

AVAILABILITY OF SOIL PHOSPHORUS BY ANION EXCHANGE RESIN

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ABSTRACT

The change of any component in soil-solution-resin system has a significant effect on the amount of phosphorus sorbed by resin. The effect is caused by the distribution of P at equilibrium in each phase of the system. The amount of phosphorus retained by soil or remaining in soil solution may not be neglected.

The distribution of phosphorus in soil-solution-resin system may be described by the combination of balance equation and adsorption isotherm:

$$T \cdot Q = P_R + \frac{T \cdot A}{1 + K/c} + c$$

By this equation the real amount of desorbable phosphate (Q) may be obviously determine.

"T" is the amount of soil suspended in 100 cm³ of water indicating the ratio of soil : solution. The term describing the amount of phosphorus sorbed on the soil may be modelled by the Langmuir isotherm of parameters "A" and "K". The BET isotherm may be used for the phosphorus sorption of the ion exchange resin. So with the help of P_R—the amount of phosphorus sorbed by resin—the phosphorus content of equilibrium-solution (c) may be determined. The model was successfully applied for several soils of Hungary, with different amounts of resin and extreme ratios of soil : solution. On the analogy of the above mentioned studies soil-solution system may be described as well.

РЕЗЮМЕ

Количественное изменение любого компонента в системе почва-раствор-смола в значительной мере влияет на количество фосфора адсорбированного ионообменной смолой. Причиной этого является то, что при равновесии фосфор входит в состав каждого элемента этой трехкомпонентной системы и количество фосфора, оставшегося в почве или растворе, зависит от содержания фосфора в смоле. Распределение фосфора в равновесной системе почва-раствор-смола можно описать комбинацией уравнения баланса и сорбционной изотермы:

$$T \cdot Q = P_{R.} + \frac{T \cdot A}{1 + K/c} + c$$

При помощи уравнения можно определить скорректированное количество десорбированного фосфора (Q). Параметр T—количество почвы, суспендированной в 100 мл воды. Адсорбированный фосфор в почве характеризуется изотермами Лангмюра с параметрами A и K. Фосфор в смоле характеризуется изотермой БЕТ. С помощью этого, зная P_{R.} — фосфор, связанный ионообменной смолой — можно рассчитать равновесное количество фосфора в растворе (c). Эту модель успешно использовали для шести различных почв Венгрии при различных количествах смолы и крайних соотношениях почва : раствор. Аналогично можно описать систему почва : раствор.

ÖSSZEFOGLALÁS

A talaj-oldat-gyanta rendszerben bármelyik komponens mennyiségének változtatása jelentősen befolyásolja az ioncserélő gyantával kivont foszfor mennyiségét. A hatás oka az, hogy egyensúly esetén a foszfor a rendszer mindhárom fázisában jelen van és a talajon maradó, illetve az oldatba jutó foszfor mennyisége nem hanyagolható el a gyantán megkötött foszfor mennyiségéhez képest. A talaj-oldat-gyanta egyensúlyi rendszerben a foszfor megoszlása leírható a mérlegegyenlet és a szorpciós izoterma kombinálásával.

$$T \cdot Q = P_{\text{fgy}} + \frac{T \cdot A}{1 - K/c} + c$$

Az összefüggéssel a Q korrigált deszorbeálható foszfor mennyiség egyértelműen meghatározható, T a 100 ml vízben szuszpendált talaj mennyisége — a talaj : oldat arány kifejezője. A talajon megkötött foszfort leíró komponens A és K paraméterű Langmuir izotermával modellezhető. Az ioncserélő gyanta foszfor megkötésének leírására a BET izoterma használható. Ezzel P_{fgy} — az ioncserélő gyantán megkötött foszfor — ismeretében az oldatban levő egyensúlyi foszfortartalom (c) kiszámítható. A modellt eredményesen alkalmaztuk hat különböző magyarországi talajon, különböző gyantamennyiségek és szélsőséges talaj : oldat arányok mellett. Analóg módon leírható a talaj : oldat rendszer is.

INTRODUCTION

The low solubility of phosphorus compounds and their strong sorption on soil make important to study the availability of soil phosphorus and the further development of soil analytical methods. Among the numerous soil phosphorus methods the most perspectives are the physico-chemically explainable methods modelling soil phosphorus availability.

According to one of them, root phosphates uptake may be modelled with phosphate sorption by anion exchange resin. The form of the method so far adopted is not enough (Barrow and Shaw, 1977). The results of the determination are highly effected by several factors. One of them is the quantity of soil phosphorus which may query the possibility of standardization of the method.

