

## THE USE OF <sup>137</sup>CS DIFFUSION TO ASSESS CHANGES IN PORE GEOMETRY OF ALLOPHANE SOILS RESULTING FROM DRYING

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### SUMMARY

The apparent diffusion coefficient of an anion in soil which is the product of the diffusion coefficient of the anion in solution and the soil geometric and interaction factors, was used to assess pore geometric changes in allophane soil resulting from drying. The diffusion method was based on the boundary condition of a planar source diffusing into an infinite medium.

Drying, re-wetting and equilibrating at a matric suction of 20 k Pa produced decreases in pore volume and the apparent diffusion coefficient, and an increase in bulk density. These changes in diffusion were considered to have resulted more from changes in bulk density and volumetric moisture content than drying itself.

Compared at a common bulk density it can be said that for allophane soils, drying re-arranged soil particles and rendered the soil inert. The extent of structural changes accompanying drying was indicated by changes in slope of a plot between geometric and interaction factors versus volumetric moisture content. Structural change was least for freeze drying to be followed by a larger but equal change for air and oven drying.

### INTRODUCTION

The allophane soils are widely distributed throughout the Caribbean and Andean lands, the Pacific areas of Indonesia, Japan and New Zealand, and the United States (MAEDA et al, 1977). They are physically characterized by their low bulk density, high natural water content and high liquid limit, though the plasticity index may be small. However, drying increases the bulk density, reduces the surface area and water holding capacity and generally produces a coarse-texture

material which in some instances is non-plastic. Changes in physical properties with drying are irreversible and serve as a useful distinguishing feature between allophanes and other crystalline soils (SWINDALE, 1964).

The effects of drying on allophane soils are manifested in the field through marked differences in physical properties between the surface soil with a variable drying history, and the continuously moist or undried sub-soils (MAEDA et al, 1977). The surface soil is usually friable and shows good aggregation, with a well defined and stable interaggregate void space, while the sub-soil is massive, though still relatively permeable.

A major difficulty in accounting for difference in the physical behaviour between various allophane soils is a lack of understanding of structure especially in the size range,  $10^{-2}$   $\mu\text{m}$  to  $10^3$   $\mu\text{m}$ . The physical behaviour of these soils is still related to allophane content rather than size, shape, and arrangement of particles and their accompanying voids (MAEDA et al, 1977). The situation is further complicated by the irreversible changes in nature, size and interparticle bonding of the "structural units" upon dehydration.

A quantification of structure in the range  $10^{-2}$   $\mu\text{m}$  to  $10^3$   $\mu\text{m}$  is needed to refine a proposed model for physical properties of allophanes (MAEDA et al, 1977). This is preferred for undried allophane soils. However, it is not always possible and at times even not relevant to work with undried allophane soils. Surface soils, for example, have a variable and largely unknown drying history and a comparison of their properties would have to be based on air-dried samples. There is difficulty also in obtaining a representative subsample of a wet allophane soil which contains predominantly sand and gravel. Some of the very methods of structural characterization require the use of an initially dry soil, for example, the determination of surface area by nitrogen adsorption (GREGG and SING, 1969) or pore

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size distribution by water vapour adsorption (ROUSSEAU and WARKENTIN, 1976). It is important therefore to assess the relative effects of various methods of drying on soil structure. The method of drying producing the least structural change may then be used in sample preparation where drying is unavoidable.

The effects of various methods of drying on the plasticity of allophane soils (WARKENTIN and MAEDA, 1974) and on clay content (KUBOTA, 1972 cited by MAEDA et al, 1977) have been measured previously and inferences with respect to structure have been made. The author is however not aware of a more direct assessment of soil structural changes arising from drying. In this study therefore, changes in the pore geometric factors, tortuosity and porosity, arising from various methods of drying are assessed from the apparent diffusion coefficient of  $^{36}\text{Cl}$  in previously dried and undried samples of allophane soils.

#### MATERIALS AND METHODS

The allophane soil samples used are briefly described in Table 1. The physical properties of  $\text{N}_2$  and  $\text{N}_4$  were described previously by WARKENTIN and MAEDA (1974). Comparisons of the apparent diffusion coefficient of  $^{36}\text{Cl}$  in allophane samples previously freeze-dried, air-dried, oven-dried or with no previous drying referred to as undried, were made at a matric suction of 20 kPa and a variable bulk density, and at a fixed density of  $0.7 \text{ gm/cm}^3$  for matric suctions ranging from 20 kPa to 200 kPa. This provided an assessment of the relative changes in pore geometric factors with methods of drying.

