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INTERACTIONS OF MOLYBDATE
AND PHOSPHATE WITH SOILS

A thesis presented in partial fulfilment of
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ABSTRACT

Using four New Zealand soils, it was found that pH, extractable Al, citrate-dithionite-bicarbonate-Al, oxalate Fe, and crystalline Fe appeared to be important soil properties in both P and Mo sorption. Allophane appeared less important in the sorption of Mo than in the sorption of P.

For the sorption of Mo, the initial, rapid removal of Mo was followed by a slow, continuing removal of Mo from solution. An estimate of equilibrium Mo concentration was obtained by extrapolation of the relationship between solution Mo and $1/t$ to $1/t = 0$, i.e. $t = \infty$. The effect of ionic strength on Mo sorption appeared to be kinetically controlled at low final Mo concentrations ($< 5 \mu\text{mol l}^{-1}$), but appeared to be absolute at high final concentrations ($> 10 \mu\text{mol l}^{-1}$).

Isotherms for the sorption of Mo by both topsoils and subsoils, at equilibrium and 40 hr, and by synthetic hydrous ferric oxide gel (Fe gel) and allophane at 40 hr, could be described by three Langmuir equations. Values for the free energies of sorption for each region of sorption, which were remarkably similar for the different sorbents, indicated that sorption in regions I and II corresponded to chemisorption reactions, whereas sorption in region III involved a more-physical type of sorption. Fe gel appeared to be a satisfactory model for Mo sorption by soils.

Isotherms for the sorption of P by the four soils, Fe gel, and allophane during 40 hr were described by three Langmuir equations. Because the free energies of sorption for each region, for both Mo and P, were very similar, the sites for sorption and types of sorption reaction for both anions are probably similar. Synthetic allophane chemisorbed

much less Mo than P, relative to Fe gel, and this was attributed to kinetic charge effects.

Sorption of Mo by Fe gel in each region was affected differently by changes in pH and ionic strength, and the charge relationships for each region were also different. These data, along with the three distinct free energies of sorption obtained for Mo, suggested that three distinct sorption reactions were involved. The data suggested that sorption of Mo in regions I and II involved ligand-exchange chemisorption of MoO_4^{2-} for $-\text{OH}_2^+$ and $-\text{OH}$, respectively, resulting in the formation of a bidentate complex. Sorption in region III was considered to involve sorption at a plane distant from the sorbing surface.

The Langmuir equation developed to describe competitive sorption was not obeyed for Mo and P, but the sorption of Mo, in the presence of P, could be described by three simple Langmuir equations. It appeared that Mo and P competed for similar surface sites.

Solution P increased the amounts of sorbed Mo that could be desorbed, relative to Cl. The amounts of Mo desorbed by both Cl and P decreased with time after addition of Mo to soils. This was attributed to a shift in the form of sorbed Mo. Chemical fractionation of sorbed Mo suggested that the absorption of adsorbed Mo was also occurring. For several soils to which Mo had been added in the field, no Mo was desorbed by P solutions.

Solution:soil ratio affected only the rate at which P was removed from solution, not the final equilibrium concentrations. Incubating soil with P prior to the addition of Mo reduced both chemisorption and more-physical sorption of Mo. For a soil that had received annual

additions of phosphate and lime for 22 yr, the chemisorption of added Mo was reduced by both fertilizer P and lime, whereas the more-physical sorption maxima were only reduced by lime additions. The results were discussed in terms of both the persistence and plant-availability of Mo added in the field situation.

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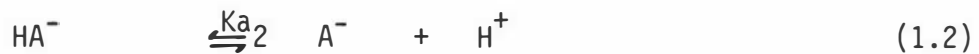
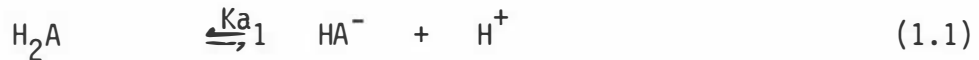
CHAPTER 1

SORPTION OF ANIONS WITH PARTICULAR
REFERENCE TO PHOSPHATE AND MOLYBDATE

1A. Anion Sorption by Soils and Soil Components

1A.1 Introduction

In the pH range, 3.5 - 9.0, which commonly occurs in soils, elements that may exist in anionic form include As, B, Cl, F, I, Mo, N, P, S, Se, and Si. The form of the element which occurs in solution depends on the pH and the dissociation constants of the acid form of the element; for example, considering the acid, H_2A , which follows a two-step dissociation:



The distribution of the ionic species H_2A , HA^- and A^- , is given by equations (1.3) and (1.4):

$$pK_{a1} = pH + \log \frac{[H_2A]}{[HA^-]} \quad (1.3)$$

$$pK_{a2} = pH + \log \frac{[HA^-]}{[A^-]} \quad (1.4)$$

Consequently, the anionic species which predominates depends on pH, and pK_{a1} and pK_{a2} values. Values of pK_a for the acid forms of the elements occurring as anions in the soil solution are given in Table 1.1.

In this review, all species (both undissociated and dissociated) will be denoted by the element, unless otherwise stated; for example, P may refer to H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-} , depending on the conditions being examined.

There has been no general review of the nature of the reactions

Table 1.1 pKa values of acid forms of elements commonly occurring in soils as anionic species

Element	Acid	pKa ₁	pKa ₂	pKa ₃
As	H ₃ AsO ₄	2.3	6.9	11.5
B	B(OH) ₃	9.2		
Cl	HCl	-7.0		
F	HF	3.2		
I	HI	-9.5		
Mo	H ₂ MoO ₄	4.0	4.2	
N	HNO ₃	2.1	7.2	12.0
P	H ₃ PO ₄	-1.4		
S	H ₂ SO ₄	-3.0	1.9	
Se	H ₂ SeO ₃	2.5	8.0	
Si	Si(OH) ₄	9.5	12.0	

All pKa values taken from Sillen and Martell (1964), except that for Mo which is taken from Sillen and Martell (1971).

between anions and soils; reviews have generally concentrated on the reactions of one element, such as P (Wild, 1949; Larsen, 1967; Syers and Williams, 1977) or S (Harward and Reisenauer, 1966). This review will consider anion retention by soils and soil components; the nature of retention and the retaining surfaces; the chemistry of such surfaces; and the mechanisms of the reaction between anions and the retaining surfaces.

1A.2 Anion Retention by Soils and Soil Components : Precipitation and Sorption Concepts

Retention is a general term used to describe the removal of ions from solution by soils and soil components, but it gives no indication of the specific reaction or mechanism involved. Whether anion retention involves precipitation from solution or sorption* at the surfaces of soil components is an argument that is still continuing.

A summary of the arguments for P retention involving precipitation or sorption reactions is outside the scope of this review (see Larsen, 1967; Syers and Williams, 1977). The arguments for precipitation as the mechanism of P retention are primarily based on the fact that discrete Fe and Al phosphate compounds can be formed in pure solutions at pH values corresponding to those commonly occurring in soils (Cole and Jackson, 1950a,b; Kittrick and Jackson, 1955a, b, 1956). This approach also attempts to fit soil solution concentrations to P mineral solubility isotherms (Lindsay et al., 1959; Larsen and Widdowson, 1970).

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

Ryden (1975) has collated solution P data from several workers and shown that the data fail to follow any definite solubility isotherm, indicating that solution P concentrations are not necessarily controlled by a precipitation reaction. Although the concept of P sorption was proposed earlier than that of precipitation (Russell and Prescott, 1916; Mattson, 1931), only recently have results shown that most P retention data are more easily explainable in terms of P sorption concepts (Hsu, 1964; Hingston et al., 1967, 1968b; Ryden and Syers, 1976).

Because many of the other anions (e.g. As, Mo, Se) occur in trace amounts in soils, the concept of precipitated forms of these ions existing in soils has been proposed less frequently than for P, because the soil solution would be undersaturated with respect to any solid phase compounds. Vlek and Lindsay (1977a) have shown that, for Mo retention by several Colorado soils, only the very rarely occurring $PbMoO_4$ could sustain the observed soil solution Mo concentrations. Even early investigations of trace element retention assumed that these anions were held at the soil component surface by a sorption reaction (Olson and Jensen, 1940; Sieling, 1946; Deans and Rubins, 1947; Jones, 1957). The high solubility of compounds of the halides, N, and to a lesser extent S, has also precluded the concept of precipitation as the mechanism of retention for these anions.

In general, it would appear that anion retention involves sorption reactions and the mechanism of retention can best be understood by assuming such reactions. Sorption reactions, however, may be chemisorption reactions and, as such, involve the formation of a chemical bond (Adamson, 1967) which may be considered as the formation of a new compound, although chemisorption is generally limited to a thickness of

one layer of sorbing ion. Kurtz et al. (1946) and de Boer (1950) have pointed out that there is essentially no difference between the chemical forces which hold an ion at a sorbing surface and those involved in the precipitation of a comparable discrete phase. This may have given rise to much of the conflict in the past.

For the remainder of this review, anion retention will be considered to involve sorption reactions.

1A.3 Soil Components Important in Anion Sorption

1A.3.1 Nature of the components

The nature of the soil components important in anion retention might possibly be expected to be as diverse as the anions themselves. A study of the literature, however, reveals that the dominant components involved in anion sorption appear to be common to most anions.

Early studies showed that anion retention was generally greatest in soils rich in Fe and Al. For some anions, the relationship between anion retention and the amounts of Fe and Al has not been investigated very thoroughly; namely As (Misra and Tiwari, 1963) and Se (Geering et al., 1965; Cary et al., 1967). For other anions, however, the nature of the sorption surface has been defined more narrowly, mainly by two techniques: (1) relating anion retention to chemical fractions of the soil, and the effect on anion retention of removing these fractions, and (2) studies of the sorption of anions by synthetic soil components.

Although not constituting direct proof that certain components are involved in anion sorption, correlation with several soil properties is consistent for many anions. Good correlations have been obtained between anion retention and free Fe and Al oxides and hydrous oxides^{*}

* Differences between oxides and hydrous oxides are discussed in a following section. In the rest of this study, the term "oxide" will refer to both oxides and hydrous oxides unless otherwise specified.

(those removed by citrate-dithionite-bicarbonate, CDB, which does not differentiate between crystalline and amorphous oxides) for As (Deans and Rubin, 1947), B (Sims and Bingham, 1968b), Cl (Sumner and Reeve, 1966), Mo (Jones, 1956; Barrow, 1970; Theng, 1971), P (Saunders, 1965; Ramulu et al., 1967; Syers et al., 1971), S (Chao et al., 1962) and Si (Beckwith and Reeve, 1963). Correlations obtained between anion retention and the amounts of CDB-Fe and -Al are often direct, or more conclusively, a correlation is obtained between reduction in anion sorption after chemical treatment and the amounts of CDB-Fe or -Al. Good correlations between P sorption and oxalate-extractable Fe and/or Al have been obtained by Williams et al. (1958), Saunders (1965), and Syers et al. (1971), but this fraction has not been investigated for other anions. Short-range order (amorphous) Al, extracted with boiling 0.5M NaOH, has been correlated with anion sorption for B (Sims and Bingham, 1968b; Bingham et al., 1971) and S (Chao et al., 1962; Gebhardt and Coleman, 1974b).

The oxalate reagent extracts short-range order Fe and Al (Gorbunov et al., 1961; Schwertmann, 1964) and many of these components are also extracted along with crystalline Fe, and some crystalline Al, oxides by CDB reagent (Gorbunov et al., 1961). Hence, the good correlations between anion retention and CDB-extractable Fe and Al do not allow any distinction between the relative importance of short-range order and crystalline oxides. For P sorption, it has been shown that short-range order components appear to be more important (Williams et al., 1958; Saunders, 1965; Syers et al., 1971). Short-range order oxides of Al include short-range order aluminosilicates (allophane); the presence of allophane in soils results in large amounts of anions being retained by soils. Allophane has been shown to be important in the retention

of B (Bingham et al., 1971), Cl (Gebhardt and Coleman, 1974a), Mo (Theng, 1971; Gonzalez et al., 1974), P (Saunders, 1965; Gebhardt and Coleman, 1974c), S (Gebhardt and Coleman, 1974b), Se (Rajan and Watkinson, 1976) and Si (Beckwith and Reeve, 1963; McKeague and Cline, 1963).

The difficulty of drawing conclusions concerning the relative importance of soil properties from correlations between anion retention and soil properties arises from the fact that the soil properties may themselves be correlated to a considerable degree. For example, Saunders (1965) and Syers et al. (1971) have demonstrated that oxalate Fe and Al and soil organic matter are well correlated. The good correlations obtained between anion retention and Fe and Al components in a wide variety of soils, however, points to the importance of these soil components in anion sorption.

Studies of the sorption of anions by synthetic soil components give good indirect evidence of the relative importance of the different components. Extensive studies have been made of P sorption by pure components, and reviews of these investigations (Ryden, 1975; Syers and Williams, 1977) show that short-range order hydrous oxides of Fe and Al, as well as allophane, sorb up to 100 times more P than their crystalline counterparts, which in turn sorb considerably more P than do crystalline layer silicates and calcium carbonate. Retention of other anions by soil components has not been studied so extensively, but similar conclusions can be reached. Thus, short-range order Fe and Al gels have been shown to sorb considerably more As (Sieling, 1946), B (Sims and Bingham, 1967, 1968a), Mo (Jones 1956, 1957; Resienauer et al., 1962), and S (Chao et al., 1964; Aylmore et al., 1967) than their crystalline counterparts, which in turn sorb greater amounts than crystalline layer silicates.

An interesting variation to studying sorption by pure soil components has been to coat soil particles or minerals with synthetic Fe and Al gels. It has been shown that the retention of B (Sims and Bingham, 1968b), Mo (Jones and Smith, 1972), and S (Chao et al., 1964) can be increased considerably by this technique. Such experiments could have direct relevance to the field situation. With the knowledge that Fe and Al oxides, especially those that have short-range order, sorb markedly greater amounts of anions than crystalline components, their distribution and occurrence in soils will now be discussed.

1A.3.2 Distribution of oxides in soils

The considerable experimental evidence that Fe and Al oxides are important in anion retention has only recently been followed by investigations into the distribution of these oxides in soils. This has mainly been carried out by the use of the electron microscope in studying materials that appear amorphous to X-rays.

Greenland et al. (1968) showed that old, highly-weathered soils contained considerable free iron oxides, present as small discrete particles which were frequently aggregated. They found no evidence of iron oxide coatings. Such coatings, however, have been observed on layer silicates in less weathered soils (Roth et al., 1969) and gel coatings of unknown composition have been observed in a wide range of recent soils by Jones and Uehara (1973), who state that the use of less-sophisticated electron microscope techniques in earlier studies could have hindered detection of such coatings. Laboratory studies have shown that both "ferric hydroxide" gels (Follett, 1965; Greenland and Oades, 1968) and "aluminium hydroxide" gels (El-Swaify and Emerson, 1975) can be precipitated on to soil minerals and are very important

in affecting physical and chemical properties of soils. Oxide coatings of Al have been regarded as being more important in determining soil properties than Fe coatings by Tweneboah et al. (1967) and Deshpande et al. (1968), although their studies were carried out on relatively strongly-weathered soils. On less-weathered soils, aluminosilicate gels (allophane), alone or in combination with Fe (Kirkman, 1973), are very important in determining chemical and physical properties of soils (Mitchell et al., 1964).

Studies on the sorption of aluminium by clay minerals have shown that polymeric hydroxy aluminium species may sorb on clay minerals (Shen and Rich, 1962; Brown and Newman, 1973). The formation of these polymers has a large effect on the properties of the sorbents (Hsu and Bates, 1964; de Villiers and Jackson, 1967). Depending on the amounts of Al present, these hydroxy polymers may form polymeric Al gels or crystalline Al hydroxides (Hsu and Bates, 1964).

The persistence of short-range order Fe and Al oxides over long periods of time could be questioned, given that in laboratory studies such oxides age rapidly to more crystalline oxides. The presence of organic anions (Schwertmann, 1966), and Si (Tran Vinh An and Herbillon, 1969; El-Swaify and Emerson, 1975) in the solution, however, can retard and inhibit the crystallization process. Schwertmann (1966) has proposed that the presence of other anions, such as P, could also hinder the crystallization of amorphous oxides. Jenne (1968) has also suggested that ferric oxide may undergo reduction/oxidation reactions with organic matter, which would result in ferric oxide being continually reprecipitated.

The high anion retention by synthetic Fe and Al oxides, and their relatively wide distribution in soils, indicates that such surfaces are

important in anion retention. Hence, the study of pure oxide systems, which are much simpler than mixed soil systems, as models for the soil system would appear to be justifiable and should lead to a better understanding of anion sorption by soils.

1A.4 Properties of the Metal Oxide - Aqueous Interface

1A.4.1 Origin of charge

When a crystalline solid is immersed in an electrolyte solution, a charge can develop at the surface by one of two methods: (1) unequal dissolution of the lattice ions making up the solid, referred to as incongruent dissolution, and (2) unequal sorption of electrolyte cations and anions. The most extensively studied crystalline solid/solution interfaces are the silver halides, at which the surface charge depends on lattice Ag^+ and halide ions, and the charging process leads to development of a potential difference between solid and solution. The Ag^+ and halide ions have been termed "potential-determining ions" (p.d.ions) (Overbeek, 1952). Electrified interface systems were later extended to hydrous metal oxide systems (Parks and de Bruyn, 1962) and, since then, have been studied extensively. The term, hydrous metal oxide, refers to solids which have as their only constituents, one or more metallic cations combined with the elements of water, hydrogen, and oxygen. Included are the metal hydroxides and oxyhydroxides, and also metal oxides, which may have hydrated surfaces a few atomic layers in thickness (Onoda and de Bruyn, 1966).

The development of charge may be illustrated by the example of a metal oxide. For a broken oxide surface, exposure to an aqueous solution results in the hydration of surface layers (O'Connor et al., 1956;

Parks and de Bruyn, 1962). In order to complete the coordination shell of the surface atoms, hydroxyl ions are bound to exposed M^+ , and protons bound to exposed O^- . This hydrated surface can be considered analagous to the surface of a hydrous oxide. Similarly, for edges of crystalline and short-range order aluminosilicates, broken surfaces incorporate OH^- and H^+ to complete their coordination shell. These hydrated surfaces (represented as $M-OH$) have an amphoteric nature and the sorption and desorption of protons, equation (1.5) and (1.6) below, result in a variable charge surface:



For oxide systems, the lattice metal and oxygen atoms are considered to be p.d.ions, by analogy with the silver halide system, and the proton and hydroxyl ions are also defined as p.d.ions (Parks and de Bruyn, 1962). The potential of the oxides surface is, therefore, dependent on the concentration of H^+ and OH^- in solution. Such surfaces are defined as constant potential surfaces, in contrast to surfaces such as layer silicates, where the surface charge of the particle is determined by interior lattice imperfections, which are classified as constant charge surfaces (van Olphen, 1963).

Before considering the effects of solution parameters on oxide surfaces, and possible explanations of the effects, it is necessary to consider models of the electrical double layer which have been proposed to explain the behaviour of charged interfaces.

1A.4.2 Electrical double layer models

The principal aim of double layer theory is to describe the spatial distribution of charge and potential close to an interface. Many models have been proposed, but all of them are based on simplified

models, initially proposed by Gouy (1910) and Chapman (1913), and later modified by Stern (1924).

1A.4.2.1 Gouy - Chapman - Stern theory

The Gouy - Chapman model proposes that the ionic double layer may be considered to consist of a surface charge (σ) uniformly distributed over a plane, and in contact with a solution containing ions which may be regarded as uniform point charges. Ions in solution are attracted or repulsed by coulombic forces, depending on the charge on the surface and the ion under consideration. The charge on the surface is compensated for by ions of opposite charge in solution, termed counter ions. A theoretical model of the Gouy - Chapman double layer may be derived by considering the distribution of ions in electrolyte solutions under electrostatic forces, and equations obtained for the distribution of charge and potential in solution (for example, see Adamson, 1967; Aveyard and Haydon, 1973). Fig. 1.1A shows the distribution of potential and charge for the Gouy - Chapman model. The equations obtained show that the charge depends on the concentration of the counter ions, the charge on the counter ion, and the potential at the surface.

The simple Gouy - Chapman theory was found to have several important shortcomings, the most important being the assumption that ions in solution are point charges, and the consequent neglect of ionic diameters. Stern (1924) modified the theory by introducing the fact that ions could not approach the surface to a distance closer than their effective diameters. The distribution of charge and potential in the Stern model is illustrated in Fig. 1.1B. The charge on the surface (σ_0) is balanced by the charge on the ions at the distance of closest approach (σ_{st}) plus the charge on the ions in the diffuse layer (σ_d), i.e. Stern

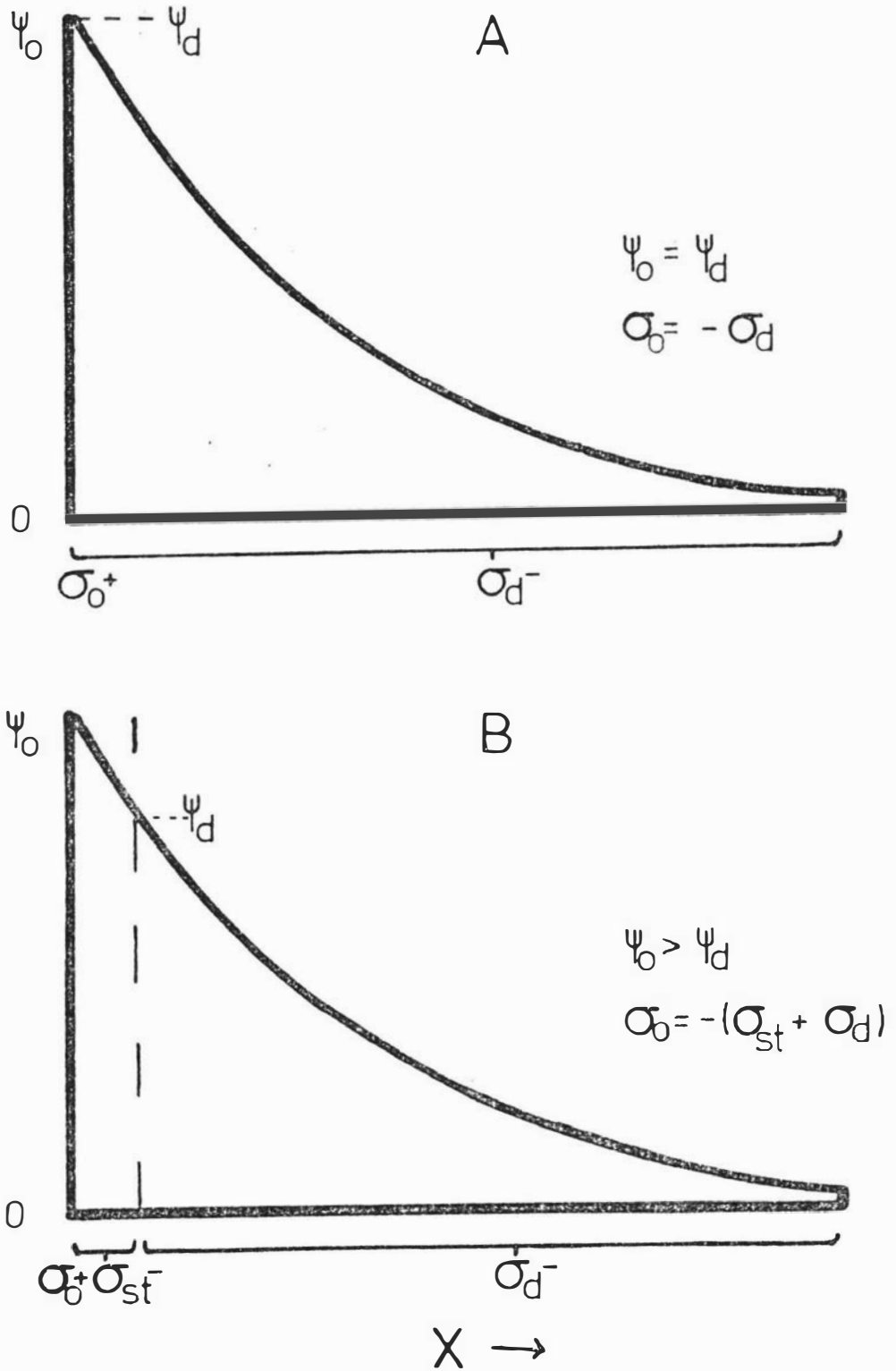


Fig. 1.1 Distribution of potential and charge at a positively-charged interface. A = Gouy - Chapman model and B = Stern model. ψ = potential, σ = charge, x = distance from the surface; subscripts 0, st, and d denote the surface, the Stern layer, and the diffuse layer, respectively.

divided the double layer up into an inner compact layer and a diffuse Gouy - Chapman layer.

Stern also introduced a new concept that recognized that, at short distances from the surface, there may exist a specific "chemical" interaction between the ions and the surface. Hence, the potential of an ion at a charged interface would be a combination of the potential due to specific chemical attraction between the surface and the ion, plus the potential due to coulombic attraction between the ion and the surface. By considering both these potential terms, the distribution of charge at the Stern layer can then be calculated (Adamson, 1967).

1A.4.2.2 The Gouy - Chapman - Stern - Grahame double layer

From studies of the mercury-electrolyte interface, Grahame (1947) proposed that further subdivisions of the double layer could be made. Observing the strong sorption of ions at the interface, Grahame proposed that ions could be sorbed into a plane of direct contact with the surface by complete or partial removal of both the ion, and the surface, hydration sheaths. The locus of centres of such ions is called the inner Helmholtz plane (i.H.p.), in contrast the locus of centres of hydrated ions that are not so strongly sorbed, the outer Helmholtz plane (o.H.p.) (Fig.1.2A). The o.H.p. corresponds to the Stern layer of Fig. 1.1B.

Ions that are in direct contact with the surface are termed specifically sorbed ions (s.s.ions). This type of sorption is possible if the ion concerned is weakly hydrated or if a high sorption energy exists between the specific ion and the surface. S.s. ions can sorb on oppositely - charged surfaces out of all proportion to their concentration in solution, relative to non-specifically sorbed ions (Hingston et al., 1967), and can show super-equivalent sorption, resulting in reversal of

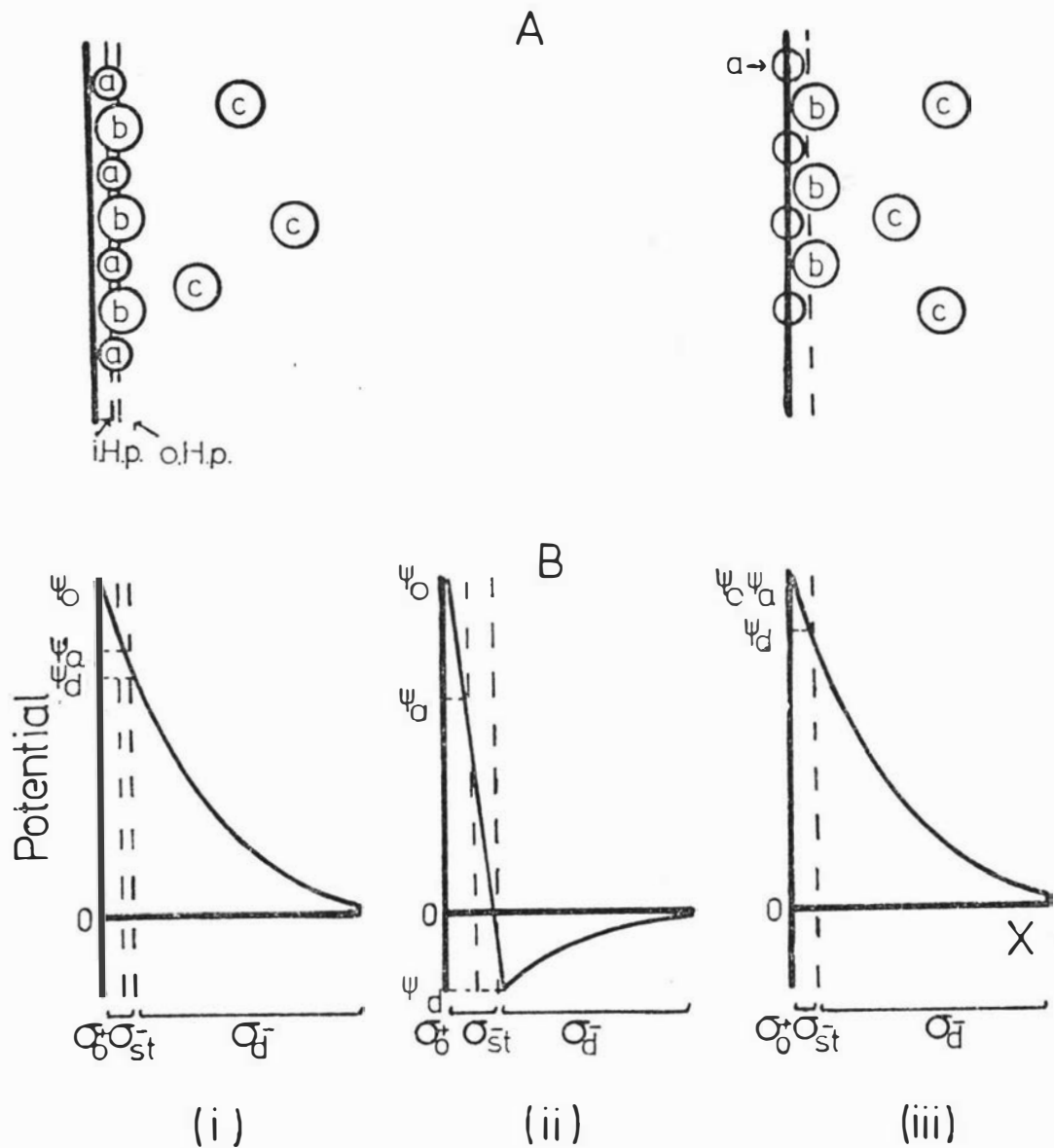


Fig. 1.2 Models of different positively-charged surfaces (A) and distribution of potential and charge at these surfaces (B). (i) Stern-Graham model, (ii) charge reversal arising from superequivalent sorption of anions, and (iii) constant-potential surface. a = specifically sorbed anion in the inner Helmholtz plane in (i) and at the surface in (iii), b = anion at the plane of closest approach (outer Helmholtz plane), c = counter ion in diffuse layer, ψ_a = potential in plane of specifically sorbed anion, and other terms as defined in Fig. 1.1

the sign of the diffuse layer potential, ψ_d (Fig. 1.2(ii)). Breeuwsma and Lyklema (1973) have defined specific sorption as any sorption for which the sorption energy differs from the coulombic energy. The term specific sorption was initially developed by Grahame (1947) for sorption at polarizable metal electrodes where there was no charge transfer across the interface and the distinction between surface and sorbing ions was clear. Hence, specifically sorbed ions can be physically distinguished from the surface and superequivalent sorption clearly has no effect on the surface charge (Breeuwsma and Lyklema, 1973). For metal oxide system, however, counter ions can become p.d. ions and the distinction between surface and solution becomes unclear. It is normally assumed that p.d.ions are integral parts of the solid surface and, hence, p.d.ions are no longer regarded as s.s.ions and a new surface of potential (ψ_0, ψ_a) is formed (Fig. 1.2(iii)). Therefore, p.d.ions may be distinguished from s.s.ions; these s.s.ions are assumed to sorb at the solution side of the interface. This distinction is clear if specific sorption involves primarily ionic interactions. When covalency is involved, however, the distinction between surface and sorbed ion becomes unclear and s.s.ions may also become p.d.ions. Such effects will be discussed in subsequent sections.

