Phosphate sorption by Egyptian, Ethiopian and German soils and P uptake by rye (*Secale cereale* L.) seedlings

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Summary - Zusammenfassung

Phosphate sorption was studied in samples (0 - 20 cm depth) of five soils from Egypt (pH 7.4 - 8.7), four soils from Ethiopia (pH 3.9 - 5.3) and six soils from Germany (pH 3.3 - 7.2). Sorption parameters were calculated according to *Pagel* and *Van Huay* (1976) and according to Langmuir (*Syers* et al., 1973). Phosphate sorption parameters and oxalate extractable Fe and Al (Fe_{ox}, Al_{ox}) were related to the phosphate uptake by young rye plants in Neubauer pot experiments.

P sorption parameter after *Pagel* and *Van Huay* (A) correlated significantly positively with the Fe_{ox} and Al_{ox} content in acid (r = 0.73) as well as in calcareous soils (r = 0.89) if the whole equilibrium concentration range (0 - 14 mg P/L) was considered. The relations calculated after Langmuir (B) were similar.

P uptake by rye in acid soils was negatively correlated with the affinity constant n (r = -0.76, (A)). In calcareous soils, a negative correlation between P uptake and affinity constant was calculated in the lower P equilibrium range (0 - 2.8 mg P/L) only for (B). Thus, P uptake decreased with increasing strength of P bonding to soil.

From these results it is concluded that phosphate sorbed to Fe/Al oxides is an important P source for plants in acid and calcareous soils.

Phosphatadsorption von ägyptischen, äthiopischen und deutschen Böden und Phosphatentzug von Roggenkeimpflanzen

Die Phosphatadsorption wurde in Proben (0 - 20 cm Tiefe) von 5 Böden aus Ägypten (pH 7,4 - 8,7), 4 Böden aus Äthiopien (pH 3,9 - 5,3) und 6 Böden aus der Bundesrepublik Deutschland (pH 3,3 - 7,2) studiert. Alle Sorptionsparameter sind nach *Pagel* und *Van Huay* (1976) und nach Langmuir (*Syers* et al., 1973) berechnet worden. Die Parameter der Phosphatadsorption und Gehalte an oxalat-extrahierbarem Eisen und Aluminium (Fe_{ox}/Al_{ox}) wurden zur Phosphataufnahme durch junge Roggenpflanzen (Neubauer-Methode) in Beziehung gesetzt.

Es zeigte sich, daß die P-Adsorption sowohl in sauren (r = 0,73) als auch in kalkhaltigen Böden (r = 0,89) signifikant positiv mit dem Gehalt an Fe_{ox}/Al_{ox} korrelierte, wenn der Ansatz von Pagel (A) verwendet wurde. Die Beziehung von Langmuir (B) brachte ähnliche Relationen. Dies galt für die Betrachtung des gesamten Bereichs der Adsorptionsisotherme (0 - 14 mg P/L).

Die P-Aufnahme der Roggenpflanzen korrelierte negativ mit der Affinitätskonstante n für die Phosphatadsorption in den sauren Böden (r = -0,76 (A), signifikant). Bei Kalkböden galt dies nur für den Bereich niedriger P-Konzentrationen (0 - 2,8 mg P/L) in der Lösung, wie sie für Vegetationsversuche zutreffen. Das heißt, die P-Aufnahme sank erwartungsgemäß mit steigender Bindungsintensität. Parameter der P-Adsorptionsisotherme charakterisierten dies jedoch nur in niederen Konzentrationsbereichen sinnvoll. Aufgrund dieser Zusammenhänge, sowie der korrelativen Beziehungen zwischen P-Adsorption und Gehalten an Fe_{ox}/Al_{ox} auch in Kalkböden, wird geschlossen, daß die an solchen Oxiden adsorbierte P-Fraktion hier ebenfalls zur P-Versorgung der Pflanze dient.

