THE REACTIONS AND MECHANISMS OF INORGANIC PHOSPHATE SORPTION BY SOILS

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Abstract

A review of the literature relating to the reactions and mechanisms involved in the sorption of inorganic phosphate (P) by soils and soil components suggested several topics for further research, the results and interpretations of which are presented in this thesis. Soils which contrasted in components and properties considered to be important in P sorption sorbed between 210 and 3350 µg P/g during 40 hr from 0.1M NaCl at a final P concentration of 10 µg P/ml. Contrasting soils provided a more reliable basis for the interpretation of data obtained in investigations of the reactions and mechanisms of P sorption by soils. Sorption of P was described by four first-order reactions for each soil. The rate constant for a particular reaction was also similar for each soil, implying that the same series of reactions were involved in P sorption. The decrease in extractability and isotopic exchangeability of sorbed P with increasing time, following P addition, coupled with increased recovery of P by citrate-dithionite-bicarbonate extraction indicated that adsorption was followed by absorption. Elimination of the differences between the amounts of P sorbed from various support media during 40 hr, when an estimate of the equilibrium condition was made, pointed to the implications of time-dependent sorption in the interpretation of P sorption data. Virtually complete replaceability by K of Ca removed from solution in response to P sorption was obtained. Retention of Ca to balance the increased negative charge arising from P sorption, and not the precipitation of a calcium phosphate, is indicated. Time-dependent sorption affected significantly the interpretation of P sorption data using the Langmuir equation. For equilibrium data, the P sorption isotherm for each soil was described by three distinct Langmuir equations, each corresponding to a particular P concentration range or region (0 to 0.02, 0.08 to 0.80, and 1.0 to > 20 µg P/ml). The sorption energy constant of a Langmuir equation corresponding to a particular region was very similar for each soil and suggested similar sorption mechanisms for each soil. Charge and pH relationships of P sorption by two soils and Fe gel demonstrated that three distinct P sorption mechanisms caused the deviation of P sorption data from a single Langmuir equation. The same mechanisms were involved in P sorption by soils and Fe gel. Data suggested that the mechanisms involved the ligand exchange reactions $-OH_2^+$; $H_2PO_4^-$, $-OH$; $H_2PO_4^-$, and $-OH$; HPO_4^{2-} at the hydrous-oxide surface. These mechanisms are in accord with the three Langmuir sorption energy constants obtained for each soil. The reactions and mechanisms of P sorption established have important implications to the plant availability of soil and fertilizer P, and provide a basis for the interpretation of other P sorption data.

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CHAPTER 1

REVIEW OF LITERATURE

1.1 Introduction

The role of phosphorus in pasture and crop production is well established. Because of the increasing cost of phosphate fertilizers, the phosphate requirements of soils in relation to agricultural production have been emphasised recently (Syers, 1974). Also, phosphorus has been implicated as one of the major causative factors in the eutrophication of waters (Mackenthun, 1965; Vollenweider, 1968; Syers _et al_., 1973 a). Furthermore, losses of phosphorus from agricultural land are believed to be important in phosphorus-induced eutrophication of natural waters (Lee _et al_., 1969; Ryden _et al_., 1973). Knowledge of the dynamics of phosphorus in soil-water systems is essential to an understanding of the availability of phosphorus to plants in both terrestrial and aquatic environments.

Probably the most important link in the non-biological dynamics of phosphorus in the environment is the interaction that occurs between dissolved inorganic orthophosphate (hereafter refer to as P) and other inorganics, both dissolved and particulate. Studies of the interaction of P with soils and soil components and, more recently, with other materials of environmental interest such as lake and stream sediments and those used in sewage treatment, have produced a voluminous literature. A commensurate understanding of the system, however, has not been achieved (Jacks, 1966). This situation has largely arisen from the confusion surrounding the types of reactions and mechanisms involved in the interaction of P with particulate materials.

A definition of some of the terms used in this review is required. "Retention" will be used as a general term for the removal of P from solution by soils and soil components, when no distinct reaction type or mechanism is implied. The term "sorption"*, however, is used to denote retention of P at surfaces, as opposed to its precipitation, with other ions, from solution. In the case of sorption, a definite mechanism or series of mechanisms are frequently implied.

Several reviews, which include discussion of the nature of P retention by soils and soil components are to be found in the literature (Wild, 1949; Kurtz, 1953; Hemwall, 1957; Larsen, 1967, Syers and Williams, 1975). In this review the development of concepts concerning the reaction type and mechanism of P retention are discussed with respect to the importance of sorption reactions, which have been emphasised in recent years. The type and properties of the sorbing surface are also discussed in detail, because of their importance in explaining many aspects of the P sorption mechanism.

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* The term "sorption" is used because of the confusion surrounding the exact nature of the reaction. Distinction between adsorption and absorption reactions is made in a later section.

1.2 Phosphate Retention - General Considerations

Concepts and interpretations of the nature of P retention by soils and soil components have tended to follow a cyclical development moving from those involving a sorption reaction, to a precipitation reaction, and returning more recently to a sorption reaction. A brief overview of the development of P retention concepts is given below.

1.2.1. The development of P retention concepts

Although the early works of Leibig (1840) and Way (1850) demonstrated that soils retain P to a greater extent than other anions, Warrington (1868) was the first to conduct laboratory experiments to evaluate the type of reaction involved in the retention of P by soils. Based on the retention of P by "ferric oxide" and "alumina", Warrington suggested that P was retained at the oxide surface by a chemical reaction.

Russell and Prescott (1916) substantiated this work by demonstrating that P retention by soils during acid extraction could be described by the Freundlich adsorption equation. Furthermore, they noted that P retention was diminished in the presence of organic anions. On the basis of these observations and that precipitation was unlikely under the pH conditions used (pH $\simeq$ 1), Russell and Prescott (1916) proposed that P was retained by a sorption reaction. As discussed later, the fit of data to a sorption equation is not incontrovertible proof of a sorption reaction.

The concept that P is retained by a sorption reaction was developed further by Mattson (1927, 1930, 1931) who recognised and demonstrated, using electrokinetic techniques, the importance of the pH dependent charge of "soil colloids" in P retention. The effects of P (and other anions) on the isoelectric point of soil colloids could only be explained by a chemisorption reaction. These studies were remarkably advanced in the light of more recent work in this area, and the conclusions compare favourably with those of Breeuwsma and Lyklema (1973) and Hingston <u>et al</u>., (1972).

Subsequent work by Ford (1933), Ravikovitch (1934), Davis (1935), Toth (1937), and Kurtz <u>et al</u>. (1946) again suggested that P retention by soils involved a sorption reaction. Although precise mechanistic concepts were not tested, Ravikovitch (1934) viewed the reaction as an anion exchange phenomenon. This observation was based on the effects of pH on P sorption. In contrast, using chemical and X-ray techniques, Ford (1933) suggested that P sorption was nonpolar in character and involved a chemical reaction at the sorbing surface.

Despite the evidence accumulated to the contrary, Low and Black (1947) proposed that kaolinite retained P by precipitation with Al dissociated from kaolinite. The solution P concentrations, however, were sufficiently high to disrupt the kaolinite structure. Later work by Low and Black (1950), at P concentrations more comparable to those of the soil solution, implied a chemisorption reaction at surface OH groups. Russell and Low (1954) later demonstrated that surface-bound Al was requisite to P sorption.

The concept that P retention involved a precipitation reaction attracted further attention in the 1950's. On the basis that Al and Fe phosphates could be formed and identified in solutions of similar composition to the soil solution, and from consideration of the solubility equilibria of P compounds, Haseman <u>et al</u>. (1950 a, b) and Cole and Jackson (1950 a, b) postulated that P retention involved a precipitation reaction. Cole and Jackson (1950 a, b) determined the solubility product of variscite and constructed its solubility isotherm. It was concluded that P retention by neutral to acid soils could be explained by the variscite-barrandite-strengite ($Al\ PO_4$ - $(Al, Fe)\ PO_4$ - $Fe\ PO_4$) isomorphous series.

Kittrick and Jackson (1955 a, b, 1956) developed these concepts further. Using electron microscopy, they demonstrated the formation of ferric phosphate over the pH range of 4.3 to 7.0 during the treatment of hydrous ferric oxide with a 1M phosphate solution at room temperature (Kittrick and Jackson 1955 a). The electron micrographs were taken to represent the formation of discrete-phase P compounds. Using solution precipitation techniques at elevated temperatures, Kittrick and Jackson (1955 b) also prepared variscite and strengite which were identified by X-ray diffraction. Based on their previous work (Kittrick and Jackson, 1955 a), it was considered that these P compounds, despite their method of preparation, represented the products of P retention by soils. The P concentrations maintained in solution (Kittrick and Jackson, 1955 b), however, were very much higher than would be expected for the soil solution, with the exception of that in close proximity to a fertilizer granule. The common-ion effect of the components of the soil solution, on the solubility of variscite and strengite, was proposed (Kittrick and Jackson, 1955 b) as an explanation for the lower P concentrations characteristic of the soil solution. Data presented to substantiate this explanation could also be attributed to the sorption of P released by the dissolution of variscite and strengite.

The work described above led to attempts to correlate P concentrations in equilibrium aqueous extracts of soils (e.g., the "phosphate potential", Aslying 1954; Schofield, 1955) to solubility isotherms of various Fe, Al, and Ca phosphates. This was done with a view to identifying the discrete phosphate compounds which were believed to govern the solution P concentration and the chemical mobility of P in soils (Clark and Peech, 1955, 1960; Lindsay et al., 1959; Larsen and Court, 1961; Chakravarti and Talibudeen, 1962; Withee and Ellis, 1965; Murrmann and Peech, 1968; Larsen and Widdowson, 1970; Webber and Mattingley, 1970; Jensen, 1971; Talibudeen, 1974). This approach is still to be found in the soils literature, despite the generally inconclusive data obtained, and the considerable limitations of the approach. The value and validity of this approach are discussed below in relation to the concept of P sorption.

Interest in P sorption by soils and soil components was revived by the work of Olsen and Watanabe (1957), Shapiro and Fried (1959) and Rennie and McKercher (1959) who realised that the mobility of P in soils could best be described by P sorption isotherms. The interpretation of P retention by both soils and soil components, has tended to follow this approach over recent years (Hsu and Rennie 1962; White and Beckett, 1964; Hsu, 1964; Bache, 1964; Muljadi et al., 1966; Hingston et al., 1967, 1968 b, 1972; Syers et al., 1973 b). This has allowed development of more flexible models of P retention by soils with respect to fertilizer practice and environmental studies (Woodruff and Kamprath, 1965; Bache and Williams, 1971; Taylor and Kunishi, 1971). The same approach has also formed the basis for studies of the mechanism of the P sorption reaction (Hingston et al., 1967, 1972).

1.2.2 The nature of P retention

1.2.2.1 The validity of precipitation and sorption concepts. Although Wild (1954)had shown that the P concentration of the soil solution showed little or no correspondence to solubility isotherms of discrete P compounds, Taylor and Gurney (1962) appear to have been the first workers to present data that questioned the precipitation concepts described above. Taylor and Gurney (1962) demonstrated that the P and Al concentrations of the aqueous extracts of the soil used were compatible with the existence of variscite. When the soil was treated with dilute acid, however, the ion product of variscite, fell below the variscite solubility isotherm. This suggested that the soil could maintain lower P concentrations than predicted from the solubility isotherm of variscite.

Raupach (1963) also obtained evidence that the existence of variscite in soils was unlikely. By analysis of data presented by other workers, he demonstrated that Al concentrations in the soil solution were determined by hydrolysis products of species formed during the dissolution of aluminium hydroxide.

Further evidence suggesting the inapplicability of solubility criteria in describing the retention of P by soils is presented in Fig. 1.1. Data drawn from several reports of the P concentrations in aqueous extracts of a wide range of soils with different fertilizer and lime additions, are plotted over the solubility isotherms for variscite, strengite, hydroxy-apatite, octocalcium phosphate, and dicalcium phosphate dihydrate, assuming a Ca concentration of 3.2×10^{-3}M. This approach has been used extensively to postulate the existence of discrete P compounds in soils, and to demonstrate their importance in determining the P concentration of the soil solution. In most previous studies the pH range has been limited and consequently only Al and Fe, or Ca phosphates were included (Lindsay et al., 1959; Larsen and Court, 1961). The data in Fig. 1.1 suggest that phosphate concentrations, expressed as pH_2PO_4, vary from about 5.5 to 6.5, showing no apparent dependence on pH, and little tendency to conform to any particular solubility isotherm, being generally undersaturated with respect to all compounds over the pH range 5.5 to 6.5.

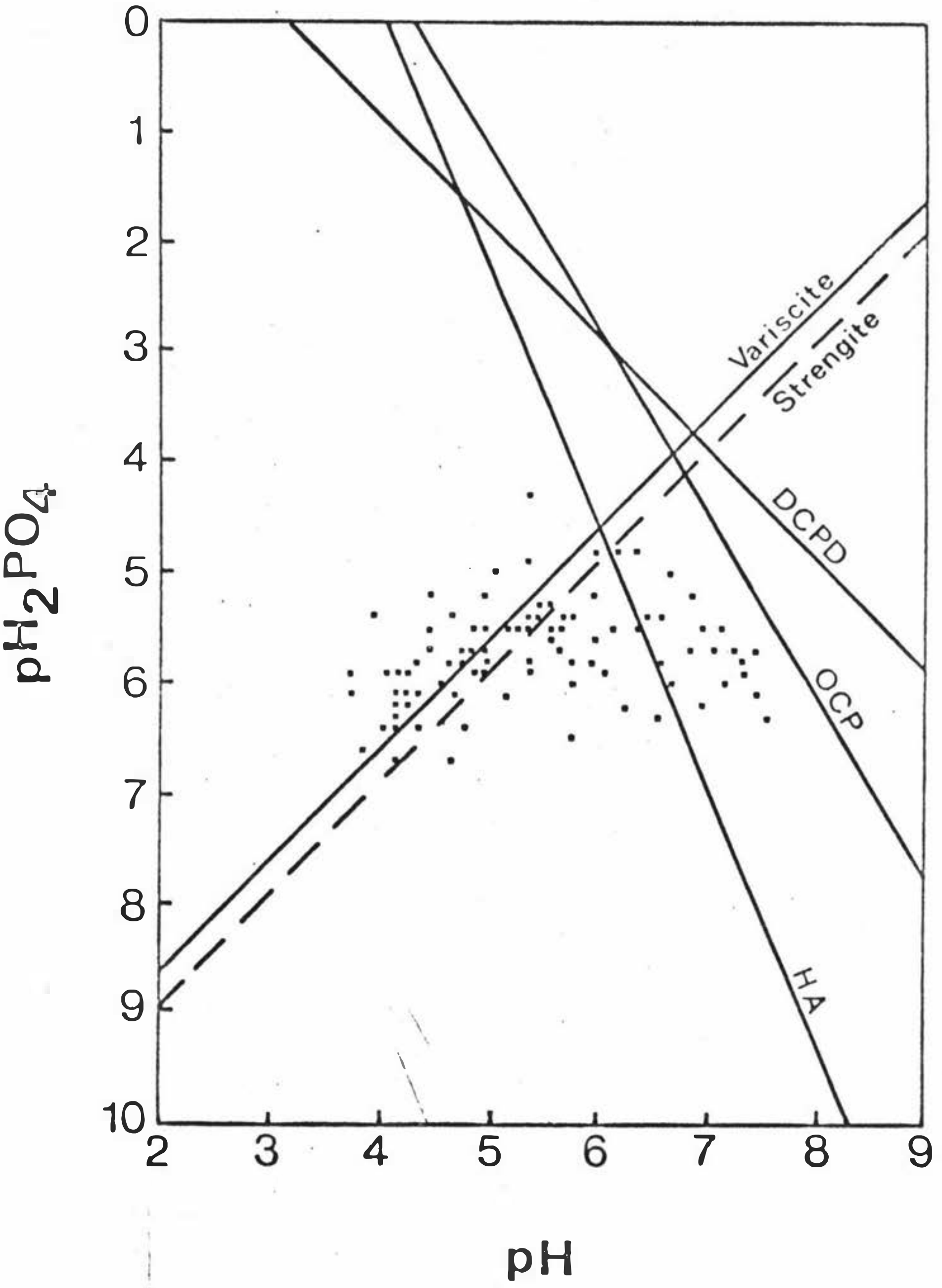

FIG. 1.1 Solubility isotherms for various phosphate minerals as a function of pH, and data for the P concentrations of soil solution extracts. Solubility isotherms after Lindsay and Moreno (1960). P concentration data for soil solution extracts from Clark and Peech (1955), Lindsay *et al.* (1959), Clark and Peech (1960), Taylor and Gurney (1960), Larsen and Court (1961), Chakravarti and Talibudeen (1962), and Withee and Ellis (1965).

That some workers have reported agreement between P concentration data and solubility isotherms would appear to be fortuitous, and is not a good criterion for the existence of discrete P compounds in soils, as demonstrated by Taylor and Gurney (1962). Furthermore, solubility isotherms, such as those in Fig. 1.1, take no account of complex ion formation from which even higher solution P concentrations would be predicted (Van Wazer, 1958; Galal-Gorchev and Stumm, 1963; Morgan and Stumm, 1970).

Evidence against a precipitation concept has also been presented by Hsu and Rennie (1962) for amorphous "aluminium hydroxide" and by Hsu (1964) for soils. After treating a soil (Hsu, 1964) with solutions of varying initial P concentration, the supernatants were removed and replaced by a second solution containing 5 μg P/ml. A summary of the results is given in Table 1.1. Hsu (1964) argued that if P was originally retained by a precipitation reaction, removal of P from solution would continue in the second treatment. If a sorption reaction was involved, however, removal of P would continue only in those systems for which the final P concentration after the first treatment was less than 5 μg/ml. In systems where the final P concentration after the first treatment was greater than 5 μg P/ml, P would be released to solution. The data in Table 1.1 suggest that a sorption reaction is involved. Similar results were obtained for "aluminium hydroxide"(Hsu and Rennie, 1962).

Quantitative data on the solubility of variscite and strengite have been presented by Bache (1963, 1964). Using buffers to maintain pH, Bache (1963) showed that the solubility of variscite and strengite was congruent only below pH values of 3.1 and 1.4, respectively. This is in agreement with solubility data for variscite, previously reported by Kittrick and Jackson (1955 c). Above these pH values P concentrations remained fairly constant, being one to three orders of magnitude greater than those predicted by Fig. 1.1. Based on the effects of pH, and solution to solid ratio on the solubility product, incongruent dissolution was attributed to hydrolytic decomposition of the surface, producing "Fe and Al hydroxides" capable of sorbing P from solution. Bache (1963) concluded that only highly crystalline forms of variscite and strengite, the formation of which is improbable in soils (Lindsay _et al._, 1962), are likely to conform to thermodynamic solubility criteria similar to those used to

TABLE 1.1 The amount of P removed by a soil from solutions of different initial P concentrations (first treatment), and the distribution of P removed from solution during the first treatment between soil and solution after replacing the final solutions from the first treatment with solutions initially containing 5 μg P/ml (second treatment). Data from Hsu (1964).

First treatment			Second treatment		
Initial P concentration (μg/ml)	Final P concentration (μg/ml)	P removed from solution (μg/g)	Initial P concentration (μg/ml)	Final P concentration (μg/ml)	P removed from solution * (μg/g)
2.5	0.5	20	5	2.3	27
5.0	1.3	37	5	3.1	19
20	8.9	111	5	6.2	- 12
30	15.8	142	5	7.7	- 27
60	42.8	172	5	10.0	- 50

* negative values indicate release of P.

calculate the isotherms in Fig. 1.1. In recently fertilized soils however, it is well established that the P concentration and low pH of the solution in the vicinity of a fertilizer granule (4.0 M and 1.48, respectively, at the metastable triple point of monocalcium phosphate and dicalcium phosphate dihydrate; Huffman and Taylor, 1963) are influential in the formation of a wide variety of discrete P compounds by reaction with soil components. Lindsay et al. (1962) have identified at least thirty different compounds after soils and soil components had been allowed to react with saturated solutions of five fertilizer salts. The dominant products were complex phosphates of iron, aluminium, and calcium in neutral to acid soils, and calcium phosphates in calcareous soils. All compounds, however, supported higher P concentrations than the surrounding soil, ranging from approximately 62 µg P/ml in the case of calcium reaction products to 0.31 µg P/ml for iron and aluminium reaction products. The rates of dissolution were in a similar order to their solubilities (Huffman et al., 1960).

The facts that the reaction products isolated by Lindsay et al. (1962) maintained higher P concentrations than the surrounding soil, and that Bache (1964) showed that hydrous oxides of iron and aluminium maintained very much lower P concentrations, by a sorption reaction, than those maintained by variscite and strengite, suggest that the persistence of discrete P fertilizer reaction products in soils is unlikely. Reversion of the P in fertilizer reaction products to sorbed forms has been predicted (Huffman and Taylor, 1963; Bache 1964). The rate at which this occurs will depend largely on the nature and solubility of the discrete phases, and the degree of saturation of the sorbing surface of soil components.

The above discussion suggests that an understanding of P retention is facilitated by assuming a sorption reaction. However, de Boer (1950) has pointed out that there is essentially no difference between the chemical forces which may hold an ion or molecule at a sorbing surface and those involved in the precipitation of a comparable discrete phase. It is this fact that has probably led to the confusion with respect to the reaction involved in P retention by soils and soil components. Sorption, however, requires that as the process continues, the structure of the sorbent remains essentially unchanged, whereas surface activity changes appreciably. Consequently, concentrations maintained in solution at high sorbent saturation will be greater than those at low sorbent saturation. In contrast, precipitation implies a constant surface activity. The retention of P by soils and soil components fits the conditions of sorption reactions described above (Table 1.1), although the non-reversibility of P sorption complicates this simple interpretation, as will be discussed in a later section.

1.2.2.2 The time dependence of P sorption. Although the retention of P by soils and soil components complies with the conditions of sorption, a reaction involving only true adsorption implies a rapid reaction rate with a well defined sorption maximum. The sorption of P in laboratory experiments is characterised by an initially fast reaction, followed by a slow reaction which frequently does not attain a true equilibrium condition (Rennie and McKercher, 1959; Hsu, 1964; Sholten, 1965; Fox and Kamprath, 1970; Evans and Syers, 1971). This is particularly true for soils and to some extent for soil components (Sholten, 1965; Chen et al., 1973 a). In many studies, however, the approach to equilibrium has not been reported.

Although the rapid initial reaction has frequently been attributed to a true adsorption reaction (Rennie and McKercher, 1959; Hsu, 1964) the origin of the slow reaction has rarely been discussed. Larsen and Widdowson (1971), Chen et al. (1973 a) and Talibudeen (1974) have implied a slow reversion of adsorbed P to discrete P compounds. This explains to some extent the reported (Talibudeen, 1958; Evans and Syers, 1971; Larsen and Widdowson, 1971) decrease in isotopic exchangeability of sorbed P with time of sorption. It does not, however, fully explain the continued slow sorption of P with time.

Sholten (1965) has reported that only up to 80% of P sorbed by naturally-occurring goethite is extracted by 0.1 M NaOH, suggesting that not all the sorbed P was held at the surface (Williams et al., 1967). The additional P was recovered after dissolution of the goethite in a reductant solution. These observations suggest that an absorption reaction may follow the initial adsorption reaction, although more quantitative data are required, particularly with regard to P sorption by soils.

In this review no distinction will be made with respect to P sorption mechanisms, between adsorption and absorption reactions, the latter being considered as adsorption at "internal surfaces".

The potential effect of an absorption reaction on the rate of the overall P sorption reaction is expected to be appreciable, and may have a direct bearing on the interpretation of many aspects of P sorption by soils and soil components.

1.2.3 P sorption surfaces in soils

1.2.3.1 Nature of the P sorption surface. Two approaches may be adopted to elucidate the surfaces important in the sorption of P by soils. Both provide only circumstantial evidence, but the weight of evidence available provides a useful basis from which a model P sorption surface may be proposed.

The first method relies upon an evaluation of P sorption by soils before and after a chemical treatment designed to remove a particular component or components. The change in P sorption can then be related to the amounts of various soil components removed by chemical treatment. Studies of this type have been reported extensively (Leaver and Russell, 1957; Williams *et al.*, 1958; Bromfield, 1965; Saunders, 1965; Ramulu *et al.*, 1967; Syers *et al.*, 1971). Although the results of these studies have been somewhat inconclusive because of the interrelationships between many soil properties, all have pointed to the importance of secondary Fe and Al oxides and hydrous oxides. In a detailed study of 300 New Zealand soils, Saunders (1965) found that P sorption was closely correlated with the amounts of short-range order (amorphous) Fe and Al components. Similar results were reported by Williams *et al.* (1958) for Scottish soils and by Bromfield (1965) for Australian soils.

The findings summarised above are not unexpected in view of the fact that short-range order hydrous oxides of Fe and Al are, in general, more reactive than their crystalline counterparts (Gorbunov *et al.*, 1961; Schwertmann, 1964; Syers and Williams, 1975). This is substantiated by the data of Syers *et al.* (1971). These workers showed that although short-range order Al components were more important than short-range order Fe components in P sorption by Brazilian soils, the decrease in P sorption following removal of short-range order components by oxalate was considerably greater than that following removal of crystalline components by dithionite. The effect of isomorphous substitution on the reactivity of crystalline hydrous oxides may also be important. Norrish and Taylor (1961) noted that Al may be substituted for Fe in soil goethites by up to 30%, reducing the size of the crystallites, increasing the surface area, and presumably reactivity with respect to P sorption.

Although the dependence of P sorption on the content of short-range order Fe and Al hydrous oxides is well established, problems are inherent in studies similar to those discussed above in that the components which are highly correlated with P sorption may themselves be interrelated to a considerable extent (Saunders, 1965; Syers et al., 1971). This is illustrated by the high correlations frequently found between organic matter content and P sorption (Williams et al., 1958; Harter, 1969). The high correlation probably arises from the influence of organic matter on the crystallinity of hydrous metal oxides (Schwertmann, 1966).

A second approach to establish the relative importance of soil components in P sorption involves evaluation of P sorption by "pure" soil components, and comparison of the results obtained to the expected forms, amounts, and distribution of similar components in soils. The sorption of P by various soil components has been studied extensively. Soil components tested have included crystalline alumino-silicates (de Haan, 1965; Muljadi et al., 1966; Kafkafi et al., 1967, Pissarides et al., 1968; Kafkafi and Bar-Yosef, 1969; Kuo and Lotse, 1972; Chen et al., 1973 a b), short-range order alumino - silicates (Cloos et al., 1968), short-range order hydrous oxides of Fe and Al (Hsu and Rennie, 1962; Gastuche et al., 1963; Bache, 1964), crystalline oxides and hydrous oxides of Fe and Al (Hingston et al., 1967, 1968 b; Chen et al., 1973 a,b; Breeuwsma and Lyklema, 1973; Kuo and Lotse, 1972), and calcium carbonate (Cole et al., 1953; Kuo and Lotse, 1972; Griffin and Jurinak, 1973). It is important, however, to distinguish those components which are likely to be of greatest importance in P sorption by soils. This is governed not only by the absolute amount of a particular component and its sorption capacity, but also by the distribution of the component in soils, e.g., as coatings.

Table 1.2 lists the amounts of P sorbed by various soil components at given final P concentrations (approximately 3 μg P/ml). Because of the lack of uniformity in the experimental

TABLE 1.2 Sorption of P by various soil components at final P concentrations of approximately 3 µg P/ml under the experimental conditions specified.

Component	P sorbed (µg/g)	Final P concentration (µg/ml)	Experimental conditions			Ref.**
			pH	Support medium	Shaking time(hr)	
Hydrous ferric oxide gel*‡	14,290	5.0	5.5	0.1M NaOAc	2.4	(1)
" " " " *§	21,700	3.1	5.0	"	24	(2)
" " " " *§	29,700	3.3	7.7	0.1M $NaNO_3$	48	(3)
" " " " *§	50,000	2.95	5.5	"	11	(3)
Short-range order aluminum hydroxide *‡	3,900	3.8	5.0	1M NaOAc	0.5	(4)
Goethite* §	5,800	2.7	4.2	0.1M $NaClO_4$	48	(3)
Haematite* §	1,150	3.1	4.0	H_2O	3	(5)
Gibbsite* §	7,130	3.1	5.0	"	24	(6)
Kaolinite+	465	3.0	5.0	"	"	(6)
Montmorillonite+	110	3.0	6.5	"	72	(7)
Calcite*‡	60	2.8	9.2	"	Variable	(8)
Calcite*‡	25	3.0	7.0	"	24	(9)

*Synthetic, +Natural, ‡ Dried, § Undried.

**(1) Leaver and Russell, 1957; (2) Bache, 1964; (3) J.R. McLaughlin, pers. comm; (4) Hsu and Rennie, 1962; (5) Breeuwsma and Lyklema, 1973; (6) Muljadi *et al.*, 1966; (7) Pissarides *et al.*, 1968; (8) Cole *et al.*, 1953; (9) Kuo and Lotse, 1972.

conditions used, and sorbent preparation and pretreatment, a detailed comparison of the data in Table 1.2 cannot be made. Differences in the amounts of P sorbed by the various components are, however, of sufficient magnitude to indicate their relative importance in a mixed component system, such as a soil. Data suggest that crystalline Fe and Al components (e.g., haematite, gibbsite, and α-alumina) generally sorb 5 to 10 times more P than crystalline aluminosilicates or calcium carbonate. In contrast, short-range order components, such as Fe gel, sorb approximately 10 to 100 times more P than their crystalline counterparts and approaching 1000 times more P than crystalline aluminosilicates or calcium carbonate.

The difference in P sorption by crystalline as compared to short-range order components is in accord with the data for soils discussed above, and the differences in the surface area of these components. Furthermore, it is well established that a considerable proportion of the oxides and hydrous oxides of Fe and Al in weakly-to moderately-weathered soils has short-range order character (Mitchell et al., 1964). Consequently, the importance of short-range order, and to some extent crystalline oxides and hydrous oxides of Fe and Al, in P sorption by soils is likely to outweigh that of crystalline aluminosilicates. Even when the higher pH of calcareous soils is taken into account, the presence of only small amounts of short-range order or even crystalline oxides and hydrous oxides may reduce to minor significance the contribution of calcium carbonate to the overall sorption of P by these soils.

1.2.3.2. Distribution of oxides and hydrous oxides in soils. The distribution of the oxides and hydrous oxides of Fe and Al in soils, and the way in which other surfaces may be affected by them, is also of importance in relation to P sorption by soils. The electronmicroscope has played a particularly important role in evaluating this distribution.

For highly-weathered soils, Greenland et al. (1968) reported that hydrous Fe oxides occurred primarily as discrete particles within the clay fraction, although small amounts of hydrous-oxide coatings were observed on the clay surfaces. More extensive hydrous Fe oxide coatings have been reported for clays in less strongly-weathered soils (Roth et al., 1969; Kirkman, 1973).

The coating of clay minerals with hydrous Fe oxides has also been demonstrated in laboratory studies. Follett (1965) noted that "ferric hydroxide" was precipitated on the basal surfaces of kaolinite from a mixed solution-suspension. A similar observation was reported by Greenland and Oades (1968) for "ferric hydroxide" gel, although during mixed precipitation with kaolinite, goethite showed little tendency to associate with the clay surface.

The occurrence of hydroxypolymers of Al on clay mineral surfaces has also been noted by Shen and Rich (1962) and Jackson (1963). Tweneboah et al. (1967) and Deshpande et al. (1968) also reported that aluminous coatings were extensive in soils and that they had a major influence on the physical, and presumably chemical, properties of soil clays. Furthermore, the fixation of hydroxy-aluminium polymers by vermiculite has been observed by Hsu and Bates (1964). de Villiers and Jackson (1967), and Brown and Newman (1973) have also demonstrated that the pH-dependent charge of soil clays arises from coatings of "hydroxy aluminium".

The importance of coatings at clay surfaces in P sorption by soils has frequently been emphasised (Coleman, 1944; Russell and Low, 1954; Hsu, 1965). Consequently, the coexistence of hydrous oxides and crystalline aluminosilicates in soils, especially if the hydrous oxides form coatings on the latter, emphasises further the minor role that crystalline aluminosilicates are likely to have in the sorption of P by soils.

The surface of naturally-occurring calcium carbonate also shows quite different properties to its chemically pure equivalent in terms of pH and solubility relationships. It has been suggested that these differences arise from surface coatings of organics and possibly hydrous oxides (McGeorge, 1935; Buehrer and Williams, 1936; Olsen and Watanabe 1959; Lahav and Bolt, 1963; Chave, 1965).

There seems little doubt that, with the possible exception of highly-weathered soils, oxides and hydrous oxides of Fe and Al occur extensively as coatings on soil mineral particles, particularly crystalline aluminosilicates within the clay-sized fraction as well as calcium carbonate in the case of calcareous soils. Such coatings, in conjunction with the greater surface area of the clay-sized fraction, accentuate the potential of oxides and hydrous oxides in P sorption.

Consequently, the use of Fe and Al oxides and hydrous oxides as a model for the P sorption surface in soils seems justified. Even in soils where aluminosilicates, particularly short-range order aluminosilicates, make a significant contribution to the overall sorption of P, the oxide-surface model remains valid, as will be discussed below.

1.3 The Oxide-Aqueous Interface

The hydrous metal oxide*-aqueous interface is highly complex and its behaviour and role with respect to P sorption has only recently begun to be understood. An appreciation of the properties and structure of the interface is essential to the development of any mechanism to describe the P sorption reaction. The structure of the surface, and the development and distribution of charge are discussed below. Terms are also defined which will be used in the subsequent discussion of the P sorption mechanism.

1.3.1 Oxide structure and origin of charge

The structure of Fe and Al oxides, is essentially similar, and the chemical formula will be denoted by M_2O_3, where M = Fe or Al. Although packing varies between different types, each metal ion is usually in distorted octahedral coordination with six oxygen ions, and each oxygen ion in coordination with four metal ions. Without implying ionic character, the distribution of charge can be considered in the following way. The structure requires that the triple positive charge of each metal ion is shared between six oxygen ions; effectively 0.5 units of positive charge in each direction. The dual negative charge of each oxygen ion, however, is shared between four metal ions; i.e., 0.5 units of negative charge in each direction, bringing about charge balance within the undisrupted structure.

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*With the exception of the considerations of oxide structure and charge development (Section 1.3.1), the term hydrous oxide is used hereafter in this review. It has been demonstrated that the surface of even anhydrous oxides, such as haematite, are characterised by a hydrated surface, a few atomic layers in thickness (Onoda and de Bruyn, 1966).

At the broken surface, two extreme cases may arise. Fig. 1.2. A assumes fracture along M – O bonds, exposing the unfilled coordination shells of metal ions. This represents 0.5 units of positive charge for each broken bond, giving rise to unit positive charge at each exposed metal position. A similar situation develops at exposed oxygen positions, producing unit negative charge. A mixture of the two extreme conditions will give rise to a net positive or negative charge at the broken surface.

Exposure of the broken oxide surface to an aqueous solution, results in the hydration of surface layers (O'Connor <u>et al</u>., 1956, Parks and de Bruyn, 1962; Onoda and de Bruyn, 1966). The hydration step may be envisaged as an attempt by exposed atoms at the broken surface, to complete their coordination shells of nearest neighbours. This is accomplished by incorporation of OH^- at M^+ and H^+ at O^- (Fig. 1.2.B), and represents a state of zero charge at the surface. It can be seen, therefore, that the hydrated oxide surface may be considered analagous to the surface of a hydrous oxide which may also be represented by Fig. 1.2.B. The similarity between the properties of a hydrated oxide surface, and the surface of a hydrous oxide will become apparent in the subsequent discussion. The hydrated surficial structure (Fig. 1.2. B) facilitates transfer of charge (H^+ and OH^-) between the surface and solution.

The structural models for short-range order aluminosilicates and the edge faces of crystalline aluminosilicates, represent a surface structure similar to that of hydrous oxides. Exposed aluminium, silicon, and oxygen atoms of the octahedral and tetrahedral units attempt to complete their coordination by the incorporation of OH^- and H^+ to produce a hydrated surface similar to that represented in Fig. 1.2.B.

1.3.2 Charge properties of the interface

1.3.2.1 <u>Amphoteric behaviour and pH dependence of charge</u>. The amphoteric behaviour of the hydrous-oxide surface arises from the residual charge of unfilled coordination shells (Fig. 1.2.A), and the hydroxylated nature of the surface subsequent to hydration (Fig. 1.2.B). Amphoteric properties may be represented (Fig. 1.2.B and 1.2.C, and equations (1.1) and (1.2) below) as the sorption and de-

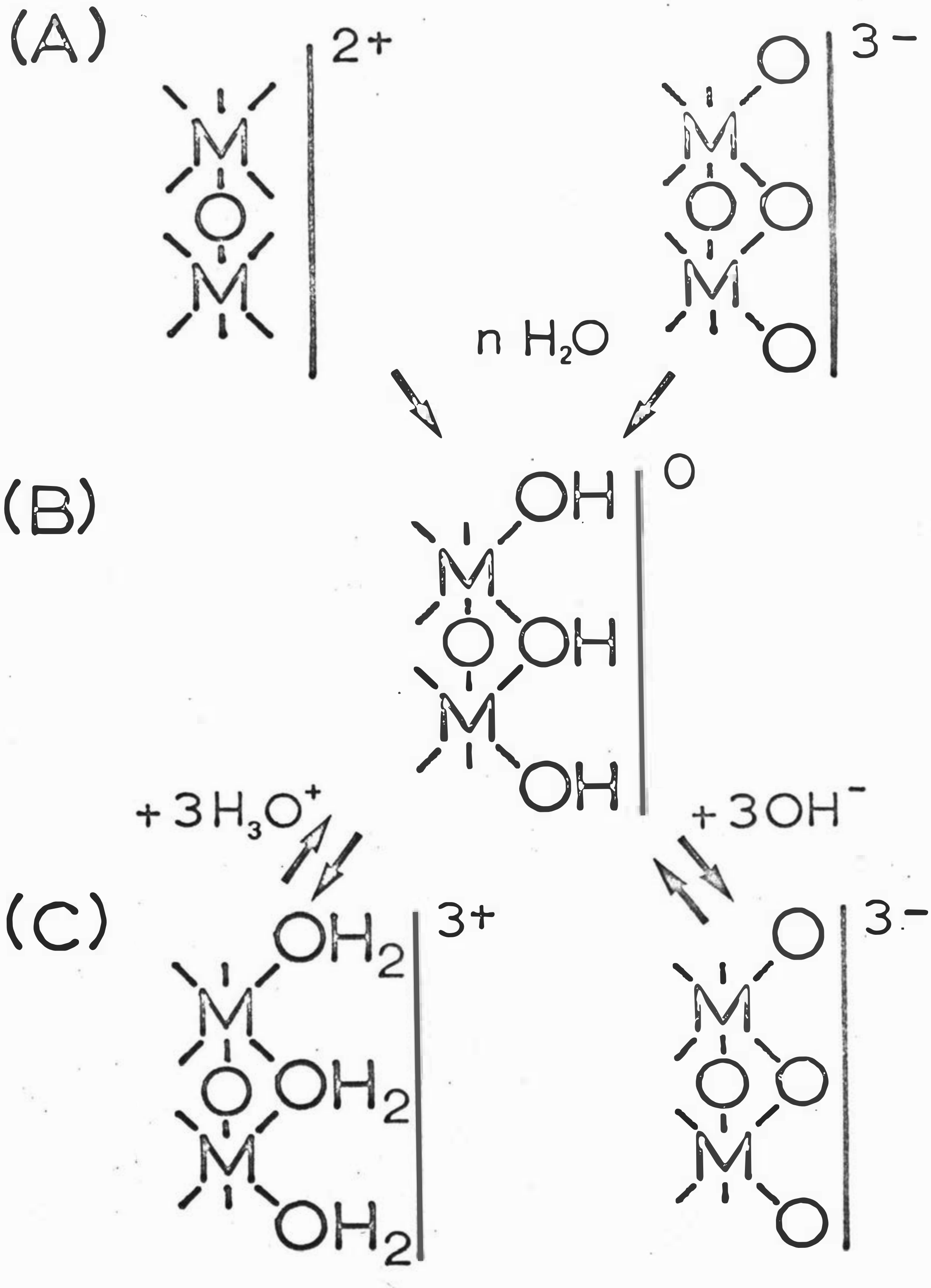


FIG. 1.2 Schematic representation of the hydration of a broken oxide surface and the subsequent development of charge.