1A.4.3 Distribution of charge at oxide surfaces

1A.4.3.1 Variation of charge in the absence of specific sorption

The charge on hydrous metal oxides is determined by the p.d.ions, H^+ and OH^- . An excess of one of these ions determines the net charge of the surface, and, hence, the charge on the surface is given by equation (1.7):

$$\sigma_0 = F (\bar{\nu}_{H^+} - \bar{\nu}_{OH^-}) \quad (1.7)$$

where Γ_{H^+} , Γ_{OH^-} , are the sorption densities of H^+ and OH^- , respectively (strictly speaking, the surface excess, but the solution concentration is assumed to be negligible compared to the sorbed ions). The uptake of H^+ or OH^- is most readily determined by potentiometric titrations of oxides (Bolt, 1957; Parks and de Bruyn, 1962; Yopps and Fuerenstau, 1964; Atkinson et al., 1967). Such titrations are usually carried out in various concentrations of suitable electrolytes (KCl or KNO_3), whose ions are assumed to be non-specifically sorbed. The uptake of H^+ (or OH^-) is determined by the difference in titres and the appropriate blank solution. An example of a titration curve for a metal oxide is given in Fig. 1.3A. The point of common intersection of the curves can be shown to be the condition of zero net surface charge (Parks and de Bruyn, 1962) and the pH at the point of zero charge (p.z.c.) is denoted as pH (p.z.c.). Therefore, at pH (p.z.c.):

$$(\Gamma_{H^+} - \Gamma_{OH^-}) = 0 \quad (1.8)$$

The charge on the surface at pH values different from the p.z.c. is then defined relative to this zero point and charge - pH curves obtained. At pH values above pH (p.z.c.), σ_o is negative and below pH (p.z.c.), σ_o is positive. It can be seen from Fig. 1.3A that, at constant pH, the magnitude of the charge increases with increasing electrolyte concentration, in agreement with predictions from theoretical double layer equations.

1A.4.3.2 Variation of charge in the presence of specifically-sorbed anions

When titration curves of metal oxides move away from the unique crossover point, usually at high electrolyte concentration (Fig. 1.3B), then one of the ions of the electrolyte is a s.s.ion. The direction

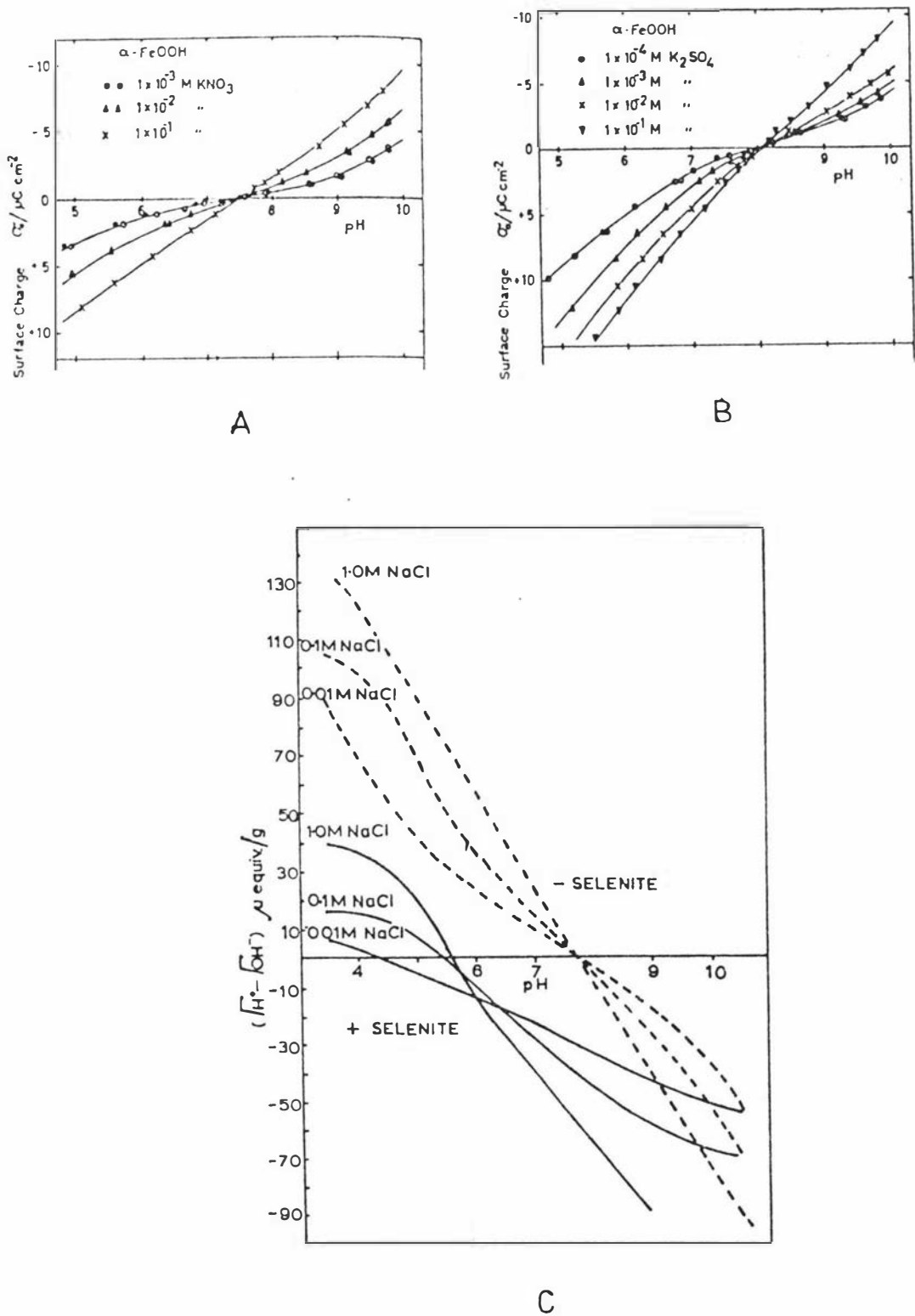


Fig. 1.3 Surface charge-pH curves for goethite in the presence of different anions, showing the effect of anion sorption on pH (p.z.c.) of oxides. A = in the presence of KNO_3 solutions of different ionic strength and B = in the presence of K_2SO_4 solutions of different ionic strength; both from Yates and Healy (1975). C = in presence and absence of selenite at various NaCl concentrations, from Hingston et al. (1968a); charge in presence of selenite calculated, not experimentally determined.

of shift of pH (p.z.c.) has been found to differ for different anions sorbing on hydrous metal oxides (Hingston et al., 1968a, 1972; Breeuwsma and Lyklema, 1973; Ryden et al., 1977a).

The contradictory results reported for the shift of pH (p.z.c.) appear to have partly arisen because of the definition of where ions are located with respect to the "surface" of the metal oxide. Breeuwsma and Lyklema (1973) consider that specific sorption takes place in the Stern Layer at the i.H.p. (Fig. 1.2A); the increase in negative charge subsequent to specific sorption of anions promotes the sorption of H^+ on the surface, hence the pH must increase to make the surface charge zero. This is illustrated in Fig. 1.3B for S sorption on goethite. A similar increase in pH (p.z.c.) subsequent to S sorption of haematite has been observed by Breeuwsma and Lyklema (1973). Hingston et al. (1967, 1968a, b, 1972) have concluded that specific sorption of anions results in a decrease in pH (p.z.c.) (Fig. 1.3C). They define the surface of the oxide to begin at the i.H.p. and call specific sorption a ligand-exchange reaction. Their data for the surface charge in the presence of a specifically-sorbed anion, however, is not measured by H^+ , OH^- sorption, but by measuring OH^- release and by assuming an increase in surface negative charge subsequent to anion sorption. This approach is questionable because it assumes that the sorption of anions results in an increase in surface negative charge, i.e., the mechanism is assumed in calculating the charge-pH curves. Recent studies (Ryden et al., 1977a) have shown that the pH (p.z.c.) of hydrous ferric oxide gel, as measured by potentiometric titration, decreases subsequent to P sorption. These workers ascribed this shift to the formation of a ferric phosphate-like surface, rather than in terms of specific sorption. The difference between the data of Ryden et al. (1977a) and Breeuwsma

and Lyklema (1973) does indicate that the reaction between P and the surface is different from that for S, even though both are described as s.s. anions (Hingston et al., 1967). Further evidence for this difference has been presented by Yates and Healy (1975), who showed that P sorption by goethite occurred by ligand-exchange, whereas S sorption did not involve ligand exchange. This points to the need for a more precise definition of specific sorption.

1A.4.3.3 Points of zero charge of soil components

No oxide or hydrous oxide of a specific formula has a definite pH (p.z.c.) (Parks, 1965). The value depends on the origin, history, purity, crystallinity, temperature of preparation, and the degree of hydration of the sample. Compilation of pH (p.z.c.) values for Fe and Al oxides and hydrous oxides (Ryden, 1975), however, shows that the values fall in the range 8.0 - 9.5, with Al oxides and hydrous oxides generally showing higher values than those for Fe. This implies that, at acid soil pH values, hydrous oxides of Fe and Al would be expected to be positively charged. Silica gels, on the other hand, have a pH (p.z.c.) of approximately 3.0 and would be negatively charged at normal soil pH values.

The pH (p.z.c.) values for crystalline aluminosilicates are not so definite. The permanent negative charge of such minerals would be expected to be constant at all pH values. Such crystalline aluminosilicates, however, can have hydrated edge faces, on which a pH-dependent charge could arise in much the same manner as for hydrous metal oxides. These hydrated edge atoms could be either Si or Al, which would in turn affect whether they were positively or negatively charged at a given pH, because the pH (p.z.c.) of Si and Al hydrous oxides differ widely.

The surface charge of such complex oxides will be the sum of the net positive and negative charges (Parks, 1967) and the pH (p.z.c.) of crystalline aluminosilicates could, therefore, occur at pH values where there are localised centres of charge. Short-range order aluminosilicates would also be expected to show the same properties. Although the "structure" of such minerals is not definitely known, models proposed independently by Cloos et al. (1969) and van Reeuwijk and de Villiers (1970) appear to have general acceptance. These models propose a permanent, negatively-charged core, arising from isomorphous substitution of Si by Al, surrounded by a hydroxy Al coating, which would be expected to have a pH-dependent charge. Hence, the pH (p.z.c.) of such aluminosilicates would fall at a pH where the net charge was zero, even though localized centres of positive charge could exist at pH values greater than the determined pH (p.z.c.).

The existence of pure Fe and Al hydrous oxides in soils is doubtful, and it is often postulated that they exist as mixed gel systems with silica (Tran Vinh An and Herbillon, 1969) or with silica and organic matter (Mattson et al., 1950). Such mixed gel systems would have different pH (p.z.c) from the pure components, as discussed above. Tadros and Lyklema (1969) reported that impurities, including Al_2O_3 in SiO_2 , increased pH (p.z.c.) from approximately 3.0 to 6.0. Mattingley (1975) has urged that greater attention be paid to such mixed gel systems, which are expected to have more relevance to the soil situation than pure oxide systems.

1A.4.4 Distribution of potential at oxide surfaces

The distribution of potential in the double layer is usually determined by measurement of electrokinetic phenomena, involving relative motion between a charged surface and the bulk solution. This enables

measurement of the zeta potential, the potential at the plane of shear when the charged particle moves. The position of this shear plane, relative to other double layer planes, is not precisely known, because it is not possible to locate it relative to the solid surface (Aveyard and Haydon, 1973). The zeta potential is often assigned to the potential at the Stern layer boundary, ψ_d (Fig. 1.2A) (Hunter and Wright, 1971; Breeuwsma and Lyklema, 1973), although there is evidence that it may be located further away from the surface (Adamson, 1967). Measurement of the zeta potential may provide evidence for the occurrence of specific sorption, because the plane of specific sorption is always located on the solid side of the zeta potential plane, and consequently the exact location of the plane of specific sorption is less important than for surface charge measurements.

The zeta potential is related to surface potential and hence, to electrolyte concentration and pH for oxide systems. The pH where the zeta potential is zero is known as the isoelectric point, pH (i.e.p.). In the absence of specific sorption, the charge in the diffuse layer depends only on the surface charge, and hence:

$$\text{pH (i.e.p.)} = \text{pH (p.z.c.)} = \text{pH}^0 \quad (1.9)$$

In the presence of s.s. anions, the potential in the diffuse layer is changed (Fig. 1.2B) and pH (i.e.p.) also changes. Specific sorption of anions makes ψ_d more negative, and therefore, relative to no specific sorption, less OH^- must be added to a positive oxide surface to make $\psi_d = 0$. Therefore, pH (i.e.p.) would be expected to drop relative to pH^0 when specific sorption occurs. Decreases in pH (i.e.p.) subsequent to anion sorption by oxides has been found for As (Anderson et al., 1976), S (Breeuwsma and Lyklema, 1973), and for a range of anions (Wakatsuki et al., 1974). Both Wakatsuki et al. (1974) and Anderson et al. (1976)

assumed that the decrease in pH (i.e.p.) was a consequence of a decrease in surface potential subsequent to anion sorption, i.e., the sorbing anions are p.d. ions. However, Fig. 1.2B shows that a reduction in the diffuse layer potential as a result of specific sorption would lead to a change in pH (i.e.p.) without any change in surface charge, as proposed by Breeuwsma and Lyklema (1973). Wakatsuki et al. studied sorption of several anions (As, B, Cl, Mo, N, P, S, Se, Si, V) and listed these anions in order of the minimum anion solution concentration required to give charge reversal on a given oxide at a constant pH. By comparing the order of anions with ionic potential and general solubility, they concluded that specific sorption of anions which required the lowest concentration to give charge reversal involved covalent bond formation. The fact that pH (i.e.p.) is dependent on a potential at a distance from the surface, however, would appear to limit its value as a tool in mechanistic studies of anion sorption.

Studies of change in pH (p.z.c.) and pH (i.e.p.) subsequent to specific sorption indicate that the term specific sorption, inherited from the more easily-defined electrode surfaces (Grahame, 1947; Bockris et al., 1963), is perhaps not applicable at oxide surfaces. For example, it is important to know whether specific sorption involves ligand-exchange (Hingston et al., 1967, 1968a, b, 1972) with surface p.d.ions or involves sorption at a plane distinct from the surface (Breeuwsma and Lyklema, 1973) if an understanding of sorption mechanisms is to be reached.

Non-specific sorption of anions (and cations) does not affect the surface charge, per se, the ions merely compensate the surface charge and are distributed at the o.H.p. and over the diffuse layer (Fig. 1.1B). Such ions are easily removed from the surface and are only sorbed in

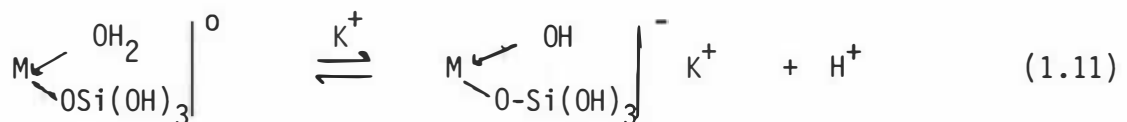
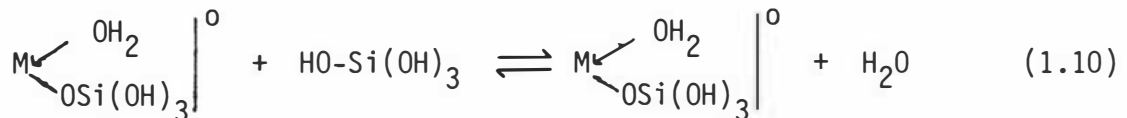
proportion to their concentration in solution (Hingston et al., 1967). Anions sorbed in this way could be classed as being physically sorbed at the oxide surface; Cl, N, and ClO_4^- behave as physically sorbed anions at oxide surfaces.

Specifically-sorbed ions are sorbed out of all proportion to their concentration in solution (Hingston et al., 1967) and may induce charge reversal at the sorbing surface (Fig. 1.2B). Although anions such as P and S are both classed as specifically-sorbed ions, P appears to bond by ligand-exchange whereas S does not (Yates and Healy, 1975), and the shift in pH (p.z.c.), subsequent to sorption at iron oxide surfaces, is in different directions relative to pH^0 (Breeuwsma and Lyklema, 1973; Ryden et al., 1977a). Thus, it would seem necessary to re-classify specifically sorbed anions into two groups. One, those that are strongly held at the surface and undergo ligand-exchange reactions with the surface, i.e., they may affect the surface charge and are, in fact, p.d.ions, such as As, F, Mo, P, Se, and Si; these ions are postulated to form strong covalent bonds with the surface (Wakatsuki et al., 1974) and hence would constitute chemisorbed ions (P has been proposed to undergo chemisorption reactions with oxide surfaces by Breeuwsma and Lyklema, 1973; Ryden et al., 1977a). Two, those anions, such as B and S, that do not appear to be held as strongly at the surface, yet are classed as specifically sorbed, i.e., they are more-strongly held than anions such as Cl and N. There is no sharp dividing line between physical and chemical sorption, although the extremes are easily distinguishable (Adamson, 1967), and anions such as B and S could be classed as intermediate sorption types, not undergoing ligand-exchange, chemisorption reactions but more strongly held than physically-sorbed anions.

1A.5 Generalized Models of Anion Sorption

Whereas there have been many studies of anion sorption, few have involved a precise mechanistic approach, and results are often interpreted in terms of the generalized anion sorption models. The only general models for anion sorption have been obtained by Quirk and co-workers (Hingston et al., 1967, 1968a, b, 1972; Bowden et al., 1973, 1974, 1977). Because other anion sorption studies (e.g. Barrow, 1970; Theng, 1971; Obihara and Russell, 1972; Gebhardt and Coleman, 1974a, b, c; Gonzalez et al., 1974) often interpret their results in terms of the general models, these models require critical evaluation.

It is often difficult to understand what the models of Hingston et al. propose, but they are based largely on the experimentally-determined "adsorption envelopes" (Fig. 1.4), which are plots of maximum sorption of an anion at each pH versus pH. Hingston et al. (1967, 1968b, 1972) have shown that maxima and/or breaks in these plots occur at pH values which are well correlated with the pKa of the conjugate acid of the sorbing anion. From these results they concluded that, for specific sorption of anions to occur, species able to donate and accept a proton must exist simultaneously at the surface. The exact mechanisms proposed are not clear, but the authors state that an increase in negative charge upon sorption is a necessary requirement and that specific sorption involves ligand-exchange. For example, the sorption of Si is proposed as:



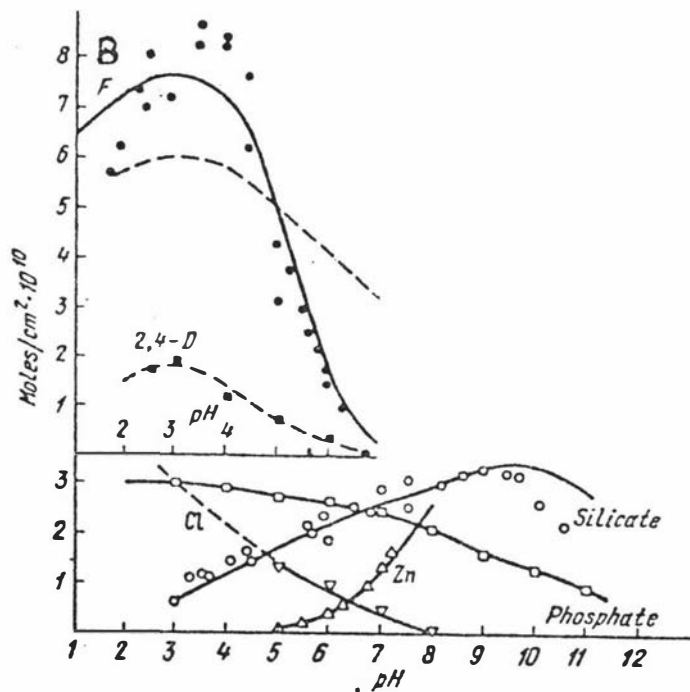
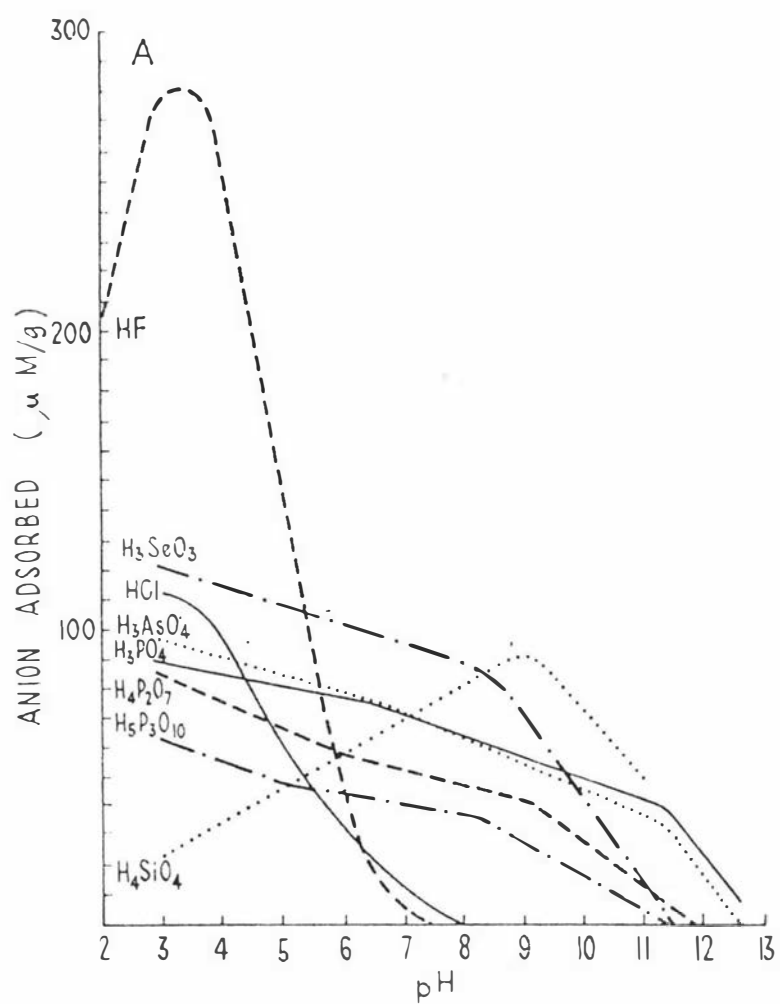


Fig. 1.4 Maximum sorption-pH curves ("adsorption envelopes") for sorption of various anions by goethite. A = experimental curves from Hingston et al. (1968b), and B = calculated envelopes (solid lines) and experimental points from Bowden et al. (1975). Dashed line for F places anion in Stern layer.

It is never made clear why an increase in negative charge is conditional for specific sorption of anions; for example, why equation (1.10) alone could not be the sorption reaction. Specifically-sorbed anions of completely dissociated acids, e.g., F, S, are said to sorb only on positive charged surfaces by proton donation from the surface, enabling the anion to then displace surface -OH. While fully dissociated anions can only sorb at positive surfaces, partially dissociated anions are said to sorb at surfaces which may be negatively charged because "acid dissociation of the sorbing species provides protons which react with surface -OH to form water which is readily displaced by the anion". The weakness in the theories developed by Hingston et al. is that they do not consider the surface charge on the oxide, which would be expected to change with pH, as discussed in section 1A.3. Thus, the theoretical adsorption envelopes developed by Hingston et al. (1970) do not correspond well with experimentally obtained envelopes, except at $\text{pH} = \text{pK}_a$. These envelopes were based solely on consideration of the sorbing species with no regard to the change in surface charge with pH.

Although breaks and/or maxima in sorption envelopes have been found at or near pK_a values by other workers (Theng, 1971; Obihara and Russell, 1972), they have not always been found for P sorption (Chen et al., 1973a; Huang, 1975). Therefore, although the experimental work of Hingston et al. appears to indicate that there is a significant relationship between sorption and the form of anion in solution, to maintain that this is the only important parameter is an oversimplification.

A recent model from the same school of workers (Bowden et al., 1973, 1974, 1977) has attempted to improve the Hingston model, and a

theoretical model has been developed, based primarily on the Stern model of sorption (Section 1A.4.2.1). The model developed proposes that: (1) pH-dependent charge on the surface is developed by protonation and deprotonation reactions with oxo, hydroxo, and aquo ligands in a surface phase; (2) specific sorption (not involving ligand-exchange) is pictured as taking place in a second plane at some distance from the first plane. Bowden et al. then compared model titration curves, sorption isotherms and sorption envelopes with experimental data for goethite (Fig. 1.4B). Comparison of experiment and theory in the absence of specific sorption (Bowden et al., 1977) is good, but in the presence of specifically sorbed ions, the data presented are for a wide concentration range and conclusive comparisons are hard to make. To fit theoretical curves to experimental data for F sorption, Bowden et al. (1973, 1974) proposed that F sorbs in the same plane as potential-determining H^+ and OH^- . Close comparison of predicted and experimental curves for other s.s.ions at low concentrations may have necessitated the same postulate. The model of Bowden et al., therefore, predicts that anion sorption cannot be generally regarded as ligand-exchange. The observation that anion sorption often results in OH^- release (Reisenauer et al., 1962; Rajan et al., 1974) is qualitatively explained in terms of displacement of the anion acid dissociation equilibrium, even though pH changes can occur during sorption of fully dissociated anions (Reisenauer et al., 1962). The observed fact that anions can sorb on negative charged surfaces is qualitatively explained by the Stern chemical interaction potential between the surface and the sorbing ion, whereas at high solution concentrations, anion sorption is said to be limited by electrostatic repulsion rather than by all surface sites which can be occupied being filled.

Bowden et al. (1973, 1977) state that their model is an obvious oversimplification and is at best, only a qualitative explanation of observed experimental facts. The apparent disregard of ligand-exchange as a mechanism of anion sorption would appear to limit the applicability of the model, although it does leave open the possibility of anion exchange with potential determining H^+ and OH^- , and predictions based on this need to be investigated. Their recognition of surface charge and acidity as being of importance is an improvement on the models of Hingston et al., but the oversimplification of the Stern model appears to limit the use of the model. Any generalized theory must account for differences in the extent of anion sorption, differences in strength of bonding of anions, competition effects between anions, the effects of pH on anion sorption, and the effect of anion sorption on double layer parameters, such as $pH(p.z.c.)$ and $pH(i.e.p.)$. Such theories would need to consider both surface parameters and properties of the sorbing ion, as well as consideration and testing of the proposed double layer theories to oxide surfaces. Bowden et al. (1977) have pointed out that the concept of plane oxide surfaces is a gross oversimplification and before reasonable models can be proposed, concepts such as $p.d.ions$, and $s.s.ions$, need to be rationalized, given the increasing experimental evidence that there is no clear distinction between them (Wakatsuki et al., 1974; Anderson et al., 1976; Bowden et al., 1977; Ryden et al., 1977a).

In conclusion, although anion sorption on oxide surfaces shows some similarities for many anions, there is no overall sorption model that can adequately fit the wide range of sorption properties seen. Further discussion of definite mechanistic postulates for anion sorption will be limited to those for Mo and P.

1A.6 Sorption and Desorption in the Presence of Competing Anions

1A.6.1 Competitive sorption

Studies of competitive sorption by soils and soil components can help lead to an understanding of the sorption reaction and may also be useful in understanding results that are a consequence of anion competition in field situations. Competitive sorption is here taken to mean sorption of anions in the presence of other anions which are expected to compete for sorption sites.

