Compaction Effect on the Gas Diffusion Coefficient in Soils

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ABSTRACT

Gas diffusion is important in determining the aeration status of soils for crop production and in providing estimates of transport of volatile chemicals at waste disposal or chemical spill sites. This study investigated the effects of compaction on the gas diffusion coefficient in four soils. The experiment involved equilibrating bulk loose soil to a known matric potential in a pressure chamber, compressing the equilibrated moist soil in metal cores at a given applied stress, and measuring the concentration of N_2 diffusing through these cores into a diffusion chamber. The diffusion coefficient was calculated by fitting an analytical solution of the transient diffusion equation to the measured N_2 concentration in the diffusion chamber as a function of time. The diffusion coefficient of N_2 in four soils at four water contents and four applied loads varied exponentially as a function of air-filled porosity and was nearly the same function for all four soils. At an air-filled porosity of $\approx 10\%$, the diffusion coefficient was close to zero, reflecting a discontinuity in the pathways at an air-filled pore space of 10% or lower. A model for predicting the diffusion coefficient of gases in soils based on the diffusion coefficient of individual soil constituents was tested with the data set. For known shape factors for soil solid and soil water, the model overpredicted the diffusion coefficient for all four soils. A reduction factor suggested in the literature to account for blocked air slightly improved predictions. The ratio of the measured to predicted diffusion coefficient vs. degree of air-filled saturation suggests a second-degree correction factor to account for blocked air in soils.

THE EXCHANGE of gases between the soil and the atmosphere can occur by both convection and diffusion. Diffusion has been recognized as the most important process determining not only the aeration of soil for crop production (Glinski and Stepniewski, 1985; Hillel, 1980) but also the transport of volatile chemicals at waste disposal or chemical spill sites (Baehr, 1987; Thorstenson and Pollock, 1989) and the transport of naturally occuring radioactive gases, such as radon, from mine tailing sites and basements (Nielson et al., 1984). Because of the difficulty of measuring the gas diffusion coefficient of soil, many studies have been undertaken to develop relationships between the gas diffusion coefficient and some easily measured soil properties like air-filled porosity. A review of these studies has been given by Glinski and Stepniewski (1985). Table 1 summarizes some of the relationships in the literature between the gas diffusion coefficient and easily measurable soil properties. Except for studies by Currie (1983) and Stepniewski

(1981), there is limited information on the effects of compaction on the gas diffusion coefficient of soils.

Currie (1983) proposed that, for a unimodal pore-size distribution, the gas diffusion coefficient (D) is related to the fourth power of the air-filled porosity (f_a),

$$\frac{D}{D_o} \alpha f_a^4 \qquad [1]$$

where D_o is the gas diffusion coefficient in air. For a bimodal pore-size distribution such as aggregated soils, Currie suggested that the gas diffusion coefficient follows a fourth-degree exponential function of air-filled porosity for interaggregate pores and a linear relationship for intraaggregates pores. Since soil compaction narrows the pore-size distribution, Currie (1984) suggested that the exponential form of the diffusion relationship shifts to the linear form as soil compaction increases. Using five different levels of compaction on 1- to 2-mm aggregates, Currie (1984) showed that the linear relationship between the gas diffusion coefficient and air-filled porosity was nearly the same for all levels of compaction. However, the exponential relationships varied (became less steep) with an increase in soil compaction. Stepniewski (1981) proposed a linear relationship between the log of the diffusion coefficient and the soil bulk density and water content.

Since the work of de Vries (1950, 1952), limited research (Rust et al., 1957) has been reported on prediction of the gas diffusion coefficient in soil based on its primary or secondary constituents. Based on the electrical conductivity theory, de Vries (1950) suggested that the apparent diffusion coefficient of a gas in soil can be calculated from the weighted mean diffusion coefficient of its constitutents like soil solids, soil water, and soil air. Since the diffusion coefficient of soil solids is practically zero and that for soil water is about 10^{-4} times that of soil air (i.e., often negligible), the diffusion coefficient of soil air can be written as:

$$D = \frac{k_a X_a D_o}{k_s X_s + k_w X_w + k_a X_a} \qquad [2]$$

where X and k are the volume fraction and weighting constants, respectively; and subscripts s, w, a correspond to solid, water, and air, respectively. The value of X_a in Eq. [2] is same as the air-filled porosity, f_a. Since the diffusion coefficient of gases present in air

Table 1. Various formulations used in the literature to represent the diffusion coefficient of gas in soils. Variables D and D_o are diffusion coefficients of a gas in soil and air, respectively; ρ_b is bulk density; W is mass wetness; f_a is air-filled porosity; f is total porosity; k_s is a weighting factor for soil solids; A is a correction factor for blocked air; r, u, m, v, a, b, and c are empirical constants; $\bar{d}$ and RMSE are the bias and root mean square error defined by Eq. [13] and [14].