Introduction

The determination of phosphate fertilizer requirement based on soil testing is still controversial. There are various reasons for this. Specific plant parameters for the acquisition of phosphate by plants (root morphology, uptake parameters: I_{max}, K_m, etc.) and parameters of phosphate availability (buffer power, effective diffusion coefficient) of soils are not considered by conventional soil tests (*Jungk* and *Claassen*, 1989).

The determination of phosphate sorption and desorption curves of soils may be helpful in obtaining more information about P concentration in the soil solution and buffering by the solid phase. P sorption parameters may, therefore, be a useful tool for describing phosphate availability. *Pagel* et al. (1982) used P sorption parameters for the calculation of fertilizer recommendations. But especially the transformation of fertilizer phosphate in calcareous soils is still controversial. For calcareous soils, *Ryan* et al. (1985), *Borreo* et al. (1988) and *Solis* and *Torrent* (1989) have recently

shown a close relationship between P sorption and oxalate or dithionite/bicarbonate extractable Fe, indicating that perhaps both Ca phosphate precipitation and phosphate adsorption to calcite play a minor role compared with sorption to Fe-oxides.

The aim of this investigation was to determine the relationship between P sorption parameters according to *Pagel* and *Van Huay* (1976) and *Langmuir* (*Syers* et al., 1973), and the content of oxalate extractable Fe and Al as well as P uptake by rye seedlings in 15 soil samples from Ethiopia, Egypt, and Germany, widely differing in texture, pH, $CaCO_3$ content, and oxalate extractable (labile) Fe and Al (Fe_{ox}/Al_{ox}).

Material and Methods

The origin and several characteristics of the soil samples are described in Table 1. The samples were taken from the Ap horizon (0 - 20 cm) of arable land, air dried and 2 mm sieved.

Determination of P sorption

P sorption was measured according to *Ozanne* and *Shaw* (1967) modified by *Pagel* et al. (1982). 10 g soil material and 100 ml 0.01 M $CaCl_2$ solutions containing 0 - 200 mg P/kg soil were shaken on an end-over-end shaker for 2 h. Suspensions were then left for another 24 h at about 20°C. After centrifugation and filtration, phosphate was determined in the filtrate according to *Murphy* and *Riley* (1962). Sorbed phosphate (mg/kg soil) was calculated from the difference between the initial and the equilibrium phosphate concentration of the filtrate. The P-sorption capacity at the highest P addition of 200 mg/kg soil is considered as the experimental P sorp-

tion maximum (Table 2). The equilibrium concentration X-GLB (Table 2) of each soil was determined as the intercept of the sorption isotherm with the x axis (examples in Fig. 1). At this P concentration, the quantity of P sorption and P desorption is equal.

Calculation of sorption parameters

Pagel and *Van Huay* (1976) suggested the following adsorption equation (Eq. 1) for the linearized isotherm:

$$y = n \sqrt{x} + b \qquad \text{(Eq. 1)}$$

y = sorbed phosphate (mg/kg soil)

x = P concentration (mg/L) of the filtrate after shaking

n = affinity constant $\sqrt{mg \cdot L/kg^2}$, a measure of the shape of the sorption curve

b = theoretical phosphate desorption extrapolated to x = 0 (mg/kg soil).

b is the intercept of the sorption isotherm with the y axis (for example in Figure 2: b = -88 mg/kg for soil Lobenstein).

The parameters of the Langmuir isotherm were calculated according to the linearized form (Eq. 2) by means of linear regression analysis (*Syers* et al., 1973):

$$\frac{C}{x/m} = \frac{1}{K_1 \cdot K_2} + \frac{C}{K_2} \qquad \text{(Eq. 2)}$$

C = equilibrium phosphate concentration (mg/L) after 2 h shaking

x/m = sorbed phosphate (mg/kg)

K_1 = affinity parameter of the P sorption (L/mg)

K_2 = sorption maximum (mg/kg)

