

The quantitative effect of chemical phosphate mobilization by carboxylate anions on P uptake by a single root. I. The basic concept and determination of soil parameters

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Dedicated to *Albrecht Jungk* on the occasion of his 70th birthday

Accepted 26 January 2000

Summary – Zusammenfassung

Model calculations on the uptake of inorganic nutrients by single roots and root systems do not include chemical nutrient mobilization by root exudates. In this paper, a model description of Nye (1984) was applied to the case of a single root (cylindrical case) and chemical mobilization of phosphate (P) by carboxylates. Experimental results are reported which allow the quantification of soil parameters required for the model calculations. These include the solubilizing effect of carboxylates on P. The experiments showed a strong positive correlation between carboxylate adsorption to the soil solid phase and chemical P mobilization by the carboxylate. Below a concentration of adsorbed citrate and oxalate of $10 \mu\text{mol g}^{-1}$ soil no mobilization occurred in the 3 soils which were investigated. Differences in pH did not affect P solubility, but did, however, affect the quantity of adsorbed carboxylate and thereby the mobilization of P. Citrate and oxalate have a greater ability to mobilize soil P as compared with oxaloacetate and malate. Model calculations which are based on these experimental results are presented in a second paper.

Key words: P-mobilization / root exudates / carboxylates / P-uptake / modeling

Der quantitative Effekt einer chemischen Phosphatmobilisierung durch Carboxylate auf die P-Aufnahme durch eine Einzelwurzel. I. Theoretische Grundlagen sowie die Bestimmung der Bodenparameter

Mathematische Aufnahmemodelle zur Berechnung der Aufnahme von anorganischen Nährstoffen durch eine Einzelwurzel und durch Wurzelsysteme berücksichtigen nicht die chemische Mobilisierung durch Wurzelauflösungen. Für die durchzuführenden Aufnahmeberechnungen wird ein Modell von Nye (1984) auf den Fall einer Einzelwurzel unter Einbeziehung der chemischen Mobilisierung von Phosphat durch Carboxylate modifiziert. Zusätzlich wird über experimentelle Ergebnisse zur Mobilisierung von P durch Citrat und Oxalat in verschiedenen Böden berichtet. Sie dienen zur Ermittlung von Parametern, die für die Aufnahmeberechnungen in einer nachfolgenden Publikation notwendig sind. Die Untersuchungen zeigten eine positive Beziehung zwischen Carboxylatadsorption an die Bodenfestphase und chemischer P-Mobilisierung. Unterhalb einer Konzentration an adsorbiertem Citrat oder Oxalat von $10 \mu\text{mol g}^{-1}$ Boden wurde kein P durch Citrat mobilisiert. Unterschiede in den pH-Werten hatten keinen direkten Einfluß auf die P-Löslichkeit, wirkten aber indirekt über die Beeinflussung des Adsorptionsverhaltens der Carboxylate. Der Vergleich der Effizienz verschiedener Carbonsäureanionen bezüglich der P-Mobilisierung zeigte, dass Citrat und in abgeschwächtem Maße Oxalat sehr viel effizienter als Malat und Oxalacetat waren.

Introduction

Plant roots absorb inorganic nutrients from the soil solution. Nutrients are transported to the root surface mainly by diffusion and mass flow, the transport mechanism for phosphate (P) being mainly diffusion (Oliver and Barber, 1966).

Mathematical models which describe the uptake of nutrients by roots include soil and plant parameters, assuming that the nutrient desorption from the soil solid phase is initiated by the decrease of the nutrient soil solution concentration which itself is a result of the uptake by the roots (Claassen and Barber, 1976; Nye and Tinker, 1977; Cushman, 1979; Yanai, 1994). Chemical mobilization of P by root exudates is not included. However, the increase of nutrient solubility by chemical mobilization increases

nutrient absorption by roots, especially at low initial nutrient solubility (Nye, 1966).

Di- and tricarboxylic acid anions have the ability to increase P solubility also in P fixing soils. The soil P fraction which is mobilized mainly consists of Fe/Al associated P (Earl et al., 1979; Lopez-Hernandez et al., 1979; Fox et al., 1990; Gerke, 1992, 1994). Citrate and oxalate seem to be the most efficient anions in mobilizing P (Fox et al., 1990; Gerke, 1995).

Several plant species are known to increase the efflux of di- and tricarboxylic acid anions as a result of P deficiency, e.g. *Medicago sativa* L. (Lipton et al., 1987), *Lupinus albus* L. (Dinkelaker et al., 1989; Neumann et al., 1999; Gerke et al., 1994), *Brassica napus* L. (Hoffland et al., 1989), *Trifolium pratense* L. (Gerke et al., 1995) and *Beta vulgaris* L. (Beißner, 1997). Citrate is the main anion in leguminous plant species (Gerke, 1995) whereas oxalate dominates in *Beta vulgaris* L. and *Spinacea oleracea* L. (Gerke, 1995;

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Beißner, 1997; Keller and Römer, 1998). In graminaceous species, carboxylate efflux is also increased with decreasing P supply, however, the efflux is lower by a factor of 10–50 than that of leguminous plant species (Gerke, 1995; Egle et al., 1999).

These findings suggest that chemical mobilization of P by carboxylates can strongly improve P acquisition of plants grown in soils low in available P. The quantitative relation between the excretion of mobilizing agents and its effect on P uptake by the roots is still unknown. Mathematical descriptions of the processes involved allow the possibility of obtaining such information about this gap of knowledge. Models not only require adequate mathematical equations but also the determination of independently measured soil and plant parameters. In the first paper the mathematical model and experiments are described, by which the parameters can be determined. A second paper considers the effect of different soil and plant parameters on uptake of chemically mobilized P.

Materials and methods

Theoretical considerations

As an example of coupled diffusion processes, Nye (1983; 1984) derived a model of nutrient absorption by a single root as a result of chemical nutrient mobilization. This model will be briefly developed and discussed with respect to the boundary conditions which are required. For a planar soil-root interface, Nye (1983) developed the following equations (eq. 1–3).

$$\Delta X = b_X (\Delta X_1 - \lambda \Delta Y_1) \quad (1)$$

$$\frac{\Delta X_1}{\Delta_0 X_1} = f_1 + \lambda \left(\frac{D_Y}{D_Y - D_X} \right) \cdot (f_2 - f_1) \frac{\Delta_0 Y_1}{\Delta_0 X_1} \quad (2)$$

$$\frac{\Delta Y_1}{\Delta_0 Y_1} = f_2 \quad (3)$$

X, Y = concentration of the mobilized (X) and mobilizing (Y) species in soil

X₁, Y₁ = soil solution concentrations of the mobilized and mobilizing species

b_X, b_Y = buffering of X and Y

λ = interaction coefficient (∂X₁/∂Y₁)_X

$$f_1 = \operatorname{erfc} \frac{x}{2} \sqrt{D_X t}$$

$$f_2 = \operatorname{erfc} \frac{x}{2} \sqrt{D_Y t}$$

D_X, D_Y = effective diffusion coefficients of X and Y

x = distance from the root-soil interface

Two boundary conditions for the equations are required. The concentration of X and Y in solution at the soil-root

interface changes abruptly at t = 0 by the quantity of Δ₀X₁ and Δ₀Y₁. The second assumption is, that the excretion of the mobilizing agent (Y) affects the solubility of P (X) and therefore P diffusion, but that the diffusion of the mobilizing agent is not affected by the P depletion in the rhizosphere.

Both conditions are reasonable assumptions. For example, the mobilizing effect of citrate on the P solubility in P fixing soils did not depend on the mode of P application (continuous vs. single) over a wide range of citrate concentrations in soil (Gerke, 1994). Fox et al. (1990) found similar results for other carboxylates. We therefore conclude that it is an acceptable simplification to assume that the mobilizing agent is already excreted at t = 0.