(A) Broken surface

(B) Hydrated surface

(C) Development of charge

sorption of protons by M-OH (Parks and de Bruyn, 1962; Sedek *et al.*, 1970; Lyklema, 1971 a; Huang and Stumm, 1973), although other charge distributions have been proposed, notably Hingston *et al.* (1967).

$$M - OH_2^+ \text{ (surface)} \rightleftharpoons M - OH \text{ (surface)} + H^+ \qquad (1.1)$$

$$M - OH \text{ (surface)} \rightleftharpoons M - O^- \text{ (surface)} + H^+ \qquad (1.2)$$

In contrast to constant-charge surfaces such as crystalline aluminosilicates, where charge arises from isomorphous substitution, oxide surfaces are classified as constant-potential surfaces. That is, the potential of the surface may be kept constant by maintaining the bulk concentration of solutes, whose chemical reaction with the surface gives rise to the potential. A constant-potential surface, therefore, may be defined as one for which a chemical reaction occurs between the surface and a solute species in the contacting solution (Morgan and Stumm, 1970). The solute species are known as potential determining (p.d.) ions. Hydrous oxides of Fe and Al, and soil components with similar surface structure, are constant-potential surfaces by virtue of equations (1.1) and (1.2). Because protons and hydroxyl ions are the p.d. ions, hydrous oxides have constant potential at constant pH.

The relationship between pH and surface charge is of obvious importance with respect to the interaction of the surface with other species in solution. This relationship is evaluated from titration curves for the surface. These are expressed as a variation in the sorption density of p.d. ions with pH (Parks and de Bruyn, 1962; Yopps and Fuerstenau., 1964; Atkinson *et al.*, 1967; Huang and Stumm, 1973), examples of which are given in Fig. 1.3. The curves are obtained from data for the titration of an oxide suspension in a suitable electrolyte (e.g., KCl or NaCl) at different ionic strengths, with acid or base. The uptake of H^+ (or OH^-) is determined from the difference in pH between the suspension and the corresponding blank solution. The point of inflexion and intersection of the titration curves at different ionic strengths can be shown, from double-layer theory (Parks and de Bruyn, 1962), to be the condition of zero surface charge. The pH at which this condition arises is termed the point of zero charge (p.z.c.) and is denoted pH (p.z.c.) (Fig. 1.2.B).

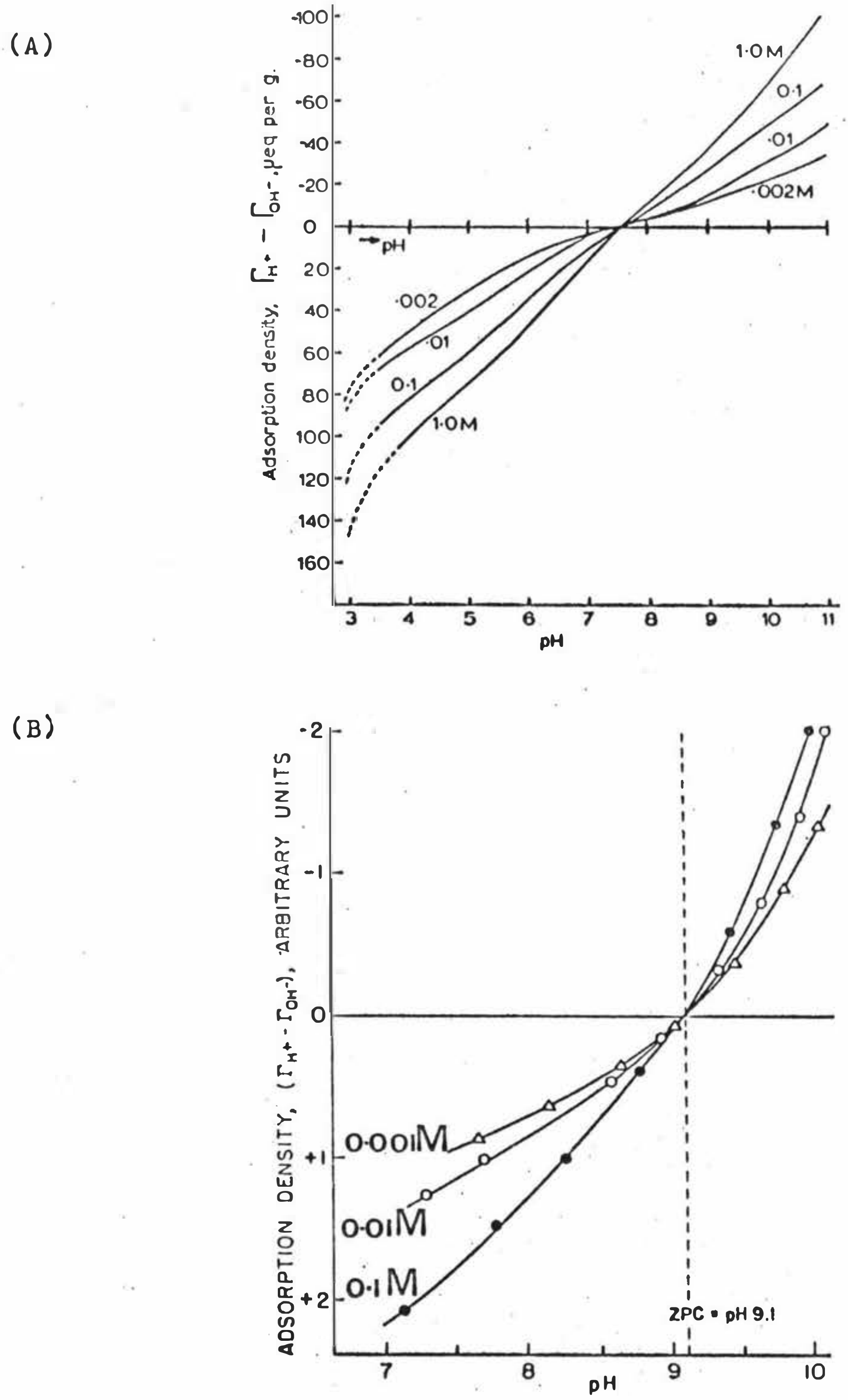


FIG. 1.3 Titration curves (surface charge - pH relationships) for two oxides.

(A) Sorption of potential determining ions (H^+ and OH^-) by goethite as a function of pH and molar concentration of KCl. From Atkinson et al. (1967).

(B) Sorption of potential determining ions by α-alumina as a function of pH and molar concentration of KCl. From Yopps and Fuerstenau (1967).

At pH (p.z.c.) :

$$\Gamma_{H^+} = \Gamma_{OH^-} \qquad (1.3)$$

where Γ denotes the sorption density of the p.d. ion, expressed in equivalents per unit area. The net sorption density at any pH may then be calculated with reference to the condition at the pH (p.z.c.) :

$$(\Gamma_{H^+} - \Gamma_{OH^-}) = 0 \qquad (1.4)$$

Sorption density is related to surface-charge density (σ_0) by the expression :

$$\sigma_0 = F (\Gamma_{H^+} - \Gamma_{OH^-}) \qquad (1.5)$$

where F is the Faraday constant. Consequently, at pH values above pH (p.z.c.), σ_0 is negative (i.e., $\Gamma_{H^+} > \Gamma_{OH^-}$) whereas below pH (p.z.c.), σ_0 is positive (Fig. 1.3).

1.3.2.2 <u>Points of zero charge for soil components and soils</u>. Knowledge of pH (p.z.c.) of an oxide or similar surface is essential to the prediction of surface charge. No oxide or hydrous oxide of a given formulation has a unique pH (p.z.c.) (Parks, 1965, 1968). The exact value depends on the origin, history, purity, crystallinity, temperature of preparation and degree of hydration of the sample. Nevertheless, the values given in Table 1.3 suggest that pH (p.z.c.) of various Fe and Al oxides and hydrous oxides all lie within the region of pH 8 to 9.5. The pH (p.z.c.) of Al oxides and hydrous oxides, however, tends to be somewhat higher than that of Fe oxides and hydrous oxides.

The pH - dependent charge at the edge faces of "clean" crystalline aluminosilicates will be determined by equations (1.1) and (1.2) applied to the edges of the octahedral and tetrahedral layers. Experimentally determined pH (p.z.c.) values tend to be lower (Parks, 1968) than those for oxides and hydrous oxides (Table 1.3). The exact meaning of experimentally determined pH (p.z.c.) values of crystalline aluminosilicates, however, is complicated by the permanent negative charge arising from isomorphous substitution. The high and low pH (p.z.c.) values expected for the edges of the octahedral (Al) and tetrahedral (Si) layers, respectively (Table 1.3), suggest that the net pH (p.z.c.) of the edge faces of crystalline aluminosilicates may be approximately neutral. It will probably also depend on the degree of isomorphous substitution in each layer. Tadros and Lyklema (1969) reported that impurities, including Al_2O_3, in silica, increased pH (p.z.c.) to approximately 6. Furthermore, the possibility of localised centres of pH-dependent charge with pH (p.z.c.) above 7, cannot be discounted.

TABLE 1.3 Values of pH (p.z.c.) of various oxides and hydrous oxides.

Oxide or hydrous oxide	pH(p.z.c.)	Reference
Goethite	7.6	Atkinson _et al._ (1967)
Goethite samples	7.8 - 8.3	Hingston _et al._ (1972)
Haematite	9.0	Atkinson _et al._ (1967)
Haematite	8.5	Breeuwsma and Lyklema (1971)
Fe gel	8.1	Kinniburgh _et al._ (1975)
Gibbsite	8.3	Kinniburgh _et al._ (1975)
Gibbsite samples	7.8 - 9.5	Hingston _et al._ (1972)
Pseudoboehmite	9.2	Alwitt (1972)
α-alumina	9.1	Yopps and Fuerstenau (1964)
γ-alumina	8.5	Huang and Stumm (1973)
Al gel	9.4	Kinniburgh _et al._ (1975)
Silica	~ 3	Tadros and Lyklema (1968)

Similar considerations may be applied to short-range order aluminosilicates (allophane). Although allophane, by definition, shows very limited structural organisation, several structural models have been proposed, based on X-ray fluorescence, infra-red, differential thermal, and chemical analyses (Fields and Schofield, 1959; Wada, 1967; Cloos *et al.*, 1968, 1969; Udagawa *et al.*, 1969; van Reeuwijk and de Villiers, 1970). All of these models suggest possible sites for proton sorption and desorption. Extensive isomorphous substitution of Al for Si (Cloos *et al.*, 1968), however, complicates estimation of pH (p.z.c.). The influence of localised centres of high pH (p.z.c.) are again likely to be of particular importance.

That soils carry pH-dependent charge has been appreciated for some time (Mattson, 1927; Schofield, 1949; Mehlich 1960). Recently, the ionic composition of the soil solution has also been shown to affect the net charge carried by soils, as would be predicted from the discussion above (Mekaru and Uehara, 1972; van Raij and Peech 1972). Furthermore, the association of variable charge with hydrous oxides in soils has been demonstrated by Hussain and Kyuma (1970) and Swahney and Norrish (1971).

The measurement of pH-dependent charge for whole soils, however, may lead to a misrepresentation of the situation at hydrous-oxide surfaces within the soil. van Raij and Peech (1972) determined the pH (p.z.c.) of three tropical soils. Values of between 3 and 4 for surface horizons and 4 to 6 for the B horizons were obtained, suggesting that the soils were dominated by negative charge at their respective pH values. The determination of positive and negative charge components at various pH values by ion uptake techniques (Schofield, 1949; van Raij and Peech 1972) suggests that components, with net positive charge, exist up to pH values of at least 7. This observation is in accord with charge characteristics of "pure" hydrous-oxide surfaces. Consequently, localised centres of positive charge, or high pH (p.z.c.), at hydrous-oxide and similar surfaces in soils, may be of particular importance with respect to P sorption by soils.

1.3.3 The electrical double layer at the interface

1.3.3.2 The Gouy-Chapman and Stern models. The Gouy-Chapman model of the electrical double layer (Gouy, 1910; Chapman, 1913) is the most frequently used model to describe the distribution of charge (σ) and potential (ψ) at a charged solid-solution interface

(Fig. 1.4.A). Ions in close proximity to the interface are subject to Coulombic attraction and repulsion, depending on the charge of the surface and ion under consideration. Ions of opposite charge to the surface, and which compensate the surface charge, are termed counterions. Thermal motion of the ions tends to distribute the ions, which are influenced by surface charge, throughout the solution in the vicinity of the surface. A theoretical treatment of this topic is given by van Olphen (1963) and Aveyard and Haydon (1973).

Theory predicts that the thickness (l) of the diffuse layer, i.e., the distance from the surface over which the distribution of ions is affected by the surface charge, is determined by :

$$l \simeq 3.3 \times 10^{-7} \quad z^{-1} \; c^{-0.5} \qquad (1.6)$$

where z is the charge on the counterion and c is the concentration of the counterion in solution. Potential and charge distribution (Fig. 1.4.A) may be visualised by considering the diffuse double layer as a parallel plate condenser of variable distance (l) between the plates. The capacitance (C) is given by :

$$C = \frac{\sigma_o}{\Psi_o} = \frac{\epsilon}{4\pi l} \qquad (1.7)$$

where σ_o is the net surface charge, Ψ_o the surface potential and ϵ the dielectric constant, usually of water.

Equation (1.7) illustrates the effect of the ionic strength of an indifferent electrolyte on the charge at an oxide surface (Fig. 1.3). Because the oxide surface is a constant-potential surface, that is Ψ_o is constant at constant pH, an increase in ionic strength decreases l (equation 1.6) and σ_o increases in a positive or negative manner, Fig. 1.3 depending upon the pH relative to pH p.z.c.

The Gouy-Chapman model, however, is not applicable to the distribution of potential close to the surface. Ions have finite size and, the distance of closest approach of their centres to the surface is limited to a few tenths of one nanometer. Consequently, the surface potential of the Gouy-Chapman theory is in effect the potential at the plane of closest counterion approach (Ψ_d, Fig. 1.4.A). The Stern theory distinguishes between the surface potential (Ψ_o) and the potential at the plane of closest approach (Ψ_d). Potential decreases linearly between Ψ_o and Ψ_d whereas beyond the plane of closest approach, the distribution of potential is described by the Gouy-Chapman theory (Fig. 1.4.B).

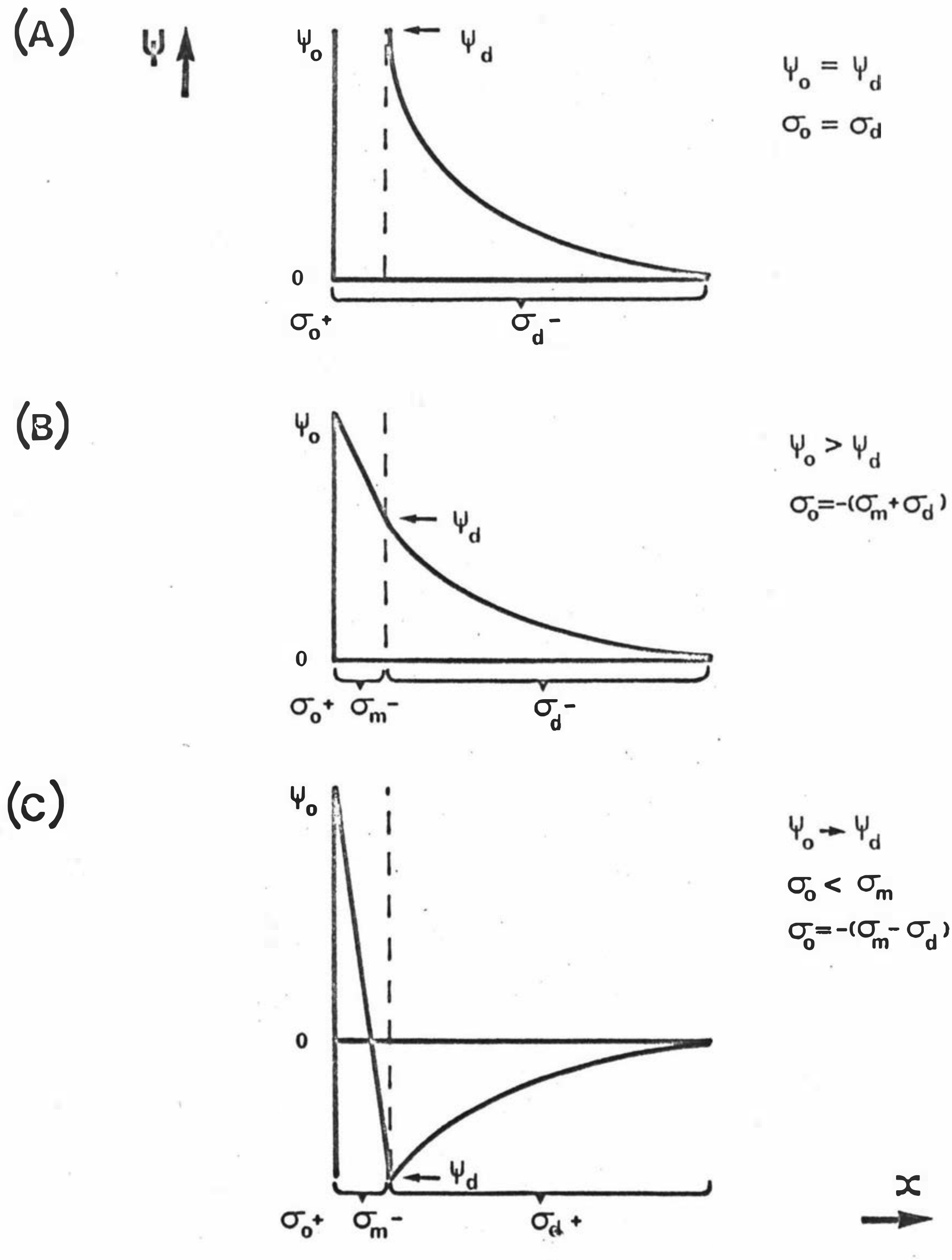


FIG. 1.4 Distribution of charge and potential at a positively charged hydrous-oxide surface.

(A) Gouy-Chapman model

(B) Stern model

(C) Charge reversal arising from superequivalent sorption of counterions.

ψ = potential, σ = charge, x = distance from the surface; subscripts o, m, and d denote the surface, the plane of closest approach (Stern layer) and the diffuse layer, respectively.

1.3.3.2 Interaction of counterions with the surface.

The Stern model also allows for the interaction, which may be more or less ionic or covalent in character, between counterions and the surface itself. The double layer may be further differentiated to distinguish this condition (Fig. 1.5.A). Direct interaction of counterions with the surface implies that the plane of closest approach to the surface (the inner Helmholtz plane; i.H.p.) is nearer to the surface than that (the outer Helmholtz plane, o.H.p.) for counterions distributed only in the diffuse layer. The difference in closeness of approach is usually equivalent to the thickness of one molecular layer of water. This is attributable to the loss of the hydration shell of the counterions which interact with the surface (Fig. 1.5.A). The three potential terms Ψ_o , Ψ_B and Ψ_d are also defined in Fig. 1.5.A.

Some counterions, having direct interaction with the surface, show super-equivalent sorption which may result in surface charge reversal (Fig. 1.4.C). The sorption of P at a hydrous-oxide surface illustrates this phenomenon, which is termed specific sorption.

The hydrous-oxide surface acquires charge by sorption of H^+ and OH^-. These species may be considered to be held at a plane equivalent to the i.H.p., and the locus of their centres is considered to be the plane of Ψ_o . Consequently, Ψ_o and Ψ_B (Fig. 1.5.A and 1.5.B) become indistinct. This situation presents no problem in considering counterions at the o.H.p. and in the diffuse layer, because Ψ_d remains distinct.

During specific sorption at a constant potential-surface, however, counterions become p.d. ions, and the distribution of potential at and close to the surface depends upon the interaction of the surface with at least two solute species (Fig. 1.5.B). It is still possible to distinguish, on a conceptual basis, between Ψ_o and Ψ_B when specific sorption involves primarily ionic interaction. The situation is particularly complex, however, when covalency is involved between the surface and sorbed species. In the latter case, which is particularly relevant to P sorption, it may be more convenient to consider that a new surface has formed. The literature relating to surface chemistry suggests that the properties of the constant-potential surface, subsequent to specific sorption, are ill-defined. This has given rise to problems in the development of P sorption mechanisms which have

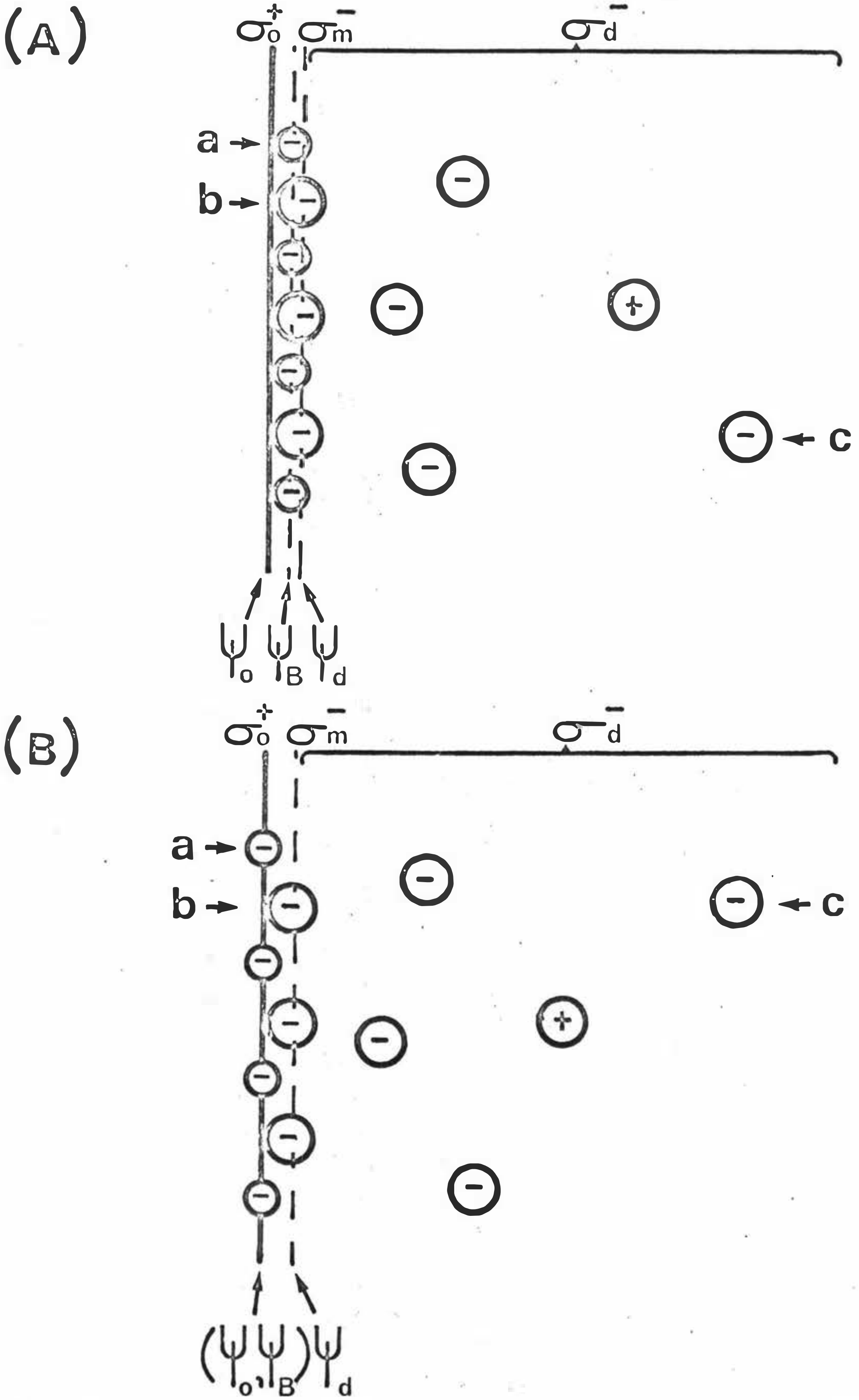


FIG. 1.5 Schematic representation of anion - sorption types at different positively-charged surfaces.

(A) Constant - charge surface.

(B) Constant - potential surface.

a = specifically sorbed anion at the inner Helmholtz plane in (A) and at the surface in (B), b = anion at the plane of closest approach (outer Helmholtz plane), c = counterions in the diffuse layer, ψ_B = potential at plane of specific sorption, other terms as defined in Fig. 1.4. Adapted from Aveyard and Haydon (1973) frequently been based on an interpretation of shifts in pH (p.z.c.) (Hingston et al., 1967, 1968 a) subsequent to the specific sorption of P. This is discussed in a later section.

The conceptual problems discussed above, may be overcome to some extent by the measurement of zeta potential, although theoretical problems in its measurement have detracted from its general acceptance. A position close to the edge of the Stern layer or the o.H.p. (Fig. 1.5) is frequently considered to be the slipping or shearing plane. The slipping plane develops between the bulk solution and the water which moves with charged particles when a sol is subject to an external potential in electrokinetic experiments. The potential at this plane, which is probably close to the plane of ψ_d , is the zeta potential. Consequently, the locus of specific sorption with respect to the surface becomes less important because the zeta potential represents the condition of the Stern layer as a whole.

Zeta potential is related to surface potential, and consequently to electrolyte concentration and pH. The pH at which the zeta potential is zero is termed the isoelectric point (pH (i.e.p.)). In the absence of specific sorption pH (i.e.p.) = pH (p.z.c.). When ions sorb at the i.H.p. (specific sorption), changes in charge and potential occur close to the surface. Consequently, the potential at the slipping plane shifts. A shift is also observed in pH (i.e.p.), which for the specific sorption of anions is to a lower pH (Lyklema, 1971 b).

1.3.3.3 Porous interface model. Because hydrous-oxide surfaces are constant-potential surfaces, charge distribution at the surface may not be exactly comparable to that at the constant-charge surface. Lyklema (1968, 1971 a) has pointed out that surface charge-pH curves (Fig. 1.3) imply a steady increase in surface charge as the pH moves away from pH (p.z.c.). Furthermore, he demonstrated that for silica, the more porous the surface, the higher was the charge that developed. Experimentally determined sorption densities of H^+ (or OH^-) were also considerably greater than the value predicted from the expected number of surface sites calculated from surface area and structural considerations. The high surface charge, however, was not reflected to a proportionate extent in zeta-potential measurements.

Lyklema (1968) postulated that a surface, porous to both p.d. ions and counterions, accounted for the anomalously high surface-charge densities developed at the silica surface. This model is similar to the concept of an expanded hydrated surface, several atomic layers thick, over which charge is developed (Onoda and de Bruyn, 1966; Wright and Hunter, 1973).

That the surface is also porous to counterions (Lyklema 1968, 1971 a) was included to account for the low values of zeta potential relative to surface charge. The size of anions and the porosity of the surface to them when the surface is positively charged is difficult to conceive. The influence of a porous surface on the kinetics of P sorption and the possibility that P may be absorbed. (Sholten, 1965; Evans and Syers, 1971) should not be overlooked.

1.4 The Type and Mechanism of Phosphate Sorption

Sorption has been classified into two basic types, namely physical sorption and chemisorption. Sorption type, however, is not always well defined, but some knowledge of it is essential if a sorption mechanism is to be considered (Kitchener, 1965). Hayward and Trapnell (1964) define the difference between physical and chemisorption in terms of the occurrence of electron transfer. During chemisorption, electron transfer occurs between the sorbent and the sorbate, whereas electron transfer is absent in physical sorption reactions. Consequently, the energy of chemisorption will be similar to that of bond formation in a chemical reaction, a criterion frequently used to distinguish between physical sorption and chemisorption (de Boer, 1950).

The sorption type of P at hydrous-oxide and similar surfaces, may be discussed and evaluated in relation to the way in which it differs from that of other anions and the dependence of it on the pH of the ambient aqueous phase. From these considerations and those concerning the nature of the hydrous-oxide surface, possible mechanisms of P sorption may be developed.

1.4.1 Sorption type

1.4.1.1 Non-specific and specific sorption. The development of positive charge at the hydrous-oxide surface implies a diffuse double layer of anions, as discussed above. Many anions merely compensate the positive charge by their distribution at the o.H.p. and over the diffuse layer. Such anions show conventional ion-exchange properties, such as ease of displacement by other anions added at similar or higher concentration, sorption in proportion to their concentration in solution, and exclusion from the double layer when the surface becomes negatively charged at high pH values. Anions held at the surface in this way are said to be non-specifically sorbed and include nitrate, chloride, and perchlorate.

The pH (p.z.c.) is measured in solutions of salts of non-specifically sorbed anions (and cations) because the surface charge, *per se*, is not affected by them; that is they cannot become p.d. ions over low to moderate concentration ranges. Non-specific sorption is a physical sorption type, in terms of the definition of Hayward and Trapnell (1964).

On the other hand, phosphate and other anions including arsenate, selenite, silicate, and fluoride (Hingston *et al.*, 1968 a, b) which have a specific affinity for the metal of the hydrous-oxide surface, are sorbed out of all proportion to their concentration in solution and may induce charge reversal (Fig. 1.4.C) at the sorbing surface. Charge reversal during P sorption is implied by data presented by Breeuwsma and Lyklema (1973) and Hingston *et al.* (1974). As discussed previously, charge reversal is indicative of specific sorption, i.e., sorption at the i.H.p.

Other properties of specifically-sorbed anions include the ability to be sorbed even in the pH range where negative surface charge is predicted (Hingston *et al.*, 1968 a, 1972) and the lack of normal ion-exchange behaviour. Furthermore, specific sorption affects other properties of the sorbing surface, including cation exchange capacity (Toth 1937; Davis 1945; Mehlich, 1964; Mekaru and Uehara, 1972) and the pH (p.z.c.) (Hingston *et al.*, 1967; Breeuwsma and Lyklema 1973). Because specifically-sorbed anions alter surface charge, they may be defined as p.d. ions. Consequently specific sorption constitutes a chemisorption reaction.

1.4.1.2 Experimental verification of specific sorption.

Distinction between specific and non-specific sorption can be made experimentally by determination of the titration curves of hydrous oxides in the presence and absence of the anion under consideration (Hingston *et al.* 1967; 1968 a, Breeuwsma and Lyklema, 1971; 1973). Controversy has developed, however, between these groups of workers in terms of the effects of specific sorption on the position of pH (p.z.c.) and the use of such data in the interpretation of anion sorption mechanisms. Unfortunately no data are available to illustrate the effects of P sorption on the position of titration curves for various hydrous-oxide surfaces. Data for other anions, however, provide a useful basis for a discussion of the possible effects of P sorption and their implications to the P sorption mechanism.

Because the specific sorption of anions occurs within the Stern layer, shifts occur in the values of pH (p.z.c.) and pH (i.e.p.) of the sorbing surface. Shifts in the pH (p.z.c.) and pH (i.e.p.) have been used to distinguish between specific and non-specific sorption of both anions and cations. Breeuwsma and Lyklema (1973) have demonstrated that the specific sorption of sulphate by haematite, shifts the pH (p.z.c.) to a higher pH value (Fig. 1.6.A) whereas pH (i.e.p.) shifts to a lower pH value. The shift in pH (i.e.p.) to a lower pH is in agreement with electrokinetic data presented by Mattson (1931) for the sorption of P and silicate by "soil colloids" . Explaining these shifts, Lyklema (1971 b) has argued that, because specific sorption occurs within the Stern layer, σ_m (Fig. 1.4.B) becomes more negative. Consequently, to maintain the condition $\sigma_o = -(\sigma_m + \sigma_d) = 0$; $\sigma_d = 0$, the net positive charge of the surface must increase. This is achieved by the sorption, of H^+ or desorption of OH^-, shifting pH (p.z.c.) to a higher pH value. The pH (i.e.p.) shifts to a lower pH value because the slipping plane occurs on the outer edge of the Stern layer. Subsequent to specific sorption of anions, restoration of the potential at the slipping plane (nominally Ψ_d) to zero (Fig. 1.4.B) requires an addition of H^+ to the suspension, to satisfy the condition $\sigma_o = -\sigma_m$; $\Psi_d = 0$

An alternative description has been given by Hingston *et al.* (1968 a) who apparently consider the surface to be represented by the i.H.p., and that specifically sorbed anions are p.d. ions. Consequently, in the determination of surface charge-pH curves in the presence of specifically-sorbed anions, the effects of anion sorption

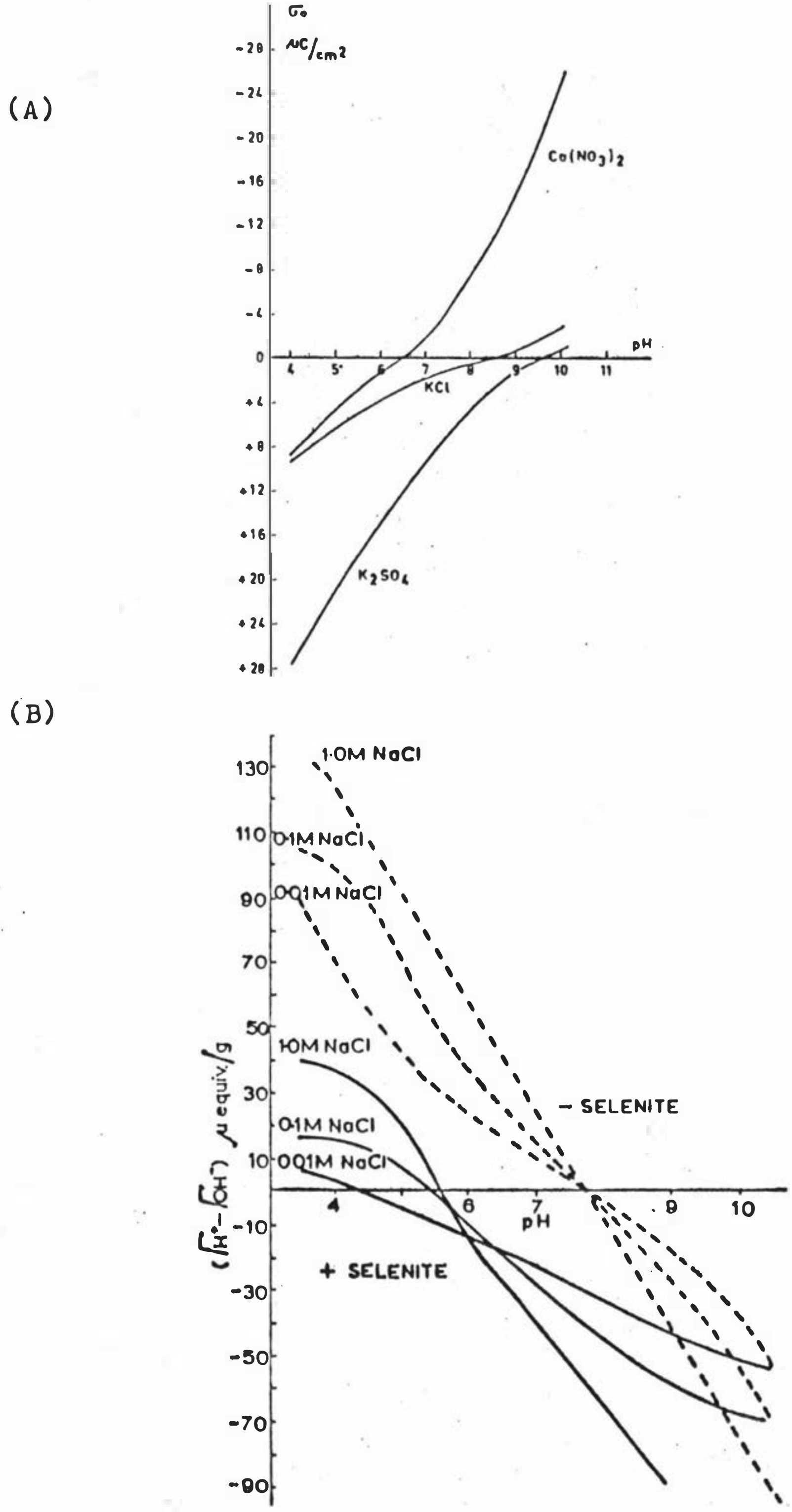


FIG. 1.6 Two representations of the effects of specific-anion sorption on the pH (p.z.c.) of oxide and hydrous-oxide surfaces.

(A) Surface charge - pH curves for haematite in the presence of 10^{-3}N solutions of KCl and K_2SO_4. Curve for 10^{-3}N $Ca(NO_3)_2$ illustrates the effect of specific calcium sorption. From Breeuwsma and Lyklema (1973).

