mineralogical Characteristics of Maury Silt Loam, Pembroke Silt Loam, Henry Silt Loam, Burgin Silty Clay Loam, Eden Silty Clay Loam, Yolo Loam, and Huntington Loam.

Soil Type (location sampled)	% Sand	% Silt	% Clay	Predominant Clay ¹	External Surface Area m ² /gm	Total Surface Area m ² /gm
Maury silt loam (Fayette County)	1.39	75.11	23.50	A1-interlayered vermiculite	27.35	64.84
Pembroke silt loam (Nelson County)	2.91	76.90	20.19	Mica	29.40	67.91
Huntington loam (Greenup County)	45.94	37.93	16.13	Vermiculite, Montmorillonite	32.70	69.29
Henry silt loam (Calloway County)	1.70	81.00	17.20	Montmorillonite	--	--
Eden silty clay loam (Grant County)	2.70	66.76	30.54	Vermiculite, Mica	53.50	166.62
Burgin silty clay loam (Fayette County)	2.00	69.80	28.20	A1-interlayered montmorillonite	49.29	113.33
Yolo loam (Davis, Calif.)	41.80	39.95	19.15	Montmorillonite	41.20	76.23

¹ Probable clay mineral which is predominant in the clay fraction.

porous plates. Three different porous plates were used in order to obtain diffusivity values over a large soil moisture range. The three plates had bubbling pressures of 0.2, 1.0, and 3.0 bars.

After the soils were packed in the cells, each soil sample was water saturated, the cell was attached to a dropflow counter as described by Doering and Decker (1964), and a pressure slightly less than the bubbling pressure of the porous plate was applied to the system. Each sample was dewatered once to the lowest water content possible with a given porous plate. The dewatering process was done to stabilize the soil mass and insure a more uniform soil medium. The soil was then resaturated with water and again attached to the drop-flow counter for a measurement. The drop-flow counter recorded the water outflow from the soil as a function of time. After the soil water attained equilibrium, the cell was removed, resaturated, and another trial made.

The diffusivity values were calculated by using Gardner's solution of the diffusion equation (1962). The boundary and initial conditions of these experiments were the same as those used in Gardner's solution.

Capillary-Diffusion (Inflow Method)

The method used to measure the soil water diffusivity coefficients by the inflow method is similar to that employed by Bruce and Klute (1956). Diffusivity values were obtained for the same soils as in the outflow method.

Soils were uniformly packed by hand into an acrylic column 50 cm in length. The column was composed of fifty 1-cm rings, 2-cm in diameter. The rings were held in a horizontal position by placing the rings in a slightly larger column which was open on one side to permit the rings to be taken out separately and easily.

To furnish a water supply with a given tension to the system, a buret containing a side-arm was used. The side-arm was open to the atmosphere, and consequently, the water held in that position was at atmospheric pressure. A porous plate was connected to the buret by plastic tubing. Before the start of the diffusion process, the tygon tubing from the buret was connected to the porous plate and filled with water. During the filling operation the side-arm and the tubing to the porous plate were shut off by clamps. The porous plate was

attached to the soil column and the height of the side-arm was adjusted to the desired level. Once the porous plate was firmly fitted to the soil column, the clamps were removed, permitting water to flow into the system under tension. A diagrammatic sketch of the experimental system is given by Bruce and Klute (1956).

After the diffusion process was completed, the porous plate was separated from the column and the gravimetric water content was determined for each of the 1-cm rings in the column.

The capillary-diffusion coefficients were calculated using equation (1) which is the solution of the diffusion equation corresponding to the initial and boundary conditions:

$$D(\theta) = \frac{1}{2t} \frac{dx}{d\theta} \int_{\theta_i}^{\theta} x \, d\theta \quad (1)$$

where θ is moisture content on a volume basis, t is the time in minutes, x is the distance in cm, and θ_i is the initial water content of the soil, and $D(\theta)$ is the capillary-diffusion coefficient which is assumed to be a unique function of θ .

Self-Diffusion

Self-diffusion coefficients were measured for Maury, Huntington, Pembroke, Eden, Henry, Burgin, and Yolo soils using a modification of the method used by Phillips and Brown (1968).

Subsamples of each soil at each of several water content were prepared as follows. The soils were passed through a 40-mesh sieve. The samples, each containing 40 gms of oven-dry soil, were wetted with distilled water to obtain the desired moisture content. After soil water equilibrium had been obtained, 2μ Ci of tritiated water was added to one sample of each water treatment. Each sample was then thoroughly mixed periodically with a spatula during the following day in order to insure a uniform distribution of tritiated water throughout the soil sample.

The soil samples containing either tritiated water or normal water were packed into lucite cylinders, each measuring 2 cm in length and 1.92 cm in

diameter. To start the diffusion process, one end of a cylinder containing tritiated water was placed against one end of a cylinder containing normal water at an equal water content. Copper discs were placed at the ends of each of the cylinders, and a "C" clamp was used to hold the cylinders in close contact. Masking tape was placed around the cylinders at the interface to prevent evaporation. The "C" clamp holding the cylinder was enclosed in a plastic bag and placed in a desiccator above a free water surface to further reduce evaporation. At the end of the diffusion period, approximately 4-10 hours, depending on the water content of the soil, the half-cells were separated and the soil from each cylinder was stored in a small air-tight jar. The soil was mixed periodically for one day to obtain a uniform distribution of the tritiated water within the sample. A known weight of subsample was taken from each jar and placed into a liquid scintillation counting vial. The scintillation liquid was made up according to the following recipe: 500 ml toluene, 500 ml dioxane, 104.0 gms naphthalene, 6.60 gms PPO, and 0.130 gm POPOP. The vials were shaken by hand and placed in cold storage over night before counting. The self-diffusion coefficients were calculated using equation (2) which is equation (7) of Phillips and Brown (1964):

$$D = \pi F^2 h^2 / t \quad (2)$$

where D is the self-diffusion coefficient in cm^2/sec , π is 3.1416, F is the fraction of the tritiated water molecules which diffused across the interface of the initially tagged and untagged soil sample, h is the length of the half-cell in cm, and t is the time of the diffusion process in seconds.

The method used to measure the self-diffusion of water in soil by using ^{36}Cl as a tracer of water is identical to that used for tritiated water with the exception that ^3H was replaced by ^{36}Cl .

Vapor Diffusion (Inflow Method)

A method similar to that reported by Jackson (1964a) was used to measure the diffusion coefficients of water vapor into relatively dry soils. The same soils were used in this experiment as were used to measure the self-diffusion coefficients of tritiated water.

An acrylic plastic column 10 cm long and 2 cm in diameter was constructed. The column was composed of 0.5 cm and 1.0 cm rings which were held in place by tape and sealed with paraffin over the entire length of the column. One end was sealed with a rubber stopper which was coated with paraffin. Soil which had been dried at 50 C was carefully packed into the column and quickly placed in a desiccator above a free water surface. This produced an atmosphere of approximately 100 percent relative humidity. The only water that could enter the soil system had to do so by vapor movement from the open end of the column.

After the diffusion process was completed, the column was sectioned, and the moisture content of each ring section was determined gravimetrically. The vapor diffusion coefficients were calculated with the use of equation (1) since the initial and boundary conditions were identical to those in the development of equation (1).

DATA AND RESULTS

Physical and Mineralogical Characteristics

The six Kentucky soils: Maury, Eden, Henry, Burgin, Pembroke, and Huntington; and one California soil, Yolo, used in this study are described in Table I. This table shows the particle size distribution, the dominant clay mineral present, and total and external surface area of each of these soils.

Figures 1 and 2 show the relationship between water retention of the soils as a function of the water tension. The differences found among the various soils can be related to the characteristics found in Table I. The soils with higher clay contents hold more water for a given tension than do the other soils, and the slopes of the moisture release curves indicate that the release of the water is slower in the soils with the higher clay contents.

Capillary-Diffusion (Outflow Method)

Figures 3 and 4 show the measured diffusivity values of the soils studied as a function of the water content on a volume basis. The values shown in the figures represent the average coefficients measured at several water contents. The method of averaging the values consisted of plotting all

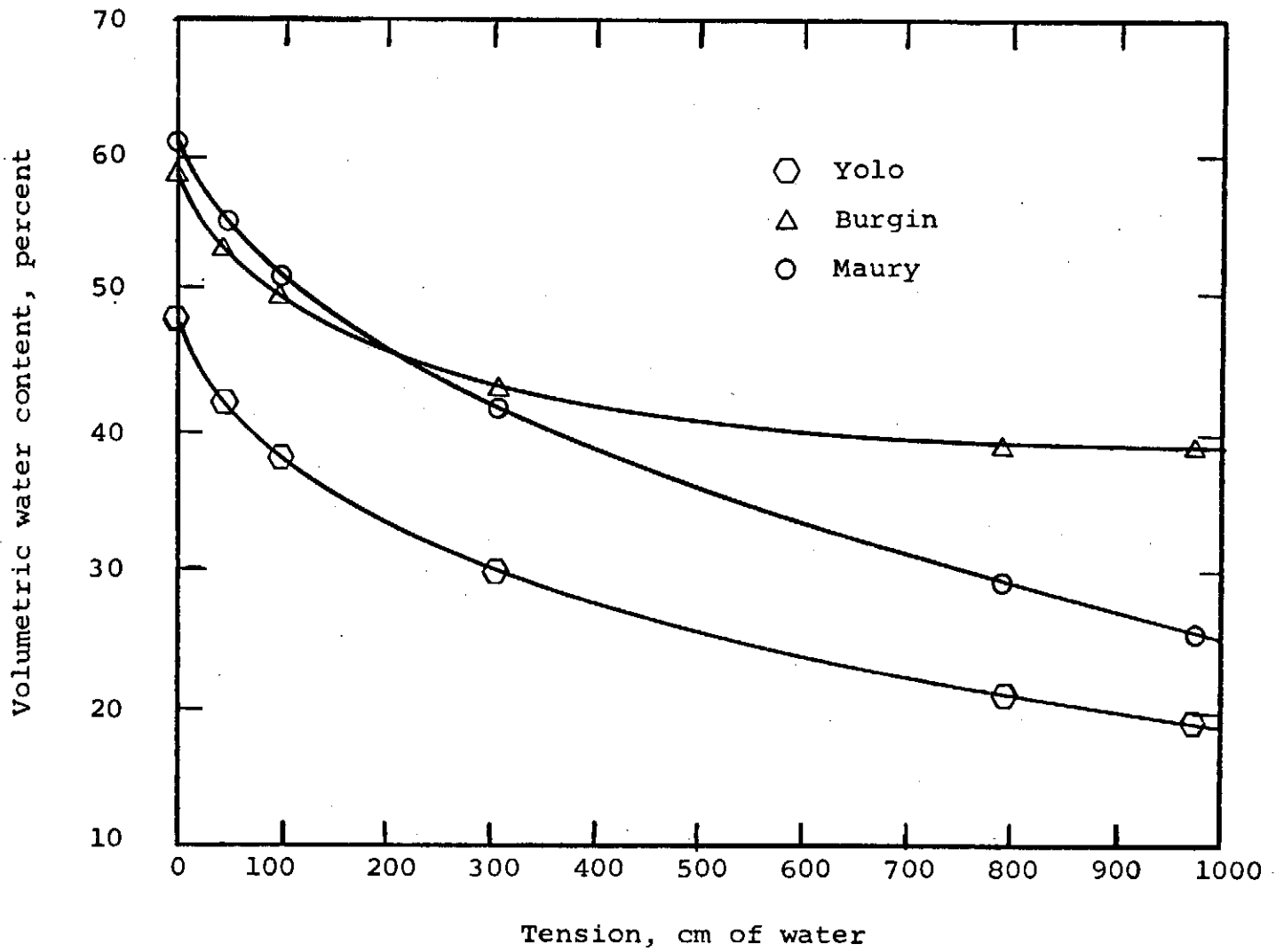


Figure 1. Soil-water retention curves of Yolo loam, Burgin silty clay loam, and Maury silt loam.