The second condition can be interpreted in a way that the depletion of P in the rhizosphere does not affect the adsorption behaviour and diffusion of the mobilizing carboxylate species. Introducing equations 2 and 3 in equation 1 gives equation 4.

$$\Delta X = f_1 b_X \Delta_0 X_1 + \lambda b_X \Delta_0 Y_1 \left(\frac{D_X f_2 - D_Y f_1}{D_Y - D_X} \right) \quad (4)$$

From equation 4 the changes of P concentrations in the soil as a result of P uptake by a single root is calculated by integration over the range 0 > x > ∞ (equation 5).

$$\int_0^{\infty} \Delta X dx = \int_0^{\infty} f_1 b_X \Delta_0 X_1 dx + \int_0^{\infty} \lambda b_X \Delta_0 Y_1 \left(\frac{D_X f_2 - D_Y f_1}{D_Y - D_X} \right) dx \quad (5)$$

The first term in equation 5 describes changes in P concentration in the rhizosphere without interaction with citrate, the second term describes changes in P concentration as a result of chemical mobilization. This term is denoted M_X (equation 6).

$$M_X = \int_0^{\infty} \lambda b_X \Delta_0 Y_1 \left(\frac{D_X f_2 - D_Y f_1}{D_Y - D_X} \right) dx \quad (6)$$

The amount of carboxylate which accumulates in the rhizosphere by root exudation (M_Y) is given in equation 7.

$$M_Y = \int_0^{\infty} \Delta Y dx \quad (7)$$

Equation 8 is a solution of equation 7 under the assumption that changes in P (X) do not affect the solubility of the carboxylate (Y).

$$\Delta Y = b_Y \Delta Y_1 \quad (8)$$

Combining equations 3, 7, 8 gives equation 9.

$$M_Y = \int_0^{\infty} b_Y \Delta_0 Y_1 f_2 dx \quad (9)$$

Dividing equation 6 by equation 9 gives equation 10.

$$\frac{M_X}{M_Y} = \lambda \frac{b_X}{b_Y} \frac{\int_0^{\infty} \frac{D_X f_2 - D_Y f_1}{D_Y - D_X} dx}{\int_0^{\infty} f_2 dx} \quad (10)$$

Integration leads to equation 11.

$$\frac{M_X}{M_Y} = -\lambda \frac{b_X}{b_Y} \left(\frac{1}{1 + \sqrt{D_Y/D_X}} \right) \quad (11)$$

The first term in equation 11 – $\lambda b_X/b_Y$ – is equivalent to the solubilizing effect of Y on X, which can be shown to be equivalent to $(-\partial X/\partial Y)_{X_1}$ (Nye, 1984). This term describes the amount of P which must be removed from soil at a given carboxylate accumulation to keep the P concentration in the soil solution (X_1) constant. Equation 11 describes the uptake of chemically solubilized P (M_X) by the excretion of the carboxylate (M_Y) in the case of a planar soil-root interface. The extension to the cylindrical geometry is required to calculate uptake of mobilized P by a single root.

The approximations of equation 12 and 13 can be used in the cylindrical case (Nye, 1984) with a = radius of the root; t = time of uptake.

$$f_1' \approx \sqrt{\frac{a}{r}} \operatorname{erfc} \frac{r-a}{2\sqrt{D_X t}} \quad (12)$$

$$f_2' \approx \sqrt{\frac{a}{r}} \operatorname{erfc} \frac{r-a}{2\sqrt{D_Y t}} \quad (13)$$

Combining equations 12 and 13 with equations 6 and 9 and rearrangement gives equation 14.

$$\frac{M_X}{M_Y} = -\lambda \frac{b_X}{b_Y} \left(\frac{1}{1 + \sqrt{D_Y/D_X}} \right) \left(\frac{1}{\left(\frac{\sqrt{\pi D_Y t}}{4a} \right) + 1} \right) \quad (14)$$

If the diffusion coefficients in water of X and Y (D_{1X} , D_{1Y}) are the same, then equation 14 can be simplified to equation 15.

$$\frac{M_X}{M_Y} = -\lambda \frac{b_X}{b_Y} \left(\frac{1}{1 + \sqrt{b_X/b_Y}} \right) \left(\frac{1}{\left(\frac{\sqrt{\pi D_Y t}}{4a} \right) + 1} \right) \quad (15)$$

This equation is correct if $D_X t/a^2$ is small. This is the case if the considered time of uptake is $< 10^{-5}$ s, with an average D_Y of 10^{-9} cm² s⁻¹. The error is less than 3%. At higher t values, this equation is less correct, however it may nevertheless provide an estimate of P uptake or P influx as a result of chemical mobilization for a given excretion or efflux of the mobilizing agent.

The three parameters λ , b_X , and b_Y are required for the calculation of the influx of chemically mobilized P into a single root as evident from eq. 15. To determine these parameters for a defined concentration of the carboxylate in soil, the adsorption of the carboxylate and orthophosphate were investigated in model experiments. λ was calculated from the desorbed P at a defined carboxylate adsorption to soil. Carboxylate and phosphate buffering were calculated by fitting the adsorption data to the simple Langmuir or by the Freundlich adsorption isotherm with r^2 values always above 0.92.

Adsorption experiments

Twenty g of air dried and 2 mm sieved soil (soil parameters see Tab. 1) were weighed into 500 ml PVC bottles. Fifty ml of a carboxylate solution containing 0–80 mmol Na-carboxylate L⁻¹ in a 0.1 M NaCl matrix were added. The pH of the solution was adjusted with NaOH or HCl to reach the desired pH after 16 hours of equilibration. The PVC vessels were closed and shaken with an end over end shaker. After equilibration the suspensions were filtered through a 0.45 μ m membrane and P, Al and Fe concentrations were determined in the filtrate by ICP-ES. Carboxylates in the filtrates were determined by HPLC on a 30 cm Polyspher OAK column (Merck, Darmstadt, Germany). The samples were eluted with 0.1 M H₂SO₄. Details of the chromatographic procedure are described by Gerke (1995). If the citrate concentrations in the equilibrium solution were < 0.1 mM, the filtrates were preconcentrated on strong basic anion exchangers by solid phase extraction as described by Gerke et al. (1994).

Table 1: Characteristics of the soils used.

Tabelle 1: Kenndaten der verwendeten Böden.

	pH (0.01 M CaCl ₂)	C _{org} [% w/w]	CaCO ₃ [% w/w]	Fe _o * [mg kg ⁻¹]	Al _o * [mg kg ⁻¹]
Ferralsol	5.5	0.3	–**	2925	3544
Podzol	5.5	3.3	–**	1225	1390
Luvisol	7.0	1.1	0.2	1955	672
Fluvisol	6.9	1.1	0.7	2050	680

* oxalate extractable Al or Fe according to Schwertmann (1964)

** below detection limit

Results

Citrate adsorption studies were measured on a Ferralsol a Luvisol and a humic Podzol (Fig. 1, 2). The adsorption depended greatly on the pH of the equilibrium solution. In the Ferralsol and the Luvisol, both low in organic carbon, citrate adsorption decreased markedly as the pH increased (Fig. 1), whereas in the Podzol citrate adsorption was higher at pH 6.4–6.7 compared with pH 5.4–5.6 (Fig. 2).

Figures 3–5 show the P solubility in relation to the concentration of adsorbed citrate. In all soils, P mobilization is a function of the concentration of citrate on the soil solid phase.