(B) Surface charge - pH curves for goethite in the presence and absence of selenite at various NaCl concentrations; charge contribution from sorbed selenite included in computation of surface charge. From Hingston <u>et al</u>.(1968 a).

and OH displacement from the surface are included in the computation of surface charge. This is achieved using the equation :

$$\sigma = \sigma_0 - \sigma_A + \sigma_{OH} \qquad (1.8)$$

where σ = the net surface charge in the presence of specific anion sorption, σ_0 = the surface charge in the absence of specific sorption, σ_A = the negative charge contributed by the anion, and σ_{OH} = the negative charge lost by displacement of OH^- . The effect of this interpretation on the relative position of titration curves for goethite in the presence and absence of the specific sorption of selenite is illustrated in Fig. 1.6.B. The data suggest that pH (p.z.c.) shifts to a lower pH value. Hingston et al. (1967, 1968 a) have postulated, therefore, that specific sorption of anions is conditional on an increase in the negative charge of the surface. A similar shift in pH (p.z.c.) to lower pH values has been reported for the sorption of silicate by goethite (Hingston et al., 1972), although it is not clear how the titration curves in the presence of silicate were obtained.

A flaw is apparent, however, in the arguments of Hingston et al. (1968 a) in that the charge contribution to the surface by the anion cannot be known without implying a mechanism. Consequently, the assumption that specific sorption of anions is conditional on an increase in the negative charge of the surface is a reflection only of the method by which the titration curves (Fig. 1.6.B) were obtained. Despite the apparently cyclical arguments involved in this assumption, it has been included in many P sorption mechanisms which have been based on the interpretation of data similar to that in Fig. 1.6.B (Hingston et al., 1968 b, 1972; Mott, 1970)

The approach used by Hingston et al. (1968a) measures a change in a double-layer property similar to pH (i.e.p.), because the specifically-sorbed anion is considered to be a p.d. ion. This is not invalid because specific sorption implies retention at the i.H.p., which for hydrous oxides cannot be distinguished from the surface, as discussed above (Fig. 1.5). Furthermore, the inclusion of P, or other specifically-sorbed anions, as p.d. ions facilitates an explanation of the increase in cation exchange, the reduction or elimination of non-specific anion sorption, and charge reversal which may occur during the specific sorption of P. The fact that P sorption may continue even when the surface is negatively charged can also be explained.

Because surface charge density-pH curves represent the variation in a relative quantity with respect to pH, inclusion of the charge contributed by specific sorption can only be made if the precise mechanism is known. Consequently, the approach used by Breeuwsma and Lyklema (1973) is considered to be a more reliable test for specific anion sorption. Preliminary work in this laboratory (J.R. McLaughlin, pers. comm.), using an experimental approach similar to that of Breeuwsma and Lyklema (1973), suggests that the titration curves of Fe gel in the presence of P show a shift in pH (p.z.c.) to a lower pH value, giving a graphical relationship similar to that in Fig. 1.6.B. This suggests a difference in the type of specific anion sorption between P and, for example, sulphate (Fig. 1.6.A). Because P sorption is strongly covalent in character (Syers and Williams, 1975), the nature of the surface subsequent to P sorption is likely to be different to that subsequent to specific sorption of anions such as sulphate, for which the interaction with the surface is probably more ionic. Consequently, in the presence of sorbed P, the titration curve for a particular sorbent may tend towards that of a corresponding P compound. The shift in pH (p.z.c.) of Fe gel to a lower pH value in the presence of P, is in accord with the above suggestion, because a value of 2.8 has been reported for the pH (p.z.c.) of strengite (Chang and Jackson, 1957 a). The shift in pH (p.z.c.) during P sorption, and its implications to the exact nature and mechanism of the interaction between P and the sorbing surface, requires further investigation.

1.4.2 The mechanism of P sorption

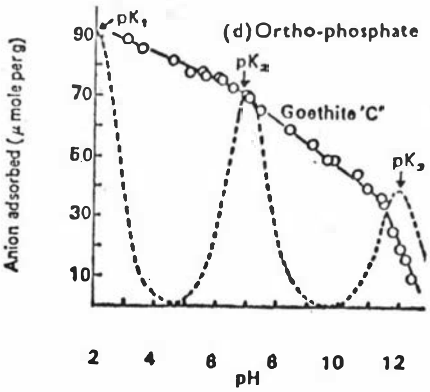
Several studies have been concerned with the mechanisms of P sorption (Hsu and Rennie, 1962; Bache, 1964; Muljadi et al., 1966; Kafkafi et al., 1967; Hsu, 1968; Cloos et al., 1968). At best these studies have been both qualitative and speculative in nature. The studies of Hingston et al. (1967, 1968 a, 1968 b, 1972) and Breeuwsma and Lyklema (1973) again provide the most reliable data with respect to an evaluation of the P sorption mechanism, in that they have presented quantitative data.

The specific sorption of P involves interaction between the coordination shells of the metal ion at the hydrous-oxide surface and the P group. Consequently the sorption mechanism must involve a ligand exchange reaction. This has been implied in most recent studies (Hingston *et al.*, 1968 b, 1972), although previous workers had frequently assumed a simple ion-exchange reaction (Hsu and Rennie, 1962; Muljadi *et al.*, 1966). In the following discussion, ligand exchange reactions will be written in the form $-L_o$; L_s. where $-L_o$ is the ligand originally present at the surface which exchanges with L_s, the ligand originally present in solution.

1.4.2.1 pH and charge relationships. Evaluation of the P sorption mechanism has frequently relied on the pH dependence of P sorption and associated changes in surface charge. Hingston *et. al.* (1967, 1968 b, 1970, 1972) have based much of their proposed anion sorption mechanisms on the shape of the "adsorption envelope" and shifts in pH (p.z.c.). The adsorption envelope may be defined as the relationship between maximum P sorption at a given pH, and the pH of the system (solid line Fig. 1.7.A). The adsorption envelope suggests a break in the slope at pH values close to pK_{a2} and pK_{a3} of H_3PO_4, with an overall sorption maximum at approximately pK_{a1}. Similar adsorption envelopes have been obtained for P sorption by several soils (Obihara and Russell, 1972), emphasising the validity of the hydrous-oxide surface as a model surface for the sorption of P by soils.

Hingston *et al.* (1968 b, 1972) implied that at pH values below pK_{a2}, P sorption occurs by the ligand exchange $-OH_2^+$; $H_2PO_4^-$, which is in agreement with data presented by Hsu (1968). This mechanism has also been supported recently by Sawhney (1974) based on cation exchange measurements. Hingston *et al.* also implied that the breaks in the adsorption envelope correspond to a change in the dominant sorption mechanism. The reasons for this are not entirely clear but these workers argue that P sorption continues at a negatively charged surface because acid dissociation of the sorbing species (i.e., $H_2PO_4^-$ or HPO_4^{2-}) at the surface provides "protons which can react with surface $-OH$ to form water which is readily displaced by the anion". This process, they argue, occurs most readily at the pK_{a2} value. Consequently, not only is surface $-OH_2^+$ believed to form by direct protonation, but it was suggested that this is a prerequisite for P sorption at surface $-OH$. The deprotonation of P species, particularly $H_2PO_4^-$, during sorption at surface-OH,

(A)



(B)

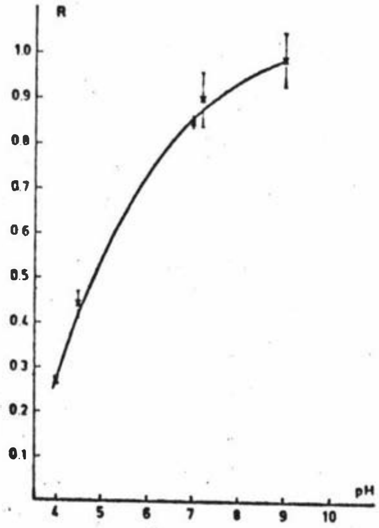


FIG. 1.7 Relationships between P sorption and pH.

(A) "Adsorption envelope" for P sorption by goethite. Solid line is the experimentally determined envelope; dashed line is the calculated envelope. From Hingston *et al.* (1972).

(B) Relationship between pH and the ratio R (mole:mole) of the amount of H^+ required to maintain pH during P sorption by haematite to the amount of P sorbed. From Breeuwsma and Lyklema (1973).

fits the assumption that P sorption is conditional on an increase in the negative charge of the surface. This assumption is included in all P sorption mechanisms based on the work of Hingston et al. (Hingston et al., 1967, 1968 b 1972; Mott 1970). The limitations of this assumption have already been discussed.

Hingston et al. (1970) developed a theoretical treatment for their proposed mechanism scheme, from which an adsorption envelope could be calculated (dashed line, Fig. 1.7.A). These do not correspond at all well with experimentally determined envelopes, apart from the maxima at the pK_a values which were established from experimental data. The poor correspondence between the theoretical and experimental approach, probably arises from the fact that the pH dependence of charge at the hydrous-oxide surface was not included in the theoretical treatment.

Breeuwsma and Lyklema (1973) also obtained an adsorption envelope, similar to that presented by Hingston et al. (1972), for P sorption by hematite. They showed, however, that over the pH range of 4 to 9, the ratio R (mole/mole) of the amount of H^+ required to maintain pH during P sorption to the amount of P sorbed, increased steadily from a value tending to zero, to one approaching unity, (Fig. 1.7.B). This suggests no fundamental change in the sorption mechanism at pH $\simeq pK_{a2}$ as proposed by Hingston et al. (1967, 1972). The ligand exchange reactions - OH_2^+; $H_2PO_4^-$, $-OH_2^+$; HPO_4^{2-}, $-OH$; $H_2PO_4^-$ and $-OH$; HPO_4^{2-} were proposed to account for the relationship in Fig. 1.7.B, because only the third and particularly the fourth reaction are likely to occur at higher pH values where the ratio, R, approaches unity. A similar sequence of reactions has recently been proposed by Sawhney (1974) to explain the different changes in cation exchange capacity (increase in negative charge) subsequent to P sorption by soils of different pH. This study provides one of the few links between mechanisms developed to describe P sorption by soil components and those developed to describe P sorption by intact soils.

Although some aspects of the P sorption mechanism are now known, none of the mechanisms discussed above has been supported by adequate quantitative data. The precise mechanism, or mechanisms of P sorption, and their relationship to pH and solution P concentration, still require evaluation. Consequently, many other aspects of P sorption can still not be explained. Furthermore, an adequate identity between the mechanisms involved in P sorption by soil components and soils themselves, remains to be established.

1.4.2.2 The form of P sorbed. Recent work by Atkinson et al. (1974) and Russell et al. (1974), based on the I.R. spectra of goethite subsequent to P sorption, has suggested that the form of P sorbed is PO_4^{3-}. This confirms an earlier report by Gastuche et al. (1963). These observations are difficult to reconcile with the sorption mechanisms discussed above, which involved only $H_2PO_4^-$ and HPO_4^{2-} species. Hingston et al. (1974), however, have implied the sorption of PO_4^{3-}, although no explanation was given.

The P adsorption envelope for goethite (Fig. 1.7.A) indicates that maximum P sorption occurs at a pH value lower than 2.5 where the dominant P species in solution are H_3PO_4 and $H_2PO_4^-$. The complete deprotonation of P species at this pH seems improbable because of the high pK_{a3} value of H_3PO_4 (12.32; Butler, 1964). Furthermore, if PO_4^{3-} is the actual P species sorbed, the maximum P sorption, or at least an increase in P sorption would be expected close to pK_{a3}. At this pH the proportion of PO_4^{3-} increases rapidly, and if the arguments of Hingston et al. (1970) are accepted, the energy of deprotonation of HPO_4^{2-} is at a minimum. The adsorption envelope (Fig. 1.7.A) however, indicates that P sorption decreases rapidly above pH 11.

The observation that PO_4^{3-} appears to be the form of P sorbed, may be the result of the method used. In the preparation of samples on which I.R. spectra were determined (Russell et al., 1974), a drying step was involved, in some cases using temperatures as high as 250°C. Drying is known to induce structural changes at hydrous-oxide surfaces (Onoda and de Bruyn, 1966), and is illustrated by the differences in pH (p.z.c.) of dried and undried samples (Parks, 1968). It is possible that similar changes in surface structure could account for the observation that PO_4^{3-} appears to be the form of P sorbed. The translocation of protons at the surface, subsequent to P sorption, could also explain the apparent sorption of PO_4^{3-}. The P sorption mechanism, per se, would, however, still be controlled by protonated species and the charge at the surface.

The discussion above suggests that direct sorption of PO_4^{3-} is unlikely. Consequently, an evaluation of the P sorption mechanism will probably be facilitated by consideration of the amounts of $H_2PO_4^-$ and HPO_4^{2-} species in solution, and the distribution of charge at the sorbing surface, for various pH values.

1.5 Interpretation of Sorption Data

The description and interpretation of P sorption in quantitative terms is an essential part of an extension of the considerations discussed above to more practical applications. A quantitative description of P sorption is also useful in predicting and reinforcing concepts concerning the mechanism of P sorption, and in evaluating the factors which influence the process.

The use of sorption isotherms to describe P sorption has become common practise in recent years. The meaning of sorption isotherms and the transformation of sorption data into useful quantitative forms is discussed below.

1.5.1 The sorption isotherm

A sorption isotherm describes the relationship, at constant temperature, between the amount of sorbate retained by a sorbent and that maintained in the phase contacting the sorbent. Sorption isotherms were originally developed to describe sorption in gas-solid systems. Phosphate sorption, however, involves a liquid-solid system and the extention of gas sorption theory to solute sorption from aqueous systems requires evaluation.

Giles <u>et al</u>. (1960) have described and classified the isotherm types which may be expected for solute sorption (Fig. 1.8.A). Type-S represents a strong intermolecular attraction between sorbed species, whereas type-C represents a constant partition of sorbate between the sorbent and solution. Type-L (Langmuir type) is the most commonly-occurring isotherm type in liquid-solid systems and assumes a limit to sorption upon the completion of a monolayer of sorbate species at the surface. When a high affinity exists between sorbate and sorbent, isotherms of type-H are characteristic.

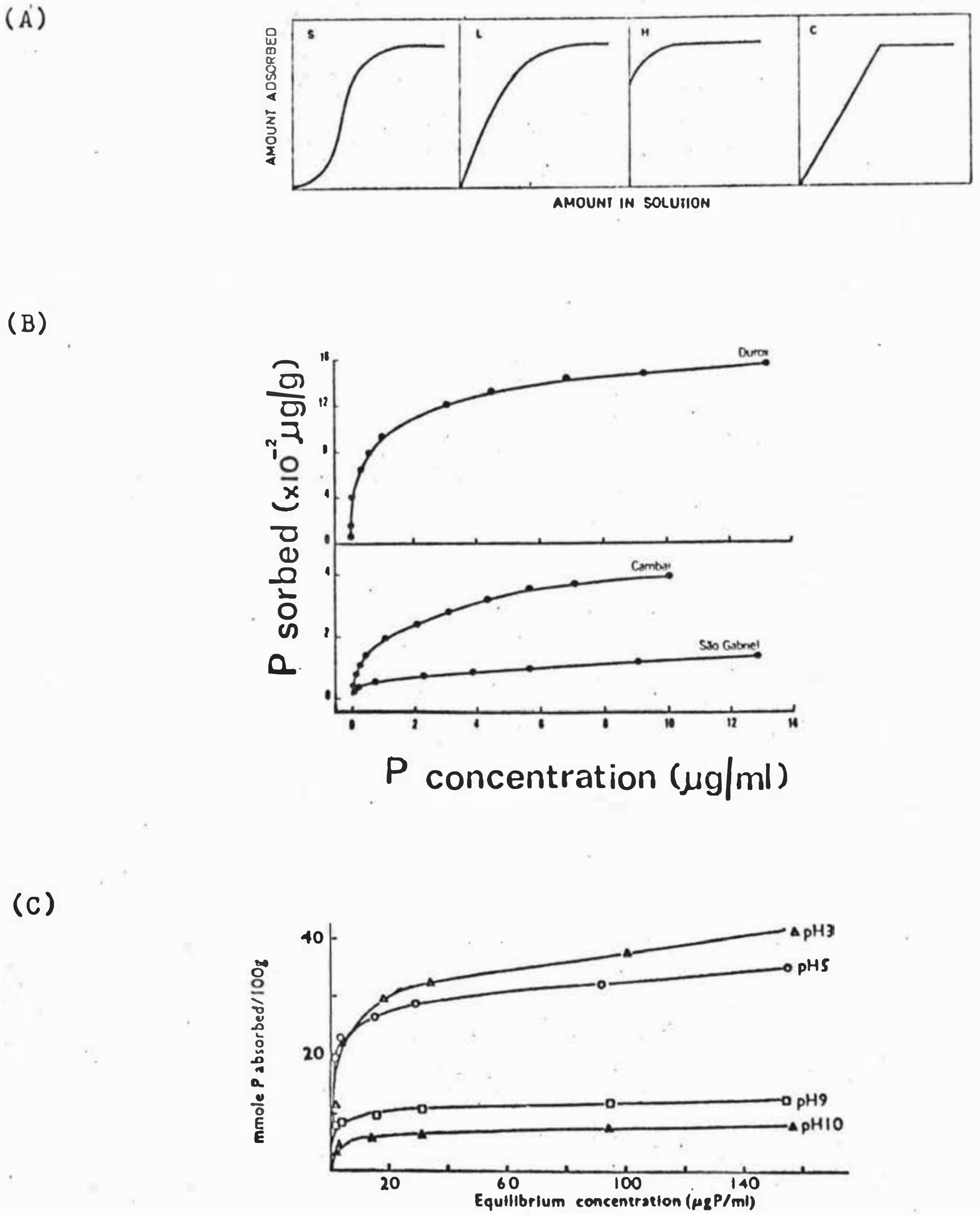


FIG. 1.8 Isotherms for solute sorption.

(A) Classification of isotherm type. From Giles (1970).

(B) Typical isotherms for the sorption of P by soils. From Syers _et al._ (1973 b).

(C) Isotherms for the sorption of P by gibbsite at various pH values. From Muljadi _et al._ (1966).

Sorption isotherms for P are determined for soils and soil components by making various additions of P to a suspension of known solid:solution ratio. After shaking for a suitable period of time, depending on the objectives of the experiment, the amount of P remaining in solution and that sorbed is determined independently (Hsu and Rennie, 1962; Muljadi et al., 1966). In many cases, however, and exclusively for soils, the difference between the initial and final solution P concentrations is used as a measure of the amount of P sorbed. Although this procedure is not as rigorous as the separate determination of the amounts sorbed and in solution, satisfactory results are obtained. Furthermore, Kipling, (1965) and Giles (1970) have suggested, from theoretical considerations, that the difference procedure is valid for aqueous systems.

Sorption isotherms for P have been determined for soils with a variety of theoretical and practical objectives in view (Olsen and Watanabe, 1957; Shapiro and Fried, 1959; Hsu, 1964; Woodruff and Kamprath, 1965; Taylor and Kunishi, 1971; Syers et al., 1973 b). Isotherms typical of those obtained are presented in Fig. 1.8.B. The isotherms are generally of the L-type with a greater or lesser degree of H-type character, suggesting a variable degree of high affinity interaction between P and the soils. Similar isotherms with generally a greater amount of H-type character (Fig. 1.8.C) have been obtained for P sorption by various soil components (Bache, 1964; Muljadi et al., 1966; Chen et al. 1973; Breeuwsma and Lyklema 1973). It is possible that the isotherm type reflects the mechanism, or mechanisms, involved in P sorption, as will be discussed below.

The value of sorption isotherms in providing a direct evaluation of the degree and extent of P sorption at various solution P concentrations is immediately apparent. This relationship, however, is complicated by non-reversibility, if desorption is also considered. The sorption isotherm also provides a basis for the evaluation of numerous other parameters, including sorption maxima, and relative values for free energy and entropy of the sorption reaction. If kinetic data are obtained, the activation energy of the sorption reaction may also be determined. Some of these parameters have been determined for P sorption by soils and soil components (Olsen and Watanabe, 1957; Fried and Shapiro, 1959; de Haan 1965; Kuo and

Lotse 1974 a, b); and are particularly useful in evaluating the P sorption mechanism.

To obtain this information, however, it is frequently necessary to transform sorption data, and test its fit to equations developed to describe sorption. The equations most frequently used to describe P sorption are the Freundlich and Langmuir equations. The latter equation is particularly useful because it is developed from a physico-chemical model involving a sorption maximum at monolayer coverage.

1.5.2 The Freundlich equation*

Early work on the sorption of gases by various solids and of dissolved organics by charcoal, suggested that sorption data could usually be described by an equation of the form :

$$x = A c^{1/n} \quad (n < 1) \qquad (1.9)$$

where, in the case of solute sorption, x = the amount of sorbate removed from solution per unit weight of sorbent, c = the solution concentration maintained, and A and n are constants. Expressed in logarithmic form, sorption data conforming to equation (1.9) will fit at least one linear relationship of slope $\frac{1}{n}$

The logarithmic form of equation (1.9) was the first to be used to describe the retention of P by soils (Russell and Prescott, 1916) and conformity of their data to the equation was taken as one of the first indications that P retention involved an sorption reaction. The conformity of data to a sorption isotherm equation, however, should not be taken as incontrovertible proof of a sorption reaction, as will be discussed later. The Freundlich equation has since been used in several studies of P sorption by both soils and soil components (Kurtz et al., 1946; Low and Black, 1950; Kuo and Lotse, 1974 a, b).

The form of the Freundlich equation appears to be purely empirical. Henry (1922, quoted by Kipling, 1965) has shown that for dilute solutions the term $\frac{1}{n}$ can be given thermodynamic identity, if

---

*Not developed by Freundlich but used extensively by him in early adsorption work (Giles, 1970).

monolayer sorption is assumed. The value of n was shown to be related to the difference between the free energy of the "clean" surface and that when a complete monolayer was formed. The value, n is also related to the sorption maximum. This treatment, however, applies only to dilute solutions.

Kitchener (1965) has pointed out that because the Freundlich equation frequently describes sorption on such heterogeneous surfaces as that of charcoal, it is particularly suited to sorption at a series of sorption sites of different sorption energies. A logarithmic plot of sorption data, however, should respond to any significant change in the dominant sorption site or mechanism. A break in the slope of an otherwise linear Freundlich relationship was obtained at a solution P concentration of 2 µg P/ml, for P sorption by several Illinois soils (Kurtz et al., 1947). Although no explanation was given, a distinct change in the dominant sorption site or mechanism is implied.

Because it is difficult to give quantitative identity to the constants in equation (1.9), the Freundlich equation is now little used to describe P sorption by soils and soil components.

1.5.3 The Langmuir equation

1.5.3.1 Derivation and test for data fit. The fact that P sorption by soils and soil components frequently conforms to the Langmuir equation, has given rise to the extensive use of this equation to describe and interpret P sorption data (Cole et al., 1953; Olsen and Watanabe, 1957; Shapiro and Fried, 1959; Rennie and McKercher; Hsu and Rennie, 1962; Muljadi et al., 1966; Syers et al., 1973 b; Schwertmann and Knittel, 1973; Holford et al., 1974). Because the Langmuir equation was originally developed for gas adsorption, its widespread use in the soils literature to describe P sorption requires further discussion.

Langmuir (1918) visualised sorption as a dynamic process in which the surface forces were assumed to operate over a short range and intermolecular forces between sorbed molecules were small. These assumptions imply that only those molecules which strike unoccupied sorption sites can be sorbed, whereas those which strike occupied sites are reflected back into the bathing phase (gas or solution depending on the situation under consideration). Consequently, a limiting condition of monolayer sorption is imposed.

For solute sorption, the rate of sorption per unit area (R_a) can be expressed :

$$R_a = c (1 - \theta) e^{-E/RT}. \qquad (1.10)$$

where θ is the fraction of the surface covered with sorbed molecules; c is the concentration which is proportional to the number of molecules striking the surface per unit time and area, and $e^{-E/RT}$ is an activation term representing the ratio of collisions resulting in sorption to the total number of collisions, E being the activation energy of sorption reaction.

The number of molecules (v) desorbing from the surface per unit time and area, is given by :

$$v = j\, e^{-E'/RT} \qquad (1.11)$$

where $e^{-E'/RT}$ is an activation term for desorption, E' is the activation energy of desorption, and j is a constant depending on temperature. The rate of desorption (R_d) may therefore be written :

$$R_d = j\theta e^{-E'/RT} \qquad (1.12)$$

At equilibrium the rates of sorption and desorption are equal, and equations (1.10) and (1.12) may be equated :

$$c (1 - \theta) e^{-E/RT} = j\theta\, e^{-E'/RT} \qquad (1.13)$$

Because the heat of the sorption reaction (ΔH) is given by :

$$\Delta H = E - E' \qquad (1.14)$$

and must be negative for sorption to occur, equation (1.13) may be simplified :

$$c = j\ e^{\Delta H/RT}\ \frac{\theta}{(1 - \theta)} \qquad (1.15)$$

For a constant temperature, ΔH may be assumed to be constant (i.e. independent of surface coverage). The fractional surface coverage (θ) may be represented by x/b, where x is the amount sorbed per unit area (or weight) and b is the sorption maximum, equivalent to a complete monolayer. Equation (1.15) can now be written in the form :

$$c = \frac{x/b}{K(1-x/b)} \tag{1.16}$$

where $K = 1/j\ e^{\Delta H/RT}$. Rearrangement of equation (1.16) gives the typical form of the Langmuir equation :

$$x = \frac{bKc}{1+Kc} \tag{1.17}$$

Equation (1.17) may be expressed in several linear forms (see equations (1.18) (1.19) and (1.20) below). Conformity of sorption data to one of these equations however, does not constitute undisputable proof that the sorption reaction under consideration conforms to the model on which the Langmuir equation is based. Additional information is required (Brunauer _et al._, 1966). For example, the values of b and K should be consistent with the assumed mechanism. Furthermore, because the value of b depends on the surface area of the sorbent, it should be possible to estimate its value from theoretical considerations. Chemisorption, however, depends not only on the surface area but also on the number of active sites available on a particular component.

In the case of P sorption, the relationship between the surface area and the number of sorption sites on a particular sorbent may not be as direct as at first assumed. This is illustrated by P sorption at the edge faces of crystalline aluminosilicates and the possibility of an absorption reaction. Nevertheless, the amount of P sorbed by soil components at solution P concentrations of approximately 3 μg/ml (Table 1.2), suggests that P sorption, and probably b values, are in proportion to the relative number of sites that may be predicted for each component, based on structural and pH considerations. Comparison of the size of the phosphate group to the apparent area occupied by each sorbed group (Muljadi _et al._, 1966; Chen _et al._, 1973 b), however, may not be valid, because the nature of packing at the surface is not known. Furthermore, the implication of a "porous" surface (Lyklema, 1968) precludes a simple comparison between surface area and b values for P sorption.

As will be discussed later, few reliable estimates of K values for P sorption are available. This fact and the confusion that still surrounds the exact P sorption mechanism, prevents comparative assessment of K values.

1.5.3.2 The validity of applying the Langmuir equation to P sorption.

The application of the Langmuir equation to P sorption by soils and soil components has frequently been criticised (Hsu and Rennie, 1962; Gunary, 1970; Bache and Williams, 1971; Kuo and Lotse, 1974 a, b). Criticism has usually been based on an apparently poor fit of P sorption data to the Langmuir equation. It has usually been implied that P sorption is not amenable to the rigorous conditions implicit in the derivation of the equation (Gunary, 1970). The constancy of ΔH, at constant temperature, with surface coverage has also been questioned in the case of P sorption (Bache and Williams, 1971; Kuo and Lotse, 1974 a, b). Breeuwsma and Lyklema (1973) also pointed out that poorly-defined sorption maxima, frequently implied by P sorption isotherms, does not comply with the monolayer assumption. It is probable, however, that the apparently poor fit of P sorption data to the Langmuir equation, arises from insufficient data (Syers *et al.*, 1973 b) or the assumption that only one sorption site or mechanism is involved.

The condition that ΔH is independent of surface coverage, implies that all sorption sites for a given P sorption mechanism are uniform, and that no lateral interaction occurs between sorbed species. This condition appears rigorous, even for the sorption of gases. Most surfaces are heterogeneous, and at low concentrations, sorption takes place at sites having the highest affinity or sorption energy (Brunauer, 1961). Consequently, a plot of Δ H against fractional surface coverage (θ) will be a decreasing function. Lateral interaction between sorbed species, however, increases the heat of sorption, giving an increasing function for a plot of Δ H against θ (Brunauer, 1961; Adamson, 1967). These opposing interactions may be expected to produce a Δ H value which is approximately constant, and conformity to the Langmuir equation is shown for a greater number of situations than may at first seem likely (Brunauer, 1961).

For solute sorption, and especially when a chemisorption reaction is involved (Brunauer et al., 1966), the conditions imposed by the Langmuir equation may be more adequately satisfied than for gas sorption. A chemisorption reaction involves direct chemical interaction at sorption sites. This approximates chemical bond formation, and a near uniform heat of sorption may be expected. Furthermore, because the surface is bathed in solvent, interaction between sorbed species will be relatively weak (Giles, 1970). Surface heterogeneity will also be relatively less important in chemisorption reactions, especially when a strong interaction is involved between sorbent and sorbate.

The P sorption mechanisms discussed previously seem particularly suited to Langmuir interpretation. For a given pH, there is a finite number of sorption sites of a particular type at the hydrous-oxide surface. Also, because the mechanism involves ligand exchange with surface groups, sorption in excess of monolayer sorption is precluded. The value of ΔH will also be constant because all proposed mechanisms have involved a chemisorption reaction. The hydrated surface and the affinity of P species for Fe and Al, will minimise lateral interaction. Consequently, P sorption by soils, and particularly by soil components, may approach ideal Langmuir behaviour.

1.5.4 P sorption and desorption isotherms

1.5.4.1 Application of the Langmuir equation to P sorption

Although the Langmuir equation assumes an equilibrium condition, many studies of P sorption, particularly those involving soils, have not met this condition. Nevertheless, for the studies discussed, the lack of attention given to the equilibrium condition does not appear to affect the general conclusions that may be drawn from them.

For the reasons discussed in the previous section, the Langmuir equation is particularly suited to describe P sorption by soils and soil components. In order to evaluate the constants relating to the sorption maximum (b) and the sorption energy (K), equation (1.17) may be rearranged to give three linear forms :

$$\frac{c}{x} = \frac{c}{b} + \frac{1}{Kb} \tag{1.18}$$

(b = slope^{-1}, K = slope/intercept)

$$x = b - \frac{x}{Kc} \tag{1.19}$$

(b = intercept, K = - slope $^{-1}$)

$$\frac{1}{x} = \frac{1}{Kbc} + \frac{1}{b} \tag{1.20}$$

(b = intercept^{-1} , K = intercept/slope)

Each equation has advantages for particular concentration ranges. Equation (1.18), the most commonly used form, accommodates a concentration range of approximately two orders of magnitude, whereas equation (1.19) is more suited to a concentration range of less than two orders of magnitude. Because of its reciprocal nature, equation (1.20) is suited to only a narrow concentration range, usually less than one order of magnitude, and is particularly sensitive to changes in the value of K.

Early applications of the Langmuir equation to P sorption by soils and soil components (Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Hsu and Rennie, 1962) generally covered a high P concentration range. These studies suggested that although P sorption was described by the Langmuir equation over most of the concentration range, deviations from a linear relationship occurred at solution P concentrations in excess of approximately 15 μg P/ml. The studies of Shapiro and Fried (1959) using soils, and de Haan (1965) using various aluminosilicates, suggested a curvilinear relationship when P sorption data were plotted according to the Langmuir equation. It was shown, however, that the relationship could be transformed into two linear portions, although an explanation of the different K and b values, obtained over different solution P concentration ranges, was not given.

In a study of P sorption by kaolinite, gibbsite, and pseudoboehmite, Muljadi et al. (1966), using an inspection method suggested by Bache (1964), concluded that P sorption isotherms could be split into three distinct portions or "regions" (I, II, and III) corresponding to distinct solution P concentration ranges. Region I corresponded to <3.1 μg P/ml, region II to between 3.1 and 31 μg P/ml, and region III to between 31 and 3100 μg P/ml. Region III was a linear isotherm, but the very high solution P concentrations suggest that sorption may not be the dominant reaction, based on the work of Russell and Low (1954) and Chen _et al_. (1973a). Both regions I and II, however, could be described by a Langmuir equation. The sorption energy (K) for each region however, was very similar, suggesting that regions I and II could be described by essentially the same isotherm if the b values for each region were summed.

The similarity in K values obtained by Muljadi _et al_. (1966) suggests that isotherm differentiation by inspection is not satisfactory. This approach has been criticised by Syers _et al_. (1973 b). To a large extent, the method depends on the scale adopted for plotting the x-c isotherm. It should be noted, however, that the K values obtained by Muljadi _et al_. (1966) were not only comparable between regions I and II , but also between the different sorbents used.

Data similar to that presented by Muljadi _et al_. (1966) have recently been reported by Chen _et al_. (1973 b) for kaolinite and α-alumina, and by Karim _et al_. (1973) for soils. Covering a somewhat lower concentration range, Chen _et al_. (1973 b) suggested that region I may be composed of two Langmuir relationships, again emphasising the limitation of the inspection technique.

Syers _et al_. (1973 b) used equations (1.18) and (1.19) to evaluate P sorption by three contrasting Brazilian soils over the solution P concentration range of 0 to approximately 14 μg P/ml. This range corresponds to region I and part of region II as defined by Muljadi _et al_. (1966). Syers _et al_. (1973 b) demonstrated that the Langmuir equation itself, and the two linear relationships given by the experimental data, could be used to differentiate regions of apparently different sorption energies (Fig. 1.9). The "breaks" in the overall relationship, from one linear portion, or region to the next, occurred at approximately 2 μg P/ml for the soils used. After correction, which partially eliminated the effects of one sorption region on the Langmuir constants obtained for the other, each region could be represented by a distinct

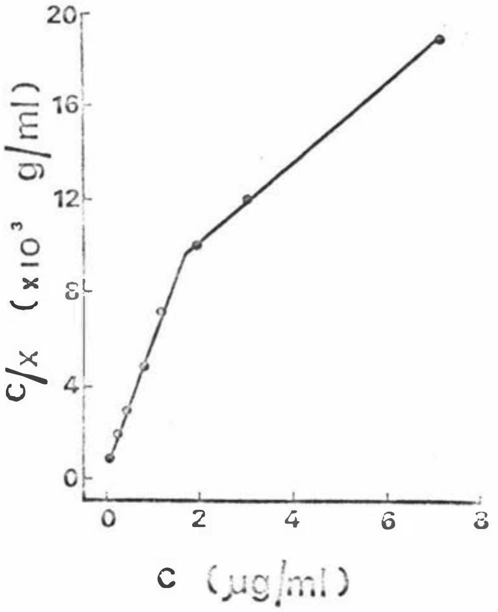


FIG. 1.9 Isotherm for P sorption by a soil showing two distinct linear portions over the final P concentration range of 0 to 8 µg P/ml, using the Langmuir equation in the form of equation (1.18). From Syers *et al.* (1973 b).

Langmuir equation. Very similar results have recently been reported by Holford et al. (1974) for P sorption by English and Australian soils.

For a given region, the K values obtained by both Syers et al. (1973 b) and Holford et al. (1974) were comparable This is particularly true in the case of the second sorption region corresponding to solution P concentrations greater than approximately 2 µg/ml. Furthermore, the K values obtained for the second region are of a similar order of magnitude to those obtained by Muljadi et al. (1966) over an equivalent concentration range for P sorption by the aluminous components discussed previously.

The possibility of a third Langmuir relationship corresponding to very low P concentrations has also been suggested by Syers et al. (1973 b) and Chen et al. (1973 b) for soils and aluminous soil components, respectively. This was supported by Schwertmann and Knittel (1973), who reported the existence of two, or possibly three, Langmuir sorption regions below solution P concentrations of 3 µg/ml, for P sorption by several Bavarian soils.

1.5.4.2 Implications of multiple Langmuir relationships.

The studies discussed above are in accord with the fact that P sorption isotherms are usually of a mixed H-, L-type (Fig. 1.8). An illustration of the dependence of isotherm type on sorption energy (K), has been given by de Boer (1953). Isotherms A, B, C and D (Fig. 1.10) are drawn for sorbents with uniform K values of 10^{-3}, 10^{-2}, 10^{-1}, and 10^{0} respectively (all relative units). These isotherms are perfect L-type isotherms, each described by a single Langmuir equation. Isotherms E and F (Fig. 1.10), however, represent sorption at a surface with two types of sorption sites or K values. Isotherm E assumes a heterogeneous surface for which the K has a value of 10^{-1} over 10% of the surface but only 10^{-3} over the remainder. Isotherm F assumes a K value of 10^{-1} over half the surface and a K value of 10^{-3} over the other half. Isotherms E and F, which are mixed H-, L-type isotherms, are typical of P sorption isotherms (Fig. 1.8). Similar isotherms would be obtained by assuming three distinct K values, although the H-type character would be accentuated.

The difference between the arguments of de Boer (1953) and Brunauer et al. (1966), discussed previously, with respect to

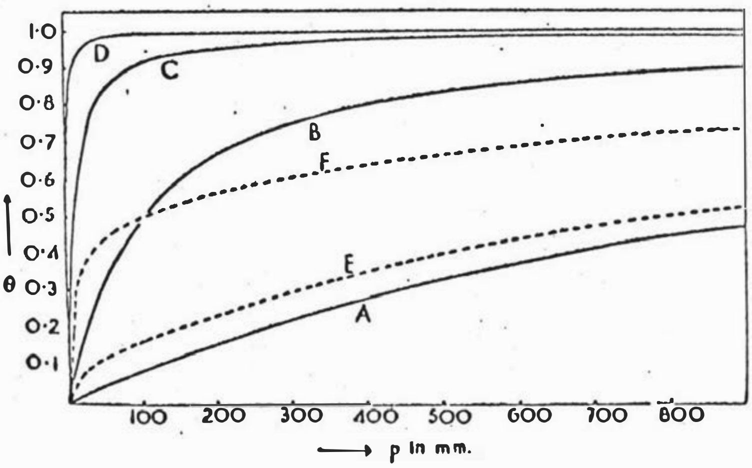


FIG. 1.10 Sorption isotherms constructed from the Langmuir equation assuming a uniform surface or K value (isotherms A, B, C, and D) and two distinct populations of sites or K values (isotherms E and F). From de Boer (1953).
Θ = fractional surface coverage, p = pressure (c.f., concentration).

surface heterogeneity is that de Boer (1953) assumes homogeneity within the overall heterogeneous character of the surface. The considerations of Brunauer et al. (1966) can be taken to apply to a group of sites of distinct K values rather than to the surface as a whole.

