Suggested Short Title:

DIFFUSION OF ANIONS IN ALLOPHANE SOILS

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EFFECTS OF TEMPERATURE, BULK DENSITY AND DRYING ON THE APPARENT DIFFUSION COEFFICIENT OF ^{36}Cl IN SOIL

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ABSTRACT

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Effects of Temperature, Bulk Density and Drying on the Apparent Diffusion Coefficient of ^{36}Cl in Soil

The Apparent Diffusion Coefficient of an anion in soil was evaluated to determine its potential in the characterisation of pore geometry. The effects of temperature, bulk density and drying of the soil on the apparent diffusion coefficient of ^{36}Cl were investigated. The diffusion method chosen was based on the boundary condition of a planar source diffusing into an infinite medium.

The measured diffusion coefficient equals the diffusion coefficient in solution multiplied by soil geometric and interaction factors. The change of viscosity of water with temperature accounted for a large part of the variation of the geometric and interaction factors with temperature; the remainder of the variation must be due to changes in bound water. For a given moisture content, increasing the bulk density increased the geometric factors such as diffusion path length. With the allophane soils, freeze-drying reduced the geometric and interaction factors; oven-drying and air-drying produced an equal reduction which was greater than that produced by freeze-drying.

RÉSUMÉ

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Les effets de la température, de la densité apparente et de l'assèchement sur le coefficient de la diffusion apparente du Cl^{36} dans le sol.

Le coefficient de diffusion apparente d'un anion dans le sol fut évalué dans le but de déterminer son potentiel dans la caractérisation de la géométrie des pores. Les effets de la température, de la densité apparente et de l'assèchement du sol sur le coefficient de diffusion apparente du Cl^{36} furent étudiés. La méthode de diffusion ainsi sélectionnée était basée sur les prémisses d'une source ayant la forme d'un plan se diffusant perpendiculairement à l'infini.

Le coefficient de diffusion ainsi mesuré égale le coefficient de diffusion en solution multiplié par les facteurs géométrique et d'interaction du sol. Le changement de viscosité de l'eau en fonction de la température était responsable dans une large mesuré de la variation des facteurs géométriques et d'interaction en fonction de la température, le reste de la variation devait être dû à des changements de l'eau adsorbée. Pour une teneur donnée d'humidité, l'augmentation de la densité apparente augmentait les facteurs géométriques, tel la distance de la diffusion. Avec les sols à allophane, l'assèchement par gel réduisait les facteurs géométriques et d'interaction; l'assèchement au four et à l'air ambiant produisaient une réduction égale qui était plus grande que celle produit par l'assèchement par gel.

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Gordon D. Holder

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CHAPTER 1

INTRODUCTION

The apparent diffusion coefficient of anions in soil is potentially a good tool to be used in the characterisation of pore geometry. The coefficient includes a tortuosity factor and a factor indicating the heterogeneity of pores, two important parameters in pore geometry. There is also the possibility that dead-end porosity, a third important parameter in pore geometry, could be measured by comparing the diffusion coefficients for transient and steady-state conditions.

The derivation of the apparent diffusion coefficient is based on the two parameter approach of tortuosity and porosity. The adequacy of such an approach has been questioned in the presence of dead-end pores. Therefore, despite its possible uses, the nature of the apparent diffusion coefficient is indistinct. It is doubtful whether the geometric and interaction factors contained in the apparent diffusion coefficient are separable. In spite of the many measurements, little attention has been paid to the possible effects of temperature, bulk density, and differences in methods of determination, on the apparent diffusion coefficient of anions in soil.

The objectives of this study were:

(1) To evaluate the effects of temperature on the apparent diffusion coefficient.

(2) To evaluate the effects of bulk density on the apparent diffusion coefficient.

(3) To review the literature on dead-end porosity and determine whether or not it is possible to measure dead-end porosity by diffusion.

(4) To evaluate the extent of structural changes due to drying of allophane soils by a comparison of the apparent diffusion coefficients measured in the undried and dried soils.

(5) To compare diffusion coefficients determined by different methods on a soil at constant bulk density, temperature and moisture content.

CHAPTER II

LITERATURE REVIEW

1. *The Diffusion Equations*

Diffusion is defined as the process by which matter is transported from one part of a system to another as a result of random molecular motions. In the classical experiment in which iodine and water are brought into contact without mixing, it is observed that after a time there is a net transfer of iodine into the water region. Such a transfer in the absence of convection currents is described as diffusion.

Each molecule in the iodine solution behaves independently of the others, which it seldom meets, and because of its constant collision with solvent molecules, each has a random haphazard motion. It moves sometimes towards a region of higher, and at other times towards a region of lower concentration showing no preferred direction of motion. The motion of a single molecule can be described in terms of the familiar "random walk" picture, and whilst it is possible to calculate the mean square distance travelled in a given interval of time, it is not possible to say in what direction a given molecule will move in that time (Crank, 1970).

This picture of random molecular motions, in which no molecule has preferred direction of motion, has to be reconciled with the fact that a transfer of iodine molecules from the region of higher to that of lower concentration is nevertheless observed (Crank, 1970).

Consider any horizontal section in the iodine solution and two thin, equal elements of volume one just below and one just above the section. Though it is not possible to say which way any particular iodine molecule will move, in a given interval of time, it can be said that on average, a definite fraction of molecules in the lower element of volume will cross the section from below, and the same fraction of molecules in the upper element will cross the section from above. Thus simply because there are more iodine molecules in the lower element than in the upper one, there is a net transfer from the lower to the upper side of the section as a result of random molecular motions.

Fick (1855) put diffusion on a theoretical basis by showing that the diffusion of substances through solutions obeyed the same mathematical laws that Fourier had derived for the conduction of heat in solids. Since the time of Fick, theoretical and experimental aspects of diffusion have undergone spectacular advances both in single and multi-phase systems (Barrer, 1951; Jacobs, 1935). For a multi-phase system such as a porous material, diffusion takes place almost exclusively through the fluid phase (gas or liquid or both). The solid matrix complicates matters by altering the diffusion path length and the cross-sectional area available for diffusion (Jackson *et al*, 1963).

The diffusion path length and the effective cross-section are extremely complicated properties of each porous material, and, in certain cases, both may be functions of space and time. Accounting for these factors in diffusion equations is usually accomplished by inclusion of the two parameters, porosity and tortuosity, which are assumed to be constants. The manner in which the two parameters have been used in diffusion equations has not been universal. Furthermore, the adequacy of the two parameter treatment has been questioned (Currie, 1960; Goodknight et al, 1960; Klute, 1959).

1.1 The First Order Diffusion Equation

Quantitative measurements of the rate at which a diffusion process occurs are usually expressed in terms of a diffusion coefficent. The diffusion coefficient is defined as the rate of transfer of the diffusing substance across a unit cross-sectional area divided by the space gradient of concentration of the substance at the section (Jackson, et al, 1963). Thus, if $q = \frac{Q}{t}$ is the amount of substance transferred in time t, A the cross-sectional area, c the concentration, and x the space coordinate, then

$$\bar{q}_x = \frac{Q}{t} = - D_o A \frac{\partial c}{\partial x} \qquad (1)$$

is a definition of the diffusion coefficient D_o, in one dimension. Similarly, expressions can be written for $\bar{q}_y$ and $\bar{q}_z$ using the assumption that the medium is isotropic. Hence,

$$\bar{q}_y = -D_o A \frac{\partial c}{\partial y} \qquad y = \text{the } y \text{ space coordinate}$$

$$\bar{q}_z = -D_o \frac{\partial c}{\partial z} \qquad z = \text{the } z \text{ space coordinate}$$

The definition of diffusion coefficient can be unambiguous only if the units of $\bar{q}$, A, and c, and x in equation (1) are carefully specified (Hartley and Crank, 1949). As Hartley and Crank (1949) have noted, concentration can be expressed in a number of different ways, thus necessitating that all the components of Equation (1) carry an index to indicate the frame of reference used.

In general, the concentration c should have the same quantity reference as q, and the volume should be of the same length reference as A and x. The use of different frames of reference for components of the same equation requires the use of appropriate conversion factors. This is particularly true in porous materials where the frame of reference may be the entire bulk medium (designated by the subscript m) or the fluid phase (designated by the subscript f). In some cases the fluid phase must be further designated as gas or liquid or both (Jackson <u>et</u> <u>al</u>, 1963).

Writing equation (1) in reference to the entire porous medium would give

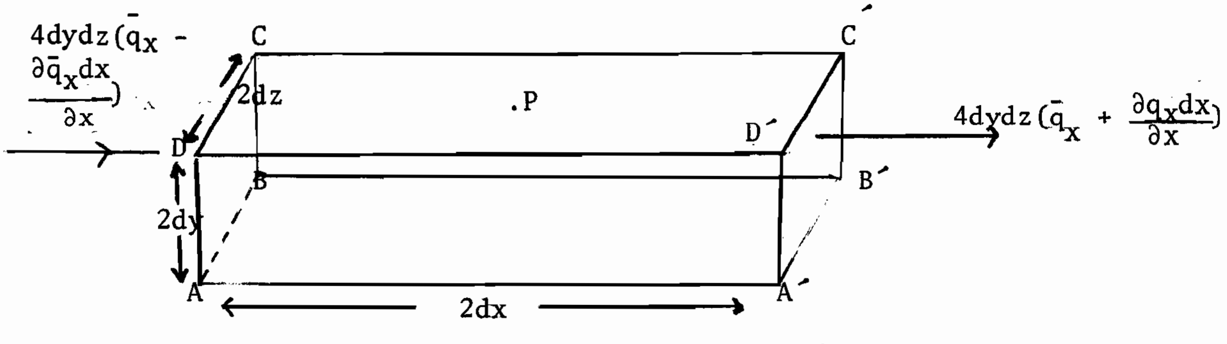
$$\bar{q}_x = - D_o A_m \frac{\partial \mathbb{C}_m}{\partial X_m} \qquad (2)$$

where $\bar{q}$ refers to the quantity of diffusing substance (frequently the mass) per unit time and does not need to be referred to the medium or fluid reference. If two or more substances are diffusing simultaneously, then the equation can be re-written for each substance and $\bar{q}$ would carry an appropriate index (Hartley and Crank, 1949).

The use of C_m, the quantity of diffusing substance per unit volume of porous medium, departs from the more commonly used definition of concentrations, but it is the only correct definition that can be used for a two-component system when one component is the porous medium (Jackson et al, 1963). Its use is not without precedent (Fukuda, 1956; Tiselius, 1934). In many systems, however, it is more convenient to measure the concentration with reference to the fluid phase.

1.2 *The Second Order Diffusion Equation*

The first order equation in the previous section is commonly referred to as 'Fick's first law'. By itself, Fick's first law is sufficient to describe only steady (or stationary) state diffusion. For transient state diffusion, one needs to introduce another law, namely, the law of conservation of matter expressed in the equation of continuity. The analysis is as follows:



(Crank, 1970)

Assuming that the medium is isotropic, consider a parallel pipe whose sides are parallel to the axes of coordinates and are of lengths 2dx, 2dy, 2dz. Let the centre of the element be at P(x, y, z) where the concentration of the diffusing substance is c, let ABCD and A'B'C'D' be the faces perpendicular to the axis of x as in the diagram. The rate at which the diffusing substance enters the element through the face ABCD in the plane x - dx is given by

$$4\, dydz\, (\bar{q}_x - \frac{\partial \bar{q}_x}{\partial x} dx) \qquad (3)$$

Where $\bar{q}_x$ is the rate of transfer through unit area of the corresponding plane through P. Similarly the rate of loss of diffusing substance through the face A'B'C'D' is given by

$$4dydz\, (\bar{q}_x + \frac{\partial \bar{q}_x}{\partial x} dx) \qquad (4)$$

The contribution to the rate of increase of diffusing substance in the element from these two faces is thus equal to

$$- 8\, dxdydz\, \frac{\partial \bar{q}_x}{\partial x} \qquad (5)$$

Similarly from the other faces one obtains

$$- 8\, dxdydz\, \frac{\partial q_y}{\partial y} \quad \text{and} \quad - 8\, dxdydz\, \frac{\partial \bar{q}_z}{\partial z}$$

But the rate at which the amount of diffusing substance in the element increases is also given by

$$8\, dxdydz\, \frac{\partial C}{\partial t} \qquad (6)$$

This results from the equation of continuity which states that if the rate of diffusion into a volume element is greater than the rate of diffusion out of that element, then the volume element must be storing the excess solute, and increasing in its solute concentration (Hillel, 1971).

Hence $$8 \; dxdydz \frac{\partial C}{\partial t} = - 8 \; dxdydz \left(\frac{\partial \bar{q}_x}{\partial x} + \frac{\partial \bar{q}_y}{\partial y} + \frac{\partial \bar{q}_z}{\partial z}\right) \qquad (7)$$

and $$\frac{\partial c}{\partial t} + \frac{\partial \bar{q}_x}{\partial x} + \frac{\partial \bar{q}_y}{\partial y} + \frac{\partial \bar{q}_z}{\partial z} = 0 \qquad (8)$$

Now, if the diffusion coefficient D_o is constant, then

$$\bar{q}_x = - D_o \frac{\partial c}{\partial x}$$ and equation (8)

becomes

$$\frac{\partial c}{\partial t} = D_o \left\{\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right\} \qquad (9)$$

If it is further assumed that diffusion is one dimensional then equation (9) reduces to

$$\frac{\partial c}{\partial t} = D_o \frac{\partial^2 c}{\partial x^2} \qquad (10)$$

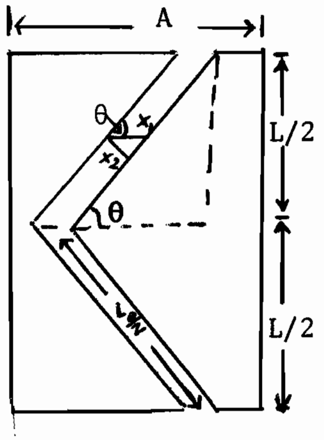
which is a mathematical expression of Fick's second law of diffusion.

1.3 Geometric factors: Porosity and tortuosity

Fick's first law of diffusion is given as

$$\bar{q}_x = - D_o A \frac{\partial c}{\partial x} \qquad (11)$$ [symbols explained earlier]

As stated earlier, the solid matrix through which a substance is diffusing complicates matters by altering the diffusion path length



Simplified porous media.
The symbols A, X_1, and X_2
represent areas, L and Le
represent lengths.
(Porter et al, 1960)

and the cross-sectional area available for diffusion. These factors can be accounted for by the inclusion of the two parameters, porosity and tortuosity, in the diffusion equation (Jackson et al, 1963). In addition to path length and cross sectional area which are collectively known as 'Geometric Factors', (Porter et al, 1960), interaction factors (i.e. interaction between the diffusing substance and the matrix) must also be accounted for.

The major effects of the geometric factors are illustrated in the diagram above, in which a simplified 'water' filled pore in a solid of unit depth is represented. The porosity, S, of the solid is equal to X_1/A. However, the cross-sectional area available for flow perpendicular to the direction of microscopic flow is X_2, which is equal to $X_1 \sin \theta$.

$$\sin \theta = L/Le$$
$$\therefore X_2 = X_1 (L/Le)$$

Thus, the effective fraction of the total area A available for flow is not the porosity $S = X_1/A$ but X_2/A.

$$\text{But}\quad \frac{X_2}{A} = \frac{X_1(L/Le)}{A} = S\ (L/Le)$$

The macroscopic distance between points is identified as L, and the actual distance through which diffusion must take place is identified as Le. Since Le is larger than L, Δx (∂x) in a porous medium is larger than the macroscopic distance between points by the factor Le/L.

Rewriting Fick's first law to account for these geometric factors in a porous medium

$$\bar{q}_x = - D_o[AS(L/Le)]\ \frac{\Delta C}{\Delta x(Le/L)} = - D_oAS\ (L/Le)^2\ \frac{\Delta C}{\Delta X} \qquad (12)$$

Approximately the same results are obtained when more complicated pore geometric models are considered. This treatment has been used in the oil industry literature for quite some time (Wyllie, 1952). Since ionic diffusion takes place only through the water in unsaturated media, the fraction θ of the volume occupied by water should be used instead of the porosity, S in equation (12).

Thus by accounting for the 'geometric factors', $\bar{q}_x$ becomes

$$\bar{q}_x = - D_o(L/Le)^2\theta A\ \frac{\partial C}{\partial X} \qquad (13)$$

where θ is volumetric moisture content.

1.4 *Interaction factors – Viscosity and Chemical Interactions.*

Interactions between the diffusing ions and the charged surfaces of the matrix (e.g. in the case of diffusion of ions through soils), act so as to decrease the diffusivity. The viscosity of water is also increased in the immediate vicinity of the mineral surfaces (as in the case of soil as the matrix) and this tends to reduce diffusivity. Porter et al (1960), combined these two factors and represented them in the equation by γ.

The steady state equation could thus be written as

$$\bar{q}_x = - D_o \gamma [L/Le]^2 \, \theta A \frac{\partial C}{\partial X} \tag{14}$$

It is doubtful for diffusion of many substances in soils, that the various chemical and physical factors can be separated, evaluated or enumerated (Jackson et al, 1963).

However, more recently, Kemper et al (1964) used separate symbols for these two effects. The effect of the viscosity of water on diffusion was accounted for by α in equation(14), where α is the relative mobility or fluidity of the water. Van Schaik and Kemper (1966) evaluated α from Cl^- diffusion in Na-bentonite at moisture contents equivalent to approximately 2.5 and 5 molecular layers of water on each surface, viz. $\theta = 0.61$ and $\theta = 0.75$ respectively. Values of α were 0.50 for $\theta = 0.61$ and 0.65 for $\theta = 0.75$. In this treatment α is a weighted relative fluidity because viscosity changes with distance from the clay surface. Similar values of α were found in a Ca-bentonite system for comparable values of θ. In soil, Porter et al (1960) estimated α as about 0.8 at 0.33 bar water suction.

Negative adsorption on the other hand was accounted for in equation (14) by the factor γ. This adsorption of free electrolyte in soil or clay causes a greater exclusion of anions from small pores and from narrow films of water connecting large pores. The factor γ is most important for anions because the cations exchange with a mobile fraction of the adsorbed cations and effectively by-pass this restriction (Van Schaik et al, 1966). Van Schaik and Kemper (1966) estimated γ to be about 0.5 for Cl^- diffusion in Na- or Ca-saturated bentonite. The influence of negative adsorption in Ca-clay was expected to be smaller than in the Na-clay, but a greater heterogeneity of pore size in the clay apparently balanced the greater negative adsorption in the Na-clay.

Thus equation (14) can be rewritten as

$$\bar{q}_x = - D_o \alpha \gamma [L/Le]^2 \theta A \frac{\partial C}{\partial X} \qquad (15)$$

The term $D_o \alpha \gamma \theta [L/Le]^2$ is called the effective diffusivity, D_p (Olsen and Kemper, 1968). However, other authors use different symbols, e.g. Kemper et al (1960) described $D_o \alpha \gamma [L/Le]^2$ as De, Jackson et al (1963) used D_m. Hence, to avoid confusion, the following are used in this review.

$$\begin{aligned} D_o &= \text{diffusivity in water} \\ D_m &= D_o \alpha \gamma [L/Le]^2 \\ D_p &= D_o \alpha \gamma [L/Le]^2 \theta \qquad (16) \end{aligned}$$

Hence $D_p = D_m \theta$ (Olsen et al, 1968; Jackson et al, 1963)

Thus equation (15) may be written in a number of ways depending on the frame of reference used for expressing concentration. The symbols preferred are those of Jackson et al (1963).

Hence,

$$\bar{q}_x = -\theta D_p A_m \frac{\partial C_f}{\partial X_m} \qquad (17)$$

or,

$$\bar{q}_x = -\theta D_m A_m \frac{\partial C_m}{\partial X_m}$$

Similarly, for Fick's Second Law of Diffusion

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial X^2_m} \qquad (18)$$

or,

$$\frac{\partial C_f}{\partial t} = D_m \frac{\partial^2 C_f}{\partial X^2_m} \qquad (19)$$

Thus, regardless of the concentration reference, the diffusion coefficient is D_m (Jackson et al, 1963).

Or if D_p is preferred, equation (19) becomes

$$\frac{\partial C_f}{\partial t} = \frac{D_p}{\theta} \frac{\partial^2 C_f}{\partial X^2_m} \qquad (20)$$

where θ is volumetric moisture content

1.5 Diffusion plus Reaction

It is necessary to consider the possibility of interaction between the diffusing ion and the soil particles. This interaction has been accounted for in the diffusion equation by the inclusion of a capacity factor (Gardner, 1965; Olsen and Kemper, 1968).

