DETERMINATION OF THE ORIGINALLY ADSORBED SOIL PHOSPHORUS BY MODIFIED FREUNDLICH ISOTHERM

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ABSTRACT: Phosphorus adsorption was studied on four different Hungarian soil samples previously treated with phosphorus. Six different isotherm models were fitted to the P adsorption data. All the models took into account the amount of phosphate originally adsorbed (**Q**). The models applied were the Langmuir isotherm, a Freundlich isotherm with a calculated exponent and 3 Freundlich isotherms with different constant exponents (1/1, 1/2 and 1/3).

The aim of the comparison was to select the model whose parameters gave the best characterisation of the phosphorus adsorbing ability of the soil and the amount of phosphorus originally adsorbed (**Q**). It should be possible to fit the model to the measured data with low residual variance and to evaluate the parameters fairly independently of each other.

In all respects a Freundlich isotherm function with a constant 1/3 exponent was found the most suitable for the description of phosphorus adsorption. This Freundlich isotherm can be expressed as:

$$\mathbf{P_{ads.} = k \cdot c^{\frac{1}{3}} - Q}$$

A linear correlation was found between the phosphorus treatments and the originally adsorbed phosphorus quantities (**Q**) calculated using the model. This indicates that the ratio of phosphorus - in the sorbed and bound states - does not depend on the size of the phosphorus dose.

The value of the **k** factor characteristic of the shape of the sorption curve is near to constant within each soil, so it is characteristic of the given soil. The value of **Q** is thus clearly capable of characterising the labile P value of the soil.

INTRODUCTION

Soils very rarely behave as ideal systems, for which the adsorption isotherms were originally elaborated. A certain quantity of phosphate ions is always present in the adsorbed state on their surfaces, so the quantity of originally adsorbed phosphorus (**Q**) must be taken into consideration when fitting the isotherms (Bache and Williams, 1971):

$$\textbf{P}_{\textbf{ads.}} = \textbf{f (c)-Q}$$

where **P**$_{\textbf{ads.}}$ is the quantity of phosphorus adsorbed on the soil during the adsorption studies,

c is the P concentration of the equilibrium solution, and

f(c) is the general form of the adsorption isotherm correlation.

When a form modified by the phosphorus content originally present in the adsorbed state is applied, this quantity can be determined with the aid of ion exchange resin (Fitter and Sutton, 1975), or from the isotopically exchangeable phosphorus content (E value; Olsen and Watanabe, 1957, Bache and Williams, 1971), possibly with the help of the Olsen method (Nychas, 1982), in the course of measurements independent of the adsorption isotherm.

The value of **Q** can also be calculated by extrapolating the adsorption curve to zero equilibrium concentration (Fitter and Sutton, 1975). The value of **Q** determined in this manner is highly dependent on the model applied (Barrow, 1978).

The first Freundlich and Langmuir isotherm models applied did not always fit satisfactorily, so more and more complicated multifactorial models were elaborated and applied, such as the 2-term Langmuir (Syers et al., 1973, Holford et al., 1974), BET (Taylor and Ellis, 1978), Gunary (1970). Although these parameters had a physico-chemical interpretation, the goodness of fit could chiefly be attributed to the increasing flexibility of the functions as the number of parameters rose. However, not only the goodness of fit, but also the reliable

determination of the parameters is of importance in the present case, since these
are
to be used to characterise the soil status. The chances of this succeeding decline as
the number of parameters rises, since the parameters cannot be estimated
independently of each other. This problem is particularly strongly felt when
samples of a given soil are subjected to different treatments. It would be expected
that for any soil some of the parameters would be constants characteristic of the
soil, while others would depend on the treatment. Experience, however, shows
that the parameters of multifactorial models do not satisfy these expectations.

The theoretical problem of the independent estimation of the coefficients is
further complicated by the practical difficulty that the fitting of the models is
carried out by non-linear regression, or iteration.

The linearised solutions previously applied were also erroneous. In the
case of the Langmuir isotherm, for example, the original form was:

$$P_{ads.} = \frac{A}{1 + K/c}$$

and the linearised form:

$$\frac{\mathbf{c}}{\mathbf{P_{ads.}}} = \frac{\mathbf{K}}{\mathbf{A}} + \frac{\mathbf{1}}{\mathbf{A}} \cdot \mathbf{c}$$

