Relationship between phosphorus intensity and capacity parameters in Finnish mineral soils

I Interpretation and application of phosphorus sorption-desorption isotherms

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Abstract. The interpretation and application of two types of P isotherms were elucidated by means of sorption-desorption graphs of two surface soil samples.

The isotherm expressing the retention or removal of P as a function of P application indicates the direction and extent of reactions at a given initial stage. The isotherm describing the sorption or desorption as a function of P concentration in the final solution after events illustrates the P buffering power of the soil. By using simultaneously the isotherms of both types, all information included can be integrated and the graphs can be used as a dynamic model describing P exchange.

Introduction

The availability of soil phosphorus to plants, the contribution of eroded soil material to phosphorus loadings of waters as well as the significance of sediment in the phosphorus budget of streams and lakes can be estimated by means of solubility of phosphate. This intensity parameter reflects the easiness of removal of the nutrient from the soil to solution, whereas the capacity parameter is related to the quantity of nutrient which can be removed before the intensity parameter is lowered to a certain level.

The relationship between intensity and capacity factors is of practical importance. Phosphorus bound by soil or sediment material becomes available by desorption when the plants or algae reduce the concentration of soluble phosphate in the soil solution or water below that prevailing in the solution in equilibrium with soil or sediment.

The relationship between the intensity and capacity parameters can be studied by P isotherms of various types. After SCHOFIELD(1955) introduced the concept of phosphate potential, numerous investigators have studied the theoretical aspects involved and techniques of measurement as well as its

application as an index of phosphate availability. The assumptions implicit in the use of phosphate potential are discussed in detail e.g. by WHITE and BECKETT (1964). Later, the principle of determination has been applied by TAYLOR and KUNISHI (1971) to estimating phosphate equilibria on stream sediments and soils and by BACHNICK (1977) to estimating the contribution of erosion to phosphate loadings into lake waters. However, in their method of application attention was not paid to the disparities between isotherms of various kinds and on the suitability of a particular isotherm for a given purpose. The purpose of the present study was to elucidate the nature of different sorption-desorption curves and their applicability for various purposes.

Material and methods

The sorption and desorption of P from and to solutions of various P concentrations were investigated with two surface mineral soil samples. Sample 51 was a fine sand clay (52 % clay) with pH 5.3 ($CaCl_2$) and 4.9 % organic carbon. Sample 61 was a silty clay (42 % clay) with pH 4.5 and 11.9 % organic carbon.

Standard phosphate solutions containing 0.010, 0.020, 0.050, 0.100, 0.200, 0.300, 0.500 and 1.000 mg P per liter were prepared from KH_2PO_4. One gram of soil was weighed into centrifuge tubes and 50 ml of standard solution was added. The suspension was shaken for one hour, allowed to stand for 23 hours, shaken for 10 minutes and centrifuged. The supernatant solution was filtered through a 0.2-μm membrane filter and analysed for phosphate by the molybdenum blue method, using ascorbic acid as reductant (ANON. 1969). Net adsorption or desorption was calculated on the basis of changes in the P concentrations occurred during the 24-hour equilibrium time.

Results and discussion

Figure 1 shows two different sorption-desorption isotherms obtained for the soil samples studied. The lines A_1 and A_2 represent the removal and retention of phosphorus as a function of phosphorus in original solutions. The isotherm followed the equation $y = a + bx$, where y is the sorbed or desorbed P mg/kg soil and x the initial concentration of phosphorus solution (mg/l). On the basis of this line, it can be estimated how much the soil sample will retain or release phosphorus when being in contact with a solution of a given phosphorus concentration.