Table 1: Origin and some characteristics of the soil samples from Ethiopia (E), Egypt (Eg) and Germany (G)
Tabelle 1: Herkunft sowie einige Kennwerte der äthiopischen (E), ägyptischen (Eg) und deutschen (G) Bodenproben

No.	Location, soil type		< 2 μm	CaCO₃	pH	C-org.	DL-P[1]	CaCl₂-P[1]	Olsen-P[5]	Fe_ox[3]	Al_ox[3]
			%	%	0,1 M KCl	%	mg/kg			mg/g	
1	Bürgel, Calcic Cambisol	G	43	37	7,2	1,73	9	1,4	35,0	1,90	1,50
2	Dölau, Ferro-Orthic Podzol	G	11	0	6,0	0,91	115	5,5	43,7	0,66	0,52
3	Lobenstein, Dystric Ranker	G	32	0	3,3	4,06	15	1,2	21,9	4,46	2,41
4	Eisenberg, Vertic Cambisol	G	40	0	6,6	1,45	36	0[4]	13,6	2,14	1,05
5	Milzau, Haplic Phaeozem	G	30	0,1	6,9	1,61	140	2,8	42,4	1,44	1,28
6	Schlöben, Dystric Cambisol	G	17	0	5,3	0,88	35	1,2	36,1	1,70	0,58
7	Woliso, Ferralsol	E	56	0	5,3	0,51	0,1	0[4]	0	7,81	2,63
8	Gutin, Cambisol	E	61	0	3,9	3,76	0,1	0,2	0,8	9,03	6,00
9	Dergea, Acrisol	E	51	0	3,9	0,68	0,1	0[4]	2,0	6,49	3,78
10	Balkase, Vertisol	E	45	0	4,8	2,03	8	0[4]	14,9	7,98	1,93
11	Etay El-Baroud, Anthropic Gleysol	Eg	59	3	7,4	0,92	116	2,0	24,4	1,87	1,73
12	El-Satah, Eutric Regosol	Eg	13	12	8,1	0,11	15	0,1	7,7	0,11	0,15
13	Wadi-El-Awage, Lithosol	Eg	11	11	8,5	0,07	20	0,1	2,3	0,076	0,05
14	Wadi Abu-Gerf, Lithosol	Eg	11	13	8,7	0,10	23	0[4]	2,2	0,095	0,20
15	El Amerya, Yermosol	Eg	37	44	7,7	1,05	29	2,6	88,9	0,45	0,40

1) lactate soluble after *Egner* and *Riehm* (*Thun* et al., 1955)
2) 0,01 M CaCl₂ extractable P, 10 g: 100 ml
3) oxalate extractable Fe and Al after *Schwertmann* (1964)
4) detectable only in traces
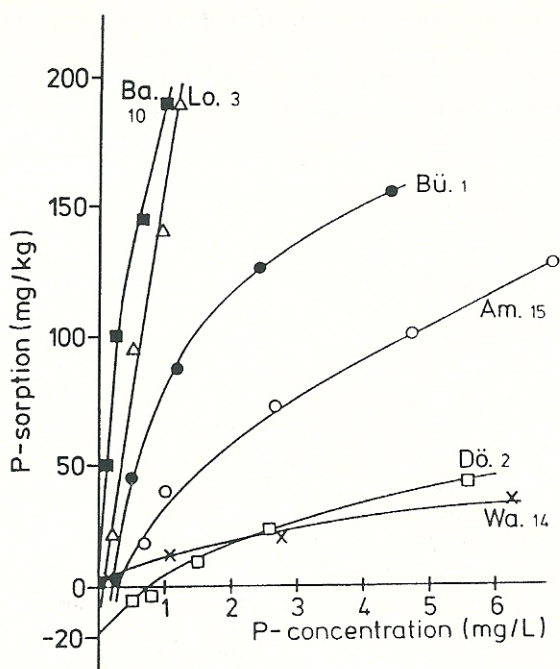5) sodiumbicarbonate extraction

Figure 1: Sorption curves of 6 soil samples Balkase (Ba), Lobenstein (Lo), Bürgel (Bü), El Amerya (Am), Dölau (Dö) and Wadi Abu Gerf (Wa).
Abbildung 1: Adsorptionskurven der 6 Bodenproben Balkase (Ba), Lobenstein (Lo), Bürgel (Bü), El Amerya (Am), Dölau (Dö) und Wadi Abu Gerf (Wa).