The second order diffusion equation then becomes

$$\frac{\partial C_f}{\partial t} = \frac{D_p}{(b + \theta)} \frac{\partial^2 C_f}{\partial X^2_m} \qquad (21)$$

or

$$\frac{\partial C_m}{\partial t} = \frac{D_m}{(b' + 1)} \frac{\partial^2 C_m}{\partial X^2_m}$$

The expressions $(b + \theta)$ and $(b' + 1)$ are called capacity factors (Olsen and Kemper, 1968). This term is intended to be analagous to "heat capacity", (in the case where equations of heat flow are used to solve problems in diffusion) meaning the quantity of heat required to raise the temperature of a body one degree. Thus the capacity factor (Equation [21]) is the amount (g) of diffusible ion per cubic centimeter of soil required to increase the solution concentration by one unit (g per milliliter of soil solution) [Olsen and Kemper, 1968].

A capacity factor will need to be measured in all cases of anion diffusion in soil where the anion is adsorbed or reacts to form a solid phase. Fortunately, some ions are not adsorbed by the solid phase, e.g. Cl^- and NO_3^- and as such b and b' are zero.

1.6. Factors affecting the Apparent Diffusion Coefficient

Factors affecting the apparent diffusion coefficient include, temperature, moisture content, tortuosity factor, viscosity of water, negative adsorption, concentration and properties and concentration of the counter-diffusing ions.

1.6.1. Temperature

It is believed that the apparent diffusion coefficient is temperature dependent (Gardner, 1965). However, no data is available at the moment to verify this except for diffusion in solutions. It can be seen that in the apparent diffusion coefficient, temperature would affect viscosity as well as D_o, the diffusion coefficient of the ionic species in solution.

1.6.2. Moisture Content

The apparent diffusion coefficient D_m of an ionic species diffusing in soil varies in a linear or non-linear manner with moisture content depending upon whether or not the ionic species is adsorbed by the matrix (Olsen and Kemper, 1968). In the case where the ions are adsorbed by the solid phase, the relationship is non-linear. When the ionic species in solution is not adsorbed by the solid phase (viz. Cl^- or NO_3^-), the relationship is linear (Porter _et al_, 1960; Olsen and Kemper, 1968). The effects of θ on D_p or D_m are both physical and chemical. As θ decreases in a given soil, the cross-sectional area available for diffusion becomes smaller, the path length increases, and the viscosity and negative adsorption terms in Equation (16) become more important as the water film decreases in thickness (Olsen and Kemper, 1968). Thus the diffusion coefficient decreases with decreasing water content as illustrated in Table 1 (Gardner, 1965). The data of Klute and Letey (1958) for glass beads showed a similar reduction with decreasing water content.

TABLE 1. Diffusion Coefficients in Soils

Solute	Soil Texture	Water Content	D_m cm^2day^{-1}	$D_m(x10^{-5})$ cm^2sec^{-1}	$D_m(x10^{-5})/\theta$ cm^2sec^{-1}	Reference
Cl^-	Clay	0.450	0.500	0.580	1.95	Porter _et al_ (1960)
	Clay	0.250	0.160	0.190	-	-do-
	Loam	0.250	0.350	0.410	2.20	-do-
	Loam	0.100	0.065	0.080	2.20	-do-
RbCl	Loam	0.470	0.120	0.140	0.35	Patil _et al_ (1963)
	Loam	0.278	0.043	0.050	0.35	-do-
	Loam	0.172	0.034	0.040	0.35	-do-
Cl^-	Silt	0.427	1.150	1.330	5.64	Romskens & Bruce (1964)
	Silt	0.248	0.275	0.320	5.64	-do-
	Sand	0.402	1.200	1.390	5.73	-do-
	Sand	0.168	0.042	0.050	5.73	-do-

1.6.3 *Geometric and Interaction Factors.*

These factors were treated to some length in the derivation of the apparent diffusion coefficient. Reference is therefore made to sections 1.3 and 1.4 in Chapter II.

1.6.4 *Concentration*

It has been suggested that the apparent diffusion coefficient is concentration dependent (Gardner, 1965). Van Schaik and Kemper (1966) measured the diffusivity of Cl^- in steady-state and transient systems with concentration of Cl^- varying between 0.001 and 0.15M and the effect on D_p was small.

It is generally accepted that concentration effects are probably not too important in soils except at very high concentrations (Paul, 1965; Lewis and Quirk, 1962; Olsen and Kemper, 1968).

1.6.5 *Properties and Concentration of the Counterdiffusing Ions.*

Whenever possible with soil, self-diffusion coefficients have been measured using isotopes because of their convenience and accuracy (Olsen and Kemper, 1968). When two different ions are involved in diffusion then the participating ions have a mutual diffusion coefficient that depends on the individual diffusion coefficients and on their respective concentrations as shown by Equation 22.

$$D_{12} = \frac{D_1 D_2 (Z_1 C_1 + Z_2 C_2)}{Z_1 C_1 D_1 + Z_2 C_2 D_2} \qquad (22)$$

In this equation D is the diffusion coefficient, C the ion concentration, Z the valence of the ions; the subscripts 1 and 2 represent respectively, the given ion and the co-diffusing or counter-diffusing ion (Jost, 1952). The equation indicates that the diffusion coefficient of the ion present in low concentration will largely control the mutual diffusion coefficient. Diffusion of one ion species is changed if an appreciable electrical diffusion potential is caused by differential diffusion rates of other ions. Since there are generally many mobile cations in the adsorbed phase and these ions shift readily to 'buffer' diffusion potentials, these potentials remain small in soils with appreciable exchange capacity.

The mutual inter-diffusion coefficient from Equation 22 is a function of the concentration of the ions. Simple solutions of the diffusion equation require that $D_{12p}/(b + \theta)$ is a constant, where D_{12p} refers to a porous system. There may be important ranges of concentration where the variation of D_{12p} for anions is sufficiently small that an average value can be used for an approximate solution. The non-exact nature of methods for measuring diffusion coefficients in soils (Olsen and Kemper, 1968) would appear to justify the use of average co-diffusion or counter-diffusion coefficients, estimated from self-diffusion coefficients, in solving practical problems like ion movement to plant roots.

1.7 *Anion versus Cation Diffusion*

Diffusion of cations differs from that of anions in that cations may participate in diffusive movement while they are adsorbed on clay minerals. Anions are either not adsorbed, or, when they are adsorbed, the adsorption forces are usually so strong and the adsorption sites are so far apart that practically no exchange takes place between anion adsorption sites without the anions going through the energy level characteristic of the equilibrium solution. Cation-exchange-sites are often sufficiently close together that weakly held cations (participating in the diffuse layer) can trade positions without attaining the high energies characteristic of the equilibrium solution. This mutual exchange of positions of adsorbed cations contributes to the overall cation inter-diffusion (Olsen and Kemper, 1968).

So far, much of what has been said, refers to anion diffusion in the soil matrix. A concise account of the diffusion equations treated for cation diffusion can be obtained from Olsen and Kemper (1968).

1.8 Significance of $(L/Le)^2\alpha\gamma$ as Measured by a Particular Anion for a Particular Soil.

Apparently values of $(L/Le)^2\alpha\gamma$ measured for diffusion of one anion in a soil are good estimates of these values for other anions of equal valence. For instance, values of $(L/Le)^2\alpha\gamma$ obtained by using Cl^- (Porter et al, 1960), may be combined with reported (Moreno, 1957; Salvinien et al, 1954) values of D_o for P in solution (5×10^{-6} cm^2 sec^{-1}) to obtain values of D_p for P practically identical to those measured by steady-state measurements on the same soil by Olsen et al (1965).

However, Olsen et al (1965) observed that measured values of D_p for P (by transient-state) were slightly lower than calculated values of D_p estimated from Cl^- diffusion and the relationship $D_p = (L/Le)^2\alpha\gamma\theta D_o$. The calculations were based on the assumption that the effect of the factors $\alpha\gamma(L/Le)^2\theta$ on diffusion of Cl^- was the same as on diffusion of P. In reality, over half of the P was present as HPO_4^{2-} ions. Negative adsorption will be greater for divalent anions which could account for the lower values of D_p found by diffusion of ^{32}P. In addition the values for D_p obtained by the transient-state method (Olsen et al, 1965) should be about 20 per cent larger because in these transient measures of D_p using an isotope in one block of soil diffusing into another block, the appropriate capacity factor is the isotopic dilution capacity factor C'/C, whereas they used $\partial C'/\partial C = b + \theta$. These capacity factors were not identical because for their systems $C' = bC + \theta C + \text{constant}$ (Olsen and Kemper, 1968). These results (Olsen et al, 1965) further illustrate the necessity of measuring a capacity factor when D_p is to be determined by a transient state method.

2. *Dead-end Porosity and its Determination*

The importance of dead-end pores in this project is two-fold, since:

(a) any characterisation of the pore geometry of a porous material must take into account an assessment of dead-end pores in that material (Jackson and Klute, 1967a).

(b) It has been suggested that the transient state diffusion equation may be inadequate in the presence of dead-end pores. (Klute, 1959; Goodknight, Klikoff and Fatt, 1960).

2.1 Dead-end Pore Volume of Pumice

Soils developed from volcanic ash of which pumice is a major constituent have unique physical (Cochran et al, 1967) and chemical properties (Chichester, 1967). To a large extent, these properties are related to the vesicular (or dead-end pore) structure of the particles.

This led Borchardt et al (1968) to measure the vesicular pore size distribution of pumice using mercury intrusion techniques and also to obtain preliminary information on the characteristics of samples from different origins. They found that vesicular pores constituted about 98 per cent of the fine porosity (<120μ diameter) in 1 - 0.5 mm fractions of pumice. Average diameters of internal pores of pumice were found to be in the range of 3 to 7μ.

The type and amount of vesicular pores in pumice supposedly depends upon gas pressure and viscosity in the magma at the time of eruption (Williams, 1942). It is therefore likely that pumice ejected from different volcanoes will have different vesicular pore-size distributions. This was investigated by Borchardt et al (1968), and it was found that pumice samples from different sources exhibited distinguishing pore-size distribution curves.

2.2 Fick's Second Law and its Validity

Goodknight et al (1960) appear to have been the first to suggest that equation (18) may be inadequate in the presence of dead-end pores. In fact, it was Klute(1959) who first questioned the adequacy of the use of two pore structure parameters, porosity and tortuosity, in the treatment of non steady-state diffusion. It was pointed out that dead-end pore volume (defined as volume which contains the flowing or diffusing species but through which there is no flux during steady-state diffusion) may alter diffusion behaviour.

The basis for questioning the adequacy of Equation 18 by Goodknight _et al_ (1960) is that local disequilibria between the concentrations in the active and dead-end pore space cannot be neglected. A mathematical treatment of non steady-state diffusion was presented by these workers, which included an expression for the dead-end pore volume. However, no mention was made of a possible means of determining the dead-end pore volume in the laboratory.

Therefore to assess whether or not the transient state diffusion equation is adequate in the presence of dead-end pores would involve some measurement of dead-end pore volume.

2.3 Dead-end Pore Volume: Measurement by Jackson and Klute.

Jackson and Klute (1967a) proposed a method for measuring dead-end pore volume based on diffusion measurements. According to these workers, dead-end pore volume is defined as the volume which contains the flowing or diffusing species, and acts as a source or sink during transient behaviour, but does not contribute to steady-state fluid flow or diffusion. The precise geometry of the dead-end pore volume is somewhat obscure. Dead-end pores may be cavities i.e. pores with only one opening. Pendular bodies of fluid that can only exchange fluid through a vapour phase or thin film with the main body of the pore fluid may also act as dead-end pore volume. Adsorption of the fluid by the solid phase can also contribute to dead-end pore volume. Therefore, as stated earlier, an estimate of dead-end pore volume is necessary for: (a) the proper evaluation of transient flow measurements, (b) description of the soil pore geometry.

Jackson and Klute (1967a) suggested the following relationship.

$$V_{f2}/V_m = 1 - \frac{D_{tr}}{D_{ss}} \quad \ldots \quad (23)$$

Where V_{f2} is volume of dead-end pores
V_m is total pore volume
D_{tr} is transient-state diffusion coefficient
D_{ss} is steady-state diffusion coefficient

Equation (23) was based on the following mathematical reasoning:

In a porous system, the diffusion of a substance takes place through the fluid which is held in the pore volume. In the mathematical description of the diffusion process, the frames of reference are the same as described in Section 1.1. These reference frames are further divided into the pore volume contributing to flow (subscript 1) and dead-end pore volume (subscript 2).

Hence for one dimensional diffusion

$$\bar{q}_m = - D_m \frac{\partial C_{m1}}{\partial X_m} \quad \ldots \quad (24)$$

where C_{m1} = concentration of 'active' diffusant
(See Equation (1) for other symbols)

$$C_m = C_{m1} + C_{m2} = (1 + K)\, C_{m1} \quad (25)$$

where C_{m2} is the concentration of diffusant in the dead-end pores.

$$K = C_{m2}/C_{m1}$$

Applying the equation of continuity to equation (24) and including a source term, yields

$$\frac{\partial C_{m1}}{\partial t} = \frac{-\partial q_m}{\partial X_m} + S \qquad (26)$$

where S is a source term for 'active' diffusant, and is the amount of diffusant produced per unit time per unit volume of porous medium.

Therefore,

$$S = -\frac{\partial C_{m2}}{\partial t} \qquad (27)$$

Since the source for 'active' diffusant is the dead-end pore volume:

Combining Equations (24) and (27) with Equation (26) gives

$$\frac{\partial C_{m1}}{\partial t} + \frac{\partial C_{m2}}{\partial t} = \frac{\partial}{\partial X_m}\left[D_m \frac{\partial C_{m1}}{\partial X_m}\right] \qquad (28)$$

Using Equation (25) in Equation (28)

$$\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial X_m}\left[\frac{D_m}{1+K} \cdot \frac{\partial C_m}{\partial X_m}\right] \qquad (29)$$

If K and D_m are constant, then Equation (29) reduces to

$$\frac{\partial C_m}{\partial t} = D_{tr} \frac{\partial^2 C_m}{\partial X_m^2} \qquad (30)$$

(Where $D_{tr} = D_m/(1 + K)$)

Now $K = C_{m2}/C_{m1}$

But $C_{m1} = \frac{M_1}{V_m} = \frac{M_1}{V_{f1}} \times \frac{V_{f1}}{V_m} = C_{f1}\frac{V_{f1}}{V_m}$ (31)

Where M_1 and M_2 are the amounts of diffusant in the active and dead-end pores; V_m, V_{f1} and V_{f2} are the total volume, 'active' pore volume, and dead-end pore volume respectively.

Similarly, $C_{m2} = C_{f2} \; V_{f2}/V_m$ (32)

Substituting for K in equation (30)

$$D_{tr} = \frac{D_m}{1 + \frac{C_{f2}}{C_{f1}} \frac{V_{f2}}{V_{f1}}} \qquad (33)$$

where D_{tr} is transient-state diffusion coefficient

D_m is steady-state diffusion coefficient

The assumption here is that since C_{f2}/C_{f1} is difficult to specify, it is reasonable to assume that these concentrations are nearly equal. Therefore let $C_{f2}/C_{f1} = 1$

$$\frac{D_{tr}}{D_m} = \frac{1}{1 + \frac{V_{f2}}{V_{f1}}} \qquad (34)$$

$$\frac{D_{tr}}{D_m} = \frac{V_{f1}}{V_{f1} + V_{f2}}$$

But $V_m = V_{f1} + V_{f2}$

$$1 - \frac{D_{tr}}{D_m} = 1 - \frac{V_{f1}}{V_m}$$

$$1 - \frac{D_{tr}}{D_m} = \frac{V_{f2}}{V_m}$$

Hence from the ratio D_{tr}/D_m, the fraction of dead-end pores could be calculated.

Evidence to support this analysis was given by Jackson and Klute when it was mentioned that Goodknight and Fatt (1961) had a differential equation in their analysis which was similar to Equation (29). The time lag equation for a system of dead-end pores differed from the equation for a system without dead-end pores by a factor of $(1 + V_{f2}/V_{f1})$, which, when combined with the diffusion coefficient, resulted in equation (33). The results of the two different approaches indicate that equation (33) is valid when the dead-end pores are of nominal pore size or smaller, as well as for larger orifice-connected-chambers used in the experimental apparatus of Goodknight and Fatt (1961).

2.3.1 *Jackson and Klute Criticized*

Almost immediately after their publication Jackson and Klute (1967a) were subjected to heavy criticism from Philip (1967). Philip's view was that the presence of dead-end pores manifests itself during diffusion in a porous material through *changes* with *time* and *space* in the ratio of the quantity of diffusing material in dead-end pores and that in active pores. The variation of this ratio in transient systems embodies the total physical influence of dead-end pores on diffusion. If this ratio were not to vary, the experimental detection of dead-end pores by diffusion studies would be impossible and dead end porosity per se would be of neither theoretical nor practical interest in diffusion studies. It would simply be one more factor influencing 'tortuosity'.

Philip expressed surprise that Jackson and Klute (1967a) proposed a method based on the assumption that the *ratio* is a constant K. Jackson and Klute further adopted a value of K which implied that there is no local concentration difference (and therefore no exchange of diffusant) between active and dead-end pore space. This value is only suitable for a system in which the concentration in both types of pore-space is continuous and everywhere in local equality. Therefore, on the basis of their assumptions, Jackson and Klute should have arrived at the result that the diffusion coefficient is the same for steady and transient systems.

They apparently did not arrive at this logical conclusion because of confusion in their interpretation of equation (24) in this review. Jackson and Klute identified D_m as the steady state diffusion coefficient, and this was in fact their error, which resulted in their inconsistent results.

Looking at equation (24) again,

$$\bar{q}_x = - D_m \frac{\partial C_{m1}}{\partial X_m}$$

Dm is clearly therefore a diffusion coefficient based on the gradient of C_{m1}; but a steady-state experimental measurement of diffusivity determines the ratio of q_x to the gradient of the physically observable concentration, i.e. of $(C_{m1} + C_{m2})$ where C_{m2} is 'the concentration of diffusant in dead-end pores', (based on unit volume of the medium).

With this correction, then

$$C_m = (C_{m1} + C_{m2}) = (1 + K)\, C_{m1}$$

Hence, for steady-state diffusion

$$\bar{q}_x = - \frac{D_m}{(1 + K)} \frac{\partial C_m}{\partial X_m}$$

That is, steady-state diffusion $(D_{ss}) = \frac{D_m}{1 + K}$ which is also equal to D_{tr}.

Hence $D_{ss} = D_{tr} = \frac{D_m}{(1 + K)}$

A note was then published by Jackson and Klute (1967b) accepting that their mathematical analysis was based on the wrong assumptions and that their interpretation of Fick's first law (Equation 24) was wrong. In fact, their analysis should have yielded, $D_{ss} = D_{tr}$ as shown by Philip (1967). They pointed out that C_{f2} / C_{f1} could be <1 during absorption and >1 during desorption, hence D_{tr} may be > or < D_{ss}. However, available experimental data was insufficient to elucidate this point.

2.4 *Philip's Method of Measuring dead-end pore volume*

Diffusion in a porous medium is conventionally described (on a Darcy's scale) as linear diffusion down a gradient of concentration it is being understood that the concentration C_m is averaged over a volume which is large compared with that of the individual pore. Such a description is appropriate when (i) the diffusion process would indeed be linear if it took place in a space unencumbered by the solid matrix material of the medium, and (ii) local disequilibrium of concentration (i.e. disequilibrium on the Darcy's scale) is unimportant. The second of these requirements need be invoked only when transient phenomena are to be considered. When these requirements are met, the diffusion may be described by Equation (18).

2.4.1 *Philip's analysis*

Let the concentration of diffusant contained in active and dead-end porosity be C_{m1} and C_{m2} respectively. Both concentrations (as well as C_m which equals $C_{m1} + C_{m2}$) are based on unit volume of the medium. Then the equations governing transient diffusion in the system are:

$$\frac{\partial (C_{m1} + C_{m2})}{\partial t} = D_m \frac{\partial^2 C_m}{\partial X^2_m}$$

$$\frac{\partial C_{m2}}{\partial t} = K (\alpha C_{m1} - C_{m2})$$

Hence, α is the ratio of dead-end porosity to active porosity and K, the transfer coefficient for local diffusion between active and dead-end porosities, has the dimension $(\text{time})^{-1}$.

Philip (1968) presented a solution where the system is effectively semi-infinite with a step-function change of concentration at the surface of the column. From the mathematical analyses (Philip, 1968) it is clear that transient diffusion into a medium with dead-end pores has the following properties:

1. Net diffusion into the active porosity initially obeys a $(\text{time})^{1/2}$ law. A second $(\text{time})^{1/2}$ law, corresponding to a smaller apparent diffusivity, is established for sufficiently large τ (where $\tau = Kt$).
2. Diffusion into the dead-end porosity initially obeys a $(\text{time})^{3/2}$ law. At sufficiently large t or (τ) a $(\text{time})^{1/2}$ law is established.
3. Total diffusion into the medium initially obeys a $(\text{time})^{1/2}$ law. A second $(\text{time})^{1/2}$ law, corresponding to a larger apparent diffusivity, holds for sufficiently large t (or τ).