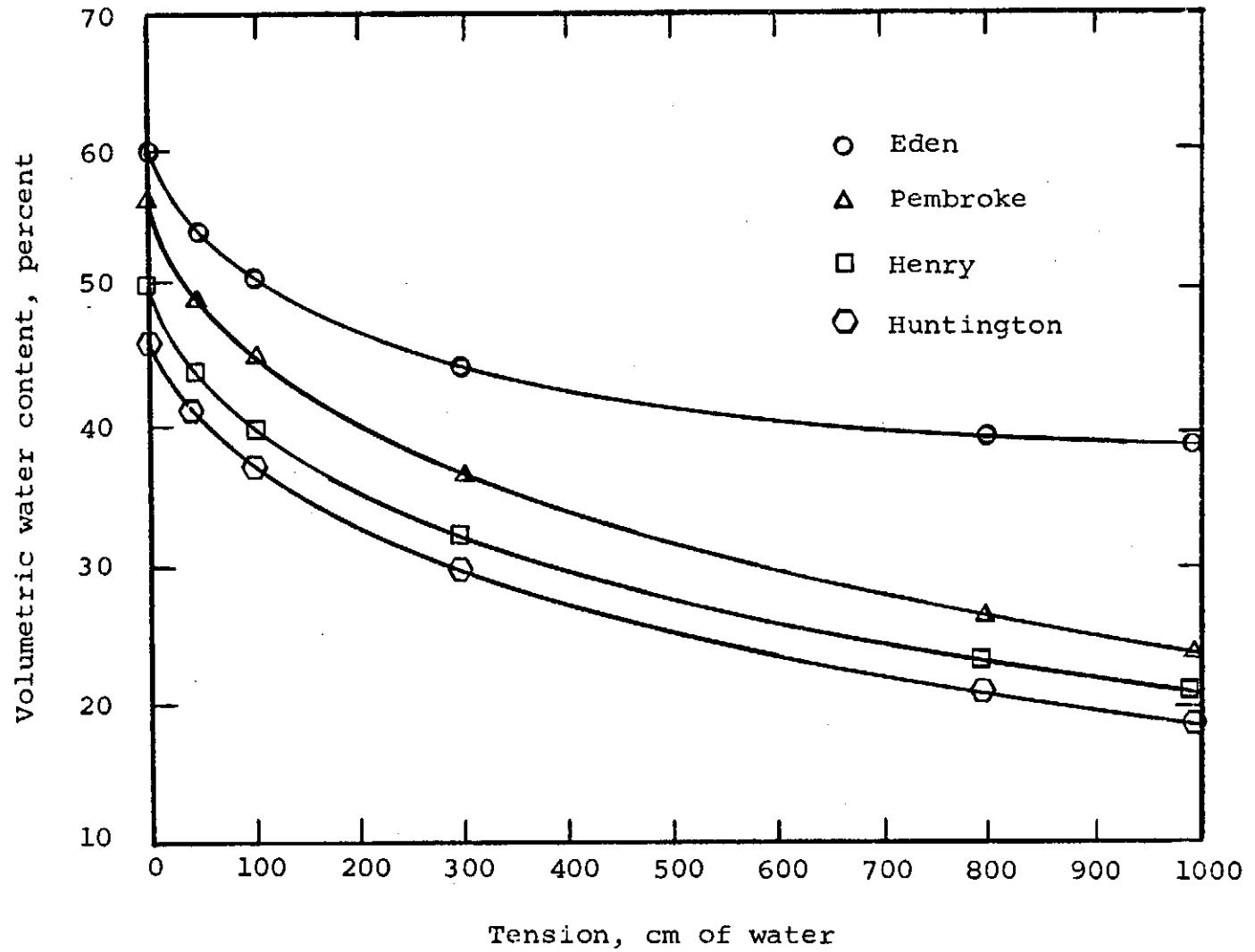


Figure 2. Soil-water retention curves of Eden silty clay loam, Pembroke silt loam, Henry silt loam, and Huntington loam.

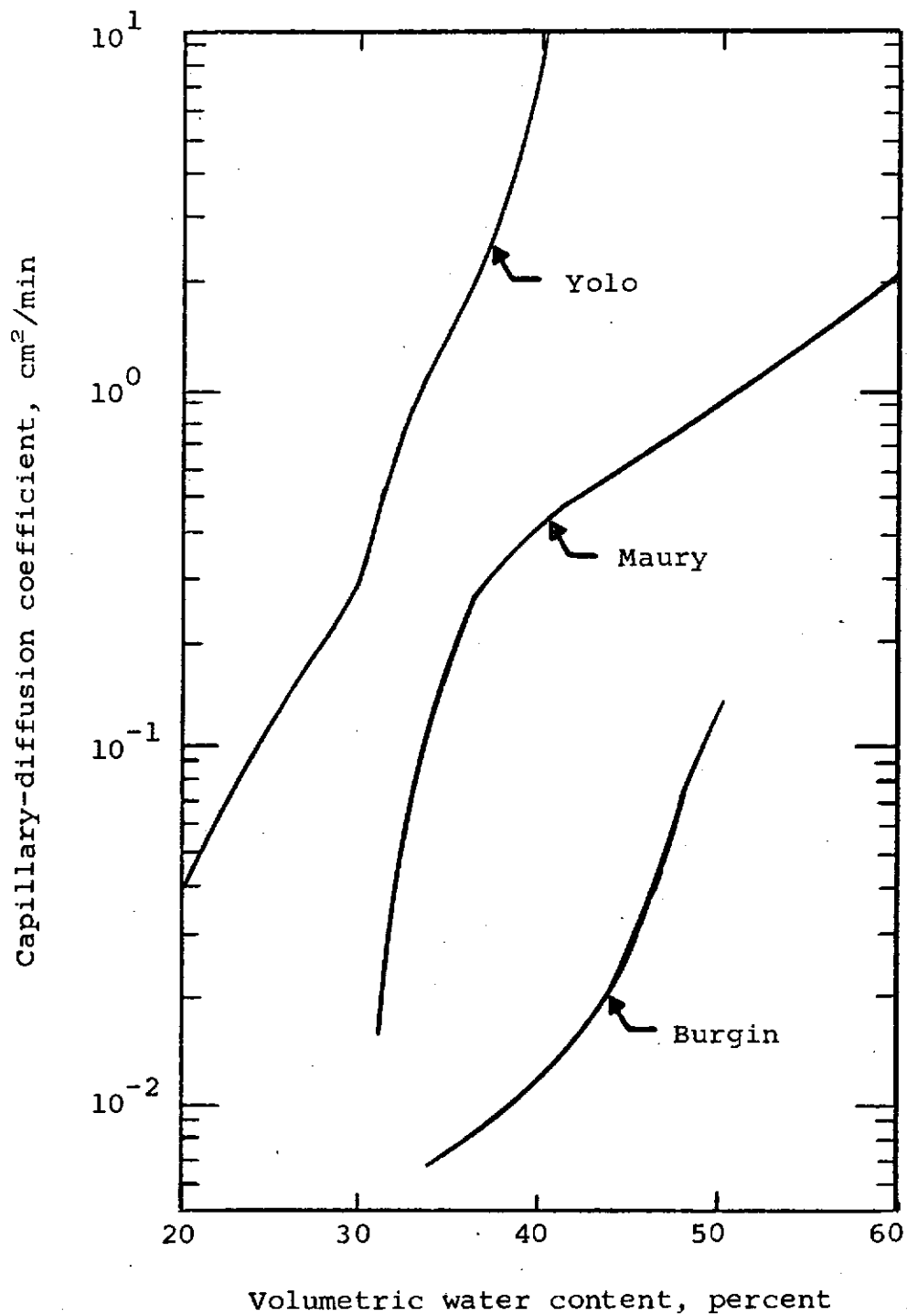


Figure 3. Capillary-diffusion coefficients as a function of volumetric water content as measured by the outflow method for Yolo loam, Maury silt loam, and Burgin silty clay loam.

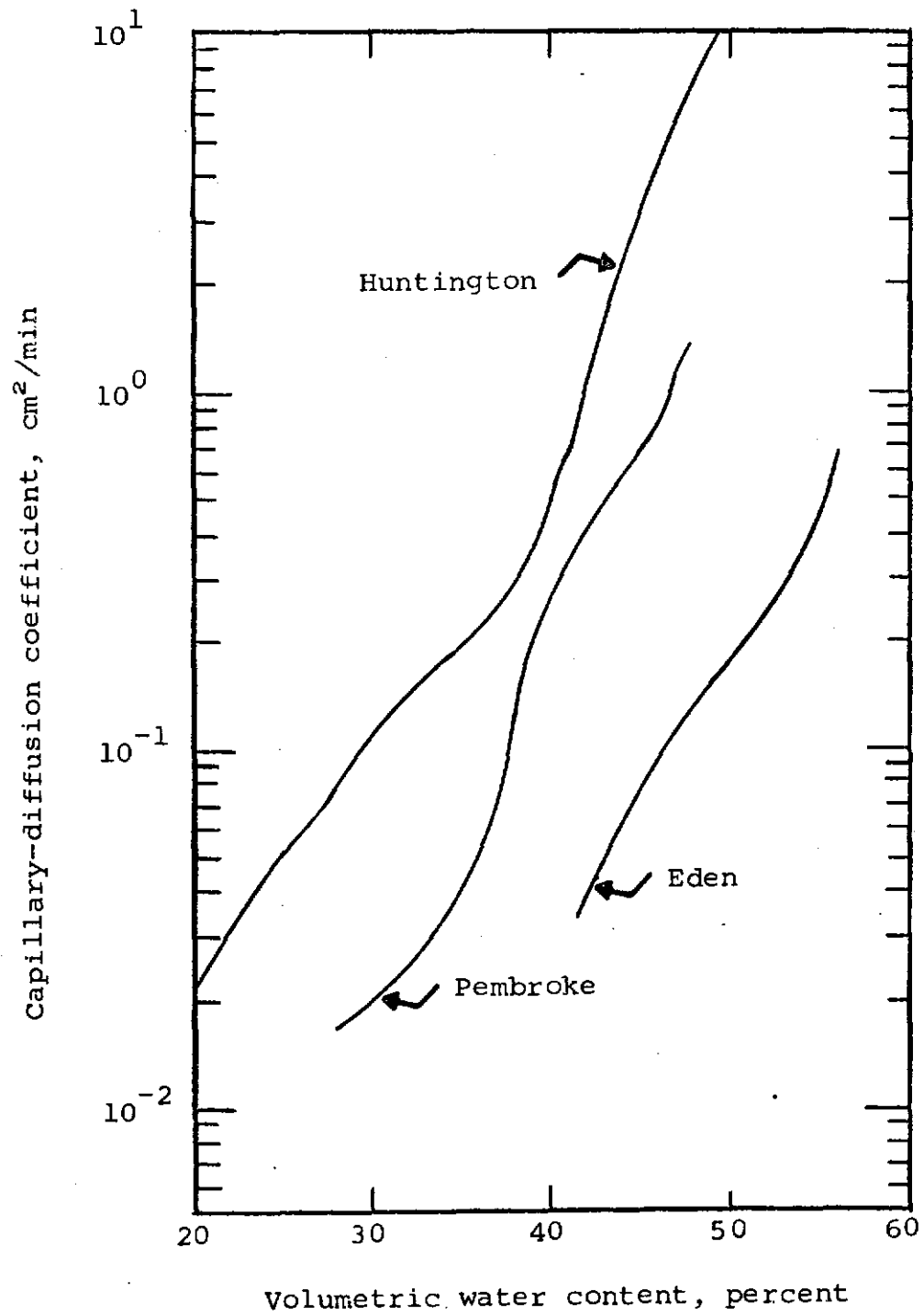


Figure 4. Capillary-diffusion coefficients as a function of volumetric water content as measured by the outflow method for Pembroke silt loam, Eden silty clay loam, and Huntington loam.

the obtained diffusivity values versus the water content on a volume basis and drawing a smooth curve through the greatest concentration of points. This method seems preferable to that of taking a simple mean, because this method permits a smooth curve to be drawn through the points which gives a better representation of the entire range for comparing the diffusivity values of the different soils. In order to measure the diffusion coefficients over a large range of water contents, it was necessary to combine data from three different porous plates, each with a different bubbling pressure. The water content range was divided into three segments for measurement of the diffusion coefficients: water contents corresponding to tensions of 0 to 0.2, 0.1 to 0.9, and from 0.8 to 1.2 bars. The overlapping tensions from one plate to another permitted a smooth transition in coefficients in going from one plate to another. The first and last few values obtained for each pressure increment were discarded.