When linear regression involving the smallest mean squares method is
applied, the best solution is obtained when the sum of the squares of the
differences between the measured ($\mathbf{P_{ads.meas.}}$) and calculated ($\mathbf{P_{ads.calc.}}$) values of
the quantity of P adsorbed on the soil is minimum. The best solution is thus:

$$\sum \left(P_{ads.meas.} - P_{ads.calc.} \right)^2 = \min imum$$

By contrast, the condition for a minimum difference between the sum of
mean squares for the linearised correlation mentioned above is:

$$\sum \left(\frac{c}{P_{ads.meas.}} - \frac{c}{P_{ads.calc.}} \right)^2 = \min imum$$

This differs from the best solution in two respects, since it contains
reciprocals of the dependent variable ($\mathbf{P_{ads.}}$), which are multiplied by the

independent variable (**c**). The distortion involved in using reciprocals is that the error of $\mathbf{P_{ads.}}$ values having lower absolute values receives greater weight, while that of $\mathbf{P_{ads.}}$ values with higher absolute values receives less weight. This error proves to be especially serious, since the measurement of low values generally takes place in the region of the measurement limit. By forming a reciprocal, errors committed here are magnified and become decisive in the estimation of the regression parameter. Multiplication with the independent variable (**c**) has the opposite effect, but is unable to compensate for the above effect.

The "linearisation" of the Freundlich isotherm model leads to similar errors:

$$\mathbf{P_{ads.} = k \cdot c^{\frac{1}{n}}} \qquad\qquad \ln\left(P_{ads.}\right) = \ln(k) + \frac{1}{n} \cdot \ln(c)$$

The use of a logarithm masks the variation, so again the weight of $\mathbf{P_{ads.}}$ values with lower absolute values increases compared with those having greater absolute values (Kemény and Deák 1990).

It is impossible to make this erroneous linearisation if the Langmuir isotherm or the Freundlich isotherm is corrected using the values originally adsorbed on the soil (**Q**).

If consideration is given to the quantity of P originally adsorbed on the soil (**Q**), the form of the Freundlich isotherm is (Fitter and Sutton, 1975):

$$\mathbf{P_{ads.} = k \cdot c^{\frac{1}{n}} - Q}$$

In the course of the present work, emphasis was placed on the interpretation of a reduced number of parameters, even at the expense of a slight reduction in the goodness of fit and a narrowing of the range over which the model is valid.

Studying the adsorption of phosphorus on acidic Hawaii soils, Davis (1935) observed that the correlation between the phosphorus bound to the soil and the concentration of the equilibrium solution could be characterised by a simple root function. Among the whole root exponents tested (**n**=1, 2, 3, 4), the best fit was obtained for **n**=3, i.e. for a 1/3 power exponent.

Barrow (1978) found a value of **n**=2.5 to be the best. Hartikainen (1991) used phosphate solutions with a very low concentration (0-0.5 $mg.dm^{-3}$) to

determine the sorption isotherm. In this narrow range the isotherm can be taken as linear to a good approximation, i.e. the value of the square root component is **n**=1.

Phosphorus sorption results obtained over the last few decades with the aid of adsorption isotherms suggests that, for the description and interpretation of binding processes, the parameter introduced last, **Q**, is the bearer of more useful information, particularly from a practical point of view, than all the other sorption parameters. The role of **Q** was not significant earlier because it had a value close to zero as long as the soils were not fertilized. As the result of intensive fertilization the quantity of P present in the soil in the adsorbed state has risen, making it essential to take **Q** into account.

In the course of our work the aim has been to determine the value of **Q** as accurately as possible and to study the effect on **Q** of earlier phosphorus fertilization and the time which has passed since fertilization.

MATERIAL AND METHODS

Four typical Hungarian soils were used in the studies, the characteristic data of which are presented in Table 1. For each soil, soil samples with various phosphorus contents were also required. The soils were thus treated with 0, 10, 20, 40, 80, 160, 320 or 640 mg.kg^{-1} phosphorus in the form of an aqueous solution of KH_2PO_4. Soils mixed with these quantities of phosphorus were incubated at constant moisture content (60% of water holding capacity) and incubated at room temperature for 1, 7 or 19 months.

In order to study the phosphorus sorption of the incubated soil samples, the soils were shaken for 24 hours with increasing quantities of phosphorus (0-100 mg.dm^{-3} KH_2PO_4 in aqueous solution) in a 1:10 soil:water system.

The quantity of phosphorus remaining in the solution was determined to calculate the quantity of phosphorus adsorbed on the soil.

RESULTS AND DISCUSSION

Six different isotherm models were fitted to the data series for the phosphate concentration of the equilibrium solution (**c**) and the phosphate adsorbed by the soil (**P$_{ads.}$**).

All the models applied were corrected with the **Q** value.

