

# **PHOSPHATE ADSORPTION-DESORPTION IN SELECTED VERTISOLS**

**A thesis submitted to the  
Andhra Pradesh Agricultural University  
in part fulfilment of the requirements  
for the award of the degree of  
MASTER OF SCIENCE IN AGRICULTURE**

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## CERTIFICATE

Ms. S. SHAILAJA has satisfactorily prosecuted the course of research, and the thesis entitled "PHOSPHATE ADSORPTION-DESORPTION IN SELECTED VERTISOLS" submitted is the result of original research work and is of sufficiently high standard to warrant its presentation to the examination. We also certify that the thesis or part thereof has not been previously submitted by her for a degree of any university.

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## CERTIFICATE

This is to certify that the thesis entitled "Phosphate adsorption-desorption in selected Vertisols" submitted in partial fulfilment of the requirements for the degree of Master of Science in Agriculture in the major subject of Soil Science and Agricultural Chemistry of the Andhra Pradesh Agricultural University, Hyderabad, is a record of the bonafide research work carried out by Ms. S. Shailaja under our guidance and supervision. The subject of the thesis has been approved by the Student's Advisory Committee.


No part of the thesis has been submitted for any other degree or diploma. All assistance and help received during the course of the research work have been duly acknowledged by her.


  
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## ABSTRACT

Title : Phosphate adsorption-desorption in selected Vertisols

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Phosphate (P) adsorption-desorption characteristics of surface samples of 4 Vertisols were studied. The phosphate adsorption capacity of these soils was low, and ranged from 35 to 80  $\mu\text{g g}^{-1}$  of soil at 0.2  $\mu\text{g ml}^{-1}$  equilibrium solution P concentration. The Langmuir equation described the adsorption reasonably accurately at all solution P concentrations, and was much more accurate than the Freundlich, Gunnary, Tempkin and Dubinin-Radushkevich equations. P adsorption at 0.2  $\mu\text{g P ml}^{-1}$  equilibrium solution P concentration calculated from Langmuir isotherm was positively correlated with DTPA extractable Fe, but was not correlated with clay content. Neither P fertilization

history nor the P source used (Potassium-dihydrogen phosphate vs. ammonium polyphosphate) affected P adsorption in BR-1 soil (soil Nos.1a-1d). Relative efficiency of different extraction techniques for desorption of adsorbed P decreased in the following order: electro-ultrafiltration (EUF) (400 V, 80°C) > sodium bicarbonate > EUF (200 V, 20°C) > calcium chloride. Phosphorus desorption was equivalent to, respectively, 74%, 63%, 50% and 3% of the P adsorbed.

## I. INTRODUCTION

The low phosphorus (P) status of most Indian soils has been fully demonstrated by numerous agronomic experiments (Tandon, 1987), and a recent analysis has shown that the response of dryland crops such as sorghum differ among soil orders, with the magnitude of the responses being ranked: Alfisol > Entisol > Vertisol (Kanwar, 1986). The causes of these differences among soils in crop response are not understood. An improved understanding to predict P responses of crops under rainfed agriculture is necessary because of the high potential productivity of these soils and the likelihood that cropping intensity will increase markedly on them in the future. Increasing cropping intensity will cause depletion of available P in the soil, and with improved cropping systems, crop demands for nutrients will increase. Accurate prediction of nutrient requirements is highly desirable, because the cost of fertilizer is a constraint limiting fertilizer use by small farmers.

Olsen's soil test (extraction with 0.5 M  $\text{NaHCO}_3$ ) is used throughout India for the prediction of soil P status. A single critical limit is used throughout India, on all soils except <sup>acid</sup> and soils for all crops (Indian Society of Soil Science, 1979). No serious criticism of this test had been made until recently, when both AICRPDA and ICRISAT indicated that crops on Vertisols did not respond to fertilizer P even when low Olsen-P values were obtained (ICRISAT, 1985). Mechanisms suggested were higher P fixation (Venkateswarlu, 1987) or a much lower critical limit for

Vertisols when compared to other soils (Sahrawat, 1988). At present the uncertainties over the P status of Vertisols are unresolved; the reason for this lies in the emphasis given in past research.

In India, research on P has given great emphasis to agronomic experiments measuring the response of crops to P, especially in irrigated agriculture, relatively little emphasis has been given to dryland agriculture. Basic studies on the chemistry of soil P have received little attention. The past research has been directed mainly towards evaluating soil test methods adopted from temperate climate agriculture, using empirical characterisation methods such as simple P fixation procedures and the soil P fractionation technique of Chang and Jackson (1957). However, there is now an urgent need to use methodological approaches for assessing soil P status that are more relevant to soil-plant studies. Two approaches have so far not been adequately evaluated for assessing P availability in Indian soils. First, phosphorus adsorption and desorption isotherms which consider P adsorption and release for assessing the relationship between P in solution and that adsorbed on soil surfaces. Second, electro-ultrafiltration (EUF) was strongly advocated by a group of German Scientists (Nemeth, 1979).

The aim of the present study was to understand the behaviour of phosphorus in Vertisols with the following objectives:

1. To investigate the phosphate adsorption characteristics of selected Vertisols and to assess the equations that best describe the relationships between solution P and adsorbed P.
2. To study the desorption of adsorbed P, using different extractants, to attempt to select the best technique for soil testing.

## II. REVIEW OF LITERATURE

### II.1. BEHAVIOUR OF P IN INDIAN VERTISOLS

The recent workshop on "P in Indian Vertisols" (ICRISAT, 1988) showed that there have been few studies on the behaviour of P in Vertisols and that responses to P cannot be predicted reliably. Additionally, the causes of the poor predictability were not clearly understood. The salient details and the need for evaluating e.g. adsorption isotherm are given below:

#### II.1.1 Soil-test/crop response relationships

The recognition that responses to added P are uncertain and unpredictable, is only recent. Earlier, the general recommendations for critical limits for the Olsen's soil test ( $0.5M NaHCO_3$ ) were assumed to apply throughout India on all calcareous soils and for all crops. The limits used are 5 and 10  $\mu g P g^{-1}$  soil to separate deficient, possibly deficient and more deficient soils were based on many experiments under ICAR coordinated experiments (Indian Society of Soil Science, 1979). It is presumed that these experiments were conducted mainly on the light textured soils of the Indo-Gangetic Plains, Northern India, and under irrigation. However, recent research at ICRISAT Center has shown that these critical limits appeared to be satisfactory for grain sorghum grown on Alfisols, but not on Vertisols, for e.g. a large response to added P was obtained on the benchmark Alfisol (Patancheru Series) when the Olsen's-P was less than 5  $\mu g g^{-1}$  soil. But on the other hand sorghum on

Vertisol responded little to applied P unless the 0.5 M NaHCO<sub>3</sub> extractable P level was less than 2.5 ug g<sup>-1</sup> soil. Although this research indicated that the critical limit for Olsen's-P may be lower on Vertisols than on other soils, it did not investigate the causes of this phenomenon. Nevertheless, this apparently lower limit for Vertisols was consistent with other findings in India for which fixation was implicated.

### II.1.2 Phosphorus fixation

Earlier, a common lack of responses was observed by AICRPDA Scientists, and had been attributed to high fixation of added P by Vertisols. It was implied that lack of response may reflect an inadequate rate of fertilizer P than other soils. This high fixation hypothesis (Venkateswarlu, 1987) was based on the fact that Vertisols do adsorb appreciable proportion of P; measurements were made with rates of added P similar to the amounts of fertilizer P that would be added by farmers. Additionally, claims of high P fixation were also based on the fact that most Vertisols have a high clay content, and the assumption that all clays have a high P adsorption capacity.

The difficulty in assessing the relevance of past P fixation measurements is due to the fact that high concentrations of P were added to soils. The relative adsorption capacity of different pure clay minerals kaolinite, illite, montmorillonite have been characterized (Indian Society of Soil Science, 1979). More recently, studies on the two ICRISAT benchmark soils, a Vertisol and an Alfisol, have indicated that P fixation by the

Vertisols should not be high. Past studies show that most of the clay in the Indian Vertisols was Smectitic i.e. of the swelling 2:1 lattice type, the dominant clay mineral was usually montmorillonite which usually does not have capacity to adsorb appreciable amounts of phosphate (El-Swaify *et al.*, 1985). However, Vertisols contain appreciable amounts of calcium carbonate, commonly 2-10% (Benchmark soils of India, 1982). It has been generally found that P adsorption is not always closely related to  $\text{CaCO}_3$  content (Goswami and Sahrawat, 1982) perhaps the critical factor was the quality of  $\text{CaCO}_3$  which would affect P availability by its effects on precipitation and as an adsorber.

### II.1.3 Phosphorus fractionation

Chemical characterization of different forms of inorganic phosphorus on four benchmark Vertisols with a range in extractable ( $0.5\text{M NaHCO}_3$ ) P showed that these soils have similar amounts of the different forms of P to other Vertisols in India. These results indicated that Ca-P was the dominant form followed by Fe-P with very low amount of Al-P. Interestingly, the levels of Fe-P in the Vertisols were similar to those found in the Alfisols (ICRISAT, 1985).

### II.1.4 Equilibrium P concentration

The research mentioned previously was primarily empirical in nature, in which various assessments of soil P status of soils were correlated with responses of soils to added P. A better



approach would be to use the "Equilibrium P concentration" method for studying adsorption to assess the amount of P to be added to result in a P concentration in solution of  $0.2 \text{ ug ml}^{-1}$ . This value, if continuously maintained in solution cultures, is adequate for good growth by many crop species. It was suggested that phosphate adsorption at this standard equilibrium P concentration in solution would provide information about phosphate fertilizer requirements (Beckwith, 1965). Fox *et al.* (1974) and Jones and Benson (1975) demonstrated the utility of phosphate adsorption curves for assessing the residual effects of phosphate fertilizer and their usefulness in transferring soil management information among soils with different mineralogy and also confirmed that a concentration of  $0.2 \text{ ug P ml}^{-1}$  in solution was adequate for many crops. The advantages of equilibrium concentration were shown by recent studies on the benchmark Vertisols and Alfisols at the ICRISAT Center. These soils differed only a little in their phosphate adsorption behaviour in that adsorption in the Vertisol changed little with depth, and a similar pattern was obtained with Alfisols with the exception of high adsorption occurred in the B horizon. The amount of fertilizer P to be added to obtain  $0.2 \text{ ug ml}^{-1}$  equilibrium P concentration after incubation for 6 days at  $25^{\circ}\text{C}$  varied between 28 to  $38 \text{ ug P g}^{-1}$  soil up to a soil depth of 160 cm. These results clearly indicated that phosphate adsorption is not high in the selected Vertisols studied (Sahrawat, 1988).

### II.1.5 ~~Isotopically exchangeable P~~

Recent studies have also shown that Vertisols have the capacity to adsorb phosphate a little more strongly than Alfisols, all the adsorbed phosphate is easily exchangeable by  $^{32}\text{P}$  and little phosphate is adsorbed in a non-exchangeable form (Warren and Sahrawat, 1988). This partly explains why crops do not respond to P fertilizer when their soil test value is low. Although solution concentration is low, it is clear that adsorbed P is readily released to the solution phase.

This major new advance will be the further consideration of equilibrium P concentration in the solution phase of soils, in relation to adsorption and desorption of P from the solid phase. Relatively, little research has been done on either in India. Elsewhere in the world much more effort has been given to adsorption than to desorption, partly because of the much greater ease of making such measurements. However, desorption studies are much more relevant to the field situation where a soil is supplying phosphorus to crop roots.

One specialized method for studying P desorption has been recently developed is electro-ultrafiltration (EUF) which can be used for desorption of P.

## II.2. USE OF ADSORPTION ISOTHERMS FOR DESCRIBING ADSORPTION

An adsorption isotherm describes the relationship between concentration of adsorbed and dissolved species under specified conditions i.e. temperature, time, and shaking period etc. A

number of adsorption isotherms have been used to describe the phosphate adsorption in different soils but there have been few studies on the Vertisols (Sahrawat, 1988).

On forty soils ( $\text{pH} > 5.0$ ) from southern England and eastern Australia, the Langmuir isotherm accurately described P adsorption, provided it was assumed that adsorption occurred on two types of surfaces with contrasting bonding energies (Holford *et al.*, 1974). Phosphate adsorption data for twenty-nine soils were found to fit the Freundlich adsorption isotherm better if an estimate of native labile P was first added to the adsorption data and the sum plotted against intensity (Fitter and Sutton, 1975). The exponent from the isotherm thus obtained was closely related to exchangeable Al (in acid soils) and exchangeable Ca (in neutral and calcareous soils).

Studies with fourteen rice soils belonging to red loam, lateritic, shallow black, alluvial and coastal saline soils showed that phosphate adsorption obeyed the Freundlich isotherm (Gaikwad and Patnaik, 1969).

Warren and Sahrawat (1988) fitted P adsorption measurements on a range of tropical soils to the Freundlich equation. The adsorption capacity of a Vertisol (from ICRISAT Center) was found to be modest in comparison to the Oxisols and Inceptisols. The results indicated that fertilizer P is not permanently fixed by the Vertisols, and is easily exchangeable with <sup>32</sup>P. Sekhon and

Bansal (1988) also showed that phosphate adsorption from six Indian Vertisols fitted the Langmuir adsorption isotherm well.

A major advantage of the Langmuir isotherm was that it was possible to calculate the adsorption maximum and relative bonding energy for P adsorption (Olsen and Watanabe, 1957). Phosphate adsorption data for clay, sandy clay, loam and sandy clay loam soils showed that although Langmuir equation gave a good fit, there was a significant curvature, but the best fit was obtained by introducing a square root term in the Langmuir equation accounting for more than 99.8% of the variation in phosphate adsorption (Gunary, 1970).

The adsorption of phosphorus by four Saskatchewan soils of different colloid content was described well by the Langmuir isotherm when the final phosphorus concentrations were less than 20 ug P ml<sup>-1</sup>. The percentage phosphorus saturation of the adsorption maximum was closely correlated with the phosphorus concentration in the soil suspension. The total adsorbed phosphorus of four soils was not correlated with the phosphorus concentration of the soil solution, but varied considerably depending on the colloid content of the respective soils (Rennie and McKercher, 1959).

The adsorption of phosphate by calcium carbonate and Ca-kaolinite at low phosphate concentration in solution was described by Langmuir adsorption isotherm, indicating that a monolayer of phosphate was formed on the surface. The calculated

surface saturation was  $25 \text{ ug P g}^{-1}$  for calcium carbonate and  $187 \text{ ug P g}^{-1}$  for Ca-kaolinite (Kuo and Lotse, 1972).

The adsorption of added inorganic phosphate by  $A_1$  horizons of three contrasting soils from Rio Grande do Sul, Brazil, which varied appreciably in their ability to adsorb P, was examined using the Langmuir adsorption isotherm (Syers *et al.*, 1973). Two linear relationships were obtained indicating the presence of two populations of sites for phosphate adsorption.

Bache and Peaslee (1975) investigated the phosphate adsorption and desorption in five soils collected in Kentucky from the Alligator, Crider, Pembroke and Zanesville soil types, covering a wide range in clay content (16 to 51%). For some soils, the Langmuir adsorption isotherm was curvilinear when the P concentration in the equilibrium solution was greater than  $10 \text{ ug P ml}^{-1}$ .

In four important soil series of the Punjab, P <sup>ad</sup>desorption conformed to the Langmuir isotherm in three soils, but not in the fourth soil (Bahl *et al.*, 1986). The Freundlich adsorption isotherm, however, described well the phosphate adsorption in all soils. Phosphorus was most strongly adsorbed in fine textured soil. Soils having high adsorption capacity also had higher soil P buffering capacity, but this decreased with increase in applied P.

These results showed that, in general, phosphate adsorption in many soils can be described well by the Langmuir or Freundlich

adsorption isotherms but such studies on the Vertisols are lacking on a world scale.

### II.3. FACTORS AFFECTING PHOSPHORUS ADSORPTION IN SOILS

Several soil components such as clay, calcium carbonate and amorphous materials affect phosphate adsorption (Indian Society of Soil Science, 1979; Goswami and Sahrawat, 1982; Syers *et al.*, 1971). Phosphate adsorption in Vertisols and the factors affecting this, were poorly characterised.

Syers *et al.* (1971) studied P adsorption in surface samples of fifteen soils developed on a range of parent materials and varying widely in crystalline iron oxide content. They found that the soils adsorbed between 60 and 490  $\mu\text{g P g}^{-1}$  of the P added (500  $\mu\text{g P g}^{-1}$  added as  $\text{KH}_2\text{PO}_4$ ). Although P adsorption was well correlated with exchangeable Al ( $r=0.84$ ), removal of exchangeable Al caused only a relatively small decrease in the amount of P adsorbed. Removal of amorphous Fe and Al components by oxalate treatment reduced P adsorption by 19 to 100 percent compared to that of the untreated sample. The amount of P adsorbed by untreated samples was less well correlated with oxalate extractable Fe ( $r=0.47$ ) than extractable Al ( $r=0.78$ ), suggesting that amorphous Fe components are less active per unit weight than amorphous Al in the adsorption of added P, adsorption of added P following citrate-bicarbonate-dithionite (CBD) extraction was well correlated with the amounts of amorphous aluminosilicates in the soils ( $r=0.99$ ).

Phosphorus adsorption by aluminium complexed with organic matter in acid soils was studied by using Al-peat. Phosphate was strongly adsorbed by Al-peat. The data suggested that phosphate removal from solution was due to both the adsorption of complex Al-phosphate cations by the peat and the precipitation of amorphous Al-hydroxy phosphate (Bloom, 1981).

The capacity of tropical acid soils in Nigeria to adsorb phosphorus varied among the soils, but in general the more strongly weathered soils from eastern Nigeria adsorbed more phosphorus than those from western Nigeria. At low concentrations of phosphorus in the equilibrium solution, adsorption was satisfactorily described by the Langmuir isotherm. Adsorption was significantly correlated with sesquioxides and exchangeable Fe and Al contents (Udo and Uzu, 1972).

The phosphate adsorption by 290 samples (top soil and sub soil) of nine soil orders from humid tropics and the seasonally dry tropics carried out in the United Kingdom indicated that the samples from Entisols, Alfisols, Mollisols and Ultisols generally had lower than average adsorption indices. Vertisols had higher than average and Histisols, Inceptisols, Oxisols and Spodosols varied greatly in their adsorption index (Burnham, 1982).

Willet and Higgins (1978) reported that clay formed a part of a complex gel consisting of hydrated  $\text{Fe}_2\text{O}_3$  and associated  $\text{Si}(\text{OH})_4$  in the soil and thus provided sites for P adsorption. Organic matter, on the other hand, served as a source of

reduction processes, resulting in the reduction of ferric-iron to ferrous-iron which increases phosphorus desorption.

The influence of three anions (sulphate, silicate, and fluoride) on phosphate adsorption parameters was studied using the Langmuir equation in three markedly different soils. A black soil (Vertisol) had the highest P adsorption maximum followed by the lateritic and the alluvial soil. Sulphate did not cause any significant reduction in the P adsorption maximum, but its presence caused a significant decrease in phosphate bonding energy in all soils. The presence of fluoride resulted in a significant reduction in the adsorption maximum of the alluvial soil with lower reduction in the black and lateritic soils, while the reduction in bonding energy was highest in the lateritic soil with less reduction in the alluvial soil and least in the black soil (Kundu *et al.*, 1988).

The effect of soil components on phosphate adsorption was studied in profiles of the soils belonging to the Alfisol, Inceptisol and Entisol orders from the Mysore Plateau (Manikandan and Sastry, 1988). Removal of iron oxides by citrate-bicarbonate-dithionite (CBD) and clay-sized amorphous material, extracted by 0.5 N NaOH showed that nearly 93% of the variation in phosphate adsorption was caused by these two components. The clay fraction contributed least to the phosphate adsorption. The amount of phosphate adsorbed by the clay-sized fraction was significantly related to the amorphous material contained in the clay and the octahedral polyhydroxy aluminium component of the



amorphous materials.

The "two-surfaces" Langmuir equation was used to study high-energy and low-energy phosphate-adsorbing surfaces in 24 calcareous soils derived from Jurassic limestone in south western England (Holford and Mattingly, 1974). Adsorption by the high-energy P-adsorbing surfaces was closely correlated with dithionite-soluble iron hydrous oxides, while adsorption by the low-energy P adsorbing surfaces was closely correlated with organic matter content and the total surface area of  $\text{CaCO}_3$  but not the  $\text{CaCO}_3$  content of the soil. These results explain why the relationship between phosphate adsorption and  $\text{CaCO}_3$  is not always close. The specific surface area of the calcium carbonate component in 24 calcareous soils, derived from Jurassic limestone in Sherborne series, was an inverse hyperbolic function of the percentage of  $\text{CaCO}_3$  (ranging from 16 to about  $500 \text{ m}^2 \text{ g}^{-1}$ ). The total surface area of calcium carbonate was a linear function of the percentage of  $\text{CaCO}_3$  and ranged from 4.0 to  $8.5 \text{ m}^2 \text{ g}^{-1}$  soil (Holford and Mattingly, 1975a). The adsorption of phosphate in 24 calcareous soils derived from Jurassic limestones was not attributed solely to adsorption, but appeared to result from precipitation (Holford and Mattingly, 1975b); the dithionite soluble iron present in these soils adsorbed about  $3400 \text{ ug p g}^{-1}$  of iron. The amount of P adsorbed by iron in the limestone (if present as goethite) ranged from 5 to  $18 \text{ ug g}^{-1} \text{ CaCO}_3$  more than for pure calcite of similar surface area. The localised adsorption of P on iron oxide surfaces in the limestones could moreover provide P rich nuclei for the precipitation of basic

calcium phosphate.

Tropical soils did not show a higher P-adsorption capacity than the British soils (Lopez-Hernandez and Burnham, 1974b). This result was ascribed to the fact that free iron oxides in British soils were more reactive to phosphate than those of the tropical soils, which was due to the greater crystallization of these materials in tropical soils. Phosphorus adsorption capacity was determined by the amount of active forms of iron and aluminium. When adsorption was compared in different soil orders in tropical soils, there was a great variability in Oxisols; within the Oxisols, hardened laterite adsorbed least phosphorus. All the Ultisols studied had low P adsorption capacities. The Vertisols adsorbed moderate to high amounts of P. In general, Entisols had the lowest P adsorption capacity whereas the Inceptisols examined had high P adsorption capacities. Extractable Al was well correlated with phosphate adsorption in tropical and British soil groups (Lopez-Hernandez and Burnham, 1973).

Juo and Fox (1977) studied the phosphorus adsorption characteristics of soil materials from selected soil profiles belonging to Alfisol and Ultisol orders of West Africa which was mainly related to soil mineralogy, which in turn was related to the parent material, surface area, and free Fe oxide content of the soils. Alfisols and Ultisols derived from basalts had the highest P adsorption capacity. The Fe oxides in the soils derived from basaltic materials existed as very fine discrete

particles in the clay fraction; specific surface area of the Fe oxides was about  $300 \text{ m}^2 \text{ g}^{-1}$  which was much higher than the area of the Fe oxides derived from the acidic parent rock ( $50 \text{ m}^2 \text{ g}^{-1}$ ). These results showed that the specific surface area characteristics of the oxide minerals present in the soil was a key factor affecting the P adsorption characteristics of the soils.

The phosphate adsorption and buffering capacities of Alfisols and adjoining Entisols collected from different altitudes of Eastern Hills of Meghalaya indicated that Entisols and the soils of higher altitudes possessed a larger P adsorption capacity and buffering capacity than the Alfisols and the soils of medium and lower altitudes. The higher P adsorption capacity of Entisols could be attributed to the presence of amorphous Al (Munna Ram *et al.*, 1987).

The Langmuir adsorption isotherm accurately described the adsorption of P by 32 surface soil samples collected from Chotanagpur region of Bihar in India (Singh and Singpuri, 1986). Soil pH was linearly related to the P adsorption maximum and the bonding energy constant. Oxides of Fe and Al were also significantly correlated with P adsorption maximum.

Soils with a high content of organic matter (colloidal) had very low capacities to adsorb P (Fox and Kamprath, 1971). Soluble P fertilizer was readily leached from such soils; the addition of large amounts of exchangeable Al almost completely

prevented leaching of P.

The P adsorption characteristics of calcareous soils (pH 8.6 to 8.7) from Haryana showed that the adsorption capacity of the soils was positively correlated with surface area, clay, and  $\text{Fe}_2\text{O}_3$  (Gupta *et al.*, 1977).

The correlation between pH and phosphate retention for a group of pedologically similar soils differing mainly in pH was significant. Phosphate retention decreased with increasing pH (Lopez-Hernandez and Burnham, 1974a). Exchangeable Al and acetate-extractable Al decreased with increasing pH which in turn decreased phosphate retention.

In summary, the soil components affecting phosphorus adsorption include iron and aluminium oxides, clay and clay sized amorphous materials. The specific surface area of the calcium carbonate is also responsible for P adsorption in calcareous soils. Clay content has been reported to be of low importance for phosphate adsorption. The surface area and characteristics of the oxide minerals present in the soil appear to be the most important factors determining P adsorption by a soil.

#### II.4. FACTORS AFFECTING PHOSPHORUS DESORPTION IN SOILS

Ethylene diamine tetra acetic acid ( $\text{EDTA}^{2-}$ ) was reported to be the most effective agent in extracting phosphorus from P treated sediments because this chelating agent can complex iron and thereby release phosphorus adsorbed on the surface of iron

compounds in soil. Fluoride was also found to extract considerable amounts of phosphorus. The amount of phosphate desorbed was relatively high in the first two desorptions (Kuo and Lotse, 1974).

Desorption of added P using anion exchange resin from five soils was highly correlated ( $r=0.99$ ) with the values of "n" which is a unique characteristic of each soil calculated from parameters of the Langmuir equation. Decreasing n values among the soils indicated greater adsorption capacities. Neither desorption maximum nor bonding energy was correlated with the relative increase in extractable P. The data showed that n derived from Langmuir equation provided an index of the adsorption-desorption properties of soils (Bache and Peaslee, 1975).