2.4.2 *Actual Determination of Dead-end Porosity [Philip, 1968].*

The solutions obtained by Philip are rather simpler in form than those of Goodknight et al (1960) and of Goodknight and Fatt

(1961); and they appear better adapted to the detection of dead-end porosity by diffusion observations.

The required experiment consists of the observation of diffusion consequent on the imposition of a step-function change of concentration at one end of a long column of the medium (or on the bringing together of two long columns of different initial uniform concentrations). The measurement required is of the cumulative flux I(t). The ratio of the final to the initial value of $dI/d(t^{\frac{1}{2}})$ then yields an estimate of $(1 + \alpha)^{\frac{1}{2}}$. (This follows from a comparison of Equation (21) and Equation (24) in Philip's paper (1968). The experiment is terminated before any concentration change occurs at the remote end(s) of the column(s).

2.4.3 *Magnitude of K. Practical significance of dead-end Porosity in Diffusion.*

The various solutions of Philip (1968) indicate that, for τ values greater than 5, the process is virtually indistinguishable from a simple diffusion process. At τ values of this magnitude, concentration changes in the active porosity operate too slowly to produce local disequilibria of any magnitude. An assessment of the practical importance of dead-end porosity in diffusion depends on the translation of the results of Philip back into physical time, and this requires an estimate of K (where $\tau = Kt$).

2.4.4 Order of Magnitude of K and t range for which Dead-end Porosity is important.

Suppose that the characteristic length of the diffusion path in an individual dead-end pore is equal to λ which may be identified with the characteristic pore dimension for the medium. Then the characteristic time for equilibration by diffusion in the dead-end pore is $\kappa(\lambda^2/D_o)$. (D_o is preferred to D_m in the expression because the effect of tortuosity will tend to be less important for the processes in an individual pore than for the medium as a whole; but the substitution of D_m for D_o would not influence the subsequent agrument materially). K varies inversely as the time and is therefore $\kappa'(D_o/\lambda^2)$ where $\kappa' = 1/\kappa$ and κ equals a constant. The duration of the initial period during which dead-end porosity influences the phenomenon is 5 in τ-time and hence $\kappa(5\lambda^2/D_o)$ in physical time. But during an initial interval of duration t_1, the depth of penetration of the diffusion process into the medium is $(\kappa' D_m t_1)^{\frac{1}{2}}$, so that the depth of penetration for $t_1 = \kappa(5\lambda^2/D_o)$ is $(5D_m/D_o)^{\frac{1}{2}}\lambda$. It is thus concluded that the initial period during which dead-end porosity has an influence is equal to the time taken for the diffusion process to penetrate a few pore lengths into the medium (Philip, 1968).

The distances over which diffusion in soils and porous media are of concern to scientists are usually large relative to the characteristic pore length. It is clear that, under such circumstances, deviations from simple diffusion behaviour due to dead-end porosity can, at most, constitute a perturbation over a small initial period which is of no practical importance and is difficult to detect experimentally.

The present conclusion may seem surprising in view of the attention that Goodknight _et al_ (1960) and others have given to this problem, and of the fact that Goodknight _et al_ cite experimental results in support of their calculations. The following aspects of the work of these authors must be borne in mind, however.

1. Their experiments were for the mathematically similar, but physically quite different, process of flow of a compressible gas. For that process, the 'diffusivity' in dead-end porosity may, in principle, be much less than that in the active pores (if dead-end pore diameter is sufficiently small). No similar reduction of dead-end pore diffusivity holds for a molecular diffusion process.
2. In any case, the experiments of Goodknight _et al_ were performed on an artificially constructed system in which the 'dead-end pores' were a number of chambers (of volume 50 to 174 cm^3) connected to the medium through 'orifices' that were, essentially, flow resistances of length 5 to 10 cms. Such experiments cannot be considered as evidence that dead-end porosity produces significant deviations from simple diffusion behaviour in real porous media (even for the process of compressible gas flow) [Philip, 1968].

2.5 *Turner's Work*

Immediately after the work of Jackson and Klute (1967a; 1967b) and Philip (1967), came a letter by Turner (1968) in which it was claimed that dead-end porosity could be determined. It was stated that Turner (1958; 1959) presented a model and a test of the model, whereby the amount of dead-end space (defined as that which can store dissolved material but which does not allow fluid flow) and the size distribution of these pores can be determined.

A method was proposed (Turner, 1958) whereby the flow structure of a system, or the physical structure (including dead-end porosity) of a packed bed or porous solid, might be analysed in terms of a model chosen (a) to approximate hydrodynamically to the system under investigation, and (b) so that its effect on a flow of fluid containing a sinusoidally varying concentration of solute can be mathematically analysed.

To test the proposed method, physical models of known dimensions resembling the postulated ones were made. The object was then to determine the dimensions of the models based on the earlier proposals (Turner, 1958) and compare them with the known dimensions (Turner, 1959).

It was found that the calculated values of the parameters (namely depth of 'pockets' and length of channels) were in the region of the actual values. However, the calculated values were rather sensitive to small errors, and were on the whole laborious to calculate.

Despite the claims of Turner (1968), the method proposed, although theoretically sound, appears too sensitive to small errors (requiring some parameters to be measured to within 0.1 per cent, others less accurate) to be of any consequence to soils. Again criticisms similar to those levelled against Goodknight and Fatt by Philip (1968) could well be levelled against Turner, with respect to the physical dimensions of the test model.

It appears that the conclusions of Philip (1968) with respect to deviations from simple diffusion behaviour due to dead-end porosity and consequently the actual determination of dead-end porosity by diffusion, are still valid. For although the method and model of Turner appears to give information which would be difficult or impossible to obtain in any other way, it also seems that for a soil such information would also be very difficult or impossible to interpret.

3 *Choice of Methods for Measuring the Apparent Diffusion Coefficient.*

3.1 *Criteria of a Suitable Method*

In selecting a suitable method for measuring the apparent diffusion coefficient it was decided that the criteria to use were (a) Precision, and (b) Convenience. The latter with respect to this project entails: simplicity of apparatus, technique and calculations; suitability for limited quantities of soil; and flexibility with respect to the range of moisture contents for which D_m may be evaluated.

3.2 Precision

In an experiment, the standard error is an index of precision. To increase the precision of an experiment one has the following options either singularly or in combination:

(a) Increase the number of samples (or measurements)
(b) Refine the experimental technique
(c) Re-organise the experimental design.

In this particular case the former two are important. Bearing in mind that the quantity of soil is limited, option (a) is not quite advisable. This leaves option (b) as the only possible means of increasing precision. Refinement of technique has been achieved in over 90 per cent of the literature by the use of radio-tracer techniques as opposed to straightforward chemical techniques as used by Hüsted and Low (1954); Porter et al (1960) and Dutt and Low (1961) .

3.3 Convenience

Convenience is an arbitrary criterion and depends on the person or persons involved, objectives and environment of work, among other things. In this section, it is proposed to consider the experimental variants which make one experimental technique different from another, and to see whether or not they are "convenient" based on the criteria for convenience given earlier. The experimental variants include things such as:

(a) Transient state versus steady-state methods.

(b) Self diffusion versus interdiffusion.

(c) Anion diffusion as opposed to cation diffusion.

3.3.1 Transient State versus Steady-state

Two main methods have been used to measure diffusion coefficients in porous materials: (a) steady-state (Husted and Low, 1954; Dutt and Low, 1961; Olsen et al, 1965; Van Schaik et al, 1966; Van Schaik and Kemper, 1966). (b) Transient state (Bloksma, 1957; Klute and Letey, 1958; Fletcher, 1960; Schofield and Grahan-Bryce, 1960; Porter et al, 1960; Lai and Mortland, 1961; Lewis and Quirk,1962; Olsen et al, 1962; Gast, 1962; Graham-Bryce, 1963 (a); 1963 (b); Patil et al, 1963; Nakayama and Jackson, 1963; Phillips and Brown, 1964; Brown et al, 1964; Olsen et al, 1965; Van Schaik and Kemper, 1966; Van Schaik et al, 1966).

However, steady-state diffusion experiments are difficult to to set up, particularly at high moisture tensions (Porter et al, 1960). Transient diffusion systems can more readily be set up at these tensions.

On the other hand, transient state methods require an estimation of the capacity factor to obtain a value for the apparent diffusion coefficient (D_m). So far, methods have not been developed to measure a capacity factor for anions other than phosphate (Olsen and Kemper, 1968). However, by a suitable choice of anions, the term b in the capacity factor may be eliminated.

3.3.2 *Self-diffusion versus Interdiffusion*

Interdiffusion, by which one species of ion moves in one direction while another moves in opposite direction is complicated because the two kinds of ions do not have the same behaviour (Lai and Mortland, 1961). The simplest and most rigorous kind of diffusion study that can be made is that of self-diffusion in which the difference between two interdiffusing substances vanishes. Foreign ions are not introduced into the system for self-diffusion measurements; consequently, the results are more straight forward than those of interdiffusion of dissimilar ions (See Section 1.6.5 in Chapter II).

3.3.3 *Anions versus Cations as the Ionic Species*

As indicated earlier, diffusion of cations differs from that of anions mainly in that cations may participate in diffusive movement while they are adsorbed on clay minerals. This tends to add complications to the diffusion equations (Olsen and Kemper, 1968). To avoid complications it is better to work with anions which are not adsorbed or, when adsorbed the adsorption forces are so great, and the adsorption sites so far apart, that practically no exchange takes place between anion adsorption sites without the anions going through the energy level characteristics of the equilibrium solution (Olsen and Kemper, 1968). Better still are the anions Cl^- and NO_3^-, which are not adsorbed by the solid phase and hence the complications of having to determine a capacity factor are eliminated.

3.4 Most Suitable Method(s)

Therefore, the method or methods to be chosen must be, 'transient state self-diffusion of radio-active chlorine(or Nitrate) in soils.'

Fick's second law which characterises transient state diffusion can have an infinite number of solutions depending on the boundary conditions chosen. In the literature, the two most widely used methods are based on the following boundary conditions:

(a) Extended source; (b) Planar source.

The method based on the solution for Fick's second law for an extended source has been used by: Klute and Letey (1958); Schofield and Graham-Bryce (1960); Gast (1962); Graham-Bryce (1963a; 1963b; 1963c); Brown et al (1964), and Van Schaik et al (1966).

The method based on the boundary condition of a planar source has been used by Lai and Mortland (1961) and Nakayama and Jackson (1963). The former used clay pastes at or near saturation while the latter used a much wider range of soil suctions.

Hence, methods based on solution of Fick's second law for either set of boundary conditions can be considered suitable for this project.

4 Analysis of Method Chosen

4.1 Solution of Fick's Second Law for Instantaneous Sources or Plane Sources

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial X^2} \qquad (35)$$

It can be seen by differentiation that a possible solution to Equation (35) is

$$C = \frac{A}{t^{\frac{1}{2}}} \quad e^{-x^2/4D_m t} \qquad (36)$$

where A is an arbitrary constant

The equation (36) is symmetrical with respect to x = 0, tends to zero as x approaches infinity positively or negatively for t > 0, and for t = 0 it vanishes everywhere except at x = 0, where it becomes infinite. The total amount of substance, M, diffusing in a cylinder of infinite length and unit cross-section is given by

$$M = \int_{-\infty}^{+\infty} C_x dX$$

and if the concentration distribution is that of Equation (36) it can be seen that on writing

$$x^2/4D_m t = \xi^2, \quad dx = 2(D_m t)^{\frac{1}{2}} \, d\xi$$

that $$M = 2AD_m^{\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-\xi^2} \, d\xi = 2A(\pi D_m)^{\frac{1}{2}} \qquad (37)$$

Equation (37) shows that the amount of substance diffusing remains constant and equal to the amount originally deposited in the plane x = 0. Thus, on substituting for A in equation (36) the following is obtained

$$C_x = \frac{M}{2(\pi D_m t)} \quad e^{-x^2/4D_m t}$$

and this is therefore the solution which describes the spreading by diffusion of an amount of substance M deposited at time t = 0 in the plane x = o (Crank, 1970).

The above solution applies to the case where M is deposited at x = o and diffusion is allowed in both the positive and negative directions along the x-axis, that is, diffusion is symmetrical about x = o. Consider the case where a definite quantity Q of substance is deposited as a uniform and infinitely thin layer on the surface and allowed to diffuse into an infinitely thick diffusion medium, then

$$Q = \frac{M}{2} \int_{0}^{+\infty} C\,dx$$

$$\text{Hence} \qquad C_x = \frac{Q}{2(\pi D_m t)^{\frac{1}{2}}} \, e^{-x^2/4D_m t}$$

(Barrer, 1951). Where C_x is the concentration of the diffusing substance at time t, and distance x from the initial boundary and D_m is the diffusion coefficient. This is the basis of the experimental technique of Lai and Mortland (1961) [based on the procedure used by Anderson and Richards (1946) for measuring self-diffusion coefficients of lead in lead sulfide and by Jakubovic <u>et al</u> (1958) for resins] which can be used for the evaluation of D_m.

4.2 Mathematical Treatment of Lai and Mortland Technique for the Evaluation of D_m

According to the experimental conditions described in section 4.1, the total radio-activity of the clay plug was measured at the surface of the plug. A portion of the activity underneath the surface is absorbed by the clay, and this kind of absorption follows the familiar exponential law

$$I = I_o e^{-kx}$$

where I_o is the measured activity without absorption, and I, the activity observed through an absorber of thickness x with absorption coefficient k. Therefore, any radio-active tracer at a distance x below the surface will contribute an amount of measured total activity at the surface proportional to

$$C_x e^{-xk} \quad dx$$

Therefore, the total activity recorded at the surface of the clay plug will be

$$A_o = \frac{Q}{\sqrt{(\pi D_m t)}} \int_0^\infty e^{-(x^2/4D_m t \quad + \quad kx)} \, dx$$

Similarly, when the plug has been sliced down to a depth x below the original surface, the radio-activity measured at the new surface will be given by

$$A_x = \frac{Q}{\sqrt{(\pi D_m t)}} \int_0^\infty e^{-(x^2/4D_m t \quad + \quad kx)} \, dx \qquad (38)$$

Putting

$$y = \frac{x}{2\sqrt{(D_m t)}} + k[\sqrt{(D_m t)}]$$

and integrating between $y = y_o = k\sqrt{(D_m t)}$ and $y = \infty$, the following equation will be obtained:

$$A_o = Qe^{k^2D_mt}(1 - \mathrm{erf}y_o) \qquad (39)$$

where erf(y) is called the error function or probability integral. Equation (38) can also be written as

$$A_x = Qe^{k^2D_mt} (1 - \mathrm{erf}y) \qquad (40)$$

Combining Equations (39) and (40)

$$\frac{A_x}{A_o} = \frac{1 - \mathrm{erf}y}{1 - \mathrm{erf}y_o} \qquad (41)$$

If $A_x/A_o <1$, when the measurement of activity of the clay plug is made at any appreciable depth below the original boundary surface, since erf $y_o < 1$, equation (41) can be reduced approximately to

$$\mathrm{erf}\ y = 1 - A_x/A_o \qquad (42)$$

The values of A_o and A_x can be obtained from experiments to be described and the value of y can be found from erfy in any standard probability tables (Selby, 1975). A plot of y versus x should result in a straight line passing through the origin. The diffusion coefficient D_m can be evaluated from this straight line for which the equation is

$$y = \frac{x}{2\sqrt{D_mt}} + y_o$$

CHAPTER III

MATERIALS AND METHODS

1. *Materials*

1.1 *Clay Samples*

Brief descriptions of the samples used are given in Table 2. The physical properties of N2 and N4 were described by Warkentin and Maeda (1974), and those of Chateauguay clay loam by Shaykewich and Warkentin (1970). Chateauguay clay loam, the only non-allophanic sample used was primarily a reference sample.

1.2 *Radio-active Tracer*

The radio-active tracer used throughout the study was ^{36}Cl a β-emitter. It was applied to the soil in the form of NaCl in quantities small enough not to warrant consideration of counter-diffusion, or an unbalance in electrical neutrality.

Activity was measured with a Geiger Mueller Tube (Picker Nuclear) having an operating voltage of 900 volts. This was connected to a "BAIRD ATOMIC" general purpose scalar (Model 146). The average background was 40 counts per minute (cpm) and counting time was set at 2 minutes.

2. *Methods*

The diffusion method based on the boundary condition of a planar source was selected for measurement of the diffusion coefficient.

The method based on the extended source was used to test objective 5, Chapter I. The latter method provided very inconsistent data, and is briefly described in the appendix.

2.1 Planar Source

2.1.1 Soil Preparation

For each soil, the size fraction used was smaller than 0.5 mm. Samples were compacted to desired bulk densities in plastic syringes ($3\ cm^3$ Stylex), and leached with 0.1 M $CaCl_2$. Leaching was considered essential as allophanic material could have quite large anion exchange capacities below a pH value of 5.5 (Fieldes and Schofield, 1960). The samples were then equilibrated at the desired soil suction on a porous plate in a pressure plate apparatus.

2.1.2 Labelling and Radio-active Assay

A syringe containing the soil sample at the desired bulk density and moisture content was equilibrated in a constant temperature bath at 25°C. A smooth level surface was obtained by slicing along the top edge of the syringe with a razor. A tiny drop ($<10\lambda$) of ^{36}Cl labelled sodium chloride was deposited as a thin film on top of the soil in the syringe. The amount of radio-active substance added to each syringe was of a magnitude to give the most desirable counting rate. For the particular geometry conditions of the counter used in this study, the total radio-activity used in each measurement was about 0.5 to 1.0 μC. After labelling, the syringe was covered with "Parafilm" in order to prevent evaporation and placed in a constant temperature bath at 25°C.

After a time, t, (the magnitude of which varied with moisture content, the soil, and the size of the syringe), the syringe with the labelled soil was placed in a vertical position directly under the counter and activity was measured for two minutes. This was the activity at zero distance (x = 0). The syringe was removed and some of the soil extruded. The extruded length (x) was recorded and sliced off with a razor blade. The activity of the remaining plug was measured. This was repeated a number of times and the extruded length (x) and activity of the remaining plug were recorded each time.

During the preliminary work, the extruded length was measured indirectly from the scale on the syringe. However, in the actual study, x was measured directly with a centimetre scale placed alongside the syringe. The mathematics and a model calculation are presented in Section 4.2 of Chapter II and Appendix A respectively.

2.2 *Moisture Content*

The moisture content of each sample was determined by weighing, after the activity of the entire sample had been measured.

TABLE 2. Description of Source and Moisture Content of Undried Soils.

Laboratory Number	Name	Depth (cms)	Location	Co-ordinates	Moisture % Content by Weight
CC1	Chateauguay Clay loam	10 - 20	Chateauguay, Quebec	45° 8' N 74° 2.5' W	-
N_4	Murasakino	About 150	Kitakami Tonhoku	39° 18' N 141° 07' E	139.4
N_2	Memuro	15 - 40	Memuro Hokkaido	42° 54' N 143° E	46.1
75 - 4	Memuro	30 - 40	Memuro, Hokkaido	- do -	77.6
74 - 2	-	About 100	St.-Marie, Martinique	14° 46' N 61° 01' W	48.6
74 - 4	-	50	Plateau Borcher, Martinique	14° 46' N 61° 07' W	232.6

CHAPTER IV

RESULTS AND DISCUSSION

1 *Effect of Temperature on the Apparent Diffusion Coefficient*

Gardner (1965) mentioned that the diffusion coefficient for anions may vary with temperature, but there was no data to support the statement. Comparison of diffusion data can only be meaningful if the data are reduced to the same temperature. In the literature, a large percentage of the diffusion measurements were done at 25°C (Dutt and Low, 1961; Olsen et al, 1965; etc.). However, some measurements were taken for systems equilibrated at different temperatures (Philip and Brown, 1964; Nakayama and Jackson, 1963; Graham-Bryce, 1963a).

Hence there is a need to determine the effect of temperature on anion diffusion in soil in order to:

(a) Evaluate the effect of temperature on the apparent diffusion coefficient and its components.

(b) To obtain a coefficient which can be used for adjusting diffusion values to a common temperature base.

1.1 *Justification of Method*

To investigate the effect of any single factor on a given process (diffusion) or a particular property of that process, other factors known or suspected to affect that process must be held constant. In this case therefore, moisture content and bulk density must be kept constant, without making the experiment too complicated. It was found that equilibrating all samples to a constant soil suction (0.2 bar) was adequate for keeping moisture content relatively constant. Using an initially moisture-saturated soil paste, pouring it into syringes of constant height and allowing them to equilibrate at a constant soil suction also provided a reasonably constant bulk density (Table B.1 in Appendix B).

