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Impedance Factor for Chloride Diffusion in Soil as Affected by Bulk Density and Water Content

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Angenommen: 11. November 1990

Summary - Zusammenfassung

The influence of soil bulk density and water content on the impedance factor (f) was studied by measuring bulk diffusion of chloride from one soil block to another differing in Cl^--concentration. An increase in bulk density from 1.38 to 1.76 g cm^{-3} at a constant gravimetric moisture content of 7% decreased f by a factor of 3, at 10% to 12% there was nearly no effect on f, while at higher soil moistures of 16% to 20%, f increased almost linearly with increasing bulk density. With increasing soil volumetric water content, (θ), f increased linearly at all soil bulk densities. At the same θ, the impedance factor decreased with increasing soil bulk density. The relationship between θ and f as established by *Barraclough* and *Tinker* (1981) agrees well with the results obtained here for bulk densities of 1.38 and 1.56 g cm^{-3} and water contents higher than 18% (v/v). However, at lower values of θ, measured f values were higher than predicted by these authors. On the other hand, f values for a bulk density of 1.76 g cm^{-3} at all water contents were clearly below the values of these authors.

Wirkung von Lagerungsdichte und Wassergehalt auf den Hemmfaktor der Chloriddiffusion im Boden

Es wurde der Einfluß von Lagerungsdichte und Wassergehalt des Bodens auf den Hemmfaktor (f) der Ionendiffusion im Boden untersucht. Hierzu wurde die Chloriddiffusion gemessen, die von einem Bodenblock höherer in einen Bodenblock niedrigerer Cl^--Konzentration erfolgt. Der Anstieg der Lagerungsdichte von 1.38 auf 1.76 g cm^{-3} führte bei einem konstanten gravimetrischen Wassergehalt von 7% zur Abnahme von f um den Faktor 3, bei 10 - 12% bestand kein Einfluß auf f, bei 16 - 20% stieg f mit der Lagerungsdichte an. Mit der Zunahme des volumetrischen Wassergehaltes (θ) stieg f in allen Fällen linear an. Bei gleichem θ nahm f hingegen mit steigender Lagerungsdichte ab. Die von *Barraclough* und *Tinker* (1981) gefundene Beziehung zwischen θ und f stimmt mit unseren Ergebnissen bei Lagerungsdichten von 1.38 - 1.56 g cm^{-3} und Wassergehalten über 18 Vol.-% gut überein. Bei niedrigem θ sind die hier gefundenen f-Werte dagegen höher und bei einer Lagerungsdichte von 1.76 g cm^{-3} sind sie bei allen Wassergehalten niedriger als bei diesen Autoren.

Introduction

The importance of nutrient ion mobility (expressed by the diffusion coefficient) for plant nutrition is well established (*Olsen* and *Kemper*, 1968; *Nye* and *Tinker*, 1977; *Barber*, 1984). Understanding the diffusive transport of ions from soil to plant roots requires knowledge of the impedance or tortuosity factor (f). This factor is also required to calculate the effective diffusion coefficient (D_e), and is often defined by

$$f = (L/L_e)^2 \qquad [1]$$

where L is the straight-line distance between two points, and L_e is the actual or effective distance of solute movement through the soil between the same two points. This definition interprets f to depend only on the tortuosity of the diffusive pathway. However, other phenomena such as the change of electrical charges and water viscosity near the surface of the soil matrix may also have an influence on f. Therefore, the term impedance factor is preferred here rather than tortuosity factor. The definition is based on the method of measurement of f in soil as expressed by Eq. [2] (*Nye* and *Tinker*, 1977)

$$f = D_e/D_l \qquad [2]$$

where D_e is the effective diffusion coefficient of anions such as chloride or bromide which are not strongly sorbed on soils, and D_l is the diffusion coefficient of the same ion in free bulk water.

