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ADSORPTION OF SULPHATE BY SOILS

A thesis presented in partial
fulfilment of the requirements for
the degree of Master of Philosophy
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ABSTRACT

Studies of sulphate adsorption, phosphate sorption and surface charge on soils of varying anion sorption ability which had been incubated, each with several rates of calcium hydroxide, have indicated that:

- (i) The amounts of both sulphate and phosphate sorbed from 0.1M NaCl can be correlated with surface positive charge, but whilst there is a 1:1 relationship between the amounts of sulphate adsorbed and surface positive charge phosphate is sorbed in amounts well in excess of the amounts of positive charge present.
- (ii) Although there is a requirement for some positive charge on the surface before sulphate adsorption can occur in both 0.1M NaCl and 0.025M CaCl_2 , there is a strong selectivity for sulphate over non-specifically adsorbed ions such as chloride.
- (iii) Sulphate is adsorbed from 0.025M CaCl_2 in excess of the amounts of surface positive charge initially present ($y = 1.51x + 1.45$), an observation which is consistent with a closer approach of sulphate to the surface in the presence of calcium such that the actual surface charge is modified.

These findings point to a predominantly electrostatic link between sulphate and the surface, with the changes in sulphate adsorption with pH being dependent on changes in surface positive charge. Sulphate adsorption was strongly reduced (10 - 60%) by increasing pH, and in a study of competitive sorption was also significantly (10 - 30%) reduced by addition of phosphate. An investigation with one soil showed that the measured charges in sulphate adsorbed on phosphate addition were highly correlated with measured changes in surface positive charge, and there was some evidence for phosphate having a larger effect on surface positive charge at low pH.

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CHAPTER 1

INTRODUCTION

A fundamental property of soil is its ability to retain anions. Percolating rainfall washes anions in the soil solution down through the profile and potentially out of the root zone. Although anions such as phosphate, molybdate and selenate are held strongly by the soil surface with only small amounts in the soil solution, others such as sulphate, nitrate, and chloride are often at higher concentrations in the soil solution and subject to leaching.

Although the significance of sulphate leaching to the cycling of sulphur varies between soils (Gregg et al., 1977), New Zealand has a sufficiently moist climate to suggest that a fuller understanding of the factors controlling leaching is justified. One of these factors is the ability of the soil to adsorb sulphate.

Soils vary in their adsorption capacity for sulphate, and sulphate adsorption is affected by farm management practices such as liming and phosphate addition (Kamprath et al., 1956). There is limited information on the magnitude of these effects however, and on the significance of changes in adsorption to the mobility of sulphate in soils. Moreover, there is some debate as to the degree to which sulphate interacts with the soil surface. Sulphate is relatively loosely held compared to phosphate but is adsorbed in amounts that are out of proportion to its concentration in solution when compared with some other ions such as chloride and nitrate, suggesting there is more than a simple electrostatic interaction involved in adsorption.

Accordingly, a study of sulphate adsorption was undertaken, not only as a means of assessing the effects of lime and phosphate on sulphate mobility, but also as a means of investigating the interaction between sulphate and the surface. The former consideration has implications to sulphur balance models for predicting the sulphur

requirements of pastoral sites (Cornforth and Sinclair, 1982), and the latter, to previously proposed mechanisms for the adsorption of sulphate by soils and soil components (Parfitt, 1978; Rajan, 1979b; Bowden et al., 1980a).

The effect of liming was studied on soils incubated with varying rates of calcium hydroxide and in a separate experiment the effect of competition with phosphate was assessed by adding sulphate to these soils in conjunction with phosphate.

There is an extensive literature on phosphate sorption in soils, and studies of sulphate adsorption were rationalised by comparing the results obtained to those for phosphate sorption and for a non-specifically adsorbed anion, chloride, in the same soils. This comparison provided interesting insight into adsorption mechanisms for sulphate, and particularly into the significance of surface positive charge to sulphate adsorption in soils.

CHAPTER 2

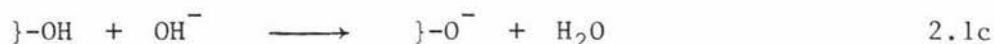
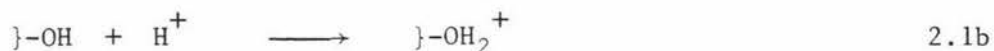
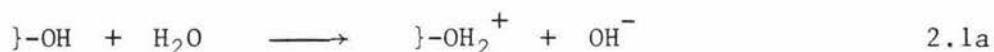
REVIEW OF LITERATURE

2.1 Anion Sorption by Soil and Soil Components

This thesis attempts to make a contribution to the study of sulphate adsorption by soils. Accordingly, a general review of anion sorption is presented with emphasis on the concepts and terminology essential to an understanding of sorption mechanisms.

2.1.1 Soil components important in anion sorption

Sorption of anions occurs at exposed hydroxyl groups on the surfaces of soil colloids (Parfitt, 1978; Harrison and Berkheser, 1982). These groups can undergo reaction with water, hydroxyl, or hydrogen ions as follows:



and thus have a charge which can be positive or negative depending on pH. A convenient model (Parfitt, 1978; Uehara and Gilman, 1981) considers the $-\text{OH}$ group to have a charge of zero, the $-\text{OH}_2^+$ group to have a single positive charge, and the $-\text{O}^-$ group to have a single negative charge. In reality however, the actual charge on the exposed $-\text{OH}$ group, which is co-ordinated to cations below the surface, will depend on the internal lattice of the particular colloid.

The major soil constituents having amphoteric surfaces similar to those described above include goethite, ferrihydrite and other iron oxides, and oxides of aluminium such as gibbsite, imogolite and allophane (Parfitt, 1980). Short range order hydrous oxides have abundant exposed hydroxyl groups, and sorb up to 100 times more

phosphate than their crystalline counterparts (Ryden, 1975). Correlation studies (Harward et al., 1962), and studies of pure components (Parfitt, 1978) have shown that these hydrous oxides of iron and aluminium, and to a lesser extent other cations, are the principal soil components involved in anion sorption but the edges of layer-lattice clays may also develop a positive charge at exposed Al-OH, or Si-OH groups (Bolt, 1979). Many of these hydrous oxides are present as coatings on other soil mineral surfaces in soils (Wada and Harward, 1974).

2.1.2 The soil colloid/soil solution interface

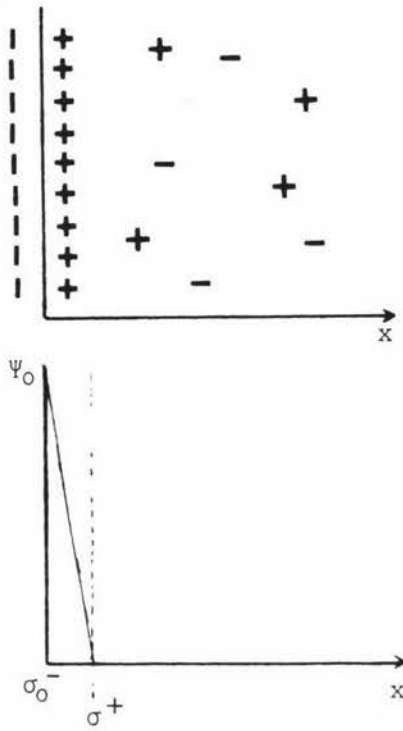
2.1.2.1 Constant charge surfaces.

Most layer-lattice clays exhibit a permanent negative charge, due to isomorphous substitution in the alumino-silicate lattice (Schofield, 1949). The surfaces of these minerals have a measurable and relatively constant charge density which is unaffected by change in pH. The charge on the colloid surface creates an electrostatic potential, in response to which, ions will be attracted or repelled.

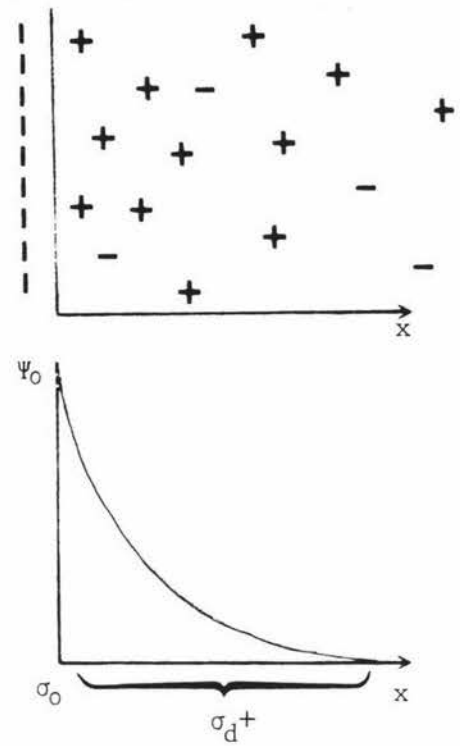
The historical development of a model for the distribution of charge and potential close to a colloid/solution interface is represented in Fig. 2-1 (Bear, 1960; Hope, 1977; Bohn et al., 1979).

These models all assume that surface charge is confined to a plane and is evenly distributed over the surface. They vary in complexity from the simple ion-pair model of Helmholtz (Fig. 2-1a), through the diffuse layer theory developed by Gouy in 1910 (Fig. 2-1b), to the double layer theories of Stern (1924) and Grahame (1947). Both of the latter theories assume that charge on the surface (σ_0) is balanced by charge on ions at a distance of closest approach (σ_{st}), the Stern layer, plus charge on ions in a diffuse layer (σ_d). This diffuse layer contains ions of opposite charge to the surface (counter-ions) and ions of similar charge to the surface (co-ions). The Stern-Grahame model contained elements of both the Helmholtz and the Gouy-Chapman model but benefited from considering the finite dimensions of ions in solution, when previous approaches had treated ions as point charges.

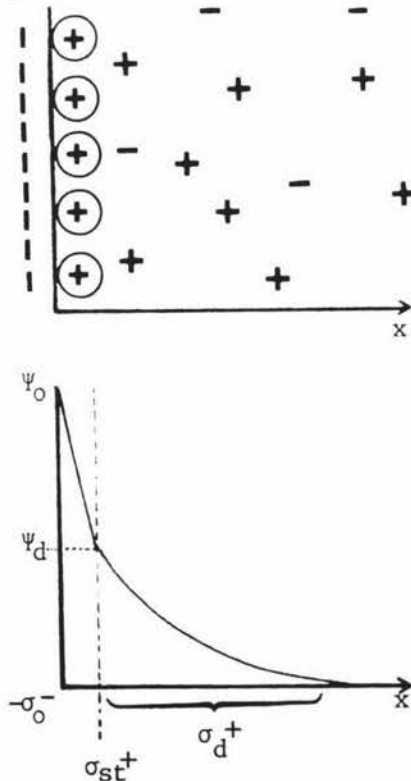
(a) Helmholtz 1879



(b) Gouy 1910



(c) Stern 1924



(d) Stern-Grahame 1947

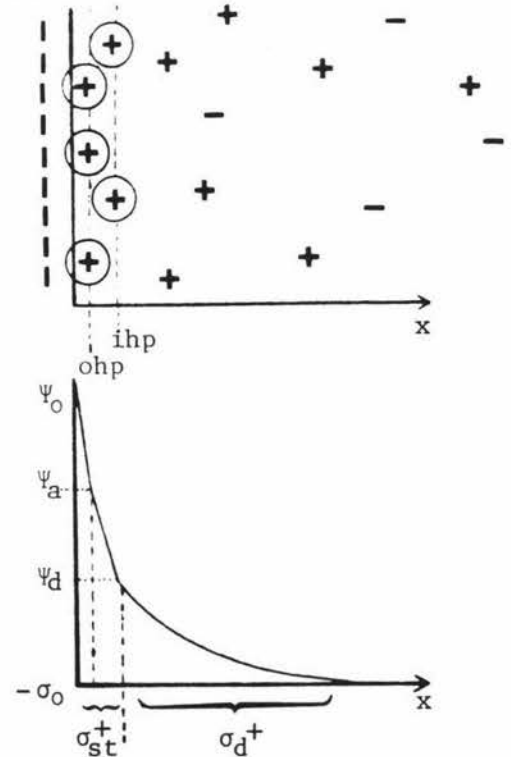


Fig. 2-1

Models for the distribution of ions and potential close to the soil/solution interface. A schematic representation of (a) ion pair (b) diffuse layer, and (c) (d) double layer models where ψ = potential, σ = charge, x = distance from the surface, and the subscripts o, st, a and d denote the surface, the stern layer, the plane of sorption of a specifically sorbed anion, and the diffuse layer respectively. A point charge is represented as + or - but where the finite size of ions is recognised is used. ihp and ohp refer to the inner and outer-Helmholtz planes respectively.

Some ions are more strongly adsorbed than others, and Grahame (1947) proposed that these ions could be sorbed into a plane of direct contact with the surface by complete or partial removal of the hydration sheaths of both the ion and the surface. The locus of centres of such ions is called the inner-Helmholtz plane (i.h.p.), while the locus of centres of ions that are not so strongly adsorbed is the outer-Helmholtz plane (o.h.p.). Sorption in the i.h.p. implies some form of specific interaction between the surface and the adsorbing ion, and becomes possible when the ion concerned is weakly hydrated, or if a strong adsorption potential (chemical or coulombic) exists between the specific ion and the sorption surface (Bowden, 1973).

For a constant charge surface, the electrostatic potential at short distances from the surface varies in response to changes in concentration and valence of the ions in the supporting electrolyte (Uehara and Gilman, 1981).

In the simple case of the Gouy-Chapman theory (Fig. 2-1b), the charge in the diffuse layer is given by

$$\sigma_d = \left(\frac{2n \cdot \Sigma \cdot k \cdot t}{\Pi} \right)^{1/2} \sinh \left(\frac{ze\psi^0}{zkt} \right) \quad 2.2$$

(van Olphen, 1963), where σ_d is the charge in the diffuse layer (in this case equal to $-\sigma_0$, the charge density of the surface), n is the concentration of the equilibrium solution in moles per cm^3 , Σ is the dielectric constant of the medium, z is the valence of the counter-ion, e is the charge on an electron, h is Plancks constant, and ψ^0 is the surface potential.

The surface charge is constant for these surfaces and a change in valence or concentration of the electrolyte therefore results in a decrease in the potential difference between surface and solution. This is accomplished by a reduction in the distance that the double layer extends into the solution; i.e. the "thickness" of the double layer is reduced according to the following expression (Bear, 1960);

$$\ell \approx \frac{1}{3 \times 10^7 \cdot z \cdot \sqrt{c}} \quad 2.3$$

where ℓ is the thickness of the ionic double layer, and c is the molar concentration.

The Gouy-Chapman theory described above is inadequate for colloids having a high surface charge density, giving unrealistically high values for the number of ions close to the surface. When the finite size of ions is considered however, expressions can be derived for the charge accommodated close to the surface (σ_{st}) using the Stern-Grahame model (van Olphen, 1963). When this is done the ions in the Stern layer quantitatively reduce the surface charge density of the colloid, and the diffuse portion of the double layer (eq 2.2) then develops on a colloid surface of lower charge density.

Both of the above treatments predict that the thickness of the double layer will vary with the valence and concentration of the supporting electrolyte. In reality however, some cations approach closer to the surface than others and show a selectivity for sorption. This is related to the individual ion characteristics, such as hydrated radius and polarisability (Bohn et al., 1979; Bolt, 1979), and these ions which approach close to the surface will have an additional effect in decreasing the thickness of the ionic double layer (Bolt, 1979).

As shown in Fig. 2-1, the concentration of counter-ions decreases from the particle surface outward, while the concentration of ions of similar charge increases in the same direction, with the total ionic concentration decreasing in a direction away from the surface. Anions are thus repelled from the negatively charged surface and an increase in anion concentration in the bulk solution is observed when salt solutions are added to clay minerals (Schofield, 1949; Bear, 1960). This is referred to as anion exclusion, or negative adsorption, and the exclusion distance is greater for divalent ions such as sulphate than for chloride, particularly when present in a mono-monovalent salt such as sodium chloride (Bolt, 1979). Thus, less anion exclusion will occur in calcium chloride, than in sodium chloride, but this effect may be small unless specific adsorption of calcium grossly reduces the extent of the double layer (Bolt, 1979).

This has implications to the measurement of surface positive charge in soils (Barber and Rowell, 1972) (Section 2.1.3). An anion approaching a charged surface may be simultaneously attracted

to positive sites, whilst being repelled from the negatively charged clay colloid (Bohn et al., 1979; de Haan, 1964).

2.1.2.2 Variable charge surfaces. For hydrous oxides and other similar surfaces, surface charge varies according to the solution pH (eq. 2.1). At any given pH there is a characteristic potential difference between the surface and the bulk solution which will remain constant (eq. 2.2) regardless of changes in the ionic strength of the supporting electrolyte.

Thus, in contrast to the constant charge surfaces previously described, the effect of increasing either the valence or concentration of the supporting electrolyte will be to increase the screening effect on surface charge and thus allow increased sorption of H^+ or OH^- ions to maintain the surface potential constant.

The pH at which an equivalent number of positive and negative sites is present is termed the point of zero charge (pzc) (Parks, 1967), and at this pH an increase in ionic strength has no effect on surface charge.

At a pH higher than the pzc the surface will carry a net negative charge, whilst at a pH lower than the pzc the surface has a net positive charge. This does not mean that positive groups do not exist at pH values above the pzc; the co-existence of small amounts of positive and negative sites at the pzc has been reported for various oxides (Kraus et al., 1958; Amphlett, 1960). The pzc values for several hydrous oxides are presented in Table 2-1, and it is apparent that some oxides will be predominantly negatively charged at normal soil pH values, but that appreciable amounts of positive charge may be present on some Fe and Al surfaces (Greenland and Mott, 1978).

Table 2-1. The point of zero charge values of several hydrous oxides found in soils.

<u>Oxide</u>	<u>pzc</u>
SiO ₂	2.0
TiO ₂	4.5
MnO ₂	4.0
Fe ₂ O ₃	6.5-8.0
Al ₂ O ₃	7.5-9.5

2.1.3 Non-specific adsorption and the measurement of surface charge

Ions which are adsorbed only when the surface is oppositely charged and which can be displaced off the surface by a saturating concentration of any other counter-ion, are referred to as non-specifically adsorbed ions. The adsorption of these 'indifferent' ions can be used to measure the surface charge in soils (Schofield, 1949), and the amounts of electrolyte ions adsorbed can be predicted by double-layer models (eq. 2.2; Barber and Rowell, 1972; van Raij and Peech, 1972), even in soils containing both constant and variable charge surfaces.

The proportions of monovalent, divalent and trivalent ions of like charge adsorbed from a mixed electrolyte by non-specific adsorption can be estimated from ion exchange equations. Several ion exchange equations have been proposed, differing in the way in which they treat ions in solution (Bohn et al., 1979), but the Gapon equation (eq. 2.4) is usually preferred because it deals with easily measurable concentrations in solution.

$$\frac{(\text{Ads} - \text{Cl})}{(\text{Ads} - \text{SO}_4^{\frac{1}{2}})} = K_G \cdot \frac{(\text{Cl}^-)}{(\text{SO}_4^{2-})^{\frac{1}{2}}} \quad 2.4$$

Here the surface complexes of chloride (Ads - Cl) and sulphate (Ads - $\text{SO}_4^{\frac{1}{2}}$) are in meq g^{-1} , and the solution ions are in moles l^{-1} .

The ability of a soil to adsorb 'spectator' anions or cations is assessed by equilibrating the soil several times with a particular electrolyte, then displacing the adsorbed ions off the surface with a second electrolyte and measuring their concentration in solution (Schofield, 1949; Section 3.3).

The results obtained by this method may be affected by negative adsorption (Section 2.1.2). Several workers have suggested that corrections for negative adsorption of anions and cations will cancel out in most soils (van Raij and Peech, 1972; Morais et al., 1976), but this will only be correct at the pzc, and may not be applicable when ions of different valence are involved. Barber and Rowell (1972) found a correction of 20-40% was required for surface positive charge in one soil containing both constant and variable charge surfaces. Although positive charge can be measured in soils with a

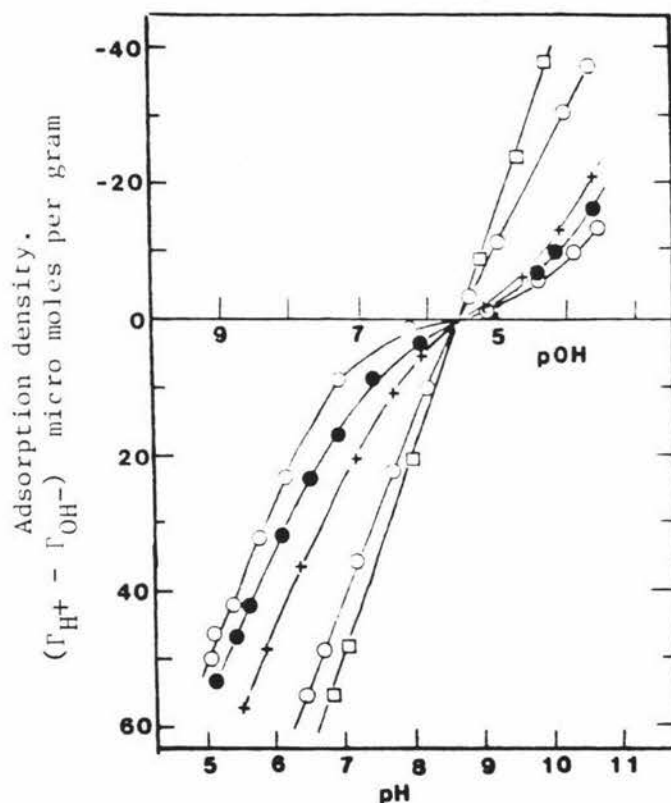
high reserve of surface negative charge (Black and Waring, 1976; Espinoza et al., 1975), if no correction is made for negative adsorption surface positive charge will be underestimated.

Positive and negative sites may be in close proximity in soils, and in dilute electrolyte solution diffuse double layers will extend further into the electrolyte, leading to overlap and cancellation of adjacent negative and positive sites (Barber and Rowell, 1972; van Raij and Peech, 1972) with parallel decreases in measurable surface charge values but no effect on net surface charge.

An alternative method for measurement of surface charge involves the use of acid/base titrations. Since surface charge depends on the amounts of potential determining H^+ or OH^- ions sorbed by a variable charge surface it is possible to determine the relationship between surface charge and pH by titrating the surface with acid and base. If this titration is performed in different concentrations of the same indifferent electrolyte, a plot of H^+ sorption (positive charge) or OH^- sorption (negative charge) against pH for each electrolyte yields several curves, which intersect at the point of zero charge of the oxide surface.

In the absence of specific adsorption (see Section 2.1.4) the pzc is equal to the iso-electric point (iep), the pH where the charge on the surface due to sorption of H^+ and OH^- alone is zero. The point of zero charge, as determined by titration, is referred to as the point of zero salt effect (pzse) and is often observed to differ from the point of zero net charge (pznc), which is the point of zero charge determined by adsorbed ion methods. The titration method usually gives a higher value for pzse than the pznc, and higher values for the charge at pH values away from the pzse (Parfitt, 1980). This appears to be related to the presence of organic matter and exchangeable Al ions (van Raij and Peech, 1972; Parker et al., 1979). Several reactions consume H^+ in soils, and changes in the amounts of H^+ added to soils cannot readily be equated with changes in surface charge. Parker et al. (1979) estimated that 30-90% of acid or base lost from titration did not contribute to a change in surface charge in one soil containing both constant and variable charge surfaces.

Fig. 2-2 Determination of the point of zero charge of oxide surfaces by potentiometric titration (Parks and de Bruyn, 1962).



Adsorption density of potential determining ions on ferric oxide as a function of pH and ionic strength: temperature, 21° ; indifferent electrolyte KNO_3 .

The adsorbed ion retention method is thus the preferred method for estimating the surface charge characteristics of soils, and provided the anion and the cation do not have a specific affinity for the surface, will provide a reliable estimate of the charge on the soil's surface (Sposito, 1981). The potentiometric titration method measures only net charge and not the actual amounts of positive and negative charges present, but it has found widespread application in the characterisation of oxides and pure soil components.

2.1.4 Specific sorption and the definition of the surface

Non-specifically adsorbed anions are visualised as being adsorbed in the outer-Helmholtz plane, or in the diffuse layer (Fig. 2-1). When sorption is in excess of that predicted from ion-exchange considerations (eq. 2.4), specific sorption is implied. Specifically sorbed anions approach to within the Stern layer distance from the surface, and it is thought sorption can occur on neutral or even net negatively charged surfaces (Grahame, 1947; Hingston et al., 1967, 1972), although there is a conflict in the literature as to the degree to which these anions interact with the surface and alter surface charge. Apparent inconsistencies have arisen through differing concepts of the surface and different definitions of surface charge. Some workers consider anions sorbed in the inner-Helmholtz plane to constitute part of the surface (Hingston et al., 1967, 1968, 1972; Bowden et al., 1980a), and report changes in surface charge on anion sorption (Rajan, 1976; Parfitt, 1978; Bowden et al., 1980a), while others maintain a distinction between the sorbed anion and the surface (Grahame, 1947; Breeuswma and Lyklema, 1971, 1973).

When oxide surfaces are titrated with acid or base in the presence of specifically adsorbed anions, the pzse shifts to a lower pH. That is, less OH^- must be supplied to obtain equal amounts of positive and negative charge on the surface. This is generally interpreted as evidence that the specifically sorbed anion increases surface negative charge (Mekaru and Uehara, 1972; Sawhney, 1974; Morais et al., 1976). However, if the anion is considered to remain distinct from the surface, adsorption results in a decrease in the amount of OH^- sorbed, and a consequent reduction in the amount of negative charge on the oxide surface (Breeuswma and Lyklema, 1973; Yates and Healy, 1975, Keng and Uehara, 1974; Gallez et al., 1976).

The distinction between non-specific and specific sorption, and the effect of sorption of any ion on surface charge will thus depend on how the surface is defined. Recent workers (Sposito, 1981; Barrow, 1981) have presented a unified definition of the surface which, by clearly specifying terminology, attempts to overcome many apparent contradictions in the sorption literature (Fig. 2-3).

Fig. 2-3. A unified definition of the sorption surface

$\sigma_s = \sigma_p + \sigma_v$	σ_a	σ_β	σ_d
Structural Surface	Inner sphere	Outer sphere	Diffuse layer

The basic tenet of the model is that

$$\sigma_s + \sigma_a + \sigma_\beta + \sigma_d = 0, \text{ where}$$

σ_p = permanent charge due to isomorphous substitution.

σ_v = variable charge.

σ_s = the charge on the oxide surface (iep : $\sigma_s = 0$).

σ_a = "Inner sphere complex charge" resulting from strong adsorption of ions other than H^+ or OH^- which can become potential determining ions. e.g. phosphate.

σ_β = "Outer sphere complex charge", perhaps equatable with the o.h.p of the Stern-Grahame model.

σ_d = Diffuse layer charge.

By definition there are no water molecules interposed between the surface functional group and the ions in the inner sphere. This close proximity allows covalent interactions to play a major role in the bonding mechanism, imparting stability to the complex (Sposito, 1981). The surface encompasses σ_a so the surface has zero charge (pzc) when $\sigma_s + \sigma_a = 0$

The experimentally determined preference of some ions over others of the same valence (Section 2.1.2.1), necessitates a layer of ion specificity distinct from the surface (σ_β), and further evidence for a β plane comes from studies which indicate that some ions approach closer to the surface than others (Breeuswma and Lyklema, 1973; Barrow, 1981), albeit in response to surface charge. Colloids remain

in aqueous suspension as long as they remain charged but in calcium media Breeuswma and Lyklema (1973) found some colloids did not migrate to the same extent in an electric field. This suggested that calcium could approach closer to the charged particle than sodium, and neutralise the negative charge on the colloid. Despite this apparent specificity, calcium did not appear to be adsorbed when the colloid was neutral or carried a net positive charge. Calcium is thus said to be adsorbed in the β plane, and the division between σ_β and σ_d can then be equated with the plane of shear (Bowden, 1973) commonly described in colloid mobility studies. When $\sigma_\beta + \sigma_s + \sigma_a \neq 0$, the colloid will migrate in an electric field.

Close approach of ions to the surface (σ_β, σ_a) can cause proton association or dissociation at the surface, shifting the pzse ($\sigma_v = 0$) in different electrolytes (Sposito, 1981). Where there is equal cation and anion adsorption the surface is at the pznc, but this pH value will also be influenced by (i) the presence of selectively adsorbed ions in the β plane, and (ii) whether or not the indifferent ions enter the outer sphere (σ_β) and displace previously adsorbed ions, or effect H^+/OH^- sorption. Although the ions in the β plane are observed to move in concert with the rest of the surface in colloid mobility studies, they are not considered to be part of the surface.

The surface model described above has great value in standardising the terminology used in sorption studies, but the evidence for five distinct planes of sorption is purely empirical and Barrow (1981) suggested that a continuum of specificity for sorption may be more appropriate.

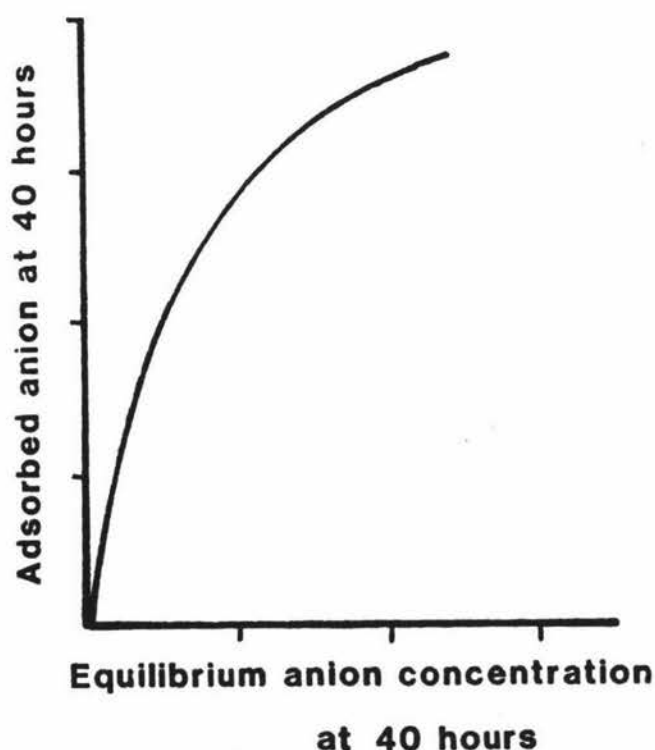
An oxide surface is a dynamic soil component, a complex and often irregular surface, which may be extended by adsorption and precipitation of ionic species, or contracted by dissolution and desorption of the solid phase species (Bowden et al., 1980b). The concept of planes of adsorption may be a gross generalisation for such a surface, and any ion may sorb with a number of different intensities depending on the molecular environment in a particular region of sorption (Bowden, 1973). When the sorption surface is mixed with other soil components, with differing charge characteristics, and a variety of ions competing for sorption an even greater continuum of

sorption intensities, and distances of approach to the surface might be expected.

2.1.5 Modelling anion sorption

Adsorption of ions from solution provides a mechanism for retention and release of anions by soils and soil components, although the degree of reversibility of the process may vary with different anions and different soil components. Sorption isotherms relating the quantity sorbed to the concentration in solution are convenient summaries of the adsorption properties of a particular surface (Fig. 2-4), and considerable attention has been directed towards mathematically reproducing these curves in order to model the adsorption process, with the ultimate aim of predicting the reactions of inorganic nutrients in a soil/plant system (Barrow, 1978).

Fig. 2-4. An example of a sorption isotherm



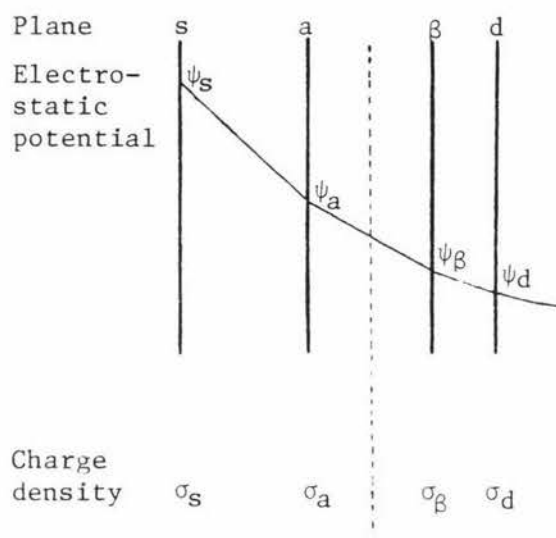
Models proposed vary from an empirical description of the data, e.g. the Freundlich equation (Holford et al., 1974; Barrow and Shaw, 1975a), to more complex models which may yield additional information on the interaction of a particular ion with the surface (Hayward and Trapnell, 1964; Hingston et al., 1972; Syers et al., 1973). Perhaps the most favoured of these is the Langmuir equation (Giles, 1970), which may give a good description of sorption data over a limited concentration range in soils (Olsen and Watanabe, 1957; Gunary, 1970). When two or more Langmuir equations are used, adsorption is additive, and a good fit to sorption over quite a wide concentration range can be obtained (Rajan and Fox, 1975; Syers et al., 1973; Ryden et al., 1977a).

Using a three surface Langmuir equation to describe sorption data, Ryden et al. (1977a) proposed that phosphate was sorbed on three energetically different types of site. They suggested mechanisms by which this might occur in soils, and provided good qualitative support for these mechanisms from the charge relationships of phosphate sorption (Rajan 1976; Ryden et al., 1977a). This is discussed in more detail in Section 2.6.

There is however, some debate as to the applicability of the Langmuir equation, developed originally for monolayer adsorption of gas molecules on uncharged surfaces, to systems where charged particles are sorbing on a charged surface (Brunauer et al., 1966; Giles, 1970; Barrow, 1978; Posner and Bowden, 1980), and also as to the justification for splitting sorption isotherms into three regions (Barrow, 1978; Posner and Bowden, 1980). To date this debate remains unresolved.

Another school of workers has recently suggested that the changes in phosphate sorption can be explained by a progressive increase in surface negativity as sorption proceeds (Bowden et al., 1977, 1980a). These workers have developed a mechanistic model using an extended double layer approach to modelling the sorption of ions on an idealised charged surface (Fig. 2-5) (Bowden et al., 1980a), assuming it becomes increasingly difficult for each increment of anion to adsorb as the negative charge on the surface increases.

Fig. 2-5. The sorption surface (Bowden et al., 1980a)



Schematic representation of the distribution of charge and of the change in potential when phosphate ions are adsorbed on an idealized planar surface (from Bowden et al. (1980)).

When an anion sorbs on this surface, it sorbs in a characteristic plane depending on its sorption affinity. Each anion has a characteristic free energy of sorption, which can be separated into arbitrary components to account for experimentally observed differences in the sorption behaviour of the different ions.

$$\Delta G_{\text{ads}} = \Delta G_{\text{coul}} + \Delta G_{\text{chem}} + \Delta G_{\text{int}} \quad 2.5$$

Here ΔG_{coul} is the non-specific component of the adsorption free energy, depending on no other property of the ion than its charge. ΔG_{chem} , which describes the specific interaction of the ion with the surface, depends on the electronic nature of both the ion and the surface. The binding forces which constitute this component are composed of co-ordination, van der Waal and polarisation forces (de Boer, 1950), and ΔG_{chem} can be positive, negative or zero. Ions can adsorb on uncharged surfaces and even surfaces of like charge if ΔG_{chem} is large enough to overcome the electrical forces of repulsion. The final component of the sorption free energy, ΔG_{int} , is the interaction component which gives specificity to coulombic

binding, being associated with the size and polarisability of the adsorbing ion, and the structured nature of the electrolyte solution at the surface. ΔG_{int} can be positive or negative and is distinguished experimentally from ΔG_{chem} in that it varies with surface potential and is zero when the surface has no charge.