A relatively high soil water content (i.e. a suction of 0.2 bar), was preferred so that the boundary conditions chosen would be valid without modification of the method (Nakayama and Jackson, 1963). Also it was felt that the volume of soil containing moisture in the vapour phase should be kept to a minimum to avoid undue loss of moisture during equilibration at higher temperatures.

At equilibrium [samples were equilibrated for two days (Lai and Mortland, 1961)] the temperature reading of the thermostat was not necessarily the temperature in the constant temperature bath. Hence, temperature was measured on an extra sample by plunging the bulb of a Hg thermometer into the soil and recording the highest temperature. As a pre-requisite the thermometer reading before use should have been no lower than two degrees below the thermostat reading. This would eliminate any significant heat transfer from the sample to the thermometer for increasing the temperature of the glass bulb and stem.

Diffusion was measured at four temperatures from 25°C to 38.5°C and the results were extrapolated to 10 degrees beyond either extreme (Fig. 1). The extrapolations were considered reasonable since:

(a) The relationship between temperature and D_m appeared linear.

(b) The temperature range over which extrapolation was carried out, did not include temperatures at which (i) the behaviour of water deviates from the normal (i.e. 4°C and lower) or (ii) the clay minerals are affected.

Interpolations of diffusion coefficients were made and presented in Table 3 along with data from the American Institute of Physics Handbook (Gray, 1972).

TABLE 3. The variation of D_m, D_o, D_m/D_o, μ, and $\frac{D_m}{D_o}\mu$ with temperature

Temp. °C	$D_m \times (10^{-5})$ $cm^2\ sec^{-1}$	$D_o \times (10^{-5})$ †$cm^2\ sec^{-1}$	D_m/D_o	†Viscosity of Water (μ), cp ‡	$\frac{D_m}{D_o} \times \mu$
20	0.87	1.80	0.48	1.000	0.48
25	1.15	2.03	0.57	0.893	0.51
30	1.42	2.28	0.62	0.801	0.50
35	1.69	2.54	0.67	0.723	0.49
40	1.97	2.80	0.70	0.658	0.46
45	2.24	3.09	0.72	0.610	0.44

† Interpolated from data given in the American Institute of Physics Handbook (Gray, 1972).

‡ cp = centipoise: $g\ cm^{-1}\ sec^{-1}\ (10^2)$

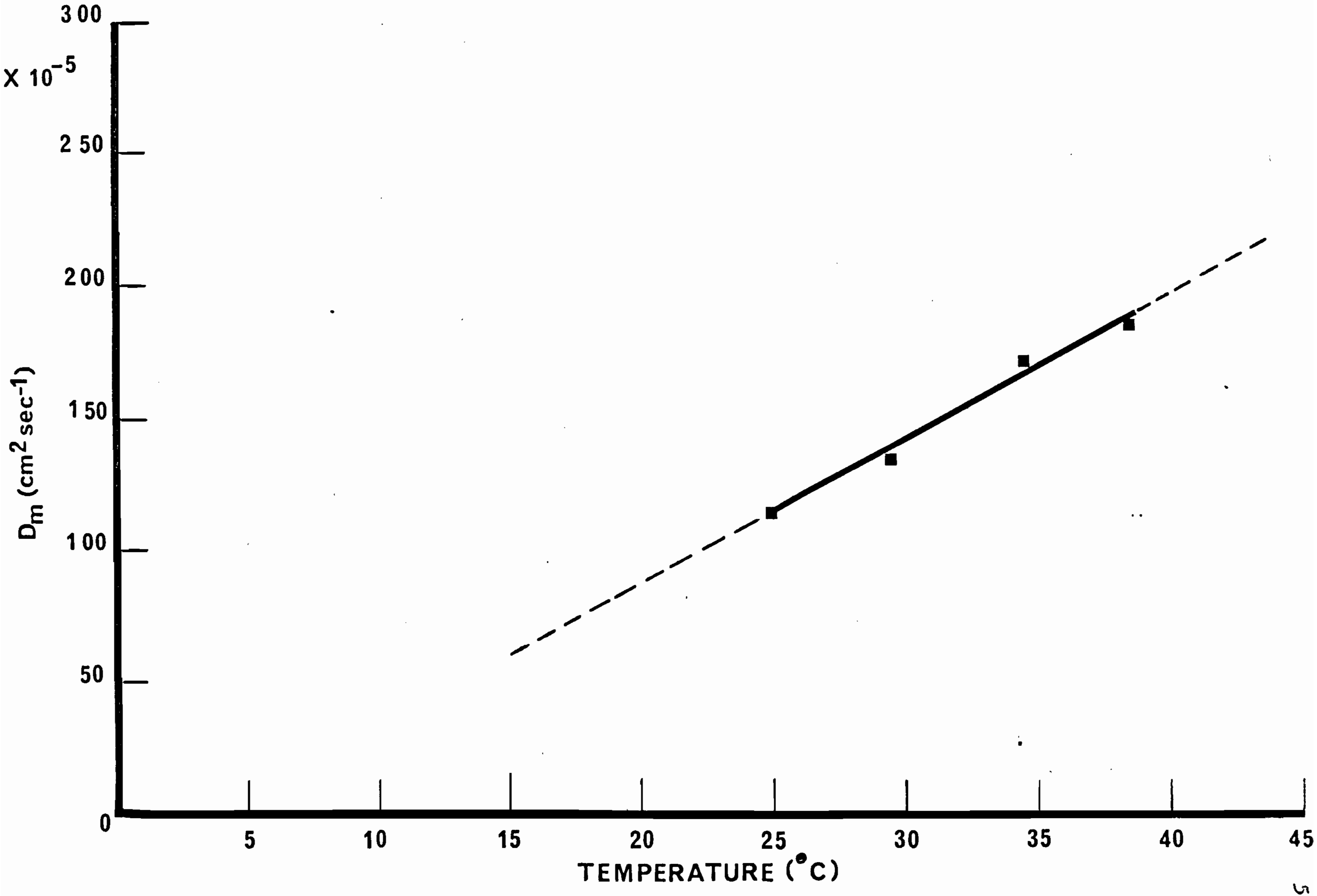


FIGURE 1. Apparent diffusion coefficient (Dm) versus temperature for Chateauguay Clay loam at 0.2 bar suction.

1.2 *Temperature and its effect on the Components of the Apparent Diffusion Coefficient*

The apparent diffusion coefficient (D_m) is linearly related to temperature (Fig. 1). However, the ratio D_m/D_o or $\alpha\gamma(L/Le)^2$ has a curvilinear relation to temperature (Fig. 2). To further understand the curvilinear relationship, an analysis of temperature effects on the components of D_m/D_o is required.

The diffusion coefficient D_m could be divided into two components

(a) one resulting from diffusion in the free water (intermicellar solution) i.e. D_o;

(b) the other resulting from diffusion in the bound water (Micellar solution) i.e. $\alpha\gamma(L/Le)^2$ or D_m/D_o.

The component in D_m/D_o most likely to be affected by temperature is the viscosity of the bound water represented by the viscosity factor α.

1.2.1 *Viscosity Factor* α

The viscosity of water decreases with increasing temperature (Table 3), and the diffusivity is inversely related to viscosity (Kemper et al, 1964). Equally true is the statement that the viscosity factor is inversely related to viscosity.

Assume therefore, that

$$\alpha = \frac{k}{\mu}$$

α = viscosity factor;

k = constant

μ = viscosity of the micellar solution at a given temperature

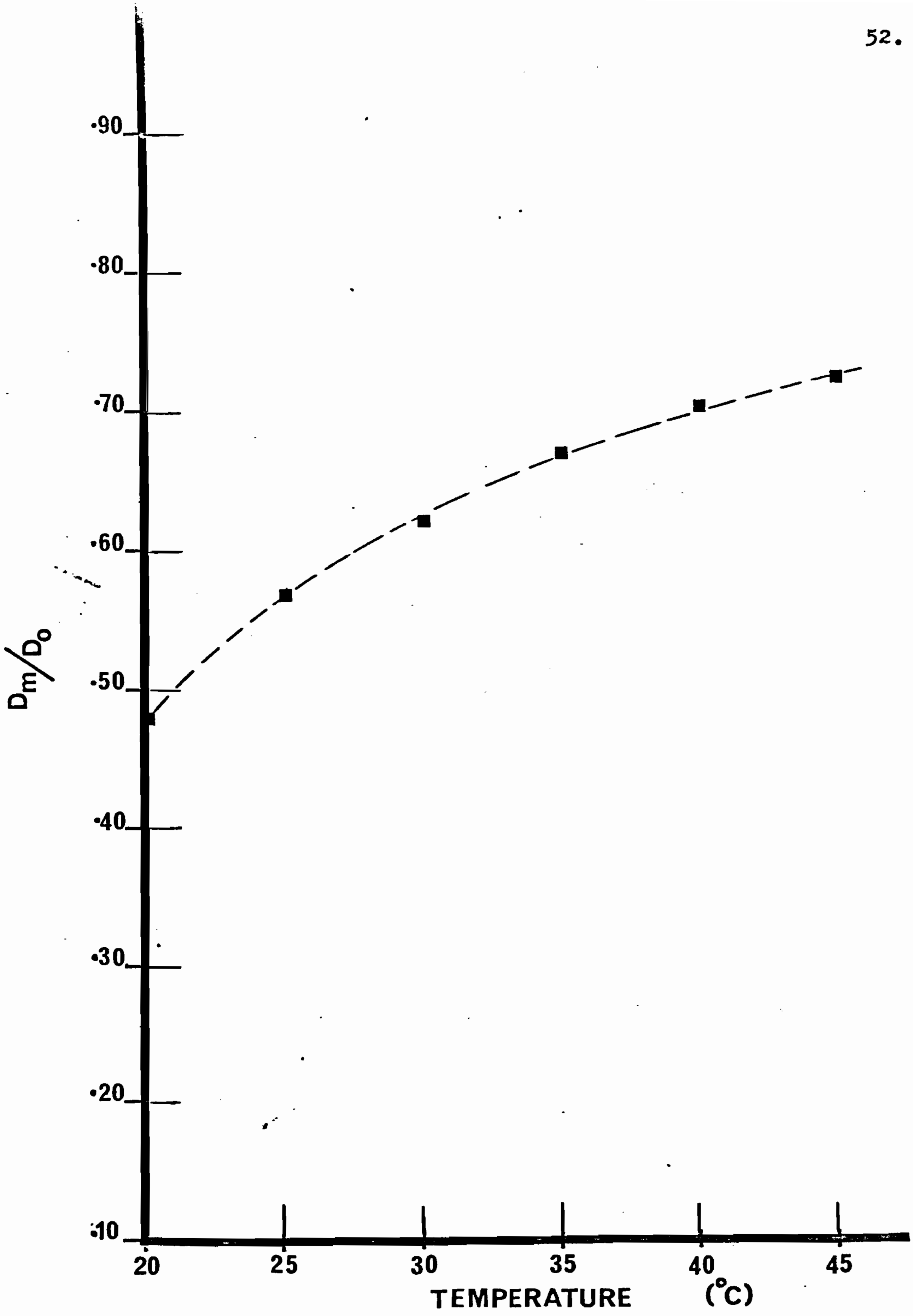


FIGURE 2. The variation of geometric and interaction factors (D_m/D_o) with temperature.

Hence, $$\frac{D_m}{D_o} = \gamma\frac{k}{\mu}(L/Le)^2$$

$$k_1\left(\frac{D_m}{D_o}\mu\right) = \gamma(L/Le)^2 \qquad k_1 = 1/k$$

Assuming that α is the only component of D_m/D_o which is a function of temperature, then $(D_m/D_o\mu)$ should be constant. Table 3 shows that $\frac{D_m}{D_o}\mu$ is not constant but decreases with increasing temperature. It is noteworthy however, that this correction for viscosity after separating D_o from D_m did account for a large part of the variability that existed in D_m/D_o (Table 3, Columns 4 and 6). The apparent variation of $[\frac{D_m\mu}{D_o}]$ could be explained as follows:

(a) a result of natural variation within the experiment. However, since the values did not fluctuate randomly about a mean but showed a well-defined trend of decreasing with increasing temperature, other sources of variation should be considered.

(b) γ or $(L/Le)^2$ varies either independently or together with temperature in a manner as shown by the variation of $\frac{D_m}{D_o}\mu$ with temperature.

(c) The assumption that k is constant may not have been valid. The actual values used for μ were for pure water. It is quite likely that the bound water, because of its quasi-crystalline structure, has a different temperature viscosity relationship than that of pure water.

1.3 A Comparison with the Approach in the Literature

The viscosity of water is closely related to its diffusivity (i.e. the diffusivity of the water molecules). Using Eyring's equations for diffusivity and viscosity, the following relation was derived (Kemper et al, 1964)

$$D = \frac{k''}{\mu}$$

Where D = diffusivity of water molecule
μ = viscosity of water
k'' = a constant containing, Planck's Constant Boltzmann's constant, lattice factors and the absolute temperature.

It was stated that the diffusion coefficients of ions should also show an inverse relationship to the viscosity of the liquid in which they were diffusing.

$$D_m/D_o = \alpha\gamma(L/Le)^2 \qquad (42)$$

In equation (42), after separating the effect of viscosity on D_o from the L.H.S, α still persists on the R.H.S.. The viscosity factor α relates to the increased viscosity of the bound soil solution. Although there is no mathematical relationship, it is logically sound to say that as an ion approaches the clay mineral surface, the viscosity increases (Low, 1960), and the apparent diffusion coefficient decreases along with, or because of, a decrease in α. Low (1958) presented activation energy data which indicated that the reduction in the apparent diffusion coefficient was greater than that accounted for by increased viscosity alone.

Therefore, while a large proportion of the variation in D_m/D_o with temperature could be accounted for by the changes in viscosity of water with temperature, viscosity alone could not account for all the variation. The remainder must be due to changes in bound water.

1.4 *A Temperature Coefficient of Diffusion*

In the apparent diffusion coefficient, the variation of D_o with temperature, which is known (Gray, 1972), is independent of soil properties. The variation of the geometric and interaction factors ($\alpha\gamma(L/Le)^2$) with temperature has been determined for Chateauguay clay loam (Fig. 2). The equation for the line in Fig. 2 could be used in the formulation of a temperature coefficient of diffusion. However, before this is attempted, the relationship between geometric and interaction factors and temperature should be determined for different soil types and soil suctions. Only then could a temperature coefficient of diffusion be formulated.

1.5 *Effect of Vapour Phase on Diffusion at Different Temperatures*

A common misconception with respect to diffusion at different temperatures is that the vapour phase would have some effect on the data. Nakayama and Jackson (1963) found that diffusion of DOH was not essentially confined to the liquid phase and that the vapour phase provided a pathway for diffusion. They speculated that vapour diffusion increased with decreasing water content in the same proportion as liquid diffusion decreased. With respect to ionic diffusion the pathway is essentially the liquid phase for:

(a) during the process of evaporation, the liquid surface acts as a semi-permeable membrane (Hillel, 1971) allowing only water molecules to escape. Hence the labelled chloride ions are confined to the liquid film.

(b) Mass transfer of the vapour is non-existent in the absence of potential gradients (e.g. temperature gradients). Hence a so-called "sea-breeze" effect is eliminated.

2 *Effect of Bulk Density on the Apparent Diffusion Coefficient*

Increasing the bulk density (D_b) of a soil sample reduces the pore space and alters the pore geometry. It is likely that the diffusion path-length is altered by a change in bulk density, hence the apparent diffusion coefficient changes.

In the literature, bulk density is implied to affect the diffusion coefficient indirectly as a result of its relation with volumetric moisture content. Olsen et al (1965), in assessing the effect of bulk density on the apparent diffusion coefficient, simply stated that because the volumetric moisture content is related to bulk density then it is essential to compare methods of measuring the diffusion coefficient at the same bulk density. In fact values of the diffusion coefficient taken from the literature have not been readily comparable since measurements were not done at the same bulk density. Data presented by Gardner (1963) [Table 1] to illustrate the relationship between moisture content and the diffusion coefficient is of limited use as no mention was made of the bulk density values at which diffusion measurements were made.

Graham-Bryce (1963a) investigated the effect of bulk density on the apparent diffusion coefficient in heteroionic soils. The results presented could be questioned on the grounds that volumetric moisture content was not given in his discussion.

Therefore, an investigation of the effect of bulk density on the apparent diffusion coefficient was undertaken for the following objectives:

(a) To determine whether bulk density has a direct effect on D_m or an indirect effect stemming from its relation to volumetric moisture content.

(b) To determine whether or not a simple relationship exists between D_b and D_m. If so, could such a relationship be used for converting values of D_m to a common D_b base?

(c) To confirm that the method used for diffusion is in fact measuring diffusion and not some other transfer phenomena.

Since bulk density is related to volumetric moisture content, it was decided to measure the diffusion coefficient at different moisture contents for a known constant bulk density. Repeating this for several values of bulk density, one is then able to compare the apparent diffusion coefficient at a convenient but constant volumetric moisture content (Figs. 3, 4 and 5). The range of bulk density values selected for Chateauguay clay loam was determined by the nature of the apparatus (plastic syringes). In the case of N4 soil, a range of bulk density from 0.5 to 0.8 g cm^{-3} was possible, but because of shrinkage, it was narrowed from 0.6 to 0.8 g cm^{-3}.

The high volumetric moisture range was necessary for reasons already mentioned and extrapolations of the curves in Figs. 3 and 4 were justified on the grounds that the apparent diffusion coefficient (D_m) or effective diffusivity (D_p) is a linear function of θ (Porter et al, 1960; Olsen et al, 1968).

The results are presented in Figs. 3, 4 and 5. Presenting the data in the form of figures of D_m/D_o vs θ or D_p/D_o vs θ was preferred to that of simply D_m or D_p vs θ. A plot of D_m/D_o vs θ had been used previously by Porter et al (1960) and D_p/D_o vs θ was derived from the statement (Olsen and Kemper, 1968) that D_p is a linear function of θ for ions not adsorbed on the clay. Since D_o is constant for a constant temperature, then D_p/D_o vs θ should also be linear.

The advantages of using these plots were:

(a) $D_m = \beta D_o$ where $\beta = \alpha\gamma(L/Le)^2$

In this way, the variation of β with θ or D_b can be had directly.

(b) The slope of a plot of D_p/D_o vs θ gives the average β or $\alpha\gamma(L/Le)^2$ over that moisture range.

(c) Since D_o is constant, the trends shown in Figs. 3 and 4 reflect similar trends as plots of D_m or D_p vs θ.

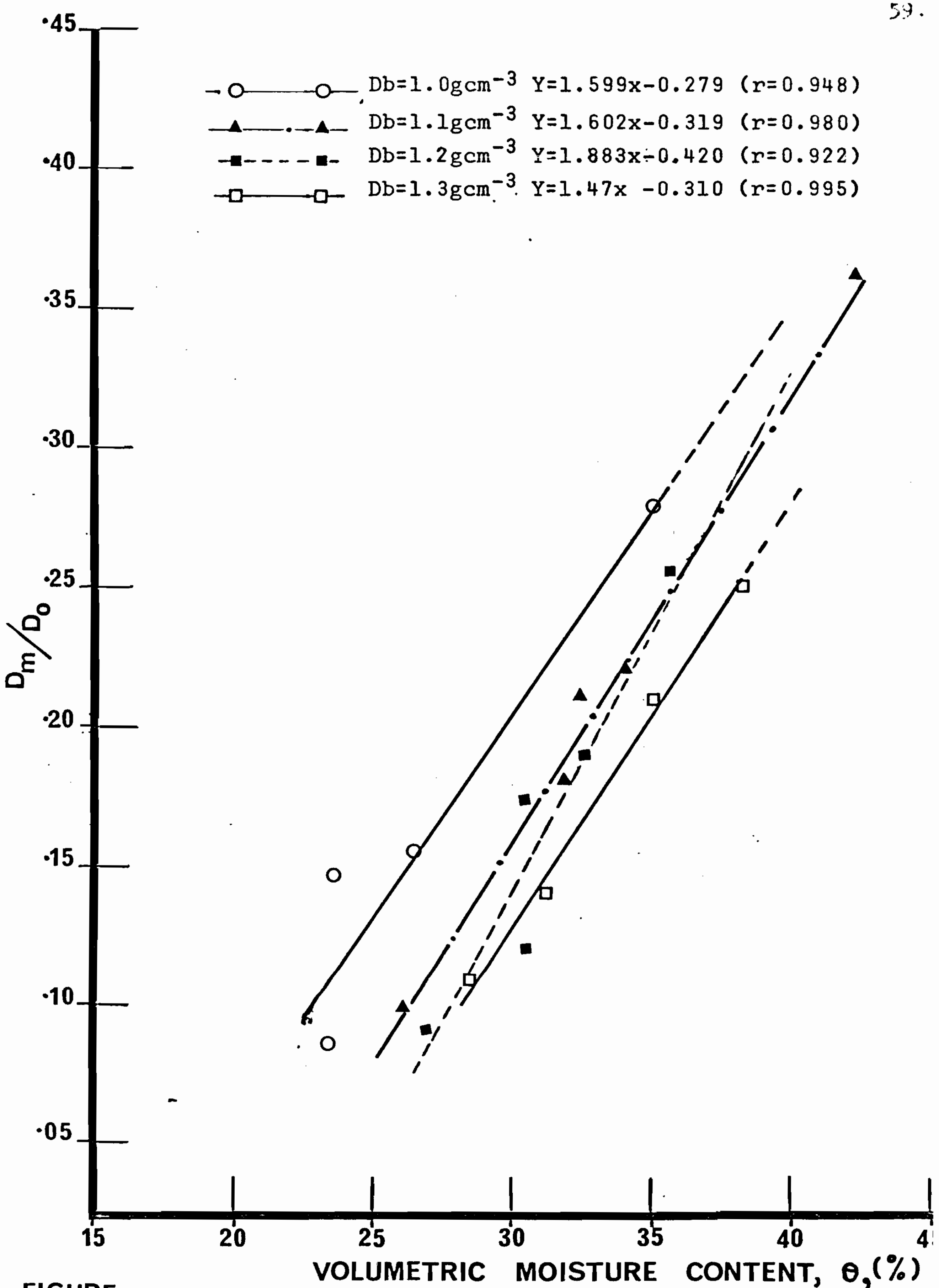


FIGURE 3. Geometric and interaction factors (D_m/D_o) versus volumetric moisture content (θ), for Chateauguay clay loam at different bulk densities (Db).