Several authors (*Porter* et al., 1960; *Rowell* et al., 1967; *Warncke* and *Barber*, 1972; *Barraclough* and *Tinker*, 1981) have shown that the mobility of these anions in soil depends mainly on water content whereas, at the same moisture level, bulk density of the soil is of minor influence. The objective of this work is to determine the effect of soil water content and bulk density on the impedance factor. These values are necessary to calculate P diffusion coefficients in soil (*Bhadoria* et al. 1991a, 1991b).

Material and Methods

Procedure. For this study the subsoil (70 - 90 cm) of a Luvisol from loess (Hottenrode) was used. The soil has the following characteristics: 16% clay, 81% silt, 3% sand, 0.17% organic carbon, pH (H_2O) 5.8. For each experiment two series of subsamples were prepared. One of the series received chloride in the form of $CaCl_2$ at a rate of 10 mg kg^{-1} soil (treated) and the other identical series received the same amount of salt in the form of $Ca(NO_3)_2$ (untreated). This was done to avoid influence on diffusion due to ion concentration difference. After 4 days of equilibration the soil was

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air-dried and sieved to pass a 2 mm sieve. For the diffusion experiments the treated and untreated soils were uniformly wetted with distilled water. The soils were thoroughly mixed and kept in covered buckets for 2 days for equilibration. The soil having water contents of 7.2, 9.8, 12.5, 16.6, 19.7 and 23.1% (w/w) was then placed into diffusion cells and compacted to bulk densities of 1.38, 1.56 and 1.76 g cm^{-3} as described by *Kaselowsky* et al. (1990). Because at a bulk density of 1.76 g cm^{-3} the point of water saturation was surpassed this treatment could not be included at the gravimetric water content of 23% (w/w).

Each diffusion unit comprised two half cells which consisted of a piece of plastic pipe with an inner diameter of 4.2 cm and a length of 1.8 cm giving a soil layer of 1.8 cm.

After compaction, the cells with the treated and the untreated soil blocks were joined, sealed with parafilm and kept at a constant temperature of 25°C for diffusion. After periods of time ranging from 4 to 109 h, the cells were separated. In the untreated soil core, chloride was determined by shaking the soil with bi-distilled water for one hour with 1:5 soil/water ratio. A 50 ml aliquot of the extract solution was transferred to a beaker. 2 ml of 5 M $NaNO_3$ buffer solution was added to maintain a constant ionic strength. A chloride specific electrode was placed in the solution with a reference electrode and millivolt readings were recorded. Chloride concentration was determined from a calibration curve obtained from a series of standards containing 1 to 200 mg Cl L^{-1}. To compensate for drift in the mV readings, the calibration curves were obtained before, in-between and at the end of sample readings.

Diffusion coefficient. Effective diffusion coefficients (D_e) of chloride in soil were calculated from the simplified equation of *Schofield* and *Graham-Bryce* (1960)

$$D_e = \left(\frac{Q}{Q\infty}\right)^2 \cdot \frac{\pi L^2}{4t} \qquad [3]$$

where Q is the amount of chloride that diffused across the interface of the treated and untreated soil cores in time t, Q∞ is equal to one-half of the total chloride added to the treated soil and L is the length of the half cell (1.8 cm). This equation is valid for finite boundary conditions if $Q/Q\infty$ is $<$ 0.5. The experiments were carried out accordingly.

D_e calculated from Eq. [3] was then used to determine the impedance factor (f) from equation [2]. The D_l value used was 1.85 x 10^{-9} m^2 s^{-1} (*Porter* et al., 1960). Each D_e-value represents the mean of three replicates.

Results and Discussion

Effect of diffusion period on the diffusion coefficient

The diffusion coefficients (D_e) and Q/Q∞ measured after different periods of time are presented in Table 1. D_e was almost constant over this time even when Q/Q∞ reached a value of 0.74. However, the variability among replicates was higher when diffusion periods were shorter. Herewith in agreement *Barraclough* and *Tinker* (1981) have pointed out that a period is desirable which allows diffusion to extend some distance into the soil sample. The effects of artefacts in the surface of the two soil blocks due to preparation can thus be minimized. The similarity between D_e values obtained beyond 13 hours indicates that the method is reliable.