The method was introduced by Amer et al (1955). Chlorid saturated strong-base anion exchange resin (Dowex 2) was used. 1 g of soil, 1 g of ion exchange resin and 100 cm³ of water were used for studies. The ion exchange capacity of 1 g of resin was found much higher than the phosphate supply of 1 g soil. According to Amer (1955) concluded that resin could sorb all the amount of phosphate supplied by soil.

Cooke (1963) and Hislop (1968) worked on further development and standardization of the method. They proved, that the relative amount of soil, resin and water, the ratio of soil : resin surface, the temperature of the suspension as well as the period and intensity of shaking highly effect the amount of phosphate sorbed by ion exchange resin. Consequently the values of these factors have to be kept constant. But Hislop (1968) found, that in some cases the amount of resin also may be a limiting factor of phosphate sorption.

According to Barrow (1977) phosphate concentration in the equilibrium solution significantly affects phosphate distribution in soil-solution-resin system. The starting point of authors mentioned above as well as of Amer (1955) was that at equilibrium the phosphat concentration of solution may be considered as zero. If it was true —according to Barrow— the amount of phosphate sorbed by resin would be propor-

tional to the quantity of desorbable soil phosphate. Whereas he found that the amount of phosphate extracted by resin from soil may be not proportionally, if the quantity of soil phosphate is large.

The phosphate sorption of resin as well as of soil reach equilibrium, consequently the phosphorus concentration in equilibrium solution even theoretically may not be zero.

The equilibrium of soil-solution-resin system is characterized by the distribution of the quantity of desorbable soil phosphate (Q) between the three phases:

$$Q = P_R + P_{\text{solution}} + P_{\text{soil}} \quad (1)$$

The amount of phosphate sorbed by resin (P_R) depends not only on the quantity of desorbable soil phosphate (Q) but amount of phosphate actually retained by soil (P_{soil}) and the phosphate in the solution (P_{solution}) should be taken into account to. On the base of this experimental and calculated data Barrow (1977) emphasized that the amount of phosphate extracted from soil depends on several factors as the quality and quantity of resin applied, the ratio of soil: solution and the amount of soil phosphorus reserve.

MATERIALS AND METHODS

A chloride form, strong-base anion exchange resin (Varion AD) was used. 0–10 g of soils were suspended in 100 cm³ of distilled water with 0–4 g of resin in bottles. The suspensions were shaken for 0.5–48 hours. After shaking the resin was separated from the suspension by a nylon sieve (mesh size 0.3 mm), and washed with distilled water. Then, after addition of 20 cm³ of 0.5 M Na₂SO₄ it was heated in water bath for 45 minutes. Then the solution was added into a 50 cm³ calibrated flask, while the resin was heated for further 15 minutes in water bath with the addition of 10 cm³ of 0.5 M Na₂SO₄. This solution was also added to the flask. The resin was washed over again with 10 cm³ of 0.5 M Na₂SO₄ and this solution was also added to the flask. The amount of phosphorus in the collected solutions was determined by the Murphy and Riley method (1962).

The model was used successfully for several soils. In this study the application of the model is shown on two soils. One of the soil is an acid clay soil from Hajdú-böszörmény while the other is a calcareous sandy soil from Órbottyán. Their phosphorus content was 8.8 and 8.1 ppm by the Olsen method and 21 and 27 ppm by ammoniumlactate-acetate extraction method.

Desorption studies were conducted on soil samples treated with 0 and 100 µg P/g of soil, and incubated at 60%, of water capacity for one year.

Three sequences of experiments were conducted:

- The study of adsorption on anion exchange resin (Varion AD); 1, 2 and 4 g of resin were shaken with 100 cm³ of solution containing 50; 100; 200; 1000 and 2000 µg of P for 16 hours. The amount of phosphate in solution and on resin were determined.

- The study of desorption in soil-solution system; In this experiment different ratios of soil: solution were adjusted. The samples were shaken for periods of 0.5, 2, 24 and 48 hours in two replications. For adjusting the different ratios of soil: solution 0.1, 0.5, 1, 5 and 10 g of soil were added to 100 cm³ of water. In this way the ratios of soil: solution varied from 1 : 1000 to 1 : 10. After shaking solutions were separated and their phosphorus content was determined (Table 1.).

Table 1.