A detailed derivation of the extended double layer model is beyond the scope of this review, but expressions can be derived for the relationship between the activity of ions in solution and on the surface from electrochemical considerations. This leads to expressions for the sorption of H^+ or OH^- on the surface, for the changes in surface charge with pH, and ultimately for the charge, or sorption of other ions, in sorption planes further from the surface (Bowden et al., 1974, 1977, 1980a).

The model leads to twelve simultaneous equations which must be solved for seven unknowns (charge and potential terms), after the assignment of values to numerous parameters, such as the maximum amount of charge that can be accommodated in each plane (N), and binding constants (K_i) for each ionic species present.

Assuming electrical neutrality ($\sigma_s + \sigma_a + \sigma_b + \sigma_d = 0$) several simplifying assumptions yield the equations necessary to solve for charge and potential in each plane, but even so, the assignment of values to the parameters and variables is not a simple matter. Several parameters, such as the binding constants for OH^- and H^+ , the maximum number of surface sites, and the capacitance, are determined from potentiometric titration curves. These empirically derived curves may however be insensitive to changes in the value of some parameters and large errors could result (Barrow et al., 1980a, b). The titration curve method, although suitable for the oxide surfaces for which the model was developed, is not applicable to soils (Parker et al., 1979), and this places a limitation on the use of the model in mixed mineral systems. The model can be solved by trial and error (Bowden, 1973; Bowden et al., 1977), or by using computer optimisation techniques (Barrow et al., 1980a, b), but methods of measuring some parameters independently would be preferable (Barrow et al., 1980a).

Historically, a wealth of information on the interactions of

anions with oxide surfaces has accumulated from an Australian group of workers (Hingston et al., 1967, 1968, 1971, 1972), and the model of Bowden et al. (1977, 1980a) reproduces this data. The underlying assumption in much of this early work (Hingston et al., 1967, 1968, 1972) was that sorption would always increase net surface charge and this concept has persisted to the present model (Barrow, 1978; Bowden et al., 1980a, b).

Considerable emphasis is placed on the ability of the model to reproduce data for the charge relationships of phosphate and sulphate sorption (Bowden et al., 1980a), but there are problems in the original method used to assess surface charge (Hingston et al., 1972). Hope (1977) suggested that the method, involving a series of titrations of anion, adsorbent + anion, and adsorbent, depended on the validity of the ligand exchange mechanism proposed (Hingston et al., 1972), and the method also depends on the assumption that the charge on the adsorbed anion will be equal to the average charge on the anion in solution. This may be open to question.

The success of the latest model does not lie in its ability to reproduce data. There is an interdependence of parameters, coefficients, and experimental observations that makes it difficult to draw mechanistic conclusions from this correlation. Two surface Langmuir equations (Syers et al., 1973; Rajan and Fox, 1975) accounted for P sorption over a similar concentration range of phosphate in solution, and the method used to measure surface charge (Hingston et al., 1972) may be too indirect to be of any significance.

Evidence for a consistent increase in surface negative charge on phosphate sorption is by no means conclusive, being limited to a few studies of changes in surface charge on oxides (Hingston et al., 1972; Rajan, 1976) and several observations on the shift in pzse (Hingston et al., 1972; Breeuswma and Lyklema, 1973). This contrasts with evidence that surface negative charge does not change in a certain range of sorption (Rajan, 1976; Ryden et al., 1977a), where H_2PO_4^- exchanges with OH^- on the surface.

Mathematical models, such as that proposed by Bowden et al. (1980a), are by nature generalisations but the general trends observed in both data and generated curves give good support to the model.

Changes in pH (Bowden et al., 1980a), ionic strength (Barrow et al. 1980b), and competition with other ions (Bowden et al., 1977; Bowden et al., 1980b) have been shown to have readily predictable effects on sorption in oxide systems, and this has implications to the sorption of anions by soils.

There will be difficulties however in applying the model to soils as it depends largely on potentiometric titration curves, and there is also a difficulty in characterising the soil surface sufficiently to apply an extended double layer approach.

Although oxide components similar to those studied by Bowden et al (1977, 1980a, 1980b) may be important in soils (Fordham and Norrish, 1979), it is found that laboratory prepared oxides have a much higher pzc than those found in soils (Barrow et al., 1983). This is probably because of adsorbed organic matter (van Raij and Peech, 1972) and previously adsorbed phosphate or silicate (Barrow et al., 1983). Consequently, whereas most soil oxides carry a net negative charge at soil pH values, the studies of Bowden et al. (1977, 1980a, 1980b) were performed on positively charged surfaces, without the complicating effects of having both positive and negative charge on the same surface, and this may affect the results obtained.

Although highly weathered tropical soils, or soils with relatively simple mineral assemblages, may behave predictably and lend themselves to modelling with some degree of success (Bowden et al., 1980b), it is the qualitative predictions from the model which have greatest application to soils. The model has shown an ability to successfully predict sorption under varying experimental conditions, suggesting that it emphasises the correct features of sorption and is a good approximation of the way in which ions in solution react to an oppositely charged surface.

2.1.6 Phosphate sorption by soil components and soils

2.1.6.1 The surface-phosphate complex.

Infra red spectroscopic techniques have indicated that phosphate forms a binucleate complex of the type $\text{Fe} - \text{O} - \text{P} - \text{O} - \text{Fe}$ on both evacuated (Parfitt et al., 1975, 1977), and air-dry films (Parfitt and Atkinson, 1976) of

goethite and other oxides. The evidence consisted of changes in the spectra of both phosphate and the surface, indicating stretching of $P = O$ and $P - O - (Fe)$ bonds and almost complete replacement of surface OH groups by phosphate (Parfitt et al., 1977).

Studies at a range of pH values, and at higher concentrations of phosphate in solution (Parfitt, 1979), have indicated that phosphate forms a binucleate complex at a range of surface coverage (Parfitt, 1978). This may contrast with the one point attachment of phosphate to the surface proposed by Ryden et al. (1977a) at high phosphate additions, but some blurring of spectra was observed, which could result from interactions of the type proposed (Ryden et al., 1977a). The broadening of infra-red adsorption bands observed was attributed to hydrogen bonding by Parfitt (1978) however, with different amounts of hydrogen bonding occurring on different oxides.

Parfitt (1977) obtained evidence for surface OH groups in soils, suggesting that the similarity of sorption isotherms in soils and oxides indicated a binucleate phosphate complex was also formed in soils. The ligand exchange mechanisms proposed by several workers (Hingston et al., 1972; Rajan and Fox, 1975; Ryden et al., 1977a) provide support for this approach, particularly when phosphate is visualised as replacing two surface groups (Rajan, 1975a, 1976, 1979b), and Barrow and Shaw (1975b) have suggested that the slow formation of binucleate complex in soil might account for the observed decrease in isotopic exchangeability of P with time.

2.1.6.2 Phosphate sorption studies. There is an extensive literature on phosphate sorption, and although there is some conflict in the mechanisms proposed by various workers (Muljadi et al., 1966; Hingston et al., 1972; Rajan, 1975a, 1976; Ryden et al., 1977a; Bowden et al., 1980a) there are several general trends which are commonly reported for phosphate sorption in both soil components and soils.

(i) Phosphate addition increases net surface negative charge in soils (Schalscha et al., 1974; Sawhney, 1974), and shifts the pzse in oxide studies (Hingston et al., 1972; Breeuswma and Lyklema, 1973).

(ii) Uptake of H^+ , release of OH^- and concomitant changes in pH may occur when phosphate interacts with the soil surface (Rajan, 1976; Ryden et al., 1977a).

(iii) Sorption shows a dependence in ionic strength (Mattson et al., 1950; Barrow, 1972), and is generally greater in calcium rather than sodium media (Volkwiess et al., 1973; Ryden and Syers, 1975).

(iv) Phosphate competes strongly with other anions (Hingston et al., 1971; Bowden et al., 1980b).

(v) Observed sorption maxima show a dependence on pH (Barrow, 1970; Bowden et al., 1980a), with characteristic inflexions in these 'adsorption envelopes' (Hingston et al., 1967) at pH values corresponding to the dissociation constants of the ionic species.

Any sorption model or mechanism proposed must be compatible with these observations. Two contrasting approaches to describing phosphate sorption; the extended double layer model (Bowden et al., 1980a,b; Barrow et al., 1980a,b), and the three surface Langmuir approach (Ryden et al., 1977a,b,c), have shown an ability to qualitatively predict both changes in sorption, and changes in surface charge during sorption. Some of the limitations of the extended double layer approach have already been discussed, but a general review of phosphate sorption follows with emphasis on the qualitative description of data provided by these two groups of workers.

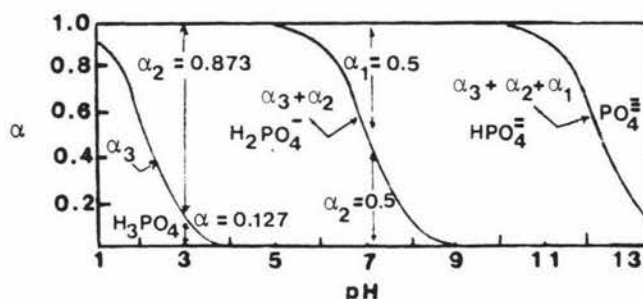
The phosphate anion undergoes hydrolysis in solution,



and the proportions of monovalent, divalent and trivalent ions of phosphate present in solution vary at different pH values as shown in Fig. 2-6.

Fig. 2-6

Distribution diagram for phosphoric acid



Distribution diagram for phosphoric acid. A vertical line is divided into segments proportional to the fraction α , (after Butler, 1964).

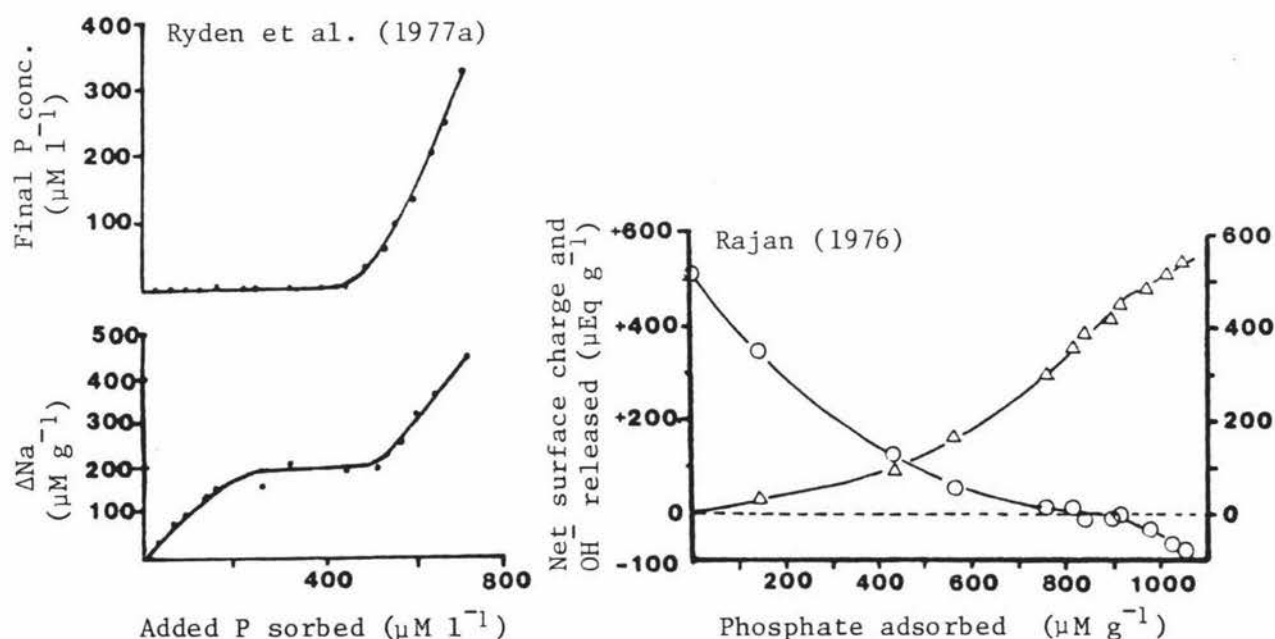
The model of Bowden et al. (1980a) suggested that HPO_4^{2-} was the major ion sorbed by goethite, although in much of the pH range studied H_2PO_4^- was the predominant form in solution. Many other workers have proposed, and provided evidence for, some sorption of monovalent ions (H_2PO_4^-) however (Muljadi et al., 1966; Bræuswma and Lyklema, 1973; Rajan, 1975b; Rajan and Fox, 1976; Parfitt, 1977; Ryden et al., 1977a), and Bowden et al. (1980a) suggested different results might be obtained under different conditions.

If HPO_4^{2-} is the phosphate ion sorbing then changes in apparent sorption maxima with pH (Hingston et al., 1967, 1968, 1972), can be explained. At low pH, maximum sorption occurs because of a large electrostatic component to sorption. This electrostatic component decreases as pH increases but the activity of HPO_4^{2-} , which has a high binding constant, increases 10 fold for every pH unit increase also, so pH changes have only a slight effect on P sorption. Towards neutral pH, where the proportion of HPO_4^{2-} is relatively constant, sorption depends more on changes in the electrostatic component and decreases more rapidly with increasing pH (Bowden et al., 1980a). If the method Bowden et al., (1980a) used to measure surface

charge can be accepted (Section 2.6) observations on the change in surface charge with phosphate sorption suggest HPO_4^{2-} is sorbed at a wide range of pH values. The charge conveyed to the surface is always less than -2 however, as sorption in plane a (Fig. 2-5) causes uptake of H^+ or release of OH^- from the surface and some degree of preservation of surface charge.

Other workers have postulated mechanisms for sorption of H_2PO_4^- in order to explain charge and hydroxyl release data of soil components (Muljadi et al., 1966; Rajan, 1976; Ryden et al., 1977a).

Fig. 2-7 Effect of phosphate on surface charge



An isotherm for the sorption of P by Fe gel; and, the relationship between the difference (ΔNa) in the Na uptake by Fe gel in the presence and absence of added P for the same addition of Na, and the amount of added P sorbed.

Phosphate adsorption on hydrous alumina. Net surface charge (O) and OH^- released (Δ) plotted against P adsorbed.

The data of Rajan (1976) (Fig. 2-7a) suggest a rapid neutralisation of surface positive charge, which slows as the amount of phosphate on the surface increases. This is supportive of the data of Ryden et al., (1977a) (Fig. 2-7b) who inferred a decrease

in positive charge from increased sodium adsorption. It is unlikely that Ryden et al. (1977a) were measuring a real decrease in positive charge. Only under fortuitous conditions of electrolyte concentration, giving mutual cancellation of adjacent negative and positive sites, could increased Na sorption correspond to decreased positive charge. This is only a problem in the low concentration range where phosphate is thought to sorb on positive sites however, and here, an increase in sodium adsorption may indicate HPO_4^{2-} is sorbing to increase surface negative charge.

There is significant agreement between the results of Ryden et al. (1977a) and Rajan (1976) however, and these data, and hydroxyl release (pH change) data (Ryden et al., 1977a), give good qualitative support for a general mechanism of phosphate sorption proposed by Ryden et al. (1977a).

Phosphate was considered to sorb on three different types of site (Ryden et al., 1977a). Firstly, on positive sites to give a neutral surface, and no release of hydroxyls; secondly, on neutral sites to give no change in surface charge and displacement of OH^- by phosphate, viz ligand exchange; and thirdly by completely reversible potential-determining sorption on neutral or negative sites. Sorption in this region involved weak bonding to surface Fe atoms, and sorption of Na (negative charge) increased in proportion to the amount of P sorbed. Rajan and co-workers (Rajan and Fox, 1972; Rajan and Perrot, 1975; Rajan, 1976) had postulated a similar series of ligand exchange mechanisms involving displacement of adsorbed silica, OH_2^+ , or OH groups in the lower range of sorption ($< 800 \mu\text{mole g}^{-1}$), but found that disruption of hydrous alumina occurred at higher phosphate concentrations exposing new sites for sorption.

The third category of sorption (Ryden et al., 1977a, c) with consequent increase in surface negativity, was not observed by Rajan (1976), and although this may be due to fundamental differences in the nature of the oxide surface studied, it can also be explained by the method of measuring surface charge. Easily desorbable-P may not stay on the surface when charge is estimated by the entrapped ion method used by Rajan (1976) and no increase in surface negative charge would be observed.

Ryden and Syers (1975) had observed that many of the effects of calcium and ionic strength on phosphate sorption could be explained by kinetic effects in sorption studies. These effects could be eliminated by a graphical technique which projected sorption to infinite time. There was however, a real effect of ionic strength in increasing the more-physical sorption of phosphate (Ryden et al., 1977c). With increasing ionic strength, and in calcium media, they postulated that more phosphate could approach the surface due to compression of the ionic double layer and enhanced screening of the negative charge that accumulated at the surface during sorption. Similarly, increased sorption at positive sites was observed with increasing ionic strength and in calcium media (Ryden et al., 1977a), but there was no evidence for sorption of phosphate on positive sites resulting from specific adsorption of calcium.

An extended double layer approach (Barrow et al., 1980a; Bowden et al., 1980a) also successfully predicted the effects of ionic strength and calcium on phosphate sorption (Barrow et al., 1980b).

At low pH when the surface (goethite) carried a net positive charge, increasing ionic strength decreased the positive potential in the plane of sorption for P and sorption was reduced. When the surface carried a net negative charge, sorption was increased, the high ionic strength tending to reduce the negative potential at short distances from the surface (Bowden et al., 1980b). This is consistent with the effects measured by Ryden et al. (1977b) who thought sorption in region 1 occurred on positive sites when the surface carried a net negative charge. The effect of calcium was additional to that of ionic strength, and Bowden et al. (1980b) suggested that the specific adsorption of calcium in a plane of close approach to the surface reduced the negative electrostatic potential in this region and enabled more phosphate to be sorbed in an adjacent plane.

The sorption of phosphate by soils is complicated by the observation that an initial rapid reaction is followed by a continuing and slow reaction which makes sorbed-P less available (Mattingly, 1975).

Barrow and Shaw (1975a, b) had previously proposed a three compartment model to account for this continuing decrease in P

concentration in the equilibrating solution during sorption studies (Rajan and Fox, 1975).



A secondary reaction occurred after sorption, accounting for continuing sorption, and a decrease in isotopic exchangeability of P with time (Barrow and Shaw, 1975a). It was suggested that P remained on the initial sorption site but in a form which was not readily displaced and a bidentate ring structure was proposed (Section 2.1.7.1) (Kafkafi et al., 1967).

Ryden and co-workers (Ryden and Syers, 1977b; McLaughlin et al., 1977) suggested that the formation of binuclear complexes was not sufficient to account for a slow reaction on P sorption. The irreversibility of overall phosphate sorption was attributable to the conversion of easily desorbable-P in region 3 (Ryden et al. 1977b) to chemisorbed forms, which were not desorbed and only slowly isotopically exchangeable. Later studies (McLaughlin et al., 1977; Ryden et al., 1977c), on a variety of sorbents, showed that the shift of P into chemisorbed forms resulted from the diffusion of chemisorbed-P into occluded, or within gel surfaces. This regenerated external surfaces for sorption.

Although, Bowden et al. (1980a) considered there was no need to postulate two or more kinds of surface with different affinities to explain the sorption of phosphate (Muljadi et al., 1966; Syers et al., 1973; Ryden et al., 1977), the behaviour which gave rise to these mechanisms being more easily explained by an increase in negative charge as sorption increased (Bowden, 1973; Bowden et al., 1980a), there are some advantages in the more empirical approach of Ryden et al. (1977a, b, c). These mainly centre on the applicability of the approach to soil systems.

2.1.7 Sulphate adsorption by soil components and soils

2.1.7.1 The surface-sulphate complex. Although most workers agree that phosphate is sorbed in close approach to the surface (Parfitt, 1978), there is some debate as to the applicability of a ligand

exchange mechanism to sulphate adsorption. Infra-red spectroscopy studies have yielded different results under different conditions. Sulphate was thought to form a binucleate complex on suspensions of crystalline oxides (Parfitt and Russel, 1977; Parfitt and Smart, 1978), but was only in single co-ordination with the surface in co-precipitated films of aluminium hydroxide (Serna et al., 1977).

The close co-ordination of sulphate to the surface may partly be an artifact of the techniques used. Non-specifically adsorbed anions such as chloride and nitrate are adsorbed by electrostatic interaction with a surface, but appear to replace surface OH groups on iron-oxides when infra-red spectroscopy samples are evacuated (Parfitt and Russel, 1977; Harrison and Berkhieser, 1982). Similarly, Serna et al., (1977) have shown that sulphate replaces OH groups only after evacuation to remove surface water.

In apposition to this, Parfitt and Smart (1978) found sulphate replaced two surface groups on crystalline iron oxides with both air-dry and evacuated samples and Harrison and Berkhieser (1982) reported similar results with hydrous iron-oxides. Parfitt and Smart (1978) proposed that sulphate formed a binucleate bridging complex by ligand exchange with surface $-OH$ and $-OH_2^+$ groups. They suggested that the requirement for a surface $-OH_2^+$ group before sorption could occur accounted for the marked pH dependence of sulphate sorption.

This ligand exchange mechanism cannot be easily extended to soils. Studies in less ordered systems (Serna et al., 1977) suggest sulphate forms a single electrostatic link with the surface and hydroxyl ions in suitable position for sulphate to effect a bidentate ligand exchange may be less common on soils than on oxide surfaces. In addition, the presence of competing ions and a dominantly negative surface may affect the interaction between surface and sulphate in soils.

2.1.7.2 Sulphate adsorption studies. Sulphate is adsorbed by soils less strongly than phosphate (Hasan et al., 1970; Haque and Walmsley, 1973), and more strongly than non-specifically adsorbed anions such as chloride (Hingston et al. 1972). Aylmore et al. (1967) suggested that sulphate adsorption was largely irreversible on iron and aluminium

oxides but experience with soils (Chao et al. 1963, 1965; Barrow, 1967) tends to suggest that adsorbed sulphate is in rapid equilibrium with solution sulphate. Isotopic exchange results (Harward et al., 1962; Barrow and Shaw, 1977) indicate that adsorbed sulphate is in kinetic equilibrium with sulphate in the soil solution and adsorption/desorption studies have shown little hysteresis in soils (Harward et al., 1962; Barrow, 1967).

There are some similarities between sulphate and phosphate sorption, and these have prompted several workers to suggest that both anions are sorbed by similar mechanisms (Parfitt, 1978; Rajan, 1979b) in soil components and soils. It has been suggested that sorption of either anion will increase the surface negative charge (Hingston et al. 1967; Rajan 1979b; Barrow et al., 1980a), and a ligand exchange mechanism has been proposed for sulphate (Parfitt, 1978).

In contrast to phosphate however, evidence for ligand exchange during sulphate adsorption is not conclusive. Sulphate sorption promoted a release of hydroxyl ions (Chao et al., 1965; Mekaru and Ueharu, 1972; Couto et al., 1979), but the relationship between sulphate adsorbed and hydroxyl release was not consistent at all levels of sulphate addition (Rajan, 1978, 1979a, b). Initially only small amounts of hydroxyl were released per equivalent of sulphate adsorbed, but as the amount of sulphate added increased, proportionally more hydroxyl seemed to be displaced. Rajan (1979a, b) explained this by suggesting that sulphate was preferentially sorbed by ligand exchange, displacing $-\text{OH}_2^+$ in the low sorption range and $-\text{OH}$ at high levels of sulphate addition. This was consistent with an almost 1:1 relationship between the equivalents of sulphate sorbed and reduction in surface positive charge in the low sorption region. At high sorption, the proportion of sulphate sorbing by displacement of $-\text{OH}_2^+$ decreased and only small changes in surface positive charge were observed.

In these studies, surface charge was measured by an ion retention technique, whereby the amounts of indifferent ions retained in the diffuse layer, before and after sulphate adsorption, were displaced off the surface by five equilibrations with calcium and measured in solution.

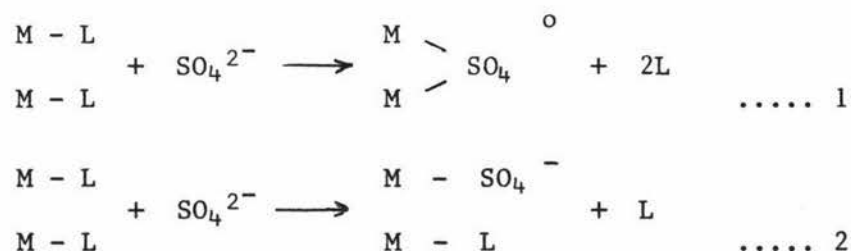
A decrease in surface positive charge recorded by this method makes no distinction as to whether sulphate is electrostatically linked or covalently bound to the surface, as in either case, when sulphate is neutralising positive charge, chloride adsorption is reduced and measured positive charge will decrease (Rajan, 1978).

Similarly, when a shift in the pzse is observed in oxide studies it is often assumed that sulphate has increased the net negative charge of the surface (Hingston et al., 1972; Pyman et al., 1979), but this depends on how the surface is defined. A shift in the point of zero salt effect would be recorded if the sulphate anion sorbed in an inner plane to other ions of the support medium (e.g. within the σ_β plane of Fig. 2-4), but this does not necessarily imply covalent co-ordination between sulphate and the surface (Yates and Healy, 1975).

Although Rajan found that sulphate decreases surface positive charge on sorption, the final surface, after sorption, was close to neutral (Rajan, 1978, 1979b). It was only at very high rates of addition (0-10 meq $l^{-1}S$) to allophane that a negative charge could be induced.

Rajan suggested that a bidentate ligand exchange left a neutral surface on hydrous alumina (Rajan, 1978), but a monovalent ligand exchange mechanism accounted for situations where an increase in surface negative charge was observed on sorption (Rajan, 1979a, b). The following mechanisms were proposed for sorption of sulphate on hydrous iron and aluminium surfaces (Fig. 2-8);

Fig. 2-8. A general mechanism for sulphate sorption



where M is the metal atom and L the ligand (mainly $-OH$, or OH_2^+).

The initial charge on the site could be either positive or neutral, with reaction 1 favoured on a net positive surface, and reaction 2 on neutral, and net negative surfaces, i.e. at higher concentrations of sulphate in solution. Parfitt and Smart (1978) proposed a mechanism similar to reaction 1 for sulphate adsorption on iron oxides.

These ligand exchange mechanisms are in conflict with the observations of Yates and Healy (1975). They compared the sorption of phosphate, sulphate and nitrate on goethite and on α -chromia. Fe(III)-oxide and Cr(III)-oxide behave very similarly in their aqueous chemistry, except that ligand exchange reactions occur much more slowly on α -chromia than goethite. The two oxides showed similar capacities to adsorb sulphate, and nitrate, but markedly different abilities to sorb phosphate. It was concluded that of the three anions studied, only phosphate underwent ligand exchange with α -chromia and probably with goethite.

The adsorption of an ion on a hydrous metal surface can be compared to similar reactions which occur when the same ion interacts with a metal ion in solution (Schindler, 1981). Evidence from co-ordination chemistry (Eigan, 1960; Hester and Plane, 1964; Prue, 1966) suggests that sulphate does not form inner sphere complexes with metal ions in solution. Raman spectra studies showed that in a series of metal ions including Al^{3+} , In^{3+} , Cu^{2+} , Zn^{2+} , and Mg^{2+} , only In^{3+} showed evidence of direct association with sulphate ions. The interaction between sulphate and the other cations occurred primarily through intervening water molecules, indicating there was an ionic interaction between sulphate and soluble cations. If this can be extrapolated to hydrous metal oxide surfaces it would suggest that sulphate forms an ionic bond with the surface. There are however, two major differences between co-ordination complexes formed between an anion and a metal ion in solution and adsorption on a cationic surface (Schindler, 1981). Firstly, anion adsorption is only partly reversible (for phosphate particularly, in contrast to sulphate) and secondly, lateral interactions between the adsorbed species, or between the anion and other regions of the surface, might take place to complicate the interaction between surface and anion.

There is some evidence for a dependence of sulphate adsorption capacity on the amounts of positive charge on oxide surfaces and soils,

which may also suggest that sulphate is adsorbed through an electrostatic link with the surface. Hingston et al. (1972) suggested that anions which were completely dissociated at normal soil pH (e.g. SO_4^{2-} , F^-) were only adsorbed on a positive surface, and that sulphate adsorption (in moles) was equal to the amount of chloride that could be adsorbed in the absence of sulphate. Accordingly, Hingston et al. (1972) proposed a ligand exchange mechanism involving adsorption of HSO_4^- at positive sites. Although Rajan's studies (1978, 1979a,b) suggested a 1:1 relationship between equivalents of sulphate adsorbed and positive charge neutralised at low concentrations of sulphate, the ratio increased (1:1:6) as adsorption tended to a maximum. It has recently been shown that a very pure iron oxide adsorbs four times as much sulphate as chloride (Harrison and Berkhieser, 1982) but most studies have suggested that a lower ratio of sulphate adsorbed to chloride adsorbed is appropriate in soils.

Black and Waring (1976, 1979) observed that one equivalent of sulphate was adsorbed per equivalent surface positive charge in a range of soils, and data for surface charge in different electrolytes (van Raij and Peech, 1972; Morais et al., 1976) indicated that the equivalents of sulphate and chloride adsorbed were of a similar magnitude in soils. Against this, Gebhardt and Coleman (1974a,b) have shown that tropical soils adsorb twice as many equivalents of sulphate as chloride. They considered that this was evidence for sulphate being adsorbed as HSO_4^- on positive sites (Hingston et al., 1972), but the evidence for HSO_4^- adsorption at anything other than low pH values (<4.0) is very limited and most workers prefer to consider SO_4^{2-} to be the anion adsorbed (Barrow et al., 1983).

Sulphate adsorption capacities are usually lower than those reported for phosphate (Barrow, 1970a; Parfitt and Smart, 1978), but Rajan (1979b) has shown that sulphate, selenite, and phosphate have similar adsorption maxima on hydrous alumina. The ratio of sulphate adsorbed to phosphate sorbed in soils decreases with increasing pH (Barrow, 1970a) and sulphate is a very poor competitor with phosphate (Kamprath et al., 1956; Chao, 1964). Under constant pH conditions (except where OH^- or HCO_3^- were added), Chao (1964) found that the adsorption of sulphate was reduced by several anions but unaffected by others (Fig. 2-9).

Fig. 2-9. Effect of other anions on sulphate adsorption

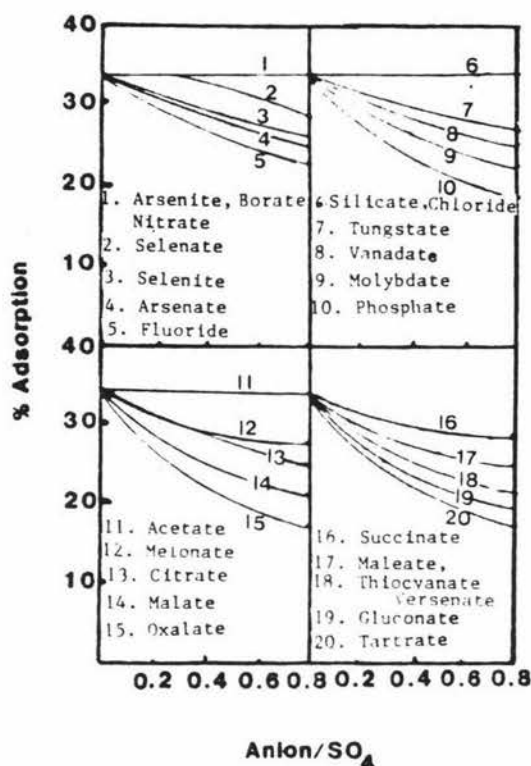


Fig. 2.9a

Sulfate adsorption from a 0.005N Na₂SO₄ solution by the Quillayute soil as affected by various proportions of inorganic (upper) and organic (lower) anions.

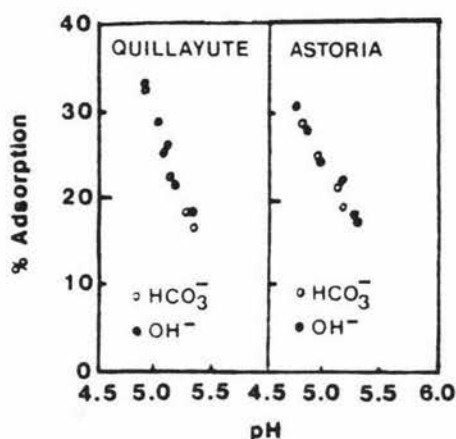


Fig. 2.9b

Sulfate adsorption from a 0.005N Na₂SO₄ solution at different pH levels caused by the presence of variable proportions of HCO₃⁻ or OH⁻ ions.

Kamprath et al. (1956) have shown that sulphate adsorption by soils is virtually eliminated when phosphate is present and it has been suggested that this competitive effect of phosphate has implications for the movement of inorganic-S in soils (Kamprath et al., 1956; Saunders, 1974; Metson and Blakemore, 1978).

The double layer model of Bowden et al (1980a) suggests that competition results from changes in the electrostatic potential when phosphate sorbs in a plane adjacent to that in which sulphate sorbs. If phosphate and sulphate were sorbed in the same plane, sulphate might be expected to have an effect on phosphate sorption. Sulphate has a slight effect on phosphate sorption on goethite (Parfitt, 1982), but the effects are just detectable and only significant at higher pH (>6.5). It is likely therefore that phosphate is sorbed in an

inner plane relative to sulphate (Breeuswma and Lyklema, 1973) and that phosphate sorption reduces the electrostatic potential at distances further from the surface (Bowden et al., 1980a, b). There is support for this in the binding constants (K_i ; Bowden et al., 1977) for the two anions on goethite. A value of 6.4 has been suggested for sulphate (Barrow et al., 1980a) and 7×10^6 for phosphate (Bowden et al., 1980a), compared to values of 0 - 0.5 allocated to non-specifically adsorbed anions.

Sulphate adsorption shows a dependence on the electrostatic potential of the surface (Barrow et al., 1983). Adsorption thus changes with ionic strength and pH, and although there is little information on the effect of ionic strength or accompanying cation on adsorption, several workers have observed a decrease in sulphate adsorption with increasing pH (Kamprath et al., 1956; Chao et al., 1963; Barrow, 1970a; Black and Waring, 1979). The effect of pH is considerably larger for sulphate than phosphate (Barrow, 1970a), and Kamprath et al. (1956) have suggested that little sulphate is adsorbed above pH 6.0 in most soils. Changes in sulphate adsorption with pH have been explained by increased competition with hydroxyl ions on aluminium surfaces by some workers (Miller, 1924; Marion and Thomas, 1946), and by changes in surface charge by others (Hingston et al., 1972; Black and Waring, 1979).

The present study incorporates a comparison of chloride, sulphate and phosphate sorption by soils of varying pH in which the greater significance of surface positive charge to the adsorption of sulphate will be emphasised.

2.2 Implications of Adsorption to the Mobility of Sulphate in Soils

Soluble sulphate fertilisers are applied to New Zealand soils to supplement an available nutrient pool consisting of soil solution sulphate, and sulphate adsorbed on soil colloids (During, 1972; Metson, 1979). Sulphate which exists in the soil solution will be displaced by incoming leaching water but sulphate held on the soil

surface is less susceptible to leaching (Barrow, 1967). Adsorbed sulphate is nonetheless in equilibrium with soil solution sulphate, so the primary determinant of the potential loss of nutrient is the amount of water moving through the profile. The observation that soils have differing abilities to adsorb sulphate (Saunders and Hogg, 1971; Metson, 1979) suggests that leaching losses might also be affected by the ability of the soil to adsorb sulphate (Barrow, 1967; Rhue and Kamprath, 1973).

