PHOSPHOROUS DISSOLUTION INTO WATER FROM SOIL SURFACE

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ABSTRACT

Water erosion can carry away the fertilized upper soil layer and deposit it in rivers and lakes. Some part of sorbed phosphate ions will release into the water and potentially can cause environmental pollution and eutrification of surface waters. How phosphate ions are desorbed from the soil particles - sooner or later - fertilized with P - are discussed in this paper. A calcareous loamy soil of pH_{H_20} 7.9 was incubated with 0, 80 and 320 mg kg^{-1} P and then equilibrated with several rates of P. After shaking and centrifugation the solid phase was shaken12 times with distilled water and the desorbed quantity of P was calculated. Using the adsorption equation, a new model was constructed to describe the one-step and multi-step desorption. Parameters of the model help to calculate the reversible and irreversible fraction of sorbed P. Higher fertilizer P rates produced higher rates of desorbable P. This model, developed by combining a modified Freundlich equation and the mass balance equation, makes it possible to describe multi-step desorption and the calculation of potentially desorbable P in soil.

INTRODUCTION

When calculating the phosphorus pollution of surface waters, it is extremely important to know how much phosphate may be dissolved or desorbed into the water from the surface of soil particles washed into rivers or lakes by erosion, since the quantity of phosphate ions in solution is closely related to the growth of algae which cause eutrophication. In a model experiment set up to examine this question the soil was fertilised with P and then incubated. Phosphate ions were then adsorbed onto these soils. This was followed by aqueous desorption in 12 steps to model the more and more dilute solution phase affecting the surface of soil particles due to water movement in surface waters. It was possible to calculate the maximum quantity of desorbed P by expressing this multi-step desorption in mathematical form.

Some of the P bound to the soil is present in a readily dissoluble form, while the remainder is strongly bound. Only a fraction of the P applied to the soil dissolves in an equilibrium extract prepared with water or dilute salt solution. This simple desorption step can be repeated several times consecutively on the soil sample. If a soil was previously treated with P fertiliser, the quantity of P desorbed through the multiple repetition of the desorption steps may approach the quantity applied in the course of the treatments (Loch and Jászberényi, 1995).

Multi-step desorption can be illustrated by means of a cumulative function. In this case the total quantity of P entering solution in the given step and in previous steps is plotted as a function of the P concentration of the equilibrium solution in each step. The points obtained in this way can be formally fitted to a Langmuir isotherm correlation (Fried and Shapiro, 1956).

A true desorption isotherm can be obtained if the soil P quantity minus the quantity entering solution is plotted as a function of the P concentration of the equilibrium solution. If this is preceded by adsorption and multi-step desorption is carried out to retrieve the adsorbed quantity, the points characteristic of the various steps in the desorption are usually located above the adsorption isotherm. According to Kafkafi et al. (1967), this is due to the fact that in the course of adsorption some of the P applied to the soil becomes strongly bound and does not thus take part in the development of the equilibrium state. The distance between the adsorption and desorption curves becomes negligible if there is a space of only 12 hours between the two processes, or if this period does not exceed 5 days (Muljadi et al., 1966). Barrow and Shaw (1975) dispute the fact that a further substantial quantity of P cannot become more strongly bound during the desorption process. The degree of binding depends on the length of the process and may be significant even if only 2 days pass between adsorption and desorption. When modelling multi-step desorption they used a combination of Freundlich isotherms, taking into account the binding process, which takes place more slowly than sorption.

Okajima et al. (1983) studied the reversibility of desorption and the hysteresis of the adsorption and desorption processes. The decline in the P content of the soil was illustrated as a function of the logarithm of the equilibrium concentration. Approximate straight lines were obtained, the slope of which was characteristic of the reversibility of the process.

The objective of the present work was to use a correlation method elaborated for the evaluation of adsorption data (Tolner and Füleky, 1995) to develop a model suitable for the description of multi-step desorption.

MATERIALS AND METHODS

A calcareous loamy soil of pH_{H_20} 7.9 was used in the model experiment. The soil was incubated with 0, 80 and 320 mg kg^{-1} P and then equilibrated with several rates of P. After shaking and centrifugation the solid phase was shaken12 times with distilled water and the desorbed quantity of P was calculated.

The desorption curves were fitted using non-linear regression. The optimum values of the parameters of the non-linear function were determined by minimising the sum of the squares of the measured and calculated values using a simple step-wise iteration procedure (Bojarinov and Kafarov, 1973).