Anions such as Cl and N, termed non-specifically sorbed anions (Hingston et al., 1967), are found to be non-competitive with specifically sorbed anions, such as Mo, P, S, etc. For example, Kinjo and Pratt, (1971) found that both P and S showed a large preferential sorption over N on several tropical soils.

When both the anions present are strongly sorbed, the results are not as clear-cut. Hingston et al. (1967, 1968b) have proposed that the ion, which when present alone increases the charge to the greatest extent, is sorbed preferentially. Fig. 1.5 illustrates the effect of Si on P sorption and is said to be proof of the above statement, i.e., Si only reduces P sorption when the sorption envelopes cross, or, in other words, when more Si is sorbed than P. This is also proposed to explain the known dependence of competitive sorption on pH (Hingston et al., 1968b; Gorlach et al., 1969; Obihara and Russell, 1972). The limitation to the hypothesis that anion sorption results in an increase in negative charge has been discussed previously. Similarly, for competitive sorption, the requirement of anion sorption increasing negative charge is only a qualitative proposal that has no direct proof.

Hingston et al. (1971) studied the competitive sorption between

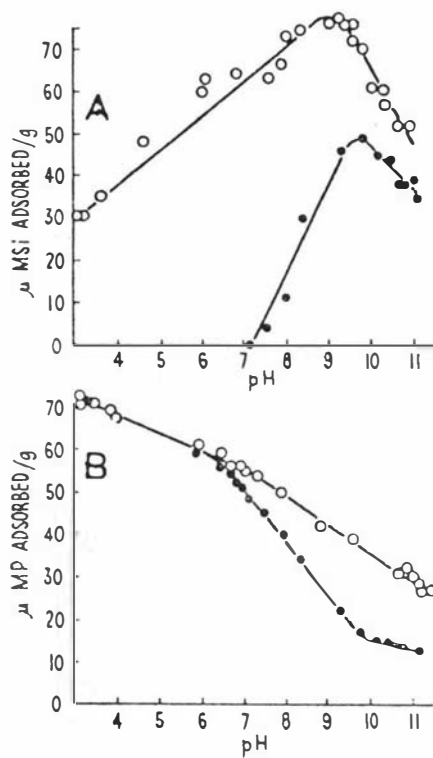


Fig. 1.5 Sorption maxima-pH curves for Si and P sorbing on goethite in the absence and presence of competing anions. A = Si sorbed in absence (o) and presence (●) of P, and B = P sorbed in the absence (o) and presence (●) of Si; both from Hingston et al. (1968b).

P and As, and P and Se, and concluded that three types of sites occurred: those common to both anions and those common to one anion only. This conclusion was reached by considering that the decrease in As (or Se) sorbed when P was added (compared to that sorbed in the absence of P) was a measure of the sites that are common to both P and As (or Se). This ignores the fact that some As may remain sorbed at common sites and hence, the decrease in As sorption will underestimate the number of common sites. Using the maximum sorption capacity of each type of site, obtained from Langmuir equations, Hingston et al. calculated that the area occupied by an anion in the presence of a competitor was much less than in the absence of the competing anion, and therefore, concluded that the competing anion aided in the formation of multi-bridging ligands bound to Fe atoms. The fact that the sum of the calculated sorption maxima for common sites plus P-only sites was greater than the sorption maximum for P in the absence of competing anions, while the experimental data indicated that less P was sorbed in the presence of a competitor, however, suggests that the approach used was in error. The classification of surface sites into three types, although theoretically possible, seems questionable because the chemical nature of all three types of sites could be the same, but the amounts of each anion sorbed would depend on solution concentration of that anion. Also, because oxide surfaces are heterogeneous (Parks and de Bruyn, 1962), this may lead to more than one type of site for each anion even in the absence of competitors, but this fact was not considered by Hingston et al. Such surface heterogeneity may lead to sorption obeying multi-Langmuir equations, and the sorption maxima calculated would be erroneous.

The fact that at any pH value the maximum amount of anion sorbed depends on the identity of the anion, and the consequence that one anion may sorb on sites which appear to be unavailable to the other anion, prevent any simple analysis of competitive sorption.

1A.6.2 Desorption of anions

Before considering desorption by competing anions, it is necessary to look at desorption in the absence of competing anions and at constant pH. In the absence of competing anions, and at constant pH and ionic strength, the sorption of specifically sorbed anions is known to be irreversible, whereas non-specifically sorbed anions are reversibly sorbed. Irreversibility of sorption has been found for P (Kafkafi et al., 1968; Hingston et al., 1974; Ryden and Syers, 1977) and for other anions (Hingston et al., 1974). Although such desorption reactions are expected to be important in the supply of plant nutrients, there have been few quantitative investigations. Hingston et al. (1974) proposed that the irreversibility of anion sorption arose because of the formation of a bidentate surface complex, and considered the fact that anions such as F were reversibly sorbed was evidence for their proposal. For the desorption of P, Ryden and Syers (1977) have presented evidence that only weakly-held (more-physically sorbed) P is desorbed at constant pH and ionic strength. They state that specific sorption (or chemisorption) of P is completely irreversible, which is in agreement with the definition of a chemisorption reaction (Adamson, 1967).

In this section, competing anions are limited to inorganic anions: competition between inorganic and organic anions may be complicated by the dissolution of oxide surfaces (Earl et al., 1977) and is beyond the scope of this review. In the presence of competing s.s.anions,

considerably more sorbed ion can be desorbed than in the presence of non-specifically sorbed anions such as Cl and N (Evans and Syers, 1971; Obihara and Russell, 1972; Rajan and Watkinson, 1976). Hingston et al. (1967, 1968b) have proposed that anions are desorbed only when competitors can occupy sites in addition to those occupied by the anion, and hence, increase the negative charge of the surface, thereby allowing hydrolysis of the sorbed anion. Consequently, anions such as Cl and N cannot desorb anions such as P because they are non-specifically sorbed and therefore, cannot make the surface more negative.

Qualitative evidence of this hypothesis has been presented by Obihara and Russell (1972), who showed that displacement of sorbed P by Si (or vice-versa) did not proceed until after a certain amount of competing anion was sorbed, i.e., once the surface charge had been increased.

Rajan and Watkinson (1976), however, found that P displaced sorbed Se at low P concentrations at almost a 1:1 ratio, i.e., without any increase in negative charge prior to desorption.

Given that specific sorption of anions appears to involve formation of a strong bond with the surface by ligand-exchange with surface bound $-OH_2^+$ and $-OH$, it would seem likely that desorption of such strongly-held anions by a competitor would also involve ligand displacement. Ligand-displacement reactions commonly occur in coordination chemistry and often involve displacement of one anion by another (Cotton and Wilkinson, 1966). Desorption behaviour can then be explained in terms of the effectiveness of the competing anion to displace the s.s.ion. through the formation of a new bond with the surface metal atom. The ability of s.s. anions to displace other s.s.anions would depend on the respective anions. For example, the fact that S does not desorb P (Evans and Syers, 1971), even though S is considered to be specifically

sorbed and to increase the surface negative charge (Hingston et al., 1967, 1968b, 1972) can be explained in terms of the inability of S to form a stronger bond with the surface metal atoms than does P.

The fact that ions such as P may bond as both chemisorbed and more-physically sorbed species (Holford and Mattingly, 1975; Ryden et al., 1977a), depending on the solution P concentration, however, indicates that careful determination of the form of the anion sorbed is required before the effect of a competing anion can be quantified. Thus, while some workers have found that Si and HCO_3^- can displace P at high P concentrations (Hingston et al., 1968b; Nagarajah et al., 1968), other workers (Chen et al., 1973a) found that, at low solution P concentration, both these anions had little or no effect on P sorption, whereas anions such as F were able to displace P even at low solution concentrations.

1A.7 Sorption Isotherms

A sorption isotherm is a plot of the concentration of a substance sorbed on a solid against the concentration (or pressure) of that remaining in the external phase, and obtained at experimental conditions of constant temperature. Isotherms can yield a sizeable amount of information on the nature of the reaction between the sorbent and the sorbate, and on the heat, free energy, and entropy of the sorption reaction.

For solutes sorbing on solids, Giles et al. (1960) classified isotherm shapes into four main classes (Fig. 1.6). The classes, determined by their initial slope, are: S, L (Langmuir), H (high affinity), and C (constant partition). A theoretical basis for this classification has been developed (Giles et al., 1974), based largely on parameters

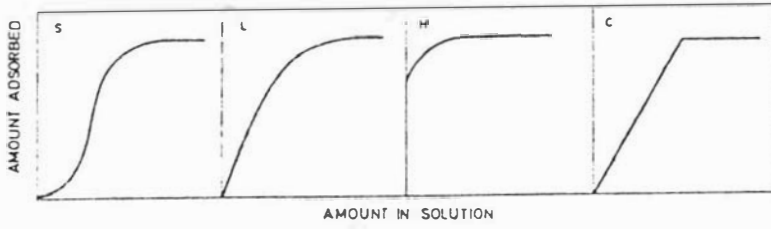


Fig. 1.6 Classification of isotherms for solute sorption.
From Giles (1970).

of the solvent and any second solute, and their effect on the energy of activation for removal of solute from the surface. Type S indicates strong intermolecular attraction between the solute molecules and weaker attraction to the surface. Type L is the common type of isotherm, resembling the standard Langmuir isotherm for gaseous sorption, and assumes that monolayer coverage of the surface limits sorption. Type H is caused by very high solute-substrate affinity, whereas type C, indicating constant partition of solute between solid and solution, is caused by solutes which penetrate into the solid more readily than does the solvent.

Investigations into gas phase sorption have produced several equations which isotherms may follow; the Freundlich, Langmuir, B.E.T., and Temkin equations are obeyed in different situations, depending on the conditions of the experiment and nature of the reacting components. The Freundlich and Langmuir equations are commonly used in sorption investigations with soils and will be discussed here.

1A.7.1 The Freundlich equation

This equation was developed empirically in early sorption studies, Freundlich being one of its main users. The common form is:

$$x/m = k c^{1/n} \quad (1.12)$$

where x and m are the masses of the substance sorbed and sorbent, respectively; c is the concentration of sorbing species in solution when equilibrium is reached; and n is an empirical constant, usually greater than unity. Expressed in logarithmic form, a sorption isotherm will fit at least one linear relationship of slope, $1/n$.

Although the Freundlich equation is based on experimental data, Kipling (1965) has shown that it can be derived for dilute solutions, by combining an expression for the free energy on the surface with the

Gibbs adsorption isotherm. The constant ($1/n$) is related to the monolayer capacity of the surface and also to the difference in free surface energy between a solute-free surface and a surface covered with a monolayer.

1A.7.2 The Langmuir equation

This equation was theoretically derived by Langmuir (1918) for sorption of gases by solids under equilibrium conditions. Langmuir assumed sorption was a dynamic process where a proportion of the gas molecules striking the surface adhere and the remainder rebound into the gas phase. Intermolecular forces are assumed to be negligible and the heat of sorption is assumed to be the same for all sites, and not to depend on the fraction, θ , of sites occupied. Therefore, molecules which strike occupied sites are reflected back into the gas phase, imposing a limiting condition of monolayer sorption. Derivation of the Langmuir equation is based on the rate of sorption equalling the rate of desorption, and may be found in many standard texts (e.g. Brunauer et al., 1966). The final form of the equation for gas sorption is:

$$\theta = \frac{kp}{1 + kp} \quad (1.13)$$

where θ is the fractional surface coverage, p is the equilibrium gas pressure, and k is a constant related to the free energy of sorption. Langmuir assumed k was constant, and for this to be true, the heat of sorption must be constant or nearly constant. Brunauer et al. (1966) have shown that this can hold true without having an energetically uniform surface on which sorbed molecules do not interact with each other. At low θ , sorption takes place on sites possessing the highest energies. As surfaces are usually heterogeneous, a plot of heat of sorption versus θ is usually a decreasing function. Lateral inter-

actions between sorbed molecules increases the heat of sorption. As the number of sorbed molecules increases, the lateral interactions increase, and consequently, a plot of heat of sorption due to lateral interactions versus θ is an increasing function. These two opposing effects, in certain cases, compensate for each other, making the heat of sorption approximately constant. Also, the variation of the entropy term in k may compensate partially for the variation of the enthalpy term. The conditions postulated by Langmuir are obtained more often in solute sorption than in gas or vapour sorption (Giles, 1970). Interactions between adjacent molecules on the surface are relatively weak due to the solvent preventing such interactions, and the solvent-covered surface is less heterogeneous because the solvent is often retained in high energy regions. The limitation of monolayer formation is also more likely to occur for chemisorption than for physical sorption reactions (Brunauer et al., 1966).

For sorption from solution, p in equation (1.13) can be replaced by c , the concentration of solute in solution (strictly speaking, activities should be used, but if solutions are sufficiently dilute, the activity coefficient is assumed to be unity). The fractional surface coverage, θ , is given by x/b , where x is the amount of solute sorbed, and b the amount sorbed at monolayer coverage. Consequently, the Langmuir equation becomes:

$$x/b = \frac{kc}{1 + kc} \quad (1.14)$$

Equation (1.14) may be expressed in several linear forms:

$$c/x = 1/kb + c/b \quad (1.15)$$

$$1/x = 1/kbc + 1/b \quad (1.16)$$

$$x = b - x/kc \quad (1.17)$$

If plotted data conform to one of these linear forms, values for b and k can be obtained from the straight-line plots. The form of the Langmuir equation that is used often depends on the concentration range being studied. Equation (1.16) allows better examination of data at very low concentration values and over a narrow range, because of its reciprocal nature. Equations (1.15) and (1.17) are best suited to studying wider concentration ranges at higher concentration values.

The fact that isotherm data conform to one of these linear forms is not sufficient for establishing that a set of isotherms obeys the Langmuir equation, as pointed out by Brunauer et al. (1966). The b and k values obtained from such plots should be consistent with each other, and b values obtained from the isotherms should correspond to calculated values where it is possible to calculate b .

For ideal conditions, and for sorption of non-electrolytes from solution, it can be shown that k is equivalent to the equilibrium constant of the sorption reaction (Graham, 1953; Aveyard and Haydon, 1973). All the assumptions of the Langmuir derivation, plus the assumption that the activity coefficients of occupied and unoccupied sites are the same, must be made. Therefore, for an ideal system, the standard free energy of sorption, ΔG^0 , can be calculated:

$$\Delta G^0 = -RT \ln k \quad (1.18)$$

For the sorption of ions from solution, however, the relationship is not as simple (Aveyard and Haydon, 1973). In this case, the standard free energy of sorption is a function of both the chemical attractive force and the electrical potential difference between the solid surface and the bulk of the solution, and is defined as:

$$\Delta G = \Delta G_{\text{chem.}} + z_{+,-} e^{-} \psi_d \quad (1.19)$$

where $\Delta G_{\text{chem.}}$ is the free energy of sorption due to non-coulombic attractions, ψ_d is the electric potential in the plane of the sorbed ions (Fig. 1.1B), assuming Stern sorption, $z_{+,-}$ is the charge on the sorbing species, and e^- is the electric charge. The free energy term will not be a constant unless ψ_d is small compared to $\Delta G_{\text{chem.}}$. This may arise through a large $\Delta G_{\text{chem.}}$ and/or ψ_d being suppressed by the presence of a high concentration of non-sorbing electrolyte. If ψ_d varies as sorption proceeds, the effect is to progressively reduce the magnitude of the free energy of sorption as the extent of sorption increases. This is the reason given by Bowden et al. (1973, 1977) for the reduction in ion sorption at high solution concentrations.

When the surface has more than one type of site, the overall sorption isotherm will be a combination of individual isotherms. The isotherm shape will then depend on the sorption energy constant (k) of each site. This is illustrated in Fig. 1.7, which is taken from de Boer (1953). Isotherms A, B, C, and D are drawn for sorbents with uniform k values of 10^{-3} , 10^{-2} , 10^{-1} , and 10^0 , respectively. Isotherms E and F represent sorption at a surface with two types of sorption types or k values. Isotherm E assumes a heterogeneous surface for which k has a value of 10^{-1} over 10% of the surface, but only 10^{-3} over the remainder. Isotherm F assumes a k value of 10^{-1} over half the surface and a k value of 10^{-3} over the other half.

Where a surface has more than one type of site, a satisfactory method of testing the fit of such isotherm data is to treat different sites as distinct surfaces in equilibrium with the same mobile phase. Each surface is assigned a characteristic sorption maximum and sorption energy constant. This method has been successfully applied to P sorption (Muljadi et al., 1966; Syers et al., 1973; Holford et al., 1974; Ryden et al., 1977a) and Mo sorption (Theng, 1971) on soils and soil components.

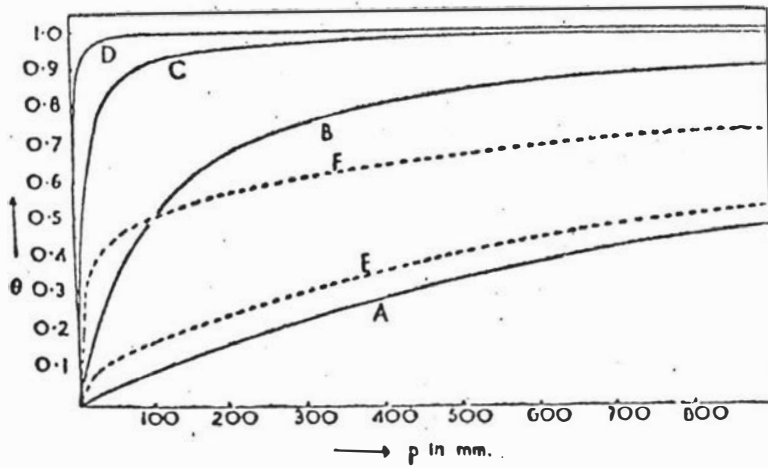


Fig. 1.7 Sorption isotherms generated from the Langmuir equation assuming a uniform surface or k value (isotherms A, B, C, and D), and two distinct populations of sites or k values (isotherms E and F). From de Boer (1953).

1B. Phosphate and Molybdate Sorption by Soils and Soil Components

1B.1 Introduction

In the first part of this review, it has been shown that P and Mo retention in soils appears to involve sorption reactions, primarily at oxide surfaces in soils. General models of anion sorption, including P and Mo, have also been discussed.

To test the validity of generalized models of anion sorption, fit of experimental data from a wide range of workers is required. The sorption of P has been investigated extensively, and several explanations proposed for the nature of the sorption reaction. This review will examine investigations that have lead to a clearer understanding of the P sorption reaction, and critically examine proposed models.

Investigations and explanations of Mo sorption data have often been based on P sorption data. Thus, Mo sorption will be examined and the validity of comparisons between P and Mo sorption discussed. The time dependence of both P and Mo sorption also will be examined, both separately and by comparing the behaviour of the two anions.

1B.2 Sorption of P by Soils and Soil Components

1B.2.1 Use of sorption equations for evaluating P sorption

The Freundlich and Langmuir equations has been used in evaluating P sorption isotherms. In this review, consideration will only be given to studies that have used sorption equations in an attempt to understand P sorption mechanisms. The Langmuir equation can be particularly helpful as it allows evaluation of a sorption maximum and a relative sorption energy.

Fit of sorption data to single Freundlich (Low and Black, 1950;

Kuo and Lotse, 1974), or Langmuir (an extensive list of references is given by Syers and Williams, 1977), equations has been taken to indicate that a single sorption reaction operates for P sorption by soils and soil components. Many of these studies, however, were made over large, and often high, concentration ranges. For example, Kuo and Lotse (1974) fitted P sorption data on goethite, over the concentration range of 30 - 3000 $\mu\text{mol l}^{-1}$, to a single Freundlich equation. Kitchener (1965) has pointed out that because the Freundlich equation frequently describes sorption on such heterogeneous surfaces as that of charcoal, it is particularly suited to sorption at a series of sorption sites of different sorption energies. Sorption data have often been found to deviate from a single Langmuir equation (Olsen and Watanabe, 1957; Gunary, 1970), and this has lead some workers to dismiss the use of the Langmuir equation in studying P sorption from soil solution (Hsu and Rennie, 1962; Gunary, 1970; Bache and Williams, 1971). The fact that deviations from a single Langmuir equation, especially at low concentrations, can be accounted for by fitting sorption data to more than one equation tends to over-ride such suggestions. Also, the fact that multiple Langmuir equations appear to be obeyed by a wide range of soils indicates that much of the early work, where soils were found to obey only a single Langmuir equation, could be due to insufficient data points at low concentration (Syers et al., 1973). Consequently, much of this work is not particularly useful in understanding the mechanism of P sorption.

By inspection of the sorption isotherm, Muljadi et al. (1966) split the isotherms for sorption of P by synthetic soil components into three regions, each with distinct Langmuir equations. These regions were assigned to separate chemical reactions. The method of inspection has been criticised by Syers et al. (1973) because it underestimates

the magnitude of sorption in each region at low solution concentrations. Using the same method as Muljadi et al. (1966), Chen et al. (1973a) split P sorption isotherms for kaolinite but suggested that the poor agreement of calculated and experimental data at low concentrations indicated that their region I may consist of two Langmuir equations. The data of Muljadi et al. were obtained at relatively high concentrations ($> 10^{-4}$ M P) and this could result in the method overlooking high energy regions which would be occupied first at low concentrations.

For concentrations less than $600 \mu\text{mol l}^{-1}$, P sorption data for soils deviating from a single Langmuir equation have been found to fit two Langmuir equations by Syers et al. (1973), Holford et al. (1974), and Rajan and Fox (1975), and for soil components by Rajan et al. (1974), Rajan (1975), and Rajan and Perrott (1975). In many of these investigations, however, fit of data to two distinct Langmuir equations was obtained by assuming the existence of two types of sites and adjusting the Langmuir equation parameters until the calculated isotherms agreed with the experimental. The sorption energy constants (k) of the two Langmuir equations are generally widely different (as opposed to those found by Muljadi et al. (1966) which were very similar in value), suggesting the existence of at least two different types of sites for P sorption. It is noteworthy that the range of k values obtained for each region by Syers et al. (1973), Holford et al. (1974), and Rajan and Fox, (1975) are remarkably comparable, considering that the isotherms were determined on soils from completely different geographical areas. The k values obtained for the second region by each of these workers are of similar magnitude to those obtained by Muljadi et al. (1966) for P sorption by aluminous soil

components, over an equivalent concentration range. For P sorption by synthetic allophanes, Rajan and Perrott (1975) obtained k values that were lower than the equivalent k values obtained for soils by the other workers, but they were still of the same order of magnitude.

The implications of the two-term Langmuir equations to the mechanism of P sorption was not thoroughly investigated by any of the above workers. Syers et al. (1973) and Holford et al. (1974) suggested that the high and low energy regions could correspond to P sorption on different soil components, although no evidence was presented to support this hypothesis. Rajan (1975) and Rajan and Perrott (1975) suggested that sorption in regions I and II corresponded to ligand-exchange of P with $-\text{OH}_2^+$ and $-\text{OH}$, respectively, and presented OH^- release data that were said to confirm the hypothesis, although the non-integral ratio of P sorbed: OH^- release places some doubt as to whether the data support the mechanisms.

Syers et al. (1973) found that at low concentrations ($<10 \mu\text{mol l}^{-1}$), two Langmuir equations did not sufficiently describe the experimental data, suggesting the presence of further sites of high affinity for P. This has also been suggested by Chen et al. (1973a) for P sorption by aluminous soil components. Schwertmann and Knittel (1973) reported the existence of two, possibly three, regions obeying Langmuir equations at concentrations less than 10^{-4}M for P sorption by several German soils. For P sorption by several New Zealand soils and also soil components, Ryden et al. (1977a) reported the existence of three Langmuir regions over the concentrations range $0 - 300 \mu\text{mol l}^{-1}$. In contrast to other workers, who have assumed a number of different sites, Ryden et al. obtained three different regions by resolution of the experimental data. The first region obeying a Langmuir equation

was at lower concentrations than previously investigated ($<1.5 \mu\text{mol l}^{-1}$). Ryden et al. (1977a) also presented charge, pH, and ionic strength relationships that corresponded to each region of sorption and were able to propose definite mechanisms of P sorption for each region. The Langmuir k values obtained enabled calculation of free energies of sorption for each region. From the magnitude of these free energies of sorption, regions I and II were considered to involve chemisorption reactions, and region III to involve a more-physical sorption reaction. The mechanism proposed by Ryden et al. will be discussed the following section.

1B.2.2 Mechanisms of P sorption

Although use of the Langmuir sorption equation has indicated the existence of two, and probably three, regions of P sorption at concentrations less than $300 \mu\text{mol l}^{-1}$, there have been few quantitative investigations of the mechanisms of P sorption over this concentration range. The mechanisms proposed have been based primarily on the effects of pH on P sorption (Hingston et al., 1967, 1968b; Breeuwsma and Lyklema, 1973) and release of hydroxyl ions during P sorption (Breeuwsma and Lyklema, 1973; Rajan et al., 1974; Rajan, 1975), although more-recent studies considered ionic strength effects (Helyar et al., 1975; Ryden et al., 1977a) and calculation of sorption energies (Huang, 1975; Ryden et al., 1977a).

The specific sorption of anions has been discussed (Section 1A.3.3.2) and specific sorption of P is assumed to involve ligand-exchange of P with surface ions coordinated to the central metal atom of hydrous oxide surfaces. Ligand-exchange has been implied in most studies (Hingston et al., 1967, 1968b; Breeuwsma and Lyklema, 1973; Rajan et al., 1974; Ryden et al., 1977a), although the

sorption model of Bowden et al. (1973, 1974, 1977), as discussed previously, proposed that P sorption occurs in the Stern layer of the double layer, and presumably does not involve ligand-exchange. Also sorption in the region III proposed by Ryden et al. (1977a) would not involve ligand-exchange. For sorption at a hydrous oxide surface, ligand-exchange involves formation of a strong covalent bond, and hence could be termed chemisorption (Breeuwsma and Lyklema, 1973; Ryden et al., 1977a).

The P sorption mechanisms proposed by Hingston et al. (1967, 1968b, 1972) have been discussed in section 1A.5. Although the apparent sorption maxima and/or breaks in sorption envelopes at pH values corresponding to pKa values of P species have been observed for P sorption by soils (Obihara and Russell, 1972) and soil components (Breeuwsma and Lyklema, 1973), no such breaks have been observed by Chen et al. (1973a) and Huang (1975). The mechanisms proposed by Hingston and co-workers presumably imply that at pH values less than pH (p.z.c.), P sorption occurs by ligand-exchange of P with $-OH_2^+$, plus ligand-exchange of P with $-OH$ by acid dissociation of the sorbing species to provide H^+ which react with surface $-OH$ to give OH_2^+ , enabling ready displacement by the sorbing anions. The fact that P sorption can occur at negatively-charged surfaces is explained by this second ligand-exchange reaction. The condition that P sorption involves an overall increase in negative charge, assumed by Hingston et al., but never proven, has been shown by Ryden et al. (1977a) not to be a necessary requirement for P sorption.

Data for the release of OH^- subsequent to P sorption by haemitite (Breeuwsma and Lyklema, 1973), hydrous alumina (Rajan et al., 1974; Rajan, 1975), and short-range order aluminosilicates (Rajan and Perrott,

1975) have been used to propose P sorption mechanisms. Breeuwsma and Lyklema found that over the pH range of 4.0 to 9.0, the ratio (R) of the moles of H^+ required to maintain constant pH during P sorption to the amount of P sorbed, increased steadily from a value close to zero to one approaching unity (Fig. 1.8A). They found that R was independent of the P concentration in solution. Contradictory to this, Rajan et al. (1974) found that the ratio R increased from near zero to approximately unity as the amounts of P sorbed on hydrous alumina, at pH 5.1 and 6.2, increased (Fig. 1.8B). Rajan (1975) found that R had a constant value of 1.44 (Fig. 1.8C) as P sorption on hydrous alumina, at pH 8.5, increased up to values where disruption of the polymeric substrate seemed likely. Both Breeuwsma and Lyklema (1973) and Rajan et al. (1974) have proposed ligand-exchange reactions involving exchange of $H_2PO_4^-$ and HPO_4^{2-} with $-OH_2^+$ and $-OH$, the change in R values with (a) pH, being explained by Breeuwsma and Lyklema as due to a change in both the predominant P species in solution and the predominant surface exchange group, as pH increased, and (b) P sorbed, explained by Rajan et al. as being due to ligand-exchange of the positively-charged $-OH_2^+$ at low concentration and the neutral $-OH$ at higher concentrations. Rajan (1975) proposed that an R value greater than unity obtained for P sorption on hydrous alumina could be due to a reaction involving formation of a binuclear aluminium phosphate complex. The use of data based on H^+ consumption to keep constant pH during P sorption appears to be insufficient evidence on which to base mechanisms. There is no means of differentiating between H^+ consumption and OH^- release, and the R values obtained are often non-integral, enabling different combination of mechanisms to be proposed.