2.2.1 Sulphate retention

2.2.1.1 Measurement. In New Zealand a sulphate retention quick test has been developed (Barrow, 1967; During and Martin, 1968; Saunders and Hogg, 1971) which ranks soils according to their ability to adsorb sulphate. Soils are shaken for 16 hours with a solution of 0.01M CaCl_2 containing 50 ppm S, and the amount of sulphate retained calculated after a correction for sulphate present in the soil. This correction is made through a parallel extraction with 0.01M CaCl_2 . The amount of sulphate released to this solution is subtracted from that left in solution after the extraction with CaCl_2 containing 50 $\text{mg l}^{-1}\text{S}$ (Gregg et al., 1977; Gregg and Goh, 1978; Saunders, pers. comm.) as shown in equation 2.8.

$$\% \text{ S retn.} = \frac{(50 + x) - y}{50} \times \frac{100}{1} \quad 2.8$$

Here, y is the amount of sulphate left in solution after shaking the soil with 0.01M CaCl_2 containing 50 $\text{mg l}^{-1}\text{S}$, and x is the amount of sulphate released into 0.01M CaCl_2 .

The purpose of the parallel extraction with CaCl_2 alone is to correct for sulphate which may be released to the solution from the soil. The validity of this approach is open to question. There is a rapid equilibrium between sulphate on the surface and sulphate in solution so it is unlikely that the soil will release the same amount of sulphate to 0.01M CaCl_2 as it does to the same solution containing 50 $\text{mg l}^{-1}\text{S}$.

There thus seems little justification for a correction for S released to 0.01M CaCl_2 in laboratory studies of sulphate retention,

and a single equilibration with 0.01M CaCl_2 containing 50 ppm S (Barrow, 1967; During and Martin, 1968) has been used in the current study.

2.2.1.2 Sulphate retention of New Zealand soils. The major soil groups of New Zealand have been classified for their ability to retain sulphate (Saunders and Hogg, 1971), and grouped into three classes of sulphate retention; low (0 - 30%), medium (30 - 50%) and high (> 50%). Typically, soils derived from siliceous parent materials such as brown-grey earths, yellow-grey earths, and yellow-brown earths have low sulphate retention values, while soils derived from volcanic parent materials, particularly the yellow-brown loam soils tend to have a higher ability to retain sulphate (Saunders and Hogg, 1971).

Sulphate retention values are reduced by liming or large additions of phosphate fertiliser however, and for many soil groups sulphate retention values show appreciable variation (Saunders and Hogg, 1971). The limited data available from the analysis of trial sites suggested that lime was rapid and effective in reducing the S-retention value of the 0 - 7.5cm depth in low and medium retention soils (Saunders and Hogg, 1971). Phosphate fertilisation also reduced sulphate retention, but these changes seemed more the result of a gradual increase in P status over a number of years (Saunders and Hogg, 1971; Saunders, 1974). Few conclusions can be drawn as to the significance of these effects however, as only the upper 20cm of the soil was examined for changes in S-retention and there is limited information available on the practical implications of differences in S-retention of the magnitude observed.

A strong correlation between P-retention, as assessed in a similar quick-test procedure (Saunders and Hogg, 1971), and S-retention has been reported in subsoils (Hogg et al., 1970; Saunders and Hogg, 1971) but S-retention values were low in topsoils at a wide range of P-retention values. This further suggests that S-retention will be influenced by factors such as pH and phosphate content of soils, in contrast to P-retention which varies little with phosphate status (Saunders, 1974) and pH (Bailey et al., 1976).

2.2.2 Sulphate movement

Numerous column and lysimeter studies have demonstrated that although New Zealand soils have varying abilities to adsorb sulphate, some soils had very limited capacity to retain sulphate against percolating water (Waters, 1957; Cooper and Hogg, 1966; Hogg and Toxopeus, 1965; Muller, 1975; Hogg, 1981). It is difficult to estimate the practical significance of such studies, not only because of the effects of air-drying and sieving soils on the availability of sulphate (Williams, 1967), but also because the drainage characteristics of a packed soil column may bear little resemblance to those of a field soil.

Field studies have also suggested that soils of low S-retention are susceptible to leaching (During and Martin, 1968; Gregg et al., 1977; Gregg and Goh, 1978; Smith et al., 1983), and sulphate has been measured in the drainage waters of low S-retention soils (During and Martin, 1968; Smith et al., 1983). Although sulphate is more resistant to leaching in highly retentive soils (During, 1972; During and Cooper, 1974), some movement of fertiliser sulphate has still been recorded in these soils (Saunders and Hogg, 1971; During and Cooper, 1974), particularly in the upper horizons. For medium retaining soils there is little information available. Gregg and Goh (1978) demonstrated that sulphate accumulates in medium S-retention soils, under rainfall conditions sufficient to cause considerable movement of sulphate in low retention soils, and Saunders et al. (1969) suggested that reserves of adsorbed sulphate in these former soils would protect soils from deficiency for 1-2 years if fertiliser was withheld.

Sulphate movement is not completely dependent on the ability of soils to adsorb sulphate however, leaching losses can also be influenced by water holding capacity, texture, and the rate of water percolation through the soil, factors which interact with the depth of root penetration and the availability of subsoil sulphate for plant nutrition (Gregg and Goh, 1978).

2.2.3 The plant availability of adsorbed sulphate

The definition of rooting depth and the depth at which plant uptake occurs is crucial to an understanding of leaching and nutrient availability. Plants may obtain sulphate from varying depths in soils (Gregg et al., 1977; D. Horne, pers. comm.) and reserves of sulphate at depth may be adequate for the nutrition of deep rooting plants (Ensminger, 1954; Thomson and Neller, 1963; Gregg et al., 1977). It is often necessary therefore to include some estimate of root uptake, and/or rooting depth in an estimate of sulphate losses from a soil/plant system. Sulphur response trials can be used to infer leaching losses of fertiliser sulphate (During and Cooper, 1974; During and Martin, 1978), but Gregg and co-workers (Gregg et al., 1977; Gregg and Goh, 1978) have used ^{35}S to demonstrate that adsorbed sulphate at depth may be accessible to roots in some soils and unavailable in others.

Both grass and clover roots were obtaining sulphate from 100cm depth in a sandy soil of low S-retention, whereas sulphate at 60cm depth in a soil of higher sorption capacity and silt loam texture was largely unavailable to plants. There were also variations in plant uptake with season, which were attributed to the drying out of surface horizons in Spring. In this situation, uptake of nutrients and moisture is greatest from subsurface horizons, and a high availability of sulphate in subsoils could be an advantage.

Adequate nutrition of a grass/clover pasture is often dependent on maintaining clovers against strong competition for nutrients from the grass component of the sward, with grasses having a deeper and more extensive root system (Nye and Tinker, 1976). Luxury amounts of sulphate may thus be required to maintain healthy clover growth (Walker and Adams, 1958; McNaught, 1970; Saunders and Cooper, 1975). Although in incipient sulphur deficiency clovers are affected earlier than grasses, sulphur deficiency also limits the growth of symbiotic nitrogen fixing bacteria. Grass growth may thus be quickly limited by lack of N (During, 1972), so for a mixed pasture the sulphate content of the upper 15cm may be all important. In one trial (During and Cooper, 1974) responses to sulphate were recorded, even though high levels of adsorbed sulphate were present at 15 to 45cm depth in a high sorbing soil. Similar results had been reported on

another soil and During (1972) suggested that soils that did not retain sulphate in upper horizons would show a tendency to grow sulphur deficient grass/clover pasture if rainfall and timing of fertiliser applications were favourable to leaching.

It is commonly observed that subsoils show an accumulation of adsorbed-S, and higher affinities for sulphate than topsoils (Metson, 1979). This is not only because of changes in mineralogy (Ensminger, 1954; Harward and Riesenauer, 1966), but also because of decreased pH (Ensminger, 1954; Kamprath et al., 1956) and lack of competition from the more strongly adsorbed phosphate ion (Ensminger, 1954; Barrow, 1967). While these accumulations may be unavailable because of low pH and aluminium toxicity effects on root growth (Ensminger, 1954; Metson, 1979), they are certainly unavailable to shallow rooting crops and during early stages of the establishment of deeper rooting plants.

Sulphate at considerable depth has been shown in other situations to be available to plants, and to make a significant contribution to plant nutrition (Blakemore et al., 1969; Gregg et al., 1977), but this may not always be the case. Although adsorbed sulphate is in equilibrium with soil solution sulphate (Barrow, 1969; Barrow and Shaw, 1977) it may be less available in soils of high adsorption capacity (Barrow, 1967). When the affinity of the soil for sulphate is high, reaction between soil and sulphate slows diffusion to the roots, (Barrow, 1969), resulting in a different pattern of uptake, relatively slow at first, but maintained at this level such that uptake is spread over a longer period (Barrow, 1970b).

Nutrient availability may thus be limited by slow diffusion and the need for a high root density to exploit the soil volume (Nye and Tinker, 1976). This is certainly the case for phosphate, an anion which interacts strongly with the surface in most soils (Lewis and Quirk, 1967), but less attention has been directed towards the effect of soil interaction on sulphate movement. A few studies in which sulphate was plentiful, have indicated that sulphate accumulates at the root when it is transported by convection in excess of requirements (Wray and Tinker, 1969^{*}; Wray, 1971^{*}), but under other conditions zones of sulphate depletion around roots were observed (Saunders, 1971^{*}).

^{*} Quoted by Nye and Tinker (1976).

It seems apparent that the availability of sulphate in soils is to some degree dependent on the strength and extent of adsorption, not only because of the effect of leaching in removing sulphate from a depth where it is plant available, but also because the adsorption surface acts as a store of sulphate and affects the diffusion of plant available sulphate to the zone of uptake. These considerations provide the incentive for a study of sulphate sorption and the effects of lime and competition with phosphate on the soils' ability to adsorb sulphate.

CHAPTER 3

MATERIALS AND METHODS

3.1 Soil Collection and Chemical Characterisation

The bulk samples of soil used in this study were collected from pastoral sites, air-dried and passed through a 2mm sieve. The soils were chosen to have varying mineralogies (Table 3-1), and had varying abilities to resist changes in pH.

Several chemical analyses were performed on these bulk samples of soil.

3.1.1 Extractable-sulphate

Subsamples (5g) of soil were shaken with 25 mls of either 0.01M CaCl_2 (Barrow, 1967) or 0.04M $\text{Ca}(\text{HPO}_4)_2$ (Searle, 1979) for 16 hrs on an end-over-end shaker, centrifuged (15 mins, 5000 rpm), filtered (Whatman No 5), and an aliquot of solution retained. These aliquots were dried down overnight, analysed by the method of Johnson and Nishita (1952), and compared to standards in the range 0 - 80 $\mu\text{g S}$ using a Pye Unicam SP 1800 spectrophotometer at 670 nm.

For estimation of adsorbed sulphate, the level of CaCl_2 - extractable sulphate was subtracted from that extracted by $\text{Ca}(\text{HPO}_4)_2$ in the same soil (Searle, 1979).

3.1.2 Extractable-phosphate

3.1.2.1 Olsen-P. One gram of soil was shaken with 20 mls of Olsen reagent (0.5M NaHCO_3 , adjusted to pH 8.5 with NaOH) for 30 minutes, centrifuged (5 mins, 10,000 rpm), filtered (Whatman No 5) and analysed for phosphate.

Table 3-1 Classification of soils collected

Soil	N.Z. Great Soil Group	Parent Material	Notes on clay mineralogy
Patua loam (topsoil)	Strongly leached YBL (1)	Andesitic volcanic ash	22% clay, of which 23% is allophane, 67% volcanic glass (4)
Patua loam (subsoil)	Strongly leached YBL (1)	Andesitic volcanic ash	30% clay, of which 80% is allophane, 20% volcanic glass (4)
Egmont loam	Mod. leached YBL (1)	Andesitic volcanic ash over tephric loess	25% clay, of which 68% is allophane, 26% volcanic glass, 6% halloysite (4)
Ramiha silt loam	Mod. leached YBE-YBL intergrade (9)	Siliceous loess over greywacke gravels	25-30% clay, of which most is vermicullite, some illite, contains allophane (9)
Taupo sandy loam	YBPS	Taupo pumice rhyolitic tephra	14% clay, of which 100% is allophane (9)
Okaihau gravelly clay	Strongly leached BL with ironstone nodules (1)	Basalt	30% clay, of which 36% is kaolin, 50% gibbsite, 16% free Fe O (1)
Kumeroa hill soil (f.s.l.)	YGE/YBE intergrade (2)	Moderately consolidated silty sandstone	20% clay, mainly vermicullite, montmorillonite, and hydrous mica (2)
Konini silt loam	YBE (6)	Siliceous sandstone and mudstone	Soil classification unit shows considerable variation (8)
Wainui silt loam (si l)	YBE/YGE intergrade (7)	Consolidated sandy silt stone	- -
Tokomaru silt loam	YGE	Siliceous loess	23% clay, predominance of 12 and 14A clay particularly mica/illite, some vermicullite (3)

References:

- | | | |
|--------------------------|------------------------|--------------------------|
| 1) NZ Soil Bureau (1981) | 2) Campbell (1977) | 3) Pollok (1975) |
| 4) NZ Soil Bureau (1982) | 5) Cowie (1978) | 6) NZ Soil Bureau (1954) |
| 7) Campbell (1978) | 8) De Rose, pers.comm. | 9) McLaughlin (1983) |

The method adopted for estimation of dissolved inorganic phosphate was a modification of the vanadomolybdate method of Murphy and Riley (1962) (Watanabe and Olsen, 1965), with adsorbance measured at 712 nm using a Pye Unicam SP 1800 spectrophotometer.

3.1.2.2 NaOH-P. Soils were prewashed with 0.1M NaCl (30 mins) then extracted with 0.5M NaOH (1g:100 ml) for 16 hrs, centrifuged (15 mins, 5000 rpm), and filtered (Whatman No.5). A small aliquot (< 2 ml) was taken for phosphate determination (Watanabe and Olsen, 1965) and a similar aliquot for determination of a background adsorbance for each soil at 712 nm (McKay, 1982). Both of these aliquots were neutralised with dilute HCl prior to analysis for phosphate (Watanabe and Olsen, 1965).

3.1.3 Sulphate-retention

A 5g sample of soil was shaken with 25 mls of 0.01M CaCl_2 containing 50 mg l^{-1} S for 16 hrs, centrifuged (10 mins, 5000 rpm), filtered, and the solution analysed for sulphate.

Percent S-retention was then calculated as follows:

$$\% \text{ S-retn.} = \frac{50 - x}{50} \times \frac{100}{1} \quad 3.1$$

where x is the measured concentration of sulphate in mg l^{-1} (During and Martin, 1968).

3.1.4 Phosphate-retention

A 5g sample of soil was shaken for 16 hrs with 25 mls of P-retention solution (1000 mg l^{-1} P as KH_2PO_4 in 0.2M sodium acetate, adjusted to pH 4.65 with acetic acid). The suspension was centrifuged (10 mins, 5000 rpm), filtered (Whatman No.5) and the solution analysed for phosphate as in Section 3.1.2. The percent P-retention was then calculated from the difference between phosphate added, and phosphate remaining in solution (Saunders and Hogg, 1971; Saunders, 1974).

3.1.5 pH

1g soil:25 mls H_2O or 1M KCl (NZ Soil Bureau, 1968). The suspension was stirred, left overnight, stirred again, and pH measured by means of a glass electrode, 60 seconds after cessation of stirring.

3.1.6 Organic carbon

A Leco induction furnace (model 765-000) was used to estimate organic carbon levels according to the procedure of Tabatabai and Bremner (1970).

3.2 Soil Incubation

Samples of each bulk soil were incubated with several rates of calcium hydroxide or calcium chloride to obtain a range of pH values for each soil. During incubation, sufficient water was added to wet the soils to a moist, friable condition (approximately 60% of field capacity), and the soils were maintained in this condition (with daily mixing and aeration) for a period of 10 weeks with regular checks (≈ 3 weeks) on pH.

After 10 weeks, when the pH values of the soils had become relatively static the soils were air-dried, sieved (2 mm), and stored for future study. The following chemical analyses (as outlined in Section 3-1) were performed on incubated soils; soil pH, $CaCl_2$ and $Ca(HPO_4)_2$ -extractable sulphate, Olsen and NaOH-extractable-phosphate, and S and P-retention.

3.3 Surface Charge Characterisation of Soils

The adsorption of chloride, and sodium or calcium from 0.1M NaCl and 0.025M $CaCl_2$ solutions was measured by an ion retention method, with a correction for ions held in the entrained electrolyte made on the basis of the weight and concentration of electrolyte

(van Raij and Peech, 1972). This method has disadvantages in that

- (i) the concentration of electrolyte close to the adsorbing surface will not be equal to the concentration in the bulk solution,
- (ii) high background concentrations of ions are often obtained making it difficult to measure an increase due to adsorption and
- (iii) adsorption of water by surfaces may lead to inaccurate estimates of the amount of electrolyte entrained.

Despite these difficulties this method is preferred over an alternative which involves washing the soil with alcohol prior to displacement of adsorbed ions, because this may cause changes in the double layer environment existing during adsorption (Rajan, 1975, 1976).

A 3g sample of soil was shaken with 30 mls of solution (0.1M NaCl, or 0.025M CaCl₂) in weighed centrifuge tubes for 2 hrs, centrifuged (15 mins, 5000 rpm), the solution decanted, and the soil retained for three further washes with 0.1M NaCl or 0.025M CaCl₂. On the third wash, the decanted solution was retained for pH, chloride and sodium or calcium analysis. The tubes were then weighed to account for entrained ions, and stored overnight. The following day the soils were equilibrated with five, ten minute, washes with 0.1M KNO₃ using a similar procedure. All of these five washing solutions were filtered through the same filter paper (Whatman No 5), and collected for chloride, and sodium or calcium analysis.

Chloride was analysed by an Orion specific ion electrode attached to an Orion 901 microanalyser when charge was assessed in 0.025M CaCl₂, but for later studies (charge in 0.1M NaCl) a more sensitive titrimetric method (Vogel, 1979) using potassium chromate as indicator was preferred.

Sodium and calcium were analysed by atomic adsorption at 589 nm and atomic emission at 422.7 nm respectively, in the presence of 0.2% caesium and strontium using a Varian-Technicon atomic adsorption spectrophotometer.

The measured amounts of these ions in the total filtrate were then corrected for entrained ions, and the amounts of ions retained by surface charge calculated by difference.

3.4 Phosphate Sorption

A 1g sample of soil was shaken with 40 mls of 0.1M NaCl containing varying additions of phosphate as KH_2PO_4 (300 - 500 mg kg soil^{-1}) for 40 hours (McLaughlin et al., 1977; Ryden et al., 1977a), centrifuged (15 mins, 5000 rpm), and filtered (Whatman No 5). An aliquot of the filtrate was analysed as described in Section 3.1, and the sorbed-P estimated by difference after correcting for 'native-P' already on the surface. Ryden et al. (1977b), have suggested that this surface-bound pool of phosphate can be estimated by extraction with NaOH (Section 3.1.2).

3.5 Sulphate Adsorption

Sulphate adsorption was estimated in 0.1M NaCl, a medium which has been extensively used for phosphate sorption studies (Ryden, 1975; Hope, 1977), and in a similar ionic strength calcium media, 0.025M CaCl_2 . Samples of soil, 5g, were shaken for 40 hrs with each of these solutions containing varying additions of sulphate (0 - 800 mg kg soil^{-1} added as K_2SO_4), centrifuged (15 mins, 5000 rpm), and filtered (Whatman No 5). Adsorbed sulphate was estimated from the difference between sulphate remaining in solution and sulphate added, with a correction for 'native-sulphate' as estimated by $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extraction (Searle, 1979).

3.6 Competitive Sorption

3.6.1 Sorption of phosphate and sulphate

In several soils the competitive sorption of phosphate and sulphate was assessed by equilibrating the soil for 40 hrs in 0.1M NaCl containing equimolar amounts of phosphate and sulphate at a soil:solution ratio of 5g:25 mls as outlined above.

It was considered desirable that competitive effects be

Table 3-2 Additions of phosphate applied to different
soils during competitive sorption studies

Soil	Phosphate Addition mM kg^{-1}	Soil	Phosphate Addition mM kg^{-1}
Patua subsoil	6.24	Egmont	6.24
	*7.80	Ramiha	6.24
	*10.90	Okaihau	2.50
		Taupo	5.00
Patua topsoil	6.24	Tokomaru	5.00

* Added to Patua topsoil in conjunction with
7.8 mM kg^{-1} of sulphate in a second study
in which surface charge was also assessed.

studied in a similar concentration range for each soil type, and accordingly different amounts of phosphate and sulphate were applied to different soils (Table 3-2).

There is a problem in competitive adsorption studies however, because when sulphate adsorption is reduced by phosphate addition, a higher concentration of sulphate is observed in solution than when a similar amount of sulphate is added without P. It is thus difficult to estimate the quantitative effect of equimolar additions of P on sulphate adsorption.

In this study, because sulphate adsorption isotherms had previously been determined we were able to compare the amounts of sulphate adsorbed in the presence of P to that which might normally be present on the surface at a similar concentration in solution in the absence of competition, and thus express the results as a percent reduction in adsorption capacity for each soil.

Competitive sorption results for the Patua subsoil indicated that phosphate had a much greater effect on sulphate adsorption at some pH values than others, and a short study was initiated to compare changes in sulphate adsorption to changes in surface charge on phosphate sorption.

3.6.2 Effect of phosphate on sulphate adsorption and surface charge

For the Patua subsoil, the adsorption of sulphate from a solution containing 7.80 mM kg^{-1} of sulphate by soil samples of differing pH in the presence of both 7.80 mM kg^{-1} and 10.90 mM kg^{-1} of phosphate was compared to the adsorption of sulphate in the absence of any phosphate addition, according to the procedure outlined in Section 3.5, 3.6.1, at a soil:solution ratio of 5g:25 mls.

In a parallel experiment, 3g samples of soil were shaken with 30 mls of 0.1M NaCl containing similar additions of P per gram soil, and the surface charge was estimated by a procedure similar to that described in Section 3.3. In this case the initial 2 hour equilibration had been replaced by a 40 hour sorption equilibration in the same media, so only three subsequent washes with 0.1M NaCl

were considered necessary. These soils were not left overnight prior to displacement of sodium and chloride by 0.1M KNO_3 and in the only other alteration in procedure (Section 3.4) chloride was analysed by titrimetry (Vogel, 1979).

For both parts of this experiment duplicate soil samples were shaken without phosphate. In the case of the sulphate adsorption study this was used as a check on the adsorption isotherms for each soil, and for the surface charge measurements as a check on the previously determined levels of surface positive and negative charge in these soils.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Chemical Properties of Unincubated Soils

The soils selected for this study varied in their ability to sorb phosphate, as shown by their P-retention values (Table 4-1). Only soils with high P-retention capacities adsorbed large quantities of sulphate. Soils of low to medium P-retention showed little or no ability to retain sulphate (Table 4-1). These results are in agreement with those of previous workers (Saunders and Hogg, 1977; Nguyen, 1981).

The soils with a large capacity to sorb anions (Table 3-1) had mineralogies dominated by allophane and free iron oxides. In contrast, those containing predominantly layer lattice clays had a much lower ability to sorb phosphate and adsorbed very low amounts of sulphate.

The soils varied in phosphate status as indicated by Olsen-P values, and organic carbon content but were predominantly of low pH (Table 4-1). The amounts of surface bound phosphate (NaOH-extractable; Ryden and Syers, 1977), and sulphate ($\text{Ca}(\text{HPO}_4)_2$ -extractable; Searle, 1979) showed considerable variation, perhaps reflecting different fertiliser histories and different sorption capacities in the soils studied. Barrow (1967) has suggested that the initial sulphate level in a soil may be a useful index of sulphate adsorption capacity.

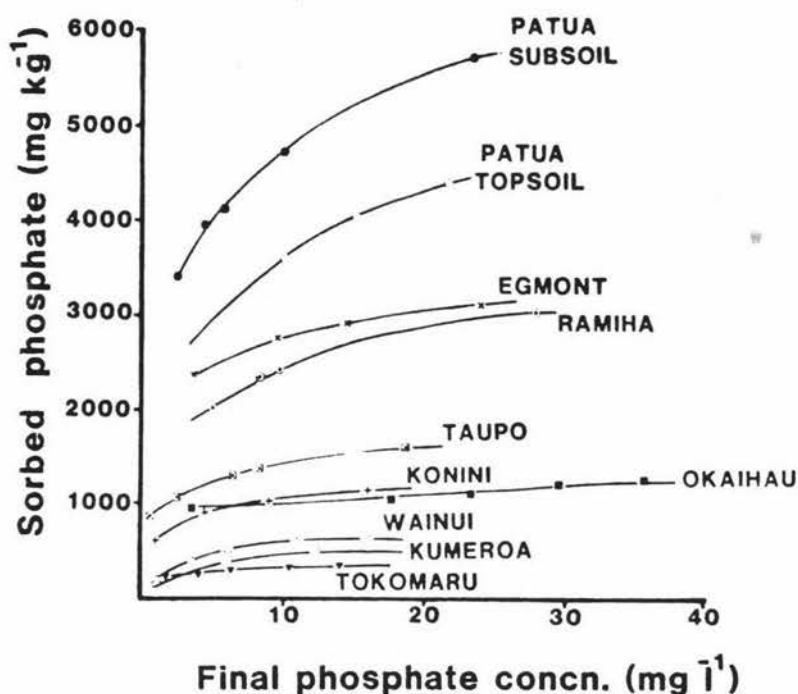
Sorption isotherms for these soils (Fig. 4-1) showed that there was an approximately 15-fold difference in the amount of phosphate a soil sorbed at an equivalent concentration (20 mg l^{-1}) in solution compared to the amount of sulphate adsorbed. The ranking of soils in order of sorption capacity for sulphate was similar to that for phosphate, but some differences did exist. These might be attributed to the dependence of sulphate sorption on soil pH and phosphate status (Kamprath et al., 1956).

Table 4-1

Chemical characterisation of unincubated soils

Soil	pH	Olsen-P	NaOH-P	CaCl ₂ -S	Ca(H ₂ PO ₄) ₂ -S	Adsorbed S	S-retention	P-retention	% Org.C
		mg kg ⁻¹					%		
Patua topsoil	5.45	2.3	280	15.5	43.0	144.5	51	90	12.5
Patua subsoil	5.60	0.7	435	3.0	160.0	43.0	81	98	6.6
Egmont	6.55	30.0	971	4.5	58.0	53.5	41	91	2.9
Ramiha	5.00	7.0	330	2.5	45.0	42.5	55	87	6.7
Taupo	5.05	26.0	419	6.5	29.0	22.5	15	65	2.3
Okaihau	5.85	5.2	175	22.5	101.3	79.0	28	60	6.0
Kumeroa	6.00	18.0	126	6.2	12.5	6.3	10	30	12.4
Konini	5.25	6.7	160	2.5	10.0	7.5	17	48	3.2
Wainui	5.10	7.6	111	3.5	19.0	15.5	15	31	3.4
Tokomaru	5.20	10.2	149	7.5	13.0	5.5	5	23	5.3

(a) Phosphate



(b) Sulphate

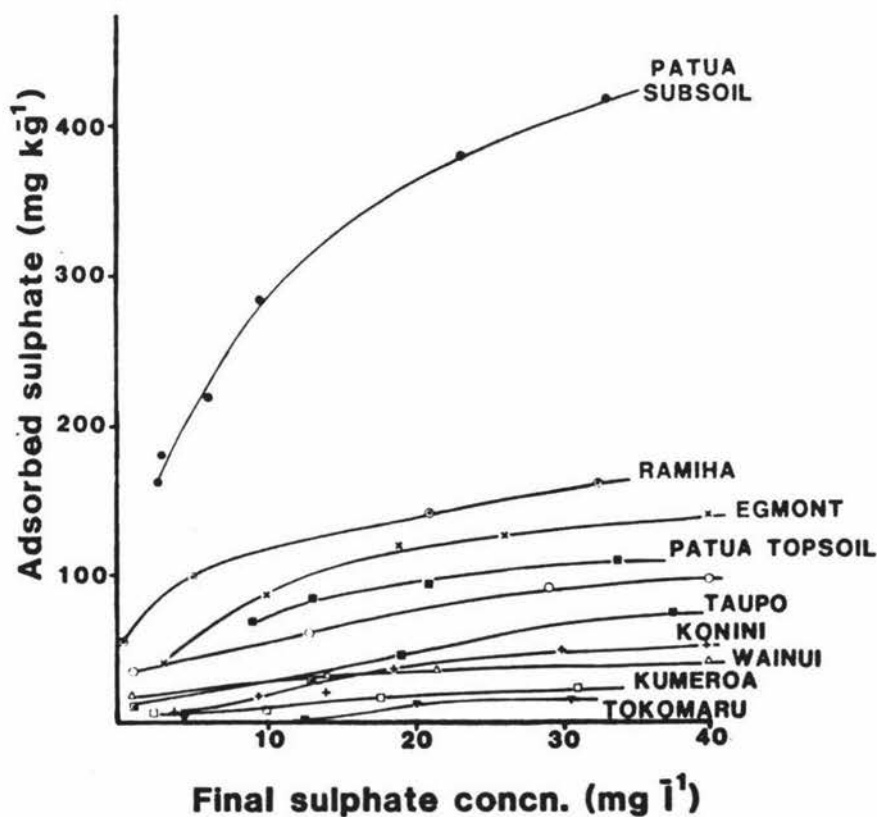


Fig. 4-1 Phosphate sorption and sulphate adsorption in unincubated soils; a) phosphate b) sulphate. Here the final anion concentration is the solution concentration after 40 hrs, and the amount on the surface is adsorbed sulphate for sulphate, and sorbed phosphate for phosphate.

A preliminary aim of this study had been to obtain soils of varying capacity to adsorb sulphate, and at a solution concentration of 20 mg l^{-1} , which may approximate that present in the soil solution (Russell, 1973), the amounts of sulphate on the surface varied by a factor of 25 for the soils collected (Fig. 4-1b).

4.2 Effect of Incubation on Soil Chemical Properties

Incubation with varying rates of Ca(OH)_2 was successful in producing soils covering a wide range of pH values (Table 4-2, 4-3, Appendix I). In the absence of calcium hydroxide, incubation produced slight reductions in pH, but at medium and high rates of calcium hydroxide large increases in pH were observed.

4.2.1 Extractable sulphate and phosphate levels

In all cases available sulphate levels, as measured by an extraction with calcium phosphate, increased on incubation (Table 4-2, and Appendix I). The size of this increase was greater at high rates of Ca(OH)_2 . It is probable that liming stimulated the microbial flora, and resulted in increased mineralisation of organic sulphur to sulphate during incubation.

This increased quantity of sulphate was then distributed between surface and solution. The adsorbed pool of sulphate initially increased with pH, but showed a tendency to decrease in the higher pH range, apparently limited by a decrease in the capacity of the soil to adsorb sulphate (Section 4.5). As a result of this, levels of CaCl_2 -extractable sulphate exhibited marked increases at high pH, but otherwise paralleled the changes in available sulphate shown by $\text{Ca(HPO}_4)_2$ -extractable sulphate levels.

It was interesting to note that when incubation caused slight reductions in pH (e.g. at zero and low rates of Ca(OH)_2 application) CaCl_2 -extractable sulphate levels also decreased. This decrease in CaCl_2 -extractable sulphate was balanced by an increase in adsorbed sulphate, suggesting that a decrease in pH on incubation produces a

Table 4-2 Extractable sulphate levels in several incubated soils

	CaCl ₂ -S	Ca(HPO ₄) ₂ -S	Adsorbed -S		CaCl ₂ -S	Ca(HPO ₄) ₂ -S	Adsorbed -S
pH	mg kg ⁻¹			pH	mg kg ⁻¹		
<u>Wainui</u>				<u>Konini</u>			
* 5.07	3.5	19.0	15.5	* 5.25	2.5	10.0	7.5
4.70	4.0	20.5	16.5	4.70	2.0	15.0	13.0
5.01	6.5	22.5	16.0	4.91	2.0	17.5	15.5
5.30	10.0	26.0	16.0	5.30	1.8	18.0	16.0
5.70	11.0	28.0	17.0	5.50	2.5	19.0	16.5
6.10	10.0	27.0	17.0	5.70	3.0	19.0	16.0
6.40	13.0	28.0	15.0	6.10	6.5	23.0	16.5
<u>Ramiha</u>				<u>Patua</u>			
* 5.00	2.5	45.0	42.5	* 4.61	3.0	160.0	157.0
4.70	1.5	48.0	46.5	5.30	1.8	168.0	166.2
5.13	1.2	48.0	46.8	5.80	4.1	173.0	169.2
5.40	1.5	50.8	49.3	6.10	6.6	177.0	170.0
5.80	6.0	52.5	46.5	6.50	10.5	180.0	170.0
6.10	9.1	51.3	42.5	6.70	16.0	185.0	170.0
6.60	20.0	63.0	43.0	7.00	24.5	177.0	153.0

* Unincubated soil.

Table 4-3 Extractable phosphate levels in several incubated soils

Olsen-P NaOH-P			Olsen-P NaOH-P			Olsen-P NaOH-P		
pH	—mg	kg ⁻¹ —	pH	—mg	kg ⁻¹ —	pH	—mg	kg ⁻¹ —
<u>Tokomaru</u>			<u>Wainui</u>			<u>Konini</u>		
* 5.20	10.2	149	* 5.10	7.6	111	* 5.25	6.7	160
4.80	18.8	132	4.70	13.2	101	4.70	8.1	133
4.90	14.5	124	5.01	12.9	105	4.91	7.6	136
5.10	13.2	123	5.30	10.1	107	5.30	6.0	127
5.50	13.3	133	5.73	8.3	107	5.50	6.2	141
5.80	13.1	129	6.10	5.8	103	5.70	5.2	127
6.10	12.6	131	6.40	6.6	93	6.10	5.7	124
<u>Taupo</u>			<u>Ramiha</u>			<u>Patua</u>		
* 5.05	26.0	419	* 5.00	5.0	330	* 5.61	0.7	435
4.70	37.0	427	4.70	6.9	225	5.30	0.7	420
4.85	23.0	422	5.13	5.7	251	5.80	0.5	425
5.00	22.0	399	5.40	5.0	238	6.10	0.6	420
5.40	19.1	432	5.80	4.8	237	6.50	0.4	420
5.75	17.1	432	6.10	5.0	245	6.72	0.9	415
6.05	14.0	404	6.60	5.5	235	6.98	0.6	420

* Unincubated soils.

redistribution of sulphate in favour of the adsorbed pool.

Changes in Olsen-P and in the levels of surface-bound inorganic-P, (NaOH-P; Ryden and Syers, 1977), (Table 4-3, and Appendix I) did not reflect the increased levels of inorganic sulphur observed in incubated soils. Changes in Olsen-P value were significant to the classification of values as indicating low (0 - 9), medium (10 - 20), or high (21+) availability of phosphate, and were inversely related to the pH of soils after incubation, i.e. Olsen values tended to decrease as pH increased.

The Olsen reagent extracts soil solution phosphate, phosphate which is readily desorbed from the soil surface, and a portion of adsorbed P which is not isotopically exchangeable, but which may become available in the longer term (Ryden and Syers, 1977). Changes in Olsen-P levels with pH may thus be a combination of several factors. These include changes in the nature and extent of sorption (Section 4.4), changes in inorganic P levels due to mineralisation and immobilisation, and changes in the portion of P extracted by the Olsen reagent or the efficiency of the Olsen extraction (P.Sorn-srivichai, per. comm.). In the absence of further information, few conclusions can be drawn as to the significance of each of these effects in the current study.

NaOH-extractable P levels decreased on incubation (Table 4-3), but were relatively unaffected by changes in the rate of calcium hydroxide addition. Ryden et al. (1977b) have suggested that adsorbed phosphate becomes occluded in short-range order material with increasing time of sorption, and this provides a mechanism for the consistent reduction in NaOH-P observed in incubated soils.