The amounts of phosphate desorbed from soils by successive extractions with 0.01 M  $\text{CaCl}_2$  solution was far less than the amount of P adsorbed. A comparison of the P desorption parameters showed that the mobility of P was higher in alkaline soils than the acid soils. Diffusion was the main process limiting the rate of release of adsorbed P in soils (Vig and Dev, 1976).

The rate of phosphate adsorption and desorption by hematite and gibbsite indicated that the rate of phosphate adsorption was rapid initially and decreased with prolonged reaction time (Kuo and Lotse, 1973). The total perturbation energy of adsorbed phosphate molecules and the potential energy of the last adsorbed molecules were high, and therefore the amount of phosphate

desorbed was initially rapid. By consecutive desorption the interaction energy as well as the potential energy of adsorbed phosphate decreased and the desorption curve levelled off.

The residual effects of continuous P application to a soil were evaluated by measuring the labile P and available P content with the 0.01 M  $\text{CaCl}_2$  and 0.5 M  $\text{NaHCO}_3$  extraction methods (Vig *et al.*, 1979). A linear relationship between the quantity and intensity factors of P in these soils was observed. The desorption mechanism appeared to involve rapid dissolution of amorphous P compounds and the slow dissolution of crystalline P compounds. The process was diffusion controlled.

Biswas and Ghosh (1987) found that the phosphate desorption kinetics shortly after adding different P carriers of varying water soluble P to an alkaline soil were mostly described by the parabolic-shape diffusion equations. The desorption rate constants were however, greater in their soil samples treated with diammonium phosphate and decreased with the fall in the water soluble P content of the fertilizer or with prolonged incubation.

The release of P from the solid phase in to solution was a slow process, and it followed first order reaction kinetics. Phosphorus released was mostly from the labile fraction of surface P. Desorption of P was a diffusion-controlled process and the rate of P release increased with P status of the soil (Dhillon *et al.*, 1986).

Nakos (1987) found that from 24 to 75% of the adsorbed P from 54 Greek forest soils could subsequently be extracted with Olsen's P extractant. The amount of P desorbed was significantly negatively correlated with clay and free iron oxide contents of the soils.

Following a 100 h reaction with Cl-resin and 300 h reaction with bicarbonate-resin, the concentration of anions complementary to phosphate was the critical variable affecting the transfer of P from soil to resin. Solution concentrations of  $\text{H}_3\text{O}^+$  and  $\text{Ca}^{++}$  and P indicated that desorption of P by  $\text{OH}^-$  and dissolution of calcium phosphates, controlled P release from soils. The amount of P extracted by  $\text{HCO}_3^-$ -resin was higher than those extracted by Cl-resin from an acid soil, but there was little difference in the amounts of P extracted from a calcareous soil by the two resins. Bicarbonate-resin extracted a constant proportion of isotopically exchangeable P from different soils whereas Cl-resin did not. Anion exchange resins could provide a convenient means for producing desorption curves for soils (Bache and Ireland, 1980).

The electro-ultrafiltration (EUF) technique utilises the combination of electrodialysis and ultrafiltration for desorption of ions. It is directly proportional to the voltage and temperature of operation and inversely proportional to the binding power of the ions. Through a wide choice of voltage and temperature combinations, it is possible to separate several nutrient fractions having different binding power which indicates differential availability to plants. Using EUF, the nutrients

are extracted by water. It has been found that the best correlations with plant availability were obtained with the amounts of P extracted by EUF in 30 min. at 200 V and 20°C and amounts of P extracted by six successive extraction with 0.5 N NH<sub>4</sub>Cl. When the voltage was increased from 200 V to 400 V and the temperature was raised from 20°C to 80°C, the amount of P extracted by EUF could be five times higher than the amounts extracted under constant condition of 200 V and 20°C (Nemeth, 1979).

Biddappa (1976) measured the release of adsorbed phosphorus by Olsen's extractant in 4 rice growing soils of Orissa. He found that the quantity of phosphorus desorbed decreased with successive desorptions, but the quantity of phosphorus desorbed after 4 desorptions was almost constant. These results clearly showed that the phosphorus was being released at a constant rate to the solution, to replenish P taken up by roots. Dalal (1974) found that the phosphate desorption process was well described by two constant rate equations, based on the co-efficient term (i.e. rate factor) and constant term (i.e. the initial solution P). Further, these constants were significantly correlated with amorphous Al content of soils. As the rate factor increased, the solution P concentration decreased with the increase in amorphous Al content.

Manikandan and Sastry (1986) found that the relative efficiency of three extractants to desorb P from six soil profiles belonging to Alfisol, Inceptisol and Entisol collected



from the Mysore Plateau (pH 4.6 to 8.3) decreased in the order: Bray's (0.03 N  $\text{NH}_4 + 0.025$  N HCl) > Olsen's (0.5 M  $\text{NaHCO}_3$ ) > Dyer's (1% citric acid). More than 90% recovery was obtained with Olsen's and Bray's reagent, but in each case the maximum attainable recovery with Bray's reagent was higher than that with Olsen's reagent. The recovery with Dyer's reagent ranged from 75.3 to 88%. The maximum attainable recovery with Olsen's reagent decreased with increase in the time allowed originally for phosphate adsorption.

#### II.5. PHOSPHORUS SUPPLY PARAMETER

Khasawneh (1971) stated that quantity, intensity and buffering capacity of soils determined the supply of P to growing roots of plants. Khasawneh and Copeland (1973) proposed the use of a "supply parameter" which combines the effect of above factors in predicting the availability of P to plants. In a greenhouse study, the total P removed by rice and wheat was found to be correlated significantly with the phosphorus supply parameter and cumulative P release of phosphorus in three soils differing in soil characteristics (Singh and Sarkar, 1985). In another greenhouse experiment, the total amount of P removed by wheat was also found to be correlated well with the supply parameter. A highly significant linear relationship was found to exist between cumulative P desorption and the supply parameter, indicating that either of these two indices could successfully define P supply capacity of the soil (Vig *et al.*, 1978).

### III. MATERIALS AND METHODS

#### III.1. SOILS AND THEIR CHARACTERISTICS

##### III.1.1 Collection and preparation of soil samples

Surface (0-15 or 0-20 cm) samples of Vertisols were collected from benchmark sites in Andhra Pradesh, Madhya Pradesh and Maharashtra states. The soil samples were air dried and ground to pass through a 2 mm sieve before use.

##### III.1.2 Characteristics of soil series

Details about locations of the Vertisols used are given in Table 1. Of the Vertisols studied, the Kasireddipalli series was a Typic Pellustert developed on basaltic alluvium; it occurred on lower pediments and in depressions in Medak and adjoining districts of Andhra Pradesh. This soil was deep, clayey, imperfectly drained, strongly to very strongly alkaline and calcareous. It tended to become saline and sodic because of poor drainage (Benchmark Soils of India, 1982).

The Barsi series was a Typic Chromustert, developed on fine basaltic alluvium. It was a deep, very clayey, moderately well drained, calcareous soil and occurred in Sholapur and Osmanabad districts of Maharashtra. (Benchmark Soils of India, 1982).

The Begamganj series belonged to the fine, montmorillonitic, hyperthermic family of Entic chromusterts developed on fine basaltic alluvium. It was a very deep soil with clay content of about 58% and it develops wide cracks in a dry state. The soil

reaction was mildly alkaline. The exchange complex was 83 to 95% saturated by divalent cations (ICAR, 1985).

Table 1: Details of soils used.

Soil Series No.	State	Site
1a Kasireddipalli	Andhra Pradesh	ICRISAT 1 (BR-1) no P applied in the previous season
1b "	"	" 10 kg P ha <sup>-1</sup> applied in the previous season
1c "	"	" 20 kg P ha <sup>-1</sup> applied in the previous season
1d "	"	" 40 kg P ha <sup>-1</sup> applied in the previous season
2 "	"	ICRISATII(BW-6)
3 Barsi	Maharashtra	Barsi
4 Begamganj	Madhya Pradesh	Bhopal

### III.2. METHODS OF SOIL ANALYSIS

#### III.2.1 Characteristics of soils

Some important characteristics of the soils are given in Tables 2a, b; for this analysis, soil pH was determined with a glass electrode in 1:2 soil : water suspension (Jackson, 1967), particle size distribution was determined by the hydrometer method (Gee and Boudier, 1986) and calcium carbonate content by acid neutralization method (Jackson, 1967). Oxalate extractable Fe and Al were determined as described by Tamm's modified method (IITA, 1979), DTPA extractable Fe was extracted by the method

suggested by Lindsay and Norvell (1978). Exchangeable Al was extracted with 1N KCl (Barnhisel and Bertsch, 1982) and total phosphorus was determined by digestion with perchloric acid (Olsen and Sommers, 1982).

### III.2.2 ~~Extractable~~ P

Calcium chloride extractable P was determined calorimetrically in the extracts obtained by shaking each soil sample (2 g) with 0.01 M  $\text{CaCl}_2$  (20 ml) (Olsen and Sommers, 1982). Olsen's extractable P was determined by extracting soil (2g) with 0.5 M  $\text{NaHCO}_3$  (40 ml). Electro-ultrafiltration (EUF) P was determined by extracting soil (2 g) using an automatic programmed EUF machine (Nemeth, 1979) which measures 3 fractions: 0-5 min 50 V, 20°C; 5-30 min 200 V, 20°C; 30-35 min 400 V, 80°C. The contents of P in the extracts was determined by the developing colour with ascorbic acid (Olsen and Sommers, 1982).

Table 2a: Selected physical and chemical characteristics of the Vertisols used.

Soil No.	pH	Clay	CaCO <sub>3</sub>	DTPA extrac- table	Oxalate extrac- table	IN KCl extrac- table	Oxalate extrac- table
	1:2	%	%	Fe	Fe	Al	Al
----- ug g <sup>-1</sup> soil -----							
1a	8.4	53	6.1	5.6	720	1.4	1315
1b	8.4	53	5.8	5.8	845	1.6	1480
1c	8.4	53	5.7	5.6	815	1.6	1320
1d	8.4	53	5.9	5.7	825	2.2	1430
2	8.5	52	5.2	5.9	690	2.6	1010
3	8.6	61	11.1	6.9	878	2.2	1528
4	8.0	48	2.4	6.8	795	1.7	1025

Table 2b: Extractable and total P content of soils.

Soil No.	NaHCO <sub>3</sub> -P	CaCl <sub>2</sub> -P	EUf-P	Total-P
	----- ug g <sup>-1</sup> -----			
1a	2.2	0.20	21.6	150
1b	2.4	0.20	24.2	150
1c	2.4	0.20	28.8	150
1d	3.0	0.20	20.2	150
2	3.5	0.40	16.2	250
3	2.1	0.43	28.7	325
4	7.4	0.47	16.0	406

### III.3. PHOSPHORUS ADSORPTION STUDIES

#### III.3.1 Determination of phosphate adsorption characteristics of the soils

For determining phosphate adsorption characteristics of the soils, the method suggested by Fox and Kamprath (1971) was followed :

Duplicate soil samples (2 g) were placed in 50 ml centrifuge tubes, 25 ml of 0.01 M  $\text{CaCl}_2$  solution containing 0, 20, 40, 60, 80, 100, 150, 200, 250, 300, 400 and 450  $\mu\text{g}$  of P as potassium dihydrogen phosphate or ammonium polyphosphate was added. The tubes were incubated at  $25 \pm 1^\circ\text{C}$  for 6 days, and shaken intermittently twice each day. After 6 days, the samples were centrifuged at 3000 rpm for 10 min and filtered through Whatman No 1 filter paper. Since there were no significant differences between the duplicates, except for soil 1a and 1d, the average value was used to calculate the amount of P in solution. The P content in the clear solution was determined by developing colour with ascorbic acid (Olsen and Sommers, 1982). The difference in the amount of P added and that recovered in solution was considered to be adsorbed.

To get a stock solution containing  $50 \mu\text{g P ml}^{-1}$ , 0.21965 g of potassium dihydrogen phosphate or 0.20819 g of ammonium polyphosphate respectively, were dissolved in 0.01 M  $\text{CaCl}_2$  and made up to one litre with 0.01 M  $\text{CaCl}_2$ . From this stock solution, working solutions were prepared.

### III.3.2 Fitting of phosphorus adsorption data to five equations

The phosphate adsorption data were fitted to five equations for evaluating the goodness of fit. The different equations used are described below:

(i) Freundlich equation (Ratkowsky, 1986)

$$Y = \alpha x^\beta$$

(ii) Langmuir equation (Ratkowsky, 1986)

$$Y = \frac{\alpha \beta x}{1 + \beta x}$$

(iii) Tempkin equation (Barrow, 1978)

$$Y = K_1 \ln (K_2 C)$$

(iv) Gurnary equation (Ratkowsky, 1986)

$$Y = \frac{x}{\alpha + \beta x + \gamma/x}$$

(v) Dubinin - Radushkevich equation (Dalal, 1979)

$$\ln X = \ln X_m (-Be^2)$$

where,

X is the P concentration in solution

Y is the amount of P adsorbed per unit of soil

$\alpha$ ,  $\beta$ ,  $\gamma$ ,  $K_1$ ,  $K_2$  are coefficients which reflect the relative rates of adsorption and desorption of P at equilibrium

x is the amount of P adsorbed (mmol P kg<sup>-1</sup> soil)

X<sub>m</sub> is the adsorption maximum (mmol P kg<sup>-1</sup> soil)

e is adsorption potential and is defined as:

$$e = RT \ln \left( \frac{1+1}{C} \right)$$

C is the equilibrium concentration ( $\text{mmol P L}^{-1}$  soil)

is constant

R is a gas constant  $8.3147 \times 10^{-3} \text{ KJ deg}^{-1} \text{ mole}^{-1}$  and

T is absolute temperature (293.15 K at  $20^{\circ}\text{C}$ ).

### III.4. PHOSPHORUS DESORPTION STUDIES

Phosphorus desorption after providing a range of adsorbed P in the soil samples was determined using three procedures.

#### III.4.1 ~~Desorption by calcium chloride~~

Soil samples with adsorbed P after separating solution P were used for the desorption study. Soil samples were shaken with 20 ml of 0.01 M  $\text{CaCl}_2$  in duplicates for 20 hrs and the contents were centrifuged at 3000 rpm for 10 min and filtered through Whatman No 1 filter paper. This process was repeated for the second time and the desorbed P during each desorption was determined as described earlier. Correction was made for the solution retained during the adsorption run.

#### III.4.2 ~~Desorption by sodium bicarbonate~~

Soil samples used for adsorption studies, after separating the solution P were shaken with 40 ml of 0.5 M  $\text{NaHCO}_3$  for 20 hrs, the contents were centrifuged at 5000 rpm for 10 min and filtered through Whatman No 1 filter paper. The samples were subjected to two desorption cycles and the amount of P desorbed was determined as described earlier.



### III.4.3 Desorption by Electro-ultrafiltration (EUF) technique

The soil samples after adsorption studies were subjected to EUF desorption. The EUF desorption was carried out at two different voltage and temperature combinations: 200 volts voltage and 20°C temperature; 400 volts voltage and 80°C temperature. The samples were extracted two times and P desorbed during each extraction was determined separately.

### III.4.4 Fitting of phosphorus desorption data to two equations

The phosphate desorption data were fitted to Freundlich and Langmuir equations for evaluating the goodness of fit. The equations used were those described earlier for the phosphorus adsorption studies.

## III.5. PHOSPHORUS BUFFERING CAPACITY

The buffering capacity (b) was calculated from Langmuir equation at 0.2 ug ml<sup>-1</sup> soil equilibrium p concentration by using the equation :  $b = \frac{q}{c}$

where,

b = buffering capacity

q = quantity factor

c = intensity factor

### III.6. PHOSPHORUS SUPPLY PARAMETER

Phosphorus supply parameter (SP) was calculated using the expression described by Khasawneh and Copeland (1973):

$$SP = \sqrt{qc} / \sqrt{K_1 K_2}$$

where  $q$  = P adsorbed per gram of soil

$c$  = equilibrium concentration i.e.  $0.2 \text{ ug ml}^{-1}$

$d$   $K_1$  and  $K_2$  are constants determined by plotting  $\frac{1}{c}$  versus  $\frac{1}{q}$  ( $K_1$  is reciprocal of intercept of  $\frac{1}{q} \times \frac{1}{c}$  plot, and  $K_2$  is slope of the plot of  $\frac{1}{q} \times \frac{1}{c} \times K_1$ ).

#### IV. RESULTS AND DISCUSSION

The amounts of P to be added to bring soils to an equilibrium solution concentration of  $0.2 \text{ ug P ml}^{-1}$  was selected as the basis for characterising their P adsorption capacities. This was chosen as the basis at Beckwith's (1965) suggestion, that the standard equilibrium P concentration used should be  $0.2 \text{ ug P ml}^{-1}$ , and other work showing that this concentration in solution cultures was adequate for optimum growth of many crops (Fox *et al.*, 1974; Jones and Benson, 1975).

The adsorption data obtained with different Vertisols were fitted to the five adsorption equations described earlier (materials and methods).

The P adsorption isotherms (actual values) for all the soils (Fig.1,2,3 and 4) and P adsorption isotherms (by fitted values) for all soils by the Langmuir equation (Fig.5-11) and the P adsorption isotherm for BW-6 (soil No.2) by the Tempkin, Dubinin-Radushkevich isotherm (Fig.12-13) were determined.

The amounts of P adsorbed at  $0.2 \text{ ug ml}^{-1}$  equilibrium solution P concentration in soils with the Langmuir isotherm when both potassium dihydrogen phosphate and ammonium polyphosphate were used as sources of P were similar irrespective of the source of P (Table 4). The amounts of P required in all the soils to obtain  $0.2 \text{ ug mg}^{-1}$  of P in equilibrium solution would be rated low (10-100 ug/g) according to the criterion suggested by Juo and Fox (1977).

The fit of the data to the five isotherms (Table 3) gave variable conformity to the equations used. The Dubinin-Radushkevich and the Langmuir equations gave the closest fit to the adsorption data. The Tempkin equation also gave a very good fit, but the Freundlich and the Gunary equations gave poorer and variable fit. Data in Table 3 also showed that  $R^2$  values of the Dubin-Radushkevich equation (e) were slightly higher than the  $R^2$  values of the Langmuir (b) and Tempkin equation (c) but all the three equations had  $R^2 > 0.90$  for all soils. The Freundlich (a) and Gunary (d) equations however accounted for much lower variability (avg.  $R^2$  0.38). Although the variability in the fitted data  $R^2$  values for the Dubin-Radushkevich equation (e) were similar to the values of  $R^2$  for the Langmuir equation (b), the Langmuir equation was preferred; when the observed values were fitted, the Langmuir equation gave a better fit at all concentrations where as the Dubin-Radushkevich equation was flattened at higher concentrations (Fig.9 and 13).

Table 3: Co-efficient of determination ( $R^2$ ) indicating goodness of fit to various adsorption isotherms.

Soil No.	Freundlich (a)	Langmuir (b)	Tempkin (c)	Gunary (d)	Dubinin-Radushkevich (e)
1a	0.49	0.97	0.96	0.69	0.99
1b	0.49	0.98	0.97	0.87	0.99
1c	0.48	0.97	0.91	0.05	0.98
1d	0.44	0.98	0.95	0.82	0.99
2	0.37	0.99	0.96	0.12	0.99
3	0.28	0.99	0.97	0.00	0.99
4	0.18	0.99	0.98	0.13	0.99
Average	0.39	0.98	0.96	0.38	0.99

Table 4: Phosphorus adsorption parameters calculated from the Langmuir isotherm.

Soil No.	A			B		
	a	b	c	a	b	c
1a	182.82	1.46	41.32	192.50	1.44	43.90
1b	182.46	1.34	38.62	182.09	1.42	40.35
1c	203.36	1.05	35.23	204.82	1.11	37.20
1d	182.46	1.11	34.25	199.53	1.52	46.50
2	203.36	1.30	41.94	187.48	1.50	43.40
3	215.31	2.48	71.37	217.87	2.53	73.30
4	196.61	3.40	79.51	212.48	3.01	79.90

A =  $\text{KH}_2\text{PO}_4$  used as source of P

B = Ammonium polyphosphate used as source of P

a = adsorption maximum

b = bonding energy

c = P  $\mu\text{g g}^{-1}$  retained by the soil at  $0.2 \mu\text{g ml}^{-1}$  solution P

Correlations between the amount of P adsorbed at  $0.2 \mu\text{g ml}^{-1}$  equilibrium solution P concentration with the various soil characteristics showed that it was significantly correlated only with DTPA extractable Fe ( $r=0.965^*$ ), for both ammonium polyphosphate and potassium dihydrogen phosphate as P carriers. The correlations with other soil characteristics were not significant (Table 5).

This data indicated that the amount of P adsorbed by the BR-1 soil fertilized in the previous season (soil No.1a-1d) at 0.2 ug ml<sup>-1</sup> equilibrium P solution concentration were similar and ranged from 35-40 ug P g<sup>-1</sup> (Fig.1 and 3). It can be concluded that fertilization of this Vertisol (0, 10, 20 and 40 kg P ha<sup>-1</sup>) in the previous season had no effect on phosphate adsorption.

Table 5 : Co-efficients of correlation between the amount of P retained by soil at 0.2 ug P ml<sup>-1</sup> equilibrium solution concentration and soil characteristics.

Characteristics	a <sub>1</sub>	b <sub>1</sub>
pH	-0.487	-0.484
Clay	0.079	0.099
CaCO <sub>3</sub>	0.058	0.082
DTPA Fe	0.965*	0.964*
Oxalate Fe	0.258	0.321
IN KCl Al	0.034	0.105
Oxalate Al	-0.234	-0.166

\* = Significant at 1% level

a<sub>1</sub> = KH<sub>2</sub>PO<sub>4</sub> used as source of P

b<sub>1</sub> = Ammonium polyphosphate used as source of P

The data using the Langmuir adsorption parameters showed that adsorption maximum (a) and bonding energy (b) were also similar irrespective of the source of P (Table 4). Barsi soil (soil No.3) showed high adsorption maximum followed by other soils. Barsi soil (soil No.3) had also the highest content of CaCO<sub>3</sub>, clay, DTPA and oxalate extractable Fe and Al (Table 2).

Similarly, the bonding energy (b) which indicates the tenacity or energy with which P is bound to the soil particles showed that phosphate was held with less tenacity in all the Vertisols (Table 4). In Barsi series (soil No.3), P was held with less energy as compared to other soils and this soil also showed high adsorption maximum. Thus release of P from the Barsi soil (soil No.3) must be high. This indeed was confirmed from the results of an experiment where P was added at a rate of 100  $\mu\text{g P g}^{-1}$ , the amount of P retained by this soil after 6 days of equilibrium was greater than in other soils. Desorption with 0.5 M  $\text{NaHCO}_3$  solution also indicated that more P was desorbed from the Barsi soil (soil No.3) than the Begamganj soil (soil No.4) (Table 6).

Table 6: The relationship between P adsorption, clay % and  $\text{CaCO}_3$  content of soils.

Soil No.	P added $100 \mu\text{g g}^{-1}$	P adsorbed by the soil after incubation $\mu\text{g g}^{-1}$	P retained by the soil after 0.5 M $\text{NaHCO}_3$ desorption $\mu\text{g g}^{-1}$	Clay %	$\text{CaCO}_3$ %
1	100	90.63	46.63	53	6.1
2	100	92.75	56.50	52	5.2
3	100	96.25	64.25	61	11.0
4	100	95.25	74.65	48	2.4



A comparison of the amount of P adsorbed and  $\text{CaCO}_3$  % of soils showed that the amount of P adsorbed by the Barsi soil (soil No.3) and the Begamganj soil (soil No.4) were similar though the  $\text{CaCO}_3$  % was markedly different (11.0, 2.4%) in the two soils. The relationship between the amount of P adsorbed by the soil and clay indicated that though the clay content was markedly different in the Barsi soil (soil No.3) and the Begamganj soil (soil No.4), the amount of P adsorbed by these soils was similar. In case of the two Vertisols (Kasireddipalli series) from two locations at the ICRISAT Center, BR-1 soil (soil No.1a-1d) and BW-6 soil (soil No.2), showed that the amounts of clay (52%) and P adsorbed by these soils were also similar (89.63 and 92.75  $\mu\text{g P g}^{-1}$ ) (Table 6). These results indicated that perhaps the amount of clay and  $\text{CaCO}_3$  % are not important for P adsorption and that the nature and quality of clay and  $\text{CaCO}_3$  play an important role in P adsorption.

There was no significant correlation between the amount of P adsorbed at  $0.2 \mu\text{g P ml}^{-1}$  equilibrium solution concentration and the amount of clay and  $\text{CaCO}_3$  (Table 5). Clay content *per se* has been reported to be a relatively less important factor in phosphate adsorption (Sahrawat, 1988; Manikandan and Sastry 1988; Lopez-Hernandez and Burnham, 1974b and 1982) and the type of clay was important in this regard. The specific surface of the carbonate component was reported to be an inverse hyperbolic function of the percentage of  $\text{CaCO}_3$ , (Holford and Mattingly, 1975a). Phosphorus adsorption may be closely related to the

quality of  $\text{CaCO}_3$  but not with the  $\text{CaCO}_3$  content (Goswami and Sahrawat, 1982).

The buffering capacity of the soils at  $0.2 \text{ ug ml}^{-1}$  equilibrium solution P concentration calculated from the Langmuir adsorption isotherm, was found to decrease in the BR-1 Vertisol (soil No.1a-1d) with the application of phosphatic fertilizer in the previous season (Table 7). The lower buffering capacity factor in the fertilized soil indicated the increased presence of P in the solution phase. With the addition of P to the soil, the average strength of P adsorption by soil solution increased more rapidly than the amounts of adsorbed P (Table 7). Sheppard and Racz (1984) however reported it in terms of desorption buffering capacity determined immediately after fertilizer P application and indicated that the higher buffering capacity (desorption) probably resulted from relatively large amounts of superficially adsorbed P at that time.