RESULTS AND DISCUSSION

Two correlations were considered when describing the equilibrium set up during desorption. One of these is the sorption isotherm, which characterises the distribution of P between the solid and solution phases of the soil suspension. The other is a material balance which states that only the quantity of P present in the soil in the adsorbed state prior to desorption can be distributed between the two phases. This quantity may differ from the P previously entering the soil due to sorption, and the parameters of the sorption isotherm also may not necessarily correspond to those of the adsorption isotherm. The purpose of the model is to make it possible to determine these parameters by carrying out regression on the series of equilibrium concentrations obtained during desorption.

It is assumed that the modified Freundlich isotherm found to give the best evaluation of the adsorption data is suitable for the description of the distribution of P between the solid and solution phases (Tolner and Füleky, 1995):

$$P_{ads} = k.c^{1/3} \qquad (1)$$

where P_{ads}= quantity of P adsorbed on the soil in the equilibrium state of the sorption process; c= P concentration of the equilibrium solution; and k= constant.

The P quantity present in the soil in the adsorbed state prior to carrying out desorption is designated as Q. This decreases to a value Q_1 in the course of equilibration. The difference enters solution (P_{sol}). The quantity of P still adsorbed on the soil at equilibrium (Q_1) can thus be calculated as the difference between the quantity originally in the adsorbed state (Q) and that entering solution (P_{sol}):

$$Q_1 = Q - P_{sol} \qquad (2)$$

If the initial solution contained no P (c_0=0), P_{sol} can be calculated from the concentration of the equilibrium solution (c_1) with the help of the soil:solution ratio (S) (Tolner and Füleky, 1987):

$$P_{sol} = \frac{c_1}{S} \qquad (3)$$

In the course of the studies, the soil:solution ratio was 1:10, i.e. S = 0.1 kg dm^{-3}. At a concentration of c_1 = 1 mg dm^{-3} the quantity of P entering solution (P_{sol}) is thus 10 mg of P per kg soil.

By combining correlations (2) and (3), the quantity of P still in the adsorbed state after equilibrium has been achieved (Q_1) can be given as a function of the concentration of the equilibrium solution (c_1) and the soil:solution ratio (S):

$$Q_1 = Q - \frac{c_1}{S} \qquad (4)$$

This material balance correlation is a straight line function. This satisfies one of the conditions for the equilibrium developing during desorption. The other condition is the sorption isotherm characteristic of the distribution between the solution and the solid phase (1). The point of intersection of the curves or straight lines depicting the two conditions indicates the solution concentration (c_1) and the quantity still adsorbed (Q_1) in the equilibrium state (Fig. 1). While the quantity of P adsorbed on the soil decreases in the course of equilibration from Q to Q_1, the P concentration of the solution phase increases from the initial value of 0 (c_0=0) to the equilibrium value of c_1.

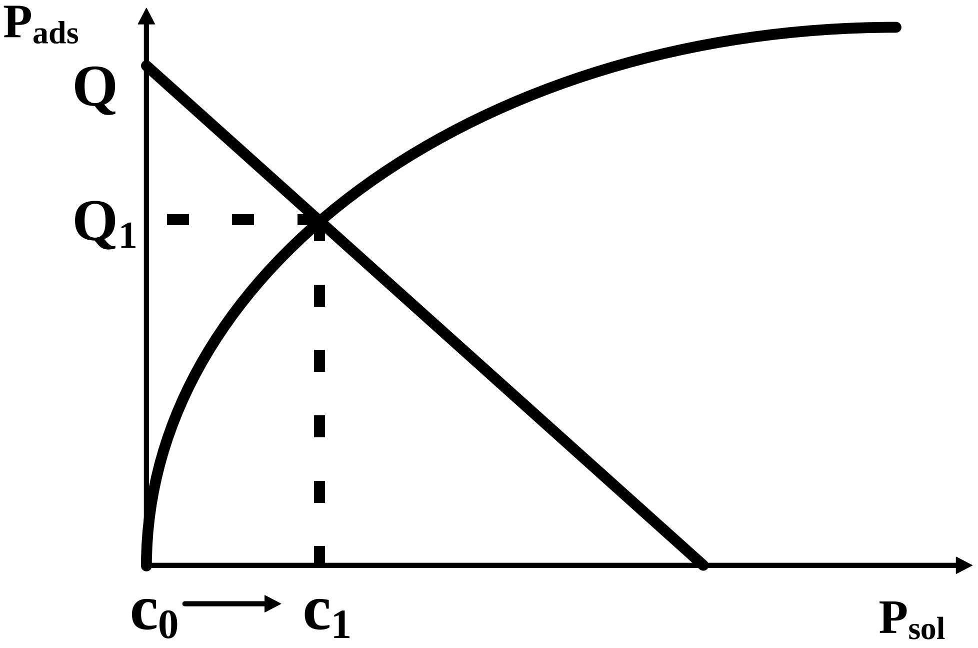

Fig. 1. One step desorption. The point of intersection of the curves or straight lines depicting the two conditions indicates the solution concentration (c_1) and the quantity still adsorbed (Q_1) in the equilibrium state.