4.2.2 Phosphate and sulphate retention

Incubation with calcium hydroxide had little effect on the P retention values of soils with high and low sorption capacity, but there were small changes observed with medium phosphate retention soils (Fig. 4-2). All changes in P-retention were insignificant to the classification of soils as being either low (0 - 30), medium

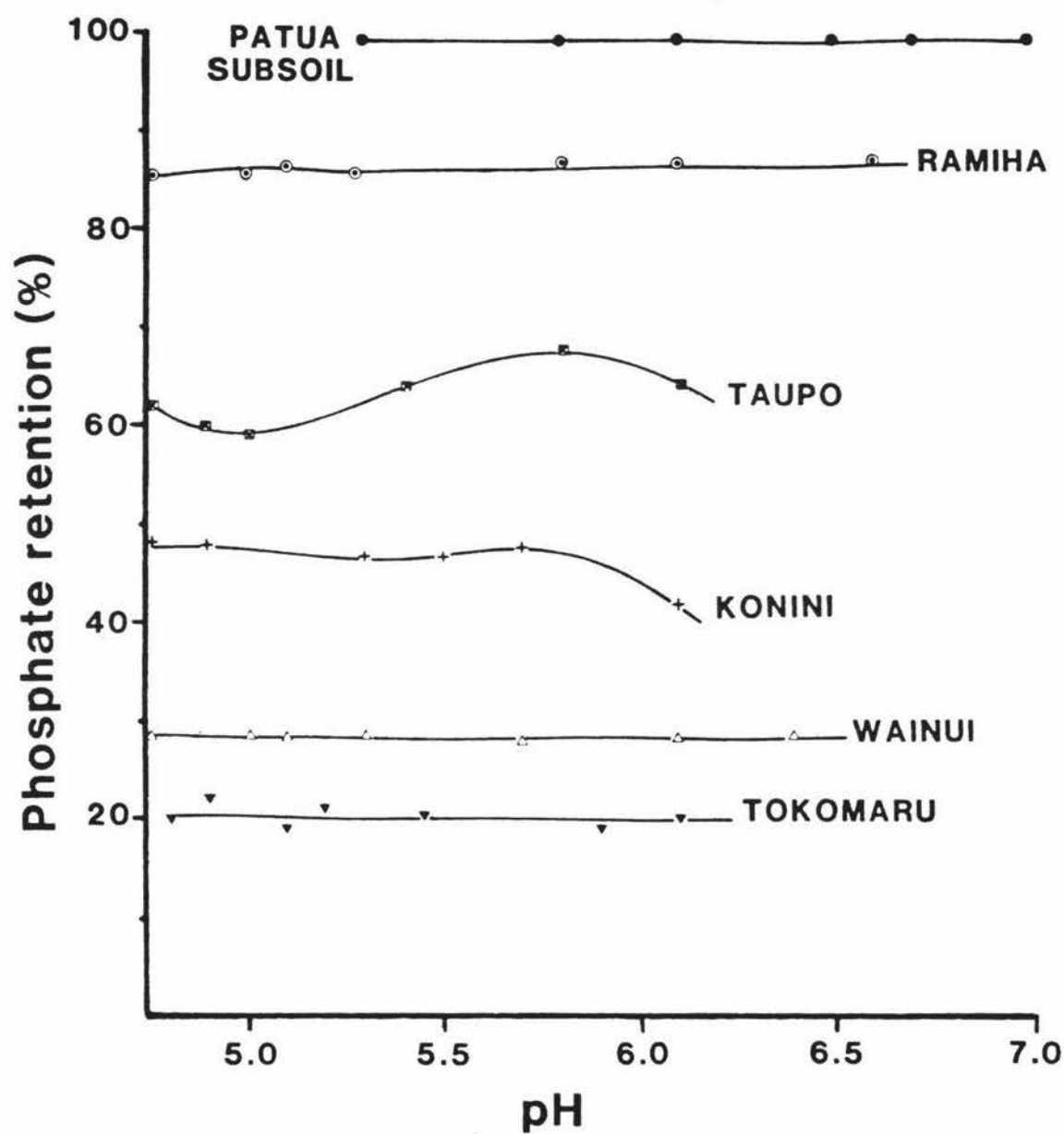


Fig. 4-2

The relationship between phosphate retention value and pH in several incubated soils.

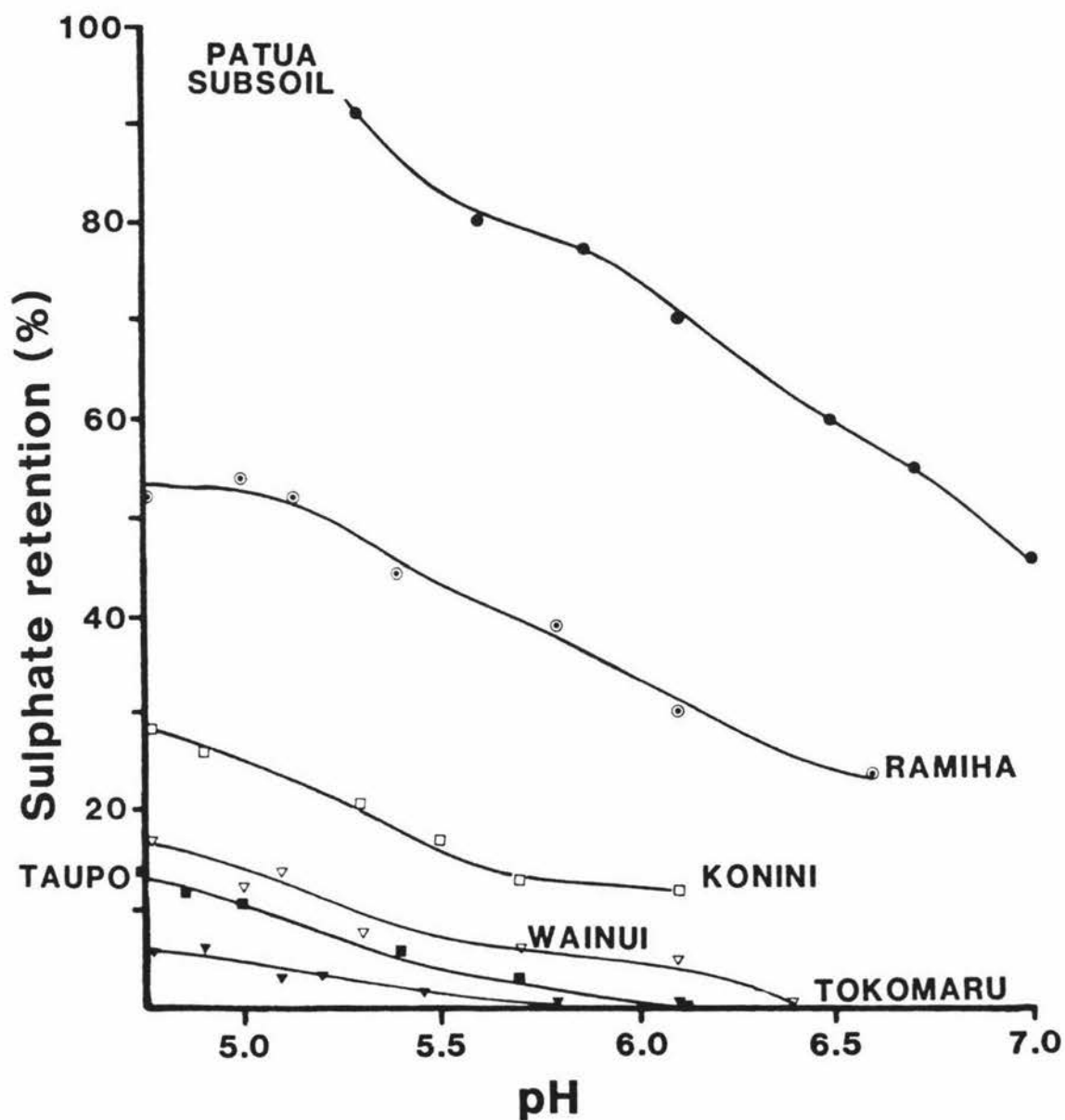


Fig. 4-3

The relationship between sulphate retention value and pH in several incubated soils.

(31 - 60), high (61 - 85), or very high (86+) P-retaining.

This is not surprising, given that the P-retention reagent is strongly buffered at pH 4.65 so that soil pH would be expected to have little effect on the values obtained. Determination of the final pH of the P-retention extracts (data not presented) confirmed that only slight changes (± 0.2) in the pH of the reagent occurred when the soils were shaken with the P-retention solution. The small variations in the P-retention values of medium P-retaining soils appeared to be related to these small changes in pH.

In contrast to P-retention, calcium hydroxide significantly reduced S-retention in all soils (Fig. 4-3). In the lower S-retaining soils, liming virtually eliminated the ability of the soil to retain sulphate at pH values greater than 6.0. Even soils of high S-retention were strongly affected by liming. On both medium and high S-retaining soils a progressive decrease in sorption capacity was observed with increasing pH, and a change in pH of 2 pH units, from 4.8 to 6.8, reduced the retention of sulphate from a 50 mg l^{-1} solution by half in these soils.

In the current study, a single equilibration with 50 mg l^{-1} S was preferred as the method for estimating S-retention (Section 2.2.3). Other workers (Gregg et al., 1977; Saunders, pers. comm.) have suggested that S-retention values should be corrected for S released in a preliminary extraction with 0.01M CaCl_2 . If this was done, then low sulphate-retaining soils showed measurable, but variable, S-retention values, even at pH 6.5 (Appendix II).

4.3 Surface Charge Characteristics of Soils

4.3.1 Measured pH in water and potassium chloride

All soils had a lower pH in 1M KCl than in water (Table 4.4 and Appendix III). This indicated that the soils carried a net negative charge and were at a higher pH than the point of zero charge (pzc) (Mekaru and Uehara, 1972; Parfitt, 1980). There is a

Table 4-4. A comparison of net surface charge and
pH values in H₂O and KCl for the Patua soils

	<u>pH</u>				<u>Net Negative Charge</u>	
	H ₂ O	KCl	ΔpH	meq kg ⁻¹	CaCl ₂	NaCl
					——meq kg ⁻¹ ——	
Topsoil						
L ⁰	4.80	4.56	0.24	.029	72.5	82.0
L ₁	5.34	4.94	0.40	.017	104.5	112.0
L ₂	5.70	5.33	0.37	.007	130.2	122.0
L ₃	5.90	6.63	0.27	.000	156.0	150.0
Subsoil						
L ₀ ⁰	5.27	5.18	0.09	.003	24.0	47.0
L ₁	5.80	5.47	0.33	.005	49.1	79.0
L ₂	6.08	5.72	0.36	.003	73.6	94.7
L ₃	6.53	6.00	0.53	.002	86.8	104.2
L ₄	6.72	6.16	0.56	.001	109.8	114.0
L ₅	6.98	6.50	0.48	.001	130.6	124.0

tendency for workers to attach undue significance to the magnitude of the ΔpH ($\text{pH}(\text{H}_2\text{O}) - \text{pH}(\text{KCl})$) value (Mekaru and Uehara, 1972; Keng and Uehara, 1974; Smith, 1978; Black and Waring, 1979), and Bowden (1973) has suggested that ΔpH values can be used to determine the net charge characteristics of soils. The absolute magnitude of the ΔpH value has no quantitative meaning, however, because pH is measured on a log scale. Even when the results were expressed as the amounts of H^+ released to 1M KCl and water, respectively, and subtracted to determine changes in H^+ activity, the amounts of H^+ released had little relation to the net charge on the soil colloid as estimated by adsorbed ion methods (Section 4.3.2).

The absolute changes in H^+ activity measured were several orders of magnitude smaller than those possible on the basis of surface charge measurements. This suggests that ΔpH values are not a reliable indicator of the absolute amounts of net charge in soils.

There are a number of reactions which can consume or release H^+ in soils, particularly in soils containing variable charge materials, and the changes in H^+ activity measured may thus not be directly attributable to H^+ displaced off negatively charged sites in soils. Additionally, ions other than H^+ and OH^- may be neutralising charged sites in these soils, particularly in soils to which calcium was added to change pH.

4.3.2 Surface charge by sorption of electrolyte ions

Although all soils contained appreciable amounts of surface negative charge, surface positive charge was also detected in many soils. The amounts of positive charge varied from 0 - 43 meq kg^{-1} soil and surface negative charge from 50 - 163 meq kg^{-1} (Fig. 4-5, Fig. 4-6, Appendix III).

The apparent co-existence of positive and negative surface charge is consistent with the suggestion that positive and negative charges are spatially separated on soil colloids, and do not neutralise each other in most soils (Espinoza et al., 1975; Black and Waring, 1976, 1979).

Full data for charge determined in 0.1M NaCl, and 0.025M CaCl_2 systems (Appendix III) will not be presented. There were several general trends which are summarised below, and these are illustrated by the results for the allophanic Patua soil and the 2:1 clay mineral dominated Tokomaru soil (Fig. 4-7).

(i) Measurable amounts of surface negative charge were generally greater than the amounts of surface positive charge and all soils carried a net negative charge in the pH range investigated.

(ii) Surface negative charge increased with pH and this increase was most marked in soils with a high content of variable charge materials, viz. amorphous Fe and Al constituents. The Tokomaru soil showed a moderately high CEC, which was mainly due to permanent charge, with some variable charge probably attributable to organic matter and edge sites of clay minerals.

(iii) Surface positive charge was very low in the soils dominated by more crystalline clay minerals but there were appreciable amounts of positive charge in the volcanic soils, particularly at low pH.

(iv) This positive charge decreased with increasing pH but even at pH 7.0 some soils, e.g. the Patua soils, contained appreciable amounts of surface positive charge.

(v) For the Patua soil, surface negative charge was higher and surface positive charge lower in the topsoil. This was probably a result of a higher organic carbon content and phosphate content in the topsoil than the subsoil.

When all soils were considered, the amounts of surface charge (positive, negative or net) measured in 0.1M NaCl were very similar to those measured in 0.025M CaCl_2 (Fig. 4-4, 4-5, 4-6). There were some differences observed however in the amounts of electrolyte ions adsorbed from 0.1M NaCl and 0.025M CaCl_2 by individual soils, perhaps attributable to differences in the pH of the final equilibration solution used to measure surface charge (Table 4-5).

The pH values for the fourth shaking solution of several soils were higher by about half to one pH unit in 0.1M NaCl than in 0.025M CaCl_2 . An increase in pH per se should be reflected in increased

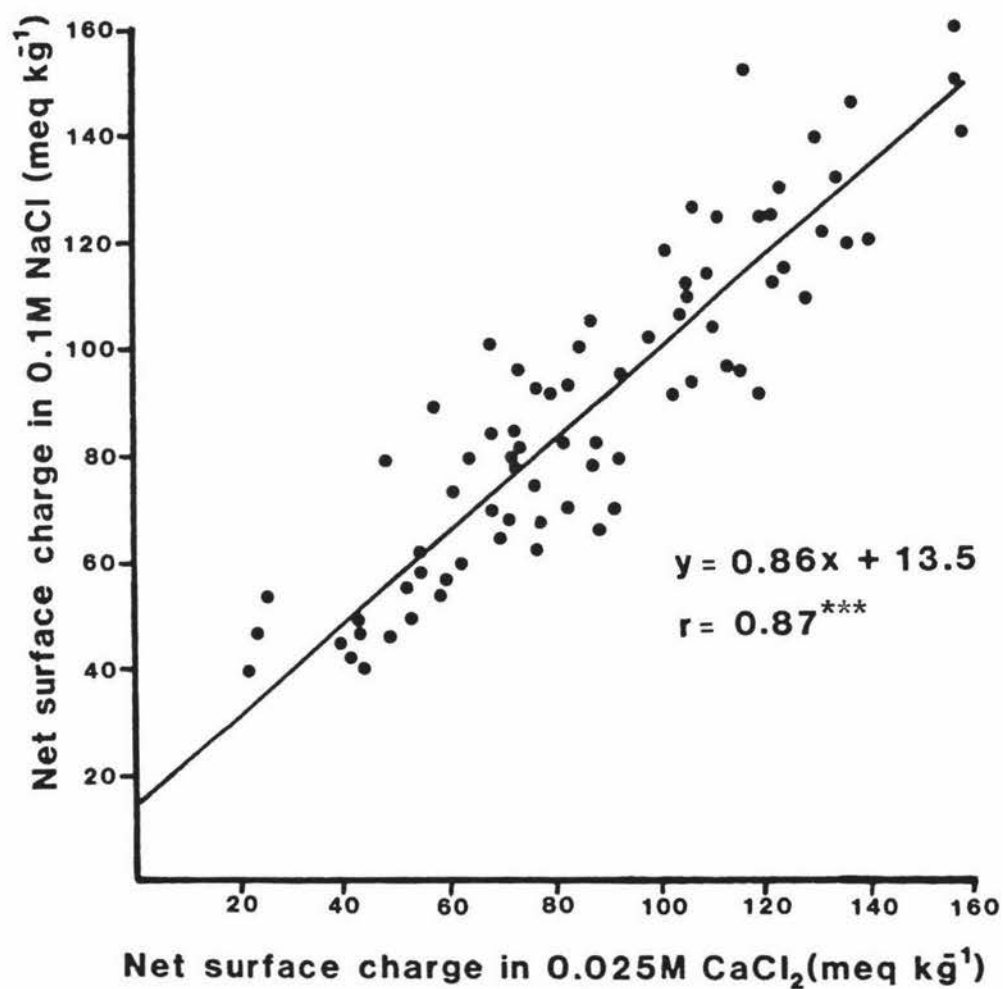


Fig. 4-4

The relationship between net charge in 0.1M NaCl and net charge in 0.025M CaCl₂.

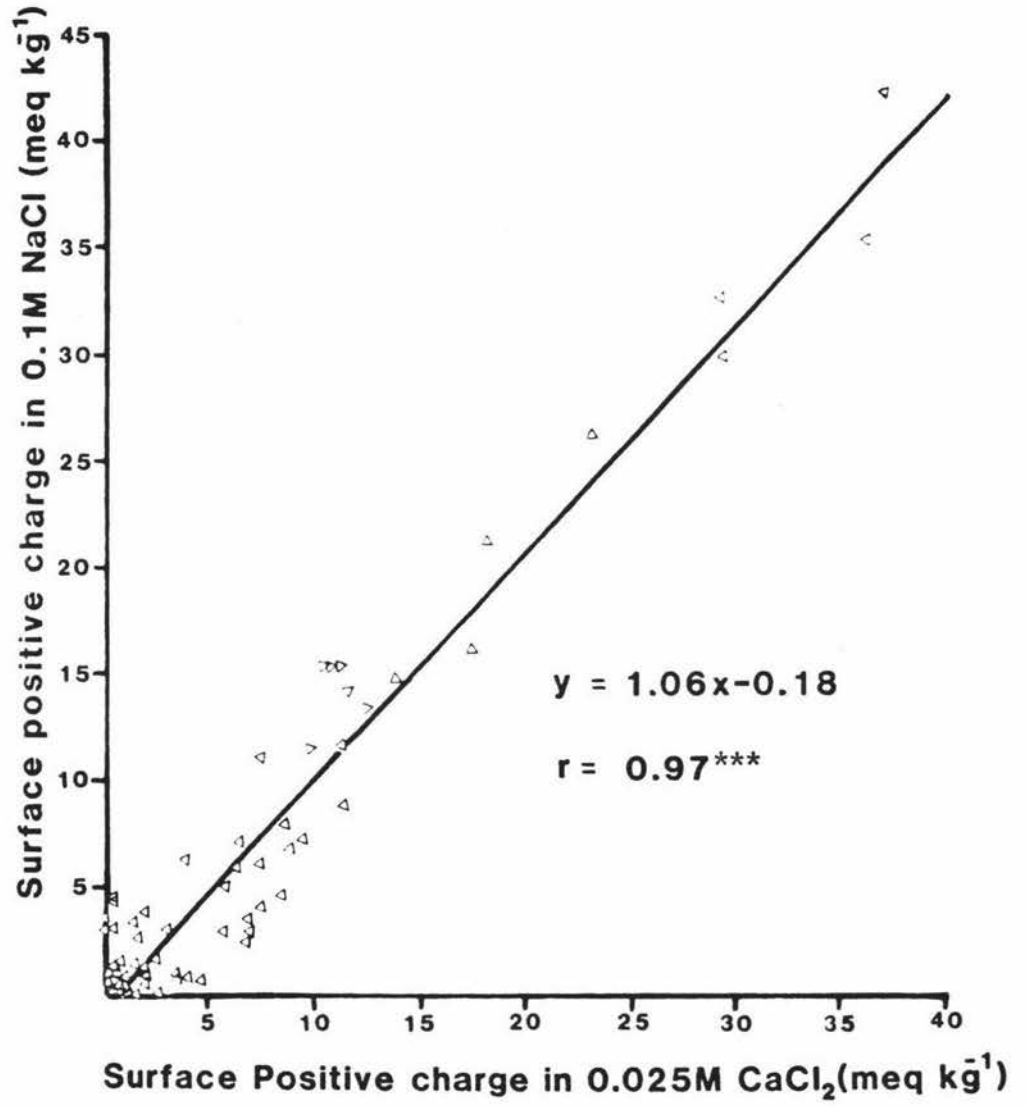


Fig. 4-5 The relationship between positive charge in 0.1M NaCl and positive charge in 0.025M CaCl₂.

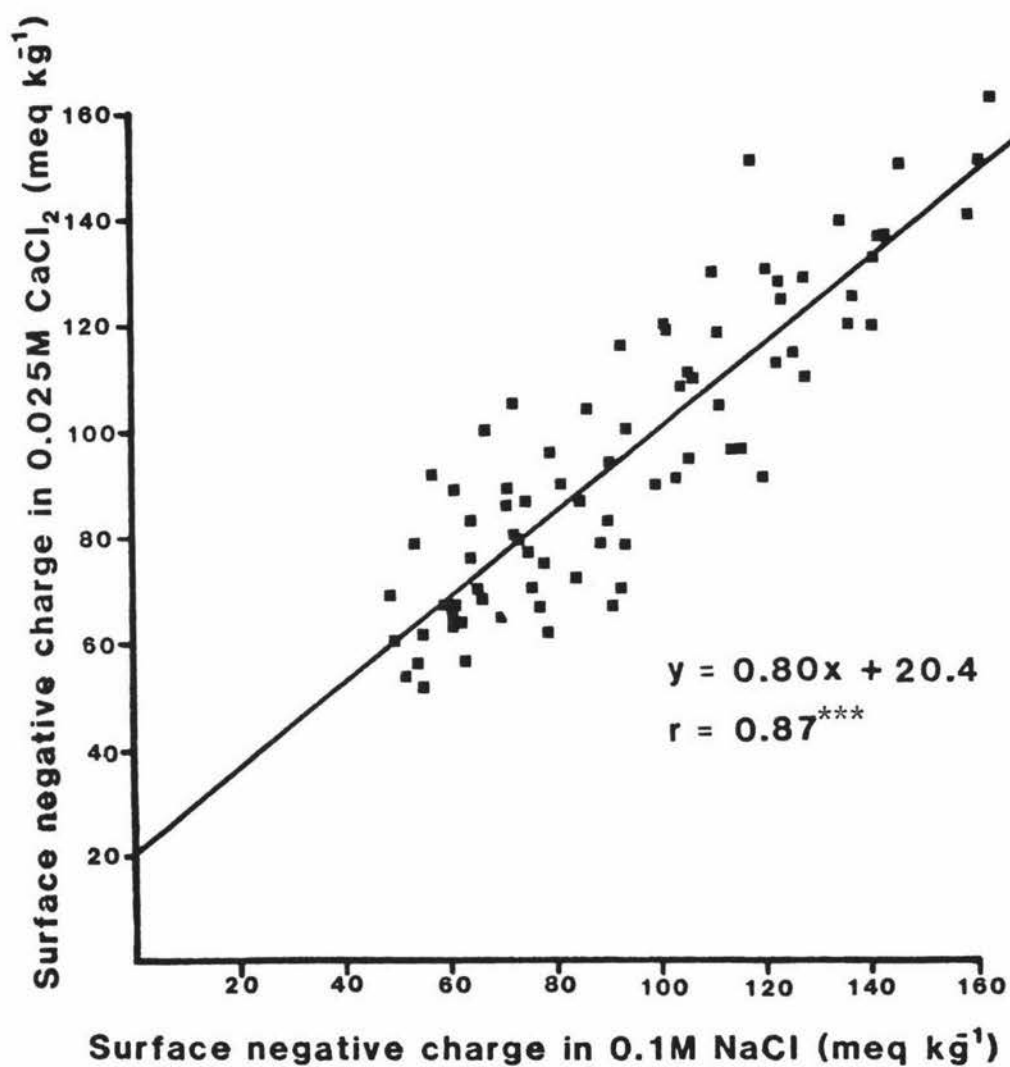


Fig. 4-6

The relationship between negative charge in 0.1M NaCl and negative charge in 0.025M CaCl₂.

Table 4-5 A comparison of pH values for some incubated soils,
prior to and during charge measurement in 0.1M NaCl
and 0.025M CaCl₂ (pH values are for the final
equilibrating charge measurement solution)

	pH				pH		
	H ₂ O	NaCl	CaCl ₂		H ₂ O	NaCl	CaCl ₂
<u>Ramiha</u>	* 5.00	5.55	4.85	<u>Egmont</u>	* 6.55	6.50	5.52
L ₀	4.70	5.00	4.76	L ₀	6.07	6.30	5.62
L ₁	5.13	6.00	5.20	L ₁	6.35	6.54	6.07
L ₂	5.40	6.33	5.76	L ₂	6.80	6.85	6.27
L ₃	5.80	6.65	6.10	L ₃	7.10	7.05	6.50
L ₄	6.12	6.81	6.40	L ₄	7.30	7.16	6.70
L ₅	6.60	7.05	6.60				
<u>Kumeroa</u>	* 5.97	6.96	6.10	<u>Patua</u>	* 5.61	6.30	5.31
L ₀	5.54	6.60	5.40	<u>Subsoil</u>			
L ₁	6.06	6.90	6.35	L ₀	5.30	5.80	5.12
L ₂	6.60	7.19	6.83	L ₁	5.80	6.20	5.53
L ₃	7.11	7.26	7.10	L ₂	6.10	6.35	5.82
L ₄	7.52	7.44	7.43	L ₃	6.53	6.60	6.01
				L ₄	6.72	6.70	6.21
				L ₅	6.98	7.02	6.45

* Unincubated soil.

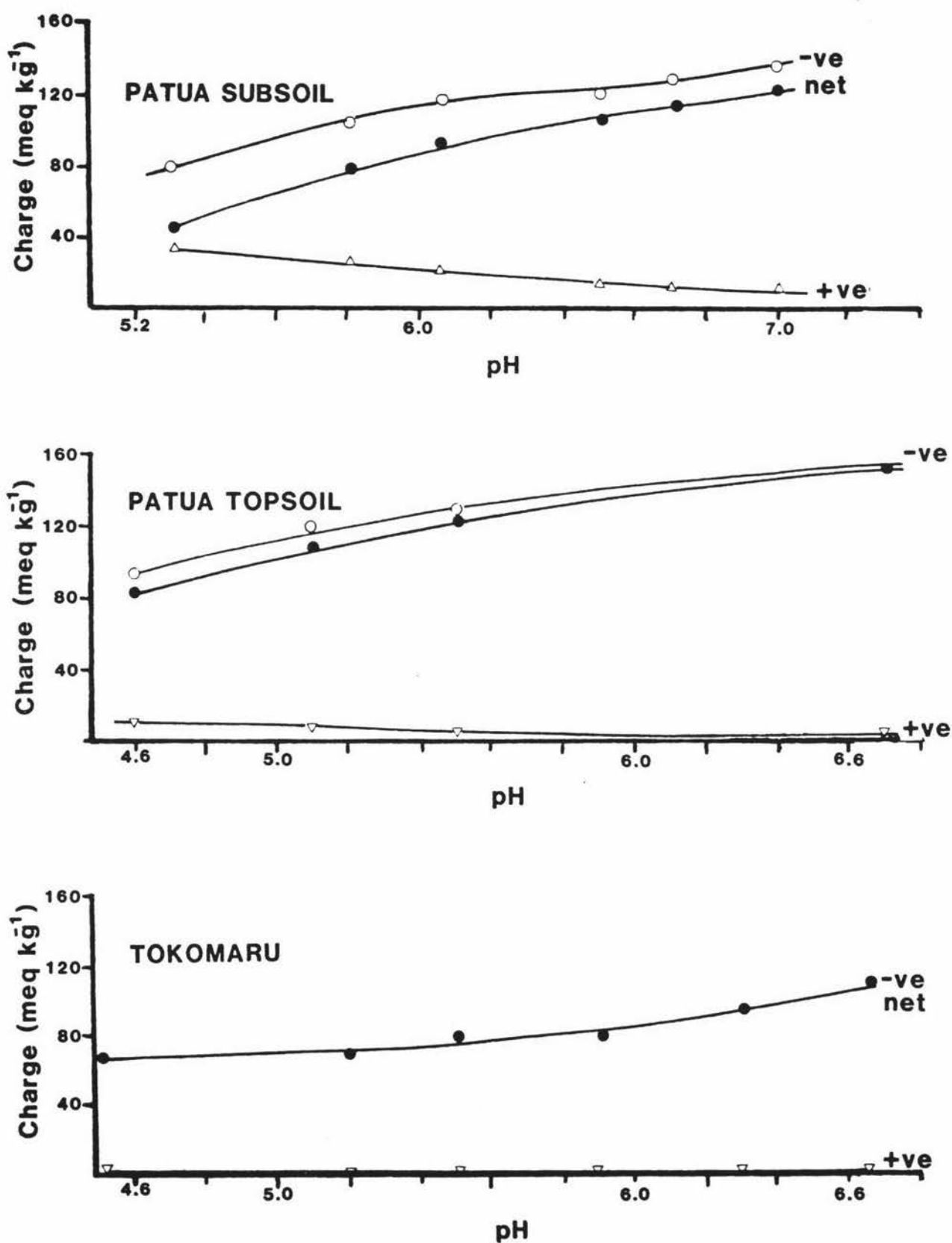


Fig. 4-7 The relationship between surface charge and pH in Tokomaru and Patua soils after incubation.

negative and decreased positive surface charge in the sodium media. The relationship between the amounts of calcium adsorbed and the amounts of sodium adsorbed ($y = 0.80x + 20$) was consistent with this suggestion, but there was some scatter in the data ($r = 0.87^{***}$). Certainly there was no evidence for calcium being specifically adsorbed in amounts greater than the surface negative charge (Na-sorption) in these soils.

Despite some differences in the behaviour of ions in calcium and sodium media (Bolt, 1979) and differences in the pH of the final equilibration solution, good agreement between charge in 0.1M NaCl, and charge in 0.025M CaCl_2 has been demonstrated. This relationship has significance to sulphate adsorption studies in these soils (Section 4.5).

4.4 Phosphate Sorption in Incubated Soils

Incubation with calcium hydroxide caused changes in phosphate sorption in all soils, although the differences in sorption within a soil were relatively small compared to the range of sorption capacities existing between soils (Fig. 4-8).

There was a clear dependence of sorption on pH in individual soils (Fig. 4-9), and the effect of calcium hydroxide appeared to be larger at higher solution concentration. Only limited information was obtained at low concentrations of phosphate in solution however, so few conclusions can be drawn as to the significance of pH to the sorption of phosphate in the concentration range significant for soils ($0 - 1 \text{ mg l}^{-1}$; Parfitt, 1982).

The data presented (Fig. 4-9) suggests that sorption is at a maximum at low pH (< 5.0), decreases with liming, and passes through a minimum in most soils, before increasing again in the higher pH range (6 - 7). From the isotherms presented in Fig. 4-9, and additional data (Appendix IV), a pH range in which the sorption minimum would occur can be identified for each of the soils. This maximum occurs somewhere between the pH values on either side of the pH at which minimum sorption was observed (Fig. 4-10).

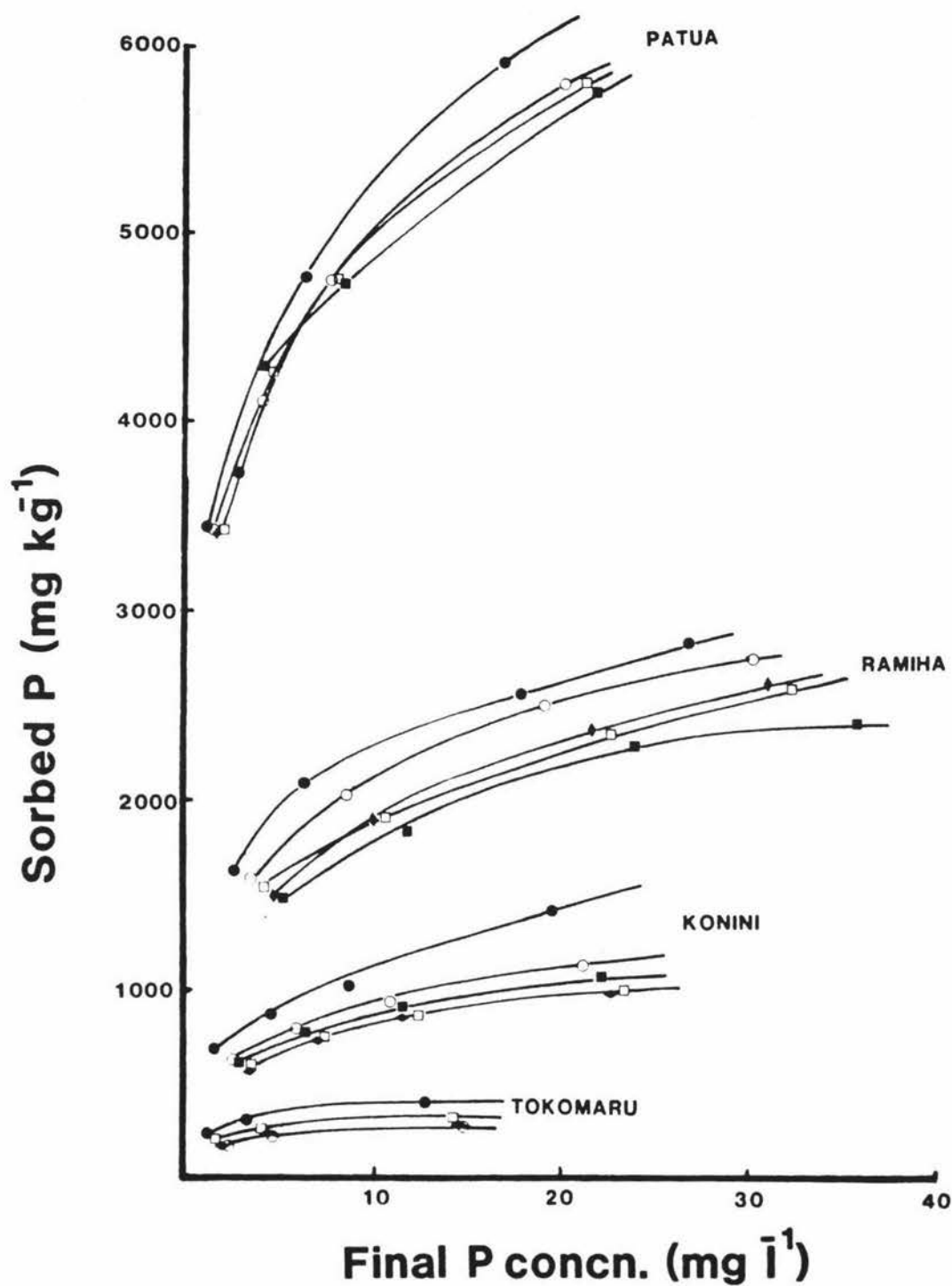


Fig. 4-8

Phosphate sorbed from 0.1M NaCl by several soils with a range of capacities to sorb anions. Here the final P concentration is the concentration of phosphate in solution at 40 hrs and sorbed P is phosphate on the surface.