Because P sorption is described by at least two, and possibly three, distinct Langmuir equations, the same number of distinct populations of sorption sites is implied. Full evaluation of P sorption by the Langmuir equation requires, therefore, test for data fit over the complete solution P concentration range of the x-c isotherm, starting as close as is experimentally feasible, to the origin. Emphasis at the very lowest P concentrations is essential if sorption sites of the highest K value are to be detected. This is necessary because each experimentally determined point on the isotherm, represents the sum of P sorption within each population of sites for the observed solution P concentration. Little attention has been given to the low (0-0.05 µg P/ml) concentration range of P sorption isotherms in the studies discussed above. This is the concentration range of particular relevance to the soil solution of many soils.

A detailed isotherm is also required because each Langmuir relationship is only observed over a limited concentration range (Syers et al., 1973 b; Holford et al., 1973). The lack of experimental detail, particularly over the solution P concentration range of 0 to 1 µg/ml, accounts for the fact that some workers have obtained curvilinear relationships when the Langmuir equation was applied to P sorption data (Gunary, 1970; Bache and Williams, 1971). This has led to the criticism of the Langmuir equation, as applied to P sorption, discussed previously.

The exact origin of the deviations of P sorption data from a single Langmuir relationship, remains obscure. Muljadi et. al. (1966) have attributed P sorption over the solution P concentration range of 0 to 31 µg P/ml to sorption at adjacent surface -OH groups. The basis of this interpretation is questionable, however, because of the method by which the sorption regions were differentiated. Syers et al. (1973 b), suggested that distinct sorption mechanisms, probably involving different soil components, may explain deviations from a single Langmuir equation. A similar explanation has been given by Holford et al. (1974).

At present no experimental data are available to explain the deviations of P sorption data from a single Langmuir equation. The similarity of K values obtained in many of the studies discussed previously, suggest, however, that the distinct populations of sorption sites, implied by different K values, may in fact represent distinct sorption mechanisms at the same surface. The effects of non-equilibrium and limited experimental data, particularly at low solution P concentrations, leaves the interpretation and implications of this effect, open to question.

1.5.4.3 The nature and implications of P desorption isotherms. Desorption (or release) of sorbed P may be evaluated subsequent to a sorption step by replacement of the equilibrium solution with a washing solution of equal ionic strength and pH, but containing no P (Muljadi et al., 1966; Kafkafi et al., 1967; Syers et al., 1970; Hingston et al., 1974). Despite the ease of conducting such an experiment, and the importance of desorption in relation to the supply of soil P to plants, desorption of sorbed P by soils and soil components has received little attention.

The desorption of sorbed P is characterised by a hysteresis effect (Muljadi et al., 1966; Hingston et al., 1974). Hysteresis implies that sorption is only partially reversible; that is the isotherm obtained for the desorption step does not follow the same path as that for the sorption step (Adamson, 1967). Desorption of P by soils and soil components follows an isotherm representing larger amounts of sorbed P for a given solution P concentration, than is represented by the sorption isotherm. It should be noted, however, that desorption hysteresis only occurs for desorption at constant pH (Muljadi et al., 1966; Hingston et al., 1974). If the pH is increased sufficiently, the desorption isotherm has been shown to correspond to the P sorption isotherm obtained at the pH of the desorption step (Muljadi et al., 1966; Kafkafi and Bar-Yosef, 1969; Breeuwsma and Lyklema, 1973).

Several attempts have been made to describe the hysteresis effect of P sorption and desorption. Using aluminous soil components, Muljadi et al. (1966) observed that above solution

P concentrations of 3 μg/ml sorption was to some extent reversible on washing at constant pH. P sorption at less than 3 μg/ml, however, was not reversible. It was suggested that during the desorption step, sorbed P underwent a phase change in which it became more tightly bound to the surface. A more detailed study of the desorption of P from kaolinite was reported by Kafkafi et al. (1967) from surface saturations corresponding to solution P concentrations no greater than 3 μg/ml. Over this concentration range, sorption was found to be largely irreversible. Other data implied that the isotopic exchangeability of sorbed P decreased during the desorption step. To some extent this may have been an artefact of the method used. Kafkafi et al. (1967) suggested that hysteresis arose from a "fixation" process whereby sorbed P was reoriented at the surface, to establish a stable, six-membered ring structure between P (HPO_4^{2-}) and adjacent surface sites (Al at the edge face of kaolinite). This mechanism implies that for each P group "fixed", one P group is released. Desorption data do not seem to support this prediction.

Hingston et al. (1974) evaluated the desorption of sorbed P from gibbsite and goethite, in terms of the change in surface charge induced by the desorption process. It was noted that desorption decreased the negative charge of the surface, as measured by ion uptake. This is in direct contrast to an earlier assumption of Hingston et al. (1967, 1968 b) that an increase in the negative charge of the surface is requisite to desorption of sorbed P, by other anions.

Hingston et al. (1974) have proposed that sorption is reversible only if the change in surface charge per mole P sorbed or desorbed is the same for both the sorption and desorption steps. To illustrate the non-reversibility of P sorption, it was shown that the change in charge per mole of P desorbed was two to six times greater than that during the sorption step. The greater change in charge during the desorption step, as compared to the sorption step, was attributed to preferential desorption of OH^-, or sorption of H^+. No pH data, however, were presented. This interpretation of the desorption mechanism (Hingston et al., 1974) is questionable because it involves the assumption that each mole of P sorbed contributes to the negative charge of the surface. The limitation of this condition has been discussed previously.

The preceding discussion suggests that a virtually complete lack of understanding surrounds the meaning of P desorption isotherms and the desorption mechanism. A more quantitative evaluation of the sorption mechanism is required before the desorption mechanism can be explained. The desorption of sorbed P, however, may not be fully explained, even when a desorption mechanism is formulated. The effect of phase changes (Muljadi et al., 1966; Kafkafi et al., 1967; Chen et al., 1973 a) and the possible absorption of P (Sholten, 1965; Evans and Syers, 1971) may also be of importance in explaining the non-reversibility of P sorption.

1.6 General Conclusions and Research Needs

Although the nature and implications of the work reviewed in the preceeding sections have been discussed in some detail, an overview of the more salient points is valuable. This is particularly true with respect to an evaluation of research needs.

The time dependence of P sorption has received little attention in much of the work discussed in this review, and the question of the precise nature of the sorption reaction arises. Some experimental data (Sholten, 1965; Evans and Syers 1971) and the porous double layer model proposed by Lyklema (1968, 1971 a), suggest that an absorption reaction may be important in the overall sorption of P. The implications of this to other aspects of P sorption, such as desorption and isotopic exchangeability of sorbed P, cannot be known until the occurrence of absorption is established. It is also important to know whether an absorption step can be distinguished from a true adsorption reaction, in terms of the mechanisms involved in P sorption. Furthermore, the influence of the time dependence of P sorption on the interpretation of data obtained in both laboratory and field experiments is not known.

The Langmuir equation has been used increasingly in recent years to describe P sorption by soils and soil components. The use of the Langmuir equation has important implications to an evaluation of P sorption mechanisms and possibly, to an estimation of the ease with which plants may obtain P from soils after a fertilizer addition (Bache and Williams, 1971; Holford et al., 1974). A more complete understanding of the implications of the fit of P sorption data to the Langmuir equation and the deviations from a single linear relationship are limited by the lack of quantitative data. Furthermore, failure to recognise the importance of an equilibrium condition leaves much of the interpretation of existing data open to question. A complete evaluation of P sorption data using the Langmuir equation, will be facilitated by experimental data, obtained for the equilibrium condition, covering in detail a wide solution P concentration range.

Recent developments in an understanding of the P sorption mechanism have also been stressed in this review. Advances in this direction are represented by the increased awareness of the importance of the properties of the hydrous-oxide surface to the P sorption mechanism. Although the work of Hingston et al. (1967, 1968 b, 1972) has defined more clearly the type of sorption reaction involved, many questions still surround the exact mechanism and the precise nature (i.e., degree of covalency) of the chemical bond formed between P and the surface. Furthermore, identity of P sorption mechanisms, developed using soil components, with those which operate for whole soils, is still required. The measurement of change in cation exchange capacity during P sorption may be valuable in this regard, as well as in establishing a sound quantitative basis for a P sorption mechanism. Finally, a better understanding of the sorption mechanism would provide a much more reliable basis for the interpretation of P sorption data and its application to practically-orientated areas of interest.

In subsequent Chapters, some of the research areas outlined above are investigated with a view to developing a better understanding of the type of reaction, and the mechanisms involved in P sorption by soils. Four soils having contrasting properties considered to be important in P sorption are used in all the studies described to provide a more reliable basis for the extension of interpretations to other soils. For these soils, the extent and origin of the time dependence of P sorption are investigated and the nature of the reactions involved are discussed. The effects of time-dependent P sorption on the interpretation of the data obtained using contacting solutions of different ionic composition are also evaluated. These effects are investigated with a view to establishing more reliable experimental conditions for use in subsequent P sorption studies. A particularly important objective in this regard is that of developing a method by which the equilibrium P concentration can be estimated. Such an estimate is required in the interpretation of P sorption by soils using the Langmuir equation. The implications of the interpretation of P sorption using the Langmuir equation to P sorption mechanisms are also evaluated, based on the charge relationships of P sorption as determined by cation uptake.

CHAPTER 2

SOILS AND SOIL PROPERTIES

2.1 Introduction

Various interpretations concerning the reactions and mechanisms involved in the sorption of inorganic phosphate (P) by soils, have usually been based on data obtained with soils having rather similar properties. These interpretations have frequently been extended to explain P sorption by soils with very different properties. Generally applicable concepts of P sorption, however, should be based on data obtained for soils which contrast in terms of properties considered important in P sorption. By using contrasting soils, any differences in P sorption characteristics, which may be a reflection of reaction type and mechanism, may be detected. More importantly, any interpretation of P sorption should have a more sound foundation if based on results which show similar patterns for widely-different soils.

In this study the properties of four contrasting New Zealand soils are evaluated. The properties are discussed in relation to the ability of the soils to sorb added P from solution. The suitability of the soils for studies of various aspects of the reactions and mechanisms involved in P sorption is also discussed.

2.2 Materials and Methods

Horizons of Egmont black loam (BC) developed from andesitic tephra, Okaihau gravelly clay (B2) developed from olivine basalt, Porirua fine sandy loam (B1) largely developed from greywacke-derived sands, and Waikakahi silt loam (B3Ca) largely developed from calcareous sandy mudstone, were collected from the reference sites for these soils (New Zealand Soil Bureau, 1968). The soils were air dried and material passing a 2 mm sieve was used for all analyses.

Soil pH was determined using 10^{-1}M NaCl at a solution:soil ratio of 40:1. Exchangeable Ca and Al were determined by four successive washings of a 1-g sample of soil in a 50-ml centrifuge tube with 1M KCl; Ca in solution was determined by flame emission spectrophotometry, and Al in solution by colorimetric analysis (Rainwater and Thatcher, 1960). Free Fe oxides and hydrous oxides were determined by extraction with citrate-dithionite-bicarbonate (CDB) and colorimetric analysis (Jackson, 1956); Al extracted by the CDB reagent was also determined following destruction of citrate by evaporation with HNO_3-H_2SO_4 and ignition at 450°C. Short-range order Fe and Al components were determined by extraction with acid ammonium oxalate (Williams et al., 1971) and colorimetric analysis (Rainwater and Thatcher, 1960). An estimate of crystalline Fe was obtained by subtracting short-range order Fe from CDB-Fe. Water-dispersable clay was separated by centrifugation and decantation (Jackson, 1956) following dispersion of 8 g of soil in 60 ml of distilled water for 16 hr on an end-over-end shaker. Surface area was determined using a B.E.T. apparatus.

Sorption of inorganic P in this and subsequent studies was evaluated by variations of the same basic method. One-gram samples of soil were shaken with 40 ml of 10^{-1}M NaCl, containing an appropriate amount of P, in 50-ml polycarbonate centrifuge tubes (Oak Ridge-type) on an end-over-end shaker at 23°C for specified time periods. Each system also contained 40 μg $HgCl_2$/ml to minimise possible microbial activity (Environmental Protection Agency, 1971). After shaking, the suspensions were centrifuged at 10,000 rpm at 23°C for 5 min, and the supernatant solutions were passed through a 0.45 μm 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 source of added P in all studies, except where specified, was KH_2PO_4.

The method of Murphy and Riley (1962) was used, except where specified, for the determination of dissolved inorganic P in all extracts and absorbance was measured at 712 nm using a Unicam SP 1800B spectrophotometer.

2.3 Results and Discussion

The four soils were selected according to characteristics known to be of potential importance in P sorption. In this way it was possible to evaluate P sorption in relation to soil components and properties. These characteristics include pH, exchangeable Ca and Al, $CaCO_3$, crystalline Fe (CDB-Fe minus short-range order Fe), CDB-Al, short-range order Fe and Al, total and water-dispersable clay, and surface area; values for these parameters are given in Table 2.1.

Soil pH increased from 4.4 for Porirua and Okaihau soils to 8.1 for the calcareous (27% $CaCO_3$) Waikakahi soil, whereas exchangeable Al ranged from 0 mmoles/100g in Waikakahi soil to 1.03 mmoles/100g in Egmont soil. Egmont soil, developed from andesitic tephra, contained the largest amount (133 mmoles/100g) of short-range order Al ("allophane") whereas Porirua and Waikakahi soils contained less than 6 mmoles/100g and Okaihau soil contained an intermediate amount (18 mmoles/100g) of this component. It appears that 1M KCl, used to remove exchangeable Al, extracts some non-exchangeable Al from the allophanic Egmont soil. Okaihau soil contained an appreciable amount (139 mmoles/100g) of crystalline Fe. With the exception of Egmont soil, a greater amount of Al was extracted by the CDB reagent than by acid ammonium oxalate. The high value of 124 mmoles/100g for CDB-Al in Okaihau soil suggests that an appreciable amount of Al is substituted in the crystalline Fe components of this soil or that some of the gibbsite present is extracted by the CDB reagent. Norrish and Taylor (1961) noted that increasing substitution of Al for Fe (up to 30%) in soil goethite limits the size of the crystallites, suggesting a possible increase in P sorption by such material.

Isotherms for the sorption of added P from 10^{-1}M NaCl (Fig. 2.1) indicate that the four soils differed appreciably in their ability to sorb P during 40 hr, over a final P concentration range of 0 to approximately 10 µg P/ml. The amounts of P sorbed at a final P concentration of 9 µg P/ml varied from approximately 3350 µg P/g to 230 µg P/g for Egmont and Waikakahi soils, respectively. Differences in the amounts of P sorbed by the soils, for a given addition of P, can be explained on the basis of the widely differing soil characteristics, discussed previously (Table 2.1). Soil components of most importance in relation to P sorption appear to be short-range order Fe and Al, crystalline Fe, and CDB-Al (Table 2.1, Fig. 2.1). The relationship of these and similar soil components to the amounts of P sorbed by soils have been studied by several workers (Williams et al., 1958; Saunders 1965; Syers et al., 1971) with rather similar conclusions being obtained to the ones in the present study.

Although the ability of $CaCO_3$ to sorb P is well established (Cole et al., 1953), it is apparent that the $CaCO_3$ in Waikakahi soil

TABLE 2.1 Some characteristics of the soils used

Soil	Horizon	Depth	pH	Exchangeable		$CaCO_3$	Crystalline	CDB	Short-range order		Clay		Surface area
				Ca	Al		Fe	Al	Fe	Al	Total	Water dispersable	
		(cm)		(mmoles/100g)		(%)*	(mmoles/100g)				(%)*	(%)	(m^2/g)
Egmont black loam	BC	43-61	6.6	1.17	1.03	0	21.0	78	19.5	133	41	0.7	52
Okaihau gravelly clay	B2	23-40	4.7	0.00	0.57	0	139	124	5.2	18.0	31	3.5	64
Porirua fine sandy loam	B1	20-33	4.7	0.40	0.72	0	7.3	10	3.3	5.6	15	8.5	9.2
Waikakahi silt loam	B3Ca	41-56	8.1	n.d.†	0.00	27	17.6	8.0	4.3	4.6	n.d.	11	17.8

* Data from New Zealand Soil Bureau (1968).

† not determined.

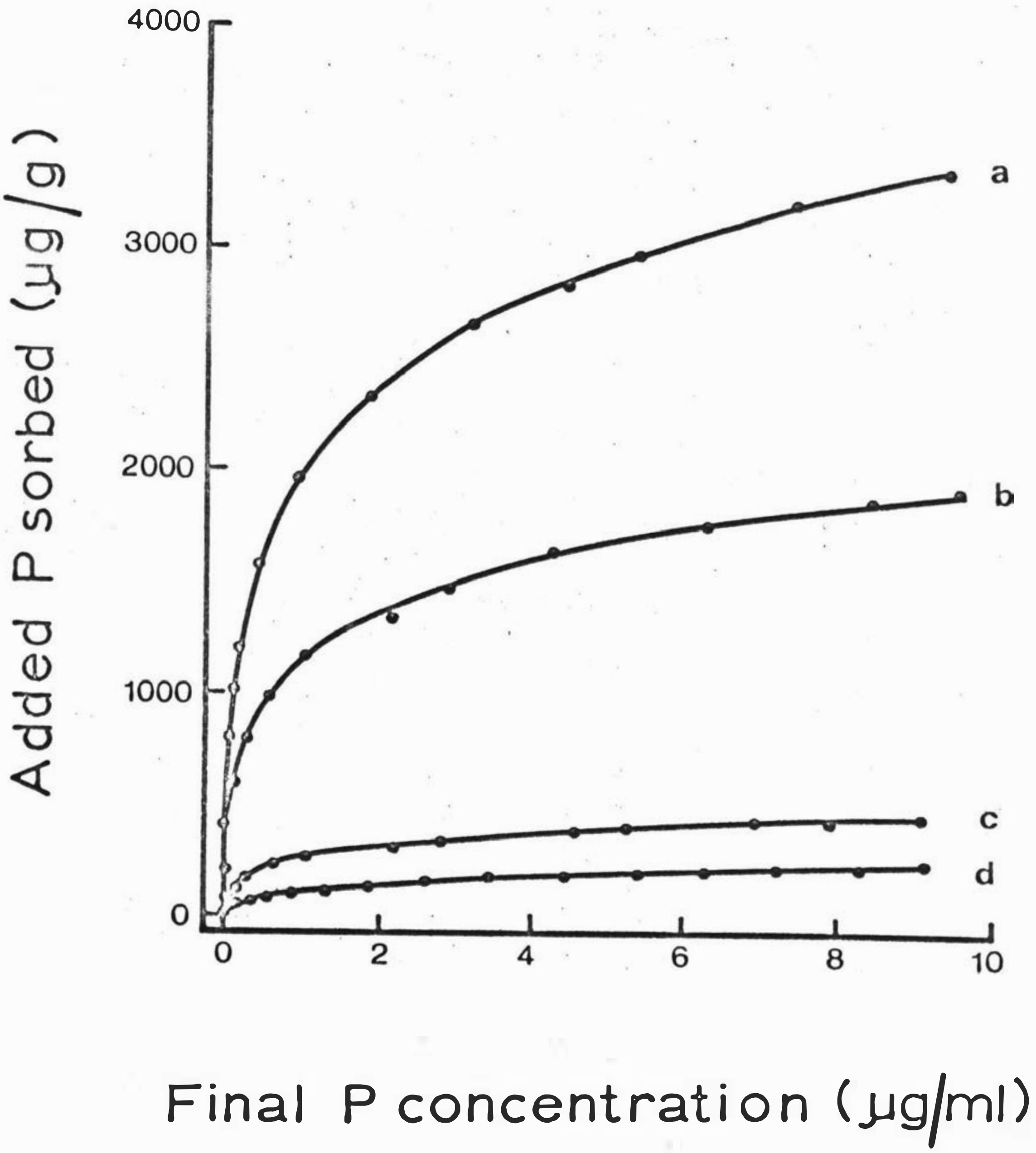


FIG. 2.1 Isotherms for P sorption by soils during 40 hr from 10^{-1}M NaCl over a final P concentration range of 0 to 10 µg P/ml. a = Egmont, b = Okaihau, c = Porirua, d = Waikakahi.

does not compensate, in terms of P sorption, for the rather low amounts of Fe and Al components in this soil. Even though the amounts of Fe and Al components in Waikakahi soil are similar to those in Porirua soil, except for crystalline Fe, the amount of P sorbed by Waikakahi soil is somewhat less over the final P concentration range (Fig. 2.1), despite the presence of $CaCO_3$ (Table 2.1). This is probably due to the higher pH of Waikakahi soil.

The data in Table 2.1 demonstrate the contrasting properties of the soils selected for studies in this thesis. This is particularly the case for chemical and mineralogical composition in relation to P sorption (Fig. 2.1). The data suggest that the four soils cover a very wide range of soil types, for which it is possible that P sorption reactions and mechanisms may be considerably different. It is believed that the use of such contrasting soils to evaluate the reactions and mechanisms involved in P sorption will provide a more reliable basis for the extension of interpretations to many other soils.

CHAPTER 3

EXTENT AND ORIGIN OF TIME DEPENDENT PHOSPHATE SORPTION BY SOILS

3.1 Introduction

The time dependence of the sorption of inorganic phosphate (P) by soils and soil components has been demonstrated in numerous studies (Kurtz et al., 1946; Rennie and McKercher, 1959; Hsu, 1964; Chen et al., 1973 a; Kuo and Lotse, 1974 a, b). The nature, extent, and origin of time dependent P sorption, however, have received little attention.

Furthermore, the effect of time, as an experimental variable in P sorption studies, has frequently been overlooked in data interpretation. Although quantitative data on the time dependence of P sorption are limited, several attempts have been made to explain this phenomenon. These include the slow transfer of P from Al-to Fe-bound forms (Hsu, 1964), increasing interaction of sorbed P species with increasing surface saturation (Kuo and Lotse, 1974 a, b) or the slow crystallisation of sorbed P to form discrete-phase P compounds (Chen et al., 1973 a).

The purpose of this study was to evaluate the rate and extent of P sorption, measured as the change in solution P concentration with time, in terms of the rate constants involved. Based on a procedure for the fractionation of sorbed added P an explanation of the time dependence of P sorption is proposed.

3.2 Materials and Methods

Air dried $\leqslant$ 2 mm samples of horizons of Egmont, Okaihau, Porirua and Waikakahi soils were used in this study.

The time dependence of P sorption for one P addition to each soil was evaluated at time intervals of 0.017 (1 min) to approximately 190 hr. The level of P added to each soil was chosen to give approximately the same solution P concentration at a time of approximately 190 hr. The additions were 3200, 2000, 500, and 250 µg P/g for Egmont, Okaihau, Porirua, and Waikakahi soils, respectively. The appropriate amount of P was added in a 5-ml aliquot, at recorded times, after commencing to shake 1-g samples of each soil in 35 ml of 10^{-1}M NaCl containing 40 µg $HgCl_2$/ml. Additions of P were made at times such that, as shaking was continued, only the time of contact between P and soil varied. The total shaking time for all systems was approximately 190 hr.* After this time, the tubes were centrifuged and dissolved inorganic P was determined in the supernatants. For the shortest times of contact, soil and solution phases were separated directly by Millipore filtration at 0.45 µm. The sorption of P from various additions of P to Porirua soil was also determined by the same method for recorded contact times between approximately 70 and 140 hr.

The isotopic exchangeability during 24 hr, and a fractionation of added P sorbed by Okaihau and Porirua soils, from P additions of 2000 and 500 µg/g, respectively, was determined after P sorption had continued for times between 48 to 192 hr. For isotopic exchangeability studies 2.28 µCi carrier-free ^{32}P was added to each system, 24 hr prior to the separation of soil and aqueous phases. Solution ^{32}P concentration was determined by the following method. A 3-ml aliquot was added to 10 ml of Triton-toluene scintillation cocktail in a vial, for counting in a Packard-Tricarb liquid scintillation spectrometer. Blank aqueous extracts of each soil were used for quench correction. Solution ^{31}P concentration was also determined. Exchangeability of sorbed P was calculated, based on isotope dilution theory.

After the appropriate sorption period, each system was extracted in two successive, 16-hr treatments with 40 ml of 0.1M NaOH. This was followed by extraction with citrate-dithionite-bicarbonate (CDB) solution at 75° C (Jackson, 1956) and subsequent extraction with 40 ml of 1M NaOH. Inorganic P in the 0.1M and 1M NaOH extracts was determined following neutralisation, by the usual procedure. Inorganic P in CDB extracts was determined by the method described

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*Particle breakdown during long shaking periods was found to be unimportant. After shaking samples of each soil for between 1 and 7 days, it was found that, for a particular soil, the same amount of P was sorbed during a subsequent 24-hr P sorption step, regardless of the length of the previous shaking period.

by Weaver (1974). The amounts of inorganic P extracted by CDB reagent and by 1M NaOH were summed. Soils to which no P was added were extracted using the same procedures, and data obtained were used to correct for native soil P.

3.3 Results

3.3.1 Time dependence of P sorption

The sorption of added P, measured as the decrease in solution P concentration, as a function of time, is illustrated in Fig. 3.1 by data for the Okaihau and Waikakahi soils with P additions of 2000 and 250 μg/g, respectively. The relationships in Fig. 3.1 are typical of those obtained for all the soils used. The relationship is characterised by an extremely rapid decrease in solution P concentration (Fig. 3.1.A.1, and 3.1.B.1), which over a period of < 0.17 hr (10 min) was reduced to half its initial value for the Okaihau soil. After the initially rapid decrease in solution P concentration, the rate (tangential slope of Fig. 3.1) of removal of P from solution decreased considerably. Solution P concentration showed little tendency, however, to attain an equilibrium value, even at times up to 180 hr (Fig. 3.1.A.2 and 3.1.B.2). Equilibrium at some time in excess of 180 hr, however, is implied by the overall shape of Fig. 3.1.

The exponential character of the relationship in Fig. 3.1, suggests that the change in solution P concentration with time, is characterised by first-order reaction kinetics. First-order reactions conform to the equation :

$$\frac{dc}{dt} = -kc \qquad (3.1)$$

where c = solution P concentration at time t, and k = reaction-rate constant.

Conformity of the decrease in solution P concentration to first-order reaction kinetics was evaluated using the integral form of equation (3.1) :

$$\log c = \log a - \frac{kt}{2.303} \qquad (3.2)$$

where a = the initial solution P concentration. Although a single

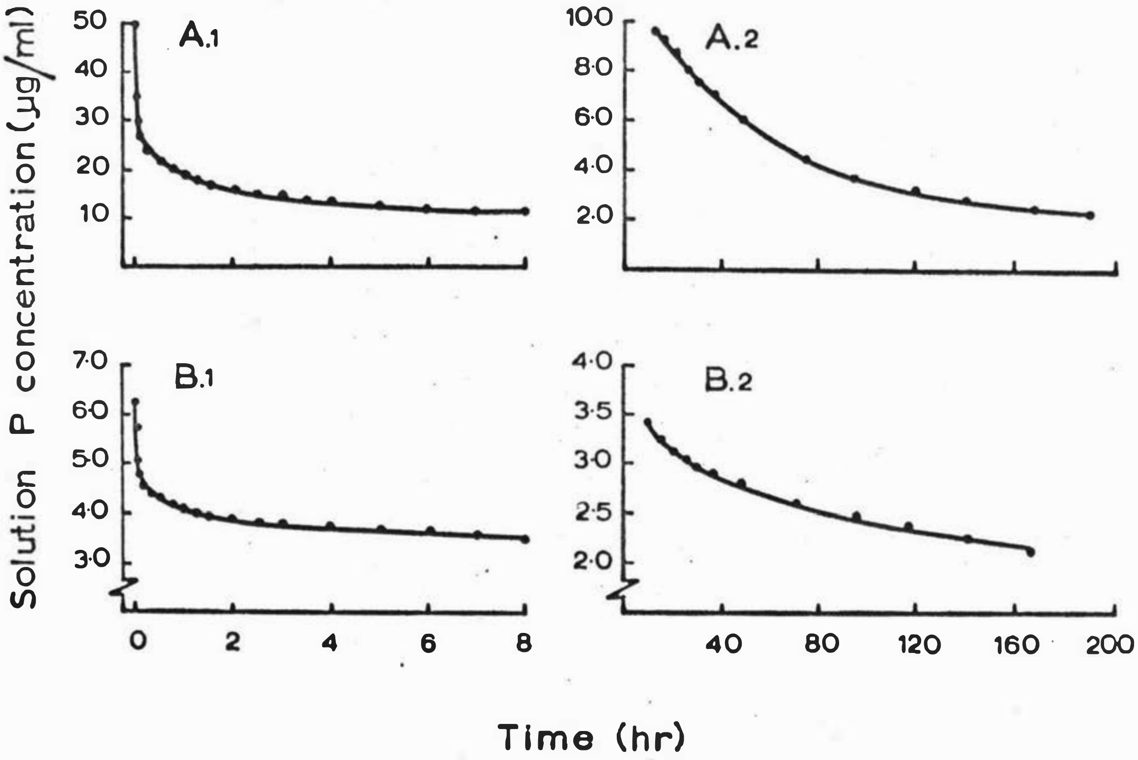

FIG. 3.1 Relationship between solution P concentration and time during the sorption of added P by Okaihau and Waikakahi soils. A = Okaihau soil, P added = 2000 µg P/g; B = Waikakahi soil, P added = 250 µg P/g (1) = 0 to 10 hr; (2) = 0 to approximately 190 hr.

linear relationship was not obtained when data were plotted in the form of equation (3.2), six linear portions were obtained for each soil over the time interval 0 to 190 hr. This is illustrated by data for Okaihau soil (Fig. 3.2). For each soil, each linear portion of the semi-log plot corresponded to approximately the same time intervals as those indicated in Fig. 3.2 for Okaihau soil. These are approximately 0 to 0.05 hr, 0.05 to 0.5 hr, 0.5 to 3 hr, 3 to 10 hr, 10 to 60 hr, and > 60 hr for the six linear portions, respectively.

Fig. 3.2 suggests that the decrease in solution P concentration is controlled by more than one first-order reaction (Amer _et al._, 1955; Ulrich _et al._, 1962). At times in excess of approximately 60 hr, however, the decrease in solution P concentration conforms to a single first-order reaction, which describes the change in solution P concentration for times up to at least 190 hr.

The relationship in Fig. 3.2 may be resolved using the method described by Ulrich _et al._ (1962) and Li _et al._ (1972). This is accomplished by extrapolating the terminal (sixth) rate relationship to zero time (dashed line in Fig. 3.2.B) subtracting the delogged intercept value from preceeding values of solution P concentration, and replotting the corrected data on semi-log scales (Fig. 3.3.A). This procedure is repeated until the experimentally defined solution P concentration at zero time is reached (Fig. 3.3.B and 3.3.C). The fact that the corrected extrapolated relationship covering the time interval 0 to 0.05 hr (Fig. 3.3.C) intercepts the y axis at the experimentally defined solution P concentration at zero time, increases the credibility of the resolution method. The resolution technique generates four distinct first-order relationships. These are the extrapolated relationship in Fig. 3.2.B and the three relationships in Fig. 3.3, and are designated reactions 1 to 4, the reaction rate decreasing with increasing reaction number.

The rate constants (k) for each reaction (k = -(slope) 2.303; Fig. 3.2.B and 3.3) and for each soil are given in Table 3.1. The striking feature of these data is the similarity of a particular k value for each soil. The maximum variation within corresponding k values irrespective of the soil was less than three fold, whereas between k values, differences ranged from ten to fifty fold (Table 3.1).

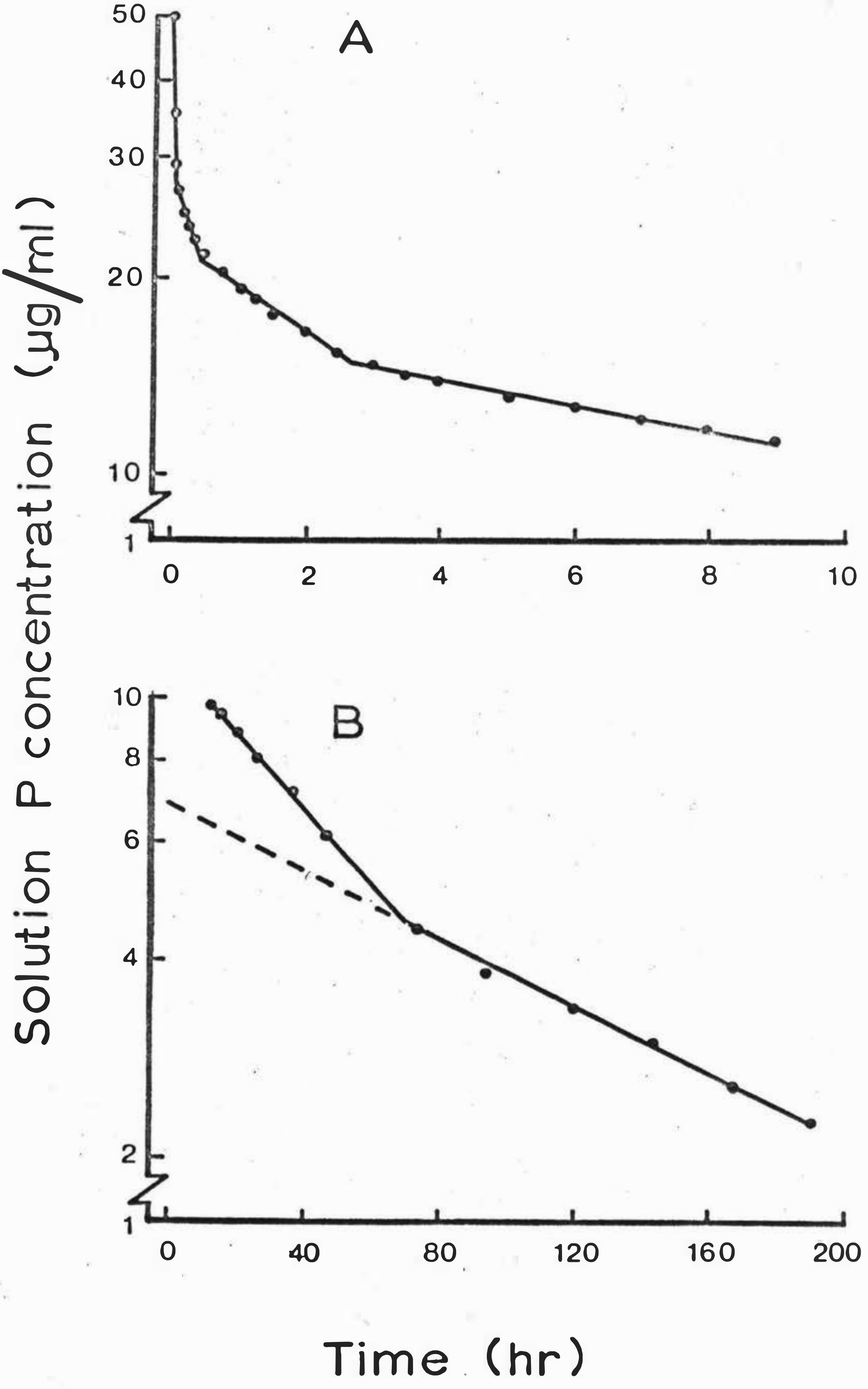

FIG. 3.2 Relationship between solution P concentration (log scale) and time during the sorption of added P (2000 µg P/g) by Okaihau soil. A = 0 to 10 hr and B = 0 to approximately 190 hr.

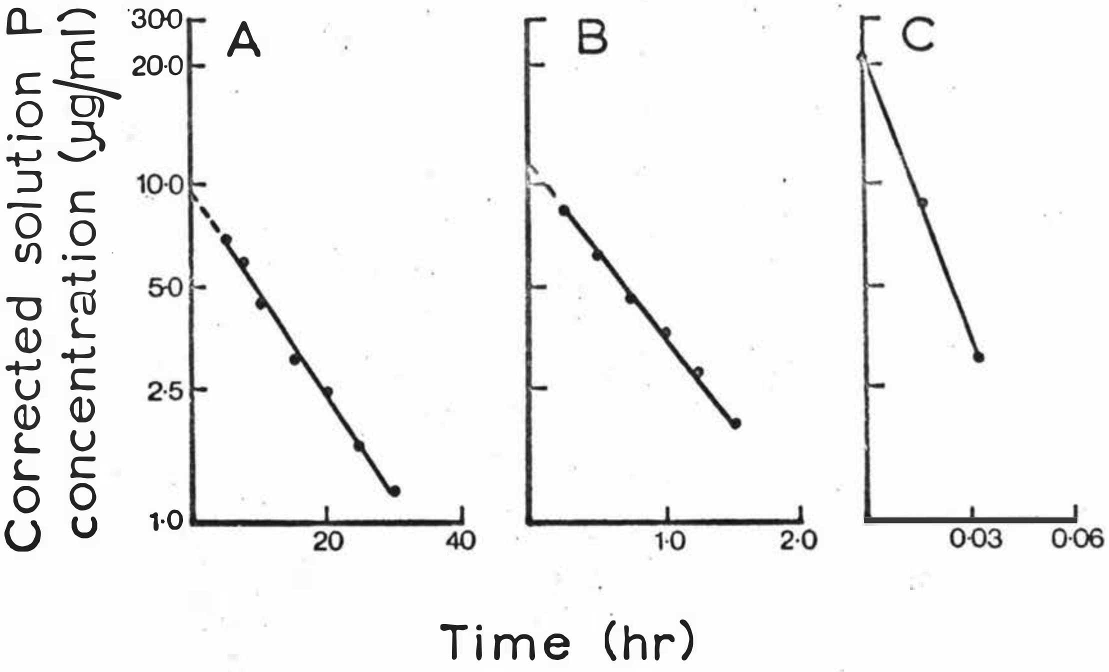

FIG. 3.3 Distinct first-order reaction relationships for the sorption of added P (2000 µg P/g) by Okaihau soil obtained after the resolution of data in Fig. 3.2 using the method described in the text. A = 0 to 33 hr, B = 0 to 2 hr and C = 0 to 0.6 hr.

TABLE 3.1 Rate constants (k) for the four reactions describing the decrease in solution P concentration during P sorption by four contrasting soils, and the time intervals over which each reaction is dominant in overall P sorption.

Soil	P added	Rate constant (hr^{-1}) and time interval (hr)			
		k_1^1	k_1^2	k_1^3	k_1^4
	(µg/g)	(0 - 0.05)	(0.05 - 2.0)	(5.0 - 40)	(>60)
Egmont	3200	45.0	1.48	0.107	0.0049
Okaihau	2000	61.1	1.16	0.072	0.0055
Porirua	500	145	2.68	0.121	0.0040
Waikakahi	250	77.8	2.09	0.121	0.0022

The similarity of corresponding k values suggests that similar reactions, possibly involving similar mechanisms, are responsible for the sorption of P by each soil. No mechanism is implied, however, by reaction-rate data.