Below a concentration of around 10 μ mol citrate g⁻¹ soil the P solubility was not markedly increased by the addition

of citrate regardless of the pH of the equilibrium solution. By increasing the concentration of adsorbed citrate, the P solubility increased exponentially, the slopes being different for the soils and pH treatments. Not only P was mobilized but so also were Fe and Al and their solubilities increased

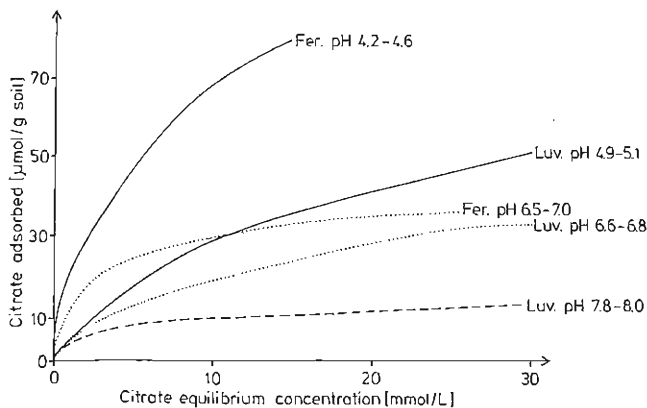


Figure 1: Citrate adsorption by a Ferralsol and a Luvisol at different pH.
Abbildung 1: Citrat Adsorption an einen Ferralsol und an eine Löß-Parabraunerde bei unterschiedlichem pH.

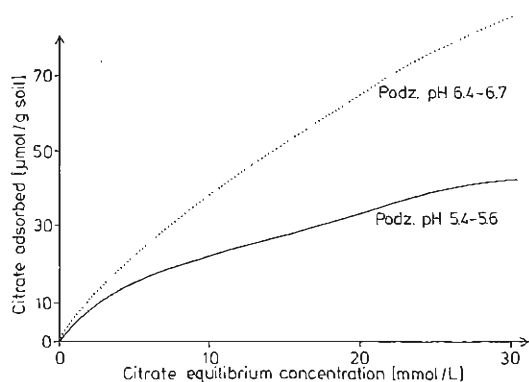


Figure 2: Citrate adsorption by a Humic Podzol at different pH.
Abbildung 2: Citrat Adsorption an einen Humuspodzol bei unterschiedlichen pH-Werten.

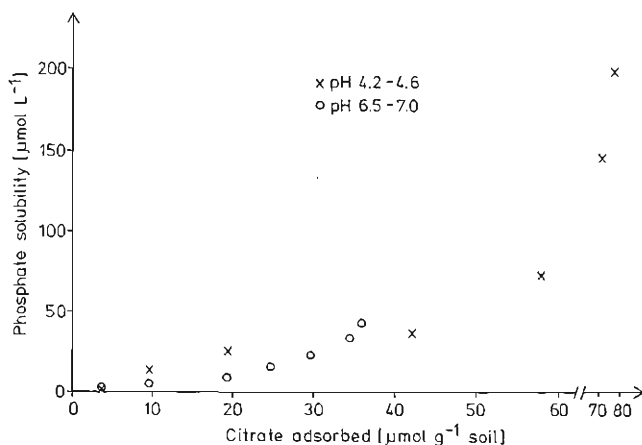


Figure 3: Phosphate solubility in a Ferralsol in relation to the amount of adsorbed citrate at different pH.
Abbildung 3: Phosphatlöslichkeit in einem Ferralsol in Abhängigkeit von der adsorbierten Citratmenge bei unterschiedlichem pH.

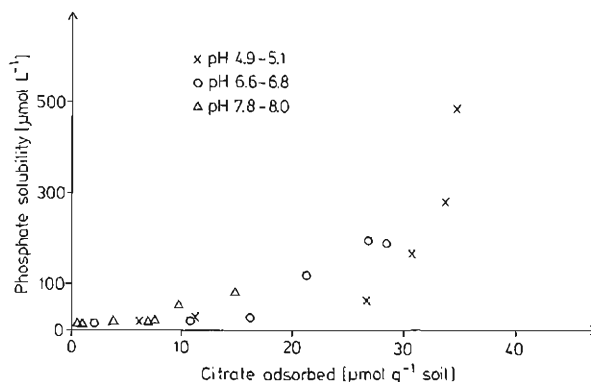


Figure 4: Phosphate solubility in a Luvisol in relation to the amount of adsorbed citrate at different pH.

Abbildung 4: Phosphatlöslichkeit in einer Löß-Parabraunerde in Abhängigkeit von der adsorbierten Citratmenge bei unterschiedlichem pH.

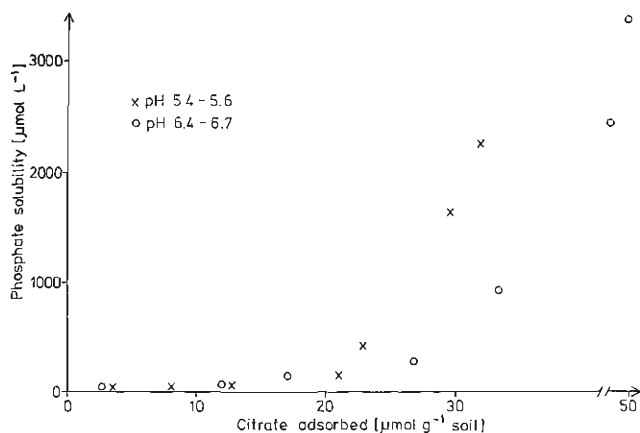


Figure 5: Phosphate solubility in a Humic Podzol in relation to the amount of adsorbed citrate at different pH.

Abbildung 5: Phosphatlöslichkeit in einem Humuspodzol in Abhängigkeit von der adsorbierten Citratmenge bei unterschiedlichem pH.

exponentially with increasing citrate concentration (data not shown).

Citrate is the most efficient carboxylate in the Ferralsol and Luvisol in mobilizing P and Fe/Al (Tab. 2). Oxalate was also very efficient in the Luvisol, whereas oxaloacetate had only a small effect on P solubility even at high concentrations in soil.

The effect of the pH on the adsorption of oxalate to a Fluvisol is shown in Fig. 6. The adsorption decreased as the pH increased.

The P solubility in the Fluvisol depending on pH and oxalate loading is a function of the concentration of oxalate at the soil solid phase. The maximum P mobilization was higher at the lowest pH value compared with the pH above 6.0 or 7.0 (Fig. 7).

Discussion

The results presented here allow the calculation of parameters which are required for the modelling of the influx of mobilized P as a result of carboxylate excretion.

Table 2: Maximum mobilization of phosphate and Fe + Al by different carboxylate anions, concentrations of the soil solutions at a concentration of 80 μmol carboxylate g^{-1} soil.

Tabelle 2: Maximale gemessene Phosphat- und Fe + Al-Mobilisierung durch verschiedene Säureanionen, Bodenlösungskonzentrationen bei einer Carboxylatkonzentration von 80 μmol g^{-1} Boden.

		Phosphate $\mu\text{mol L}^{-1}$	Fe+Al
Ferralsol pH 4.1–4.7	citrate	198.5	9420
	oxalate	28.3	1314
	malate	25.2	2810
	oxaloacetate	7.5	72
Luvisol pH 7.7–8.1	citrate	85.6	2341
	oxalate	70.4	1234
	malate	36.4	812
	oxaloacetate	32.2	972

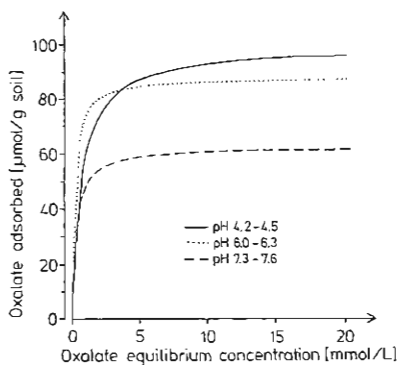


Figure 6: Oxalate adsorption by a Fluvisol at different pH.
Abbildung 6: Oxalatadsorption an einen Fluvisol bei unterschiedlichen pH-Werten.

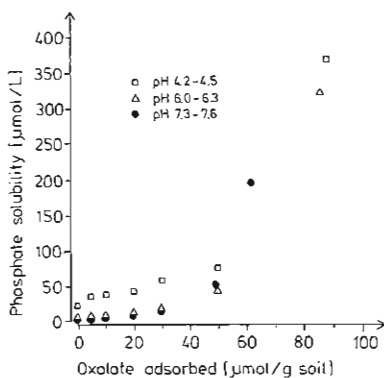


Figure 7: Phosphate solubility in a Fluvisol in relation to the amount of adsorbed oxalate at different pH.
Abbildung 7: Phosphatlöslichkeit in einem Fluvisol in Abhängigkeit von der adsorbierten Oxalatkmenge bei unterschiedlichem pH.

