

# Phosphate Diffusion Coefficients in Soil as Affected by Bulk Density and Water Content

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## Summary - Zusammenfassung

Phosphate diffusion coefficients ( $D_e$ ) were determined by the quantity of P that diffused from a soil block with P addition into a soil block without P addition. To compare the results with theoretical concepts and to quantify the influencing factors,  $D_e$  was also calculated using the equation of Nye (1968). This equation takes into account the P diffusion coefficient in water,  $D_i$ , the volumetric water content,  $\theta$ , the impedance factor,  $f$ , and the buffer power,  $b$ , of the soil. The results show that  $D_e$  strongly depends on volumetric water content whereas the effect of bulk density on  $D_e$  values was relatively small. If the weighted average buffer power was used, calculated  $D_e$  values were in good agreement with measured values at higher soil moisture contents. At  $\theta < 0.22 \text{ g cm}^{-3}$  the measured values for  $D_e$  were smaller than the calculated. This effect is attributed to incomplete contact between the two soil blocks. The only small influence of bulk density on  $D_e$  is caused by the fact that bulk density affects both  $\theta$  and  $b$  in a way which compensates each other.

## Einfluß von Lagerungsdichte und Wassergehalt auf den Phosphat-Diffusionskoeffizienten im Boden

Phosphat-Diffusionskoeffizienten,  $D_e$ , wurden mit Hilfe der P-Mengen gemessen, die aus einem Bodenblock mit P-Düngung in einen solchen ohne P-Düngung diffundieren. Um festzustellen, wie die Ergebnisse mit theoretischen Vorstellungen übereinstimmen, und um die Einflußfaktoren zu quantifizieren, wurde  $D_e$  außerdem mit Hilfe der Gleichung von Nye (1968) berechnet. Sie berücksichtigt den P-Diffusionskoeffizienten in Wasser,  $D_i$ , den Wassergehalt,  $\theta$ , den Hemmfaktor,  $f$ , und die Phosphatpufferung,  $b$ , des Bodens. Die Ergebnisse zeigen, daß der Wassergehalt großen, die Lagerungsdichte des Bodens dagegen nur geringen Einfluß auf  $D_e$  hat. Die berechneten  $D_e$ -Werte stimmen bei höheren Wassergehalten sehr gut mit den gemessenen  $D_e$ -Werten überein, wenn die mittlere gewogene Pufferung eingesetzt wird. Bei niedrigeren Wassergehalten ( $< 0.22 \text{ g cm}^{-3}$ ) sind die gemessenen  $D_e$ -Werte geringer als es die Rechnung erwarten läßt. Dieser Effekt wird auf unvollständigen Kontakt zwischen den Bodenblöcken zurückgeführt. Der geringe Einfluß der Lagerungsdichte auf  $D_e$  kommt dadurch zustande, daß diese bei konstantem gravimetrischen Wassergehalt sowohl  $\theta$  als auch  $b$  beeinflusst und sich beide Effekte kompensieren.

## Introduction

Diffusion is generally assumed to be the main mechanism of P transport from soil to plant roots (Nye and Tinker, 1977; Barber, 1984). The rate of diffusion is mainly governed by the effective diffusion coefficient and the concentration gradient between soil and plant root.  $D_e$  is affected by the cross sectional area, the tortuosity of the diffusion path and the interaction between ions in soil solution and the solid phase of the soil. The rates of cation diffusion (Graham-Bryce, 1965; Warncke and Barber, 1972a; Mullins and Edwards, 1987) and anion diffusion (Porter et al., 1960; Rowell et al., 1967; Bhadoria and Datta, 1984) increase with increasing soil water content. Bulk density, however, has no consistent influence on diffusion of ions in soil (Phillips and Brown, 1965; Warncke and Barber, 1972b; Hira and Singh, 1977).

Self diffusion coefficients of P were measured by using various modifications of two half cells in combination with radioisotope techniques (Phillips et al., 1968; Mahatab et al., 1971; Hira and Singh, 1977). However, in many applications of diffusion theory such as transport of ions from soil to plant roots, not self diffusion but bulk diffusion of an ion accompanied by or exchanged with other ions is the dominant mechanism (Nye, 1966). Warncke and Barber (1972b) and Hira and Singh (1977) tried to predict  $D_e$  using the equation of Nye (1968). They found calculated  $D_e$  values up to 100 fold higher than measured  $D_e$ .

