

## PHOSPHATE SORPTION CAPACITY OF A CALCAREOUS SOIL INFLUENCED BY ACIDIFICATION.

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### ABSTRACT

When water soluble phosphate compounds are added to soils much of the P is rendered insoluble within a few hours. The capacity of soils to retain phosphate varies widely and is influenced by many factors. One of the many parameters that have been proposed to account for the retention of phosphate by soil is thought to be pH. The changing of pH changes both the phosphorus solubility and the surface properties of soil, which will affect the phosphate adsorption maximum and the slope of soil solution-solid phase phosphorus ratio.

The present work is concerned with a detailed study and interpretation of the adsorption isotherms and sorption capacity under different levels of acidification. The phosphate-buffering capacity also was determined.

A calcareous loamy soil of  $\text{pH}_{\text{H}_2\text{O}} = 7.9$  was used for this study. The soil was incubated with 0, 80 and 320  $\text{mgP.kg}^{-1}$  soil for one month. Four acidity levels (pH 7.9, 7.3, 6.0 and 4.5) were adjusted by adding HCl and incubating the soil samples for further one month. The adsorption isotherm curves were established after 24 hours equilibration, fitting the modified two-term Langmuir equation and the modified Freundlich equation with 1/3 exponent. The phosphate buffering capacity (PBC) was determined at 0, 0.2 and 10  $\text{mg.l}^{-1}$  equilibrium concentration.

Both functions gave a good fit. The two surface Langmuir phosphorus adsorption isotherm is better for studying the phosphorus adsorption maxima parameters, while the Freundlich equation is more suitable for describing the parameters Q and (PBC).

The studying of adsorption maxima at different pH levels (7.9-4.5), demonstrates that the big change of investigated pH approximately did not change the P-adsorption maxima in the view of un- and moderate fertilized samples (0 and 80  $\text{mgP.kg}^{-1}$ ), while a close correlation was observed with P-320, where the phosphorus adsorption maxima decreases with the decreasing of acidification. At the same time this big change in acidification practically didn't change the phosphate buffering capacity calculated from the adsorption isotherms.

### INTRODUCTION

Adsorption is the net accumulation of matter at the interface between a solid phase and an aqueous solution phase. Adsorption is the predominant phenomenon at low to medium concentration of phosphate (Muljadi et al., 1966), whereas at higher concentration (1.0 M phosphate solution), precipitation and dissolution reactions occur with the formation of a new crystalline phase.

Many factors affect the amount of phosphate adsorbed by soil colloids. One of these factors is soil reaction. In humid climates, weathering and leaching processes lead sooner or later to natural acidification. Hutchinson and Havas (1980) mentioned that the acid deposition involves  $H^+$  (with  $NO_3^-$  or  $SO_4^{2-}$ ) in the rain-water, dissolved  $NH_4^+$  which produces acidity when it is nitrified, and dry deposition of  $SO_2$  which produces acidity when it dissolves and is oxidized in the soil. Barrett (1983) reviewed that the rain-fall pH is therefore not a good indicator of total acid deposition. The latter may be small compared to total acidification.

The use of ammonium sulphate as fertilizer to supply nitrogen to crops had a strongly acidifying influence on soil. The major problem was associated with the use of ammonium salts.  $NH_4^+$  is rapidly nitrified in neutral or slightly acid soils. The fertilizers of potassium are normally chloride or sulphate salts, and assuming that potassium is either taken up by plants or enters the soil reserves, the  $Cl^-$  or  $SO_4^{2-}$  will cause somewhat raising of acidity. Phosphate fertilizer have a negligible affect on pH since the phosphate is strongly held in the soil or is taken up by the crop. If the phosphate is supplied as mono or di-ammonium phosphate, as in most compound fertilizers, the ammonium will contribute to acidity in the way discussed above with ammonium salts. Basic slag and many rock phosphates raise soil pH. Thus, acid soil infertility is a major limitation to crop production on highly weathered and leached soils in both tropical and temperate regions of the world [Bache, 1980].

Two interacting factors influence the effect of pH on the adsorption of phosphate by amphoteric surfaces. One, as the pH increases the surface charge becomes increasingly negative, thereby resulting in greater electrostatic repulsion and decrease in electrostatic potential, while with the decreasing of pH the positive charge becomes to increase and consequently the electrostatic potential increases and resulting an increase of phosphorus adsorption. Generally phosphate adsorption by soil and soil compounds is a maximum in the pH range 2-4 (Parfitt, 1978 and Bowden et al., 1980 a).