As shown in Figures 3 and 4, the diffusivity values of the soils studied vary greatly with the moisture content range considered. In each case the diffusion coefficients decreased very rapidly with decreasing water content. Pore size, continuity, and number are probably the most important factors influencing capillary diffusion values at any given water content, because the textural distribution, kind of clay, bulk density, and organic matter all influence these properties. The loams, Yolo and Huntington, have higher diffusivity values than the silt loams, Maury and Pembroke, which in turn are higher than the silty clay loams, Eden and Burgin.

The greatest differences among the soils in regard to the diffusion rates were found at the higher water contents. At a water content of 40 percent on a volume basis, the diffusivity value of the Yolo loam was nearly 1000 times as great as the Burgin silty clay loam. At this same water content, the Maury silt loam was approximately 50 times greater than the Burgin. A loam has many more large pores than a silty clay loam. At water contents approaching saturation many of these large pores in a loam are filled with water. As a given pressure gradient is applied to the soil system, the largest pores drain first and more rapidly than the smaller pores as found in the soils with

relatively high clay contents. As a consequence of the pore geometry, a loam releases more water for a given period of time than a soil which contains many more small pores.

In the intermediate water content range, approximately 20 to 35 percent on a volume basis, the diffusivity values of the different soils are more nearly the same value than at the higher water contents, although the lighter textured soils still have the higher values. At a volumetric water content of 30 percent on a volume basis, the diffusivity value of the Yolo is less than 100 times as great as the Burgin silty clay loam; this is 10 times smaller than it is at 40 percent. The Maury has a value of approximately 4 times the Burgin at 30 percent water content, about $1/12$ as large as the value at 50 percent. The reason that the coefficients are more nearly the same in this drier range is due to the fact that many of the large pores in the loams and the silt loams have already drained. The number and size of pores, which are still saturated in the loams and silt loams, are more nearly equal to the number and size of pores still saturated with water in the silty clay loams. Even so, at this lower water content the equivalent radii of the pores filled with water in the silty clay loams are still smaller than those in the loams and silt loams.

Capillary-Diffusion (Inflow Method)

A second method was used to measure the capillary-diffusion coefficients of the six soils. Whereas, the first method involved introducing an applied air pressure to the soil system, the inflow method involved the flow of water into the system under a tension. In the mathematical solution of the diffusion equation, an assumption is made that the relationship between the distance of the wetted front and the square root of time required to reach that distance is linear. Nielson et al. (1962), working with California soils, have shown that this relationship holds only for a tension up to approximately 2 cm of water.

Figure 5 shows the distance of the advance of the wetted front as a function of the square root of time for the Huntington loam. With an applied tension of 2 cm of water, a linear relationship was found to exist for the

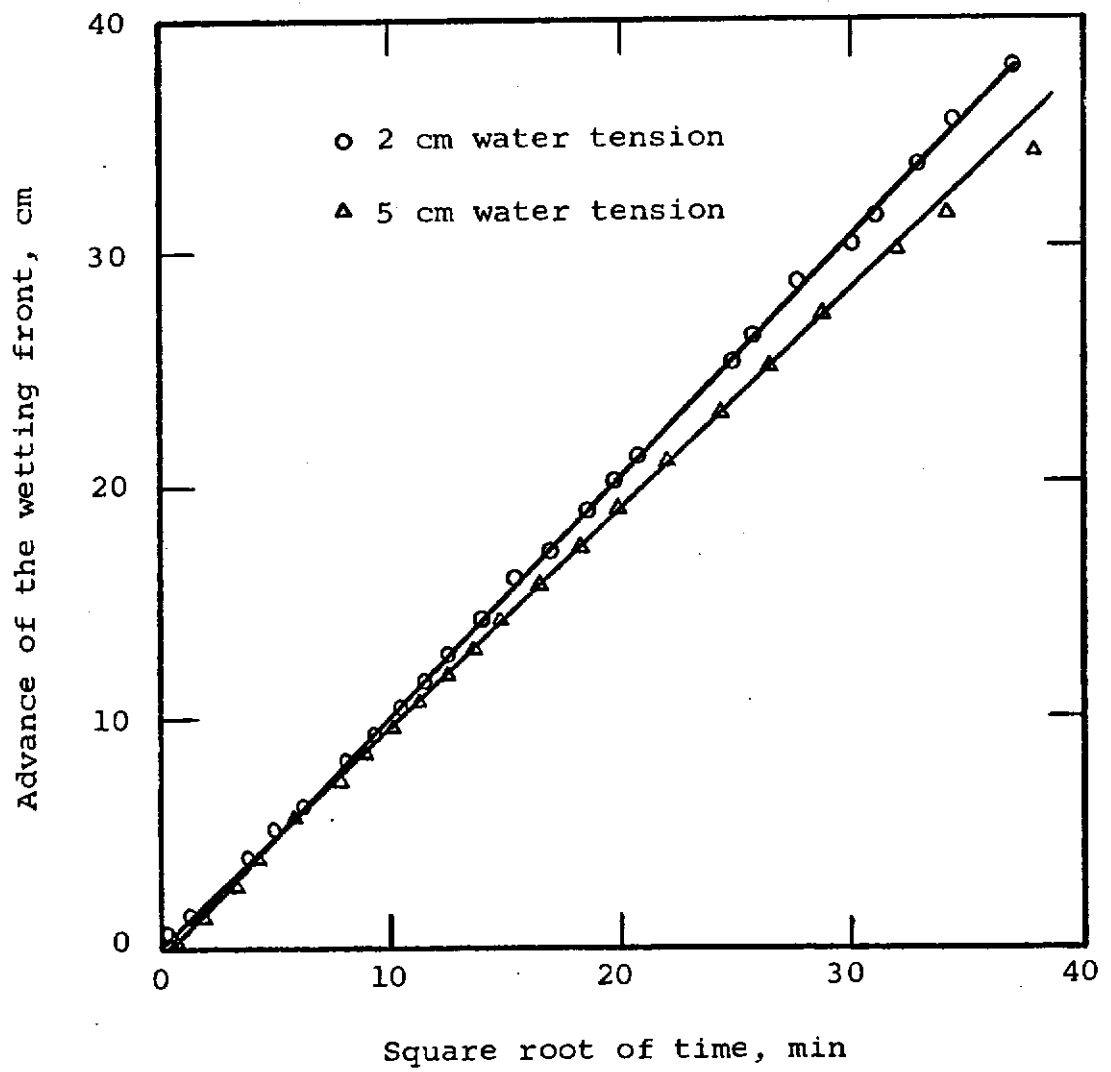


Figure 5. Relationship of advance of the wetted front and square root of time for Huntington loam.

duration of the experiment. The relationship for a tension of 5 cm of water was found to be linear for some time after which the relationship became curvilinear. The two systems yielded approximately the same diffusivity values for a given water tension, if the system with the higher tension was stopped soon after the linear relationship ceased to exist. Tensions of 10 cm of water, or greater, yielded lower diffusion values for the entire moisture content range studied. Similar relationships were found to exist for the Yolo loam, the Maury silt loam, and the Pembroke silt loam.

The distance of the advance of the wetted front as a function of the square root of time for the Burgin silty clay loam is shown in Figure 6. An applied tension of 2 cm of water resulted in a relationship that was nearly linear for the entire time of the experiment. However, the curve was not linear for a tension of 5 cm as it was for the Huntington loam and the other lighter textured soils. Greater tensions gave even more deviation from linearity. The Eden silty clay loam produced curves very similar to the Burgin.

Figures 7 and 8 show the average capillary-diffusion coefficient as a function of the water content for the inflow method. The values were averaged in the same manner as they were for the outflow method. As with the outflow method, the diffusion coefficients decrease very rapidly with decreasing water content. At the higher water contents the diffusivity values of the Yolo loam and the Huntington loam are much higher than for the Maury silt loam. Pembroke silt loam, and the Burgin silty clay loam which are in turn greater than for the Eden silty clay loam. Capillary-diffusion measurements by the inflow method yielded values for the Burgin as high as for the Maury and the Pembroke. At the lower water content, the diffusivity values of the several soils were much more nearly the same than they were at water contents approaching saturation.

Comparison of the Outflow and Inflow Methods

Although both methods are designed to measure the same diffusion coefficient, the two methods used in this study differ in their experimental design, and consequently differ in their mathematical development. Due to

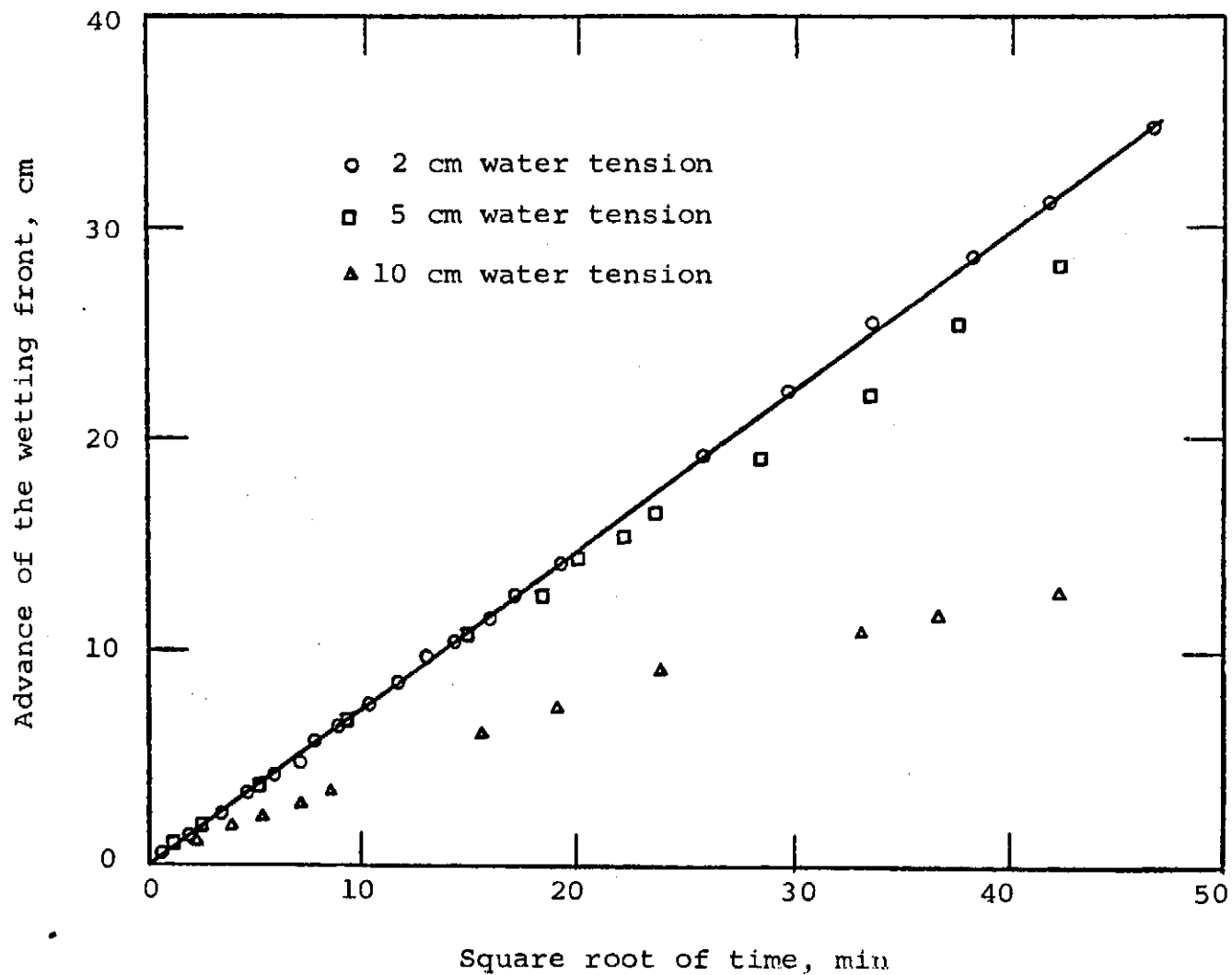


Figure 6. Relationship of advance of the wetted front and square root of time for Burgin silty clay loam.