It was the objective to study the effect of bulk density and water content in soil on the P diffusion coefficient and to compare the results with calculations based on the equation of Nye (1968) in order to find the cause for changes of  $D_e$  and to quantify the influencing factors.

## Materials and Methods

**Measurement of phosphate diffusion coefficients.** In this study the subsoil (70-90 cm below surface) of a Luvisol from loess (typic Hapludalf "Hottenrode" near Göttingen) was used. It has the following characteristics: 16% clay, 81% silt, 3% sand, 0.17% organic carbon, pH (H<sub>2</sub>O) 5.8. Effective P diffusion coefficients were measured by determining the amount of P that diffused from a soil block fertilized with 400  $\mu\text{g P g}^{-1}$  (80% KH<sub>2</sub>PO<sub>4</sub> and 20% K<sub>2</sub>HPO<sub>4</sub> dissolved in water) into an unfertilized one. To prepare the soil blocks, two diffusion half-cells were used which consisted of two pieces of plastic pipe with 4.2 cm inner diameter and 1.8 cm length thus giving a soil layer of 1.8 cm each. Two half-cells formed a diffusion unit.

The soil was moistened to 9%, 12.6% and 16.5% on a weight basis by spraying deionized water onto the soil and thoroughly mixing it, then 72 h stored in plastic bags for equilibration. Subsequently, the soil was sieved to 1 mm and packed into the diffusion cells to final bulk densities of 1.38, 1.56 and 1.76  $\text{g cm}^{-3}$ . Only in case of 24% (w/w) soil water content was raised from 16.5% by gently pipetting deionized water on top of the packed soil. Two half-cells were joined and sealed with para-film to prevent water loss. Each diffusion unit consisted of the same soil at the same water content and bulk density, except that the soil in one half cell was fertilized with 400  $\mu\text{g P g}^{-1}$  soil. There were two replicates for each treatment.

After a diffusion period of two weeks, in which the diffusion units were kept at 25°C, the two half-cells were separated, the soil blocks frozen in liquid nitrogen, sliced into 0.2 mm layers by a refrigerated microtome and their P concentration individually determined after extraction with 4 M HCl. On the basis of this measurement, a P concentration vs. distance curve was drawn. An average diffusion coefficient,  $D_e$ , for the concentration range between fertilized and unfertilized soil was obtained by using Eq. [1] (Jost, 1952).

$$D_e = \frac{M_1^2 \pi}{A^2 (C_2 - C_1)^2 t} \quad [1]$$

where

$M_1$  = the total amount of P diffused from high to low concentration in time  $t$ . This quantity was determined by graphically integrating the area under the curve of the unfertilized soil (Fig. 1 and 2).

$C_2 - C_1$  = the concentration difference between fertilized and unfertilized soil.

$A$  = the cross sectional area of diffusion, 13.8  $\text{cm}^2$ .

For details of the method see Kaselowsky et al. (1990).

**Calculation of P diffusion coefficients.** Effective diffusion coefficients,  $D_e$ , were also obtained by calculation using Eq. [2] (Nye, 1968) which is based on the assumption that P diffuses only in the liquid phase.

$$D_e = D_1 \theta f / b \quad [2]$$

$D_1$  = the diffusion coefficient in water,

$\theta$  = the volumetric water content,

$f$  = the impedance factor, and

$b$  = the buffer power.

$D_1$  was taken from Parsons (1959),  $\theta$  was obtained from water loss (105°C) and  $f$  was determined by chloride diffusion in the same soil as described by Bhadoria et al. (1991b).

**Buffer power.** A buffer curve was established by plotting  $C$ , the quantity of P soluble in 4 M HCl, as a function of  $C_1$ , the P concentration of the soil solution using the replacement method of Adams (1974). For reasons described by Bhadoria et al. (1991a) we used the average weighted buffer power,  $\bar{b}$ , obtained by dividing the buffer curve into several sections. For each section,  $i$ , a separate buffer power,  $b_i$ , was obtained by dividing  $\Delta C_i$ , the increase in HCl-P, by  $\Delta C_{1i}$ , the increase in soil solution concentration. For the same  $\Delta C_i$ , the P concentration in soil solution,  $\Delta C$ , the 4 M HCl-soluble P, increased with bulk density due to the increase in soil mass per unit of soil volume. Therefore, under the assumption that soil bulk density did