Desorption of phosphorus in soil-solution system

Soil: solution ratio g/100 cm ³	Shaking (hours)	Amount of P desorbed from soils (µg P/g soil)			
		Soil samples			
		19/0	19/100	34/0	34/100
0.1	0.5	18.05	53.30	9.40	29.75
	2.0	26.70	66.40	15.13	46.20
	24.0	21.50	74.60	19.30	67.55
	48.0	25.20	75.55	22.90	81.65
0.25	0.5	12.44	42.64	7.22	25.26
	2.0	14.76	48.10	10.10	35.26
	24.0	13.18	57.96	15.20	54.56
	48.0	11.80	55.54	16.02	63.56
0.5	0.5	10.00	37.59	5.64	25.11
	2.0	10.56	41.77	7.09	36.71
	24.0	8.32	45.61	9.89	47.51
	48.0	9.31	47.06	11.16	48.39
1.0	0.5	6.05	29.95	4.18	21.12
	2.0	6.28	31.95	4.98	26.88
	24.0	6.46	35.43	6.76	34.74
	48.0	6.55	35.48	7.60	37.22
5.0	0.5	1.84	13.65	1.58	12.43
	2.0	1.80	14.88	1.58	13.64
	24.0	1.81	16.30	1.64	16.45
	48.0	1.66	16.48	1.61	16.43
10.0	0.5	1.09	8.14	0.84	8.31
	2.0	0.93	9.01	0.77	8.86
	24.0	1.06	9.97	0.76	10.15
	48.0	1.25	9.68	0.79	10.20

Table 2.

Desorption of phosphorus in soil-solution-resin system.

Soil: solution ratio g/100 cm ³	Shaking (hours)	Amount of P sorbed by 1 g resin (µg P/g soil)			
		Soil samples			
		19/0	19/100	34/0	34/100
0.1	0.5	26.70	58.70	14.75	41.65
	2.0	30.65	76.80	17.45	52.20
	24.0	43.40	110.70	27.70	65.30
	48.0	49.80	122.25	25.25	76.40
0.25	0.5	15.10	46.74	7.74	21.02
	2.0	14.78	62.48	7.90	34.18
	24.0	24.62	83.58	19.22	65.96
	48.0	22.72	87.54	17.82	73.70
0.5	0.5	9.45	38.38	4.68	23.25
	2.0	13.12	48.71	7.27	31.10
	24.0	19.45	78.41	15.68	61.03
	48.0	18.61	76.30	16.63	69.61
1.0	0.5	7.37	32.66	3.26	21.32
	2.0	10.37	47.81	6.33	33.38
	24.0	15.63	71.69	12.75	53.48
	48.0	15.54	74.24	12.82	61.42
5.0	0.5	2.82	17.71	2.00	14.80
	2.0	6.63	33.80	4.13	24.07
	24.0	14.80	60.50	8.69	43.23
	48.0	16.00	64.09	8.96	47.99
10.0	0.5	2.37	11.81	1.49	12.06
	2.0	4.93	29.27	3.16	21.31
	24.0	12.38	52.13	6.89	38.62
	48.0	10.89	54.25	7.79	44.08

- The study of desorption in soil: solution: resin system: The experiment was similar to the above mentioned experiment in soil: solution system, but 1 g of Varion AD ion exchange resin was added to each of soil-solution combinations. After shaking the resin was separated and the amount of phosphate sorbed by resin was determined (Table 2.).
- The main tools of modelling were nonlinear regression computer programs for Commodore-64. These self-developed programs were written by the application of simplex iteration algorithm. With the use of this stepwise procedure the parameters were determined at which the sum of square of the deviation of measured and calculated values were minimal.

RESULTS AND DISCUSSION

The equation (1) introduced by Barrow and Shaw (1977) forms the base of the model. First the single terms should be analysed. The term of P_{solution} may be calculated from " P_R " provided that the formula of $P_R = f_R(P_{\text{solution}})$ is obtainable. If the formula of $P_{\text{soil}} = f(P_{\text{solution}})$ also would be known the amount of P_{soil} could be given the help of P_{solution} substituted from the inverse function of $P_R = f_R(P_{\text{solution}})$, which is $P_{\text{solution}} = f_R^{-1}(P_R)$. The inverse function is available after changing the dependent and independent variable in the original function. It is usually signed by the index f^{-1} . The transformed function (1) is:

$$Q = P_R + f_R^{-1}(P_R) + f[f_R^{-1}(P_R)] \quad (2)$$

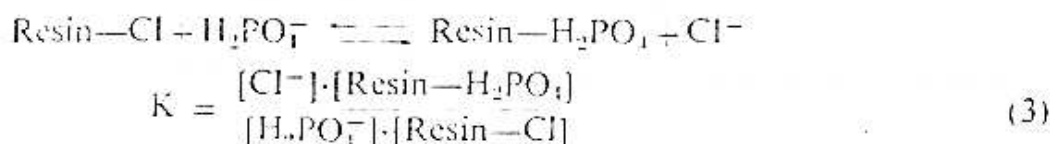
Consequently "Q", the adsorbed phosphorus on the soil may be expressed by the phosphorus sorbed on the resin. For this the shape of the functions " f " and " f_R " is necessary to know. The parameters of the functions can be determined from the equation (2) with the help of sufficient experimental data.