Author	Year	Model	$\bar{d}$	RMSE	Equation No.
Penman	1940	$\dfrac{D}{D_o} = 0.66 f_a$	0.060	0.065	[15]
Buckingham	1904	$\dfrac{D}{D_o} = f_a^2$	−0.034	0.045	[16]
Marshall	1959	$\dfrac{D}{D_o} = f_a^{3/2}$	0.037	0.044	[17]
Millington	1959	$\dfrac{D}{D_o} = \dfrac{f_a^{3.33}}{f^2}$	−0.017	0.039	[18]
Sallam et al.	1983	$\dfrac{D}{D_o} = \dfrac{f_a^{3.1}}{f^2}$	0.015	0.049	[19]
Currie	1960b	$\dfrac{D}{D_o} = r f_a^u$	0.001	0.021	[20]
Troeh et al.	1982	$\dfrac{D}{D_o} = \left(\dfrac{f_a - m}{1 - m}\right)^v$	0.001	0.020	[21]
Stepniewski	1981	$\log\left(\dfrac{D}{D_o}\right) = a + b\rho_b + cW$	0.016	0.080	[22]
de Vries	1950	$\dfrac{D}{D_o} = A\dfrac{f_a}{f_a + k_s(1 - f_a)}$	0.015	0.030	[23]

are different for a given temperature and pressure, D and D_o in Eq. [2] represents an average value for diffusion coefficient of various gases. The weighting contant k_i in Eq. [2] is defined as

$$k_i = \frac{1}{3}\sum_{a,b,c}\left[1 + \left(\frac{D_i}{D_o} - 1\right)g_a\right]^{-1} \qquad [3]$$

where g_a is a shape factor for dispersed-phase particles and is determined by the lengths of a particle in the x, y, and z coordinate directions (a, b, and c). Assuming soil particles are ellipsoidal, de Vries (1966) suggested g_a values of 0.144 for quartz, 0.125 for feldspars, and 0.5 for peat.

When air is a continuous medium and solids and water are dispersed phases, the weighting constant for air, k_a, is 1 and the weighting factor, k_i, for soil solids and soil water can be calculated from Eq. [3] as

$$k_s = k_w = \frac{1}{3}\sum_{a,b,c}\left(\frac{1}{1 - g_a}\right) \qquad [4]$$

Substitution of Eq. [3] and [4] in Eq. [2] results in the following equation that can be used to calculate the diffusion coefficient of gases in soil based on the proportion of various soil constitutents:

$$\frac{D}{D_o} = \frac{X_a}{X_a + k_s(X_w + X_s)} = \frac{X_a}{X_a + k_s(1 - X_a)} \qquad [5]$$

For soils where a certain portion of air-filled pores may be blocked and some of the pores are not contin-

uous, de Vries (1950) introduced the following reduction factor, A, to correct the calculated diffusion coefficient from Eq. [5]:

$$A = \frac{1 - X_0}{1 - 0.5X_0} \qquad [6]$$

where X_0 represents the volume fraction of blocked pores and is defined as

$$X_0 = \epsilon(1 - X_a)X_a \qquad [7]$$

where ϵ is an empirical constant. Equation [7] suggests that the volume of blocked air follows a second-degree parabola with the maximum occurring at $X_a = 0.5$. The minimum values of blocked air correspond to 0 at $X_a = 0$ and $X_a = 1.0$. The reduction factor (Eq. [6]) also follows a second-degree parabola with a minimum value at $X_a = 0.5$. De Vries (1950) found a good agreement between Penman's (1940) measured values of the diffusion coefficient and calculated values using a g_a value of 0.18 and $\epsilon = 0.4$. A value for ϵ of 0.4 is equivalent to 10% blocked air at $X_a = 0.5$.

The objectives of this study were to: (i) investigate the effects of compaction and soil wetness on the gas diffusion coefficient of four different-textured soils and (ii) test the model of de Vries (1950) for predicting the gas diffusion coefficient of soil based on the diffusion coefficient of its constituents.

MATERIALS AND METHODS

Experimental Apparatus

The diffusion apparatus used in this experiment was based on the design suggested by Rolston (1986). It consisted of
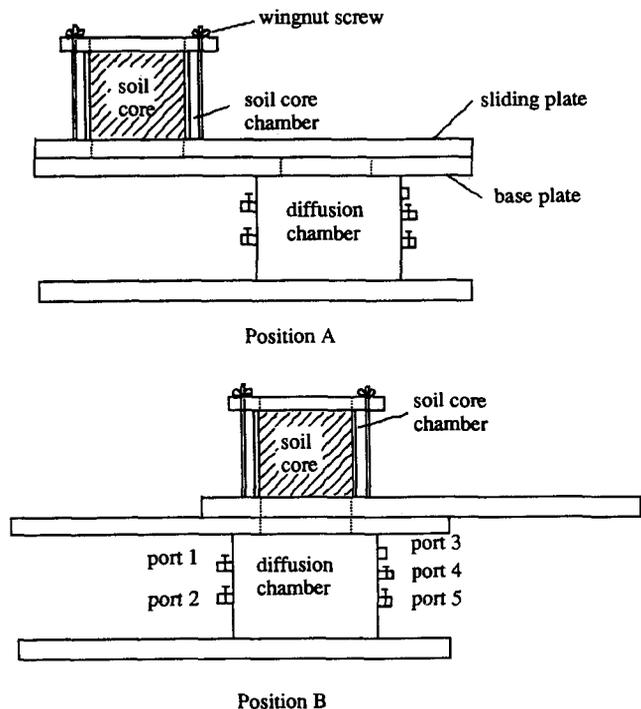

Fig. 1. A schematic representation of the chamber setup for measuring the gas diffusion coefficient of a soil.

a diffusion chamber of 460 cm³, a base plate, and a sliding plate, all made of Plexiglas (Fig. 1). The diffusion chamber had five ports. Port 1 and Port 5 were connected to a small air pump that provided circulation to achieve uniform mixing of the gases in the chamber. Port 2 had a valve that was used as an inlet to introduce Ar gas into the diffusion chamber. Port 4 had an exhaust valve that was used to balance the pressure inside and outside the diffusion chamber. Port 3 was covered tightly by a rubber septum and used as a sampling port. The septum provided a seal for the diffusion chamber and facilitated sampling of the chamber gas with a hypodermic needle.