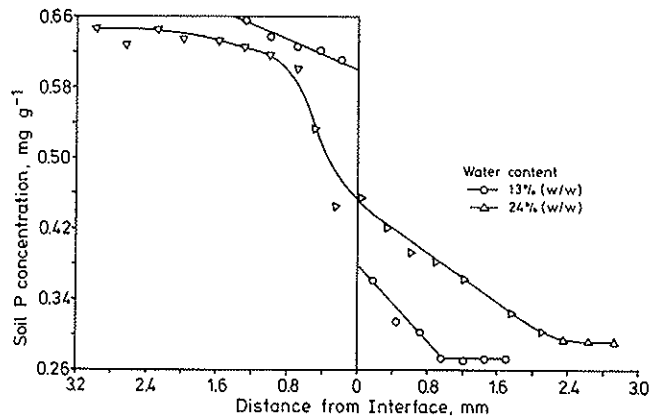
not influence soil solution concentration, buffer power is dependent on bulk density. To obtain the weighted average buffer power,  $\bar{b}$ , Eq. [3] was used

$$\bar{b} = \frac{\sum b_i \Delta C_i}{\sum \Delta C_i} \quad [3]$$

## Results

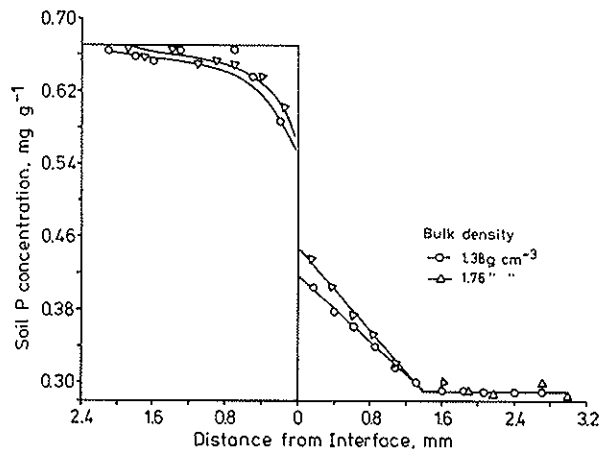
### Concentration vs. distance curve

Figure 1 shows the P distribution in soil at water contents of 13 and 24% (w/w) and at a bulk density of 1.38  $\text{cm}^{-3}$ . Similar curves were obtained (data not shown) for other treatments. An increase in water content led to higher P diffusion, indicated by greater depletion on the left side and higher enrichment on the right side (Fig. 1).



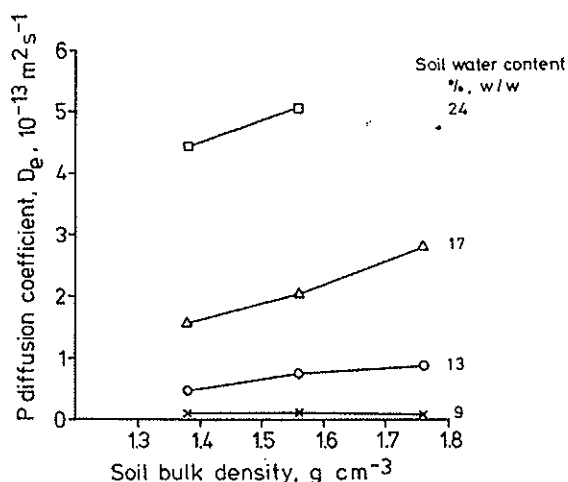
**Figure 1:** Phosphate distribution in soil (4 M HCl soluble) after a two weeks diffusion period at two soil water contents and a bulk density of 1.38  $\text{g cm}^{-3}$

**Abbildung 1:** Phosphatverteilung im Boden (4 M HCl-löslich) nach zweiwöchiger Diffusionszeit bei zwei Wassergehalten und einer Lagerungsdichte von 1.38  $\text{g cm}^{-3}$



**Figure 2:** Phosphate distribution of P in soil (4 M HCl soluble) after a two weeks diffusion period at two bulk densities and a water content of 17% (w/w)

**Abbildung 2:** Phosphatverteilung im Boden (4 M HCl-löslich) nach zweiwöchiger Diffusionszeit bei zwei Lagerungsdichten und einem Wassergehalt von 17 Gew.-%