Extrapolation of the graph to zero addition of P ($x = 0$) yields the amount of phosphorus soluble in pure water. Thus, the term a in the equation, the intersecting point of the line on y-axis, describes the quantity of water soluble phosphorus (mg/kg) and theoretical maximum of desorption at the soil-solution ratio of 1 to 50. The intersecting points for the soil samples 51 and 61 are −8.4 and −5.4 mg/kg, respectively. They correspond well with

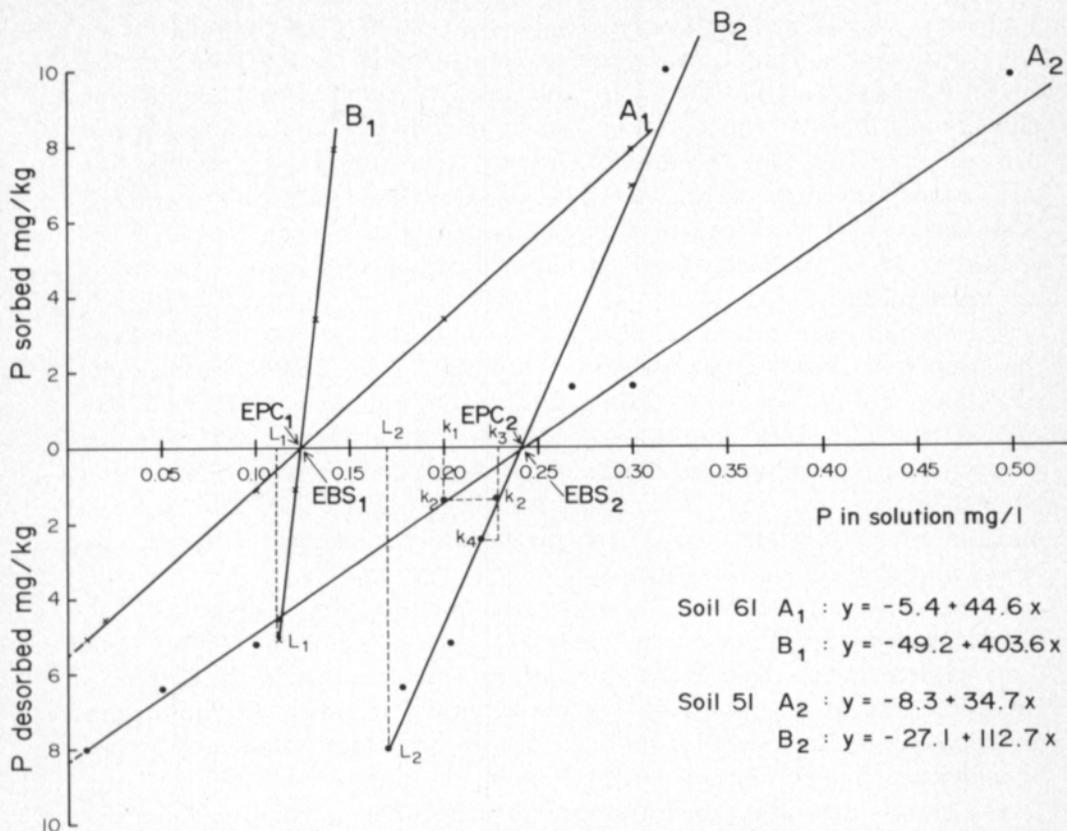Figure 1. Desorption and sorption of P as function of P in the initial solution (lines A_1 and A_2) and as function of P in final equilibrium solution (lines B_1 and B_2).

the quantities of P desorbed in the water treatment (9.8 and 5.5 mg/kg) when using the soil-water ratio of 1 to 60. The intersecting point on the x-axis ($\gamma = 0$) expresses the phosphorus concentration in the recipient water, where no net phosphorus exchange occurs upon addition of the soil sample to the aqueous system. This point can be termed the equilibrium bathing solution (EBS).

The term b in the equation for the isotherm of type A (see Fig. 1) is the tangent of the isotherm and describes the effectiveness of the desorption or sorption. The greater it is, the more markedly the total adsorption by the sample increases with incresing P concentration in the bathing solution above the EBS. Correspondingly, below the EBS the total desorption decreases with increasing P concentration in the bathing solution the more steeply the greater the value of b is.