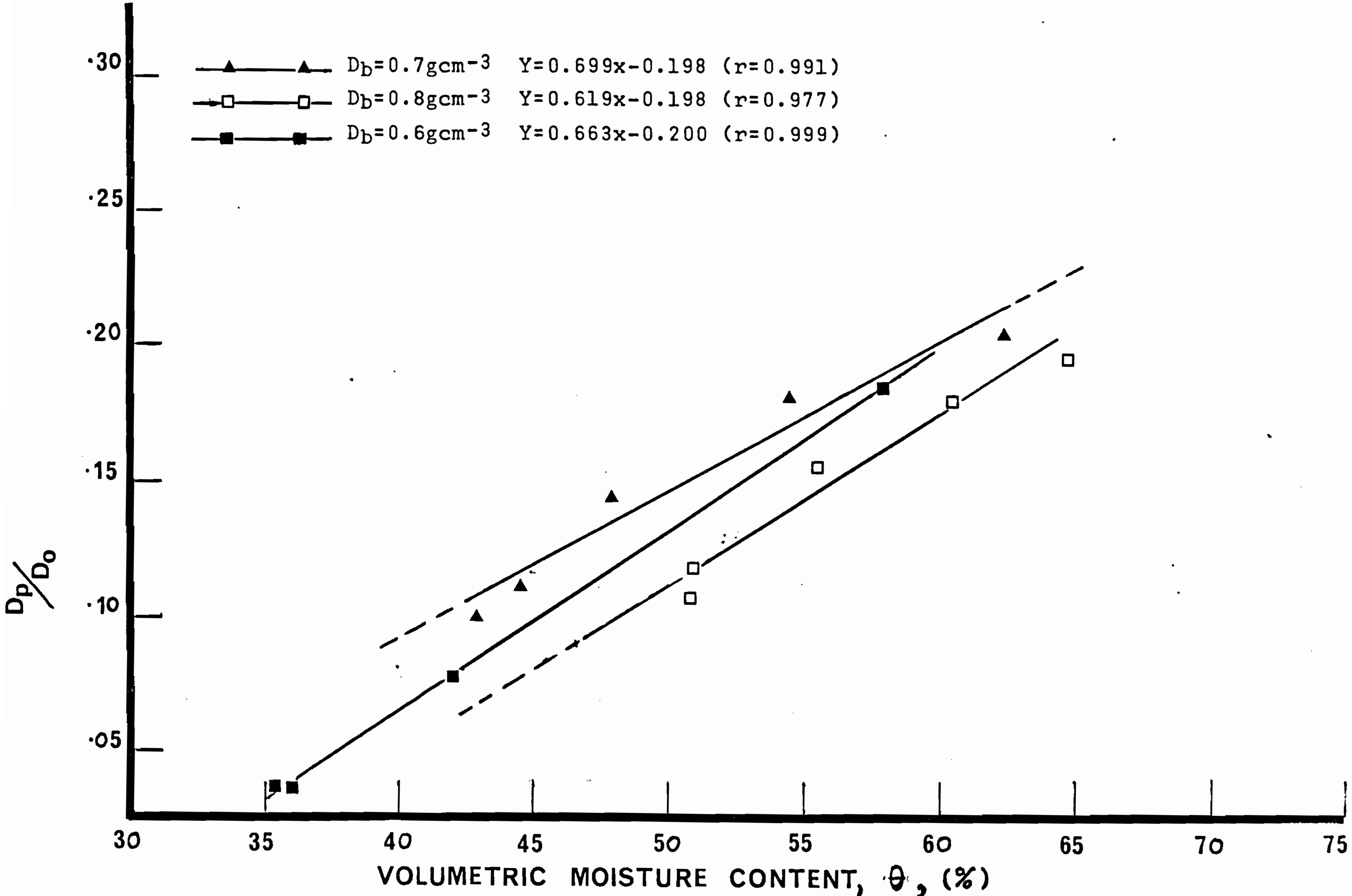


FIGURE 4. Geometric and interaction factors x volumetric moisture content, (D_p/D_o), versus the volumetric moisture content (θ), for N4 Soil at different bulk densities (D_b).

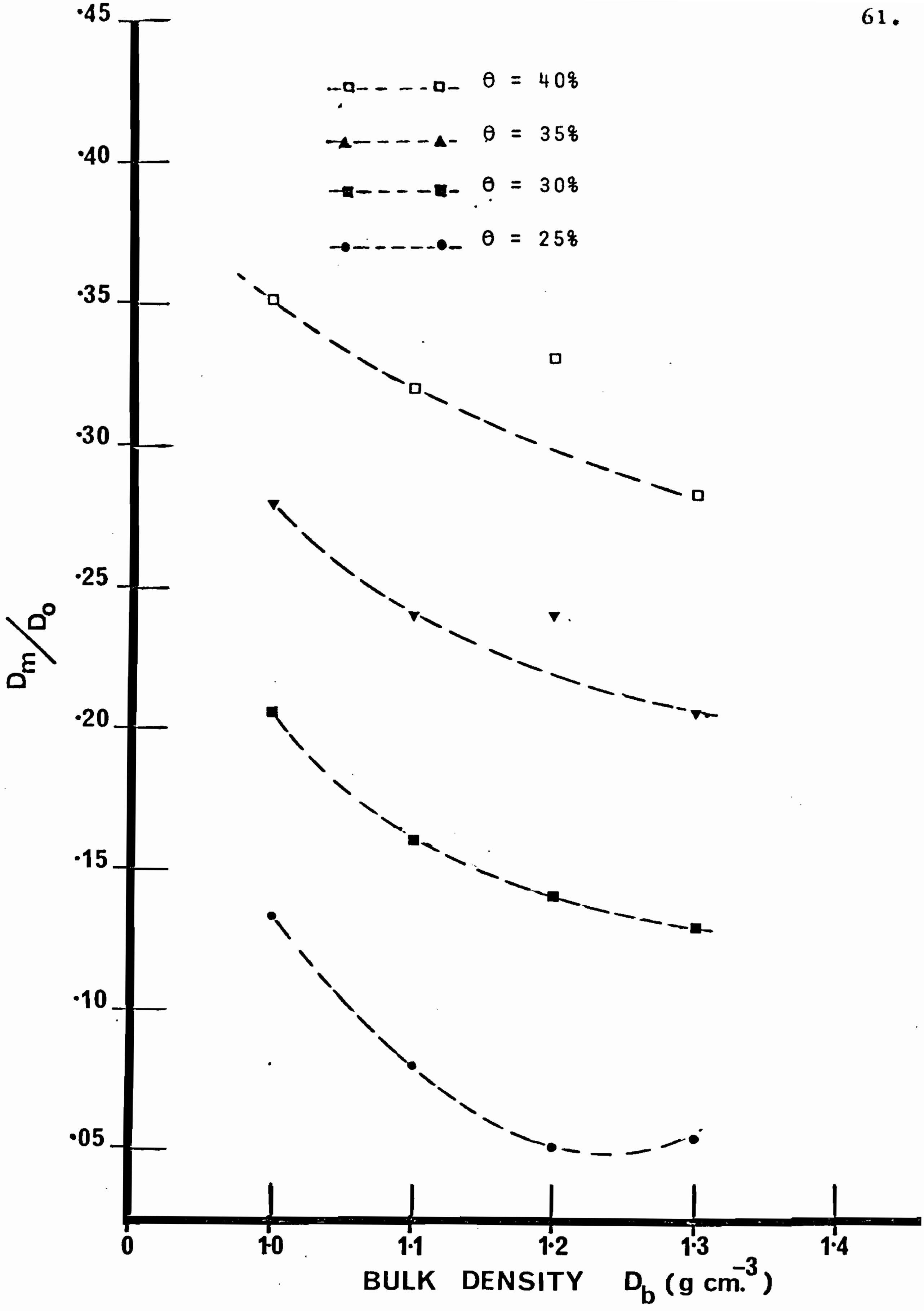


FIGURE 5. Geometric and interaction factors, (D_m/D_o) versus bulk density at different volumetric moisture contents (θ), for Chateauguay clay loam.

Each point in Figs. 3 and 4 represents the mean of three or four values of D_p/D_o or D_m/D_o. The coefficient of variation (Tables B2-B7, Appendix B) ranged from 5.5 per cent to 30 per cent. In a large number of cases, the high variability could be partly accounted for by a high variability in volumetric moisture content.

2.1 *Chateauguay Clay Loam*

Throughout the study, this soil was used as a standard or reference. Fig. 3 shows that it is possible to separate bulk density and volumetric moisture content and investigate the effect of each on D_m/D_o. It confirms that D_m/D_o is a linear function of volumetric moisture content, a fact established by Porter et al (1960). This along with Fig. A1 confirms that the method is measuring diffusion. Fig. 3 shows that as bulk density increases, D_m/D_o decreased. In the lower range of bulk density (1.0 to 1.2 g cm^{-3}) the change of D_m/D_o with bulk density is greater than in the higher range (1.2 to 1.3 g cm^{-3}). This trend became greater as the moisture content decreased.

One possible explanation of the decrease in D_m/D_o with bulk density is that the diffusion path length is increased with increasing bulk density.

Consider the curve for the volumetric moisture content of 25 per cent. At a bulk density of 1.0 g cm^{-3} the D_m/D_o value is lower than that for 30 per cent moisture content. The tortuosity factor $(L/Le)^2$ decreases with decreasing moisture content as the path length Le increases.

Increasing the bulk density from 1.0 g cm^{-3} to 1.2 g cm^{-3} would increase the volumetric moisture content from 25 to 30 per cent provided there was no change in the volume of soil water. The value of D_m/D_o at a bulk density of 1.0 g cm^{-3} and 25 per cent moisture content was not significantly different from that at a bulk density of 1.2 g cm^{-3} and 30 per cent moisture content. Although there was a change in bulk density, there was no significant change in the ratio of free water to bound water in the soil sample. As a result D_m/D_o was constant.

Holding the volumetric moisture content constant (25 per cent), while increasing the bulk density from 1.0 to 1.2 g cm^{-3} would mean a decrease in the volume of water in the soil. This favoured a decrease in the ratio of free water to bound water. The diffusion path length increased as more ions diffused along the surface film rather than in the bulk solution. The tortuosity factor $(L/Le)^2$ decreased and likewise the apparent diffusion coefficient (D_m).

Increasing the bulk density from 1.2 to 1.3 g cm^{-3} for a volumetric moisture content of 25 per cent caused no significant change in D_m/D_o. Although there had been a reduction in the volume of water, the water was essentially present in the bound form. Ions diffused along the clay surfaces, and provided there was no significant change in surface area due to re-arrangement of soil particles, then the diffusion path length should have been constant. Hence D_m/D_o was constant.

As volumetric moisture content was increased above 25 per cent, e.g. at 40 per cent, the range of bulk density was such that a significantly large portion of the water existed as free water throughout. Changing the bulk density from 1.0 to 1.2 g cm^{-3} produced a smaller change in D_m/D_o than at 25 per cent moisture content, as diffusion was largely in the free water. The change between 1.2 g cm^{-3} and 1.3 g cm^{-3} suggested that diffusion was not confined to bound water as in the case of 25 per cent moisture content. The diffusion path length was smaller and increased with bulk density on account of the diminishing free water.

Therefore, bulk density influenced the apparent diffusion coefficient through:

(a) a change in free water content in the high range of volumetric moisture content;

(b) a change in the wetted surface area in the lower range of volumetric moisture content.

The assumption used throughout, has been that the viscosity factor (α) and the negative adsorption factor (γ) do not change with bulk density. In fact they do. The negative adsorption factor (γ), which is a measure of heterogeneity of pore size, could well be affected by bulk density more in the lower range of bulk density than in the higher. At low values of bulk density, a change in bulk density is brought about by closing interparticle spaces and this could influence heterogeneity to a greater extent than particle re-arrangement at higher bulk density values. As bulk density increases at a constant moisture content, the ratio of free to bound water decreases and α is likely to change especially at low values of moisture content. The extent of such a change is not known. Therefore, it is difficult to say which component of D_m/D_o or $\alpha\gamma(L/Le)^2$ is affected by bulk density. It may well be that the components of D_m/D_o are inseparable (Jackson et al, 1963).

2.2 N4 Soil

The results are presented in Fig. 4. The curve of D_p/D_o vs θ for a bulk density of 0.6 g cm^{-3} fell between curves for bulk density values of 0.7 and 0.8 g cm^{-3}. It was thought that shrinkage at the bulk density of 0.6 g cm^{-3} could have reduced the final average bulk density to a value intermediate between 0.7 g cm^{-3} and 0.8 g cm^{-3}. This was investigated on equivalent samples and it was found that shrinkage at 3.0 bars suction (highest suction for that soil) increased the bulk density from 0.6 g cm^{-3} to 0.63 g cm^{-3}. The relative positions of the three lines cannot therefore be explained with the information available.

2.3 Bulk Density Coefficient of Diffusion

D_o is independent of soil properties and a variation of the apparent diffusion coefficient with bulk density is essentially a result of a variation of the geometric and interaction factors with bulk density. Fig. 4 illustrates the latter relationship. Similarly, before any formulation of a bulk density coefficient of diffusion is undertaken, the relationship between geometric and interaction factors and bulk density should be obtained for different soil types. The formulation is made complex since volumetric moisture content does influence the shape of the curve. In the higher range of volumetric moisture contents, free water appeared more important than bound water, whereas the reverse held true for the lower range of volumetric moisture contents.

3. *Effect of Drying on the Apparent Diffusion Coefficient*

Physical properties of allophanes are often studied on samples which have been dried. It is known that drying changes the structure of the soil, some drying techniques to a greater extent than others. The diffusion coefficient is evaluated here as a measurement of the relative effects of drying.

3.1 *Effect of Drying on the Apparent Diffusion Coefficient at a Variable Bulk Density.*

Consider the soil sample 74-4 (Table 4). In the undried state, at a suction of 0.2 bars, the volumetric moisture content was 78.2 per cent and the bulk density 0.21 g cm^{-3}. After drying the sample at 110°C, re-wetting and equilibrating at 0.2 bars, the volumetric moisture content was 35.6 per cent and the bulk density 0.95 g cm^{-3}. Drying caused a substantial change in bulk density and volumetric moisture content. (At 85 per cent saturation, the volumetric moisture content of the undried sample was 78.2 per cent, that of the oven-dried sample 55 per cent).

TABLE 4. Volumetric Moisture Content (θ), Bulk Density (D_b), Apparent Diffusion Coefficient (D_m), Geometric and Interaction Factors (D_m/D_o), Per Cent Saturation, Ratio of Diffusion Path Lengths (Le_1/Le_2), and Ratio of Bulk Densities (D_{b1}/D_{b2}) for the Selected Allophane Samples.

Soil	Treatment	Volumetric Moisture Content θ	Bulk (D_b) Density g cm^{-3}	D_m (x 10^{-5}) cm^2 sec^{-1}	D_m/D_o = $\alpha\gamma(L/Le)^2$	% saturation	*$\{\frac{Le_1}{Le_2}\}^2$	*$\frac{Le_1}{Le_2}$	D_{b1}/D_{b2}
N4	Undried	0.760	0.50	1.55	0.76	94	0.74	0.86	0.65
	Freeze dry	0.736	0.60	1.72	0.85	95	0.67	0.82	0.78
	Air dry	0.710	0.69	1.15	0.57	96	1.00	1.00	0.90
	Oven dry	0.710	0.77	1.15	0.57	96	-	-	-
N2	Undried	0.616	0.69	1.13	0.56	83	0.81	0.90	0.75
	Oven dry	0.531	0.92	0.92	0.45	81	-	-	-
74 - 2	Undried	0.620	0.81	1.42	0.70	89	0.91	0.95	0.77
	Oven dry	0.552	1.05	1.29	0.64	91	-	-	0.77
74-4	Undried	0.782	0.21	1.72	0.85	85	0.07	0.26	0.22
	Oven dry	0.356	0.95	0.12	0.06	56	-		

* Subscript 1 refers to undried, freeze dried or air dried;
Subscript 2 refers to oven dried only.

There was a 30 per cent reduction in void volume due to drying. Despite the usefulness of this information, it tells nothing of the change in diffusion path length which is apt to accompany any substantial change in void volume. In this respect, it was felt that a measure of the apparent diffusion coefficient in the sample before and after drying could contribute some information with respect to changes in pore geometry.

Drying (irrespective of the type of drying), produced a decrease in volumetric moisture content upon re-wetting and equilibrating at 0.2 bar. This suggested that drying has altered the soil structure, produced a loss in pore volume, increased bulk density, and decreased the apparent diffusion coefficient D_m. Assuming that for any one soil, the interaction factors, α and γ, are constant, then a change in the apparent diffusion coefficient would be a direct result of a change in the diffusion path length, Le. Columns 8 and 9 (Table 4) show that drying produced an increased path length.

As mentioned in Section 2.1 Chapter IV, a change in bulk density would result in a change in the diffusion path length. Using the bulk density of the oven-dried sample as a base, then the ratio of the bulk density of the undried sample to that of the oven-dried sample should correlate with the corresponding ratio of diffusion path lengths of any one soil, provided the same degree of saturation was maintained (See Column 7, Table 4). Fig. 6 shows that there is good correlation ($r = 0.993$) between the ratio of bulk densities and that of diffusion path lengths. This illustrates that:

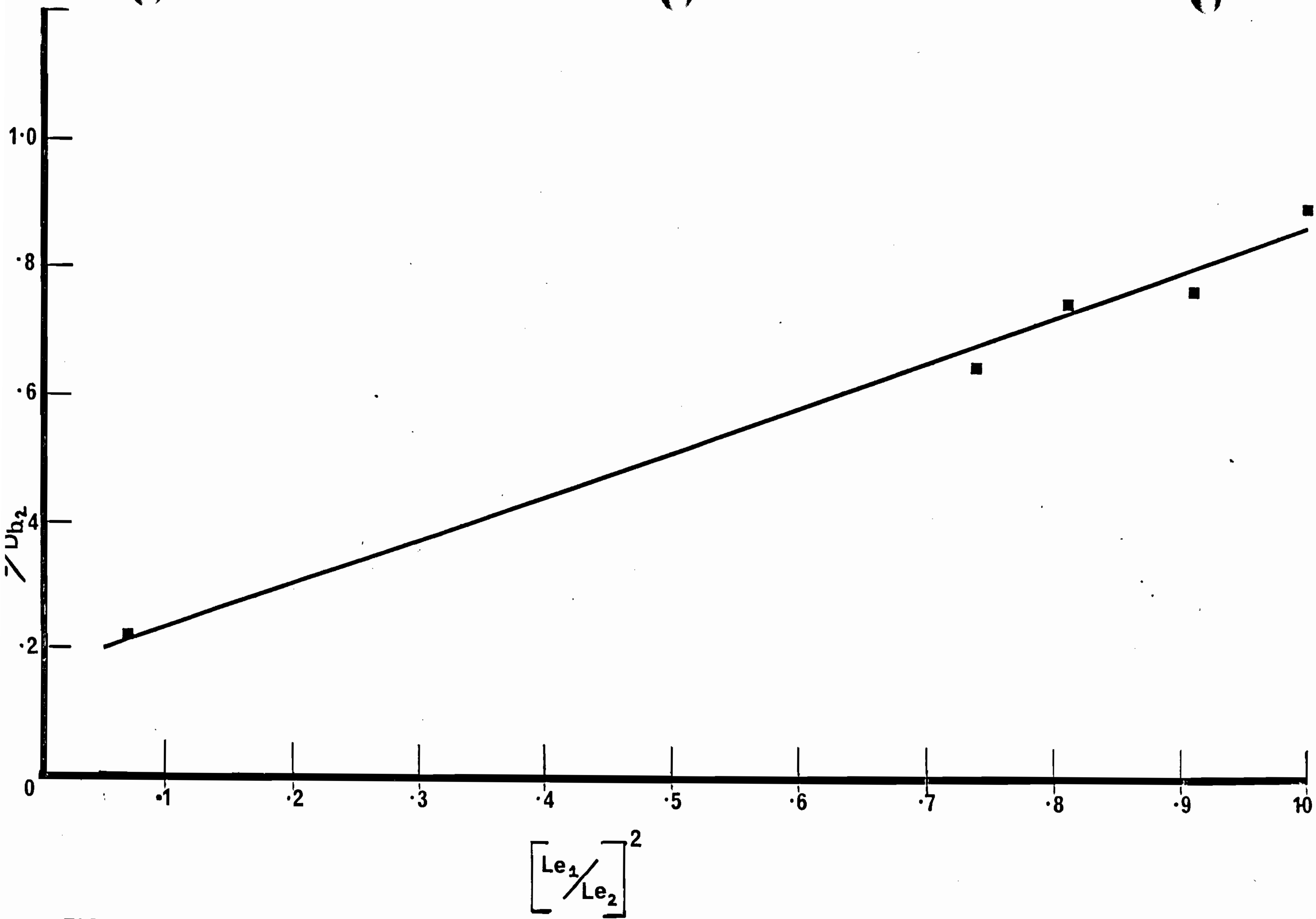


FIGURE 6. Ratio of bulk densities [Db1/Db2] versus ratio of diffusion path lengths [Le1/Le2]^2 of undried and oven-dried samples at 0.2 bar suction.