The P supply parameter was calculated for the Vertisols with the Langmuir isotherms for BW-6, Barsi and Begamganj soils (soil Nos.2, 3 and 4). This parameter determined the ability of a soil to supply P to growing roots. The Barsi (soil No.3) and Begamganj (soil No.4) soils had similar supplying parameters (Table 7) and higher when compared to BW-6 (soil No.2). These soils had a similar buffering capacity which indicated similar capacity of these soils to supply P to the growing roots. Higher buffering capacity indicated higher P supply parameter value.

Table 7: Buffering capacity and P supply parameter calculated from Langmuir isotherm.

Soil No.	'Buffering capacity	Supplying parameter
1a	159.90	-
1b	152.20	-
1c	145.50	-
1d	140.20	-
2	166.48	2.34
3	238.60	2.51
4	236.80	2.54

The maximum attainable recovery was calculated from the values of cumulative P desorbed and P initially retained by each soil using different extractants. The percentage of phosphate extracted by different reagents followed the order: EUF (400 V, 80°C) > sodium bicarbonate > EUF (200 V, 20°C) > calcium chloride. Average recovery of 74% was obtained with EUF (400 V, 80°C) followed by sodium bicarbonate (63%), but the recovery with sodium bicarbonate was found to be more consistent (Fig.16-23). Hingston *et al.* (1972, 1974) suggested that only those ions which can increase the negative charge of the soil in the presence of phosphate can desorb added phosphate. In addition to the higher concentration of HCO<sub>3</sub> ions in the Olsen's reagent, the higher pH of Olsen's reagent can increase the negative charge of the soil thereby resulting in consistent recovery.

The desorption of phosphate by different extractants (Tables 8, 9, 10 and 11) indicated that the recovery in the Begamganj soil (soil No.4) with EUF (400 V, 80°C) was more than 100%. These data clearly indicated that the applied P was not fixed by the soil, it was adsorbed on the soil particles and was desorbed and may be available to the plant in due course.

The desorption data were fitted to Freundlich and Langmuir equations. A good fit to the first desorption data was obtained by the Langmuir isotherm ( $R^2=0.95$ ) (Fig.14) but a poorer fit was obtained with the Freundlich isotherm ( $R^2=0.55$ ) (Fig.15).

The data on the desorption of the adsorbed phosphate from the soils by different extractants showed that the first extraction desorbed the highest amount of phosphate, and the amount desorbed decreased with the successive extractions (Tables 8, 9, 10 and 11). During the initial extraction, the surface coverage might have been relatively high and hence the amount of phosphate desorbed was also relatively high. By successive extractions the surface coverage would have decreased and hence the desorption might have gradually decreased (Kuo and Lotse, 1973). The rapid release of phosphate during the first extraction was characteristics of the more labile fraction of P. Similar behaviour of soil P during desorption was also reported by Vig *et al.* (1979) for alluvial soils of Punjab. The desorption of soil P is known to be proportional to the number of occupied sites (Kuo and Lotse, 1974); it is obvious that higher amount of P may be desorbed with initial extractions. EUF

(400 V, 80°C) among the extractants used released the highest amount of phosphate during the first desorption.

The phosphate desorption during the second desorption was well described by the Langmuir isotherm ( $R^2=0.95$ ) for all soils except Barsi. The reason for the deviation from the normal behaviour for this particular soil is unknown and needs further investigation. However, a poorer fit to the phosphate data in the second desorption was obtained with the EUF both at high voltage and high temperature (400 V, 80°C) and at low voltage and low temperature (200 V, 20°C) for all the soil samples.

A graph between cumulative P desorbed ( $\mu\text{g g}^{-1}$  soil) versus P retained ( $\mu\text{g g}^{-1}$  soil) indicated that EUF (400 V, 80°C) extracted the highest amount of P followed by sodium bicarbonate for all the soils except soil No. 1d and 2. Calcium chloride desorbed the least amount of phosphate (Fig.24-27).

Table 8: Desorption of adsorbed P from soils by  
0.01 M CaCl<sub>2</sub> reagent.

Soil No.	P added	Desorption No.		Cumulative P desorbed	Maximum attainable recovery %
		I	II		
-----ug g <sup>-1</sup> of soil-----					
1a	40	0.8	1.3	2.2	6.0
1b	40	0.7	0.6	1.3	3.0
1c	40	0.7	0.5	1.2	3.0
1d	40	0.6	0.5	1.1	3.0
2	40	0.6	0.3	0.9	2.0
3	40	0.2	0.1	0.3	0.8
4	40	0.3	0.0	0.3	0.6
Mean					3.0

Table 9 : Desorption of adsorbed P from soils by  
0.5 M NaHCO<sub>3</sub> reagent.

Soil No.	P added	Desorption No.		Cumulative P desorbed	Maximum attainable recovery %
		I	II		
-----ug g <sup>-1</sup> of soil-----					
1a	40	14.2	4.6	18.8	48
1b	40	18.4	6.6	25.0	64
1c	40	18.1	6.7	24.8	64
1d	40	17.4	9.2	26.6	68
2	40	18.4	6.2	24.6	63
3	40	15.6	8.1	23.7	60
4	40	20.8	7.6	28.4	72
Mean					63

Table 10 : Desorption of adsorbed P from soils by  
EUF (200 V, 20°C).

Soil No.	P added	Desorption No.		Cumulative P desorbed	Maximum attainable recovery %
		I ----- -ug g <sup>-1</sup>	II ----- of soil-----		
1a	40	13.0	2.4	15.4	39
1b	40	7.0	4.4	11.4	29
1c	40	14.0	6.6	20.6	52
1d	40	13.0	6.4	19.4	49
2	40	12.5	4.8	17.3	44
3	40	21.0	10.8	31.8	80
4	40	20.5	3.0	23.5	59
Mean					50



Table 11 : Desorption of adsorbed P from soils by  
EUF(400 V, 80°C).

Soil No.	P added	Desorption No.		Cumulative P desorbed	Maximum attainable recovery %
		I	II		
-----ug g <sup>-1</sup> of soil-----					
1a	40	20.0	3.2	23.2	59
1b	40	29.5	4.4	33.9	86
1c	40	17.0	5.8	22.8	58
1d	40	22.5	3.2	25.7	66
2	40	16.0	3.0	19.0	48
3	40	22.0	11.2	33.2	83
4	40	38.0	9.8	47.8	120
<b>Mean</b>					<b>74</b>

## V. SUMMARY AND CONCLUSIONS

The critical limit (level) of extractable P in soil above which a response to P application is likely was considered to be  $5 \text{ ug g}^{-1}$  soil (Indian Society of Soil Science, 1979). However, studies made at ICRISAT on P response of crops like sorghum on Vertisols showed that response to P application was obtained when soil P levels were usually less than  $2 \text{ ug g}^{-1}$  soil compared to Alfisols which under similar condition give very good response to P application when P level was less than  $5 \text{ ug g}^{-1}$  soil. A knowledge of the ability of the soils to sorb added phosphate was implicit in the development of an efficient fertilizer program for these Vertisols.

The P adsorption study was made by equilibrating the soils with different amounts of P in solution (as  $\text{KH}_2\text{PO}_4$ ) for six days. The distributions of added P in solution and adsorbed phases were computed from the amounts remaining in solution. The P desorption studies were conducted with the treated soils using different extractants and EUF technique. P adsorption data were fitted to five equations : Freundlich, Langmuir, Tempkin, Gunary and Dubinin-Radushkevich. The Langmuir isotherm gave consistent and good fits to the data at all concentrations followed by the Dubinin-Radushkevich isotherm. The amounts of P adsorbed at  $0.2 \text{ ug ml}^{-1}$  equilibrium solution P concentration in these soils calculated from the Langmuir isotherm were low and ranged between  $35\text{-}80 \text{ ug P g}^{-1}$  of soil. The amounts of P adsorbed by these soils were similar whether potassium dihydrogen phosphate or ammonium polyphosphate were used as the source of P. The amounts of P

adsorbed (35-40  $\mu\text{g g}^{-1}$  soil) by a Vertisol at ICRISAT Center (BR-1) (soil No.1a-1d) at 0.2  $\mu\text{g ml}^{-1}$  solution P concentration were not affected by P fertilization (0-40 kg P  $\text{ha}^{-1}$ ) in the previous season. This indicated that P fertilization in the previous season had little effect on P adsorption. P adsorbed by the soils at equilibrium solution P concentrations were positively correlated with DTPA extractable Fe but were not with clay or  $\text{CaCO}_3$  content. A comparison of the P adsorption at 0.2  $\mu\text{g ml}^{-1}$  equilibrium solution by the Barsi (soil No.3) and Begamganj (soil No.4) soils indicated that they adsorbed the same amount of P though the content of  $\text{CaCO}_3$  (11% VS, 2.5%) and clay (61% VS, 48%) varied markedly in these two soils. Sahrawat (1988) suggested that the soil components involved in phosphate adsorption could be  $\text{CaCO}_3$  content and its quality and the nature of clay minerals present. The adsorption maximum and bonding energy calculated from the Langmuir isotherm were similar irrespective of whether the source of P was potassium dihydrogen phosphate or ammonium polyphosphate.

The bonding energy which was indicative of the energy with which P was bound to the soil particles indicated that P was held with less tenacity in all the Vertisols studied. The buffering capacity of a Vertisol at ICRISAT Center (soil No.1a-1d) decreased with the application of phosphatic fertilizer in the previous season. The lower buffering capacity factor in the P fertilizer added soils was associated with the increased amounts of P in the solution phase. The P supply parameter which

determined the ability of the soil to supply P to the roots indicated that the Barsi (soil No.3) and the Begamganj (soil No.4) soils had similar supplying capacity. Besides this, these soils had similar buffering capacity indicating that the capacity of the soil to supply P to growing roots would be similar.

Relative efficiency of different extractants to desorb P decreased in the order: EUF (400 V, 80°C) > sodium bicarbonate > EUF (200 V, 20°C) > CaCl<sub>2</sub>. The average attainable recovery of 74% was obtained with EUF (400 V, 80°C) followed by sodium bicarbonate; CaCl<sub>2</sub> desorbed the least amount of P. But in each case the maximum attainable recovery with sodium bicarbonate was more consistent. The attainable recovery percentage in the Bagamganj soil (soil No.4) with EUF (400 V, 80°C) was more than 100% (i.e. 120%) indicating that very little of the applied P was fixed. This study clearly establishes that P adsorbed by the soil particles was easily desorbed and may be available to the plants in due course. The desorption of the adsorbed phosphate from soils by different extractants showed that the first extraction desorbed the highest amount of phosphate, whereas the amount of P desorbed decreased with the successive extractions. On a cumulative P desorbed basis, EUF (400 V, 80°C) desorbed the highest amount of P followed by sodium bicarbonate for all soils. In all cases CaCl<sub>2</sub> desorbed the least amount of phosphate.

From the results of this study, it could be concluded that the Vertisols investigated have low phosphate adsorption capacity, and the adsorbed P was easily desorbable.

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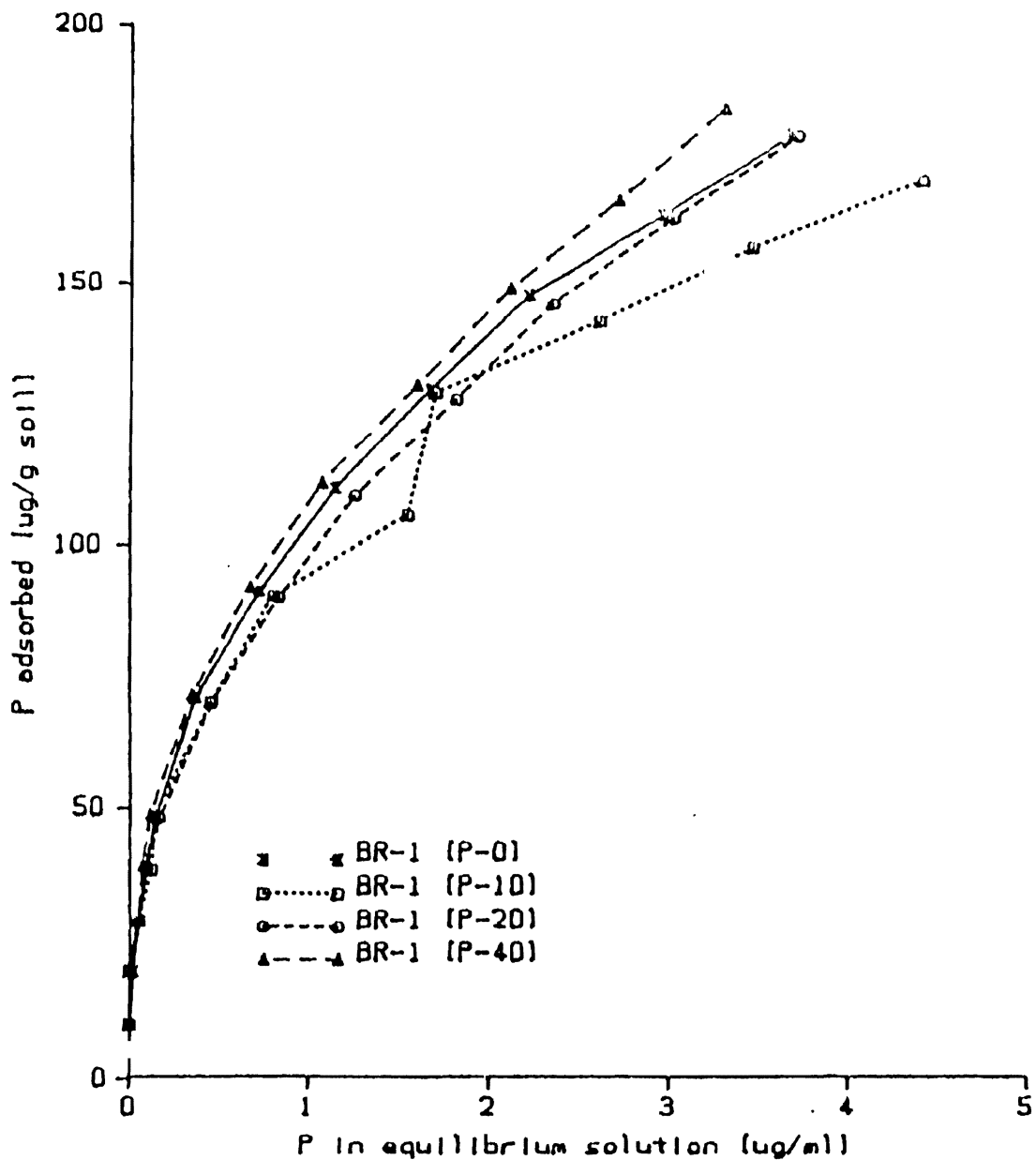


Fig. 1. Relationship between adsorbed P and P concentration in solution after adsorption for BR-1 soil fertilized in the previous season, potassium dihydrogen phosphate used as source of P.

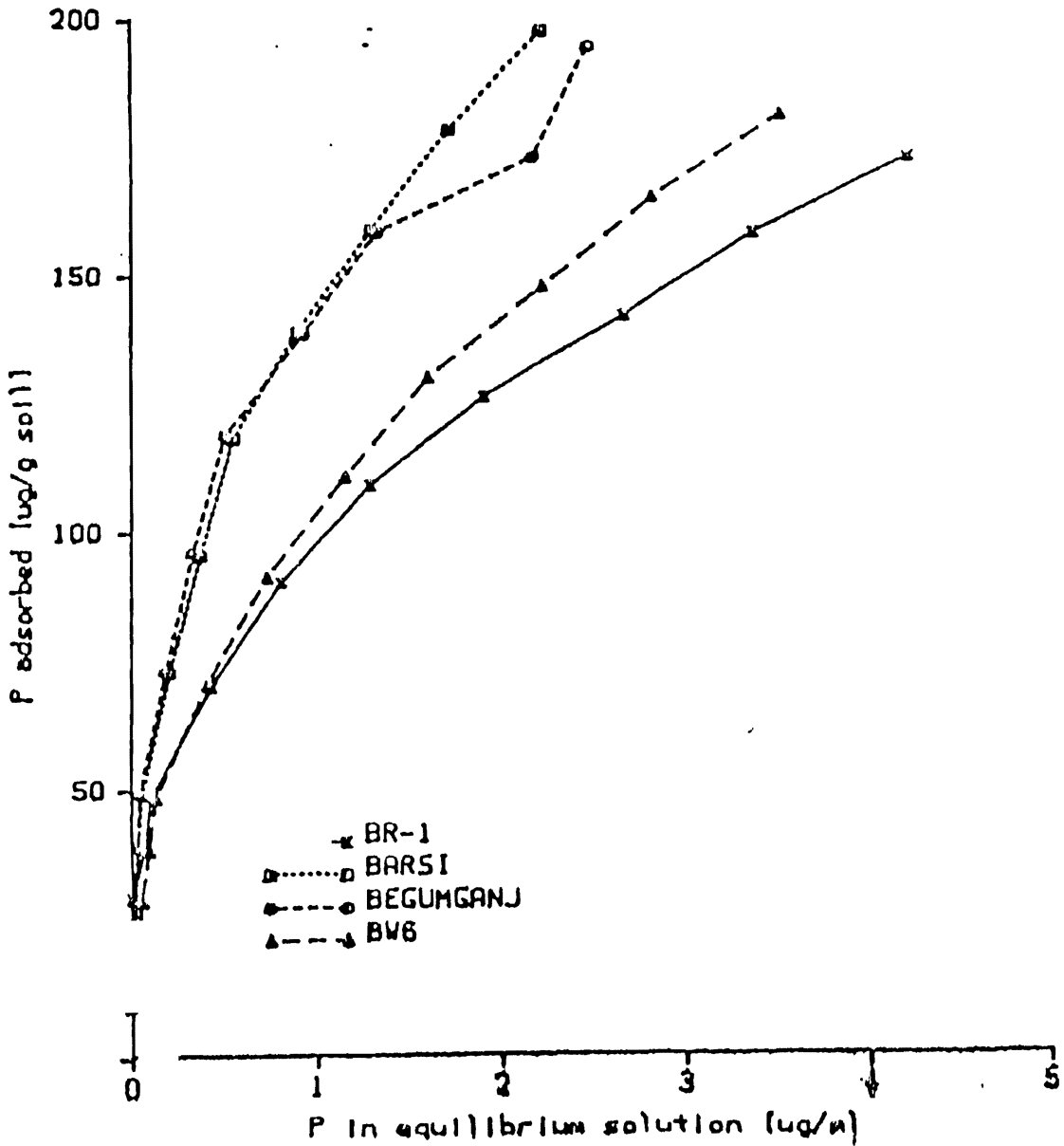


Fig. 2. Relationship between adsorbed P and P concentration in solution after adsorption for selected Vertisols, potassium dihydrogen phosphate used as source of P.

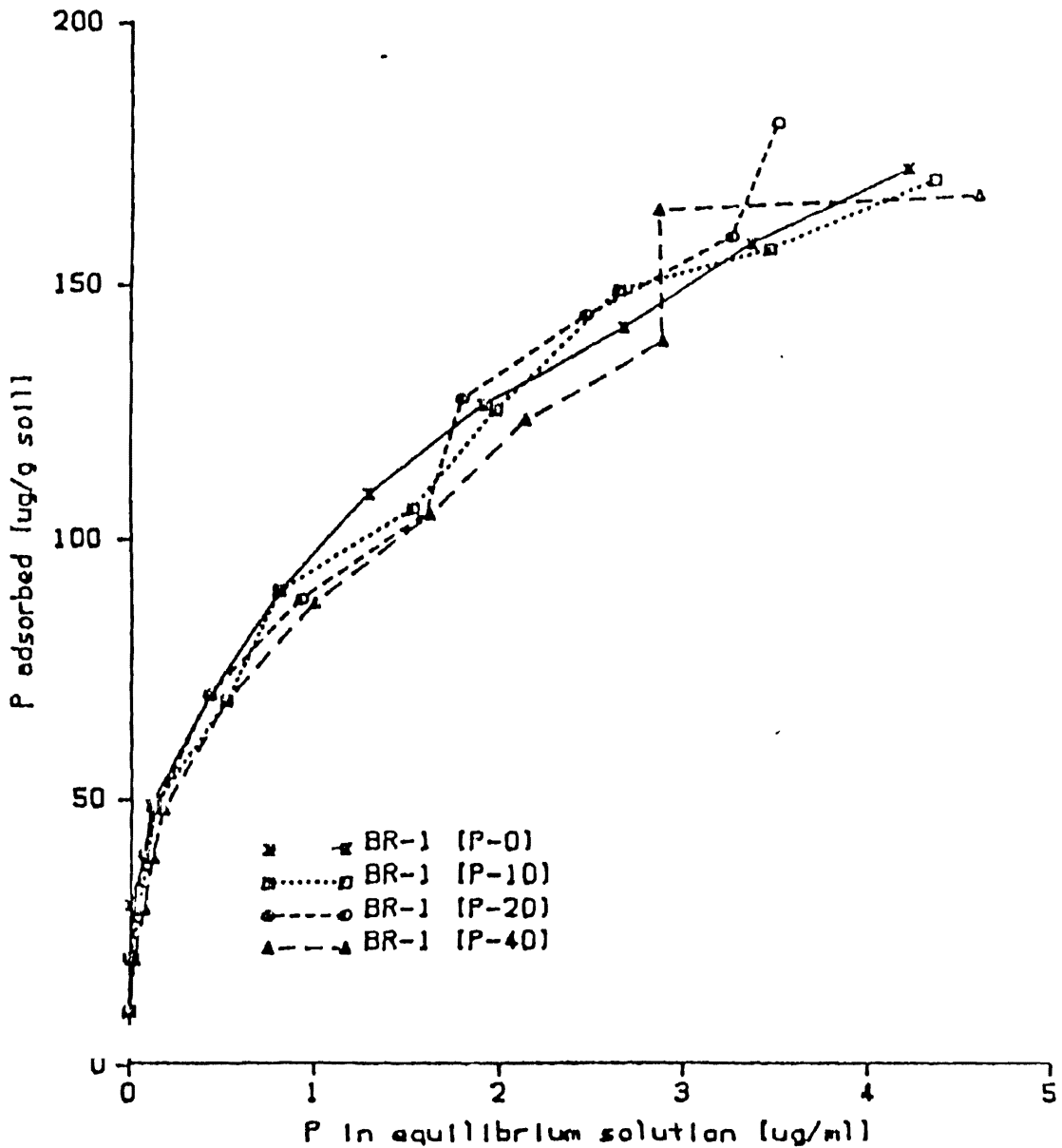


Fig. 3. Relationship between adsorbed P and P concentration in solution after adsorption for BR-1 soil fertilized in the previous season, ammonium polyphosphate used as source of P.

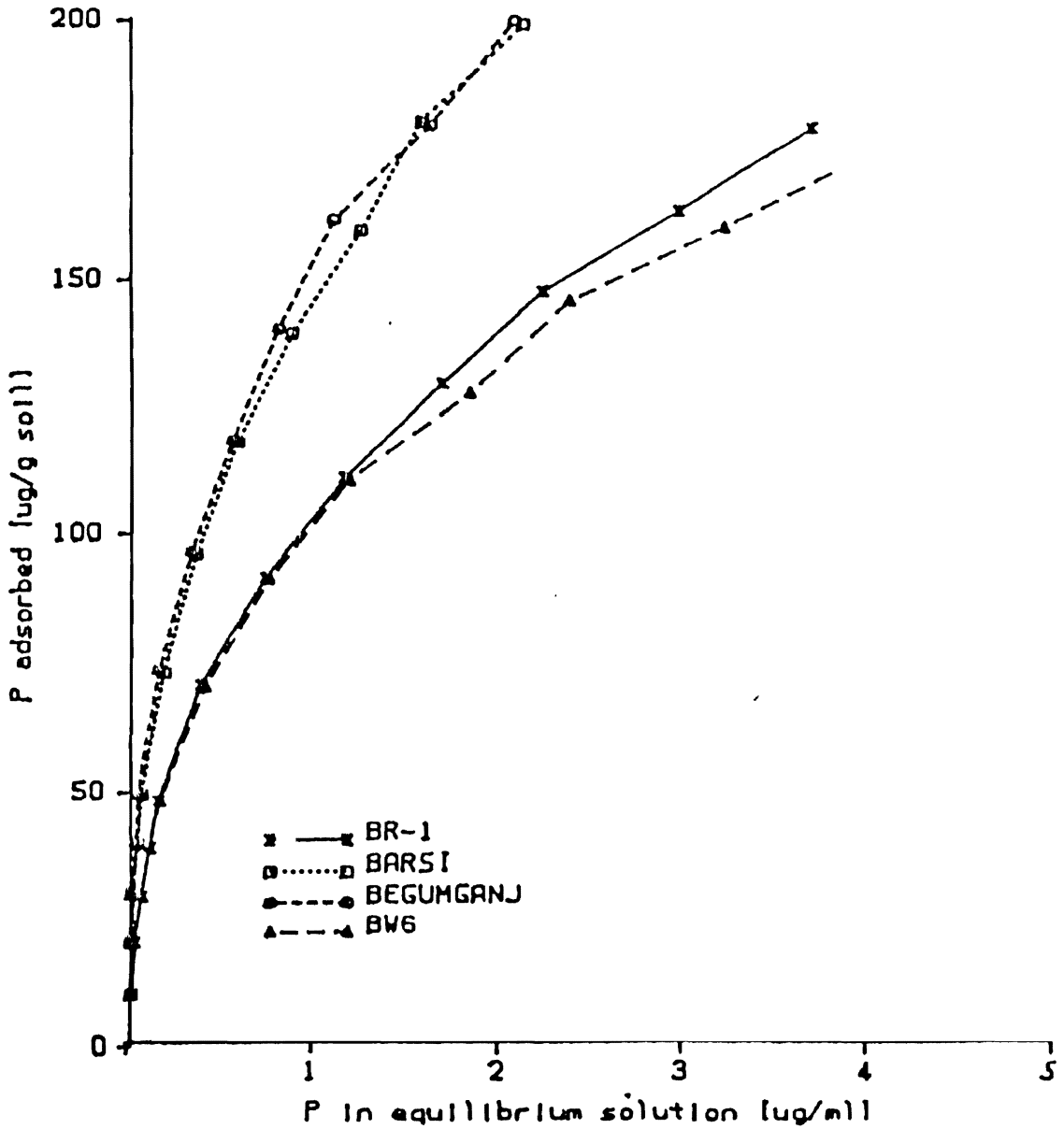


Fig. 4. Relationship between adsorbed P and P concentration in solution after adsorption for selected Vertisols, ammonium polyphosphate used as source of P.