The phosphorus adsorption have been studied by many workers. Phosphate sorption by soils has been shown to be influenced by pH (Mokwunye, 1975; White and Taylor, 1977). The effect of pH on phosphate sorption is probably the least understood [Barrow, 1987]. While some reports have shown that phosphate sorption decreased with increase in pH in the acidic pH range (Parfitt, 1977; Friesen et al., 1980), others have shown that phosphate sorption increased with increase in pH (Amarasiri and Olsen, 1973; Mokwunye, 1975). There is also some evidence to show that phosphate sorption decreased with increase in pH up to 5-6, beyond which it increased [Barrow, 1987].

The buffer capacity for phosphate differs widely for different soils and, is generally high in soils with high surface areas containing iron and aluminium. In some soils from Britain, the buffer capacity increased with clay content and with the amount of extractable phosphate the soil contained, but decreased with increasing calcium carbonate content (Webber and Mattingly, 1970).

This study is to investigate the adsorption isotherms and sorption capacity, as well as the phosphate-buffering capacity under different levels of acidification.

## **MATERIAL AND METHODS**

The phosphorus experiment was carried out on a calcareous loamy soil from Keszthely, Hungary. The soil samples were incubated for one month at room temperature at field water capacity moisture level with different rates of phosphorus (0, 80 and 320 mgP).

$\text{kg}^{-1}$ ). Four acidity levels (pH 7.9, 7.3, 6.0 and 4.5) were adjusted by adding HCl. The soil samples were incubated for a further one month at room temperature. Phosphorus adsorption was determined on these samples as follows: 1 g soil was equilibrated with 10  $\text{cm}^3$  of aqueous phosphate solution (0, 5, 10, 20, 40, 80, 100, 160, 240, 320, 640  $\text{mgP} \cdot \text{kg}^{-1}$ ) for 24 hours. The phosphorus contents of the centrifuged solutions were determined spectrophotometrically.

Modified two-term Langmuir and modified Freundlich equations were fitted to the adsorption data (Tolner and Füleky 1995) as:

$$\text{Adsorbed} \cdot \text{amount} = \frac{A_1 K_1 c}{1 + K_1 c} + \frac{A_2 K_2 c}{1 + K_2 c} - Q \quad \text{two term Langmuir}$$

$$\text{Adsorbed} \cdot \text{amount} = k \cdot c^{\frac{1}{3}} - Q \quad \text{modified Freundlich}$$

where  $Q$  is the quantity of originally adsorbed ions on the soil.

The buffer capacity of the soil P system may be described by the phosphorus adsorption isotherm. As a result of the differentiating of the adsorption equation, the buffer capacity at any concentration (BC) could be calculated as:

$$BC = \frac{dP_{ads.}}{dc} = \frac{1}{3} \cdot \frac{k}{\sqrt[3]{c^2}}$$

assuming that the adsorption reduces exponentially according to the Freundlich isotherm with a 1/3 exponent.

## RESULTS AND DISCUSSION

The amount of phosphate adsorbed, expressed in  $\text{mgP} \cdot \text{kg}^{-1}$  soil is plotted against the equilibrium concentration of the bulk solution in  $\text{mgP} \cdot \text{l}^{-1}$  applying modified Langmuir two-term and modified Freundlich with 1/3 exponent equations to give the corresponding adsorption isotherms.

Both functions gave a good fit. The two surface Langmuir phosphorus adsorption isotherm is better for studying the phosphorus adsorption maxima (Fig. 1). The primary process is considered to be the adsorption which dominates at lower equilibrium concentrations and reflects the adsorption of phosphorus on the high energy site surface ( $A_1$ ), while the secondary process is the adsorption which takes place on the low energy site surface ( $A_2$ ) occurring at higher equilibrium concentration. The latter is usually quantitatively higher compared to that occurring on the high energy site surface.