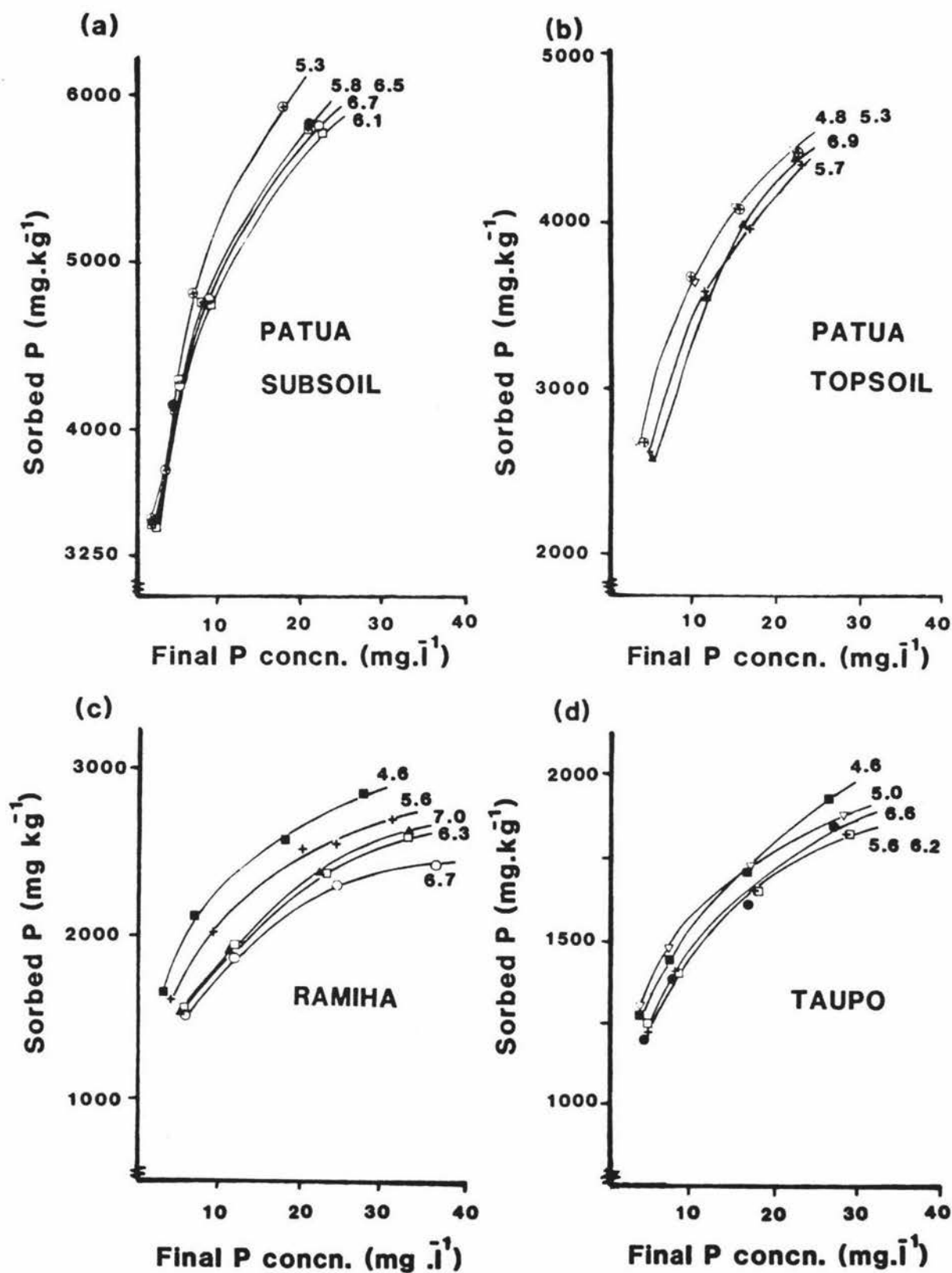


Fig.4-9

Phosphate sorbed from 0.1M NaCl by incubated soils, each at a range of pH values. Here the final P concentration of phosphate in solution at 40 hrs, and sorbed P is phosphate on the surface.

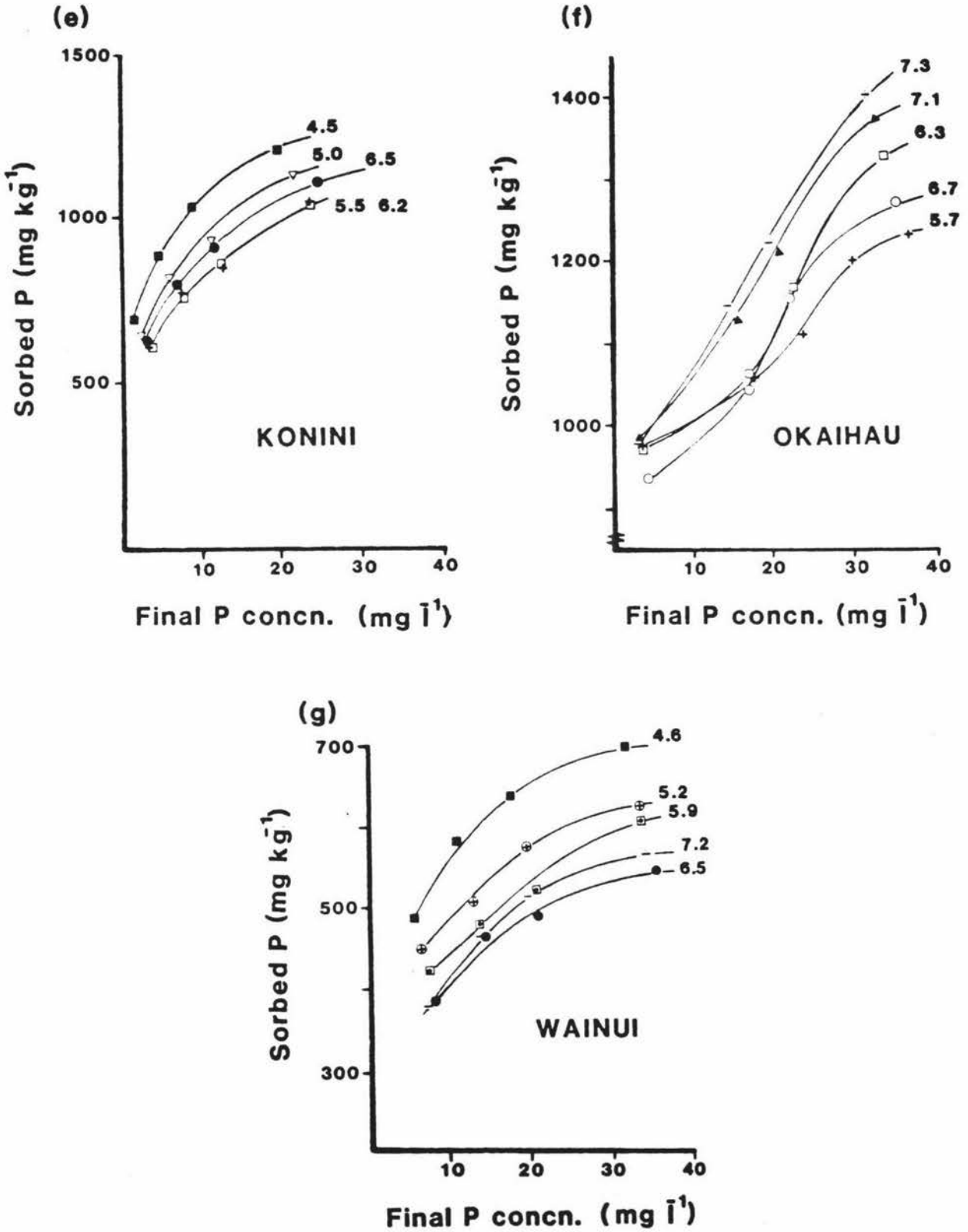


Fig. 4-9 Phosphate sorbed from 0.1M NaCl by incubated soils, each at a range of pH values. Here the final P concentration of phosphate in solution at 40 hrs, and sorbed P is phosphate on the surface.

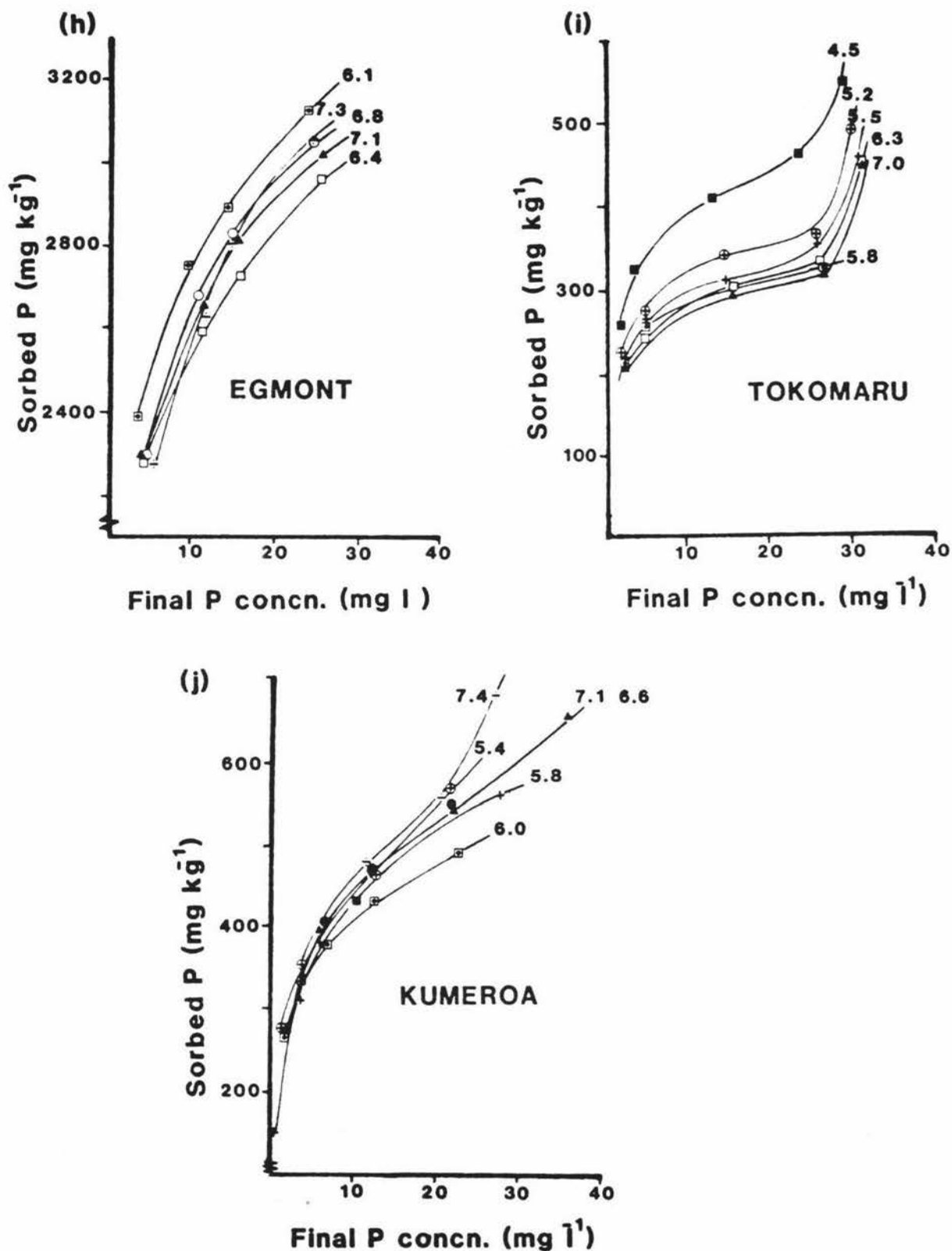


Fig. 4-9

Phosphate sorbed from 0.1M NaCl by incubated soils, each at a range of pH values. Here the final P concentration of phosphate in solution at 40 hrs, and sorbed P is phosphate on the surface.

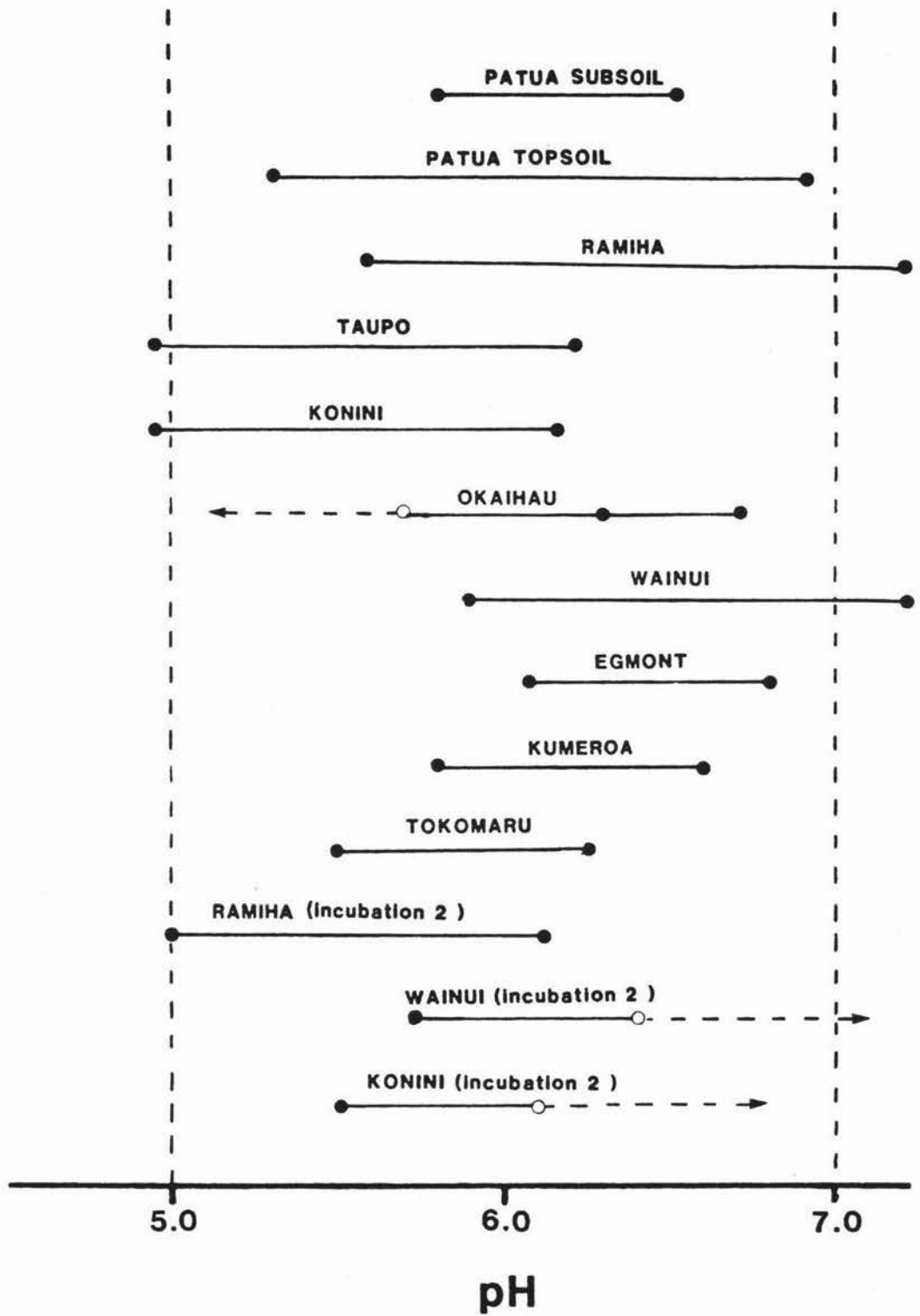


Fig. 4-10 The pH range in which apparent minima for phosphate sorption occurred in incubated soils. Here ●—● indicates that the apparent minimum occurred in the indicated range, but where the results do not preclude a minimum at higher or lower pH ●—○ is used.

Although in these studies it was not possible to locate precisely the pH at which sorption was a minimum (Fig. 4-10), it is apparent that there is no common point at which sorption will begin to increase with liming in all soils (Fig. 4-10). This dependence of phosphate sorption on pH is similar to that reported for a goethite surface (Bowden et al., 1980b) (Section 2.1.5). Here it was suggested that the sorption of phosphate will initially decrease with increasing pH due to increasing surface negativity, but at some stage this effect will be outweighed by an increase in the proportion of the HPO_4^{2-} ion in solution. It has been suggested that this ion has a higher affinity for the surface (Bowden et al., 1980a, b).

There are a number of different surfaces which can sorb phosphate and the proportions of these surfaces which are active in sorption will change with pH and in different soils. Variable charge materials will consistently show a decrease in positive and an increase in negative surface charge with increasing soil pH, but the rate of change of surface charge will vary in different soils. This suggests that the pH of minimum sorption will also vary among soils.

Alternatively, a change in the pH of minimum sorption may be due to the effects of calcium content of soils on phosphate sorption. Slight increases in ionic strength can be expected when calcium is displaced off the surface by sodium ions, or released into the sorption medium from the soil solution, and the ratio of calcium to sodium changed in the sorption media of soils limed at different rates (Table 4-6).

Calcium concentrations in the sorption media of the Patua subsoils were increased 20-fold by incubation with calcium chloride, and 13-fold by incubation with an equivalent rate ($4.3\text{g Ca kg soil}^{-1}$) of calcium hydroxide. This disparity arises because of an increase in the cation exchange capacity of the soil as the pH increases, such that an increasing proportion of the calcium applied is held on the soil surface, and not displaced by 0.1M NaCl in the limed soil. Lower amounts of calcium hydroxide ($2.0\text{g Ca kg soil}^{-1}$) were necessary to change the pH of the Wainui soil and the changes in calcium concentration of the sorption media were smaller. Changes of 2 - 3-fold were observed however, and a 3-fold change in calcium concentration was observed in the Patua topsoil.

Table 4-6 Calcium concentrations of 0.1M NaCl extracts of some incubated soils after different levels of calcium addition

Soil	(Ca ²⁺)		Soil	(Ca ²⁺)		Soil	(Ca ²⁺)	
	pH	mM l ⁻¹		pH	mM l ⁻¹		pH	mM l ⁻¹
<u>Patua</u> <u>Subsoil</u>	* 5.60	0.10	<u>Patua</u> <u>Topsoil</u>	* 5.40	0.60	<u>Wainui</u>	* 5.10	0.45
L ₀	5.30	0.10	L ₀	4.80	0.60	L ₀	4.70	0.45
L ₁	5.80	0.40	L ₁	5.30	1.05	L ₃	5.70	0.80
L ₂	6.10	0.70	L ₂	5.70	1.40	L ₅	6.40	1.05
L ₃	6.50	0.81	L ₃	6.90	2.20	** CaCl ₂ ⁵	4.92	1.10
L ₄	6.80	1.02				L ₀	4.60	0.45
L ₅	7.00	1.30				L ₆	5.20	0.73
** CaCl ₂ ³	5.15	0.60				L ₇	5.90	1.00
** CaCl ₂ ⁵	4.80	1.90				L ₈	6.50	1.10
						L ₉	7.21	1.40

* Unincubated soil.

** Soil incubated with CaCl₂ at equivalent rate of calcium to that indicated.

Table 4-7 Solubility calculation for calcium and phosphate concentrations in the sorption media of Kumeroa and Tokomaru soils ($K = (P)(Ca)$), where
 $K_{sp} = 2.19 \times 10^{-7}$ for Dicalcium phosphate (DCP)
 $K_{sp} = 2.75 \times 10^{-7}$ for Dicalcium phosphate dihydrate (DCPD)

Level of P added	Tokomaru				Kumeroa			
	Soil pH	(Ca ²⁺) mM l ⁻¹	(P) mM l ⁻¹	K x10 ⁻⁷	Soil pH	(Ca ²⁺) mM l ⁻¹	(P) mM l ⁻¹	K x10 ⁻⁷
1	4.50	0.16	0.04	0.06	5.42	0.98	0.04	0.40
2		0.15	0.11	0.17		0.97	0.11	1.07
3		0.15	0.42	0.62		0.99	0.19	1.88
4		0.15	0.75	1.10		0.92	0.40	3.66 **
5		0.15	0.93	1.40		0.92	0.68	6.24 **
1	5.20	0.25	0.05	0.12	5.80	0.90	0	0
2		0.24	0.14	0.34		0.88	0.11	0.97
3		0.24	0.46	1.09		0.96	0.19	1.83
4		0.24	0.81	1.95		1.13	0.92	10.35 **
5		0.23	0.96	2.22 *		0.87	1.69	14.70 **
1	5.51	2.70	0.06	0.16	6.00	1.16	0.04	0.46
2		2.58	0.14	0.36		1.16	0.11	1.28
3		0.27	0.47	1.28		0.12	0.20	2.32 *
4		0.27	0.82	2.17		0.12	0.40	4.63 **
5		0.26	0.99	2.57 *		0.12	0.73	8.94 **
1	5.84	0.31	0.06	0.20	6.60	0.14	0.04	0.55
2		0.31	0.15	0.47		0.14	0.11	1.55
3		0.31	0.49	1.52		0.14	0.20	2.57 *
4		0.31	0.84	2.56 *		0.14	0.40	5.32 **
5		0.30	0.99	2.97 **		0.14	0.70	9.80 **
1	6.30	0.36	0.06	0.21	7.10	0.16	0.04	0.64
2		0.35	0.16	0.56		0.15	0.11	1.70
3		0.36	0.49	1.74		0.16	0.19	3.03 **
4		0.35	0.84	2.95 **		0.16	0.39	6.37 **
5		0.36	0.99	3.52 **		0.16	0.70	10.92 **
1		0.40	0.06	0.24		0.19	0.04	0.75
2		0.40	0.15	0.61		0.19	0.11	2.10
3		0.40	0.50	1.99		0.19	0.20	3.82 **
4		0.40	0.84	3.37 **		0.20	0.38	7.47 **
5		0.40	0.99	3.91 **		0.19	0.70	13.50 **

* Indicates K_{sp} of DCP is exceeded.

** Indicates K_{sp} of DCPD is exceeded.

Barrow et al. (1980) have shown that calcium has a co-operative effect in increasing phosphate sorption, and the data of Ryden and Syers (1975), for sorption of 40 hours, suggests that sorption in calcium media will be 25-50% greater than sorption in sodium media at comparable ionic strength.

It is tentatively suggested, therefore, that differences in the pH of minimum sorption in various soils may be attributed to differences in the nature of the surfaces which sorb phosphate and to differences in the amounts of calcium in the sorption medium.

Phosphate sorption isotherms for some of the soils showed inflexions towards the y-axis (Fig. 4.9), perhaps indicating that phosphate was precipitating in the sorption media. Analysis of these media showed that the concentrations of phosphate and calcium in solution were sufficient to exceed the solubility products of both dicalcium phosphate, and dicalcium phosphate dihydrate (Table 4-7). Such a mechanism will only occur at high P concentration in solution, however, and is unlikely to be significant in soils, in situations other than directly after fertiliser application.

The formation of a discrete phase calcium carbonate surface is not likely to be significant to the sorption of phosphate at higher rates of calcium hydroxide application. Isotherms for sorption on calcium carbonate are almost linear, and the amounts adsorbed in pure systems (Kuo and Mikkelsen, 1979) are relatively low compared to the amounts sorbed by soils in this study.

4.5 Sulphate Adsorption by Incubated Soils

4.5.1 Sulphate adsorption in 0.1M NaCl

All soils had a lower ability to adsorb sulphate than phosphate, but the ratio of P adsorbed:S adsorbed at any one anion concentration in solution was not consistent between soils. For example, at 20 mg l⁻¹ S or P, the Patua subsoil adsorbed approximately 15 times more phosphate

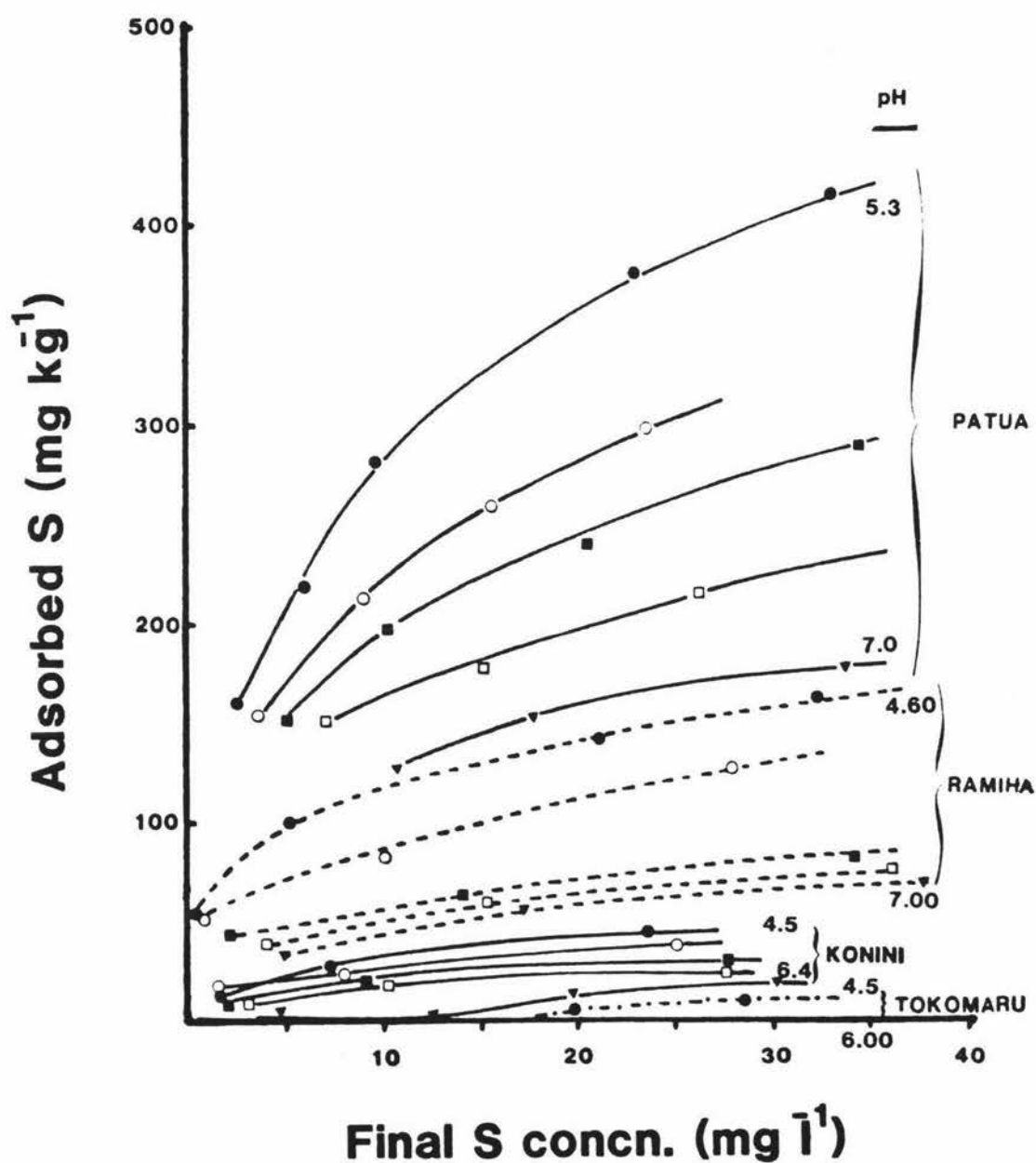


Fig. 4-11 Sulphate adsorbed from 0.1M NaCl by several soils with a range of capacities to sorb anions. Here the final S concentration is the solution sulphate concentration at 40 hrs, and adsorbed sulphate is the amount on the surface.

than sulphate, but the ratio of P adsorbed:S adsorbed in the Konini soil was almost 40:1.

The adsorption capacity of incubated soils showed a dependence on pH (Fig. 4-11, 4-14, 4-15); decreasing with increasing rates of calcium hydroxide. In contrast to phosphate sorption (Fig. 4-8) changes in sulphate adsorption were of a similar magnitude to the differences in adsorption capacity observed between soil types (Fig. 4-11). The absolute changes in the amounts of anion sorbed at any given concentration in solution (e.g. 20 mg l^{-1}) were greater for phosphate than sulphate (Fig. 4-12). When these changes were expressed as a percent of maximum sorption (i.e. sorption observed at lowest pH) however, the observed decreases were much greater for sulphate than phosphate (Fig. 4-13). Liming produced a maximum reduction in sorption capacity of only 30% for phosphate, while changes in sulphate sorption ranged from 40 - 100%.

The shape of sulphate adsorption isotherms showed some dependence on the absorption capacity of the soil. Lower sorbing soils (4-14c,e,f; 4-15e,f,g,h) typically had S shaped isotherms. A low initial slope became steeper with increasing sulphate concentration in solution and then levelled off to approach a maximum in the range $25 - 40 \text{ mg l}^{-1}$ sulphate. Higher sorbing soils (4-14a,b,d; 4-15a,b,c,d) had their steepest slope at very low sulphate concentrations ($0 - 10 \text{ mg l}^{-1}$) and then levelled off to approach a maximum in the high solution sulphate range ($> 30 \text{ mg l}^{-1}$).

The observed differences in the shape of adsorption isotherms may be related to the desorption of sulphate from the soil colloid. When soils are equilibrated with low or zero rates of sulphate addition, some sulphate may be desorbed. The amount of sulphate remaining on the surface is then calculated as the difference between the previously determined levels of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ -extractable in these soils, and the amount of sulphate released to solution.

In the low sorbing soils, less sulphate than expected appears to be desorbed into 0.1M NaCl . This apparent hysteresis between the adsorption and desorption of sulphate suggests that either (i) sulphate adsorption is partially irreversible, and a small portion of the surface inorganic pool of sulphate cannot be desorbed, or

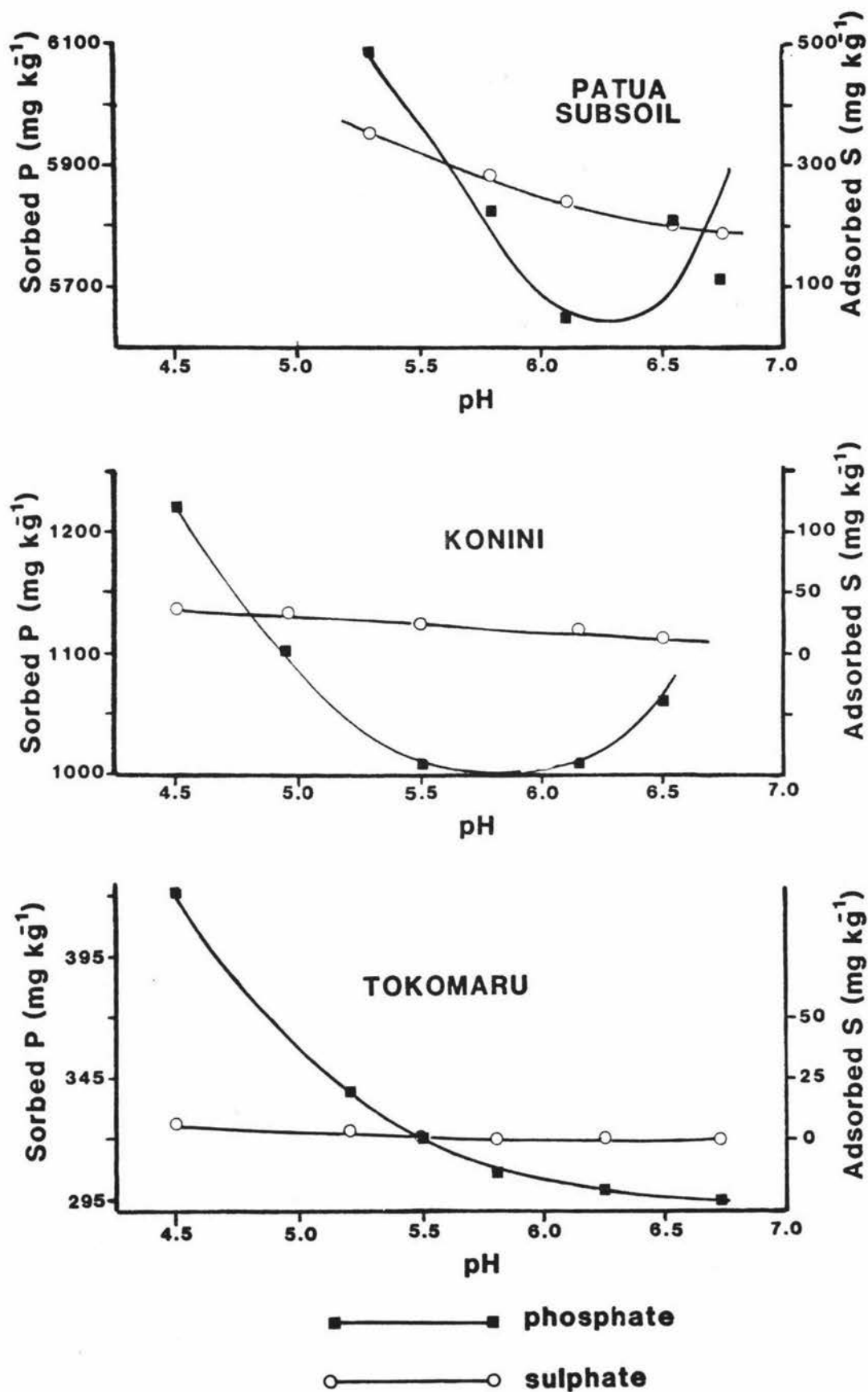


Fig. 4-12

The amounts of phosphate and sulphate on the surface at an anion concentration of 20 mg l^{-1} in three incubated soils each at a range of pH values.

