

A Method for Determining Phosphate Diffusion Coefficients by Bulk Diffusion in Soil

Joachim Kaselowsky*, Pratapbhanu B.S. Bhadoria**, Norbert Claassen* and Albrecht Jungk*

* Institut für Agrikulturchemie, Georg-August-Universität, von Siebold-Str. 6, D-3400 Göttingen, F.R. Germany,

** Humboldt Research Fellow from the Indian Institute of Technology, Kharagpur 721 302, India

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Summary - Zusammenfassung

A method is described for the determination of phosphate diffusion coefficients by bulk diffusion in soil using the concentration distance method. Two soil blocks only differing in phosphate concentration are brought into contact. After a diffusion period of two weeks the soil blocks are separated, frozen in liquid nitrogen and sliced into layers about 0.02 cm thick by means of a refrigerated microtome. The soil samples are extracted with 4 N HCl, a procedure which fully recovers the added amount of fertilizer P and thus includes the total amount of P that diffuses from one soil block to the other. A concentration distance profile for P and a calculation of the P diffusion coefficient is presented.

Eine Methode zur Bestimmung des Phosphat-Diffusionskoeffizienten im Boden

Es wird eine Methode zur Bestimmung des Phosphat-Diffusionskoeffizienten vorgestellt. Zwei Bodenblöcke unterschiedlicher P-Konzentration wurden in Kontakt gebracht. Nach zwei Wochen wurden die Blöcke getrennt, in flüssigem Stickstoff schockgefroren und in Schichten von 0,02 cm Dicke an einem Gefriermikrotom zerlegt. Die Bodenproben werden mit 4 N HCl extrahiert, ein Verfahren, das die Menge des gedüngten Phosphats quantitativ erfasst und damit die gesamte Phosphatmenge wiedergibt, die vom einen in den anderen Bodenblock diffundiert. Ein Konzentrations-Entfernungsprofil für P und eine Berechnung des P-Diffusionskoeffizienten wird gezeigt.

Introduction

Diffusion is the main mechanism of phosphate transport from the soil to the root surface (Bouldin, 1961; Barber, 1962). The amount diffusing is mainly determined by the mobility of P in the bulk soil, which depends on the effective diffusion coefficient (D_e). Because of the difficulties of measuring it, D_e is often calculated using the equation from Nye (1968), but measurements of D_e are desirable.

Progress in this field is restricted by a lack of convenient methods for the determination of bulk diffusion coefficients. Measurements of self diffusion of ions in soils have been made by Graham-Bryce (1963a, b). The self diffusion coefficients were determined by placing a soil sample labelled with ^{32}P in contact with an identical but unlabelled sample and measuring the amount of isotope transferred to the unlabelled core in a given time. Phillips and Brown (1964, 1965) and Phillips et al. (1968) used the same technique but measured self diffusion coefficients by analyzing the concentration vs. distance curves of an ion.

In self diffusion the ion exchanges with its own isotope and the environment remains unchanged. This is not the case with bulk diffusion because of the interaction between the ions in soil solution and the solid phase of the soil.

Vaidyanathan and Nye (1966) used a resin paper, and Römer and Schilling (1988) a resin block as a sink for the diffusion of ions. In this case difficulties can arise from short experimental periods which cause diffusion only very near to the absorbing surface of the resin. Another problem

with adsorbed ions is that the total diffusible amount cannot be determined exactly. If radioactive materials are used the diffusion coefficient of the total isotopically exchangeable nutrient is determined. However, Hendriks et al. (1981) have shown that only 50% of the isotopically exchangeable P is depleted by plants from rhizosphere soil. Therefore, only this fraction is included in P diffusion from soil to plant roots.

This paper presents a method to measure the amount of P moving from a soil block of high to one of low concentration by bulk diffusion. Furthermore the concentration vs. distance profile will be shown. Both can be used to evaluate the effective diffusion coefficient. In this paper only the amount moving from high to low concentration will be used to determine the effective diffusion coefficient of P.

Material and Methods

The subsoil (70 - 90 cm) of a silty loam soil derived from loess (location "Hottenrode") was used in this study. The soil has the following characteristics: 16% clay, 81% silt, 3% sand, 0.17% organic carbon, pH (H_2O) 5.8. The soil was ground and passed through a 2 mm sieve. For the determination of the diffusion coefficient, soil samples were fertilized with P by a solution containing 80% of the P as KH_2PO_4 and 20% as K_2HPO_4 . The pH of this mixture was similar to the soil pH. Fertilizer levels varied from 0 to 40 mg P/100 g soil. The P solution was sprayed in portions on the soil surface and thoroughly mixed under. Water was

added to make a paste. The paste was stirred by hand once a day for a period of 8 days in order to ensure equilibration of P with the soil and to obtain uniform distribution. Afterwards the soil was dried at 45 - 50°C in a forced air current oven and then crushed, and ground with a mortar. The soil was then moistened to 15% (w/w). Before being packed, the moist soil was sieved to 1 mm to obtain a smooth and homogeneous soil core.