The determination of $P_R = f_R(P_{\text{solution}})$ function.

The function can be characterized by saturation curve. According to the literature two models are proposed. The model suggested by Barrow and Shaw (1977) deduced from chemical equilibrium, while Taylor (1968) offers a model described by BET isotherm. For a good choice it is necessary mathematically analyse the models and then the chemical meaning of them should be determined. Hereupon may be studied the goodness of the fit of the functions to the measured data. Namely by the help of goodness of fitting only can not choose the adequate model because different functions may present the same shape in a given interval.

For the demonstrative comparison, the functions offered by Barrow and Taylor were simplified, because in the interval of our study only a slight proportion of the resin capacity was utilized.

The equation introduced by Barrow and Shaw (1977) was deduced from the chemical equilibrium of phosphate linkage with one valence.



In the equation (3) the elementary cation unit of the resin was designated.

As the result of the deduction Barrow gives the following equation for the amount of phosphate adsorbed by resin (P_R):

$$P_R = \frac{1}{2} c \cdot R \cdot V \cdot (\text{Cl}_{R_0} - P_R) K \quad (4)$$

where " c " is the concentration of phosphorus in the solution of " V " volume; " R " is the amount of the resin; Cl_{R_0} is the initial amount of Cl^- sorbed on the resin as the capacity of resin. " K " is the equilibrium constant from equation (3). Taking into

account, that "R" and "V" are given and the amount of phosphorus sorbed on resin compared with the capacity of resin is negligible ($Cl_{R_0} \gg P_R$), these parameters may be combined into one constant:

$$k' = \sqrt{R \cdot V \cdot Cl_{R_0}} / K$$

Therefore, Eq. (4) takes the form

$$P_R = k' \cdot \sqrt[3]{c} \quad (5)$$

The base of deduction was that phosphate ions link with one valence to the ion exchange resin.

According to Taylor (1978) in the case of less saturation as in the studied interval as well, phosphate ions linked mainly by two valences to the resin surface. Taking it into consideration deduction is



$$K_2 = \frac{[Cl^-]^2 \cdot [\text{Resin}_2 - HPO_4]}{[HPO_4^{--}] \cdot [\text{Resin} - Cl^-]^2} \quad [Cl^-] = 2 \cdot [\text{Resin}_2 - HPO_4]$$

$$[HPO_4^{--}] = \frac{4 \cdot [\text{Resin}_2 - HPO_4]^2}{K_2 \cdot [\text{Resin} - Cl]^2} \quad (6)$$

Since only a small part of the capacity of resin is utilized, $[\text{Resin} - Cl]$ and its square may be considered constant; $k'' = 4/(K_2 \cdot [\text{Resin} - Cl]^2)$. After the transformation of Eq. (6) and substitution of k'' using the $c = [HPO_4^{--}]$ notation:

$$P_R = k'' \sqrt[3]{c} \quad (7)$$

Using the power form of Eq. (5) and (7) the amount of phosphorus sorbed by resin can be expressed as

$$P_R = k' \cdot c^{1/2} \quad P_R = k'' \cdot c^{1/3} \quad (8)$$

It is similar to the formula of Freundlich empirical isotherm:

$$P_R = k \cdot c^n \quad (9)$$

Where "n" is a parameter depending on the type of linkage of phosphate ions. In this case "n" was 1/2 or 1/3. In solution-resin system (at low equilibrium concentration) the equilibrium distribution might be described by Freundlich isotherm. So the type of linkage may be determined by the parameter "n" resulted from the calculations. However in the same system the type of linkage, as well as the value of "n" changes depending on phosphate saturation of the resin (Taylor, 1978). The value of "n" could be estimated only as a constant, consequently this model is not an adequate approach for resin-solution system. The problem is the same in soil-solution system.

The model described by BET isotherm.