Table 1: Effect of diffusion period on Q/Q∞ and D_e for Chloride (average of three replicates)

Tabelle 1: Wirkung der Diffusionsdauer auf Q/Q∞ und auf D_e für Chlorid (Mittel aus 3 Messungen)

Time (hours)	Q/Q∞	D_e 10^{-10} m^2s^{-1}
4	0.13	2.98
8.25	0.22	4.14
13	0.23	2.87
24	0.32	3.01
51	0.47	3.06
109	0.74	3.55

Effects of bulk density and soil water content on the impedance factor

Impedance factors (f) as a function of bulk density at six water contents (w/w) are shown in Fig. 1. Within each group gravimetric moisture content was kept constant. As a result of compaction, θ increased as bulk density increased but water tension stayed about the same. This is the situation when soil is being compacted in the field. At soil moistures of 9.8 and 12.5% (w/w) there was little or no effect on f when bulk density increased from 1.38 to 1.76 g cm^{-3}. At 7.2% moisture, the increase of bulk density decreased f by a factor of 3. This may be attributed to insufficient contact at the interface of the relatively dry soil blocks (*Bhadoria* et al., 1991b). At higher soil water content (16% - 20%, w/w) f increased markedly as bulk density increased. This result is in agreement with *Warncke* and *Barber* (1972). They concluded that compaction of the soil caused part of the liquid discontinuities to be filled, resulting in a less tortuous diffusion path and therefore an increase in f. At the highest water content (23%, w/w) an increase in bulk density again had no effect on f, (as far as can be judged from the two data points) indicating that this effect occurs only in a certain range.

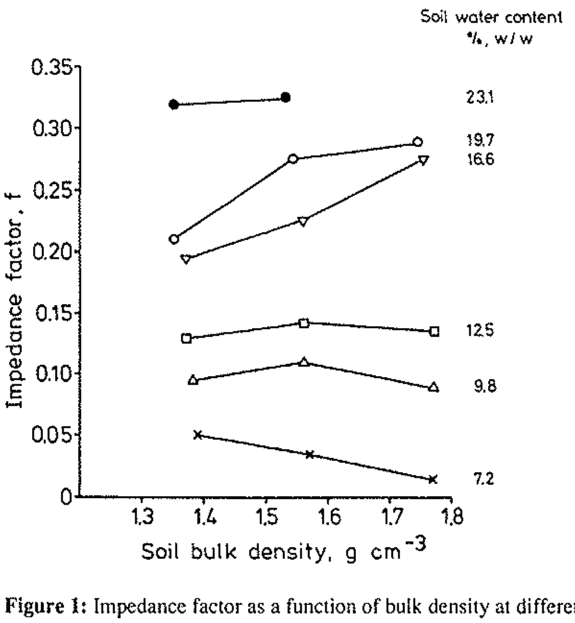

Figure 1: Impedance factor as a function of bulk density at different gravimetric soil water contents

Abbildung 1: Der Hemmfaktor als Funktion der Lagerungsdichte bei verschiedenen gravimetrischen Wassergehalten im Boden

The volumetric water content (θ) of the soil, which determines the cross sectional area of the diffusion pathway, increases with an increase in bulk density provided the gravimetric water content is kept constant. Because of the results of Fig. 1, if θ is constant, f should decrease when soil bulk density is increased. As shown in Fig. 2, impedance factors increased linearly with an increase in the volumetric water content irrespective of soil bulk density.