The remarkably uniform values of k_1^4 at widely different additions of P to Porirua soil (Table 3.2) indicate that the reaction is similar for each P addition. The P additions, ranging from 25 to 1600 µg/g, resulted in very large differences in solution P concentration at 136 hr (0.005 to 23.1 µg P/ml).

3.3.2 Fractionation of sorbed P

The data in Fig. 3.4 for Okaihau and Porirua soils indicate that although the amount of added P sorbed increases with time (c.f., Fig. 3.1.A.2 and 3.1.B.2), the proportion which remains isotopically exchangeable within 24 hr, shows a steady decrease between 48 and 192 hr. Almost identical results were obtained for both Okaihau and Porirua soils. At 48 hr, approximately 50% of the added P sorbed remained exchangeable, but this value decreased to approximately 35% at 192 hr.

The decrease in amount of exchangeable P was concurrent with changes in the amount of added P sorbed which was recovered in two successive 0.1M NaOH extractions and a subsequent CDB extraction of the soils. For the Okaihau soil (Fig. 3.4.A), the amount of NaOH-extractable P (NaOH -P) showed only a small increase with time which was not commensurate with the increase in the amount of P sorbed. The increase in CDB-extractable P (CDB-P) however, accounted for the observed increase in P sorbed between 48 and 192 hr. Summation of NaOH-P and CDB-P at each time gave between 98 to 100% recovery of added P sorbed.

Changes in the amounts of NaOH-P and CDB-P for Porirua soil showed a slightly different pattern (Fig. 3.4.B). Between 48 and approximately 144 hr, the increase in NaOH-P was comparable to the increase in the amount of P sorbed. Between 144 and 192 hr, however, the amount of NaOH-P tended to become constant, and an increase, commensurate with that for the amount of P sorbed, was observed for CDB-P. Recovery of 95 to 100% of added P sorbed, was obtained.

TABLE 3.2 Values of the rate constant (k_1^4) for the decrease in solution P concentration at times greater than 60 hr for various P additions to Porirua soil.

P Added (μg/g)	k_1^4 (hr^{-1})
25	0.0054
75	0.0064
250	0.0054
500	0.0040
1000	0.0046
1600	0.0054

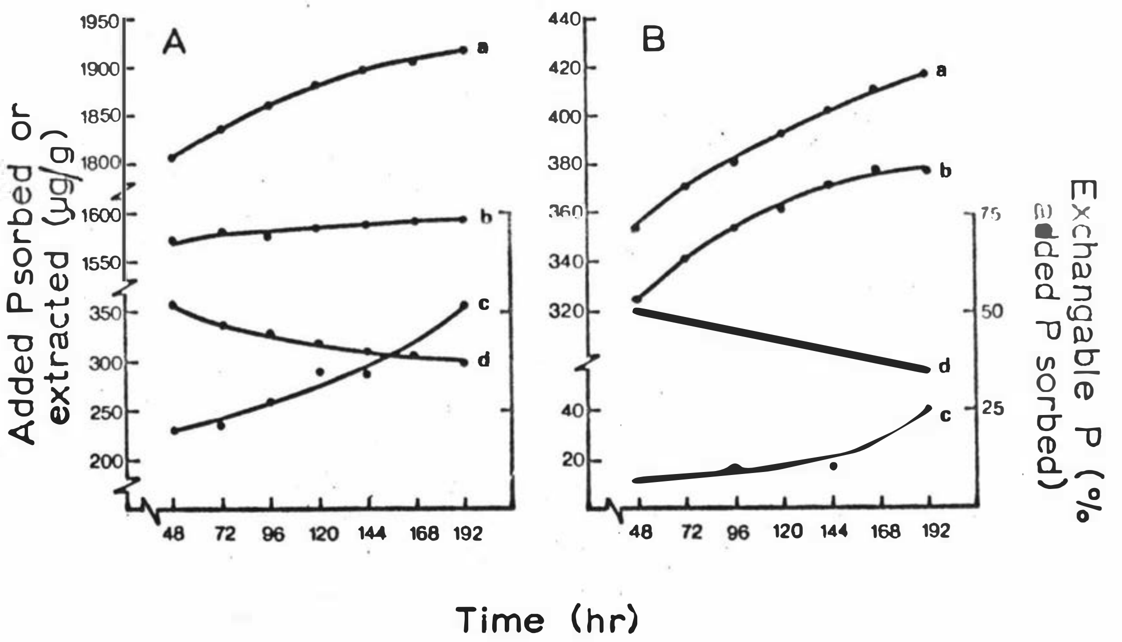

FIG. 3.4 Relationship between added P sorbed (a) between 48 and 192 hr, the amount of sorbed added P extracted by two successive 0.1M NaOH treatments (b), that extracted by a subsequent CDB treatment (c), and that exchangeable to ^{32}P (d) during the same 48- to 192-hr time interval for Okaihau and Porirua soils.

A = Okaihau soil; P added = 2000 µg/g,

B = Porirua soil; P added = 500 µg/g.

3.4 Discussion

3.4.1 Extent and nature of time-dependent P sorption

Although the time dependence of P sorption has frequently been reported in the literature relating to P sorption, the extent and significance of this process does not appear to have been appreciated fully. This is because the change in the amount of P sorbed has usually been monitored with time (Olsen and Watanabe, 1957; Rennie and McKercher, 1959). The data in Fig. 3.1 and 3.4 suggest that at times in excess of approximately 20 hr, the amounts of P sorbed increased by only a small percentage, relative to that already sorbed. For example, at 48 hr the amount of added P sorbed by Okaihau soil (Fig. 3.4.A) is 1810 µg P/g, whereas at 192 hr, a value of 1915 µg P/g is obtained, an increase of only 5.8%. Over the same time period, however, the solution P concentration decreases from 6.15 to 2.25 µg P/ml (Fig. 3.1.A.2), a change of 63.4%. This effect is even more significant when solution P concentrations fall below 1 µg P/ml. The disparity between the relative change in solution P concentration and the amount of P sorbed has received little attention in the literature. This observation points to the importance of obtaining an estimate of the equilibrium condition. Although the relationship in Fig. 3.1.A.2 and 3.1.B.2 appears to be approaching an asymptote, an estimate of the equilibrium P concentration cannot be made. The effect of the time dependence of P sorption on various aspects of P sorption data interpretation, is demonstrated in subsequent chapters, where a method of estimating equilibrium P concentration is proposed.

The conformity of P sorption data to first-order reaction kinetics suggests that the kinetics of P sorption may be more simple than has been assumed in previous studies (Kuo and Lotse, 1974 a, b). Sorption of P by kaolinite and α-alumina (Chen et al., 1973 a) has also been shown to conform to first-order reaction kinetics. The pattern of decrease in solution P concentration with time reported by Chen et al. (1973a) was similar to that observed for soils in the present study.

The similarity of rate constants for a particular time interval (Table 3.1) for all soils, implies that the same series of reactions, possibly involving the same mechanisms, are involved in P sorption by each soil, despite their contrasting properties. The rate constant (0.001 hr^{-1}) obtained by Chen *et al.* (1973 a) for P sorption by α-alumina at $25^{\circ}C$ at times $>$ 24 hr is also comparable to the k_1^4 values obtained for soils at times $>$ 60 hr in this study. A sorption reaction, similar to that for soils at times $>$ 60 hr, is suggested.

3.4.2 Origin of time-dependent sorption

The amounts of P sorbed by the four soils during the first 0.083 hr (5 min) ranged from 28 to 48% of that added, or from 37 to 49% of that sorbed at approximately 180 hr. The extremely rapid decrease in solution P concentration over this time interval, probably represents a true adsorption reaction. Such a reaction possibly occurs at the most reactive surfaces of soil components. Similar conclusions have been drawn by Rennie and McKercher (1959), Hsu (1964), Chen *et al.* (1973 a), Kuo and Lotse (1974 a, b).

The decreasing rate of P sorption (Fig. 3.1) may also be predicted if it is assumed that P sorption continues by a true adsorption reaction at sites of decreasing adsorption energy (Syers *et al.*, 1973 b; Kuo and Lotse, 1974 a, b). Less than approximately 50% of added P sorbed, however, remains isotopically exchangeable after 48 hr. Furthermore, total recovery of added P sorbed is not attained by two extractions with 0.1M NaOH (Fig. 3.4). Consequently, it seems highly unlikely that the decrease in solution P concentration, between at least 48 and approximately 180 hr, arises from a true adsorption reaction. Added P sorbed was also not recovered by one extraction with 1M NaOH (data not presented). Virtually complete recovery of added P sorbed was attained following extraction with CDB reagent subsequent to the two 0.1M NaOH extractions. The fact that two 0.1M Na^{O}H extractions are expected to remove "surface bound" , or adsorbed P (Williams *et al.*, 1967) and the CDB reagent solubilises free Fe oxides and hydrous oxides (Jackson, 1956), implies the movement of surface adsorbed P into Fe retaining components.

Based on the data in Fig. 3.4, it is proposed that the time dependence of P sorption at times in excess of, and probably very much less than 48 hr, arises from the absorption, or diffusive penetration of P into retaining components, followed by the regeneration of surface adsorption sites. Consequently if the initial first-order reaction (Fig. 3.3.C, Table 3.1) is assumed to represent true adsorption, diffusive penetration of P into retaining components is probably the rate limiting step in the reaction described by the rate constant k_1^4 (Fig. 3.2.B, Table 3.1).

Although the distinction between surface adsorbed or non-occluded P, and absorbed or occluded P, based on extraction with NaOH and CDB reagents (Williams _et al._, 1967) is somewhat empirical, it appears to provide a useful operational separation of adsorbed as opposed to absorbed P. Given the fact that OH^- may also be absorbed, and thereby desorb some absorbed P, and the fact that NaOH solubilises some Al components such as short-range order aluminous components, not all NaOH-P is strictly adsorbed P. Nevertheless, the tendency for NaOH-P to attain a constant value, and the commensurate increase in CDB-P when this condition is reached (Fig. 3.4), implies that added P sorbed consists of two distinct fractions. The difference between the relative changes in NaOH-P and CDB-P for Okaihau and Porirua soils (Fig. 3.4) probably reflects the somewhat empirical basis of the fractionation procedure, and the considerable differences between these soils in terms of components of potential importance in P sorption (Table 2.1).

Previous workers (Chen _et al._, 1973; Talibudeen, 1974) have indicated that the slow decrease in P concentration with time arises from the slow formation of discrete P compounds. Data obtained in this study suggest this is not the case. Discrete Fe and Al phosphates would have been dissolved in the NaOH extraction (Chang and Jackson, 1957 b). Also, discrete Ca phosphates would not have been recovered in either extraction (Williams _et al._, 1967), and would have given rise to consistently low recoveries of added P sorbed.

3.4.3 Implications of an absorption reaction

The data obtained in this study demonstrate the extent of time dependent P sorption and provide a rational basis for explaining this effect. The implications of the study to the interpretation of other aspects of P sorption are numerous.

The concept of diffusive penetration, or absorption, offers an explanation for the frequently reported observation that P sorption is a diffusion-controlled process even in well mixed systems (Cloos *et al.*, 1968; Kuo and Lotse, 1974 a, b). The apparent decrease in the exchangeability of sorbed P with increasing sorption time (Fig. 3.4), and the dependence of exchangeable P values on the time allowed for exchange (McAuliffe *et al.*, 1947; Russell *et al.*, 1954; Li *et al.*, 1970) may also be explained. The similarity between the time dependence of P sorption (this study) and P exchange (Li *et al.*, 1971) is remarkable. Furthermore, an absorption reaction may also partially explain the hysteresis effect during desorption of sorbed P (Syers *et al.*, 1970, Hingston *et al.*, 1974), and the rapid decreases which frequently occur in the availability of fertilizer P applied to soils.

The data, however, provide no indication of whether the mechanism involved in the absorption reaction is distinct from that involved in adsorption. Furthermore, it is difficult to interpret the meaning of the two first-order reactions described by the rate constants k_1^2 and k_1^3 between the extreme reactions (described by k_1^1 and k_1^4) which have been attributed to dominantly adsorption and absorption reactions, respectively. It is possible that the overall relationship (Fig. 3.2) represents not only a shift from an adsorption to an absorption reaction, but also more than one distinct P sorption mechanism. The possibility that absorption is equivalent to adsorption at "internal surfaces" is discussed in subsequent chapters.

CHAPTER 4

CATION AND IONIC STRENGTH RELATIONSHIPS OF PHOSPHATE SORPTION BY SOILS

4A. Origin of cation and ionic strength effects on phosphate sorption by soils

4A.1 Introduction

One of the principle experimental variables which has a considerable effect on the results obtained in inorganic phosphate (P) sorption studies with soils is the ionic composition, both species and concentration, of the solution containing P which is placed in contact with the soil during a P sorption experiment. This solution is referred to as the support medium.

Although several support media have been used in P sorption studies, the rationale for the choice has rarely been explained or justified. Schofield (1955) suggested the use of 10^{-2}M $CaCl_2$ in conjunction with the expression of solution P concentration values in terms of "phosphate potential" ($\frac{1}{2}pCa + pH_2PO_4$) on the basis that cation exchange is minimised by the use of calcium, and chloride at this concentration has no specific replacing power. This support medium has been used subsequently in numerous studies with varied objectives (White and Beckett, 1964; Ozanne and Shaw, 1967; Barrow, 1970; Gunary, 1970; Taylor and Kunushi, 1971). Other support media have included KCl (Mattson et al., 1950) and NaCl (Syers et al., 1970) whilst many workers have used distilled water containing added P and associated cations (Shapiro and Fried, 1959; Rennie and McKercher, 1959; Hsu, 1964; Woodruff and Kamprath, 1965).

Attempts to quantify and explain support medium effects on P sorption arising from different salt concentrations and cation species have relied upon concepts of solubility of phosphate compounds, believed to form in soils (Wild, 1950; Volkweiss et al., 1973) or the sorption of P at a dominantly negatively charged surface (Mattson et al., 1950; Barrow, 1972).

This study is concerned with an evaluation of support media effects on P sorption by four contrasting unfertilised soils and presents data which enable rationalisation of ionic strength, cation, and pH effects of the support media in terms of overriding kinetic considerations.

4A. 2 Materials and Methods

Air dried < 2 mm samples of horizons of Egmont, Okaihau, Porirua, and Waikakahi soils were used in this study.

The effects of support media (water; 10^{-4}M, 3 x 10^{-2}M and 10^{-1}M NaCl; and 10^{-4}M, 10^{-3}M, and 10^{-2}M $CaCl_2$ on P sorption were evaluated using the basic method described previously (Chapter 2)and a shaking period of 40 hr. Because all the support media were chloride salts only the cation will be used to describe the medium. Additions of P varied with the soil and the support medium used, to give a final P concentration range of 0 to approximately 10 µg/ml. The maximum additions of P required were 5000, 3000, 900, and 750 µg P/g for Egmont, Okaihau, Porirua, and Waikakahi soils, respectively, in the 10^{-2}M Ca systems. In addition to P concentration, Ca or Na concentrations and pH were measured in all supernatants, Ca and Na being determined by flame emission spectrophotometry.

The amount of Ca sorbed during treatment of Egmont, Okaihau, and Porirua soils with solutions of 10^{-2}M and 10^{-3}M Ca in the absence of added P, and that which was subsequently replaced by washing with 1M KCl solution were also determined. Non-replaceable Ca was calculated from the values for added Ca sorbed, replaceable Ca, and native exchangeable Ca.

Effects of pH on P sorption from 10^{-2}M Ca and 10^{-1}M Na, over the pH range observed in initial experiments, were determined for one level of P addition to Egmont, Okaihau, and Porirua soils; these P additions were 3000, 1500, and 400 µg/g of soil, respectively. Additions of P, based on P sorption isotherms obtained as described above, were different for each soil in order to obtain comparable final (40-hr) P concentrations. The desired range in pH was obtained by adjusting the pH of 35 ml of solution containing 1 g of soil, over a period of several hours, using 0.01M NaOH or 0.01M HNO_3. The P addition was made in a 5-ml aliquot and the systems shaken for 40 hr.

Kinetic effects of P sorption were determined for each soil at two additions of P in 10^{-4}M and 10^{-2}M Ca, and in 10^{-1}M Na, containing 40 µg of $HgCl_2$/ml in order to minimise microbial activity. Additions of P used were 750 and 2500 µg P/g for Egmont soil, 600 and 1500 µg P/g for Okaihau soil, 100 and 700 µg P/g for Porirua soil, and 50 and 500 µg P/g for Waikakahi soil. The appropriate amount of P was aded in a 5-ml aliquot 0, 1, 2, 3, and 4 days after commencing to shake 1-g samples of each soil in 35 ml of a given support medium. Shaking was continued for 40 hr. Consequently, the total time of shaking was the same for each system but the contact time between soil and added P ranged from approximately 40 to 144 hr. The supernatant solution of all systems was separated after no more than 144 hr and dissolved inorganic P determined.

4A.3 Results

4A.3.1 Effect of support media on P sorption

The composition and concentration of the support media had a marked effect on P sorption by the four soils, as indicated by the isotherms obtained with a 40-hr shaking period over both high (Fig. 4.1) and low (Fig. 4.2) final P concentration ranges. For Egmont, Okaihau, and Porirua soils, P sorption was the highest from 10^{-2}M Ca and the lowest from water. At final P concentrations in excess of 0.1 µg/ml, the amounts of P sorbed from 10^{-2}M Ca were between 1.5 and 2.5 times greater than the amounts sorbed from water. At lower final P concentrations, less than 0.1 µg/ml (Fig. 4.2), differences between the isotherms obtained using different support media were less. Isotherms for P sorption from 10^{-3}M Ca and 10^{-1}M, and 3 x 10^{-2}M Na by these three soils were somewhat similar, particularly at low final P concentrations, and plotted between the isotherms obtained with 10^{-4}M and 10^{-2}M Ca systems. Isotherms for Egmont and Porirua soils using 10^{-4}M Na were identical to those obtained using water.

The arrangement of isotherms for the Waikakahi soil appears to be somewhat different. It should be noted, however, that even in "water" systems the Ca concentration maintained in solution by the Waikakahi soil is of the order of 10^{-3}M. Consequently, the arrangement of isotherms is more similar to that for the other soils than a cursory examination would suggest.

For the three noncalcareous soils, the difference between the amounts of P sorbed from 10^{-4}M Ca and water were inversely related to

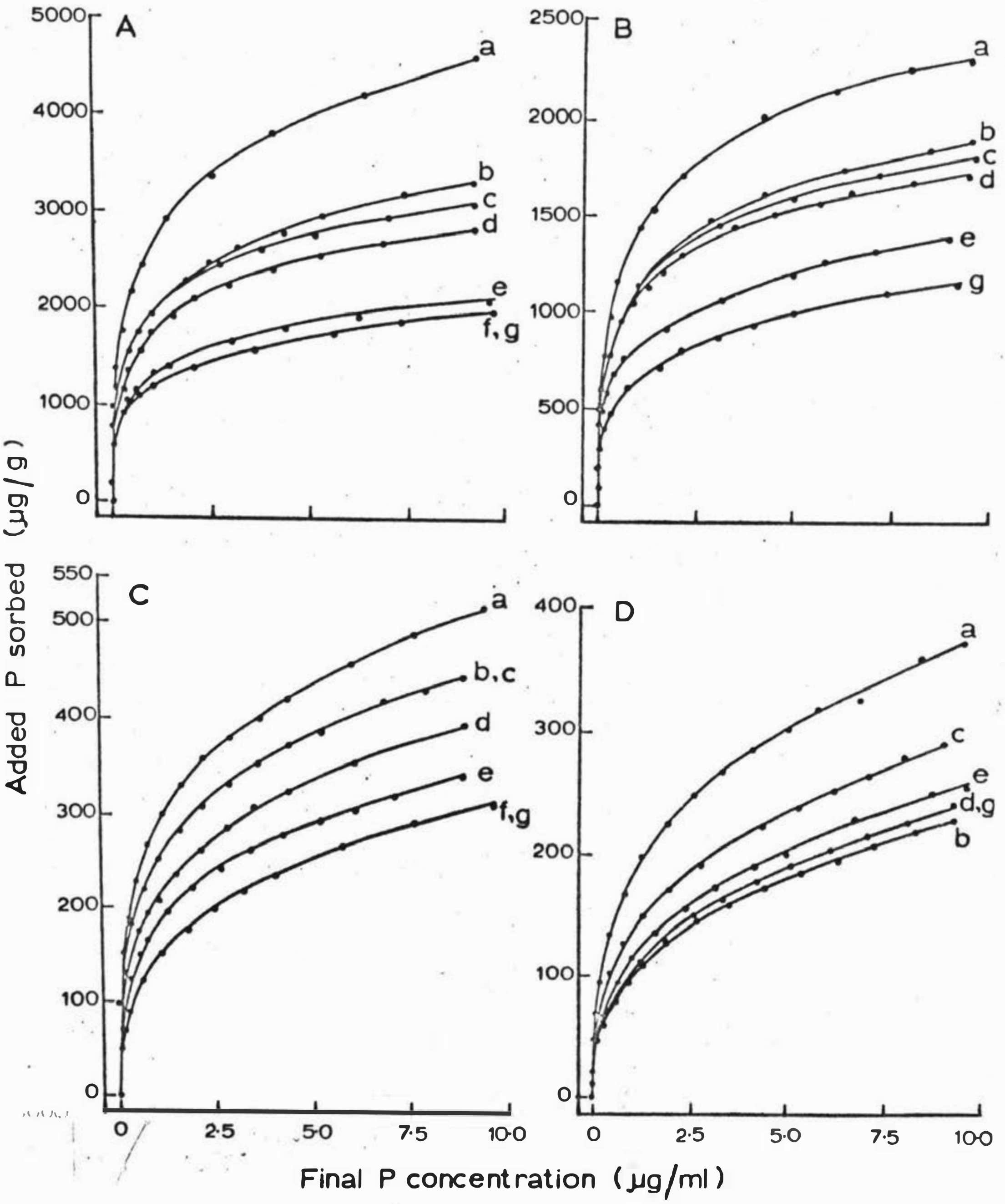

FIG. 4.1 Isotherms for P sorption by soils during 40 hr from various support media over a final P concentration range of 0-10 µg/ml. A = Egmont, B = Okaihau, C = Porirua, D = Waikakahi. a = 10^{-2}M Ca, b = 10^{-1}M Na, c = 10^{-3}M Ca, d = 3 x 10^{-2}M Na, e = 10^{-4}M Ca, f = 10^{-4}M Na, g = water.

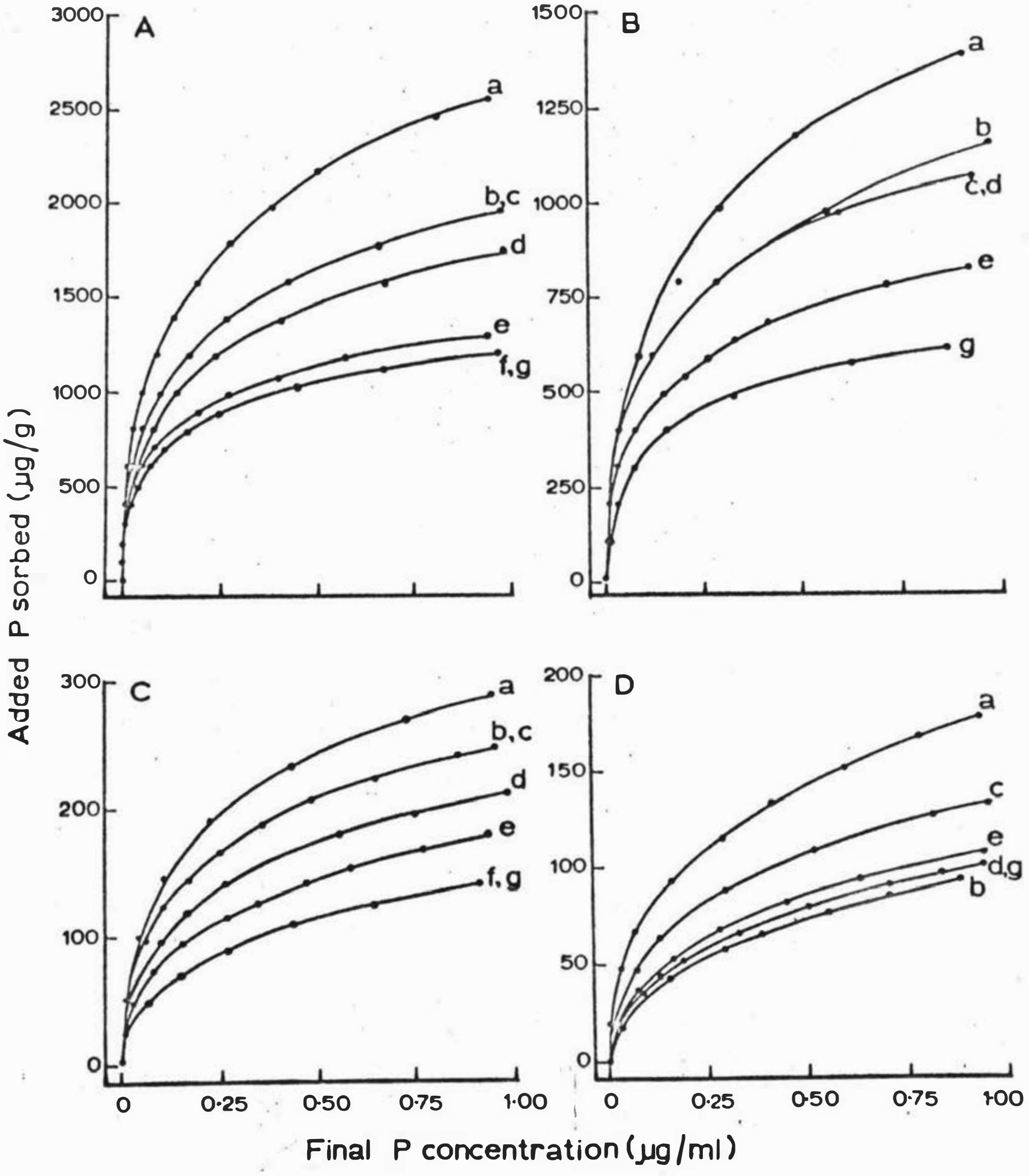

FIG. 4.2 Isotherms for P sorption by soils during 40 hr from various support media over a final P concentration range of 0-1 µg/ml. A = Egmont, B = Okaihau, C = Porirua, D = Waikakahi. a = 10^{-2}M Ca, b = 10^{-1}M Na, c = 10^{-3}M Ca d = 3 x 10^{-2}M Na, e = 10^{-4}M Ca, f = 10^{-4}M Na, g = water.

amounts of exchangeable Ca in the soil (Table 2.1), differences being the largest for the Okaihau and Porirua soils, and least for Egmont.

4A.3.2 Causes of support media effects on P sorption

The causes of the effect of support media on P sorption (Fig. 4.1 and 4.2) may arise from differences in ionic strength and cation species, pH, and kinetic effects. The results obtained in this study allow these factors to be isolated and discussed separately.

4A.3.2.1 Ionic strength and cation species. The data in Fig. 4.1 and 4.2 indicate that an increase in ionic strength of the support medium enhances P sorption, as evidenced by the increase in P sorption between H_2O, 10^{-4}M, 3 x 10^{-2}M, and 10^{-1}M Na systems, and H_2O, 10^{-4}M, 10^{-3}M, and 10^{-2}M Ca systems. Reasons for the effect of ionic strength on P sorption are discussed below. Ionic strength alone, however, does not account for all of the observed differences in P sorption. Despite the higher ionic strength of 10^{-1}M Na systems, P sorption was less than from 10^{-2}M Ca systems. The 3 x 10^{-2}M Na support medium was included in the study because it has an ionic strength equivalent to 10^{-2}M Ca. The difference in the P sorption isotherms obtained in these two support media suggest that the species of cation has a considerable effect on P sorption.

The higher amounts of P sorbed from Ca than from Na systems of comparable or even higher ionic strength may be due to the specific sorption of divalent Ca by oxides and hydrous oxides of Fe and Al (Kurbatov et al., 1951; Bonner et al., 1966; Grimme, 1969). Such specific sorption leads to an increase in the positive charge of the surface (Kolarik, 1962; Morgan and Stumm, 1964; Kinniburgh et al., 1975), a property not shown by Na (Kinniburgh et al., 1975). In the absence of added P, Egmont, Okaihau, and Porirua soils sorbed varying amounts of Ca from 10^{-2}M and 10^{-3}M Ca systems (Table 4.1), a significant proportion of which (up to 78%) could not subsequently be replaced by K. The amounts of sorbed Ca which were not replaceable by K varied for the three soils and depended on the amount of Ca added; values ranged from 0.14 to 1.16 mg Ca per g of soil, being the highest for Okaihau soil in 10^{-2}M Ca. The way in which the specific sorption of Ca by oxides and hydrous oxides of Fe and Al

TABLE 4.1 Amounts of Ca sorbed from 10^{-2} and 10^{-3}M Ca systems and amounts of sorbed Ca which are non-replaceable by K

Soil	System	Ca added (mg/g)	Ca sorbed (mg/g)	Non-replaceable Ca* (mg/g)
Egmont	10^{-2}M Ca	16.00	2.00	0.60
	10^{-3}M Ca	1.60	0.36	0.28
Okaihau	10^{-2}M Ca	16.00	2.00	1.16
	10^{-3}M Ca	1.60	0.32	0.24
Porirua	10^{-2}M Ca	16.00	0.80	0.35
	10^{-3}M Ca	1.60	0.34	0.14

*Ca non-replaceable with K.

produces an apparent increase in P sorption is discussed below.

4A.3.2.2 pH effects. Data for the average ambient pH values of the supernatants of the various support media following a 40-hr sorption period indicate that with the exception of Waikakahi soil, which is buffered at approximately pH 8.0 by the $CaCO_3-CO_2-H_2O$ equilibria, the lowest pH values were recorded in 10^{-2}M Ca, whereas the highest pH values were obtained in 10^{-4}M Na and/or water (Table 4.2). For Porirua soil, the order of increasing pH values of the supernatants of the support media was the same as the order of decrease in P sorption from the respective support media. This may at first suggest that the support media effects are merely due to pH effects on P sorption. The fact that support media effects on P sorption by Waikakahi soil, however, were similar to those obtained with the other three soils (Fig. 4.1 and 4.2), despite virtually equivalent pH values in all support media for Waikakahi soil (Table 4.2), suggests that support media effects on P sorption cannot adequately be explained by pH differences. This is substantiated by the data for Egmont soil. Although the pH values in 10^{-2}M Ca, 10^{-3}Ca, 10^{-1}M Na, and 3×10^{-2}M Na were similar, large differences in the amounts of P sorbed from these media were observed (Fig. 4.1 and 4.2).

A further evaluation of the effect of pH on P sorption from 10^{-2}M Ca and 10^{-1}M Na systems was facilitated by adjusting the pH of these two systems to various values within the range of pH values obtained with other support media (Table 4.2). The effect of pH on the final P concentrations maintained from P additions of 3,000, 1,500, and 400 µg/g to Egmont, Okaihau, and Porirua soils, respectively, is illustrated by data in Fig. 4.3. The final P concentrations maintained in dilute, relative to the more concentrated, support media are many times greater than would be expected if pH accounted for the differences. For example, if the difference in P sorption by Egmont soil from 10^{-2}M Ca, compared to 10^{-1}M Na, was solely a pH effect, final P concentrations would have been 3.40 and 4.25 µg/ml, respectively (*a and *b in Fig. 4.3.A). The effects of support media, other than pH, on final P concentration are even more pronounced with dilute support media. Observed effects on final P concentration in water, relative to 10^{-1}M Na, are 115, 14.1, and

TABLE 4.2 Effect of support media on supernatant pH values (average values over the isotherm)

Soil	pH value in						
	10^{-2}M Ca	10^{-3}M Ca	10^{-4}M Ca	10^{-1}M Na	3×10^{-2}M Na	10^{-4}M Na	Water
Egmont	6.78	6.79	7.28	6.70	6.83	7.33	7.34
Okaihau	4.74	4.84	5.77	5.05	5.62	-	6.33
Porirua	4.44	4.79	5.36	4.55	4.88	5.90	5.79
Waikakahi	7.97	7.91	8.13	8.05	8.09	-	7.99

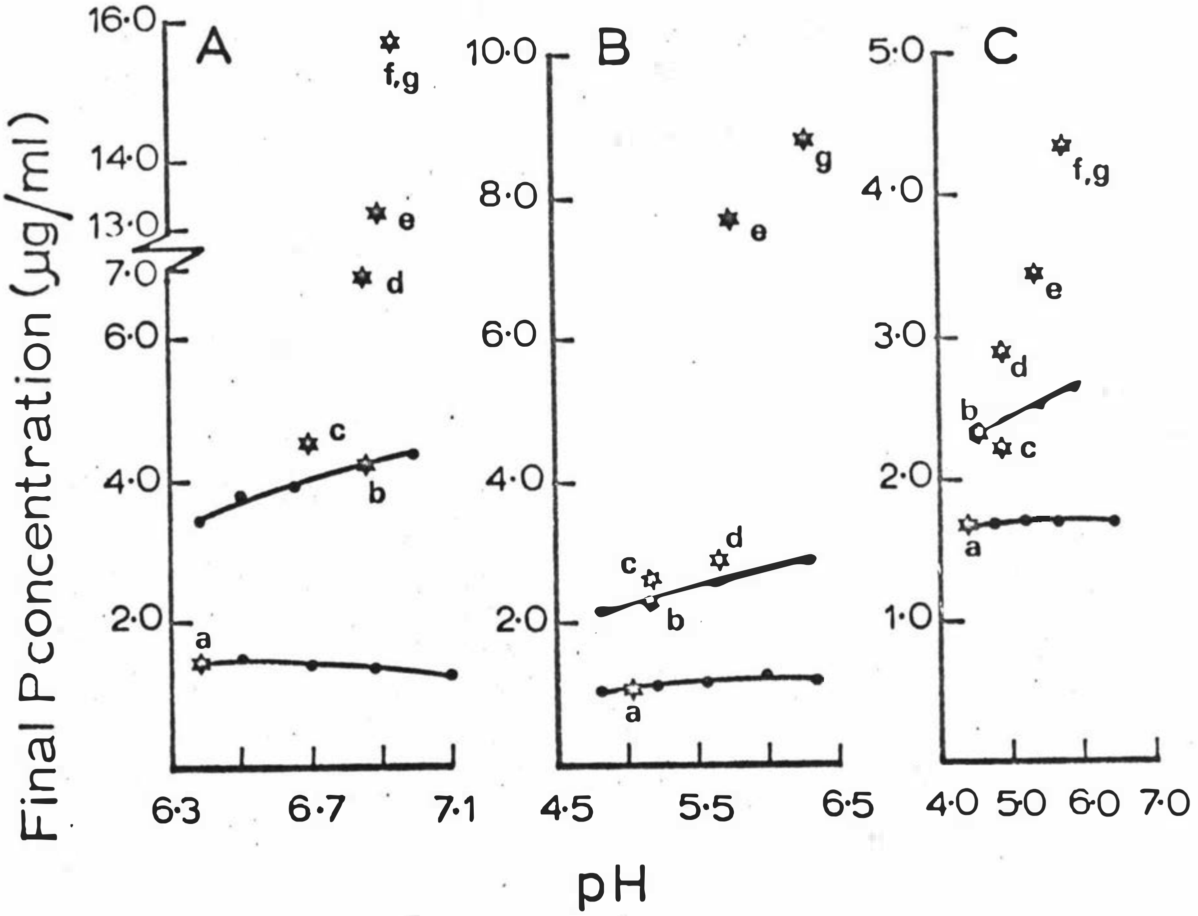

FIG. 4.3 Relationship (✱) between final P concentration and ambient pH induced by various support media for given additions of P to three soils, and dependence (●) of final P concentration maintained in 10^{-2}M Ca and 10^{-1}M Na systems upon pH adjustment over the range of ambient pH values induced by the other support media. A shaking time of 40 hr was used.
A = Egmont, P added = 3,000 µg/g; B = Okaihau, P added = 1,500 µg/g; C = Porirua, P added = 400 µg/g. a = 10^{-2}M Ca, b = 10^{-1}M Na, c = 10^{-3}M Ca, d = 3 x 10^{-2}M Na e = 10^{-4}M Ca, f = 10^{-4}M Na, g = water.

5.25 times greater, for Egmont, Okaihau, and Porirua soils, respectively, than can be accounted for by differences in pH (Fig. 4.3).

Although pH does affect the amounts of P sorbed from a given support medium, it does not account for the differences in P sorption from different support media. Rajan and Fox (1972) also concluded that pH effects on P sorption were small compared to support medium effects, although no data were presented to support their conclusion.

4A.3.2.3 Kinetic effects. The sorption isotherms (Fig. 4.1 and 4.2) suggest that at very low final P concentrations, isotherms obtained in different support media are equivalent. As final P concentration increased, the isotherms diverged rapidly and then maintained a fairly constant difference, which slowly increased (e.g., Egmont) or decreased (e.g., Porirua), depending on the relative approach to the maximum sorption. This observation led to an investigation of the kinetic effects of P sorption.

The rate of P sorption by the soils was initially very rapid, and this was followed by a progressively slower reaction which proceeded for several days (Fig. 4.4) and even weeks, as discussed in Chapter 3. The approach to equilibrium at times in excess of approximately 40 hr with Egmont, Okaihau, Porirua, and Waikakahi soils using high (2,500, 1,500, 700, and 500 µg P/g, respectively) and low (750, 600, 100, and 50 µg P/g, respectively) in 10^{-2}M Ca, 10^{-4}M Ca, and 10^{-1}M Na varied appreciably (Fig. 4.4). For a given time, the proximity to equilibrium depended on the support medium and the level of added P, as illustrated by the shape and relative position of the sorption rate curves. The data in Fig. 4.4 suggest a greater initial rate of P sorption from 10^{-2} M Ca compared to 10^{-1}M Na and 10^{-4}M Ca systems. Consequently, the magnitude of the differences in P sorption obtained in different support media at 40 hr appear to depend largely on the proximity to equilibrium. Extrapolation of the curves in Fig. 4.4 to probable equilibrium positions suggests convergence, implying the elimination of support medium effects.