They also provide information about the mechanism of P mobilization. As shown by the close relationship between P solubility and adsorbed citrate or oxalate, the initial adsorption of the carboxylate to the soil solid phase is essential for the mobilization of P. *Kirk* (1999) modelled the effect of citrate on P desorption by assuming that a part of soil P is affected by the application of citrate whereas

another fraction of soil P is unaffected. From a physico-chemical point of view this assumption is not justifiable. Adsorption of citrate to the soil solid phase will affect the solubility of the entire soil P fraction which is adsorbed.

In all four soils investigated, changes in pH over a wide range had a relatively small effect on P solubility compared with the effect of the carboxylate anion. These results indicate that Ca-P precipitates do not constitute the principal fractions mobilized. The close relationship between Al/Fe solubility and P solubility also shows that it is the Fe/Al-associated P that is mainly mobilized. This is in agreement with previous results (*Earl et al.*, 1979; *Fox et al.*, 1990 *Gerke*, 1992, 1994).

The mechanisms are ligand exchange between the organic anion and the orthophosphate anion, and the dissolution of P sorbing Fe- and Al- sites (*Gerke*, 1992). Both mechanisms are interconnected because dissolution requires the adsorption of the organic anion to the soil solid phase as the initial step (*Cornell and Schindler*, 1987). Hence P mobilization is a function of the concentration of the initially adsorbed carboxylate, as shown in the present paper.

Below a concentration of 10 μmol citrate or oxalate g^{-1} soil, the P mobilization is negligible or small. *Jones and Darrah* (1994) investigated the effect of citrate and malate on the P solubility at different pH and found no effect of citrate in 6 of 7 soils which were investigated. This is in accordance with the present results. However, the carboxylate concentration which can accumulate the rhizosphere of mobilizing plant species is unknown in most cases. *Dinkelaker et al.* (1989) and *Gerke et al.* (1994) found more than 50 μmol citrate g^{-1} soil in the proteoid rhizosphere of white lupin under non-sterile conditions. *Gerke et al.* (1995) found citrate concentrations in the rhizosphere of *Trifolium pratense* L. of about 12 μmol g^{-1} soil within 1 mm distance to the soil/root interface. From the concentration profile it was further concluded that, in close proximity to the roots, the citrate concentration in the rhizosphere soil may be even higher. However measurements made at a planar soil/root interface should not be taken to be directly applicable to cylindrical roots in soil. This has recently been emphasized by *Geelhoed et al.* (1999). Nevertheless, these results indicate, that under non-sterile conditions an accumulation of citrate in the rhizosphere may occur which is higher than 10 μmol g^{-1} soil.

Acknowledgements

The helpful criticism by *P. H. Nye* on an earlier version of the manuscript and the constructive comments by *E. A. Kirkby* are gratefully acknowledged.

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The quantitative effect of chemical phosphate mobilization by carboxylate anions on P uptake by a single root. II. The importance of soil and plant parameters for uptake of mobilized P

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Dedicated to *Albrecht Jungk* on the occasion of his 70th birthday

Accepted 26 January 2000

Summary – Zusammenfassung

Model calculations were made in order to quantify the effect of carboxylate excretion on phosphate (P) uptake by a single root.

The uptake of chemically mobilized P increased exponentially with increasing concentration of adsorbed citrate or oxalate in soil because of the exponential relationship between adsorbed carboxylate and the solubilizing effect of carboxylate on P.

The effect of local citrate excretion compared with uniform citrate excretion along the whole root was also calculated. Local exudation increased the uptake of chemically mobilized P because the higher concentration of citrate increases the solubilization of P. Additionally the effect of citrate excretion by root clusters e.g. proteoid roots was evaluated. Uptake of chemically mobilized P by root clusters was much higher than that of single roots, especially if the ratio of P buffering to citrate buffering was high. This is often the case in P fixing soils where by definition P buffering is high and citrate buffering is low because of the short time of reaction between root excreted citrate and rhizosphere soil. The reason for the superiority of cluster roots lies in the fact that most of the mobilized P is transported away from a single root to be absorbed by neighbouring roots in the clusters. This phenomenon demonstrates the strong ecological significance of cluster roots in relation to nutrient mobilization.

The calculations on the effect of oxalate excretion by sugar beet roots on the uptake of mobilized P show that under P fixing conditions the influx of mobilized P will exceed that of P transported by diffusion to the root surface by a factor of 1.5–6.0.

Key words: P-mobilization / root exudates / carboxylates / P-uptake / modeling / proteoid roots

Der quantitative Effekt einer chemischen Phosphatmobilisierung durch Carbon-säureanionen auf die P-Aufnahme durch eine Einzelwurzel. II. Die Bedeutung von Boden- und Pflanzenparametern für die Aufnahme von mobilisiertem P

Um die Bedeutung der Carboxylatausscheidung für die Phosphataufnahme durch eine Einzelwurzel quantitativ zu erfassen, wurden Modellberechnungen durchgeführt.

Die Aufnahme von chemisch mobilisiertem P stieg mit zunehmender Konzentration an adsorbiertem Citrat oder Oxalat im Rhizosphärenboden exponentiell an. Dies ist auf die exponentielle Beziehung zwischen dem adsorbierten Carboxylat im Boden und dem Mobilisierungsfaktor von Carboxylat auf Phosphat zurückzuführen.

Es wurde ferner der Effekt einer lokalen gegenüber einer gleichmäßigen Ausscheidung von Citrat auf die Aufnahme von mobilisiertem P untersucht. Die lokale Ausscheidung erhöhte die Aufnahme von mobilisiertem P aufgrund der Erhöhung des Mobilisierungseffekts von Citrat auf Phosphat.

Weiterhin wurde die Wirkung der Citratausscheidung von Wurzelclustern auf die Aufnahme von mobilisiertem P untersucht. Die P-Aufnahme war in den Wurzelclustern sehr viel höher, als bei einer Einzelwurzel, besonders dann, wenn das Verhältnis von Phosphatpufferung zu Citratpufferung hoch war. Dies ist häufig der Fall in P-fixierenden Böden, in denen definitionsgemäß die Phosphatpufferung hoch und die Citratpufferung aufgrund der geringen Reaktionszeit zwischen Citrat und Rhizosphärenboden gering ist. Der Grund für die Überlegenheit von Clusterwurzeln bezüglich der Aufnahme von mobilisiertem P liegt darin, dass das mobilisierte, von der Einzelwurzel wegdiffundierende P von benachbarten Clusterwurzeln aufgenommen wird, während dies bei einer Einzelwurzel nicht der Fall ist. Diese Ergebnisse zeigen die große ökologische Bedeutung von Wurzelclustern in Bezug auf die Nährstoffmobilisierung.

Die Modellberechnungen zum Einfluss einer Oxalatausscheidung von Zuckerrübenwurzeln auf die Aufnahme von mobilisiertem P zeigen, daß der Influx von mobilisiertem P um den Faktor 1,5–6,0 höher ist als der Influx des diffusiv antransportierten P.

Introduction

In a preceding paper, we presented a mathematical model which allows the calculation of uptake of chemically

mobilized nutrients (Gerke et al., 2000). We also reported experimental data on the mobilization of phosphate (P) induced by several carboxylates. In the present paper we conduct sensitivity analysis to evaluate the effect of soil and

We focus on the effect of citrate and oxalate efflux on the influx of mobilized P, the effect of root clusters and concentrated local exudation of mobilizing agents on the acquisition of mobilized P.