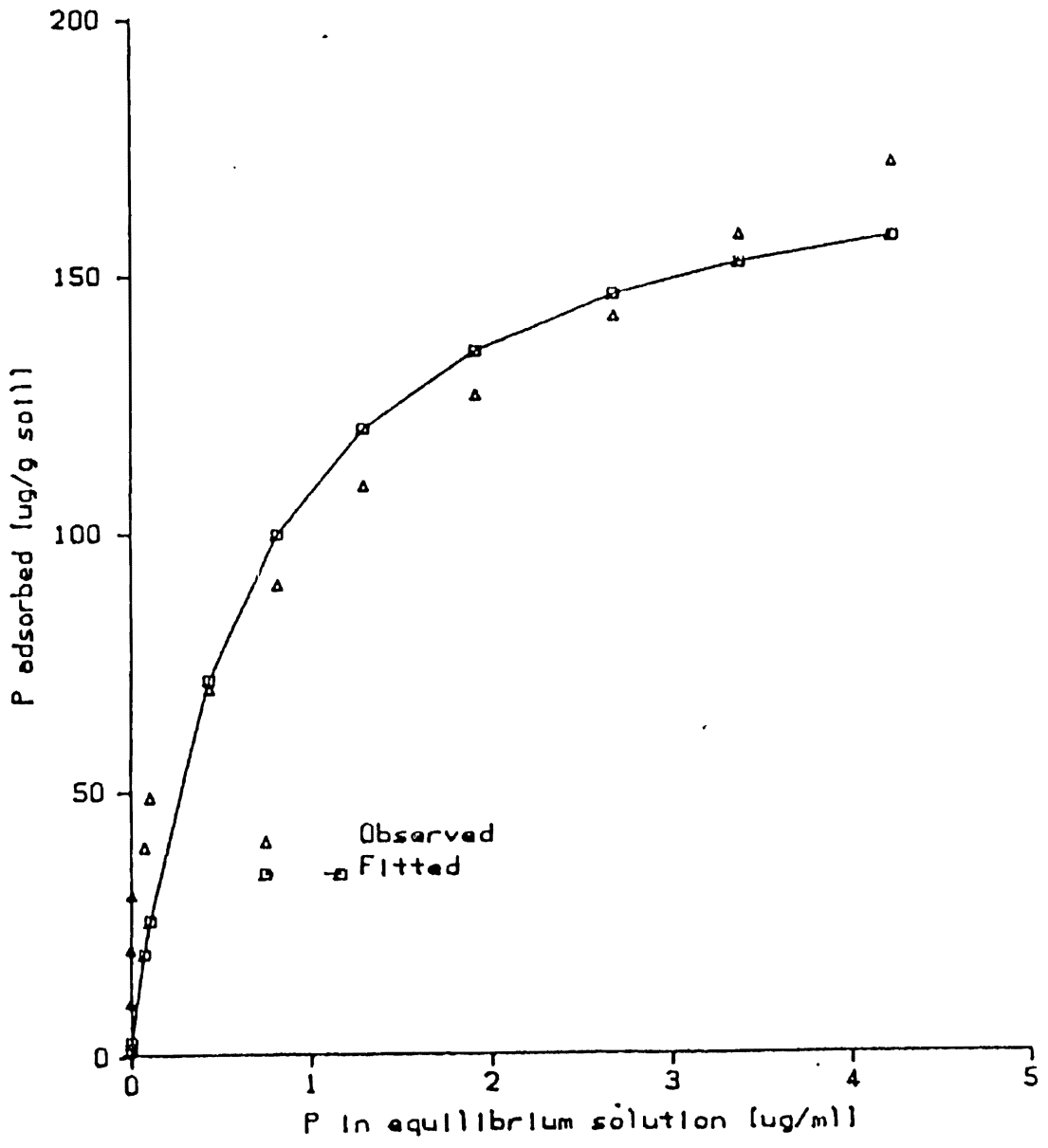


Fig. 5. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Langmuir is shown by continuous line with observed points for BR-1 (no applied P) soil.

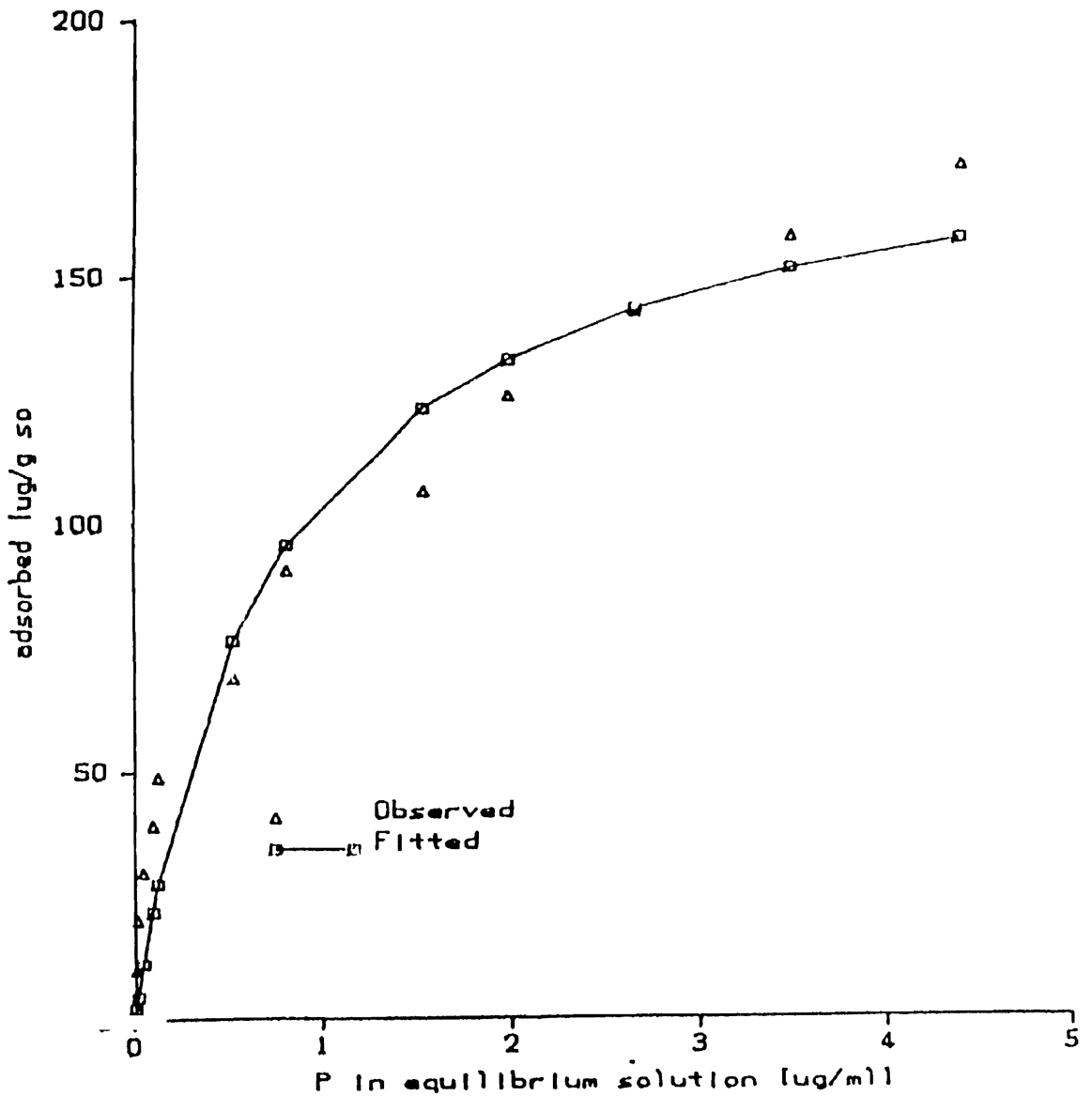


Fig. 6. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Langmuir is shown by continuous line with observed points for BR-1 (10 kg P ha<sup>-1</sup> applied in the previous season) soil.



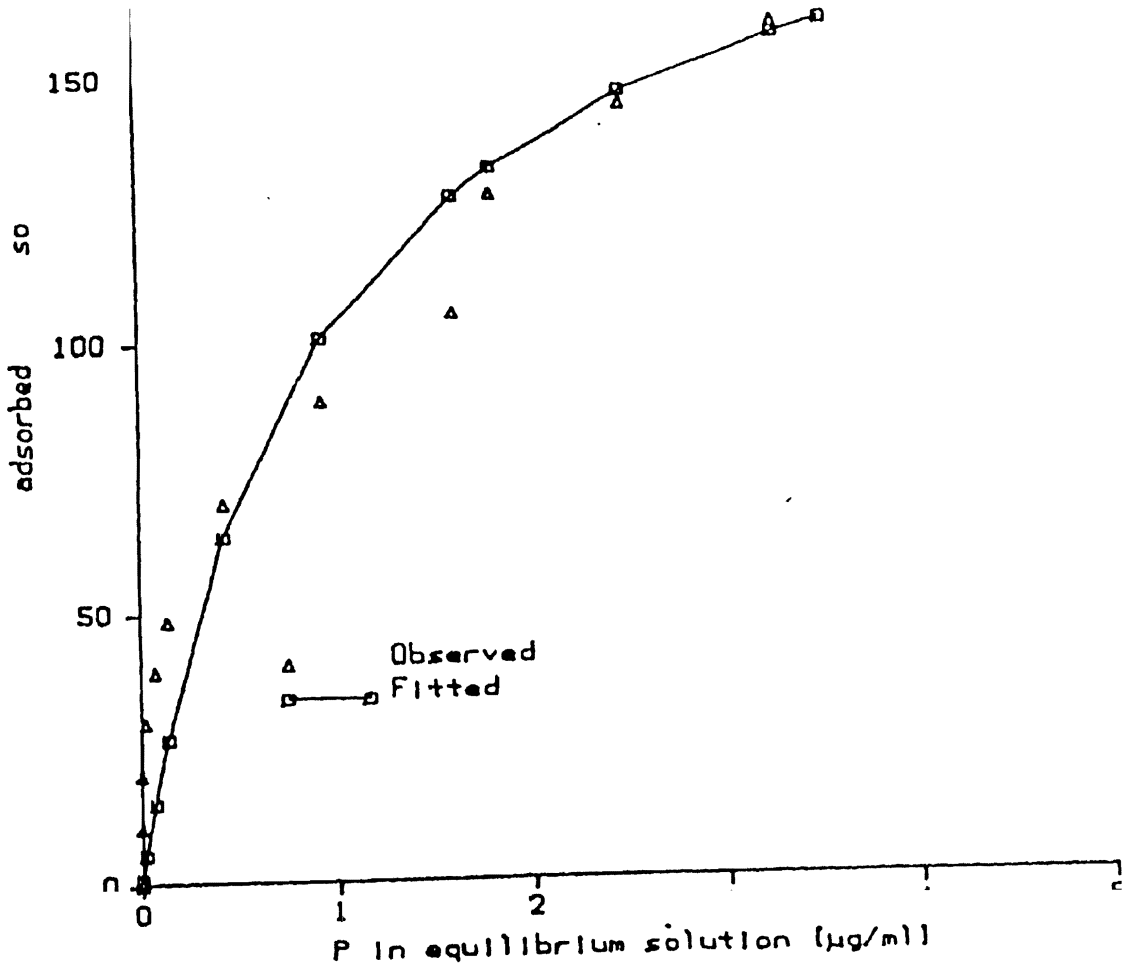


Fig. 7. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Langmuir is shown by continuous line with observed points for BR-1 (20 kg P ha<sup>-1</sup> applied in the previous season) soil.

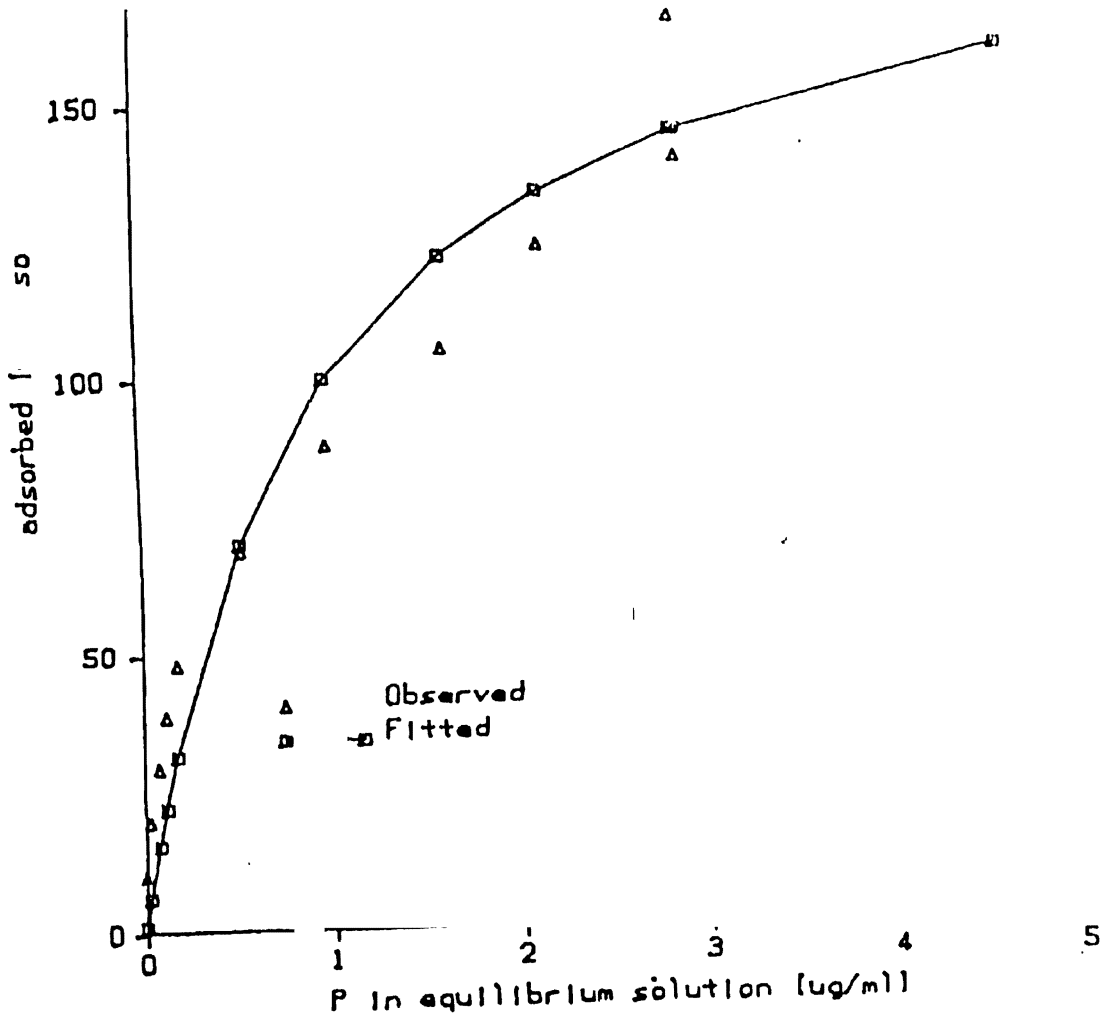


Fig. 8. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Langmuir is shown by continuous line with observed points for BR-1 (40 kg P ha<sup>-1</sup> applied in the previous season) soil.

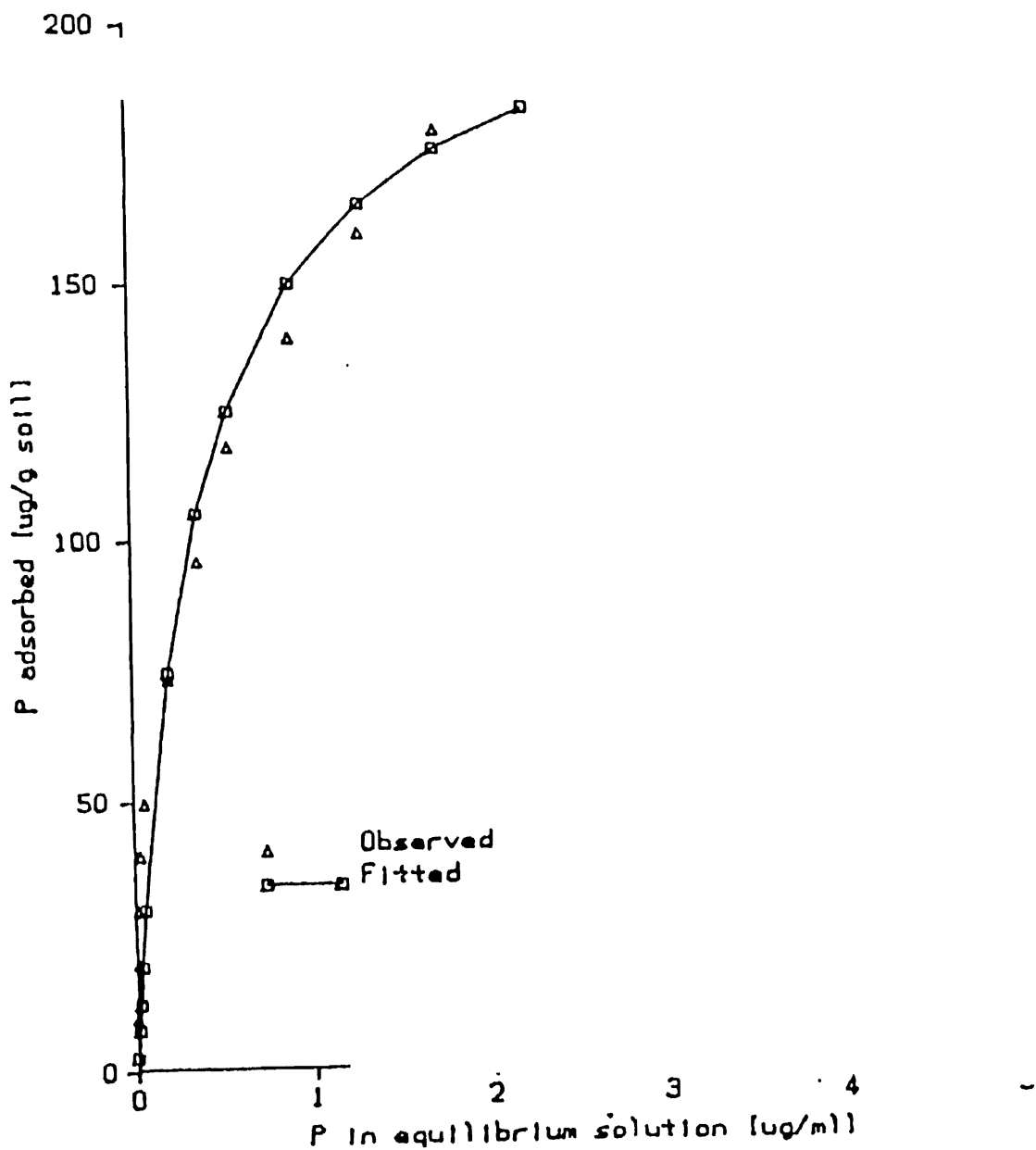


Fig. 9. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Langmuir is shown by continuous line with observed points for Barsi soil.

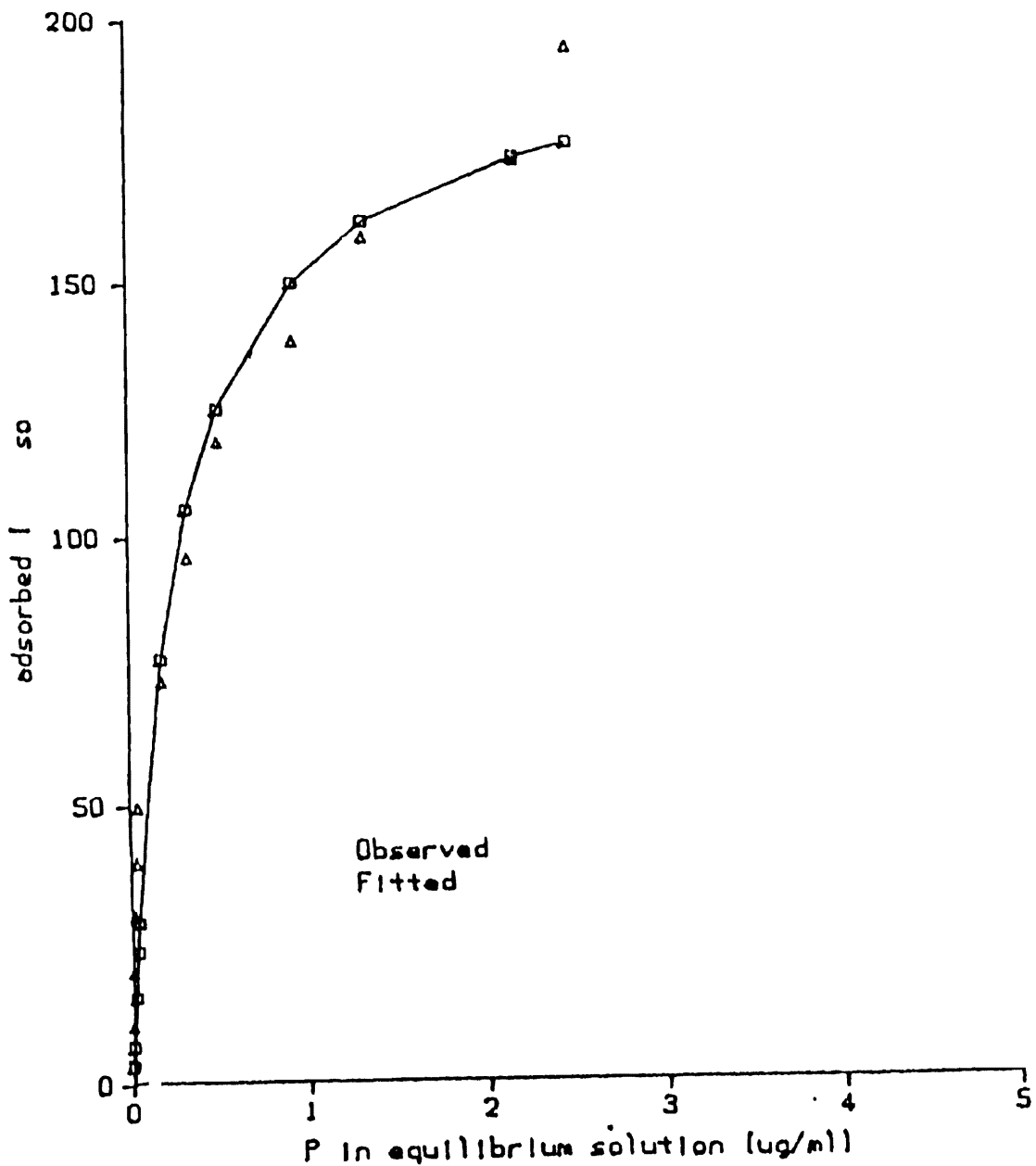


Fig. 10. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Langmuir is shown by continuous line with observed points for Begamganj soil.