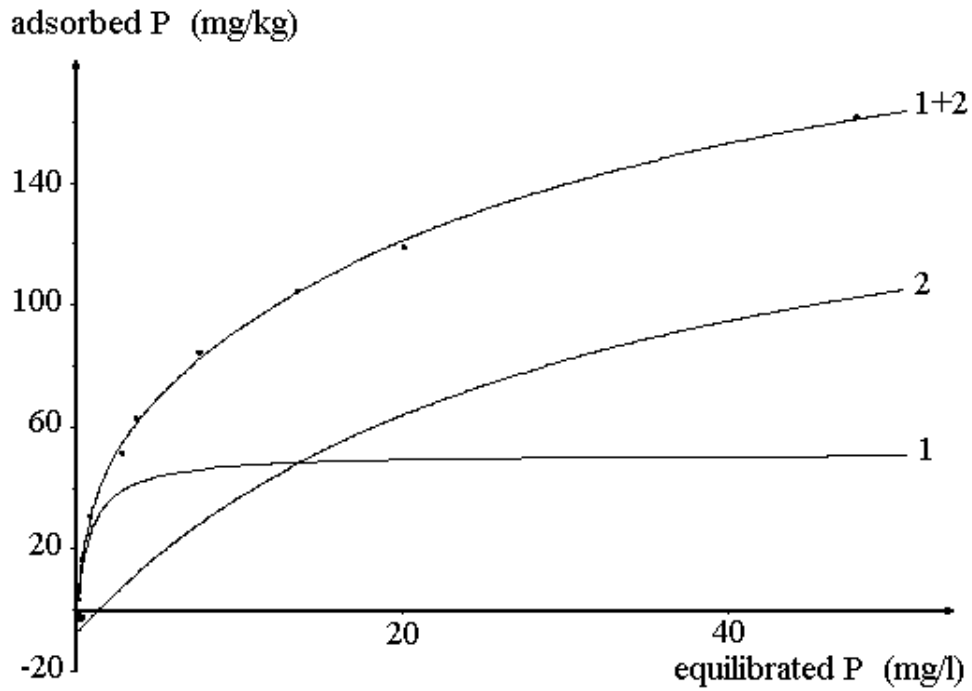


Figure 1. Modified Langmuir two-surface equation for phosphorus sorption of soil at  $P_0$  and pH 7.86.

The Freundlich equation is more suitable for describing the parameter "Q" where Q is the maximum desorbable phosphorus (Table 1).

Table 1. Maximum desorbable phosphorus "Q" applying modified Freundlich function.

pH	( Q )		
	P-zero	P-80	P-320
4.5	21.95	33.94	85.12
6.0	20.93	32.92	75.00
7.3	19.45	29.01	71.93
7.9	19.42	38.22	95.39

A general feature in Q columns is the continual increase of Q values with the increasing of P-fertilization, at the same time, the Q value has some fluctuation in its relation

with the different levels of pH and there is no clear consistent trend in this relationship. The increasing of Q related to the increasing of P-fertilization was recorded by Barrow 1984.

The studying of adsorption maxima ( $A_1 + A_2$ ) at different pH levels, (7.9-4.5), some fluctuations appeared in the case of P-zero and P-80 without any consistent trend with changing of pH, while a close correlation was observed with P-320, where the phosphorus adsorption maxima decreases with the increasing of pH. The statistical values of phosphorus adsorption maxima calculated from modified Langmuir 2-term isotherm were plotted against pH in Figure 2. This Figure demonstrates that the big change of investigated pH approximately did not change the P-adsorption maxima in the view of un- and moderate fertilized samples (0 and 80 mgP.kg<sup>-1</sup>), only some random changes were observed. These findings are in accordance with those of Eze and Loganathan (1990), who claimed that the effect of pH on phosphate sorption at low P-concentration (10 ppm initial P concentration), did not have any striking influence on phosphate sorption within the pH range 3.5-6.5 and the