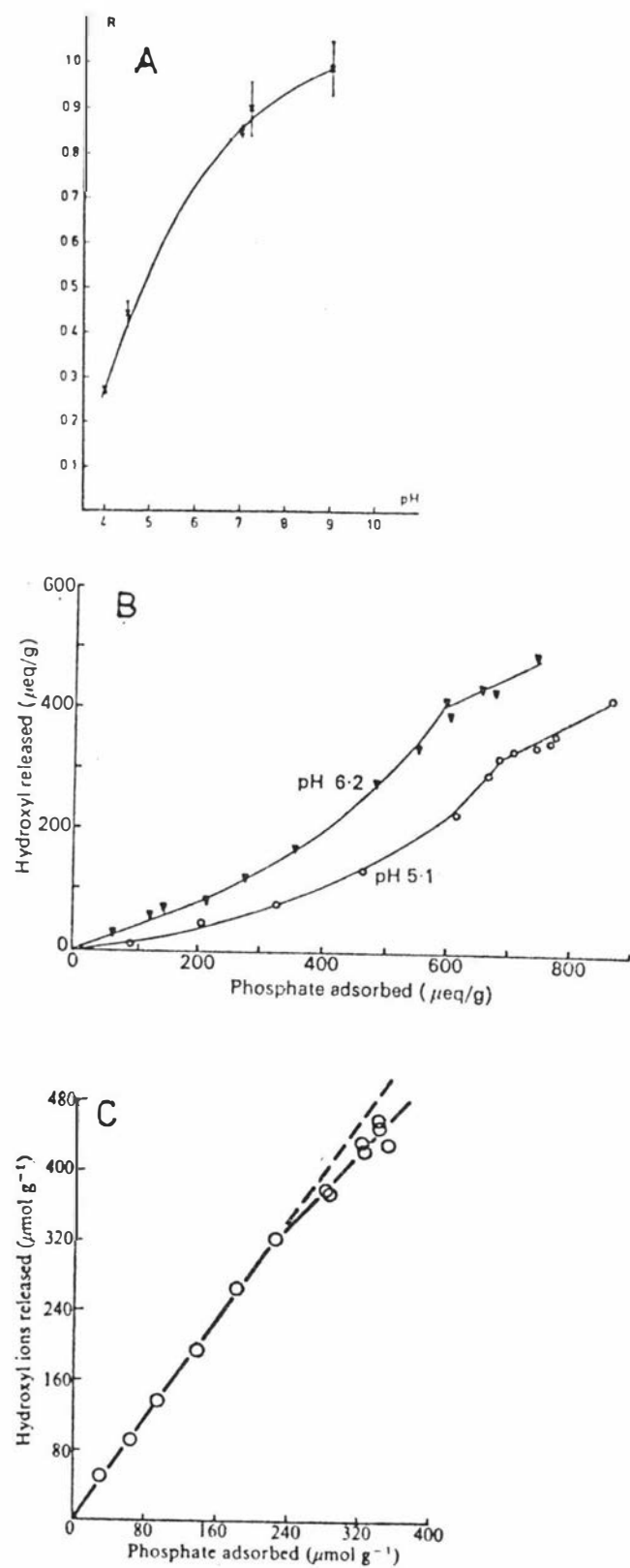


Fig. 1.8 Relationships between acid consumed to maintain constant pH during sorption, and pH (A), or P sorbed (B and C). A = relationship between the ratio R (mole:mole) of H^+ consumed:P sorbed on haemitite and pH; from Breeuwsma and Lyklema (1973). B = relationship between hydroxyl released (H^+ consumed) and P sorbed by hydrous alumina at pH 5.1 and 6.2; from Rajan et al. (1974). C = relationship between hydroxyl released (H^+ consumed) and P sorbed by hydrous alumina at pH 8.5; from Rajan (1975).

The study of Ryden et al. (1977a) is one of the first to link P sorption by soils with that by soil components. As discussed earlier, they found that P sorption obeyed a three-term Langmuir equation. Sorption of P in region I did not cause an increase in pH, changed the surface charge (Fig. 1.9), and was dependent on both pH and ionic strength; sorption in region II did not change surface charge, caused an increase in pH and was independent of both ionic strength and pH; and sorption in region III increased surface charge, was independent of pH, and was dependent on ionic strength. Based on these data, plus free energies of sorption obtained from Langmuir equations, sorption in regions I and II was assigned to ligand-exchange chemisorption of P with -OH_2^+ and -OH , respectively, whereas region III was assigned to a "potential-determining, more-physical sorption" at a ferric phosphate-like surface subsequent to sorption in regions I and II. The use of "potential determining" is perhaps contradictory, in that sorption involving ligand exchange with -OH_2^+ can also be classed as potential determining because it affects the charge on the surface. Sorption in region III could possibly be equated with the Stern model of sorption proposed by Bowden et al. (1973, 1974, 1977), whose experimental data are mainly in the same concentration range as that of region III of Ryden et al. (1977a).

The free energy of sorption obtained by Ryden et al. (1977a) for their region III is very similar to that calculated by Huang (1975) for the single region he found to describe P sorption by hydrous Al oxide. Huang studied P sorption in the solution concentration range of 10^{-4} M to 10^{-3} M P, which is within the range of region III of Ryden et al. By dividing the overall free energy of sorption into electrostatic, solvation, and chemical interaction terms, Huang (1975)

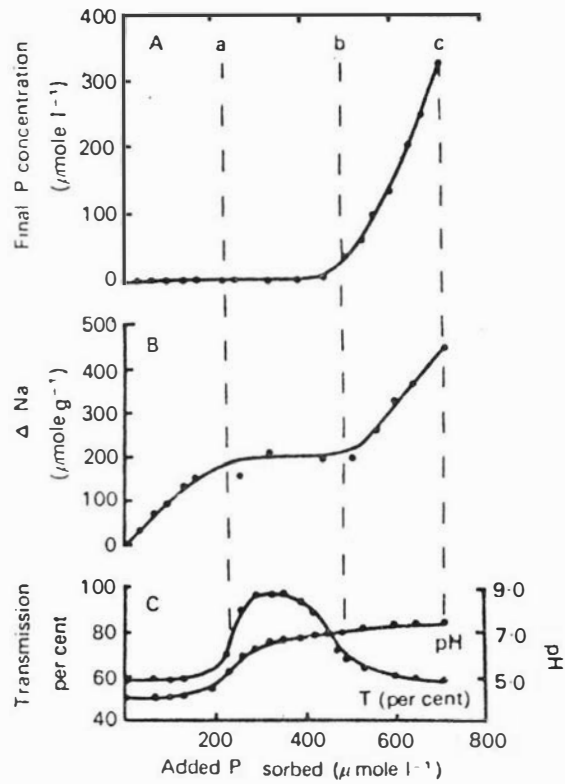
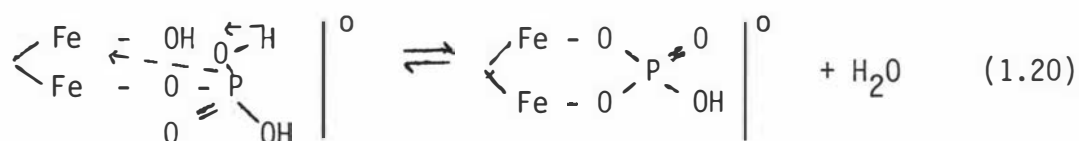


Fig. 1.9 Relationship between P sorbed by Fe gel and the double layer charge, as reflected by Na uptake (B), and transmission (C). From Ryden et al. (1977a).

showed that the chemical free energy term, which had a constant value of -16 kJ mol^{-1} , dominated the overall free energy, which had an approximate value of -19 kJ mol^{-1} . Thus, Huang concluded that specific chemical sorption was important in this concentration range.

Whereas most studies of P sorption mechanisms have concentrated on solution measurements, recent work has investigated the structure of the solid phase subsequent to P sorption (Russell et al., 1974, Parfitt et al., 1975, 1976; Parfitt and Atkinson, 1976). From infrared (i.r.) spectra of crystalline goethite, which has a surface structure that is well-defined, Russell et al. (1974) and Parfitt et al. (1976) found, over the pH range of 3.5 to 9.0, that P appeared to bond as a bidentate ligand to adjacent Fe atoms by replacement of adjacent A-type hydroxyls, i.e., hydroxyls singly-coordinated to Fe atoms. The well-defined structure of goethite allowed differentiation in the i.r. spectra of the different -OH groups and led to the conclusion that A-type hydroxyls were replaced. These studies have been extended to other Fe minerals, including "ferric hydroxide" gel (Parfitt et al., 1975) and also to gibbsite, and it has been concluded that P bonds as a bidentate ligand on all such surfaces. Although the initial i.r. studies were made on oxide surfaces that were dried subsequent to P sorption, recent i.r. spectra (Parfitt and Atkinson, 1976) on wet goethite films have found spectra similar to those for the dried complexes and have confirmed that the bidentate ligand structure was not an artefact of the drying process. The P-oxide surface complexes were, however, prepared in solution at solution P concentrations that were not detectable. There is no guarantee, therefore, that at higher solution P concentrations a different form of sorbed P could exist in conjunction with the bidentate groups. Possible formation of

binuclear complexes has been included in P sorption mechanisms by Rajan (1975) and Ryden et al. (1977a). Ryden et al. (1977a) showed that formation of a binuclear complex would not affect the observed charge and pH effects, but Rajan (1975) postulated that formation of the binuclear complex involved OH^- release. From the charge relationships of P sorption (Ryden et al., 1977a) and the i.r. spectra of sorbed P groups (Parfitt et al., 1976; Parfitt and Atkinson, 1976), it would appear that the formation of a binuclear complex subsequent to initial displacement of $-\text{OH}_2^+$ or $-\text{OH}$, involves reaction of a proton of the sorbed species with surface $-\text{OH}$:



Such a displacement reaction would partly explain the observations of Hingston et al. (1967, 1968b) that P sorption was at a maximum when protonated sorbing species were present.

In conclusion, it appears that P sorption by soils and oxides, at low concentrations ($< 10 \mu\text{mol l}^{-1}$) involves ligand exchange with coordinate $-\text{OH}_2^+$ and $-\text{OH}$ and possible formation of binuclear complexes. At high concentrations, formation of a weaker complex between P and the surface appears likely.

1B.3 Sorption of Mo by Soils and Soil Components

In contrast to P, the sorption of Mo by soils and soil components has not been studied extensively. Early investigations (Barshad, 1951; Stout et al., 1951) showed that Mo was strongly held by soils and soil clays. Subsequently, sorption isotherms and the effect of pH on Mo sorption have been evaluated. As discussed in section 1A.2, the dominant soil surfaces involved in Mo sorption appear to be hydrous

metal oxides. Consequently, many sorption investigations have involved pure oxides as the sorbent, although the well-defined surface and double layer structure of such oxides have not been utilized in any detailed investigations. Many workers have relied on apparent similarities between Mo and P sorption to predict Mo sorption mechanisms, without obtaining detailed data that would enable confirmation of the mechanisms.

1B.3.1 Sorption isotherms for, and the effect of pH on, Mo sorption

Many workers have shown that maximum sorption of Mo by both soils and soil components occurs at acid pH values (Barshad, 1951; Jones, 1956, 1957; Reisenauer et al., 1962; Reyes and Jurinak, 1967; Hingston et al., 1968b, 1972; Tuev, 1969; Theng, 1971; Gonzalez et al., 1974), with maximum sorption usually occurring in the pH range 2.5 to 4.5, depending on the sorbent used. The fact that the pH of maximum sorption is near to the pK_{a2} of molybdic acid (4.0; Sillen and Martell, 1971) has been taken as evidence (Theng, 1971; Gonzalez et al., 1974) that Mo bonds to soil surfaces by a mechanism similar to that proposed by Hingston et al. (1967, 1968b, 1972). Maximum sorption, however, is often observed at pH values less than 4.0 (Jones, 1957; Tuev, 1969) and depends on the oxide sorbent (Jones, 1957; Reisenauer et al., 1962; Tuev, 1969). At acid pH values close to 7.0, and above pH 7.0, Mo sorption falls off markedly (Jones, 1957; Reyes and Jurinak, 1967), and above pH 8.5, very small amounts of Mo are sorbed.

The Mo sorption isotherms determined in almost all studies cover a wide range of concentration, with very little data available at low

final solution concentrations ($< 1.0 \mu\text{mol l}^{-1}$). Although analytical determinations are often difficult in this range, the Mo concentrations in the soil solution commonly correspond to this range and thus, it is most important to have data at such concentrations.

Sorption of Mo has been shown to fit both the Freundlich (Reisenauer et al., 1962; Vlek and Lindsay, 1977b) and Langmuir (Reyes and Jurinak, 1967; Theng, 1971; Gonzalez et al., 1974) equations. Figures 1.10 and 1.11 show data plotted according to the different sorption equations and illustrate the wide concentration range over which attempts have been made to fit the equations. Both Reisenauer et al. (1962) and Vlek and Lindsay (1977b) found that Mo sorption did not conform to a simple Langmuir equation over a final concentration range of $0 - 10 \mu\text{mol l}^{-1}$, but found that data over this range appeared to conform to the Freundlich equation. Sorption data have been fitted to multiple Langmuir equations for haemitite (Reyes and Jurinak, 1967) and soil clays (Theng, 1971). At pH 4.0, Reyes and Jurinak found two distinct Langmuir regions (Fig. 1.11), one reaction being essentially complete at a final solution concentration of $100 \mu\text{mol l}^{-1}$, and the other being essentially complete at $550 \mu\text{mol l}^{-1}$. Theng (1971) found that Mo sorption by two allophanic clays each followed a simple Langmuir equation in the concentration range of $2.0 - 50 \mu\text{mol l}^{-1}$, whereas a layer-lattice clay showed two distinct regions of sorption in the same range, each region conforming to a different Langmuir equation. At pH 7.8 for haemitite, and pH 5.5 for the lattice clay, only one Langmuir equation was observed in both studies.

The absence of good, reliable data at low concentrations in all these studies makes it difficult to assess the validity of using the Langmuir equation to resolve experimental data. For example, in

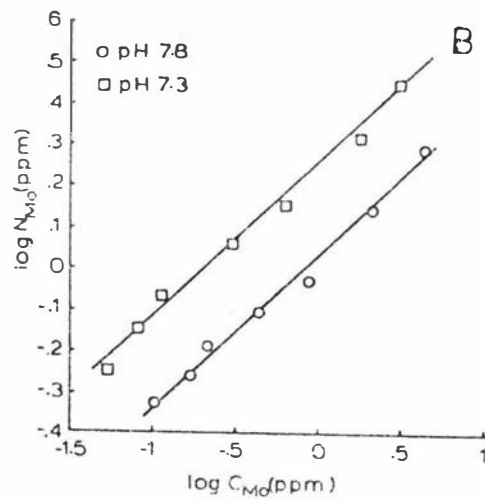
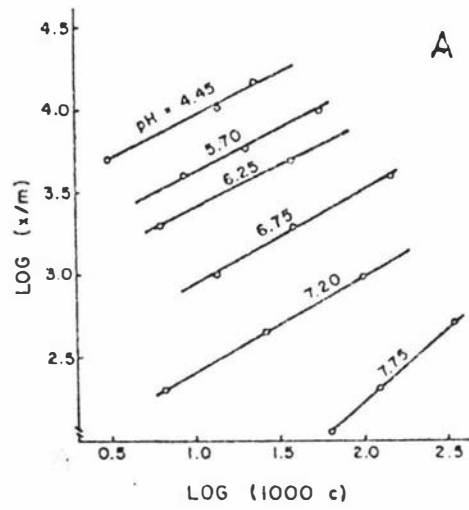
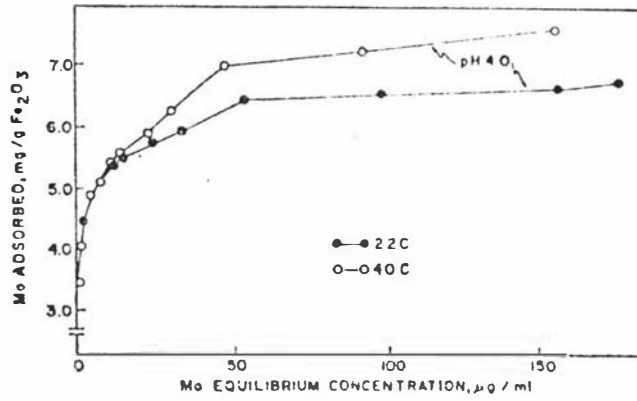
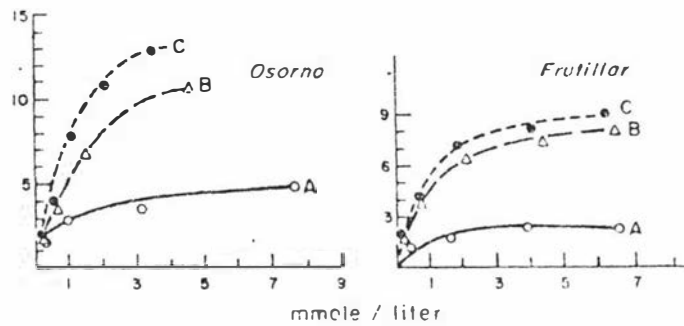


Fig. 1.10 Isotherms for sorption of Mo by hydrous Fe oxide (A) and several Colorado soils (B) evaluated by using the Freundlich equation. From Reisenauer et al. (1962) (A), and Vlek and Lindsay (1977b) (B).



A



B

Fig. 1.11 Isotherms for sorption of Mo by haemitite (A) and two Chilean soils (B) evaluated by using the Langmuir equation. From Reyes and Jurinak (1967) (A), and Gonzalez et al. (1974) (B).

Fig. 1.11, Gonzalez et al. (1974) used only five points between concentration limits of 0.2 and $70 \mu\text{mol l}^{-1}$ to obtain b and k values from the Langmuir equation. As discussed previously, extension of studies of P sorption to very low concentrations enabled fit of data to two or three equations, whereas previous studies at high concentration ranges had not found these relationships. The form of the Langmuir equation used in studies of Mo sorption has generally been equation (1.15), which is best for studying a wide range of concentration, rather than equation (1.16), which allows better investigation at low, and over a narrow range of, concentrations.

1B.3.2 Mechanisms of Mo sorption

Based, as they are, on limited sorption and pH data, many of the proposed mechanisms are very speculative and often rely on similarity with other data determined for P sorption. Reisenauer et al. (1962) have made the most comprehensive study, although much of their data were obtained at high final solution Mo concentrations. They found that sorption of Mo by hydrous Fe oxide was accompanied by a stoichiometric release of 2OH^- ions and one molecule of water, although at low concentrations ($< 0.5 \text{ mmol l}^{-1}$), deviations from this simple stoichiometry appear in their data. These authors concluded that Mo sorption involved the following reaction:



Obviously (1.21) is a very simple mechanism, giving no indication of the nature of the sorption reaction or the surface groups involved.

Reyes and Jurinak (1967) concluded that Mo sorption by haemitite, at acid pH values, involved two distinct reactions, with each following a different Langmuir equation. One reaction involved sites covering 80% of the surface, and the other involved sorption at the other 20%.

From a comparison of the surface areas of potential sorbing species, and potential sorbing sites (OH groups), they considered that the tetrahedral, $H_xMoO_4^{x-2}$, was the sorbing anion, but no precise mechanisms were given. They did, however, conclude that sorption of polymeric forms of Mo was not occurring, by comparing observed and calculated sorption maximum values.

Barrow (1970), Theng (1971), and Gonzalez et al. (1974) have all concluded that Mo is sorbed at oxide surfaces by the mechanisms proposed by Hingston et al. (1967, 1968b, 1972). Gonzalez et al. (1974) point out, however, that many of the results are only qualitatively consistent with the theories of Hingston et al., i.e., sorption maxima at or near pKa values. Barrow (1970) has shown that the change in Mo sorption with pH could be predicted reasonably accurately by assuming that both proton donor, $HMoO_4^-$, and proton acceptor, MoO_4^{2-} , are necessarily present at the sorbing surface, as proposed by Hingston et al., but then goes on to point out that good predictions can also be obtained if it is assumed that Mo sorption depends only on the concentration of $HMoO_4^-$. The limitations of the theories of Hingston et al. have been discussed previously.

In conclusion, studies of Mo sorption have only been semi-quantitative and do not allow any conclusive mechanisms to be proposed. Resolution of sorption isotherms, using the Langmuir or Freundlich equations, has not been integrated with other experimental data, and due to the wide concentration ranges studied, fit of data to the sorption equations is very inconclusive. Although many investigators assume a similarity between Mo and P sorption, there has been no detailed experimental investigation of the similarities. The assumption that Mo and P sorption mechanisms are similar requires quantitative

investigation, with more emphasis on the nature of the Mo sorption reaction, which appears to be poorly understood in comparison with that for P sorption.

1B.4 Time-Dependent P and Mo Sorption

In the preceding discussion, no distinction was made between the adsorption and absorption of anions, where adsorption refers to retention of anions at external soil surfaces, and absorption of ions refers to retention at internal soil surfaces, presumably by movement of the adsorbed ions through external surfaces. When discussing retention, with respect to retaining surfaces, and the mechanisms of retention, no distinction was necessary between adsorption and absorption and the overall reaction was referred to as sorption. In discussing the time-dependence of P and Mo sorption, distinction will be made between the two types of sorption.

1B.4.1 Time-dependence of P sorption

That P sorption continues over long-time periods is well known (Kurtz et al., 1946; Hsu, 1964; Fox and Kamprath, 1970; Barrow and Shaw, 1975a, b; Ryden and Syers, 1975). This time-dependent sorption continues if the soil is in contact with large volumes of solution or at normal soil moisture contents. The pattern of P retention is generally a fast initial uptake followed by a slow, continuing uptake. Following the initial fast uptake, an apparent steady state may be reached; sorption investigations are often made during this steady-state period (Rennie and Mckerchar, 1959; Muljadi et al., 1966; Chen et al., 1973a). At these short-time periods, however, a true equilibrium situation is not reached (Ryden and Syers, 1975; Munns and Fox, 1976), and use of the Langmuir equation, which is derived for an equilibrium

situation, is questionable. While such considerations are frequently overlooked, Ryden et al. (1977a) have shown that P sorption appears to obey similar Langmuir equations at 40 hr and equilibrium.

The decrease in exchangeability of P (Talibudeen, 1958) and extractability of P (Kafkafi et al., 1967; Barrow, 1974) with time is well known. Barrow and Shaw (1975a, b) have shown that both are related to the continuing sorption reaction.

Most workers appear to agree that the ongoing P sorption reaction appears to involve a shift in the form of P held at the surface from a loosely-held to a more-strongly held type (Talibudeen, 1958; Barrow, 1975a, b; Ryden et al., 1977b), but the nature of the shift is often subject to speculation. Barrow and Shaw (1975a, b) have divided soil P into three compartments: solution P, adsorbed P, and P tightly held in a form not in direct contact with the soil solution.

Conversion of adsorbed P to the tightly-held form has been proposed to involve the formation of precipitated P minerals (Larsen and Widdowson, 1971; Chen et al., 1973b; Talibudeen, 1974). Studying P sorption on Al minerals, Chen et al. (1973b) produced electron micrographs of the proposed new mineral form of P, although these workers were unable to explain why seeding the solution with crystalline Al phosphate did not increase the rate of the reaction, as would be expected for the proposed precipitation reaction.

Other workers have proposed that the continuing sorption reaction (and related decrease in extractability of P) is a result of a shift in sorbed P from a monodentate to a bidentate form (Kafkafi et al., 1967; Hingston et al., 1974; Barrow and Shaw, 1975b; Munns and Fox 1976) although such a mechanism has no experimental justification. Although the formation of bidentate P complexes appears to be highly likely

(Parfitt et al., 1975), it is difficult to understand how a change from monodentate to bidentate bonding would allow further P sorption sites to be formed, enabling continuing P sorption.

Ryden et al. (1977b) have shown that 10^{-1} M NaOH completely recovers the P sorbed on soils and soil components during short times (<48 hr), but at longer-time periods complete recovery is only obtained by extraction with CDB reagent or HCl digestion of soil components. It is considered that NaOH extracts surface-bound P (Williams et al., 1967) and Ryden et al. proposed that the increase in CDB-P at constant NaOH-P was due to the movement of chemisorbed P into short-range order mineral structures, i.e., an absorption reaction. This absorption reaction was proposed to require the presence of short-range order material, as synthetic goethite, with negligible amounts of short-range order material, showed no increase in sorbed P at times greater than 48 hr. Although the fractionation procedure used was somewhat empirical, the increase in CDB-extractable P would seem to disprove that the slow reaction involved a change from mono- to bidentate bonding, as both forms should be extracted with NaOH. Ryden et al. (1977b) proposed that the absorption of chemisorbed P resulted in regeneration of surface sites, thus allowing a shift of more-physically sorbed P to chemisorbed P and allowing a continued uptake of P. This shift in the form of P sorbed (more-physical to chemisorbed) accounted for the decrease in isotopic exchangeability and desorption of P with time (Ryden and Syers, 1977).

1B.4.2 Time-dependence of Mo sorption

The sorption of Mo over long periods of time appears to follow a very similar pattern to the sorption of P. The amount of Mo sorbed, after an initial rapid uptake, slowly increases with time (Reyes and

Jurinak, 1967; Gorlach et al., 1969; Barrow, 1970; Barrow and Shaw, 1975c). With increasing time of contact between soil and Mo, the added Mo becomes more difficult to desorb with solutions at iso-pH and ionic strength (Gorlach et al., 1969), by anions such as P and HCO_3^- (Gorlach et al., 1969; Jones and Smith, 1972; Barrow, 1973) or by hydroxyl (Smith and Leeper, 1969; Barrow, 1973).

Barrow and Shaw (1975c) found that the decrease of Mo in soil solution and in the effectiveness of Mo for plant growth could be explained by empirical equations similar to those for P. Using the same approach as that used for P, Barrow and Shaw (1975c) compartmentalized Mo into three forms: solution Mo, sorbed Mo in equilibrium with solution Mo, and tightly-held Mo not in contact with solution Mo. Although such a classification enables rationalization of the observed behaviour, it does not give a clear understanding of the actual mechanism of time-dependent sorption. Smith and Leeper (1969) and Barrow (1973) have observed decreases in NaOH-extractable Mo when Mo was incubated with soil. By analogy with P, it is expected that surface-bound Mo is extracted with NaOH. Smith and Leeper (1969) and Barrow and Shaw (1975c) have proposed that the decrease in NaOH-extractable Mo signifies that sorbed Mo is being reorganised at the surface to less soluble forms. Smith and Leeper (1969) showed that much of the Mo not recovered by NaOH was extracted by CDB reagent, as found for P by Ryden et al. (1977b), and stated that this confirmed that Mo was being converted to more crystalline forms at the colloid surfaces. Barrow and Shaw (1975c) proposed that the surface reorganization may involve changing the Mo-surface bond from monodentate to bidentate. Such a change in bond would be expected to depend on pH. Barrow and Shaw (1975c), however, found that the time-dependent sorption

of Mo was independent of pH, which places doubt on their suggested mechanism.

In conclusion, reasons for the time-dependent sorption of Mo are not well understood. There is a definite need for investigations into extractants that remove a known fraction of soil Mo, so that the origin of the time-dependent sorption can be better identified.

1B.5 General Conclusions and Research Needs

Although each Section of this Chapter has included a discussion of the implications and the weaknesses of previous work, a general overview is valuable, particularly with regard to evaluating future research needs.

The importance of oxides of Fe and Al in anion sorption has received considerable attention, but there has been little detailed investigation into comparisons between sorption by these oxides and by soils. This is especially so for Mo, where there have been few, if any, detailed studies of Mo sorption by soils and soil components at realistic final solution concentrations. It has been shown that the oxide surfaces are well characterised, and this would appear to be of use in any mechanistic investigations.

Although it has been shown that sorption isotherms may give valuable information on the nature of the sorption reaction, isotherms for the sorption of Mo have only been obtained at unrealistically high solution concentrations. Evaluation of Mo sorption mechanisms may also allow rationalisation of more practical Mo behaviour in soils, such as the effects of lime on availability of both native and added Mo.

The nature and mechanisms of P sorption appear to be well understood, but there have been few detailed comparisons of P and Mo sorption mechanisms. Obtaining good relationships between P and Mo

sorption may allow the well-detailed information for P sorption to be used in evaluation of Mo sorption mechanisms. It has been shown that there is some disagreement about the nature of the reaction between oxide surfaces and anions, and detailed studies of individual anions are needed before general anion mechanism proposals can be evaluated.

This review has shown that recent investigations have given insight into the slow reaction between P and soil with regard to the occurrence of an absorption reaction. Similar patterns have been observed for Mo sorption, although again there has been little detailed research.

It has been shown that competition and desorption have not been studied extensively. Evaluation of the sorption mechanisms of anions in the absence of competitors may allow rationalisation of the effects of competitors, and desorption by other anions, on anion sorption. This may be particularly valuable with regard to the behaviour of Mo and P in the field situation, where large amounts of P are added to soils along with, or subsequent to, very small additions of Mo.

In subsequent Chapters, some of the research areas outlined above are investigated. Four soils, both topsoils and subsoils, were chosen in order to obtain detailed information on Mo sorption and also to compare the importance of soil components in Mo and P sorption. The effects of time and ionic strength on Mo sorption are investigated in order to establish reliable experimental conditions for subsequent studies. The use of the Langmuir equation is evaluated for interpretation of Mo sorption isotherms, both at equilibrium and during short-time periods. The data obtained are examined for information on the nature of the Mo sorption reaction.

A comparison of Mo and P sorption is also made, both by soils and

synthetic soil components, and similarities and differences discussed. The mechanism of Mo sorption is investigated, based on the implications of the fit of data to the Langmuir equation, similarities between Mo and P sorption, the effect of pH and ionic strength on Mo sorption, and the charge relationships of Mo sorption.

The mechanisms proposed for Mo sorption (and those for P sorption) are then used, in conjunction with the Langmuir equation, to rationalize competitive sorption between Mo and P. Desorption of Mo by solution P and extraction of Mo with several reagents, as a function of time after the addition of Mo are investigated and changes in these parameters are discussed in terms of the form of sorbed Mo and also the slow, continuing reaction between added Mo and soils.