(a) As the bulk density increases, the diffusion path length increases. This supports the relationship between bulk density and D_m/D_o for Chateauguay (Fig. 5).

(b) The assumption that the interaction factors, α and γ, are constant for any given soil sample is valid within limits. Although it is possible that values of the negative adsorption factor (γ) may not be equal for a sample given different treatment, Fig. 6 suggests that the differences are small. The same could be said for viscosity factor (α).

(c) A comparison of bulk densities could be used as an index of relative diffusion path lengths for a given sample which has undergone a structural change. The need for using the apparent diffusion coefficient could be questioned on the grounds that for the four soil samples used, changes in the pore geometry could have been adequately described in terms of change in volumetric moisture content (at a constant % saturation) and bulk density.

Sample N4 was dried in three ways, and although Table 4 indicates a decreased volumetric moisture content and increased bulk density for samples which were dried, the values of D_m did not decrease as would have been expected. The D_m values indicate that air drying and oven drying produced the same structural change in N4 soil. Freeze drying altered pore structure in such a way that D_m increased above that of the undried sample. This change in pore structure may not have been real because the N4 samples used for freeze drying might not have been from the bulk sample used for other treatments.

3.2 Effect of Types of Drying on the Apparent Diffusion Coefficient at a Constant bulk density.

To look critically at the changes in the apparent diffusion coefficient or its components due to different types of drying, the bulk density of all samples must be constant. A value of 0.7 g cm^{-3} was selected. Diffusion was measured at different moisture contents and D_p/D_o or $\alpha\gamma\theta(L/Le)^2$ was plotted against volumetric moisture content.

The results are presented in Figs. 7 and 8. Each point represents the mean of four values; the original data is presented in Appendix B. The figures show that:

(a) drying altered the slope of each line. Freeze drying reduced the slope to a smaller extent than oven drying for 75-4 soil. For N4 soil, air drying and oven drying, when compared with freeze drying produced an equal reduction in slope.

(b) for any common moisture content, the oven-dried N4 samples had a higher average diffusion coefficient than the air-dried samples. Similarly for 75-4 soil, at 45 per cent moisture content by volume, the freeze-dried

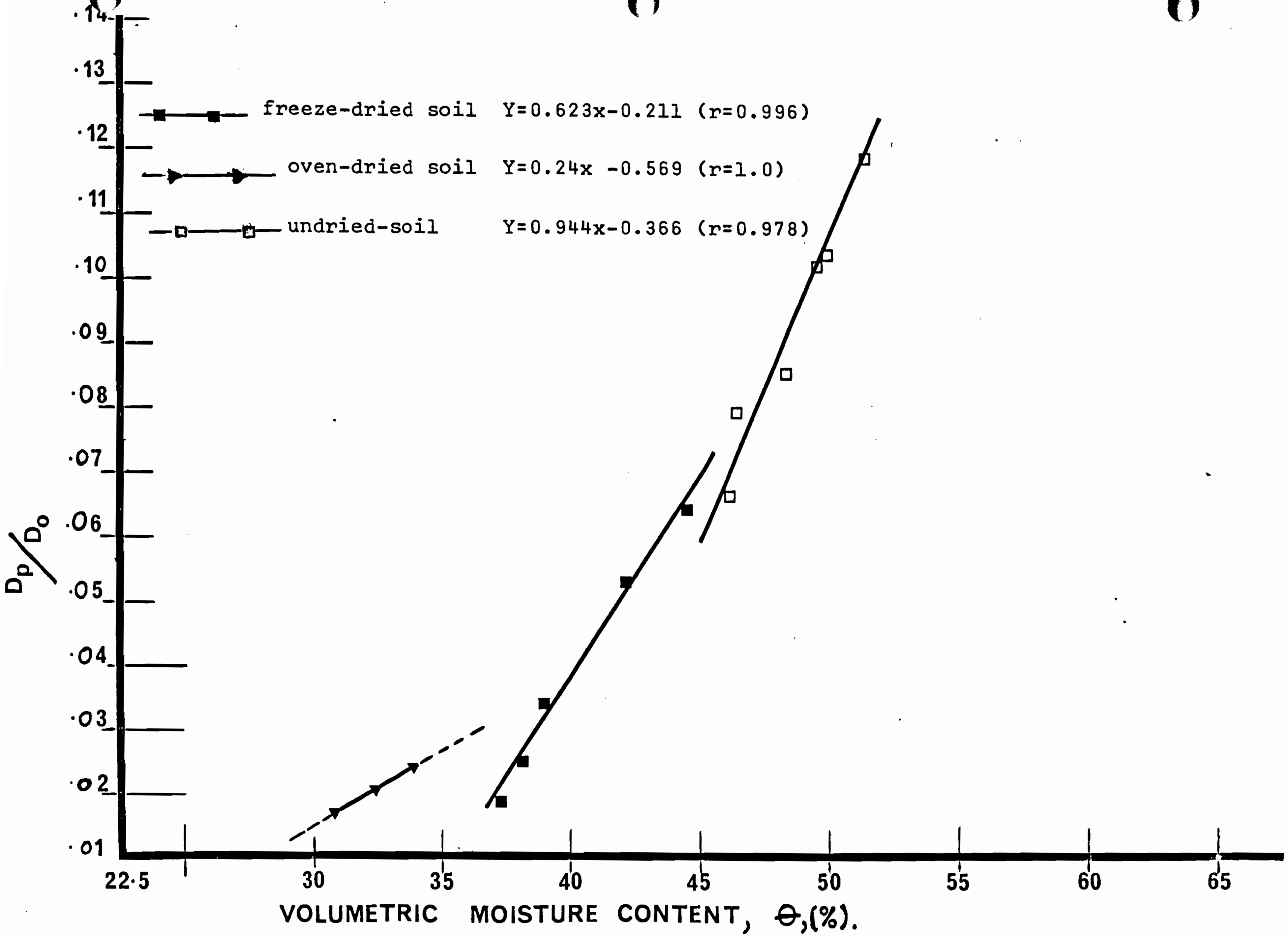


FIGURE 7. Geometric and interaction factors x volumetric moisture content (D_p/D_o) versus volumetric moisture content (θ), for undried, freeze-dried and oven-dried 75-4 soil samples at a bulk density of 0.7 gcm^{-3}.

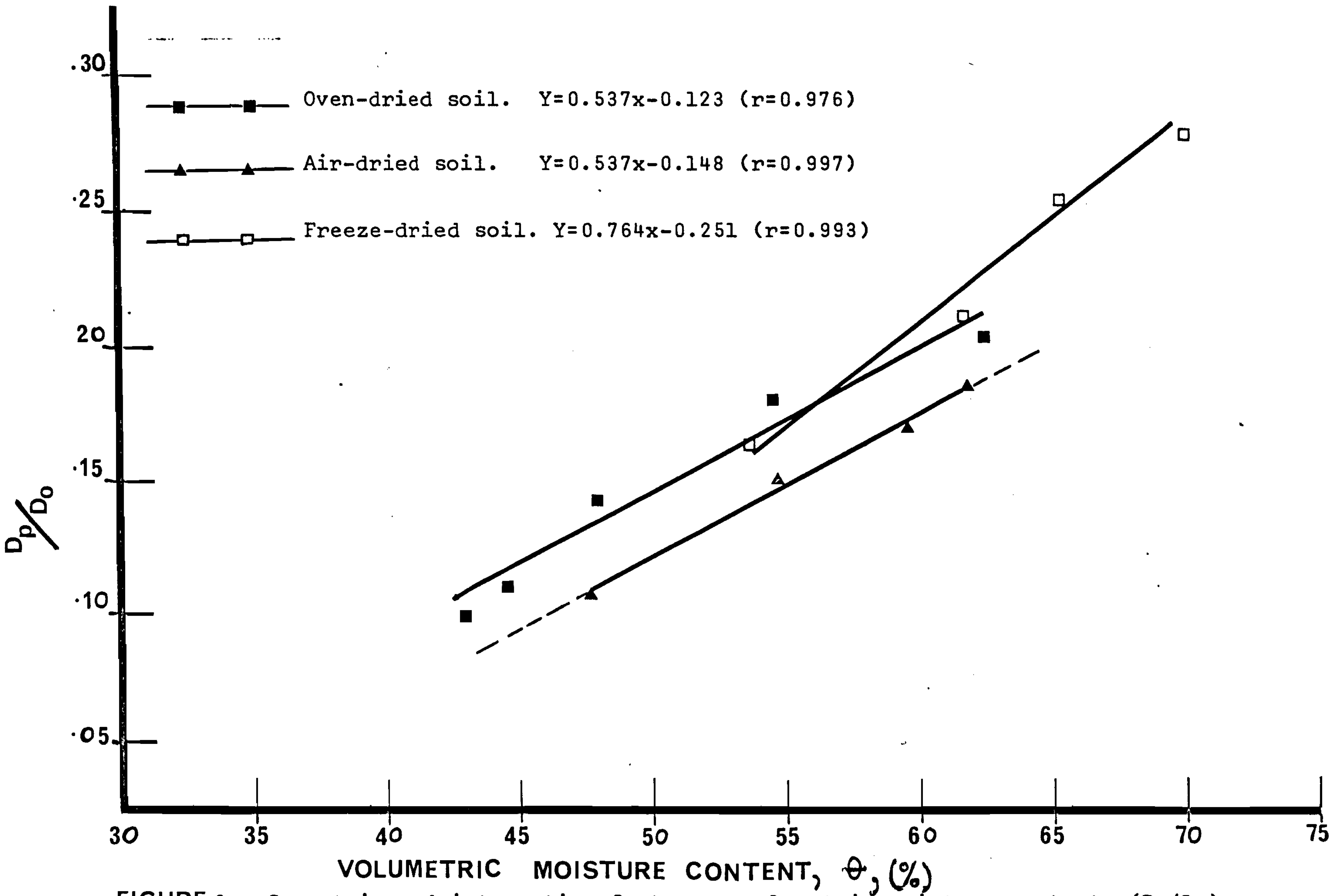


FIGURE 8. Geometric and interaction factors x volumetric moisture content, (D_p/D_o) versus volumetric moisture content (θ) for freeze-dried, air-dried, and oven-dried N4 soil samples at a bulk density of 0.7 gcm^{-3}.

samples had a higher average diffusion coefficient than that of the undried samples. For the same soil, at 35 per cent moisture content by volume, the oven-dried samples had a higher average diffusion coefficient than that of the freeze-dried samples.

(c) drying reduced the water holding capacity of soils, freeze drying to a smaller extent than oven-drying. The range of suction used for each drying treatment was the same for any one soil.

Observations (a) and (c) suggest that drying, irrespective of type, caused a re-arrangement of soil particles. This resulted in a reduction in potential water holding pores, dead-end or otherwise, and a decrease in geometric and interaction factors as indicated by the slope. Observation (b) suggests that drying rendered the soils inert (cf. a sand as an example of an inert soil, and a clay as an example of an active soil). An inert sample would have a larger apparent diffusion coefficient than an active or less inert sample at a common volumetric moisture content, because of a much smaller diffusion path length.

From a consideration of the effect of drying on the apparent diffusion coefficient, it can be said that for allophanes, drying re-arranges soil particles and renders the soil inert. The extent of re-arrangement is indicated by the changes in slope due to different types of drying.

4 *Some Problems Encountered During the Study.*

Problems encountered included: setting the diffusion time, determination of moisture content and range of moisture content, compaction on extrusion, compacting moist soils to known bulk densities, shrinkage of samples, and use of the extended source as a set of boundary conditions.

4.1 *The Diffusion Time*

One of the assumptions for the method based on the boundary condition of an instantaneous source, was that the medium into which diffusion was taking place was infinite. Diffusion should have taken place for such a time duration that $dC_O/d_X = 0$ at the remote end (C_O = initial concentration of the diffusing ion). In the literature Lai and Mortland (1961) quoted one to two days as a suitable time and Nakayama and Jackson (1963) one to twenty days. In fact, three hours was found to be the best time duration for the size of apparatus and moisture range used (3 cm^3syringes). This illustrates that the time duration of diffusion has to be determined by trial and error for a given set of conditions.

4.2 *Determination of Moisture Content and Range of Moisture Content.*

Moisture Content. The counting time of each reading was 2 minutes and there were 5 to 7 readings per sample. This meant that on the average, each sample was exposed for at least 10 to 14 minutes. Ideally, the moisture content should have been determined with sub-samples extruded from each syringe before labelling as was done initially. However, with the bulk density experiments, minimum disturbance was desirable and it was more convenient to determine the moisture content of each sample after the ^{36}Cl activity was measured, i.e. after a 10 to 15 minutes loss of moisture by evaporation. Moisture contents measured at the two different times on N4 soil samples are presented in Table 5. The data indicate that there was no significant differences between the two at the 0.1 probability level. Hence moisture loss by evaporation was negligible.

TABLE 5. Moisture Content by Weight Before and After the Measurement of Activity.

	Moisture Content by wt. measured before labelling	Moisture Content by wt. measured after the radioactive assay
Sample I	104.1	103.7
	118.6	118.1
	120.6	121.2
Mean	114.4	114.3
Sample II	123.7	120.6
	126.8	121.2
	104.2	100.8
Mean	118.2	114.2

Moisture Range: Lai and Mortland (1961) confined their diffusion studies to the relatively high values of moisture contents. This was considered essential if the boundary condition of a planar source was to be maintained.

Dry soils have a large affinity for water or a large suction. A drop of aqueous radio-tracer placed on a dry soil would tend to move rapidly into the soil due to the high soil suction. This situation lends itself more to the condition of an extended source rather than a planar one.

Nakayama and Jackson (1963) modified the method of diffusion based on a planar source, by fitting the soil column with a filter paper disc and applying the aqueous radio-tracer to the disc. This facilitated the measurement of the apparent diffusion coefficient over a wide range of moisture content by volume (3 to 40 per cent).

In this study, it was felt that the modification with a filter paper disc could have increased the range of moisture content. However, it was not sure whether diffusion coefficients as measured with the modified method were the same as those measured with the unmodified method. The filter paper disc would introduce a rate limiting step into the diffusion process.

As a preliminary test, four syringes of Chateauguay clay loam equilibrated at 0.2 bars were used as follows: three were fitted with discs and labelled (with the radio-tracer) and the fourth was labelled without the disc. The results in Table 6 indicate that the disc could have reduced the diffusion coefficient and there was need for a more detailed study. Therefore, the diffusion coefficient was measured on a further eight samples of Chateauguay clay loam, four with discs and four without, each at a bulk density of 1.1 $g\ cm^{-3}$ and equilibrated at 0.75 bars suction. The results in Table 6 indicate that there was no significant difference between the means of the two treatments at the 0.1 probability level.

TABLE 6. Volumetric Moisture Content (θ), Bulk Density (D_b), and Apparent Diffusion Coefficient (D_m), of Chateauguay clay loam samples with and without Discs.

Treatment	Volumetric Moisture Content %	Bulk Density g cm^{-3}	D_m (x 10^{-5}) cm^2 sec^{-1}	D_m (x 10^{-5}) cm^2 sec^{-1} corr.* to θ=42%
Preliminary Experiment				
discs	51.3	1.01	1.08	0.88
	42.3	0.92	1.18	1.17
	46.7	0.94	1.24	1.11
no discs	42.6	0.98	1.32	1.30
At 0.75 bars (10 p.s.i)				corr. to θ = 31.0%
discs	31.50	1.10	0.34	0.34
	31.20	1.10	0.35	0.35
	32.68	1.10	0.43	0.41
	43.40	1.10	0.82	0.59
no discs	31.7	1.10	0.38	0.37
	30.9	1.10	0.39	0.39
	30.8	1.10	0.36	0.36
	35.7	1.10	0.56	0.48

*corrected

The suction of 0.75 bar was considered the wet range and an attempt to make a comparison in the dry range failed on account of the small adhesive force between the disc and the dry soil. It was therefore decided not to use the discs and to confine the study to the relatively low range of soil suction, below 3 bars.

4.3 Compaction on Extrusion

A certain degree of compaction was unavoidable in extruding the samples from the syringes. This resulted in an underestimation of the extruded distance (x) which may be accounted for by the use of "correction factors" (Appendix C).

The correction factors are listed in Table 7. In the majority of cases, diffusion was measured in the upper 3 cms of the soil plug. Hence, for Chateauguay clay loam, no correction appeared necessary for bulk density values of 1.1, 1.2, and 1.3 g cm^{-3}.

Table 7. Changes in Bulk Density (D_b), on Account of Extrusion and the Appropriate Correction Factors.

	Chateauguay Clay Loam			N4		
	D_b before extrusion	D_b after extrusion	Correction Factor	D_b before extrusion	D_b after extrusion	Correc-tion Fac.
U.P	1.00	1.11	1.11	0.55	0.63	1.14
L.P	1.00	1.15	1.15	0.55	0.58	1.05
U.P.	1.10	1.15	1.04	0.60	0.64	1.07
L.P	1.10	1.24	1.13	0.60	0.63	1.05
U.P	1.20	1.23	1.03	0.70	-	-
L.P	1.20	1.29	1.08	0.70	-	-
U.P	1.30	1.29	-	0.80	-	-
L.P	1.30	1.43	1.10	0.80	-	1

Legend: U.P - upper portion - 3 cms length
L.P - lower portion - varied length
D_b - bulk density (g cm^{-3})

The values in the Table represent the mean of four values, in no instance did the coefficient of variation exceed 4 per cent.

Consider an extrusion of 4 mm. This could have been measured to the nearest 0.5 mm with a 15-cm rule, and a correction factor of 1.11 may have been worthwhile for such a thickness. However, for extrusions less than 4 mm, because of the error involved in actually measuring the thickness of the slice, it may not have been worthwhile correcting the values. To be consistent, the correction factor of 1.11 was used at all times for a bulk density of 1.0 g cm^{-3}.

No correction factor was required for N4. At a bulk density of 0.6 g cm^{-3}, there was a small degree of shrinkage which facilitated easy extrusion. For bulk densities of 0.7 and 0.8 g cm^{-3} extrusion was not possible on the lathe without the syringe collapsing. As such, the syringes were sliced lengthwise and extrusion made with negligible compaction. Slicing followed by extrusion was not possible with the Chateauguay clay loam at the bulk density of 1.0 g cm^{-3} for the cohesion was not sufficient to hold the plug together.

4.4 *Compacting Moist Soils to Known Bulk Densities*

Consider the following example: It is desired to compact an initially wet soil to a known bulk density using the following data.

What weight of wet soil is required?

Data:
Required bulk density = 1.10 g cm^{-3}
Vol. of Container = 3.43 cm^{3}
Initial Moisture Content by Weight = 77.5%

Solution:

$$\text{Bulk density} = \frac{\text{Mass of dry soil}}{\text{Volume of Soil}} = \text{g cm}^{-3}$$

Hence, mass of dry soil required = (1.10 x 3.43) g
Wt. of wet soil required = [(1.10 x 3.43) + (1.10 x 3.43) x 0.775] g
= dry soil + moisture
or = [(1.10 x 3.43) x 1.775] g.