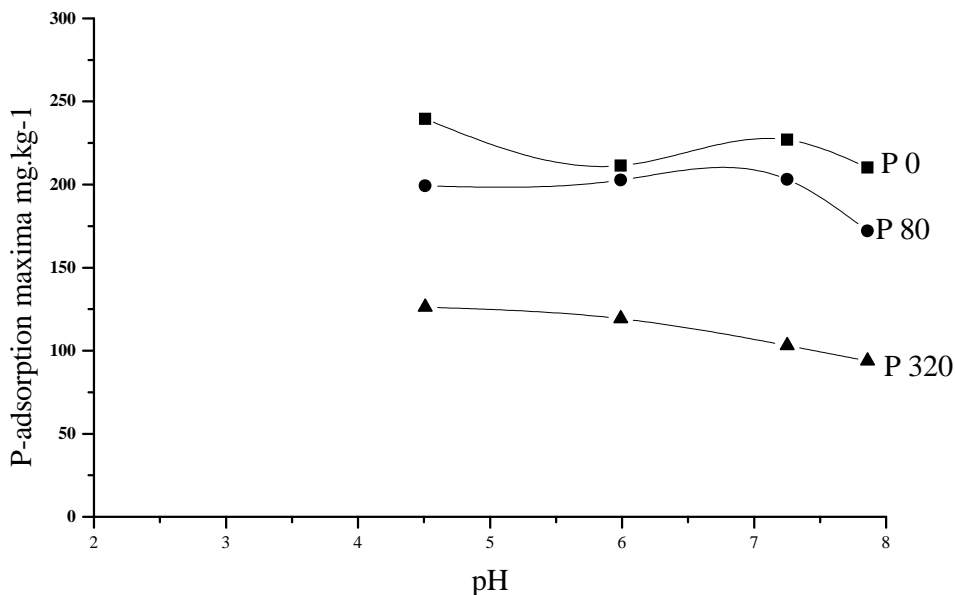


Figure 2. Phosphorus adsorption maxima of soils as a function of previously added-P and acidification.

data appear to follow the trend observed for the high P-concentration. At low P-concentration, the number of phosphate ions sorbed is low, and these ions are sorbed mainly at high affinity sites possibility by the "two points attachment" mechanism of (Taylor and Ellis 1978). Therefore these sorbed phosphate ions cannot be easily replaced by the increasing concentration of hydroxyl ions under conditions of increasing pH.

The results obtained at high phosphorus fertilization doses, where the P-adsorption maxima decrease with the increasing of pH, are in agreement with Parafitt (1977) and Frissen et al. (1980) who said that phosphate sorption decreased with increasing in pH in the acidic region. Shang et al. (1992) stated that the rate of adsorption of both organic and inorganic phosphate by Al and Fe precipitates generally decreased as pH increased.

Phosphate may, in fact, be preferentially adsorbed by surfaces as  $\text{HPO}_4^{2-}$  rather than as  $\text{H}_2\text{PO}_4^-$  (Taylor and Ellis, 1978; Bowden et al., 1980 a). As the pH increases from 2 to 7, the concentration of the divalent ion ( $\text{HPO}_4^{2-}$ ) increases 10-fold for each unit in pH, a change that partially offsets the decrease in electrostatic potential. Thus, phosphate adsorption by amorphous hydroxy-Al surfaces (Kwong et al., 1979) decreases relatively slowly until pH 7 is reached. Above pH 7, the concentration of  $\text{HPO}_4^{2-}$  increases at a progressively slower rate whereas the decrease in surface potential continues; hence, adsorption decreases more quickly.

In this course it could be summarized that, the effect of pH on phosphate sorption process appears through out its effects on the responsible adsorbent materials, by increasing or decreasing the net positive or negative charges, electrostatic potential and aqua-site numbers, and also by dissolving calcium carbonate as a result of HCl treatments. Considering the main materials responsible for phosphate retention in the soils, (they are iron and aluminium oxides), and their positively charged sites increase if the pH is made low enough, so, the P-adsorption increases if the pH is low. Stumm and Morgan (1981) found that the development of surface charges of oxides are controlled by the suspension pH. Shang et al., (1992) said that the effect of pH on adsorption can be firstly attributed to the change of interfacial characteristics of the Al precipitates. The surface excess positive charge of Al-precipitate decreased with the increasing of pH from 4.5 to 6.5, at the same time the adsorption of phosphate ions increased the surface negative charge, consequently the average negative charge increased with increasing solution pH, hence, the electrostatic repulsion increased and subsequently a decrease in P-adsorption appeared. Additively, in water system studies, the change of pH influenced somewhat the changing of the numbers of aqua-sites (Shang et al., 1992) where, the aqua-sites on the surface react with phosphates, the increasing of pH decreased the number of aqua-sites and subsequently decreased the positive charge and increased the hydroxo-sites and negative charges on the surfaces. So, the decrease in aqua-sites with increasing pH would decrease the phosphate sorption during later stages as shown in Figure 2, when the surface becomes increasingly negatively charged, the reaction would be less sensitive to increasing pH, this result was confirmed by Shang et al., 1992, i. e., the hydroxo-sites react more slowly than the aqua-sites. So, where the hydroxo-sites expected to provide the main reaction sites, the reaction would not be decreased substantially by raising pH compared to the adsorption at the beginning which was due to the aqua-sites.

The decreasing of P-adsorption maxima associated with the increasing of pH could be explained by one of the soil properties at which the electrostatic potential of adsorption is decreased as pH increased, resulting decreasing of the adsorption (Barrow 1984). Finally, with the increasing of pH, the charge on the clay due to dissociation of edge hydroxyls, might lead to an increase in the negative charge on the adsorbent, and lessened the tendency for adsorption.