Model parameters

In the previous paper (Gerke et al., 2000) we developed an equation which allows the quantification of M_X/M_Y (equation 1).

$$\frac{M_X}{M_Y} = -\lambda \frac{b_X}{b_Y} \left(\frac{1}{1 + \sqrt{b_X/b_Y}} \right) \left(\frac{1}{\left(\frac{\sqrt{\pi D_Y t}}{4a} \right) + 1} \right) \quad (1)$$

M_X is the uptake or the influx of mobilized nutrient into a single root, M_Y is the excretion or efflux of mobilizing agent. If not otherwise mentioned the time of uptake t is 1000 [s] and the root radius a is 0.01 cm. For the calculation of the effective diffusion coefficient of citrate (D_Y), other information is needed, the volumetric water content, the impedance factor and the buffering b_Y . The volumetric water content was set to 30% (v/v), the impedance factor f was calculated from the volumetric water content with the aid of simple linear regression equations developed by Kaselowsky (1990, p. 32, 33). Carboxylate buffering (b_Y) and phosphate buffering (b_X) were calculated from the adsorption curves (Gerke et al., 2000).

The solute interaction coefficient $-\lambda$ describes the increase of P solubility as a result of the increase of carboxylate solubility at a definite concentration of P in the soil. This parameter was calculated from figures 3, 4, 5 and 7 of the preceding paper (Gerke et al., 2000) where carboxylate solubility and P solubility were measured at each level of carboxylate application. As outlined by Nye (1984), the first term in equation 1 describes the effect of the excretion of mobilizing agent on nutrient solubility; the product of the second and third term quantifies the proportion of chemically mobilized nutrient which is taken up by the root.

Results

Effect of adsorbed citrate and oxalate on the solubilizing effect of phosphate by citrate

The results of the previous paper showed that the P mobilization by citrate or oxalate depends on the quantity of adsorbed carboxylate (Gerke et al., 2000). From Fig. 1–3 it

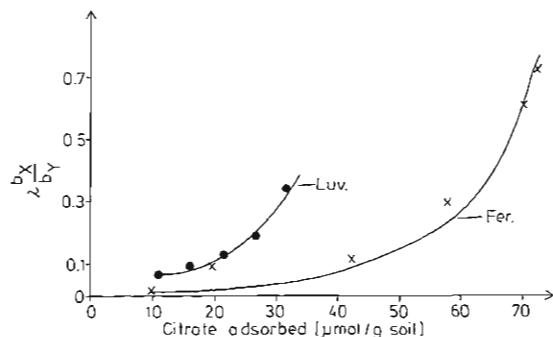


Figure 1: Relationship between adsorbed citrate and the solubilizing effect of citrate on phosphate in a Ferralsol at pH 4.2–4.6 and a Luvisol at pH 6.6–6.8. The curves show the fit of the function $y = ab^x$.

Abbildung 1: Beziehungen zwischen der adsorbierten Citratmenge und dem Mobilisierungsfaktor von Citrat auf Phosphat in einem Ferralsol bei pH 4,2–4,6 und einer Löß-Parabraunerde bei pH 6,6–6,8. Die Kurven stellen die statistische Anpassung mittels einer Exponentialfunktion der Form $y = ab^x$ dar.

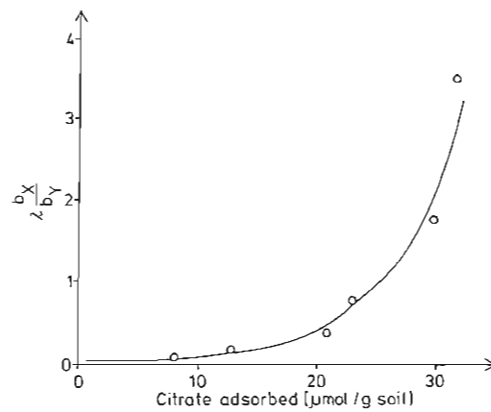


Figure 2: Relationship between adsorbed citrate and the solubilizing effect of citrate on phosphate in a Humic Podzol at pH 5.4–5.6. The curve shows the fit of the function $y = ab^x$.

Abbildung 2: Beziehung zwischen der adsorbierten Citratmenge und dem Mobilisierungsfaktor von Citrat auf Phosphat in einem Humuspodzol bei pH 5,4–5,6. Die Kurve stellt die statistische Anpassung mittels einer Exponentialfunktion der Form $y = ab^x$ dar.

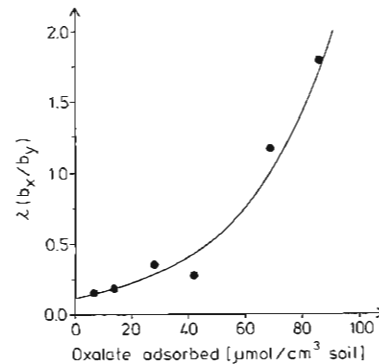


Figure 3: Relationship between the solubilizing effect of oxalate on phosphate in a Fluvisol at pH 7.3–7.6. The curve shows the fit of the equation $y = ab^x$.

Abbildung 3: Beziehung zwischen der adsorbierten Oxalatkmenge und dem Mobilisierungsfaktor von Oxalat auf Phosphat in einem Fluvisol bei pH 7,3–7,6. Die Kurve stellt die statistische Anpassung mittels einer Exponentialfunktion der Form $y = ab^x$ dar.

is evident that the solubilizing effect $-\lambda b_X/b_Y$ is related to the quantity of adsorbed citrate or oxalate. The curves were fitted by an exponential function $y = ab^x$. The r^2 values varied between 0.77 (Ferralsol) and 0.98 (Luvisol).

In order to determine the effect of citrate on the influx of mobilized P [$\text{mol } 10^{-14} \text{ s}^{-1} \text{ cm}^{-1}$ root length], the citrate efflux was assumed to be 28 [$\text{mol } 10^{-14} \text{ s}^{-1} \text{ cm}^{-1}$]. This is in the order of magnitude which was measured as an average value of the whole root system of alfalfa and red clover starved of P (Gerke, 1995). Adsorbed citrate strongly affects the influx of mobilized P (Fig. 4, 5).

The influx of mobilized P increases exponentially in the Ferralsol and Luvisol and reaches a maximum in the Podzol. In this soil, the influx of mobilized P was highest and exceeded values of 9 [$\text{mol } 10^{-14} \text{ s}^{-1} \text{ cm}^{-1}$] which was about a factor of 3 higher than the maximum influx in the other two soils.

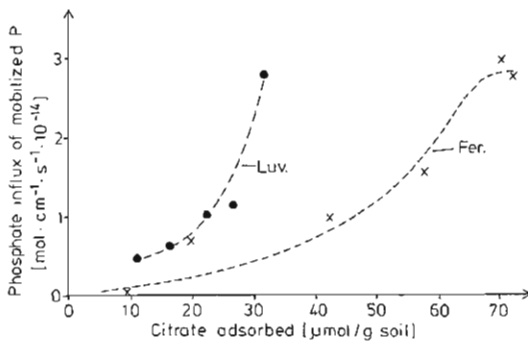


Figure 4: Relationship between adsorbed citrate and the influx of mobilized P by a single root in a Ferralsol at pH 4.2–4.6 and a Luvisol at pH 6.6–6.8. The curves describe the supposed function between the two parameters.

Abbildung 4: Beziehung zwischen der adsorbierten Citratmenge und dem P-Influx aufgrund chemischer Mobilisierung durch eine Einzelwurzel in einem Ferralsol bei pH 4,2–4,6 und in einer Löß-Parabraunerde bei pH 6,6–6,8. Die Kurven stellen eine Interpretation der Beziehung dar.

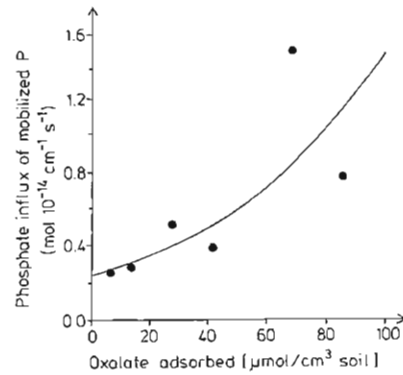


Figure 6: Relationship between adsorbed oxalate and the influx of mobilized P by a single root in a Fluvisol at pH 7.3–7.6. The curve describes the supposed function between the two parameters.