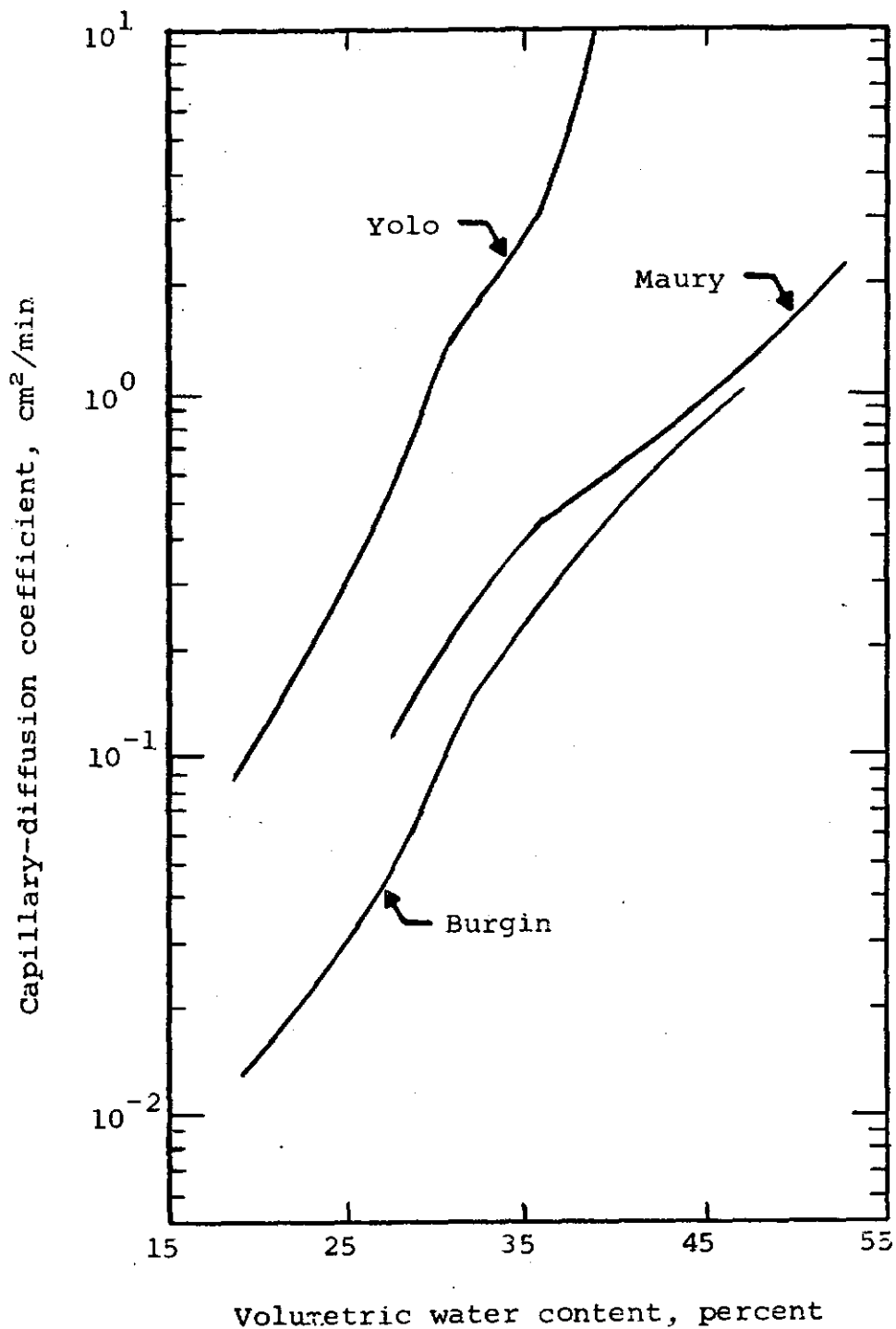


Figure 7. Capillary-diffusion coefficients as a function of volumetric water content as measured by the inflow method for Yolo loam, Maury silt loam, and Burgin silty clay loam.

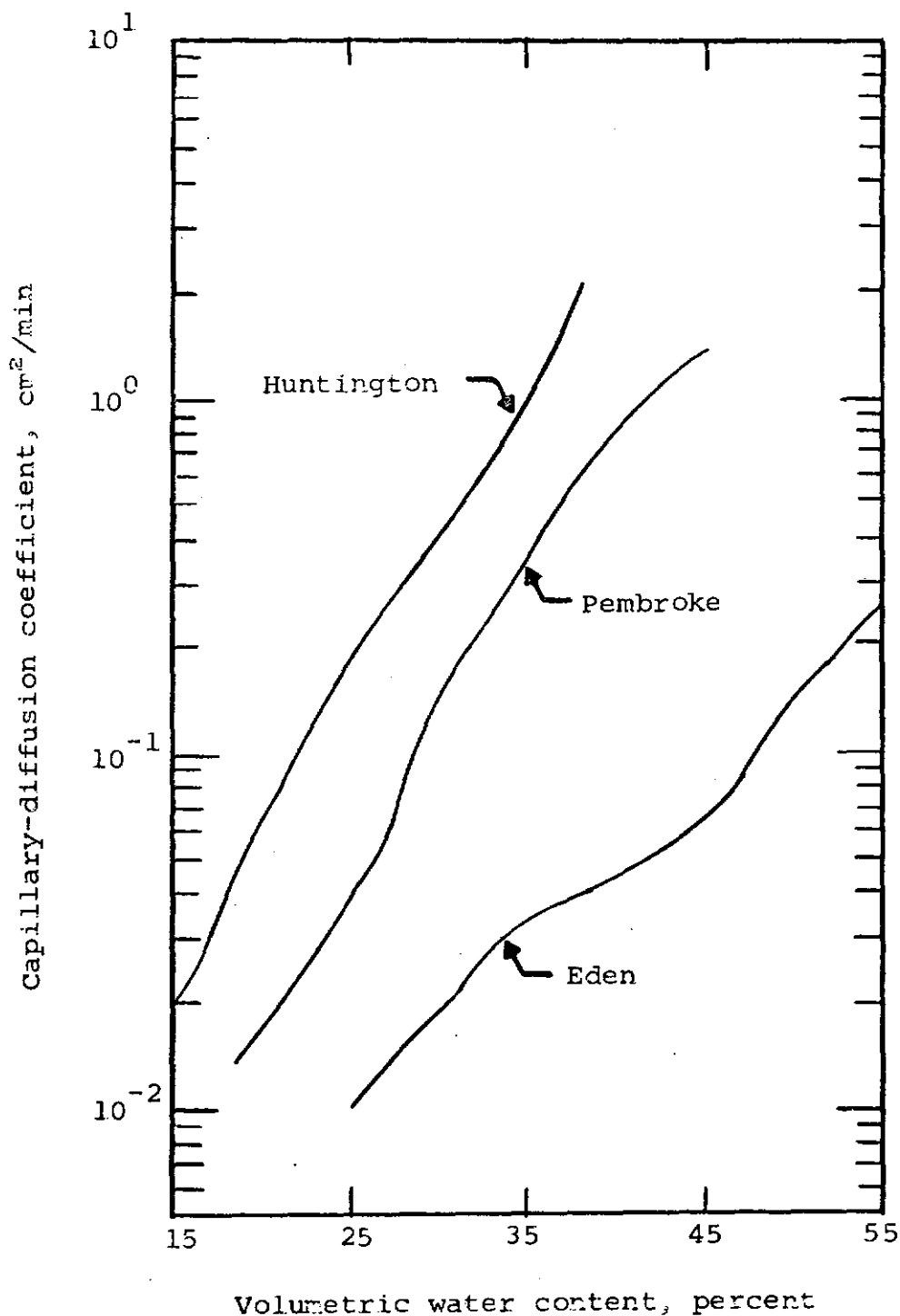


Figure 8. Capillary-diffusion coefficients as a function of volumetric water content as measured by the inflow method for Pembroke silt loam, Eden silty clay loam, and Huntington loam.

this difference, and due to possible hysteresis effects, it is important that these two methods be compared to see if both yield the same diffusivity values for various soils and over a large range of soil water contents.

A comparison of the soil water diffusivity values of the two methods appears in Figures 9 and 10. The curves representing the Maury silt loam, Yolo loam, and Eden silty clay loam show very good agreement over the water content range measured. In the intermediate range diffusion coefficients for Pembroke determined by the outflow method were lower than those measured by the other method. The diffusion values of the Pembroke were somewhat variable. The outflow method produced smaller values than the inflow method over the entire soil moisture range for the Huntington loam.

Although some differences existed in the five previous soils discussed, the general agreement between the two methods was acceptable. However, the Burgin silty clay loam values measured by the two methods differed greatly over the entire range of moisture content. The inflow method was more than an order of magnitude greater than the outflow method. The outflow method consists of packing a quantity of soil into a given volume and then wetting the system. As the soil wetted, the Burgin swelled, resulting in a reduction of the soil porosity. The inflow method starts with an air-dried soil. Consequently, the pore geometry of the soil differs from one method to another, resulting in a slower rate of water movement in the outflow method.

It would appear that either method would be satisfactory for measuring the capillary-diffusion coefficients of soil water for soils that do not contain appreciable amounts of expanding clays. Although the Yolo loam and the Eden silty clay loam contain montmorillonite, relatively little difference in the magnitude of the capillary-diffusion coefficients as measured by the inflow and outflow methods was measured. If the soil swells quickly upon wetting, such as has been observed for Eden silty clay loam in the field, then the difference of values obtained by the two methods should be small. On the other hand, if the soil swells slowly upon wetting, such as has been observed with Burgin silty clay loam in the laboratory, then the difference of values obtained by the two methods should be relatively large.

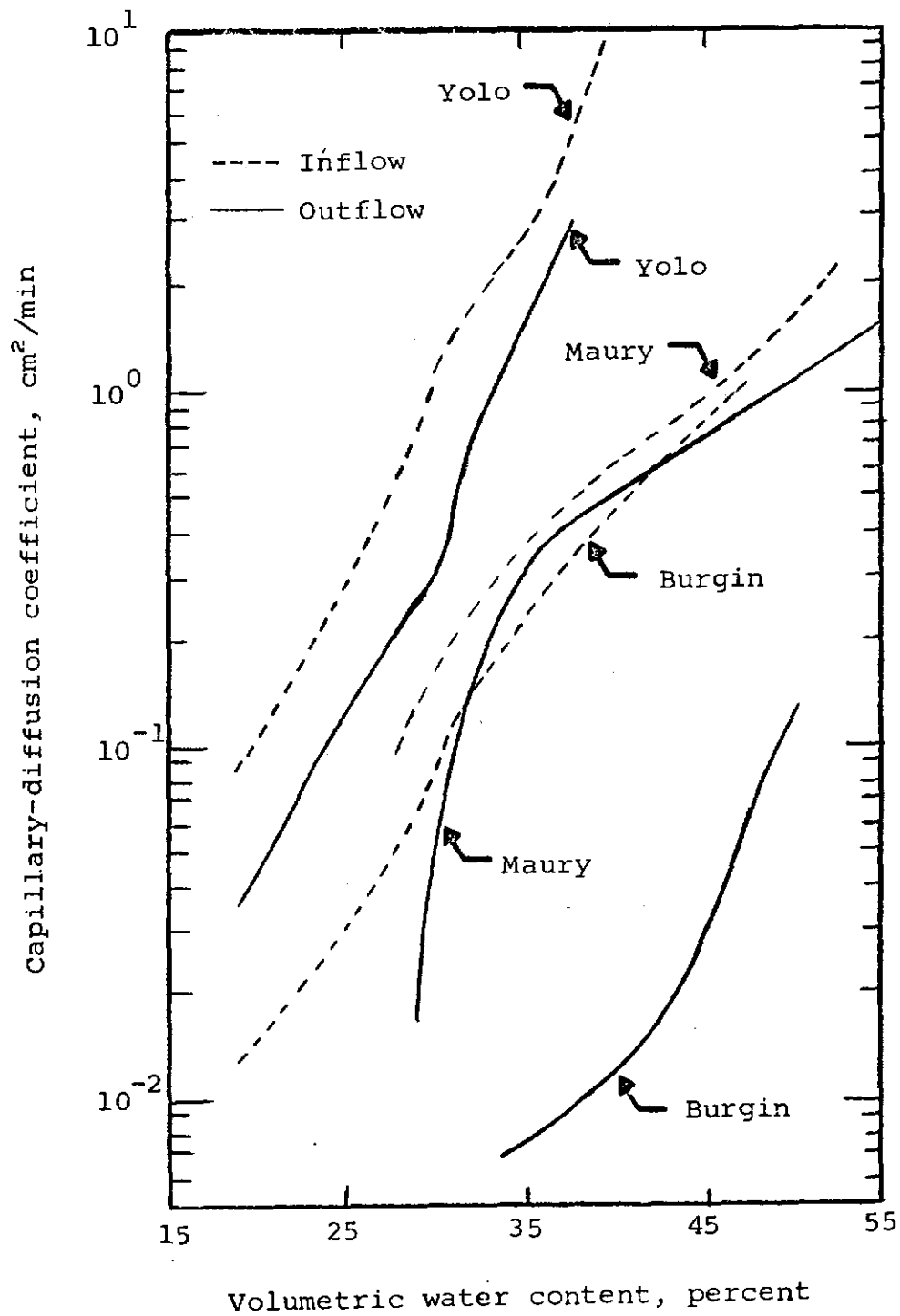


Figure 9. Comparison of inflow and outflow capillary-diffusion coefficients for Yolo loam, Maury silt loam, and Burgin silty clay loam.