Taylor (1978) described the alteration of phosphate ion linkage with one or two valences by the BET isotherm:

$$P_R = \frac{A_R}{1 - \frac{c}{c_0}} \cdot \frac{1}{1 + \frac{1}{b} \cdot \frac{1}{c/c_0}} \quad (10)$$

where P_R represents the amount of phosphate sorbed by resin, "b" is constant, c represents the phosphate concentration of the equilibrium solution, "A" is the value of saturation in the case of bivalence linkage; " c_0 " is the solution concentration when the active places on the resin surface are saturated with bivalence linked phosphate ions. The value of c_0/b being the quotient of two constants is constant too and it is indicated as "B". Taking into account the amount of the resin "R":

$$P_R = \frac{R \cdot A_R}{1 - \frac{c}{c_0}} \cdot \frac{1}{1 + \frac{B}{c}} \quad (11)$$

In this case of low equilibrium concentration if $c \ll c_0$ then $c/c_0 \approx 0$. The result is formally similar to Langmuir isotherm. On the base of measured data the goodness of the fitting of the calculated model is shown in Fig. 1.

The relation of resin-solution system with the calculated parameters is:

$$P_R = \frac{1068 \cdot R}{1 - \frac{c}{120.6}} \cdot \frac{1}{1 + \frac{656}{c}} \quad (12)$$

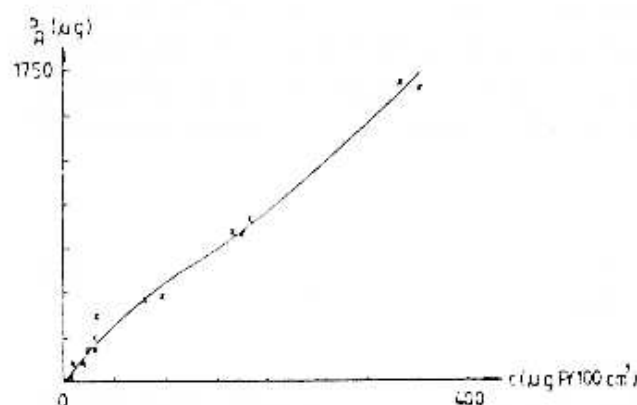


Fig. 1. Distribution of phosphorus in resin-solution system.

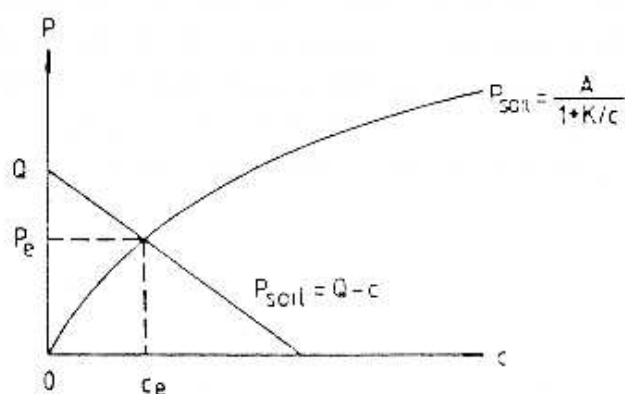


Fig. 2. Distribution of phosphorus in soil-solution system at constant ratio.

P equilibrium; c equilibrium; $P_{soil} = \frac{A}{1 + K/c}$

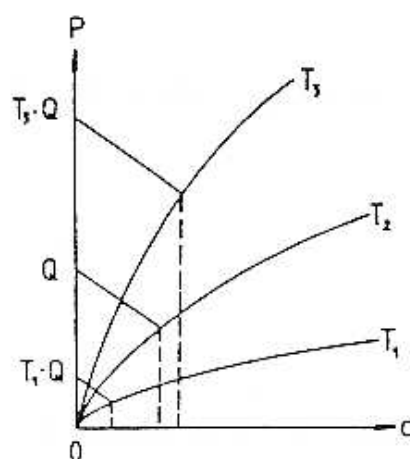


Fig. 3. Distribution of phosphorus in soil-solution system at different ratios.

$T_1 = 1$ g soil; $T_2 = 1$ g of soil; $T_3 = 1$ g of soil.

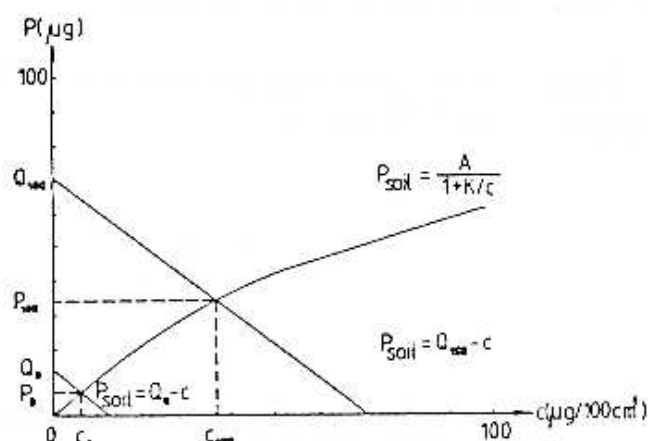


Fig. 4. Distribution of phosphorus in soil-solution system, soil No. 19.