The base plate was constructed with two slots, to ensure alignment of the soil core with the opening in the base plate. Vacuum grease was used between the sliding plate and the base plate. The soil core was held in the core chamber by a fine metal screen, which in turn was supported by a metal wire frame. Two rubber O-rings, one at the top of the base plate in a slot around the opening and the other immediately underneath the soil core chamber, were used for sealing purposes.

A tank of compressed gas mixture containing 90% Ar and 10% N_2 was used to fill the diffusion chamber and to set the initial gas concentration of the diffusion experiment. Argon and N_2 were used because they are relatively inert. Also the diffusivity and solubility of Ar in water is approximately same as that of O_2.

A mass spectrometer (Model LKB-9000 GC/MS, KBL-Produkter, Bromma, Sweden)[1] was used to analyze the concentration of N_2 in the diffusion chamber. Either a 7.6 by 0.3 cm (3 ft. by 1/8 in.) stainless steel column packed with 0.25/0.177 mm (60/80 mesh) molecular sieve 5A followed by a 25.4 by 0.3 cm (10 ft. by 1/8 in.) stainless steel column packed with 0.149/0.125 mm (100/120 mesh) Carbosieve S-II (Supelco, Bellefonte, PA), or a 3-m-long 0.3-cm (1/8 in.) o.d. stainless steel column packed with 0.25/0.177 mm (60/80 mesh) Tenax GC was used in this experiment. Room temperature during the course of this study varied from 18.5 to 23.0 °C with a mean value of 20.2 °C and a standard deviation of 0.6 °C.

Soils

Soils used in this study were four of the seven soils used by Gupta et al. (1990, unpublished data) in soil compaction studies. The soils were Sharpsburg silty clay loam (fine, montmorillonitic, mesic Typic Argiduoll) from Nebraska, Miles loamy sand (fine-loamy, mixed thermic Udic Paleustalf) from Texas, Blount silty clay loam (fine, illitic, mesic Aeric Ochraqualf) from Ohio, and Cecil loamy sand (clayey, kaolinitic, thermic Typic Kanhapludult) from Alabama. These soils are representative of areas where soil compaction is a major problem. Detailed characterization on particle-size distribution and other hydraulic and mechanical properties are given in Gupta et al. (1990, unpublished data).

Bulk samples of the surface soil were shipped to Minnesota, where they were air dried, ground, and passed through a 2-mm sieve. Particle size (Table 2) was determined by direct sieving for the sand fraction and by the pipette method for the silt and clay fraction (Gee and Bauder, 1986). Organic matter content was measured by using the wet combustion method (Nelson and Sommers, 1982).

Soil Core Preparation

Gas diffusion coefficients were measured on soil cores that were compressed at four applied stresses and were at four initial water contents. The procedure for core preparation involved saturating loosely packed, large (2–3-kg)

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[1] The trade names are for the benefit of readers and do not imply endorsement from the University of Minnesota.

Table 2. Particle-size analysis and the organic C (OC) content of the four soils used in this study

Soil series	Subgroup	Sand (0.05–2.00 mm)	Silt (0.002–0.05 mm)	Clay (<0.002 mm)	OC	Tex-ture†
		%	%	%	g kg⁻¹	
Sharpsburg	Typic Argiudoll	6.4	56.6	37.0	21.0	sicl
Miles	Udic Paleustalf	82.5	11.5	6.0	2.0	ls
Blount	Aeric Ochraqualf	15.9	56.2	27.9	27.0	sicl
Cecil	Typic Hapludult	78.5	16.7	4.8	6.0	ls

† sicl - silty clay loam; ls = loamy sand.

samples of air-dried soil on a pressure plate overnight and then desorbing the saturated soil in a pressure plate apparatus to a known pressure head (Gupta et al., 1990, unpublished data). The equilibrating pressure heads were 3.3, 10.0, 50.0, and 150.0 m. The average water content corresponding to the above four pressure heads for all four soils used in this study are given in Table 3.

Soil cores were prepared by compressing a known weight of moist soil in metal cores using an Instron Universal Testing Machine. The procedure involved stacking and taping together three metal cylinders (7.6 cm in diam. by 7.6 cm high), pouring a known weight of moist soils into the rings, and compressing (1 cm h⁻¹) the soil at both ends with metal pistons until the given applied mechanical load was achieved. Treatments of applied mechanical loads were 0.225, 0.445, 0.900, and 1.800 kN. These loads translated to applied mechanical stresses of 49.3, 98.7, 197.4 and 394.7 kPa in this study (Gupta et al., 1990). The middle core was separated from the end cores using a thin cutting wire, and was used for the gas diffusion measurements. Gupta and Larson (1979) found that cores compressed using the above procedure had minimal variation in soil packing along the length of the core. The bulk density of the middle core was calculated from the mass of the wet soil in the core, soil water content, and the core volume. Porosity of all four soils varied from 0.45 to 0.66, 0.41 to 0.62, 0.39 to 0.52, and 0.38 to 0.46 at applied stresses of 49.3, 98.7, 197.4, and 394.7 kPa, respectively.