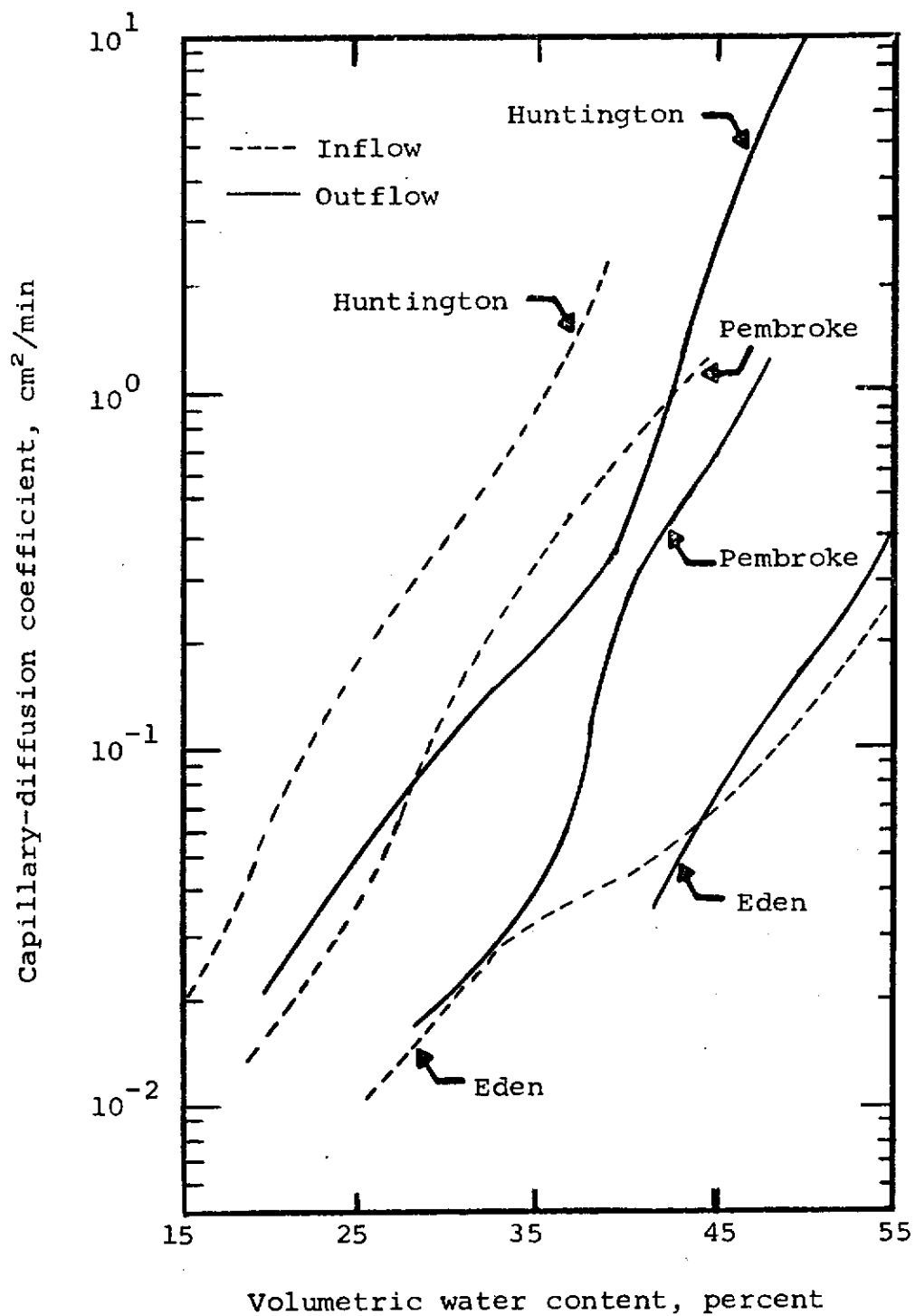


Figure 10. Comparison of the inflow and outflow capillary-diffusion coefficients for Huntington loam, Pembroke silt loam, and Eden silty clay loam.

Self-Diffusion

Figures 11, 12, and 13 show the self-diffusion or molecular coefficient of the water molecule as a function of the water content on a volume basis for the seven soils used in this study. The resulting curves are similar in shape for each of the soils; however, the diffusion coefficients differ among water contents for the various soils.

Each curve shows a rapid decrease in the self-diffusion coefficients as the water content decreases from near saturation to approximately 30 to 40 percent water on a volume basis. At some given water content for each soil, the diffusion coefficient begins to increase as the water content is further reduced. This increase continues until a water content of about 5 to 10 percent is reached. As the water content was reduced to near zero, the diffusion coefficients decreased very rapidly.

All researchers reporting self-diffusion coefficients for given soils have found the diffusion coefficients to be constant over a large portion of the water content range, in most cases from a water content of about 15 to 20 percent on a volume basis to saturation. The results of this work are not in agreement with other workers on this finding, since as the water content decreased from near saturation to approximately field capacity, the diffusion coefficients decreased.

Figures 14, 15 and 16 show the self-diffusion coefficients as a function of the number of water layers on each mineral surface. It would appear reasonable to expect a decrease in the diffusion coefficient with a decrease in the water content if the water is entirely in the liquid form. The three most important factors influencing the diffusion of a water molecule in a soil-water system with water contents in the range of plant growth are: (1) path length of the diffusing molecule, (2) the attraction of the mineral surface for the polar water molecule, and (3) the viscosity of the soil water. Low (1961) has advanced the theory that the water on the mineral surface is somewhat ordered out to a distance of approximately 50 Å when the clay is saturated with monovalent ions. Kemper et al. (1964) found that the mobility of water

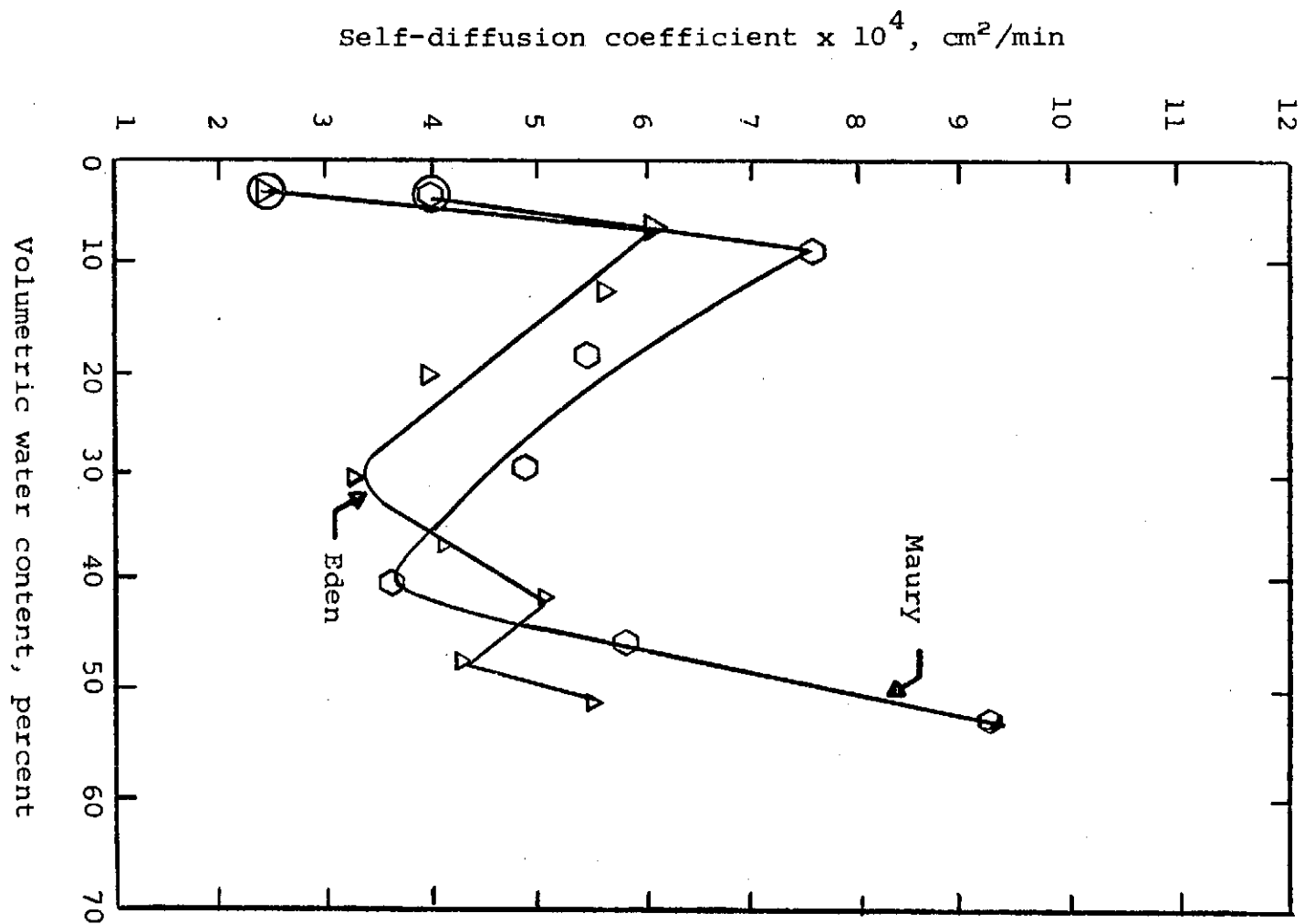


Figure 11. Self-diffusion coefficients as a function of volumetric water content for Maury silt loam and Eden silty clay loam. The encircled characters represent the coefficients obtained by the method of Jackson (1964), the non-enclosed characters represent the coefficients obtained by the method of Phillips and Brown (1968). Each data point in the figure represents the average of four values.

