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SORPTION AND DESORPTION OF INORGANIC PHOSPHATE  
BY SOILS AS INFLUENCED BY COMPETING INORGANIC  
AND ORGANIC ANIONS

by

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Introduction

Anions play a very significant role in the retention and plant availability of soil and fertilizer inorganic phosphate (P). Evidence that different inorganic and organic anions can modify P retention was presented by many workers prior to 1950 ( Kurtz et al., 1946; Dean and Rubins, 1947; Swenson et al., 1949 ). The exact mechanisms of this effect was little understood. In addition, a range of chemical extractants have been used to assess the available P status of soils; these included citrate, tartrate, fluoride, arsenate, and other anions capable of forming stable complexes with Fe and Al in soils.

It is now well recognised that microorganisms and root excretions greatly modify the chemical environment in the rhizosphere. Organic compounds found in the root exudates of several plants ( reviewed by Rovira, 1965 ), and produced by microorganisms, include many organic acids known to form strong complexes with metal ions. Such compounds may be an important factor affecting the mobility of P in soils.

There is now a reasonable amount of information concerning the reactions of certain anions with soil components. The significance of inorganic and organic anions in the soil solution, and their effect on P sorption and desorption by soil components and soils, however, is not so well documented. Recent studies by Deb and Datta ( 1967 a, b ), Hingston et al. ( 1970, 1971, 1974 ), Nagarajah et al. ( 1968, 1970 ), and Barrow ( 1974 a, b ) have enabled a better understanding of the extent to which competing anions influence the uptake and release of P by soil components and soils.

The literature pertaining to the uptake and release of P by soils, as influenced by other anions, is reviewed in three sections :

- I. The mechanism of P sorption by soil components and soils,
- II. The influence of competing inorganic and organic anions on the sorption of P by soil components and soils, and
- III. The influence of competing inorganic and organic anions on the desorption of sorbed P from soil components and soils.

Sorption reactions may conveniently be divided into adsorption reactions ( concentration of ions at solid surfaces due to removal from solution ) and absorption ( diffusive penetration of ions into retaining components ).

I. THE MECHANISM OF P SORPTION BY SOIL  
COMPONENTS AND SOILS

The removal of P from solution by soil components and soils has been studied by many workers. It is now widely recognized that on addition of P fertilizers to soil, the P contained in the largely water-soluble compounds is rapidly removed from the soil solution by soil components and held in a relatively unavailable form. This immobilisation of P occurs in soils by two mechanisms, namely sorption and precipitation. At low P concentrations ( $\ll 10^{-4}M$ ) in the soil solution, however, retention appears to be the result of a sorption-reaction (Cole *et al.*, 1953; Bache, 1964; Muljadi *et al.*, 1966), and it is the mechanisms of such a reaction that will be considered in this section. Information on the mechanism of sorption of other anions will be included to provide a more general theory.

A. Mechanism of P sorption by soil components

P sorption studies have been conducted using a wide range of "pure" soil components. Those considered to influence the amount of P sorbed by soils are :

- short-range order and crystalline oxides and hydrous oxides of Fe and Al
- clay minerals ( layer silicates )
- short-range order aluminosilicates
- calcium carbonate
- humic substances

The ability of these components to sorb P generally decreases in the order : short-range order hydrous oxides of Fe and Al, and short-range order aluminosilicates > crystalline oxides and hydrous oxides of Fe and Al > clay minerals > calcium carbonate >> humic substances ( Gorbunov, 1959; Gastuche *et al.*, 1963; Fox *et al.*, 1971 ).

## 1. Oxides and hydrous oxides of Fe and Al

Oxides and hydrous oxides of varying crystallinity occur in virtually all soils. The short-range order components take the form of gels, whereas crystalline components are more common in strongly-weathered soils. The ability of these components to sorb P varies considerably. Short-range order Fe and Al components, which may occur as coatings on silicate minerals or as discrete phases, usually sorb more P than crystalline components ( Gorbunov, 1959; Syers and Williams, 1975 ), because of the greater surface area giving rise to a larger number of sites in the former.

Data for the sorption of P by "amorphous aluminium hydroxide" was found by Hsu and Rennie (1962) and Hsu (1965) to follow two adsorption curves, using the Langmuir adsorption equation. The initial reaction occurred very rapidly and was practically complete in a matter of hours, while the second occurred at a much slower rate. The initial rapid reaction was thought to be an immediate adsorption of the added P resulting from the displacement of weakly held hydroxyl ions located at the surface. The subsequent less rapid reaction was thought to be due to a surface adsorption on similar short-range order hydrous oxides continuously developed during the experiment by a weathering process ( Hsu, 1965 ).

Muljadi et al. (1966) found that the adsorption isotherms obtained from P sorption studies using kaolinite, gibbsite, and pseudoboehmite could be divided "by inspection" into three distinct regions. The regions were designated I, II, and III, and it was suggested that these regions were related to the affinity of P for at least three energetically different reactive sites. A similar isotherm-splitting technique was used by Bache (1964) for gibbsite and short-range order hydrous ferric oxide.

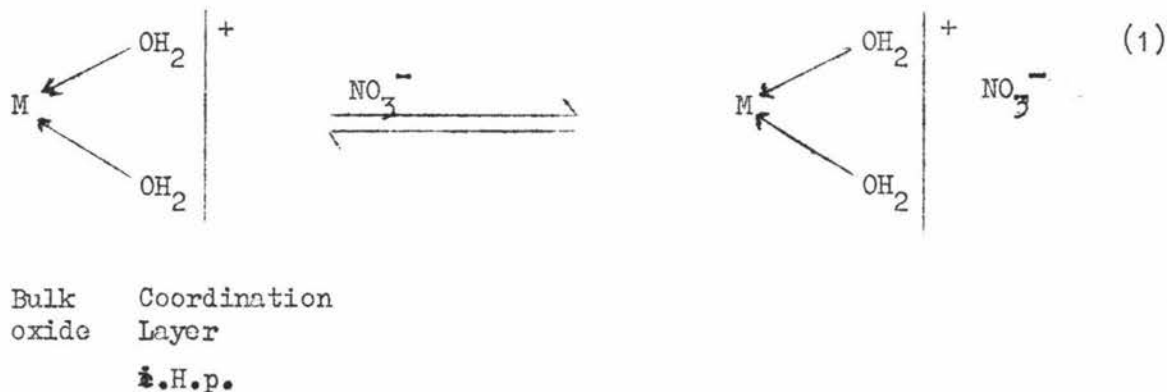
The simplest mechanism proposed by Muljadi et al. (1966) is that region I ( sites with a high affinity for P ) corresponds to P exchange with an -OH counterion of an  $-Al(OH)_2$  group situated on the edge face of the crystal. This grouping would be common to oxides, hydrous oxides, and kaolinite. The reaction sites responsible for sorption in region II were considered to be similar to those of region I, because the binding energy values (  $K_1$  ) for regions I and II, calculated from the Langmuir adsorption equation, were similar. If this

was true, however, there should be no distinct boundary between the two regions ( since  $K_1 = \text{slope/intercept}$  ). Region III was thought to be associated with the occlusion or diffusive penetration of P into a short-range order or semicrystalline regions of the surface ( Muljadi et al., 1966 ).

These rather simple mechanisms proposed by Muljadi et al. (1966) have been modified as a result of more recent work by Hingston et al. ( 1967, 1970, 1972 ). They consider that anion adsorption occurs by two distinct mechanisms. An anion added to a hydrous oxide system may be :

(a) electrostatically attracted if the net surface charge is positive, but does not exchange with a ligand in the inner Helmholtz plane ( i. H.p ). These anions are weakly held, and have no effect on the charge of the surface. This is referred to as non-specific adsorption, examples being  $\text{NO}_3^-$  and  $\text{Cl}^-$ , and may be described by Scheme 1.

SCHEME 1

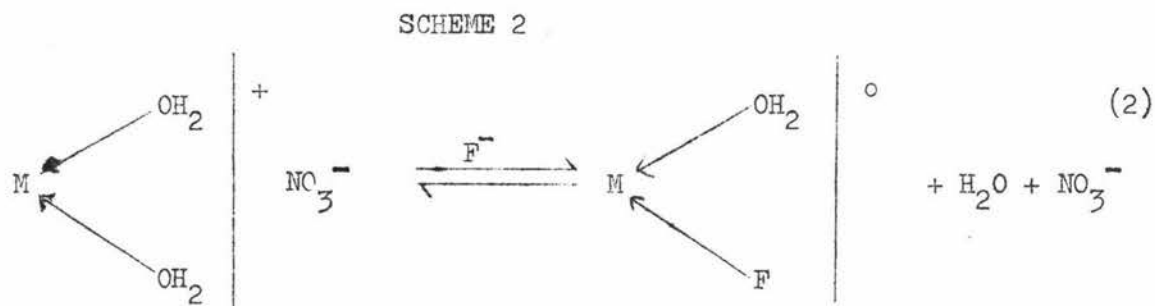


Alternatively the anion may :

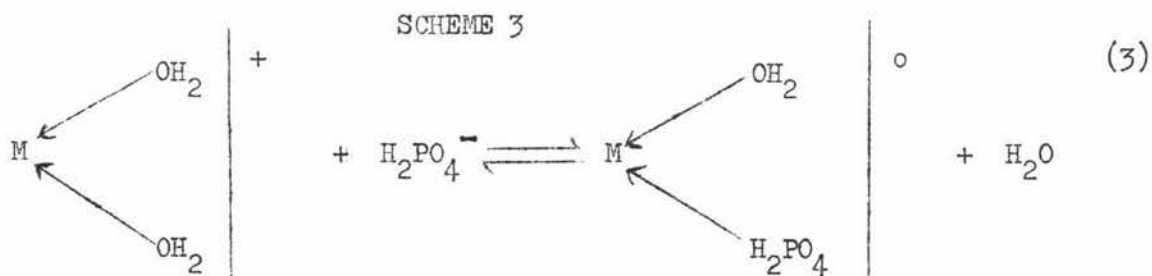
(b) exchange with a surface ligand and form partly covalent bonds with lattice cations. This is referred to as specific adsorption, and can occur whether the surface has a net positive or negative charge. The amount of anion adsorbed is far greater than would be expected for non-specifically adsorbed species, which are adsorbed according to their relative abundance in solution. Most anions fall into the specifically adsorbed category and are generally derived from weak acids.

At pH values where the acid is fully dissociated ( e.g.,  $\text{F}^-$  ) specific adsorption occurs only to the extent of the positive charge

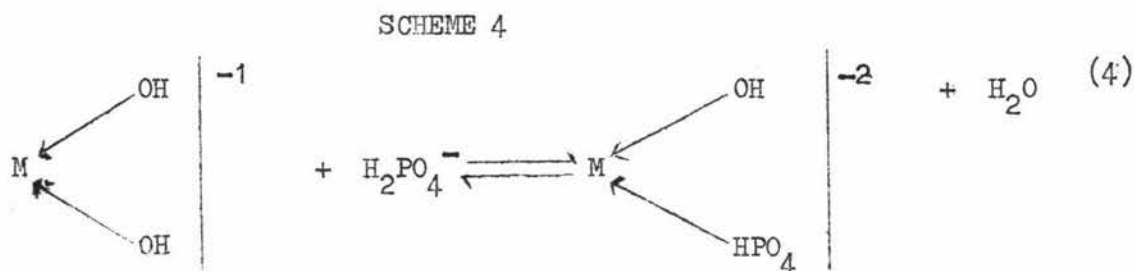
of the surface ( see Scheme 2 ) and little specific adsorption occurs at pH values more alkaline than the zero point of charge ( z.p.c ) ( Hingston et al., 1972 ).



For an incompletely dissociated acid ( e.g.,  $\text{H}_2\text{PO}_4^{2-}$  ) specific adsorption at a positively charged surface is thought to occur by an exchange reaction, as described in Scheme 3 ( Hingston et al., 1972; Breeuwsma and Lyklema, 1973 ).



When the pH is higher than the z.p.c., maximum adsorption, according to Hingston et al. ( 1967, 1970 ), is determined by the proportion of ions in solution that are able to donate and accept protons, and enter the coordination layer by effecting a ligand exchange, displacing  $\text{H}_2\text{O}$  and/or  $\text{OH}^{-}$ , as seen in Scheme 4.



Hingston et al. ( 1970 ) have suggested that, in all cases, specific adsorption renders the surface more negatively charged. Breeuwsma and

Lyklema (1973), however, argue that negative charge does not always increase with specific adsorption of P. Recent work in this laboratory by Rydon and McLaughlin (pers. comm.) using soils and a hydrous ferric oxide gel has added support to the claim of Breeuwsma and Lyklema (1973).

Hingston et al. (1967) demonstrated that for monobasic acids, silicate, and borate, there is an adsorption maximum at the  $pK_a$  of the acid. For orthophosphate and other polybasic acids, however, there is a discontinuity at each  $pK_a$  value, the one at the highest  $pK_a$  value being the most marked. The observation of the approximately 1:1 correlation between the pH at maximum adsorption and the  $pK_a$  value suggests that specific adsorption depends on the ease of dissociation of the conjugate acid at the surface. At or near the  $pK_a$  value the energy required to abstract a proton is at a minimum, the proton being required for the removal of a surface OH, as in Scheme 4.

In the case of orthophosphate, both anions which can accept or donate protons ( $H_2PO_4^-$ ,  $HPO_4^{2-}$ ) are present in equal concentrations at the  $pK_{a2}$  of orthophosphoric acid. According to Kafkafi and Bar-Yosef (1969), because  $HPO_4^{2-}$  can contribute more negative charge to the surface than does  $H_2PO_4^-$ , the molar amounts of P sorbed decrease as the pH and the proportion of  $HPO_4^{2-}$  increase. This interpretation has been criticised by Breeuwsma and Lyklema (1973) who found that sorption at  $pH = pK_{a2}$  did not deviate from that at other pH values when the amount of acid required to keep the pH constant during the sorption of P by hematite was considered.

A number of workers have used these concepts to explain the observed effects of pH on anion sorption, not only by oxides and hydrous oxides of Fe and Al, but also by other soil components, and soils. Examples may be found in the work of Beckwith and Reeve (1963) for silicate, Sims and Bingham (1968) for borate, Reisenaur et al. (1962) for molybdate, Geering et al. (1968) for selenite, Harward and Reisenaur (1966) for sulphate, and Watson et al. (1973) for the herbicide, 2, 4-D.



## 2. Clay minerals

Sorption of P by clay minerals ( layer silicates ) has been studied widely ( de Haan, 1965; Muljadi et al., 1966; Kuo and Lotse, 1972 ). It is widely recognised that active aluminium ( that located on crystal surfaces ) is capable of removing small but significant amounts of P from solution. The general constitution of the aluminosilicate lattice involves sheets of Al and Si layers; the Al layers may be simply alternating with Si layers ( 1:1 type, e.g., kaolinite ) or be bounded on both sides by Si sheets ( 2:1 type, e.g., montmorillonite, vermiculite ). Successive Al atoms in the Al layer share O-atoms with tetra-coordinated Si of the upper ( or lower ) Si layer, in addition to sharing OH. At the edge of the lattice, pairs of Al atoms which normally share bonds with -OH groups ( thus forming the edge-situated hydroxy Al atoms ) are believed to be bonded preferentially to P groups if present at satisfactory concentration ( de Haan, 1965 ). The result would then be a bonding between edge-Al and  $\text{H}_2\text{PO}_4^-$  ions comparable to the situation between Al and Si sheets.

Muljadi et al. (1966) and Kuo and Lotse (1972) have postulated that the mechanism of P sorption by kaolinite is similar to that for P sorption by hydrous oxides of Al; namely, the replacement of water molecules and/or  $\text{OH}^-$  at the surface of the active component.

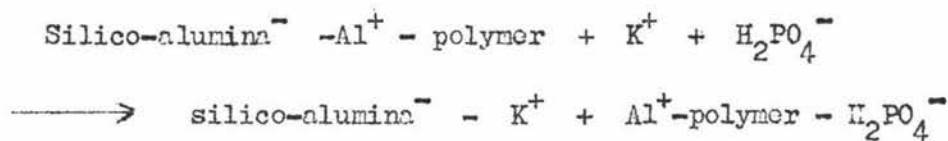
Kafkafi and Bar-Yosef (1969) demonstrated that the slope of the curve of sorbed P on the surface of kaolinite, as a function of pH, had discontinuities at two points, one at pH 7.0 and the other at pH 10.5. The close relationship between these pH values and the  $\text{pK}_{a2}$  and  $\text{pK}_{a3}$  values for orthophosphoric acid suggests that the mechanism of P sorption at clay mineral surfaces is the same as that proposed by Hingston et al. ( 1967, 1970 ) for oxides and hydrous oxides of Fe and Al ( i.e., specific adsorption ).

## 3. Short-range order aluminosilicates

Of the short-range order components, allophane-like materials have been shown to be particularly effective in the sorption of P. Hypothetical models of allophane presented by Fieldes and Schofield (1960) and Udagawa et al. (1969) suggest that the structure of the aluminosilicate in its electrostatically neutral state is such that a hole in the uncompleted Al tetrahedron will conveniently house an

oxygen atom. Thus, in the presence of water it is likely that this site will be occupied by a coordinated water molecule. These tetrahedral Al sites have special affinities for anions containing oxygen, and P sorption is therefore assumed to occur by a ligand exchange reaction with water molecules ( Fieldes and Schofield, 1960 ).

Cloos et al. (1968) studied P sorption by allophane-like synthetic aluminosilicates. Kinetic plots of P sorption showed two linear portions, I and II, with distinctly different slopes. These were assumed to result from two diffusion processes occurring in the course of time. They suggested that portion I may be related to a double exchange reaction involving:



This implies that  $\text{H}_2\text{PO}_4^-$  may be specifically adsorbed through exchange reactions with OH groups associated with  $\text{Al}(\text{OH})_2^+$  ions and hydroxy-Al polymers ( e.g.,  $\text{Al}_6(\text{OH})_{12}^{6+} \cdot 12\text{H}_2\text{O}$  ). For portion II, Cloos et al. (1968) suggested that molecular absorption or occlusion of P was possible, a mechanism similar to that proposed for Region III by Muljadi et al. (1966).

#### 4. Calcium carbonate

It is generally believed that calcium carbonate plays an important role in the sorption of P by calcareous soils, although the significance of this component relative to the more reactive Fe and Al components is not clear. Although both Cole et al. (1953) and Kuo and Lotse (1972) have shown that P sorption by  $\text{CaCO}_3$  could be described by the Langmuir adsorption equation at P additions of less than 15  $\mu\text{g}/\text{ml}$ , their data were inadequate to delineate a two-slope Langmuir plot at low final solution P concentrations, as reported by Griffin and Jurinak (1973).

A more intensive study by Griffin and Jurinak (1973) led these workers to conclude that the interaction of P with the calcite surface resulted from a heterogeneous nucleation process, visualized as follows :

The initial adsorption of P takes place on a limited number of specific surface sites. As adsorption proceeds, site coverage increases to the extent that lateral interaction occurs between the adsorbed ions, which eventually results in surface clusters of  $\text{H}_2\text{PO}_4^-$  ions. These clusters then serve as centers ( heteronuclei ) from which crystal growth can occur. This interpretation was corroborated by the electron microscope studies of Stumm and Leckie (1970) who showed that exposure of calcite crystals to P solutions resulted in the development of amorphous or semicrystalline clusters of  $\text{H}_2\text{PO}_4^-$  on the surface which gradually change into surface nuclei and ultimately into hydroxylapatite.

Somasundaran and Agar (1967) provided a detailed account of the surface charge properties of  $\text{CaCO}_3$  and related these to the ability of  $\text{CaCO}_3$  to sorb anions from solution. Differential hydrolysis reactions appear to result in the development of a net charge on the surface of the calcite particle. The potential-determining ions are  $\text{Ca}^{2+}$ ,  $\text{H}^+$ ,  $\text{HCO}_3^-$ , and  $\text{OH}^-$ , producing a net positive charge at pH values less than 9.5 ( the z.p.c. ) and a net negative charge at pH values greater than 9.5 ( Somasundaran and Agar, 1967 ). Thus, anions can be adsorbed non-specifically by electrostatic attraction to the calcite particle at pH values below the z.p.c., or, in the case of  $\text{H}_2\text{PO}_4^-$ , specifically adsorbed by ligand exchange with bicarbonate ions and/or carbonate ions existing at the surface of the calcite particle. According to Kuo and Lotse (1972), the relative adsorption strength of P and other anions present will depend on the "solubility" of the compound formed with surface  $\text{Ca}^{2+}$  ions.

##### 5. Humic substances

Humic substances are probably of very limited direct importance in the sorption of P by soils. This is because the functional groups in such compounds require very low pH values for protonation to occur. Humic substances, however, may influence the sorption of P by soils in two ways :

- (a) In the presence of humic substances, P sorption by soils may be reduced. This is attributed to the formation of complexes between the humic acid and active Al and Fe ( Gorbunov, 1959; Gaur, 1969 ).

- (b) Levesque and Schnitzer (1967) demonstrated that Fe- and Al- fulvic acids could interact with P to form stable complexes. In the low (1:1) molar metal: fulvic acid ratio preparation, P occurred as the orthophosphate ion bonded through the metal to fulvic acid. In contrast, in the high (6:1) ratio preparation, a considerable proportion of P occurred as the metal phosphate mixed physically with fulvic acid-metal phosphate.

The significance of humic substances, in particular organic anionic polymers, as competing agents in the sorption of P by soils will be discussed in greater detail in Section II.

#### B. Mechanism of P sorption by soils

Because of the very complex nature of soils it has been difficult to postulate mechanisms for P sorption by a whole soil system. Attempts to relate mechanisms of P sorption developed using pure components to whole soils have rarely been made. To extend such mechanisms to whole soil systems, however, it is necessary to know which components are important in P sorption by soils. In an attempt to identify the components involved in P sorption by soils, many workers have used selective chemical dissolution techniques to remove certain components from the soil ( Williams *et al.*, 1958; Bronfield, 1965; Syers *et al.*, 1971 ), and have attempted to relate the decrease ( or increase ) in P sorption to the particular components removed. These procedures have demonstrated that the sorption of added P is generally better correlated with Al parameters than with Fe parameters. The use of selective dissolution techniques, however, is unsatisfactory for two main reasons. Firstly, the removal of one soil component by a chemical extractant may expose P sorption sites which play little or no role in P sorption by the untreated soil. Secondly, anions present in the chemical extractant used, if not removed by washing, may effectively compete with P for sorption sites.

The cation-exchange capacity (CEC) of soils is known to increase as a consequence of the sorption of P ( Toth and Bear, 1947; Coleman and Mehlich, 1948 ). The increase in negative charge has been attributed to the replacement of  $-OH_2$  and/or  $-OH$  groups by  $H_2PO_4^-$  at the surface

of a component, with a subsequent shift in the z.p.c. of the surface to lower pH values ( Hingston et al., 1970 ). More cations are therefore required to balance the additional negative charge produced by the specific adsorption of anions. Lowering of the z.p.c. in tropical soils, as a consequence of specific adsorption of anions, has been clearly demonstrated by Van Raij and Peech (1972) and Mekarua and Uehara (1972).

Using six Connecticut soils, Sawhney (1974) observed that at low pH values (  $< 5.0$  ), the increase in CEC resulting from P sorption occurred mainly by replacement of octahedrally coordinated water molecules on mineral surfaces. At higher pH values (  $> 6.0$  ), increases in CEC were largely due to replacement of hydroxyls by polyvalent phosphate ions. Further, for soils of temperate regions, Sawhney (1974) showed that oxides and hydrous oxides of Fe and Al, rather than layer silicates, were primarily responsible for the increase in CEC as a result of P sorption. Similar results were reported by Mekarua and Uehara (1972) for tropical soils. These workers observed a positive sorption of  $\text{NO}_3^-$  or  $\text{Cl}^-$  in ferruginous tropical soils. Negative sorption of these ions occurred, however, as soon as  $\text{SO}_4^{2-}$  was added, which tends to support the view that specifically adsorbed anions increase the negative charge.