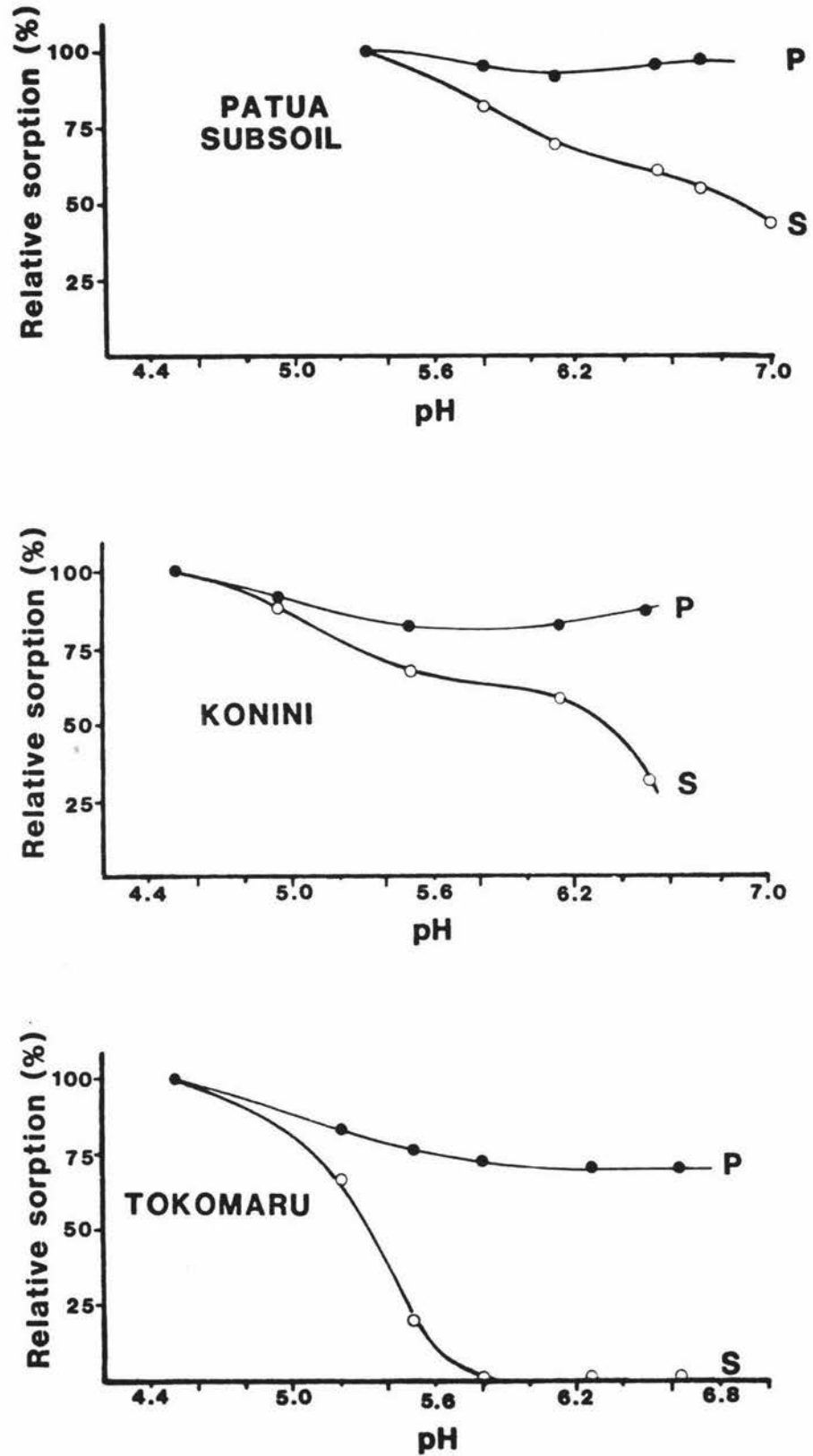
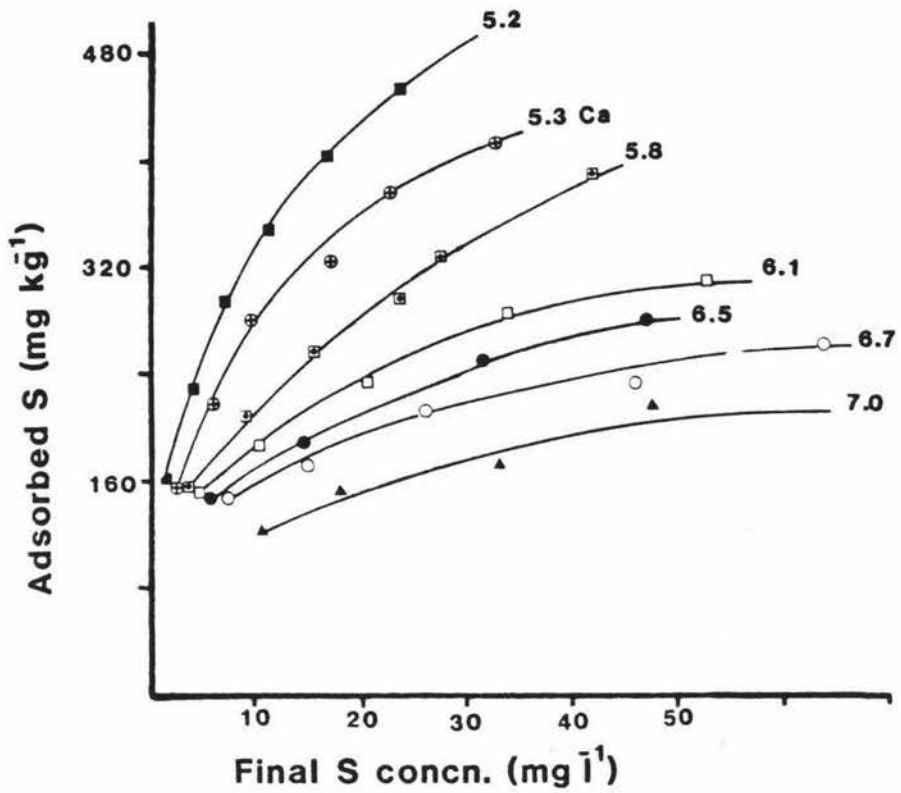


Fig. 4-13

The relative amounts of sulphate and phosphate on the surface at an anion concentration of 20 mg l^{-1} in three incubated soils each at a range of pH values, where the results are expressed as a percentage of sorption at the lowest pH.

(a) PATUA SUBSOIL



(b) RAMIHA

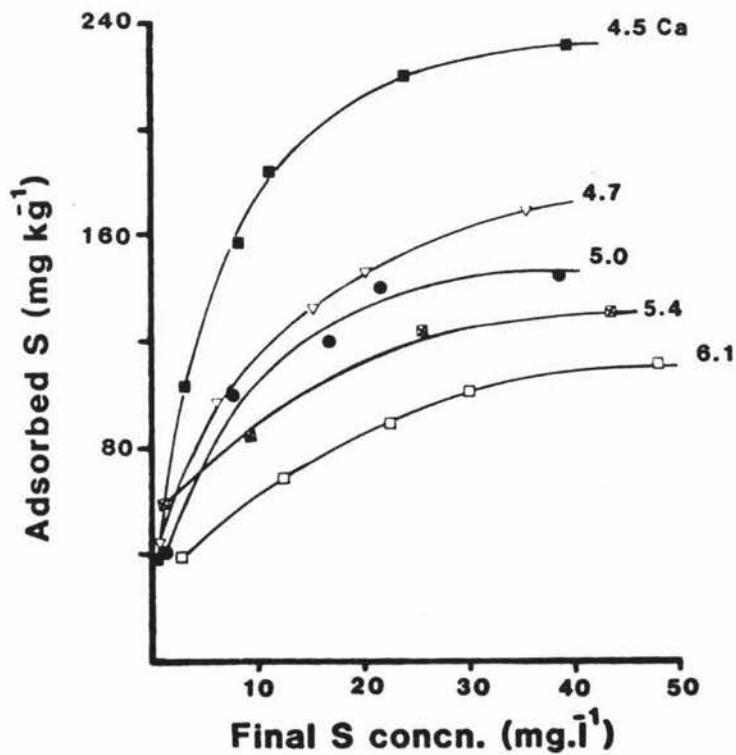
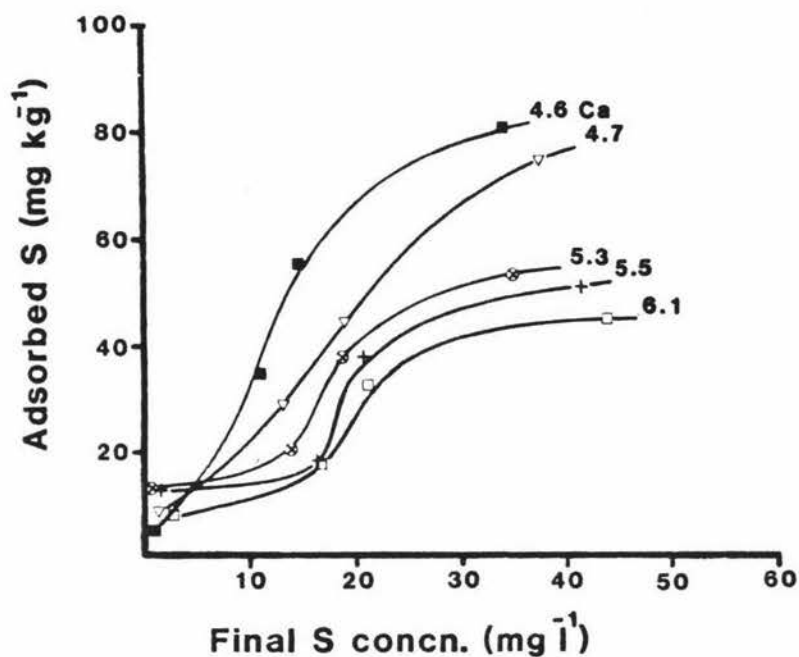


Fig. 4-14

Sulphate adsorbed from 0.1M NaCl by soils incubated with calcium hydroxide or calcium chloride. Here the final S concentration is the concentration of sulphate in solution at 40 hrs, adsorbed S is the amount on the surface, and soils incubated with calcium chloride are indicated by Ca.

KONINI



(d) TAUPO

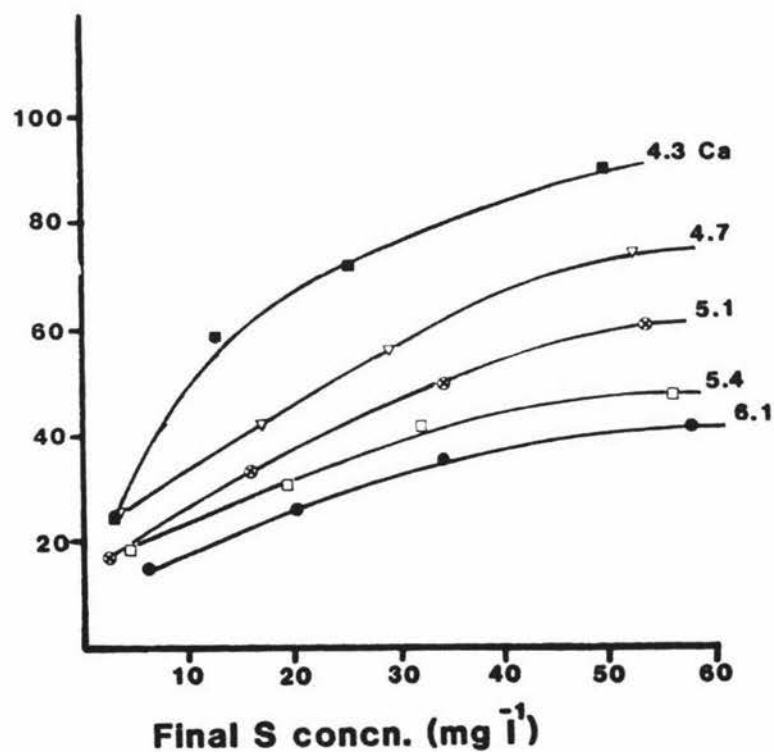
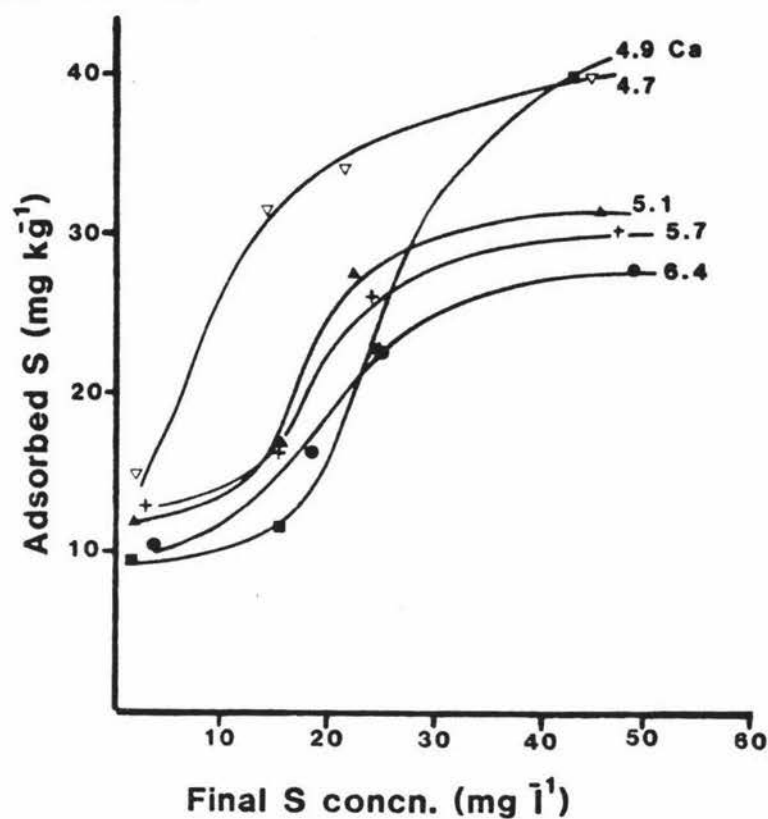


Fig. 4-14

Sulphate adsorbed from 0.1M NaCl by soils incubated with calcium hydroxide or calcium chloride. Here the final S concentration is the concentration of sulphate in solution at 40 hrs, adsorbed S is the amount on the surface, and soils incubated with calcium chloride are indicated by Ca.

(e) WAINUI



(f) TOKOMARU

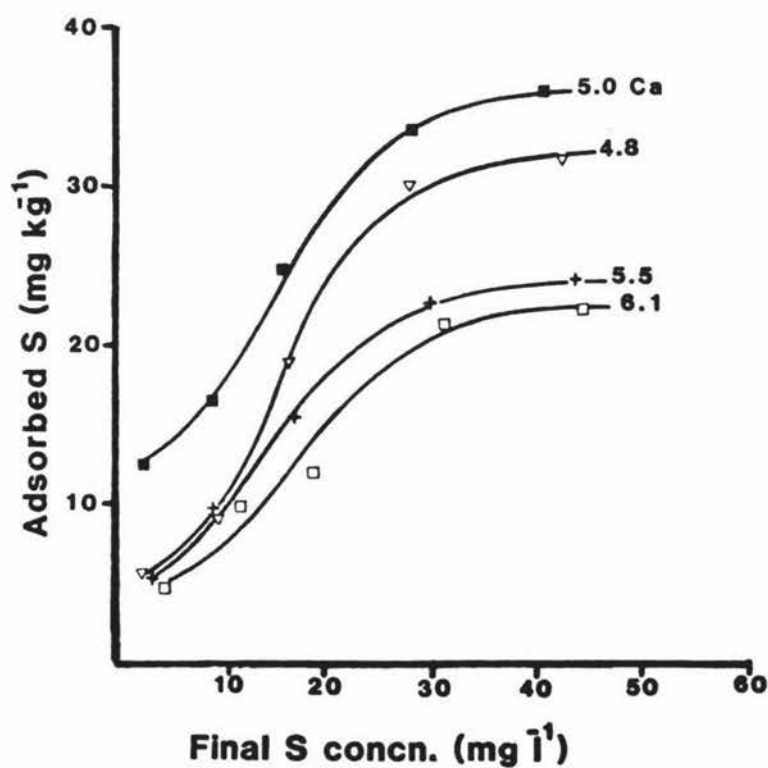
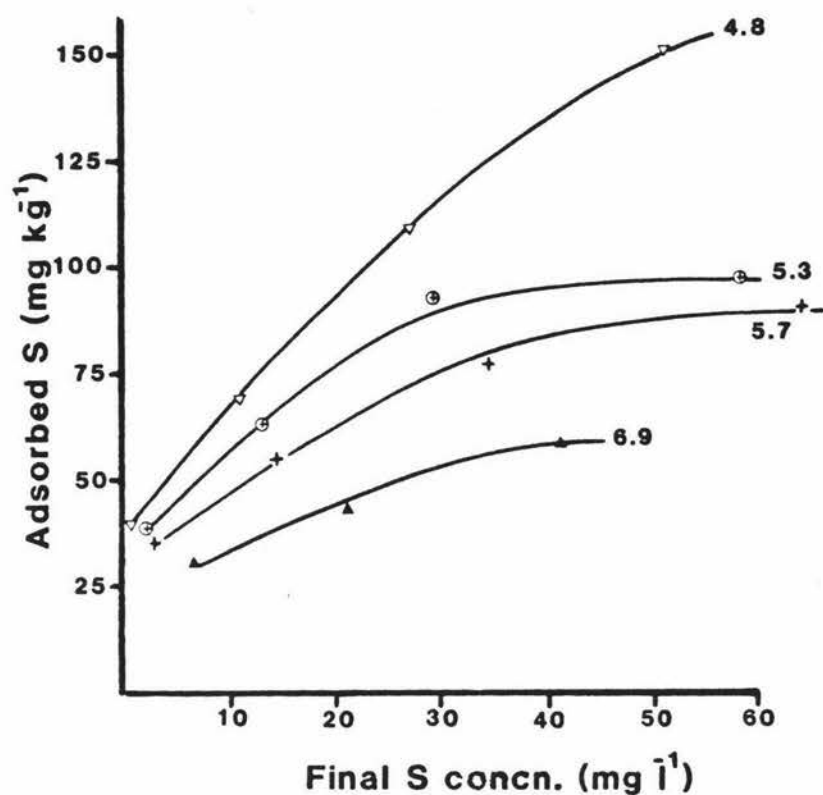
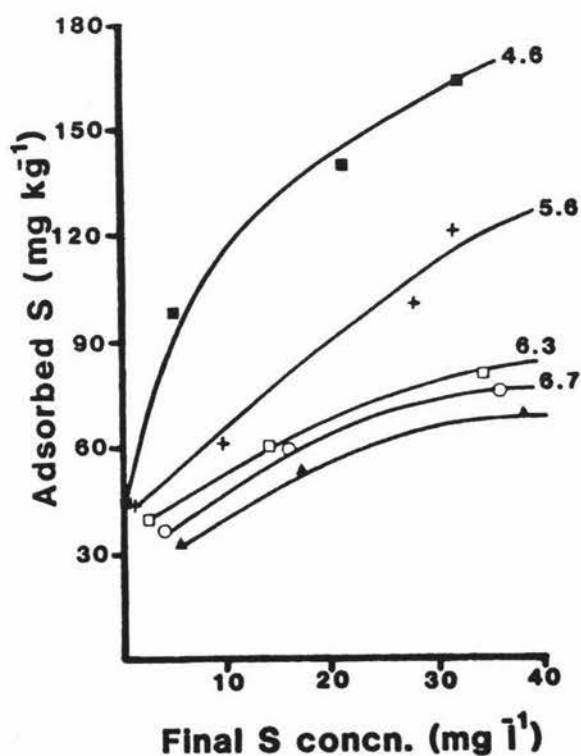


Fig. 4-14

Sulphate adsorbed from 0.1M NaCl by soils incubated with calcium hydroxide or calcium chloride. Here the final S concentration is the concentration of sulphate in solution at 40 hrs, adsorbed S is the amount on the surface, and soils incubated with calcium chloride are indicated by Ca.



(b) RAMIHA



(c) EGMONT

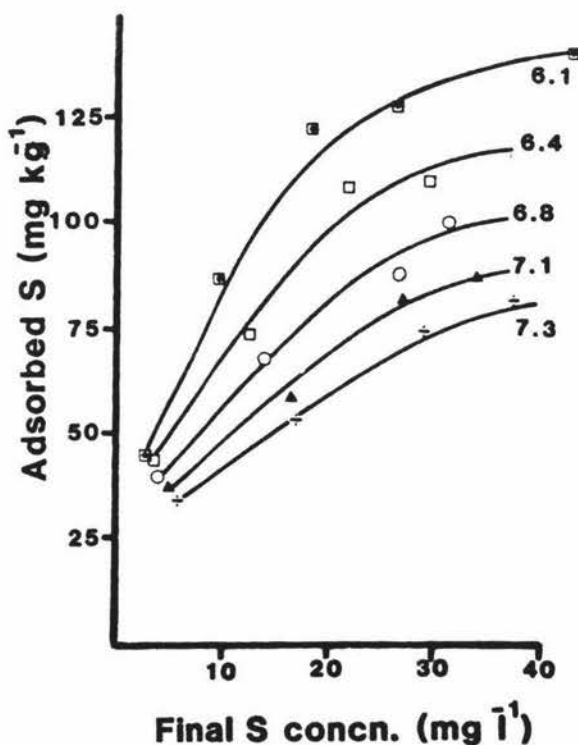
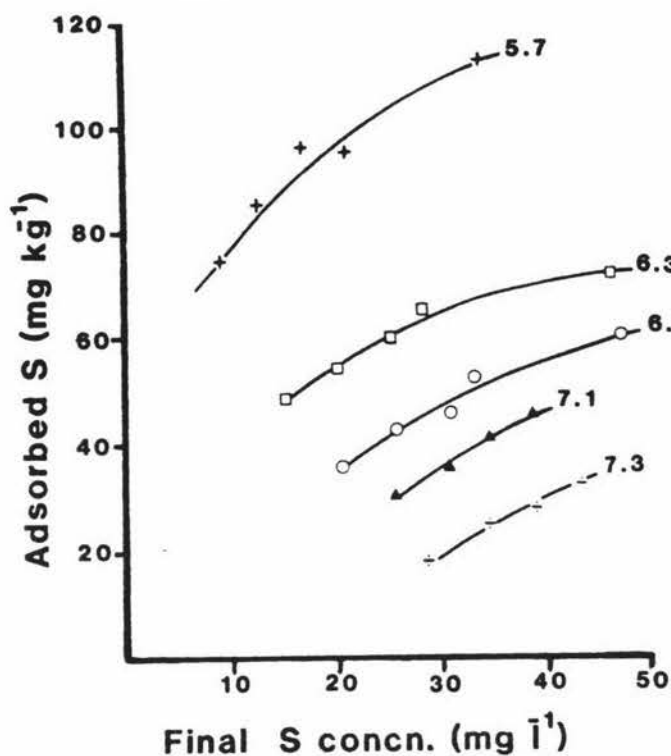


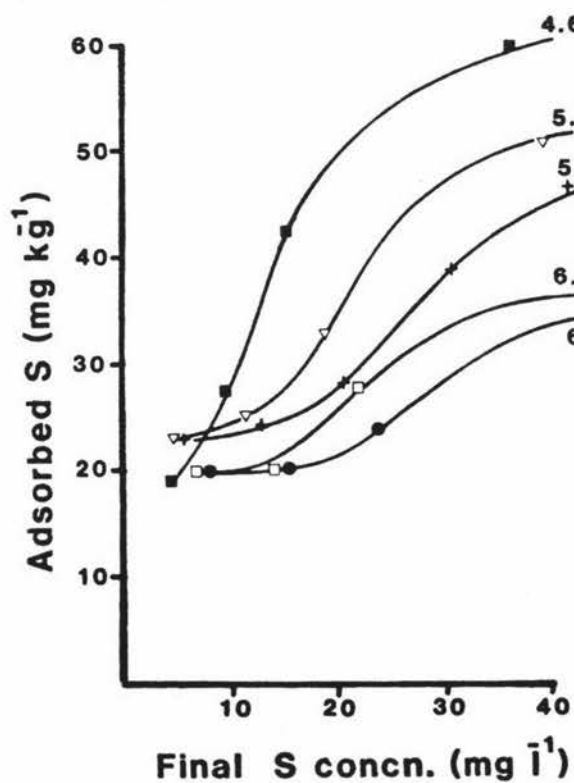
Fig. 4-15

Sulphate adsorbed from 0.1M NaCl by soils after incubation with calcium hydroxide to give a range of pH values (5.0 - 7.0). Here the final S concentration is the concentration of sulphate in solution at 40 hrs, and adsorbed S is the amount of sulphate on the surface.

(d) OKAIHAU



(e) TAUPO



(f) KONINI

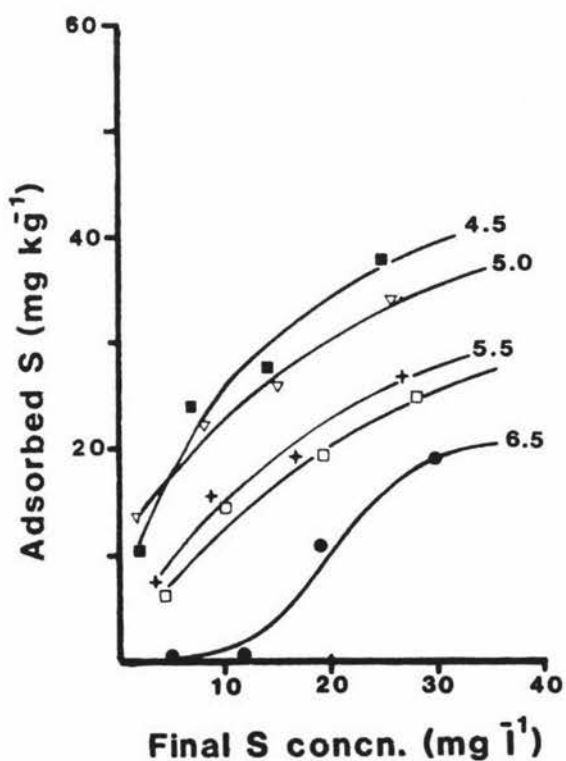


Fig. 4-15 Sulphate adsorbed from 0.1M NaCl by soils after incubation with calcium hydroxide to give a range of pH values (5.0 - 7.0). Here the final S concentration is the concentration of sulphate in solution at 40 hrs, and adsorbed S is the amount of sulphate on the surface.

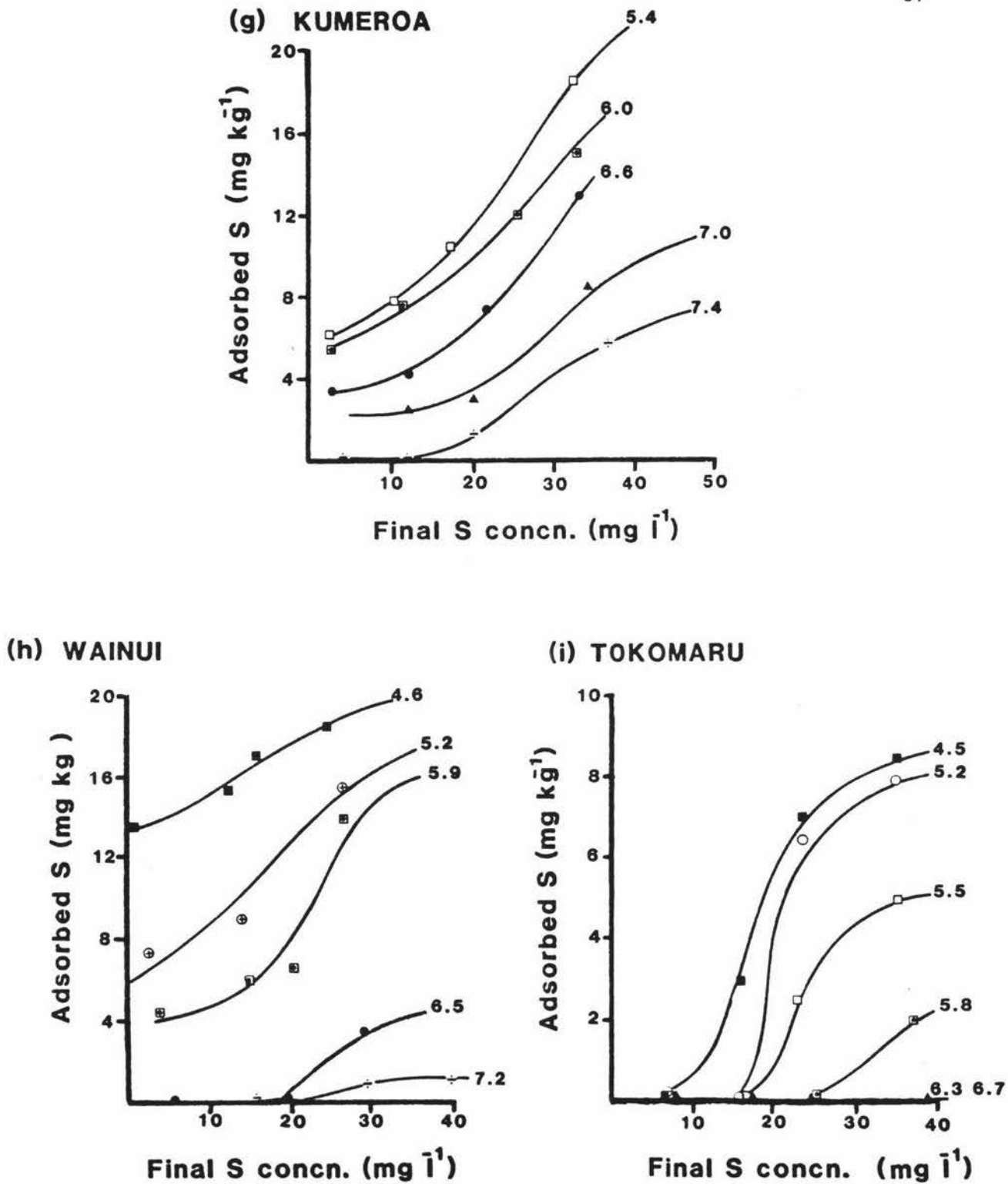


Fig. 4-15

Sulphate adsorbed from 0.1M NaCl by soils after incubation with calcium hydroxide to give a range of pH values (5.0 - 7.0). Here the final S concentration is the concentration of sulphate in solution at 40 hrs, and adsorbed S is the amount of sulphate on the surface.

(ii) that there are errors in the assumption that $\text{Ca}(\text{HPO}_4)_2^-$ extractable sulphate represents a discrete surface pool of sulphate, which is in complete equilibrium with the 0.1M NaCl sorption medium.

There is indirect support for the latter explanation. When adsorbed plus solution sulphate is estimated by calcium phosphate extraction and analysed by reduction (Johnson and Nishita, 1952), a small amount of reducible organic-S may be included in the measurement (Searle, 1979). Differences in the amount of reducible organic-S released into NaCl, and CaHPO_4 may thus explain some apparent hysteresis in sorption isotherms, and these effects will be more noticeable in the low sorbing soils, which have lower levels of inorganic sulphur.

The amounts of sulphate adsorbed at 20, 30 and 40 mg l^{-1} sulphate in solution were all highly correlated with the measured surface positive charge in 0.1M NaCl (Table 4-8). There was a tendency for sulphate adsorption to approach a maximum in all soils and for convenience an apparent maximum for sulphate adsorption was assumed at 40 mg l^{-1} sulphate in solution. Slight changes in sulphate on the surface were still occurring at this solution concentration in several soils however, particularly those of high adsorption capacity.

At 40 mg l^{-1} of sulphate in solution, 95% of the variation in sulphate adsorption could be accounted for by differences in surface positive charge, and the relationship between equivalents sulphate adsorbed, and surface positive charge was close to 1:1 (Fig. 4-16). Significantly, as the amount of positive charge on the soil surface tended to zero very little sulphate was adsorbed. This suggests that the ability of a soil to adsorb sulphate is dependent on the presence of surface positive charge.

Some variation in the data at low charge, and low levels of adsorbed sulphate may be accounted for by a difficulty in measuring small amounts of surface positive charge. A large correction for entrained chloride ions means that chloride desorbed by 0.1M KNO_3 is measured against a high background (25 - 40 mg l^{-1}) concentration. Further variation may be attributable to negative adsorption of chloride and sulphate (Section 2.1.2).

There was very little correlation between the amounts of surface negative charge and sulphate adsorbed ($r = -0.06$), suggesting that sulphate is adsorbed on positive sites in a manner which is

Table 4-8 The relationship between sulphate adsorbed
by soils and surface positive charge
(both measured in 0.1M NaCl).

(S) in solution mg l ⁻¹	Correlation Coefficient	Regression Coefficient	Significance
20	0.98	0.66	***
30	0.98	0.74	***
40	0.98	0.80	***

Table 4-9 The relationship between sulphate adsorbed
by soils and surface positive charge
(both measured in 0.025M CaCl₂)

(S) in solution mg l ⁻¹	Correlation Coefficient	Regression Coefficient	Significance
40	0.98	1.41	***
50	0.98	1.51	***

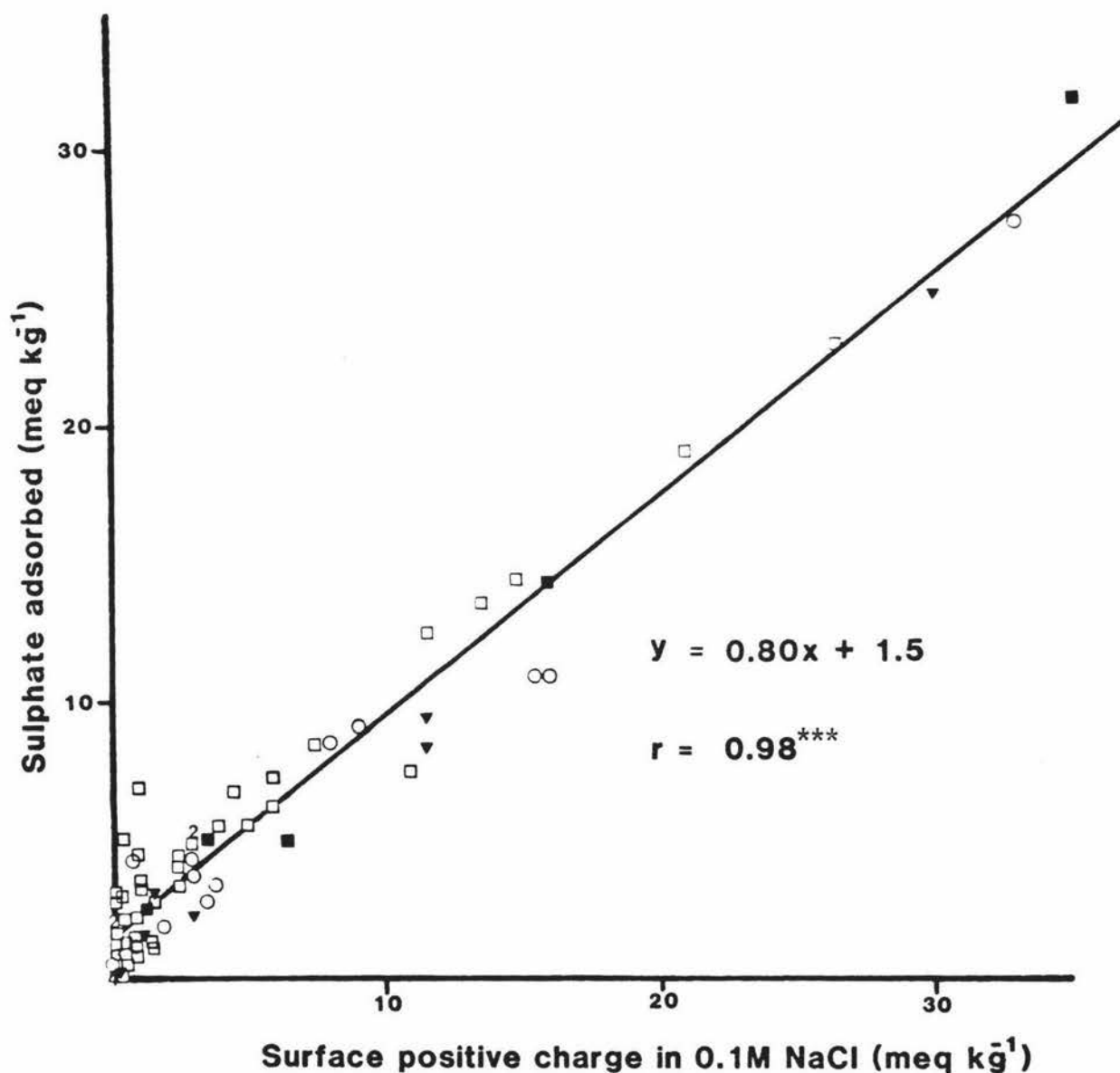


Fig. 4-16 The relationship between sulphate on the surface at 40 mg l⁻¹ S in solution, and surface positive charge, both measured in 0.1M NaCl.

Legend:

- ▼ unincubated soil
- soil incubated with water only
- soil incubated with calcium hydroxide
- soil incubated with calcium chloride

relatively independent of surface negative charge. The dependence of sulphate adsorption on positive surface charge might suggest that sulphate is non-specifically adsorbed, but consideration of the conditions under which this study was conducted suggests otherwise. These results were obtained in a medium which was 0.1M in chloride, so if sulphate was non-specifically adsorbed, chloride would be in sufficient concentration to eliminate sulphate adsorption altogether. This was not the case and a preferential adsorption of sulphate on positive sites is apparent.