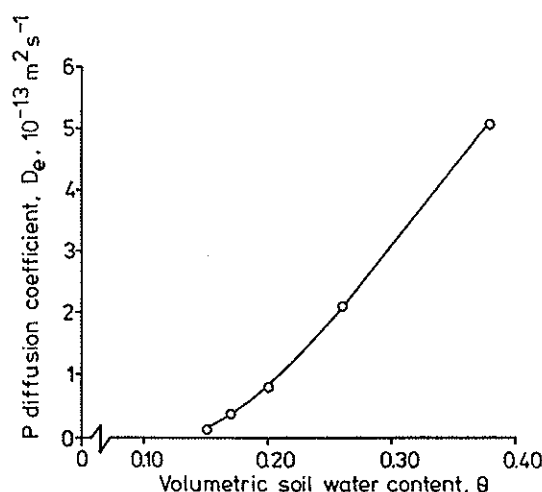


**Figure 3:** Phosphate diffusion coefficient as a function of soil bulk density at different gravimetric moisture levels

**Abbildung 3:** Phosphat-Diffusionskoeffizient als Funktion der Lagerungsdichte des Bodens bei unterschiedlichem gravimetrischen Wassergehalt

At the lower water content, the concentration vs. distance curve abruptly changed at the interface of the soil blocks. This is attributed to insufficient contact between the two soil blocks at low water content resulting in an interface resistance and therefore an under-estimation of  $D_e$  for P as pointed out by Crank (1975, p. 40). Secondly, the curves do not show the regular s-shape which is according to Crank (1975, p. 122) to be expected in case of a concentration dependent diffusion coefficient.

Figure 2 shows the P distribution in soil at a water content of 16.5% (w/w) measured at two bulk densities of 1.38 and 1.76 g cm<sup>-3</sup>. The curves are almost identical which indicates that at the same gravimetric moisture content bulk density is of minor importance for P diffusion in this soil.



**Figure 4:** Phosphate diffusion coefficient as a function of volumetric soil water content at a bulk density of 1.56 g cm<sup>-3</sup>

**Abbildung 4:** Phosphat-Diffusionskoeffizient als Funktion des volumetrischen Bodenwassergehaltes bei einer Lagerungsdichte von 1.56 g cm<sup>-3</sup>.

#### Measured and calculated P diffusion coefficients

The measured P diffusion coefficients are related to bulk densities and water contents of the soil (Fig. 3). The increase of bulk density from 1.38 to 1.76 g cm<sup>-3</sup> at a moisture level of 13 and 17% (w/w) increased  $D_e$  by a factor of 2 while there was almost no effect at 9% (w/w) moisture. In contrast soil water content changed  $D_e$  by a factor of 6 when soil moisture increased from 12.6 to 24% at a bulk density of 1.56 g cm<sup>-3</sup>. As shown in Fig. 4 at a bulk density of 1.56 g cm<sup>-3</sup> the P diffusion coefficient increased almost linearly with water content.

Table 1 summarizes the  $D_e$  values calculated using Eq. [2] and its components. The impedance factor,  $f$ , increased with

**Table 1:** Measured and calculated P diffusion coefficients at different bulk densities and water contents

**Tabelle 1:** Gemessener und berechneter P-Diffusionskoeffizient bei unterschiedlichen Lagerungsdichten und Wassergehalten des Bodens

bulk density g cm <sup>-3</sup>	water content		f <sup>+</sup>	$\bar{b}$	$D_e$ calc. <sup>++</sup>	$D_e$ meas. <sup>+++</sup>	$\frac{D_e \text{ calc.}}{D_e \text{ meas.}}$
	g g <sup>-1</sup>	g cm <sup>-3</sup>					
1.38	0.09	0.12	0.07	210	0.36	0.10	3.60
	0.13	0.17	0.13	210	0.94	0.43	2.19
	0.16	0.22	0.19	210	1.77	1.59	1.11
	0.24	0.33	0.32	210	4.47	4.45	1.00
1.56	0.09	0.15	0.08	237	0.45	0.10	4.50
	0.11	0.17	0.10	237	0.64	0.37	1.73
	0.13	0.20	0.14	237	1.05	0.79	1.33
	0.17	0.26	0.21	237	2.05	2.09	0.98
	0.24	0.38	0.36	237	5.14	5.05	1.02
1.76	0.09	0.16	0.05	268	0.26	0.08	3.25
	0.12	0.20	0.10	268	0.66	0.46	1.43
	0.13	0.22	0.13	268	0.95	0.90	1.05
	0.17	0.29	0.21	268	2.02	2.82	0.72

<sup>+</sup>f values from Bhadoria et al. (1991b)

<sup>++</sup> calculated by Eq. [2],  $D_i$  is  $0.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

<sup>+++</sup> measured  $D_e$  values using Eq. [1], average of two replicates

an increase of volumetric water content while  $\bar{b}$  remained constant at the same bulk density. These changes of  $\theta$  and  $f$  resulted in calculated  $D_e$  values which differ by a factor of about 10.