The Langmuir isotherm is thus:

$$P_{ads.} = \frac{A}{1 + K/c} - Q \tag{1},$$

The two-term Langmuir isotherm is:

$$P_{ads.} = \frac{A_1}{1 + K_1/c} + \frac{A_2}{1 + K_2/c} - Q \tag{2},$$

The Freundlich isotherm is:

$$P_{ads.} = k \cdot c^{\frac{1}{n}} - Q \tag{3}.$$

The Freundlich isotherms with 3 different constant exponents are:

with a 1/3 exponent:

$$P_{ads.} = k \cdot c^{\frac{1}{3}} - Q \tag{4},$$

with a 1/2 exponent:

$$P_{ads.} = k \cdot c^{\frac{1}{2}} - Q \tag{5},$$

with a 1/1 exponent:

$$P_{ads.} = k \cdot c - Q \tag{6}.$$

The aim of the comparison was to select the model whose parameters gave the best characterisation of the phosphorus-adsorbing ability of the soil and the amount of originally adsorbed phosphorus (Q). This model should make it possible to fit the measured data with low residual variance, and to estimate the parameters independently of each other. In the case of non-linear functions, however, the independent estimation of the parameters is impossible even using special experimental design (Adler et al 1977).

In the case of non-linear functions an added difficulty is that the iteration methods used to calculate the parameters are not always accurate. We can never be sure that the model parameters found during the calculation to be optimum are really the best solutions for the whole of the interpretation range, rather than being only local optima for part of the range. A direct search, non-linear regression calculation method was used (Tolner and Füleky, 1987) to calculate the parameters of models which cannot be linearised. This efficient technique, which can be applied even for functions which are difficult to handle, is not completely free of this error, though the several thousand steps in the search, starting from ten different places, leads to a relatively reliable result.

Naturally, the unequivocal solution provided by linear regression cannot be achieved in every case even with this method, so, wherever possible, it is worth applying linear regression.

On the basis of the reliability of the regression calculation, the correctly linearised function models (**4**, **5** and **6**) are preferable to models calculated by iteration only (**1**, **2** and **3**).

A further distinction can be made between the applicabilities of the above models on the basis of the independence of parameter estimation. In general it can be said that the more parameters a model contains, the less possible it is to estimate them independently of each other. On the other hand, model containing a larger number of parameters can usually be fitted better. The most important parameter in the present case is the quantity of phosphorus originally adsorbed (**Q**). It should thus be possible to estimate this value as independently as possible from the other parameters.

The problem arising from the correlation between the parameters will be illustrated using the Freundlich isotherm.

When the Freundlich isotherm was fitted to the series of soil samples from Orosháza (8) treated with 320 mg.kg^{-1} phosphorus and incubated for 1 month, values of **1/n** = 0.16, **k** = 379 and **Q** = 555.0 mg.kg^{-1} were obtained. If the exponent was taken to be 1/3, i.e. **1/n** = 0.33, the other values became **k** = 108 and **Q** = 240.5 mg.kg^{-1}. The residual variance of regression was practically the same, being 6 and 8 mg.kg^{-1}. The curve fitting is shown in Fig. 1.

It is clear from the figure that the two types of function differ considerably from each other in the range which contains no measured points. The fact that a **Q** value of 555.0 mg kg^{-1} is unrealistic is obvious if we consider that the soil was given a treatment of 320 mg.kg^{-1}, while in the case of the untreated sample a value of **Q** = 27.3 mg.kg^{-1} was obtained for the originally adsorbed quantity. It is unlikely that, as the result of the treatment, the increase in the quantity of adsorbed phosphorus will be greater that the quantity applied. In reality, some of the phosphorus applied will be transformed during incubation into a strongly bound form, so that the value remaining in the adsorbed state (**Q**) will be smaller that the quantity of phosphorus applied (P treatment). The **Q** = 240.5 mg kg^{-1} value obtained with the 1/3 exponent is thus realistic.

After the six model functions mentioned above had been fitted to the measured data, the function parameters and the residual variance values characteristic of the goodness of fit were calculated. The residual variance was calculated by dividing the deviance (sum of squares) by the degrees of freedom, i.e. by the difference between the number of measured data and the number of function parameters, and by extracting the square root of the value obtained. This is characteristic of the goodness of fit for models calculated using both non-linear and linear regressions. The residual variance values for the Orosháza soil are shown in Table 2.

On the basis of the residual variance values characteristic of the goodness of fit, the curve fitting was classified as satisfactory or unsatisfactory. Taking each line in Table 2 separately, the variance value and those which did not exceed twice this value were included in the satisfactory group. In addition, values which did not exceed the mean variance of the experimental data (15 mg.kg^{-1}) were also classified in this group. The remaining curve fits were placed in the unsatisfactory group. These latter were marked *.