The apparent diffusion coefficient of anionic species in soil ( $D_m$ ) is a product of its diffusion coefficient in water ( $D_0$ ); a geometric factor relating diffusion path length ( $L_e$ ) to the macroscopic distance between points ( $L$ ) and referred to as the tortuosity factor [ $L/L_e^2$ ]; factors accounting for

viscosity of soil water on diffusion ( $\alpha$ ) and for ionic interference between the diffusing ion and the matrix ( $\gamma$ ). Porosity, a second geometric factor, is also included in the apparent diffusion coefficient ( $D_p$ ) as the volumetric moisture content ( $\theta$ ), since ionic diffusion in unsaturated media is confined to the liquid phase (PORTER et al, 1963; JACKSON et al, 1963; KEMPER et al, 1964). The apparent diffusion coefficients are generally written as  $D_p$  and  $D_m$  where  $D_m = D_0 \alpha \gamma (L/L_e)^2$  and  $D_p = D_m \theta$ .

Following drying, the soils were either leached with  $0.1 \text{ M CaCl}_2$  and poured into  $3 \text{ cm}^3$  "stylex" plastic syringes, or compacted to a bulk density of  $0.7 \text{ gm/cm}^3$  in similar syringes before leaching with  $0.1 \text{ M CaCl}_2$  solution. Leaching was considered essential as allophane material could have quite considerable anion exchange capacities below a pH value of 5.5 (FIELDS and SCHOFIELD, 1960). The samples were then equilibrated at the desired soil suction on a porous plate in a pressure chamber.

A syringe containing the soil sample at the desired bulk density and soil water potential was first equilibrated at  $25^\circ\text{C}$  before radio-active labelling. The radio-active trace used was  $^{36}\text{Cl}$ , a  $\beta$ -emitter. It was applied to the soil in the form of  $\text{NaCl}$  in quantities small enough not to warrant consideration of counter diffusion, or an unbalance in electrical neutrality, though adequate for the desirable counting rate. A tiny drop of  $^{36}\text{Cl}$  labelled sodium chloride was deposited as a thin film to a smooth, level soil surface in the syringe. For the particular geometric conditions of the counter used in the study, the total radio-activity used in each measurement was about  $0.5$  to  $1.0 \mu\text{C}$ . After labelling the syringes were sealed with "parafilm" and maintained at  $25^\circ\text{C}$ .

Activity was measured with a Geiger Mueller tube (Picker Nuclear) operating at 900 volts in surroundings with an average background radiation of 40 counts per minute. After a time  $t$ , the magnitude of which varied with

Table 1. Description of source and moisture content of undried soils.

Laboratory Number	Name	Depth (cms)	Location	Co-ordinates	Moisture Content by Weight (%)
N <sub>4</sub>	Murasakino	About 150	Kitakami Tohoku	39° 18' N 141° 07' E	139.4
N <sub>2</sub>	Memuro	15 - 40	Memuro Hokkaido	42° 54' N 143° E	46.1
75 - 4	Memuro	40 - 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' N	232.6

moisture content and the soil, the syringe with the labelled soil was placed in a vertical position directly under the counter and activity was measured for two (2) minutes.

This was the activity at zero distance ( $x=0$ ). An extruded length of soil ( $x$ ) was removed and the activity of the remaining plug measured. The process was repeated several times and a series of thicknesses of the extruded soil ( $x$ ) and activity of the remaining plug were recorded. The apparent diffusion coefficient was calculated from Fick's second law for the particular boundary conditions of a substance diffusing from a planar source into an infinitely thick medium (CRANK, 1970).

An approximate solution for diffusion from a planar source was presented by LAI and MORTLAND (1961) and is

$$\text{erf } y = 1 - \left( \frac{A_x}{A_0} \right)$$

where

erf  $y$  = the error function or probability integral  
 $A_0$  = total activity at  $x=0$   
 $A_x$  = activity of plug with extruded length ( $x$ ) removed.