Using the Q_1 and c_1 values characteristic of the equilibrium state, the general form of the sorption correlation (1) becomes:

$$Q_1 = k \cdot c_1^{1/3} \qquad (5)$$

The equilibrium soil suspension is centrifuged. Distilled water is again added to the solid soil phase after separation from the liquid phase and the desorption phase is thus repeated. From the point of view of this new equilibration, the quantity of P adsorbed on the soil prior to the desorption step is equivalent to the quantity which remained in the adsorbed state in the previous step (Q_1).

In the second step, the quantity of P still adsorbed on the soil will be Q_2 after equilibrium has been reached, and the concentration of the equilibrium solution c_2. The material balance for the second step is thus:

$$Q_2 = Q_1 - \frac{c_2}{S} \qquad (6)$$

If the value of Q_1 from equation (4) is substituted into equation (6):

$$Q_2 = Q - \frac{c_1 + c_2}{S} \qquad (7)$$

As the result of a similar derivation, the equation valid for the third desorption step will be:

$$Q_3 = Q - \frac{c_1 + c_2 + c_3}{S} \tag{8}$$

The correlation for the equilibrium states arising in the three consecutive desorption steps is illustrated in Fig. 2

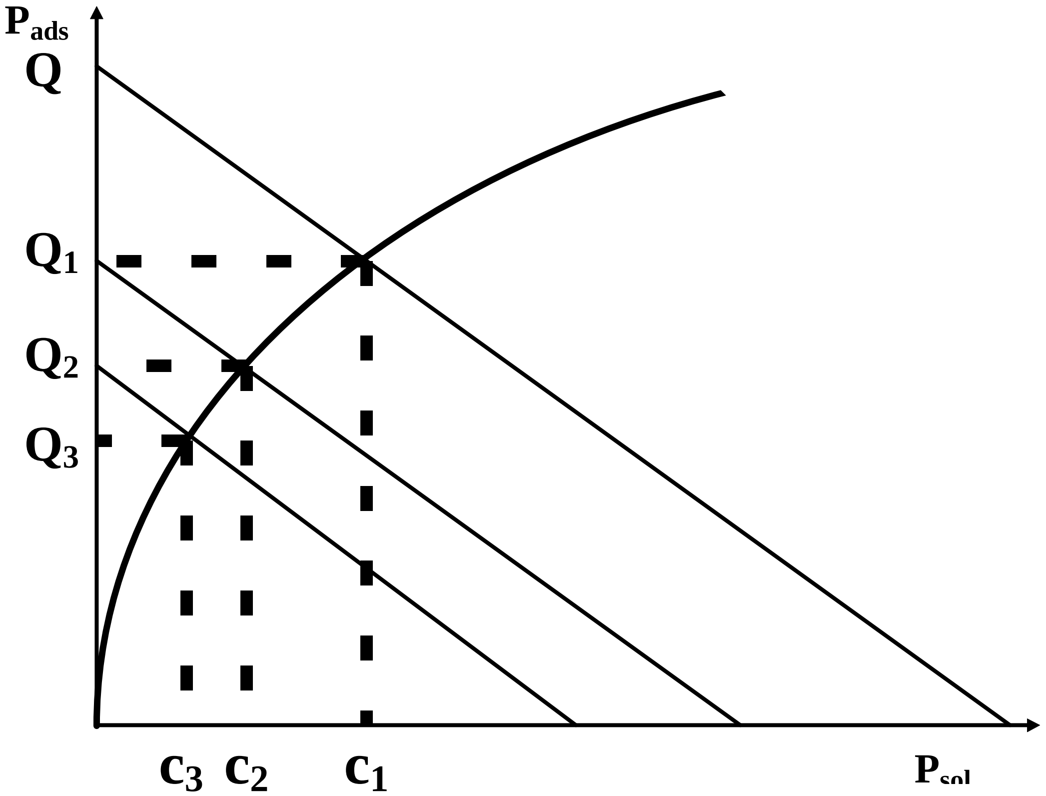

Fig. 2. Equilibrium states in case of multi-step desorption.