Buffering capacity was calculated with the aid of the Freundlich isotherm, first at the  $0.2 \text{ mg.l}^{-1}$  equilibrium concentration (which is very close to a 0 equilibrium concentration), since this characterises the maximum buffering capacity of the system. In addition, the buffering capacity was determined at an equilibrium concentration of  $10 \text{ mg.l}^{-1}$ .

The buffering capacity values for phosphorus at an equilibrium concentration of  $0.2 \text{ mg.l}^{-1}$  are presented in Fig. 3. The phosphorus buffering capacity depends to a great extent on the degree of previous phosphorus stress (Fig. 3), in the case of higher P input the PBC values are lower.

The smallest two values of (BC) occurred at the highest P-fertilization and higher pH levels, at the same time the big changes of pH did not change the phosphate buffering capacity, except the values associated at high phosphorus additions (320 mgP/kg soil) and high pH 7.3 and 7.9. Their values are lower than those obtained at low P-additions and low pH levels. So, in acidic soils and at low phosphorus fertilizations, the phosphorus buffering capacity values (BC) seem to be higher than the others. The PBC values

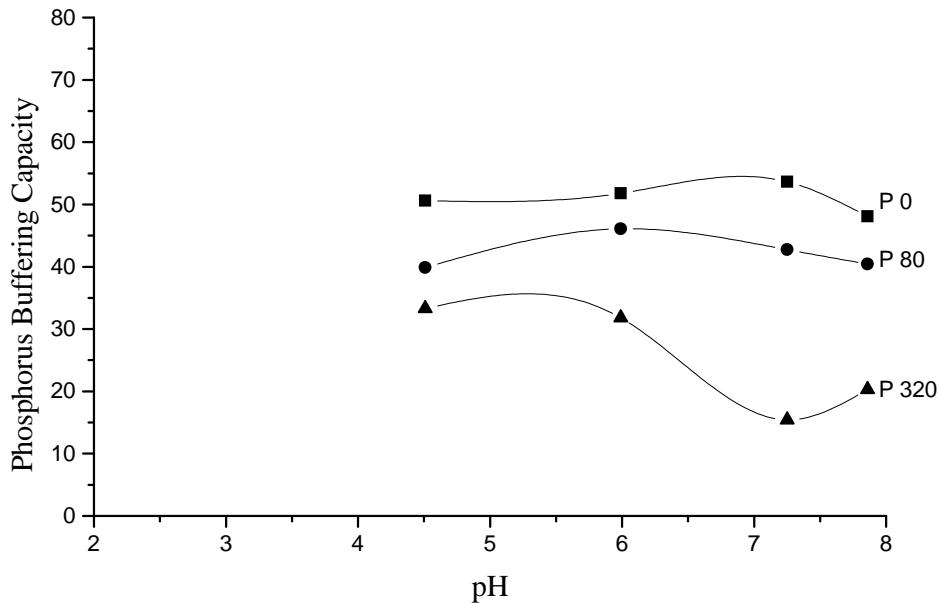


Fig. 3. Effects of P impact and soil acidity on P Buffering Capacity at  $0.2 \text{ mg.l}^{-1}$  equilibrium P concentration.

calculated at an equilibrium concentration of  $10 \text{ mg.l}^{-1}$  showed a pattern identical to that found at low concentration, except that they were approximately ten times smaller.

At the higher P-fertilization, the more adsorbed P is converted into non-exchangeable P either by the formation of stable crystalline phosphates or by penetration of the P ions into the surface, and the low capacity factor refers to the lower (desorption) section.

## CONCLUSION

Both functions, the modified two-surfaces Langmuir and the Freundlich models, are good for fitting the data of sorption. The two surface Langmuir phosphorus adsorption isotherm is better for studying the phosphorus adsorption maxima parameters while the Freundlich equation with  $1/3$  exponent is more suitable for describing the parameters "Q" and "PBC".

When studying of adsorption maxima ( $A_1 + A_2$ ) tendencies amongst different pH levels (7.9-4.5), some fluctuations appeared in the case of P-zero and P-80 soil phosphorus

levels without any consistent trend with changing of pH, while a correlation was observed at P-320, where the phosphorus adsorption maxima decreased with the increasing of pH.