The isotherm of type A expresses the premises and starting state of desorption and sorption but gives no information about the P concentration in the final solution obtained when the sample is brought into equilibrium with solutions of various initial concentrations. On the contrary, the graphs B_1 and B_2 (see Fig. 1) describe the removal or retention of P as a function of P in the final equilibrium solution. They conform to the equation $y = a + bx$, which is of the same form as that discussed above, but where y would be sorbed or desorbed P mg/kg soil and x the final P concentration in the

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equilibrium solution. This type of line allows to estimate the quantity of P to be sorbed by the sample in order to reach a certain concentration in the equilibrium solution. On the other hand, the isotherm indicates how low or high the equilibrium concentration can be so that a certain desorption has been possible. In contrast to the isotherm of type A, this graph does not give intimations about the magnitude of sorption or desorption to be expected when the sample is placed in a given solution, but it expresses the final concentration of the bathing solution after a certain sorption or desorption has taken place.

The sorption-desorption graph of type B describes the P buffer power of the sample. Its intersecting point on the x-axis, termed EPC (equilibrium phosphate concentration) according to TAYLOR and KUNISHI (1971), expresses the maximum concentration the soil or sediment can maintain without phosphorus addition under circumstances in question. Above this point, no desorption is possible. This means, e.g., that the EPC describes the maximum level to which the P concentration in the resipient water can be raised by the sediment or eroded soil.

The term a in the isotherm B is a characteristic of a particular sample. The graph can be assumed to converge the y-axis with an increasing solution-soil ratio without intersecting it. This results from the fact that in the buffering curve the intersecting point on the y-axis would express the equilibrium phosphate concentration of 0 mg/l which, in turn, does not allow any net phosphate exchange. Thus, departing from its meaning in the isotherm A, the term a in the equation for the isotherm B does not give information about the maximum desorption.

The slope b of the isotherm of type B describes the "phosphate buffer power" of the sample. The higher its value is, the greater the ability of the sample is to maintain the phosphorus intensity level against any changes in the system, i.e. the more effectively the sorption tends to decrease the P concentration in the equilibrium solution above the EPC, and, inversely, the more strongly an increase in the P concentration of the final solution is counteracted by a decrease in desorption below the EPC. As anticipated, the isotherms A and B intersect in the same point on the x-axis. This point, characteristic of a particular sample, is of great practical significance as discussed above.

The buffering curves expressing P exchange as a function of the final P concentration are used e.g. by TAYLOR and KUNISHI (1971) and BACHNICK (1977) for estimating the contribution of sediment, eroded soil and stream bank material to phosphate loadings into stream and lake waters. On the basis of these isotherms they have estimated the desorption or sorption to be expected when the sample comes into contact with a solution of a given concentration or has been brought into equilibrium with the solution of the P concentration prevailing in the recipient water. However, by adding a sample to the aqueous system, it is possible to reach this equilibrium concentration only if no net phosphate exchange takes place. It must be taken into account that, if any desorption occurs, the concentration in the solution does increase. Therefore, it is necessary first to investigate the magnitude of

desorption possible under prevailing circumstances (isotherm of type A). Thereafter the equilibrium concentration corresponding to the P desorption can be estimated (isotherm of type B).

As stated above, the buffering graphs are likely to converge the y-axis. This results in that below a certain limit value (L_1 and L_2 in Figure 1) the isotherm of type B gives no reliable information. This means that the isotherm B for soil sample 61 does not express the magnitude of desorption so that the P concentration in the final solution would be e.g. 0.05 mg/l. In fact, under the experimental conditions used in the present study this equilibrium concentration is not possible. Therefore, extrapolation of the lines may give misleading results.