The above example illustrates the calculation of the weight of wet soil for a desired bulk density. The problems associated with this procedure were (a) obtaining a constant initial moisture content, (b) ensuring uniform compaction.

Constant Initial Moisture Content: This was obtained by equilibrating the soil sample in an atmosphere of constant relative humidity for at least three days. The undried sample was equilibrated in a saturated vapour chamber and the freeze-dried and air-dried samples in a dessicator.

Uniform Compaction: This was achieved at the lower range of bulk density by tapping the sample container. The freeze-dried N4 sample at a bulk density of 0.8 g cm^{-3} posed the greater problem. The soil when dry was very fluffy with a very low bulk density, and its volume was several times that to which it was to be compacted. Compaction was done in stages by exerting a uniform force through a lever. Although the final average bulk density of the sample was 0.8 g cm^{-3}, the distribution was questionable.

4.5 Shrinkage of Samples

Allophane soils can undergo significant volume changes with small changes in moisture content. So to maintain a relatively constant bulk density for some soil samples, it was necessary to work at low soil suctions, and to disregard the bulk density values affected most by shrinkage. For N4 the bulk density of 0.5 g cm^{-3} had to be discarded.

4.6 Diffusion Based on the Boundary Condition of an Extended Source

One of the objectives of this work was to investigate whether or not diffusion coefficients as obtained by different methods were the same. The method of diffusion based on an extended source, although used quite extensively in the literature (Section 3.4, Chapter II) was not successful in this study. The method used (outlined in Appendix D) was simple and inexpensive, but yielded results which were highly inconsistent and at least four times larger than those obtained for the same soil and similar conditions of bulk density and moisture content by the planar source method. The large inconsistencies associated with replicates of a given soil, could be due to the following difficulties:

(i) Proper Contact: Initially, it was believed that proper contact could be achieved quite easily by bringing the two half cells together (Van Schaik and Kemper, 1966). In practice however, proper contact could be achieved only by actually pushing the soil samples together with an applied force. This tended to: (a) move soil solution (both labelled and unlabelled) from one half cell (or syringe) to the next, i.e. mass movement of soil solution; (b) alter the bulk density in each half cell; (c) make separation difficult as the boundary became very indistinct. In the very wet range separation of the half cells was the problem. In the dry range ensuring proper contact without forcing the samples together was difficult as the samples shrunk and moved relative to the syringes. It was believed that an improvement to this method could well have been the use of an anion exchange membrane (Schofield and Graham-Bryce, 1960) between the two half cells.

(ii) Labelling: The labelling procedure outlined in the method (Appendix D) was necessary so as to control moisture content and bulk density. This involved a two-week storage period to ensure a uniform distribution of the radio-active tracer. This length of time could well have been inadequate.

(iii) Fungal Growth: After a two-week storage period, the soil became permeated with fungal hyphae which could have influenced the diffusion coefficient. This was reduced by adding a few drops of formaldehyde to the wet soil.

(iv) Non-Uniform Bore of Syringes: The 10 cm^3 "stylex" syringes used were of a non-uniform bore. At the base of each syringe, the bore or diameter was larger for a length of 1 mm before tapering into a smaller uniform diameter. Two such syringes clamped together (Appendix D) gave rise to a non-uniform bore which must have contributed to the complicated problem of proper contact.

CHAPTER V

SUMMARY AND CONCLUSIONS

The effects of temperature, bulk density and drying on the apparent diffusion coefficient were studied. The use of diffusion for the determination of dead-end porosity was reviewed. The important points arising from this work are:

(a) The apparent diffusion coefficient is a linear function of temperature. The geometric and interaction factors (D_m/D_o) show a non-linear relationship with temperature. The change of viscosity of water with temperature, accounted for a large part of the variation of the geometric and interaction factors; the remainder must have been due to changes in bound water.

(b) For a given moisture content, increasing the bulk density reduced the apparent diffusion coefficient. This was accounted for by a reduction in the tortuosity factor as a result of an increased diffusion path length.

(c) From the point of view of characterisation of pore geometry, dead-end porosity still remains an important parameter. The literature review has shown that for a soil, dead-end porosity is difficult to determine.

The physical models proposed are better suited for the determination of dead-end porosity in large flow structures. Data using such models for soils would be both difficult to obtain and interpret.

(d) Drying, irrespective of type, produced a decrease in the average geometric and interaction factors; oven-drying and air-drying produced an equal reduction which was greater than that produced by freeze-drying. Drying rendered the soil inert.

The method of determination of the apparent diffusion coefficient based on the boundary condition of an extended source diffusing into an infinite medium was not successful in this study. A comparison of diffusion coefficients determined by different methods was therefore not presented.

It is proposed in this study that changes in the apparent diffusion coefficient on account of bulk density and drying are related mainly to changes in geometric factors. It still appears that the geometric and interaction factors are inseparable. However, in the moisture range over which the study was conducted, changes in interaction factors seemed relatively small. At lower water contents where water is essentially in the bound form, interaction factors are likely to assume a greater or equal importance in accounting for changes in the apparent diffusion coefficient.

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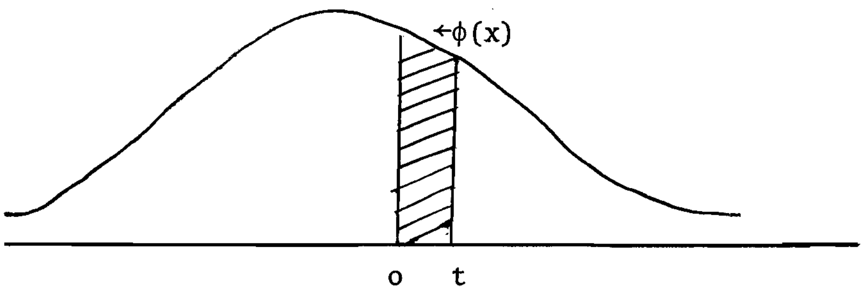
APPENDIX A

Model Calculation for the boundary condition of a planar source diffusing into an infinitely long medium

The solution of Fick's second law for instantaneous or planar sources, and a mathematical treatment of Lai and Mortland technique for the evaluation of D_m were presented in Sections 4.1.1 and 4.1.2 of Chapter II, respectively. Here, a typical data sheet and the evaluation of D_m is presented.

To better understand the data sheet, one must refer to a set of standard probability tables or normal curve of error (Selby, 1975). According to these tables:



given a curve $\phi(x)$, then the shaded area is

$$\int_0^t \phi(x)dx = \tfrac{1}{2}\mathrm{erf}(t/\sqrt{2})$$

Where $\frac{1}{2}\,\mathrm{erf}(t/\sqrt{2})$ represents the error function associated with the normal curve.

For this particular example, the value y is to be evaluated and y is given by:

$$\mathrm{erf}\,y = (1 - A_x/A_o)$$

[Section 4.1.2 Ch. II]

$$\text{hence} \quad \tfrac{1}{2}\mathrm{erf}\,y = (1 - A_x/A_o)/2 = \int_0^t \phi(x)\,dx$$

$$\text{where} \quad y = t/\sqrt{2}$$

The value of t for a corresponding value of $(1 - A_x/A_o)/2$ is obtained from tables and y calculated.

A plot of y versus x is made (Fig. A1) and the slope is related to D_m as follows:

$$\text{Slope} = \frac{1}{2\sqrt{D_m t}}$$ where t is the diffusion time in secs.

$$D_m = \frac{1}{t(2\ \text{slope})^2}$$

From Fig. AI,

$$\text{Slope} = 0.787$$

$$D_m = 1.91 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$$

In Table A1, the distance x was expressed to the nearest 1/10 mm. These values were not measured but calculated from the graduation on the syringe scale. Where x was measured, it could only be obtained to the nearest 0.5 mm.

The fact that Fig. A1 is a straight line, indicates that the experiment follow the given theoretical equations and diffusion is being measured (Lai and Mortland, 1961). Deviations from the straight line at low values of y are expected since the condition that $A_x/A_o \ll 1$ is not met at such values (Lai and Mortland, 1961). Deviations at higher values of y indicate that there is a change in concentration at the remote end, and the diffusing medium is no longer infinite.

DATA SHEET

Temp. 35°C Sample no: VIII Title: Temp. coefficient Date: 13.8.76

Time labelled: 3.44 p.m. Time assayed: 9.34 p.m.

Average background: #40 cpm Container #: 118/15

Initial Position of Plunger: 3 cm^3

x (mm)	A_x cp/2 min.	Corrected A_x	$(1-\frac{A_x}{A_o})$	$(1-\frac{A_x}{A_o})/2$	t	$y = t/\sqrt{2}$
0.0	5598	2759	-	-	-	-
5.7	3861	1891	0.3148	0.1574	0.4064	0.2870
8.6	2760	1340	0.5143	0.2572	0.6974	0.4930
10.0	-	-	-	-	-	-
11.5	1542	731	0.7350	0.3675	1.1148	0.7880
12.9	-	-	-	-	-	-
14.3	712	316	0.8855	0.4427	1.5775	1.1150
15.8	-	-	-	-	-	-
17.2	371	146	0.9473	0.4736	1.9366	1.3690
18.6	-	-	-	-	-	-
20.1	222	71	0.9743	0.4871	2.2300	1.5770
21.5	-	-	-	-	-	-
22.9	-	-	-	-	-	-
24.4	-	-	-	-	-	-

t = 5 hours 50 minutes = 21 000 secs

s = 0.787

$D_m = 1.91 \times 10^{-5}$ $cm^2\ sec^{-1}$

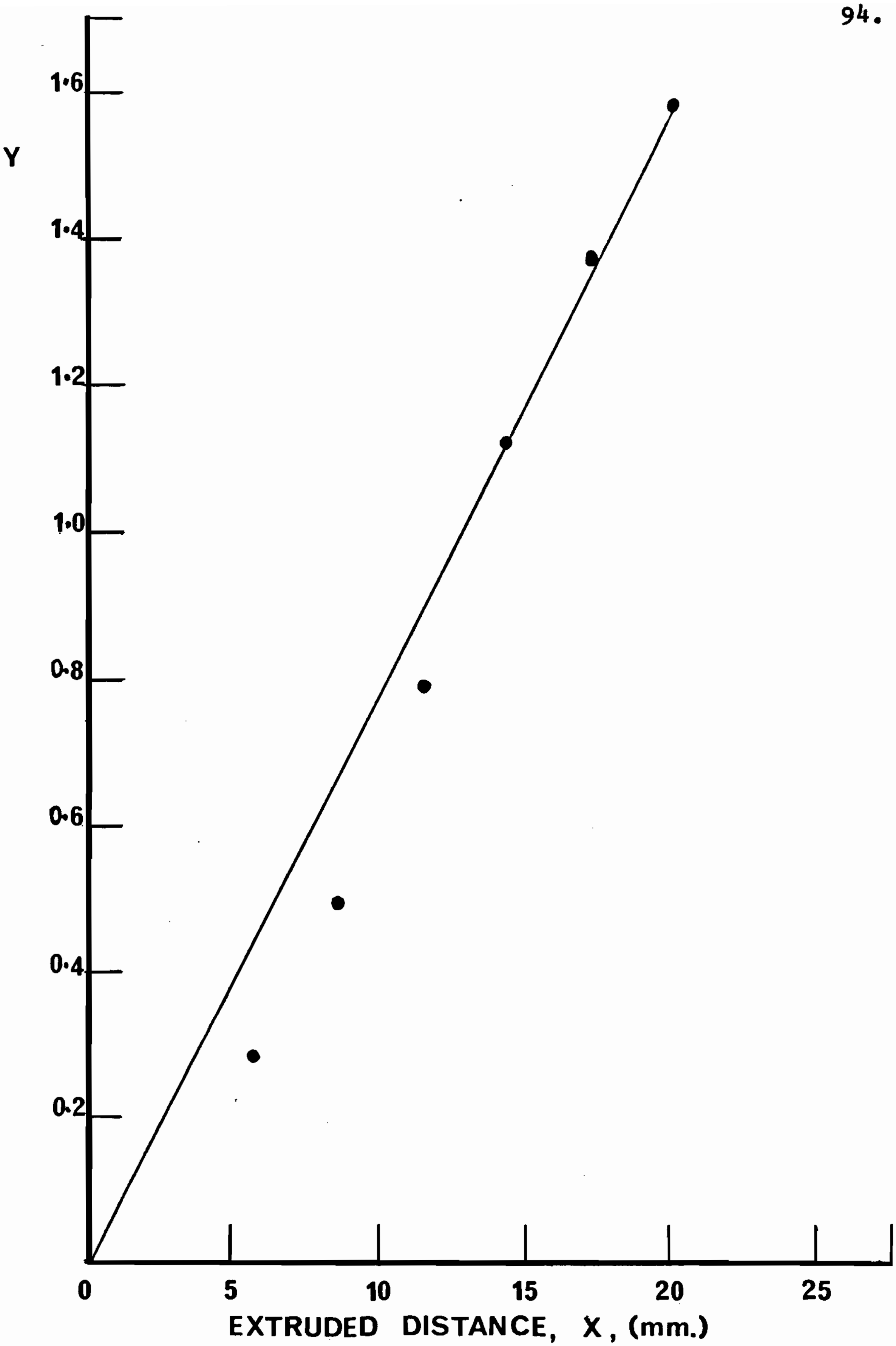


FIGURE A.1. The values of Y (Equation 42) versus the extruded distance x.

APPENDIX B

TABLE B1. Volumetric Moisture Content (θ), the Apparent Diffusion Coefficient, D_m, Bulk Density and the Geometric and Interaction Factors (D_m/D_o), for Chateauguay clay loam at Different Temperatures.

Temp. °C	Volumetric Moisture Content (θ)	D_m (x 10^{-5}) $cm^2 sec^{-1}$	Bulk Density g cm^{-3}	D_m/D_o	Mean θ±S.D.	C.V.%	Mean D_m±S.D	C.V.%
25.0	0.510	1.18	1.0	0.581	0.50± 0.008	1.6	1.16± 0.13	11.1
	0.490	1.04	1.0	0.512				
	0.500	1.08	1.0	0.531				
	0.500	1.33	1.0	0.654				
29.5	0.489	1.40	1.0	0.689	0.490± 0.003	0.6	1.35± 0.11	7.8
	0.486	1.46	1.0	0.718				
	0.491	1.31	1.0	0.645				
	0.493	1.22	1.1	0.600				
34.5	0.545	1.74	1.0	0.856	0.526± 0.029	5.5	1.72± 0.15	9.0
	0.545	1.91	1.1	0.940				
	0.528	1.54	1.2	0.758				
	0.484	1.67	1.0	0.822				
38.5	0.535	1.86	0.9	0.915	0.529± 0.033	6.2	1.86± 0.01	0.4
	0.563	1.86	1.0	0.915				
	0.532	1.87	1.1	0.920				
	0.484	1.85	1.0	0.910				

TABLE B2. Volumetric Moisture Content (θ), the Apparent Diffusion Coefficient (D_m) and the Geometric and Interaction Factors (D_m/D_o), of Chateauguay clay loam at a Bulk Density of 1.0 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 sec^{-1}	D_m/D_o	Mean θ±S.D.	C.V.%	Mean D_m/D_o ± S.D.	C.V.%
0.234 0.235 0.234 0.234	0.162 0.179 0.175 0.156	0.080 0.088 0.086 0.077	0.234±0.001	0.2	0.083±0.005	6.2
0.246 0.234 0.227	0.356 0.277 0.245	0.175 0.136 0.121	0.236±0.010	4.1	0.144±0.028	19.4
0.271 0.274 0.257 0.255	0.378 0.339 0.280 0.237	0.186 0.167 0.138 0.117	0.264±0.010	3.6	0.152±0.031	20.1
0.340 0.325 0.343 0.389	0.556 0.476 0.537 0.648	0.274 0.234 0.264 0.319	0.349±0.028	8.0	0.273±0.035	12.9

TABLE B3. Volumetric Moisture Content (θ), the Apparent Diffusion Coefficient (D_m) and Geometric and Interaction Factors (D_m/D_o) of Chateauguay clay loam at a Bulk Density of 1.1 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) $cm^2 sec^{-1}$	D_m/ D_o	Meanθ± S.D	C.V.%	Mean D_m/D_o ± S.D.	C.V.%
0.259	0.173	0.085	0.259± 0.003	1.1	0.101±0.014	13.5
0.263	0.194	0.095				
0.257	0.228	0.112				
0.257	0.230	0.113				
0.282	0.195	0.096	0.281±0.004	1.2	0.106±0.024	22.6
0.284	0.230	0.113				
0.282	0.277	0.136				
0.276	0.163	0.080				
0.357	0.556	0.274	0.323±0.023	7.1	0.207±0.045	22.0
0.308	0.358	0.176				
0.309	0.391	0.192				
0.317	0.375	0.184				
0.336	0.401	0.197	0.339±0.011	3.3	0.214±0.017	7.9
0.342	0.471	0.231				
0.339	0.435	0.214				
0.312	0.350	0.172	0.318±0.008	2.5	0.184±0.023	12.8
0.315	0.344	0.169				
0.327	0.429	0.211				
0.409	0.640	0.315	0.422±0.018	4.2	0.36±0.063	17.5
0.434	0.822	0.404				

TABLE B4. Volumetric Moisture Content (θ), the Apparent Diffusion Coefficient (D_m), and Geometric and Interaction Factors (D_m/D_o) of Chateauguay clay loam at a Bulk Density of 1.2 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) $cm^2 sec^{-1}$	D_m/D_o	Mean θ±S.D.	C.V.%	Mean D_m/D_o ± S.D	C.V.%
0.268	0.206	0.101	0.268±0.002	0.8	0.089±0.010	10.9
0.268	0.188	0.093				
0.270	0.170	0.084				
0.265	0.161	0.079				
0.307	0.384	0.189	0.303±0.005	1.5	0.171±0.013	7.7
0.306	0.350	0.172				
0.299	0.322	0.158				
0.298	0.338	0.166				
0.297	0.196	0.096	0.304±0.006	2.0	0.114±0.019	16.7
0.303	0.279	0.137				
0.309	0.205	0.101				
0.308	0.248	0.122				
0.329	0.362	0.178	0.325±0.003	1.0	0.188±0.013	7.1
0.325	0.405	0.199				
0.326	0.406	0.200				
0.321	0.355	0.175				
0.369	0.537	0.264	0.356±0.01	2.8	0.249±0.018	7.2
0.353	0.496	0.244				
0.345	0.460	0.226				
0.357	0.535	0.263				

TABLE B5. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m), and Geometric and Interaction Factors (D_m/D_o) of Chateauguay clay loam at a bulk density of 1.3 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 sec^{-1}	D_m / D_o	Mean θ±S.D	C.V.%	Mean D_m/D_o ± S.D.	C.V.%
0.277	0.256	0.126	0.283±0.004	1.5	0.116±0.030	25.5
0.287	0.239	0.118				
0.283	0.294	0.145				
0.284	0.153	0.075				
0.312	0.214	0.105	0.312±0.002	0.6	0.138±0.025	18.3
0.311	0.293	0.144				
0.315	0.278	0.137				
0.311	0.337	0.166				
0.342	0.377	0.185	0.350±0.012	3.3	0.204±0.061	30.1
0.346	0.381	0.187				
0.344	0.308	0.152				
0.367	0.596	0.293				
0.379	0.491	0.242	0.382±0.003	7.3	0.252±0.014	5.5
0.385	0.484	0.238				
0.384	0.542	0.267				
0.381	0.526	0.259				

TABLE B6. Volumetric Moisture Content (θ), The Apparent Diffusion Coefficient (D_m) and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o), for Oven-dried N4 soil at a Bulk Density of 0.6 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 $sec.^{-1}$	D_p/D_o	Mean θ± S.D.	C.V.%	Mean D_p/D_o ± S.D.	C.V%
0.351	0.195	0.034	0.354±0.003	0.7	0.037±0.003	8.1
0.355	0.211	0.037				
0.356	0.230	0.040				
0.366	0.217	0.039	0.360±0.009	2.6	0.036±0.003	6.9
0.364	0.196	0.035				
0.346	0.194	0.033				
0.364	0.203	0.036				
0.438	0.409	0.088	0.421±0.019	4.4	0.078±0.016	20.5
0.424	0.415	0.087				
0.401	0.301	0.059				
0.566	0.576	0.163	0.581±0.019	3.3	0.185±0.023	12.3
0.576	0.685	0.194				
0.609	0.709	0.212				
0.572	0.600	0.169				