The material balance for multi-step desorption can be written in general form for step n:

$$Q_3 = Q - \frac{c_1 + c_2 + c_3}{S} \tag{9}$$

The other correlation describing the equilibrium state is the sorption isotherm characterising the distribution between the solution and the solid phase. The form of equation (1) for the nth desorption step is:

$$Q_n = k.c_n^{1/3} \tag{10}$$

The lefthand side of equations (9) and (10) are identical, so this is also true of the righthand sides. The equation thus obtained is suitable for the calculation of multi-step desorption:

$$Q - \frac{\sum_{i=1}^{n} c_i}{S} = k.c_n^{\frac{1}{3}} \qquad (11)$$

This is analogous to the correlation expressing adsorption (1) (Tolner and Füleky, 1995), except that there is a complex term ($Q - \Sigma c_i /S$) on the left instead of Q_1, expressing the quantity of P remaining in the soil in the desorbable state after the given step. In equation (11) c_1, c_2, ... c_i, ... c_n is a decreasing series of equilibrium concentrations determined by measurements, S is the soil:solution ratio (1:10), while Q and k are parameters calculated by regression.

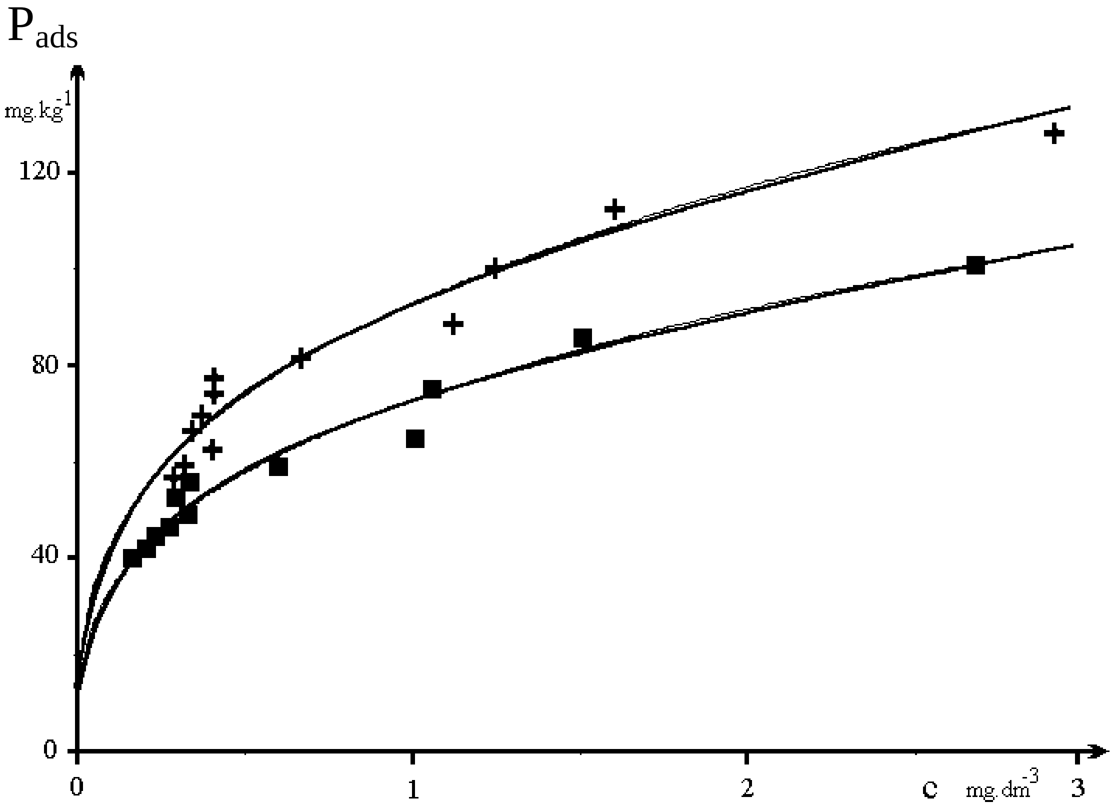

Fig. 3. The model close fit with measuring dates. The upper curve is on the dates of sample with previously 80 mg/kg P added to soil. The other curve is on dates of control soil.

After the regression calculations, equation (11) can be seen in Fig. 3 to give a close fit with the model. The Q values were calculated by means of regression. Parameter Q, i.e. the quantity of P adsorbed on the soil, was used to examine the percentage of freshly applied P which could be retrieved by means of multi-step desorption. First it is necessary to determine the quantity of P which was bound in the course of adsorption prior to the desorption steps.

It can be concluded that a multi-step desorption process for soil P can be well described using a model derived from the adsorption model. The quantitative parameter obtained using the desorption model can be interpreted as the quantity of P present in the soil in the adsorbed state, and can be used to characterise the reversibility of P binding.

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