For each soil, two soil cores were prepared at each of the 16 combinations of four soil water contents and four applied mechanical loads. This corresponded to a total of 128 soil cores for the four soils used in this study. Since some of the samples at high water content and at high mechanical load had no measurable gas diffusion, the data for these cores are not included here. Some additional samples that were disturbed while handling were also discarded. The data corresponds to a total of 105 samples, out of which 20 samples belong to Sharpsburg silty clay loam, 33 samples belong to Miles loamy sand, 25 samples belong to Blount silty clay loam, and 27 samples belong to Cecil loamy sand.

Experimental Procedure

The first step in the experiment was to place the soil core on the sliding plate (Position A, Fig. 1). The wing nuts

Table 3. Gravimetric water content (W) of loosely packed soils at four pressure heads.

Soil	Water content			
	3.3 m	10.0 m	50.0 m	150.0 m
	g g⁻¹			
Sharpsburg	0.36	0.34	0.28	0.25
Miles	0.06	0.06	0.05	0.05
Blount	0.34	0.31	0.30	0.29
Cecil	0.06	0.05	0.04	0.03

were tightened to prevent gas diffusion along the seal between the sliding plate and the core cylinder wall. Two C-clamps were used to hold the base and the sliding plate together to prevent gas diffusion between the sliding plate and the base. During this time, all valves on the Ar gas tank and diffusion apparatus were closed. The air-circulation pump was turned on and Ports 1 and 5 were opened to circulate the gas in the diffusion chamber. The valves of the Ar gas tank, the inlet valve of the diffusion chamber (Port 2), and the outlet valve (Port 4) that allowed the gas to escape from the diffusion chamber to the atmosphere were then opened. The Ar gas was injected into the diffusion chamber for 3 to 5 s, and then Port 2 was closed, followed immediately by the closing of Port 4. A gas sample was taken from the chamber to determine the initial N_2 concentration (C_o) in the diffusion chamber. The C-clamps were then slightly loosened and, while pressing down on the sliding plate, the sliding plate was carefully slid to Position B, and a stop watch was started. The C-clamps were tightened again while continuing to press on the sliding plate.

After the core was over the diffusing chamber, the chamber was sampled through the septum (Port 3) for gas concentration at various times. A 1.2-mL gas sample was taken with a 5-mL syringe at 0, 3, 10, 20, 30, 40, 50, 60, 75, and 90 min after the start of the experiment. The gas sample from the diffusion chamber was injected into the mass spectrometer for N_2 analysis. Although extraction of the sample from the chamber will result in a pressure difference (1.2 × 100/460 = 0.26%) between the chamber and the outside atmosphere, the convective flux of gases due to pressure gradient was assumed small.

Theory of the Experiment and Data Analysis

Conservation of mass in combination with Fick's law gives the following differential equation for one-dimensional unsteady-state diffusion of a gas constituent in unsaturated porous media:

$$f_a \left(\frac{\partial C}{\partial t} \right) = D \left(\frac{\partial^2 C}{\partial x^2} \right) \qquad [8]$$

where D is the diffusion coefficient $(m^2 \, s^{-1})$, C is the concentration of diffusing gas per gas phase volume $(g \, m^{-3})$, f_a is the air-filled porosity, t is time (s), and x is coordinate position (m).

Referring to Fig. 2, the boundary conditions for Eq. [8] are:

$$C = C_S \qquad x = 0, \qquad t > 0 \qquad [9a]$$
$$C = C_L = f(t) \qquad x = L, \qquad t > 0 \qquad [9b]$$

where L is the length of the soil core, C_S is the concentration of the diffusing gas in the atmosphere $(g \, cm^{-3})$, and C_L is the concentration of the diffusing gas in the diffusion chamber at time t. During the experiment C_S remains constant, whereas C_L increases with time due to the flux of the gas diffusing into the chamber.

The initial conditions for the experiment are:

$$C = C_S \qquad 0 \le x < L, \qquad t = 0 \qquad [10a]$$
$$C = C_o \qquad x = L, \qquad t = 0 \qquad [10b]$$

where C_o is the initial concentration of N_2 in the diffusion chamber $(g \, cm^{-3})$.

Applying the above boundary and initial conditions to Eq. [8] yields the solution (Carslaw and Jaeger, 1959, p. 128; Rolston, 1986) for the concentration of N_2 in the chamber, C_L:
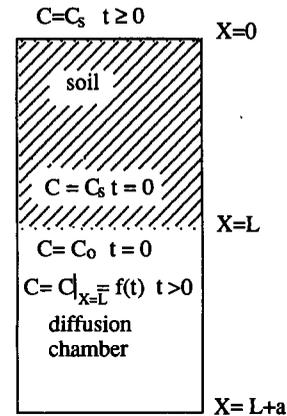

Fig. 2. Initial and boundary conditions of the diffusion experiment. C is the concentration of diffusing gas, C_s is the concentration of diffusing gas in the atmosphere, C_o is the concentration of diffusing gas initially in the diffusion chamber, L is the length of the soil core, X is coordinate position, a is the length of the diffusion chamber, and t is time.

$$\frac{C_L - C_s}{C_o - C_s} = \sum_{n=1}^{\infty} \frac{2h \exp(-D\alpha_n^2 t/f_a)}{L(\alpha_n^2 + h^2) + h} \qquad [11]$$

where $h = f_a/aE_c$, E_c is the air content of the chamber (1.0 m^3 air m^{-3} chamber), a is the volume of the chamber per unit area of the soil column, and α_n with $n = 1, 2, 3, \ldots$ are the positive roots of $(\alpha_n L) \tan(\alpha_n L) = hL$.