In order to obtain data which are more relevant to the field situation, the effect of previously added P and lime on Mo sorption is studied and the behaviour explained in terms of the effects of P and lime on the forms of Mo sorbed, using information obtained previously in the study.

CHAPTER 2

SOILS, GENERAL METHODS, AND SOIL PROPERTIES

2.1 Introduction

The sorption of Mo is often assumed to involve a similar mechanism to that of P (Hingston et al., 1967, 1968b, 1972; Theng, 1971). Few comparisons of the sorption of these two anions by contrasting soils, however, have been made.

The relative contribution of different soil properties to P sorption has been investigated extensively and the important parameters established (Saunders, 1965; Syers et al., 1971). There have been few studies of the relationship between Mo sorption and soil properties, pH and the amounts of citrate-dithionite-bicarbonate-extractable components being the only soil properties examined in relation to Mo sorption (Jones, 1957; Barrow, 1970; Theng, 1971). Relative differences between the sorption of P and Mo have been ascribed to pH effects (Barrow, 1970), but the significance of other soil properties is not known. In order to meaningfully compare the sorption of the two anions by soils, contrasting soils are required. This enables more generalised statements to be made with regard to the soil properties that are important for sorption of both P and Mo, and also allows differences between the sorption of the two anions to be better understood.

2.2 Soils

Topsoils and subsoils of Okaihau gravelly clay, Ramiha silt loam, Dannevirke silt loam, and Tokomaru silt loam were collected. Sampling and soil details are given in Table 2.1. The predominant mineralogical components of the soils are: kaolinite, gibbsite, and free crystalline

Table 2.1 Site data for soils used in the study

Soil		Sampling depth (cm)	Grid reference	New Zealand soil classification	Parent material
Okaihau	Topsoil	0 - 10	N150/310456	very strongly leached	Olivine basalt
	Subsoil	23 - 40		brown loam	
Ramiha	Topsoil	0 - 30	N149/209278	strongly leached	Loess-derived mainly from greywacke and some volcanic ash
	Subsoil	30 - 50		yellow-brown loam-yellow- brown earth intergrade	
Dannevirke	Topsoil	0 - 20	N149/381410	strongly leached	Loess-derived mainly from greywacke and some volcanic ash
	Subsoil	30 - 50		yellow-brown loam-yellow- brown earth intergrade	
Tokomaru	Topsoil	0 - 15	N149/115319	moderately gleyed,	Loess-derived mainly from greywacke
	Subsoil	35 - 50		central yellow-grey earth	

iron oxides (Okaihau); vermiculite, vermiculite-chlorite, and allophane (Ramiha); chlorite, vermiculite, and allophane (Dannevirke); and mica/illite and vermiculite, with some crystalline iron oxides (Tokomaru). Further details on the Okaihau and Dannevirke soils have been published by New Zealand Soil Bureau (1968) and on the Ramiha and Tokomaru soils by Pollok (1975).

The soils were air dried and material passing a 2-mm sieve was used.

2.3 General Methods

2.3.1 Soil properties

Soil pH was determined at a 2.5:1 solution:soil ratio in water (New Zealand Soil Bureau, 1968). Extractable Al was determined by successively washing 1-g samples of soil four times with 10 ml of 1M KCl and analyzing for Al colorimetrically (Rainwater and Thatcher, 1960). Short-range order (amorphous) Fe and Al components were determined by extraction with acid ammonium oxalate (Williams et al., 1971) followed by colorimetric analysis for Fe and Al (Rainwater and Thatcher, 1960). Free oxides and hydrous oxides of iron were determined by extraction with citrate-dithionite-bicarbonate (CDB) and colorimetric analysis (Jackson, 1956). An estimate of crystalline Fe was obtained by subtracting oxalate-Fe from CDB-Fe. The amount of CDB-Al was determined after extraction and colorimetric analysis, which involved prior destruction of citrate (Williams et al., 1971). An estimate of the amount of non-crystalline inorganic material was determined from the quantity of hydroxyl ions released by 8.5×10^{-1} M NaF at pH 6.8 (Perrott et al., 1976).

2.3.2 Sorption determinations

Soil samples (1-g) were shaken with 40 ml of the appropriate solution (except in experiments where the solution:soil ratio was varied) in 50-ml polycarbonate tubes on an end-over-end shaker at 23°C. For periods of contact between soil and solution greater than 40 hr, $147 \mu\text{mol HgCl}_2 \text{ l}^{-1}$ was added to limit microbial activity. After the required shaking period, the tubes were centrifuged at 15,000 r.p.m. at 23°C and the supernatant solutions filtered through a 0.45 μm Millipore filter. An aliquot was then taken for analysis. The amount of sorbed anion was calculated as the difference between total anion added and the amount remaining in solution. In each case, Mo was added as solutions of Na_2MoO_4 and P as solutions of KH_2PO_4 .

2.3.3 Analysis for Mo and P

Inorganic P was determined by the method of Murphy and Riley (1962), absorbance being measured at 712 nm on a Unicam SP1800B spectrophotometer.

Two methods were evaluated for the determination of Mo in extracts. The first was the method of Piper and Beckwith (1948), as modified by Bingley (1959, 1963), which involves colour development by dithiol. The second was the method of Haddad et al. (1975), which involves colour development of a molybdenum-thiocyanate-rhodamine B complex. The dithiol method requires solvent extraction of the Mo-dithiol complex into isoamyl acetate, the absorbance of the green complex being measured at 680 nm. The rhodamine B method involves the formation of the complex in aqueous solution, the resulting red-blue complex being read at 600 nm. Both methods required prior removal of organic matter. To achieve this, aliquots of soil extracts were evaporated to dryness and organic matter subsequently destroyed.

For NaCl extracts of soils, treatment with acid hydrogen peroxide was used to destroy organic matter but for NaOH extracts of soils, ignition for 3 to 4 hr at 550°C was required before hydrogen peroxide treatment (Gupta and McKay, 1965). Excess peroxide was then destroyed by heating to 130-140°C.

2.4 Results and Discussion

2.4.1 Evaluation of analytical methods for determining Mo

Recovery of Mo added to several soil extracts is shown in Table 2.2. Both methods gave good recoveries. Because the solvent extraction procedure was more time-consuming, and because a comparison of the two methods showed them to be equally effective, the rhodamine B method was used during the study.

2.4.2 Comparison of Mo and P sorption isotherms

Isotherms for the sorption of Mo and P from 10^{-1} M NaCl during 40 hr by topsoils and subsoils of Okaihau, Ramiha, Dannevirke, and Tokomaru soils, over the concentration range of 0 - 100 $\mu\text{mol l}^{-1}$, are shown in Fig. 2.1 to 2.4.

The isotherms were all of a similar shape and type, but the relative extent of sorption varied considerably for the two anions and also between soils. The data in Table 2.3 are a summary of some of the sorption data obtained from the isotherms, enabling a more direct comparison to be made.

The amounts of Mo sorbed by topsoils at each of the two solution Mo concentrations decreased in the order Okaihau > Ramiha > Dannevirke > Tokomaru. Due to the different shape of the sorption isotherm for each soil, the order of sorption was not the same at 5 $\mu\text{mol Mo l}^{-1}$ as at

Table 2.2 Recovery of Mo added to soil extracts, using two different methods for the determination of Mo

Soil	Recovery (%) of Mo added at the following levels ($\mu\text{mol Mo}^*$)		
	0.010	0.050	0.100
Dithiol Method			
Ramiha	92	95	98
Dannevirke	105	98	102
Rhodamine B Method			
Okaihau	100	102	98
Ramiha	108	102	100
Dannevirke	105	101	101
Tokomaru	98	102	100

* Added to 20 ml of soil extract.

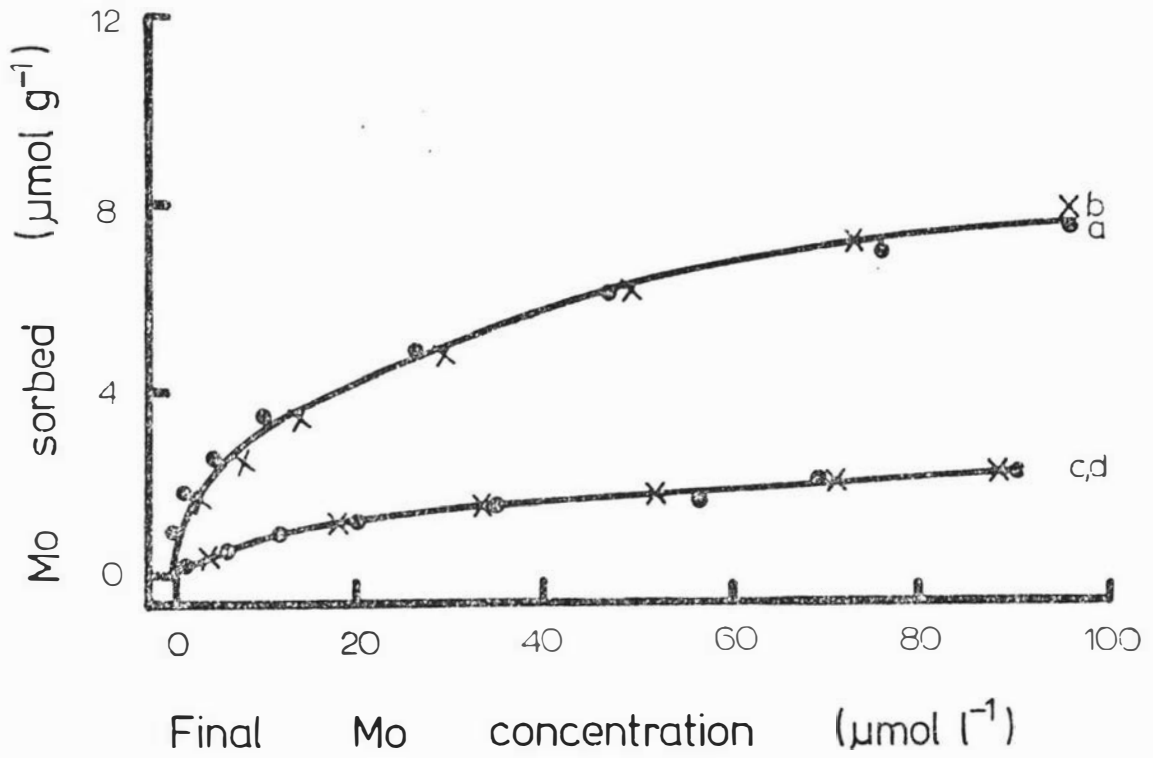


Fig. 2.1 Isotherms for the sorption of Mo from 10^{-1}M NaCl during 40 hr by Okaihau (a), Ramiha (b), Dannevirke (c), and Tokomaru (d) topsoils.

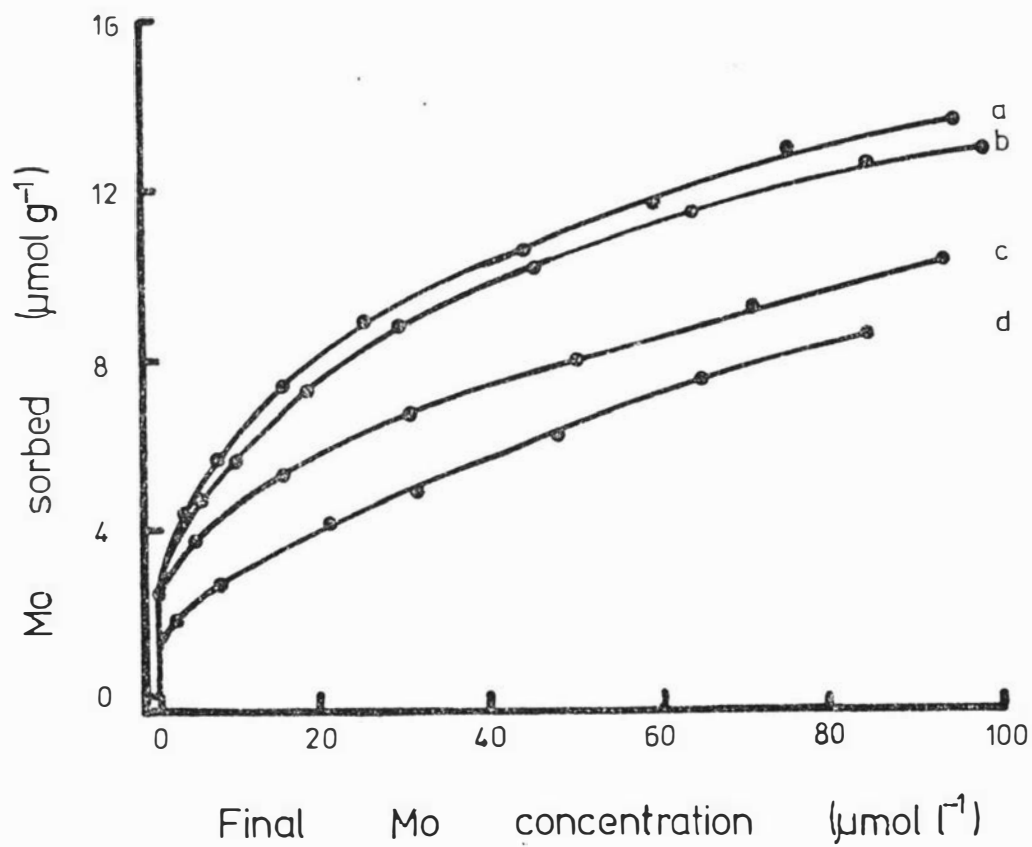


Fig. 2.2 Isotherms for the sorption of Mo from 10^{-1}M NaCl during 40 hr by Okaihau (a), Ramiha (b), Dannevirke (c), and Tokomaru (d) subsoils.

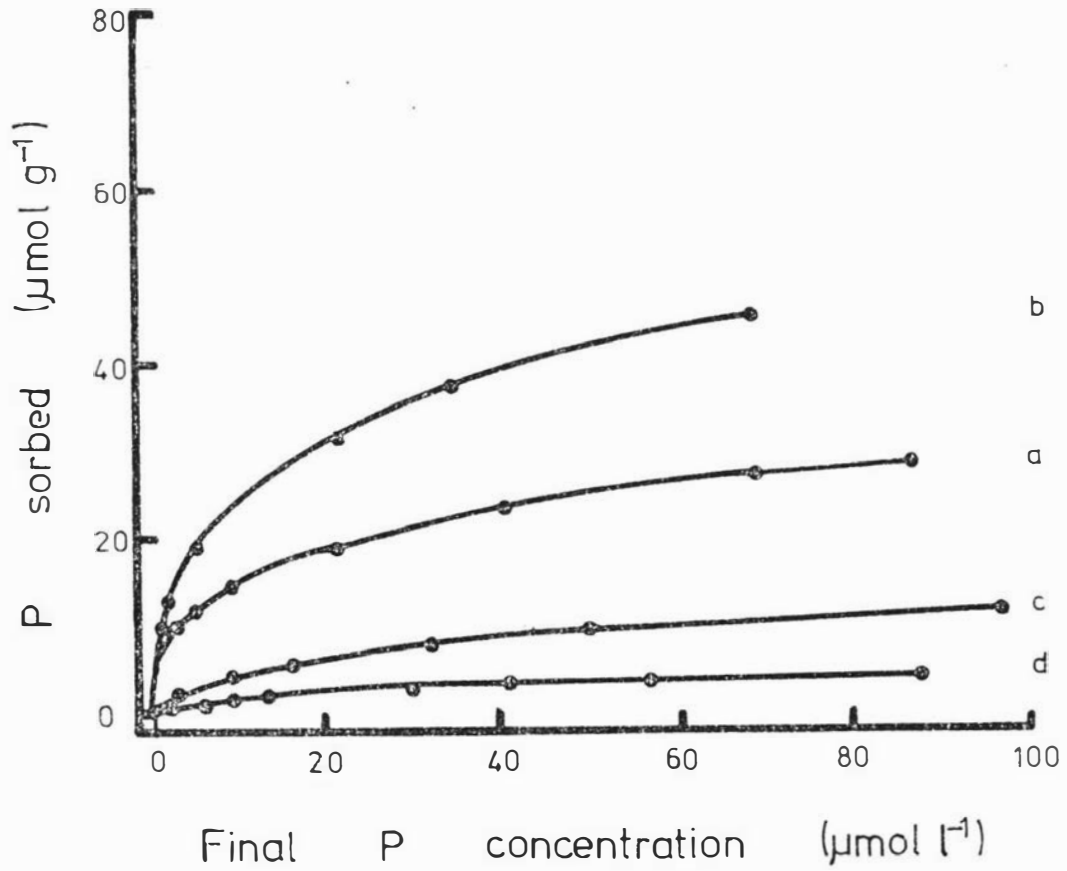


Fig. 2.3 Isotherms for the sorption of P from 10^{-1}M NaCl during 40 hr by Okaihau (a), Ramiha (b), Dannevirke (c), and Tokomaru (d) topsoils.

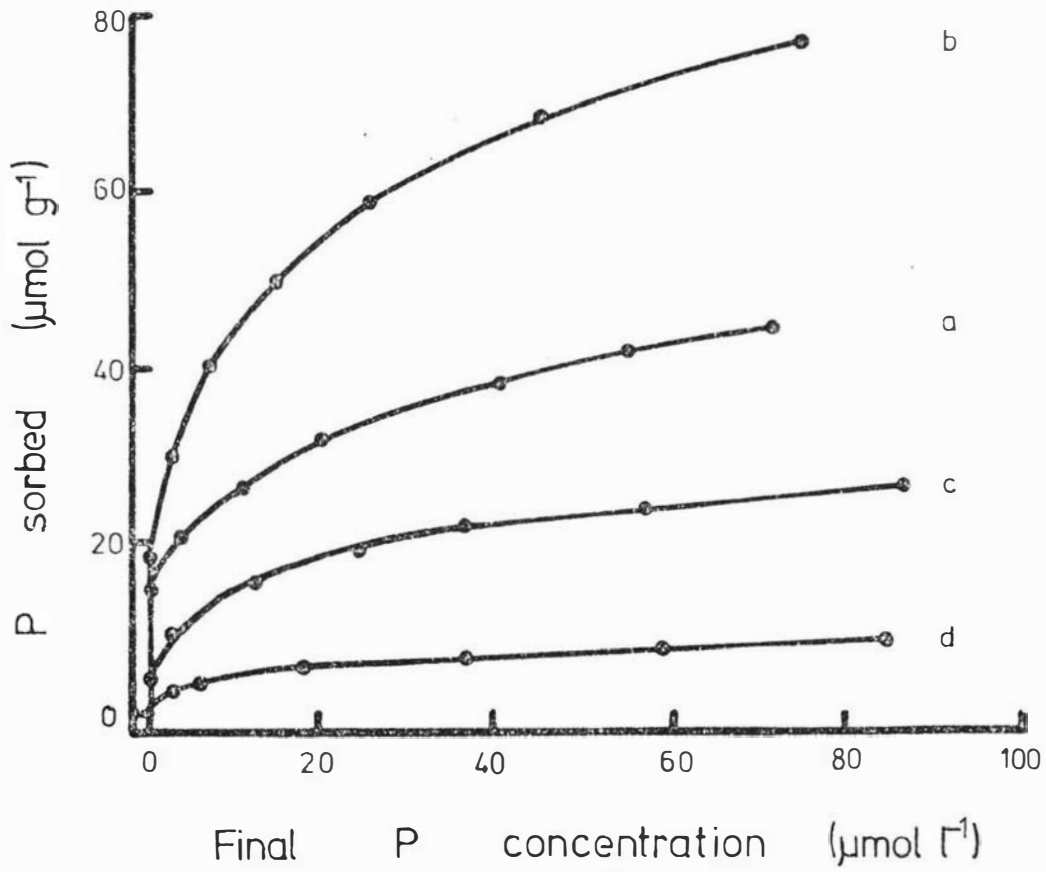


Fig. 2.4 Isotherms for the sorption of P from 10^{-1} M NaCl during 40 hr by Okaihau (a), Ramiha (b), Dannevirke (c), and Tokomaru (d) subsoils.

Table 2.3 Amounts of Mo and P sorbed by soils, and the ratio of P and Mo sorbed from 10^{-1} M NaCl during 40 hr at two final solution Mo and P concentrations

Soil		Mo sorbed		P sorbed		P sorbed:Mo sorbed	
		$\mu\text{mol g}^{-1}$		$\mu\text{mol g}^{-1}$			
Solution concentration		$\mu\text{mol l}^{-1}$					
		5	70	5	70	5	70
Okaihau	Topsoil	2.90	6.78	11.4	27.5	3.9	4.1
	Subsoil	4.62	12.45	21.3	44.3	4.6	3.6
Ramiha	Topsoil	2.25	6.95	17.9	45.8	8.0	6.6
	Subsoil	4.15	11.82	35.8	75.7	8.6	6.4
Dannevirke	Topsoil	0.72	2.20	3.1	10.3	4.3	4.7
	Subsoil	3.60	8.47	10.8	24.8	3.0	2.9
Tokomaru	Topsoil	0.55	2.20	1.1	4.2	2.0	1.9
	Subsoil	2.15	9.65	3.4	8.1	1.6	0.84

70 $\mu\text{mol Mo l}^{-1}$. For subsoils, the relative order of sorption remained the same over the whole concentration range. For P sorption during 40 hr, the order of sorption was Ramiha > Okaihau > Dannevirke > Tokomaru, over the concentration range of 0 - 100 $\mu\text{mol P l}^{-1}$, for both topsoils and subsoils.

A comparison of the Mo and P sorption data indicates the following: (1) for both topsoils and subsoils, Okaihau, Ramiha, and Dannevirke soils sorbed considerably more P than Mo at any one final solution concentration, whereas Tokomaru topsoil and subsoil sorbed approximately equimolar quantities of P and Mo; (2) the relative order of sorption between soils was different for the two anions. The ratio of P:Mo sorbed (Table 2.3) for Ramiha and Dannevirke soils was greater than the ratio for Okaihau and Tokomaru soils, indicating that the amounts of Mo sorbed, relative to P, were much less for Ramiha and Dannevirke soils. Reasons for the differences in anion sorption will be discussed in the following Section and subsequent Chapters.

2.4.3 Relationship of Mo and P sorption to soil properties

Values for pH, extractable Al, crystalline Fe, CDB-Al, short-range order Fe and Al, and OH^- released by fluoride for the four soils are given in Table 2.4.

The sorption of Mo and the ratio of Mo:P sorbed have been found to correlate closely with soil pH (Barrow, 1970). The pH of the solution is also known to affect the amount of Mo sorbed by soil clays (Theng, 1971) and it has been postulated that pH affects the mechanism of both Mo and P sorption (Hingston et al., 1967, 1968b). The pH values for the soils used in this study are not widely different and pH differences do not account for the observed differences in Mo sorption. Extractable Al is often related to P sorption (Syers et al., 1971) and inversely related to pH. The values for extractable Al for the soils used in the present

Table 2.4 Soil properties which may affect Mo and P sorption

Soil		pH	Extractable Al	Crystalline Fe	CDB-Al	Short-range order		OH ⁻ released by NaF
						Fe	Al	
					mmol 100 g ⁻¹			
Okaihau	Topsoil	5.6	0.34	128.0	69.2	3.5	14.2	63.2
	Subsoil	5.1	0.44	122.9	81.4	9.0	18.9	88.2
Ramiha	Topsoil	5.4	0.77	10.9	37.2	15.8	35.6	112.6
	Subsoil	5.5	0.25	4.2	58.4	23.0	83.0	233.6
Dannevirke	Topsoil	5.8	0.06	8.4	16.2	9.1	14.2	52.4
	Subsoil	5.9	0.43	23.2	23.6	12.1	15.9	81.2
Tokomaru	Topsoil	5.3	0.25	5.9	5.6	4.6	3.6	16.9
	Subsoil	5.2	0.76	16.8	6.6	3.7	4.8	35.3

study show large variations and again there is no obvious relationship between Mo sorption and extractable Al.

Both short-range order Fe and Al, and crystalline Fe and Al have been related to P sorption (Saunders, 1965; Syers et al., 1971). Short-range order components are generally regarded as being the more important. Jones (1957) and Theng (1971) have reported that CDB-extractable Fe (which includes both crystalline and short-range order Fe) is important in Mo sorption. In contrast, Barrow (1970) found that CDB-Al was more important in Mo sorption. Considering their importance in P sorption, it is strange that no study of the relationship between short-range order components and Mo sorption has been made, although oxalate-extractable Mo is often used as a test for plant-available Mo (Grigg, 1953; Gupta and McKay, 1966).. From the data in Table 2.4, it appears that both crystalline and short-range order Fe and Al are related to P sorption, with the two highest P-sorbing soils, Ramiha and Okaihau, containing large amounts of short-range order and crystalline material, respectively. The relationship between Mo sorption and soil components is less obvious. The large amounts of crystalline Fe and Al in Okaihau soil equate with a relatively high Mo sorption, but the same components do not appear to influence Mo sorption by Dannevirke and Tokomaru subsoils. The data for Ramiha soil suggest that short-range order Al components are not as important for Mo sorption as for P sorption. The magnitude of short-range order Fe values would seem to equate well with the extent of Mo sorption for Ramiha, Dannevirke, and Tokomaru soils, indicating that short-range order Fe components are important in Mo sorption. The comparable extent of Mo sorption by Tokomaru and Dannevirke soils, however, can not be accounted for by the mineral components of the soil alone, and pH is one obvious factor.

Comparing P and Mo sorption by the four soils, it would appear that short-range order Al, in particular, is more important in P sorption than in Mo sorption. Short-range order aluminosilicate compounds (allophane) are known to sorb large amounts of P (Cloos et al., 1968; Rajan and Perrott, 1975), but their affinity for Mo is not known. Allophane is the dominant mineral in Ramiha soil and to a lesser extent in Dannevirke soil. Hydroxyl release by NaF gives an indication that poorly-ordered inorganic materials, especially Al components (Perrott et al., 1976), are important in Ramiha soil and to a lesser extent in Okaihau and Dannevirke soils. It is possible that the values for OH^- release from Okaihau, Ramiha, and Dannevirke soils may be artificially low due to organic matter interference. The high values for OH^- release and oxalate-extractable Al (which can be correlated with allophane content, A.S. Campbell, pers. comm.) indicate that allophane is less important in Mo sorption than in P sorption by Ramiha soil. This will be investigated in subsequent Chapters.

It is difficult to assess which properties make the largest contribution to the sorption of Mo. Crystalline Fe, CDB-Al, and short-range order Fe all seem to contribute to Mo sorption, with pH also accounting for some differences. Short-range order Al would seem to be considerably more important in P sorption than in Mo sorption.

CHAPTER 3

SORPTION OF MOLYBDATE BY SOILS AND SOIL COMPONENTS

3.1 Introduction

Detailed investigations of Mo sorption by soils and soil components have not been carried out in any previously reported studies. Sorption isotherms have often been determined over extreme ranges of concentration (Reyes and Jurinak, 1967; Gonzalez et al., 1974). Possibly because of the wide range of concentrations used, tests of data to fit one of the known sorption equations have been inconclusive.

Sorption isotherms can give useful information on the reaction between sorbate and sorbent; this includes mechanistic details, sorption capacities, heat, free energies, and entropies of the reactions, and size of the sorbate molecule and its orientation at the surface (Giles, 1970). Fit of experimental sorption data to the Langmuir equation has been helpful in developing P sorption mechanisms for soils (Olsen and Watanabe, 1957; Ryden et al., 1977a) and for soil components, which have been used as models for soil surfaces (Muljadi et al., 1966; Rajan et al., 1974; Huang, 1975; Ryden et al., 1977a).

In an attempt to better understand the nature of the sorption reactions between soils and added Mo, detailed isotherms were determined over realistic final solution Mo concentrations and tested for fit to the Langmuir equation. Factors which affect the experimental isotherm, namely ionic strength and time, were also investigated. Data for sorption of Mo by synthetic soil components were also obtained, and the validity of using such components as models for soil surfaces discussed.

3.2 Methods

For kinetic and ionic strength studies, Okaihau, Ramiha, and Dannevirke topsoils were used. For equilibrium isotherm determination, Okaihau, Ramiha, Dannevirke, and Tokomaru topsoils were used, whereas for 40-hr isotherms, all four topsoils and their subsoils were used. Synthetic hydrous ferric oxide gel (Fe gel) and synthetic aluminosilicate gel (allophane) were also used for the determination of 40-hr Mo sorption isotherms.

For kinetic studies of Mo sorption over short periods of time (0-16 hr), 1-g samples of soil plus 35 ml of 10^{-1} M NaCl were shaken for 40 hr to disperse the soil. Aliquots (5 ml), containing Mo in 10^{-1} M NaCl were then added and the soil suspensions shaken over various periods of time. Over very short times (< 4 min), the suspensions were filtered directly through a 0.45 μ m Millipore filter without initial centrifugation. For kinetic studies involving shaking times >16 hr, 1-g samples of soil plus 35 ml of 10^{-1} M NaCl were shaken on an end-over-end shaker at 23⁰C. At 0, 24, 48, 72, 96, and 120 hr after starting, 5-ml aliquots of 10^{-1} M NaCl, containing Mo, were added to the polycarbonate tubes. Shaking was then continued until a total shaking time of 144 hr was reached. The soil was in contact with added Mo, therefore, for times between 24 and 144 hr, yet the total shaking time was the same for all samples.