In order to estimate the solution P concentration of equilibrated systems without shaking for excessive periods of time,* a graphical approach was used. This involved establishing a linear relationship between a parameter of time and P concentration in solution, and extrapolating to a point corresponding to infinite time.

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*see page 97

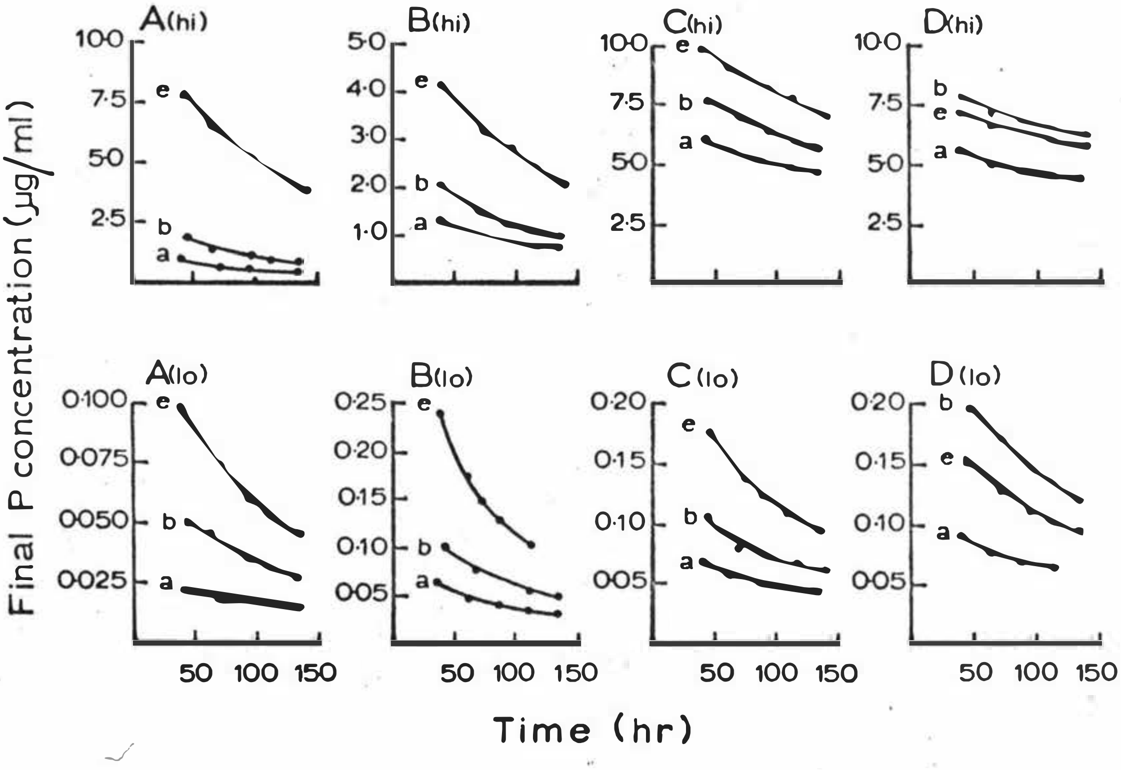

FIG. 4.4 Relationship between final P concentration in three support media and time over a period of 40 to 144 hr for two additions of P to each soil.

A = Egmont, P added (hi) = 2500 µg/g, (lo) = 750 µg/g;
B = Okaihau, P added (hi) = 1500 µg/g, (lo) = 600 µg/g;
C = Porirua, P added (hi) = 700 µg/g, (lo) = 100 µg/g;
D = Waikakahi, P added (hi) = 500 µg/g, (lo) = 50 µg/g.
a = 10^{-2}M Ca, b = 10^{-1}M Na, e = 10^{-4}M Ca.

At infinite time, the P concentration is considered to be the equilibrium P concentration. The relationship between final P concentration at time t and $^1/t$ for times from approximately 70 to 144 hr was linear for both high (Fig. 4.5) and low (Fig. 4.6) additions of P, and could be extrapolated (dashed line) to the ordinate. For a given soil and addition of P, the extrapolated relationships (Fig. 4.5 and 4.6) gave the same, or virtually the same, P concentration in solution at infinite time ($^1/t = 0$) irrespective of the support medium used.

The data in Fig. 4.5 and 4.6 suggest quite strongly that the differences in P sorption by the soils from the various support media are kinetic in origin and can be eliminated by ensuring that an equilibrium condition is attained. Consequently, isotherms for P sorption from various support media would be coincident, providing equilibrium P concentrations had been determined for each addition of P and each support medium used. Minor differences in the isotherms obtained may be due to the effects of pH induced by the different media. These differences would be small, as may be judged from the discussion of data presented in Fig. 4.3 and from the slight differences in estimates of equilibrium P concentration obtained from Fig. 4.5 and 4.6.

4A.4 Discussion

The effect of the support medium on P sorption during 40 hr (Fig. 4.1 and 4.2) has been shown to involve only a parameter of the overall sorption process, namely the rate of P sorption (Fig. 4.5 and 4.6). The following discussion of support media effects on P sorption rate assumes specific sorption of P (Hingston et al., 1967) at the amphoteric surface of Fe and Al hydrous oxides (Parks and de Bruyn, 1962) or other soil components of similar surface structure. Such surfaces will support varying positive charge densities over the range in pH values encountered in this study (Parks and de Bruyn, 1962; van Raij and Peech, 1972) as discussed in Chapter 1, and a diffuse layer of anions will develop.

An increase in ionic strength (i.e., counter ion concentration) decreases the thickness of the diffuse layer (equation 1.6),

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*Long shaking periods are undesirable because of possible effects of particle breakdown and microbial assimilation on observed changes in solution P concentration. The former can be shown to be unimportant over periods of at least seven days as discussed in Chapter 3. Microbial assimilation is difficult to evaluate but can be depressed by the use of microbial inhibitors, such as $HgCl_2$, as used in this study.

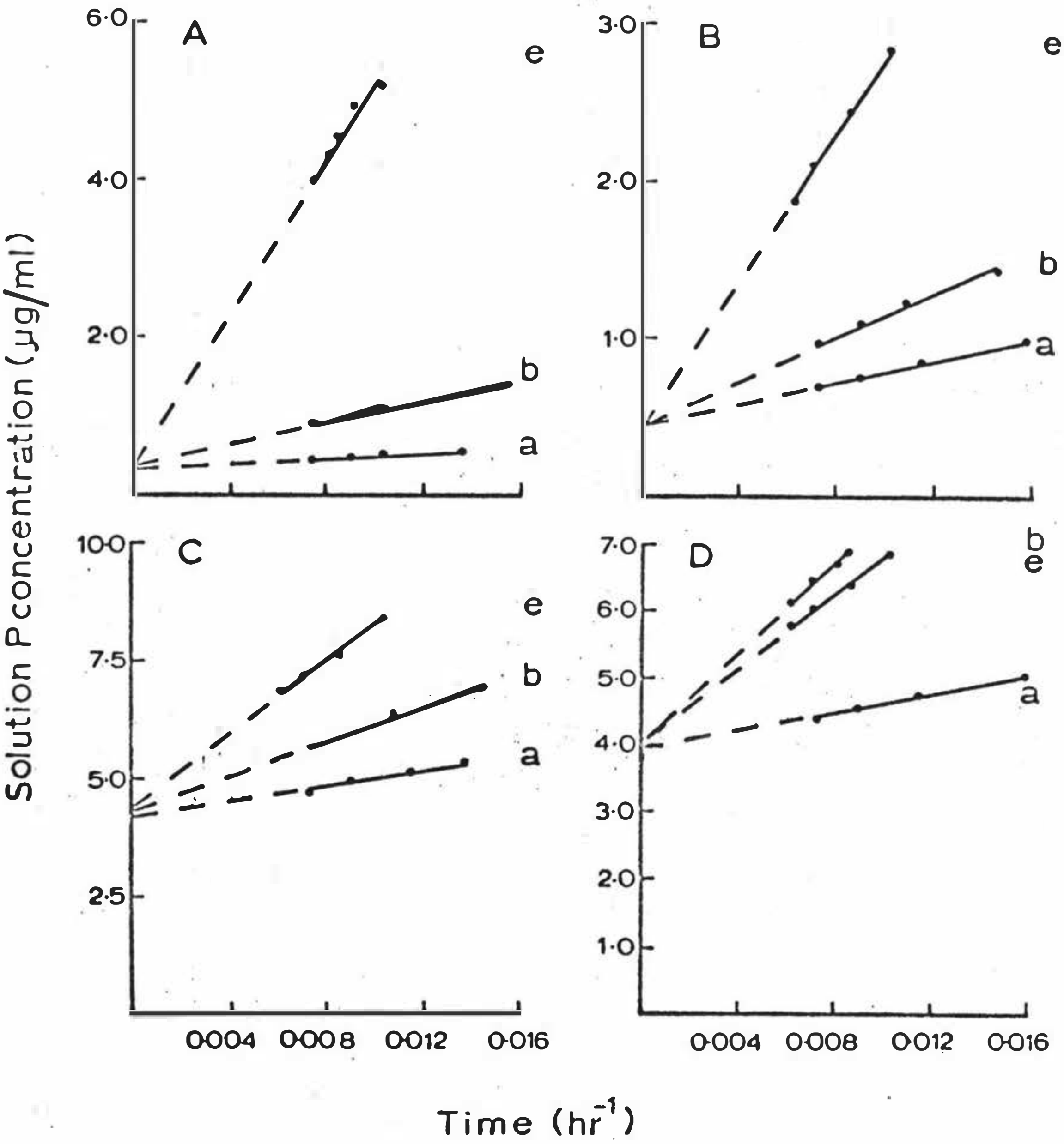

FIG. 4.5 Relationship between final P concentration, maintained in three support media from "high" additions of P, and reciprocal of time; dashed lines used to extrapolate the data to the ordinate, i.e., $1/t = 0$, $t = \infty$, to estimate equilibrium P concentration.
A = Egmont, P added = 2500 μg; B = Okaihau, P added = 1500 μg/g; C = Porirua, P added = 700 μg/g; D = Waikakahi, P added = 500 μg/g
a = 10^{-2}M Ca, b = 10^{-1}M Na, e = 10^{-4}M Ca.

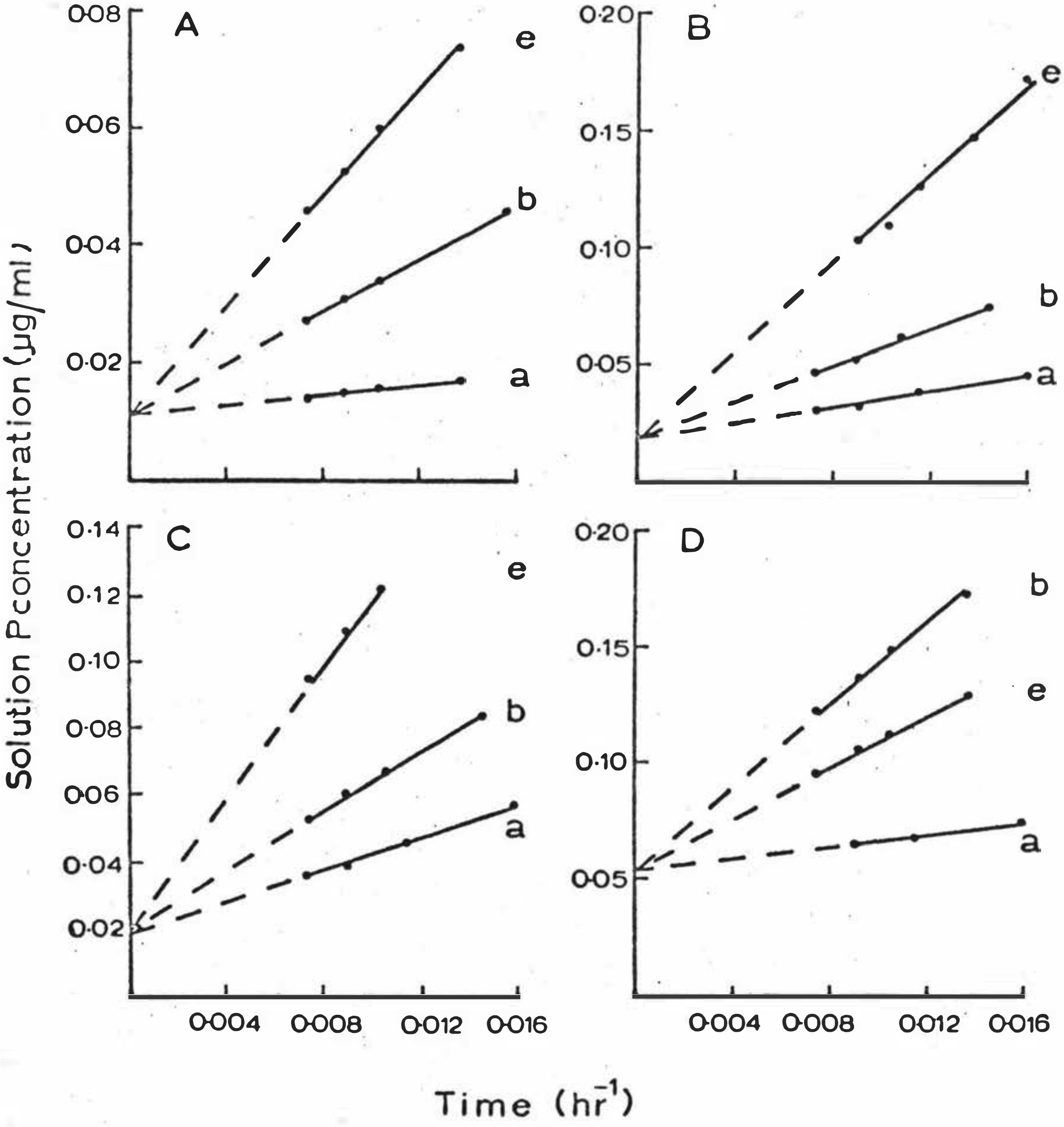

FIG. 4.6 Relationship between final P concentration, maintained in three support media from "low" additions of P, and reciprocal of time; dashed lines used to extrapolate the data to the ordinate, i.e., $1/t = 0$, $t = \infty$, to estimate equilibrium P concentration.
A = Egmont, P added = 750 µg/g; B = Okaihau, P added = 600 µg/g; C = Porirua, P added = 100 µg/g; D = Waikakahi, P added = 50 µg/g. a = 10^{-2}M Ca, b = 10^{-1}M Na, e = 10^{-4}M Ca.

and thereby the volume of the inner solution. Consequently, if the charge on the surface remains constant, the concentration of anions in the diffuse layer will increase. An increase in ionic strength at constant pH, however, also increases the surface charge (Parks and de Bruyn, 1962), and consequently the absolute amounts of anions in the inner solution. For soils, however, this effect is probably small because pH also shifts with a change in ionic strength in a direction tending to maintain surface charge.

For a given level of P addition, the proportion of chloride (common to all support media) relative to phosphate in the outer solution increases with support medium concentration. The selectivity of the surface for P relative to chloride (Hingston et al., 1972), suggests that the proportion of chloride to phosphate would not increase to the same extent in the inner solution. This assumption, in association with the effect of ionic strength on the concentration of anions in the inner solution, implies an increase in P concentration at the sorbing surface. Such an increase would enhance the initial rate of P sorption, resulting in a closer approach to equilibrium at times in excess of 40 hr in 10^{-2}M Ca, as compared to 10^{-4}M Ca systems (Fig. 4.5 and 4.6).

Cation species also affects the rate of P sorption, as evidenced by the closer approach to equilibrium in 10^{-2}M Ca as opposed to 10^{-1}M Na systems (Fig. 4.5 and 4.6). The specific sorption of Ca by hydrous metal oxides has been demonstrated by Breeuwsma and Lyklema (1973) and Kinniburgh et al., (1975), and may lead to an increase in the positive charge at the surface (Kinniburgh et al., 1975). An increase in surface positive charge will increase the initial rate of P sorption by increasing the P concentration in the inner solution. The fact that the same equilibrium P concentration was obtained in both 10^{-2}M Ca and 10^{-1}M Na systems suggests that only the rate of sorption is affected, and that P is not sorbed specifically at localised positively charged sites induced by specific sorption of Ca. For support media containing increasing concentrations of $CaCl_2$, the effects of ionic strength and specific sorption of Ca on P sorption rate are compounded.

The above discussion clearly points to the origin of the discrepancies between P sorption isotherms obtained using different support media during times less than that required to attain equilibrium. The magnitude of these discrepancies will depend on the contact time between soil and added P (Fig. 4.5 and 4.6) and will reflect the effect of different support media on the rate of P sorption. For P sorption during 40 hr, the effect of ionic strength alone on the rate of P sorption can be judged from the discrepancies between isotherms obtained using water, 10^{-4}M, 3 x 10^{-2}M, and 10^{-1}M Na systems (Fig. 4.1 and 4.2). Discrepancies between isotherms obtained using 10^{-4}M, 10^{-3}M, and 10^{-2}M Ca illustrate the compounded effects of increasing ionic strength and specific sorption of Ca, on P sorption rate. The effect of cation species alone on the rate of P sorption is indicated by the discrepancies between isotherms obtained using 3 x 10^{-2}M Na and 10^{-2}M Ca, which have the same ionic strength and similar chloride concentrations. If the equilibrium condition is estimated, however, isotherms obtained using different support media will be coincident, as implied by the data in Fig. 4.5 and 4.6.

The effect of ionic composition of the support medium on the rate of P sorption has not been considered in previous studies. In these studies "equilibration" times, or more strictly contact times between the P-containing solution and the soil, have ranged from 18 hr (Mattson et al., 1950) to 144 hr (Rajan and Fox, 1972). Consequently, support medium effects on P sorption, similar to those in Fig. 4.1 and 4.2 have previously been considered absolute. It is of interest, however, that Wiklander (1950) observed that "salt concentration", affected only the rate of isotopic P exchange rather than the actual amounts of exchangeable P, an observation in accord with those reported in this study.

The findings of the present study have several implications to P sorption studies. The importance of equilibrium in P sorption studies with soils has been shown in terms of the effects that only partial approach to equilibrium have on interpretations of the data and concepts related to P sorption mechanisms. The present findings are therefore of direct relevance to studies where interpretations are based upon the assumption that equilibrium has been attained. The equilibrium condition implied in the derivation of the Langmuir equation, which has been used extensively to describe P sorption by soils (Olsen and Watanabe, 1957; Syers et al., 1973b), is a particular case in point.

The results presented in this paper suggest that if an equilibrium condition is to be attained, the support medium employed is of practical and not theoretical concern, in as much that a rapid reaction rate is desirable in order to minimise equilibration time. In such cases a support medium of high ionic strength and containing a divalent cation is desirable. To avoid high concentrations of divalent cations and the possible precipitation of sparingly soluble phosphates in such systems at high P additions, however, a support medium of high ionic strength containing cations of soluble phosphates may be preferred (e.g., 10^{-1}M NaCl).

An equilibrium condition is not always desired, especially in P sorption experiments aimed at describing the short-term effects of P fertilizer addition, the relationships of P between aqueous and particulate phases of a runoff or stream environment, or the ability of soils and soil components to remove P from effluents. The need for careful choice of support media in studies similar to those mentioned above is evident from the results presented. The support medium should reflect the cation status as well as the ionic strength of the aqueous phase of the system under consideration.

4B. Calcium retention in response to phosphate sorption by soils

4B.1 Introduction

In the evaluation of the effect of cations and ionic strength on the sorption of inorganic phosphate (P) by soils, discussed in part A of this Chapter, it was noted that as the amount of P sorbed increased there was a concommittant increase in the amount of Ca retained by the soils. In the absence of further experimental data, these observations may imply that both Ca and P are removed from solution by a precipation reaction. Such a precipitation reaction at the surface of sorbing components in soils has been proposed (Wild, 1950; Volkweiss *et al.*, 1973) to explain the greater retention of P with increasing Ca concentration in the support medium. In this study the retention of Ca in response to P sorption by soils is evaluated to provide a better understanding of the origin of the effect.

4B.2 Materials and Methods

Air-dried < 2 mm samples of horizons of Egmont, Okaihau, and Porirua soils were used in this study.

Retention of Ca was evaluated for each soil during P sorption from 10^{-2} and 10^{-3}M Ca systems. The basic experimental system was the same as that described in Chapter 2. Additions of P, depending on the soil and support medium (see Table 4.3) were chosen to cover a final P concentration range up to 10 µg P/ml after a 40-hr sorption period. The same soils were also shaken for 40 hr with 10^{-2} and 10^{-3}M Ca containing no added P, but K (as KCl) was added in amounts equivalent to those resulting from P additions (KH_2PO_4). After the 40-hr shaking period, the supernatants were recovered by centrifugation and inorganic P concentration determined. The concentration of Ca in the supernatants was also determined by flame emission spectrophotometry.

The release of Ca and P, retained in the previous sorption step to solutions of KCl was evaluated by washing the soils four times with 20 ml of 1 M KCl. The amounts of Ca and P were determined in the combined extracts and corrected for the amounts of Ca and P carried over in the entrapped solution from the sorption step.

4B.3 Results

Isotherms for the sorption of added P during 40 hr by Egmont, Okaihau, and Porirua soils from 10^{-2} and 10^{-3}M Ca and water, have been given previously (Fig. 4.1 and 4.2). At a final P concentration of 9 µg P/ml, the amount of P sorbed by each soil from the 10^{-2}M Ca system is approximately twice that sorbed from water, whereas the amount of P sorbed from 10^{-3}M Ca is intermediate to that sorbed from 10^{-2}M Ca and water.

The retention of Ca by the soils during P sorption over a period of 40 hr, is given in Table 4.3. Data for Ca retention represent only that arising as a direct result of P sorption. Such data were computed from net Ca retention in systems containing P, corrected for Ca retention in systems containing the same concentration of all ions, but no P.

The amounts of Ca retained (Table 4.3, column 3) were independent of the amounts of Ca added, and the values for the molar ratio of Ca : P retained were rather constant, particularly for Egmont and Okaihau soils. The amounts of Ca retained which are released during washing with 1M KCl, are given in column 6 (Table 4.3). Essentially complete recovery of retained Ca is achieved. In contrast, the amounts of P desorbed (column 7) were only a small fraction of those sorbed. This fraction ranged from 0 to $<$ 5% for Egmont and Okaihau soils, and from 0 to approximately 10% for Porirua soil. The highest recoveries of sorbed P were obtained for the highest P sorption saturations. The low but slowly increasing recovery of sorbed P is reflected in the tendency of the ratio Ca : P released to decrease with increasing sorption saturation.

4B.4 Discussion

The increase in P sorption with increasing Ca concentration of the support medium (Fig. 4.1 and 4.2) and the increase in Ca retention with increasing P sorption during 40 hr (Table 4.3) illustrates two important interrelationships between support medium composition and P sorption. The origin of the increased P sorption during 40 hr with increasing Ca concentration of the support medium,was discussed in part A of this Chapter.

TABLE 4.3 Amounts of Ca and P removed from solution during 40 hr and amounts of Ca and P released by washing with 1M KCl.

Ca added	P added	Ca retained	P sorbed	Ratio Ca: P retained*	Ca released	P desorbed	Ratio Ca:P released*
mg/g					(mg/g)		
			EGMONT				
1.60	0.50	0.12	0.50	0.19	0.16	0	-
1.60	1.30	0.40	1.29	0.23	0.44	0.01	65.5
1.60	2.00	0.68	1.96	0.27	0.64	0.02	32.2
1.60	3.50	1.04	3.16	0.25	1.00	0.06	13.4
16.0	0.60	0.20	0.60	0.26	0.24	0	-
16.0	1.60	0.48	1.59	0.23	0.52	0.01	48.9
16.0	3.00	1.08	2.94	0.29	1.02	0.05	20.4
16.0	5.00	2.04	4.62	0.34	2.00	0.17	9.1
			OKAIHAU				
1.60	1.20	0.36	1.16	0.24	0.32	0.02	12.7
1.60	1.50	0.44	1.41	0.24	0.48	0.03	12.2
1.60	2.00	0.60	1.70	0.27	0.60	0.05	9.7
16.0	1.50	0.48	1.45	0.26	0.52	0.03	13.9
16.0	2.00	0.56	1.84	0.24	0.64	0.03	15.7
16.0	2.70	0.84	2.30	0.28	0.92	0.08	8.6
			PORIRUA				
1.60	0.30	0.12	0.26	0.36	0.12	0.03	3.7
1.60	0.60	0.20	0.39	0.40	0.16	0.04	2.8
1.60	0.80	0.24	0.44	0.42	0.20	0.05	3.0
16.0	0.70	0.36	0.47	0.60	0.36	0.05	5.3
16.0	0.90	0.48	0.54	0.69	0.48	0.06	6.0

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* molar basis

The fact that the ratio Ca : P retained is comparable for similar levels of P sorption, in both support media (Table 4.3), suggests that Ca retention is directly related to the extent of P sorption, and is influenced little by ambient Ca concentrations. The retention of Ca in response to P sorption may be explained by the well-established effect of P sorption on the negative charge of soils, generally measured as the cation exchange capacity, which frequently shows a considerable increase subsequent to P sorption. (Toth, 1937; Davis, 1945; Mehlich, 1960; Mekaru and Uehara, 1972; Sawhney, 1974). An increase in negative charge during P sorption requires that as P sorption proceeds, cations are also removed from the ambient aqueous phase. This is well demonstrated by the data for the retention of Ca, obtained in this study. That Ca is retained only in response to an increase in negative charge is substantiated by the fact that essentially complete recovery of retained Ca is obtained during washing with 1M KCl.

If the ratio of Ca : P retained is expressed in terms of equivalents per mole of P sorbed, obtained by multiplying column 5 (Table 4.3) by two, the increase in charge at the surface may be estimated for each level of P sorption. Values of approximately 0.4 to 0.6 equivalents/mole are obtained for Egmont and Okaihau soils. Somewhat higher values are obtained for Porirua soil. These estimates suggest that not all of the P sorbed, assuming that $H_2PO_4^-$ and HPO_4^{2-} are the sorbing species, contributes to the increase in negative charge. This is in contrast to the postulate of Hingston et al., (1968 b, 1972) that P sorption is conditional on an increase in the negative charge of the surface. The implications of this observation to the P sorption mechanism are evaluated in Chapter 6.

The fact that all of the Ca retained, but only a small fraction of the P sorbed could be released by washing with 1M KCl illustrates the difference in the type of interaction involved between the sorbing surface and Ca and P. The interaction between Ca retained in response to P sorption and the surface, appears to be purely Coulombic, Ca being distributed throughout the diffuse layer developed at the sorbing surface which, as Ca retention data implies, carries a net negative charge subsequent to P sorption. The fractional desorption of P, however, reflects the covalent character of the interaction between P and the sorbing surface.

The increasing sorption of P during 40 hr with increasing Ca concentration of the support medium (Fig. 4.1 and 4.2), and the fact that Ca retention in response to P sorption gives rather similar ratios of Ca : P retained (Table 4.3), may at first suggest that P is retained by a precipitation reaction. Such a reaction has been implied by previous workers (Wild, 1950; Volkwiess et al., 1973). Volkwiess et al (1973) have proposed that P sorption in Ca systems involves precipation of P with Ca and Al in the double layer of aluminosilicates to form a discrete-P phase resembling crandallite. These workers also implied that increasing P sorption in systems containing increasing Ca concentration, could also be explained by a precipitation reaction. The low Ca : P retained ratios and the fact that in both Ca and Na systems, the same estimate of equilibrium P concentration was obtained (Fig. 4.5 and 4.6), are not compatible with the precipitation of a calcium phosphate. In particular, however, the essentially complete recovery of retained Ca during washing with KCl, eliminates any possibility of calcium phosphate precipitation in the experiments reported in this study, and possibly many other studies reported in the literature.

CHAPTER 5

INTERPRETATION OF PHOSPHATE SORPTION BY SOILS USING THE LANGMUIR EQUATION

5.1 Introduction

The sorption of inorganic phosphate (P) by soils may conveniently be described by a sorption isotherm, which represents the distribution of P between a soil and the contacting aqueous phase at constant temperature. Sorption data may also be tested for fit against several equations derived from sorption models, some of which provide useful information concerning the sorption reaction involved. The equation developed by Langmuir (1918) is particularly useful, because from this equation, constants relating to sorption maximum and sorption energy may be calculated. Although the Langmuir equation was originally developed to describe gas adsorption by solids, an analysis of its application to sorption from aqueous solution has been given by Giles (1970).

The Langmuir equation has frequently been used to describe P sorption by soils (Olsen and Watanabe, 1957; Shapiro and Fried, 1959; Fox and Kamprath, 1970; Syers et al., 1973 b; Schwertmann and Knittel, 1973; Holford et al., 1974). The most recent of these studies, however, have shown that P sorption data are described by more than one Langmuir equation, over final solution P concentration ranges of 0 to approximately 15 μgP/ml. Interpretation of P sorption data based on the Langmuir equation is further complicated by the fact that equilibrium data have not been used, despite the equilibrium condition which is implicit in the derivation of the Langmuir equation. Evaluation of sorption data has also been hampered by the limited amount of data used by many workers, particularly at low final P concentrations (Gunary, 1970; Bache and Williams, 1971). Consequently, adequate understanding and interpretation of P sorption relationships obtained using the Langmuir equation, have not been achieved.

The purpose of this study is to evaluate the sorption of added P by four contrasting soils, under both equilibrium and non-equilibrium (40-hr) conditions, with a view to providing a more precise understanding of the Langmuir relationships involved in P sorption. A method of resolving data when more than one Langmuir equation is involved, is proposed. The effect of non-equilibrium conditions, adsorption and absorption reactions (Chapter 3), and the importance of obtaining sufficient data to adequately describe P sorption by soils, are discussed. The P sorption data obtained under equilibrium conditions are discussed in terms of the P sorption mechanism.

5.2 Materials and Methods

Air-dried, < 2 mm samples of horizons of Egmont, Okaihau, Porirua and Waikakahi soils were used in this study.

The sorption of added P was evaluated over five time intervals, ranging from 40 to approximately 140 hr. The maximum additions of P were 6000, 4000, 1600, and 1250 μgP/g for Egmont, Okaihau, Porirua and Waikakahi soils, respectively. The appropriate amount of P was added in a 5-ml aliquot at recorded times of 0 and approximately 24, 48, 72 and 96 hr after commencing to shake 1-g samples of each soil with 35 ml of 10^{-1}M NaCl containing 40 μg $HgCl_2$/ml. Shaking was continued for 40 hr. Consequently, the total shaking time for each system was the same, but the time of contact between soil and added P varied. The sorption of P during 40 hr was determined for all soils. Other contact times were known from the time at which the P addition was made and the time at which solid and aqueous phases were separated. These additional contact times were approximately 72, 96, 120 and 140 hr. After shaking, all systems were centrifuged and dissolved inorganic P determined.

Native exchangeable P was determined at four time intervals by a method similar to that described above. Carrier-free ^{32}P (2.0μCi) was added in a 1-ml aliquot at appropriate times after commencing to shake 1-g samples of each soil in 10^{-1}M NaCl containing $HgCl_2$. The times of contact between added ^{32}P and the soils were 71, 91, 113, and 135 hr, although the total shaking time for each system was constant. After 135 hr, the tubes were centrifuged and solution ^{31}P concentration determined. Solution ^{32}P concentration was determined as described previously (Chapter 3). Native exchangeable P for each time of contact was determined from isotope dilution theory. An estimate of "native sorbed P" was obtained by plotting native exchangeable P values at each time of contact against 1/t and extrapolating the resulting linear relationship to 1/t = 0 (infinite time).

5.3 Results

Data for P sorption at various levels of added P were obtained for all soils at both equilibrium and 40 hr. For reasons of simplicity, however, only equilibrium data for Porirua soil are presented in detail. These data are used to illustrate the type of data obtained and the method of data resolution. Data obtained for Egmont, Okaihau and Waikakahi soils are presented, as appropriate, to illustrate the similarity in the data obtained for all of the soils used.

5.3.1 Equilibrium and 40-hr isotherms

Data for the relationship between solution P concentration and time (plotted as 1/t) at various additions of P to the Porirua soil are given in Fig. 5.1. The cause of the progressive decrease in solution P concentration with time has been discussed previously (Chapter 3) where it was shown that for contact times $>$ 70 hr the change in solution P concentration could be described by a single first-order reaction.

Isotherms for P sorption by the Porirua and Waikakahi soils are given in Fig. 5.2 for two final P concentration ranges. The term "final P concentration" is used in this Chapter, except where specified, to denote solution P concentration data subsequent to sorption under both the equilibrium and 40-hr conditions. The term "equilibrium P concentration" is used in Figure legends when only equilibrium data are presented.

Data from which the equilibrium isotherms (a in Fig. 5.2) were constructed, were obtained by extrapolating the relationship between solution P concentration and 1/t to the ordinate ($t = \infty$), for various P additions to each soil (c.f., dashed lines in Fig. 5.1 for Porirua soil). The amount of added P sorbed at each level of P addition was computed from the equilibrium P concentration at 1/t = 0. Isotherms at 40 hr (b in Fig. 5.2) were constructed directly

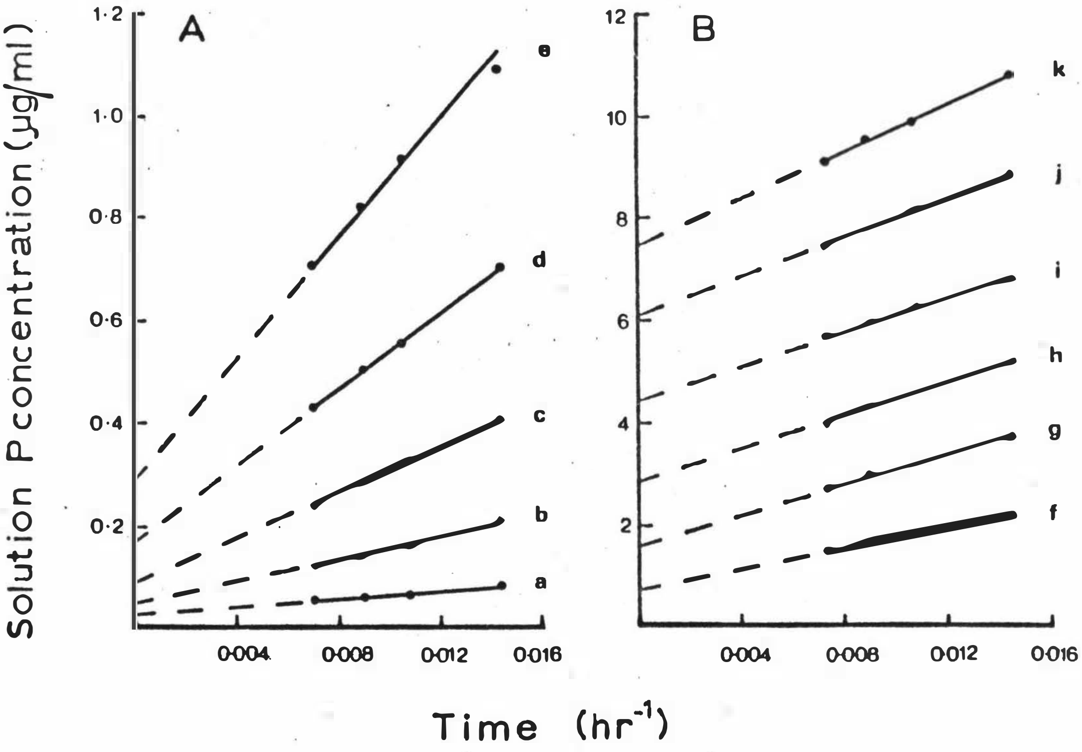

FIG. 5.1 Solution P concentration as a function of time ($^{1}/_{t}$) for various P additions to the Porirua soil. Data extrapolated to ordinate (dashed line) to obtain an estimate of equilibrium P concentration. A = Solution P concentration of 0 to 1.2 µgP/ml, B = solution P concentration of 0 to 12 µgP/ml. Added P (µg/g) a = 100, b = 150, c = 200, d = 250, e = 300, f = 400, g = 500, h = 600, i = 700, j = 800, k = 900.

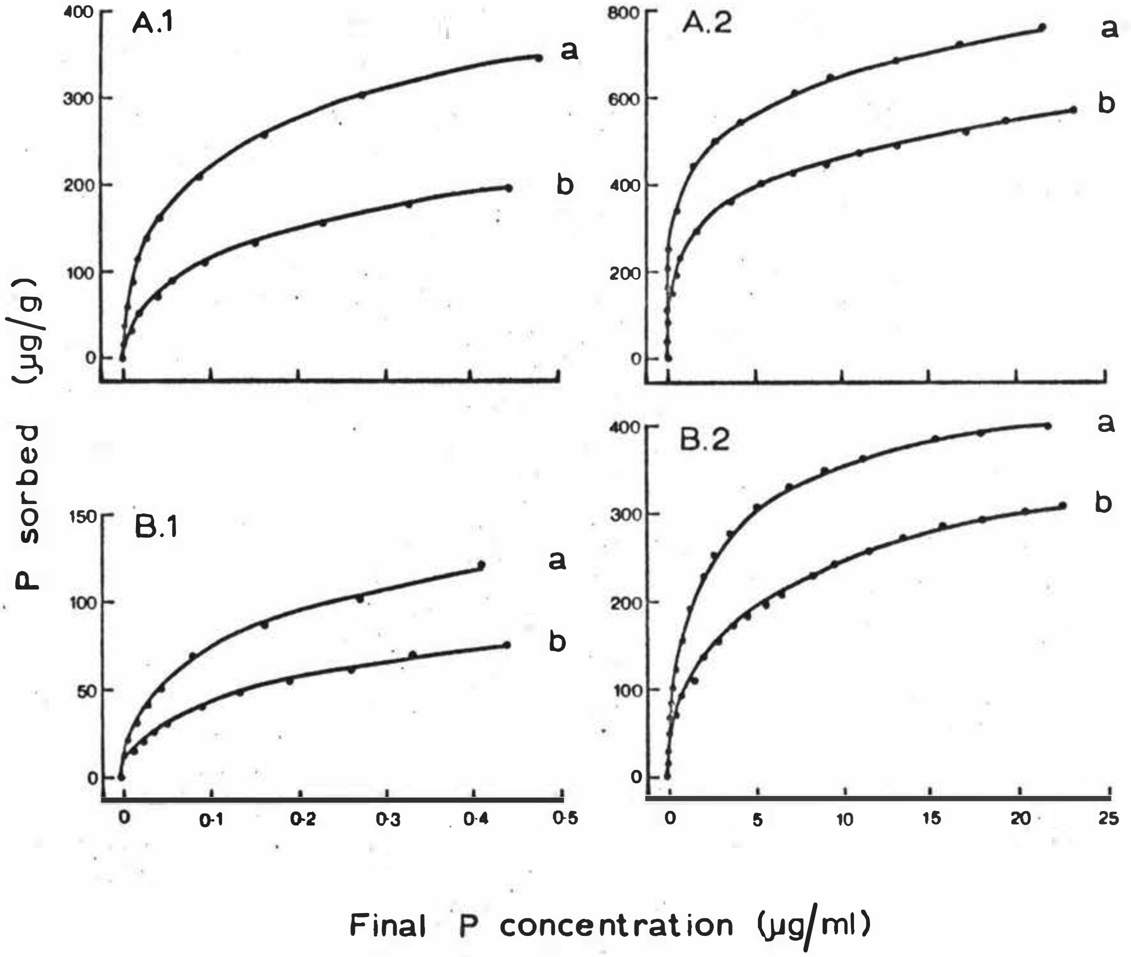

FIG. 5.2 Isotherms for P sorption by the Porirua and Waikakahi soils at equilibrium and 40 hr over two final P concentration ranges. Porirua soil, A.1 = final P concentration 0 to 0.5 µgP/ml, A.2 = final P concentration 0 to 25 µgP/ml. Waikakahi soil, B.1 = final P concentration 0 to 0.5 µgP/ml, B.2 = final P concentration = 0 to 25 µgP/ml. a = equilibrium isotherm, b = 40-hr isotherm.

from 40-hr experimental data. Values for native sorbed P (13 and 12 µg P/g for Porirua and Waikakahi soils, respectively) as determined using ^{32}P at infinite time, were added to all values of sorbed added P to give the values of "P sorbed" (ordinate in Fig. 5.2) at each final P concentration.