Values of  $A_0$  and  $A_x$  were measured and the value of  $y$  obtained from erf  $y$  in standard probability tables (SELBY, 1975). A plot of  $y$  versus  $x$  gives a straight curve with an equation

$$y = \frac{1}{2\sqrt{D_m t}} x + Y_0$$

where

$D_m$  = apparent diffusion coefficient  
 $t$  = the diffusion time in secs.  
 $Y_0 = k \sqrt{D_m t}$  with  $k$  as an absorption coefficient.

The apparent diffusion coefficient ( $D_m$ ) is then calculated from the slope of this line.

## RESULTS AND DISCUSSION

The volumetric moisture content, bulk density and apparent diffusion coefficient of four allophane samples previously dried, re-wetted and equilibrated at 20 k Pa are presented in Table 2. The N<sub>4</sub> soil received more drying treatments than the others because of the larger bulk sample available. Drying, irrespective of method, produced a decrease in volumetric moisture content upon re-wetting and equilibrating at 20 k Pa matric suction. Drying has therefore altered soil structure so that pore volume decreased, bulk density increased and the apparent diffusion coefficient ( $D_m$ ) decreased.

Assuming that for any one soil, the interaction factors  $\alpha$  and  $\gamma$  were independent of structural changes associated with drying, then a change in the apparent diffusion coefficient could be attributed directly to a change in the diffusion path length ( $L_e$ ). The data in columns 8 and 9 (Table 2) would suggest that drying resulted in an increased diffusion path length ( $L_e$ ). However, this statement is inconclusive as both bulk density and porosity, two factors known to influence the diffusion path length (HOLDER, 1978) also change with drying.

Table 2. Volumetric Moisture Content ( $\theta$ ), Bulk Density ( $D_b$ ), Apparent Diffusion Coefficient ( $D_m$ ), Geometric and Interaction Factors ( $D_m/D_0$ ), Per Cent Saturation, Ratio of Diffusion Path Lengths ( $L_{e1}/L_{e2}$ ), and Ratio of Bulk Densities ( $D_{b1}/D_{b2}$ ) for the Selected Allophane Samples at 20 k Pa matric suction.

Soil	Treatment	Volumetric Moisture Content $\theta$	Bulk ( $D_b$ ) Density g cm <sup>-3</sup>	$D_m (x 10^{-5})$ cm <sup>2</sup> sec <sup>-1</sup>	$D_m/D_0$ $\alpha\gamma(L/L_e)^2$	% saturation	* $L_{e1}/L_{e2}$	* $L_{e1}/L_{e2}$	$D_{b1}/D_{b2}$
N <sub>4</sub>	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	-	-	-
N <sub>2</sub>	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.

Correlation equation between column 9 (x) and 10(y) is:

$$y = 0.851 x - 0.0007 \quad (r = 0.969)$$

The ratio of bulk density of undried, freeze-dried and air-dried samples to that of the oven-dried samples was correlated with the corresponding ratio of diffusion path lengths. The high correlation coefficient ( $r=0.969$ ) for the equation presented in Table 2 indicates that changes in diffusion path length are largely accounted for by changes in bulk density irrespective of the method of drying. The high positive correlation supports earlier findings (HOLDER; 1978) that an increase in bulk density produces an increased diffusion path length and that the interaction factors ( $\alpha$  and  $\gamma$ ) are, within limits, independent of the structural changes arising from drying. Possible effects of drying on the diffusion path length are not readily discernible in the presence of changes in bulk density and should therefore be assessed at constant bulk density.

The relationship of apparent diffusion coefficient and volumetric moisture content for two allophane soils 75-4 and N4, dried and rewetted are presented in Figures 1 and 2. The soils were compacted to a bulk density of  $0.7 \text{ gm/cm}^3$  and the range of moisture contents correspond to a matric suction range of 20-200 k Pa. The data show that 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. For any common moisture content, oven-dried N4 soil had higher average diffusion coefficients than the air-dried soil. Similarly for 75-4 soil, at 45 percent moisture content, the freeze-dried samples had a higher average diffusion coefficient than that of the undried samples. For the same soil, at 35 percent moisture content by volume, the oven-dried samples had a higher average diffusion coefficient than that of the freeze-dried samples. Drying reduced the water holding capacity of soils, freeze drying to a smaller extent than oven and air drying.