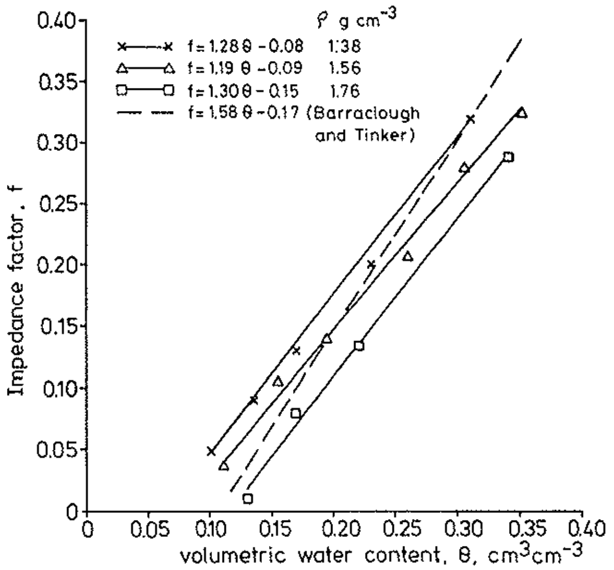

Figure 2: Impedance factor as a function of volumetric soil water content at three bulk densities

Abbildung 2: Der Hemmfaktor als Funktion des volumetrischen Wassergehalts bei drei Lagerungsdichten im Boden

With the increase of soil bulk density the lines are moved to the right. This means that at the same volumetric water content f is decreased. Because the lines are almost parallel the absolute effect of bulk density on f is about the same at all water contents. However, the relative effect is stronger in the low moisture range, where f may be up to 10 times higher in the soil of low than of high bulk density. In contrast, at $\theta = 0.30$, f increases only by 25% when bulk density decreases from 1.76 to 1.38 g cm^{-3}.

Such a strong influence of bulk density on f in relatively dry soil may however be questioned when the problems of measurement are considered. After the soil blocks were placed in contact, f was determined from the amount of Cl^- which had moved from the soil block of high into that of low concentration, assuming perfect contact between the soil blocks. However, *Bhadoria* et al. (1991b), using the same soil, have shown that at low soil moisture there is a resistance of P diffusion across the interface of the two blocks indicating insufficient contact. It is therefore likely that the f values measured at low θ are smaller than the true f values. This deviation should be larger for the compacted soil since, at the same θ, the soil has a lower gravimetric water content. At medium to high θ values there were no problems of contact between the soil blocks, measured f values are therefore more reliable.

Using medium to coarse textured soils, *Barraclough* and *Tinker* (1981) established a linear relationship between θ and f. This relation, which is included in Fig. 2, is based on their data and those of *Porter* et al. (1960) and *Rowell* et al. (1967). It can be seen that the regression of *Barraclough* and *Tinker* (1981) is in fair agreement with our results. However, the increase of f with θ is steeper than we found. Therefore, in the lower range of θ the measured f values are higher than those calculated from that regression line. Discrepancies in the low moisture range may be attributed to problems of soil contact as mentioned above.

The f values for a bulk density of 1.76 g cm^{-3} are below that regression line for all water contents. It is therefore concluded that bulk density should be taken into account when the impedance factor is calculated. The effect of bulk density on f was also observed by *Barraclough* and *Tinker* (1981). However, in calculating the regression line they included soils varying in bulk density from 1.28 to 1.76 g cm^{-3}. The soil with the largest bulk density was the most sandy. The deviation of the regression lines found here from that of Barraclough and Tinker may therefore be attributed to differences in soil texture.

In general, the results confirm that the impedance factor, f, depends largely on soil water content. This relationship, however, varies with bulk density and with soil texture. For soils of medium texture (loam) and the medium range of bulk densities a common relationship can be used to calculate f from θ.

Acknowledgements

The first author thanks the *Alexander von Humboldt-Stiftung* for the award of a post doctoral fellowship during the tenure of which the present investigation was carried out. Thanks are also due to the *Deutsche Forschungsgemeinschaft* for financial support within the priority program "Genese und Funktion des Bodengefüges".

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