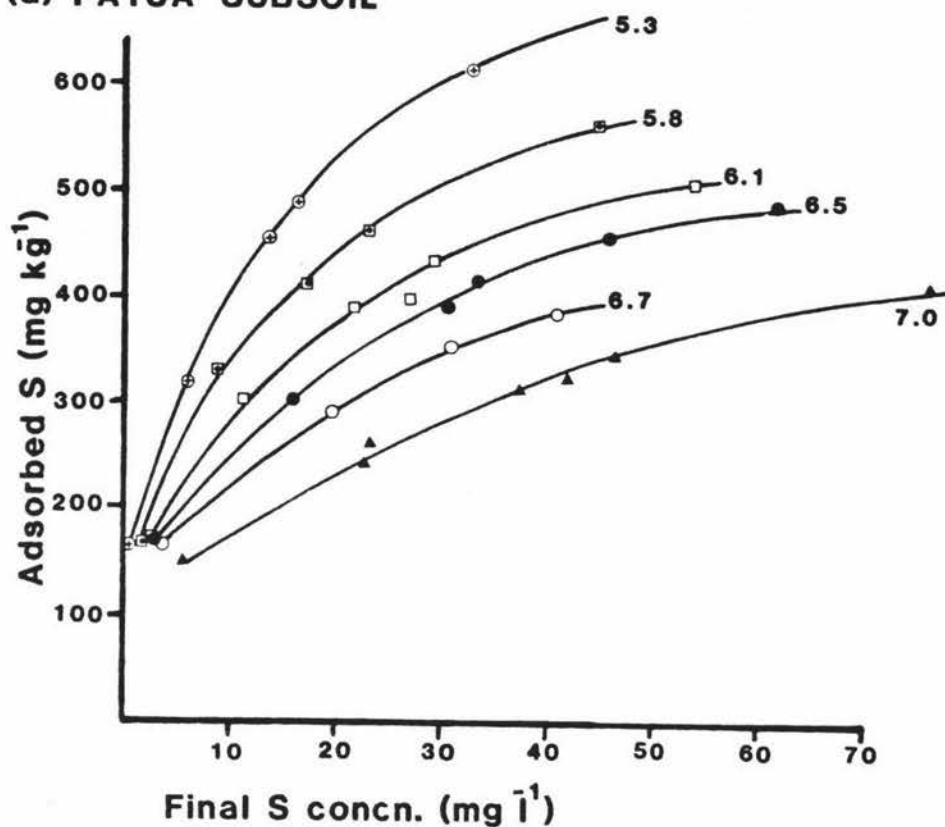
It was interesting to note that the soils incubated with calcium chloride had adsorption capacities which were also related to the levels in surface positive charge in soils (Fig. 4-16). Incubation caused slight changes in soil pH, increases in surface positive charge, and increases in sulphate adsorption.

4.5.2 Sulphate adsorption in 0.025M CaCl_2

Although the surface positive charge in 0.025M CaCl_2 was very similar to the surface positive charge in 0.1M NaCl ($y = 1.06x - 0.18$; $r = 0.97^{***}$), larger amounts of sulphate were adsorbed from 0.025M CaCl_2 than from 0.1M NaCl (Fig. 4-17). Kinetic effects can be regarded as small in sulphate adsorption studies (Barrow, 1969, 1972) with equilibrium being attained within 4 and 16 hours in most soils (Harward et al., 1962), so the increased adsorption in calcium media must be regarded as an increase in the soil's capacity to adsorb sulphate.

As with adsorption in 0.1M NaCl, adsorption isotherms in 0.025M CaCl_2 tended to approach a maximum at high concentrations of sulphate in solution. A good correlation was again obtained between sulphate adsorbed at 40 mg l^{-1} sulphate in solution and surface positive charge in 0.025M CaCl_2 ($r = 0.98^{***}$), and also at 50 mg l^{-1} sulphate in solution ($y = 1.5x + 1.5$; $r = 0.98^{***}$) (Table 4-9, Fig. 4-18). For adsorption in 0.025M CaCl_2 measurable changes in the amounts of sulphate adsorbed occurred between 40 and 50 mg l^{-1} sulphate in solution and the ratio of sulphate adsorbed to surface charge increased from 1.4 to 1.5.

(a) PATUA SUBSOIL



(b) PATUA TOPSOIL

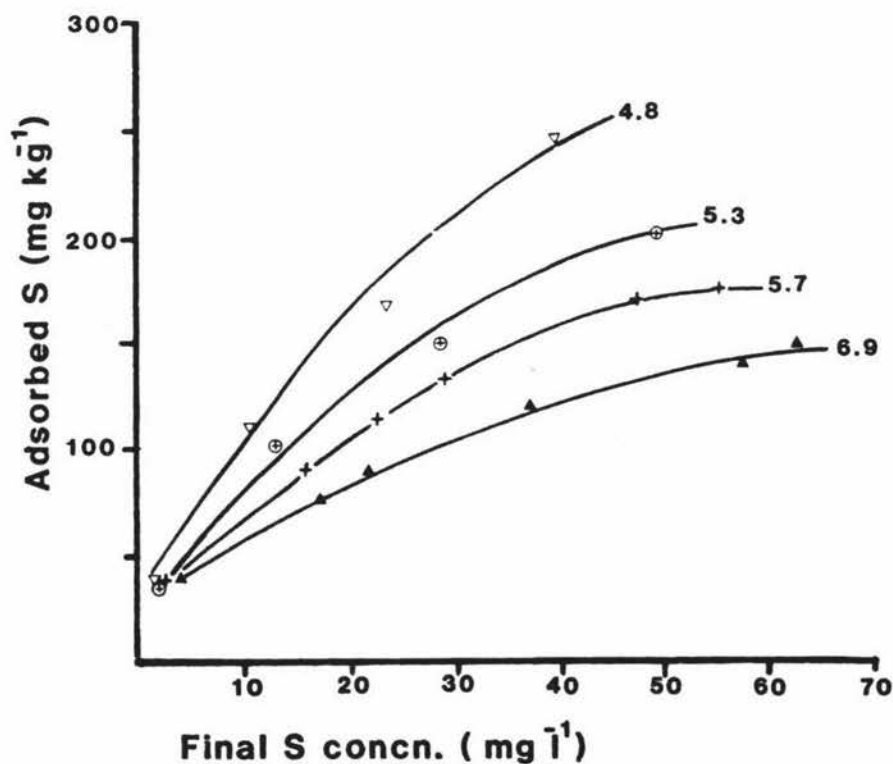


Fig. 4-17 Sulphate adsorbed from 0.025M CaCl_2 by soils incubated with calcium hydroxide to give a range of pH values (5.0 - 7.0). Here the final S concentration refers to the concentration of sulphate in solution after 40 hrs, and adsorbed S to the amount of sulphate on the surface.

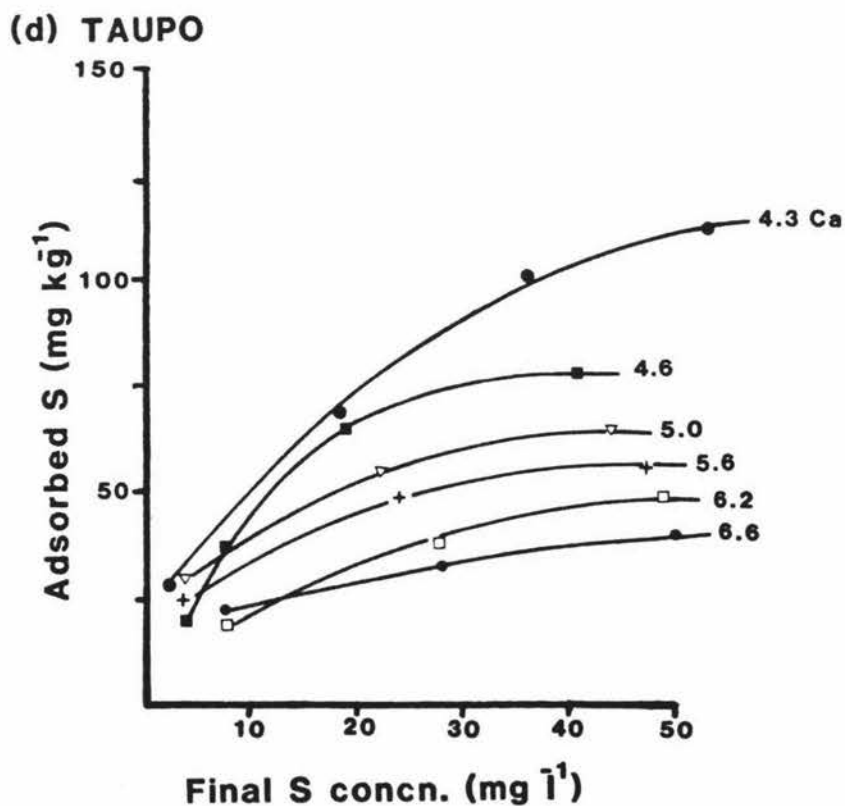
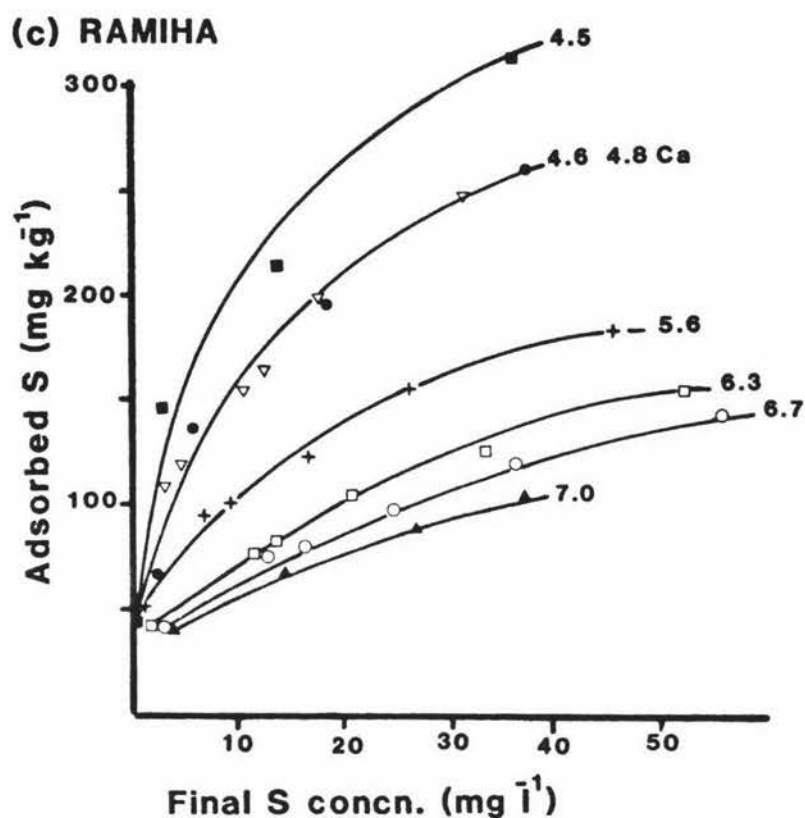


Fig. 4-17 Sulphate adsorbed from 0.025M CaCl_2 by soils incubated with calcium hydroxide to give a range of pH values (5.0 - 7.0). Here the final S concentration refers to the concentration of sulphate in solution after 40 hrs, and adsorbed S to the amount of sulphate on the surface.

(e) TOKOMARU

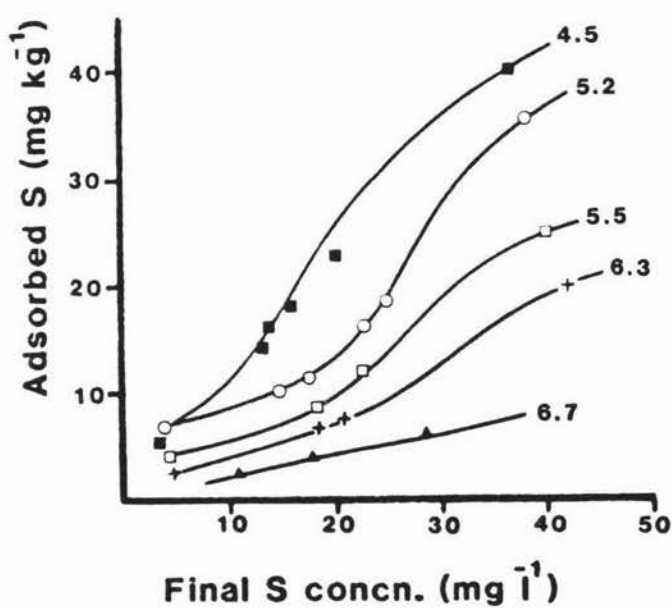


Fig.4-17 Sulphate adsorbed from 0.025M CaCl₂ by soils incubated with calcium hydroxide to give a range of pH values (5.0 - 7.0). Here the final S concentration refers to the concentration of sulphate in solution after 40 hrs, and adsorbed S to the amount of sulphate on the surface.

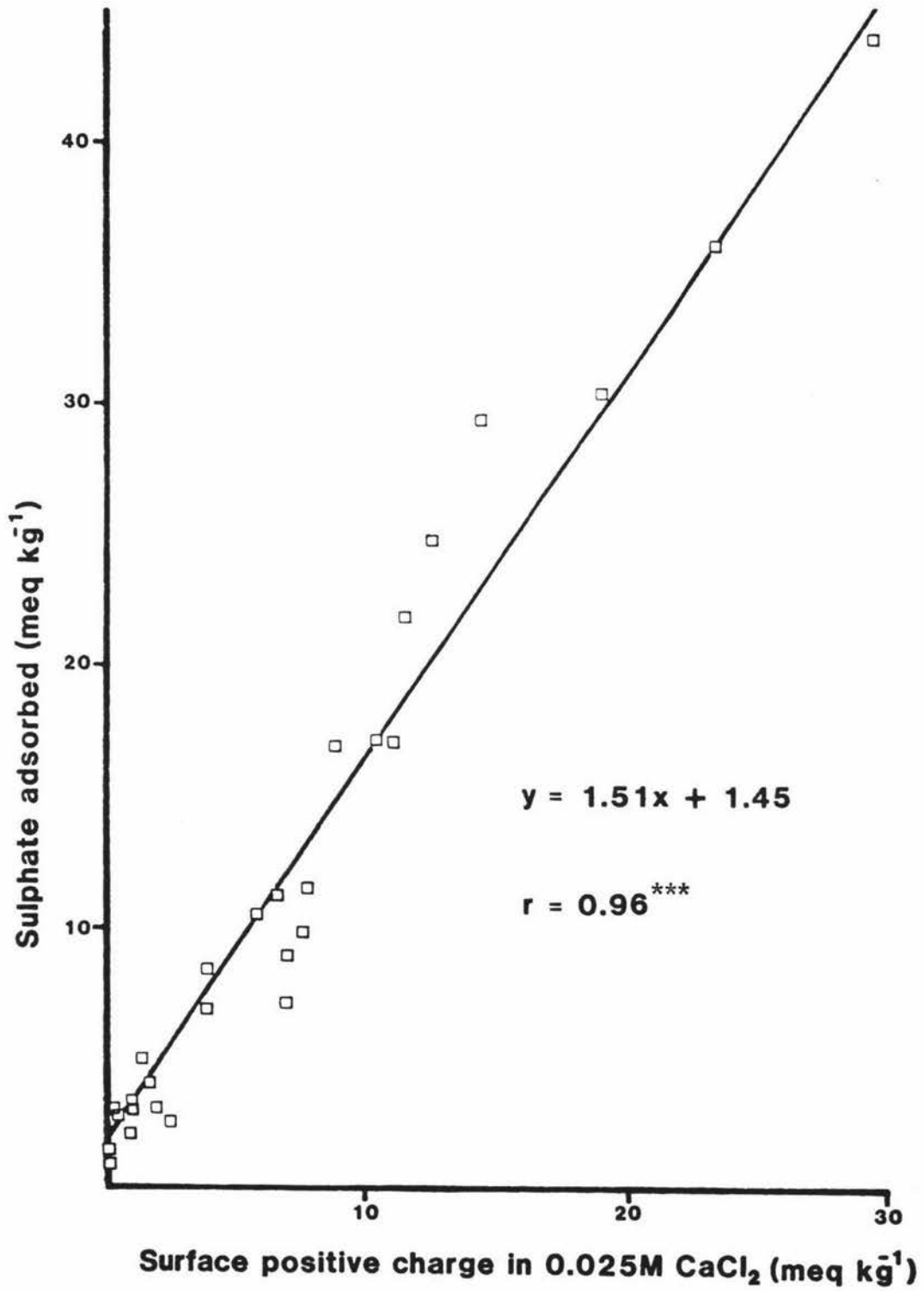


Fig. 4-18

The relationship between sulphate on the surface at 50 mg l⁻¹ sulphate and surface positive charge, both measured in 0.025M CaCl₂.

Once again, as was the case in 0.1M NaCl, only small amounts of sulphate were adsorbed from 0.025M CaCl₂ when the positive charge was zero, suggesting that there was a requirement for some positive charge on the surface before sulphate adsorption could occur.

Although the strong correlation between sulphate adsorbed and surface positive charge suggested that there was a large electrostatic influence on the bond between surface and anion, the actual quantities of sulphate adsorbed in the calcium media were considerably greater than the amounts of positive charge initially present. This is consistent with the observations of previous workers who have suggested sulphate can be specifically adsorbed (Breeuswma and Lyklema, 1971; 1973), and that sulphate is adsorbed in excess of surface positive charge (Gebhardt and Coleman, 1974; Rajan, 1975, 1979).

4.6 Competitive Sorption of Phosphate and Sulphate

When present in the sorption medium, phosphate decreased the capacity of all soils to adsorb sulphate (Table 4-10), but for all soils phosphate sorption was unaffected by the levels of sulphate applied. For all soils most of the phosphate applied was sorbed and only for the low sorbing Tokomaru soil could significant amounts of phosphate be detected in solution. The Tokomaru soil sorbed 140 mg kg⁻¹ of the 160 mg kg⁻¹ phosphate applied. Changes in the effect of phosphate on sulphate adsorption thus cannot be attributed to changes in the proportion of phosphate sorbed. Both the absolute magnitude of changes in sulphate adsorption, and the percentage reduction in adsorption varied with pH (Table 4-10).

In the lower sulphate adsorbing Tokomaru and Taupo soils there was a distinctly larger effect (% reduction in sorption) of phosphate at high pH (Table 4-10), but the opposite trend was observed in the high sorbing soil, with the effect of phosphate addition being greatest at low pH. For the soils of moderate to high sorption capacity the trend was less clear, but there was a tendency for the effect of phosphate on sulphate adsorption to increase with increasing pH.

In each case equimolar concentrations of phosphate and sulphate

Table 4-10. Effect of equimolar additions of phosphate on the amounts of sulphate adsorbed in incubated soils

Soil	pH	Phosphate addition	Equilibrium (SO ₄)	S sorbed (No P)	ΔS sorbed (with P added)	ΔS sorbed
		mM kg ⁻¹	mg l ⁻¹	meq kg ⁻¹	meq kg ⁻¹	%
Patua subsoil	5.30	6.24	17.8	21.25	3.80	17.9
	5.80		23.5	19.25	3.40	17.7
	6.10		27.8	16.75	2.00	12.0
	6.50		30.3	15.50	2.13	7.0
	6.72		34.0	14.00	0.60	4.0
	7.00		37.0	11.90	0.10	1.0
Patua topsoil	4.80	6.24	27.5	6.88	0.63	8.0
	5.30		30.8	5.78	0.25	4.0
	5.70		38.5	5.16	0.60	12.0
	6.90		40.0	3.59	0.84	21.0
Egmont	6.07	6.24	31.5	8.44	2.31	27.0
	6.35		37.0	7.34	2.80	38.0
	6.80		36.5	6.34	1.60	25.0
	7.10		39.5	5.63	1.81	32.0
Ramiha (1st incubation)	5.10	6.24	28.0	8.75	0.81	11.0
	5.40		32.3	8.00	2.31	29.0
	5.80		33.0	—	0.66	*
	6.12		35.0	6.63	1.86	28.0
	6.60		39.0	—	0.20	*
Ramiha (2nd incubation)	4.60	6.24	24.0	9.38	1.60	17.0
	5.60		32.5	7.30	1.30	25.0
	6.30		37.0	5.44	1.92	24.2
	6.70		40.0	4.88	1.30	26.0
Okaihau	5.65	2.50	23.0	6.19	0.90	14.0
	6.30		28.0	4.00	0.70	15.0
	6.70		34.3	3.19	0.20	6.0
	7.10		39.5	2.88	0.25	10.0
	7.30		43.3	2.06	0.30	15.0
Taupo (1st incubation)	4.95	5.00	33.5	3.09	0.70	22.0
	5.60		36.3	2.75	0.60	22.0
	6.20		38.7	2.25	0.90	40.0
	6.60		39.0	2.13	0.50	45.0
Taupo (2nd incubation)	4.70	5.00	27.3	3.38	0.30	8.0
	5.00		29.5	2.88	0.31	14.0
	5.40		31.3	2.55	0.63	28.0
	6.05		34.3	2.20	1.30	57.0
Tokomaru	4.90	5.00	36.0	0.25	0.22	87.0
	5.10		36.0	0.21	0.21	100.0
	5.45		36.5	0.11	0.11	100.0
	5.80		37.0	0.06	0.06	100.0
	6.10		36.5	0	0	100.0
	6.30		38.5	0	0	100.0

* Sorption isotherms were not available for these soils.

were added, but the amounts applied varied in different soils (Section 3.6). This depended mainly on the soil's capacity to adsorb sulphate, but also on the reserve of easily desorbable sulphate in soils. To enable adsorption to be studied in a similar concentration range for all soils lower amounts of sulphate and phosphate were added to soils which released large amounts of sulphate to the 0.1M NaCl medium (e.g. Okaihau soil).

Within each soil type however, the same rate of anion addition was applied to soils of different pH. These soils will have differing adsorption isotherms (Section 4.5), and sorption data will thus be obtained at different equilibrium sulphate concentrations for each soil pH. This will influence the results obtained.

Simple adsorption models (e.g. Langmuir) would suggest that:

(i) The relative (%) decrease in sulphate adsorption due to any one addition of phosphate is likely to be greater in soils with a low adsorption maximum.

(ii) The actual decrease in the amounts of sulphate adsorbed due to phosphate will be greater at high concentrations of sulphate in solution, where adsorption is close to maximum.

Both of the above considerations would lead to apparently greater competition at higher pH. This is indeed observed in the low sorbing soils, with sulphate adsorption being completely eliminated in the Tokomaru soil at high pH. The trends were less clear however, in the medium and high sorbing soils, and in the Patua subsoil the effect of phosphate was clearly greater at low pH. In an attempt to explain this observation another competitive sorption study was conducted. In this study, additional information on the effect of phosphate was provided by a comparison of changes in surface charge and changes in sulphate adsorption with phosphate addition to the Patua subsoil.

4.6.1 Effect of phosphate on surface charge

Addition of phosphate invariably resulted in a decrease in surface positive charge in the Patua subsoils, but the magnitude of the

Table 4-11 Effect of phosphate additions on surface charge
and sulphate adsorbed by Patua subsoils

Soil pH	Sorbed P mM kg ⁻¹	Surface charge			Δ S sorbed meq kg ⁻¹	Δ Positive charge meq kg ⁻¹
		— meq kg ⁻¹ —	— meq kg ⁻¹ —	— meq kg ⁻¹ —		
		-ve	+ve	net		
5.30	0	77	30.7	46.3		
	7.8	78	26.1	51.9	2.6	4.6
	10.9	87	20.7	66.3	4.7	10.0
5.80	0	105	25.8	79.2		
	7.8	96	24.8	71.2	1.9	1.0
	10.9	98	19.0	79.1	2.6	6.8
6.10	0	116	21.0	95.0		
	7.8	112	17.3	95.0	2.0	3.7
	10.9	105	15.8	89.3	2.6	5.2
6.50	0	111	15.2	95.8		
	7.8	109	*	*	1.4	*
	10.9	115	12.0	103.0	2.2	3.2
6.72	0	120	14.0	106.0		
	7.8	123	12.3	111.0	0.9	1.7
	10.9	118	11.3	107.0	1.8	2.7
7.00	0	136	11.7	124.0		
	7.8	148	11.2	137.0	1.3	0.5
	10.9	152	9.7	142.0	1.7	2.0

* missing data.

change in surface positive charge due to any one addition of phosphate decreased progressively with increased pH. In all cases however, the size of the decrease in positive charge was less than the molar amount of phosphate sorbed. Other workers have made similar observations (Hingston et al., 1972; Rajan, 1975a, b, 1979b), suggesting in some studies that a proportion of phosphate could sorb on neutral or negative sites with no effect on surface positive charge (Rajan, 1975a,b), and in others, that sorption of phosphate resulted in subsequent release of OH^- or uptake of H^+ so as to partially preserve surface charge (Bowden et al., 1980a).

The changes in surface negative charge recorded during phosphate sorption were relatively small in relation to the large reserve of negative charge in these soils, and can only be attributed to variability in the data about a mean negative charge value for each soil. Such variability can be explained by the large correction for entrained sodium and the high dilution factor (200) involved in the estimation of surface negative charge.

The decreases in surface positive charge observed related well to the measured changes in sulphate adsorption (Fig. 4-19, $r = 0.93^{***}$). Significantly, the regression line passed close to zero. When phosphate had no effect on surface positive charge, no change in the amount of sulphate adsorbed was predicted. The measured changes in sulphate adsorption were considerably smaller than the measured changes in surface positive charge. This was not altogether surprising however, as adsorption was estimated at a relatively low concentration in solution ($< 30 \text{ mg l}^{-1}$), and it is likely that larger differences would have been observed at higher solution concentrations where sorption was maximised.

The data presented for the Patua subsoil suggests that the competitive effect of phosphate results from changes in surface positive charge, and although the actual mechanism by which phosphate reduces surface positive charge is uncertain, there is evidence for a greater effect on surface positive charge at low pH.

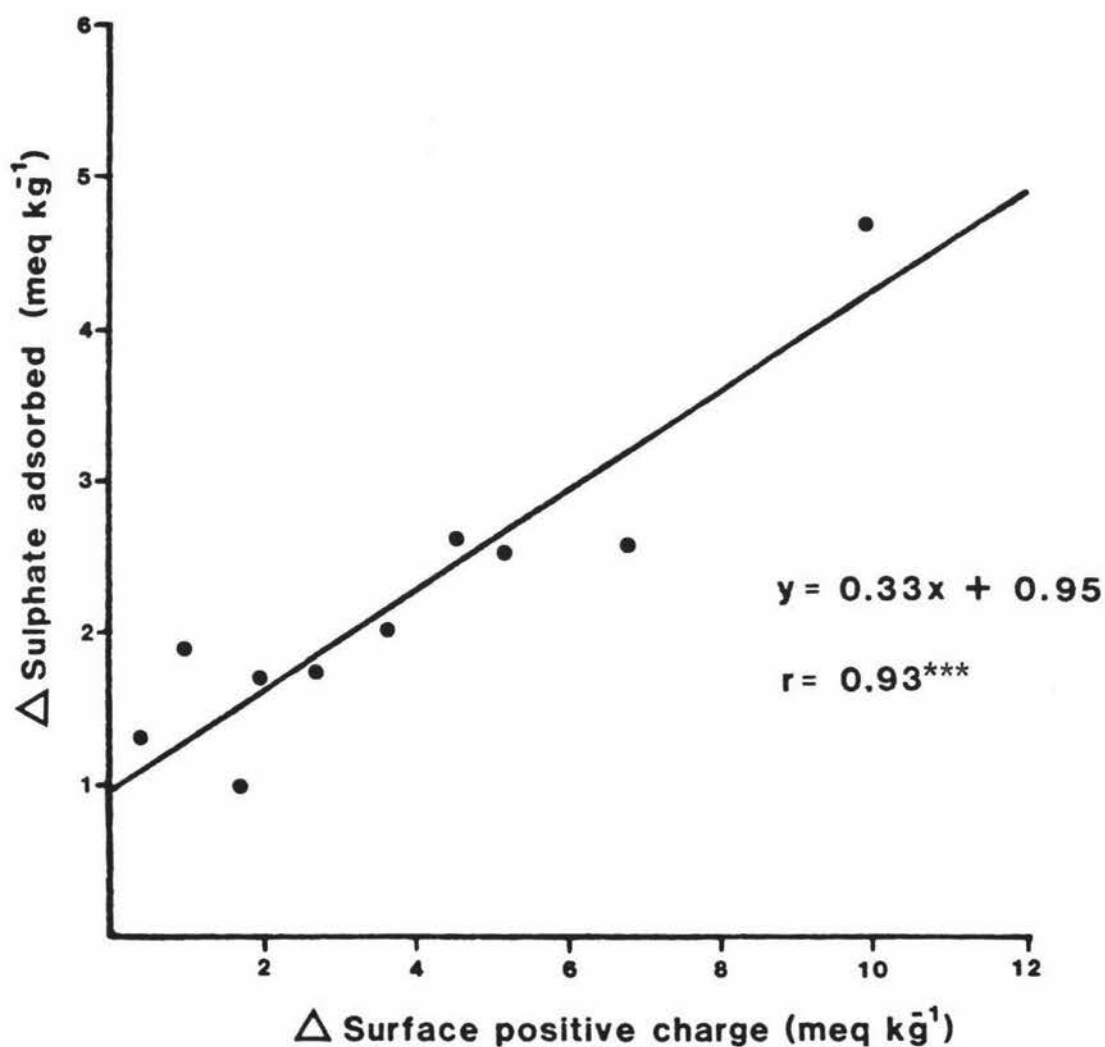


Fig. 4-19

The relationship between changes in the amounts of sulphate on the surface, and changes in surface positive charge on phosphate addition in the Patua subsoils.

CHAPTER 5

GENERAL DISCUSSION

Anion sorption studies on several soils have confirmed that there are significant differences between phosphate and sulphate sorption (Yates and Healy, 1975; Barrow et al., 1983), that soils have a much lower sorption capacity for sulphate than for phosphate (Gebhardt and Coleman, 1972; Metson, 1979); and that sulphate adsorption is proportionally more strongly affected by increased pH (Barrow, 1981).

The differences appear to be related to differences in the mechanism of sorption for the two anions. The amounts of both phosphate and sulphate sorbed in 0.1M NaCl were correlated with the amounts of surface positive charge in the soil in the same medium, but the relationship was very much stronger for sulphate (Table 5-1).

Table 5-1 The relationship between phosphate sorbed and sulphate adsorbed respectively, and surface positive charge

	Anion concentration in solution (mg l ⁻¹)	Equation of Line	r	Variation accounted for (%)
Sulphate (meq kg ⁻¹)	40	$y = 1.06x - 0.04$	0.98***	95
Phosphate (mM kg ⁻¹)	20	$y = 4.75x + 44.0$	0.70***	45

Particularly significant were the observations that
(i) while no sulphate appeared to be adsorbed in the absence of any

surface positive charge considerable sorption of phosphate (44 mM kg^{-1}) could take place, and (ii) although the apparent sorption maxima for sulphate were very similar to the amounts of positive charge initially present in the soils, the amounts of phosphate which could be sorbed were many times greater.

These observations on phosphate sorption are not new, and are explained by invoking a ligand exchange mechanism in which a strong covalent bond is formed between the phosphate group and the surface. The bond has a strong chemical component so electrostatic considerations are less important and phosphate can be adsorbed on neutral or even negative sites.

In contrast, there seemed to be a large electrostatic component to the bond between sulphate and the surface, with no sorption occurring in the absence of positive charge. A similar dependence of sulphate sorption on surface positive charge has been reported by other workers (Hingston et al., 1972; Parfitt and Smart, 1978; Black and Waring, 1976, 1979). There were however, two observations that suggested that specific adsorption played some part in the adsorption of sulphate. These were:

1. Even in the presence of high concentrations of chloride (0.025M CaCl_2 or 0.1M NaCl) sulphate appeared to be preferentially adsorbed on positive sites in soils, suggesting that there was a strong selectivity for sulphate over non-specifically adsorbed anions such as chloride.
2. There were greater amounts of sulphate adsorbed in 0.025M CaCl_2 than in 0.1M NaCl , even though there measured values for surface charge (positive, negative, and net) were very similar in these two media. This is indicative of superequivalent adsorption of sulphate, with sulphate being adsorbed in excess of the amounts of positive charge present in 0.025M CaCl_2 .

These observations are consistent with the adsorption of sulphate in a layer of ion specificity distinct from the surface but within the plane of adsorption of non-specifically adsorbed anions such as chloride. Such a plane has been proposed (β) for calcium sorption (Sposito, 1981; Bowden et al., 1980a) in idealised descriptions of the interface between surface and solution.

In calcium media, sulphate may be adsorbed even closer to the surface, causing uptake of H^+ or release of OH^- to regenerate surface positive charge (Bowden et al., 1980a; Sposito, 1981; Barrow, 1981), and this may explain why sulphate is adsorbed in excess of the amounts of surface positive charge in this medium. Several other workers (Grahame, 1947; van Olphen, 1979; Bohn et al., 1979; Bolt, 1979) have also pointed to closer approach of ions, and particularly divalent ions, to the surface in calcium media compared to sodium media because of greater compression of the ionic double layer (van Olphen, 1979), and reduced anion exclusion (Bolt, 1979). A relatively low ionic strength calcium media appeared to induce sulphate to close approach to the surface in this study, and other workers have observed 'superequivalent' sorption of sulphate at high solution concentrations of sulphate (Rajan, 1978, 1979a,b), or high ionic strength media (Gebhardt and Coleman, 1972).

As for which of the two media used most accurately approximates the soil solution, and the degree to which sulphate can be adsorbed in excess of surface charge; this is a matter of conjecture. Most workers would favour 0.025M $CaCl_2$, although this may be of too high an ionic strength to represent the soil solution (Barrow, 1967).

When added in equimolar amounts, the amounts of phosphate sorbed were unaffected by the presence of sulphate, but sulphate sorption was reduced in the presence of phosphate. This can be taken as further evidence for adsorption of sulphate in a β plane (Bowden et al., 1980b). If sulphate and phosphate were sorbed in similar planes, an extended double layer approach (Bowden et al., 1980a,b) would suggest that sulphate would have some effect in reducing phosphate sorption. This was not observed here, so it appears that sulphate is adsorbed predominantly in an outer plane to phosphate (Bowden et al., 1980a).

Although phosphate always reduced sulphate adsorption the extent and significance of this reduction varied both between soils and with pH. If phosphate had been selectively sorbed on positive sites in the low concentration range studied, as has been suggested by Ryden et al., (1977a) and Rajan (1976), surface positive charge would have been almost eliminated by the amounts of phosphate applied. This

was not the case, and there were still measurable amounts of surface positive charge present after phosphate sorption. Phosphate reduced positive charge but the magnitude of the reduction induced by any one P addition was not consistent at all pH values. A substantially greater effect of phosphate on surface positive charge was observed at low pH in a high sorbing soil studied.

On the basis of limited data, it appears that phosphate has a greater effect on surface positive charge at low pH. Other workers have reported data which is in accord with this observation (Hingston et al., 1967), with the decreased effect of phosphate at high pH being interpreted as a greater tendency for phosphate to sorb on neutral and negative sites (Breeuswma and Lyklema, 1973; Rajan et al., 1974). The ratio of H^+ consumed or OH^- released per molecule of phosphate adsorbed increased with pH (Breuswma and Lyklema, 1973; Rajan et al., 1974), suggesting that phosphate was sorbed by ligand exchange with surface OH^+ groups in the low pH range, but displaced OH^- off neutral and negative sites at high pH. If a ligand exchange mechanism can be accepted for phosphate then the release of hydroxyl ions can be used to infer changes in surface charge. Bowden et al. (1980a), used such a method to show that the effect of phosphate on surface positive charge on a goethite surface was substantially greater at low pH than in the medium (5.5 - 7.0) pH range. Although there are problems in the method these workers used to assess net surface charge (and therefore surface positive charge on goethite) the results presented were consistent with the effects of phosphate observed in the current study.