An increase in bulk density did not change  $D_e$  very much. Compared at the same gravimetric moisture content (at about the same water tension) the increase in bulk density leads to a higher volumetric water content while  $f$  remains almost constant and  $\bar{b}$  increases to the same extent as  $\theta$  increases. Therefore, changes in buffer power,  $\bar{b}$ , and volumetric water content compensate each other, when bulk density is changed.

Measured and calculated  $D_e$  values are compared in the last column of Table 1. It reveals that measured and calculated  $D_e$  values differ by a factor of 3 - 4 at lower moisture contents but they are in close agreement at higher moisture levels.

## Discussion

The close agreement between calculated and measured P diffusion coefficients at medium to higher soil water contents indicates that the theory underlying Eq. [2] describes P diffusion in soil quite realistically. The lack of agreement in the soil of lower water content is probably due to insufficient contact between the two diffusion cells. According to Crank (1975, p. 40), this is indicated by the discontinuity of the concentration-distance curve at low soil moisture (Fig. 1). Therefore, at the lower soil moisture, the calculated  $D_e$  values appear to be more realistic than the  $D_e$  values measured with this method.

The influence of bulk density and water content on P diffusion in the soil is in agreement with the theory which is expressed by Eq. [2]. The increase of water content affects  $\theta$  and therefore  $f$  while  $b$  remains constant and thus results in a more than proportional increase of  $D_e$ . The slope of the  $D_e$  vs.  $\theta$  curve (Fig. 4) is similar to the curve of the impedance factor for chloride versus  $\theta$  in the same soil (Bhadoria et al., 1991b) indicating that the tortuosity and cross-sectional area of the diffusive pathway primarily determines the change of  $D_e$  with changing  $\theta$  rather than any other interaction with the soil.

Bulk density only slightly affects  $D_e$  because at the same gravimetric water content  $\theta$  is increased,  $f$  does not change very much and  $\bar{b}$  is increased (Table 1). Thus the effects on  $\theta$  and  $\bar{b}$  largely compensate each other, Eq. [2].

Warncke and Barber (1972b) and Hira and Singh (1977) also calculated  $D_e$  values for Zn and P by using Eq. [2]. They found calculated  $D_e$  for Zn to be higher by a factor of 5 to 18 and for P by a factor of as much as 100 than measured values.

Since these authors measured  $f$  in a similar way as in the present study, and the measurement of  $\theta$  presents no problems, the discrepancies are probably caused by the determination of the buffer power. In our experiments the soil was treated in the same way for the determination of  $b$  and  $D_e$ . The same reaction time was allowed and both desorp-

tion and adsorption curves were established for determining  $b$  (Bhadoria et al., 1991a). On the diffusive pathway from the soil with high P to the soil with low P concentration desorption occurs when P diffuses out and adsorption occurs when P diffuses into the soil. Since phosphate diffusion coefficients are also dependent on the buffer power,  $b$ , and  $b$  is concentration dependent (Bhadoria et al., 1991a) the weighted average buffer power  $\bar{b}$  is superior to  $b$  because  $\bar{b}$  makes allowance for the non-linearity of the buffer curve. In case of the example presented in Fig. 1,  $\bar{b}$  is about two times higher than  $b$ .

This underlines the necessity for the correct determination of the buffer power and possibly explains why such a close agreement between measured and calculated diffusion coefficients has not been reported earlier for adsorbed ions.

The experimental results confirm the importance of the soil water content for P nutrition of plants (Römer und Schilling, 1988), because in a dry soil P transport to the root by diffusion can be reduced by a factor of 10 or more.