The total amount of sorbed phosphate $(x/_m)$ was calculated from the sum of phosphate sorbed in the experiments and the desorbable amount of P (b) at the extrapolated P concentration of zero (Fig. 2, compare Eq. 1).

Cultivation of rye plants

The method of Neubauer (*Thun* et al., 1955) was applied. 80 g of < 2 mm sieved soil material were mixed with 50 g quartz sand and 30 ml H_2O and filled into plastic vessels (9 cm · 6 cm, 4 cm deep). 100 g moistened quartz sand were added on top; 90 rye seed grains (*Secale cereale* L.) were sown and covered with 150 g moistened quartz sand. 80 seedlings were left for a growth period of 25 days. P uptake was calculated from the difference between the total P uptake of the 80 plants (shoots and roots) grown in soils and quartz sand (= control vessels). After harvesting, shoots and roots were digested at 500°C. The ash was dissolved in 4 % HCl, and phosphate was determined according to *Gericke* and *Kurmies* (1952).

Results and Interpretation

Sorption curves for selected soil samples are presented in Figure 1. They demonstrate two different tendencies. Firstly loamy or clay soils (1, 3, 10, 15; Table 1) show a much higher phosphate sorption in comparison with sandy soils (2, 14). Secondly, in the group of heavy soils, the acid soils Balkase (10) from Ethiopia and Lobenstein (3) from Germany show similarly strong phosphate sorption, whereas the calcareous soils Bürgel (1) (Germany) and El Amerya (15) (Egypt) bind much less P at the same P addition.

Description of phosphate sorption according to *Pagel* and *Van Huay* (1976)

As an example, the linear transformation of the sorption curves is presented for two soils in Figure 2. The calculated sorption parameters are shown in Table 2 for all soils.
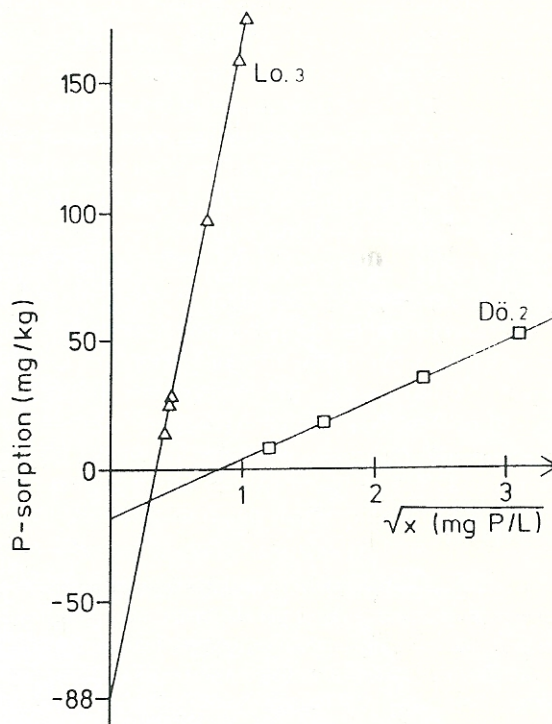

Figure 2: Sorption curves for the soil samples Lobenstein (Lo) and Dölau (Dö), linearized according to *Pagel* and *Van Huay*
Abbildung 2: Nach *Pagel* und *Van Huay* linearisierte Form der Adsorptionskurven für die Bodenproben Lobenstein (Lo) und Dölau (Dö).