$Q_{100} = 70.7$; $P_{100} = 33.1$; $C_{100} = 37.0$; $Q_0 = 13.5$; $P_0 = 7.3$; $C_0 = 6.1$; $A = 117.1$; $K = 91.7$; $K = 91.7 \frac{100 \text{ cm}^3}{\mu\text{gP}}$

The determination of $P_{\text{soil}} = f(P_{\text{solution}})$ function.

Phosphate ions on soil surface as well as on resin surface link to the positively charged positions at low equilibrium concentrations (always it is the situation at desorption).

The multivalent cations (Ca^{++} , Fe^{+++} , Al^{+++}) (linked to negative positions of soil silicates adsorb Cl^- , HCO_3^- , OH^- ions to their free valences. These ions may be replaced when phosphate ions are present. Decreasing phosphate concentration of the solution the exchange proceeds to the opposite direction –thus the sorbed phosphates are desorbed. In soils compared with resin this sorption positions are very heterogenous, and the phosphate ions may be sorbed also with other mechanisms. Therefore it is difficult to describe the sorption process in a wide interval of equilibrium concentration. So the adsorption may be modelled by the sum of various Langmuir isotherms, although the two surface Langmuir isotherm may already give sufficient result. (Osztoics, 1983). In the case of desorption at low equilibrium concentration only a part of the curve is used, so the second Langmuir isotherm may be neglected.

To elaborate the model two relationships should be taken into consideration.

The first is the adsorption –desorption isotherm, where the Langmuir isotherm is used (Olsen, 1957; Osztoics, 1984)

$$P_{\text{soil}} = \frac{A}{1 + k \cdot c} \quad (13)$$

Where “A” represents the adsorption maximum; “k” is constant. The second one is the balance equation: (Barrow and Shaw, 1977).

$$Q = P_{\text{soil}} + P_{\text{solution}} \quad (14)$$

The equation expresses that the source of the amount of phosphate retained by soil (P_{soil}) and the amount of phosphate in the equilibrium solution (P_{solution}) is the desorbable soil phosphorus (Q).

In the study 100 cm³ of solution was used so the concentration (in g/100 cm³) is equal to the amount of phosphate in the solution ($c = P_{\text{solution}}$).

By the substitution of Eq. (13) in Eq. (14), and taking into account the amount of soil (T) it gives the equation of phosphate distribution in soil-solution system:

$$T \cdot Q = \frac{T \cdot A}{1 + K/c} + c \quad (15)$$

Plotting the two functions the section of the isotherm curve and the line of $P_{\text{soil}} = Q - c$ gives the mathematical solution at equilibrium (Fig. 2.).

The effect of the change in soil: solution ratio is shown in Fig. 3. Q refers to 1 g soil.

The equation (15) solved for c :

$$c = \frac{-(K - T \cdot Q + T \cdot A) + \sqrt{(K - T \cdot Q + T \cdot A)^2 - 4 \cdot T \cdot Q \cdot K}}{2} \quad (16)$$

There are two possible mathematical solutions but only one chemical exists, calculated with the positive value of the square root.

Shaking of the different amounts of soil with water till reaching equilibrium gave pairs of values $T - c$. From these pairs of data were determined the parameters of the function (16) with nonlinear regression analysis. The results for two soils are shown in Table 3. Because of the interaction between parameters "A" and "k" their values are not reliable. The values of the adsorption maximum were found to be too low. It is possible because the measured values are far from the maximum. In this interval Langmuir isotherms plotted with different, but appropriately choessen $A - K$ parameter pairs are the same. However the value of Q is related to the shape of the isotherm and not to its concentrate parameters.

In Fig. 4, the adsorption isotherm and two balance equations $P = Q - c$ for 0 and 100 Q levels of the soil No 19 are shown.

In the figure it is shown, or it can be calculated from the function that by shaking of 1 g of soil with 100 cm³ of water until equilibrium, the concentration of the equilibrium solution is 6.1 and 37.3 $\mu\text{g P}/100 \text{ cm}^3$ in the case of samples 19/0 and 19/100 respectively. At equilibrium—as it is shown in the figure—roughly the same amount of phosphorus remain on the soil which is nearly 50% of the actual Q value. This large amount may be decreased by diminishing the ratio of soil: solution but it remains considerable.

This amount can be determined by the model so the error may be eliminated.

Determination of the equation of soil-solution-resin system.