In a comparison of the sorption of molybdate, sulphate, and phosphate by Australian soils, Barrow (1970) showed that as the pH of the soils decreased from 6 to 4, the ratio of sulphate to phosphate sorbed increased by a factor of three. This was attributed mainly to the increased ability of the surface to donate a proton to  $\text{SO}_4^{2-}$ , a suggestion which has not been demonstrated experimentally. Over the same pH range, the ratio of molybdate to phosphate sorbed increased by a factor of 20. The slope of this relationship with pH was consistent with the hypothesis that adsorption occurs when ions, capable of donating and accepting protons, exist simultaneously at the interface of the adsorbing phase with the solution.

Syers et al. (1973) demonstrated that sorption isotherms for added P ( for final solution P concentrations up to approximately  $15 \mu\text{g/ml}$  ) consisted of two linear relationships when plotted according to the Langmuir equation, indicating the presence of two populations of sites having a widely differing affinity for P. It was suggested

that these two linear relationships were the result of the differing binding energies of a range of soil components, possibly involving different mechanisms.

The rate of P sorption by soils follows two rather distinct patterns ( Kurtz *et al.*, 1946; Rennie and McKercher, 1959; Fox and Kanprath, 1970 ), namely an initially rapid adsorption reaction followed by a very much slower reaction which can proceed for many days. It has been claimed by several workers that the time-dependence of P sorption results from the diffusive penetration of P into soil materials. Autoradiography has been used to study the diffusion of P in intact soil ( Gunary, 1964 ), in soil aggregates ( Larsen and Gunary, 1965 ); and through soil to plant roots ( Lewis and Quirk, 1967 ). Mathematical expressions describing the flux of P in solids have been presented by Lewis and Quirk (1967) and Nye (1968). The penetration of P into soil crumbs was studied by Evans and Syers (1971) using autoradiographic techniques involving the low energy isotope,  $^{33}\text{P}$ . Autoradiograms of soil crumbs which had been in contact with  $^{33}\text{P}$  and  $^{31}\text{P}$  for varying periods of time showed a rather rapid penetration of P, which increased with time. This fact, along with the observed reduction in exchangeability of the sorbed added P with time, substantiates the hypothesis that the penetration of added P is a diffusion-controlled process which is rapid.

It is possible that the diffusive penetration of adsorbed P could result in the regeneration of sites for further P sorption. The rate at which regeneration occurs would depend on the P concentration in the soil solution which, in turn, determines the diffusion rate. Low P concentrations in solution would produce a slow rate of diffusion.

Any attempt to describe the mechanism of anion sorption by soils will probably be as much concerned with the characteristics of the anion as with those of the soil. The formulation of a general theory for anion sorption by soils is complicated by a number of factors. For example,  $\text{NO}_3^-$  is not strongly sorbed at any pH, whereas molybdate, which is strongly sorbed at low pH, becomes less strongly held as the pH rises; for borate the reverse is true.

II. THE INFLUENCE OF COMPETING INORGANIC AND ORGANIC ANIONS ON THE SORPTION OF P BY SOIL COMPONENTS AND SOILS

The phosphate anion is strongly sorbed by soils, especially those containing short-range order Fe and Al hydrous oxides. In a soil/soil solution/plant root system, the plant competes successfully for nitrate, sulphate, and chloride ions, but it may be greatly over-matched by the soil when competing for a high-affinity anion like phosphate. Distinct depleted zones near plant roots have been observed on autoradiograms of soils equilibrated with  $^{32}\text{P}$  ( Lewis and Quirk, 1967 ). Theoretically, P sorption by soil components and soils may be reduced by the addition of high affinity anions with the phosphate ions. Competition for sorption sites results and the anions are partitioned between the adsorbent and the soil solution in accord with their respective affinities.

One of the earliest studies of the effect of competing anions on P sorption was carried out by Mattson (1927). He observed that the citrate ion restricted P sorption by soils to a large degree, whereas the sulphate ion displaced only moderate quantities, and the chloride ion still less. Shortly after, Demolon and Bastisse (1934) observed that less P was sorbed from a solution containing another "adsorbable" anion, such as tartrate, citrate, oxalate, and silicate, than from a solution containing a largely "non-adsorbable" anion, such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , or  $\text{Cl}^-$ . Since this time a considerable amount of evidence has accumulated which shows that different organic and inorganic anions counteract P sorption by soils; it is generally agreed that organic anions are superior to inorganic anions in this respect.

A. Influence of inorganic anions on P sorption by soil components and soils

The effectiveness of inorganic anions in reducing P sorption by soil components and soils, and the factors responsible for the different affinities of the various anions to the adsorbent surface, have been studied by a number of workers ( Deb and Datta, 1967 a, b; Barrow, 1970; Hingston et al., 1970, 1971; Obihara and Russell, 1972 ).

The observation by Kinjo and Pratt (1971) that P sorption was unaffected when the concentration of  $\text{NO}_3^-$  was varied from 0.25 to 0.001 M supports the theory of Hingston *et al.* (1967) that non-specifically adsorbed anions are ineffective in reducing P sorption by soils. Similarly,  $\text{Cl}^-$  has little effect on the levels of added P sorbed ( Nagarajah *et al.*; 1968 ).

The extent to which specifically adsorbed inorganic anions compete with P for sorption sites appears to be related to the form of the anion present in solution, which in turn is influenced by the pH of the system. For example, Obihara and Russell (1972) demonstrated that the maximum adsorption of silicon from solution by three soils occurred at pH 9.2; whereas the maximum adsorption curve for P from solution showed breaks in slope at pH 6.4 and 11.6. These values compare closely with the respective  $\text{pK}_a$  values; for silicic acid the  $\text{pK}_{a1}$  value is 9.6; whereas the  $\text{pK}_{a2}$  and  $\text{pK}_{a3}$  values for phosphoric acid are 6.7 and 11.3; respectively. In a mixed solution, sufficiently concentrated in both silicate and phosphate to give maximum sorption of either anion if present alone, silicate did not affect the amount of P sorbed until the pH was above 6.5 to 7.0. At this pH, the maximum sorption curve for silicate crossed that for P. Using a range of inorganic acids, Hingston *et al.* (1970) demonstrated a high correlation between the  $\text{pK}_a$  values of the conjugate acids of the various anions and the pH values at which specific adsorption showed a marked change. This suggests that specific adsorption of anions depends on the ease of dissociation of the conjugate acids at the mineral surface.

Barrow (1970) has used the relationship between  $\text{pK}_a$  values and the pH at which the specific adsorption of anions shows a marked change to explain the results obtained for the sorption of phosphate, sulphate, and molybdate by soils. The more acid the soil, the more sulphate sorption was favoured relative to P. The amounts of sulphate sorbed, however, were much smaller than the amounts of P sorbed. Also, the more acid the soil, the more molybdate was sorbed relative to P or sulphate. In this regard, the sorption of molybdate provides an interesting contrast to P. Accurate values for the  $\text{pK}_{a2}$  of molybdic acid are difficult to obtain because of the tendency of molybdate to polymerize, but the value appears to be close to 4.0. Thus, it has been assumed by Barrow (1970) that at pH 4.0 the forms present are the fully charged  $\text{MoO}_4^{2-}$  and the partially charged  $\text{HMoO}_4^-$ . It was



concluded that the ability of molybdate to compete with P is determined by the proportion of molybdate ions present in the fully charged state.

As a competing anion, sulphate differs from molybdate in that the ratio of sulphate sorbed to P sorbed is less affected by increases in pH. The  $pK_{a2}$  for sulphuric acid is about 1.9, and hence even at pH 4.0, most of the anions are present as  $SO_4^{2-}$  and only a small proportion as  $HSO_4^-$ . Hingston et al. (1970) have suggested that the dominant mechanism of  $SO_4^{2-}$  adsorption involves the donation of a proton from the surface to the  $SO_4^{2-}$  ion, thus explaining the greater ability of sulphate to compete with P under acidic conditions.

Hingston et al. (1971) described the competitive sorption of P and selenite, and P and arsenate on oxide surfaces by a Langmuir-type exchange equation. Their results show that at any pH value the maximum amount of adsorbate on the oxide surface depends on the identity of the anion. Secondly, they postulated that the sorption sites were of three kinds: common sites, sites where only one of the competitors can be sorbed, and sites where only the other can be sorbed. Obihara and Russell (1972) did, in fact, find this to be the case for the specific adsorption of P and silicate by soils.

In mixed systems, it appears that it is possible to occupy more sites with anions than when either anion is present alone (Hingston et al., 1971). Using the anion exchange equation, these workers showed that the minimum area occupied per anion for P plus selenite on goethite B was about  $37 \text{ \AA}^2$  at pH 5; compared with  $63 \text{ \AA}^2$  for selenite and  $69 \text{ \AA}^2$  for P when sorption was measured in the absence of competitors. These data were interpreted (Hingston et al., 1971) as showing that one anion in the absence of competitors is shared between two Fe atoms on the crystal surface through a bridging link. The presence of a second anion appears to render the other Fe sites on the surface available for sorption, possibly by having two bridging ligand links attached to each Fe atom. The reason for this is not clear.

It is difficult, therefore, to arrange competing anions in order of their effectiveness in reducing P sorption by soil components and soils. Their effectiveness appears to depend on the nature and properties of the soil, the pH of the support medium, and the concentration of both P and competing anions in solution. In a mixed system of P and another anion which is specifically adsorbed, any increase in

the net negative charge resulting from the adsorption of the other anion should result in a reduction in the amount of P sorbed ( Hingston et al., 1967, 1970 ).

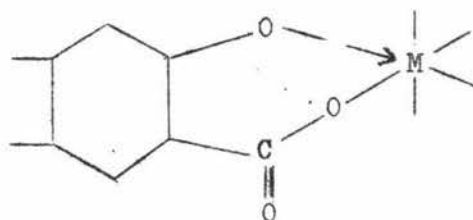
B. Influence of organic anions on P sorption by soil components and soils

That organic matter has a beneficial role in reducing the capacity of soils to sorb P, and therefore increase the availability of native and added P to plants, has been reported by Midgeley and Dunklee (1945) and Kononova (1971). Swenson et al. (1949) assigned a specific role to organic matter in making P more available to plants. They observed that certain organic anions were effective in reducing P sorption by Fe and Al components, and in liberating sorbed P from these components, at low pH. The most effective organic anions were those which were known to form stable complexes with Fe and Al. It was suggested that such anions were produced by microorganisms during the decomposition of organic matter in soils.

A large range of organic compounds have been identified in the root exudates of plants ( Rovira, 1965 ). These include many organic acids known to form strong complexes with Fe and Al. Examination of the root-soil interface under the electron microscope has revealed a slimy gel between the root and the soil colloidal particles ( Jenny and Grossenbacher, 1963; Brams, 1969 ) which has been called "mucigel". This material is considered to consist of pectic substances, chiefly partially methylated polygalacturonic acids. These acids have been shown to be highly effective in reducing P sorption by soil components ( Nagarajah et al., 1970 ) and soils ( Struthers and Sieling, 1950 ).

The effectiveness of an organic anion in reducing P sorption by soil components and soils appears to be related to the structure of the organic molecule and the pH of the system. Struthers and Sieling (1950) reported that each organic anion varies in its ability to compete with P as the pH changes. They concluded that at any pH within the range of values for agricultural soils, there are some organic anions present that are markedly effective in reducing P sorption by Fe and Al components.

Anions which would be expected to exhibit a high affinity for hydrous Fe and Al components contain a multiplicity of oxygen-containing ( carbonyl, phenolic, and carboxyl ), sulphur-containing ( sulfhydryl, thioether, and disulphide ), and nitrogen-containing ( amine and azo ) groups; these are polar donor groups (ligands) which can supply a pair of electrons to metal cation acceptors, forming chelates ( Dwyer and Mellor, 1964 ). Adjacent donor groups provide an opportunity for 5- or 6- membered ring closure, which is a feature of chelation, as shown below :



Some of these chelating compounds have been shown to be very effective competing anions ( La Fleur and Craddock, 1967; Nagarajah et al., 1970 ).

Of the range of commonly-occurring soil organic substances considered by Struthers and Sieling (1950); Bradley and Sieling (1953), Deb and Datta ( 1967 a, b ), and Nagarajah et al. (1970 ); it appears that citrate and oxalate are the most effective in reducing P sorption by soil components and soils. On the other hand, malonate, tartrate, and malate appear to be only moderately effective, whereas acetate, succinate, and lactate have little effect on the amount of P sorbed. Some of the amino acids commonly found in the rhizosphere solution ( alanine, aspartic acid, lysine, and threonine ) were virtually ineffective in reducing P sorption ( Struthers and Sieling, 1950; Nagarajah et al., 1970 ).

A significant result obtained by Nagarajah et al. (1970) in their studies on the competitive sorption of P with organic anions on kaolinite and hydrous oxide surfaces was the marked effectiveness of polygalacturonate in reducing P sorption. In contrast, the monomer galacturonate hardly decreased P sorption. Polygalacturonate is known to form stable chelates containing five- and/or six- membered rings with Fe and Al ions ( Schweiger, 1964 ). A related observation is that the polymer has been found to complex  $\text{Ca}^{2+}$ , whereas the monomer does not.

The ability of polygalacturonate to decrease P sorption by soil components may suggest that this compound can have a similar effect on soils and possibly promote the desorption of sorbed P from soils.

The bicarbonate ion has also been shown to be effective in competing with P for sorption sites ( Nagarajah et al., 1968 ). The concentration of bicarbonate in the soil solution depends on factors such as pH and soil moisture content. Burd and Martin (1924) found that the bicarbonate concentration in the soil solution of two alkaline soils with a moisture content of 12.5% varied from  $0.14 \times 10^{-2}$  M to  $0.42 \times 10^{-2}$  M.

The work of Hingston et al. ( 1967, 1970 ) on the specific adsorption of inorganic anions suggests that anions of certain weak organic acids would also be adsorbed specifically at pH values near the  $pK_a$  values. This was confirmed by Nagarajah et al. (1970) who reported that the ability of any organic anion to compete with P for sorption sites was greatest at a pH corresponding to the second  $pK_a$  value of the organic acid.

It appears from the literature that when P and an organic anion are present together, the decrease in P sorption by an adsorbent results from the specific adsorption of the organic anion which causes competition between P and the organic anion for sorption sites. Whether an organic anion is capable of decreasing P sorption or not would be determined by the relative stabilities of the Fe- and Al- organic anion complex and the Fe- and Al- phosphate complex.

III. THE INFLUENCE OF COMPETING INORGANIC AND ORGANIC ANIONS ON THE DESORPTION OF SORBED P FROM SOIL COMPONENTS AND SOILS

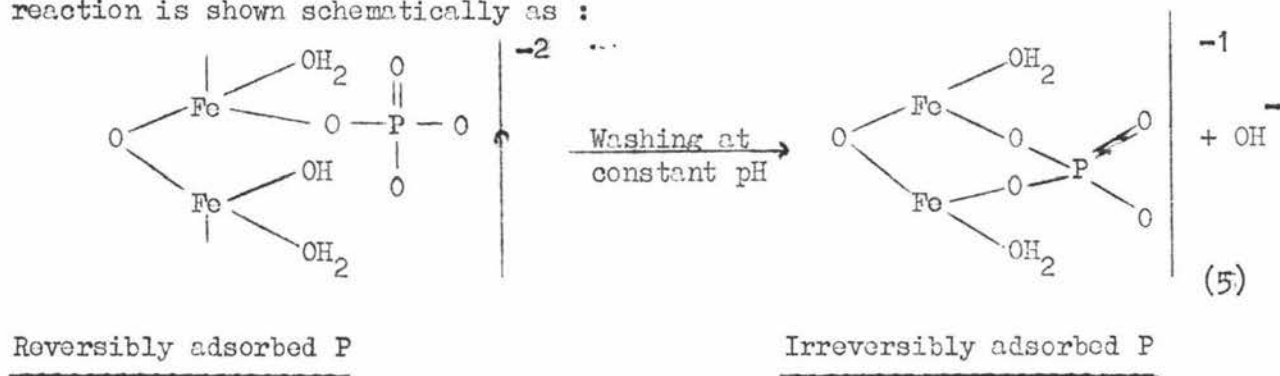
Although the mechanism of depletion of sorbed P in response to plant uptake is not completely understood, desorption must be an important step in the process, particularly when the concentration of P in the soil solution is inadequate to satisfy plant requirements. As plants progressively deplete P from the soil around their roots, the availability of the sorbed P is expected to be partly dependent on the characteristics of the desorption isotherm.

Anion exchange reactions have been described by Dean and Rubins (1947) as the substitution of one anion on the exchange complex by another anion which is present in the soil solution in greater concentration or possesses a stronger tendency to hold its position on the exchange complex. Kurtz et al. (1946) found that various anions replaced sorbed P in the following order: fluoride > oxalate > citrate > bicarbonate > borate > acetate > thiocyanate > sulphate > chloride. Borate, acetate, thiocyanate, sulphate, and chloride removed similar or smaller amounts of P than water. The stability of the complex formed between the anion and Fe or Al, compared with the Fe- or Al-phosphate complex, was thought to determine the ability of the anion to replace P (Swenson et al., 1949).

The increase in the net negative charge of Fe and Al surfaces resulting from the specific adsorption of inorganic anions led Hingston et al. (1967, 1970) to conclude that the desorption of P could only occur when the displacing anion is specifically adsorbed and present at sufficient concentrations to increase the net negative charge of the surface. They suggested, therefore, that  $\text{Cl}^-$  and  $\text{NO}_3^-$  could not desorb P because these ions are non-specifically adsorbed and cannot make the surface more negatively charged. Breuwsma and Lyklema (1973) have since claimed, however, that specific adsorption of P and other anions does not always increase the negative charge on the surface. Polybasic organic acids, such as citric, tartaric, oxalic, malic, and carbonic acids, which are found in root exudates (Rovira, 1965), conform to the requirements of Hingston et al. (1970) and have been reported to be

effective in replacing P from soil colloids ( Dean and Rubins, 1947; Swenson et al., 1949; Deb and Datta, 1967a ).

Both Muljadi et al. (1966) and Kafkafi et al. (1967) have shown that P sorption by gibbsite and kaolinite is reversible for changes in pH. When the samples were washed at constant pH, the equilibrium points did not correspond with the adsorption isotherm. Similar results were noted by Hingston et al. (1967) for selenite sorbed on goethite, and by Aylmore et al. (1967) for sulphate sorbed on Fe and Al oxides. Kafkafi et al. (1967) suggested that this irreversibility was due to the adsorbed P being relocated to positions of stronger binding to the surface which occurred when the concentration of P at the surface was reduced. Hingston et al. (1974) proposed that the P sorbed on kaolinite, which could not be desorbed on washing at constant pH, formed two coordinate bonds at the surface, whereas P which could be removed by washing was held by only one bond. The proposed reaction is shown schematically as :



This mechanism also provides an explanation for the decrease in negative charge observed during washing ( Hingston et al., 1974 ). The effect of this might be to increase the attraction between the surface and the ions remaining in solution because of the decreasing negative charge of the surface. The reason for the lack of reversibility is still incompletely understood. Evans and Syers (1971) have suggested that the diffusive penetration of P to internal surfaces with time could be involved.

The above scheme for anion desorption ( Hingston et al., 1974) may be used to explain the observation of Hingston et al. (1971) that the minimum surface area occupied per anion for P plus selenite competitively sorbed on goethite is approximately half the surface area for selenite or P when sorption is measured in the absence of competitors.

In the absence of competing anions, both P and selenite are specifically adsorbed forming bidentate ligands with surface Fe sites, whereas in the presence of both anions, monodentate ligands are formed.

Both citrate and bicarbonate have been shown to effectively desorb sorbed added P from kaolinite ( Nagarajah *et al.*, 1968 ) and from soils ( Evans and Syers, 1971 ). Nagarajah *et al.* (1968) demonstrated the effectiveness of these two anions in decreasing P sorption by kaolinite and in promoting desorption of previously sorbed P from kaolinite. Although the effects of the two anions on P sorption and desorption were similar, the concentration of the bicarbonate ion required to achieve equivalent desorption was much greater than that of the citrate ion (  $2 \times 10^{-2}$  M for bicarbonate and  $2.5 \times 10^{-3}$  M for citrate ). The pH and ionic strength of the systems were also different.

Nagarajah *et al.* (1968) suggested that at the pH of the systems used, the two anions existed in a form capable of donating and accepting protons, thus fulfilling the requirements for specific adsorption. They further postulated that the charge existing at the kaolinite surface following sorption could be made up in a number of ways depending on the sequence of sorption. When P was added before citrate or bicarbonate, a greater proportion of the charge was made up by P; the converse was true if citrate or bicarbonate was added first. When P and citrate or bicarbonate were added together, however, the resulting isotherm was very close to that obtained when citrate or bicarbonate was added first. This reflects the greater affinity of the kaolinite surface for citrate or bicarbonate, relative to P, when the anions exist together in solution. The reason for this is not clear.

Using autoradiographic techniques, Evans and Syers (1971) demonstrated that P sorbed by soil crumbs in a period of up to three weeks was essentially non-desorbable by chloride or sulphate in 7 days. The mobility of sorbed P, however, was greatly increased during desorption for 7 days with bicarbonate or citrate solutions, resulting in a complete redistribution within the crumb, and up to a 60% replacement of previously sorbed P. The applicability of such results to the practical situation appears limited because of the high anion concentrations used (  $10^{-1}$  M ) and the wide pH range observed in the extracts of the different anions.

An interesting observation was made by Barrow ( 1974, b ) in a study of the desorption of P from soils by arsenate.

With increasing time of contact between soils and P prior to arsenate addition, the proportion of the added P which was desorbed by arsenate decreased but remained independent of the level of P addition. This suggests that diffusion through the liquid phase from one adsorption site to another was not involved, because the effective diffusion coefficient would be expected to increase with an increase in the level of added P ( Lewis and Quirk, 1967 ). This conflicts with the findings of Evans and Syers (1971) who proposed a diffusive penetration of adsorbed P into the retaining component, emphasizing the need for further research in this area.

The ability of specifically adsorbed anions to desorb previously sorbed P appears to be related not only to the concentration of competing anions in solution, the pH of the system, and the length of time following P addition, but also to the properties of the associated cation ( Obihara and Russell, 1972; Barrow, 1974b ). It is probable that this effect is associated with differences in the strength of adsorption of the cation on component surfaces; cations that are specifically adsorbed ( e.g.,  $\text{Ca}^{2+}$  ); would increase the positive charge of the surface, and therefore enhance P sorption relative to non-specifically adsorbed cations ( e.g.,  $\text{Na}^+$  ). Ryden and Syers (1975), however, have shown that the effect of the associated cation on P sorption is purely kinetic.



### IMPLICATIONS OF LITERATURE TO PRESENT STUDY

The ability of inorganic and organic anions to reduce P sorption by soils, or to desorb previously sorbed P from soils, appears to be related to the amount and nature of components in the soil itself; the structure and concentration of the competing anion, and the pH of the system. The theory of specific adsorption of anions, as proposed by Hingston et al. ( 1967; 1970; 1972 ), provides an interesting explanation of the ability of anions to compete with P for sorption sites on soils and soil components. According to these workers, any increase in the net negative charge of the surface of the retaining component, resulting from the adsorption of a competing anion, should result in a reduction in the amount of P sorbed. The importance of pH in determining the charge characteristics of both adsorbent and adsorbate has also been demonstrated ( Hingston et al., 1967, 1970; Mekarua and Uehara, 1972; Sawhney, 1974 ).

The first and major difficulty in comparing the results obtained in anion sorption and desorption studies by various workers arises from the lack of uniformity in experimental conditions. In the few detailed studies of the competitive sorption and desorption of P, the effectiveness of various anions has been confused by comparisons of anion systems of widely differing concentration ( Nagarajah et al., 1968, ), of widely differing pH ( Evans and Syers, 1971 ); and of different ionic strength ( Obihara and Russell, 1972 ). In most cases this makes comparison both within and between different studies virtually impossible, thereby preventing estimations of the relative importance of each competing anion.

In most studies relating to the competitive effect of anions on P sorption and desorption by soils, the concentrations of both P and competing anions sustained in solution by the solid phase invariably have been far in excess of those found in the soil solution ( Deb and Datta, 1967 a, b; Barrow, 1974; Gebhardt and Coleman, 1974 ) because of the high levels of anions initially added. This does not provide an adequate simulation of the soil system. In many cases the levels of inorganic P added in competitive sorption/desorption studies with soils have been selected arbitrarily ( Obihara and Russell, 1972; Barrow, 1974 ) without recognising that the relationship between P sorbed by the soil and P sustained in solution can vary appreciably for different soils.