Abbildung 6: Beziehung zwischen der adsorbierten Oxalatsmenge und dem P-Influx aufgrund chemischer Mobilisierung durch eine Einzelwurzel in einem Fluvisol bei pH 7,3–7,6. Die Kurve stellt eine Interpretation der Beziehung dar.

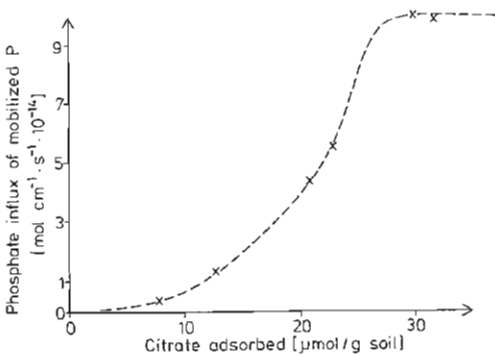


Figure 5: Relationship between adsorbed citrate and the influx of mobilized P by a single root in a Humic Podzol at pH 5.4–5.6. The curve describes the supposed function of the two parameters.

Abbildung 5: Beziehung zwischen der adsorbierten Citratmenge und dem P-Influx aufgrund chemischer Mobilisierung durch eine Einzelwurzel in einem Humuspodzol bei pH 5,4–5,6. Die Kurve stellt eine Interpretation der Beziehung dar.

In the case of the Fluvisol, we used an oxalate efflux of $6.3 \text{ [mol } 10^{-14} \text{ s}^{-1} \text{ cm}^{-1}]$ for the calculations. This value was measured for the whole root system of P starving sugar beet plants (Beißner, 1997). Also for oxalate, there is a close relationship between adsorbed carboxylate and the influx of mobilized P, which can be described by an exponential function with a relatively high r^2 (Fig. 6). However, the influx of mobilized P is lower in this case resulting from the lower efflux of oxalate compared with citrate and the higher efficiency of citrate to mobilize P.

The effect of varying citrate efflux on the influx of mobilized P

Equation 1 can also be used to calculate the effect of citrate efflux on P influx at constant solubilizing effect of citrate on P. At a definite concentration of adsorbed carboxylate, which itself is closely related to the solubilizing effect, the influx of mobilized P is linearly related to the carboxylate efflux. In the case of citrate this relationship

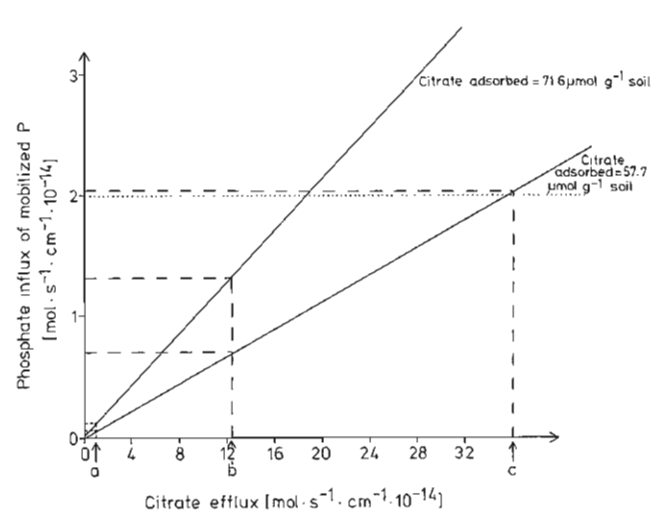


Figure 7: Relationship between citrate efflux and influx of mobilized P by a single root in a Ferralsol at pH 4.2–4.6. Arrows indicate the maximum average citrate efflux of ryegrass (a), white clover (b) and red clover (c). **Abbildung 7:** Beziehung zwischen dem Citratefflux und dem P-Influx aufgrund chemischer Mobilisierung durch eine Einzelwurzel in einem Ferralsol bei pH 4,2–4,6. Die Pfeile stellen den maximal gemessenen Citratefflux von Weidelgras (a), Weißklee (b) und Rotklee (c) dar.

is shown in figures 7–9 for the Ferralsol, Luvisol and Podzol.

At a definite citrate efflux, the influx of mobilized P in the Podzol is higher than that in the other two soils.

Calculations allow the estimation of the required P influx to satisfy the demand of the plants. Assuming a necessary P concentration of 0.3% P in the dry shoot biomass and a realistic root length/shoot weight ratio, the required P influx to reach this P concentration in the shoots can be calculated. For white lupin grown in Mitscherlich pots Gerke et al. (1994) measured a shoot dry matter of about 20 g/pot and a total root length of about 40 000 cm/pot as an average value of 8 weeks old lupin plants reasonably well supplied with P. Accordingly, the required P influx to obtain 0.3% P in the shoots can be calculated as $1.9 \text{ mol P} \cdot 10^{-14} \text{ s}^{-1} \text{ cm}^{-1}$. In

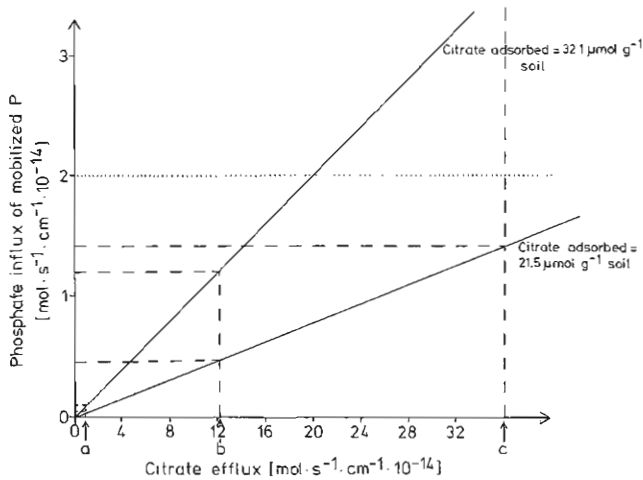


Figure 8: Relationship between citrate efflux and influx of mobilized P by a single root in a Luvisol at pH 6.6–6.8. Arrows indicate the average maximum citrate efflux of ryegrass (a), white clover (b) and red clover (c). **Abbildung 8:** Beziehung zwischen dem Citratefflux und dem P-Influx aufgrund chemischer Mobilisierung durch eine Einzelwurzel in einer Löß-Parabraunerde bei pH 6,6–6,8. Die Pfeile stellen den maximal gemessenen Citratefflux von Weidelgras (a), Weißklee (b) und Rotklee (c) dar.

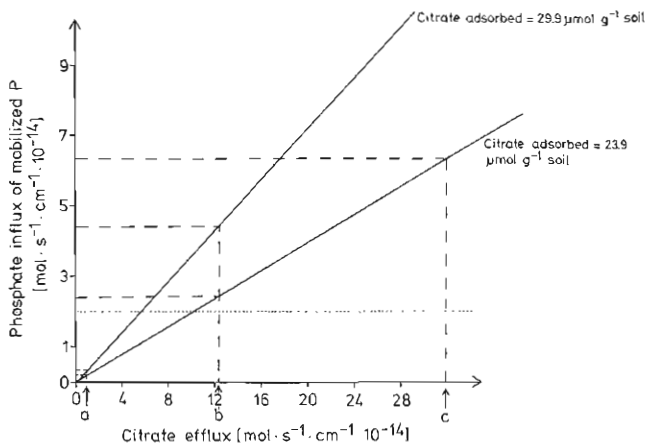


Figure 9: Relationship between citrate efflux and influx of mobilized P by a single root in a Humic Podzol at pH 5.4–5.6. Arrows indicate the maximum average citrate efflux of ryegrass (a), white clover (b) and red clover (c).