Appreciable differences between the amount of P sorbed at a given final P concentration were evident for equilibrium and 40-hr isotherms. The differences were greater for low final P concentrations, particularly for the Porirua soil (Fig. 5.2.A.1). For example, at a final P concentration of 0.06 µgP/ml for the Porirua soil (Fig. 5.2.A.1), the amount of P sorbed at 40 hr (b) was 90 µgP/g whereas at equilibrium (a) the value was 180 µgP/g. The relative difference between the amounts of P sorbed at 40 hr and at equilibrium became less, and fairly constant, over the P concentration range of 1 to approximately 25 µgP/ml (Fig. 5.2.A.2). The considerably greater discrepancies between isotherms at low, relative to high P concentrations, arise from the fact that relatively large changes in final P concentrations below 1 µgP/ml result in little change in the amounts of P sorbed. This effect has been discussed previously (Chapter 3).

Both 40-hr and equilibrium isotherms (Fig. 5.2), however, are of the same type, namely "H-type" isotherms according to the classification of Giles et al.(1960). The only difference between the isotherms is that H-type character is more accentuated at equilibrium than at 40 hr.

Although the isotherms at equilibrium and 40 hr (Fig. 5.2) are not strictly of the Langmuir type, de Boer (1953) has shown that the application of the Langmuir equation to H-type isotherms may be valid if more than one population of sorption sites is assumed.

5.3.2 Fit of data to the Langmuir equation

An evaluation of P sorption data can be made using the rearranged form of the Langmuir equation (1.20) :

$$1/x = 1/Kbc + 1/b$$

where x = amount of P sorbed, c = final P concentration, and K and b are constants relating to the sorption energy and sorption maximum, respectively. For data conforming to equation (1.20), a linear relationship, of slope $1/Kb$ and intercept $1/b$, is obtained for a plot of $1/x$ against $1/c$.

The reciprocal nature of equation (1.20) emphasises low final P concentrations and is particularly useful for evaluating sorption data obtained for the lowest measurable differences in final P concentration (i.e., in the range of 0 to 0.01 μgP/ml). Over this concentration range, however, the amounts of sorbed added P are frequently comparable to native sorbed P.

The requirement of including an estimate of native sorbed P in the values of sorbed P in isotherm studies is illustrated in Fig. 5.3 by equilibrium data for Porirua and Egmont soils. The plot of $1/x$ against $1/c$ before correction for native sorbed P (b in Fig. 5.3) was curvilinear. After correction for the amounts of native sorbed P (a in Fig. 5.3) the data conformed to the Langmuir equation (equation 1.20). The curvilinear relationships (b in Fig. 5.3) arose from the fact that at low final P concentrations ($<$ 0.01 μgP/ml), the actual amounts of P sorbed were significantly larger than those calculated from the observed final P concentrations and the amounts of added P. When the observed amount of P sorbed exceeded native sorbed P by a factor of approximately 10, the effect of the latter on data fit to the Langmuir equation became negligible (point 4 in Fig. 5.3.A). The fact that data, subsequent to correction for native sorbed P, yielded a linear relationship gives added credibility to the measurement of native sorbed P using isotopic exchangeability at infinite time.

Data points (numbered above 4) in Fig. 5.3.A showed a tendency to deviate from the linear relationship (a). The inclusion of more equilibrium data points (Fig. 5.4) for the Porirua soil, indicated that up to six linear relationships, conforming to equation (1.20), are obtained over the final P concentration range of 0 to approximately 25 μgP/ml (Fig. 5.3.A and 5.4). A single linear relationship was obtained, only if a restricted final P concentration range was considered. Similar data have been obtained for P sorption by the other three soils, at both equilibrium and 40 hr.

A complete evaluation of P sorption could not be made by direct graphical analysis of Fig. 5.3.A and 5.4 (Syers et. al. 1973 b), because the sorption maximum of the first linear relationship

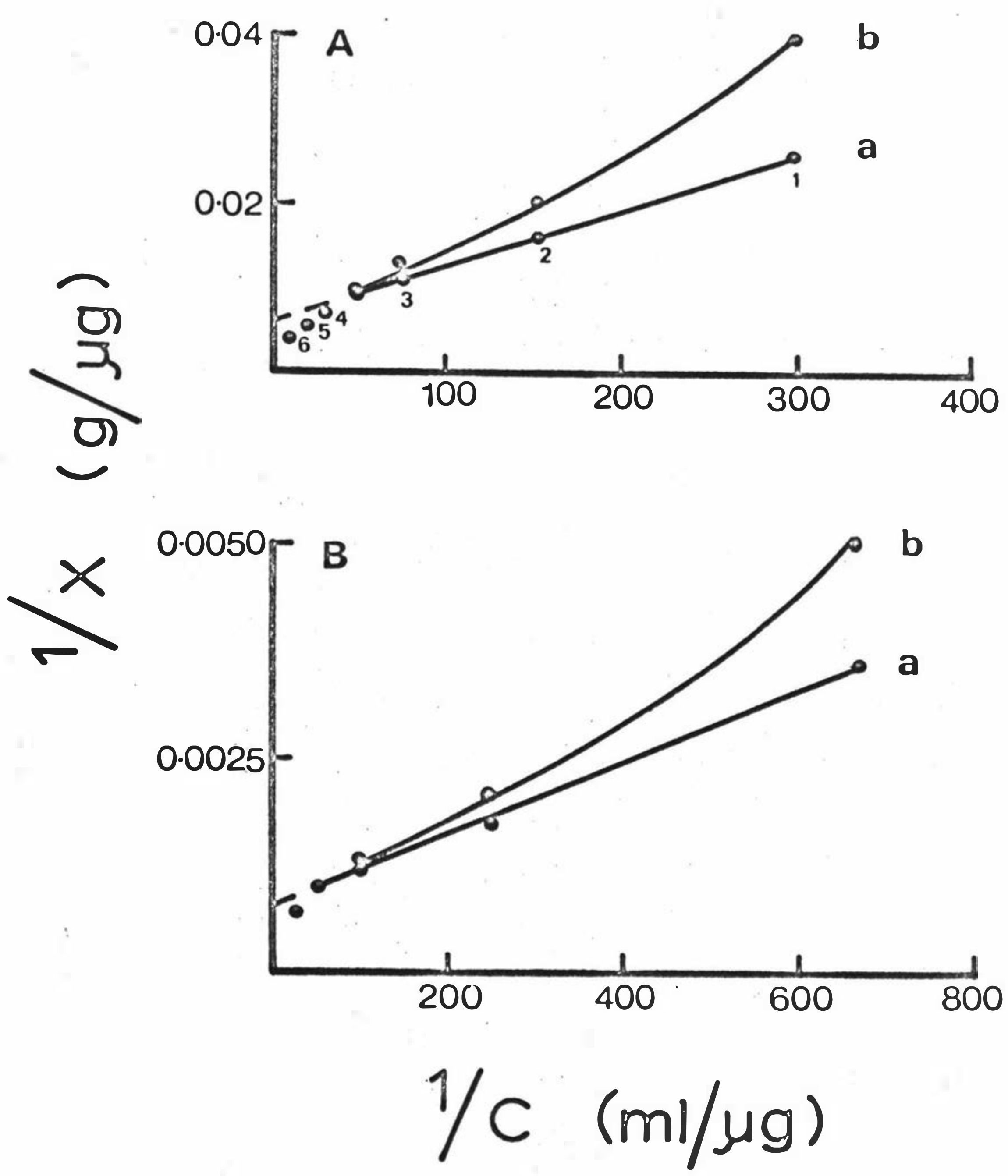

FIG. 5.3 Equilibrium P sorption isotherms for the Porirua (A) and Egmont (B) soils obtained using the Langmuir equation over an equilibrium P concentration range of approximately 0.002 to 0.05 µgP/ml before (b) and after (a) the inclusion of the amount of native sorbed P in the values of P sorbed. Data points are numbered for the Porirua soil to facilitate comparison between Figures.

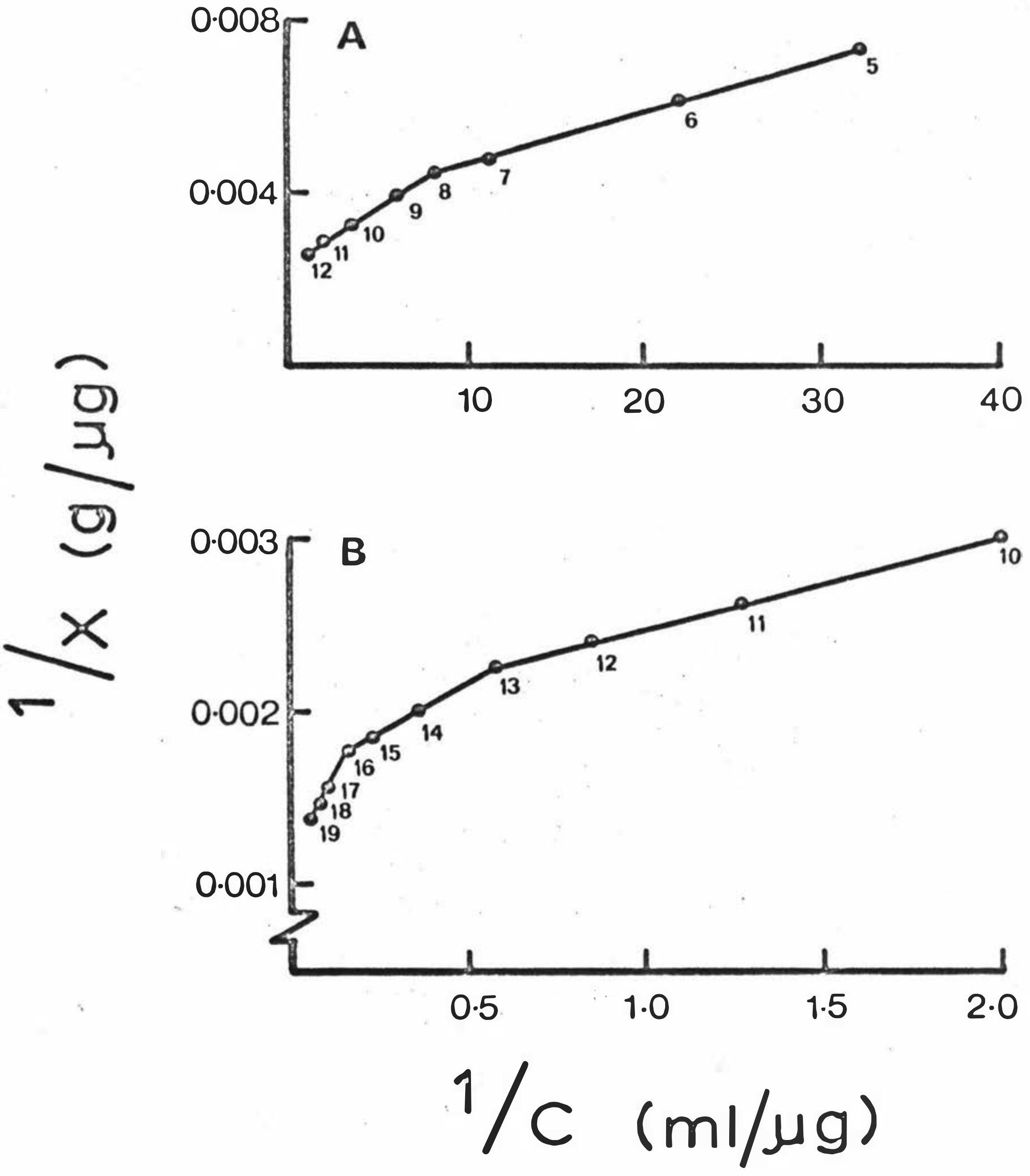

FIG. 5.4 Equilibrium P sorption isotherms for the Porirua soil over two equilibrium P concentration ranges obtained using the Langmuir equation. A = equilibrium P concentration range of approximately 0.03 to 1.00 µgP/ml, B = equilibrium P concentration range of approximately 0.5 to 25 µgP/ml.

(Fig. 5.3.A) was greater than several sorption data points (4 to 7) which deviated from it (Fig. 5.3.A and 5.4). This implied that P was sorbed with a lower sorption energy (K) concurrent with that sorbed with the higher K value which is determined by the first linear relationship. Fig. 5.3.A and 5.4 also implied that some of the linear relationships represented significant P sorption with more than one K value. Consequently, the K value of the first Langmuir relationship (Fig. 5.3.A) will be underestimated and the b value overestimated, by direct graphical analysis. A procedure for resolving compound isotherms (Fig. 5.3.A and 5.4) into distinct isotherms for which the interaction of K values is minimal, was clearly required.

5.3.3 Resolution of Langmuir relationships

Data for P sorption were resolved to determine the number of distinct isotherms involved in the overall sorption of P. This was accomplished by eliminating the effects of P sorption at one K value, upon P sorption at another K value, by a method of successive approximation of both K and b values. An outline of the steps involved is given in Table 5.1. The constants K and b were determined by linear regression analysis at the appropriate steps in the procedure (Table 5.1). The distinct relationships obtained, each conforming to a Langmuir equation, will be referred to hereafter as regions. Region I, is described by the Langmuir constants K_I and b_I, and corresponds to the lowest final P concentration range, etc.

Three distinct regions were obtained for each soil, and three to four approximations were necessary before changes of $< 5\%$ were recorded between successive approximations of a particular K value. The increase in K and decrease in b values with successive approximation (Table 5.2) illustrate the effect of simultaneous sorption with more than one K value, discussed above, on the Langmuir constants obtained at a particular approximation.

The linear relationships obtained at equilibrium, each conforming to equation (1.2), for P sorption by Porirua soil are given in Fig. 5.5. The numbered data points in Figs. 5.3.A and 5.4, which composed the six linear portions of the unresolved relationship,

TABLE 5.1 Schematic representation of the steps involved in the resolution of P sorption data to obtain the Langmuir sorption constants K and b for P sorption by soils over a final P concentration range of 0 to approximately 25 µg P/ml, using a method of successive approximation.

Step	Plot[*]	Determine
1	$1/x - 1/c$ [+]	K_I, b_I
2	–	x_I [‡]
3	–	$x_{II}' = x - x_I$
4	$1/x_{II} - 1/c$	K_{II}, b_{II}
5	–	x_{II} [‡]
6	–	$x_{III}' = x - (x_I + x_{II})$
7	$1/x_{III} - 1/c$	K_{III}, b_{III}
8	–	x_{III} [‡]
9	–	$x_I' = x - (x_{II} + x_{III})$
10	$1/x_I - 1/c$	K_I, b_I
11	–	x_I [‡]
12	–	$x_{II}' = x - (x_I + x_{III})$
Return to step 4	$1/x_{II} - 1/c$	–

Repeat steps 4 to 12 until difference between successive approximations of a particular K value is $< 5\%$.

---

[*] x = P sorbed (observed P sorbed + native sorbed P), c = final P concentration.

[+] For lowest c values (0–0.02 µg P/ml).

[‡] From preceeding K and b values for all values of c.

TABLE 5.2 Values of Langmuir sorption constants obtained at successive approximations of equilibrium P sorption data for Egmont soil by the scheme shown in Table 5.1

Approximation	K_I	K_{II} (ml/µg)	K_{III}	b_I	b_{II} (µg/g)	b_{III}
1	169	2.3	0.09	1456	2025	2967
2	184	3.9	0.14	1258	1613	3236
FINAL	190	4.6	0.14	1218	1506	3240

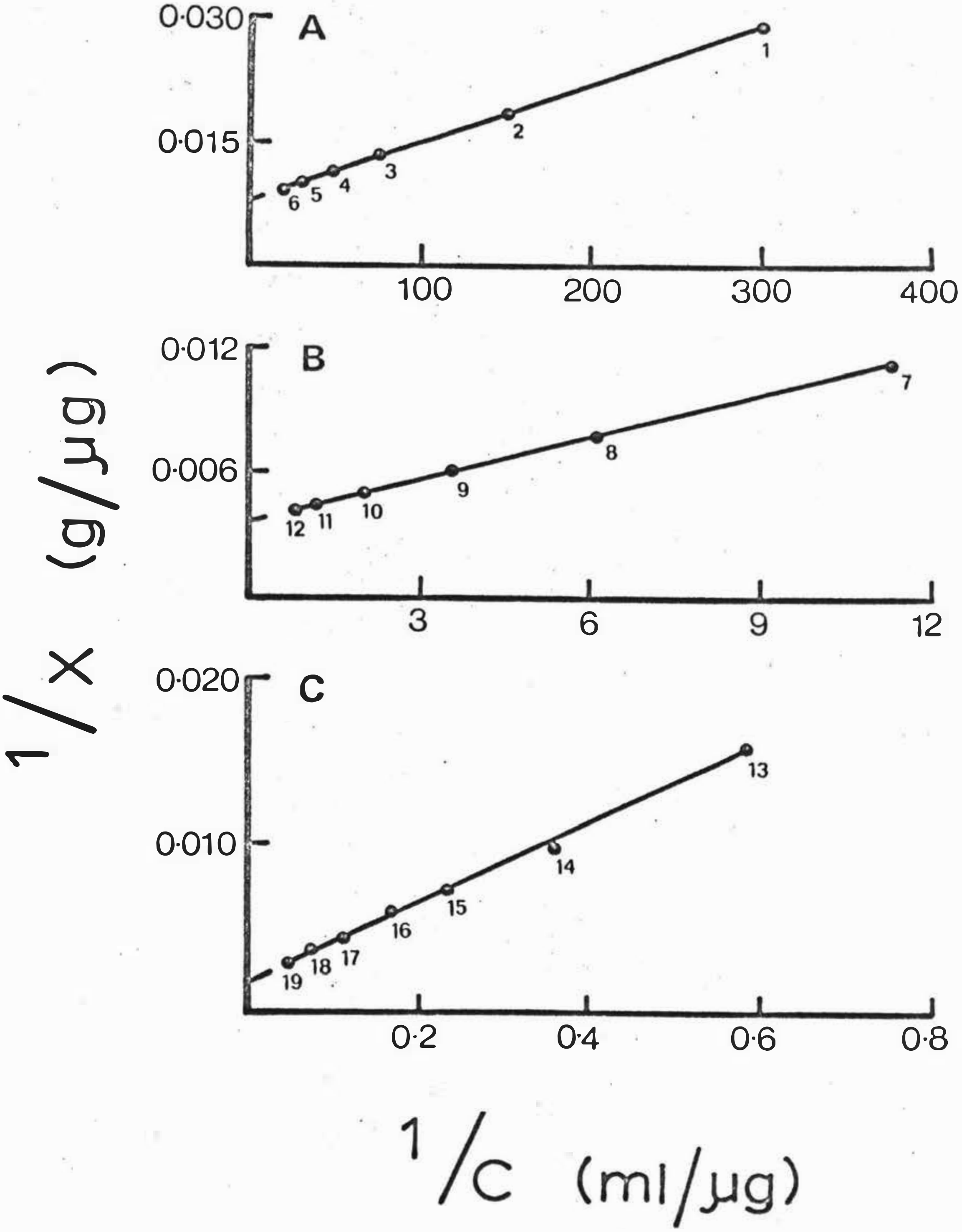

FIG. 5.5 Equilibrium P sorption isotherms for Porirua soil showing the three Langmuir relationships (regions) obtained after resolution of sorption data by successive approximation (see Table 5.1). A = region I, B = region II, C = region III.

can be seen to fit at least one of the three regions obtained (Fig. 5.5) following resolution. This observation gives credibility to the method of data resolution, which splits each observed value of P sorbed, using the successively approximated K and b values, between each sorption region.

The accuracy of this method of data resolution was tested by comparing the overall (x-c) sorption isotherm, generated by the summation of individual (x-c) isotherms calculated for each of the three sorption regions, with the experimentally determined isotherm. Experimental and generated isotherms for overall P sorption, and resolved isotherms for each sorption region for Porirua and Okaihau soils are given in Fig. 5.6. Experimental and generated isotherms for overall P sorption compared very favourably. The differences between observed and calculated values of P sorbed were generally no more than 2%. These comparisons for other soils gave similar results.

The overall isotherm for each soil was also characterised by three distinct final P concentration ranges over which at least 70 to 80% of the overall increase in P sorption was attributable to sorption in one particular region (Fig. 5.6). That is each region corresponded to a well defined final P concentration range for all soils. Region I corresponded to the final P concentration range of approximately 0 to 0.02 μgP/ml; region II, 0.08 to 0.80 μgP/ml, and region III, 1.0 to > 20.0 μgP/ml. Intermediate concentration ranges corresponded to appreciable sorption on more than one region (Fig. 5.6).

5.3.4 Evaluation of Langmuir constants

The values of the Langmuir constants, K and b, for P sorption at both equilibrium and 40 hr, and for each soil used, are given in Table 5.3. The striking feature of the data was the similarity of K values obtained for a particular region at equilibrium for all four soils. The K values varied by a factor of no more than 2 to 3 within a region, but varied by a factor of 20 to 50 between regions. Similar differences were obtained within and between K_{II}

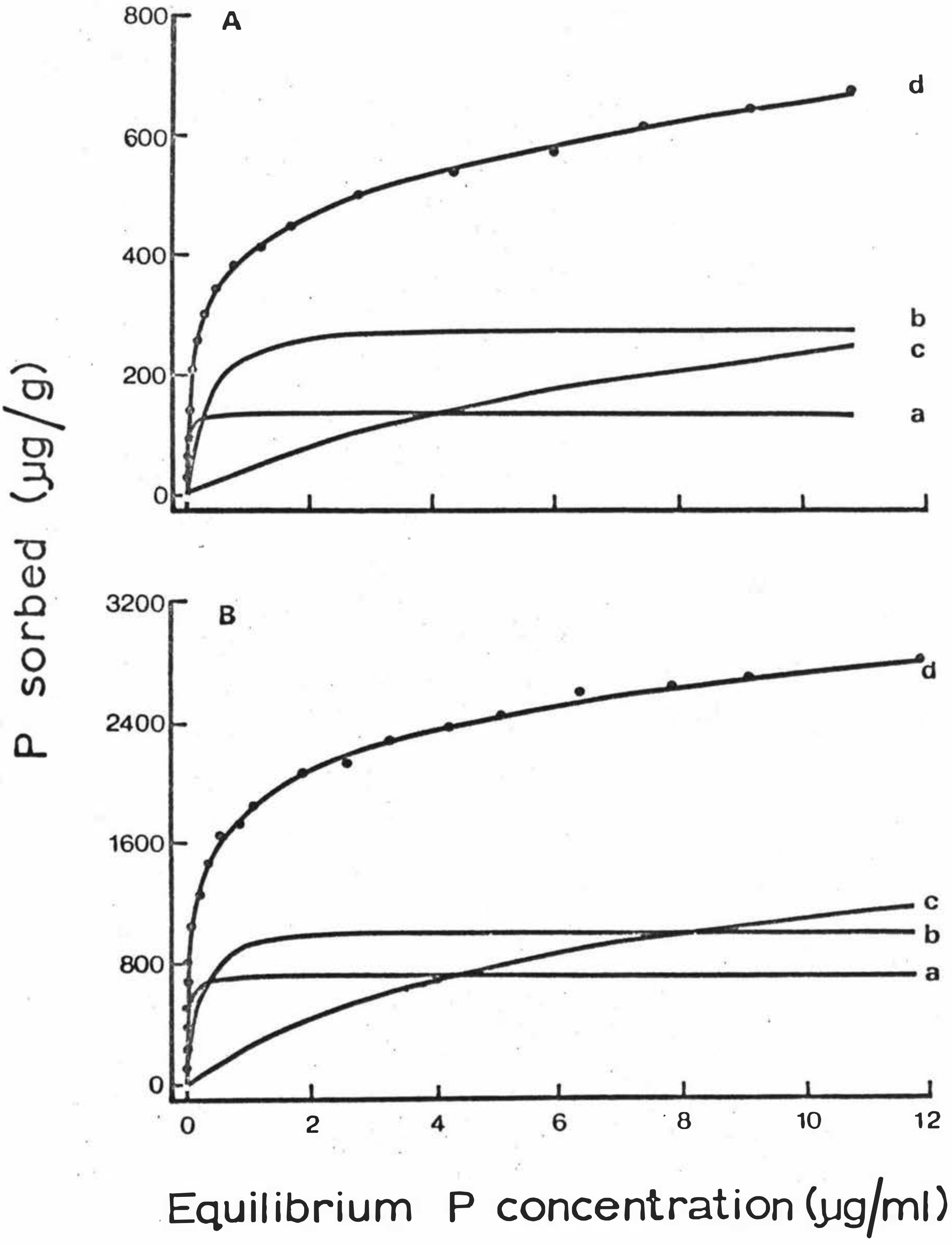

FIG. 5.6 Equilibrium P sorption isotherms for Porirua and Okaihau soils over the equilibrium P concentration range 0 to 12 μgP/ml. A = Porirua soil, B = Okaihau soil. a = resolved isotherm for region I, b = resolved isotherm for region II, c = resolved isotherm for region III, d = overall isotherm generated by summation of the resolved isotherms for regions I, II, and III. ● = experimental data points.

TABLE 5.3 Langmuir sorption constants (K and b) obtained by successive approximation of P sorption data obtained under equilibrium and 40-hr conditions for four soils.

Soil	Time	Region I		Region II		Region III	
		K_I (ml/μg)	b_I (μg/g)	K_{II} (ml/μg)	b_{II} (μg/g)	K_{III} (ml/μg)	b_{III} (μg/g)
Egmont	Equilibrium	190	1218	4.6	1506	0.18	3236
Okaihau	"	238	664	6.7	1031	0.16	1733
Porirua	"	106	130	4.7	285	0.08	529
Waikakahi	"	96	43	5.1	81	0.29	325
Egmont	40 hr	433	226	10.8	1610	0.20	2740
Okaihau	"	746	188	10.2	781	0.23	1361
Porirua	"	2037	14	12.9	163	0.19	422
Waikakahi	"	99	25	2.0	91	0.08	283

and K_{III} values for 40-hr sorption data, although considerable variation is apparent in the estimates of K_I.

Only the values of b for each region reflected the properties of each soil (Table 2.1), equilibrium b values being consistently the greatest for Egmont soil and the least for Waikakahi soil. Furthermore, 40-hr values were consistently lower than those obtained for the equilibrium condition. The relatively greater discrepancies between equilibrium and 40-hr sorption isotherms at low solution P concentrations (Fig. 5.2), was also reflected in the greater differences between equilibrium and 40-hr b_I values for each soil (Table 5.3).

5.4 Discussion

The data, presented above for the sorption of P by four contrasting soils have several implications to the interpretation of P sorption using the Langmuir equation, and to the P sorption mechanism.

5.4.1 Equilibrium and non-equilibrium isotherms

Data for P sorption by each of the four contrasting soils at both equilibrium and non-equilibrium (40 hr), can be resolved into three distinct linear relationships, each described by a Langmuir equation, and each corresponding to a well defined concentration range (Fig. 5.6, Table 5.3). The unreliability of estimates of the Langmuir constants obtained for the non-equilibrium condition, however, is illustrated by comparing the constants obtained for P sorption during 40 hr with those obtained for equilibrium, the condition inherent in the derivation of the Langmuir equation. As may be predicted, b values obtained at 40 hr are consistently lower than equilibrium b values, and considerable discrepancies are observed between estimates of both K_I and K_{II} values using 40-hr and equilibrium data.

Discrepancies between Langmuir constants for regions I and II, at equilibrium and 40 hr are particularly large. This is because the largest discrepancies occur between the overall sorption isotherm over the final P concentration range of 0 to approximately 1 μgP/ml (Fig. 5.2). Furthermore, at 40 hr the value of native sorbed P contributes disproportionately to the value of P sorbed over the lowest final P concentration range. These factors which affect K_I values obtained at 40 hr, in turn affect estimates of K_{II} and K_{III}. The value of K_{III}, however, is least affected. This is because, over the concentration range corresponding to region III, the discrepancy between equilibrium and 40-hr isotherms becomes fairly constant (Fig. 5.2). That is the 40-hr isotherm for region III is very similar to that obtained at equilibrium.

The equilibrium condition has been overlooked in most previous studies relating to P sorption by soils (Rennie and McKercher, 1959; Syers et al., 1973 b, Holford et al., 1974.). Nevertheless, non-equilibrium data (40-hr) give the same number and distribution of regions as equilibrium data (Table 5.3). Application of the Langmuir equation to non-equilibrium data is only satisfactory when absolute values of constants are not required, and may be particularly valuable in determining the origin of the Langmuir regions, as will be demonstrated in Chapter 6.

5.4.2 Importance of detailed data

The importance of having a detailed coverage of the final P concentration range, particularly the very lowest concentrations, is illustrated in Fig. 5.3.A and 5.4. It is not possible to establish the first linear relationship (Fig. 5.3.A) without three to four data points at concentrations of < 0.02 µgP/ml. Furthermore, a smaller number of data points would have implied a curvilinear relationship in Fig. 5.3.A and 5.4. This probably explains the origin of curvilinear Langmuir relationships obtained by Gunary (1970) and Bache and Williams (1971) for P sorption by several British soils.

Although previous workers have obtained deviations from a single Langmuir equation at high (Olsen and Watanabe, 1957; Rennie and McKercher, 1959) and low to intermediate (Syers et al., 1973 b; Schwertmann and Knittel, 1973; Holford et al., 1974) final P concentrations, comparison of the data obtained with that obtained in the present study is not possible because a detailed coverage of the final P concentration range was not made. Consequently, sorption data at low concentrations (0 to approximately 1 µgP/ml) have tended to be treated as one sorption region (Syers, et al., 1973 b; Holford et al., 1974). This single region represents a combination of regions I and II, as defined in this study, in terms of the K and b values obtained by other workers. The possibility that this single region comprised two regions, as observed in the present study, was however, suggested but not demonstrated by Syers et al. (1973 b).

The importance of complete data resolution is again illustrated by the work reported by Sample and Kamprath (1973) and Holford et al. (1974). These workers used computer fitting techniques, which involved the assumption of only two sorption regions. Inspection of data presented by Holford et al. (1974), however, suggests that three sorption regions were involved.

5.4.3 Implications of similar K values.

The similarity of equilibrium K values obtained for a particular region (Table 5.3), despite the contrasting properties of the soils, has implications to the P sorption mechanism. For the contrasting soils used in the present study, not only are K values for a particular region similar, but, where applicable, they compare favourably with those obtained by other workers for a wide range of soils (Table 5.4). Furthermore, K values obtained in this study are comparable with those obtained in other studies for such diverse soil components as gibbsite, kaolinite and α-alumina.

The three distinct sorption regions obtained in the present study, and the similarity of K values for both soils and soil components, (Table 5.4) strongly suggests that P sorption involves three distinct P sorption mechanisms at sites common to all sorbents. The only sites common to the soils used in this study, and the other sorbents in Table 5.4, are those of the type M-OH, where M = Fe or Al. These sites occur at the surfaces of hydrous metal oxides and short-range order aluminosilicates, and at the edge faces of crystalline aluminosilicates. The origin of the three sorption regions in the pH dependence of site charge combined with that of the distribution of P species in solution, is demonstrated in Chapter 6.

Previous workers (Syers et al., 1973 b; Holford et al., 1974) have suggested that deviations of P sorption data from a single Langmuir equation, originate from the sorption of P by different

TABLE 5.4 Values of the Langmuir sorption energy constant K (= ml/μg) for P sorption by various soils and soil components over three concentration ranges (regions).

Sorbent	Approximate concentration range (μg P/ml)			Reference**
	0 to 0.02 (I)	0.08 to 0.80 (II)	1.0 to > 14 (III)	
New Zealand soils	96 - 238‡	4.6 - 6.7*+	0.08 - 0.29*‡	(1)
Brazillian soils	-	-	0.10 - 0.12*§	(2)
Saskatchewan soils	-	-	0.08 - 0.20+§	(3)
U.S.A. Soils	-	-	0.42 - 0.27+§	(4)
English soils	-	-	0.12 - 0.46+§	(5)
Australian soils	-	-	0.09 - 0.19+§	(5)
Kaolinite API-9	-	-	0.05 - 0.10*‡	(6)
Gibbsite	-	-	0.03 - 0.04*‡	(6)
Pseudoboehmite	-	-	0.04 - 0.08*‡	(6)
Kaolinite (Wards 5)	-	1.9 - 2.8+§	-	(7)
α-alumina	-	4.4 - 7.9+§	-	(7)

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* = Corrected for sorption at lower P concentrations, where appropriate

\+ = Correction for sorption at lower P concentrations not made

‡ = Calculated from equilibrium data.

§ = Calculated from non-equilibrium data.

** (1) This study; (2) Syers et al., 1973 b; (3) Rennie and McKercher, 1959 (4) Olsen and Watanabe, 1957; (5) Holford et al., 1974; (6) Muljadi et al., 1966; (7) Chen et al., 1973 b.

mechanisms at different components. The similarity of K values for a particular region for the soils used in the present study, each of which contains different components (Table 2.1) thought to be important in P sorption, tends to discount this possibility.

The conformity of equilibrium P sorption data to three Langmuir equations, also suggests that the Langmuir equation is applicable not only to true adsorption but also to absorption (Chapter 3). Furthermore, the similarity of K_{III} and to some extent, K_{II} values, and the well-defined concentration ranges corresponding to each region at both equilibrium and 40 hr (Fig. 5.6), imply that adsorption and absorption cannot be distinguished from a mechanistic standpoint. The concept that absorption constitutes adsorption at "internal surfaces", suggested previously (Chapter 3), seems valid.

CHAPTER 6

CHARGE RELATIONSHIPS AND MECHANISMS OF PHOSPHATE SORPTION BY SOILS

6.1 Introduction

The sorption of inorganic phosphate (P) by contrasting soils may be described by three distinct Langmuir equations, or sorption regions (Chapter 5). The three distinct regions and the similarity of the sorption energy (K) values obtained for a particular region for all soils, implies that three sorption mechanisms are involved in P sorption, each operating over well defined final P concentration ranges.

The frequently reported (Davis, 1935; Mehlich 1960) increase in cation-exchange capacity, or increase in negative charge, during P sorption by soils and soil components, provides a useful basis for evaluating the mechanisms involved in P sorption. This method has been used with some success (Hingston et al., 1972; Sawhney, 1974) to evaluate the dominant sorption mechanisms within various pH ranges for soil components and soils. These studies, however, have not considered P sorption over a sufficiently wide range of final solution P concentrations, similar to that required for the construction of a sorption isotherm. Probably for this reason the results obtained by these workers have suggested that only one distinct mechanism is operative at a particular pH value. This observation does not assist with an explanation of the three sorption regions established in the previous Chapter.

In this study, charge and pH relationships of P sorption are determined for two soils and, for comparison, a hydrous ferric oxide gel (Fe gel), over the final P concentration range for which three sorption regions were obtained in previous experiments. The results are discussed in terms of three P sorption mechanisms which provide an explanation for the charge and pH relationships obtained, as well as the three Langmuir sorption regions.

6.2 Materials and Methods

Air-dried, < 2 mm samples of Egmont and Okaihau soils, and an Fe gel were used in this study. The Fe gel was precipitated from a solution containing 100 g ferric nitrate by the addition of 1M NaOH, until the pH of the suspension remained at approximately 7 for several hours. The suspension was washed and reduced in volume by centrifugation to give a suitable concentration (0.01 g/ml). After washing and concentration the gel suspension had a pH value of 3.95. The amount of Na entrapped within the gel was determined from the difference between the Na concentration of the supernatant solution, and that in an acid digest of a 5-ml aliquot of the suspension. In all cases Na was determined by flame photometry.

Sorption of P and uptake of Na by the three materials in the presence and absence of P, were determined by the following method. One-gram samples of soil and 0.05-g samples of Fe gel were shaken in 40 ml of 10^{-4}M NaCl containing various additions of P, added as a solution of Na_2HPO_4 adjusted to pH6. The maximum P additions were 2500, 1800, and 35000 µgP/g for Egmont and Okaihau soils, and Fe gel, respectively. In a parallel experiment, 1-g samples of soils, and 0.05-g samples of Fe gel were shaken in 40 ml of 10^{-4}M NaCl containing no added P but various additions of Na (as NaCl) were made, so that each system could be paired, in terms of total Na addition, with one to which P had been added. A support medium having a low Na concentration (10^{-4} Mn) was used to facilitate measurement of the changes in the solution Na concentration which occur in response to P sorption. After shaking for 40hr, the tubes were centrifuged, and aliquots taken for the determination of dissolved inorganic P in systems with added P. Solution Na concentration and pH were determined for all systems.

The relative degree of flocculation, subsequent to P sorption by Fe fel, was also measured. After shaking gel suspensions with added P, as described above, the suspensions were allowed to stand for 1.5hr. A 10-ml aliquot of the "suspension" was carefully removed from each tube at a constant depth, transferred to a 50-ml volumetric flask, and the contents brought to volume. Immediately after shaking the flask, transmission (%) was measured for each of the diluted "suspensions" at 700 nm using a 1-cm path length.