The purpose of this study is, firstly, to determine the extent to which commonly occurring inorganic and organic anions affect the sorption of P by soils and, secondly, to determine the extent to which inorganic and organic anions in the soil solution influence the desorption of both native and added sorbed P from soils. In each case, the level of P added to a particular soil is determined from the adsorption maxima of regions established using the Langmuir equation.

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SORPTION AND DESORPTION OF INORGANIC PHOSPHATE  
BY SOILS AS INFLUENCED BY COMPETING INORGANIC  
AND ORGANIC ANIONS

ABSTRACT

The extent to which inorganic and organic anions, at concentrations relevant to the soil solution, affect the sorption of added inorganic phosphate (P), and influence the desorption of both previously sorbed added P and native P, was studied using four contrasting soils. These soils varied in properties and amounts of components believed to be important in P sorption reactions in soils. In contrast to  $10^{-2}$  M  $\text{NO}_3^-$ ,  $10^{-2}$  M  $\text{SO}_4^{2-}$ , and  $10^{-3}$  M  $\text{HCO}_3^-$ ,  $10^{-3}$  M citrate and  $10^{-5}$  M polygalacturonate (PGU) were generally effective in reducing P sorption and in promoting desorption of previously sorbed added P from the four soils. In all studies, however,  $10^{-5}$  M PGU was more effective in this regard than equivalent concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and citrate. The greater affinity of P, relative to other anions, for sorption sites on components in the four soils observed for concentrations equal to or lower than those of the competing anions, is attributed to the strong covalent character of the bond formed between the phosphate ion and the Fe and/or Al constituting surface sites. Only  $10^{-2}$  M  $\text{SO}_4^{2-}$ ,  $10^{-3}$  M citrate, and  $10^{-5}$  M PGU removed detectable amounts of native P from the four soils. The importance of pH control is emphasized by the results obtained for the sorption and desorption of P in the presence of other anions. Kinetic studies of P sorption in the presence and absence of competing anions over a 6-day shaking period showed that  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  had little observable effect on the amounts of P sorbed by the soils after the initial 40-hour shaking period. In contrast; PGU produced a marked time-dependent increase in the final solution P concentration with the Egmont and Okaihau soils, while citrate, under the same conditions, caused a dramatic decrease with the Okaihau and Waiareka soils. These two observations were explained in terms of a steric hindrance effect for PGU, and an increase in microbial activity for citrate. Of the five anions studied, only  $10^{-3}$  M citrate and  $10^{-5}$  M PGU removed significant amounts of Fe and Al from the soils. A very close relationship was established between the reduction in the amount of added P sorbed and the amounts of ( Fe + Al ) removed from the

Okaihau soil by increasing concentrations of citrate. This indicates that the reduction in P sorption results primarily from the elimination of a significant number of sites rather than from a direct specific adsorption of citrate. A similar interpretation was given to explain the competitive effect of PGU.

## MATERIALS AND METHODS

### Soils

Horizons developed from Egmont black loam (BC) developed from andesitic tephra, Waiareka clay (B1) developed from weathered basaltic tuff, Okaihau gravelly clay (B2) developed from deeply weathered olivine basalt, and Porirua fine sandy loam (B1) largely developed from greywacke-derived sands, were obtained from the reference sites for these soils (N.Z. Soil Bureau, 1968). The four soils were chosen because of their range of components which are potentially important in determining the amount of inorganic phosphate (P) sorbed by soils. The soils were air-dried and material passing through a 2 mm sieve was used for all analyses.

### Anion solutions

Five inorganic and organic anions suspected of showing a range of specificity for sorption sites in soils were used in P sorption and desorption studies. These were nitrate ( $\text{NO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ), citrate, and polygalacturonate (PGU). For all experiments, anion solutions were prepared using the sodium salt and the concentrations used were approximately equivalent to the concentration ranges reported for these anions in the soil solution (Burd and Martin, 1924; Eaton et al., 1960; Larsen and Widdowson, 1968). For  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ,  $10^{-2}$ ,  $10^{-3}$ , and  $10^{-5}$  M solutions, corresponding to high, intermediate, and low soil solution concentrations were used; for citrate and  $\text{HCO}_3^-$ ,  $10^{-3}$  and  $10^{-5}$  M solutions were used; and for PGU  $10^{-5}$  and  $10^{-7}$  M\* solutions were used.

Sodium perchlorate ( $10^{-1}$  M) was used as the support medium to maintain a constant ionic strength and to serve as an indifferent electrolyte. Phosphate solutions of differing concentrations were prepared from disodium hydrogen orthophosphate ( $\text{Na}_2\text{HPO}_4$ ). Sodium hydroxide or perchloric acid were used to adjust the pH of all solutions

\* The molecular weight (M.W.) of the polygalacturonic acid preparation used ranged from 26,400 to 70,400. An M.W. of 50,000 was assumed in solution preparation.

to either pH 5.5 ( solutions added to Okaihau and Porirua soils ); or to pH 6.5 ( solutions added to Egnont and Waiareka soils ). The instability of  $\text{HCO}_3^-$  at pH values less than 6.0 prevented the preparation of a  $10^{-3}\text{M}$   $\text{HCO}_3^-$  solution at pH 5.5. For this reason  $\text{HCO}_3^-$  was used as a competing anion only in studies with the Egnont and Waiareka soils.

#### Analytical methods

Sorption of inorganic P in the presence and absence of competing anions was evaluated by shaking duplicate 1-g soil samples with 40 ml of sodium perchlorate support medium containing the appropriate amount of P and competing anion in 50-ml polycarbonate centrifuge tubes ( Oak-Ridge type ) on an end-over-end shaker at 21 C for 40 hours. After shaking the suspensions were centrifuged at 15,000 r.p.m. at 21 C for 10 minutes and the supernatant solutions were passed through a 0.45  $\mu\text{m}$  Millipore filter. An aliquot was taken for the determination of dissolved inorganic P. The amount of P sorbed was calculated as the difference between P added and P in solution after shaking.

The levels of added P required to give a final solution P concentration of 0 to approximately 10  $\mu\text{g}/\text{ml}$  varied with each soil. The maximum additions of P used were 3600, 2400, 900, and 900  $\mu\text{g P/g}$  for Egnont, Okaihau, Waiareka, and Porirua soils, respectively.

Data for the sorption of P by the four soils were evaluated using the Langmuir adsorption equation, which can be written as follows :

$$x = \frac{K_1 K_2 C}{1 + K_1 C} \quad (6)$$

where  $x$  = amount of P sorbed per gram of soil  
 $K_1$  = a constant related to the binding energy  
 $K_2$  = adsorption maximum  
 $C$  = final solution P concentration

Equation (6) can be arranged to give :

$$\frac{1}{x} = \frac{1}{K_1 K_2 C} + \frac{1}{K_2} \quad (7)$$

A plot of  $\frac{1}{x}$  versus  $\frac{1}{C}$  gives a series of straight lines ( hereafter referred to as "regions" ) from which  $K_2$  (  $y$  - intercept<sup>-1</sup> ) and  $K_1$  ( intercept/gradient ) can be obtained.

The extent to which competing anions reduce P sorption was determined for each soil using levels of added P corresponding to 40% of the adsorption maximum of the first two linear regions given by the Langmuir equation. The levels of P added to the four soils are given in Table 1 on a  $\mu\text{g/g}$  and a molar basis. Anion solutions and P solutions of appropriate concentration were added simultaneously to duplicate 1-g soil samples with sodium perchlorate as the support medium. After a 40-hour shaking period, the supernatants were recovered and the concentration of P in solution determined. The amount of P sorbed was calculated as above.

The extent to which competing anions desorb previously sorbed P was determined for each soil by shaking duplicate 1-g soil samples with 35 ml of sodium perchlorate support medium containing the appropriate amount of P for 24 hours. A 50ml aliquot of the appropriate anion solution was then added and the tubes shaken for a further 40 hours, before the concentration of P remaining in solution was determined.

The extent to which competing anions desorb native P from each soil was determined by shaking 1-g soil samples with 40 ml of support medium containing the appropriate anion for 40 hours. The amount of P in the final solution was then determined.

In addition to P concentration, the pH of all supernatants was also measured. The effect of pH on P sorption was determined for each soil by adjusting the initial pH of solutions added to 1-g soil samples with either sodium hydroxide or perchloric acid. The additions of P used were 1350, 450, 850, and 350  $\mu\text{g P/g}$  for Egmont, Waiareka, Okaihau, and Porirua soils, respectively. Following a 40-hour shaking period, the pH and P concentration in the supernatant solutions were determined.

Kinetic effects of P sorption in the presence and absence of competing anions were determined for each soil at two levels of added P. Additions of P were 1400 and 3600  $\mu\text{g P/g}$  for Egmont, 60 and 500  $\mu\text{g P/g}$  for Waiareka, 200 and 900  $\mu\text{g P/g}$  for Okaihau, and 50 and 400  $\mu\text{g P/g}$  for Porirua. Anion solutions were added only at

TABLE 1 -- Levels of P added to the four soils expressed on a  $\mu\text{g/g}$  soil ( or  $\mu\text{g}/40 \text{ ml}$  ) and a molar basis

| Soil      | Level of added P for :                             |             |                      |                      |
|-----------|--|-------------|----------------------|----------------------|
|           | Region I *   | Region II * | Region I *           | Region II *          |
|           | ( $\mu\text{g/g}$ or $\mu\text{g}/40 \text{ ml}$ ) |             | ( M )                |                      |
| EGMONT    | 200  | 1350        | $1.6 \times 10^{-4}$ | $1.1 \times 10^{-3}$ |
| OKAIHAU   | 150  | 850         | $1.2 \times 10^{-4}$ | $6.9 \times 10^{-4}$ |
| WAIIOREKA | 60   | 450         | $5.0 \times 10^{-5}$ | $4.0 \times 10^{-4}$ |
| PORIRUA   | 50   | 350         | $4.0 \times 10^{-5}$ | $2.8 \times 10^{-4}$ |

\* For 40% saturation of the adsorption maximum in each region.

their highest concentration (  $10^{-2}$ M  $\text{NO}_3^-$ ,  $10^{-2}$ M  $\text{SO}_4^{2-}$ ,  $10^{-3}$ M  $\text{HCO}_3^-$ ,  $10^{-3}$ M citrate, and  $10^{-5}$ M PGU ). The appropriate amounts of P and competing anion were added in 2-ml and 5-ml aliquots, respectively, 0, 1, 2, and 3 days after commencing to shake 1-g samples of each soil in 33 ml of sodium perchlorate support medium. Shaking was continued for a further 70 hours. Consequently, the total time of contact between P plus competing anion ranged from approximately 70 to 140 hours. The supernatant solution of all systems was recovered and inorganic P determined.

The method of Murphy and Riley (1962) was used for the determination of P in all extracts and absorbance was measured at 712nm using a Unicam SP 1800 B Spectrophotometer. Citrate and PGU solutions did not interfere in the colorimetric procedure at concentrations less than  $10^{-3}$ M and  $10^{-5}$ M, respectively. The effects of microbial activity, however, were apparent with increasing time of contact between P and citrate or PGU solutions ( Table 2.1 ), the levels of P in solution showing a marked decrease with time. Addition of  $\text{HgCl}_2$  as a microbial inhibitor, at a concentration of 40  $\mu\text{g}/\text{ml}$ , arrested this observed decrease in P levels ( Table 2.2 ). Interference from  $\text{Hg}^{2+}$  in solution was eliminated by the use of a metabisulphite-thiosulphate reagent ( Tillman and Syers, 1975 ) prior to P determination. Consequently, all experiments were conducted in the presence of 40  $\mu\text{g}$   $\text{HgCl}_2/\text{ml}$ , added with the sodium perchlorate support medium, to inhibit microbial activity.

The amounts of iron (Fe) and aluminium (Al) removed from 1-g samples of each soil by competing anions in the presence of two levels of added P during a 40-hour shaking period were determined colorimetrically by the ferron orthophenanthroline method of Rainwater and Thatcher (1960). The amounts of Fe and Al in the citrate extracts were determined after oxidation of the citrate by digestion with  $\text{HNO}_3^-$  -  $\text{H}_2\text{SO}_4$ , ignition at  $450^\circ\text{C}$ , and digestion of the residue in 0.5N HCl. This method was also used to determine Fe and Al in the citrate supernatants from the P sorption kinetic study using the Waiareka and Okaihau soils.

The relationship between P sorbed and the amounts of Fe, or Al, or ( Fe + Al ) released from the Okaihau soil in the presence of citrate was determined by shaking duplicate 1-g soil samples with

TABLE 2.1 -- Effect of polygalacturonate (PGU) and citrate on the colorimetric determination of inorganic P by the Murphy and Riley (1962) method.

| Anion system                             | Milliabsorbance values of solutions after : |         |          |
|--|---|---------|----------|
|  | 30 minutes                                  | 6 hours | 40 hours |
| 2 $\mu$ g P/50 nl                        | 205   | 204     | 202      |
| 2 $\mu$ g P/50 nl + $10^{-5}$ M PGU      | 204   | 157     | 153      |
| 2 $\mu$ g P/50 nl + $10^{-3}$ M citrate  | 203   | 196     | 136      |
| 2 $\mu$ g P/50 nl + $10^{-5}$ M citrate  | 204   | 203     | 203      |
| 10 $\mu$ g P/50 nl                       | 103   | 102     | 102      |
| 10 $\mu$ g P/50 nl + $10^{-5}$ M PGU     | 102   | 101     | 51       |
| 10 $\mu$ g P/50 nl + $10^{-3}$ M citrate | 103   | 84      | 69       |
| 10 $\mu$ g P/50 nl + $10^{-5}$ M citrate | 103   | 103     | 102      |



TABLE 2.2 --- Effect of polygalacturonate (PGU) and citrate, in the presence of  $40 \mu\text{g HgCl}_2/\text{ml}$ , on the colorimetric determination of inorganic P by the Murphy and Riley (1962) method.

| Anion system   | Milliabsorbance values of solutions after : |          |
|--|---|----------|
|  | 6 hours                                     | 40 hours |
| $2 \mu\text{g P}/50 \text{ ml} + \text{HgCl}_2$                              | 205   | 204      |
| $2 \mu\text{g P}/50 \text{ ml} + \text{HgCl}_2 + 10^{-5} \text{ M PGU}$      | 205   | 205      |
| $2 \mu\text{g P}/50 \text{ ml} + \text{HgCl}_2 + 10^{-3} \text{ M citrate}$  | 203   | 204      |
|  |   |          |
| $10 \mu\text{g P}/50 \text{ ml} + \text{HgCl}_2$                             | 103   | 103      |
| $10 \mu\text{g P}/50 \text{ ml} + \text{HgCl}_2 + 10^{-5} \text{ M PGU}$     | 103   | 102      |
| $10 \mu\text{g P}/50 \text{ ml} + \text{HgCl}_2 + 10^{-3} \text{ M citrate}$ | 103   | 103      |

40 ml of sodium perchlorate containing 0 and 850  $\mu\text{g}$  P and citrate solutions of  $10^0$ ,  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$  M concentration. After a 40-hour shaking period, P, Fe, and Al were determined in the supernatant solution following oxidation of citrate as described above. The extent to which citrate reduced P sorption was calculated from the difference between the final solution P concentrations in the presence and absence of added P.

## RESULTS AND DISCUSSION

### A. Sorption of Added P

The four soils varied appreciably in their ability to sorb added inorganic phosphate (P). At the highest levels of P addition for each soil, Egmont sorbed 92% ( 3600  $\mu\text{g}$  P added/g ), Okaihau 82% ( 2400  $\mu\text{g}$  P added/g ), Waiareka 62% ( 900  $\mu\text{g}$  P added/g ), and Porirua 54% ( 900  $\mu\text{g}$  P added/g ) of added P ( Figure 1 ). Variation in the ability of the four soils to sorb added P appears to be related to the amounts of certain components believed to be important in essentially controlling P sorption by soils ( Table 3 ).

Although the Okaihau soil has a higher surface area and contains a considerably greater amount of crystalline Fe components and associated Al ( CDB-Al ) than the Egmont soil, its ability to sorb P is not as great. This may be due to the greater amount of short-range order Fe and Al components in the "allophanic" Egmont soil. The ability of short-range order Fe and Al components, including aluminosilicates, to sorb added P is usually greater than that of the crystalline analogues ( Gorbunov, 1959; Gastuche et al., 1963; Fox et al., 1971 ).

In comparison with the Egmont and Okaihau soils, the Waiareka and Porirua soils sorbed much lower amounts of P. The latter two soils contain smaller amounts of both crystalline and short-range order Fe and Al components ( Table 3 ). The slightly greater ability of the Waiareka soil to sorb P, compared to the Porirua soil, may be attributed to the higher clay content of the former ( 68% compared to 15%, respectively ). Because the soil components thought to be involved in P sorption are themselves interrelated ( Syers et al., 1971 ), it is difficult to determine which components make the largest contribution to the sorption of P by the four soils studied.

When the sorption data for the four soils are plotted according to the Langmuir equation, described earlier, three linear relationships were obtained for each soil, suggesting the existence of three populations of sites, each with a widely differing affinity for P. Figure 2.1 demonstrates this relationship for the Waiareka

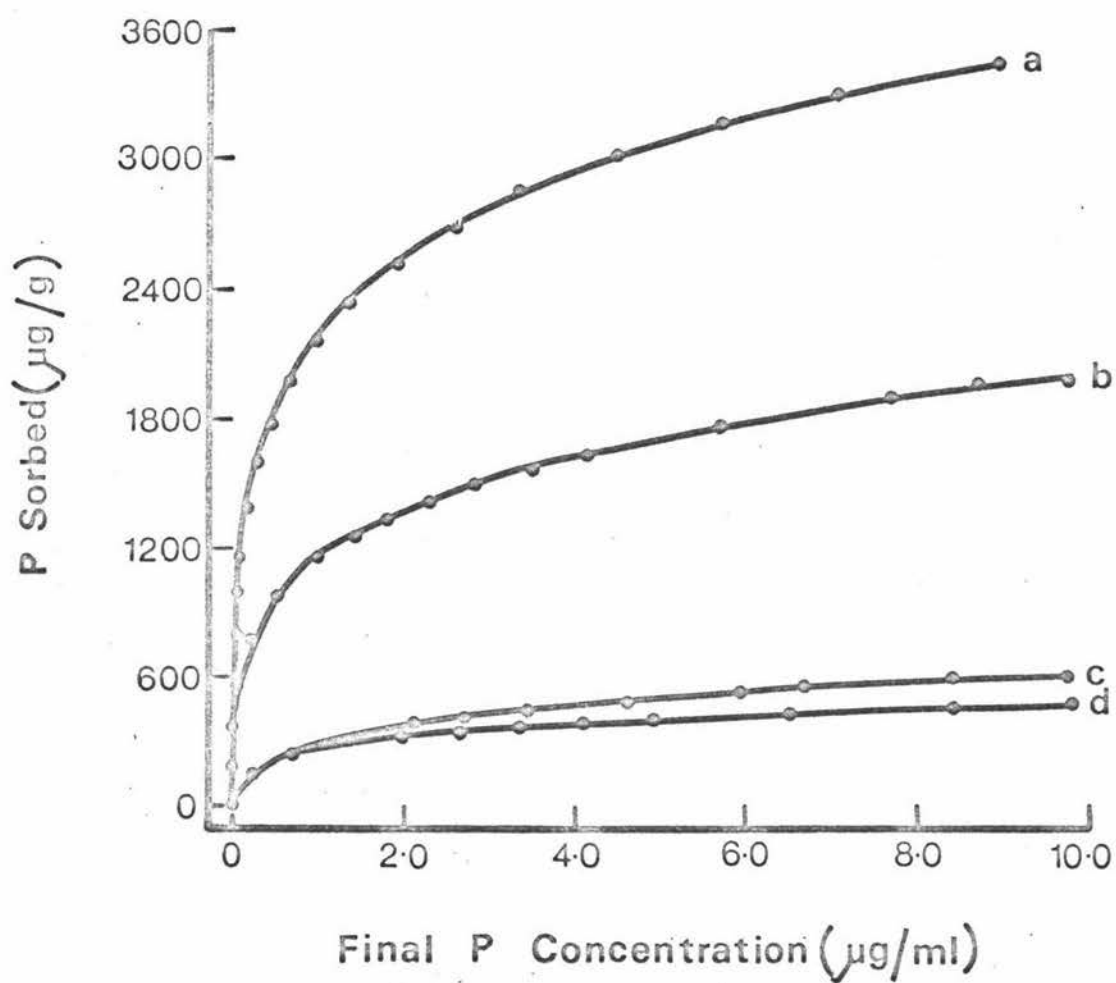


FIGURE 1 : Isotherms for the sorption of added inorganic P by the four soils following a 40-hour shaking period

- a Egmont soil
- b Okaihau soil
- c Waiareka soil
- d Porirua soil

TABLE 3 -- Some characteristics of the soils used.

| 44 Soil                 | Horizon | Depth<br>cm | pH  | Exchangeable | Crystalline | CDB  | Short-range order |      | Total clay |
|-------------------------|---------|-------------|-----|--------------|-------------|------|-------------------|------|------------|
|                         |         |             |     | Al           | Fe          | Al   | Fe                | Al   | %          |
|                         |         |             |     | mm/100 g     |             |      |                   |      |            |
| EGMONT BLACK LOAM       | BC      | 43 - 61     | 7.1 | 1.03         | 21          | 78   | 19.5              | 133  | 41         |
| OKAIHAU GRAVELLY CLAY   | B2      | 23 - 40     | 5.0 | 0.57         | 139         | 124  | 5.2               | 18   | 31         |
| WAIAREKA CLAY           | B1      | 17 - 30     | 6.3 | 0.84         | 3.5         | 18.9 | 4.8               | 10.6 | 68         |
| PORIRUA FINE SANDY LOAM | B1      | 20 - 33     | 5.0 | 0.72         | 7.3         | 10   | 3.3               | 5.6  | 15         |

Data for Egnont, Okaihau, and Porirua soils are taken from Ryden and Syers (1975)

Data for Waiareka soil were obtained employing methods described by Ryden and Syers (1975)

Clay mineralogy ( as % of < 2  $\mu$ m fraction )\*

Egnont : 75% allophane, 25% gibbsite

Okaihau : 53% gibbsite, 29% kaolinite, 24% free Fe<sub>2</sub>O<sub>3</sub>

Waiareka: 100% nontronite

Porirua : 33% interlayered hydrous mica, 31% vermiculite, 17% kaolinite

\*Data from New Zealand Soil Bureau (1968)

and Porirua soils. Binding energy values ( $K_1$ ) and adsorption maximum ( $K_2$ ) were calculated for region I (straight line plot corresponding to high  $\frac{1}{C}$  values) from (gradient<sup>-1</sup> x intercept) and (intercept<sup>-1</sup>), respectively. In order to calculate the  $K_1$  and  $K_2$  values for region II it was necessary to subtract the adsorption maximum for region I ( $K_2^I$ ) from each of the x values for the data points in region II. Figure 2.2 shows a plot of region II data for Waiareka and Porirua soils using corrected values. A third region is evident on the Langmuir isotherm for both soils at  $\frac{1}{C}$  values less than 0.3 ml/ $\mu$ g. Because region III corresponds to rather high final solution P concentrations ( $> 3.33 \mu\text{g P/ml}$ ), emphasis was placed on Regions I and II in subsequent studies.

The adsorption maximum and binding energy values obtained for regions I and II for each soil are shown in Table 4. For all soils, region I described a relatively small population of sites having a high affinity for P, compared to that of region II. The levels of added P used in subsequent experiments corresponded to 40% of the adsorption maximum for each region. It is assumed that at this level of addition most of the P will be sorbed by sites having the highest affinity for P, with little sorption occurring in a region of lower affinity. This approach appears advantageous in that the ability of an anion to compete with P for sorption sites may be related to a particular region on the isotherm having a reasonably-well defined affinity (or binding energy) for P.