For the curves fitted to the phosphorus adsorption data of four soils the following were found to be unsatisfactory:
- the Langmuir isotherm (**1**) in 29 cases (33 %),
- the two-term Langmuir isotherm (**2**) in 5 cases (6 %),
- the Freundlich isotherm with a 1/n exponent (**3**) in 3 cases (3 %),
- the Freundlich isotherm with a 1/3 exponent (**4**) in 3 cases (3 %),
- the Freundlich isotherm with a 1/2 exponent (**5**) in 19 cases (22 %),
- the Freundlich isotherm with a 1/1 exponent (**6**) in 79 cases (90 %).

It can be seen from the above that the two-term Langmuir isotherm, the 1/n exponent Freundlich isotherm and the 1/3 exponent Freundlich isotherm gave equally good fits, while the other three functions were less suitable for the description of adsorption.

In summary, as regards the joint fulfilment of the three conditions discussed up till now (the reliability of the regression calculation, the independent estimation of the parameters and the goodness of fit), the Freundlich isotherm with a 1/3 exponent (4) proved to be the best of the models tested.

To obtain further confirmation of the correctness of this choice, an examination was made of what exponent values were obtained when fitting the

original Freundlich isotherm (**3**) model, to ensure that, of the various constant exponents, the 1/3 exponent was the best.

Fig. 2 illustrates the frequency with which various **n** values were obtained for the 1/n exponent.

The height of the columns indicates the number of times the exponent value occurred in the course of curve fitting. The frequencies obtained for the 0-40 and 80-640 mg.kg^{-1} treatments are depicted separately. In the case of lower rate treatments, the 1/3 exponent value was obtained exceptionally frequently, while the exponent values showed a wider distribution for the higher treatment rates.

In the lower treatment range (0-10-20-40 mg.kg^{-1}) the exceptional frequency of the 1/3 value supports the choice of a Freundlich isotherm model with a 1/3 exponent. In the higher treatment range (80-160-320-640 mg.kg^{-1}), in addition to the 1/3 value, exponents from 1/4 to 1/8, and even values smaller than 1/8 (in a total of 16 cases), were obtained with considerable frequency. This is also illustrated by the fact that in Fig. 1 the fit is just as good if the exponent is 1/3 or 1/6 (=0.16), which can be attributed to interactions between the parameters. In the case of higher treatment rates this effect became more prominent, because at these rates no measured data were obtained in the lower equilibrium concentration range, making the shape of the curve more random, depending on the error of the individual measurements. In the case of high **n**, i.e. low 1/n values, this means that the curve is almost horizontal in the range where measured data are available (1/n -> 0, $c^0 = 1$), suddenly becoming steeper as it approaches the ordinate exis (**P$_{ads.}$**) and resulting in unrealistically high **Q** values (curve 2 in Fig. 1).

Over a smaller treatment range, the measured data give a better idea of the shape of the curve, as can be seen in Fig. 3, where the adsorption obtained for a sample of the Hajdúböszörményi soil (19), incubated for 1 month without previous treatment with phosphorus, is plotted using a Freundlich isotherm with a constant 1/3 component (**4**) or with an exponent calculated by iteration (**3**) (curves 1 and 2).

In addition to having almost identical, very low (3 and 2 mg.kg^{-1}) variance values, the exponent calculated for the Freundlich isotherm (0.34) is practically equal to 1/3. The **Q** values are also very similar, being 20.8 and 22.0 mg.kg^{-1}.

On the basis of the above, a Freundlich isotherm (**4**) with a 1/3 exponent, corrected with **Q**, the quantity of phosphorus originally adsorbed, is considered to

be the most satisfactory for the description of adsorption in the soil. In contrast to other models, this model is suitable for the description of adsorption over a wide concentration range and also in the case of an extremely high original phosphorus content.

This exponent value is in good agreement with the Freundlich isotherm exponent values to be found in the literature (**1/n**= 0.3-0.5).

The values of the parameters obtained during curve fitting using a Freundlich isotherm with a 1/3 exponent and corrected with **Q** (4) are illustrated in Table 3 for all four soils examined. All the measured data were used to study the correlation between the **Q** values calculated with the model (**4**) proposed here and the E values determined with the isotope exchange method (Osztoicsné, 1984). A close linear correlation was found (r=0.89). The slope of the straight line (Fig. 6) was 0.99, i.e. in practice, equal to 1. This shows that the values obtained with the two types of method are identical. Since adsorption studies can be carried out more simply and cheaply than isotopic measurements, the determination of **Q** using the proposed model (**4**) would give a fair approximation of the E value.