6.3 Results

6.3.1 Sorption isotherms

Sorption isotherms for Egmont and Okaihau soils, and Fe gel are given in Fig. 6.1 for the final P concentration range of 0 to 6 µgP/ml. The amounts of P sorbed by the soils do not include an estimate of native sorbed P. Isotherms for both soils and Fe gel were of a similar type (type-H) to those obtained at equilibrium in the previous study (Chapter 5).

The isotherms could also be resolved into three distinct sorption regions each described by a Langmuir equation. Each region corresponded to approximately the same final P concentration range as that obtained for the corresponding region of equilibrium data in the previous study. The values of the Langmuir sorption constants relating to sorption energy (K) and sorption maximum (b) for each of the three regions (I to III) are given in Table 6.1. The b values reflect the overall sorption of P (Fig. 6.1), but relate only to the 40-hr shaking time used. The K values, particularly K_I and K_{II}, are considerably different from the equilibrium values obtained in the previous study, and reflect the different experimental conditions used. The value of K_I for Fe gel was not determined, because of the magnitude of b_I, and the difficulty in obtaining a sufficient amount of reliable final P concentration data at the low concentrations characteristic of region I. The value of b_I was obtained by testing sorption data, after correction for an estimated b_I value, for conformity to a single Langmuir equation over the final P concentration range of 0.02 to 0.80 µgP/ml, corresponding to region II. From K and b values it is possible to estimate the amount of P sorbed in each region for a given solution P concentration which corresponds to an overall level of P sorption.

6.3.2 Charge and pH relationships

The relationship between the difference (Δ Na) between sodium uptake, in the presence and absence of P at the same level of sodium addition, and the amount of added P sorbed by each sorbent is given in Fig. 6.2. The values of Δ Na represent the increase in Na uptake due entirely to the increase in negative charge induced by P sorption (Davis, 1945; Melich, 1960; Hingston et al., 1968 b; Sawhney, 1974).

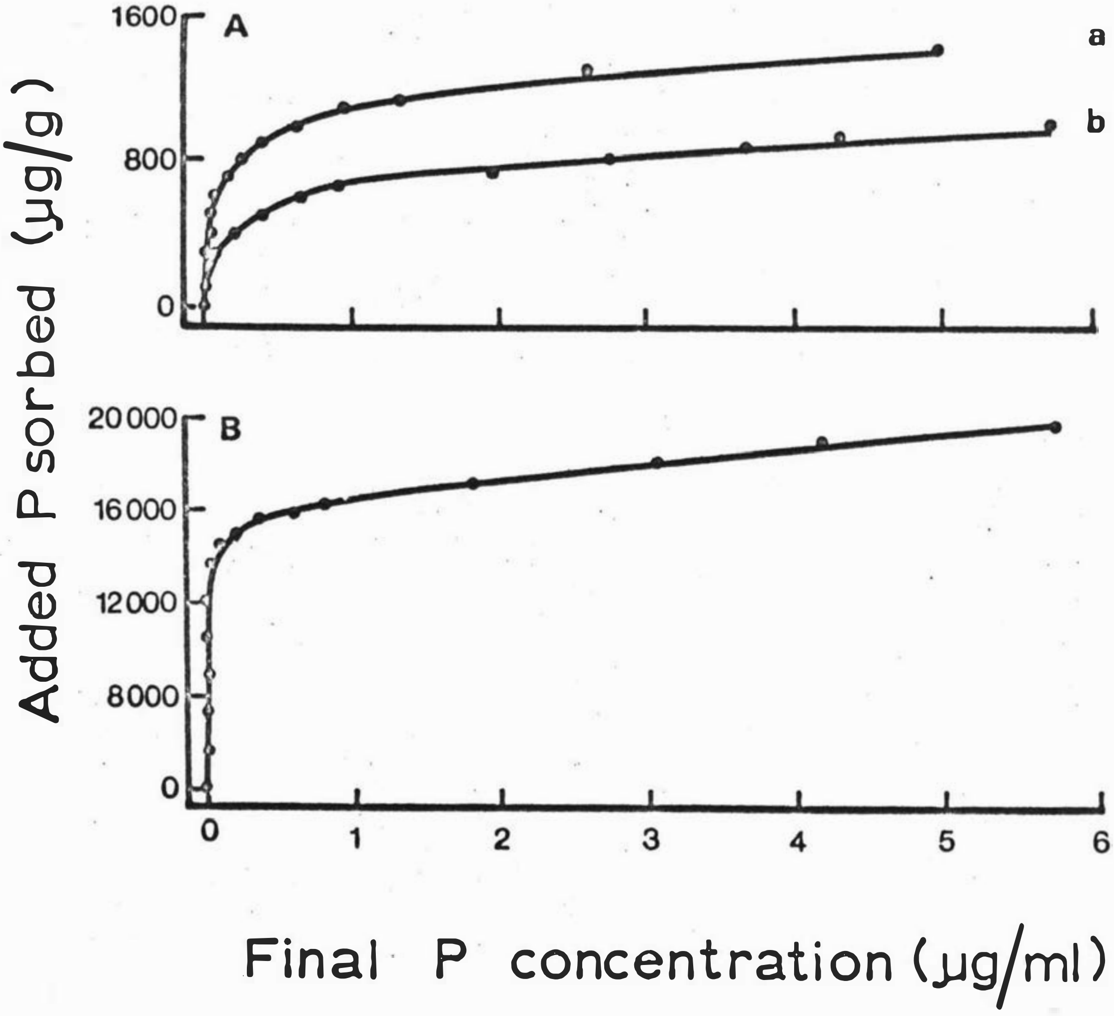


FIG. 6.1 Isotherms for the sorption of added P from 10^{-4}M NaCl by soils (A) and Fe gel (B) during 40 hr. a = Egmont soil, b = Okaihau soil.

TABLE 6.1 Values of sorption maximum (b) and sorption energy (K) for each of three (I to III) Langmuir equations (regions) describing the sorption of P by Egmont and Okaihau soils, and Fe gel.

Sorbent	b_I	b_{II}	b_{III}	K_I	K_{II}	K_{III}
		μg/g			ml/μg	
Egmont soil	248	560	1160	580	9.0	0.171
Okaihau soil	130	455	694	1470	4.8	0.110
Fe gel	7000	7500	20000	n.d.*	66	0.062

* not determined.

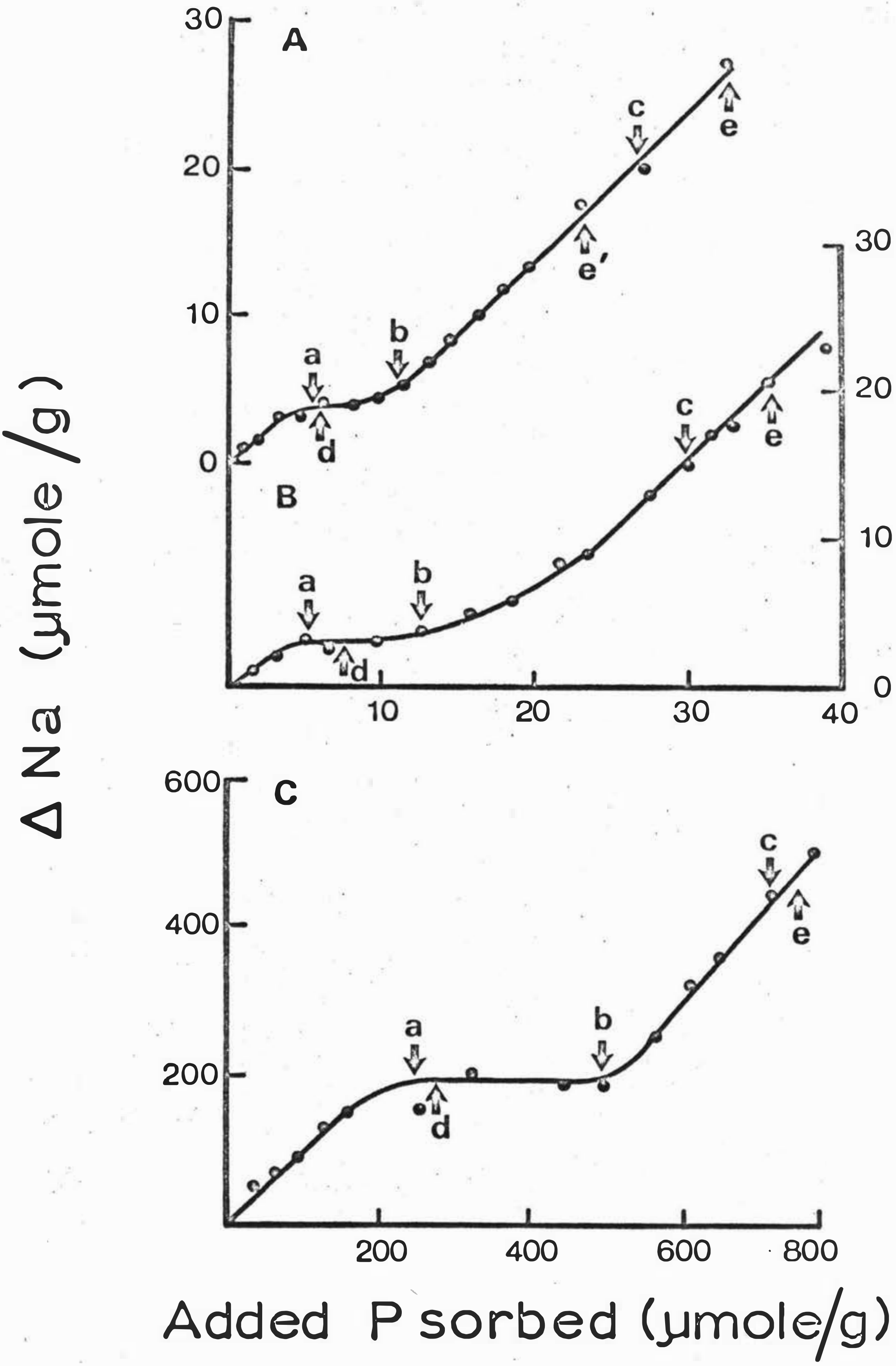


FIG. 6.2 Relationship between the difference (Δ Na) between sodium uptake, in the presence and absence of P at the same level of sodium addition, and added P sorbed for soils and Fe gel. A = Egmont soil, B = Okaihau soil, C = Fe gel. Points a, b, c, d and e refer to data in Tables 6.2 and 6.3.

The relationship between Δ Na and P sorbed is essentially the same for each soil and Fe gel, being composed of three distinct parts which are particularly apparent for Fe gel. The inflexion in each relationship represents a well-defined portion of overall P sorption for which there is no increase in negative charge of the surface; i.e., Δ Na becomes constant.

Closer inspection of the charge relationships (Fig. 6.2) suggest that the changes in slope are comparable to the sorption maximum of region I (Table 6.1 and 6.2), and the point at which sorption in region III makes a significant contribution to overall P sorption. Points a, b and c in Fig. 6.2, correspond to varying degrees of saturation of each P sorption region, values for which are calculated from respective K and b values (Table 6.1), and are given in Table 6.2. Point a on each relationship in Fig. 6.2 corresponds to approximate saturation of region I. Point b, however, corresponds to varying degrees of saturation of region II, but also to a significant saturation (approximately 5%) of region III, in terms of overall P sorption. Point c corresponds to continued sorption in region III. The higher saturation of region II for Fe gel at point b (Fig. 6.2) reflects the higher K_{II} value obtained for Fe gel and probably the greater reactivity of Fe gel relative to similar components in soils.

The ratio of Δ Na: P sorbed (i.e., increase in charge per mole of P sorbed)at points d and e is given in Table 6.3. The values of Δ Na:P for the first portion of the charge development relationship (point d in Fig. 6.2), which is equivalent to region I of the P sorption isotherms, vary from 0.6 for Egmont soil to 0.9 for Fe gel. The ratio of Δ Na:P for charge development equivalent to region III (point e) is approximately unity after correction of Δ Na values for those corresponding to region I. This suggests that for P sorption in region III, surface charge increases by one equivalent for each mole P sorbed.

The variability of Δ Na:P ratios for the two soils over region I, almost certainly reflects the relative amounts of native exchangeable cations present in the soils. For example, the amount of native exchangeable Ca in Egmont soil is 11.7 µmole/g, whereas that for Okaihau soil is approximately zero (Table 2.1). Native exchangeable cations may, in part, compensate the increasing negative surface charge arising from P sorption. This will result in lower

TABLE 6.2 Degree of saturation of each sorption region for the overall levels of P sorption by each sorbent, denoted a, b and c in Fig. 6.2 and 6.3.

Sorbent	Point *	Saturation (%) of		
		Region I	Region II	Region III
Egmont soil	a	92	29	1
	b	100	70	4
	c	100	100	63
Okaihau soil	a	93	8	1
	b	100	57	3
	c	100	97	41
Fe gel	a	100	5	0
	b	100	100	5
	c	100	100	39

*on Fig. 6.2 and 6.3 where appropriate.

TABLE 6.3 Values of the ratio of Δ Na : P sorbed at points d and e on the relationship between Δ Na and added P sorbed (Fig. 6.2).

Sorbent	Point [*]	Δ Na : P
Egmont soil	d	0.6[+]
	e	0.9[‡]
	e′	0.8[‡]
Okaihau soil	d	0.8[+]
	e	1.2[‡]
Fe gel	d	0.9[+]
	e	1.0[‡]

---

[*] On Fig. 6.2

[+] Based on b_I values for each sorbent (Table 6.1).

[‡] Based on the degree of saturation of region III calculated from K_{III} and b_{III} values (Table 6.1).

$\triangle$ Na values than expected, particularly at low overall P sorption. The increase in $\triangle$ Na:P value for region I associated with the decrease in native exchangeable cation status, and the fact that for Fe gel $\triangle$ Na:P approaches unity, suggest that unit charge arises from the sorption of each mole of P in region I. The slightly lower value of $\triangle$ Na:P (point e) for Egmont soil also reflects the greater amount of native exchangeable cations in this soil.

The development of charge, and the surface charge itself at various levels of P sorption, are also illustrated by the degree of flocculation of Fe gel suspensions, subsequent to P sorption, measured by the percent transmission at 700 nm (Fig. 6.3). Points a, b, and c correspond to the saturation of each region, as shown in Table 6.2. Fig. 6.3 shows that when region I is saturated (point a), flocculation is induced (% T increases sharply). After passing through a broad maximum the degree of flocculation (%T) decreases rapidly, i.e.,dispersion occurs, as percent saturation of region III starts to become significant (point b). This decrease continues slowly as more P is sorbed in region III (point c).

The flocculation data (Fig. 6.3) imply that net surface charge is zero when region I is saturated. The flocculation and charge development relationships (Fig. 6.2 and 6.3) also suggest that the surface is positively charged, before region I is saturated, a zero charge is maintained in region II, and the surface becomes negatively charged during sorption in region III.

Data for the pH of Fe gel systems, subsequent to P sorption, are also given in Fig. 6.3. Minimal change in pH is recorded until region I approaches saturation (point a). Beyond point a, pH increases rapidly, and then more slowly up to a value of 7.55 (point c) at the highest level of P addition. The increase in pH associated with P sorption in region II, and possibly region III, suggests release of OH^-. The more gradual pH increase above pH 6.5 probably reflects the buffering of P species in solution, which will be at a maximum at pKa_2 of H_3PO_4 (7.21; Butler, 1964). Distinct pH changes were not observed during P sorption by the two soils (data not presented). This is probably due to the buffering characteristics of a range of components, particularly organic matter, in soil systems. Small increases in pH, however, were recorded at the highest levels of P addition, particularly for the Okaihau soil which may be

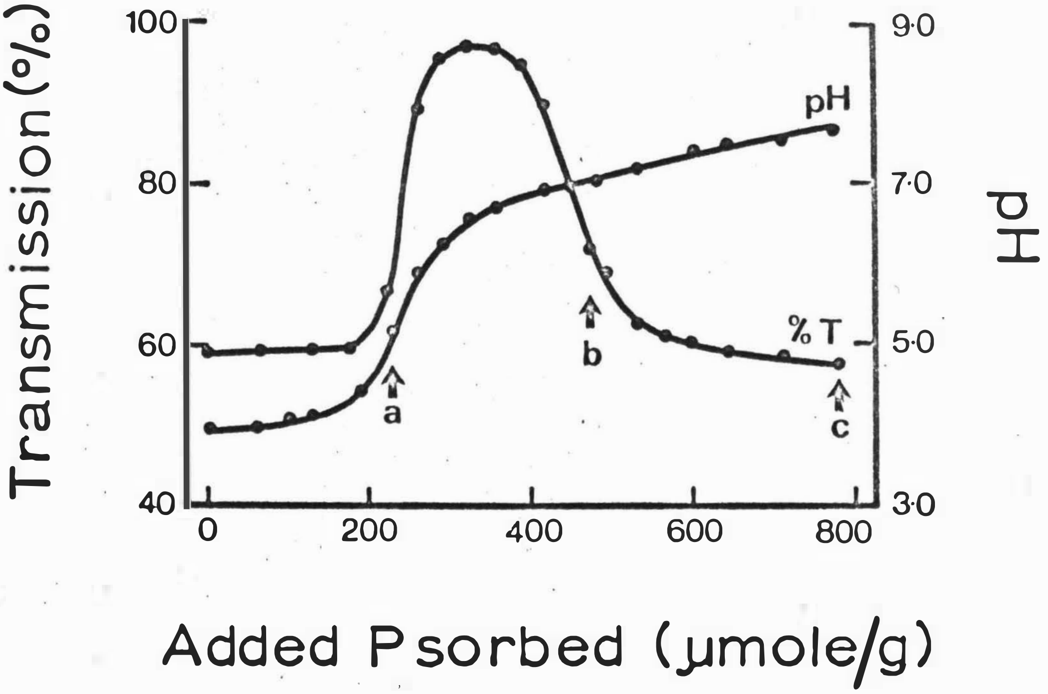


FIG. 6.3 Relationship between the degree of flocculation subsequent to P sorption measured by the transmission (% T) of Fe gel suspensions at 700 nm, the pH of suspensions subsequent to P sorption and added P sorbed. Points a, b and c refer to data in Table 6.2.

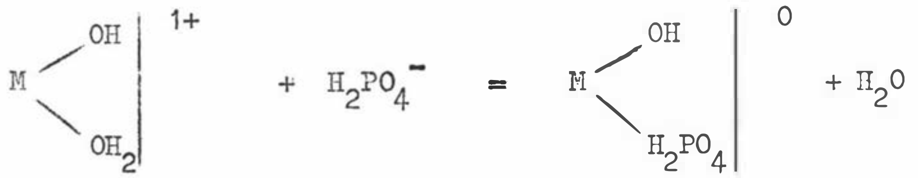
expected to show the least buffering.

6.4 Discussion

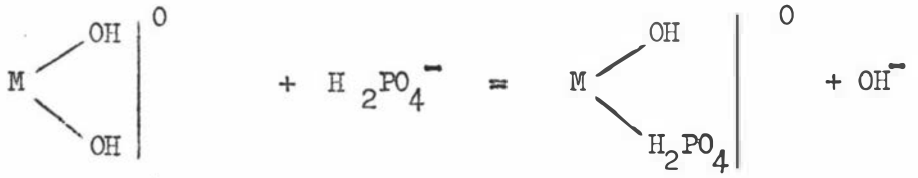
The results presented above suggest that not only does P sorption involve three distinct sorption mechanisms, each of which is described by a Langmuir equation, but also that the same mechanisms are involved in P sorption by both soils and Fe gel. This confirms the conclusions drawn in Chapter 5, based on Langmuir sorption energy (K) values. The results of this study, however, also permit a more precise evaluation of the distinct mechanism involved in P sorption in each region.

In the proposed mechanistic scheme outlined below, it is assumed that the sorbing surface can be represented by that of a hydrous oxide of Fe or Al. Such surfaces may be simply represented (Parks and de Bruyn, 1962) as $M<^{OH}_{OH_2^+}$, the proportion of $-OH_2^+$ to $-OH$ depending on the pH of the ambient aqueous phase and the point of zero charge of the surface in question (Parks and de Bruyn, 1962; Yopps and Fuerstenau, 1964; Atkinson <u>et al</u>., 1967), as discussed in Chapter 1. Ligand exchange reactions of the type $-L_o$; L_s are also assumed where $-L_o$ is the original surface group and L_s the sorbing species originally in solution.

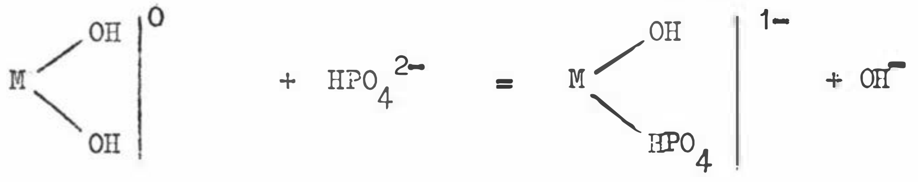
The P sorption mechanisms proposed involve the ligand exchange $-OH_2^+$; $H_2PO_4^-$ in region I, $-OH$; $H_2PO_4^-$ in region II, and $-OH$; HPO_4^{2-} in region III. When written in full (equations (6.1) to (6.3) for regions I to III, respectively) the charge and pH relationships (Fig. 6.2 and 6.3) are fully explained.



(6.1)



(6.2)



(6.3)

Equations (6.1) and (6.3) illustrate the increasing negative charge observed for P sorption in regions I and III, which is approximately one equivalent per mole of P sorbed when the probable effects of native cations are taken into account (Table 6.3). Equation (6.2) induces no change in surface charge and gives the inflexion in the charge development relationship; i.e., △Na is constant (Fig. 6.2). The increase in pH for Fe gel, subsequent to saturation of region I (Fig. 6.3), is also consistent with equations (6.2) and (6.3).

The condition of zero surface charge subsequent to saturation of region I and until significant sorption occurs in region III, implied by the flocculation of Fe gel (Fig. 6.3), is satisfied by equation (6.2). Furthermore, flocculation data imply that surface $-OH_2^+$ and -OH groups carry unit positive and zero charge, respectively. This is in contrast to 0.5 units of positive and negative charge assigned to $-OH_2^+$ and -OH groups, respectively, by Hingston et al. (1968 b, 1972).

The proposed P sorption mechanisms are also in accord with the amounts of Ca retained in response to P sorption, reported in Chapter 4B. Calcium retention data implied that a significant proportion of overall P sorption by Egmont, Okaihau and Porirua soils did not contribute to the increase observed in the negative charge of the surface (equation 6.2).

Although the above scheme of P sorption mechanisms satisfies charge and pH relationships, it must also satisfy the relative values obtained for the Langmuir sorption energy constants (Brunauer et al., 1966). If an initially positively charged hydrous-oxide surface is assumed to behave as a parallel plate condenser (double-layer theory), which will discharge under the appropriate conditions and resist subsequent build-up of charge, the relative sorption energy (K) values for each region may be explained, as discussed below.

The most energetically favourable mechanism is represented by equation 6.1. This mechanism not only depends on the relative affinity of M for $-OH_2^+$ and $H_2PO_4^-$, but also on the reduction in surface charge achieved. The condenser model predicts that this mechanism corresponding to region I, has the highest K value, which is in accord with the equilibrium, as well as non-equilibrium, K values reported in Chapter 5 and in this study (Table 6.1). The second most energetically favourable mechanism is represented by equation (6.2), corresponding to region II. Equation (6.2) induces no change in surface charge and depends only on the relative affinity of M for $-OH$ and $H_2PO_4^-$. Equation (6.3) tends to increase surface charge which may only be overcome by the affinity of M for HPO_4^{2-}. This mechanism results in the lowest K values being observed for region III.

The relative extent of P sorption in each region should also reflect the proposed sequence of mechanisms (Brunauer et al., 1966). The relative contribution of b_I to the overall sorption maximum should, therefore, depend on soil pH, due to the relatively greater amounts of $M-OH_2^+$ at lower pH values. For example, based on b values obtained in Chapter 5 (Table 5.3), the contribution of b_I to the overall equilibrium sorption maximum of Okaihau and Waikakahi soils was 19.4% and 9.5%, respectively. These soils represent pH extremes (4.8 and 8.1, respectively), for the contrasting soils used in these studies.

The above discussion has been based on the assumption that the mechanism represented by equation (6.3) describes P sorption in region III. Very recent work in this laboratory (J.R. McLaughlin, pers. comm.) suggests that P sorption in regions I and II, corresponding to equations (6.1) and (6.2), results in the development of a "ferric-phosphate like" surface, and that P sorption in region III corresponds to the sorption of phosphate as a potential determining ion at this surface (c.f., S^{2-} at the surface of Ag_2S; Iwasaki and de Bruyn, 1958). Such a mechanism would still result in unit increase in surface negative charge per mole P sorbed in region III (Figs. 6.2 and 6.3; Table 6.3), although the slow increase in pH (Fig. 6.3) seems anomalous. It is possible that this pH increase arises from the slow completion of sorption in region II which continues up to final P concentrations of approximately 2 μg P/ml. This mechanism for P sorption in region III is, however, compatible with the Langmuir sorption energy values, as discussed above.

Components having a surface structure similar to that represented above for a hydrous oxide, are ubiquitous in soils (Jackson, 1963). Such components include crystalline and short-range order Fe and Al hydrous oxides, short-range order aluminosilicates, and the edge faces of crystalline aluminosilicates. The charge relationships of P sorption by soils and Fe gel, obtained in this study and the similarity of K values for both soils and soil components, as discussed in Chapter

5, clearly demonstrate the importance of the hydrous-oxide surface in the sorption of P by widely-different soils.

Although previous workers (Hingston et al., 1968 b, 1972; Breeuwsma and Lyklema, 1973; Sawhney, 1974; Rajan, 1975) have attributed P sorption, at a particular pH value, to at least one of the mechanisms proposed above, this study represents the first quantitative evaluation of each mechanism over a wide range of final P concentration for contrasting soils and Fe gel. Final P concentrations were also realistic in terms of the P concentration of the soil solution and experiments were carried out at the pH of the soil. Furthermore, this study has identified the mechanisms involved in P sorption by Fe gel, and presumably other hydrous oxides, with those involved in P sorption by intact soils of very different chemical and mineralogical composition. Finally, the data in Fig. 6.2 demonstrate that a significant proportion of overall P sorption generates no increase in surface negative charge. This is in contrast to the assumption made by Hingston et al. (1967, 1968 b, 1972) that P sorption is conditional on an increase in the negative charge of the surface. This assumption has been included in many previously proposed P sorption mechanisms (Hingston et al., 1967; Mott, 1970).

CHAPTER 7

INTERPRETATIONS

The results of the studies discussed in the previous chapters provide a basis from which other aspects of the sorption of inorganic phosphate (P) by soils may be explained. Two areas may be defined, namely that concerning the sorption reaction and that concerning the sorption mechanism. The fact that the four contrasting soils used gave remarkably similar results, in terms of reactions and mechanisms involved in P sorption, permits extrapolation of the data obtained to a wider range of soils.

The fractionation of added P sorbed with increasing time by two soils (Chapter 3) suggested that an absorption reaction is involved in the overall sorption of P by soils. An absorption reaction is in accord with data presented by previous workers, relating to the time dependence of P sorption (Kurtz et al., 1946; Rennie and McKercher, 1959; Hsu, 1964; Evans and Syers, 1971), and the decrease in extractability and isotopic exchangeability of added P sorbed with increasing time reported on in Chapter 3 and by other workers (Talibudeen, 1958; Larsen and Widdowson, 1971; Evans and Syers, 1971).

The concept of an absorption reaction is not without support in the literature relating to the nature of reactions at the hydrous-oxide surface. Similar time-dependent reactions have been reported (Onoda and de Bruyn, 1966; Kinniburgh et al., 1975) for the sorption of protons and cations by oxides and hydrous oxides. In the study of Onoda and de Bruyn (1966), the slow sorption of protons by haematite was attributed to the movement of protons into a hydrated and expanded surface layer resembling goethite. The "porous" double layer at hydrous-oxide surfaces, proposed by Lyklema (1968, 1971 a), also implies absorption, as discussed in Chapter 1.

An absorption reaction has implications to the availability to plants of fertilizer P added to soils. Absorbed P is expected to have a very much lower potential availability to plants than adsorbed P. The kinetics involved in the diffusion of absorbed P within retaining components may be of particular importance in the supply of P to the soil solution in contact with plant roots. The kinetics involved in the release of absorbed P may also explain the low recovery of fertilizer P by plants during a particular growing season, and the fact that some soils appear to require regular additions of phosphate fertilizer to maintain adequate levels of P in the soil solution for optimum plant growth. The mechanism involved in the desorption, or release of sorbed P, however, is also of importance in maintaining an adequate supply of P for plant growth, as discussed below.

An absorption reaction also explains the time dependence frequently reported for the isotopic exchange of both added sorbed P and native sorbed P (McAuliffe et al., 1947; Russell et al., 1954). The slow exchange of ^{32}P at longer time intervals probably reflects exchange with absorbed P. The similarity between P sorption and exchange reactions (Chapter 3 and Li et al., 1970) suggests that a more reliable determination of the actual amounts of exchangeable P may be facilitated by extrapolation of exchange data to infinite time, as used to estimate equilibrium P concentrations and native sorbed P in Chapters 4 and 5.

Although the effect of ionic composition of the support medium on the kinetics of P sorption did not appear to be directly related to an absorption reaction, the investigation of this effect (Chapter 4A) illustrated the implications of the time dependence of P sorption to the interpretation of P sorption data. It is possible that differences in the amounts of P sorbed by soils, which have been attributed to experimental conditions other than time, may be eliminated if the equilibrium condition is estimated. Experimental conditions affecting the amounts of P sorbed by soils in non-equilibrium systems include soil : solution ratio, temperature, ionic composition of the support medium, and exchangeable cations. The effect of these experimental conditions has been discussed by Wild (1949), Kurtz (1953) and White and Beckett (1964). Recent work in this laboratory (G.D. Hope, pers. comm.) suggests that the effect of soil : solution ratio on amounts of P sorbed is eliminated if the equilibrium condition is estimated using the method suggested in Chapter 4. An evaluation of the role of time - dependent sorption would facilitate the choice of more reliable conditions for use in laboratory studies.

The evaluation of P sorption from the standpoint of conformity of equilibrium sorption data to Langmuir equations (Chapter 5), and the charge relationships of P sorption (Chapter 6), has provided a quantitative basis for the proposed P sorption mechanisms which cover a wide final P concentration range. The proposed P sorption mechanisms also explain the frequently reported (Syers et al., 1973b; Schwertmann and Knittel, 1973; Holford et al., 1974) deviations of P sorption data from a single Langmuir equation. Furthermore, the values of the Langmuir sorption constants obtained for P sorption by soils are in accord with the P sorption mechanisms proposed. This is a requirement for the assumption of a true Langmuir sorption model (Brunauer et al., 1966) and emphasises the previous arguments (Chapter 1) that P sorption by soils may approach ideal Langmuir behaviour.

The charge relationships of P sorption (Chapter 6) have illustrated some of the problems inherent in the interpretation of anion sorption using the models developed by Hingston et al. (1967, 1968 b, 1972). Of primary importance is the fact that a considerable portion of the overall P sorption involves no change in surface charge. This demonstrates that P sorption is not conditional on an increase in the negative charge of the surface, even though negative charge does increase during P sorption. The charge relationships also suggest that P sorption mechanisms, previously thought to apply over only restricted pH ranges (Hingston et al., 1968 b, 1972; Mott, 1970; Sawhney, 1974), contribute to P sorption at widely different pH values and solution P concentrations.

In the sorption of P by soils, the importance of the type and structure of the dominant P sorbing surface, and the pH of the system which affects the number of protonated sites and the distribution of P species in solution, are clearly apparent from the proposed P sorption mechanisms. It is suggested that the number of protonated sites(dependent on pH) is secondary in importance only to the actual number of sites, governed by the type and amounts of P-sorbing components, in determining the overall sorption of P by soils. This is illustrated to some extent by the soils used in these studies (Chapters 5 and 6). Furthermore, the relative importance of P sorption at protonated sites (sorption in region I) which is characterised by a high sorption energy, and consequently relatively small changes in solution P concentration with increasing saturation, has possible implications to the phosphate fertilizer requirements of soils. Elimination of protonated sites by saturation with P, or possibly liming, results in considerably greater changes in solution P concentration for a given

P addition.

An explanation of sorption-desorption hysteresis is also implied by the P sorption mechanisms developed. Other workers (Muljadi et al., 1966; Kafkafi et al., 1967; Hingston et al., 1974) have demonstrated that desorption shows the highest degree of reversibility over P concentration ranges corresponding to region III, as defined in Chapter 5. Sorption of P in this region possibly involves the mechanism -OH; HPO_4^{2-} which builds up the negative charge of the sorbing surface. The assumption that the surface resists charge increase (double-layer theory) implies that during desorption the exchange $-HPO_4^-$; OH^- will be facilitated. This mechanism returns site charge to zero, but its extent will be limited by the concentration of OH^- in the desorbing solution. Similar considerations with respect to the relationship between desorption and the resistance of the surface to negative charge increase during sorption in region III, maybe applied to the concept that sorption in region III involves the sorption of P as a potential-determining ion at a "ferric phosphate-like" surface.

Desorption in regions I and II is unlikely at low OH^- concentrations in solution. The exchange $-H_2PO_4$; OH^- induces no change in site charge, the latter being maintained at zero. The extent of this exchange will depend only on the relative affinity of the surface for $H_2PO_4^-$ and OH^- at the pH of the desorbing solution. Consequently, desorption of P has frequently been reported (Muljadi et al., 1966; Kafkafi et al., 1967; Hingston et al., 1974) in sorption-desorption experiments in which P concentrations subsequent to the sorption step have corresponded to significant sorption in region III. Desorption from regions I and II, however, is rarely observed, except at elevated pH (Muljadi et al., 1966; Kafkafi and Bar-Yosef, 1969). Although detailed experimental verification of such a desorption mechanism is not presently available, recent work by this author, and the change in surface charge during the desorption of P by gibbsite and goethite reported by Hingston et al., 1974, suggests that the mechanism is reasonable.

Data for the P concentration of the soil solution (Pierre and Parker, 1927; Barber et al., 1962) suggest that P sorption in regions I and II will be characteristic of field soils. Consequently the pH of the soil solution between the sorbing surface and the plant root, will be of particular importance in the ease and extent of the desorption of sorbed P and the availability of sorbed P to plants. The pH of the soil solution in the vicinity of the plant root, however, may be higher or lower than that of the soil solution as a whole, and depends on the balance between anion and cation uptake by the plant (Riley and Barber, 1969; Ozanne and Barber, 1970). An increase in the pH of the solution at the sorbing surface will facilitate the desorption of P sorbed in regions I and II, as discussed above. In the absence of any increase in pH, however, the role of organic anions released by plant roots is probably of considerable importance in the desorption of sorbed P. The possible mechanisms involved have been discussed by Nagarajah _et al._, (1968, 1970). These mechanisms however, are open to question, because they are based on anion sorption mechanisms proposed by Hingston _et al._, (1967, 1968 b, 1972), the limitations of which have been discussed previously. It is possible that sorbed P is displaced, rather than desorbed, by the partial dissolution (Earl, 1975) of sorbing components through the formation of soluble complexes between Fe and/or Al and organic ligands.

Summary

The work presented in this thesis may be summarized as follows :-

1. The development of concepts concerning the reactions and mechanisms involved in the sorption of inorganic phosphate (P) by soils was outlined in Chapter 1. Various topics requiring further research were identified.

2. Soils which contrasted in terms of components and properties considered to be important in P sorption were selected (Chapter 2) for a series of investigations relating to the reactions and mechanisms of P sorption. The use of contrasting soils provided a more reliable basis for the interpretation of the data obtained, and extrapolation to a wide range of soil types.

3. The time dependence of P sorption (Chapter 3) was described by four distinct, first-order reactions for each soil. The rate constant of a particular reaction was also remarkably similar for each of the soils used. This was taken to imply that the same sequence of reactions was involved in P sorption by each soil. Data for the fractionation of added P sorbed by two soils suggested that P sorption was not determined solely by a true surface adsorption reaction. The decrease in extractability and isotopic exchangeability of P sorbed at increasing times, coupled with the increase in the amount of sorbed P recovered by citrate-dithionite-bicarbonate extraction indicated that surface adsorbed P became absorbed, probably by diffusive penetration.

4. The implications of time-dependent sorption to the interpretation of P sorption data, were demonstrated in a study of the effects of support medium on P sorption (Chapter 4A). It was shown that differences in the amounts of P sorbed during 40 hr by soils from different support media were eliminated if an estimate of equilibrium P concentration was obtained using a graphical approach. The fact that the equilibrium P concentration was independent of support medium points to the importance of kinetic effects in the interpretation of P sorption data and is in accord with the P sorption mechanisms proposed in Chapter 6. The virtually complete replaceability by K of Ca removed from solution in response to P sorption by soils (Chapter 4B)

indicated that Ca was retained to balance the increase in negative charge arising from P sorption, rather than as a precipitated calcium phosphate, as suggested by other workers.

5. The implications of time dependent sorption to the interpretation of P sorption data using the Langmuir equation, were demonstrated in Chapter 5. The difference between the Langmuir sorption constants obtained for P sorption at equilibrium as opposed to that during 40 hr, were directly related to the extent of the absorption reaction. The similarity of equilibrium sorption energy constants for a particular sorption region for all soils implied that similar mechanisms were involved in the sorption of P by each soil. The fact that P sorption data, obtained both at equilibrium and during 40 hr, could be described by three distinct Langmuir equations also suggested that adsorption and absorption reactions could not be distinguished from a mechanistic standpoint.

6. Charge relationships of P sorption by soils and Fe gel (Chapter 6) demonstrated that three distinct mechanisms were involved in P sorption over the final P concentration range used to obtain P sorption isotherms (Chapter 5). It was also shown that the different mechanisms caused the deviation of P sorption data from a single Langmuir equation. The charge relationships of P sorption implied that the mechanisms of P sorption by soils and Fe gel are the same. One distinct mechanism was shown to be responsible for P sorption in each of the three sorption regions described by a distinct Langmuir equation. Data suggested that the mechanisms involved the ligand exchange reactions $-OH_2^+$; $H_2PO_4^-$, $-OH$; $H_2PO_4^-$, and $-OH$; HPO_4^{2-} at the hydrous-oxide surface over low, intermediate and high final P concentrations, respectively.

7. The implications of the reactions and mechanisms of P sorption by soils in controlling the levels of P in the soil solution are discussed (Chapter 7) in relation to the plant availability of soil and fertilizer P, with particular emphasis on the desorption reaction.

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