## B. Sorption of Added P in the Presence of Competing Anions

### I. As evaluated by P adsorption isotherms

The extent to which competing anions affect the P sorption characteristics of Egmont, Waiareka, Okaihau, and Porirua soils is shown in Figures 3.1, 3.2, 3.3, and 3.4, respectively. Only the highest anion concentrations were used as it was assumed that lower anion concentrations would have less effect on P sorption. For the Egmont soil, the P sorption isotherms in the presence of  $10^{-2} \text{M SO}_4^{2-}$ ,  $10^{-3} \text{M HCO}_3^-$ , and  $10^{-5} \text{M PGU}$  are so similar that they plot on the same curve (Figure 3.1). Similarly, for the Waiareka soil, the isotherms for P alone,  $10^{-2} \text{M NO}_3^-$ , and  $10^{-3} \text{M HCO}_3^-$  are plotted as one

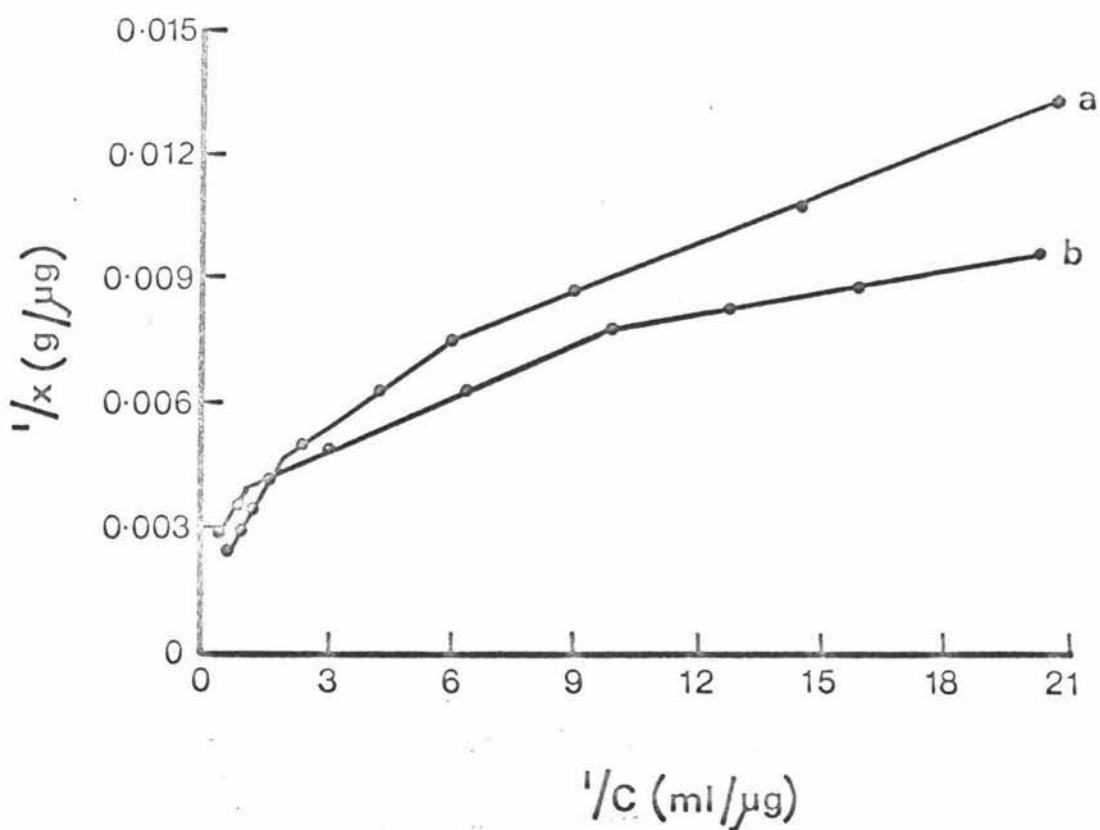


FIGURE 2.1 : Isotherms for the sorption of added inorganic P by Waiareka and Porirua soils obtained using the Langmuir adsorption equation

- a Waiareka soil
- b Porirua soil

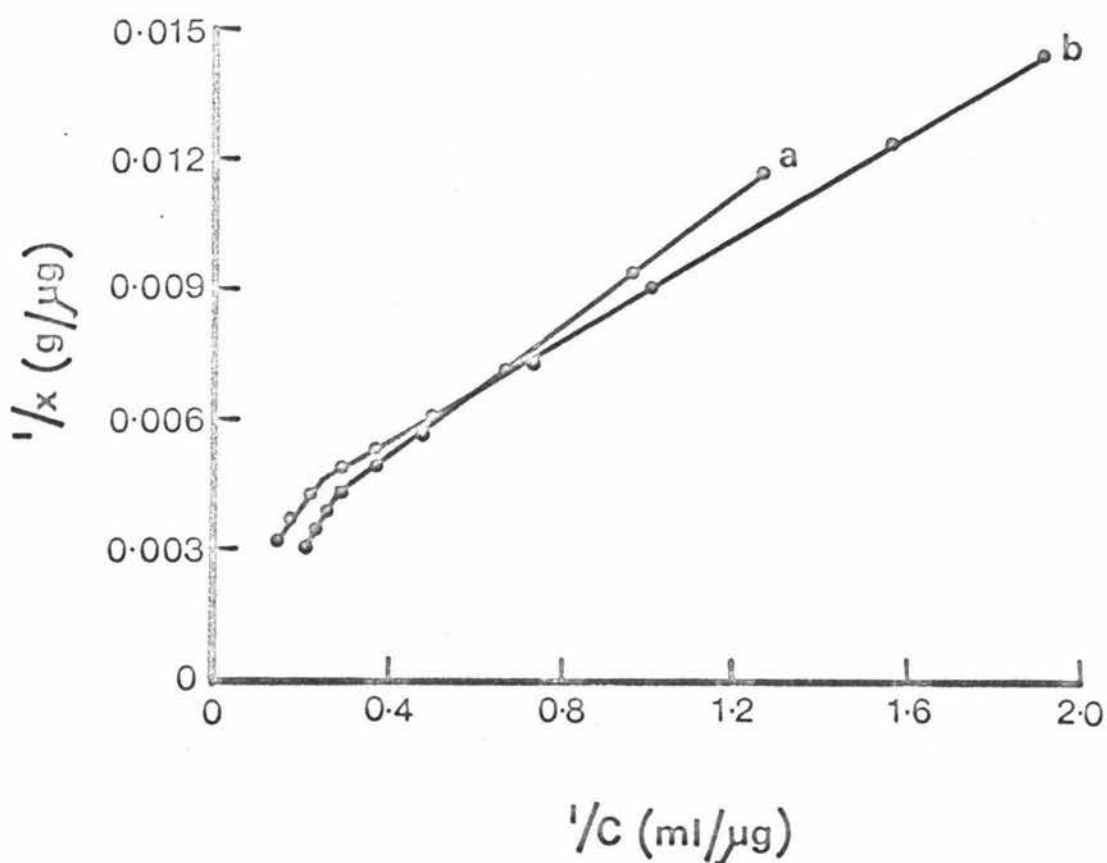


FIGURE 2.2 : Isotherms for the sorption of added inorganic P in region II by Waiareka and Porirua soils using the Langmuir adsorption equation. Data replotted after  $K_2^I$  was subtracted from each of the observed  $x$  values for region II.

- a Waiareka soil
- b Porirua soil



TABLE 4 --- Adsorption maximum ( $K_2$ ) and binding energy values ( $K_1$ ) for inorganic P sorbed in regions I and II by the four soils, calculated from the Langmuir adsorption equation following a 40-hour shaking period.

| Soil     | Adsorption maximum ( $K_2$ )<br>( $\mu\text{g/g}$ ) |           | Binding energy values<br>( $\text{ml}/\mu\text{g}^{-1}$ ) |           |
|----------|---|-----------|---|-----------|
|          | Region I  | Region II | Region I  | Region II |
| EGMONT   | 709   | 1736      | 197   | 3.92      |
| WAIAREKA | 203   | 422       | 12.0  | 0.330     |
| OKAIHAU  | 459   | 1020      | 29.1  | 2.50      |
| PORIRUA  | 164   | 339       | 33.6  | 0.477     |

FIGURE 3 : Isotherms for the sorption of added inorganic P by the four soils in the presence and absence of competing anions following a 40-hour shaking period

Figure 3.1 Egmont soil  
Figure 3.2 Waiareka soil  
Figure 3.3 Okaihau soil  
Figure 3.4 Porirua soil

a P alone  
b  $10^{-2}$ M  $\text{NO}_3^-$   
c  $10^{-2}$ M  $\text{SO}_4^{2-}$   
d  $10^{-3}$ M  $\text{HCO}_3^-$   
e  $10^{-3}$ M citrate  
f  $10^{-5}$ M PGU

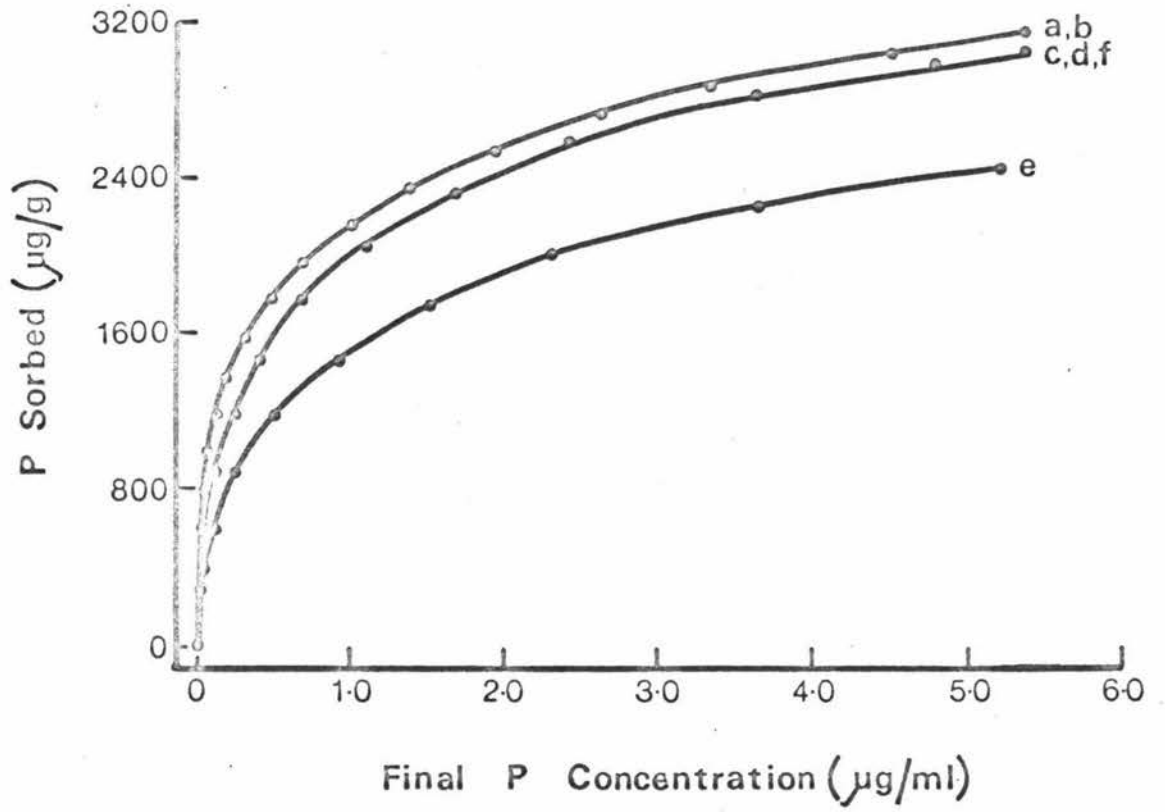


FIGURE 3.1 : Egmont soil

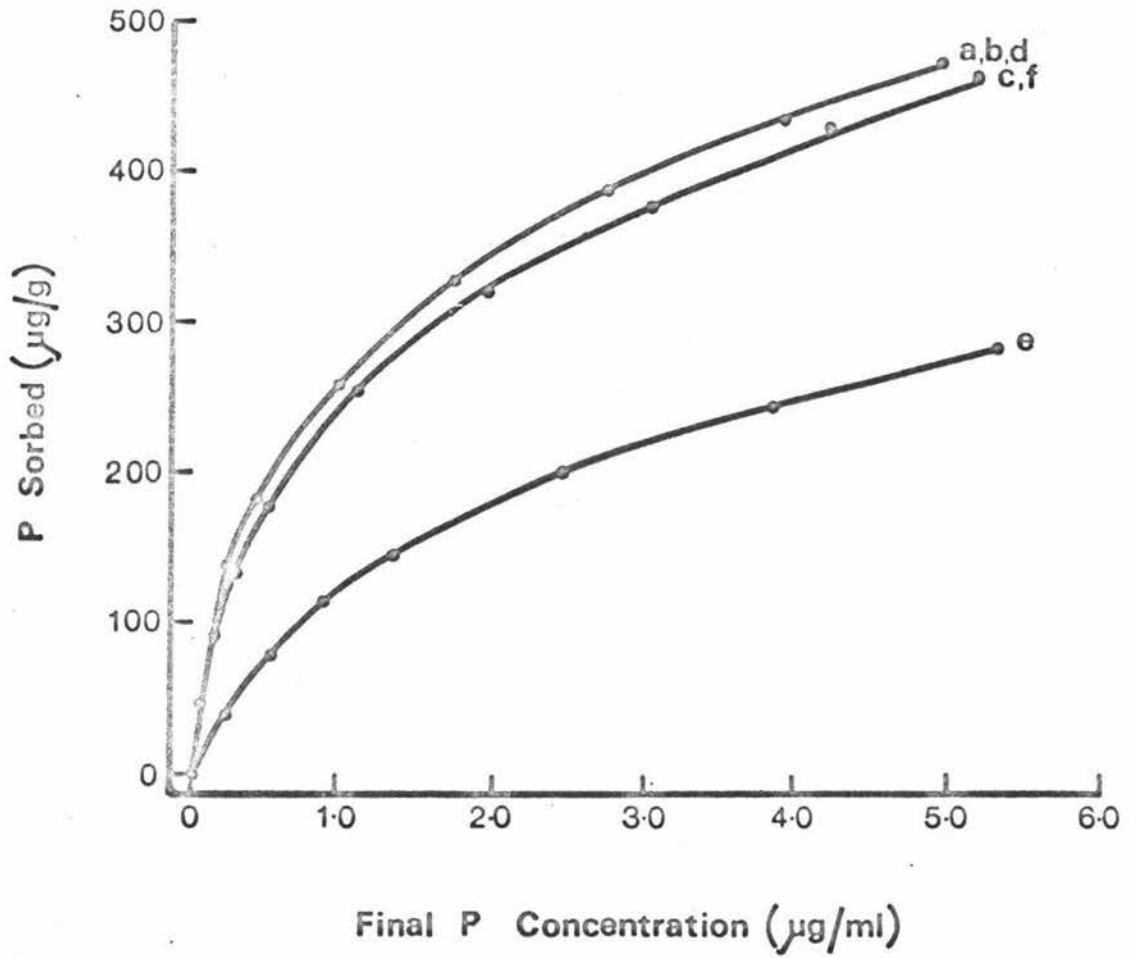


FIGURE 3.2 : Waiareka soil

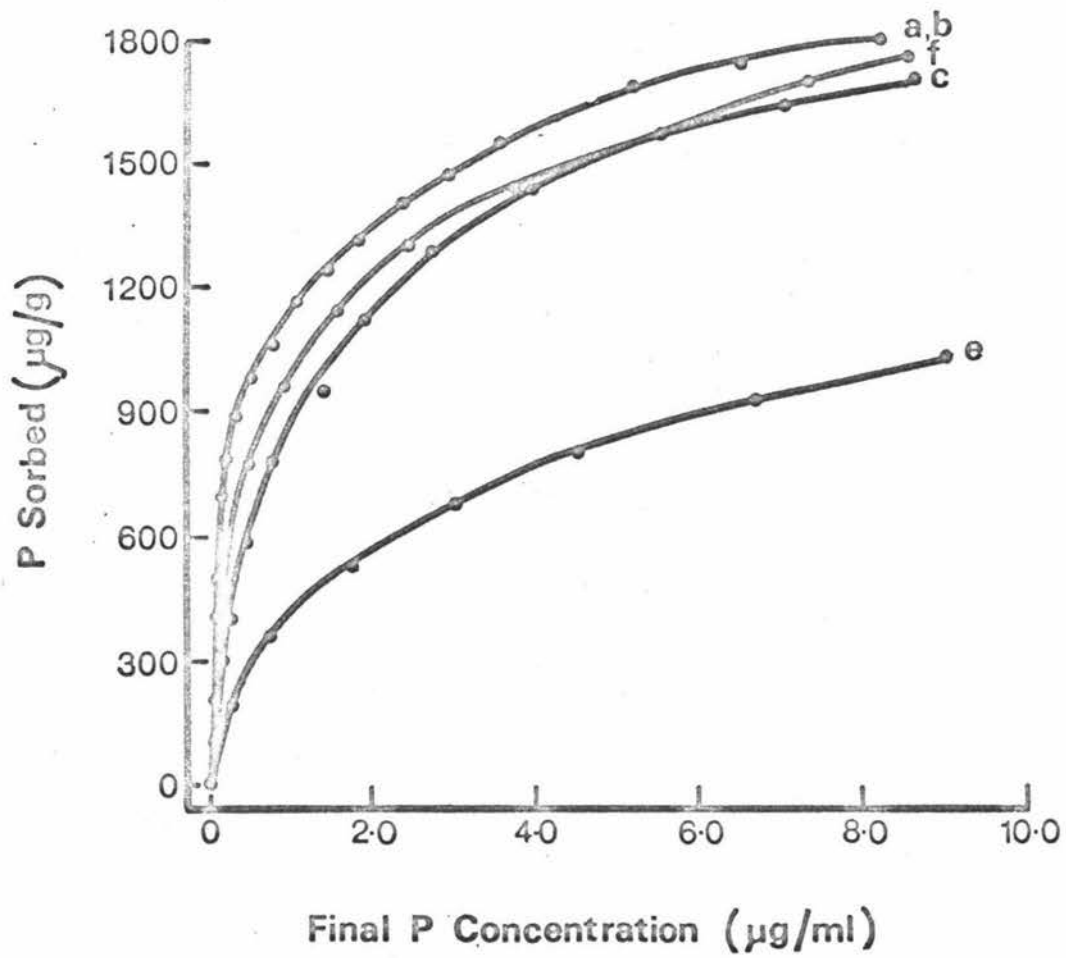


FIGURE 3.3 : Okaihau soil

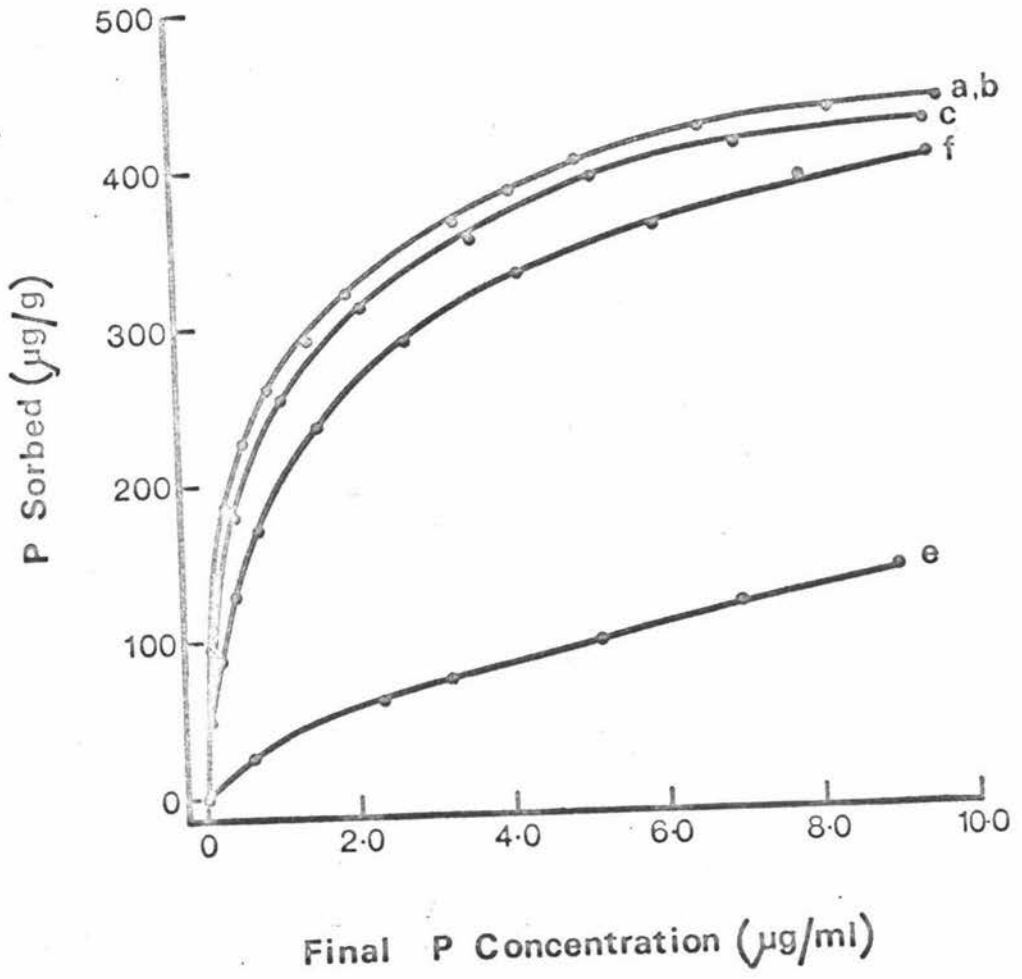


FIGURE 3.4 : Porirua soil

curve, as are the data for  $10^{-2}\text{M SO}_4^{2-}$  and  $10^{-5}\text{M PGU}$  ( Figure 3.2 ). The small differences in the amounts of P sorbed by the two soils in the presence of these competing anions at final solution P concentrations of 1 and 4  $\mu\text{g}/\text{ml}$  are shown in Table 5, to indicate the very small differences in amounts of P sorbed.

It is immediately obvious that  $10^{-2}\text{M NO}_3^-$ ,  $10^{-2}\text{M SO}_4^{2-}$ , and  $10^{-3}\text{M HCO}_3^-$  have only a limited ability to reduce the amount of P sorbed by the four soils. This observation is particularly interesting, especially in the case of  $\text{HCO}_3^-$ , which is commonly believed to be very effective in reducing P sorption by soils ( Nagarajah *et al.*, 1968 ). As discussed earlier, however, these workers used  $\text{HCO}_3^-$  concentrations (  $10^{-2}\text{M}$  ) that were much higher than that normally found under slightly acid soil conditions, and that used in this study.

In contrast,  $10^{-3}\text{M}$  citrate proved to be very effective in reducing P sorption by all soils. This was especially the case for the two soils studied at pH 5.5 ( Okaihau and Porirua ), the reduction in P sorption at a final solution P concentration of 5  $\mu\text{g P}/\text{ml}$  being 21, 42, 51, and 77% for Egnont, Waiareka, Okaihau, and Porirua soils, respectively. The effectiveness of  $10^{-5}\text{M PGU}$  in reducing P sorption was most noticeable with the Porirua soil and at low final solution P concentrations with the Okaihau soil.

## II. At defined levels of added P

The ability of competing anions to reduce P sorption by the four soils was studied using levels of added P equivalent to 40% of the adsorption maximum for regions I and II for each soil. The data in Tables 6.1, 6.2, 6.3, and 6.4 show the final solution P concentrations following a 40-hour shaking period of the soils with the specified levels of P and competing anions. The increase in P in solution as a result of the presence of a competing anion is expressed as a percentage of P in solution in the absence of competing anions. Any increase in P in solution may be interpreted as a decrease in the amount of P sorbed by the soil. It is important to point out, however, that at low levels of added P, a high percentage increase in the final solution P concentration does not necessarily indicate a large decrease in the amount of P sorbed.