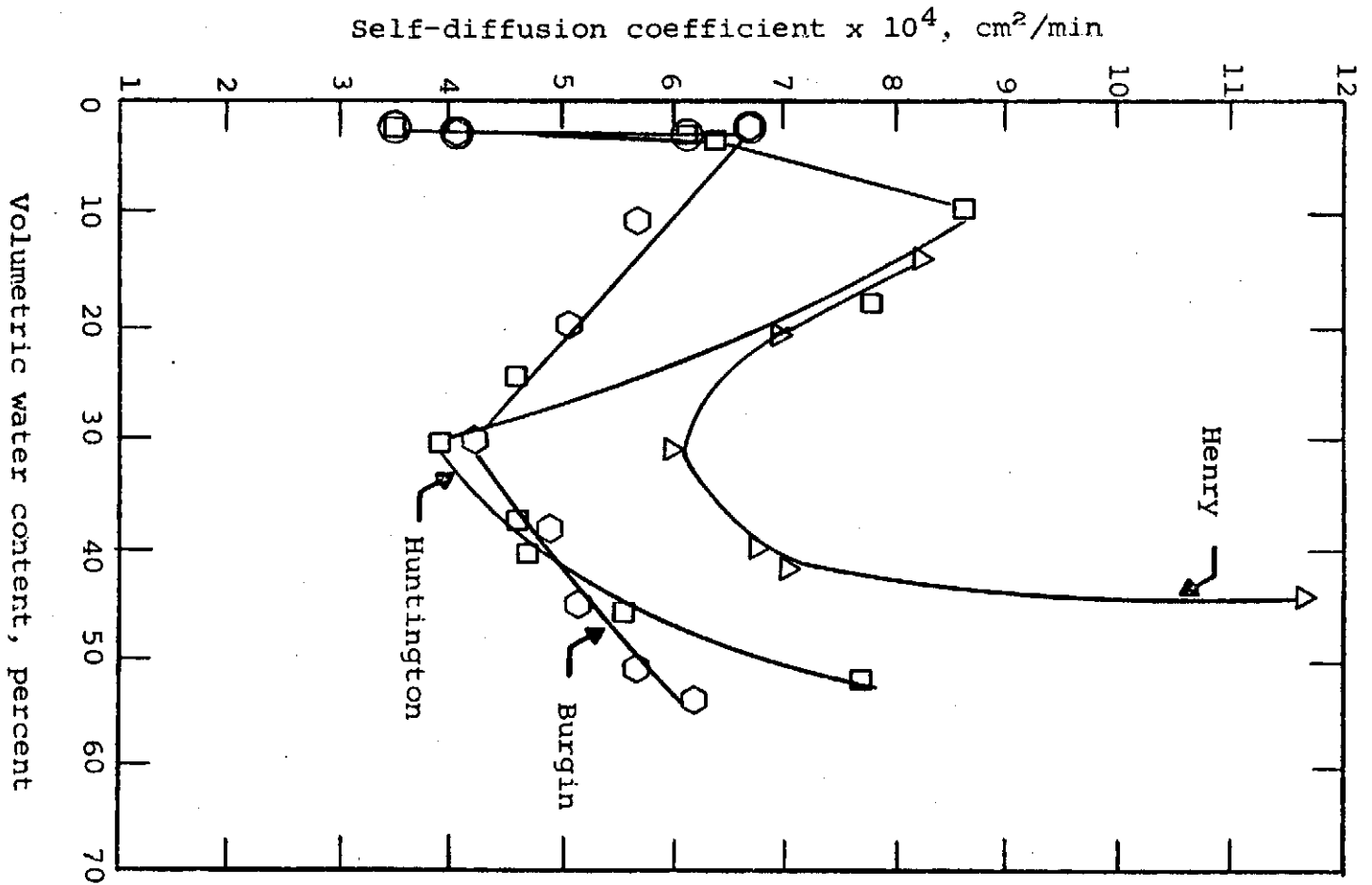


Figure 12. Self-diffusion coefficients as a function of volumetric water content for Henry silt loam, Huntington loam, and Burgin silty clay loam. The encircled characters represent the coefficients obtained by the method of Jackson (1964), the non-enclosed characters represent the coefficients obtained by the method of Phillips and Brown (1968). Each data point in the figure represents the average of four values.

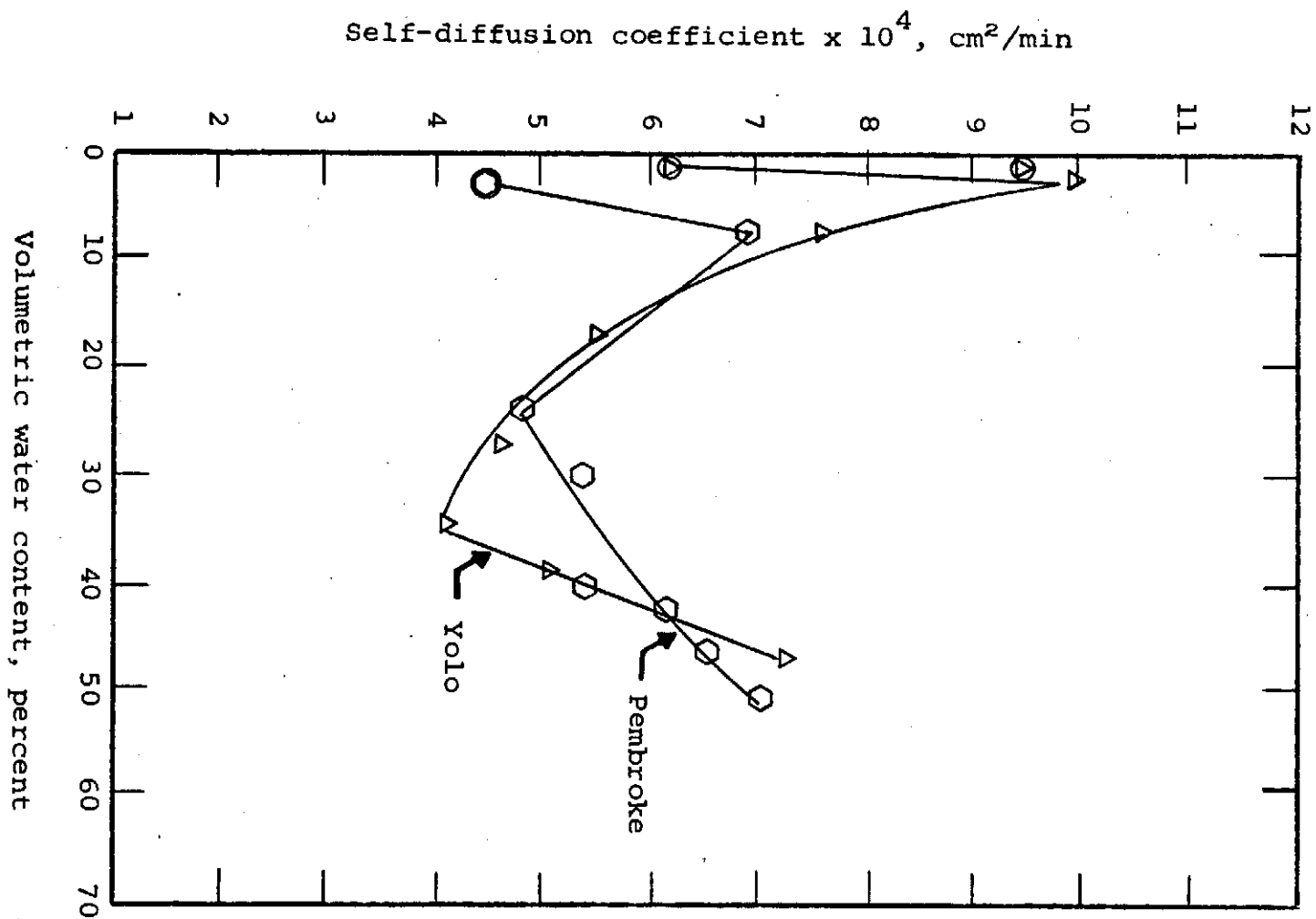


Figure 13. Self-diffusion coefficients as a function of volumetric water content for Pembroke silt loam and Yolo loam. The encircled characters represent the coefficients obtained by the method of Jackson (1964), the non-enclosed characters represent the coefficients obtained by the method of Phillips and Brown (1968). Each data point in the figure represents the average of four values.

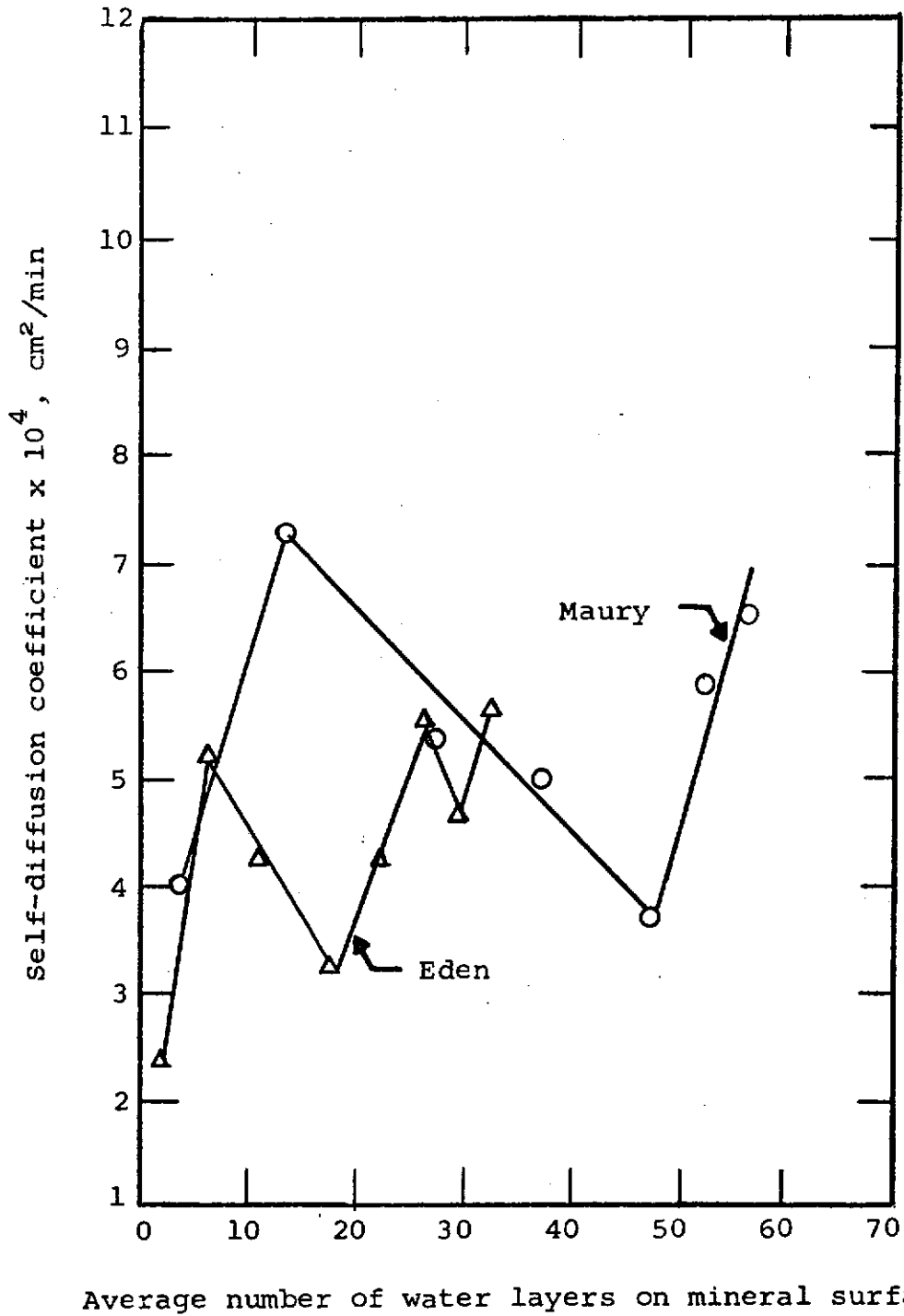
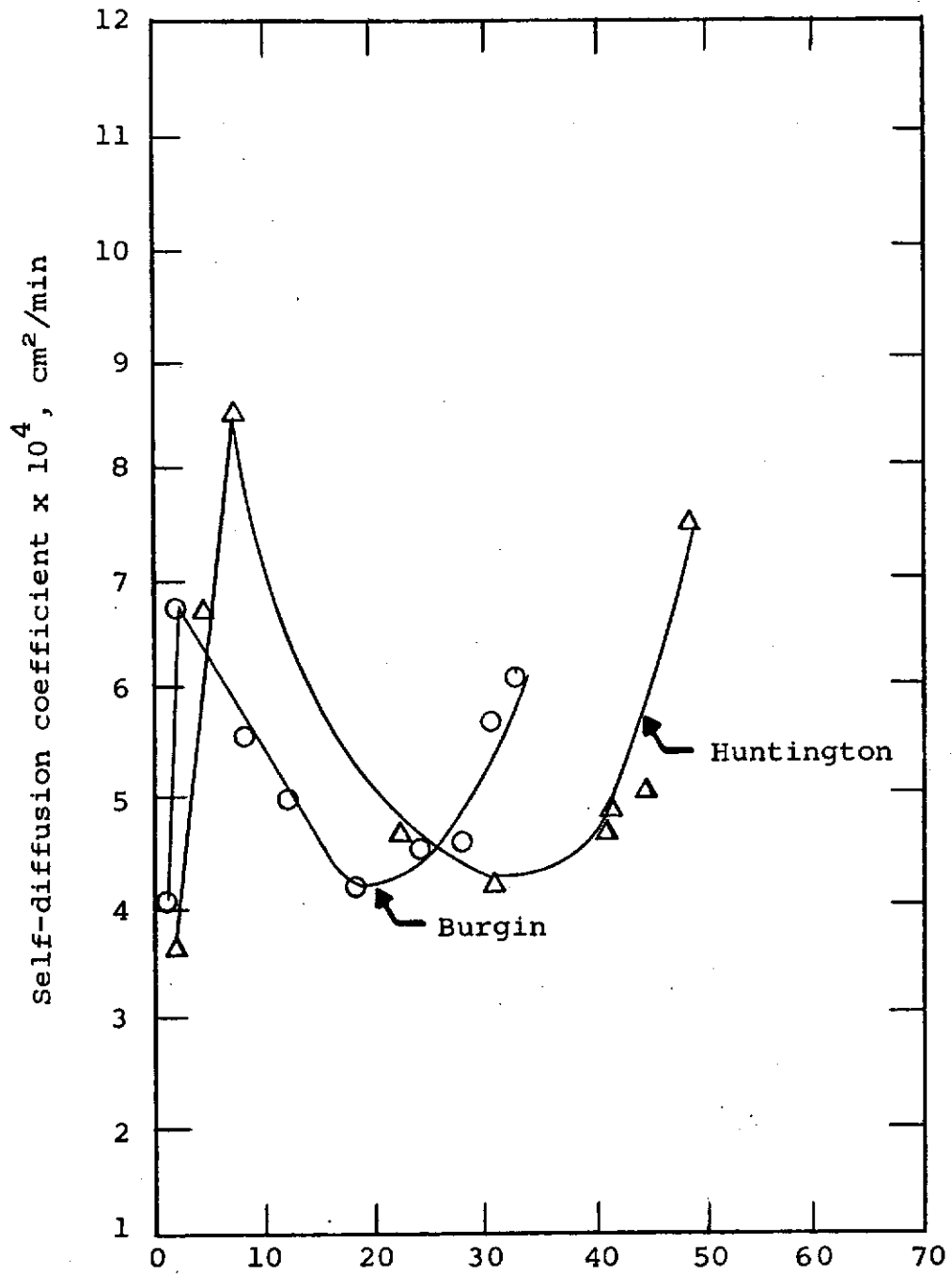