TABLE B7. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m) and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o) for Oven dried N4 Soil at a Bulk Density of 0.7 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 $sec.^{-1}$	D_p/D_o	Mean $\theta \pm$ S.D	C.V.%	Mean D_p/D_o ± S.D.	C.V.%
0.477	0.505	0.119	0.430±0.031	7.2	0.100±0.018	17.7
0.417	0.489	0.100				
0.413	0.505	0.103				
0.414	0.373	0.076				
0.439	0.507	0.110	0.446±0.014	3.1	0.112±0.011	10.2
0.431	0.475	0.101				
0.451	0.576	0.128				
0.463	0.477	0.109				
0.565	0.726	0.201	0.479±0.058	12.6	0.144±0.04	27.5
0.449	0.585	0.129				
0.458	0.487	0.110				
0.443	0.624	0.136				
0.549	0.658	0.178	0.546±0.012	2.2	0.181±0.015	8.3
0.541	0.633	0.168				
0.534	0.661	0.174				
0.561	0.732	0.202				
0.632	0.604	0.188	0.625±0.006	0.9	0.204±0.012	5.9
0.625	0.659	0.203				
0.618	0.675	0.205				
0.625	0.709	0.218				

TABLE B 8. Volumetric Moisture Content (θ), Apparent Coefficient (D_m) and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o), for Oven-dried N4 Soil at a Bulk Density of 0.8 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 sec^{-1}	D_p/ D_o	Mean θ±S.D	C.V%	Mean D_p/D_o ± S.D	C.V%
0.485	0.444	0.106	0.508±0.018	3.6	0.107±0.011	10.3
0.529	0.356	0.093				
0.515	0.455	0.120				
0.506	0.428	0.107				
0.524	0.522	0.135	0.230±0.036	15.7	0.118±0.02	16.9
0.495	0.393	0.096				
0.510	0.487	0.122				
0.559	0.273	-				
0.561	0.546	0.151	0.556±0.019	3.3	0.157±0.045	28.7
0.542	0.375	0.100				
0.541	0.624	0.166				
0.580	0.737	0.210				
0.603	0.668	0.198	0.606±0.017	2.8	0.181±0.024	13.3
0.584	0.534	0.153				
0.624	0.663	0.204				
0.613	0.555	0.167				
0.656	0.579	0.187	0.648±0.012	1.9	0.196±0.019	9.7
0.635	0.587	0.183				
0.654	0.679	0.218				

TABLE B9. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m), and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o) for air-dried N4 Soil at a Bulk Density of 0.7 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m ($x 10^{-5}$) cm^2 sec^{-1}	D_p/D_o	Mean θ± S.D.	C.V%	Mean D_p/D_o ± S.D	C.V.%
0.473	0.459	0.107	0.476±0.003	0.7	0.107±0.015	14.4
0.477	0.523	0.123				
0.480	0.471	0.111				
0.473	0.370	0.086				
0.543	0.581	0.155	0.548±0.016	3.0	0.15±0.036	24.1
0.554	0.539	0.147				
0.566	0.694	0.193				
0.528	0.405	0.105				
0.601	0.533	0.158	0.604±0.004	0.6	0.170±0.023	13.8
0.602	0.523	0.155				
0.608	0.658	0.197				
0.627	0.635	0.196	0.619±0.012	2.0	0.186±0.036	19.5
0.618	0.601	0.183				
0.629	0.529	0.138				
0.602	0.759	0.225				

TABLE B10. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m), and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o) for Freeze-dried N4 Soil at a Bulk Density of 0.7 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 sec.$^{-1}$	D_p/D_o	Mean θ± S.D		Mean D_p/D_o ± S.D.	
				C.V.%		C.V.%
0.538 0.537 0.541	0.631 0.611 0.620	0.167 0.161 0.165	0.539±0.002	0.4	0.164±0.003	1.9
0.622 0.611 0.611	0.689 0.706 0.705	0.211 0.212 0.212	0.615±0.006	1.0	0.212±0.001	2.7
0.650 0.663 0.650	0.804 0.759 0.793	0.257 0.248 0.254	0.654±0.008	1.1	0.253±0.005	1.8
0.691 0.693 0.689	0.819 0.80 0.835	0.278 0.273 0.283	0.691±0.002	0.3	0.278±0.005	1.8

TABLE B11. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m), and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o) for Freeze-dried 75.4 soil at a Bulk Density of 0.7 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 sec^{-1}	D_p/ D_o	Mean θ± S.D.	C.V.%	Mean D_p/D_o ± S.D	C.V.%
0.366	0.087	0.016	0.372±0.01	2.7	0.019±0.003	17.1
0.380	0.125	0.023				
0.361	0.111	0.020				
0.381	0.089	0.017				
0.381	0.135	0.025	0.380±0.002	0.6	0.025±0.004	14.6
0.377	0.119	0.022				
0.382	0.123	0.023				
0.380	0.162	0.030				
0.394	0.177	0.034	0.390±0.004	1.1	0.034±0.004	11.8
0.389	0.164	0.031				
0.384	0.167	0.032				
0.392	0.205	0.040				
0.420	0.323	0.067	0.422±0.003	0.8	0.053±0.012	22.4
0.427	0.225	0.047				
0.421	0.192	0.040				
0.421	0.278	0.058				
0.439	0.273	0.059	0.444±0.004	0.8	0.064±0.009	13.0
0.442	0.348	0.076				
0.447	0.295	0.065				
0.446	0.262	0.057				

TABLE B12. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m) and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o) for Undried 75-4 Soil at a Bulk Density of 0.7 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) $cm^2 sec^{-1}$	D_p/D_o	Mean θ±S.D	C.V.%	Mean D_p/D_o ± S.D	C.V.%
0.460	0.262	0.059	0.462±0.002	0.5	0.066±0.012	18.6
0.460	0.356	0.081				
0.465	0.303	0.069				
0.462	0.235	0.053				
0.467	0.296	0.068	0.465±0.002	0.5	0.079±0.009	10.9
0.462	0.351	0.080				
0.465	0.350	0.080				
0.466	0.387	0.089				
0.486	0.348	0.083	0.483±0.006	1.2	0.085±0.008	9.1
0.481	0.330	0.078				
0.489	0.399	0.096				
0.476	0.355	0.083				
0.500	0.471	0.116	0.496±0.004	0.7	0.104±0.01	9.2
0.496	0.424	0.103				
0.496	0.381	0.093				
0.491	0.443	0.107				
0.496	0.415	0.101	0.500±0.007	1.4	0.108±0.012	11.2
0.492	0.515	0.125				
0.505	0.425	0.106				
0.506	0.395	0.098				
0.512	0.478	0.120	0.514±0.04	0.8	0.118±0.003	2.4
0.519	0.472	0.120				
0.511	0.458	0.115				

TABLE B13. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m), and Geometric and Interaction Factors x Volumetric Moisture Content (D_p/D_o) for Oven-dried 75-4 Soil at a Bulk Density of 0.7 g cm^{-3}.

Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 $sec.^{-1}$	D_p/D_o	Mean θ± S.D.	C.V%	Mean D_p/D_o ±S.D.	C.V.%
0.306	0.113	0.017	0.308±0.002	0.6	0.017±0.001	5.8
0.306	0.104	0.016				
0.308	0.119	0.018				
0.310	0.115	0.018				
0.321	0.130	0.021	0.323±0.003	0.8	0.021±0.006	28.8
0.326	0.084	0.014				
0.325	0.176	0.028				
0.321	0.132	0.021				
0.342	0.178	0.030	0.338±0.003	0.9	0.024±0.007	27.3
0.336	0.173	0.029				
0.336	0.094	0.016				
0.336	0.138	0.023				

TABLE B14. Bulk Density, Volumetric Moisture Content (θ), and the Apparent Diffusion Coefficient (D_m) for N4 Soil at an equilibrium suction of 0.2 bar.

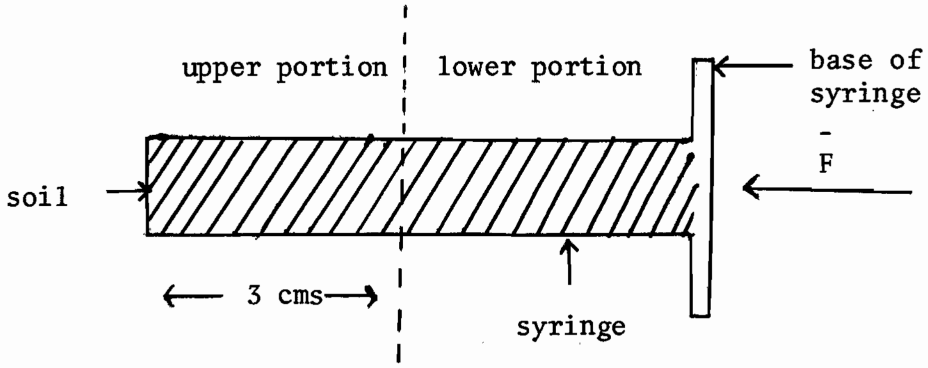
	Bulk density g cm^{-3}	Volumetric Moisture Content(θ)	D_m (x 10^{-5}) $cm^2 sec^{-1}$	Mean θ± S.D	C.V.%	Mean D_m±S.D	C.V.%
Undried	0.51 0.50 0.51 0.47	0.740 0.769 0.771 -	1.56 1.37 1.61 1.58	0.76±0.017	2.3	1.53± 0.109	7.1
Freeze-dried	0.62 0.59 0.61 0.58	0.784 0.734 0.738 0.689	1.73 1.67 1.72 1.77	0.736±0.039	5.3	1.72± 0.041	2.4
Oven-dried	0.77 0.77 0.76 0.76	0.723 0.711 0.690 0.717	1.16 1.14 1.15 1.15	0.714±0.019	2.7	1.15± 0.008	0.7
Air-dried	0.71 0.67 0.69 0.71	0.740 0.674 0.711 0.702	1.24 1.12 1.14 1.11	0.707± 0.027	3.8	1.15± 0.06	5.2

TABLE B15. Volumetric Moisture Content (θ), Apparent Diffusion Coefficient (D_m) and Bulk Density of Oven-dried and Undried Samples of Three Soil Samples at an equilibrium suction of 0.2 bar.

	Soil	Volumetric Moisture Content (θ)	D_m (x 10^{-5}) cm^2 sec^{-1}	Bulk density g cm^{-3}	Mean θ± S.D	C.V.%	Mean D_m± S.D	C.V.%
Undried	74-2	0.626 0.642 0.611 0.602	1.63 1.28 1.32 1.46	0.82 0.84 0.80 0.81	0.620 ± 0.018	2.8	1.42 ± 0.16	11.1
Oven-dried	74-2	0.540 0.525 0.595 0.547	1.16 1.22 1.34 1.44	1.04 1.00 1.13 1.05	0.552 ± 0.03	5.5	1.29 ± 0.12	9.3
Undried	N-2	0.618 0.602 0.638 0.608	1.12 1.17 1.09 1.14	0.69 0.70 0.70 0.67	0.617 ± 0.016	2.6	1.13 ± 0.03	3.0
Oven-dried	N-2	0.551 0.520 0.524 0.530	- 1.08 0.81 0.88	0.95 0.90 0.91 0.91	0.531 ± 0.014	2.6	0.92 ± 0.14	15.0
Undried	74-4	0.764 0.825 0.755 0.785	1.63 1.66 1.85 1.73	0.22 0.21 0.20 0.20	0.782 ± 0.031	4.0	1.72 ± 0.10	5.0
Oven-dried	74-4	0.358 0.368 0.372 0.328	1.02 1 1.43 1.25	1.00 0.94 0.94 0.90	0.357 ± 0.02	5.6	1.23 ± 0.21	16.0

APPENDIX C

Correction Factor for Compaction During Extrusion



In applying a force $\bar{F}$ to one end of the syringe to extrude the soil sample, movement will not occur until the static friction between the wall of the cylinder and the soil has been exceeded. The force required to initiate movement compacts the soil and increases the bulk density. Hence, there is need to correct for changes in bulk density on account of extrusion.

In making a correction, it was decided to divide the soil sample into an upper portion (3 cms in length) and a lower portion of variable length. Diffusion measurements were confined, to the upper portion of the soil sample. It was assumed that the lower portion was compacted to a greater extent than the upper portion by the extrusion force. However, before this assumption could be tested and appropriate correction factors derived, selecting a suitable moisture content for work posed a problem. It was decided to determine the correction factor at an arbitrary intermediate moisture content such that one would be "over correcting" for samples of lower moisture contents and "under correcting" for samples of larger moisture contents.

Determination of Correction Factors

A sample of known bulk density was positioned horizontally on a lathe and a force was applied to a plunger stuck in the base. The sample was extruded and divided into an upper and lower portion. The average bulk density was determined for each portion. The correction factor was given by:

$$D_{b1} \times x_1 = D_{b2} \times x_2 \quad \text{for a given mass of soil}$$

Hence,

$$x_1 = \frac{D_{b2}}{D_{b1}} x_2$$

Where x_2 = measured thickness of extruded slice;

x_1 = corrected thickness of extruded slice;

D_{b2} = Average bulk density of either the upper or lower portion

D_{b1} = Original Bulk Density of sample;

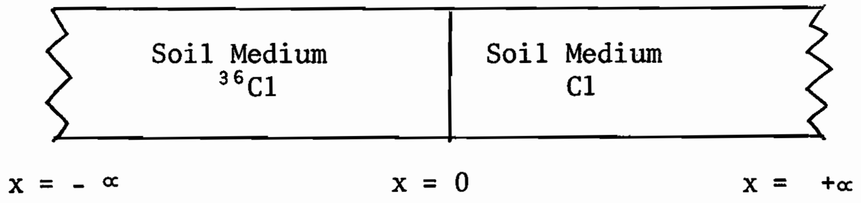
$$\frac{D_{b2}}{D_{b1}} = \text{Correction Factor}$$

For the higher values of bulk density, it was almost impossible to extrude the soil samples with the lathe. The syringes were split lengthwise, facilitating extrusion and minimising compaction. No correction factors were required in such cases.

APPENDIX D

Diffusion Method Based on the Boundary Condition of an Extended Source Diffusing into an Infinite Medium

Theory



The diagram is a schematic representation of the geometry of diffusion half-cells. Since the movement of ions is in one direction only, the diffusion equation (Fick's second law) applicable to the geometry of the above diagram is given by Equation (1) where C is the concentration of ions per unit volume in the soil medium, D_m

$$\frac{\partial C(x,t)}{\partial t} = D_m \frac{\partial^2 C(x,t)}{\partial x^2}, \qquad - \propto \; < \; x \; < \; + \propto, \quad t > 0 \; \ldots \; (1)$$

is the apparent diffusion coefficient, t is time, and x is distance. The initial conditions are given by Equations (2) and (3).

$$C(x,o) = C_o, \; -\propto < x < o \qquad \ldots \qquad (2)$$

$$C(x,o) = o, \; 0 < x < + \propto \qquad \ldots \qquad (3)$$

Since the length of the soil medium extends to $x = \pm \infty$, the concentration of ions C remains constant at $x = \pm \propto$ for all times.

The solution of Equation (1) subject to conditions expressed by Equations (2) and (3) is given by Equation (4).

$$C(x,t) = \frac{C_o}{2}\left[1 - \operatorname{erf}\frac{x}{2(D_m t)^{\frac{1}{2}}}\right] \tag{4}$$

Solutions of this general type problem can be found in Crank (1971). Equation (4) is based upon media of infinite extent but is valid also for the finite case of $x = \pm h$ as long as $C(-h, t) = C_o$ and $C(+h, t) = 0$ where t represents the time diffusion is allowed to proceed. With this in mind, the total quantity of ions Q_1 which has diffused from the region $-h < x < 0$ across the boundary $x = 0$ in in time t is given by Equation (5).

$$Q_1 = -D_m A \int_0^t \frac{\partial C(0,t)}{\partial t}\, dt = AC_o(D_m t/\pi)^{\frac{1}{2}} \tag{5}$$

Where A is the cross-sectional area of the diffusion cell. Also the total quantity of ions Q_2 remaining in the soil medium in the region $-h < x < o$ at the same time t is given by Equation(6).

$$Q_2 = AC_o h - Q_1 = AC_o h - AC_o(D_m t/\pi)^{\frac{1}{2}} \tag{6}$$

The quantity $AC_o h$ represents the total quantity of ions present in the region $-h < x < o$ at time $t = o$. Taking the ratio $Q_1/(Q_1 + Q_2) = F$ and rearranging, one obtains equation 7, an explicit expression for D_m, the apparent diffusion coefficient.

$$D_m = \pi h^2 F^2/t \tag{7}$$

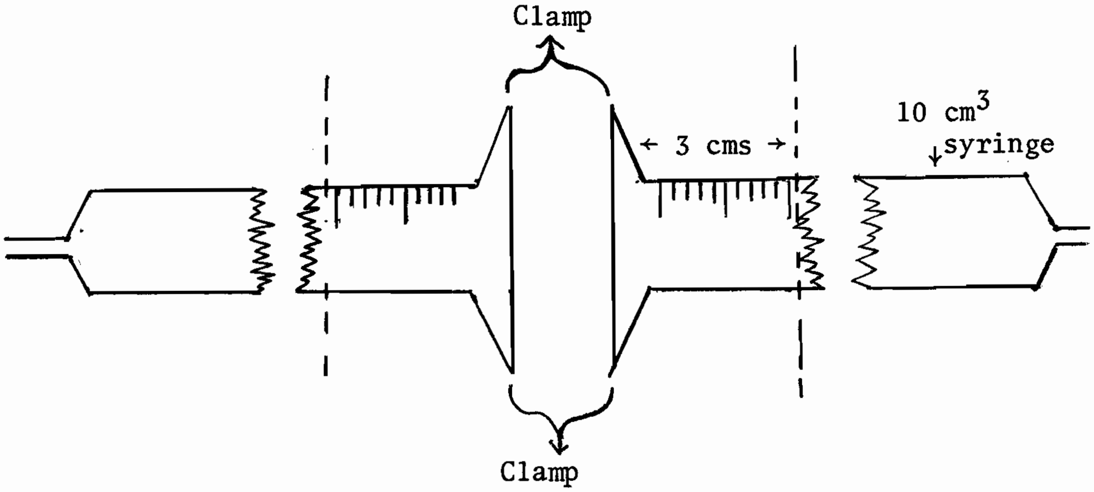
The frame of reference is with respect to the entire soil medium.

Method

10 cm^3 syringes were used as half cells. The syringes were cut along dotted lines, as shown in diagram below, to produce half-cells each of length 3 cms, and internal diameter of 1.6 cms. The bases were clamped together to provide the desired piece of apparatus for this method.

Oven-dried soil was compacted in each half cell to a desired bulk density. The packed samples were leached with $CaCl_2$ and equilibrated at desirable soil suctions. To each pair of half-cells, equilibrated at the same soil suctions, a small drop of ^{36}Cl was added to one and an equivalent volume of sodium chloride was added to the other. The half-cells were sealed with "Parafilm" and stored at 25°C for at least two weeks to obtain a uniform distribution of ^{36}Cl. At the end of storage, the cells were clamped together and a good contact was ensured by exerting simultaneous pressure on the outer ends of the soil. The cell was sealed with "Parafilm" and stored at 25°C for such time as diffusion was allowed to proceed. The half cells were separated and the total radio-activity in each was measured with the Geiger Mueller counter.

The radio-activity in counts per minute in the initially unlabelled cell is Q_1, that in the source Q_2. The length of soil in each half-cell is L, and t is the diffusion time. D_m was then calculated from Equation (7).



Arrangement of Syringes to Form the Two Half-Cells of the Extended Source Method

TABLE D.1 illustrates the in-consistent results obtained with the diffusion method based on the boundary conditions of an extended source diffusing into an infinite medium.

TABLE D I. Volumetric Moisture Content (θ), and Apparent Diffusion Coefficient (D_m), for Chateauguay Clay Loam using the Method of Diffusion based on the boundary conditions of an extended source, at a bulk density of 1.0 g cm^{-3}.

Volumetric Moisture Content (θ)	Apparent Diffusion Coefficient D_m (x 10^{-5}) cm^2 sec^{-1}	Mean θ± S.D	C.V.%	Mean D_m ± S.D.	C.V.%
0.403	0.24	0.428 ± 0.028	6.5	0.47 ± 0.24	50.7
0.423	0.46				
0.458	0.72				
0.463	1.64	0.468 ± 0.005	1.1	1.24 ± 0.43	34.9
0.469	0.78				
0.473	1.29				
0.489	1.60	0.469 ± 0.017	3.6	1.57 ± 0.06	3.6
0.461	1.60				
0.458	1.50				
0.276	24.30	0.311 ± 0.039	12.6	17.20 ± 7.79	45.3
0.353	17.36				
0.303	9.32				
0.247	0.49	0.246 ± 0.023	9.5	12.51 ± 19.94	15.9
0.231	0.14				
0.281	42.00				
0.233	7.40				
0.287	16.10	0.300 ± 0.014	4.7	13.50 ± 4.71	34.9
0.315	8.04				
0.297	16.30				