TABLE 5 --- Amounts of P sorbed at final solution P concentrations of 1 and 4  $\mu\text{g}/\text{nl}$  by the Egnont soil in the presence of  $10^{-2}\text{M SO}_4^{2-}$ ,  $10^{-3}\text{M HCO}_3^-$ , and  $10^{-5}\text{M PGU}$ , and by the Waiareka soil in the presence of P alone,  $10^{-2}\text{M NO}_3^-$ ,  $10^{-3}\text{M HCO}_3^-$ ,  $10^{-2}\text{M SO}_4^{2-}$ , and  $10^{-5}\text{M PGU}$ , following a 40-hour shaking period.

| Anion systems                        | Amounts of P sorbed ( $\mu\text{g}/\text{g}$ ) at final<br>solution P concentrations<br>of : |                           |
|--------------------------------------|--|---------------------------|
|                                      | 1 $\mu\text{g}/\text{nl}$  | 4 $\mu\text{g}/\text{nl}$ |
|                                      | EGMONT   |                           |
| $10^{-2}\text{M SO}_4^{2-}$          | 2030   | 2920                      |
| $10^{-3}\text{M HCO}_3^-$            | 1995   | 2905                      |
| $10^{-5}\text{M PGU}$                | 2020   | 2880                      |
| WAIAREKA                             |  |                           |
| P alone and $10^{-2}\text{M NO}_3^-$ | 262  | 435                       |
| $10^{-3}\text{M HCO}_3^-$            | 265  | 442                       |
| $10^{-2}\text{M SO}_4^{2-}$          | 253  | 418                       |
| $10^{-5}\text{M PGU}$                | 251  | 424                       |



TABLE 6 -- Effect of competing anions on the final solution P concentration when soils are shaken for 40 hours with solutions containing both inorganic P and anions at the indicated concentration. Amounts of added P correspond to 40% of the adsorption maxima of regions I and II of the Langmuir adsorption isotherm.

TABLE 6.1 --- Egnont soil

| Anion system                        | P in solution following addition of :            |                                       |   |                                     |
|-------------------------------------|--|---------------------------------------|---|-------------------------------------|
|                                     | 200 $\mu\text{g P/g}$ soil                       |                                       | 1350 $\mu\text{g P/g}$ soil                               |                                     |
|                                     | $\mu\text{g P}$ in solu-<br>tion per g<br>soil : | % increase<br>of P in solu-<br>tion : | $\mu\text{g P}$ in<br>solution of P in<br>per g<br>soil : | % increase<br>of P in<br>solution : |
| Soil + P                            | 0.210  | -                                     | 6.77  | -                                   |
| " " " + $10^{-2}\text{M NO}_3^-$    | 0.203  | - 3.33                                | 6.30  | - 6.94                              |
| " " " + $10^{-3}\text{M NO}_3^-$    | 0.218  | 3.60                                  | 6.98  | 2.40                                |
| " " " + $10^{-5}\text{M NO}_3^-$    | 0.288  | 23.3                                  | 7.15  | 5.00                                |
| " " " + $10^{-2}\text{M SO}_4^{2-}$ | 0.398  | 70.1                                  | 11.5  | 68.7                                |
| " " " + $10^{-3}\text{M SO}_4^{2-}$ | 0.382  | 63.2                                  | 7.93  | 16.3                                |
| " " " + $10^{-5}\text{M SO}_4^{2-}$ | 0.273  | 16.6                                  | 6.70  | 0                                   |
| " " " + $10^{-3}\text{M HCO}_3^-$   | 0.398  | 70.1                                  | 8.96  | 31.4                                |
| " " " + $10^{-5}\text{M HCO}_3^-$   | 0.203  | 0                                     | 7.34  | 7.70                                |
| " " " + $10^{-3}\text{M citrate}$   | 0.920  | 293                                   | 29.8  | 336                                 |
| " " " + $10^{-5}\text{M citrate}$   | 0.320  | 36.7                                  | 7.60  | 11.6                                |
| " " " + $10^{-5}\text{M PGU}$       | 1.16   | 396                                   | 11.9  | 75.0                                |
| " " " + $10^{-7}\text{M PGU}$       | 0.320  | 36.7                                  | 7.20  | 5.70                                |

TABLE 6.2 — Waiaireka soil

| Anion system                        | P in solution following addition of :            |                                     |  |                                     |
|-------------------------------------|--|-------------------------------------|--|-------------------------------------|
|                                     | 60 $\mu\text{g}$ P/g soil                        |                                     | 450 $\mu\text{g}$ P/g soil                       |                                     |
|                                     | $\mu\text{g}$ P in solu-<br>tion per g<br>soil : | % increase<br>of P in<br>solution : | $\mu\text{g}$ P in solu-<br>tion per g<br>soil : | % increase<br>of P in<br>solution : |
| Soil + P                            | 2.44   | —                                   | 86.6   | —                                   |
| " " " + $10^{-2}\text{M NO}_3^-$    | 2.32   | - 5.00                              | 86.4   | 0                                   |
| " " " + $10^{-3}\text{M NO}_3^-$    | 2.32   | - 5.00                              | 87.2   | 0                                   |
| " " " + $10^{-5}\text{M NO}_3^-$    | 2.47   | 1.63                                | 86.6   | 0                                   |
| " " " + $10^{-2}\text{M SO}_4^{2-}$ | 2.77   | 13.5                                | 90.7   | 4.72                                |
| " " " + $10^{-3}\text{M SO}_4^{2-}$ | 2.47   | 1.62                                | 87.0   | 0                                   |
| " " " + $10^{-5}\text{M SO}_4^{2-}$ | 2.54   | 3.90                                | 88.4   | 2.00                                |
| " " " + $10^{-3}\text{M HCO}_3^-$   | 2.07   | -15.2                               | 81.8   | - 5.54                              |
| " " " + $10^{-5}\text{M HCO}_3^-$   | 2.58   | 5.52                                | 87.2   | 0                                   |
| " " " + $10^{-3}\text{M citrate}$   | 11.2   | 360                                 | 169  | 95.5                                |
| " " " + $10^{-5}\text{M citrate}$   | 2.57   | 5.24                                | 90.5   | 5.04                                |
| " " " + $10^{-5}\text{M PGU}$       | 2.66   | 9.12                                | 91.5   | 5.76                                |
| " " " + $10^{-7}\text{M PGU}$       | 2.48   | 1.80                                | 87.6   | 0                                   |

TABLE 6.3 -- Okaihau soil

| Anion system   | P in solution following addition of :  |                             |  |                             |
|--|--|-----------------------------|--|-----------------------------|
|  | 150 $\mu\text{g}$ P/g soil             |                             | 850 $\mu\text{g}$ P/g soil             |                             |
|  | $\mu\text{g}$ P in solution per g soil | % increase of P in solution | $\mu\text{g}$ P in solution per g soil | % increase of P in solution |
| Soil + P   | 0.275                                  | -                           | 11.7                                   | -                           |
| " " "+10 <sup>-2</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.265                                  | - 3.60                      | 12.0                                   | 3.90                        |
| " " "+10 <sup>-3</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.275                                  | 0                           | 11.9                                   | 1.92                        |
| " " "+10 <sup>-5</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.386                                  | 40.0                        | 12.0                                   | 3.00                        |
| " " "+10 <sup>-2</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.858                                  | 212                         | 27.6                                   | 136                         |
| " " "+10 <sup>-3</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.484                                  | 76.0                        | 17.0                                   | 45.1                        |
| " " "+10 <sup>-5</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.382                                  | 39.0                        | 11.3                                   | 0                           |
| " " "+10 <sup>-3</sup> M citrate                       | 1.86                                   | 575                         | 85.3                                   | 624                         |
| " " "+10 <sup>-5</sup> M citrate                       | 0.250                                  | 0                           | 13.4                                   | 14.6                        |
| " " "+10 <sup>-5</sup> M PGU                           | 2.89                                   | 950                         | 27.2                                   | 133                         |
| " " "+10 <sup>-7</sup> M PGU                           | 0.798                                  | 190                         | 11.9                                   | 1.92                        |

TABLE 6.4 — Porirua soil

| Anion system   | P in solution following addition of :  |                             |  |                              |
|--|--|-----------------------------|--|------------------------------|
|  | 50 $\mu\text{g}$ P/g soil              |                             | 350 $\mu\text{g}$ P/g soil             |                              |
|  | $\mu\text{g}$ P in solution per g soil | % increase of P in solution | $\mu\text{g}$ P in solution per g soil | % increase of P in solution. |
| Soil + P   | 1.23                                   | -                           | 54.2                                   | -                            |
| " " "+10 <sup>-2</sup> M NO <sub>3</sub> <sup>-</sup>  | 1.23                                   | 0                           | 55.4                                   | 2.20                         |
| " " "+10 <sup>-3</sup> M NO <sub>3</sub> <sup>-</sup>  | 1.19                                   | 0                           | 55.3                                   | 2.00                         |
| " " "+10 <sup>-5</sup> M NO <sub>3</sub> <sup>-</sup>  | 1.20                                   | 0                           | 55.7                                   | 2.62                         |
| " " "+10 <sup>-2</sup> M SO <sub>4</sub> <sup>2-</sup> | 1.59                                   | 29.4                        | 63.2                                   | 18.4                         |
| " " "+10 <sup>-3</sup> M SO <sub>4</sub> <sup>2-</sup> | 1.31                                   | 6.54                        | 61.6                                   | 13.7                         |
| " " "+10 <sup>-5</sup> M SO <sub>4</sub> <sup>2-</sup> | 1.24                                   | 0                           | 55.9                                   | 3.10                         |
| " " "+10 <sup>-3</sup> M citrate                       | 25.4                                   | 1937                        | 195                                    | 260                          |
| " " "+10 <sup>-5</sup> M citrate                       | 1.42                                   | 15.4                        | 63.4                                   | 17.0                         |
| " " "+10 <sup>-5</sup> M PGU                           | 4.00                                   | 225                         | 73.7                                   | 36.0                         |
| " " "+10 <sup>-7</sup> M PGU                           | 1.36                                   | 10.9                        | 61.0                                   | 12.5                         |

Although  $\text{NO}_3^-$  is relatively ineffective in reducing P sorption by the soils, two interesting observations may be made from the data. Firstly, for the Egnont soil at both levels of added P and for the Okaihau soil at the lower level of added P, a small but progressive increase in the final solution P concentration was obtained with a decrease in  $\text{NO}_3^-$  concentration from  $10^{-2}$  to  $10^{-5}$  M. Secondly, it was observed that P sorption was slightly enhanced in the presence of  $10^{-2}$  M  $\text{NO}_3^-$  in the Egnont soil, a 7% increase in solution P concentration being obtained with an addition of 1350  $\mu\text{g P/g}$  soil.

Because  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  are thought to be adsorbed by a different mechanism, i.e., non-specific for  $\text{NO}_3^-$  versus specific for  $\text{H}_2\text{PO}_4^-$ ; little direct competition for adsorption sites should occur. Working with soils high in Fe components, Mekarua and Uehara (1972) also observed that more P was sorbed at higher  $\text{NO}_3^-$  concentrations. They showed that increasing the concentration of  $\text{NO}_3^-$  at pH values greater than the zero point of charge (z.p.c.) resulted in a lowering of pH, which in turn increased P sorption. Rather than suggesting that this effect was pH controlled, Ryden and Syers (1975) demonstrated that the increase in P sorption resulting from an increase in ionic strength was kinetically controlled and that, at equilibrium, this effect disappeared. This suggests that different  $\text{NO}_3^-$  concentrations affect P sorption only through the rate at which equilibrium is attained.

In contrast to  $\text{NO}_3^-$ , the ability of  $\text{SO}_4^{2-}$  to reduce P sorption by the soils decreases with a decrease in  $\text{SO}_4^{2-}$  concentration (Table 6). In most cases,  $10^{-2}$  M,  $10^{-3}$  M, and  $10^{-5}$  M  $\text{SO}_4^{2-}$  are more effective in reducing P sorption than  $\text{NO}_3^-$  at equivalent concentrations. This is particularly noticeable for the Egnont and Okaihau soils; and suggests a direct competition for sites by the two anions ( $\text{SO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ ), rather than an ionic strength effect (as with  $\text{NO}_3^-$ ).

Although  $\text{HCO}_3^-$  has been shown to be very effective in reducing P sorption by kaolinite (Nagarajah *et al.*, 1968) the results in Table 6.1 show that  $10^{-3}$  M  $\text{HCO}_3^-$  is only as effective as  $10^{-3}$  M  $\text{SO}_4^{2-}$  in reducing P sorption by the Egnont soil. For the Waiareka soil (Table 6.2) P sorption at both levels of added P was enhanced in the presence of  $10^{-3}$  M  $\text{HCO}_3^-$ . A possible reason for this

is discussed later. In contrast,  $10^{-5} \text{M HCO}_3^-$  had a very much smaller effect on the amount of P sorbed by both the Egnont and Waiareka soils. These results suggest that the ability of  $\text{HCO}_3^-$  to reduce P sorption by soils under natural conditions is not as great as that suggested by Nagarajah *et al.* (1968) probably because of the high  $\text{HCO}_3^-$  concentrations employed by these workers. The data obtained in the present study are supported by the work of Chen *et al.* (1973) who showed that  $3.75 \times 10^{-3} \text{M HCO}_3^-$  had little effect on P sorption by kaolinite and  $\alpha$ -alumina.

A very marked increase in the final solution P concentration was observed with all soils and at all levels of added P when  $10^{-3} \text{M}$  citrate was present as the competing anion. This was especially true for the Okaihau and Porirua soils. At the lower citrate concentration ( $10^{-5} \text{M}$ ), however, there was a marked decrease in the effectiveness of this anion to reduce P sorption by soils. In some cases, and particularly for the Waiareka soil,  $10^{-5} \text{M}$  citrate was only as effective as  $10^{-5} \text{M SO}_4^{2-}$ .

Polygalacturonate at a concentration of  $10^{-5} \text{M}$  was effective in reducing the sorption of P added at low levels to the Egnont, Okaihau, and Porirua soils. In two cases (Egnont and Okaihau);  $10^{-5} \text{M PGU}$  was more effective in this regard than  $10^{-3} \text{M}$  citrate at low levels of added P (200 and 150  $\mu\text{g P/g}$ , respectively). This suggests that PGU has the greatest effect on sorption sites possessing a high affinity for P. In contrast to the data obtained for the other soils, P sorption by the Waiareka soil was little affected by  $10^{-5} \text{M PGU}$ . It is important to note, however, that with all soils,  $10^{-5} \text{M PGU}$  is considerably more effective in reducing P sorption than  $10^{-5} \text{M}$  citrate.

It is of interest to compare the ability of anions to reduce P sorption by the four soils when the levels of added P and anions are compared on a molar basis. The molar concentrations of added P, corresponding to 40% saturation of the adsorption maximum of the two regions, are given in Table 1. It is clear from the data in Table 6 that  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  have little effect on the amounts of P sorbed by the four soils when the concentration of the competing anion is equal to or lower than that of added P. Also, only  $\text{SO}_4^{2-}$  shows a significant competitive effect at a much higher concentration ( $10^{-2} \text{M}$ ) than that of P. In contrast to citrate, which is effective

in reducing P sorption at concentrations (  $10^{-3}M$  ) equal to or greater than that of added P,  $10^{-5}M$  PGU is effective in reducing P sorption at concentrations less than that of added P. This observation again indicates that PGU possesses a greater ability to reduce P sorption than equivalent concentrations of citrate. The appreciable amounts of P sorbed in the presence of the highest concentrations of citrate and PGU (  $10^{-3}M$  and  $10^{-5}M$ , respectively ) demonstrate, however, the high affinity of P for sorption sites, compared with the competing anions. This probably reflects the strength of the covalent bond formed during the specific adsorption of P at a component surface.

The extent to which added anions affect the final solution pH of the four soils is determined by the level of added P and the concentration of the competing anion initially added ( Table 7 ). In general, the final solution pH increases with an increasing concentration of P and competing anion added. The slightly higher pH values obtained in P sorption studies from solutions containing  $10^{-2}M SO_4^{2-}$ ,  $10^{-3}M HCO_3^-$ ,  $10^{-3}M$  citrate, and  $10^{-5}M$  PGU may be attributed to the specific adsorption of these anions ( Hingston *et al.*, 1967 ), with the associated removal of protons from and/or release of hydroxyls to solution. Similar findings have been reported by Toth and Bear (1947) and Coleman and Mehlich (1948). The difference in pH between final solutions for a particular soil at a given level of added P and containing different anions, has been limited to 0.3 to 0.4 of a pH unit by adjusting the pH of the solutions added initially to 6.5 ( for Egmont and Waiareka soils ) or to 5.5 ( for Okaihau and Porirua soils ); these values approximate the pH values of the respective soils. This enables a better comparison of anion effects, *per se*, without serious complications arising from pH differences, at least for three of the four soils used, as discussed below.

The feasibility of comparing P sorption data when the pH values of the final solution differ by 0.3 to 0.4 of a unit may be determined from the relationship between final solution P concentration and pH ( Figure 4 ). The plot for each soil was established for one level of added P ( corresponding to 40% of the adsorption maximum of region II ). It is clear that for the Egmont, Okaihau, and Porirua soils, any increase in solution pH will result in a slightly higher final solution P concentration. For example, anions which



TABLE 7 -- Effect of anions in the presence of varying levels of added inorganic P on the final solution pH of the supernatants of the four soils recovered following a 40-hour shaking period. Solutions added to Okaihau and Porirua soils were initially adjusted to pH 5.5; whereas those added to Egnont and Waiareka soils were adjusted to pH 6.5

| Soil     | Level of added P<br>( $\mu\text{g P/g soil}$ ) | Supernatant pH values in the presence of : |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
|----------|--|--|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|          |  | P alone                                    | Nitrate           |                   |                   | Sulphate          |                   |                   | Bicarbonate       |                   | Citrate           |                   | Polygalacturonate |                   |
|          |  |  | $10^{-2}\text{M}$ | $10^{-3}\text{M}$ | $10^{-5}\text{M}$ | $10^{-2}\text{M}$ | $10^{-3}\text{M}$ | $10^{-5}\text{M}$ | $10^{-3}\text{M}$ | $10^{-5}\text{M}$ | $10^{-3}\text{M}$ | $10^{-5}\text{M}$ | $10^{-5}\text{M}$ | $10^{-7}\text{M}$ |
| EGMONT   | 0  | -  | 6.06              | 6.11              | 6.10              | 6.17              | 6.14              | 6.11              | 6.20              | 6.18              | 6.41              | 6.22              | 6.24              | 6.19              |
|          | 200  | 6.11                                       | 6.10              | 6.17              | 6.12              | 6.29              | 6.21              | 6.11              | 6.21              | 6.19              | 6.61              | 6.21              | 6.30              | 6.19              |
|          | 1350   | 6.17                                       | 6.29              | 6.27              | 6.21              | 6.33              | 6.27              | 6.21              | 6.31              | 6.29              | 6.60              | 6.23              | 6.29              | 6.19              |
| WAIAREKA | 0  | -  | 5.98              | 5.98              | 6.00              | 6.04              | 6.02              | 6.00              | 6.08              | 6.00              | 6.12              | 6.03              | 6.01              | 5.97              |
|          | 60   | 5.96                                       | 6.00              | 6.00              | 5.99              | 6.00              | 6.07              | 6.01              | 6.12              | 6.06              | 6.19              | 6.09              | 6.04              | 6.00              |
|          | 450  | 5.92                                       | 5.95              | 6.00              | 5.99              | 5.99              | 5.97              | 6.02              | 6.20              | 5.99              | 6.10              | 5.96              | 6.00              | 5.98              |
| OKAIHAU  | 0  | -  | 4.88              | 4.89              | 4.82              | 5.17              | 5.09              | 4.89              | -                 | -                 | 5.22              | 4.85              | 5.27              | 4.90              |
|          | 150  | 4.88                                       | 4.86              | 4.85              | 4.86              | 5.14              | 5.02              | 4.88              | -                 | -                 | 5.18              | 4.90              | 5.20              | 4.88              |
|          | 850  | 4.97                                       | 4.92              | 4.90              | 4.90              | 5.17              | 5.02              | 4.98              | -                 | -                 | 5.21              | 4.96              | 5.17              | 4.99              |
| PORIRUA  | 0  | -  | 4.63              | 4.65              | 4.65              | 4.74              | 4.70              | 4.68              | -                 | -                 | 4.66              | 4.60              | 4.92              | 4.68              |
|          | 50   | 4.61                                       | 4.75              | 4.79              | 4.75              | 4.86              | 4.75              | 4.73              | -                 | -                 | 4.70              | 4.64              | 4.91              | 4.70              |
|          | 350  | 4.62                                       | 4.60              | 4.70              | 4.73              | 4.76              | 4.70              | 4.70              | -                 | -                 | 4.72              | 4.70              | 4.87              | 4.71              |

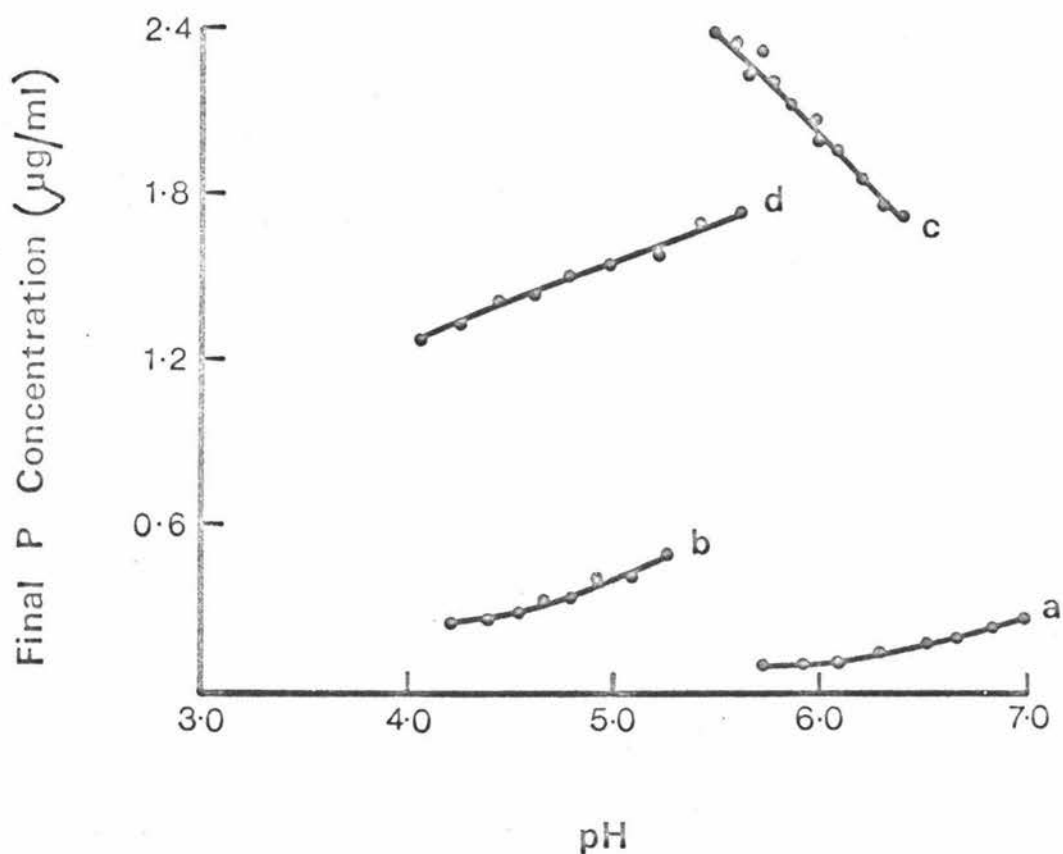


FIGURE 4 : Relationship between final P concentration and pH in the supernatants of the four soils following a 40-hour shaking period. The levels of added inorganic P for Egmont, Okaihau, Waiareka, and Porirua soils were 1350, 850, 450, and 350  $\mu\text{g/g}$  soil, respectively; these correspond to 40% of the adsorption maxima of region II.

- a Egmont soil
- b Okaihau soil
- c Waiareka soil
- d Porirua soil

increase the supernatant solution pH by 0.3 of a unit at the highest levels of P addition ( Figure 4, Table 7 ) cause a 14, 20, and 6% increase in the final solution P concentration for Egnont, Okaihau, and Porirua soils, respectively. This suggests that the competing ability of an anion producing such a higher pH may be slightly exaggerated. Failure to limit pH differences in studies reported in the literature makes interpretation of the data obtained virtually impossible.