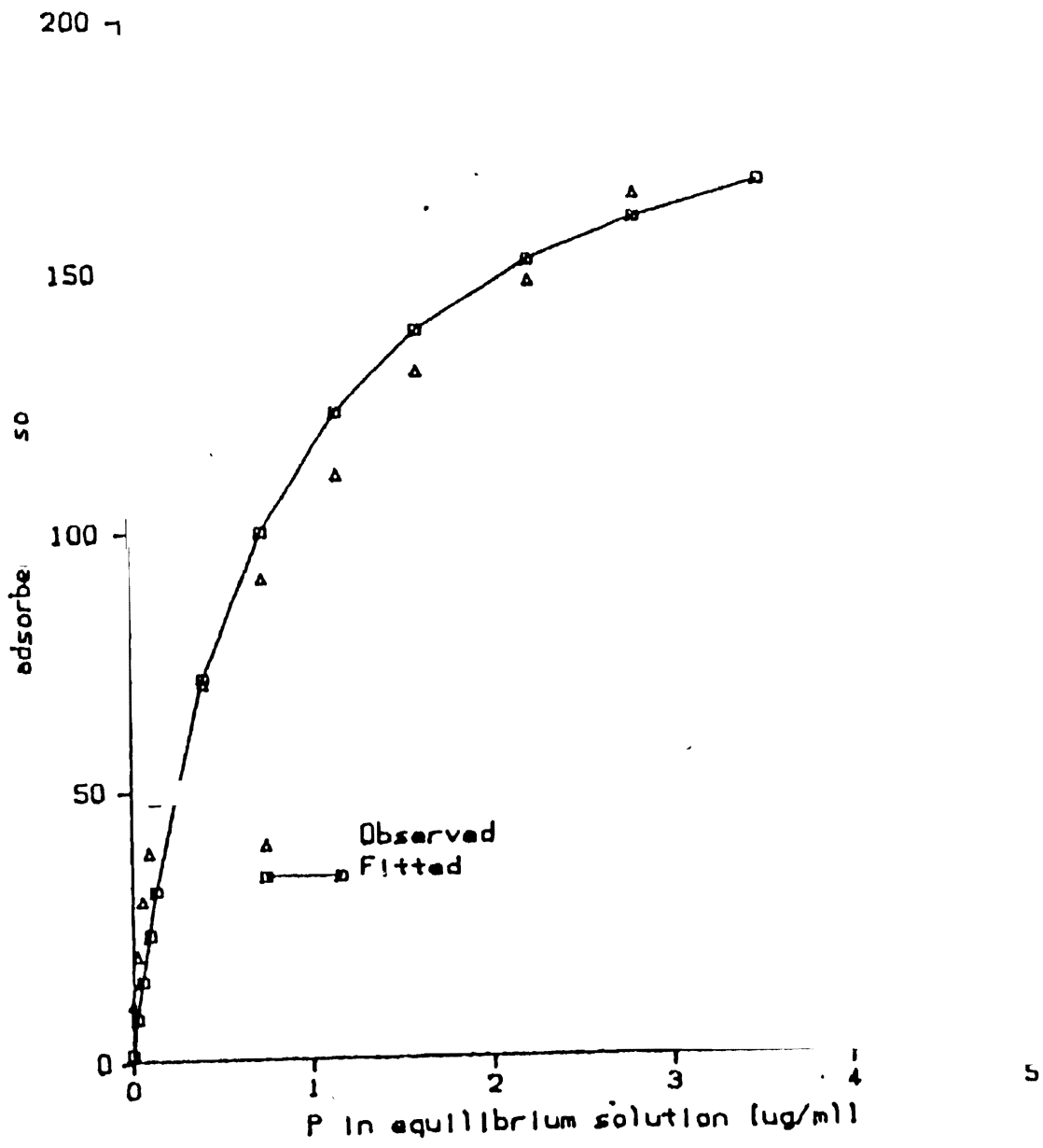


Fig. 11. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Langmuir is shown by continuous line with observed points for BW-6 soil.

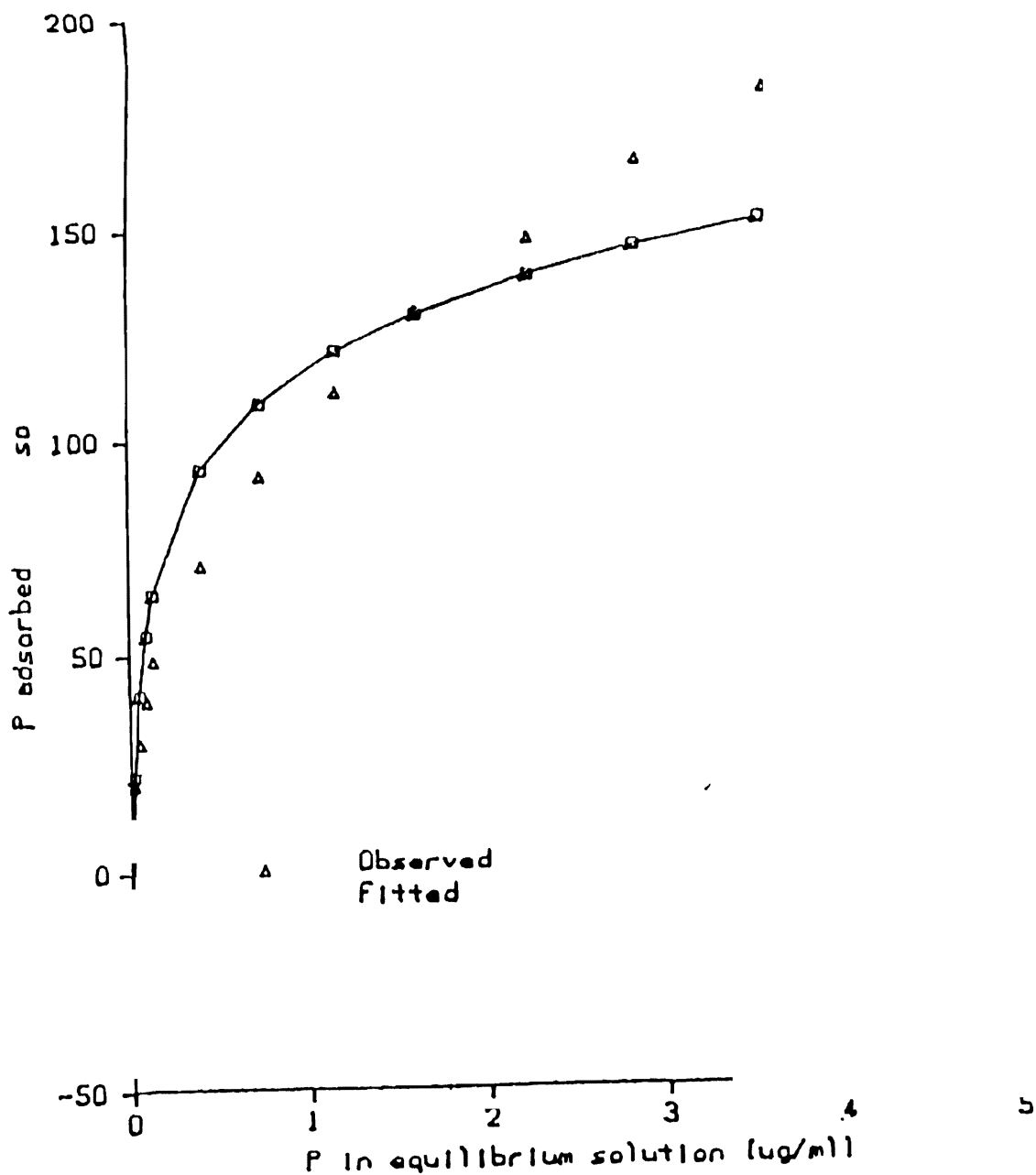


Fig. 12. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Tempkin is shown by continuous line with observed points for BW-6 soil.

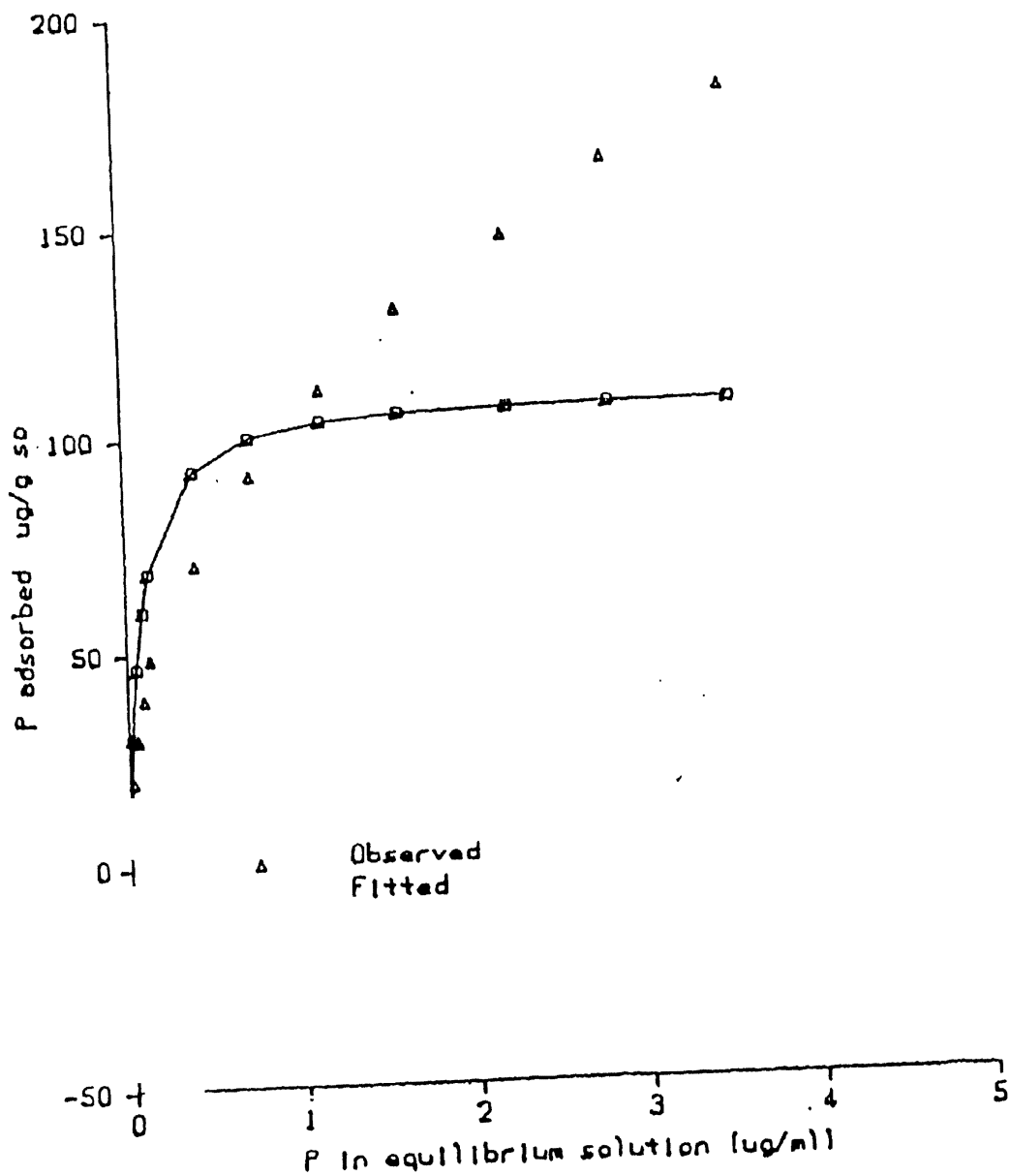


Fig. 13. Relationship between adsorbed P and P concentration in solution after adsorption, fitted isotherm according to Dubinin-Rodushkevich is shown by continuous line with observed points for BW-6 soil.

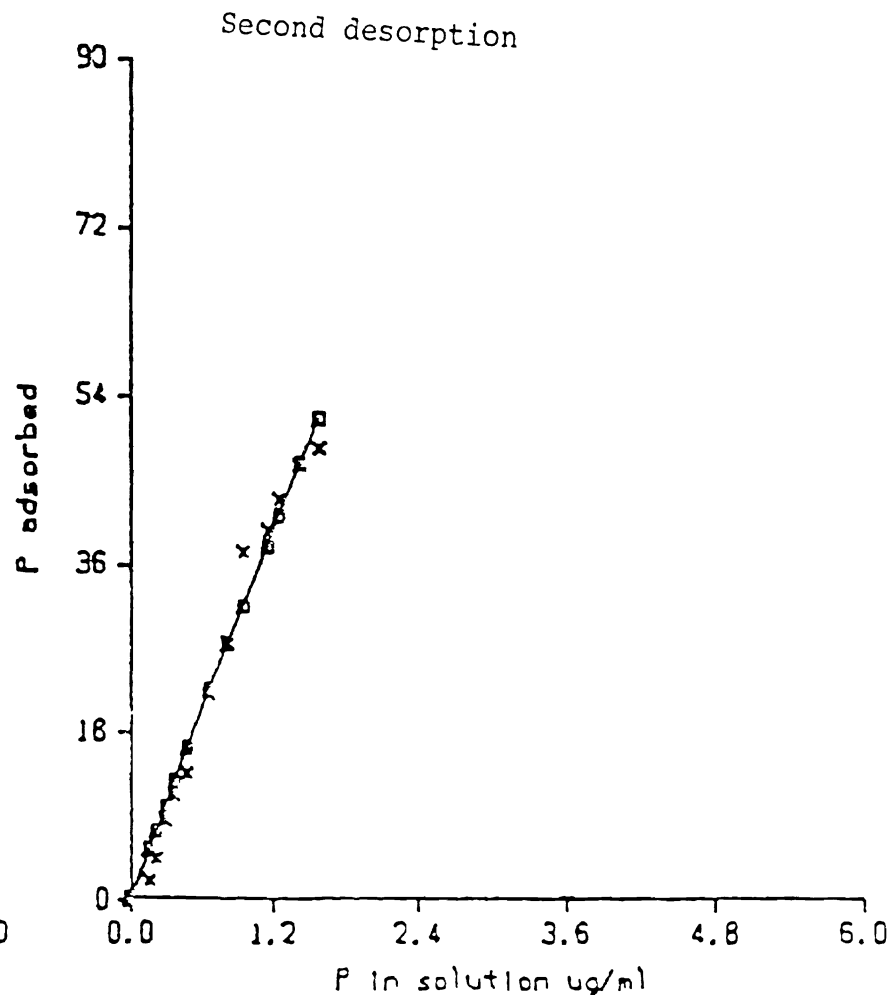
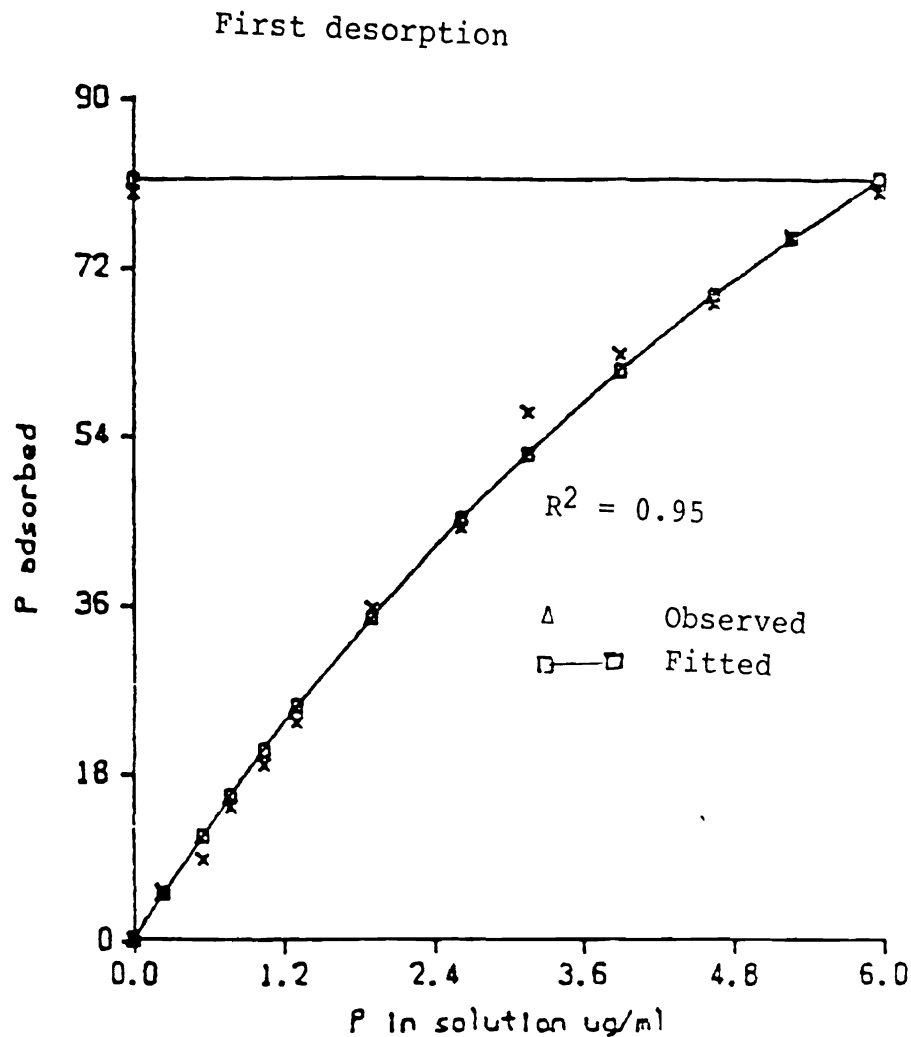


Fig. 14. Relationship between adsorbed P and P concentration in solution after first and second desorption by Olsen's extractant, fitted isotherm according to Langmuir is shown by continuous line with observed points for Begamganj soil.



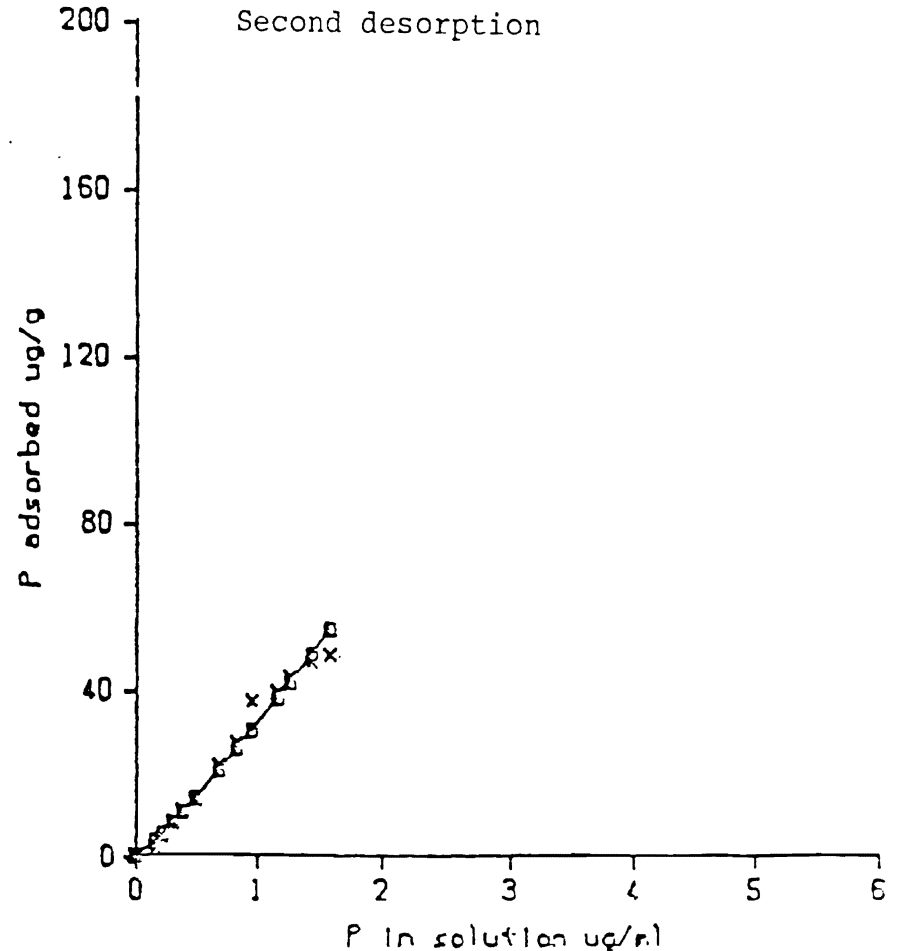
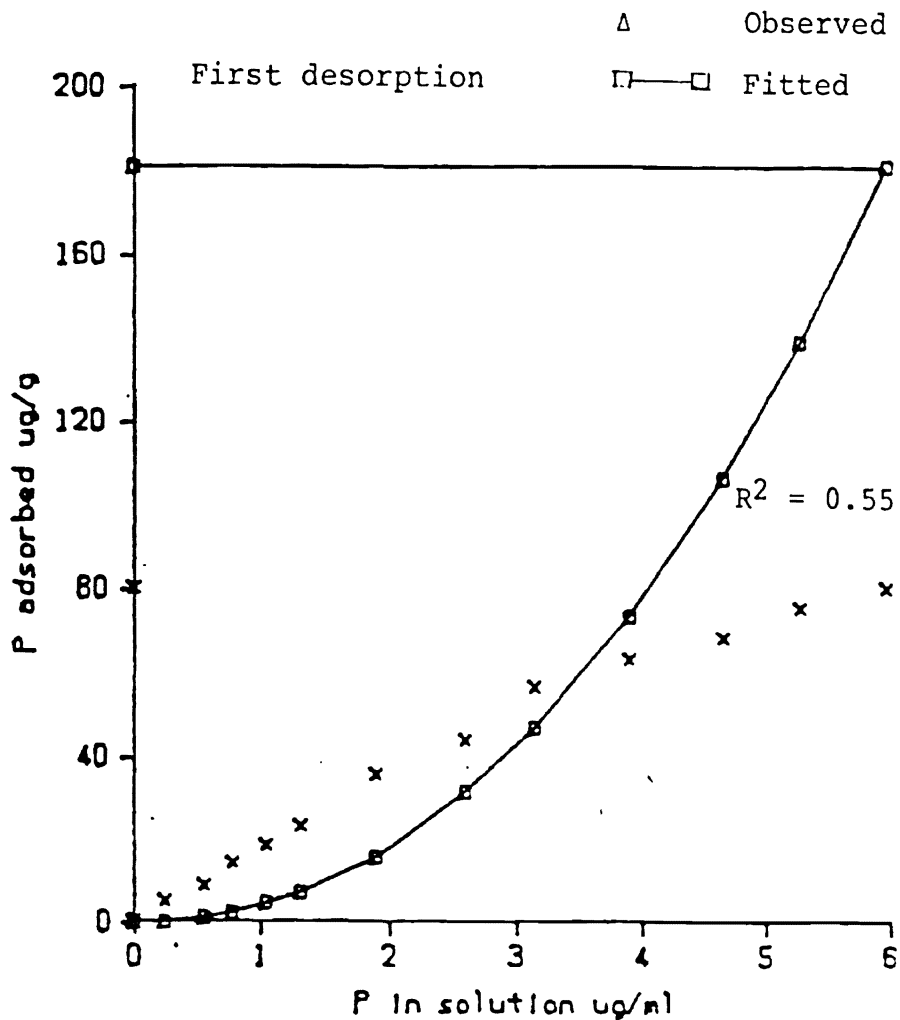


Fig. 15. Relationship between adsorbed P and P concentration in solution after first and second desorptions by Olsen's extractant, fitted isotherm according to Freundlich is shown by continuous line with observed points for Begamganj soil.

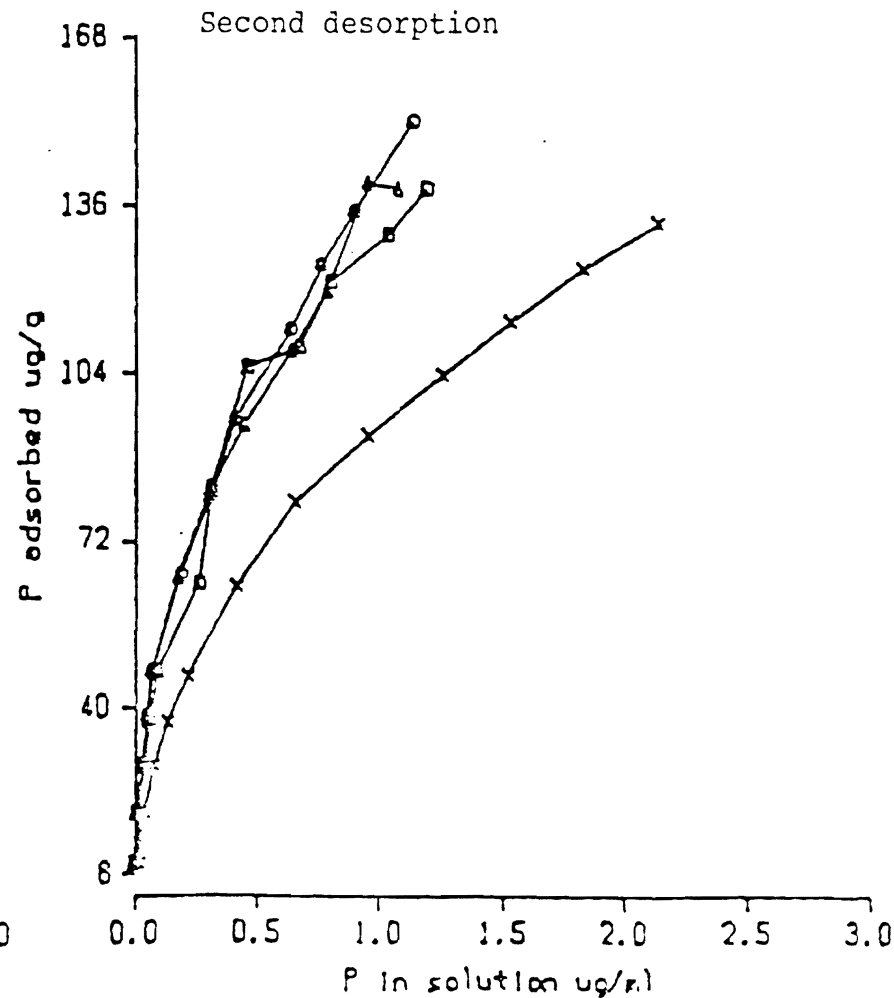
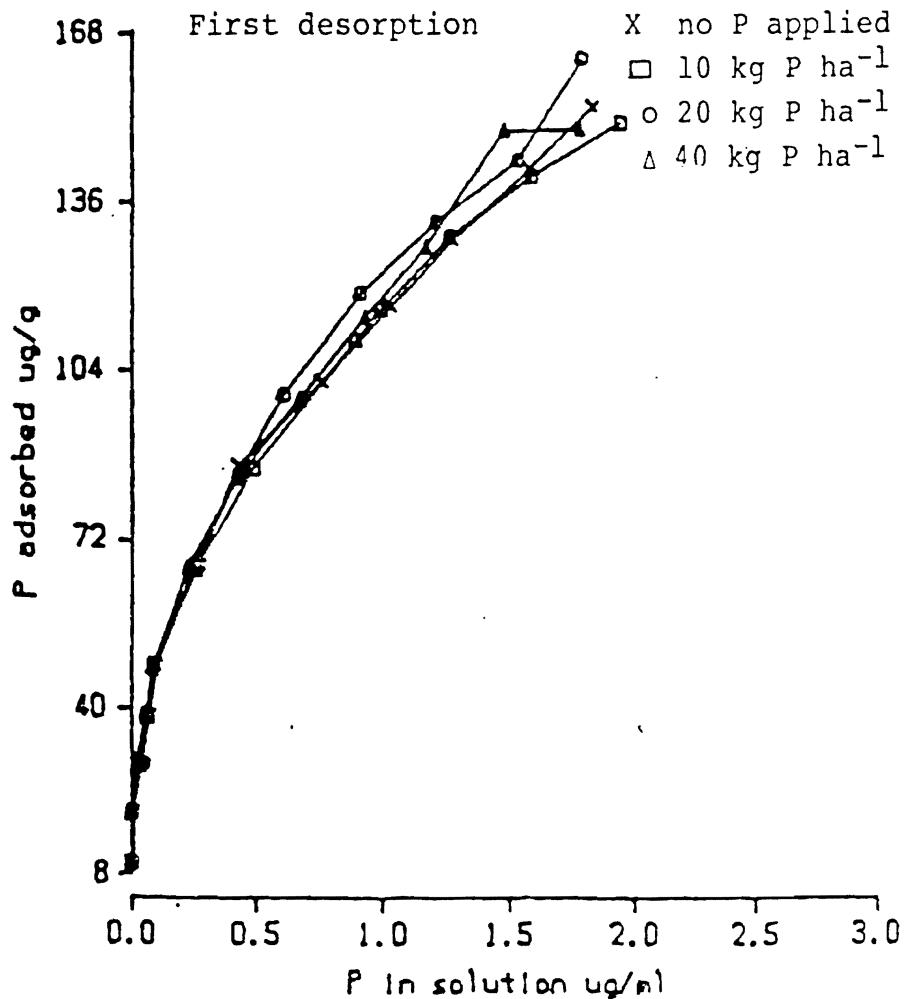


Fig. 16. Relationship between adsorbed P and P concentration in solution after first and second desorptions by calcium chloride for BR-1 soil with different P fertilization backgrounds.