By substitution of (13) Eq. in Eq. I.:

$$T \cdot Q = P_R + \frac{T \cdot A}{1 + K/c} + c \quad (17)$$

"T" is the given amount of soil; P_R , the amount of phosphorus sorbed on resin is the measured parameter, "Q", "A" and "K" parameters have to be determined similarly as in the case of soil-solution system. Nothing but variable "c", the equilibrium phosphorus concentration of the system should be determined. Taking into account the stipulation of the independency of adsorbents it may be determined from the value of P_R by transformation of Eq.(11):

$$c = \frac{-(R \cdot A_R - P_R + P_R \cdot B/c_0) + \sqrt{(R \cdot A_R - P_R + P_R \cdot B/c_0)^2 + 4P_R^2 \cdot B/c_0}}{2 \cdot P_R/c_0} \quad (18)$$

Equation (18) can be substituted in "c" of Eq.(17) A_R , B and c_0 parameters have been determined already in resin-solution system, "R" the amount of resin is given amount, so parameters "A" "K" and "Q" of the model can be obtained by regression analysis.

The complete function will not be shown here because it would not be perspicuous enough. The equation may be given also by algorithm.

The model of the resin-soil-solution system is given by Eq.17 and 18. as follows: "c" equilibrium concentration calculated from Eq.18 is substituted in the Eq.(17) so it gives the complex model. While this model is valid only for equilibrium system, measured data should be extrapolated to equilibrium. The extrapolation was made by the equation of the sum of 3 first order reactions modified by Füleky (1980):

$$P_R = A_1 + A_2(1 - e^{-k_2t}) + A_3(1 - e^{-k_3t}) \quad (19)$$

The parameters of soils No 19. and 34. resulted from the calculation are listed in Table 4. Similar results were obtained for Q in the soil-solution system (Table 3.). Larger differences were found between Q values determined by other methods.

Table 3.

Calculated parameters of the model for soil-solution system

Soil	A μg P/g soil	K 100 cm ³ /μg P	Q μg P/g soil	s
19 0	117.1	91.7	13.5	1.2
19 100	117.1	91.7	70.7	1.2
34 0	80.5	51.0	12.6	0.9
34 100	80.5	51.0	61.7	0.9

Table 4.

Calculated parameters of the model for soil-resin-solution system

Soil	A μg P/g soil	K 100 cm ³ /μg	Q μg P/g soil	s
19 0	84.8	258.0	18.1	5.0
19 100	84.8	258.0	84.8	5.0
34 0	65.2	356.9	11.4	5.1
34 100	65.2	356.9	65.2	5.1

The distribution of phosphate between soil, solution and resin may be studied on the base of the model. Fig. 5. shows the distribution of the initial 847.8 μg desorbable soil phosphorus of 10 g soil in the case of sample No. 19. (100-100 cm³ solution - 1 g resin system. Phosphate measured on exchange resin appears to be only 64 % of the amount of desorbable soil phosphorus (10 · Q). The residual 36 % is in solution and retained by soil. This systematic error may be reduced by the decrease of the amount

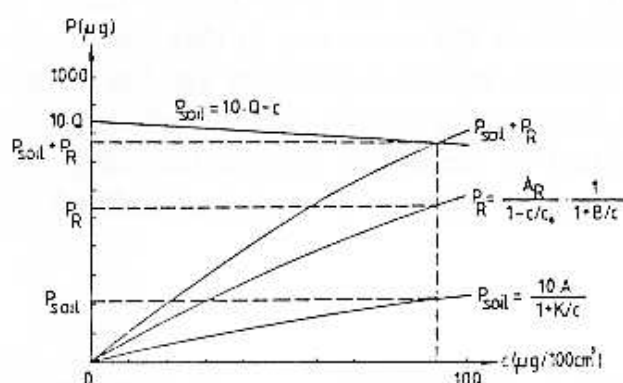


Fig. 5. Distribution of phosphorus in soil-solution-resin system, soil No. 19, 10 g of soil. $Q = 84.8 \mu\text{g/g}$ of soil; $A_R = 1068 \mu\text{g P/g}$ of resin; $A = 84.8 \mu\text{g P/g}$ soil; $K = 258.0$ $100 \text{ cm}^3/\mu\text{g P}$; $C_0 = 120.6$ $100 \text{ cm}^3/\mu\text{g P}$; $B = 65.6$ $100 \text{ cm}^3/\mu\text{g P}$