To ascertain the effect of ionic strength on the sorption of Mo during 40 hr, sorption isotherms were determined in support media of 1 M, 10^{-1} M, and 10^{-3} M NaCl. To determine the effect of ionic strength on Mo sorption for shaking periods greater than 40 hr, the procedure was similar to that given for the kinetic studies above, with three solutions of different ionic strength being used. Only four times

of contact between soil and added Mo were used, namely 144, 120, 96, and 80 hr, and only three levels of Mo were added to each soil.

In order to obtain equilibrium isotherms in 10^{-1} M NaCl, the procedure was the same as that used for determining ionic strength effects, given above. The same four times of contact between soil and added Mo were used, but at least twelve levels of addition were made to each soil to give equilibrium Mo concentrations in the range of 0 - $120 \mu\text{mol l}^{-1}$. The 40-hr isotherms were determined in 10^{-1} M NaCl for twelve to fifteen different additions of Mo to each soil to give final concentrations in the range of 0 - $120 \mu\text{mol l}^{-1}$. Low concentration levels were emphasised, with at least four final Mo concentrations being below $0.5 \mu\text{mol l}^{-1}$.

An estimate of native sorbed (non-occluded) Mo was required for evaluation of sorption isotherms, as this form of Mo would be expected to affect both the amounts of added Mo sorbed, and the final solution Mo concentration. As no method has been reported in the literature for determining native sorbed Mo, the method of Williams et al. (1967) for determining non-occluded P was used. This involved extraction of 1-g samples of soil with 40 ml of 10^{-1} M NaOH overnight. After acidification of the supernatant solution to precipitate humic acids, an aliquot was evaporated to dryness, ignited at 550°C for 3-4 hr, oxidized with acidified peroxide, and Mo determined.

Synthetic Fe gel was prepared by adding NaOH to a 0.4 M solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ until pH 7.0 was reached. The resulting gel was allowed to stand overnight and then washed with distilled water to remove excess hydroxyl ions. For the determination of isotherms for Mo sorption by Fe gel, a solution:solid ratio of approximately 40 ml:50 mg was used. Isotherms were determined in 10^{-1} M NaCl during a 40-hr shaking period.

Synthetic allophane was prepared using the method of van Reeuwijk and de Villiers (1968). A solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was slowly added

(over 10 min) to a solution of $\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$ and the suspension then adjusted to pH 6.0, this pH being maintained for 2 hr. The gel was then washed with distilled water until free of chloride. The resulting gel was amorphous to X-rays, and the Al:Al + Si molar ratio, determined by dissolution in HF and subsequent analysis for Al and Si using a Techtron atomic absorption spectrophotometer, was 0.60. For the determination of isotherms for Mo sorption by allophane, a solution:solid ratio of approximately 40 ml:40 mg was used, and sorption determined in 10^{-1} NaCl during 40 hr.

In all experiments involving shaking times greater than 40 hr, $147 \mu\text{mol HgCl}_2 \text{ l}^{-1}$ was added to each tube to limit microbial growth.

3.3 Results and Discussion

3.3.1 Effect of time on Mo sorption

The effect of time of contact between soil and Mo in solution over short- and long- time periods on solution Mo concentration is illustrated in Fig. 3.1 for Okaihau and Ramiha topsoils. Similar data were obtained for Dannevirke topsoil. The data indicate that initial uptake of Mo was extremely rapid, over 50% of the added Mo sorbed at 60 min was sorbed in 5 min. This behaviour was observed over a wide range of initial Mo concentrations. After the initial, very rapid uptake of added Mo, sorption continued for long periods of time and after 6 day (144 hr), sorption was still continuing, although at a much slower rate than that of the initial uptake of Mo. A detailed kinetic analysis of the data was not carried out. The results, however, indicated that the equilibrium condition for Mo sorption was not reached under the experimental conditions used. An estimate of the equilibrium concentration was therefore sought.

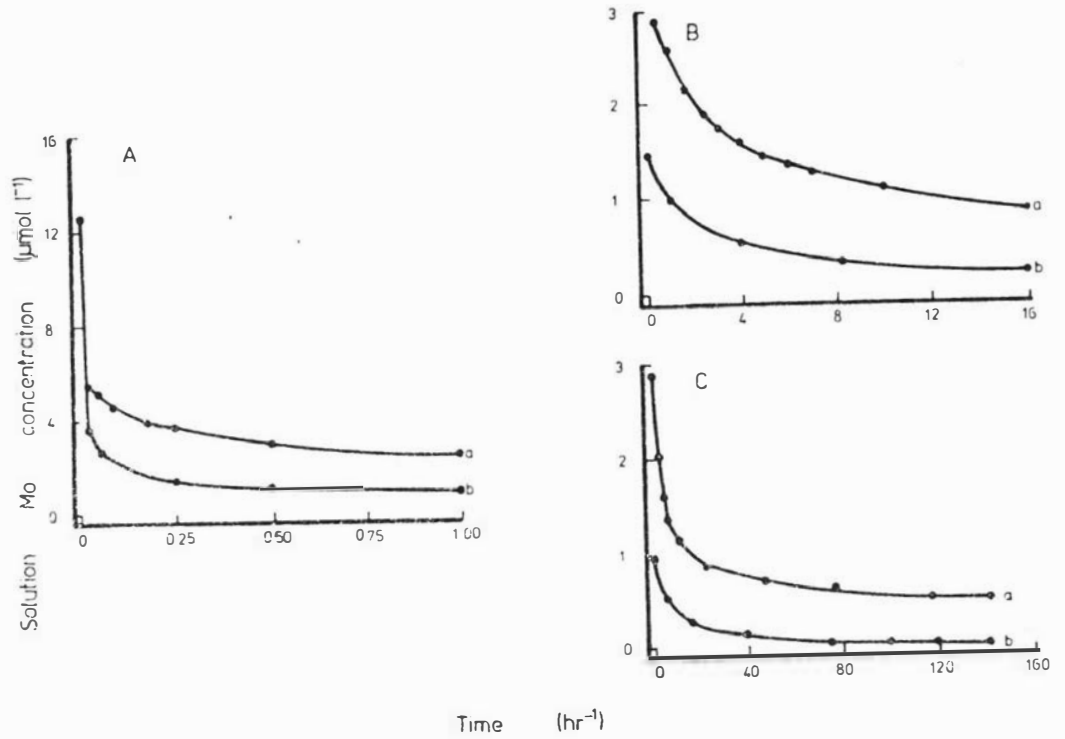


Fig. 3.1 Relationship between solution Mo concentration and time during the sorption of added Mo ($0.5 \mu\text{mol g}^{-1}$) by Ramiha (a) and Okaihau (b) topsoils. A = 0 to 1 hr, B = 0.25 to 16 hr, and C = 1 to approximately 150 hr.

For P sorption by soils, Ryden and Syers (1975) have shown that plots of solution P concentration against $1/t$ were linear over the range of 75-160 hr. By extrapolation to $1/t = 0$ (i.e., $t = \infty$), an estimate of the equilibrium concentration was obtained. Treatment of the data for Mo sorption by this method is illustrated in Fig. 3.2 for Ramiha topsoil. Similar plots were obtained for the other two topsoils (data not presented). The plots showed that, at times less than approximately 75 hr, conformation to a single straight line plot was not obtained, whereas over the time range of 75 - 150 hr, a good fit to a linear plot was obtained. An estimate of equilibrium concentrations was therefore used in subsequent investigations by data extrapolation, over the time range 75 - 150 hr, to $1/t = 0$.

3.3.2 Effect of ionic strength on Mo sorption

Isotherms for the sorption of added Mo by Ramiha topsoil from 1 M, 10^{-1} M, and 10^{-3} M NaCl during 40 hr are shown in Fig. 3.3. Similar isotherms were obtained for Okaihau and Dannevirke topsoils. At any one final Mo concentration, the amount of Mo sorbed depended on the ionic strength of the support medium and was greater at high ionic strengths. For example, at a final Mo concentration of $10 \mu\text{mol l}^{-1}$, the amounts of Mo sorbed from 1 M, 10^{-1} M and 10^{-3} M NaCl were 2.72, 2.56, and $1.92 \mu\text{mol g}^{-1}$, respectively.

The results obtained for the effect of NaCl of varying ionic strength on Mo sorption by soils during 40 hr are similar to those obtained by Barrow (1972) for Mo sorption from CaCl_2 of varying ionic strength. The data in Section 3.3.1, however, indicate that at 40 hr, Mo sorption was not at equilibrium. The tendency for the isotherms in Fig. 3.3 to converge at low solution Mo concentrations suggested also that the effect of ionic strength would disappear at equilibrium.

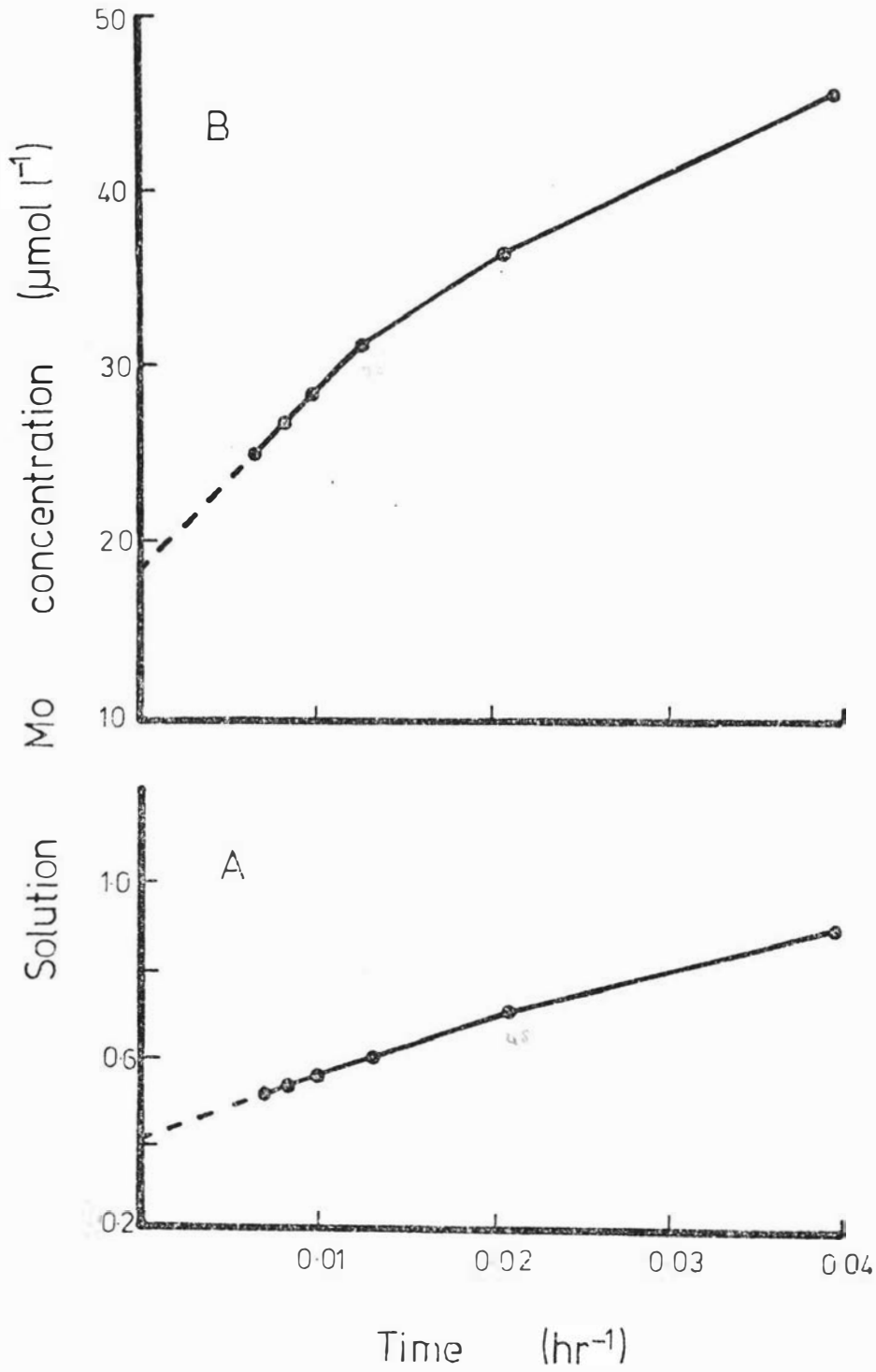


Fig. 3.2 Relationship between solution Mo concentration and reciprocal of time during sorption of added Mo by Ramiha topsoil. A = $0.5 \mu\text{mol g}^{-1}$ added Mo and B = $6.0 \mu\text{mol g}^{-1}$ added Mo.

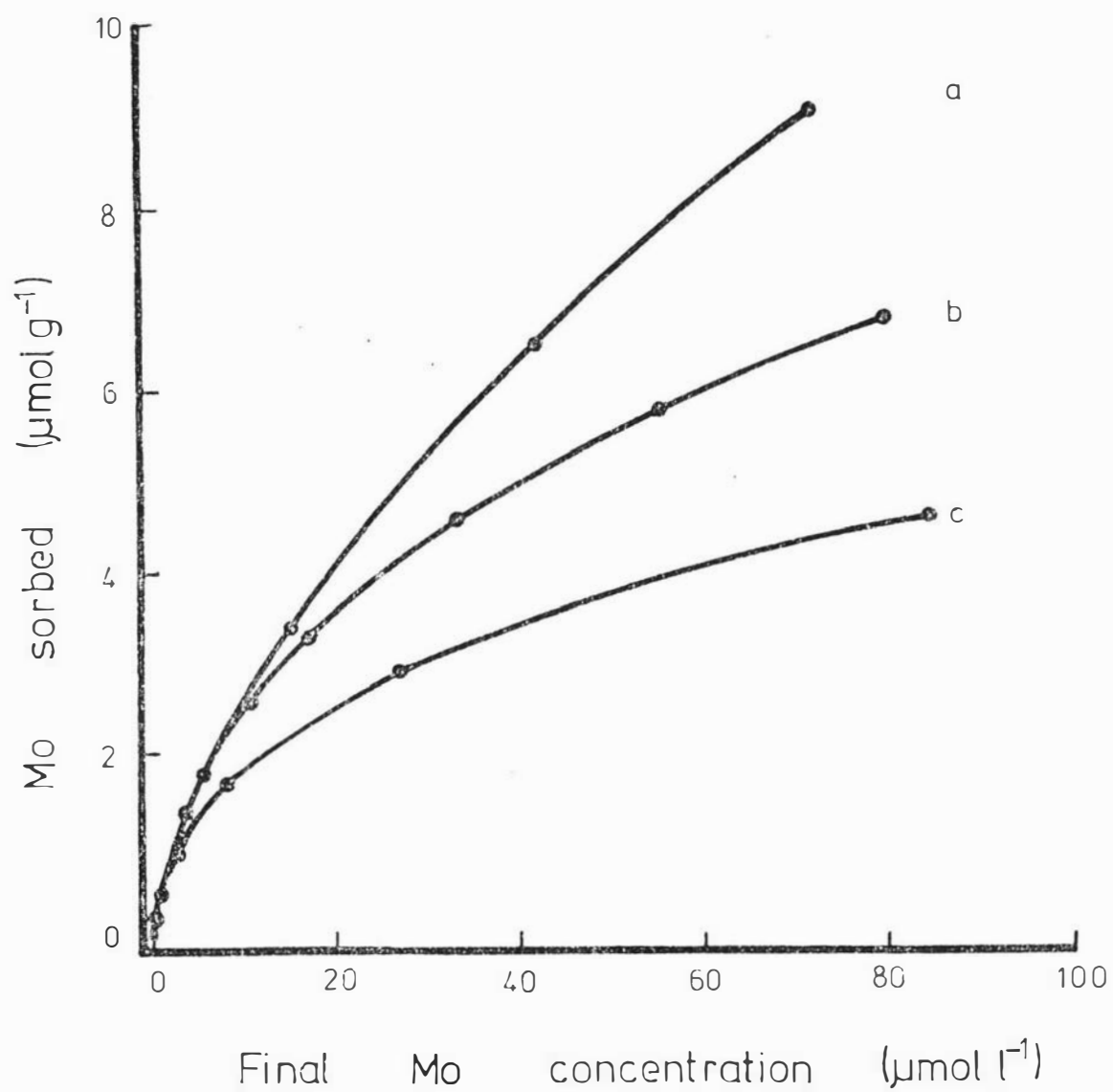


Fig. 3.3. Isotherms for sorption of Mo by Ramiha topsoil during 40 hr from NaCl solutions of varying ionic strength. a = 1M NaCl, b = 10^{-1} M NaCl, and c = 10^{-3} M NaCl.

This would be the case if the isotherms at lower Mo concentrations were closer to equilibrium.

An estimate of the equilibrium concentration was obtained by the method outlined in Section 3.3.1. Data were plotted in this way for three levels of Mo addition which gave low, intermediate, and high concentrations in solution at equilibrium for Okaihau, Ramiha, and Dannevirke topsoils. The plots, illustrated in Fig. 3.4 for Okaihau topsoil, were similar for all three topsoils.

For sorption of Mo during times between 80 and 144 hr, the amount of Mo sorbed was affected by the ionic strength of the support media, with greater amounts being sorbed at higher ionic strengths, i.e., the effect of ionic strength for these times was the same as that for sorption during 40 hr. When solution Mo concentrations were extrapolated to $1/t = 0$, the equilibrium concentrations could be estimated; these are shown in Table 3.1. At low ($<0.1 \mu\text{mol l}^{-1}$), and intermediate ($0.1\text{-}2.0 \mu\text{mol l}^{-1}$) equilibrium concentrations, the linear relationships appeared to converge, i.e., for a given Mo addition, the concentration in solution and amount sorbed appeared to be independent of ionic strength at equilibrium. At high concentrations, however, the linear relationships did not converge, i.e., the effect of ionic strength at high concentrations appeared to be absolute. A detailed statistical analysis of the data was not carried out, the results indicating patterns of behaviour that would not be altered by statistical treatment.

Because the effect of ionic strength on Mo sorption disappears at equilibrium for concentrations less than $5 \mu\text{mol l}^{-1}$, this indicates that the extent of Mo sorption, at times less than equilibrium and for low final solution Mo concentrations, differs in media of different ionic strength because of kinetic factors. Similar effects of ionic strength

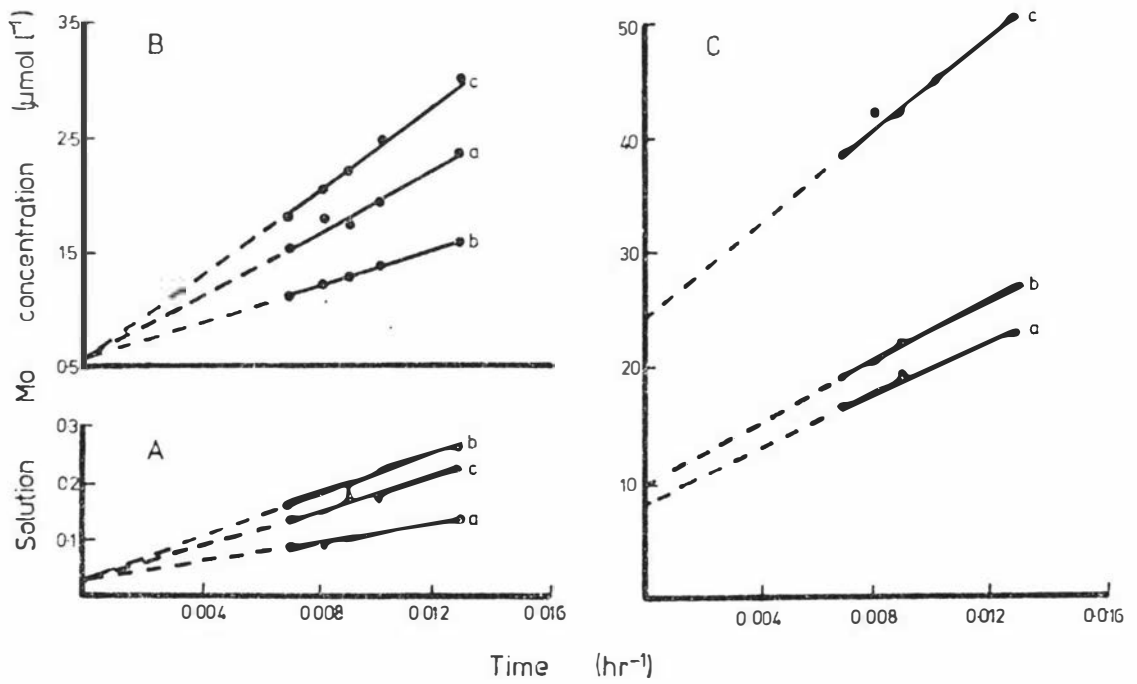


Fig. 3.4 Relationship between solution Mo concentration and reciprocal of time during the sorption of Mo by Okaihau topsoil from various support media: dashed lines used to extrapolate the data to $1/t = 0$, i.e., $t = \infty$. A = $0.80 \mu\text{mol g}^{-1}$ added Mo, B = $2.50 \mu\text{mol g}^{-1}$ added Mo, and C = $7.0 \mu\text{mol g}^{-1}$ added Mo. a = 1M NaCl, b = 10^{-1} M NaCl, and c = 10^{-3} M NaCl.

Table 3.1 Equilibrium solution concentrations of Mo following sorption by topsoils from NaCl of differing strengths, estimated by a graphical procedure

Soil	Mo addition $\mu\text{mol g}^{-1}$	Equilibrium Mo concentrations ($\mu\text{mol l}^{-1}$)			
		NaCl concentration	1M	10^{-1}M	10^{-3}M
Ramiha	0.30		0.091	0.091	0.091
	1.50		0.60	0.60	0.65
	6.00		10.10	16.50	29.10
Dannevirke	0.05		0.024	0.024	0.024
	0.50		0.83	0.89	0.91
	3.00		15.00	24.90	30.40
Okaihau	0.80		0.031	0.031	0.031
	2.50		0.59	0.58	0.57
	7.00		7.80	9.90	24.30

on P sorption by soils have been observed by Ryden and Syers (1975) and Ryden et al. (1977a). The division of ionic strength effects into kinetic effects, at low final Mo concentrations, and absolute effects, at high final Mo concentrations, implies the involvement of a sorption mechanism at high Mo concentrations which is not, or little, involved at low Mo concentrations. The implications of ionic strength effects to Mo sorption mechanisms will be further discussed in Chapter 5.

3.3.3 Evaluation of Mo sorption isotherms

3.3.3.1 Comparison of 40-hr and equilibrium isotherms

Isotherms tested for fit to the Langmuir equation have usually been determined over time periods less than those required to reach equilibrium. The Langmuir equation, however, was derived for equilibrium conditions and test of data for fit to the equation should be done using isotherms determined at equilibrium.

Equilibrium and 40-hr isotherms over the final concentration ranges of 0 - 10 and 0 - 120 $\mu\text{mol l}^{-1}$ respectively, for Ramiha topsoil are shown in Fig. 3.5. Similar data were obtained for the other three topsoils. Values for Mo sorbed take into account native sorbed Mo, estimated by extraction with 10^{-1}M NaOH. The values for native sorbed Mo were extremely small: 0.010, 0.007, 0.005, and 0.003 $\mu\text{mol g}^{-1}$ for Okaihau, Ramiha, Dannevirke, and Tokomaru topsoils, respectively, but were significant in relation to added Mo sorbed at very low solution concentrations, especially for Dannevirke and Tokomaru topsoils. For subsoils, native sorbed Mo was not significant compared to sorbed Mo.

The general shape of the isotherms was very similar for 40-hr and equilibrium isotherms, being intermediate between strong H-type and L-type (Giles et al., 1960). Over the final concentration range

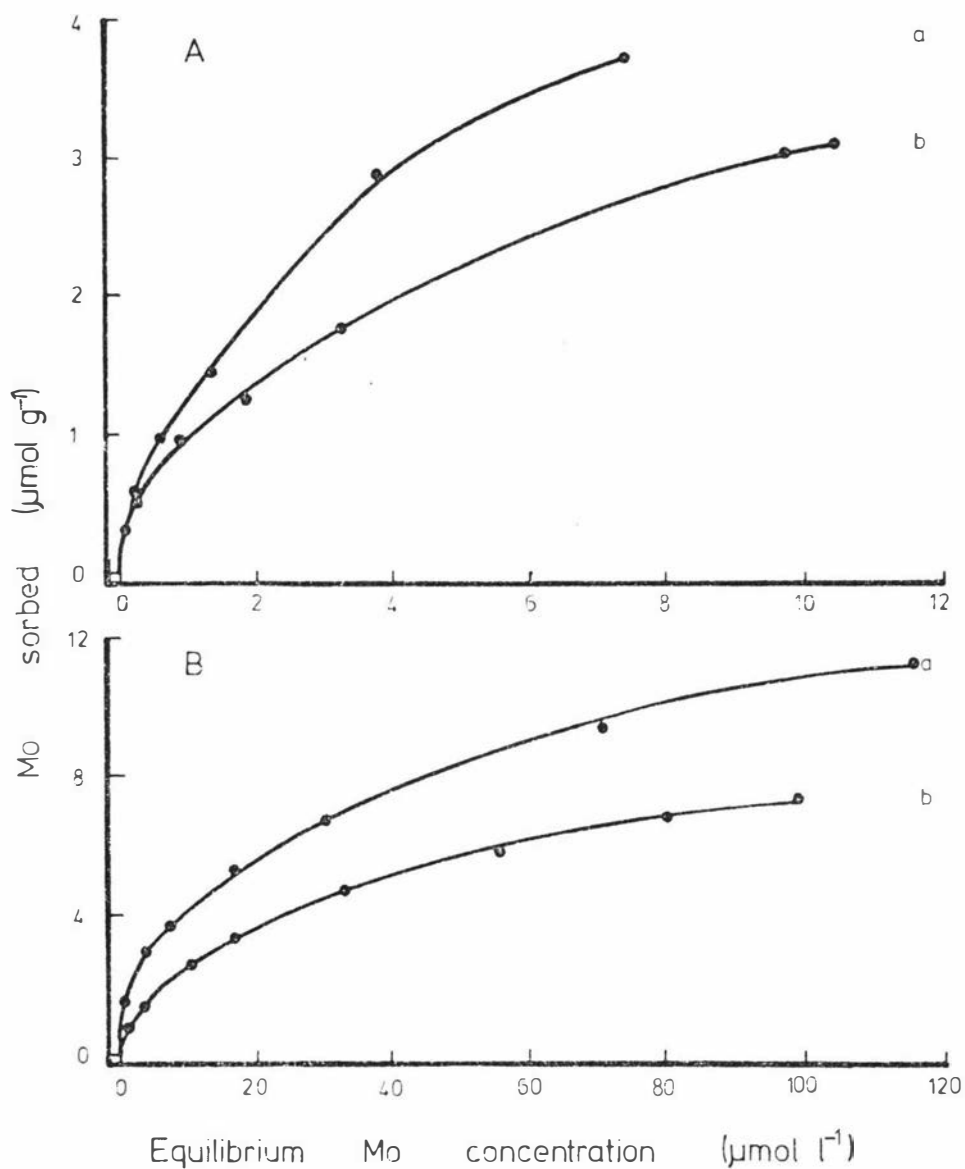


Fig. 3.5 Isotherms for the sorption of Mo by Ramiha topsoil from 10^{-1}M NaCl at equilibrium (a) and during 40 hr (b). A = final concentrations of 0 to 10 $\mu\text{mol l}^{-1}$, and B = final concentrations of 0 to 120 $\mu\text{mol l}^{-1}$.

of $0 - 1 \mu\text{mol l}^{-1}$, 40-hr and equilibrium isotherms for each soil were very similar. This is because, over this range, large changes in concentration result in only small changes in the amounts of Mo sorbed. At concentrations greater than $10\mu\text{mol l}^{-1}$, the isotherms showed very similar relative changes over a large concentration range. de Boer (1953) has shown that H-type isotherms can often be solved using the Langmuir equation by assuming more than one population of sites for sorption.

Test of fit of the data obtained in the present study to the Langmuir equation was then attempted. For this purpose, the final Mo concentration range studied was much higher than that observed under field conditions. Over such a very restricted concentration range, however, detailed evaluation would not be possible.

3.3.3.2 Evaluation of isotherms using the Langmuir equation

The form of the Langmuir equation used to test the fit of the experimental data was:

$$1/x = 1/kbc + 1/b \quad (1.16)$$

where x = the amount of Mo sorbed, c = the final Mo solution concentration, b = the sorption maximum, and k = a constant related to the free energy of the sorption reaction. If a plot of $1/x$ against $1/c$ is linear, then k and b can be evaluated from the slope and intercept of the plot. Due to its reciprocal nature, this form of the Langmuir equation allows better evaluation of data at very low concentration values, and is more sensitive to changes in k .