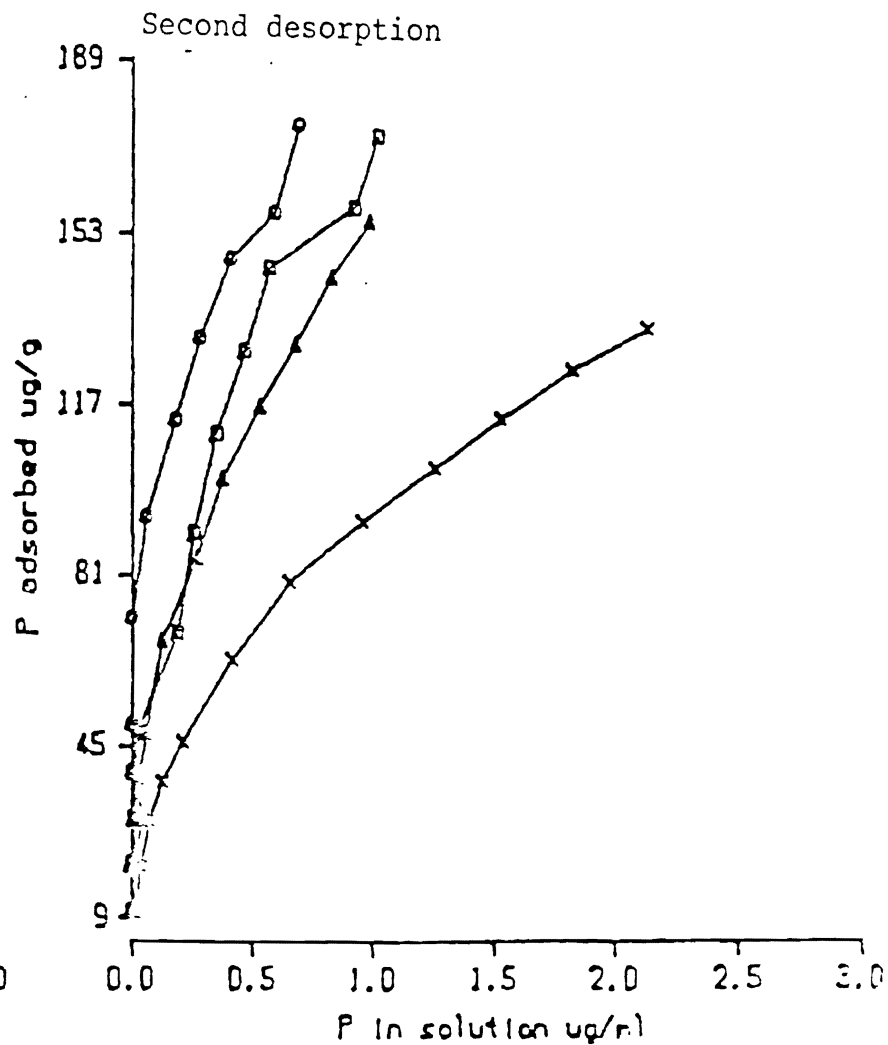
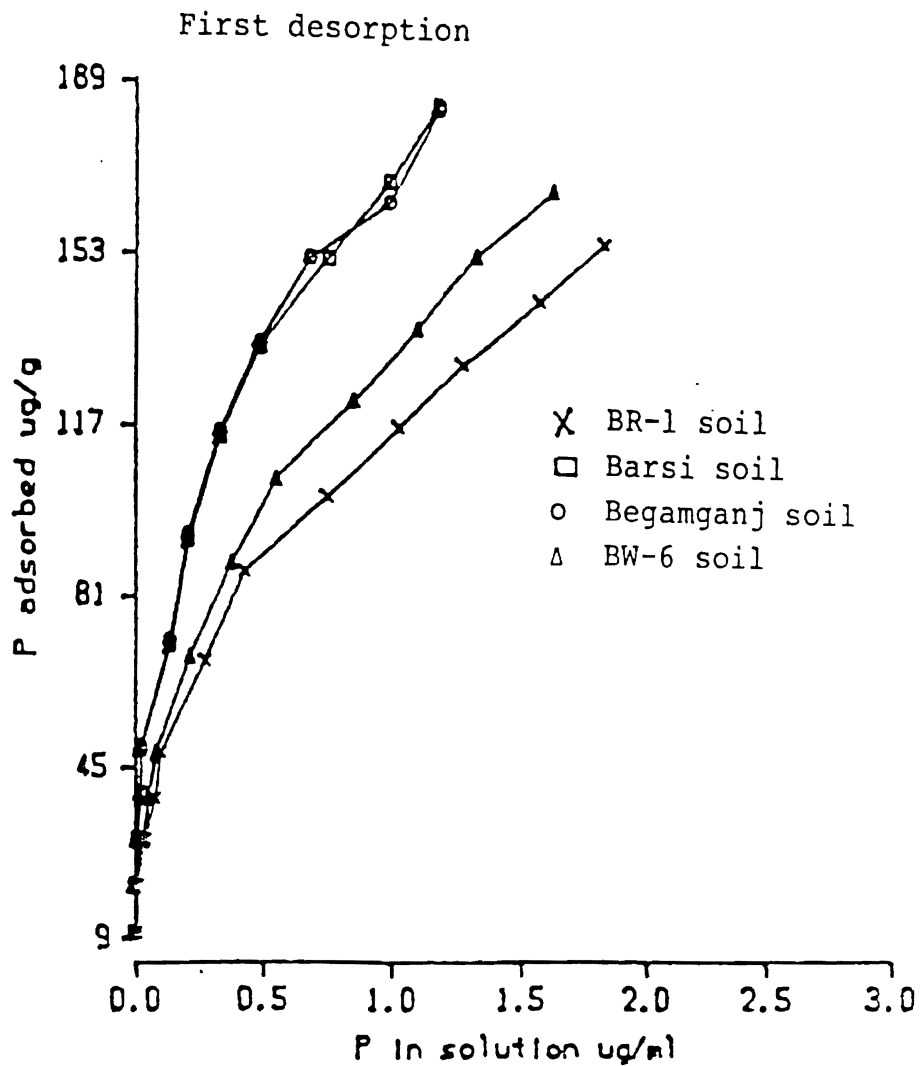


Fig. 17. Relationship between adsorbed P and P concentration in solution after first and second desorptions by calcium chloride for selected Vertisols.

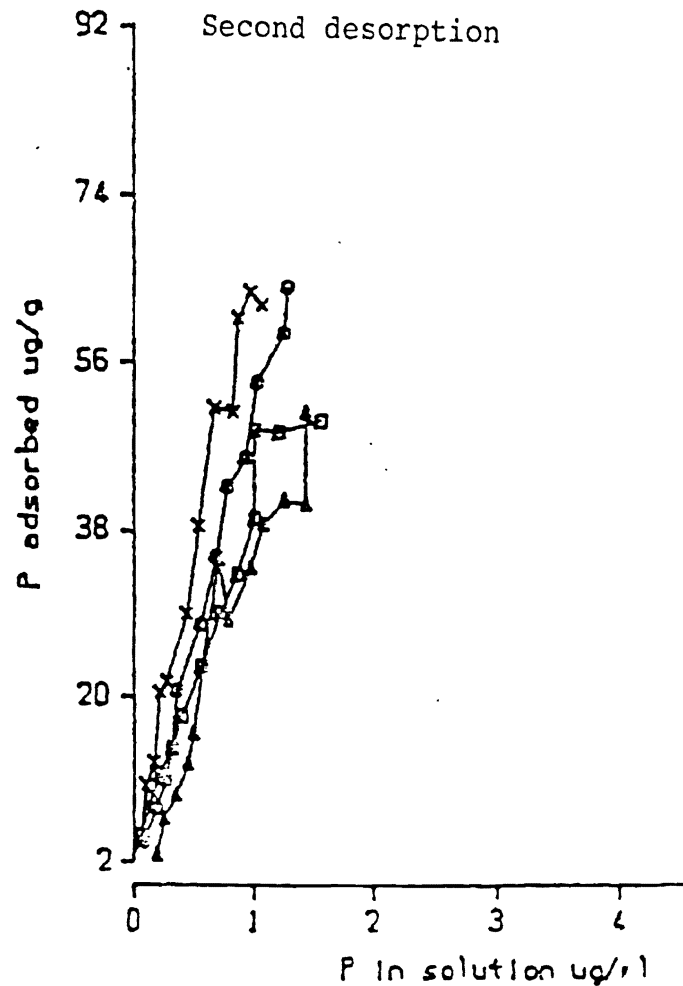
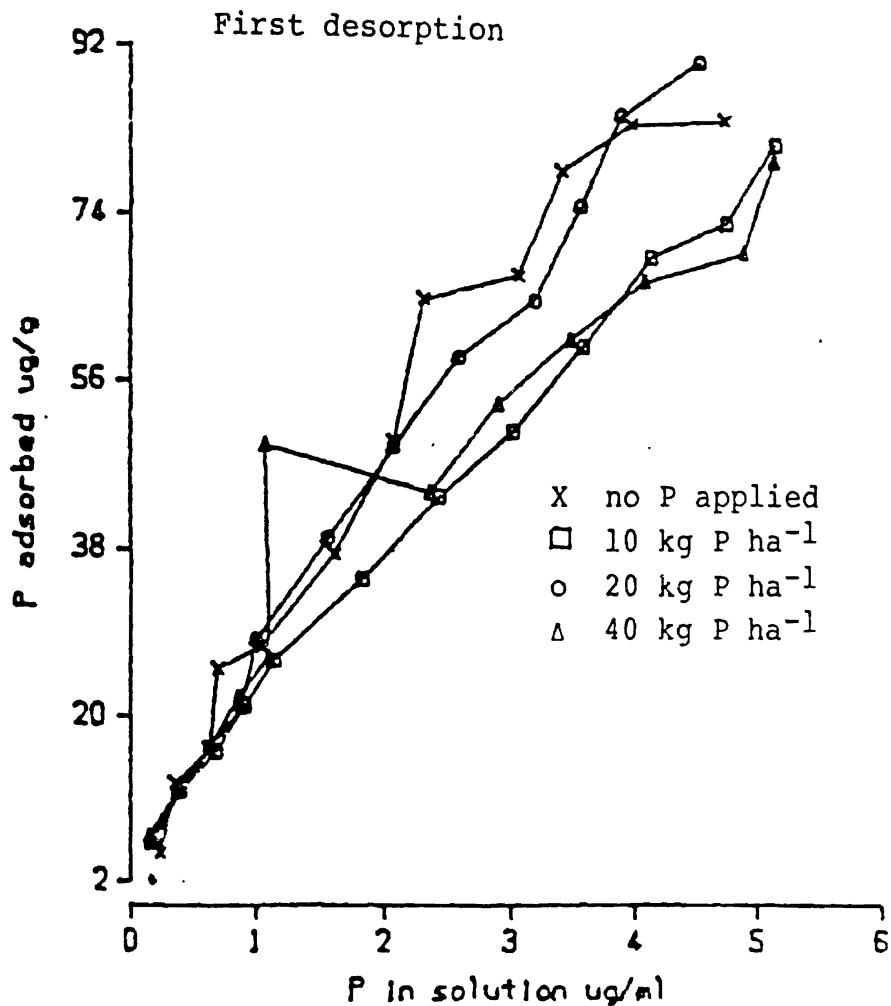


Fig. 18. Relationship between adsorbed P and P concentration in solution after first and second desorptions by sodium bicarbonate for BR-1 soil with different P fertilizatic backgrounds.

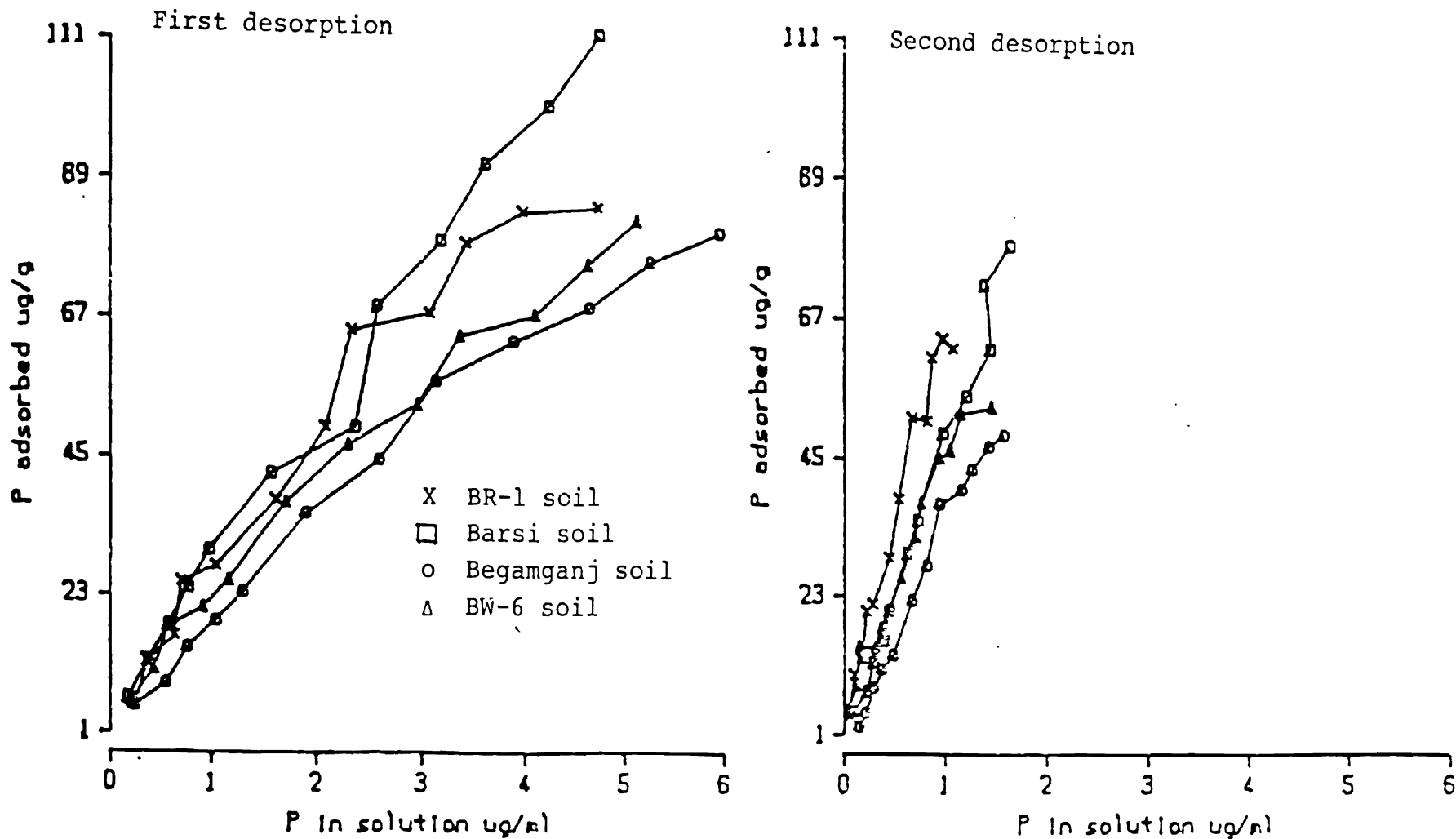


Fig. 19. Relationship between adsorbed P and P concentration in solution after first and second desorptions by sodium bicarbonate for selected Vertisols.

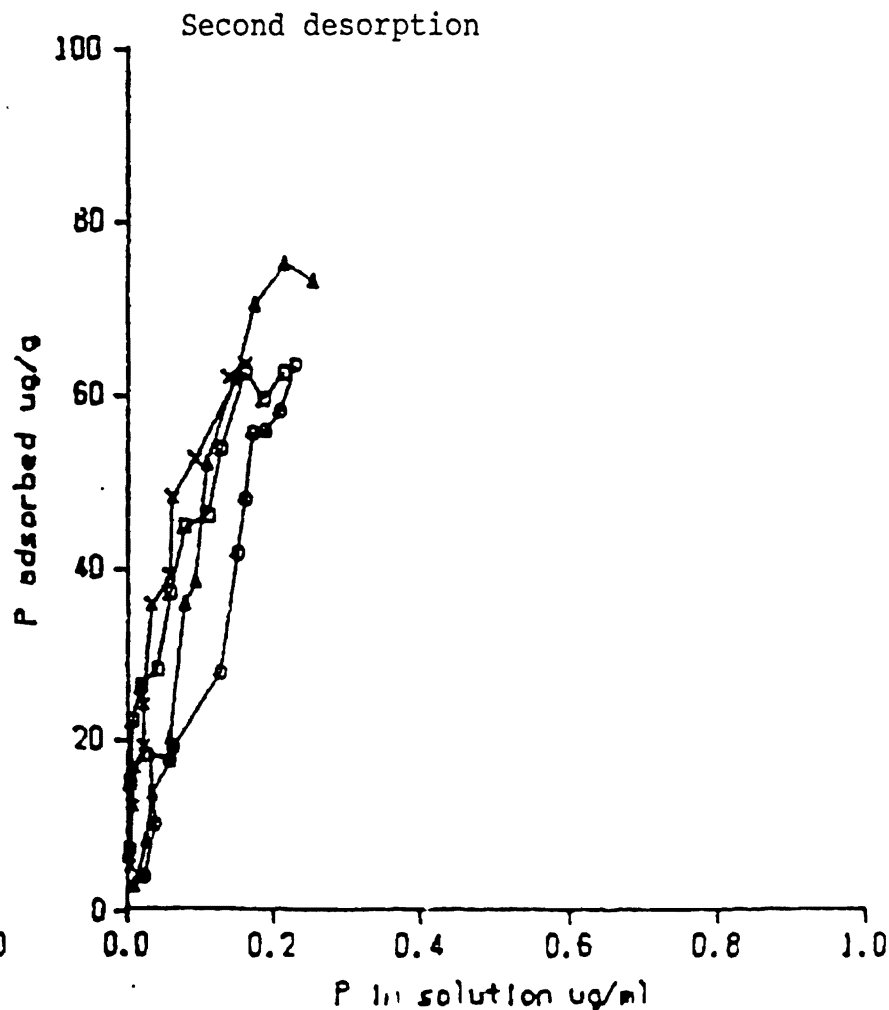
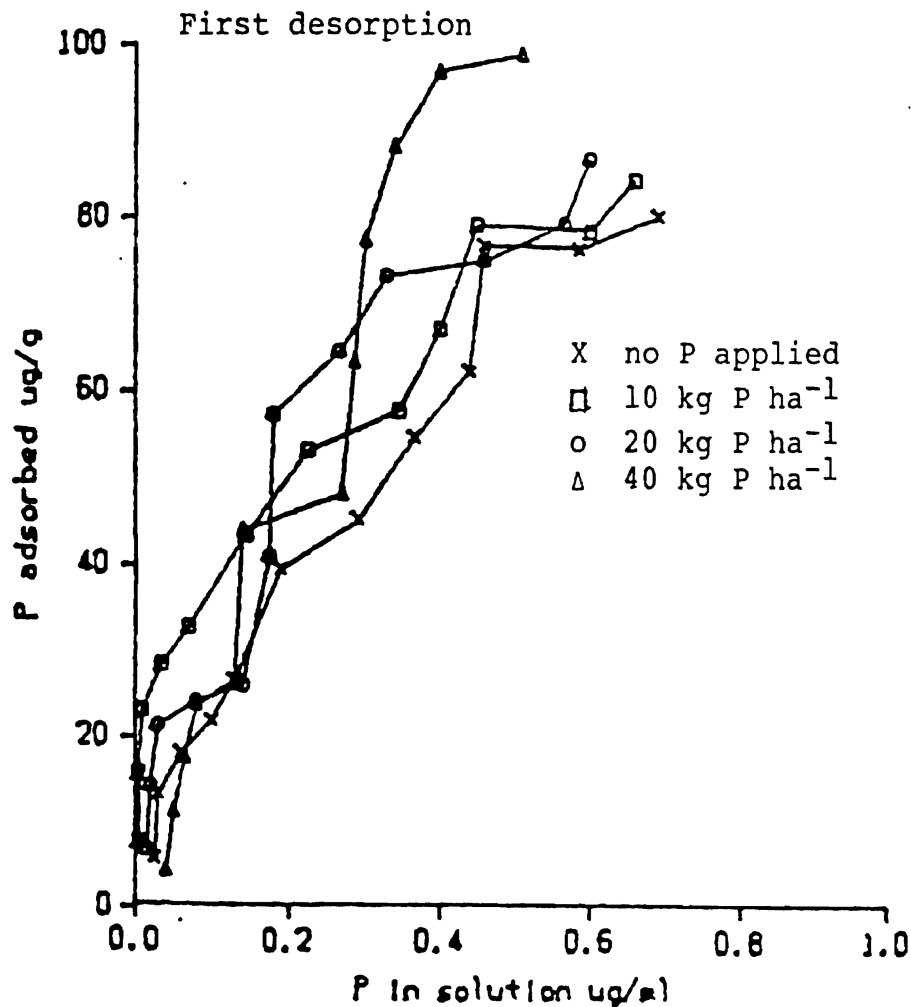


Fig. 20. Relationship between adsorbed P and P concentration in solution after first and second desorptions by electro-ultrafiltration (200 V, 20°C) for BR-1 soil with different P fertilization backgrounds.

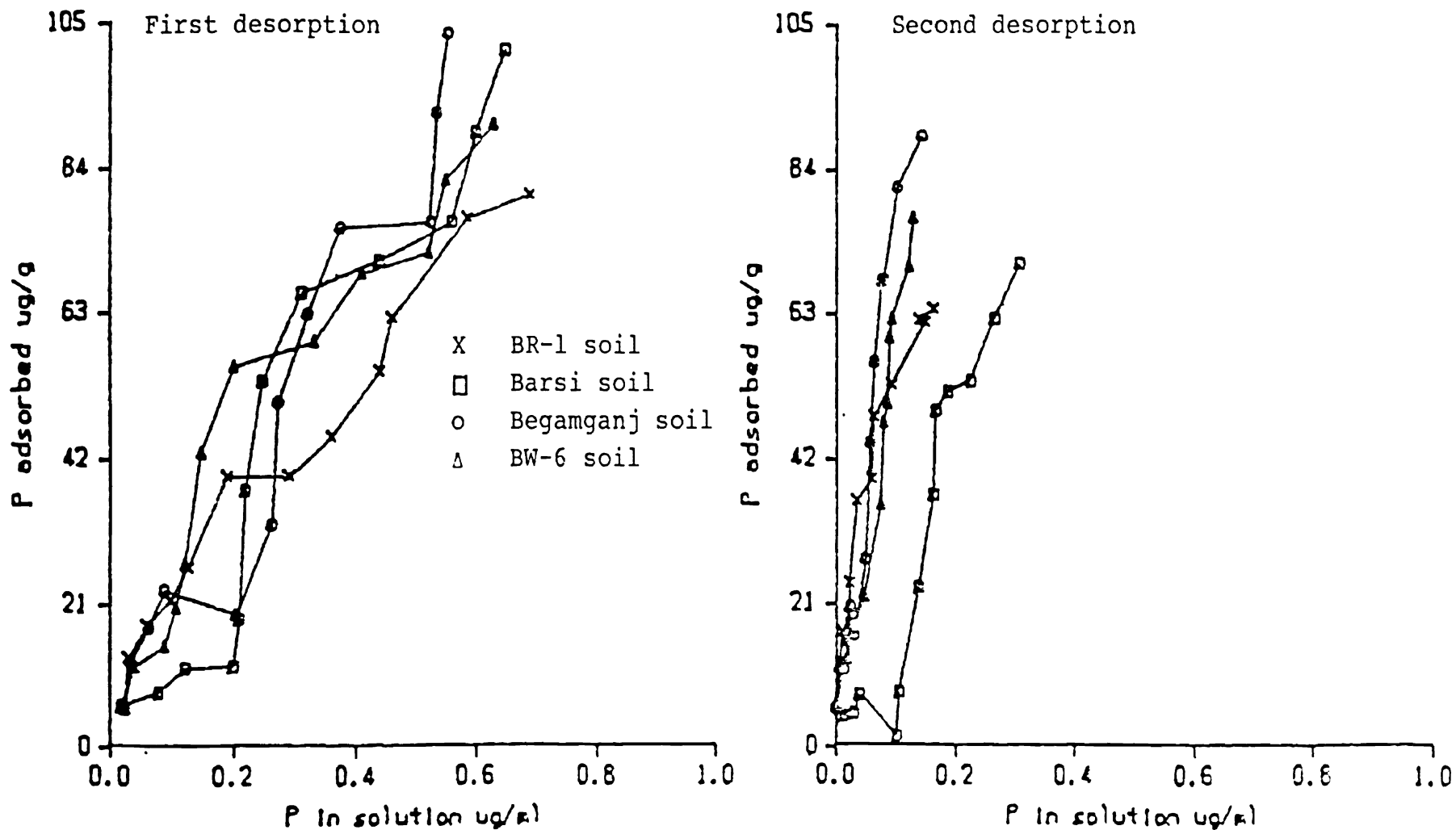


Fig. 21. Relationship between adsorbed P and P concentration in solution after first and second desorptions by electro-ultrafiltration (200 V, 20°C) for selected Vertisols.