The assumptions made in this analysis are: (i) the initial gas concentration in the soil column is uniform across the column length, (ii) the concentration of gases in the diffusion chamber is uniformly distributed, and (iii) there is no pressure gradient between the atmosphere and gases in the chamber.

The diffusion coefficient of N_2 in soil was determined by fitting Eq. [11] to the measured concentrations normalized as $(C_L - C_s)/(C_o - C_s)$ vs. time data. This fitting process was performed using the first 10 terms of Eq. [11] with trial-and-error values of D. The value of D that yielded the minimum total SSD between the measured and calculated concentrations was taken to represent the diffusion coefficient of the soil core. The SSD is defined as:

$$SSD = \sum_{i=1}^{N} \left(\frac{C_{Lm} - C_s}{C_o - C_s} - \frac{C_{Lc} - C_s}{C_o - C_s} \right)_i^2 \qquad [12]$$

where C_{Lm} is the measured N_2 concentration in the diffusion chamber at time t, C_{Lc} is the calculated N_2 concentration in the chamber for an assumed D at the corresponding time t, and N is the number of measurements for each soil sample. The diffusion coefficient was expressed as D/D_o, where D_o is the diffusion coefficient of N_2 in free air. The D_o value was calculated using Fuller's correlation as given in Liley and Gambill (1973). The calculated value of D_o for N_2-Ar diffusion in free air at 20 °C, 101 kPa pressure was 0.0698 $m^2 \, h^{-1}$. In the above analysis, the value of C_s was taken to by 0.909 kg m^{-3} (the mole fraction for atmospheric N_2 is 0.781).

Calculation of diffusion coefficients by fitting Eq. [11] to the measured N_2 concentration in the diffusion chamber assumes that Fickian diffusion was the controlling process in the experimental setup described in this study. Jaynes and Rogowski (1983) and Thorstenson and Pollock (1989) raised concerns regarding the adequacy of Fick's law to completely describe the diffusion of a gas through porous

media in a multicomponent system. These concerns relate to the contribution of Knudsen diffusion and the intrinsic coupling of diffusive and viscous fluxes that may arise due to a pressure gradient generated by diffusion of various gases with different molecular weights. Since molecular weights of the dominating gases (N_2, Ar, and O_2) in our experiment are nearly similar, we assumed that the errors due to the assumption of Fickian diffusion as the dominating mechanism would be relatively minor.

Best fit of diffusion measurements in this study to the relationships in Table 1 was tested by calculating bias (d) and RMSE.

$$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} d_i \qquad [13]$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} d_i^2} \qquad [14]$$

where d_i is the difference between the predicted–fitted and measured values of D/D_o. Standard error of the regression and coefficient of determination in Table 4 were obtained by fitting the data to Eq. [20] and [21] (Table 1) using a nonlinear regression technique.

RESULTS AND DISCUSSION

Effect of Compaction on the Gas Diffusion Coefficient

The ratio of the gas diffusion coefficient in soil to the gas diffusion in air as a function of air-filled porosity for four soils at various applied mechanical loads and soil wetness conditions is plotted in Fig. 3. The gas diffusion data basically consist of two data sets representing two groups of soils, i.e., coarse-textured soils (Cecil and Miles loamy sands) and fine-textured soils (Blount and Sharpsburg silty clay loams). The air-filled porosities of coarse-textured soils varied between 0.3 and 0.5, whereas the air-filled porosities of the fine-textured soils varied from 0 to 0.42. Corresponding normalized gas diffusion coefficients varied from 0.13 to 0.33 for the coarse-textured soils and 0.0 to 0.20 for the fine-textured soils. The higher values of the gas diffusion coefficient in the coarse-textured soils reflect the presence of large continuous pores.

Except for air-filled porosities >0.4, the relative gas diffusion coefficient for all four soils followed nearly the same relationship, i.e., an exponential decrease with a decrease in air-filled porosity. Figure 3 shows that, independent of the soil, the air-filled porosity effectively represents the effects of varying loads

and soil wetness conditions on the gas diffusion coefficient. This observation is in contrast to the findings of Currie (1984), who showed that for a 1- to 2-mm aggregated soil a different exponential function described the diffusion coefficient vs. air-filled porosity relationship at each level of bulk density. The reasons for this difference are not apparent.

At air-filled porosity >0.4, there is some scatter in the diffusion data (Fig. 3); however, there was no consistent relationship of diffusion vs. air-filled porosity as a function of either applied mechanical load or the soil wetness condition. At air-filled porosities <0.1, the gas diffusion coefficient for the two heavy soils is practically zero (Fig. 3). This is similar to the observations of Blake and Page (1948), de Vries (1950), and Grable and Siemer (1968), who suggested that at about 10% air-filled porosity, air-filled pores are mostly isolated air pockets (blocked by water films) and thus do not contribute to efficient exchange of gases between the soil and the outside atmosphere.