These observations indicate that drying, irrespective of method, 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. Comparisons at common bulk density and moisture content suggest that drying renders the soil inert (cf. a sand as an example of an inert soil, and a clay as an example of an active soil). An inert sample offers a smaller diffusion path length than

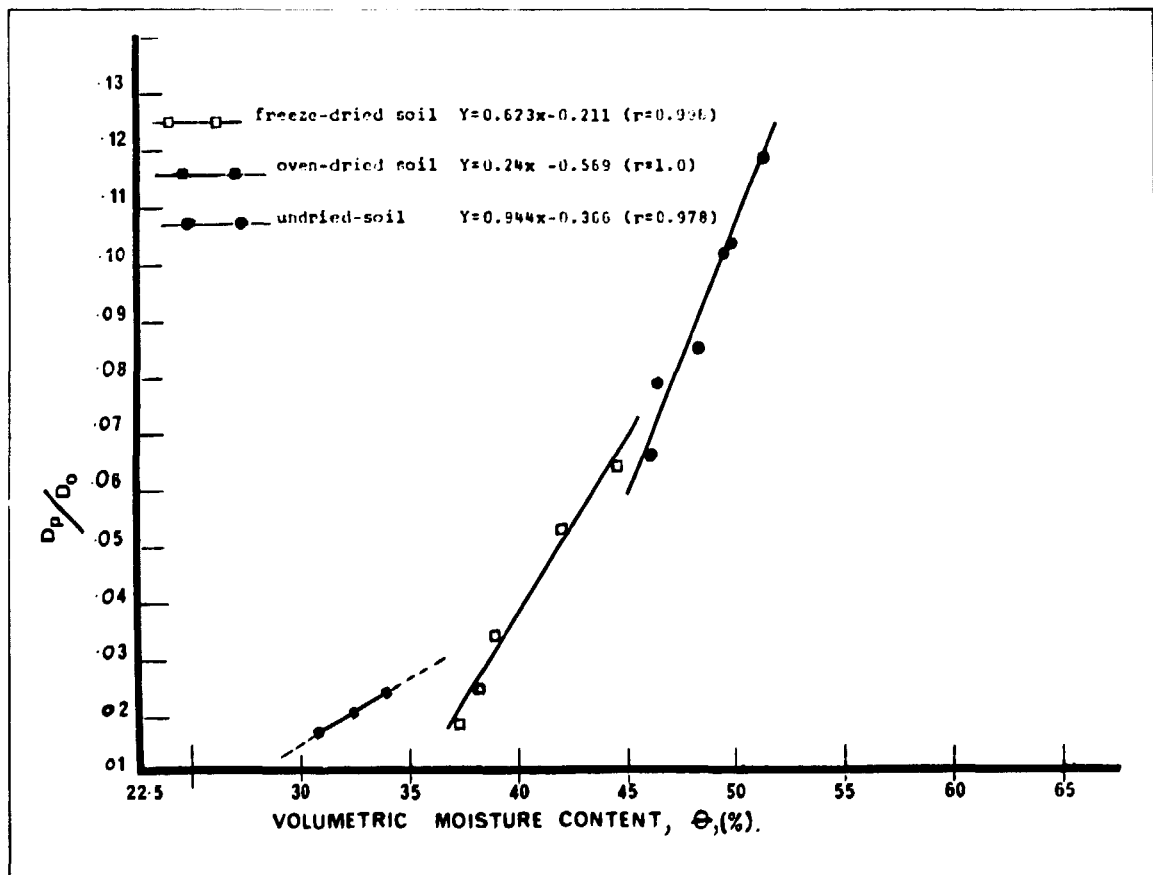


FIGURE 1 - Geometric and interaction factors  $\times$  volumetric moisture content  $[D_p/D_0]$  versus volumetric moisture

content ( $\theta$ ), for undried, freeze-dried, and oven-dried 75-4 soil samples at a bulk density of  $0.7 \text{ gm/cm}^3$