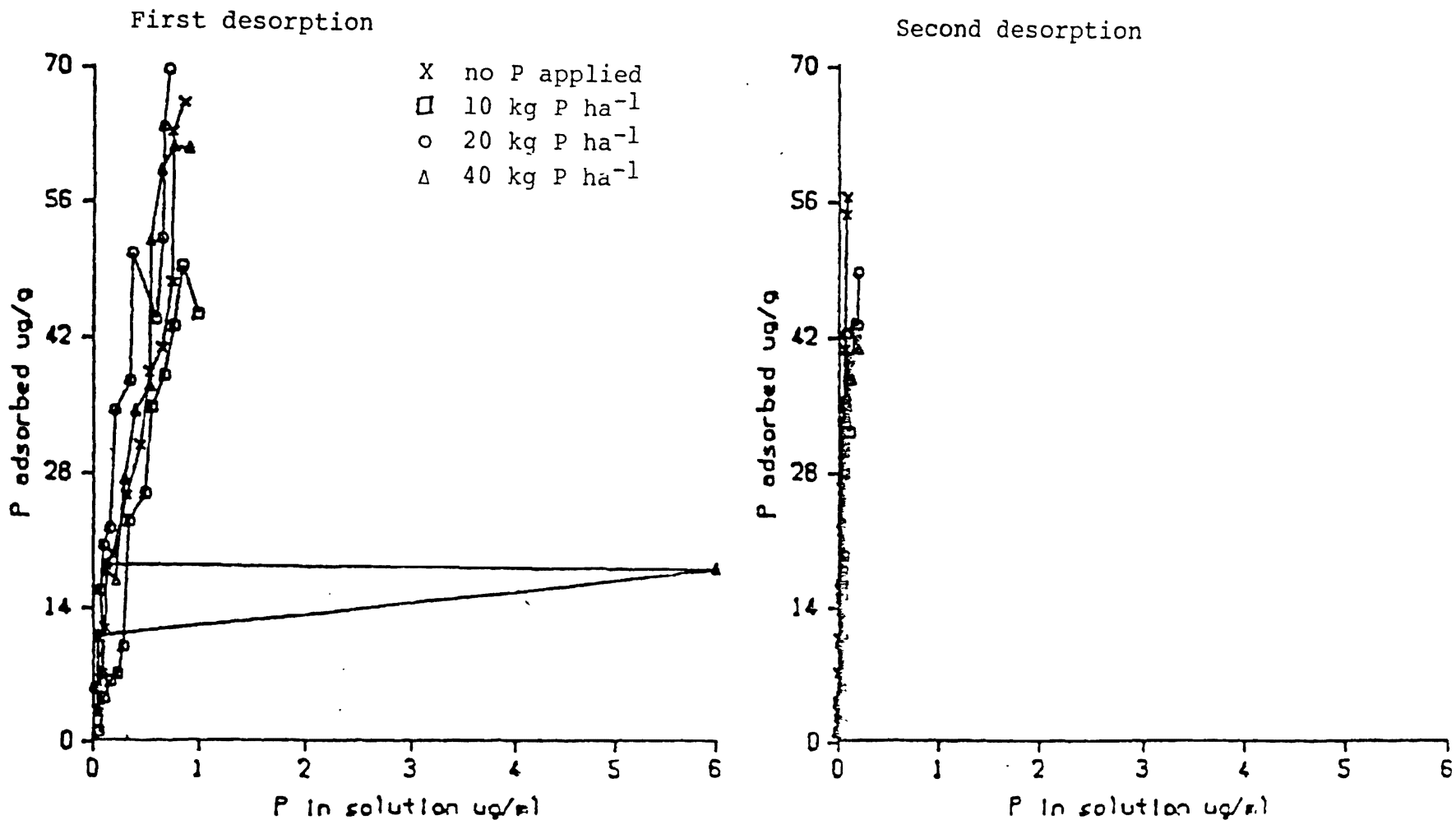


Fig. 22. Relationship between adsorbed P and P concentration in solution after first and second desorptions by electro-ultrafiltration (400 V, 80°C) for BR-1 soil with different P fertilization backgrounds.



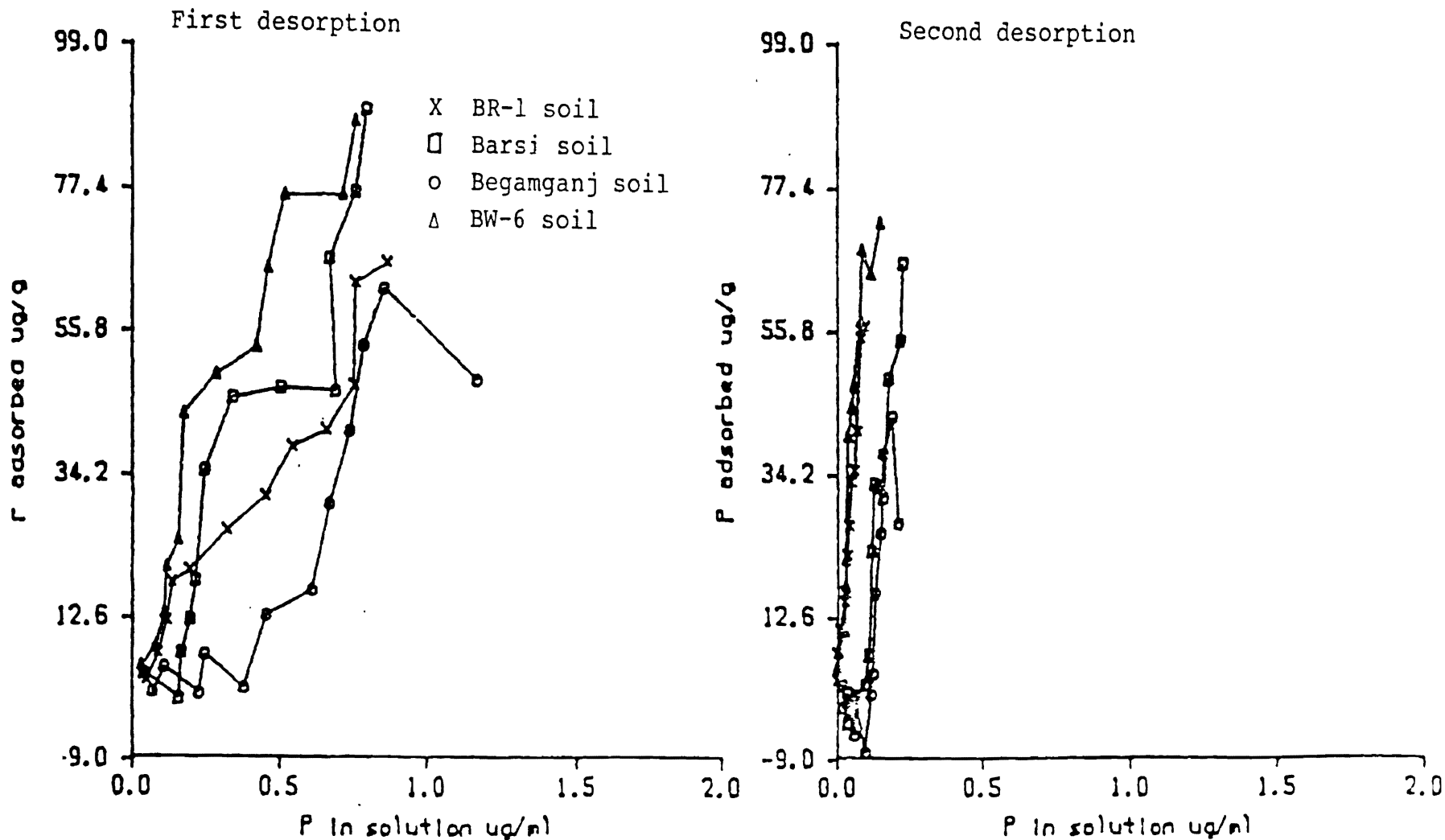
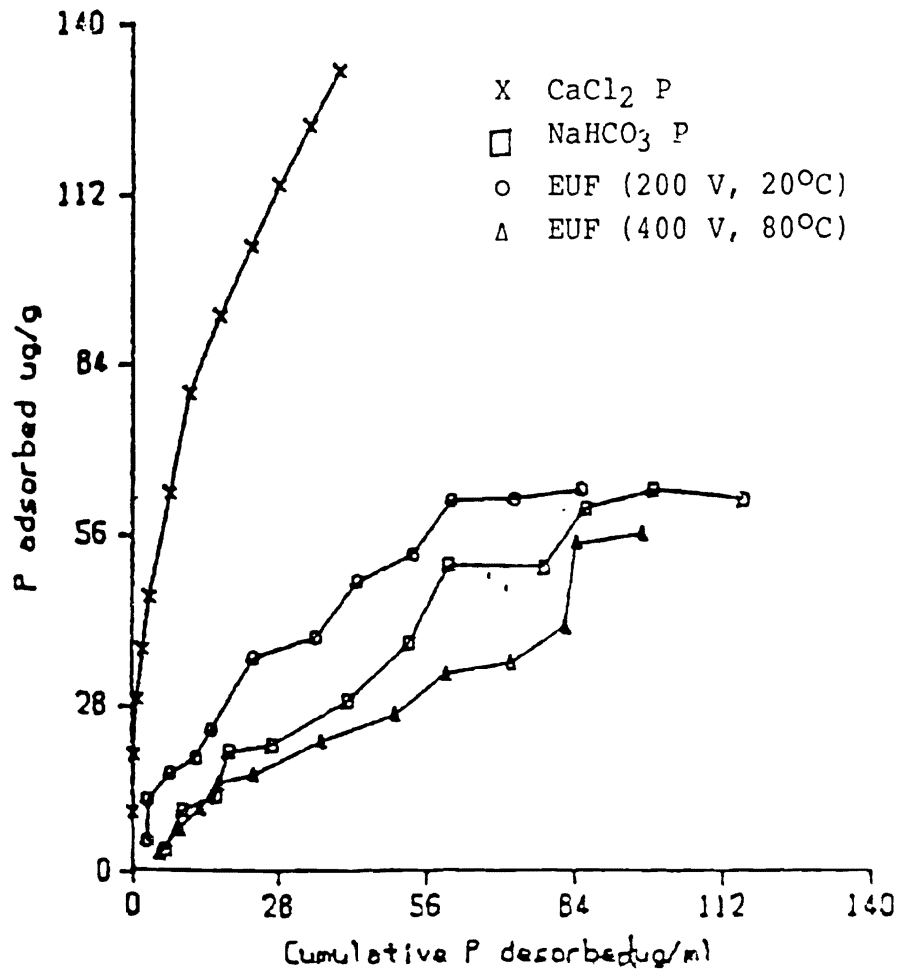


Fig. 23. Relationship between adsorbed P and P concentration in solution after first and second desorptions by electro-ultrafiltration (400 V, 80°C) for selected Vertisols.

BR-1 (no applied P) soil



BR-1 (10 kg P ha<sup>-1</sup>) soil

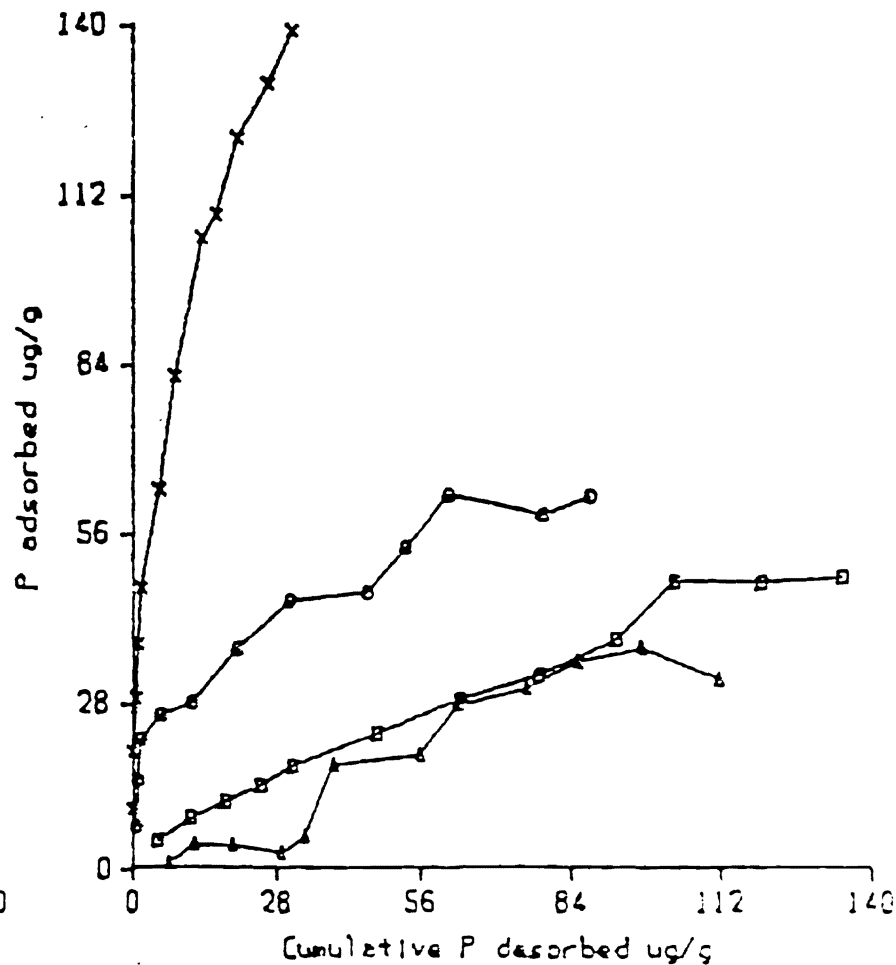
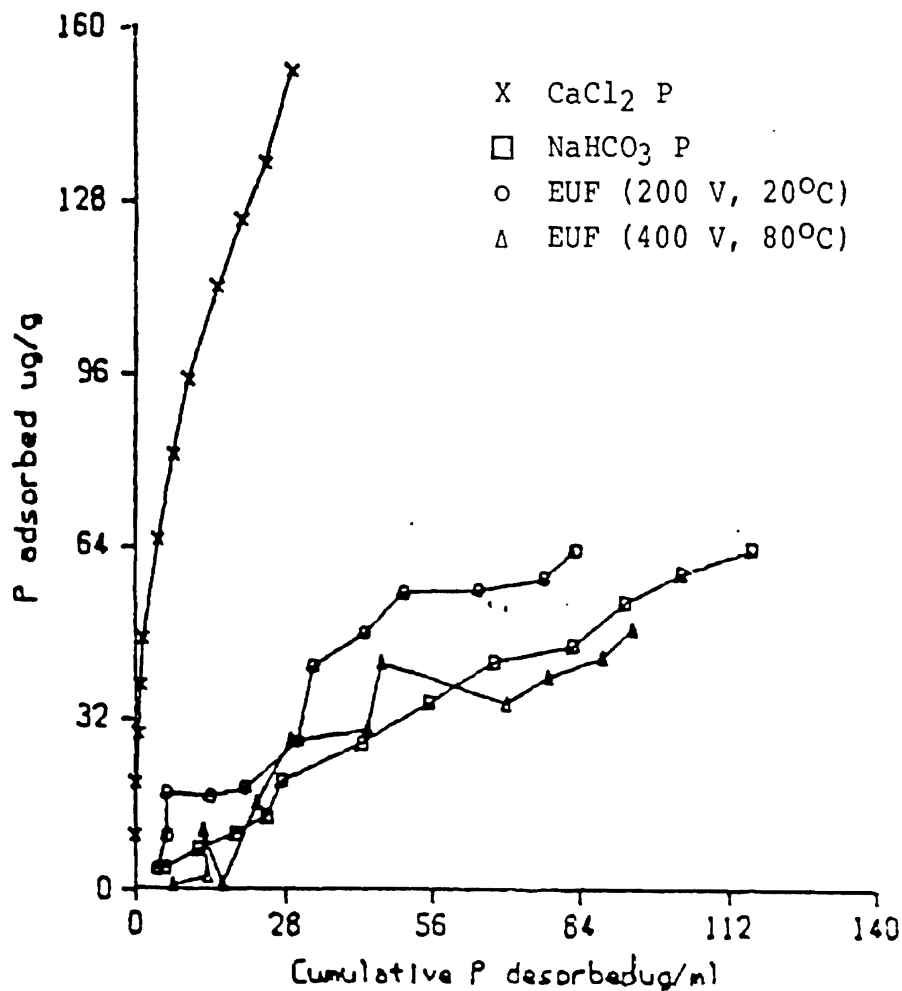


Fig. 24. Relationship between cumulative P desorbed and P concentration in solution after two desorptions by two extractants and electro-ultrafiltration.

BR-1 (20 kg P ha<sup>-1</sup>) soil



BR-1 (40 kg P ha<sup>-1</sup>) soil

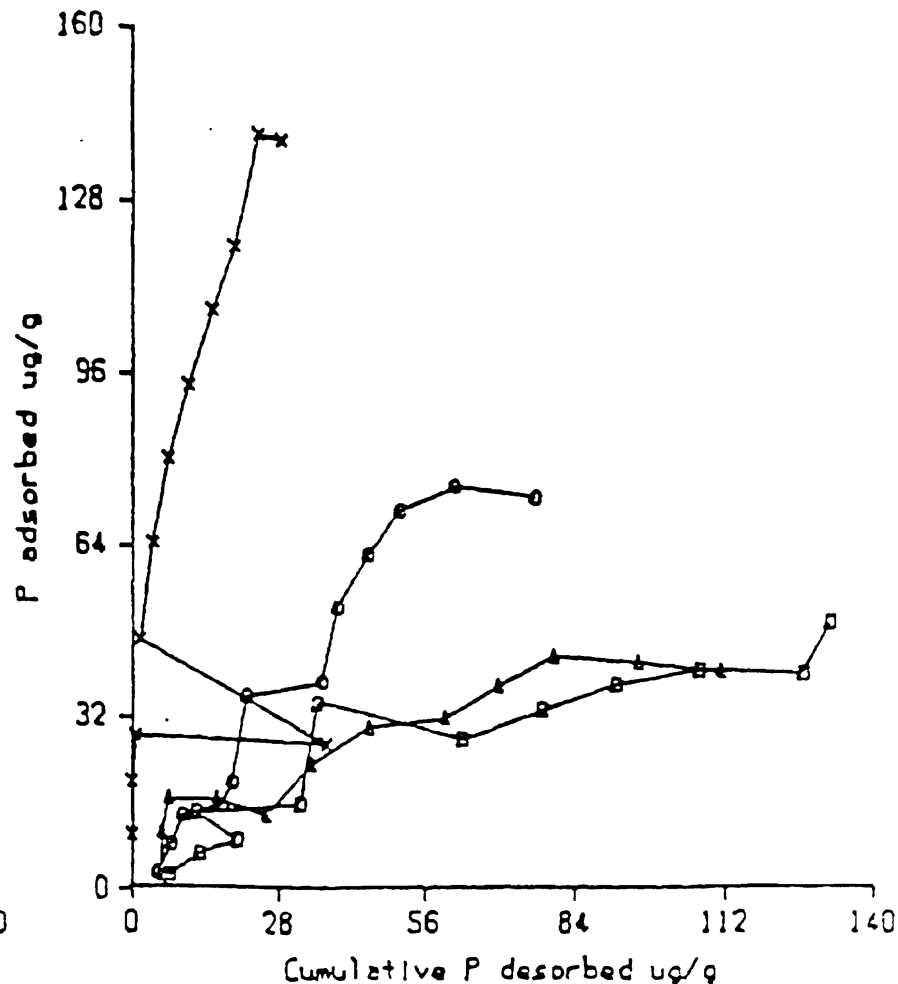
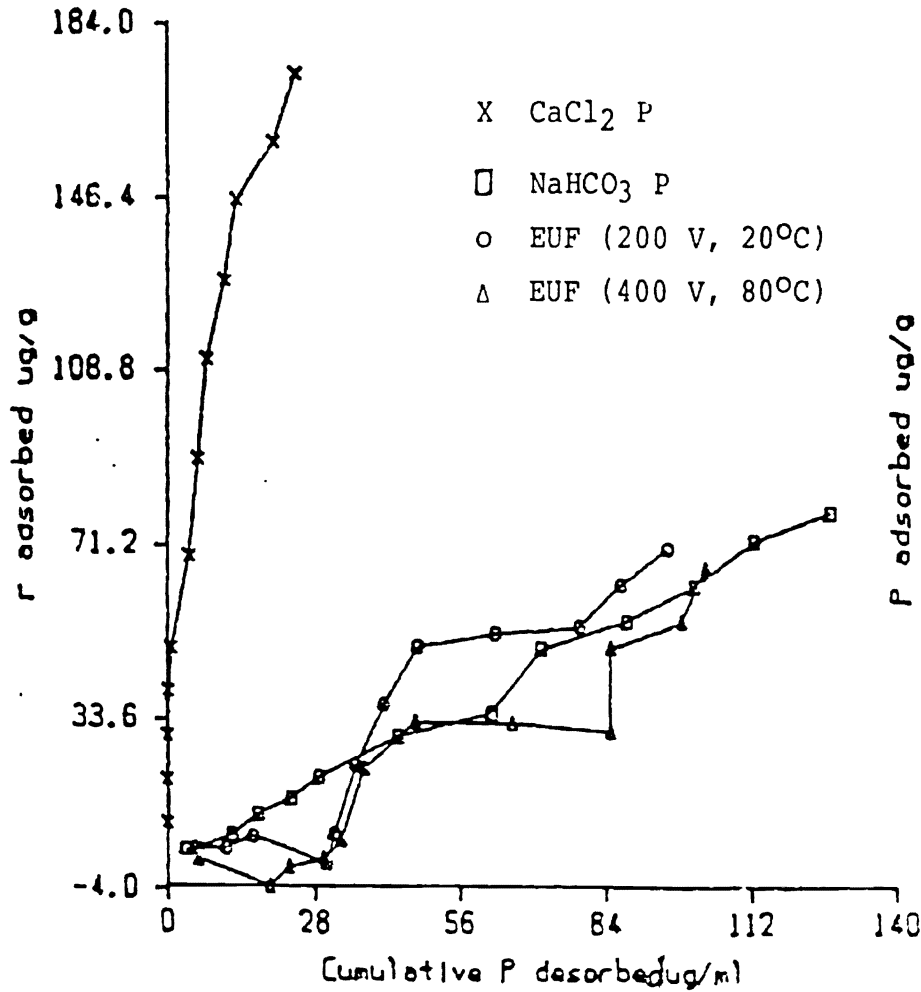


Fig. 25. Relationship between cumulative P desorbed and P concentration in solution after two desorptions by two extractants and electro-ultrafiltration.