The use of the isotherms of type A and B for various purposes can be justified on the basis of the facts discussed above. Figure 1 expresses the differences between these curves and illustrates their specific roles particularly in studies dealing with P loadings into waters. Thus, it can be estimated that when soil 51 comes into contact with a solution containing 0.20 mg P per liter (k_1), 1.4 mg P (not 4.75 mg) per kg is desorbed from the soil (k_2), leading to the equilibrium solution containing 0.23 mg P per liter (k_3). Further, it can be estimated that when the uptake by plants or algae reduces the P concentration from 0.23 mg/l to 0.22 mg/l, about 1 mg (k_1k_2) more P can be desorbed from one kg of soil.

It should be kept in mind that the isotherms are valid only under circumstances similar to those in the experiment. For example, the soil-solution ratio (WHITE and BECKETT 1964, WHITE 1966, TAYLOR and KUNISHI 1971), the salt concentration in the solution (RYDEN and SYERS 1975), or the presence of complexing agents (HARTIKAINEN 1979) may affect the sorption and desorption of P. In order to apply the results to conditions prevailing in nature the possible dependence between the slobe b of the buffering line (isotherm B) and the soil-solution ratio effect should be studied.

References

ANON. 1969. Juoma- ja talousveden tutkimusmenetelmät. Elintarviketutkijain Seura. 169 p. Helsinki.

BACHNICK, D. A. 1977. The contribution of red clay erosion to orthophosphate loadings into southwestern Lake Superior. J. Environ. Qual. 6: 217–222.

HARTIKAINEN, H. 1979. Phosphorus and its reactions in terrestrial soils and lake sediments. J. Scient. Agric. Soc. Finl. 51: 537–624.

RYDEN, J. C. & SYERS, J. K. 1975. Rationalization of ionic strength and cation effects on phosphate sorption by soils. J. Soil Sci. 26: 395–406.

SCHOFIELD, R. K. 1955. Can a precise meaning be given to "available" soil phosphorus? Soils and Fert. 18: 373–375.

WHITE, R. E. 1966. Studies on the phosphate potentials of soils. IV The mechanism of the "soil/solution ratio effect". Aust. J. Soil Res. 4: 77–85.

— & BECKETT, P. H. T. 1964. Studies on the phosphate potentials of soils. I The measurement of phosphate potential. Plant and Soil 20: 1–16.

TAYLOR, A. W. & KUNISHI, H. M. 1971. Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. J. Agric. Food Chem. 19: 827–831.

SELOSTUS

Fosforin intensiteetti- ja kapasiteettiparametrien välisestä suhteesta suomalaisissa kivennäismaissa
I Fosforin sorptio-desorptioisotermien tulkinta ja soveltaminen

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Kahden erityyppisen fosfori-isotermin tulkintaa ja soveltamista selostettiin kahdelle pinta-maanäytteelle laadittujen desorptio-sorptiosuorien avulla.

Isotermistä, jossa P:n pidättyminen tai vapautuminen esitetään fosforilisäyksen funktiona, saadaan tietoa fosforin reaktioiden suunnasta sekä sorption tai desorption todennäköisestä suuruudesta tietyn lähtötilanteen vallitessa. Siitä voidaan arvioida myös teoreettinen desorptiomaksimi k.o. uuttosuhteessa.

Isotermi, jossa P:n pidättyminen tai vapautuminen esitetään tasapainoluoksen P-konsentraation funktiona, kuvaa maan fosforinpuskurikykyä. Sen avulla voidaan siis arvioida miten korkeaksi maanesteen P-konsentraatio voi nousta tietyn lannoituksen seurauksena tai miten maasta vapautuu P:a kasvien P:n oton seurauksena.

Kummallakin isotermillä on omat sovellutusalueensa, mutta esittämällä molemmat yhtä aikaa saadaan tarkempi käsitys fosforin reaktioista k.o. näytteessä kuin käyttämällä jompaa kumpaa isotermiä yksinään. Sorptio-desorptiokäyriä voidaan soveltaa vain kohtalaisen mataliin P-liuosten konsentraatioihin, mutta niitä voidaan käyttää yhdessä maan P:n reaktioita kuvaavana dynaamisena mallina.