The big changes of pH did not change the phosphate buffering capacity, except the values associated at high phosphorus additions (320 mgP/kg soil) and high pH 7.3 and 7.9. Their values are lower than those obtained at low P-additions and low pH levels. The PBC values calculated at an equilibrium concentration of  $10 \text{ mg.l}^{-1}$  showed a pattern identical to that found at low concentration, except that they were approximately ten times smaller.



## REFERENCES

- AMARASIRI, S. L. and OLSEN, S. R., 1973: Liming as related to solubility of P and plant growth in an acid tropical soil. *Soil Sci. Soc. Am. Proc.*, 37: 716-721
- BACHE, B. W., 1980: In "Effects of Acid Precipitation on Terrestrial Ecosystems" (T. C. Hutchinson and M. Havas, ed.), pp. 173-182. Plenum, New York.
- BARRETT, C. F. ET AL., 1983: Acid Desorption in the United Kingdom, Warren Spring Laboratory, Stevenage.
- BARROW, N. J., 1984: Modelling the effects of pH on phosphate sorption by soils: *J. Soil Sci.*, 35: 283-297
- BARROW, N. J., 1987: Reactions with variable-charged soils. *Fert. Res.*, 14: 1-100
- BOWDEN, J. W., NAGARAJAH, S., BARROW, N. J., POSNER, A. M., and QUIRK, J. P., 1980 a: Describing the adsorption of phosphate, citrate and selenite on a variable-charge mineral surface. *Australian Journal of Soil Research*, 18: 49-60
- EZE, O. C. and LOGANATHAN, P., 1990: Effects of pH on phosphate sorption of some Paleudults of southern Nigeria. *Soil Sci.*, 150: 613-621
- FRIESEN, D. K. & JUO, A. S. R. and MILLER, M. H., 1980: Liming and lime-phosphorus zinc interactions in two Nigerian Ultisols: I. Interactions in the soils. *Soil Sci. Soc. Am. J.*, 44: 1221-1226
- HUTCHINSON, T. C. and HAVAS, M., 1980: Effects of Acid Precipitation on Terrestrial Ecosystems, Plenum.
- KWONG, K. F. & NG KEE and HUANG, P. M., 1979: Surface Reactivity of Aluminium Hydroxides Precipitated in the Presence of Low Molecular Weight Organic Acids. *Soil Sci. Soc. Am. J.* 43: 1107-1113
- MOKWUNYE, U., 1975: The influence of pH on the adsorption of phosphate by soils from Guinea and Sudan Savannah Zones of Nigeria. *Soil Sci. Soc. Am. Proc.*, 39: 1100-1102
- MULJADI, D. & POSNER, A. M., and QUIRK, J. P., 1966: The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. I. The isotherms and the effect of pH on adsorption. *J. Soil Sci.*, 17: 212-229
- PARFITT, R. L., 1977: Phosphate adsorption on an oxisol. *Soil Sci. Soc. Am. J.*, 41: 1064-1067
- PARFITT, R. L., 1978: Anion adsorption by soils and soil materials. *Adv. Agron.*, 30: 1-50
- SHANG, C. & STEWART, J. W. B. and HUANG, P. M., 1992: pH effect on kinetics of adsorption of organic and inorganic phosphates by sort-range ordered aluminium and iron precipitates, *Geoderma*, 53: 1- 14
- STUMM, W. and MORGAN, J. J., 1981: Aquatic chemistry. 2<sup>nd</sup> ed. Wiley, New York, 780 pp. U. S. Environmental Protection Agency, 1971. Methods of Chemical Analysis of Water and Wastes. Environmental Protection Agency, Cincinnati, Ohio.
- TAYLOR, R. W. and ELLIS, B. G., 1978: A mechanism of phosphate adsorption on soil and anion exchange resin surfaces. *Soil Sci. Soc. Am. J.*, 42: 432-436.
- TOLNER, L. and FÜLEKY, GY., 1995: Determination of the originally adsorbed soil phosphorus by modified Freundlich isotherm. *Commun. Soil Sci. Plant Anal.* 26: 1213-1231.
- WEBBER, M. D. and MATTINGLY, G. E. G., 1970: Inorganic Soil Phosphorus. I. Changes in monocalcium phosphate potentials on cropping. *J. Soil Sci.*, 21: 111-120
- WHITE, R. E. and TAYLOR, A. W., 1977: Effect of pH on phosphate adsorption and isotopic exchange in acid soils at low and high additions of soluble phosphate. *J. Soil Sci.*, 28: 48-61.