In contrast, the Waiareka soil showed a sharp decrease in final solution P concentration with an increase in pH. The contrasting behaviour of the Waiareka soil in this regard is difficult to explain although it is possibly associated with the chemical transformation or decomposition of montmorillonite suspensions with time, as reported by Brown and Miller (1971) and Steinberg *et al.* (1974). The effect of pH on the final solution P concentration obtained with the Waiareka soil may largely explain the pattern of P sorption by this soil in the presence of competing anions ( Table 6.2 ). It appears that the enhanced P sorption in the presence of  $10^{-3}M HCO_3^-$  is a result of the pH increase ( 0.28 of a pH unit, producing a 10% decrease in final solution P concentration; ( Figure 4, Table 7 ) ). Similarly, the limited ability of competing anions, in general, to reduce P sorption by the Waiareka soil may be partly attributed to the effect of pH on P sorption. Any increase in pH caused by the presence of anions leads to an overestimation of the amount of P sorbed by the Waiareka soil and an underestimation of the competing ability of that anion.

The results, therefore, suggest that pH changes have a rather small effect on the P sorption data obtained for three of the soils. The magnitude of such changes must be evaluated when considering the competitive ability of anions, as shown by the data obtained for the Waiareka soil.

### C. Desorption of Previously Sorbed Added P and Native P

The extent to which competing anions are able to desorb previously sorbed added P from the four soils is indicated by the data in Tables 8.1, 8.2, 8.3, and 8.4. The ability of the various anions to desorb P previously sorbed in 24 hours can be interpreted from the

TABLE 8 --- Effect of competing anions on the final solution P concentration when soils are shaken with inorganic P for 24 hours, competing anions added at the appropriate concentration, and shaking continued for a further 40 hours. Amounts of added P correspond to 40% of the adsorption maxima of regions I and II of the Langmuir adsorption isotherm.

TABLE 8.1 --- Egnont soil

| Anion system   | P in solution following addition of : |   |        |                                       |   |       |
|--|---------------------------------------|---|--------|---------------------------------------|---|-------|
|  | 200 $\mu\text{g}$ P/g soil            |   |        | 1350 $\mu\text{g}$ P/g soil           |   |       |
|  | $\mu\text{gP}$ in soln.<br>per g soil | % increase of P<br>in solution over<br>that after : |        | $\mu\text{gP}$ in soln.<br>per g soil | % increase of<br>P in solution<br>over that after |       |
|  | 24 hr*                                | 64 hr*  |        | 24 hr*                                | 64 hr*  |       |
| Soil + P (24 hours)                                    | 0.323                                 | -   | -      | 9.46                                  | -   | -     |
| " " " (64 hours)                                       | 0.242                                 | -   | -      | 5.01                                  | -   | -     |
| " " "+10 <sup>-2</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.219                                 | - 32.1  | - 9.5  | 4.99                                  | - 47.2  | 0     |
| " " "+10 <sup>-3</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.203                                 | - 37.1  | - 16.1 | 5.56                                  | - 40.1  | 7.5   |
| " " "+10 <sup>-5</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.234                                 | - 27.5  | - 3.3  | 4.86                                  | - 48.6  | - 3.0 |
| " " "+10 <sup>-2</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.429                                 | 32.8  | 71.0   | 9.68                                  | 2.39  | 87.3  |
| " " "+10 <sup>-3</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.281                                 | - 13.0  | 12.0   | 6.73                                  | - 28.8  | 30.2  |
| " " "+10 <sup>-5</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.219                                 | - 32.1  | - 9.5  | 5.58                                  | - 41.0  | 7.92  |
| " " "+10 <sup>-3</sup> M HCO <sub>3</sub> <sup>-</sup> | 0.257                                 | - 20.4  | 6.0    | 5.73                                  | - 39.4  | 10.7  |
| " " "+10 <sup>-5</sup> M HCO <sub>3</sub> <sup>-</sup> | 0.234                                 | - 27.5  | - 3.3  | 5.41                                  | - 42.8  | 5.05  |
| " " "+10 <sup>-3</sup> M citrate                       | 0.749                                 | 132   | 199    | 21.8                                  | 131   | 322   |
| " " "+10 <sup>-5</sup> M citrate                       | 0.249                                 | - 22.9  | 2.0    | 6.10                                  | - 35.5  | 17.9  |
| " " "+10 <sup>-5</sup> M PGU                           | 1.01                                  | 206   | 303    | 9.73                                  | 2.89  | 86.0  |
| " " "+10 <sup>-7</sup> M PGU                           | 0.367                                 | 13.6  | 50.0   | 5.94                                  | - 37.2  | 15.0  |

\* Data for soil + P alone at the appropriate time.

TABLE 8.2 -- Waiareka soil.

| Anion system                                 | P in solution following addition of :    |   |         |  |   |        |
|--|--|---|---------|--|---|--------|
|  | 60 $\mu\text{g}$ P/g soil                |   |         | 450 $\mu\text{g}$ P/g soil             |   |        |
|  | $\mu\text{g}$ P in soln.<br>per g soil : | % increase of P<br>in solution over<br>that after : |         | $\mu\text{g}$ P in soln.<br>per g soil | % increase<br>of P in soln.<br>over that<br>after : |        |
|  |  | 24 hr*  | 64 hr*  |  | 24 hr*  | 64 hr* |
| Soil + P (24 hours)                          | 2.46                                     | --  | --      | 95.1                                   | --  | --     |
| " " " (64 hours)                             | 2.02                                     | --  | --      | 78.3                                   | --  | --     |
| " " " + $10^{-2}\text{M}$ $\text{NO}_3^-$    | 1.98                                     | -- 19.5   | -- 1.90 | 78.9                                   | -- 17.0   | 0      |
| " " " + $10^{-3}\text{M}$ $\text{NO}_3^-$    | 1.99                                     | -- 19.1   | -- 1.40 | 78.4                                   | -- 17.5   | 0      |
| " " " + $10^{-5}\text{M}$ $\text{NO}_3^-$    | 1.96                                     | -- 20.3   | -- 2.92 | 78.5                                   | -- 17.4   | 0      |
| " " " + $10^{-2}\text{M}$ $\text{SO}_4^{2-}$ | 2.12                                     | -- 13.8   | 3.94    | 81.3                                   | -- 14.5   | 3.60   |
| " " " + $10^{-3}\text{M}$ $\text{SO}_4^{2-}$ | 1.99                                     | -- 19.1   | -- 1.40 | 78.3                                   | -- 17.6   | 0      |
| " " " + $10^{-5}\text{M}$ $\text{SO}_4^{2-}$ | 2.00                                     | -- 18.6   | -- 1.02 | 78.8                                   | -- 17.1   | 0      |
| " " " + $10^{-3}\text{M}$ $\text{HCO}_3^-$   | 1.64                                     | -- 33.3   | -- 18.8 | 72.2                                   | -- 24.0   | -7.72  |
| " " " + $10^{-5}\text{M}$ $\text{HCO}_3^-$   | 1.90                                     | -- 22.7   | -- 5.91 | 78.8                                   | -- 17.1   | 0      |
| " " " + $10^{-3}\text{M}$ citrate            | 8.27                                     | 235   | 305     | 151                                    | 58.7  | 92.0   |
| " " " + $10^{-5}\text{M}$ citrate            | 2.06                                     | -- 16.2   | 1.94    | 79.7                                   | -- 16.1   | 1.56   |
| " " " + $10^{-5}\text{M}$ PGU                | 2.41                                     | -- 2.0  | 17.7    | 79.9                                   | -- 15.9   | 1.70   |
| " " " + $10^{-7}\text{M}$ PGU                | 1.96                                     | -- 20.3   | -- 2.92 | 78.3                                   | -- 17.6   | 0      |

\* Data for soil + P alone at appropriate time.

TABLE 8.3 -- Okaihau soil

| Anion system   | P in solution following addition of : |  |        |                                     |   |        |
|--|---------------------------------------|--|--------|-------------------------------------|---|--------|
|  | 150 $\mu\text{g P/g soil}$            |  |        | 850 $\mu\text{g P/g soil}$          |   |        |
|  | $\mu\text{g P in soln. per g soil}$   | % increase of P in soln. over that after : |        | $\mu\text{g P in soln. per g soil}$ | % increase of P in soln. over that after. |        |
|  | 24 hr*                                | 64 hr*                                     |        | 24 hr*                              | 64 hr*                                    |        |
| Soil + P (24 hours)                                    | 0.376                                 | -  | -      | 14.5                                | -   | -      |
| Soil + P (64 hours)                                    | 0.134                                 | -  | -      | 5.92                                | -   | -      |
| " " "+10 <sup>-2</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.129                                 | - 65.6                                     | - 3.71 | 5.92                                | -59.2                                     | 0      |
| " " "+10 <sup>-3</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.108                                 | - 71.2                                     | - 19.4 | 6.02                                | -58.5                                     | 0      |
| " " "+10 <sup>-5</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.108                                 | - 71.2                                     | - 19.4 | 5.95                                | -59.0                                     | 0      |
| " " "+10 <sup>-2</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.309                                 | - 17.8                                     | 131    | 12.2                                | -15.9                                     | 97.5   |
| " " "+10 <sup>-3</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.129                                 | - 65.6                                     | - 3.7  | 9.31                                | -35.8                                     | 50.5   |
| " " "+10 <sup>-5</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.129                                 | - 65.6                                     | - 3.7  | 5.98                                | -58.8                                     | - 1.00 |
| " " "+10 <sup>-3</sup> M citrate                       | 1.45                                  | 286  | 984    | 29.6                                | 97.0                                      | 377    |
| " " "+10 <sup>-5</sup> M citrate                       | 0.107                                 | - 71.5                                     | - 20.1 | 8.91                                | -38.6                                     | 44.0   |
| " " "+10 <sup>-5</sup> M PGU                           | 0.605                                 | 60.9                                       | 315    | 14.9                                | 2.55                                      | 141    |
| " " "+10 <sup>-7</sup> M PGU                           | 0.129                                 | -65.5                                      | - 3.7  | 5.88                                | -59.4                                     | 0      |

\* Data for soil + P alone at appropriate time.

TABLE 8.4 --- Porirua soil

| Anion system  | P in solution following addition of :  |  |        |  |   |        |
|---|--|--|--------|--|---|--------|
|   | 50 $\mu\text{g}$ P/g soil              |  |        | 350 $\mu\text{g}$ P/g soil             |   |        |
|   | $\mu\text{g}$ P in soln.<br>per g soil | % increase of P<br>in soln. over that<br>after : |        | $\mu\text{g}$ P in soln.<br>per g soil | % increase of<br>P in soln.<br>over that after. |        |
|   | 24 hr*                                 | 64 hr*   |        | 24 hr*                                 | 64 hr*  |        |
| Soil + P (24 hours)                                     | 1.43                                   | -  | -      | 61.8                                   | -   | -      |
| Soil + P (64 hours)                                     | 0.726                                  | -  | -      | 42.0                                   | -   | -      |
| " " " +10 <sup>-2</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.726                                  | - 49.4   | 0      | 41.8                                   | - 32.4  | 0      |
| " " " +10 <sup>-3</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.685                                  | - 52.1   | - 5.64 | 41.8                                   | - 32.4  | 0      |
| " " " +10 <sup>-5</sup> M NO <sub>3</sub> <sup>-</sup>  | 0.685                                  | - 52.1   | - 5.64 | 42.4                                   | - 31.4  | 0      |
| " " " +10 <sup>-2</sup> M SO <sub>4</sub> <sup>2-</sup> | 1.18                                   | - 17.5   | 75.0   | 48.8                                   | -21.0   | 15.0   |
| " " " +10 <sup>-3</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.807                                  | - 43.6   | 7.20   | 45.4                                   | -26.5   | 7.23   |
| " " " +10 <sup>-5</sup> M SO <sub>4</sub> <sup>2-</sup> | 0.685                                  | - 52.1   | - 5.64 | 41.3                                   | -33.2   | - 1.66 |
| " " " +10 <sup>-3</sup> M citrate                       | 21.5                                   | 1409   | 2755   | 183                                    | 196   | 333    |
| " " " +10 <sup>-5</sup> M citrate                       | 1.20                                   | - 16.1   | 58.7   | 46.1                                   | -25.4   | 8.94   |
| " " " +10 <sup>-5</sup> M PGU                           | 3.25                                   | 128  | 332    | 50.3                                   | -18.6   | 18.8   |
| " " " +10 <sup>-7</sup> M PGU                           | 0.806                                  | - 43.6   | 7.12   | 41.8                                   | -32.4   | 0      |

\* Data for soil + P alone at the appropriate time.



increase in the final solution P concentration as a percentage of that obtained in the absence of competing anions. Also, the percentage increase in P in solution in the presence of competing anions is calculated as a function of P in solution when added P is shaken with the soils for 64 hours in the absence of anions. This, also reflects the extent to which competing anions affect the continued sorption of P in the 40-hour period following the shaking of soils with P alone for 24 hours.

For all soils and at all levels of added P, in the absence of competing anions, it is interesting to note a steady decrease in the final solution P concentration with increased time of shaking from 24 hours ( Table 8 ), to 40 hours ( Table 6 ), and to 64 hours ( Table 8 ). It is possible that an absorption reaction involving diffusive penetration ( Evans and Syers, 1971 ) and site regeneration ( Syers and Williams, 1975 ) is responsible for the continued removal of P from solution.

Zero or positive values obtained for the increase in P in solution between 24 and 64 hours when competing anions are present ( Table 8 ) indicates that the ability of a competing anion to desorb previously sorbed P overrides the ability of the soil to remove P from solution during this time, as occurs in the absence of anions. At any concentration,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  showed a limited ability to desorb previously sorbed P from the four soils studied, and, in most cases, continued removal of P from solution was observed in the presence of these anions. The exception was  $10^{-2}\text{M SO}_4^{2-}$  which desorbed a small but significant amount of P from the Egnont soil but only at the lower level of P addition ( 200  $\mu\text{g/g}$  ). This suggests that the ability of  $\text{SO}_4^{2-}$  to desorb P is largely determined by a concentration factor. Polygalacturonate at  $10^{-5}\text{M}$  was effective in desorbing previously sorbed P from the Egnont, Okaihau, and Porirua soils, but only at the lower levels of P addition. The ability of the Waiareka soil to retain previously sorbed P against desorption by competing anions, other than  $10^{-3}\text{M}$  citrate, is difficult to understand. It is possible that P is sorbed by polymeric hydroxy aluminium located in the interlayer space of nontronillonite in this soil, and in this form is largely protected from desorption by the anions used, other than citrate. Complexing of Al from interlayer polymeric hydroxy aluminium by citrate could lead to desorption of P. Although PGU can complex aluminium ( discussed later ), the very much greater size of the PGU polymer could preclude entry of this anion into the interlayer space and hence little P can be desorbed.

In contrast to these four anions,  $10^{-3}$ M citrate was very effective in desorbing previously sorbed P from all soils and at all levels of added P. The increase in P in solution in the presence of  $10^{-3}$ M citrate, expressed as a percentage of the final solution P concentration obtained in the absence of citrate and at the lower level of added P was 132, 235, 286, and 1409% for Egnont, Waiareka, Okaihua, and Porirua soils, respectively. The ability of  $10^{-3}$ M citrate to desorb previously sorbed P from the Porirua soil is consistent with the earlier observation that citrate is capable of significantly reducing the ability of this soil to sorb added P ( Figure 3.4, Table 6.4 ). With the Porirua soil,  $10^{-3}$ M citrate desorbed 41 and 42% of the P sorbed in 24 hours when 50 and 350  $\mu$ g P were added/g soil, respectively; these values correspond to an increase in P in solution of 1409 and 196%, respectively ( Table 8.4 ).

The results in Table 8 suggest that the ability of anions, other than citrate and PGU, to release previously sorbed P under conditions similar to those existing in the soil solution of weakly acid soils, has been overestimated in previous studies. This is particularly the case for  $\text{HCO}_3^-$ , which has been shown by Nagarajah *et al.* (1968) and Evans and Syers (1971) to be very effective in desorbing P from soil components and soils. The high concentration of  $\text{HCO}_3^-$  used (  $10^{-2}$ M and  $10^{-1}$ M, respectively ), often in conjunction with high pH values ( a pH of 9.5; Evans and Syers (1971) ) are only relevant to soils which have a very limited distribution. The present study has shown that  $\text{HCO}_3^-$  is virtually ineffective in desorbing sorbed P under the conditions used. It is important to emphasise the greater ability of  $10^{-5}$ M PGU than  $10^{-5}$ M citrate to desorb previously sorbed P from all soils.

The extent to which competing anions affect the final solution P concentration in the 40-hour period following the previous shaking of soils with P alone for 24 hours, is also shown in Table 8. In contrast to the data in Table 6, where an increase in P in solution in the presence of competing anions results from a direct competition for sorption sites, any increase in P in solution in this 40-hour period ( Table 8 ), relative to the P alone system, may result from the desorption of P sorbed in the previous 24-hour shaking period, as well as from a reduction in P sorption during the 40 hours which occurs in the

presence of competing anions. Although the % increase in P in solution in the presence of  $\text{SO}_4^{2-}$ , citrate, and PGU in this 40-hour period may be equal to or greater than that when P and competing anions are added simultaneously to the soils and shaken for 40 hours ( Table 6 ), the increase in the solution P concentration in the presence of anions is always greater in the latter system. This suggests that the P sorbed in the initial 24 hours is held so strongly that desorption by competing anions is restricted.

At the lower level of P addition to the four soils, and in the presence of  $10^{-2}$ ,  $10^{-3}$ , and  $10^{-5}\text{M NO}_3^-$ , it is interesting to note a decrease in the final solution P concentration compared with that for soil + P alone after 64 hours. The continued P sorption observed in the presence of  $\text{NO}_3^-$  solutions demonstrates the inability of  $\text{NO}_3^-$  to compete with  $\text{H}_2\text{PO}_4^-$  for sorption sites. The effect of increasing  $\text{NO}_3^-$  concentration on P sorption is consistent with earlier observations and is interpreted as an ionic strength effect, as reported by Ryden and Syers (1975). For the Waiareka soil, the large decrease in the final solution P concentration in the presence of  $\text{HCO}_3^-$  suggests that  $\text{HCO}_3^-$  does not desorb P or interfere with continued P sorption during the time interval of 24 to 64 hours. This can be explained by a pH effect ( Figure 4 ), discussed previously.

Data for the desorption of native P from the four soils by the anions are presented in Table 9. Only  $\text{SO}_4^{2-}$ , citrate, and PGU at the highest concentrations used were capable of removing native inorganic P from the soils, the amounts removed by each anion varying between soils. With the exception of the Egnont soil,  $10^{-3}\text{M}$  citrate removed more P than did  $10^{-5}\text{M}$  PGU, which in turn removed more P than  $10^{-2}\text{M SO}_4^{2-}$ . The total P contents of the soils used in this study, as published in New Zealand Soil Bureau Bulletin (1968), are 167, 152, 45, and 20  $\mu\text{g}/100\text{ g}$  for the Egnont, Waiareka, Okaihau, and Porirua soils, respectively. Therefore, the proportions of total native P desorbed by the respective anions are very small. The Egnont soil, in particular, demonstrates a particularly strong retention of native P.

TABLE 9 --- Effect of competing anions on the desorption of native inorganic P from the four soils in a 40-hour shaking period.

| Anion system                   | Egnont                      Waiareka                      Okaihau                      Porirua |       |       |       |
|--------------------------------|--|-------|-------|-------|
|                                | µg P desorbed/g soil   |       |       |       |
| $10^{-2}$ M $\text{NO}_3^-$    | 0  | 0     | 0     | 0     |
| $10^{-3}$ M $\text{NO}_3^-$    | 0  | 0     | 0     | 0     |
| $10^{-5}$ M $\text{NO}_3^-$    | 0  | 0     | 0     | 0     |
| $10^{-2}$ M $\text{SO}_4^{2-}$ | 0.148  | 0.110 | 0.031 | 0     |
| $10^{-3}$ M $\text{SO}_4^{2-}$ | 0  | 0     | 0     | 0     |
| $10^{-5}$ M $\text{SO}_4^{2-}$ | 0  | 0     | 0     | 0     |
| $10^{-3}$ M $\text{HCO}_3^-$   | 0  | 0     | -     | -     |
| $10^{-5}$ M $\text{HCO}_3^-$   | 0  | 0     | -     | -     |
| $10^{-3}$ M citrate            | 0  | 2.09  | 1.11  | 0.484 |
| $10^{-5}$ M citrate            | 0  | 0     | 0     | 0     |
| $10^{-5}$ M PGU                | 0.304  | 0     | 0.499 | 0.28† |
| $10^{-7}$ M PGU                | 0  | 0     | 0     | 0     |

D. Kinetics of P Sorption in the Presence and Absence of Competing Anions.

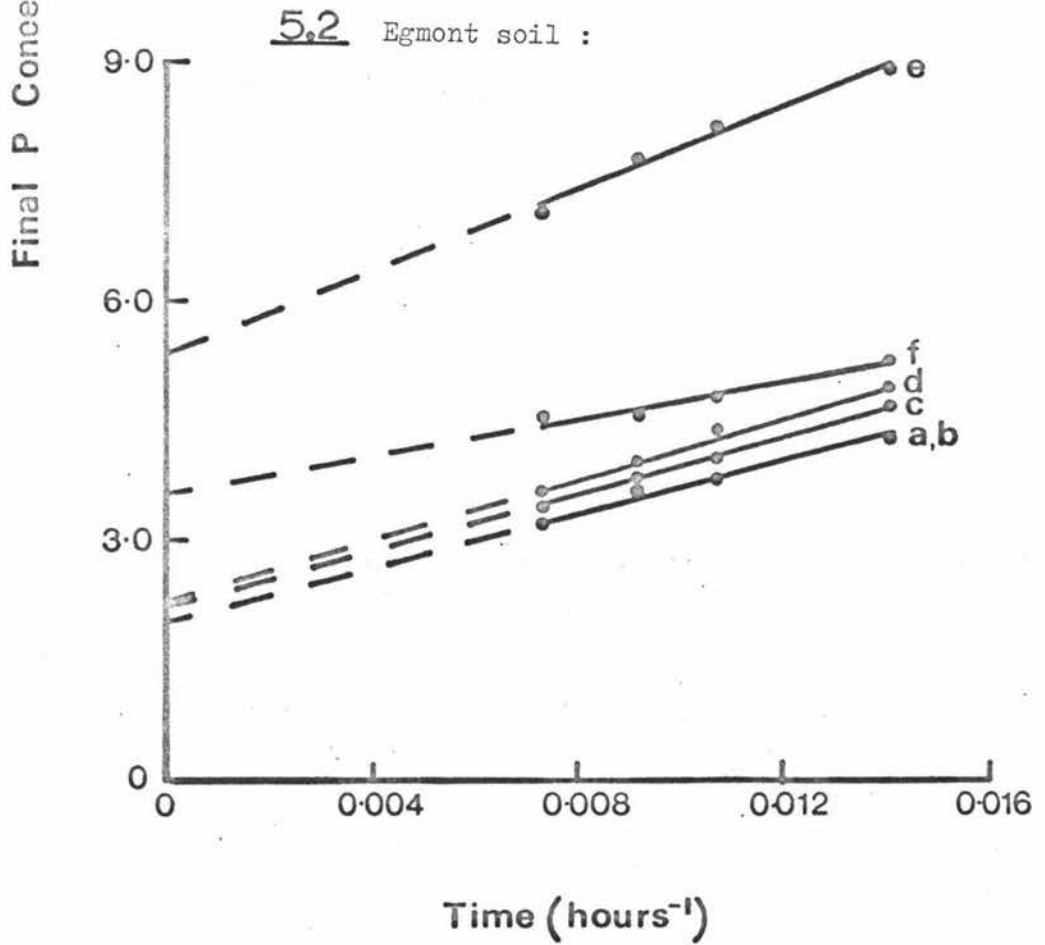
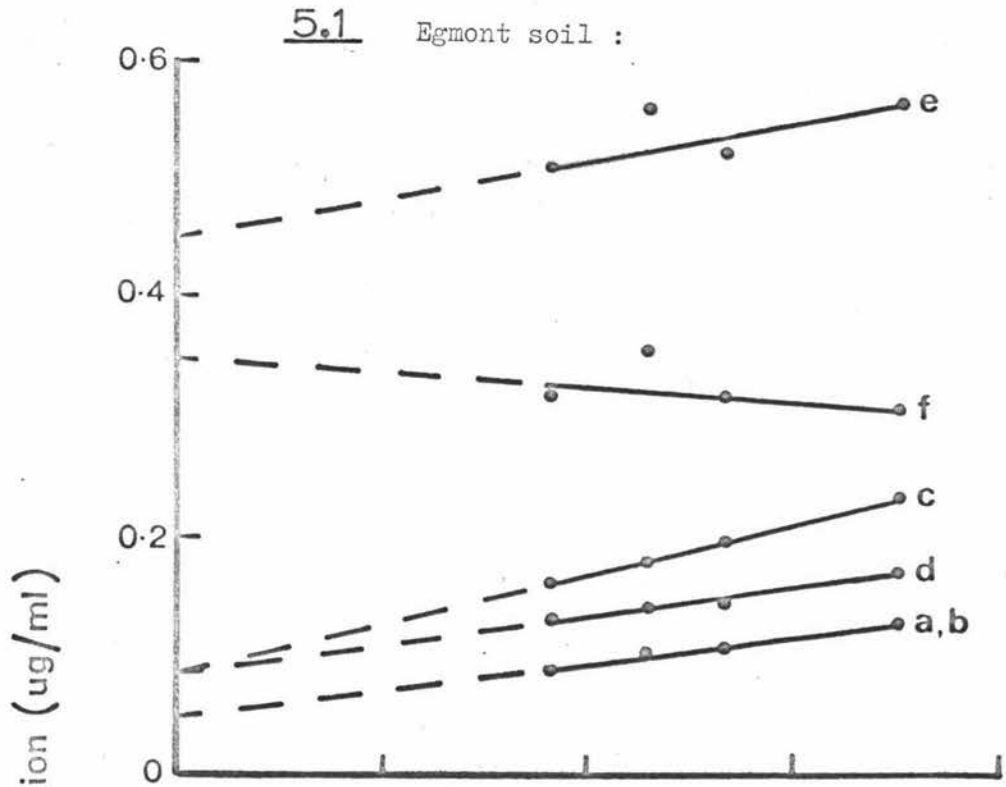
Although it has been established that  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , citrate, and PGU of differing concentrations reduce P sorption by the four soils to a varying extent in a 10-hour shaking period, it is not known whether these effects are maintained over longer periods of time. It has recently been shown ( Ryden and Syers, 1975 ) that cation valence and ionic strength of the support medium affect only the kinetics of P sorption and not the equilibrium solution P concentration. Consequently, an experiment was designed to study the kinetics of P sorption in the presence and absence of anions, such that each soil was shaken with the relevant P plus competing anion solution for 3, 4, 5, or 6 days. Two levels of added P but only the highest concentration of competing anion (  $10^{-2}\text{M NO}_3^-$ ,  $10^{-2}\text{M SO}_4^{2-}$ ,  $10^{-3}\text{M HCO}_3^-$ ,  $10^{-3}\text{M citrate}$ , and  $10^{-5}\text{M PGU}$  ) were used for each soil. A plot of final solution P concentrations against the reciprocal of time of shaking (  $\text{hours}^{-1}$  ) gave linear relationships for each competing anion ( Figure 5 ). Extrapolation of the relationship to infinite time (  $1/t = 0$  ) was used to determine the effects of the competing anions on P sorption over extended periods of time. A separate study ( Ryden and Syers, 1975 ) has shown that particle breakdown, leading to a possibly greater sorption of P, is not a problem with the Egnont, Okaihau, and Porirua soils for periods of shaking of up to six days.