An examination of columns containing k values in Table 3 indicates that no definite correlation can be expected between the **k** values and the phosphorus treatment or the incubation time. It appears that the k values are constant for a given soil, as confirmed by the negative results of linear regression analysis between the **k** values and the P treatment for each soil after various periods of incubation. The hypothetical linear correlation is:

$$\mathbf{k = m_k \cdot P_{treatment} + k_0}$$

The parameters obtained by regression analysis ($\mathbf{m_k}$: slope of the straight line, $\mathbf{k_0}$: intercept, $\mathbf{r_k}$: correlation coefficient) are presented in Table 4. The $\mathbf{r_k}$ values are not significant in two-thirds of the cases. The low $\mathbf{m_k}$ values also indicate that the regression lines are almost parallel to the $\mathbf{P_{treatment}}$ axis, i.e. there is no correlation.

A similar approach cannot be applied when studying the effect of the incubation time, since the data are insufficient, being available for only three points of time. In the $\mathbf{k_0}$ column of Table 4, the figures given for three points of time are roughly equal in value for each soil. The slight differences between them show neither a decreasing nor an increasing tendency with incubation time. It is

thus probable that the **k** values are independent not only of the phosphorus treatment, but also of the incubation time, and are constant for the soil in question.

When fitted using model (**4**), adsorption curves where the **k** parameters are in agreement, but the **Q** parameters differ run parallel to each other. This is illustrated in Fig. 4, which shows the adsorption isotherm curves obtained for samples of Orosháza soil (8) incubated for 19 months after different P treatments.

The effect of the P treatment can be expected to appear in differences in the **Q** values (Table 3), which exhibit substantial differences as the result of various phosphorus treatments and incubation times. At each point of time during incubation, linear correlation was found between the **Q** and **P$_{treatment}$** values.

$$Q = m_Q \cdot P_{treatment} + Q_0$$

The parameters obtained by regression analysis (**m$_Q$**: slope of the straight line, **Q$_0$**: intercept, **r$_Q$**: correlation coefficient) are presented in Table 5.

A glance at the **r$_Q$** correlation coefficients will show that in all 12 cases (4 soils x 3 incubation times) there is a close linear correlation between the **Q** and P treatment values. This indicates that in the course of incubation the reduction in the quantity of phosphorus present in the adsorbed phase (**Q**) is probably due to chemisorption.
The proportion of the adsorbed form in the total fixed quantity of phosphorus is constant, i.e. it does not depend on the extent of the treatment.

The steepness of the straight lines (**m$_Q$**) ranges from 0.30-0.90 for the given soil. If these values are multiplied by 100 (100.m$_Q$), they indicate the percentage of the phosphorus applied to the soil which enters the adsorbed state (**Q**), while the 100.(1-m$_Q$) values indicate the percentage of phosphorus which has become more strongly bound. It can thus be read off from the table that of the P applied to an Orosháza (8) soil incubated for 7 months, 65 % is to be found in the adsorbed state, while 35 % became more strongly bound.

The slope of the straight lines (**m$_Q$**) decreases with a rise in the incubation time (Fig. 5). This confirms the observation that, in the course of the incubation period, the phosphorus added to the soil is fixed to an ever greater extent. This effect leads to greater changes at higher treatments. In the case of lower treatments, including untreated soils, shown by the intercept (**Q$_0$**) of the straight lines, this effect is not so clear-cut, in fact a tendency to release P may even be observed.

Since the value of **k** is roughly constant, and thus characteristic, for each soil, the effect of phosphorus treatment can be concentrated in a single parameter (**Q**). As regards practical applicability, this means that it is sufficient to carry out sorption isotherm measurements, which involve several analyses, on a single occasion. These measurements can be used to determine the value of **k**. This value, which is correlated to the equilibrium constant of the adsorption expresses in itself the phosphorus sorption properties of the soil. The slope of the sorption curve depends on the value of **k**, while **Q** is given by the intercept of the sorption curve.

If the parameters of the sorption curve (**k**, **Q**) are known for a soil in a certain state, the sorption curve after any change in the phosphorus reserves of the soil, due to fertilization or fixation, can be determined after a single new analysis. Changes occurring in the phosphorus reserves of the soil through fertilization, plant uptake and adsorption can thus be traced by a simple analysis and calculation.

CONCLUSION

A Freundlich isotherm correlation with a constant 1/3 exponent is thus well suited for the description of the phosphorus sorption of the soil.

The sorption properties of the soil are characterised by the **k** parameter of the function, and the quantity of adsorbed soil phosphorus actually available to the plant by the factor **Q**.

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