If these observations can be applied to other soils, the results for the proportional decreases in sulphate adsorption due to phosphate addition can be explained.

Two opposing effects resulted in different trends in high sorbing compared to low sorbing soils and variable data in the medium - high range for sorption capacity. Firstly, a given P addition has a larger effect on surface positive charge at low pH, and this effect decreases with increasing pH. Thus, for soils with a high sorption capacity the magnitude of the reduction in sulphate adsorption induced by a given phosphate addition decreases with increasing pH.

In opposition to this however, the sulphate adsorption capacity decreases with increasing pH, and as a proportion of the adsorption capacity, the effect of a reduction in positive charge induced by phosphate addition may become greater at high pH. This effect is particularly significant for soils which have a low sorption capacity, and for these soils the effect of a given P addition increases with increasing pH.

The effect of liming on sulphate adsorption could be attributed solely to changes in surface positive charge, but other factors were needed to explain the occurrence of a minimum in phosphate sorption. The changes in phosphate sorption with pH were explained by considering changes in the form of phosphate ions in solution and by the progressive increase in surface negativity with pH (Bowden et al., 1980a). Phosphate sorption passed through a minimum in the pH range 5.2 - 6.5 in most soils, with the pH of minimum sorption varying, apparently with proportions of different surfaces that sorbed P, and/or with changes in the rate of calcium applied to soils.

The significance of surface positive charge to the adsorption of sulphate, and probably other anions, has been underemphasised in the literature. The results presented here suggest that many soils have a measureable anion exchange capacity, even at relatively high pH (> 6.0), and that positive charge can be measured in soils, even in the presence of large amounts of surface negative charge. This is consistent with previous work (van Raij and Peech, 1972; Morais et al., 1976; Black and Waring, 1979) which suggested that positive and negative sites were spatially separated on soil colloids and did not neutralise each other in most soils.

In this study the surface charge measured in 0.1M NaCl was very similar to the charge measured in 0.025M CaCl_2 when all soils were considered. This relationship was particularly strong for surface positive charge but there were some differences in the amounts of surface charge measured in individual soils in the two media. Some variation can be explained by the strong retention of calcium compared to sodium by soil colloids (Breeuswma and Lyklema, 1971, 1973; Kinniburgh et al., 1975). Ryden et al. (1977a) observed that sorption of calcium does not add appreciable positive charge to the surface,

but decreased negative charge could result from a difficulty in desorbing adsorbed calcium with potassium (Ryden and Syers, 1975). Additionally, anion exclusion would be expected to be greater in sodium media than in calcium (Bolt, 1979), such that measured negative charge will be smaller in sodium media. In apposition to these effects however are the slightly higher ionic strength ($I = 0.1M$) and the lower activity coefficient of ions in $0.025M CaCl_2$ (Butler, 1964), which should lead to greater non specific sorption in $0.1M NaCl$. It may be that many of these effects balance out in the measurement of surface charge and the correlation between charge measured in the two media may thus be rather fortuitous. Certainly, there were differences, as shown by a higher pH of the sodium media compared to the calcium media on the final equilibration for charge measurement. This in itself suggests that more negative and less positive charge should be measured in $0.1M NaCl$ compared to $0.025M CaCl_2$.

There are several practical implications of the dependence of sulphate adsorption on surface positive charge highlighted by this study. As a result of changes in surface positive charge sulphate adsorption was reduced by phosphate addition and strongly reduced by liming.

Phosphate addition can be expected to have its most significant effect on sulphate adsorption in low sorbing soils. In the current study sulphate adsorption could be eliminated by equimolar additions of phosphate to a low sorbing soil. The results for all soils suggested that when phosphate and sulphate are added together in approximately equal amounts, as in superphosphate fertiliser, phosphate sorption will be unaffected by sulphate addition but sulphate mobility will be enhanced.

The reduced ability of limed soils to adsorb sulphate was also reflected in sulphate retention (Saunders and Hogg, 1971) values. Sulphate retention (quick test) decreased as pH increased in soils incubated with calcium hydroxide, and these reductions were significant to the classification of soils as high, medium, or low sulphate-retaining.

Although During (1970) has suggested that liming initially

affects the pH of only the upper 2.5 to 5 cm of most soils, successive applications of lime will raise the pH and base status of a greater depth of soil, and may facilitate sulphate leaching. In addition, the amount of sulphate in the upper few centimetres may be all important for some crops, particularly during early growth and establishment.

Evidence suggests that liming could eliminate sulphate retention altogether in soils which initially have a limited ability to retain sulphate. This may be significant in low rainfall areas where adequate plant nutrition is dependent on the ability of the soil to retain sulphate against a small amount of percolating rainfall.

The effects of liming and phosphate fertilisation (Saunders, 1974) combine to give S-retention values a variability which is not reflected in P retention values. Although Hogg et al. (1970) and Saunders and Hogg (1971) have suggested that S-retention can be inferred from P-retention values, the results of the current study suggest that this correlation will be tenuous in fertilised topsoils. It may be therefore, that the use of phosphate retention values to infer a leaching index for sulphur balance studies (Cornforth and Sinclair, 1982) will tend to underestimate fertiliser requirements for sulphur. The results presented would suggest that the incorporation of sulphate retention values in a leaching index for sulphur would give a more reliable estimate of the potential loss of this nutrient.

There are substantial areas of low S retention soils in New Zealand which benefit from liming (During, 1972), and it is apparent that this will potentially reduce the ability of these soils to retain S. The significance of these changes cannot be estimated without recourse to lime trials in which sulphate mobility is monitored. This would be the logical projection of the present work.

Although recent reports (Gregg and Goh, 1982; Goh and Gregg, 1982) have pointed to the significance of the organic cycle as a mechanism of retaining applied sulphate, it appeared that the inorganic retention mechanism-adsorption was equally important in many soils. Both components affect the amount of sulphate retained and Goh and Gregg (1982) observed that the proportion of sulphate retained in the organic fraction increased with pH. The observation from this study,

that the adsorption of sulphate is reduced by liming suggests that whereas liming may increase the retention of sulphate in the organic fraction it will also decrease the amount of sulphate retained on the soil colloid. An increasing proportion of sulphate will thus be dependent on the organic cycle for retention in soils which are limed.

An additional aspect of the current work was the effect of phosphate on surface charge and sulphate adsorption. The results presented showed that the effect of phosphate on surface charge was different at different pH values. This is an interesting area for further study which could make a valuable contribution to current understanding of anion sorption in soil components and soils.

CHAPTER 6

SUMMARY AND CONCLUSIONS

This thesis reports on a detailed study of changes in sulphate and phosphate sorption with varying pH, and attempts to assess the practical implications of sulphate adsorption to the mobility of sulphate in soils.

A number of soils covering a range of abilities to sorb anions were each incubated with several rates of calcium hydroxide prior to sorption isotherm studies in 0.1M NaCl for both sulphate and phosphate, and also in 0.025M CaCl₂ for sulphate.

Several previously-reported differences in the sorption behaviour of sulphate and phosphate were confirmed by the results of this study. These included the observations that sulphate was adsorbed in lower amounts than phosphate, was a poor competitor with phosphate, was readily desorbed and was proportionally more strongly affected by changes in pH (pH 5.5 - 7.0) than phosphate sorption.

An ion retention method was used to assess the surface charge properties of the incubated soils in both 0.1M NaCl and 0.025M CaCl₂ and a brief study on the competitive sorption of phosphate and sulphate was conducted. The results of this study prompted a further investigation on the effect of phosphate on surface positive charge and sulphate adsorption in a high sorbing soil at several pH values (pH 5.3 - 7.0).

The main findings of this work were as follows:

- (i) Surface positive charge could be assessed by ion retention in soils, even in the presence of large amounts of surface negative charge.
- (ii) The changes in sulphate adsorption with pH were related to changes in surface positive charge ($r = 0.98^{***}$). Indeed, the ability of a soil to adsorb sulphate was directly dependent on

the amount of surface positive charge present and no sulphate was adsorbed in the absence of surface positive charge in either 0.1M NaCl or 0.025M CaCl₂.

- (iii) Although the measured amounts of surface charge (+ve, -ve, net) were very similar in 0.1M NaCl compared to 0.025M CaCl₂, and there was a strong correlation between apparent adsorption maxima for sulphate in 0.1M NaCl and surface positive charge ($y = 0.80x + 1.6$), larger amounts of sulphate were adsorbed from 0.025M CaCl₂ ($y = 1.51x + 1.5$).
- (iv) In both media, sulphate appeared to be adsorbed in preference to chloride, even though chloride was in much higher concentration in solution. This suggested that sulphate was adsorbed in an inner plane to non-specifically adsorbed ions such as chloride.
- (v) For adsorption in 0.025M CaCl₂, it was suggested that sulphate approached even closer to the surface so that surface charge was affected and adsorption was in excess of the amounts of positive charge initially present.
- (vi) Although the amounts of phosphate sorbed by soils were also correlated with surface positive charge, the correlation (0.70^{***}) was weaker than for sulphate (0.98^{***}) and the amounts of phosphate sorbed were very much greater (5 times) than the amounts of positive charge present. In contrast to the situation for sulphate, changes in phosphate sorption with pH could not be explained by a progressive increase in surface negativity with pH alone, and changes in the proportions of the various anionic species in solution had to be considered, as had been previously suggested for goethite surface (Bowden et al., 1980a).
- (vii) When phosphate and sulphate were added in equimolar amounts, phosphate sorption was unaffected by the presence of sulphate, but sulphate adsorption was reduced by the presence of phosphate.
- (viii) The effect of phosphate on sulphate adsorption varied at different pH values and in different soils. In low - medium sorbing soils, phosphate had a larger effect at high pH,

probably because of the reduced sorption capacity of soils in this pH region, but in medium - high sorbing soils the effect of the phosphate was larger at low pH.

- (ix) For one high sorbing soil studied, changes in sulphate adsorption with phosphate addition were highly correlated (0.93^{***}) with changes in surface positive charge induced by similar phosphate additions. The effect of phosphate on surface positive charge decreased with increasing pH, and this was attributed to an increasing proportion of phosphate being sorbed on neutral and negative sites as pH increased.

The major contribution of this study is that it highlights the dependence of sulphate adsorption on surface positive charge in soils. This has practical implications to the effects of pH and phosphate addition on the mobility of sulphate in soils.

APPENDIX I

Extractable sulphate and phosphate levels in soils

Soil	pH	Sulphate			Phosphate	
		CaCl ₂	Ca(HPO ₄) ₂	Adsorbed	NaOH	Olsen
		mg kg ⁻¹			mg kg ⁻¹	
Patua subsoil	*5.6	3.0	160.0	157.0	435	0.7
L ₀	5.2	1.8	168.0	166.2	420	0.7
L ₁	5.8	4.1	173.0	169.2	420	0.5
L ₂	6.1	6.6	177.0	170.0	425	0.6
L ₃	6.5	10.5	180.0	170.0	420	0.3
L ₄	6.7	16.0	185.0	170.0	415	0.9
L ₅	7.0	24.5	177.0	153.0	420	0.6
CaCl ₂ ¹	5.2	2.5	170.0	167.5	418	0.9
CaCl ₂ ²	5.1	4.0	163.0	159.0	442	0.8
Patua topsoil	*5.5	15.5	43.0	27.5	326	2.9
L ₀	4.8	22.0	43.0	21.0	305	3.5
L ₁	5.3	4.0	48.0	44.0	285	2.6
L ₂	5.7	5.0	50.0	45.0	246	2.2
L ₃	6.9	20.0	63.0	43.0	282	1.8
Ramiha	*5.0	2.5	45.0	42.5	330	5.0
L ₀	4.7	1.5	48.0	46.5	225	6.9
L ₁	5.1	1.2	48.0	46.8	251	5.7
L ₂	5.4	1.5	50.8	49.3	238	5.0
L ₃	5.8	6.0	52.5	46.5	237	4.8
L ₄	6.1	9.1	51.3	42.5	245	5.0
L ₅	6.6	20.0	63.0	43.0	235	5.5
CaCl ₂ ³	4.8	0	44.0	44.0	257	5.8
CaCl ₂ ⁵	4.5	0	40.0	40.0	244	4.2
L ₀	4.6	7.0	44.0	37.0	218	*
L ₆	5.6	11.0	50.0	39.0	207	*
L ₇	6.3	*	51.3	*	192	*
L ₈	6.7	*	58.0	*	167	*
L ₉	7.0	15.5	60.0	45.5	159	*

* Not determined

APPENDIX I contd.

Soil	pH	Sulphate			Phosphate	
		CaCl ₂	Ca(HPO ₄) ₂	Adsorbed	NaOH	Olsen
		mg kg ⁻¹			mg kg ⁻¹	
Egmont	*6.5	4.5	58.0	53.5	971	30.0
L ₀	6.1	2.5	55.3	53.0	971	*
L ₁	6.4	5.0	57.5	52.5	882	*
L ₂	6.8	9.0	58.0	49.5	934	*
L ₃	7.1	13.0	59.5	46.0	929	*
L ₄	7.3	15.5	60.0	45.0	915	*
Okaihau	*5.9	22.5	101.3	79.0	175	5.2
L ₀	5.7	20.0	120.0	100.0	198	*
L ₁	6.3	40.0	124.0	84.0	190	*
L ₂	6.7	59.0	139.0	80.0	171	*
L ₃	7.1	83.0	159.0	76.0	188	*
L ₄	7.3	97.0	164.0	67.0	174	*
Taupo	*5.1	6.5	29.0	22.5	419	26.0
L ₀	4.7	6.5	41.3	35.0	427	37.0
L ₁	4.9	8.0	38.3	30.3	422	23.0
L ₂	5.0	9.3	44.0	34.7	399	22.0
L ₃	5.4	14.5	42.5	28.0	432	19.1
L ₄	5.8	18.0	45.0	27.0	432	17.1
L ₅	6.1	20.0	46.0	26.0	404	14.0
CaCl ₂ ³	4.6	5.5	40.0	34.5	450	30.0
CaCl ₂ ⁵	4.3	2.5	39.0	35.5	427	23.0
L ₀ '	4.6	11.0	40.0	29.0	479	*
L ₆	5.0	17.0	46.3	29.3	513	*
L ₇	5.6	24.0	53.0	29.0	471	*
L ₈	6.2	28.5	55.0	26.5	484	*
L ₉	6.6	23.5	60.0	26.5	432	*
Konini	*5.3	2.5	10.0	7.5	160	6.7
L ₀	4.7	2.0	15.0	13.0	133	8.1
L ₁	4.9	2.0	17.5	15.5	136	7.6
L ₂	5.3	1.8	18.0	16.0	127	6.0

* Not determined.

APPENDIX I contd.

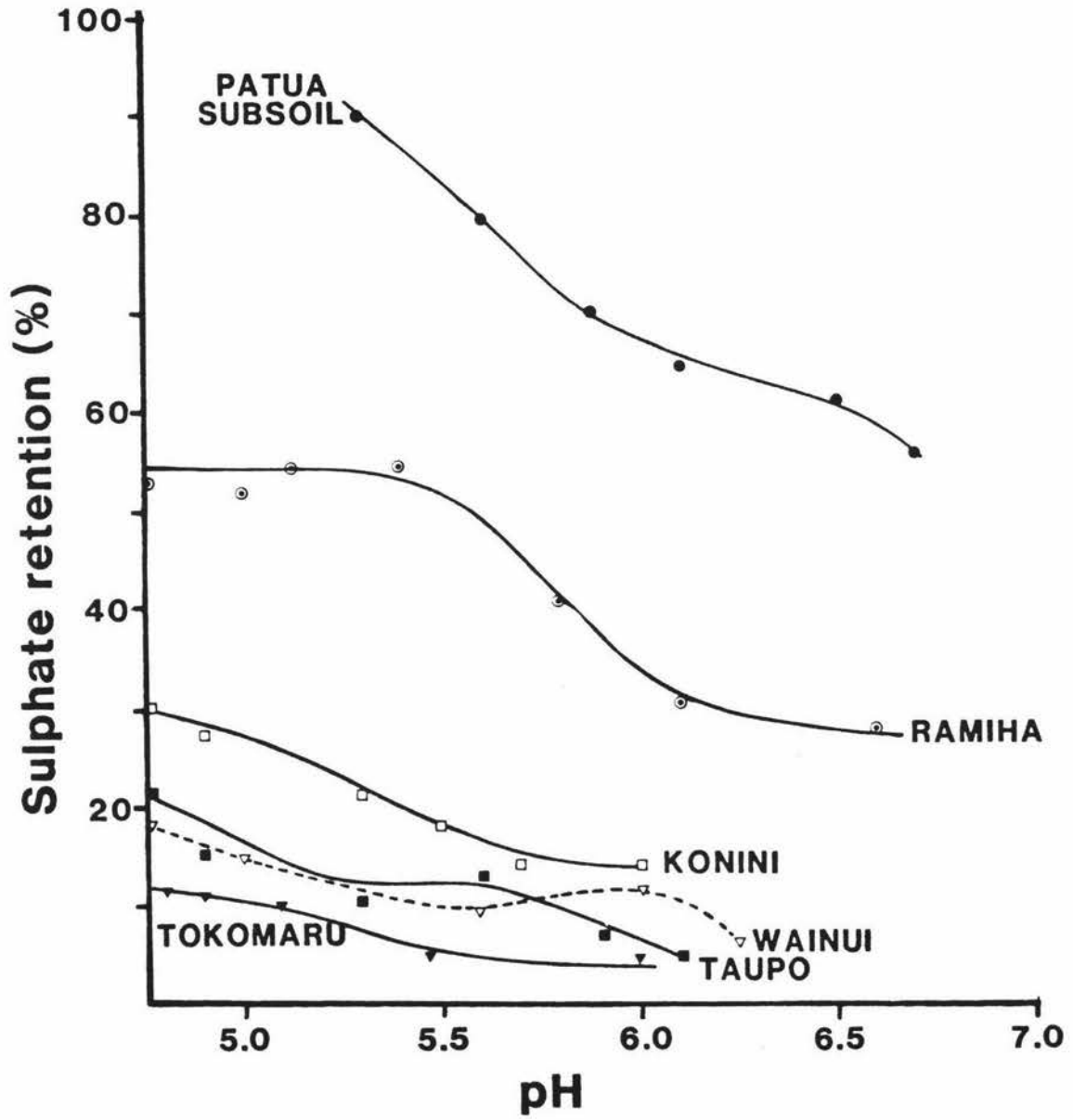
Soil	pH	Sulphate			Phosphate	
		CaCl ₂	Ca(HPO ₄) ₂	Adsorbed	NaOH	Olsen
		mg kg ⁻¹			— mg kg ⁻¹ —	
L ₃	5.5	2.5	19.0	16.5	141	6.2
L ₄	5.7	3.0	19.0	16.0	127	5.2
L ₅	6.1	6.5	23.0	16.5	124	5.7
CaCl ₂ ³	4.8	1.5	15.0	13.5	134	6.8
CaCl ₂ ⁵	4.6	1.0	10.0	9.0	142	7.4
L ₀ '	4.5	*	19.0	*	*	*
L ₆	5.0	*	22.0	*	*	*
L ₇	5.5	*	23.5	*	*	*
L ₈	6.2	*	25.0	*	*	*
L ₉	6.5	*	28.0	*	*	*
Wainui	*5.1	3.5	19.0	15.5	111	7.6
L ₀	4.7	4.0	20.5	16.5	101	13.2
L ₁	5.0	6.5	22.5	16.0	105	12.9
L ₂	5.3	10.0	26.0	16.0	107	10.1
L ₃	5.7	11.0	28.0	17.0	107	8.3
L ₄	6.1	10.0	27.0	17.0	103	5.8
L ₅	6.4	13.0	28.0	15.0	93	6.6
CaCl ₂ ³	5.2	15.0	2.5	12.5	101	10.0
CaCl ₂ ⁵	4.9	14.5	2.5	12.0	101	9.1
L ₀ '	4.6	*	18.5	*	*	*
L ₆	5.2	*	20.0	*	*	*
L ₇	5.9	*	22.0	*	*	*
L ₈	6.5	*	25.5	*	*	*
L ₉	7.2	*	28.0	*	*	*
Kumeroa	*6.0	6.2	12.5	6.3	149	18.0
L ₀	5.4	10.0	19.0	9.0	179	*
L ₁	6.1	9.0	19.0	10.0	160	*
L ₂	6.6	14.0	19.5	5.5	173	*
L ₃	7.1	12.5	20.0	8.5	172	*
L ₄	7.5	16.0	23.0	7.0	170	*

APPENDIX I contd.

Soil	pH	Sulphate			Phosphate	
		CaCl ₂	Ca(HPO ₄) ₂	Adsorbed	NaOH	Olsen
		mg kg ⁻¹			mg kg ⁻¹	
Tokomaru	*5.2	7.5	13.0	5.5	149	10.2
L ₀ ¹	4.8	12.0	19.0	7.0	132	18.8
L ₁	4.9	14.0	19.5	5.5	124	14.5
L ₂	5.1	15.0	19.5	4.5	123	13.2
L ₃	5.5	16.0	23.0	7.0	133	13.3
L ₄	5.8	19.0	25.0	6.0	129	13.1
L ₅	6.1	20.0	26.0	6.0	131	12.6
CaCl ₂ ²	4.8	10.0	18.0	8.0	124	15.5
CaCl ₂ ⁵	5.0	9.5	14.0	4.5	121	14.4
L ₀ ¹	4.5	*	23.0	*	152	*
L ₆	5.2	*	23.5	*	134	*
L ₇	5.5	*	25.5	*	134	*
L ₈	5.8	*	26.0	*	131	*
L ₉	6.3	*	27.5	*	130	*
L ₁₀	6.7	*	29.0	*	129	*

* Not determined.

APPENDIX II



Sulphate retention values of incubated soils, with a correction for S released to 0.1M CaCl_2 applied (Section 4.2.2).

APPENDIX III

Charge characteristics of soils

*Unincubated soil, CaCl_2^3 = soil incubated with CaCl_2 at same level of Ca^{2+} as indicated rate of lime.

Soil	pH		Charge in 0.025M CaCl ₂			Charge in 0.1M NaCl		
	H ₂ O	KCl	-ve	+ve	net	-ve	+ve	net
Patua subsoil	*5.61	5.20	49.2	29.4	19.8	69.0	30.0	39.0
L ₀	5.27	5.18	53.3	29.3	24.0	79.3	32.8	47.0
L ₁	5.80	5.47	72.3	23.2	49.1	105.0	26.4	79.0
L ₂	6.08	5.72	92.3	18.7	73.6	116.0	21.3	94.7
L ₃	6.53	6.00	101.2	14.4	86.8	119.0	14.8	104.2
L ₄	6.72	6.16	122.2	12.4	109.5	128.0	13.5	114.0
L ₅	6.98	6.50	142.0	11.4	130.6	136.0	11.7	124.0
CaCl ₂ ³	5.23	5.25	61.1	36.2	24.9	89.0	35.5	53.5
CaCl ₂ ⁵	5.14	4.56	71.6	37.0	34.6	89.0	42.5	46.5
Patua topsoil	*5.45	5.15	—	—	—	85.5	11.5	74.0
L ₀	4.80	4.56	81.2	8.7	72.5	90.0	7.9	82.0
L ₁	5.31	4.94	111.0	6.5	104.5	118.0	6.0	112.0
L ₂	5.70	5.33	136.0	5.8	130.2	125.0	3.0	122.0
L ₃	6.90	6.63	160.0	3.9	156.0	151.0	0.9	150.0
Ramiha	*5.00	4.34	52.0	9.8	42.2	54.0	11.6	42.4
L ₀	4.70	4.28	54.2	10.6	43.6	57.0	16.1	41.0
L ₁	5.13	4.50	64.7	11.7	53.0	70.0	14.3	56.0
L ₂	5.40	4.79	92.5	9.5	83.0	100.0	7.3	93.0
L ₃	5.77	5.10	106.0	9.0	97.0	110.0	6.8	103.0
L ₄	6.12	5.42	120.0	8.6	111.4	130.0	4.7	125.0
L ₅	6.59	6.00	145.0	7.0	138.0	150.0	3.3	147.0
CaCl ₂ ³	4.76	4.41	60.1	11.1	48.9	63.4	16.0	47.4
CaCl ₂ ⁵	4.50	4.39	60.8	17.4	43.4	65.0	16.2	48.8
L ₀ '	4.63	4.21	50.0	10.3	39.7	61.0	15.4	45.2
L ₆	5.57	4.88	90.0	7.7	82.3	94.0	11.2	82.8
L ₇	6.29	5.64	127.0	7.6	119.4	129.0	4.2	125.0
L ₈	6.73	6.17	141.0	7.1	134.0	136.0	3.0	133.0
L ₉	7.01	6.58	163.0	6.8	156.2	163.0	2.3	161.0

APPENDIX III contd.

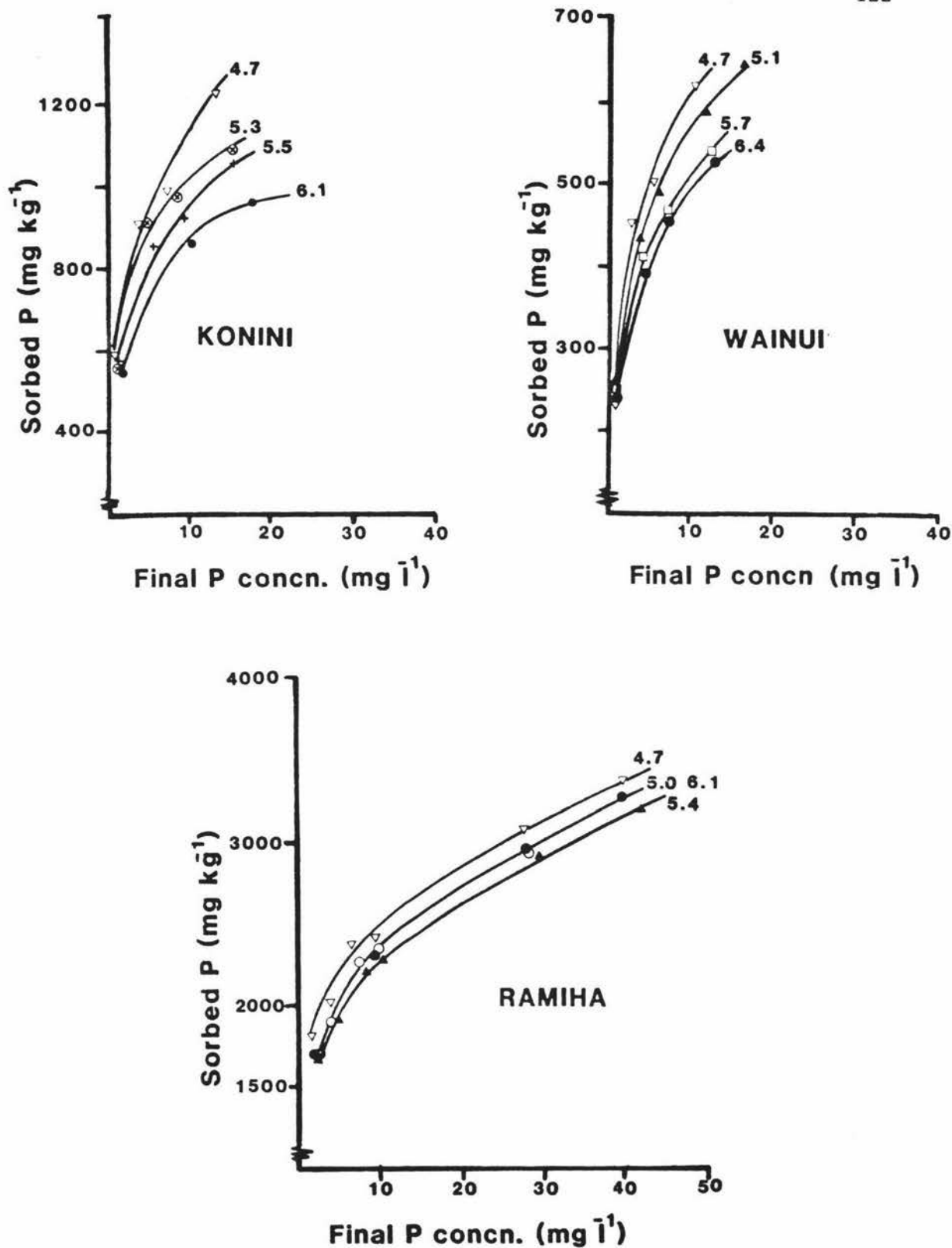
Soil	pH		Charge in 0.025M CaCl ₂			Charge in 0.1M NaCl		
	H ₂ O	KCl	-ve	+ve	net	-ve	+ve	net
Egmont	*6.55	5.70	72.5	6.6	68.6	77.0	7.1	70.0
L ₀	6.07	5.54	66.4	11.5	54.9	68.0	8.9	59.1
L ₁	6.35	5.97	84.4	7.5	76.9	87.0	6.2	93.2
L ₂	6.80	6.30	99.0	5.8	93.2	90.0	5.1	95.1
L ₃	7.08	6.65	109.6	3.2	106.4	130.0	3.0	127.0
L ₄	7.30	6.85	117.0	0.9	116.0	153.0	0.8	152.0
Okaihau	*5.85	5.40	62.8	3.5	59.3	57.0	0.7	56.3
L ₀	5.65	5.34	63.0	4.6	58.4	55.0	0.7	54.3
L ₁	6.28	5.92	74.6	3.3	71.3	70.0	0.9	69.0
L ₂	6.71	6.30	84.0	2.0	82.0	72.0	0.7	71.3
L ₃	7.08	6.70	90.4	1.4	89.0	67.0	0	67.0
L ₄	7.28	7.01	92.2	0.9	91.3	70.0	0.5	69.5
Taupo	*5.05	4.38	62.1	0.3	61.9	64.0	2.5	59.0
L ₀	4.71	4.24	63.8	2.1	61.7	76.0	3.8	72.2
L ₁	4.85	4.40	62.2	2.1	61.1	-	-	-
L ₂	5.00	4.55	65.2	2.5	62.7	-	-	-
L ₃	5.40	4.89	72.9	0.8	72.1	80.0	1.6	78.4
L ₄	5.75	5.23	91.5	0.6	90.9	-	-	-
L ₅	6.05	5.58	119.0	0.3	118.7	91.0	0.6	90.3
CaCl ₂ ³	4.56	4.23	64.5	1.1	63.4	-	-	-
CaCl ₂ ⁵	4.30	4.22	59.5	4.0	55.5	67.0	6.5	61.5
L ₀ ¹	4.57	4.18	54.4	1.4	53.0	52.0	3.3	49.0
L ₆	4.95	4.48	74.2	1.7	72.5	86.4	2.8	83.5
L ₇	5.60	5.14	110.7	0.7	110.0	105.0	0.4	104.5
L ₈	6.22	5.81	125.0	1.0	123.9	115.0	0	115.0
L ₉	6.58	6.25	134.0	2.6	131.4	139.0	0	140.0
Konini	*5.25	4.08	67.4	0.3	67.2	101.4	1.5	100.0
L ₀	4.66	4.02	57.2	0.5	56.7	92.0	3.2	89.0
L ₁	4.91	5.25	77.7	0	77.7	-	-	-
L ₂	5.26	4.51	91.1	0	91.1	-	-	-
L ₃	5.48	4.70	101.3	0	101.3	120.0	0.8	119.0
L ₄	5.67	4.93	106.4	0	106.4	-	-	-
L ₅	6.09	5.35	122.0	0	122.0	125.0	0	125.0

APPENDIX III contd.

Soil	pH		Charge in 0.025M CaCl ₂			Charge in 0.1M NaCl		
	H ₂ O	KCl	-ve	+ve	net	-ve	+ve	net
			meq kg ⁻¹			meq kg ⁻¹		
CaCl ₂ ³	4.77	4.20	78.6	0	78.6	95.8	3.4	92.4
CaCl ₂ ⁵	4.58	4.23	74.6	0	74.6	-	-	-
L ₀ '	4.50	4.06	64.0	0	64.0	83.0	3.4	80.0
L ₆	4.95	4.38	86.0	0	86.0	104.0	3.0	101.0
L ₇	5.54	4.92	104.0	0	104.0	108.0	0.9	107.0
L ₈	6.15	5.47	122.0	0	122.0	113.0	0.9	113.0
L ₉	6.48	6.00	135.0	0	135.0	120.0	0	120.0
Wainui	*5.07	4.25	69.8	8.3	61.5	-	-	-
L ₀	4.70	4.01	60.0	6.8	53.2	-	-	-
L ₁	5.01	4.27	63.6	3.4	60.2	-	-	-
L ₂	5.30	4.59	77.7	2.6	75.1	-	-	-
L ₃	5.73	4.96	85.1	3.1	82.0	-	-	-
L ₄	6.11	5.38	93.6	3.7	90.0	-	-	-
L ₅	6.40	5.73	101.5	2.8	98.7	-	-	-
CaCl ₂ ³	5.15	4.52	76.2	2.4	73.8	-	-	-
CaCl ₂ ⁵	4.92	4.51	72.5	3.7	68.8	-	-	-
L ₀ '	4.55	3.92	56.1	5.5	50.6	-	-	-
L ₆	5.20	4.50	70.9	2.0	68.9	-	-	-
L ₇	5.88	5.23	91.2	2.3	89.0	-	-	-
L ₈	6.47	5.86	105.0	4.8	100.2	-	-	-
L ₉	7.21	6.73	120.0	4.0	116.0	-	-	-
Kumeroa	*5.97	5.07	113.0	0	113.0	96.2	0	96.2
L ₀	5.40	4.81	106.0	0	106.0	94.1	0.9	93.0
L ₁	6.10	5.47	115.0	0	115.0	96.0	0	96.0
L ₂	6.60	6.12	127.0	0	127.0	110.0	0	110.0
L ₃	7.11	6.72	140.0	0	140.0	120.0	0	120.0
L ₄	7.52	7.20	158.0	0	158.0	140.0	0	140.0
Tokomaru	*5.22	4.23	72.4	0.5	71.9	80.2	1.0	79.0
L ₀	4.80	4.41	71.0	2.6	68.4	86.0	1.8	84.2
L ₁	4.87	4.62	73.5	2.0	71.5	-	-	-
L ₂	5.09	4.88	74.0	1.3	72.7	-	-	-
L ₃	5.45	5.35	79.0	1.3	77.7	62.0	1.4	60.7
L ₄	5.79	4.29	78.0	1.2	76.8	-	-	-
L ₅	6.09	4.55	90.0	2.0	88.0	83.0	1.0	82.7

APPENDIX III contd.

Soil	pH		Charge in 0.025M CaCl ₂			Charge in 0.1M NaCl		
	H ₂ O	KCl	-ve	+ve	net	-ve	+ve	net
			meq kg ⁻¹			meq kg ⁻¹		
CaCl ₂ ³	4.84	4.29	78.8	1.2	77.6	-	-	-
CaCl ₂ ⁵	5.04	4.55	78.0	2.0	76.0	75.4	1.2	73.2
L ₀ '	4.51	3.93	70.0	0.2	69.8	65.0	0.3	64.7
L ₆	5.17	4.47	77.0	0.2	76.8	67.0	0.1	66.9
L ₇	5.51	4.79	88.0	0.8	87.2	78.3	0	78.3
L ₈	5.04	5.18	93.0	0.9	92.1	78.0	0	78.0
L ₉	6.26	5.70	103.0	0	103.0	90.3	0	90.3
L ₁₀	6.65	6.14	105.0	0	105.0	111.0	0	111.0



Phosphate sorption in some incubated soils. These results refer to an earlier incubation with some of the same soils as those in Fig. 4-9.

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