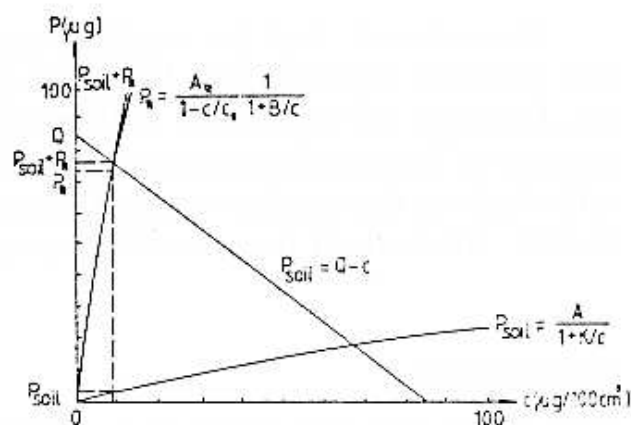


Fig. 6. Distribution of phosphorus in soil-solution-resin system, soil No. 19., 1 g of soil.

$$P_{\text{soil}} = P_R; P_R = \frac{A}{1 - \frac{c}{c_0}} \cdot \frac{1}{1 + \frac{B}{c}}; P_{\text{soil}} = Q - c;$$

$$P_{\text{soil}} = \frac{A}{1 + K/c};$$

of soil. In the case of 1 g of soil only 14% phosphate remains in the solution and on the soil. However, decrease of the amount of soil leads to an increase of the possibility of chance error derived from measuring difficulties.

The approximations with the model proved that the desorption of soil phosphate may be described by one equation. The parameters of the equation are not influenced by the ratio of soil: solution or resin: soil: solution. The effect of earlier phosphorus treatments appears to cause differences only in values of actual quantities of desorbable soil phosphate (Q). Consequently the Q value assumed by the model is useful for characterizing the phosphate supply of soils.

CONCLUSIONS

The results of the study support the statement of Barrow and Shaw (1977) that phosphate sorbed on resin (P_R) is less than the quantity of desorbable soil phosphate (Q). The deviation is larger in the case of soil with large quantity of phosphorus and it may range to 30–50%. This lack is due to the distribution of phosphorus in all of the three phases of soil-solution-resin system at equilibrium. The phosphorus retained by soil (P_{soil}) and in solution (P_{solution}) is not negligible comparing with the amount of phosphate sorbed by resin.

$$Q = P_{\text{Resin}} - P_{\text{soil}} - P_{\text{solution}}$$

The error caused by the deviation may be corrected by the adoption of the adequate model.

In the study it was found that phosphorus sorption of the resin may be modelled by BET isotherm, while the desorption of soil by Langmuir isotherm. In soil-solution-resin system the change of any component has significant effect on the amount of phosphorus sorbed by resin.

It was found, that the model is equally appropriate for 1/10–1/1000 ratios of soil: solution. It proved that desorption proceeds in the same way in this wide interval. Dilutions did not result such disaggregation which might have yielded further quantity of desorbable phosphate. However, the validity for the narrow soil: solution ratio leads to the conclusion that Q determined by the model is valid for moist soil as well, when direct determination is not possible because of technical difficulties.

REFERENCES

- AMER, F., BOULDIN, D. R., BLACK, C. A. and DUKE, F. R., 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P-32 equilibration. *Plant Soil*, 6: 391–
- BARROW, N. J. and SHAW, T. C., 1977. Factors affecting the amount of phosphate extracted from soil by anion exchange resin. *Geoderma*, 18: 309–323.
- COOKE, I. J. and HISLOP, J., 1963. Use of anion-exchange resin for the assessment of available soil phosphate. *Soil Sci.* 96: 308–
- FÜLEKY, GY., TOLNER, L. and DÖMSÖDI, J., 1980. Determination of the kinetics of soil phosphorus supply by anion exchange resin. (In Hungarian). *Agrokémia és Talajtan*, 29: 273–
- HISLOP, J. and COOKE, I. J., 1968. Anion exchange resin as a means of assessing soil phosphate status: a laboratory technique. *Soil Sci.* 105: 8–
- MURPHY, J. and RILEY, J. P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta*, 27: 31–
- OLSEN, S. R. and WATANABE, F. S., 1957. A method to determine a phosphorus adsorption maximum of soil as measured by the Langmuir isotherm. *Proc. Soil Sci. Soc. Am.* 21: 144
- OSZTOICS, A.-NÉ., 1984. Phosphate sorption in sandy soils. (In Hungarian). *Agrokémia és Talajtan*, 33: 288
- TAYLOR, R. W. and ELLIS, B. G., 1978. A mechanism of phosphate adsorption on soil and anion exchange resin surfaces. *Soil Sci. Soc. Amer. J.* 42: 432–436.