A plot of the experimental data over the whole concentration range ($0-120 \mu\text{mol l}^{-1}$) as shown in Fig. 3.6 for Ramiha topsoil, indicated several linear relationships. Values for native sorbed Mo were

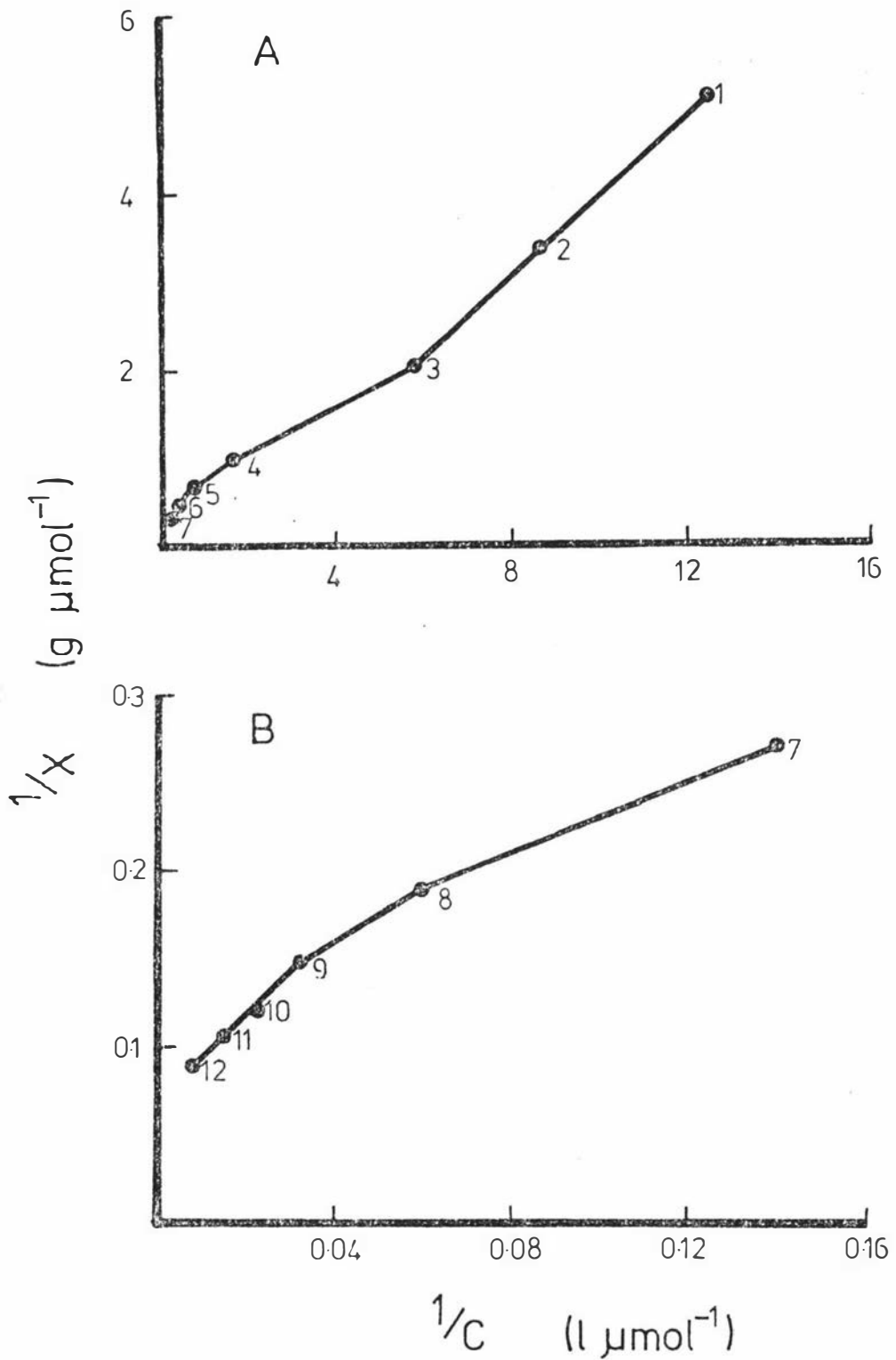


Fig. 3.6 Isotherms for the sorption of Mo by Raniha topsoil at equilibrium, plotted using the linear form of the Langmuir equation. A = equilibrium Mo concentration range of 0.05 to $10 \mu\text{mol}^{-1}$, and B = equilibrium Mo concentration range of 3.0 to $120 \mu\text{mol}^{-1}$. Data points are numbered to allow comparison between Figures.

initially considered to be insignificant (and were not included in Fig. 3.6), but in the very low concentration range ($0-0.5 \mu\text{mol l}^{-1}$), calculations showed that native sorbed Mo was important, especially for the low Mo-sorbing soils. For example, at equilibrium $c = 0.1 \mu\text{mol l}^{-1}$, native sorbed Mo was 0.76, 2.9, 8.6, and 2.0% of added Mo sorbed for Okaihau, Ramiha, Dannevirke and Tokomaru topsoils, respectively. Correction for native sorbed Mo changed the plot of $1/x$ against $1/c$ from a curved to a straight line relationship over the low concentration range, as shown in Fig. 3.7. Above final solution concentrations of $1 \mu\text{mol l}^{-1}$, native sorbed Mo was not significant and hence, did not change the relationship between $1/x$ and $1/c$.

At concentrations less than $0.5 \mu\text{mol l}^{-1}$, the data were described by one Langmuir equation. If more than one sorption reaction can occur at the surface, the most energetically favourable reaction would occur first. At higher concentrations, however, more than one type of reaction could proceed simultaneously, leading to deviation from a single Langmuir equation. Assuming the first linear relationship is primarily for one reaction, x values for this reaction can be approximated for at higher concentrations, subtracted out from total amounts sorbed, and the resulting data tested for fit to the Langmuir equation. This method has been used successfully for P sorption by Ryden et al. (1977a). By successively approximating b and k values for Langmuir plots, these workers found that three overall linear regions obeying the Langmuir equation were obtained for P sorption by soils and soil components. The method of successive approximations used to evaluate the fit of Mo sorption data to the Langmuir equation is outlined in Table 3.2

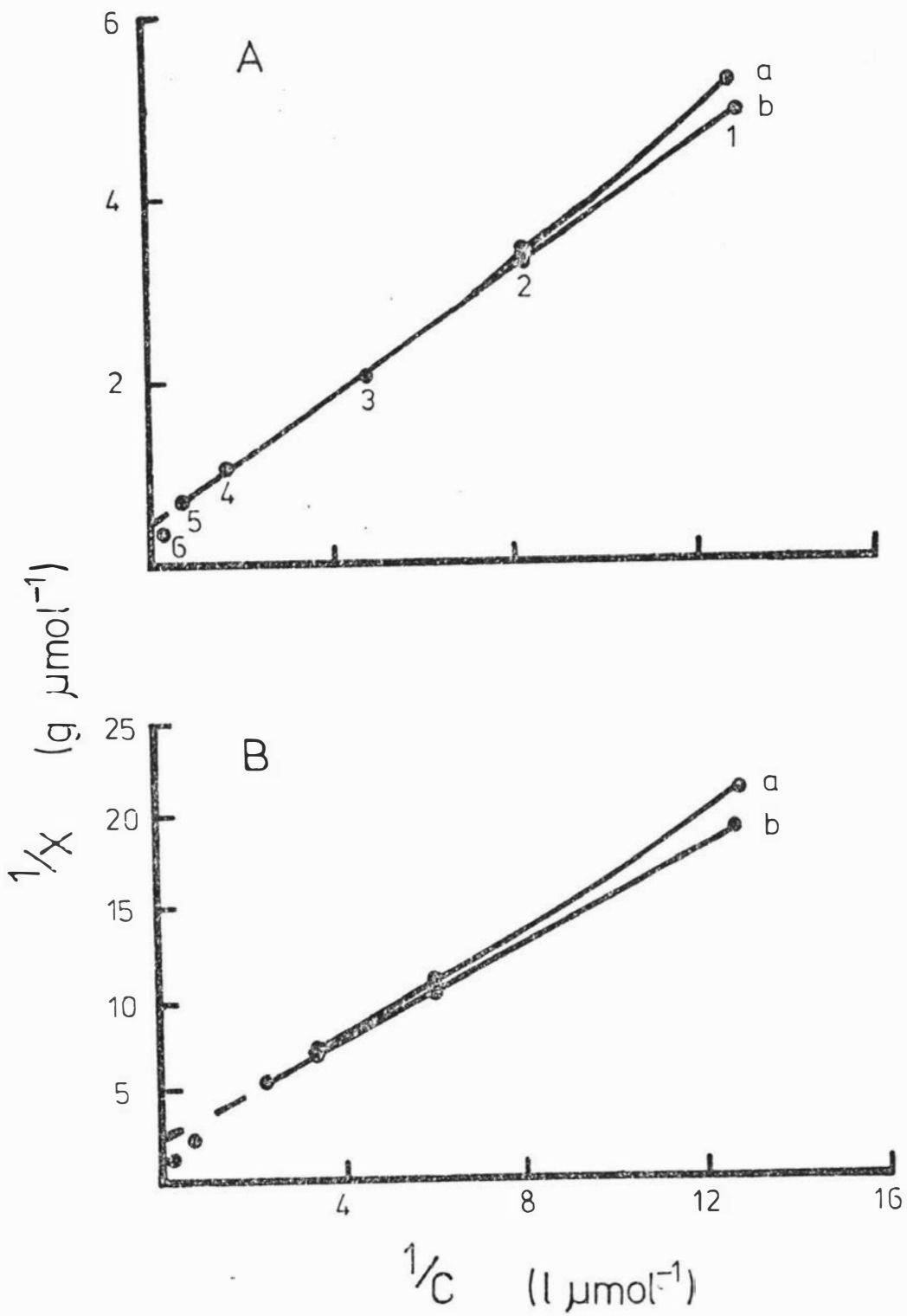


Fig. 3.7 Isotherms for the sorption of Mo by Ramiha (A) and Dannevirke (B) topsoils at equilibrium, before (a) and after (b) inclusion of native sorbed Mo, plotted using the linear form of the Langmuir equation.

Table 3.2 Outline of the method of successive approximations used to test the fit of experimental data to the Langmuir equation

Step	Plot	Determine
1	$1/x$ vs $1/c$ *	k_I, b_I
2		x_I
3		$x_{II} = x - x_I$
4	$1/x_{II}$ vs $1/c$	k_{II}, b_{II}
5		x_{II}^+
6		$x_{III} = x - (x_I + x_{II})$
7	$1/x_{III}$ vs $1/c$	k_{III}, b_{III}
8		x_{III}^+
9		$x_I = x - (x_{II} + x_{III})$
10	$1/x_I$ vs $1/c$	k_I, b_I
11		x_I^+
12		$x_{II} = x - (x_I + x_{III})$

Repeat steps 4 - 12 until difference between successive approximations of k is $<5\%$

x = Mo sorbed (added Mo sorbed + native Mo) c = final Mo concentration

* for low $c = 0 - 0.25 \mu\text{mol l}^{-1}$

+ from preceding k and b values for all values of c .

When the data were evaluated by this method, it was found that equilibrium and 40-hr isotherms could be resolved into three concentration ranges, with sorption in each being described by a distinct Langmuir equation. The data were not assumed to fit three Langmuir equations. Rather, all data points did not conform to straight line plots of $1/x$ against $1/c$ until three equations were established. Fig. 3.8 shows the data points from Fig. 3.6 after treatment by the method of successive approximations. The three concentration ranges, each with a distinct Langmuir equation, will subsequently be referred to as regions, with each region having corresponding b and k values.

Sorption isotherms for all four topsoils, both at equilibrium and 40 hr, and for all four subsoils at 40 hr, gave three Langmuir relationships. Isotherms for each region can be calculated using the b and k values, and these isotherms can then be summed over the final concentration range of 0 to $120 \mu\text{mol l}^{-1}$ to generate a "calculated" isotherm which can be compared with experimental data points, as shown in Fig. 3.9 for Okaihau topsoil. The deviation of the calculated isotherm was less than 3% at any concentration for all four topsoils and subsoils. This close agreement between observed and calculated isotherms confirms that Mo sorption in the range of 0 - $120 \mu\text{mol l}^{-1}$ can be described by three Langmuir equations.

For all soils, both topsoils and subsoils, at equilibrium and at 40 hr, each region dominated the shape of the sorption isotherm over a very similar, specific concentration range. For example, region I dominated over the range of 0 - $0.3 \mu\text{mol l}^{-1}$, region II over the range of $0.6 - 5.0 \mu\text{mol l}^{-1}$, and region III over the range of $20 - 120 \mu\text{mol l}^{-1}$. Fig. 3.9 also illustrates that sorption in region I was virtually complete at a concentration of $0.5 \mu\text{mol l}^{-1}$ and sorption in region II at

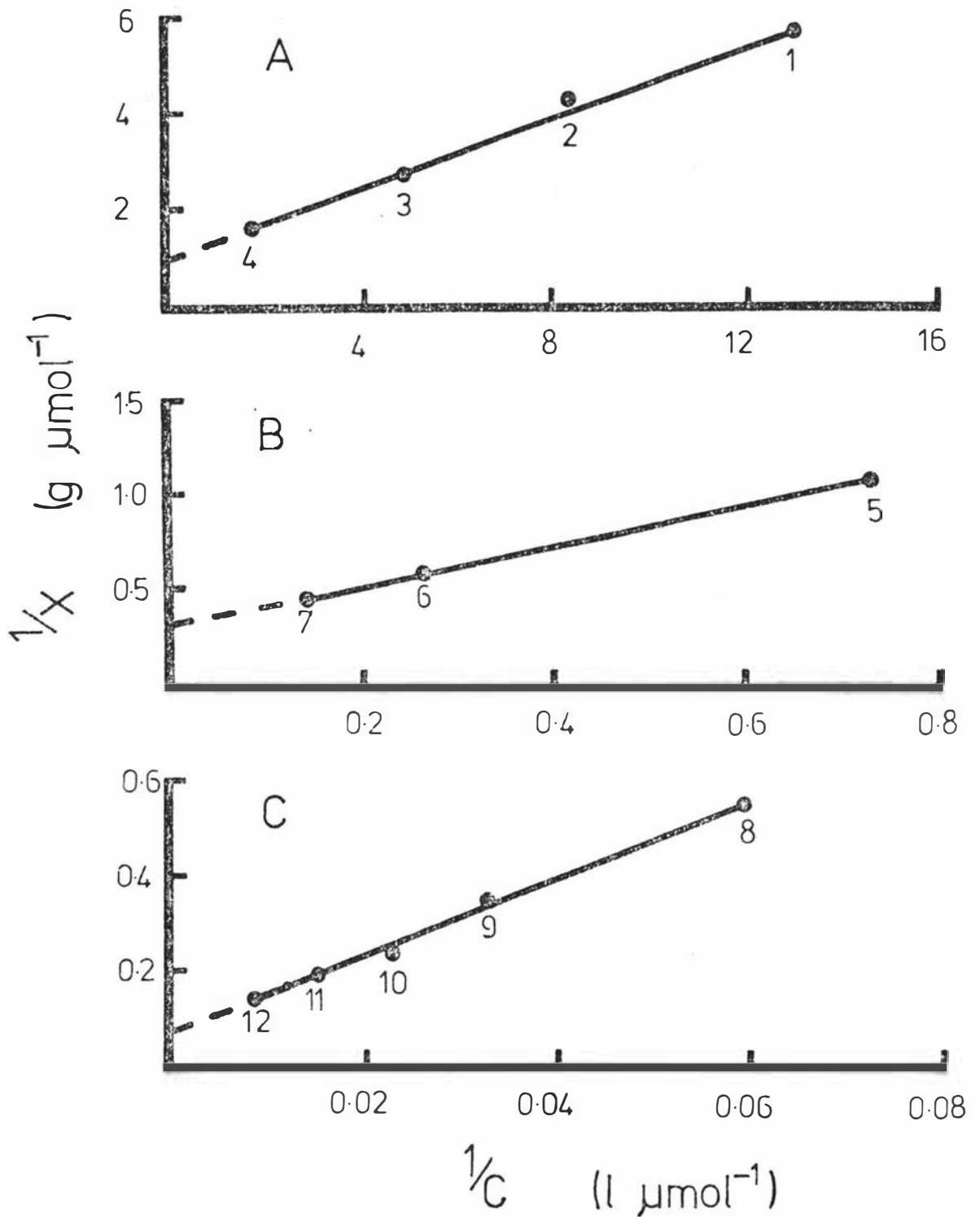


Fig. 3.8 Equilibrium isotherms for Ramiha topsoil plotted using the reciprocal form of the Langmuir equation and showing the three Langmuir relationships obtained after resolution of the data by successive approximation of the sorption constants. A = region I, B = region II, and C = region III.

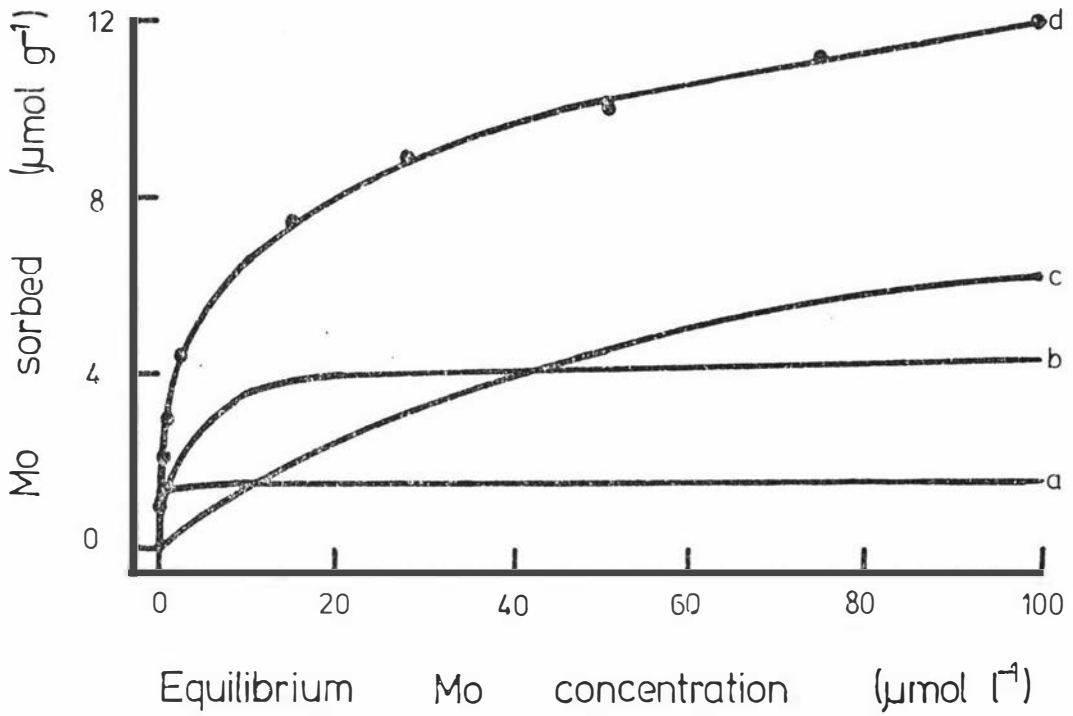


Fig. 3.9 Equilibrium isotherms for sorption of Mo by Okaihau topsoil over the concentration range of 0 - 100 $\mu\text{mol l}^{-1}$.
 a = resolved isotherm for region I, b = resolved isotherm for region II, c = resolved isotherm for region III, and d = regenerated isotherm obtained by summation of a, b, and c. ● = experimental data points.

10 $\mu\text{mol l}^{-1}$. Region III sorption continued up to concentrations greater than 120 $\mu\text{mol l}^{-1}$. The fact that sorption in region I was virtually complete at a concentration of 0.5 $\mu\text{mol l}^{-1}$ highlights the necessity of using low levels of Mo addition to yield very low final Mo concentrations in constructing sorption isotherms. Determination of isotherms at only high concentrations would lead to either deviations from a single Langmuir equation (if only a few points at low concentration were determined) or the detection of only one region obeying the Langmuir equation (probably being equivalent to region III in this study).

Table 3.3 gives values for the sorption maxima (b) and sorption energy constants (k) for each region, namely b_I , k_I , etc., for all four topsoils at equilibrium and at 40 hr, and for all four subsoils at 40 hr. Table 3.3 also gives values for the free energies of sorption, ΔG_I , ΔG_{II} , etc. Derivation of ΔG values has been discussed previously (Chapter 1) but the validity of such a derivation needs to be discussed further.

3.3.3.3. Derivation of free energies of sorption

The ΔG values were derived from the Langmuir constants (k), by equation (3.1):

$$\Delta G = -RT \ln k \quad (3.1)$$

The validity of such an equation requires some discussion.

For sorption of a non-electrolyte by an ideal surface at equilibrium, the fractional surface coverage (θ), is given by equation (3.2) (Graham, 1953):

$$\frac{\theta}{1 - \theta} = Kc \quad (3.2)$$

where K = the equilibrium constant, and c = the equilibrium concentration.

Table 3.3 Sorption maxima (b), sorption energy constants (k), and free energies of sorption (ΔG) for each region of sorption at equilibrium and 40 hr, determined from Mo-sorption isotherms for four topsoils, and at 40 hr, determined from Mo-sorption isotherms for four subsoils

Sorption Time	Soil	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}	ΔG_I	ΔG_{II}	ΔG_{III}
		$\mu\text{mol g}^{-1}$			$l \mu\text{mol}^{-1}$			kJ mol^{-1}		
Equilibrium	Okaihau Topsoil	1.47	4.35	9.90	18.89	0.479	0.0171	-41.2	-32.1	-24.0
	Ramiha Topsoil	1.01	3.57	11.77	2.75	0.159	0.0109	-37.0	-29.4	-22.9
	Dannevirke Topsoil	0.075	1.11	3.57	7.17	0.375	0.0143	-38.9	-31.9	-23.9
	Tokomaru Topsoil	0.235	1.16	3.57	21.3	0.346	0.0181	-41.5	-31.4	-24.1
40 hr	Okaihau Topsoil	0.710	3.13	10.53	14.43	0.311	0.0060	-40.5	-31.1	-21.4
	Ramiha Topsoil	0.345	2.45	11.24	3.95	0.157	0.0077	-37.3	-29.4	-22.0
	Dannevirke Topsoil	0.066	0.555	3.39	4.14	0.174	0.0120	-38.0	-29.9	-23.1
	Tokomaru Topsoil	0.131	0.990	2.94	10.04	0.206	0.0080	-39.7	-30.1	-22.1
40 hr	Okaihau Subsoil	0.96	5.78	14.93	12.24	0.227	0.0092	-40.2	-30.4	-22.5
	Ramiha Subsoil	1.39	6.06	13.16	3.73	0.119	0.0087	-37.3	-28.8	-22.3
	Dannevirke Subsoil	1.05	3.70	15.38	9.60	0.280	0.0059	-39.6	-30.9	-21.4
	Tokomaru Subsoil	0.488	1.39	14.29	40.2	0.750	0.0097	-43.3	-33.3	-22.6

This assumes that the concentrations are sufficiently dilute that the activity coefficients are unity, and that the activity coefficients of occupied and unoccupied sites are the same. The equilibrium constant (K), is related to the free energy of sorption for the reaction, ΔG , by equation (3.3):

$$\Delta G = -RT \ln K \quad (3.3)$$

ΔG is a reflection of the driving force of the reaction, or chemical affinity between the reactants. From equation (3.3) it follows that a large K value equates with a large, negative ΔG value.

Equation (3.2) is of the same form as that for the Langmuir isotherm, equation (1.14), with the equilibrium constant, K , identical to the kinetically-derived Langmuir constant (k). Hence, if equation (3.3) is valid, equation (3.1) is also valid. Aveyard and Haydon (1973) have also shown that equation (3.1) is valid for sorption from non-electrolytes using statistical thermodynamics.

For sorption from electrolytes, however, coulombic and solvation forces, as well as chemical forces, become important. The free energy of sorption is then the sum of the free energies of chemical attraction, solvation, and coulombic attraction. Solvation energies are usually negligible compared to the other two (Huang, 1975). The free energy of sorption (ΔG) is, therefore, given by equation (3.4):

$$\Delta G = \Delta G_{\text{chemical}} + \Delta G_{\text{coulombic}} \quad (3.4)$$

where ΔG_{coul} depends on the electrical potential in the plane of the sorbed ion. If the Langmuir constant (k) is used to calculate ΔG , then the value of ΔG depends on both $\Delta G_{\text{chem.}}$, the chemical driving force of the reaction, and the electrical potential in the sorbed plane, which is dependent on the magnitude of sorption (Aveyard and Haydon, 1973).

As a result, ΔG will not be constant unless the coulombic term is small compared to the chemical term, as ΔG_{Coul} will change as sorption changes. If there is a strong interaction between the sorbing ion and the surface, leading to a high ΔG_{chem} , or the electrical potential is suppressed by the presence of a high concentration of non-sorbing electrolyte, then ΔG will be constant. In such cases, ΔG will reflect the chemical affinity of the surface for the sorbing ion. For sorption involving chemisorption reactions, this would be expected.

3.3.3.4 Implications of k and ΔG values

Comparison of ΔG values for each region, obtained from equilibrium and 40-hr isotherms, showed two features: (1) ΔG values for each region for all soils were very similar; (2) for each region, and any one soil, ΔG values at equilibrium and 40 hr for both topsoils and subsoils were very similar. The similarity of ΔG_{Coul} for each region over the four soils indicates that the same sorption reactions are involved in all four soils. Although there are small differences in ΔG values between soils, all ΔG values fell in a consistent grouping. Assuming that the chemical term in the free energy expression (equation 3.4) dominates, then this indicates that for any particular region, the same chemical reaction occurs with each soil. The significant differences in ΔG values between each region indicate that each region corresponds to a different chemical reaction, with region I corresponding to the reaction with the greatest affinity between the surface and sorbing species and region II and III involving correspondingly weaker reactions. The large and negative ΔG values indicate that the reaction operating in each region involves a chemisorption type of reaction, with regions I and II involving stronger chemisorption reactions than region III. As there is often an overlap between chemisorption and physical sorption reactions (Adamson, 1967), region III could be of a more-physical sorption type

than regions I and II.

The fact that ΔG values occurred in three distinct groupings, for both topsoils and subsoils, clearly suggests that three reactions are occurring. If the ΔG values were dominated by the coulombic term in equation (3.4), then a continuum of ΔG values would be expected. This justifies the assumption that the chemical free energy dominates the overall sorption energy and consequently, each region corresponds to a separate sorption reaction.

The similarity of ΔG values, for any particular region, between equilibrium and 40-hr isotherms, also indicates that at both times the same chemical reactions are proceeding. This clearly shows that increasing the time of sorption affects only the extent of the reaction, but not the mechanisms involved. Consequently, further equilibrium isotherms were not determined.

The sorption energy constants (k), obtained from the Langmuir equation, are often used to compare sorption affinities between soils and anions (Theng, 1971; Rajan et al., 1974). As indicated in Table 3.3, however, differences in k between soils within one order of magnitude indicate only small changes in free energies of sorption and, consequently, only differences in k of greater than one order of magnitude indicate differing sorption mechanisms. Small differences in k probably reflect the different contribution of ΔG_{coul} for different soil components, which would have small effects on the overall free energy of sorption, compared to the chemical free energy of the reaction.

Sorption of Mo has been described by the Langmuir equation in previous studies by Reyes and Jurinak (1967), Theng (1971), and Gonzalez et al. (1974). Reyes and Jurinak (1967) did not give k values for

their data. Over the concentration range of 0 - 70 $\mu\text{mol l}^{-1}$, approximate k values can be determined from the data presented by Theng (1971). These k values for two allophanic clays and a kaolin-illite clay are all of the order of 0.1 $\text{l } \mu\text{mol}^{-1}$, which is comparable to region III k values obtained in the present study. No further comparisons are possible, as Theng (1971) did not obtain detailed data at low final solution concentrations. The study of Gonzalez et al. (1974) was carried out at very high final concentrations (0-7000 $\mu\text{mol l}^{-1}$) and the k values obtained cannot be compared with any of those obtained in the present study. Unless detailed data are obtained at low concentrations, use of the Langmuir equation to evaluate data obtained at high concentrations may be inaccurate and lead to misleading conclusions.

3.3.3.5 Implications of b values

The influence of time on the extent of the reaction is shown by the change in the sorption maxima (b) between 40 hr and equilibrium. The sorption maxima of both regions I and II increased by a considerable percentage, if not in absolute terms. The sorption maxima for region III differed very little between 40 hr and equilibrium. For example, the average increase, over the four topsoils, in b_I , between 40 hr and equilibrium, was 97%, the increase in b_{II} , 51%, and the increase in b_{III} , 6%. This provides further evidence that region III involves a more-physical type of sorption than regions I and II. Chemisorption reactions often occur slowly, whereas physical sorption reactions proceed much faster as there is little or no energy of activation for the latter sorption type (Adamson, 1967). The constancy of region III and the increase in the sorption maxima of regions I and II with time suggest that Mo sorbed in region III may be slowly converted to the more-strongly

bound regions I and II. For P sorption, Ryden et al. (1977b) have shown that more-weakly sorbed (region III) P is converted to chemisorbed P with time. The behaviour of sorbed Mo appears to be similar.

Sorption maxima for subsoils were generally larger than those for topsoils for each region. Compared to their topsoils, all four subsoils sorbed greater amounts of strongly-held Mo (regions I and II) and also sorbed greater amounts of Mo in region III. Differences in soil properties (Table 2.4) do not offer any simple explanation for the differences in sorption and, along with native sorbed P, which may hinder sorption of Mo if the sites for the two anions are common, probably have a combined influence on the sorption maxima changes.

3.3.4 Mo sorption by Fe gel and allophane

Hydrous iron oxides are frequently stated to be important in Mo sorption (Jones, 1957; Reisenauer et al., 1962) and have been used as models for Mo sorption by soils (Reisenauer et al., 1962). There has been no quantitative verification, however, of the use of synthetic hydrous oxides as models for Mo sorption by soils. The sorption of Mo by Fe gel was evaluated, therefore, using the Langmuir equation to provide a comparison with sorption by soils. The same procedure was used with synthetic allophane, which has been cited as an important soil component in Mo sorption (Gonzalez et al., 1974) and is known to be one of the dominant components in the Ramiha and Dannevirke soils used in this study.