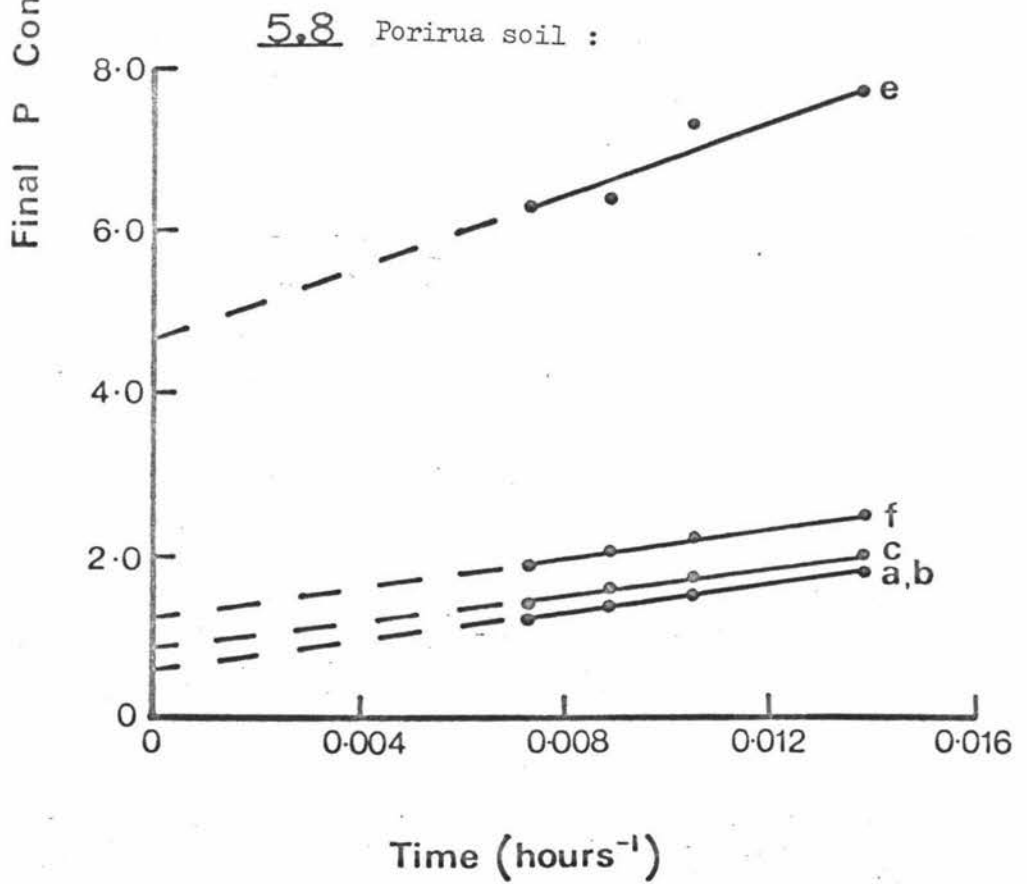
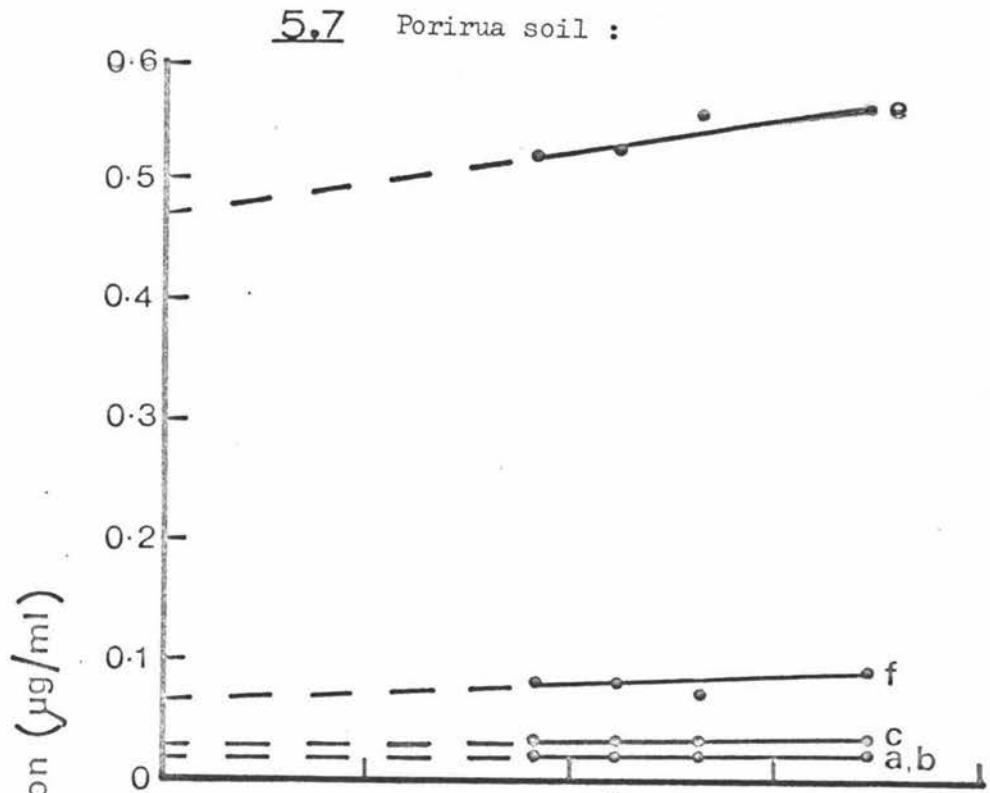
From the data presented in Figure 5 it is apparent that for all soils,  $10^{-2}\text{M NO}_3^-$  has no effect on P sorption over the entire time period, i.e., the linear relationship obtained for the final solution P concentration in the presence of  $10^{-2}\text{M NO}_3^-$  falls on that for P in solution in the absence of anions. Also, the straight-line plots of final solution P concentration in the presence of  $10^{-2}\text{M SO}_4^{2-}$  or  $10^{-3}\text{M HCO}_3^-$  with time are essentially parallel to that for P in the absence of anions. This suggests that the effects of these anions on P sorption remain constant over extended periods of time and provides an interesting contrast to the situation reported for cations ( Ryden and Syers, 1975 ). The observation that the plot of P in the final solution in the presence of  $10^{-3}\text{M HCO}_3^-$  lies below that for P alone in the Waiareka soil ( Figures 5.3 and 5.4 ) may again

Figure 5 : Effect of competing anions on the final P concentration of the four soils as a function of time. Amounts of added P correspond to approximately 40% of the adsorption maxima of regions I and II

- Figure 5.1 Egmont soil : 1400  $\mu\text{g}$  P added/g soil  
 Figure 5.2 Egmont soil : 3600  $\mu\text{g}$  P added/g soil  
 Figure 5.3 Waiareka soil : 60  $\mu\text{g}$  P added/g soil  
 Figure 5.4 Waiareka soil : 500  $\mu\text{g}$  P added/g soil  
 Figure 5.5 Okaihau soil : 200  $\mu\text{g}$  P added/g soil  
 Figure 5.6 Okaihau soil : 900  $\mu\text{g}$  P added/g soil  
 Figure 5.7 Porirua soil : 50  $\mu\text{g}$  P added/g soil  
 Figure 5.8 Porirua soil : 400  $\mu\text{g}$  P added/g soil

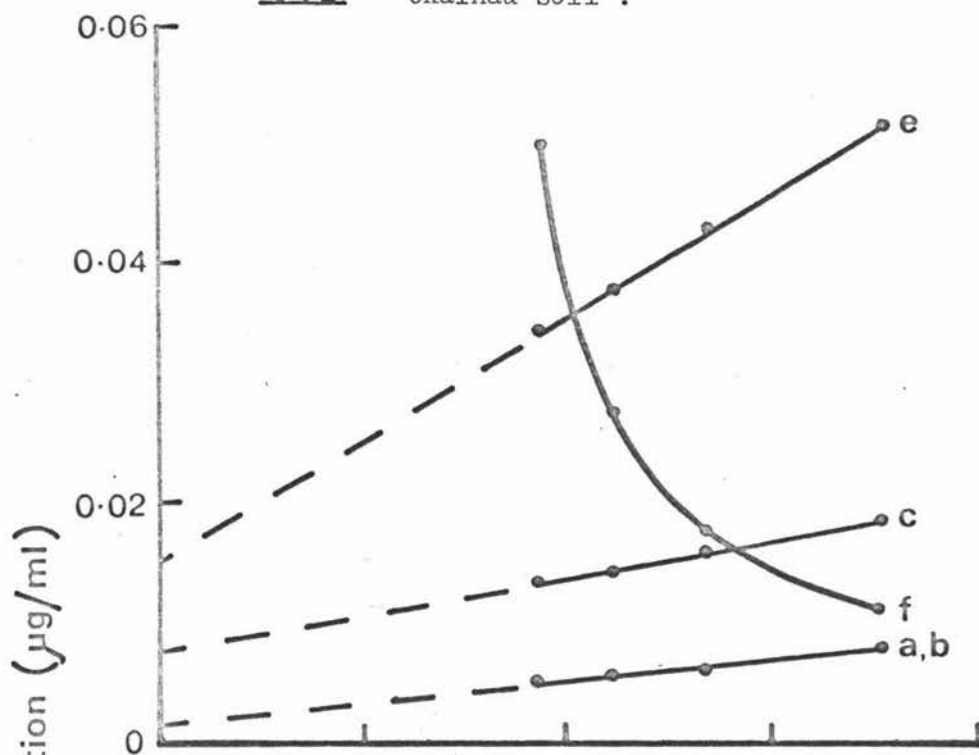
- a P alone  
 b  $10^{-2}\text{M NO}_3^-$   
 c  $10^{-2}\text{M SO}_4^{2-}$   
 d  $10^{-3}\text{M HCO}_3^-$   
 e  $10^{-3}\text{M citrate}$   
 f  $10^{-5}\text{M PGU}$



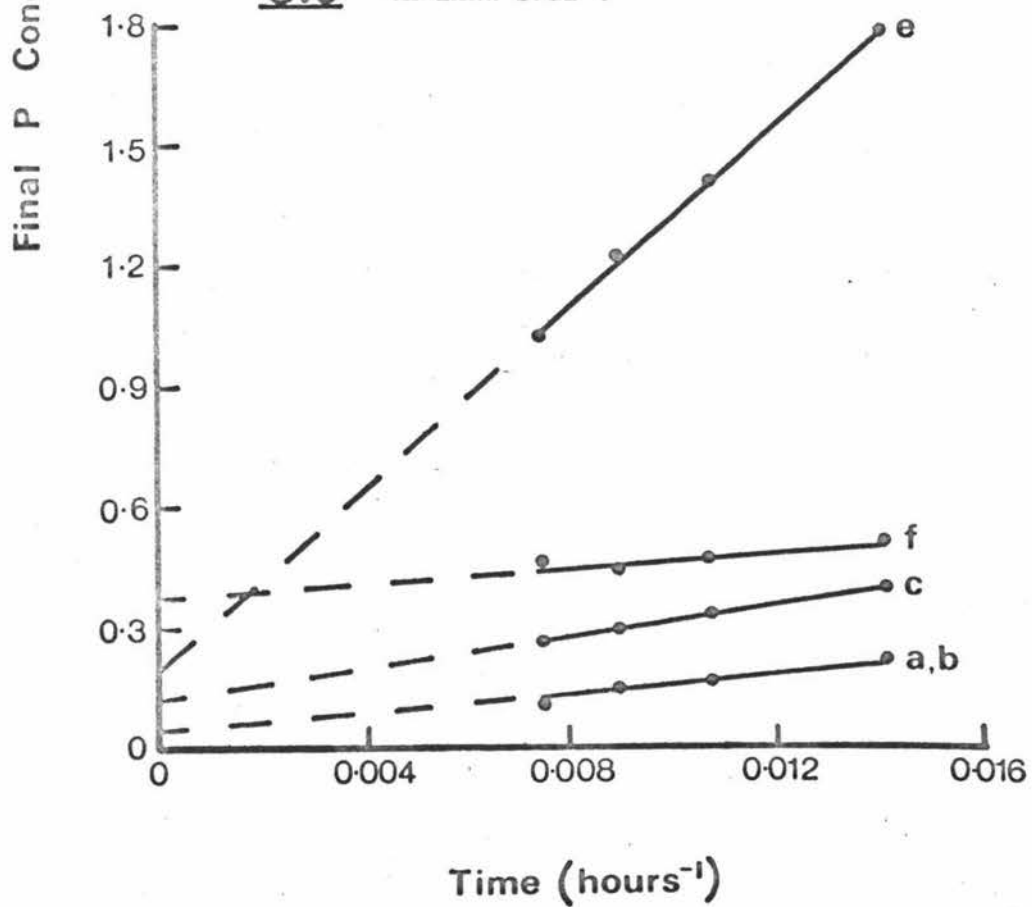


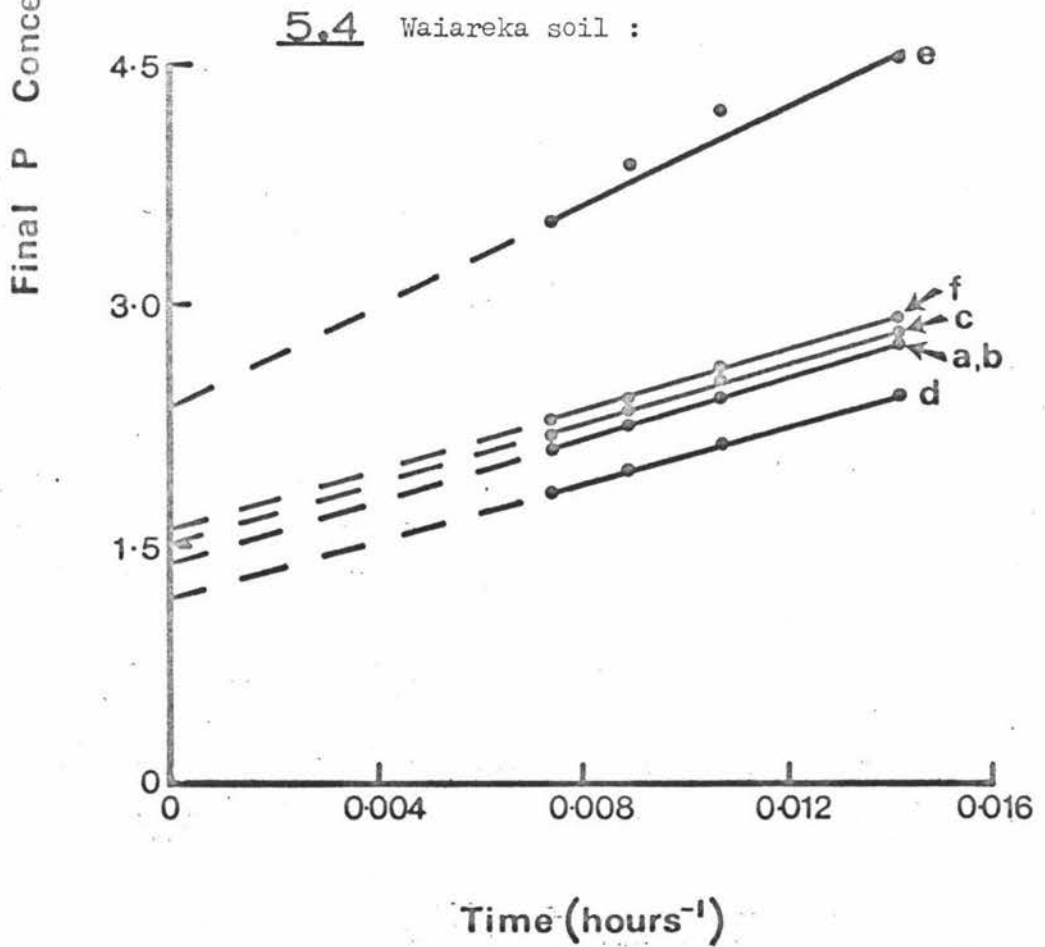
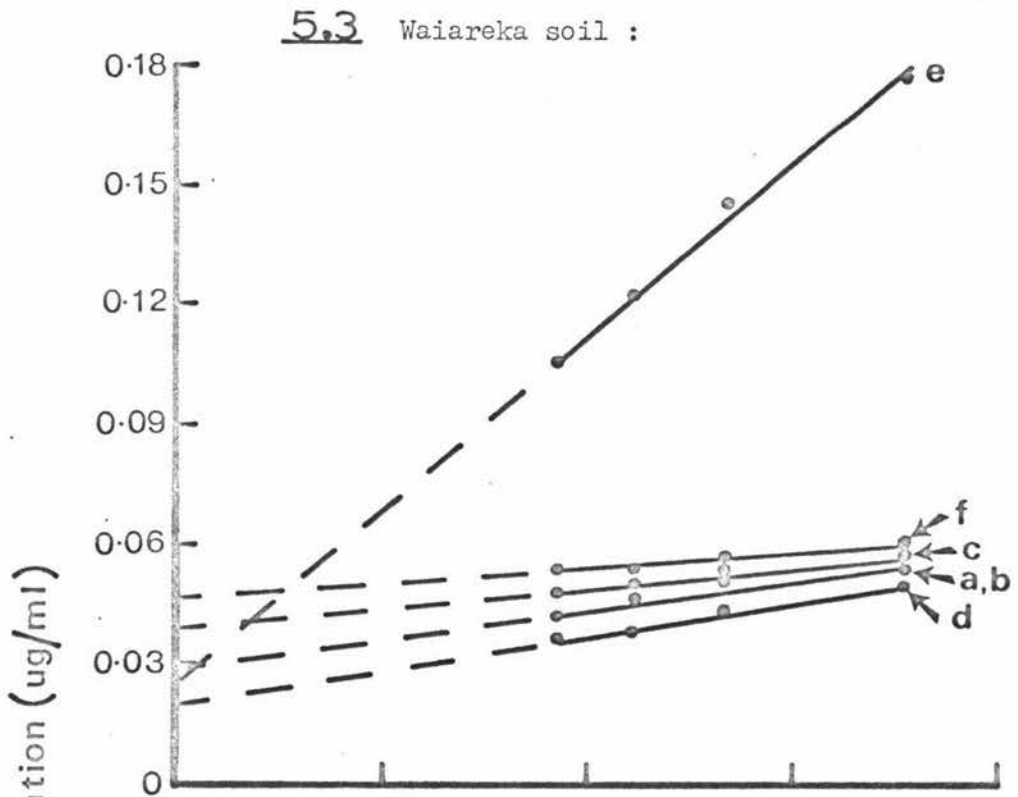


5.5 Okaihau soil :



5.6 Okaihau soil :





be explained by a pH effect ( Figure 4 ).

For both the Egnont and Okaihau soils at the lower level of added P ( Figure 5.1 and 5.5 ),  $10^{-5}$ M PGU showed an increasing ability to reduce P sorption and/or to promote P desorption with time. It is interesting to note that this effect was observed only for the two soils which have a high capacity to sorb added P. Although the reason for this is not clear, it is tentatively suggested that the large size of the PGU polymer ( M.W. ranging from 26,400 to 70,400 ) limits the rate and extent of attachment of the polymer to the adsorbent surface because of steric hindrance. With increasing periods of time, however, the active sites on the PGU polymer possibly become orientated to the surface of a component. This could explain why PGU was so effective in reducing P sorption over a 40-hour period for the Porirua soil ( Figure 3.4; Table 6 ). The results also suggest that  $10^{-5}$ M PGU may be more effective in promoting the desorption of previously sorbed P over an extended time period than the results in Table 8 for a 40-hour shaking period indicate.

For both the Egnont ( Figure 5.1 and 5.2 ) and Porirua ( Figure 5.7 and 5.8 ) soils, the plot of P in the final solution against time in the presence of  $10^{-3}$ M citrate remains approximately parallel to that for P alone, indicating no change in the effect of citrate on P sorption with time. For both the Waiareka ( Figure 5.3 and 5.4 ) and Okaihau ( Figure 5.5 and 5.6 ) soils, however, the ability of citrate to compete with P for sorption sites appears to be dramatically reduced with time. This may be explained by either of two possible reasons. Ferric iron which is initially removed from the soils by  $10^{-3}$ M citrate may be reprecipitated as hydrous ferric oxide, creating additional sorption sites. Alternatively, over time periods greater than 40 hours, the ability of  $HgCl_2$  to inhibit microbial activity in the suspensions of these two soils may decrease. The resulting build-up in microbial populations could lead to utilisation of both citrate, which is a well established energy source for microorganisms, and inorganic P, causing a reduction in the final solution P concentration.