Abbildung 9: Beziehung zwischen dem Citratefflux und dem P-Influx aufgrund chemischer Mobilisierung durch eine Einzelwurzel in einem Humuspodzol bei pH 5,4–5,6. Die Pfeile stellen den maximal gemessenen Citratefflux von Weidelgras (a), Weißklee (b) und Rotklee (c) dar.

Fig. 7–9, the P influx of 2 is marked as a threshold value. Also, in these figures, the maximum citrate efflux from ryegrass (a), white clover (b) and red clover (c) as measured by Gerke (1995), is indicated by an arrow. There are large differences between the three soils. In the Podzol, the maximum citrate efflux of red clover and also of white clover is sufficient to attain the P influx threshold value of 2 at medium to high concentrations of adsorbed citrate (Fig. 9). In the Ferralsol and Luvisol, the high citrate efflux from red clover is required to reach the influx of 2 of mobilized P (Fig. 7, 8). In all three soils, chemical

mobilization of P by citrate excretion by ryegrass roots does not contribute to a significant influx of mobilized P.

The effect of local excretion of citrate on the influx of mobilized P

A basic assumption of the results shown above is the uniform citrate excretion along the whole root, an assumption which is invalid, as discussed e.g. by Marschner et al. (1990). For several plant species, it has been shown that the efflux of carboxylates is concentrated to a small region behind the root tips as shown for rape by Hoffland et al. (1989), sugar beet (Beißner, 1997), alfalfa and red clover cultivars (Gerke, unpublished results). From this viewpoint, the effect of a local exudation of the carboxylate on the influx of mobilized P is of interest for P acquisition. For these calculations, a knowledge of the relationship between carboxylate efflux and its accumulation at the soil solid phase is required. Experimental results on this relationship are lacking at present. However hypothetical relations in the case of citrate and the Ferralsol are formulated in Fig. 10.

Two curves are assumed to cover the range of possible relationships between the two parameters, assuming the relation being linear and including implicitly the effect of microbial degradation of citrate.

In Fig. 11, the effect of a decreasing proportion of the root which excretes citrate on the influx of mobilized P from the Ferralsol is shown, assuming a constant overall citrate efflux of $10 \text{ mol} \cdot 10^{-14} \text{ s}^{-1} \text{ cm}^{-1}$. Local exudation strongly increases the influx of mobilized P especially if the excreting proportion of the root decreases. The reason for this effect is the exponential relationship between citrate concentration at the soil solid phase and the solubilizing effect, as shown in Fig. 1 and 2. The same effect is to be expected in the case of oxalate (Fig. 3). These calculations consider a single root and ignore root competition.

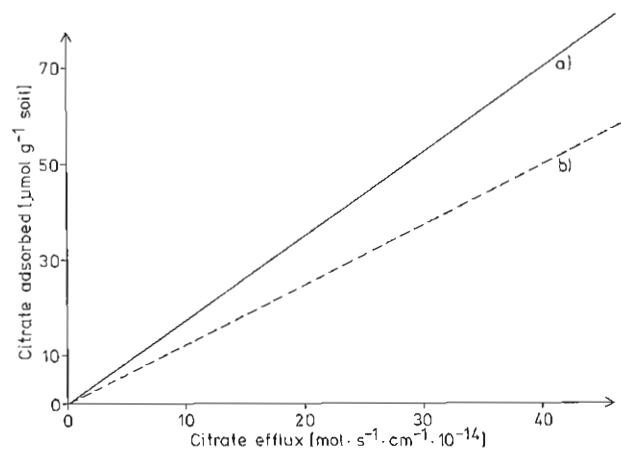


Figure 10: Hypothetical relationship between citrate efflux by a single root and accumulation of citrate in the rhizosphere soil.

Abbildung 10: Hypothetische Beziehung zwischen dem Citratefflux einer Einzelwurzel und der Citratkonzentration im Rhizosphärenboden.

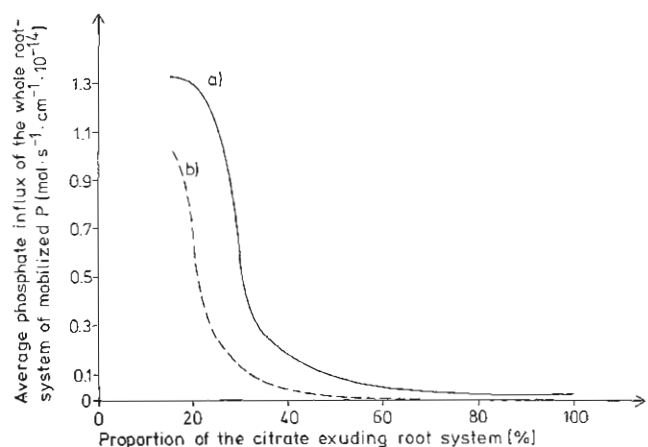


Figure 11: Relevance of the proportion of a single root which excretes citrate for the influx of mobilized P of the whole root. The data of Fig. 10 and the parameters of a Ferralsol at pH 4.2–4.6 were used for the calculations.

Abbildung 11: Bedeutung des Anteils einer Einzelwurzel an der Citrausscheidung für den P-Influx aufgrund chemischer Mobilisierung über die gesamte Wurzel. Die Beziehung aus Abb. 10 und Parameter für einen Ferralsol bei pH 4,2–4,6 wurden verwendet.

Assuming parallel oriented roots, the average half distance (r) between single roots can be calculated by equation 2 with L_v [cm root length/cm³ soil] as the rooting density.

$$r = \frac{1}{\sqrt{L_v \cdot \pi}} \quad (2)$$

Assuming values for L_v between 2 and 10, average half distances (r) between two roots of 0.18–0.40 cm are obtained. Considering the small distances of P depletion in P fixing soils < 0.2 cm (Hendriks et al., 1981), it can be assumed that the P depletion profiles of neighbouring roots often do not overlap. Root hairs, which are not considered so far, will extend the depletion zone. Root clusters, which are formed by some plant species at low P supply, can cause a very high local root density. For example, white lupin forms clusters of proteoid root which possess a high density of bottle-brush like rootlets with extensive root hair formation (Dinkelaker et al., 1989). Such a root morphology is also found in plant species of the Proteaceae, Casuarinaceae, Myricaceae, Moraceae and several species of the Fabaceae (Dinkelaker et al., 1995). Carboxylate accumulation is concentrated to the proteoid rhizosphere soil (Dinkelaker et al., 1989; Gerke et al., 1994; Neumann et al., 1999). Concentrated excretion of citrate is an advantage compared with uniform excretion along the whole root system because of the exponential relation between citrate accumulation and the solubilizing effect of citrate on P mobilization as shown previously (Fig. 11). However, there is a further marked effect of root cluster formation on uptake of mobilized P.

As shown in Fig. 12 b, the distance between root hairs of the proteoid rootlets is very low, not exceeding 0.1 cm. This is a major difference contrasting to the relatively large

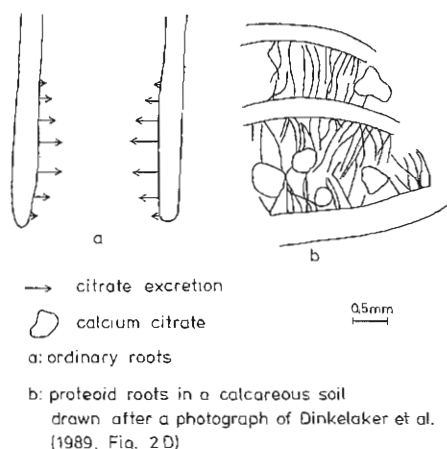


Figure 12: Average distance between single roots assuming a medium root length density in soil (a) and between proteoid roots and root hairs of white lupin after Dinkelaker et al. (1989) (b). Note the strong overlapping of the P depletion zones in the proteoid rhizosphere compared to that of single roots.