Representation of Diffusion vs. Air-filled Porosity Relationship

As discussed above, several different types of relationships have been suggested in the literature (Table 1) to represent the relationship between the normalized gas diffusion coefficient and the soil air-filled porosity. The coefficient of some of these relationships has also been used to quantify the tortuous length of the pores in the soil. For example, Penman (1940) suggested the following linear relationship between the diffusion coefficient and air-filled porosity:

$$\frac{D}{D_o} = 0.66 f_a \qquad [15]$$

where 0.66 was assumed to represent the tortuosity coefficient of the soil. In other words, the apparent path of the pore is about two-thirds the length of the real average path of diffusion in the soil. However as pointed out by Hillel (1980), since tortuosity depends on the fractional volume of air-filled pores, it stands
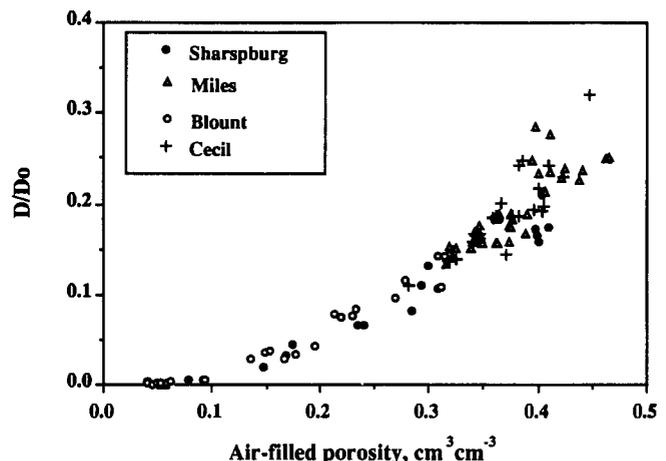
Table 4. Coefficients of Currie (1960a,b) and Troeh et al. (1982) equations (Eq. [20] and [21]) for four soils; SE and R^2 are the standard error of regression and coefficient of determination, respectively.

Soil	Currie equation†				Troeh equation‡			
	r	u	SE	R^2	m	v	SE	R^2
Sharpsburg	0.95	1.78	0.017	0.95	0.02	1.77	0.017	0.95
Miles	0.91	1.59	0.024	0.69	-0.04	1.81	0.024	0.68
Blount	1.22	1.92	0.010	0.96	0.04	1.63	0.010	0.96
Cecil	1.51	2.10	0.020	0.78	0.14	1.28	0.022	0.78

† $D/D_o = r f_a^u$.
‡ $D/D_o = [(f_a - m)/(1 - m)]^v$.

Fig. 3. Ratio of the gas diffusion coefficient in soil (D) to the gas diffusion coefficient in air (D_o) as a function of air-filled porosity for four soils that have been subjected to four mechanically applied loads at four soil wetness conditions.
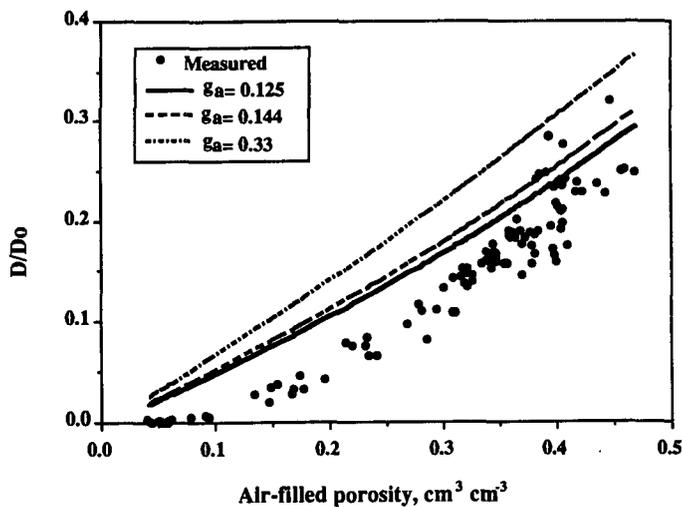
Fig. 4. A comparison of measured and calculated (no adjustment for blocked air) gas diffusion coefficients (D/D_o) as a function of air-filled porosity. Calculated values correspond to water and solid shape factors (g_a) of 0.125, 0.144, and 0.33.
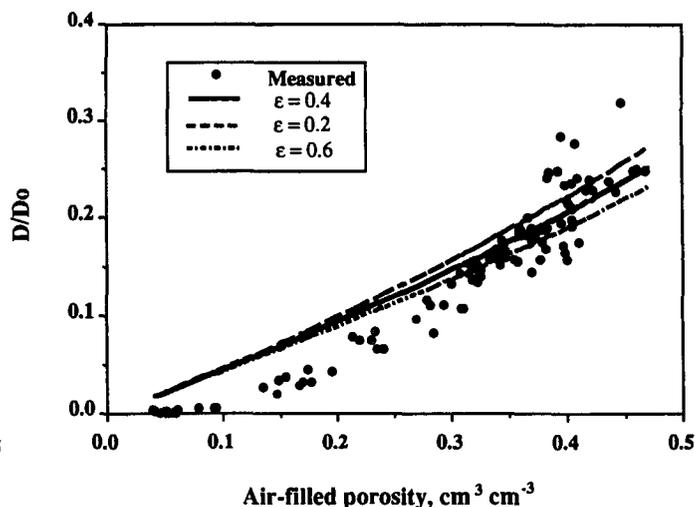