Figure 14. Relationship of self-diffusion coefficients to average number of water layers on each mineral surface for Maury silt loam and Eden silty clay loam.



Average number of water layers on mineral surface

Figure 15. Relationship of self-diffusion coefficients to average number of water layers on each mineral surface for Burgin silty clay loam and Huntington loam.

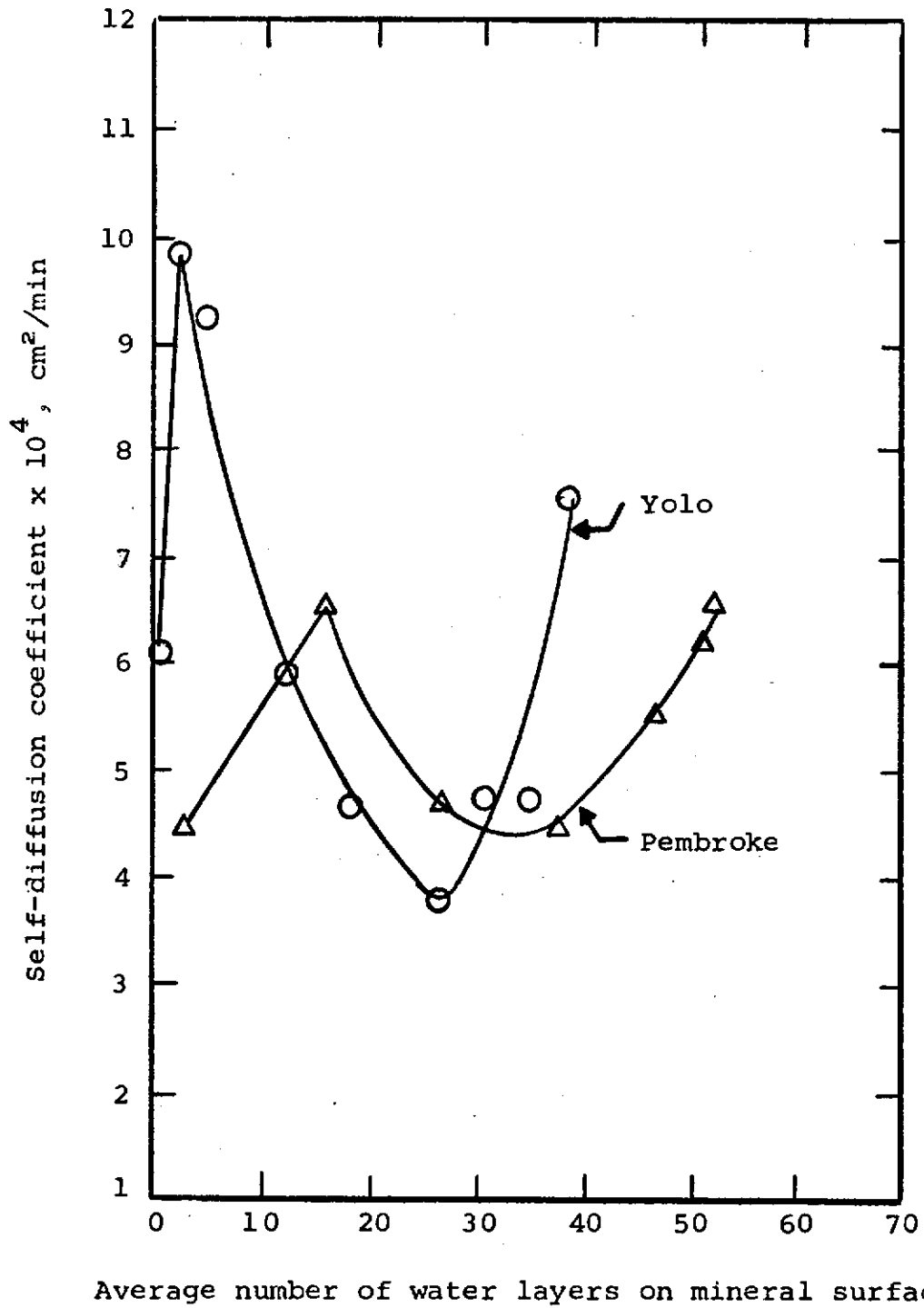


Figure 16. Relationship of self-diffusion coefficients to average number of water layers on each mineral surface for Yolo loam and Pembroke silt loam.

molecules in Na-bentonite is reduced slightly as far as 50 Å from the clay mineral surface. At 10 Å in a Ca-bentonite, the water molecules were 0.8 times as mobile as the molecules of bulk water. This could account for some decrease in the diffusion rate out to about 17 water layers assuming a Na-clay system. Since there was a decrease in the diffusion rate as the number of water layers was reduced from a saturated condition to approximately field capacity, and the number of water layers at this latter water content was greater than 20 in each case, the viscosity of the water should have had little, if any, effect on the diffusion rate. The soils in this study were Ca dominated and the viscosity should not have been affected more than 10 to 15 Å from the clay mineral surface. The decrease in the self-diffusion coefficients as the water content decreased was probably due to an increase in tortuosity, but no valid explanation can be given as to why these data do not agree with the constant diffusion coefficient values for a moisture content range from saturation to field capacity that have been previously reported in the literature by Kunze and Kirkham (1961) and Nakayama and Jackson (1963). After the self-diffusion coefficients reached a minimum value, they then increased to a maximum value as water content further decreased, because of water vapor movement. As the water contents further decreased, the attractive forces of the mineral surfaces for the water molecule were too strong to permit freedom of movement resulting in a decrease of the self-diffusion coefficients. In the loams and the silt loams the effect of vapor movement became apparent when the void pore space was no greater than three percent. In the silty clay loams void pore spaces of greater than 25 percent were necessary before vapor diffusion was detectable. These observations are related to the fact that the soils of relatively low clay contents have a greater number of large and continuous pores at water contents just below saturation.

Separation of Liquid and Vapor Self-Diffusion Coefficients

An attempt was made to separate the self-diffusion coefficients of the Huntington loam into the liquid and vapor components. The tracer used in this experiment was ^{36}Cl . The diffusion coefficient of Cl in liquid water at 25°C is $1.96 \times 10^{-5} \text{ cm}^2/\text{sec}$. This is 0.8 that of the diffusion coefficient of ^3HOH

in bulk water (Wang et al., 1953). It was reasoned that it would be possible to measure the diffusion coefficient of ^{36}Cl in a soil-water system and then multiply the value by 1.24 (diffusion rate of $^3\text{HOH} \div$ diffusion rate of ^{36}Cl) to obtain the diffusion rate of liquid water. Kunze and Kirkham (1961) have used this procedure previously. The results of this experiment are shown in Figure 17.

The diffusion coefficients of the liquid water decrease with water content until the influence of water vapor movement becomes apparent. However, the diffusion coefficients of water measured with ^{36}Cl were constant over the range of intermediate and higher water contents. The diffusion coefficients of ^{36}Cl were found to be greater than water at water contents on a volume basis of 20, 25, and 30 percent. Thus it would appear that it is impossible to directly measure the diffusion coefficient of liquid water by using the ^{36}Cl molecule as a tracer.

If one could correct for the anion exclusion volume of the ^{36}Cl , it might be possible to relate the two diffusion coefficients. However, little work has been done in calculating the anion exclusion volumes of soils under unsaturated conditions.

Relationship Between Capillary-Diffusion and Self-Diffusion Coefficients

Kunze and Kirkham (1961) presented a relationship between the self-diffusion and the capillary-diffusion coefficients. They reported that a single curve expressed the relationship between the two diffusion coefficients for each of three soils studied. The solid curve in Figure 18 is taken from the paper by Kunze and Kirkham. The points plotted in the figure represent all the diffusion coefficients collected in this work. It can be noted that there is good agreement with the curve at capillary-diffusion coefficients greater than $5 \times 10^{-2} \text{ cm}^2/\text{min}$. The values below this point deviate to the right of the curve due to the fact that the self-diffusion coefficients are increasing because of vapor diffusion.

Self-diffusion coefficients reported by Kunze and Kirkham were obtained by use of ^{36}Cl which is questionable since the differences measured