BR-1 soil



Barsi soil

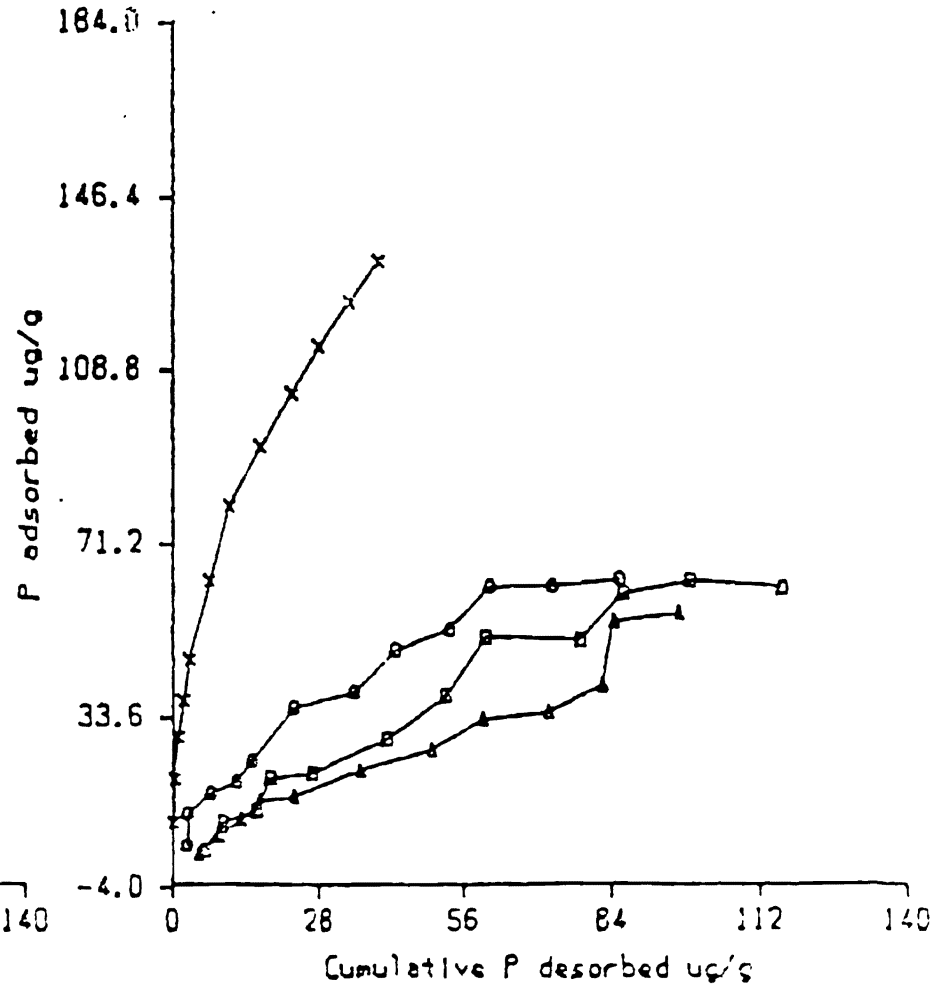
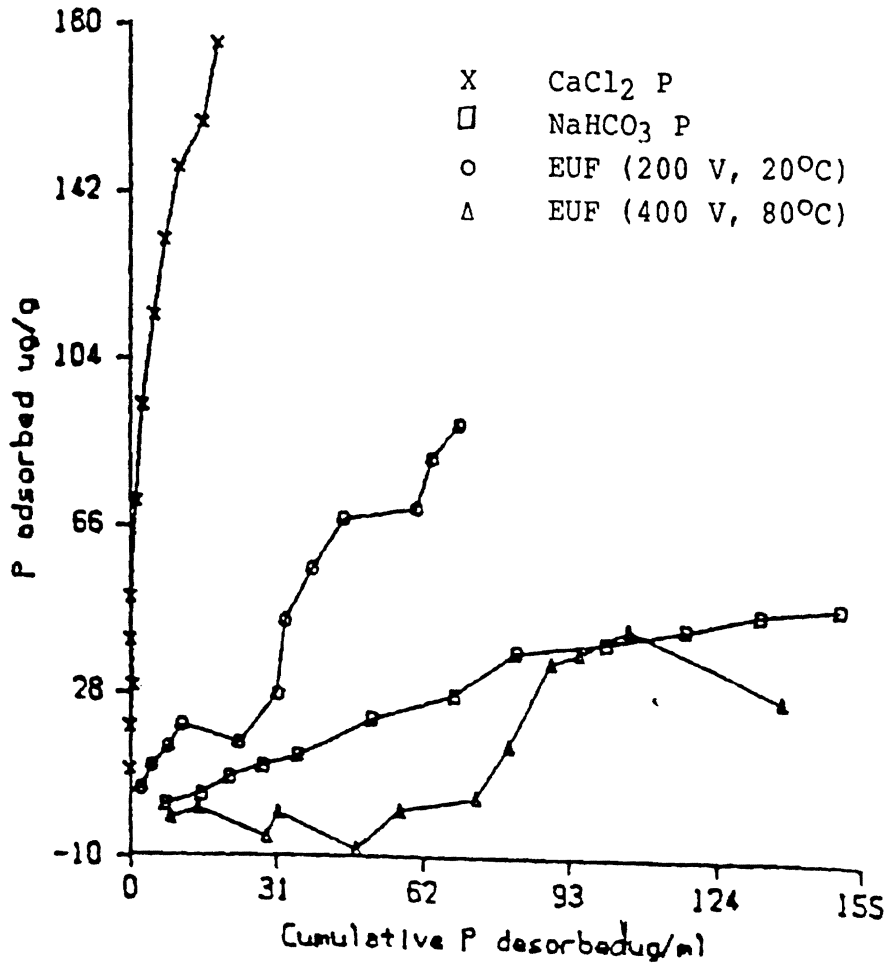


Fig. 26. Relationship between cumulative P desorbed and P concentration in solution after two desorptions by two extractants and electro-ultrafiltration.

Begamganj soil



BW-6 soil

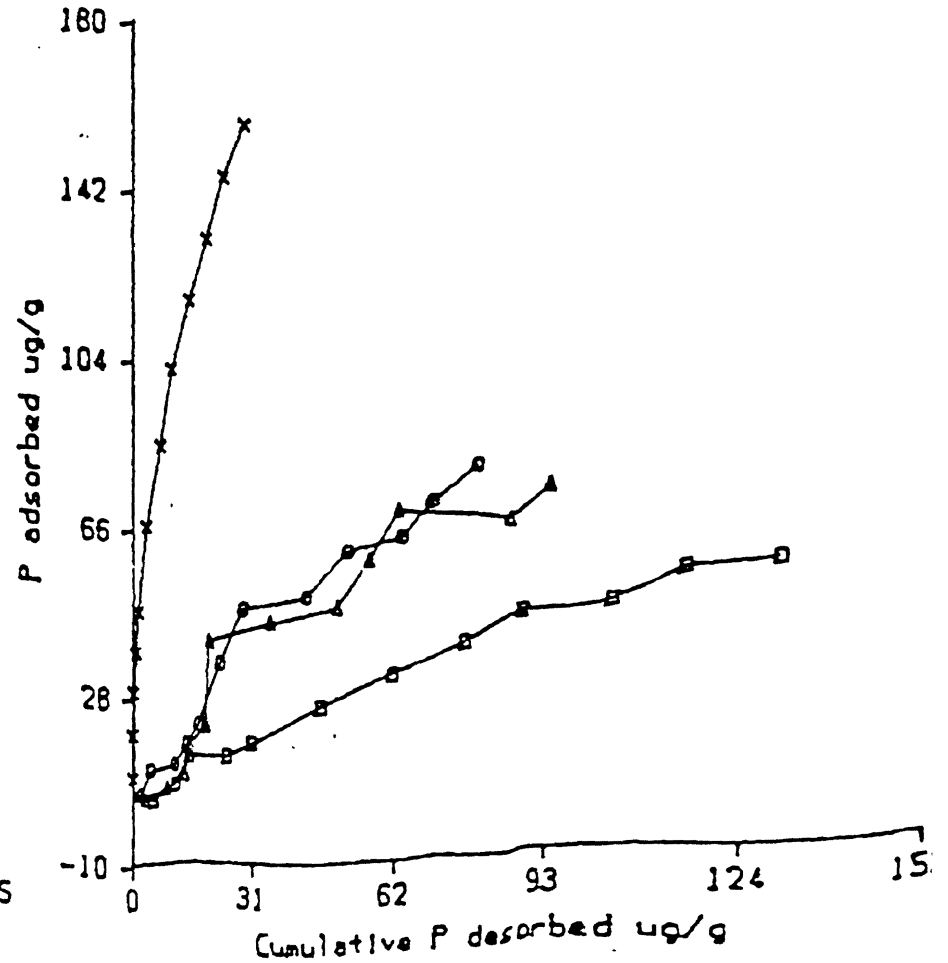


Fig. 27. Relationship between cumulative P desorbed and P concentration in solution after two desorptions by two extractants and electro-ultrafiltration.

Appendix A: The coefficient of determination ( $R^2$ ) indicating the goodness of fit according to two adsorption isotherms for the soils using ammonium polyphosphate as source of P.

Soil No.	Freundlich equation	Langmuir equation
1a	0.41	0.87
1b	0.47	0.98
1c	0.43	0.98
1d	0.35	0.98
2	0.46	0.99
3	0.07	0.98
4	0.07	0.98

Appendix B:  $R^2$  values showing the goodness of fit according to Freundlich equation for I and II desorptions of adsorbed phosphate in the soils.

Soil No.	CaCl <sub>2</sub> extraction		NaHCO <sub>3</sub> extraction		EUF (200 V, 20°C) extraction		EUF (400 V, 80°C) extraction	
	II	I	II	I	II	I	II	
1a	0.82	0.83	0.73	0.61	0.12	0.19	0.50	0.16
1b	0.87	0.86	0.45	0.60	0.17	0.18	0.97	0.90
1c	0.84	0.68	0.85	0.93	0.16	0.11	0.09	0.16
1d	0.91	0.54	0.76	0.92	0.15	0.18	0.14	0.18
2	0.86	0.94	0.80	0.57	0.14	0.19	0.07	0.10
3	0.79	0.70	0.86	0.97	0.66	0.74	0.86	0.63
4	0.82	0.61	0.27	0.99	0.23	0.19	0.46	0.40

I = First desorption

II = Second desorption

Appendix C: Calculated  $R^2$  values showing the goodness of fit according to Langmuir equation for I and II desorptions of adsorbed phosphate in the soils.

Soil No.	CaCl <sub>2</sub> extraction		NaHCO <sub>3</sub> extraction		EUF (200 V, 20°C) extraction		EUF (400 V, 80°C) extraction	
	-----		-----		-----		-----	
	I	II	I	II	I	II	I	II
1a	0.99	0.99	0.99	0.99	0.99	0.29	0.98	0.24
1b	0.99	0.99	0.99	0.99	0.97	0.40	0.99	0.91
1c	0.99	0.99	0.99	0.99	0.98	0.77	0.97	0.53
1d	0.98	0.98	0.98	0.98	0.98	0.45	0.97	0.53
2	0.99	0.99	0.99	0.99	0.99	0.25	0.98	0.20
3	0.99	0.41	0.99	0.59	0.96	0.68	0.94	0.64
4	0.99	0.99	0.99	0.99	0.89	0.16	0.85	0.58

I = First desorption

II = Second desorption



Appendix D: Amounts of P in solution (a) and P adsorbed (b) by the BR-1 soil fertilized with different amounts of P in the previous season.

P* added	P-0		P-10		P-20		P-40	
	a	b	a	b	a	b	a	b
----- ug P g <sup>-1</sup> -----								
10	0.06	9.94	0.13	9.86	0.00	10.00	0.06	9.94
20	0.06	19.94	0.25	19.75	0.06	19.94	0.38	19.63
30	0.13	29.88	0.63	29.38	0.31	29.69	1.00	28.30
40	1.00	39.00	1.25	38.75	0.94	39.06	1.50	37.40
50	1.38	48.63	1.63	48.38	1.81	48.19	2.25	46.15
75	5.50	69.50	6.63	68.38	5.44	69.56	6.63	64.33
100	10.25	89.75	10.19	89.81	11.69	88.31	12.56	87.44
125	16.25	108.75	19.25	118.25	20.13	104.88	20.38	104.63
150	24.00	126.00	24.88	125.13	22.63	127.38	26.94	123.06
175	33.63	141.38	33.31	141.69	31.06	143.94	36.31	138.69
200	42.38	157.63	43.63	156.38	41.06	158.94	36.00	164.00
225	53.00	172.00	54.88	170.13	44.19	180.81	57.88	167.13

\*Potassium dihydrogen phosphate used as source of P.

Appendix E: Amounts of P in solution (a) and P adsorbed (b) by selected Vertisols.

P* added	BR-1		Barsi		Begumganj		BW-6	
	a	b	a	b	a	b	a	b
ug P g <sup>-1</sup>								
10	0.06	9.94	0.06	9.94	0.06	9.94	0.06	9.94
20	0.06	19.94	0.19	19.81	0.13	19.88	0.38	19.62
30	0.13	29.88	0.31	29.69	0.31	29.69	0.75	29.25
40	1.00	39.00	0.50	39.50	0.50	39.50	1.25	38.75
50	1.38	48.63	0.81	49.19	0.63	49.38	1.75	48.25
75	5.50	69.50	2.63	72.38	2.38	72.63	5.19	69.81
100	10.25	89.75	4.81	95.19	4.25	95.75	9.25	90.75
125	16.25	108.75	7.00	118.00	6.44	118.56	14.56	110.44
150	24.00	126.00	11.38	138.63	11.75	138.25	20.19	129.81
175	33.63	141.38	16.38	158.63	16.75	158.25	28.00	147.00
200	42.38	157.63	21.69	178.31	27.38	172.63	36.00	164.50
225	53.00	172.00	27.94	197.06	31.13	193.38	44.25	180.75

\*Potassium dihydrogen phosphate used as source of P.

Appendix F: Amounts of P in solution (a) and P adsorbed (b) by the BR-1 soil fertilized with different amounts of P in the previous season.

P* added	P-0		P-10		P-20		P-40	
	a	b	a	b	a	b	a	b
----- ug P g <sup>-1</sup> -----								
10	0.00	10.00	0.06	9.94	0.06	9.94	0.00	0.00
20	0.31	19.69	0.06	19.94	0.13	19.88	0.25	19.75
30	0.69	29.31	0.69	29.31	0.69	29.31	0.75	29.25
40	1.25	38.75	1.56	38.44	1.25	38.75	1.00	39.00
50	1.88	48.13	1.81	48.19	2.13	47.88	1.50	48.50
75	4.75	70.25	5.75	69.25	5.81	69.19	4.44	70.56
100	9.13	90.88	10.13	89.88	10.50	89.50	8.50	91.50
125	14.44	110.56	19.50	105.50	15.81	109.19	13.50	111.50
150	21.00	129.00	21.38	128.63	22.85	127.21	20.13	129.94
175	27.88	147.14	32.94	142.06	29.56	145.44	26.63	148.38
200	37.25	162.75	43.63	156.44	38.00	162.00	34.13	165.63
225	46.31	178.63	55.45	169.56	46.75	178.25	41.63	183.38

\*Ammonium polyphosphate used as source of P.

Appendix G: Amounts of P in solution (a) and P adsorbed (b) by selected Vertisols.

P* added	BR-1		Barsi		Begumganj		BW-6	
	a	b	a	b	a	b	a	b
ug P g <sup>-1</sup>								
10	0.00	10.00	0.00	10.00	0.00	10.00	0.00	10.00
20	0.31	19.69	0.00	20.00	0.00	20.00	0.25	19.75
30	0.69	29.31	0.13	29.88	0.19	29.81	0.75	29.25
40	1.25	38.75	0.50	39.50	0.38	39.63	1.25	38.75
50	1.88	48.13	0.75	49.25	0.50	49.50	2.00	48.00
75	4.75	70.25	2.25	72.76	1.94	73.06	5.06	69.94
100	9.13	90.89	4.44	95.56	4.13	95.88	9.44	90.56
125	14.44	110.56	7.25	117.75	7.00	118.06	14.75	110.25
150	21.00	129.00	11.00	130.00	10.06	139.94	22.88	127.13
175	27.88	147.13	15.75	159.31	13.81	161.19	29.75	145.25
200	37.25	162.75	19.75	180.25	20.38	179.63	48.38	159.63
225	46.31	178.63	26.630	198.38	26.00	199.00	51.00	174.00

\*Ammonium polyphosphate used as a source of P.

Appendix H: Cumulative P desorbed from a Vertisol with different P fertilization backgrounds in 2 desorptions by 0.01 M CaCl<sub>2</sub>.

P added	P-0	P-10	P-20	P-40	P-0	P-10	P-20	P-40
	a	a	a	a	b	b	b	b
10	0.25	0.00	0.10	0.00	2.52	0.00	1.00	0.00
20	0.50	0.15	0.25	0.00	2.51	0.76	1.25	0.00
30	1.15	0.75	0.85	0.70	3.85	2.55	2.86	2.41
40	2.15	1.30	1.15	1.10	5.51	3.36	2.94	2.86
50	3.25	1.80	1.65	1.60	6.68	3.72	3.42	3.35
75	7.00	5.30	4.50	4.05	10.07	7.75	6.47	5.92
100	10.85	8.05	7.50	7.30	12.09	8.96	8.49	8.35
125	17.10	13.55	10.25	11.18	15.72	11.46	9.77	10.69
150	22.85	16.68	15.50	15.68	18.14	13.33	12.17	12.74
175	28.10	20.68	19.75	19.56	19.88	14.60	13.72	14.10
200	34.10	26.30	24.35	24.30	21.63	16.82	15.32	14.82
225	39.60	31.30	29.25	28.55	23.02	18.40	16.18	17.08

a = Cumulative P desorbed (ug g<sup>-1</sup>) in 2 desorptions by 0.01 M CaCl<sub>2</sub>.

b = Maximum attainable recovery %.

Appendix I: Cumulative P desorbed from different Vertisols in 2 desorptions by 0.01 M CaCl<sub>2</sub>.

P added	BR-1 Barsi	Begumganj	BW-6	BR-1	Barsi	Begumganj	BW-6
	a	a	a	b	b	b	b
10	0.25	0.00	0.00	0.00	2.52	0.00	0.00
20	0.50	0.00	0.00	0.00	2.51	0.00	0.00
30	1.15	0.10	0.60	0.30	3.85	0.34	2.02
40	2.15	0.30	0.25	0.85	5.51	0.76	0.63
50	3.25	1.00	0.25	1.40	6.68	2.03	0.51
75	7.00	4.15	1.40	3.48	10.07	5.73	1.93
100	10.85	5.78	2.80	6.60	12.09	6.07	2.92
125	17.10	7.53	5.30	9.35	15.72	6.38	4.47
150	22.85	10.90	7.80	13.85	19.88	8.37	6.98
175	28.10	13.28	11.05	17.85	19.88	8.37	6.98
200	34.10	20.40	15.80	21.60	21.63	11.44	9.15
225	39.60	24.40	18.80	26.10	23.02	12.38	9.70

a = Cumulative P desorbed ( $\mu\text{g g}^{-1}$ ) in 2 desorptions by 0.01 M CaCl<sub>2</sub>.

b = Maximum attainable recovery %.

Appendix J: Cumulative P desorbed from a Vertisol with different P fertilization backgrounds in 2 desorptions by 0.5 M NaHCO<sub>3</sub>.

P added	P-0	P-10	P-20	P-40	P-0	P-10	P-20	P-40
	a	a	a	a	b	b	b	b
10	6.20	5.20	5.70	7.40	62.00	53.33	57.72	74.00
20	9.60	11.20	12.00	13.20	48.30	56.18	60.76	67.26
30	16.40	18.40	18.60	20.20	56.31	61.59	63.32	68.77
40	18.80	25.00	24.80	26.60	48.21	63.69	64.00	67.99
50	26.80	31.20	27.60	32.40	55.69	64.00	57.50	67.33
75	41.20	47.90	42.40	35.80	59.02	67.50	60.63	50.96
100	52.70	63.40	55.40	63.10	58.20	70.36	61.39	69.83
125	60.20	78.10	67.90	77.86	54.20	70.36	61.59	69.83
150	78.20	92.40	82.90	91.69	60.83	70.33	64.58	70.50
175	86.20	103.40	92.40	107.10	58.76	68.03	63.34	72.33
200	99.20	119.40	103.20	126.60	61.00	71.23	63.66	75.75
225	116.20	134.40	116.40	131.60	65.24	73.09	64.58	72.36

a = Cumulative P desorbed ( $\mu\text{g g}^{-1}$ ) in 2 desorptions by 0.5 M NaHCO<sub>3</sub>.

b = Maximum attainable recovery %.

Appendix K: Cumulative P desorbed from different Vertisols in 2 desorptions by 0.5 M NaHCO<sub>3</sub>.

P added	BR-1 Barsi	Begumganj	BW-6	BR-1	Barsi	Begumganj	BW-6	
	a	a	a	b	b	b	b	
10	6.20	5.50	8.00	5.20	62.00	55.00	80.00	52.00
20	9.60	12.30	15.40	11.20	48.30	61.50	77.98	57.07
30	16.40	17.50	21.40	14.80	56.31	58.82	71.93	50.28
40	18.80	23.70	28.40	24.60	48.21	60.00	71.90	63.08
50	26.80	28.70	35.80	30.60	55.69	58.27	72.69	63.58
75	41.20	44.00	51.30	45.42	59.02	59.92	70.07	63.92
100	52.70	62.00	68.80	60.40	58.07	64.21	71.53	65.43
125	60.20	71.50	81.00	74.80	54.20	59.58	68.74	66.71
150	78.20	88.00	100.80	86.40	60.83	61.83	71.87	66.01
175	86.20	101.00	117.80	102.90	58.76	62.04	63.37	69.26
200	99.20	112.50	133.80	115.40	61.00	61.02	74.23	69.10
225	116.20	137.50	150.80	131.40	65.33	62.01	75.78	71.46

a = Cumulative P desorbed (ug g<sup>-1</sup>) in 2 desorptions by 0.5 M NaHCO<sub>3</sub>.

b = Maximum attainable recovery %.



Appendix L: Cumulative P desorbed from a Vertisol with different P fertilization backgrounds in 2 desorptions by EUF (200 V, 20°C).

P added	P-0	P-10	P-20	P-40	P-0	P-10	P-20	P-40
	a	a	a	a	b	b	b	b
8	2.90	0.90	4.10	5.20	36.25	11.25	51.25	65.00
16	3.80	1.10	6.00	7.80	23.75	6.88	37.50	48.75
24	7.20	1.80	6.00	10.10	30.25	7.56	25.00	42.44
32	12.40	5.70	14.20	14.00	39.37	17.98	44.72	44.59
40	25.40	11.40	20.60	19.40	39.29	28.93	51.96	49.36
60	23.10	20.70	30.50	22.00	40.62	35.88	52.39	38.13
80	35.00	30.70	33.40	36.60	47.36	40.69	44.47	48.83
100	42.90	45.90	42.90	39.70	47.20	49.85	47.69	43.29
120	53.50	53.20	50.60	45.20	50.42	49.74	53.79	42.16
140	61.00	61.40	65.00	51.60	49.76	49.54	57.15	42.31
160	72.70	78.80	77.50	61.60	54.01	57.01	56.75	45.06
180	85.40	87.60	83.20	76.60	57.35	58.32	65.00	51.17

a = Cumulative P desorbed ( $\mu\text{g g}^{-1}$ ) in 2 desorptions by EUF (200 V, 20°C).

b = Maximum attainable recovery %.

Appendix M: Cumulative P desorbed from different Vertisols in 2 desorptions by EUF (200 V, 20°C).

P added	BR-1 Barsi	Begumganj	BW-6	BR-1	Barsi	Begumganj	BW-6	
	a	a	a	b	b	b	b	
8	2.90	3.60	2.50	2.00	36.25	45.00	31.25	25.16
16	3.80	11.20	4.90	4.40	23.75	70.00	30.63	27.85
24	7.20	16.50	8.70	11.00	30.25	68.75	36.25	46.41
32	12.40	30.40	11.60	14.20	39.37	95.60	36.42	45.22
40	25.40	31.80	23.50	17.30	39.29	80.10	59.19	44.25
60	23.10	36.00	31.50	22.60	40.60	60.76	53.60	39.16
80	35.00	41.40	33.30	28.00	47.36	53.08	43.02	37.28
100	42.90	47.80	38.80	41.80	47.20	49.41	41.00	45.63
120	53.50	62.80	45.30	50.20	50.42	54.85	40.17	45.80
140	61.00	78.80	60.70	61.60	49.76	59.60	57.20	49.84
160	72.70	86.80	64.10	67.40	54.01	58.26	44.09	49.16
180	85.40	95.80	70.10	76.20	57.35	57.71	44.12	49.77

a = Cumulative P desorbed ( $\mu\text{g g}^{-1}$ ) in 2 desorptions by EUF (200 V, 20°C).

b = Maximum attainable recovery %.

Appendix N: Cumulative P desorbed from a Vertisol with different P fertilization backgrounds in 2 desorptions by EUF (400 V, 80°C).

P added	P-0	P-10	P-20	P-40	P-0	P-10	P-20	P-40
	a	a	a	a	b	b	b	b
8	5.00	7.00	7.10	5.60	62.50	87.50	88.75	70.00
16	9.00	11.90	13.60	5.80	56.25	74.61	85.10	36.25
24	13.20	19.90	12.80	7.20	55.46	83.79	54.01	30.25
32	16.80	28.90	16.20	15.50	53.17	91.60	58.31	65.56
40	23.20	33.90	22.80	25.70	58.88	86.04	58.31	65.56
60	36.10	39.70	29.10	34.50	62.35	69.16	51.14	59.84
80	49.90	55.90	43.40	45.40	65.53	74.39	59.13	60.32
100	59.70	63.30	46.20	59.70	64.44	69.47	52.26	65.32
120	72.00	75.70	70.00	69.50	67.51	71.15	66.89	64.86
140	82.30	85.10	78.20	80.10	66.97	70.68	66.89	64.86
160	84.40	97.10	88.20	95.70	60.76	72.11	67.12	69.40
180	96.60	111.50	93.80	110.90	63.18	77.62	65.87	73.13

a = Cumulative P desorbed ( $\mu\text{g g}^{-1}$ ) in 2 desorptions by EUF (400 V, 80°C).

b = Maximum attainable recovery %.

Appendix O: Cumulative P desorbed from different Vertisols in 2 desorptions by EUF (400 V, 80°C).

P added	BR-1 Barsi	Begumganj	BW-6	BR-1 Barsi	Begumganj	BW-6		
	a	a	a	b	b	b		
8	5.00	5.80	9.20	3.20	65.50	75.50	115.00	40.00
16	9.00	19.60	14.80	8.60	56.25	122.50	93.08	53.75
24	13.20	23.40	29.20	13.60	55.46	97.50	122.69	56.67
32	16.80	29.60	31.60	15.00	53.17	92.50	99.69	46.88
40	23.20	33.20	47.80	19.00	58.88	83.00	120.56	47.50
60	36.10	37.50	57.30	19.80	62.35	62.50	98.59	33.59
80	49.90	47.30	73.60	34.00	65.53	59.15	94.97	43.59
100	59.70	65.80	80.40	48.30	64.44	67.14	83.33	50.58
120	72.00	85.00	89.40	54.70	67.51	73.59	78.08	48.95
140	82.30	85.00	95.20	60.60	66.97	63.67	71.99	47.16
160	84.40	98.40	105.40	83.30	60.76	64.53	71.22	56.48
180	96.60	103.20	138.40	91.00	63.18	61.07	83.88	55.83

a = Cumulative P desorbed ( $\mu\text{g g}^{-1}$ ) in 2 desorptions by EUF (400 V, 80°C).

b = Maximum attainable recovery %.