Fig. 6. Comparison of measured and calculated (shape factor g_a = 0.125) diffusion coefficient (D/D_o) for three values of the empirical constant ϵ.
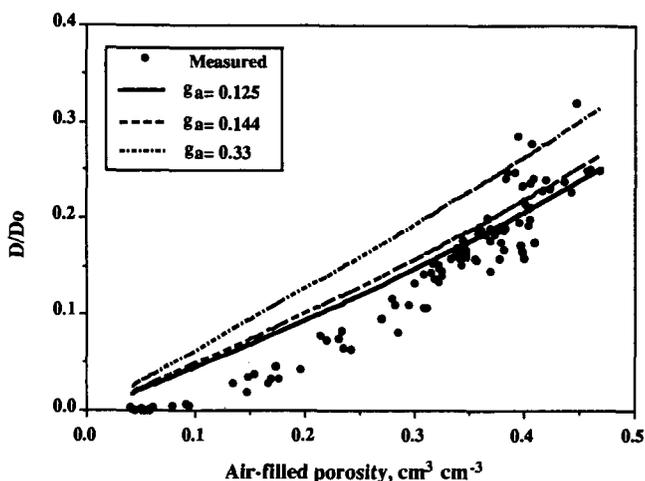

Fig. 5. A comparison of measured and calculated (adjusted for blocked air using the procedure of de Vries, 1950) gas diffusion coefficients (D/D_o) as a function of air-filled porosity. Calculated values correspond to water and solid shape factors (g_a) of 0.125, 0.144, and 0.33.

to reason that the tortuous path would decrease with an increase in air-filled porosity. Thus, Penman's (1940) constant of 0.66 for the tortuosity coefficient may hold only for a limited range of air-filled porosities (Hillel, 1980).

The gas diffusion measurements in this study were used to test the relative diffusion coefficient relationships given in Table 1. The relationships in Table 1 are separated into two groups: (i) equations where the constants are fixed (Eq. [15]–[19]), and (ii) equations where empirical constants are estimated by fitting the relationships to the data in this study (Eq. [20]–[23]). Since the constants in the second group were evaluated by fitting the equations to the data, it was expected that these equations would be a better predictor of our data. Comparison of bias and RMSE among the equations in the first group shows that the relationships suggested by Millington and Quirk (1961)

(Eq. [18]) and Sallam et al. (1984) (Eq. [19]) best describe our data (smallest $\overline{d}$ and RMSE). Among equations in the second group, the equations of Currie (1960a,b) and Troeh et al. (1982), respectively, best represent the normalized diffusion coefficient vs. air-filled porosity relationship for all four soils at various applied loads and several different water contents. The values of constants $(r, u, m,$ and $v)$ in Eq. [20] and [21] for each of the four soils are listed in Table 4. The values of $r, u, m,$ and v for the four soils together are 1.16, 1.86, 0.04, and 1.59, respectively. The value of m in Eq. [21] (Troeh et al., 1982) represents the air-filled porosity of soil when the gas diffusion coefficient is zero. For the four soils studied, this value varied between -0.04 and 0.14 (Table 4). The negative value of m for Miles loamy sand and a high value of m for Cecil loamy sand appears to be an extrapolation error of fitting a nonlinear regression to the data, which is clustered around high air-filled porosities.

It has been suggested in the literature (Shearer et al., 1973; Sallam et al., 1984) that the theoretically derived model (Eq. [18]) of Millington (1959) adequately describes the relationship between the gas diffusion coefficient and air-filled porosity of soils. For example, Sallam et al. (1984) showed that, at low air-filled porosities $(f_a < 0.15)$, the exponent β in Eq. [24] is only slightly different than the theoretically derived value of Millington (3.1 compared with 3.33).

$$\frac{D}{D_o} = \frac{f_a^\beta}{f^2}$$ [24]

We also tested this hypothesis by performing nonlinear regression on our data set. The exponent β corresponded to 3.29 for the complete data set (105 cases) and 2.58 for measurements corresponding to $f_a \leq 0.15$ (16 cases from only Sharpsburg and Blount). Standard error and R^2 for the complete data set were 0.03 and 0.77, respectively. The β values for Miles loamy sand, Cecil loamy sand, Sharpsburg silty clay loam, and Blount silty clay loam were 3.32, 3.61, 2.75, and 2.56, respectively.

Prediction of the Soil Gas Diffusion Coefficient

The relationship between the diffusion coefficient and air-filled porosity calculated using Eq. [5] for shape factors of 0.125, 0.144, and 0.33 for soil solid and soil water is shown in Fig. 4. The values of 0.144 and 0.125 represent the shape factors of quartz and feldspars, whereas 0.33 corresponds with the perfectly spherical particles (de Vries, 1966). The data shows that the calculated values using Eq. [5] are higher than the measured values at almost all air-filled porosities. We assumed that the differences between the measured and calculated values in Fig. 4 were mainly due to not accounting for blocked air-filled pores in Eq. [5]. To account for the blocked air, we adjusted the calculated values of the diffusion coefficient in Fig. 4 with a reduction factor (Eq. [6]) suggested by de Vries (1950).