According to Table 2 the Ethiopian soils (7, 8, 9, 10) and the German soil Lobenstein (3) show by far the strongest P sorption, as indicated by the experimental P sorption maximum and affinity constant n. Some calcareous soils (e.g. 12, 13, 14) show a much lower sorption indicated by low values for the experimental P sorption maximum and the constants n. Table 3 shows that the experimental P sorption maximum is significantly positively correlated with Fe_{ox} and Al_{ox} for the acid soils (pH < 7: r = 0.85[xx], 0.73[x] respectively) and for the calcareous soils (pH > 7: r = 0.89[x], 0.87[x] respectively). This also holds for the affinity constant n. In contrast, the correlation between the $CaCO_3$ content and the same sorption parameters is poor (r = 0.46; 0.45 resp.) and not significant.

Description of phosphate sorption according to Langmuir

The values of the P sorption maximum (K_2) and affinity constant (K_1), calculated for the whole P concentration

Table 2: Experimental P sorption maximum (at 200 mg P addition/kg soil), desorbable P (b), affinity constant (n) and P equilibrium concentration (X-GLB) of the soil samples, the correlation coefficient r of the isotherm and P uptake of 80 rye seedlings/pot

Tabelle 2: Experimentelles P-Sorptionsmaximum (bei Zugabe von 200 mg P/kg Boden), desorbierbare P-Menge (b), Affinitätskonstante (n) sowie P-Gleichgewichtskonzentration (X-GLB) der untersuchten Bodenproben, der Korrelationskoeffizient r der Isotherme und der P-Entzug von 80 Roggenpflanzen/Gefäß

No	P-uptake (mg)	Exper. P-sorption max. (mg P/kg)	b (mg/kg)	n ($\sqrt{mg \cdot L/kg^2}$)	X-GLB (mg P/L)	r
1	8.76	156	−26	93	0.08	0.93
2	7.79	63	−19	23	0.68	0.94
3	2.12	189	−88	254	0.13	0.98
4	6.80	149	0	67	0.002	0.96
5	8.05	140	−40	79	0.26	0.94
6	4.16	86	−5	29	0.03	0.92
7	1.94	199	0	760	0.002	0.93
8	2.34	197	−84	658	0.016	0.94
9	2.47	200	0	n.d.	0.0	n.d.
10	5.01	190	−15	212	0.005	0.95
11	4.77	149	−32	82	0.15	0.98
12	3.39	70	0	20	0.01	0.93
13	3.90	65	−4	16	0.05	0.97
14	3.61	57	−2	15	0.013	0.98
15	5.86	131	−32	63	0.26	0.97

n.d. = not determined

Table 3: Correlation coefficients (r) of the linear regression between experimental P-sorption maximum or affinity constant (n) and parameters of the calculated P-sorption isotherms (*Pagel* and *Van Huay*) and some soil characteristics

Tabelle 3: Korrelationskoeffizienten (r) der linearen Regression für die Beziehungen zwischen experimentellem P-Adsorptionsmaximum bzw. der Affinitätskonstante (n) und Parametern der berechneten P-Adsorptionsisothermen (*Pagel* und *Van Huay*) bzw. einigen Bodenparametern

	Number of soils (pH)		Affinity const. n	X-GLB	pH	Fe_{ox}	Al_{ox}	$CaCO_3$
Experim. P sorp. max.	15		0.72[xx]	−0.32	−0.74[xx]	0.84[xxx]	0.79[xxx]	
	9	(<7)	0.73[x]	−0.69[x]	−0.62	0.85[xx]	0.73[x]	
	6	(>7)	0.99[xxx]	0.67	−0.97[xxx]	0.89[x]	0.87[x]	0.46
Affinity const. n	14[1]			−0.28	−0.64[x]	0.87[xxx]	0.82[xxx]	
	8[1]	(<7)		−0.43	−0.51	0.84[xx]	0.80[x]	
	6	(>7)		0.60	−0.96[xx]	0.93[xx]	0.90[x]	0.45

[1] without soil Dergea, [x] signif. at $\alpha = 0.05$, [xx] signif. at $\alpha = 0.01$, [xxx] signif. at $\alpha = 0.001$

range is presented in Table 4 (left side). The values show that K_2 and K_1 are very high in case of the acid soils 3, 7, 8, 10 and low for the alkaline soils 12, 13, 14, in agreement with the calculations according to *Pagel* and *Van Huay*.