In order to determine whether reprecipitation of Fe or Al occurred in the kinetic study of P sorption in the presence of  $10^{-3}$ M citrate ( Figure 5 ), thereby generating sorption sites and

causing a decrease in final solution P concentration with time, the amounts of Fe and Al in the supernatant solutions of Waiareka and Okaihau soils were determined. The results in Table 10 indicate that there is no obvious decrease in the concentration of Fe and Al in the final solutions after 3, 4, 5, and 6 days of shaking. These rather constant values correspond to the rapidly decreasing final solution P concentrations in the presence of  $10^{-3}$ M citrate shown in Figures 5.3, 5.4, 5.5, and 5.6. The data suggest that Fe and Al are not reprecipitated from the citrate solutions.

The decrease in final solution P concentration in the presence of  $10^{-3}$ M citrate with time for two soils probably results from the second of the two alternatives discussed above. It is not easy, however, to explain why this decrease occurs in only two soils ( Waiareka and Okaihau ) ( Figure 5 ). It is possible that the difference in behaviour of these soils results from the different levels of microbial activity; which in turn can be related to the organic matter content of the soil horizons used. Data from the New Zealand Soil Bureau Bulletin (1968) show that the Egnont (BC), Waiareka (B1), Okaihau (B2), and Perirua (B1) soils contain 1.7, 3.4, 3.3, and 0.7% of organic carbon, respectively. This may suggest, therefore, that both the Waiareka and Okaihau soils have a potentially greater microbial population which may be stimulated by citrate to the extent that it is capable of overcoming the inhibitory effect of  $HgCl_2$  ( 40  $\mu g/ml$  ) in shaking periods greater than 40 hours.

#### E. Removal of Fe and Al from Soils by Anions

Because P sorption sites in soils are believed to occur largely on secondary Fe and Al components, it is necessary in anion sorption studies to determine whether the competing anion is being sorbed preferentially to P by these sites, or whether the anion affects P sorption by complexing the cation which forms the site. The extent to which competing anions and added P remove Fe and Al from the four soils is shown in Table 11. Very similar results were obtained when the soils were shaken with anions in the absence of P ( data not presented ).

TABLE 10 -- Amounts of iron and aluminium removed from the Waiareka and Okaihau soils by  $10^{-3}$ M citrate as a function of time of shaking in the presence of added P

| System and shaking time :                | Iron                          | Aluminium | Iron                         | Aluminium |
|--|-------------------------------|-----------|------------------------------|-----------|
|  | µmoles in solution per g soil |           |                              |           |
| OKAIHAU                                  |                               |           |                              |           |
| <u>P + <math>10^{-3}</math>M citrate</u> | <u>200 µg P added/g soil</u>  |           | <u>900 µg P added/g soil</u> |           |
| 6 days                                   | 12.7                          | 3.18      | 11.1                         | 3.78      |
| 5 days                                   | 12.7                          | 2.96      | 11.2                         | 3.56      |
| 4 days                                   | 12.7                          | 3.18      | 11.1                         | 3.61      |
| 3 days                                   | 12.8                          | 2.96      | 11.1                         | 3.70      |
| WAIAREKA                                 |                               |           |                              |           |
| <u>P + <math>10^{-3}</math>M citrate</u> | <u>60 µg P added/g soil</u>   |           | <u>500 µg P added/g soil</u> |           |
| 6 days                                   | 2.54                          | 10.5      | 2.07                         | 11.1      |
| 5 days                                   | 2.02                          | 9.63      | 2.07                         | 9.67      |
| 4 days                                   | 2.22                          | 11.9      | 2.02                         | 7.26      |
| 3 days                                   | 2.16                          | 12.3      | 2.07                         | 10.4      |

TABLE 11 — Amounts of iron and aluminium removed from the four soils by various anions in a 40-hour shaking period.

| Anion system                | Iron<br>$\mu\text{moles Fe removed/g soil}$ | Aluminium<br>$\mu\text{moles Al removed/g soil}$ |
|-----------------------------|---|--|
| <b>EGMONT</b>               |   |  |
| No anions                   | 0.095                                       | 1.38   |
| $10^{-2}\text{M NO}_3^-$    | 0.064                                       | 1.82   |
| $10^{-2}\text{M SO}_4^{2-}$ | 0.159                                       | 1.50   |
| $10^{-3}\text{M HCO}_3^-$   | 0.064                                       | 1.38   |
| $10^{-3}\text{M citrate}$   | 0.449                                       | 9.49   |
| $10^{-5}\text{M PGU}$       | 0.095                                       | 2.97   |
| <b>WAIAREKA</b>             |   |  |
| No anions                   | 0.064                                       | 1.30   |
| $10^{-2}\text{M NO}_3^-$    | 0.064                                       | 1.38   |
| $10^{-2}\text{M SO}_4^{2-}$ | 0.032                                       | 1.58   |
| $10^{-3}\text{M HCO}_3^-$   | 0.064                                       | 1.23   |
| $10^{-3}\text{M citrate}$   | 2.42  | 8.90   |
| $10^{-5}\text{M PGU}$       | 0.125                                       | 1.82   |
| <b>OKAIHAU</b>              |   |  |
| No anions                   | 0.222                                       | 1.54   |
| $10^{-2}\text{M NO}_3^-$    | 0.095                                       | 1.50   |
| $10^{-2}\text{M SO}_4^{2-}$ | 0.254                                       | 1.50   |
| $10^{-3}\text{M citrate}$   | 12.9  | 3.08   |
| $10^{-5}\text{M PGU}$       | 0.319                                       | 3.40   |
| <b>PORIRUA</b>              |   |  |
| No anions                   | 0   | 1.42   |
| $10^{-2}\text{M NO}_3^-$    | 0.032                                       | 1.58   |
| $10^{-2}\text{M SO}_4^{2-}$ | 0.125                                       | 1.94   |
| $10^{-3}\text{M citrate}$   | 2.15  | 6.82   |
| $10^{-5}\text{M PGU}$       | 0.159                                       | 2.33   |

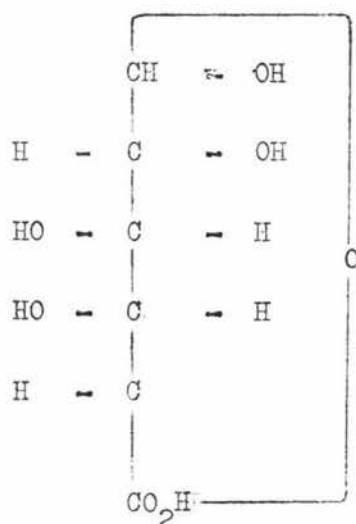
Of the five anions studied, excluding P, only  $10^{-3}$ M citrate and  $10^{-5}$ M PGU extracted significant quantities of Fe or Al from the soils ( Table 11 ). Citrate was particularly effective in removing Fe from the Fe-rich Okaihau Soil ( 12.9  $\mu$ moles Fe/g soil ), only moderately effective in the Porirua and Waiareka soils ( 2.15 and 2.42  $\mu$ moles Fe/g soil, respectively ), and removed only small amounts from the Egmont soil ( 0.449  $\mu$ moles Fe/g soil ). The reverse order was apparent for the removal of Al by  $10^{-3}$ M citrate. There appears to be no significant relationship between the amounts of Fe and Al extracted and the amounts of short-range order and crystalline Fe and Al components in the four soils ( Table 3 ).

The ability of citrate to form stable complexes with Fe and Al, and therefore to reduce P sorption has been suggested in several studies ( Swenson et al., 1949; Struthers and Sieling, 1950; Bradley and Sieling, 1953; Deb and Datta, 1967a, b; Nagarajah et al., 1970 ). These workers, however, have failed to define whether citrate removes Fe and Al from soil components by forming "soluble" complexes; or whether citrate forms complexes with Fe and Al at the surface of the component. Also, these workers have not determined the amounts of Fe and Al extracted by citrate. Low and Black (1947) demonstrated that the reduction in P sorption by kaolinite in the presence of oxalate was directly related to the amounts of Al removed, and inferred from this observation that citrate would probably show a similar effect. Evans and Syers (1971) showed that appreciable amounts of Fe were removed from soil crumbs by high citrate concentrations (  $10^{-1}$ M ). The complexing reaction may be attributed to bonding of Fe or Al ions between ionized carboxyl and alcoholic hydroxyl groups of the citrate anion ( Roberts and Caserio, 1965 ).

A comparison of the amounts of Fe and Al removed from the Okaihau soil by equivalent concentrations of citrate and PGU (  $10^{-5}$ M ) shows that the amount of Fe removed by the two anions are approximately the same ( 0.290 and 0.319  $\mu$ moles Fe/g soil, respectively ), whereas PGU removes considerably more Al than does citrate ( 3.40  $\mu$ moles/g soil and 0.79  $\mu$ moles/g soil, respectively ).

It is not clear why PGU removes greater amounts of Al than Fe from the four soils. The structure of galacturonic acid (below)

suggests that the polymer ( PGU ) is a tightly bound chain formed by H-bonding between hydroxyl and carboxyl groups ( Packer and Vaughan, 1958 ) .



It is possible that the size of the partially hydroxylated Al ion allows for more extensive complex formation with PGU than does the corresponding Fe species.

The significance of the formation of soluble complexes of Fe and Al with citrate in the sorption of added P by the Okaihau soil can be seen from the relationship between added P sorbed and the amount of Fe, Al, and ( Fe + Al ) released by citrate solutions of varying concentration (Figure 6, Table 12 ). As the concentration of citrate is increased, greater amounts of Fe and Al are removed from the soil with a corresponding decrease in the amount of added P sorbed. The relationship between added P sorbed and the amounts of ( Fe + Al ) released was particularly close ( Figure 6 ). The correlation coefficients for the relationship between % added P sorbed and the amounts of Fe, Al, and ( Fe + Al ) released by citrate solutions of varying concentration were very high, the respective values being -0.995, -0.979, and -0.998.

Although citrate may be specifically adsorbed by soil components, as claimed by Hingston *et al.* ( 1967, 1970 ) and Nagarajah *et al.* ( 1968, 1970 ), the very close relationship between added P sorbed and the amount of ( Fe + Al ) removed by citrate ( Figure 6 ) indicates that the reduction in P sorption by citrate results mainly



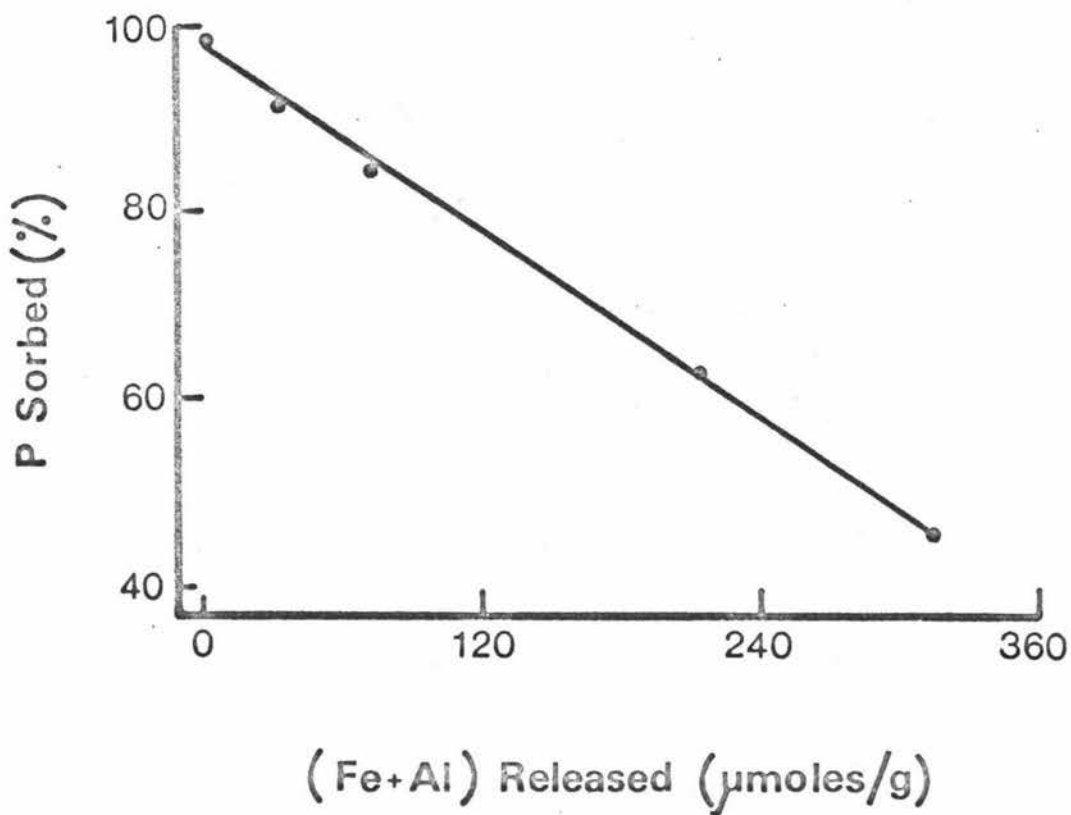


FIGURE 6 : Relationship between percentage of P sorbed and the amounts of ( Fe + Al ) removed from the Okaihau soil in a 40-hour shaking period by citrate solutions ranging in concentration from  $10^{-1}$  to  $10^{-5}$  M. Inorganic P ( 850  $\mu\text{g P/g soil}$  ) was added with citrate.

TABLE 12 -- Extent to which citrate solutions of varying concentration remove Fe, Al, and ( Fe + Al ) from the Okaihau soil, and reduce the amount of added P sorbed in a 40-hour shaking period. Inorganic P ( 850  $\mu\text{g}$  P/g soil ) was added with citrate.

| Citrate<br>concentration<br>(moles) | Final solution concentration ( $\mu\text{moles/g}$ soil ) |       |         | % added<br>P sorbed |
|-------------------------------------|---|-------|---------|---------------------|
|                                     | Fe  | Al    | Fe + Al |                     |
| $10^{-1}$                           | 231   | 81.0  | 312     | 45.5                |
| $10^{-2}$                           | 167   | 46.4  | 213     | 62.8                |
| $10^{-3}$                           | 46.3  | 26.1  | 72.4    | 84.5                |
| $10^{-4}$                           | 9.31  | 24.2  | 33.5    | 91.4                |
| $10^{-5}$                           | 0.194   | 1.27  | 1.46    | 98.5                |
| $10^0$                              | 0.452   | 0.723 | 1.18    | 99.0                |

from site elimination. A similar conclusion may be reached for PGU. It is apparent from Figure 6, however, that approximately 45% of the added P is still sorbed by the Okaihau soil in the presence of  $10^{-1}$ M citrate, indicating that not all sites are eliminated. The observation of previous workers ( Swenson et al., 1949; Bradley and Sieling, 1953; Deb and Datta, 1967 a, b ) that organic anions are generally more effective than inorganic anions in reducing P sorption by soils may, therefore, be interpreted as a greater ability of organic anions to eliminate P-sorbing sites on Fe and Al components, rather than as a direct specific adsorption effect, as proposed by Hingston et al., ( 1967, 1970 ).

CONCLUSIONS AND INTERPRETATIONS

The ability of the four soils used to sorb added inorganic phosphate (P) was strongly influenced by the amounts of certain components believed to be important in P sorption reactions in soils. The Egmont soil, which contains a high quantity of short-range order Fe and Al components, sorbed more P than the Okaihau soil which contains a greater amount of crystalline Fe components and associated Al (CDB-Al). These two soils sorbed considerably more P than the Waiareka and Porirua soils, which contain comparatively low amounts of secondary Fe and Al components.

The levels of added P used were not chosen arbitrarily, as in previous studies. Use was made of the Langmuir adsorption equation in establishing the amounts of P added to the soils. The amounts used in competitive sorption and desorption studies corresponded to 40% of the adsorption maximum for each of the first two regions on the Langmuir isotherm. This has enabled comparison of the effectiveness of the various anions at a known point on the P sorption isotherm involving sites having a reasonably well-defined affinity for P. The range of concentrations of the competing anions used was selected on the basis of limited available information on their concentration in the soil solution. This approach contrasts with that adopted in many previous studies where information on competitive sorption and desorption effects of anions has been obtained using much higher anion concentrations than those normally found in the soil solution and those used in the present study (Nagarajah *et al.*, 1968; Evans and Syers, 1971; Obihara and Russell, 1972; Barrow, 1974; Gebhardt and Coleman, 1974).

It has been shown that  $10^{-2}\text{M NO}_3^-$ ,  $10^{-2}\text{M SO}_4^{2-}$ , and  $10^{-3}\text{M HCO}_3^-$  have only a limited ability to reduce the amount of added P sorbed by the soils. Sorption of P by the Egmont and Okaihau soils was slightly enhanced in the presence of  $10^{-2}\text{M NO}_3^-$ , but this effect decreased with a decrease in  $\text{NO}_3^-$  concentration from  $10^{-2}\text{M}$  to  $10^{-5}\text{M}$ . Increasing ionic strength increases the rate of P sorption (Ryden and Syers, 1975), thus explaining the data obtained. Although  $\text{SO}_4^{2-}$  showed a greater ability than  $\text{NO}_3^-$  to reduce P sorption, the effect was only small and appeared to result from a direct competition between  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  for sorption sites, rather than from an ionic strength effect, as suggested for  $\text{NO}_3^-$ . According to Hingston *et al.* (1970) the ability of  $\text{SO}_4^{2-}$  to compete with

$\text{H}_2\text{PO}_4^-$  under slightly acid conditions is due to the formation of  $\text{HSO}_4^-$  as a result of proton donation from the charged surface. This hypothesis has not been tested experimentally.

At the two concentrations studied ( $10^{-3}$  and  $10^{-5}$  M),  $\text{HCO}_3^-$  was essentially ineffective in reducing the amounts of P sorbed by the two soils investigated (Egmont and Waiareka). It is suggested that the ability of  $\text{HCO}_3^-$  to reduce P sorption under natural conditions has been exaggerated in the past because of the high concentrations of  $\text{HCO}_3^-$  used in previous studies, often in conjunction with high pH values where competition from  $\text{OH}^-$  becomes important.

Both  $10^{-3}$  M citrate and  $10^{-5}$  M PGU were effective in reducing P sorption by the four soils. This was particularly true for the two soils having lower pH values (Okaihau and Porirua). This observation tends to support the hypothesis of Hingston *et al.* (1970) that the competing ability of organic anions is greatest at a pH corresponding to the  $\text{pK}_{a2}$  of the organic acid. According to these workers the  $\text{pK}_{a2}$  of citric acid is 4.76, and the  $\text{pK}_{a2}$  of polygalacturonic acid has been assumed to be between 3 and 5 (Nagarajah *et al.*, 1970). There is no experimental evidence, however, to support this claim.

The greater affinity of  $\text{H}_2\text{PO}_4^-$ , relative to other anions, for sorption sites on the components in the four soils obtained at concentrations equal to or lower than those of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and citrate, was attributed to the strong covalent character of the bond formed between  $\text{H}_2\text{PO}_4^-$  and the Fe and/or Al constituting surface sites. In contrast, PGU competed effectively with P for sorption sites at lower concentrations than those of the added P. For all soils,  $10^{-5}$  M PGU was more effective in reducing P sorption than citrate at the same concentration.

The ability of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  to desorb previously sorbed added P was very limited. Of these anions only  $10^{-2}$  M  $\text{SO}_4^{2-}$  showed any capacity to desorb previously sorbed P, and this was for the lower level of P addition to the Egmont soil. This again suggests that the ability of these three anions, particularly that of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ , to desorb sorbed P from soils under natural conditions has been somewhat exaggerated by previous workers. In contrast to  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ ,  $10^{-3}$  M citrate was particularly effective in desorbing previously sorbed P from all soils. This was especially

the case for the Porirua soil. Polygalacturonate at a concentration of  $10^{-5}M$  was effective in desorbing P only at low levels of previously added P to Egmont, Okaihau, and Porirua soils. In all cases, however, PGU was found to be superior to citrate at an equivalent concentration ( $10^{-5}M$ ). These findings confirm the observation of several previous workers ( Swenson et al., 1949; Bradley and Sieling, 1953; Deb and Datta, 1967 a, b ) that organic anions, in general, are more effective in desorbing P than are inorganic anions.

The extent to which competing anions affect the final solution P concentration in the 40-hour period following sorption of P by soils follows a similar pattern to their competing ability when both P and anions are added simultaneously; the extent of the change in final solution P concentration in the presence of anions is generally smaller in the former system. This is attributed to the strength of binding of the P sorbed in the 24-hour period and to the inability of anions, other than citrate and PGU to promote desorption. In the  $NO_3^-$  system sorption of P continued during the 40-hour period following  $NO_3^-$  addition.

The amounts of native P desorbed by the competing anions, studied from the four soils were very small. Only the highest concentrations of  $SO_4^{2-}$ , citrate, and PGU ( $10^{-2}$ ,  $10^{-3}$ , and  $10^{-5}M$ , respectively ) removed detectable amounts of native P. The ability of certain weak organic acids to remove P from soils accounts for the early popularity of these compounds as extractants for assessing the plant available P status of soils ( Dyer, 1894; Mattingly, 1965 ). It is also interesting to note that  $10^{-3}M HCO_3^-$  at pH 6.5 did not desorb detectable amounts of native P from the Egmont and Waiareka soils. The Olsen bicarbonate test ( Olsen et al., 1954 ) is now used extensively as a soil testing procedure, but the reagent employs a very much higher  $HCO_3^-$  concentration ( 0.5 M ) and a higher pH ( 8.5 ).

In studies of the competitive effect of anions on P sorption and desorption the need to maintain the pH of the system as closely as possible to that of the soil cannot be overemphasized. This is the case because the ability of a competing anion to affect P sorption or desorb previously sorbed P is strongly influenced by pH. Several factors are involved, including the changing proportion of ionic species present in solution, competition from hydroxyl ions, and the extent of positive charge of the surface. The pH increase observed in the present study

for each soil with increasing P and competing anion concentrations was limited to 0.3 to 0.4 of a pH unit. Such pH control allowed for a better comparison of anion effects, per se, without serious complications arising from pH differences in the systems studied. The Waiareka soil, however, showed an unusual dependence of P sorption on pH, and this effect was used to partly explain the greater ability of this soil to retain P in the presence of competing anions.

A study of the kinetics of P sorption in the presence and absence of competing anions showed that  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  had no observable effect on the amounts of P sorbed by the soils following the initial 40-hour shaking period. The marked ability of  $10^{-5}\text{M}$  PGU to decrease P sorption and to promote desorption of sorbed P with increasing time, especially at the lower level of added P with the Egmont and Okaihau soils, was attributed to the time required for the polymer to become orientated at surface sites. The dramatic decrease in final solution P concentration with the Okaihau and Waiareka soils in the presence of  $10^{-3}\text{M}$  citrate was more difficult to interpret. Because the amounts of Fe and Al in solution remained relatively constant with time in the  $10^{-3}\text{M}$  citrate system, it was tentatively suggested that microorganisms possibly overcome the inhibitory effect of the  $\text{HgCl}_2$  present and utilise both citrate and P, causing a decrease in P concentration in solution with time. This effect was more pronounced for the two soils which contained the highest amount of organic carbon ( Waiareka and Okaihau ).

Of the five anions studied, only  $10^{-3}\text{M}$  citrate and  $10^{-5}\text{M}$  PGU removed significant quantities of Fe and Al from the four soils. Citrate removed large amounts of Fe from all soils, particularly from the Fe-rich Okaihau soil. In contrast, PGU removed greater amounts of Al than Fe and also removed equal or greater amounts of Fe than did an equivalent concentration of citrate (  $10^{-5}\text{M}$  ). Although it is well established that citrate ( Bradley and Sieling, 1953; Nagarajah et al., 1968; Evans and Syers, 1971 ) and PGU ( Bradley and Sieling, 1953; Nagarajah et al., 1970 ) are particularly effective in both decreasing the amount of P sorbed and in promoting the desorption of P, the cause of these effects has remained obscure. The very close relationship established in this study between the reduction in the amount of P sorbed and the amounts of ( Fe + Al ) removed from the Okaihau soil by increasing concentrations of citrate, indicates that the reduction

in P sorption results primarily from the elimination of a significant proportion of sites, rather than from a direct specific adsorption effect as postulated by Hingston et al. (1970) and Nagarajah et al. (1970). A similar interpretation was given to explain the competitive effect of PGU.



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