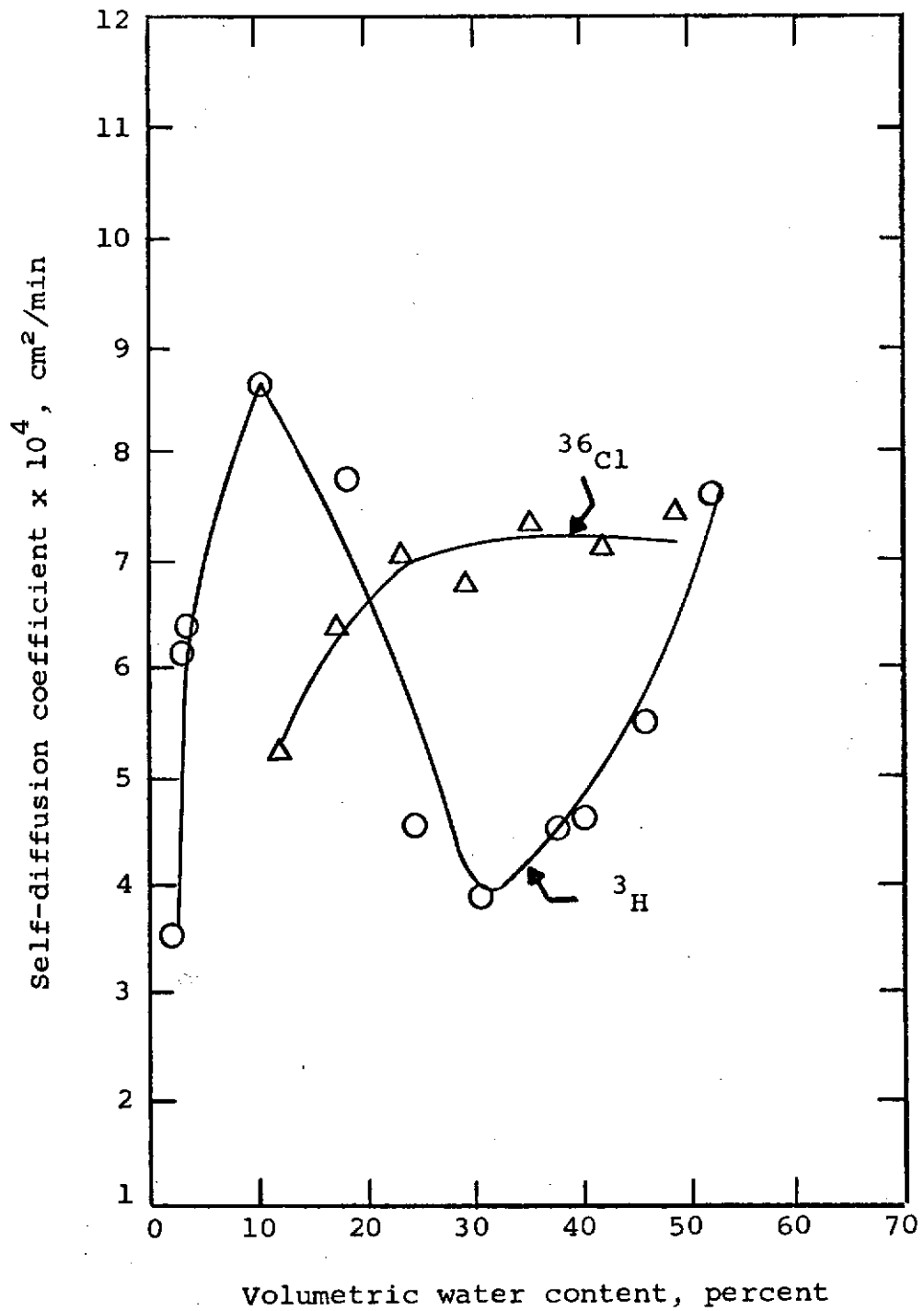


Figure 17. Self-diffusion of water in Huntington loam as measured by ^3H and ^{36}Cl .

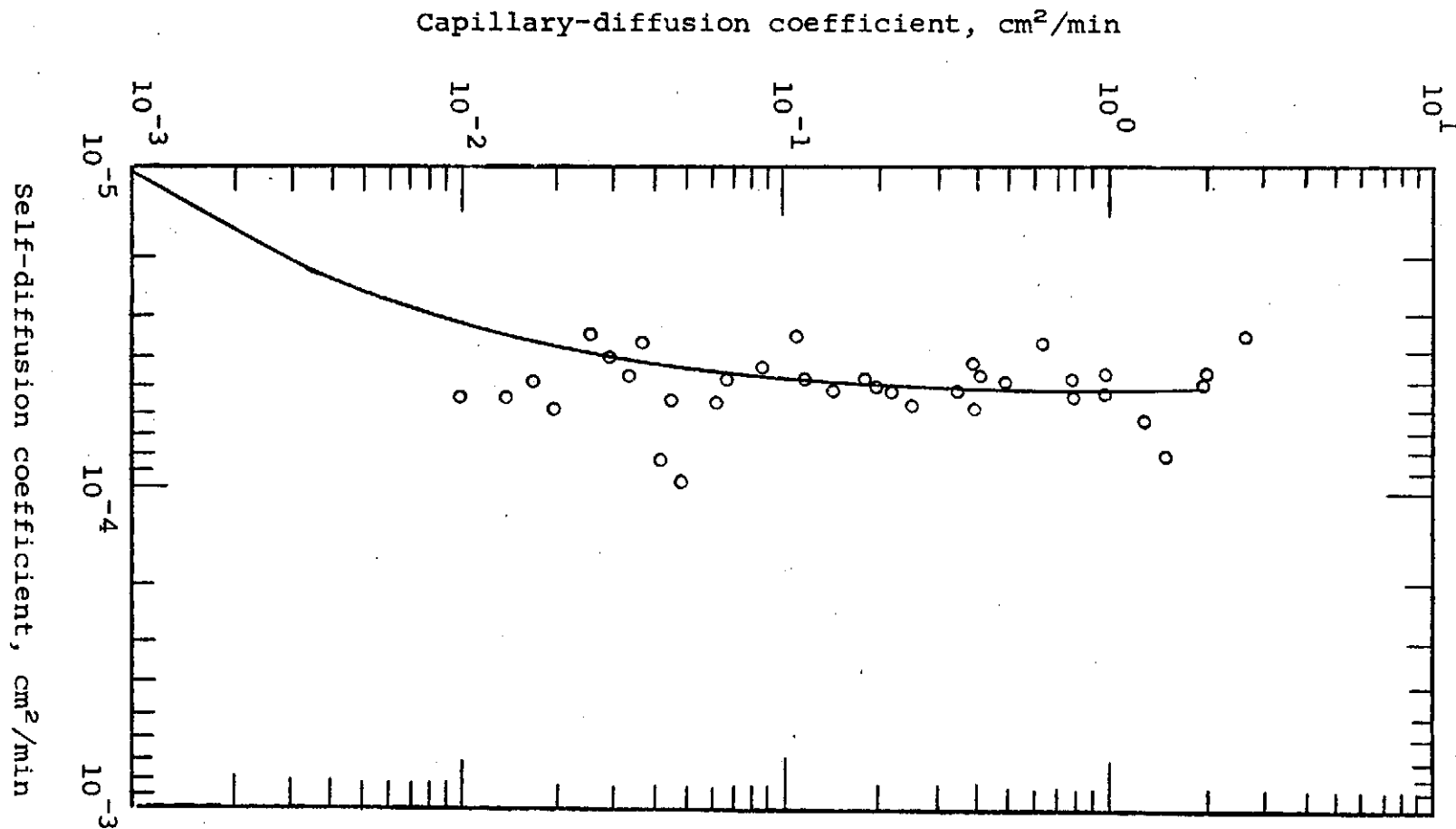


Figure 18. Relationship of capillary-diffusion coefficients as function of self-diffusion coefficients for Maury silt loam, Pembroke silt loam, Huntington loam, Yolo loam, Eden silty clay loam, and Burgin silty clay loam. The solid line represents the relationship reported by Kunze and Kirkham (1961); the points are those obtained in this work.

with ^{36}Cl and ^3HOH shown in Figure 17 for Huntington loam are large over a large water content range. However, it would appear safe to assume that a functional relationship does exist between the two diffusion coefficients for the liquid water diffusion coefficients.

Practical Considerations of Capillary-Diffusion Coefficients

Fick's first law states that the flux of water is proportional to the diffusion coefficient multiplied by the concentration of driving gradient. With the concentration gradient held constant, the higher the diffusion coefficient the greater the flux of water moving through a cross-sectional area in a given period of time.

One of the most important facets of evaporation of soil water is the ability of the saturated or unsaturated soil to transmit water upward to the soil surface. Thus, in a consideration of the loss of water due to evaporation from a soil, it is important to know the capillary-diffusion coefficients at given water contents as well as the physical, chemical, and mineralogical characteristics of the soil. A sand soil, although it has a high diffusion coefficient, may not be able to transport water upward for an appreciable distance, because the size of the capillary pores are too large to maintain the capillary rise of the water. On the other hand, a soil high in clay may not be able to transport water to the surface fast enough to meet evaporative demands, because of relatively small capillary-diffusion coefficients. When the evaporative demand is greater than the diffusive flux, the capillaries are broken and subsequent water transport is disrupted. A silt loam soil will often lose more water due to evaporation, because the sizes of the pores are such as to maintain capillary rise and the diffusion coefficient is large enough to transmit water to the soil surface fast enough to satisfy the evaporative demand.

The inflow diffusion coefficient of the Burgin silty clay loam is about an order of magnitude greater than the coefficient measured by the outflow method. This may not be too different from what is observed in field conditions. The Burgin, when initially dry, has an infiltration rate as high as the Maury silt loam. But once the soil is wetted, the soil conducts water very slowly because of the swelling effect of the clay. This reduction in the average pore

size results in a lower capillary-diffusion coefficient. Another point is illustrated with the Eden silty clay loam. The inflow and the outflow diffusivities are very similar. However, the Eden does not lose much water due to evaporation. This is a soil in which the capillary-diffusion coefficient is too small to transport water to the soil surface to meet normal evaporative demands. The Maury silt loam is known to lose a great deal of water each year due to evaporation; its evaporation rate is approximately 0.6 of open pan evaporation (Karraker et al., 1950). This observation is in agreement with the present work since the inflow capillary-diffusion and the outflow capillary-diffusion rates are nearly equal. Thus, the soil can transmit water fast enough to meet the evaporative potential and the continuity of the pore water is maintained.

Growing plants transpire enormous quantities of water which they remove from the soil. Often the soil water is not replenished by rain or irrigation over periods of weeks or months. Hence the soil acts as a moisture reservoir for the plant. Since plant roots remove water from the soil, there exists a soil moisture gradient between the plant root surface and some given distance away from the root. For a given gradient, the flux of water to the plant root will be dependent upon the diffusivity of the soil water. This work showed the diffusivity of the loams to be greater than the silt loams, which in turn were greater than the silty clay loams. This means that the loams are better able to supply the plant with water in the water content range studied. Also, due to the fact that the evaporative loss of water from the loam is not as great as that of the silt loams, the loams used in this study should be a more efficient source of water for plant growth.

SUMMARY AND CONCLUSIONS

Capillary-diffusion and self-diffusion coefficients of liquid water in unsaturated soils were determined by laboratory methods for several soils: Maury silt loam, Pembroke silt loam, Eden silty clay loam, Burgin silty clay loam, Henry silt loam, Huntington loam and Yolo loam.

Capillary-diffusion coefficients were measured by use of inflow and outflow methods. With both methods the capillary-diffusion coefficients decreased

very rapidly with decreasing water content. The soils with lower clay contents were found to have higher diffusion coefficients over the entire moisture content range studied, 0 to 1 bar tension, than the soils with the higher clay contents.

A comparison of the two methods showed that the inflow method yielded slightly higher capillary-diffusion coefficients for the Yolo, Huntington, and Pembroke. The inflow method gave coefficients about an order of magnitude greater than the outflow method for the Burgin silty clay loam. This difference was explained on the basis of the swelling property of the dominant clay mineral montmorillonite, in the soil. The two methods yielded approximately the same values for the Maury and the Eden.

The self-diffusion coefficients of the seven soils were measured over a moisture content range from air dryness to saturation using ^3HOH as a tracer of water. Each of the soils gave the same diffusion characteristics when the self-diffusion coefficients were expressed as a function of either water content or average number of water layers on the external mineral surface. As the water content decreased from saturation to near field capacity, the self-diffusion coefficients decreased very rapidly. When some critical amount of void pore space became available for the movement of water vapor, the diffusion coefficients of the soils increased very rapidly until a water content of about 5 to 10 percent on a volume basis was reached. As the water content was further reduced to air-dryness, the self-diffusion coefficients again decreased.

An attempt was made to separate the diffusion coefficients into a liquid and a vapor component by use of ^{36}Cl as a tracer of liquid water. The results showed that ^{36}Cl is not a good tracer of liquid water since the ^{36}Cl yielded higher diffusion coefficients than the water over the intermediate and higher water contents, and that these ^{36}Cl diffusion coefficients were constant, whereas the liquid diffusion coefficients decreased with decreasing water content.

A plot of the capillary-diffusion coefficient at a given water content as a function of the self-diffusion coefficient measured at the same water content

resulted in the points for all soils falling approximately on the same curve. This would suggest that a functional relationship does exist between the two diffusion coefficients. It was suggested that before a functional relationship could be derived, the liquid and vapor components would have to be separated.

By comparing the capillary-diffusion coefficients obtained by the two methods with the physical and mineralogical data, qualitative estimates of transpiration and evaporation of soil water in the field were postulated. Soils with higher inflow diffusion coefficients than outflow coefficients would not release water from the soil as rapidly as soils that have nearly equal inflow and outflow rates. However, for evaporation to occur to any great extent, the outflow rate must be fast enough to meet the evaporative demands.

Publications Resulting From the Project

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