Additionally, we calculated the Langmuir sorption parameters in a low concentration range (0 - 2.8 mg P/L) which is the most frequent range in soils (Table 4, right side). In the case of the acid soils, the sorption parameters (K_2 and K_1) are quite the same. However, the K_2 values decrease and the K_1 values increase for the alkaline soils. That means that the sorption affinity of phosphate is higher in the low concentration range.

Table 5 shows the r values for the correlation between sorption parameters and some soil characteristics for the two concentration ranges. In the case of the total isotherm, K_2 and K_1 are positively related to Fe_{ox} in both acid and alkaline soils as found from the calculation after *Pagel* and *Van Huay*. That suggests that Fe_{ox} is important for the P sorption in alkaline soils too.

The relation with $CaCO_3$ is much weaker (r = 0.44; 0.45) than with Fe_{ox} (r = 0.88[xx]; 0.83[x]). In the case of the low concentration range, K_2 is also significantly positively correlated with Fe_{ox} (r = 0.76[x]; 0.89[xx]) but weakly with $CaCO_3$ (r = 0.51). The relation between K_1 and Fe_{ox} is positive for the acid soils but negative for the calcareous soils, although, nonsignificant in both cases. That makes interpretations difficult.

P uptake and soil parameters

We calculated the relation between P uptake (Table 2) and parameters of the sorption isotherms according to

Table 4: Values of sorption maximum (K_2; mg/kg) and affinity constant (K_1; L/kg) calculated by the Langmuir equation (Eq. 2), r = correlation coefficient (between C/x_m and C)

Tabelle 4: Werte der maximalen Adsorption (K_2; mg/kg) und Affinitätskonstante (K_1; L/kg) nach Langmuir (Gleichung 2), r = Korrelationskoeffizient (zwischen C/x_m und C)

No.	P-conc: 0-14.3 mg/L		r	P-conc: 0-2.8 mg/L		r
	K_2	K_1		K_2	K_1	
pH > 7	(alkaline soils)					
1	227	0.92	0.99	217	0.98	0.98
11	232	0.61	0.99	179	0.96	0.99
12	77	0.52	0.99	41	1.75	0.97
13	73	0.27	0.92	31	1.46	0.99
14	69	0.26	0.97	29	1.37	0.99
15	200	0.51	0.99	156	0.77	0.99
pH < 7	(acid soils)					
2	98	0.34	0.99	96	0.36	0.96
3	353	2.33	0.97	353	2.33	0.97
4	178	0.84	0.99	156	1.06	0.99
5	232	0.58	0.99	166	1.00	0.99
6	126	0.41	0.99	108	0.50	0.98
7	207	301	0.99	207	301	0.99
8	363	16.0	0.99	363	16.0	0.99
10	273	2.95	0.99	273	2.95	0.99

Pagel and *Van Huay* (Table 2) or Langmuir (Table 4). Table 6 shows the results. It is evident that the P uptake was positively correlated with the phosphate equilibrium concentration X-GLB. Furthermore, P uptake decreases with increasing bonding intensity (n, K_1) considering all soils resp. the acid soils alone. The same tendency is true for the relation to Fe_{ox} and Al_{ox}. These results could be expected. In the case of the alkaline soils, we find a different behaviour. The correlation coefficients between P uptake and bonding intensity (n, K_1) as well as with Fe_{ox} and Al_{ox} were positive, considering the whole concentration range of the isotherms. In the case of the low equilibrium P concentrations (0 - 2.8 mg/L), there is a negative nonsignificant correlation between P uptake and K_1 for all soils. Because concentrations between 0 to 2.8 mg/L are usually found in the soil solution, these values should be relevant for plant P uptake. However, the positive correlation between P uptake and the Fe_{ox} and Al_{ox} content in these alkaline soils is remarkable. Because the Fe and Al oxides seem to be involved in P sorption reactions and because the bonding intensity decreases with increasing Fe_{ox} contents (Table 5; 0 - 2.8 mg/L), the results suggest the importance of P sorbed to Fe and Al oxides for P uptake. The positive correlation between P uptake and $CaCO_3$ content does not contradict with these findings.