Figure 5 shows that the calculated values of the diffusion coefficient after correction for blocked air (ϵ = 0.4) are still higher than the measured values for most ranges of air-filled porosity. Only at air-filled porosities >0.4 are calculated values of the diffusion coefficient corrected for blocked air close to the measured values. This is about the range of air-filled porosities for which de Vries (1950) showed that his calculated values matched those of Penman's (1940) measurements. Assuming that higher values of the predicted diffusion coefficient at air-filled pore space <0.4 were due to lack of proper accounting for blocked air, we further ran a sensitivity analysis of de Vries' (1950) calculations as a function of ϵ. Figure 6 shows an example of these calculations with g_a = 0.125. Although increasing the proportion of blocked air in soil brings the predicted diffusion coefficient closer to the measured values at air-filled porosities between 0.3 and 0.4, the calculated values are still higher or lower than the measured values outside the above range of porosities. Relatively little change in the calculated diffusion coefficient at air-filled pore space <0.1 also suggests that the procedure of de Vries (1950) is insensitive in accounting for blocked air at low air-filled porosities (near saturation). Since Eq. [6] and [7] are similar to an empirical adjustment of the calculated de Vries (1950) values, we propose the following simple procedure to correct for the calculated values of the diffusion coefficient from de Vries (1950) method (Eq. [5]).

Figure 7 is a plot of the ratio of the measured to calculated diffusion coefficient (correction factor) as a function of the degree of air saturation (ratio of air-filled porosity to total porosity) for g_a = 0.125. The figure shows that the value of the CF varies from 0 to 1.2 as air saturation increases from 10 to 82%. Although a ratio >1 occurs only at a few data points, it implies an underestimation of the diffusion coefficient from Eq. [5]. In general, the ratio increases from 0 to some maximum value as the air saturation increases from 0 to ≈55%. Above air saturation of 55%, the ratio is nearly constant (0.88), thereby suggesting that the effect of blocked air is minimal on the gas diffusion coefficient from air saturation of 55 to 100%. The simple linear relationship between CF and degree of air saturation from 0 to 55% is

$$CF = -0.08 + 1.5\frac{f_a}{f} \qquad R^2 = 0.89 \qquad [25]$$
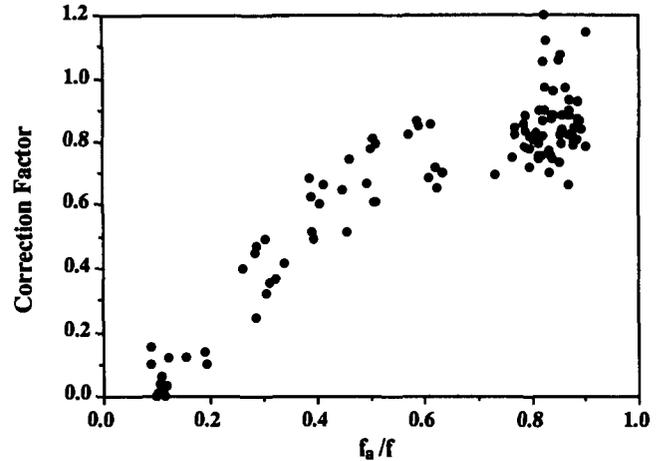

Fig. 7. Ratio of the measured to calculated diffusion coefficient correction factor (CF) as a function of degree of air saturation (air-filled porosity (f_a)/total porosity (f)).

Although the CF values also depended (data not shown) on the g_a value used for diffusion calculations (Eq. [5]), it is realistic to assume that, in mineral soils, the g_a value for soil solids and water will be close to the value of soil solids (0.125 or 0.144) because water, being a wetting agent, tends to spread around solid and assume its shape. The simple linear relationship for CF and degree of air saturation for g_a = 0.144 is

$$CF = -0.08 \pm 1.41\frac{f_a}{f} \qquad R^2 = 0.89 \qquad [26]$$

CONCLUSIONS

The gas diffusion coefficient in soils vs. air-filled porosity relationship was nearly the same irrespective of soil type, soil wetness, or soil bulk density. Exponential relationships of the form given by Currie (1960a,b) and Troeh et al. (1982) best represented gas diffusion coefficients for all four soils. At an air-filled porosity of about 10%, the gas diffusion coefficient was practically zero, thereby suggesting the presence of air as isolated pockets and a discontinuity in the pathways of air-filled pores for gas diffusion. The exponent of the commonly used theoretical model (Millington, 1959) corresponded to 3.29 for our data set. This is similar to the value (3.33) previously reported in the literature. For the data set corresponding to low air-filled porosities (<0.15), the exponent for our data was 2.58. This is considerably less than the value (3.1) reported by Sallam et al. (1984).

A model of de Vries (1950) for predicting the gas diffusion coefficient in soils based on the diffusion coefficient of its constitutents overpredicted the diffusion coefficient of N_2 for all four soils. The variation in shape factor did not account for the differences between measured and predicted diffusion coefficients. Although the reduction factor suggested by de Vries (1950) to account for blocked air slightly improved the diffusion coefficient predictions, predicted values were still higher than the measured values, especially at low air-filled porosity. Since the adjustments for blocked air suggested by de Vries are similar

to empirical corrections, we propose a simple linear relationship of the ratio of the measured to predicted diffusion coefficient vs. degree of air saturation for correcting the calculated diffusion values of de Vries.

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