Abbildung 12: Mittlerer Abstand zwischen einzelnen Wurzeln bei einer durchschnittlichen Wurzellängendichte im Boden (a) und Abstände zwischen Wurzeln und Wurzelhaaren in der Proteoidrhizosphäre von Weißer Lupine nach Dinkelaker et al. (1989) (b). Man beachte die starke Überlappung der P-Verarmungszonen in der Proteoidrhizosphäre im Gegensatz zu den Einzelwurzeln.

average distance between ordinary roots as shown in Fig. 12 a. Additionally, the depletion zones of root hairs in the proteoid rhizosphere overlap. In approximate terms all of the chemically mobilized P of the proteoid rhizosphere can be taken up by the proteoid roots, in contrast to single roots. This is of importance in relation to the influx of chemically mobilized P. This is shown in Fig. 13 in the sensitivity analysis of the ratios of buffering on the ratio of P taken up by a single root/P mobilized, shown for different values of t .

A high buffering ratio is a typical feature of soils, low in available P. Phosphate buffering (b_X) is high and the buffering of the mobilizing agent (b_Y) is often rather low, because of the short time of reaction between the excreted carboxylate and rhizosphere soil. Under these conditions, root clusters not only increase influx of mobilized P by a nonuniform excretion of mobilizing agents but also by the mechanism that nearly all the total mobilized P is taken up by the cluster roots. This is especially important, if the ratio of buffering exceeds 10 and if the time of uptake is $> 10^5$ s (Fig. 13). Under these conditions the geometry of cluster roots leads to an increased uptake of mobilized P by these roots which is about a factor of 10 or more higher than that of a single root (Fig. 13 c, at b_X/b_Y values < 10).

To evaluate the effect of P buffering on the influx of P mobilized by oxalate, we made model calculations for the case oxalate/Fluvisol. The parameters adsorbed oxalate and P buffering were varied (Fig. 14).

The effect of b_X on the influx of chemically mobilized P was small at low concentrations of adsorbed oxalate. At high concentrations of oxalate at the soil solid phase P buffering strongly affects the influx of mobilized P.

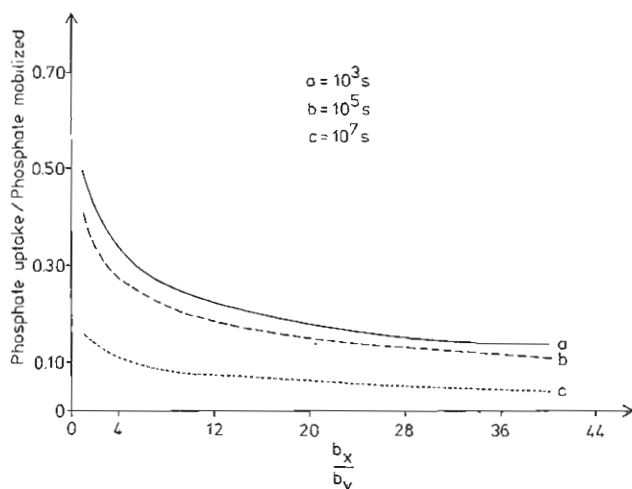


Figure 13: The importance of b_x/b_y (buffering of phosphate vs. buffering of citrate) for the proportion of chemically mobilized P which is taken up by a single root assuming different times of uptake.

Abbildung 13: Die Bedeutung von b_x/b_y (Verhältnis der Pufferung von Phosphat zu der von Citrat) für den Anteil des chemisch mobilisierten P, das von einer Einzelwurzel aufgenommen wird. Es werden dabei unterschiedliche Aufnahmezeiträume angenommen.

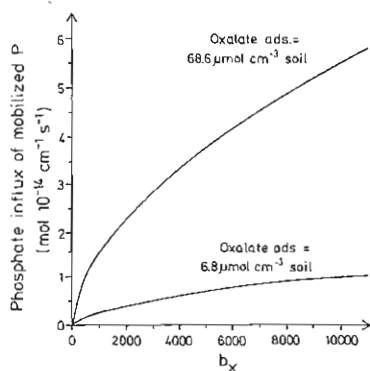


Figure 14: Effect of phosphate buffering on the influx of mobilized P by oxalate in a Fluvisol at different levels of adsorbed oxalate.

Abbildung 14: Einfluß der Phosphatpufferung auf den Influx von mobilisiertem P in einem Fluvisol bei unterschiedlichen Mengen an adsorbiertem Oxalat.

Discussion

The model proposed by Nye (1983, 1984) has been further developed to calculate the effect of carboxylate excretion on the uptake of mobilized P (Gerke et al., 2000). Sensitivity analysis of the effect of soil and plant parameters on the influx of mobilized P show the strong importance of the accumulation of the mobilizing carboxylate for the acquisition of P. An increasing accumulation of citrate (Fig. 4, 5) or oxalate (Fig. 6) increased the influx of mobilized P exponentially. The origin of this relationship lies in the fact that the solubilizing effect of the carboxylate on P increased exponentially by increasing the quantity of carboxylate which is adsorbed to the soil solid phase. This is the reason why nonuniform excretion of mobilizing agents along a single root is favourable for the uptake of chemically mobilized P.

Hoffland (1992) calculated the effect of proton excretion on uptake of chemically mobilized P from rock phosphate in a mixture with quartz sand. Sensitivity analysis showed the effect of local proton excretion on uptake of mobilized P. If the proportion of proton excreting roots decreased from 30 to 10%, P uptake increased by a factor of 7. The marked positive effect of local exudation is in agreement with the calculations in the present paper.

Such a local exudation of P mobilizing agents is of some importance for dicotyledenous plant species. Hoffland et al. (1989) showed for rape and Dinkelaker et al. (1989) for white lupin that organic acids were excreted locally. The local excretion of mainly oxalate in sugar beet is also concentrated to the zone 1.5 cm behind the root tip (Beißner, 1997). Different alfalfa and red clover cultivars excrete citrate and oxaloacetate mainly in the region 1.5 cm behind the root tip (Gerke, unpublished). Yellow lupin like white lupin also forms proteoid root clusters as a result of P deficiency (Egle et al., 1999). Similar to white lupin macroscopically visible precipitates of calcium citrate in the proteoid rhizosphere soil occur in plants grown on a calcareous soil (Marschner, pers. communication, 1993).

It seems reasonable to suppose that local exudation of P mobilizing agents can increase the influx of chemically mobilized P by a factor of 10 or more compared to uniform excretion (Fig. 12). In the case of root cluster formation (e.g. proteoid roots), a geometrical factor further increases the influx of chemically mobilized P. As calculated from the rooting density, the average half distance of single roots often exceeds 0.2 cm. In this case, P depletion profiles of single roots do not overlap. Root hairs are abundant in proteoid roots of most cluster forming species (Dinkelaker et al., 1995). The root hairs of the proteoid roots are in close proximity as shown for white lupin. Chemically mobilized P which diffuses away from the excreting root, will be taken up by neighbouring roots or root hairs. Thus, approximately all of the chemically mobilized P in the proteoid rhizosphere will be taken up by the cluster roots. As shown in Fig. 13, this is of central relevance, if the ratio of P buffering vs. citrate buffering - b_x/b_y - is high, assuming a constant solubilizing effect. This is often the case in P fixing soils, where P buffering is high and buffering of freshly excreted citrate may be low, because of the short time of reaction between soil and citrate. If the citrate is excreted by root clusters, influx of mobilized P may increase by a factor of 3–100 compared with a single root (Fig. 13). Additionally, local exudation of citrate in root clusters may cause a higher solubilizing effect as discussed before. In general, the formation of cluster roots leads to a more efficient use of assimilates (carboxylates) in the mobilization process. The induction of proteoid root cluster formation is affected by several parameters, however, P deficiency is a key factor (Johnson et al., 1994; Dinkelaker et al., 1995). Also, Fe-deficiency can induce cluster root formation in dicotyledenous species (Rosenfield et al.,