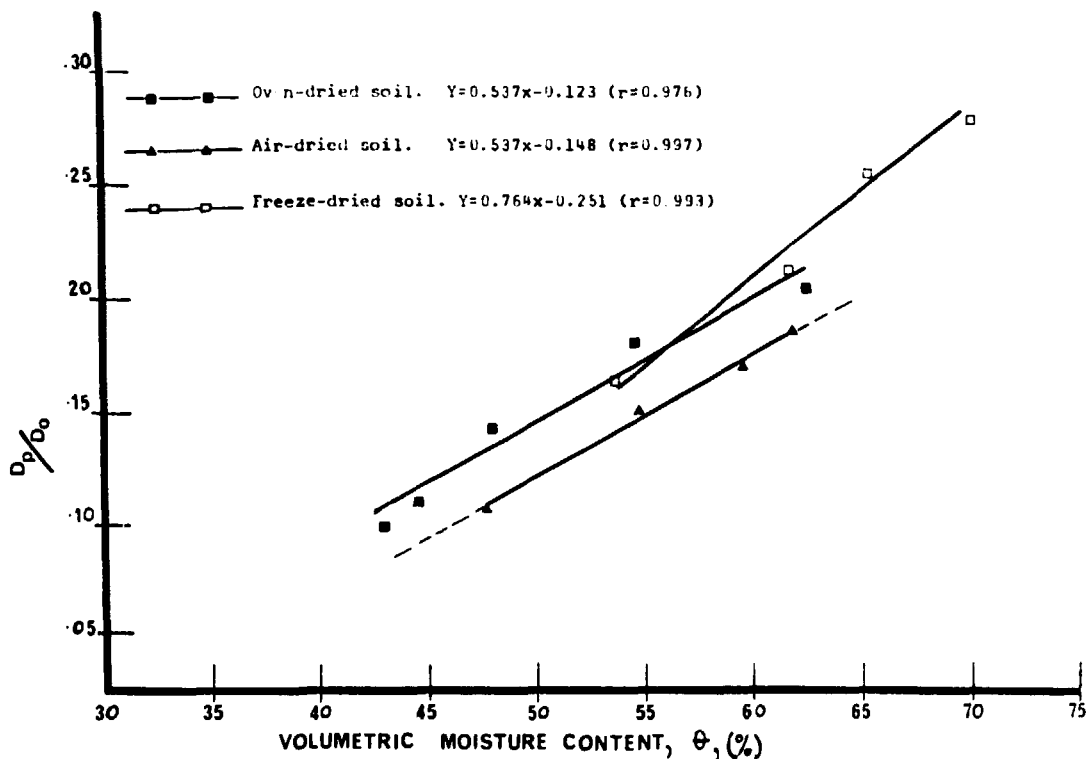


FIGURE 2 - Geometric and interaction factors  $\times$  volumetric moisture content  $[D_p/D_o]$  versus volumetric moisture

content ( $\theta$ ) for freeze-dried, air-dried, and oven-dried N4 soil samples at a bulk density of 0.7 gm/cm<sup>3</sup>.

an active sample and as the interaction factors could be considered relatively independent of changes accompanying drying, the apparent diffusion coefficient would be larger for inert than active samples.

From a consideration of the effects of drying on the apparent diffusion coefficient, it can be said that for allophane soils, drying re-arranges soil particles and renders the soil material inert. The extent of structural changes accompanying drying is indicated by the change in slope and is smaller for freeze drying than for either air or oven drying. However, oven drying while undergoing a degree of particle re-arrangement, as indexed by the slope, similar to the air-dried sample, still had a smaller diffusion path length. It is possible that oven drying also changed the nature of the "structural units".

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USO DE DIFUSÃO DE <sup>36</sup>Cl PARA AVALIAR MUDANÇAS NA GEOMETRIA DOS POROS RESULTANTES DO SECAMENTO EM SOLOS ALOFANOS

GORDON HOLDER

#### RESUMO

O coeficiente de difusão aparente de um anion em solos, que é o produto do coeficiente de difusão do anion em solução e fatores geométricos e de interação do solo, foi usado para avaliar as mudanças na geometria dos poros, resultantes do secamento, em solos alofanos. O método de difusão baseou-se na condição de contorno de uma fonte planar difundindo em um meio infinito. O secamento por congelamento reduziu os fatores geométricos e de interação, secamento por forno e por ar produziram uma reação igual, que foi maior do que a produzida por congelamento.

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