Table 5: Correlation coefficients (r) of the linear regression between P-sorption maximum (K_2) and affinity constant (K_1), respectively, and some soil characteristics, for two P concentration ranges, 8 acid soils (pH < 7)[1] and 6 calcareous soils (pH > 7)

Tabelle 5: Korrelationskoeffizienten (r) für die lineare Regression zwischen dem P-Adsorptionsmaximum (K_2) bzw. der Affinitätskonstante (K_1) und einigen Bodeneigenschaften für zwei P-Konzentrationsbereiche, 8 saure Böden (pH < 7)[1] und 6 kalkhaltige Böden (pH > 7)

	pH	P-concentration of the total isotherm (0 - 14.3 mg/L)			P-concentration range between 0 and 2.8 mg/L		
		Fe_{ox}	pH	$CaCO_3$	Fe_{ox}	pH	$CaCO_3$
K_2	< 7	0.69°	− 0.75[x]		0.76[x]	− 0.87[xx]	
	> 7	0.88[xx]	− 0.94[xx]	0.44	0.89[xx]	− 0.96[xx]	0.51
K_1	< 7	0.44	− 0.04		0.44	− 0.04	
	> 7	0.83[x]	− 0.94[xx]	0.45	− 0.62	0.68	− 0.59

1) without soil 9, [x] significant at $\alpha = 0.05$, [xx] significant at $\alpha = 0.01$, ° significant at $\alpha = 0.10$

Table 6: Correlation coefficients (r) for the linear regression between P uptake and some soil characteristics

Tabelle 6: Korrelationskoeffizienten für die lineare Regression zwischen der P-Aufnahme und einigen Bodeneigenschaften

Number of soils		X-GLB	Affinity parameters			Fe_{ox}	Al_{ox}	$CaCO_3$
			const. n 0 - 14.3	const. K_1 0 - 14.3 mg/L	const. K_1 0 - 2.8			
15	(total)	0.54[x]	− 0.54[x]	-	-	− 0.49	− 0.31	-
9	(acid soils)	0.62[x]	− 0.76[x]	− 0.48	− 0.48	− 0.74[x]	− 0.68[x]	-
6	(alk. soils)	0.38	0.82[x]	0.86[x]	− 0.68	0.72°	0.64	0.73°

[x] significant at $\alpha = 0.05$

° significant at $\alpha = 0.10$

Conclusions

In this paper a close correlation between P sorption and the contents of Fe_{ox} and Al_{ox} was found in both acid and calcareous soils. There were also positive relations between Fe_{ox}/Al_{ox} and P uptake.

The results indicate that P sorption to weakly crystalline Fe and Al oxides is perhaps initially the main P binding reaction in calcareous soils with a relatively high $CaCO_3$ and Fe_{ox}/Al_{ox} content. Fe and Al-oxide associated P seems to be more relevant for plant nutrition than phosphate precipitated with Ca or sorbed to $CaCO_3$. These results are consistent with those of *Schwertmann* and *Schieck* (1980), *Welp* et al. (1983) and *Ryan* et al. (1985).

In acid soils, phosphate availability can be characterized by the affinity constant of sorption after *Pagel* and *Van Huay* and according to Langmuir. In calcareous soils, the P availability can be satisfactorily characterized by the affinity constant after Langmuir if a realistic P concentration range (0 - 2.8 mg P/L) is used.

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