Diffusion Unit

The diffusion unit consisted of two half, open cells made of a PVC pipe, each 4.2 cm in diameter and 1.80 cm long. To allow easy removal of the frozen soil core, an axial slit was cut in the wall. Each cell was filled with soil to a constant bulk density of 1.46 g cm⁻³. Subsequently, the water content of the soil was raised from 15 to 24% (w/w) by gently pipetting deionized water on top of the packed soil without disturbing the soil surface. After moisture adjustment and a subsequent 72 hour equilibration period the two half cells, one fertilized with 40 and the other with 0 mg P/100 g soil, were gently pressed together in order to ensure good contact between them. The cells were then sealed with parafilm, placed in a plastic bag and kept at a controlled temperature of 25°C for a period of 14 days.

At the end of the diffusion period, the cells were separated and quick frozen in liquid nitrogen for 30 seconds. The frozen soil core was then cut into thin slices by a refrigerated microtome following the procedure described by *Kuchenbuch and Jungk* (1982). Several slices were combined to give samples each representing a thickness of approximately 0.02 cm. The exact thickness of each slice was calculated from the weight of the sample.

After air drying, sliced soil samples were shaken for 2 hours with 4 N HCl in a ratio of 1:50 and filtered. The P concentration of the filtrate was determined by the method of *Murphy and Riley* (1962).

Results and Discussion

Extraction with 4 N HCl

In order to test whether 4 N HCl extracts all inorganic P which was added to the soil, samples with different fertilizer P levels were extracted with this method. The percentage of

Table 1: Recovery of added P after soil extraction with 4 N HCl
Tabelle 1: Wiederfindungsrate des gedüngten Phosphats nach Extraktion des Bodens mit 4 N HCl

P added mg/100 g	P found mg/100 g	P recovered %
0	28.8	-
5	32.6	76
10	38.4	96
20	48.3	97
30	57.0	94
40	66.0	93

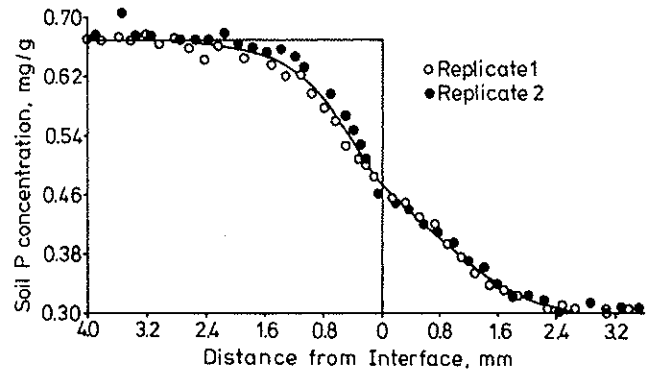


Figure 1: Concentration distance profile of P in Hottenrode silt loam at a bulk density of 1.46 g/cm³

Abbildung 1: Konzentrations-Entfernungsprofil von P im Boden Hottenrode (tU) bei einer Lagerungsdichte von 1,46 g/cm³

recovery of added P (Table 1) was 76% in the soil fertilized with 5 mg/100 g soil and varied between 93 to 97% at the higher fertilizer levels. Thus, except for the low P level, P applied to the soil was almost quantitatively recovered by 4 N HCl. This extractant was therefore suitable to determine the total amount of P which entered a diffusion cell by bulk diffusion. It may not be suitable, however, for soils where P is bound differently.

Concentration Distance Curve

Figure 1 shows the P distribution after 14 days of diffusion. Because of difficulties in the separation of the two blocks, the interface (distance = 0) was put at the point where P lost on the fertilized side was equal to the amount gained in the unfertilized block. The two replicates correspond closely indicating the reliability of the procedure.

The concentration-distance curve is convex on the fertilized side but close to a straight line on the unfertilized side. This deviation from the S-shape is probably due to a concentration dependent diffusion coefficient, as shown by *Crank* (1975, p 122). Concentration dependent diffusion coefficients can be obtained from the analysis of concentration vs distance curves as proposed by *Matano* (1933).

Effective Diffusion Coefficient

An average diffusion coefficient for P was determined from the amount of P which had moved from the high into the low P soil. This amount is obtained by integrating the area under the curve on the right hand side of Fig. 1 and then calculating D_e -values using equation (1) of *Jost* (1952, p 22), which in principle is similar to the equation used by *Phillips and Brown* (1965).

$$D_e = \frac{Mt^2 \cdot \pi}{A^2(C_2 - C_1)^2 t} \quad (1)$$

where

- D_e = the diffusion coefficient of P in soil
 M_t = the amount of P diffused in time t
 A = cross sectional area of diffusion
 $(C_2 - C_1)$ = the concentration difference between the fertilized and the unfertilized soil block.

For the results of Fig. 1: $M_t = 0.0265$ mg P/cm², $A = 1$ cm², $(C_2 - C_1) = (0.67 - 0.30) \times 1.46 = 0.5402$ mg/cm³ and $t = 1\ 209\ 600$ s (14 days). Using these values with equation (1) gives a D_e of 6.25×10^{-9} cm²/s that is similar to the diffusion coefficients for P reported by Barber (1984) and Nye and Tinker (1977).

The method has shown its advantages in determining differences of the effective P diffusion coefficient in a soil with a range of P concentrations, water contents and bulk densities as described by Bhadoria et al. (submitted). D_e -values measured with this method were fairly in agreement with D_e -values calculated by using the equation of Nye (1968).

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