## Acknowledgement

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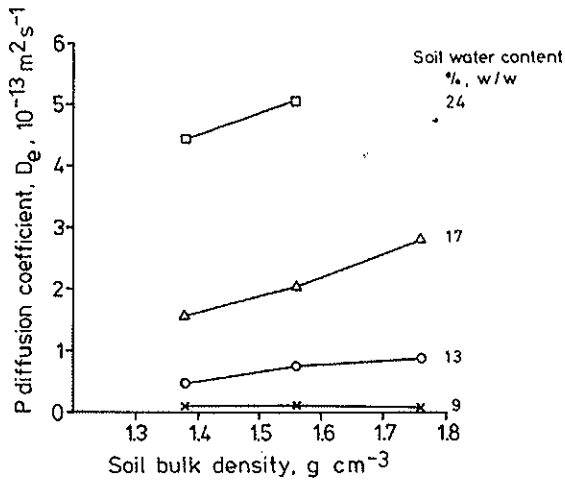


Figure 3: Phosphate diffusion coefficient as a function of soil bulk density at different gravimetric moisture levels

Abbildung 3: Phosphat-Diffusionskoeffizient als Funktion der Lagerungsdichte des Bodens bei unterschiedlichem gravimetrischen Wassergehalt

At the lower water content, the concentration vs. distance curve abruptly changed at the interface of the soil blocks. This is attributed to insufficient contact between the two soil blocks at low water content resulting in an interface resistance and therefore an under-estimation of  $D_e$  for P as pointed out by Crank (1975, p. 40). Secondly, the curves do not show the regular s-shape which is according to Crank (1975, p. 122) to be expected in case of a concentration dependent diffusion coefficient.

Figure 2 shows the P distribution in soil at a water content of 16.5% (w/w) measured at two bulk densities of 1.38 and 1.76 g cm<sup>-3</sup>. The curves are almost identical which indicates that at the same gravimetric moisture content bulk density is of minor importance for P diffusion in this soil.

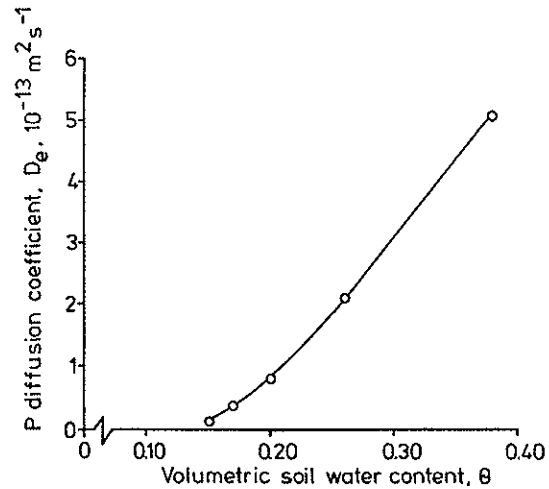


Figure 4: Phosphate diffusion coefficient as a function of volumetric soil water content at a bulk density of 1.56 g cm<sup>-3</sup>

Abbildung 4: Phosphat-Diffusionskoeffizient als Funktion des volumetrischen Bodenwasserhaltes bei einer Lagerungsdichte von 1.56 g cm<sup>-3</sup>.

#### Measured and calculated P diffusion coefficients

The measured P diffusion coefficients are related to bulk densities and water contents of the soil (Fig. 3). The increase of bulk density from 1.38 to 1.76 g cm<sup>-3</sup> at a moisture level of 13 and 17% (w/w) increased  $D_e$  by a factor of 2 while there was almost no effect at 9% (w/w) moisture. In contrast soil water content changed  $D_e$  by a factor of 6 when soil moisture increased from 12.6 to 24% at a bulk density of 1.56 g cm<sup>-3</sup>. As shown in Fig. 4 at a bulk density of 1.56 g cm<sup>-3</sup> the P diffusion coefficient increased almost linearly with water content.

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	g g <sup>-1</sup>	g cm <sup>-3</sup>					
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1.56	0.09	0.15	0.08	237	0.45	0.10	4.50
	0.11	0.17	0.10	237	0.64	0.37	1.73
	0.13	0.20	0.14	237	1.05	0.79	1.33
	0.17	0.26	0.21	237	2.05	2.09	0.98
	0.24	0.38	0.36	237	5.14	5.05	1.02
1.76	0.09	0.16	0.05	268	0.26	0.08	3.25
	0.12	0.20	0.10	268	0.66	0.46	1.43
	0.13	0.22	0.13	268	0.95	0.90	1.05
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<sup>+</sup>f values from Bhadoria et al. (1991b)

<sup>++</sup> calculated by Eq. [2],  $D_1$  is  $0.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

<sup>+++</sup> measured  $D_e$  values using Eq. [1], average of two replicates

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