Isotherms for Mo sorption by synthetic Fe gel and allophane during 40 hr are shown in Fig. 3.10. Both gel systems were at pH 6.2 prior to sorption. The isotherm for Fe gel was of a definite H-type (Giles et al., 1960), whereas the allophane isotherm was L-type, indicating a greater number of high affinity sites for Mo on the Fe gel surface than

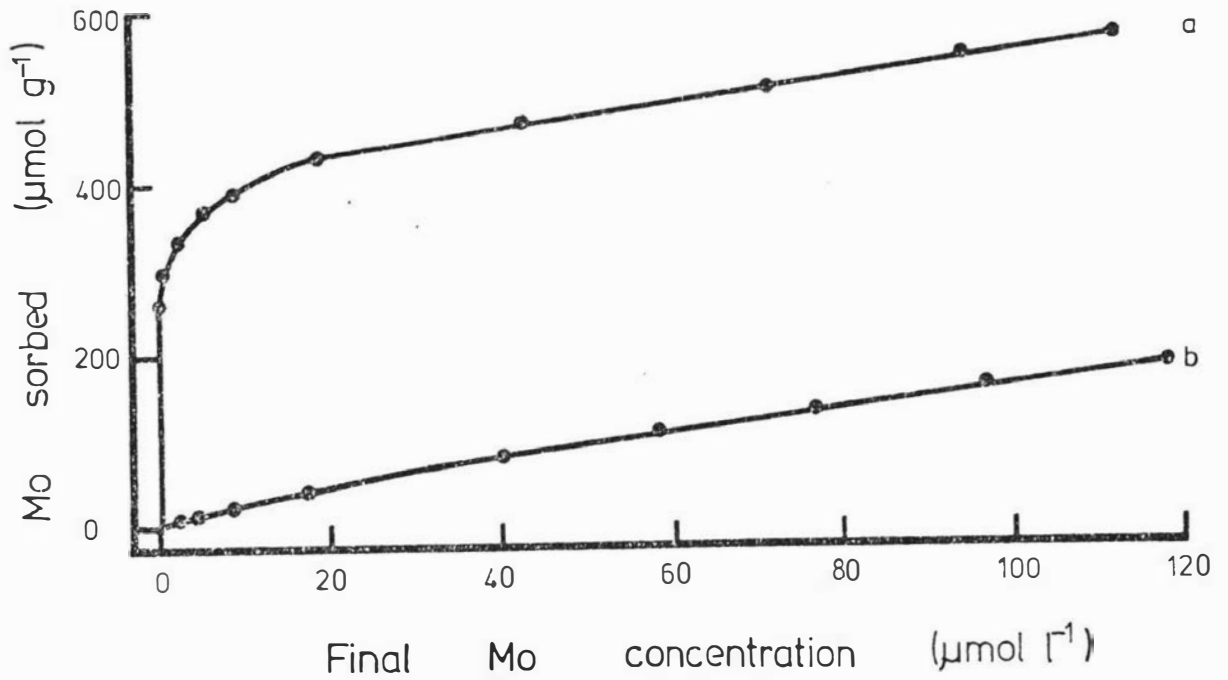


Fig. 3.10 Isotherms for the sorption of added Mo by Fe gel (a) and allophane (b) from 10^{-1}M NaCl during 40 hr at pH 6.2 over the final concentration range of 0 - 120 $\mu\text{mol l}^{-1}$.

on the allophane surface. The extent of Mo sorption by Fe gel was dominated by sorption at low final concentrations ($<1 \mu\text{mol l}^{-1}$), whereas Mo sorbed by allophane increased regularly over the whole concentration range. For example, at $c = 0.5 \mu\text{mol l}^{-1}$, Fe gel and allophane sorbed 295 and $3 \mu\text{mol g}^{-1}$, respectively, whereas at $c = 70 \mu\text{mol l}^{-1}$, they sorbed 505 and $121 \mu\text{mol g}^{-1}$, respectively.

When the sorption data for both Fe gel and allophane were tested for fit to the Langmuir equation, the isotherms could be described by three Langmuir equations. Sufficient data points were obtained in the very low concentration range ($<0.5 \mu\text{mol l}^{-1}$) for Mo sorption by Fe gel, despite the large amounts of Mo sorbed. Table 3.4 gives values for b , k , and ΔG for Mo sorption by Fe gel and allophane.

The values for b indicate that large amounts of Mo were chemisorbed (regions I and II) by Fe gel, but that very much smaller amounts of Mo were chemisorbed by allophane. Both Fe gel and allophane sorbed large amounts of Mo in region III. The different shapes of the sorption isotherms (Fig. 3.10) can, therefore, be explained in terms of differences in the amount of chemisorbed Mo.

The ΔG values for each region were very similar to those obtained for soils. It is noticeable that, although allophane sorbed small amounts of Mo in regions I and II, the sorption energies for these regions were similar to those for Fe gel and soils. The similarity of ΔG values indicates that the sorption reactions occurring in soils, synthetic Fe gel, and synthetic allophane are essentially the same for each region, even though different atoms (Fe and Al) are involved. The previously assumed fact that Fe gel is a satisfactory model for Mo sorption by soils (Reisenauer et al., 1962; Hingston et al., 1967, 1968b) is, therefore, shown to be a realistic assumption.

Table 3.4 Sorption parameters for Mo sorption by Fe and allophane gels during 40 hr from 10^{-1} M NaCl at pH 6.2^{*}

Sorbent	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}	ΔG_I	ΔG_{II}	ΔG_{III}
	$\mu\text{mol g}^{-1}$			$l \mu\text{mol}^{-1}$			kJ mol^{-1}		
Fe gel	265	115	556	58.5	0.503	0.0043	-44.0	-32.3	-20.6
Allophane	1.15	13.9	769	16.7	0.086	0.0024	-40.9	-28.0	-19.1

* pH of system with no added Mo.

The similarities in ΔG values for Fe gel and allophane, even though their b values differ widely, suggest that kinetic factors are hindering the chemisorption of Mo by allophane, but that these are not important for the more-physical sorption in region III. Possible causes of the kinetic effects will be discussed in Chapter 4.

CHAPTER 4

COMPARISON OF PHOSPHATE AND MOLYBDATE
SORPTION BY SOILS AND SOIL COMPONENTS

4.1 Introduction

Although P and Mo are often assumed to bond to soil surfaces by a similar mechanism (Hingston et al., 1968b, 1972; Theng, 1971), there has been remarkably little comparison of the sorption of these two anions.

In Chapter 3 it was shown that the sorption of Mo by soils and two soil components could be described by three Langmuir equations. Similar findings have been reported for P sorption by some New Zealand soils and Fe gel by Ryden et al. (1977a). In this Chapter, P sorption data are evaluated using the Langmuir equation and a comparison of P and Mo sorption is made. Differences in the extent of sorption of each anion by soils and soil components are discussed, and possible reasons for the differences discussed.

4.2 Methods

Both topsoils and subsoils of Okaihau, Ramiha, Dannevirke, and Tokomaru soils were used. Synthetic Fe gel and allophane, prepared as described in Chapter 3, were also used in the study.

Sorption isotherms for P were determined in 10^{-1} M NaCl during 40 hr, with P additions leading to final solution concentrations in the range of 0-300 $\mu\text{mol P l}^{-1}$. For each isotherm, between fifteen and twenty additions of P were made, with at least four giving final concentrations below 0.5 $\mu\text{mol l}^{-1}$. Isotherms for soils were determined at a solution:solid ratio of 40:1, whereas those for Fe gel and allophane

were determined at a solution:solid ratio of 800:1 and 1000:1, respectively. Sorption isotherms for Fe gel and allophane were determined at pH 6.2 (the pH of the system in the absence of P).

4.3 Results and Discussion

4.3.1 Evaluation of P sorption isotherms using the Langmuir equation

The method of evaluation of Mo sorption isotherms, involving successive approximations of data points (Table 3.2), was used on data for P sorption by soils and soil components. The P sorption isotherms for topsoils, subsoils, Fe gel, and allophane could be resolved into three regions, each described by a Langmuir equation. The concentration range over which each region dominated the overall sorption was: region I, 0 - 0.5 $\mu\text{mol l}^{-1}$; region II, 1 - 15 $\mu\text{mol l}^{-1}$; and region III, 25 - 300 (or greater) $\mu\text{mol l}^{-1}$.

Using the linear form of the Langmuir equation (equation 1.16), sorption maxima (b) and sorption energy constants (k) were calculated. From the k values, free energies of sorption (ΔG) were calculated using equation (3.1). Values for b, k, and ΔG for each region, and all sorbents, are given in Table 4.1. For any particular region, the free energies of sorption were very similar for topsoils, subsoils, and synthetic soil components, implying that similar mechanisms are operating at the different sorbing surfaces. The ΔG values are similar to those presented by Ryden et al. (1977a) for contrasting New Zealand soils. These authors also showed that the same mechanisms were involved in sorption at equilibrium and at 40 hr, and therefore, in this study only 40-hr isotherms were obtained. Based on the high ΔG values,

Table 4.1 Sorption maxima (b), sorption energy constants (k), and free energies of sorption (ΔG) for each region of sorption, for P sorption from 10^{-1} M NaCl during 40 hr

Sor bent		b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}	ΔG_I	ΔG_{II}	ΔG_{III}
		$\mu\text{mol g}^{-1}$			$l \mu\text{mol}^{-1}$			kJ mol^{-1}		
Okaihau	Topsoil	4.95	16.7	35.7	13.38	0.175	0.0043	-40.4	-29.7	-20.6
Ramiha	Topsoil	9.80	30.8	47.6	5.64	0.119	0.0044	-38.3	-28.8	-20.7
Dannevirke	Topsoil	4.74	8.00	20.8	4.40	0.059	0.0019	-37.7	-27.0	-18.6
Tokomaru	Topsoil	1.68	2.38	5.56	3.41	0.072	0.0060	-37.0	-27.5	-21.4
Okaihau	Subsoil	6.07	25.2	43.0	23.1	0.316	0.0068	-41.8	-31.2	-21.7
Ramiha	Subsoil	16.7	41.7	73.0	10.0	0.169	0.0070	-39.7	-29.6	-21.8
Dannevirke	Subsoil	5.59	15.2	33.3	12.3	0.182	0.0035	-40.2	-29.8	-20.1
Tokomaru	Subsoil	2.34	5.00	14.3	15.3	0.107	0.0026	-40.7	-28.5	-19.4
Fe gel [*]		806	400	1176	26.4	0.208	0.0030	-42.1	-30.1	-19.7
Allophane ⁺		641	588	769	4.22	0.055	0.0023	-37.5	-26.9	-19.0

* At pH 6.2.

+ For $c < 200 \mu\text{mol l}^{-1}$.

plus other evidence, Ryden et al. (1977a) proposed that sorption in regions I and II involved chemisorption, whereas sorption in region III involved a more-physical type sorption. The same approach will be adopted here.

The b values for different soils and soil components do not show any similarity. These b values reflect limits on the extent of the P sorption reaction, and are, therefore, determined by both solution parameters and the number of P sorption sites; the latter will depend on the mineralogical and chemical composition of the sorbent. The b values for any particular subsoil were greater than those for the corresponding topsoil. Comparison of sorption maxima for Fe gel and allophane indicates that Fe gel sorbed greater amounts of P in region I, but allophane sorbed greater amounts in regions II and III. Sorption of P by allophane depends on the ratio of Al:Al + Si (Cloos et al., 1968) and generalisations are not possible from the data for the allophane gel used in this study, which had an Al:Al + Si ratio of 0.60. Test of the sorption data obtained for allophane for fit to the Langmuir equation indicated that, at final P concentrations greater than $200 \mu\text{mol l}^{-1}$, fit of the data to three Langmuir equations was not good. At high final solution P concentrations, disruption of the polymer surface of allophane may occur (Rajan, 1975). Consequently, P sorption by allophane, in this study, was limited to final P concentrations less than $200 \mu\text{mol l}^{-1}$.

4.3.2 Comparison of P and Mo sorption

4.3.2.1 Extent of anion sorption

Isotherms for sorption of Mo and P by topsoils (Fig. 2.1 and 2.3), subsoils (Fig. 2.2 and 2.4), Fe gel (Fig. 3.10 and 4.1), and allophane

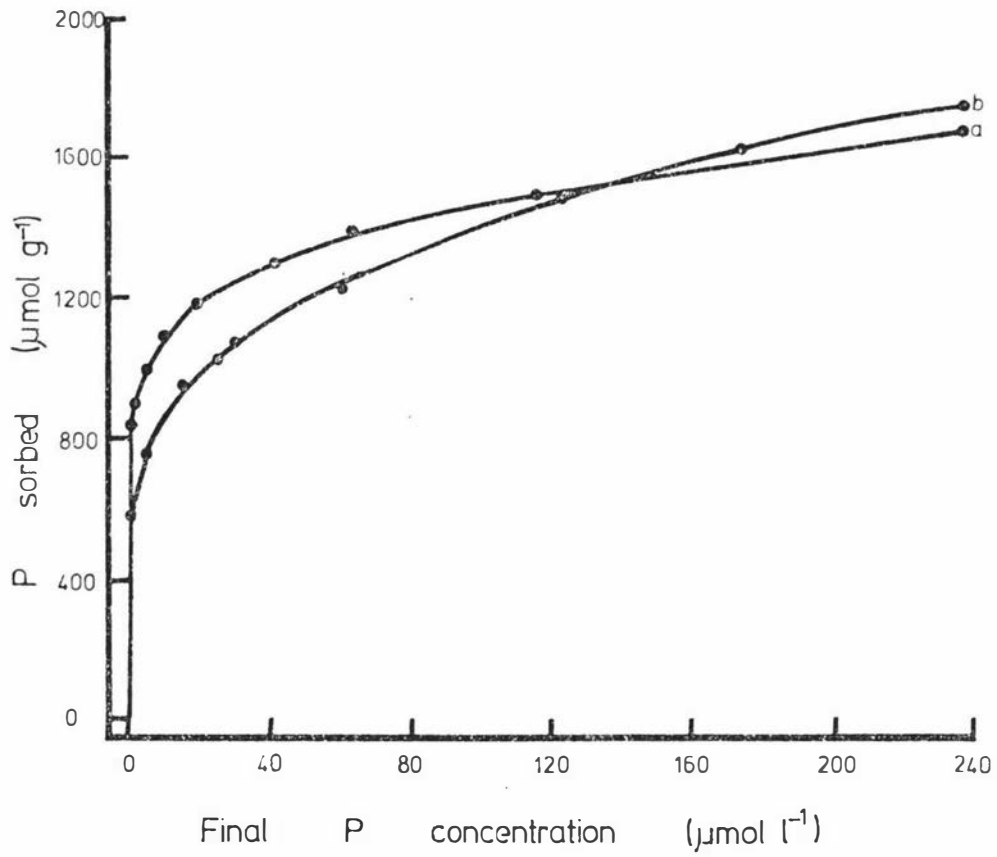


Fig. 4.1 Isotherms for the sorption of added P by Fe gel (a) and allophane (b) from 10^{-1}M NaCl during 40 hr at pH 6.2 over the final concentration range of 0 to $250 \mu\text{mol l}^{-1}$.

(Fig. 3.10 and 4.1) illustrate that P sorption isotherms were all H-type (Giles et al., 1960), whereas Mo sorption isotherms were either H-type (Fe gel and all subsoils) or more L-type (allophane and all topsoils). H-type isotherms indicate a large number of high-affinity sites for sorption, whereas L-type isotherms indicate fewer numbers of such sites. The difference in shape of the isotherms for P and Mo sorption by allophane is particularly marked, with the Mo sorption isotherm showing little H-type character, whereas the P sorption isotherm was strongly H-type.

All sorbents sorbed less Mo than P, although the ratio of Mo sorbed: P sorbed, at any one final concentration, for example, $c = 10 \mu\text{mol}^{-1}$ ranged from very low values (0.03 for allophane) to those approaching unity (Tokomaru subsoil). This ratio was also dependent on final concentration. The approach used by Barrow (1970) to compare P and Mo sorption by the amount sorbed at one single final concentration could, therefore, lead to erroneous conclusions. Native sorbed P could also decrease the sorption of Mo, although this would not account for the differences between added P sorbed and added Mo sorbed.

Table 4.2 shows the ratio of the sorption maxima of P and Mo for the three regions of the sorption isotherms, and highlights several interesting points. First, the presence of allophane in the Dannevirke and Ramiha soils greatly decreased the amount of Mo sorbed, relative to P sorbed. Second, the ratio of sorption maxima for region I was generally lower than for region II. Subtracting out values for native sorbed P from P sorption maxima for region I resulted in comparable ratios for regions I and II. This was also true for Fe gel which had no native sorbed P. The fact that the Mo:P sorption maxima ratios for regions I and II were almost equal, after subtraction of native P, for each

Table 4.2 Saturation of the P sorption complex by native sorbed P and ratios of the sorption maxima, for each region of sorption, for Mo and P sorption during 40 hr

Sorbent	$\frac{\text{Native P}}{b_I (P)}$	$\frac{b_I (Mo)}{b_I (P)}$	$\frac{b_{II} (Mo)}{b_{II} (P)}$	$\frac{b_{III} (Mo)}{b_{III} (P)}$
<u>Topsoils</u>				
Okaihau	0.28	0.15 (0.20)	0.19	0.29
Ramiha	0.36	0.036(0.056)	0.080	0.098
Dannevirke	0.69	0.014(0.046)	0.069	0.16
Tokomaru	0.71	0.078(0.273)	0.42	0.53
<u>Subsoils</u>				
Okaihau	0.13	0.16 (0.18)	0.23	0.35
Ramiha	0.17	0.083(0.12)	0.15	0.18
Dannevirke	0.22	0.19 (0.24)	0.24	0.46
Tokomaru	0.38	0.21 (0.34)	0.28	1.00
Fe gel	-	0.33	0.29	0.47
Allophane	-	0.0018	0.024	0.50

Figures in parenthesis = $\frac{b_I (Mo)}{b_I (P)}$ - native sorbed P.

$b_I (Mo)$, $b_I (P)$ etc. = b_I for Mo sorption, P sorption, etc.

individual soil, seems to indicate that there may be similar factors limiting Mo sorption, relative to P, for sorption in both regions I and II. Third, the ratio of the region III maxima was generally higher than for either of the other two regions, and was unity for the Tokomaru subsoil, i.e., the ratio of the maxima for more-physical sorption was greater than that for chemisorption, implying that the factors causing differences in the extent of chemisorption did not affect the extent of the more-physical type sorption reaction.

The reasons why the ratios differed from unity, however, are not clear. The size of the two tetrahedral anions of P and Mo are very similar, the O - O distances being in the range 2.85 - 3.20 Å for P (van Wazer, 1958) and 3.20 Å for Mo (Lindquist, 1950). This suggests that steric factors do not hinder the sorption of Mo, relative to P. The affinities of each anion for the surface, reflected by ΔG values, are also comparable. This might lead to the prediction that almost equal amounts of P and Mo would be sorbed. The ratio of Mo sorbed:P sorbed for allophane, however, shows that different sorbing components can greatly affect this ratio. Barrow (1970) has shown that the ratio of Mo sorbed:P sorbed is greatly affected by pH. Based on the theories of Hingston et al. (1967, 1968b) that anion sorption requires the simultaneous presence of a proton donor and a proton acceptor, Barrow accounted for most of the changes in the ratio of anions sorbed, although he also stated that the changes could be accounted for by only requiring the presence of the proton donor. The pK_{a2} of molybdic acid is between 3.6 and 4.0 (Aveston et al., 1964; Sasaki and Sillen, 1964) and the dominant Mo species in solution above pH 5.0 will be MoO_4^{2-} . The pK_{a2} of phosphoric acid is 7.20, and hence, for the P sorption studies, the predominant species will be $H_2PO_4^-$, and possibly HPO_4^{2-} nearer to pH 7.

Charge differences cannot be the dominant cause of the sorption differences because these would be reflected in different ΔG values, except if charge affected the kinetics of sorption. The different degree of protonation of the predominant anionic species present, however, could influence the extent of the sorption reaction and also, variations in pH may partly account for the different ratios of Mo:P sorption between soils.

4.3.2.2. Free energies of sorption

Comparison of ΔG values for P sorption (Table 4.1) with those for Mo sorption (Tables 3.3 and 3.4) clearly indicates that, for each region of sorption, ΔG values for both anions were very similar. This indicates that the driving force for the sorption of each anion is similar, even though the charge on the predominant species in solution, MoO_4^{2-} and H_2PO_4^- , respectively, differs. As discussed in Chapter 3, the free energy of sorption consists of two contributing energies, namely those of chemical and coulombic interaction. Because of the different charge on the predominant anionic species, the coulombic attractive forces for a given oxide surface would differ for each anion. These forces would be greater for Mo, as the coulombic free energy is proportional to the charge on the sorbing species, for a given oxide at constant pH. If the coulombic term dominated the overall free energy, ΔG values for Mo would be greater than those for P and, as the coulombic term varies with surface coverage, ΔG would also vary. Chemical free energies must, therefore, dominate the overall free energies of sorption. Further indirect evidence comes from the coulombic free energies calculated by Huang (1975) for Stern sorption of P species by $\gamma\text{-Al}_2\text{O}_3$. For H_2PO_4^- ΔG_{COU} varied from -3.7 to 0 kJ mol^{-1} between pH 2.0 and 8.4, whereas

ΔG_{Coul} . values for HPO_4^{2-} were twice those of the singly-charged species at any pH. Huang stated that similar values would be expected on other oxide surfaces, and it can, therefore, be concluded that

ΔG_{Chem} . terms must be large and negative to give the observed ΔG values in the present study, i.e., chemical sorption energies dominate the overall free energies of sorption.

Differences in chemical free energies of the reaction between the surface and the anionic species might be expected to be mirrored in values of stability constants for the cationic surface species and the sorbing anion. Such a relationship has been quoted by Adamson (1967) for sorption of ions by barium sulphate. Although log solubility products for P species are large and negative, for example, $\log K_s(\text{Fe}^{3+} \text{H}_2\text{PO}_4^-(\text{OH}^-)_2) = -33.5$ to -35.0 (Sillen and Martell, 1964), there are no published details for Mo. If solubility product values for Mo were slightly lower than those for P, the chemical energy would also be slightly lower. As the coulombic energy term will be slightly greater for Mo than P, a slightly lower solubility product for Mo would result in the sum of the chemical and coulombic energies for P and Mo sorption being approximately equal. Because of the low magnitude of the coulombic free energy term, and the high comparable values for the overall free energies of sorption, the chemical free energies of sorption for each anion, in each region of sorption, must be comparable. This implies that the sites for sorption must be similar for each anion. The mechanism of sorption of P by oxide surfaces has been extensively studied and also relatively well characterised; the results found for P sorption should therefore be useful in proposing mechanisms for Mo sorption. Further considerations of this will be given in Chapter 5.

4.3.2.3 P and Mo sorption by allophane

Similar structural models for allophane have been proposed independently by van Reeuwijk and de Villiers (1970) and de Villiers (1971), and by Cloos et al. (1968, 1969). The structural model postulates that amorphous alumino-silicates consist of a permanently negatively-charged silica core, the permanent negative charge arising from isomorphous substitution of Al for Si in tetrahedral coordination with oxygen. The negatively-charged core is surrounded by positively-charged monomeric, or polymeric, octahedral Al cations. As the Al:Al + Si ratio (A) increases, the maximum substitution of Al for Si is reached and six-fold Al in the polymeric hydroxy phase then increases. At A values >0.80, crystalline Al phases begin to form. Experimentally, it has been found that surface area and P sorption increase as A increases (Cloos et al., 1968; Rajan and Perrott, 1975).

Theng (1971) found that the relative extent of Mo sorption by two allophanic clays was the opposite of that expected for P sorption, i.e., the clay with the lowest A value sorbed more Mo. Figs. 3.10 and 4.1 show that P and Mo sorption by allophane, relative to sorption by Fe gel, differed markedly, i.e., much less Mo was sorbed by allophane. The data in Tables 3.4 and 4.1 show that the reduction in Mo sorption by allophane, compared to P sorption by allophane and compared to both Mo and P sorption by Fe gel, was largely a result of the small amounts of Mo that were chemisorbed by allophane.

The two obvious factors that might be expected to cause the anomalous sorption behaviour of Mo by allophane, relative to P, are steric hindrance and charge repulsion. As discussed previously, steric hindrance does not appear to be a reason, because the size of the anions of Mo and P are comparable. At pH 6.2, the predominant Mo and P species,

MoO_4^{2-} and H_2PO_4^- , are singly- and doubly-charged, respectively. The higher charge on the Mo anion could, therefore, be important in affecting the reaction. As the ΔG values for Mo and P sorption by allophane are comparable, the charge may be affecting the kinetics of the Mo sorption reaction.

Coulombic repulsion between the permanent negative charge on the silica core and the sorbing anion species would be higher for a more negative anion. This coulombic repulsion could negate the attractive forces between the Mo ion and the hydroxy - Al species. Such coulombic forces would decrease inversely with distance, indicating that sorption in region III may involve longer-range interactions with the surface, which would be unaffected by the permanent negative charge and enable large amounts of Mo to be sorbed in region III. As the A value of allophane increases, the net positive charge per Al atom in the hydroxy - Al layer decreases (Cloos et al., 1968). This could reduce attractive coulombic forces, thus reducing the approach of anions to the sorbing surface. If repulsive forces were more effective than the increasing surface area, then sorbed Mo might be expected to decrease as A increases, as observed by Theng (1971). More detailed work is required on this before definite conclusions can be reached. The work of Theng (1971) did not differentiate between different sorption sites, and increasing A values could affect each site differently.

An explanation for the large differences in the relative sorption between P and Mo for Ramiha and Dannevirke soils is now possible. Both these soils contain allophane, which is expected to be the predominant P-sorbing surface. But allophane has a much lower capacity to sorb Mo, relative to P, than has Fe gel. Thus, Ramiha and Dannevirke soils would

be expected to sorb less Mo, relative to P, than the Okaihau and Tokomaru soils, whose sorbing surfaces are predominantly Fe compounds, as discussed in Chapter 2.

CHAPTER 5

EVALUATION OF THE MECHANISMS
INVOLVED IN MOLYBDATE SORPTION

5.1 Introduction

It has previously been shown that the sorption of Mo by soils and soil components can be described by three Langmuir equations, both for sorption during 40 hr and at equilibrium. Similar observations have been made for P sorption by the same soils and soil components. The free energies of sorption for each region of sorption for both Mo and P were also remarkably similar. The reason for the fit of the data to three Langmuir equations and the close similarity in Mo and P sorption behaviour clearly require explanation.

The fact that Mo sorption by soils is dependent on pH is well established (Jones, 1957; Reisenauer et al., 1962; Reyes and Jurinak, 1967). Also, the observed effects of pH on maximum sorption of Mo has been quoted as evidence for the operation of a particular Mo sorption mechanism (Theng, 1971; Gonzalez et al., 1974). There has been little quantitative investigation, however, of the effect of pH on Mo sorption. Similarly, the stoichiometry of H^+/OH^- uptake and release during Mo sorption has not been investigated quantitatively, except at very high final Mo concentrations (Reisenauer et al., 1962). Such very high final Mo concentrations have little relevance to the field situation. The effect of the sorption of Mo on surface charge has been predicted (Hingston et al., 1967, 1968b, 1972) but no studies have been conducted to evaluate the mechanisms involved in Mo sorption.

Because of the similar free energies of sorption of Mo at 40 hr and equilibrium, it has been suggested that the mechanisms of Mo sorption

are not influenced by reaction time (Chapter 3). Also, Fe gel has been shown to be a good model surface for Mo sorption by soils. Consequently, the effect of pH on Mo sorption, the stoichiometry of the Mo sorption reaction with respect to H^+ and OH^- , and the effect of Mo sorption on double layer charge can be investigated quantitatively using 40-hr sorption studies and Fe gel. These data, along with the fit of sorption data to Langmuir equations, are used to propose Mo sorption mechanisms.

5.2 Methods

The method of preparation of the Fe gel was described in Chapter 3.

The effect of pH on Mo sorption by Fe gel was investigated using sorption from $10^{-1}M$ NaCl during 40 hr at three pH values, namely 5.0, 6.2, and 7.4. The pH was not controlled during sorption. The pH values given refer to the pH of the gel suspension in the absence of Mo. The solution:solid ratio was approximately 800:1.

The amount of acid consumed to maintain constant pH (pH 6.0) during Mo sorption by Fe gel, was measured using an automatic titrator (Radiometer), at room temperature, and under a nitrogen atmosphere to exclude CO_2 . The gel (100 mg) was pre-equilibrated in $10^{-1}M$ NaCl for 16 hr, after which time the pH of the suspension was stable. An aliquot of Mo (in $10^{-1}M$ NaCl at pH 6.0) was then added so that the total final volume was 40 ml. The acid consumed ($10^{-1}M$ HCl in $10^{-1}M$ NaCl) to maintain constant pH following Mo sorption was recorded by the automatic titrator, the acid being added initially at a rapid rate to prevent large pH changes immediately after Mo additions. After a sorption time of 4 hr, the suspension was centrifuged, filtered, and analyzed for Mo.

Isotherms were obtained for sorption of Mo by Fe gel from 10^{-4} M NaCl during 40 hr at a solution:solid ratio of 800:1. After 40 hr, the suspensions were centrifuged, filtered, and the pH measured prior to analysis for Mo. The effect of Mo sorption on double layer charge was evaluated by measuring the degree of flocculation of Fe gel which had sorbed Mo from 10^{-4} M NaCl during 40 hr at a solution:solid ratio of 800:1. The degree of flocculation subsequent to Mo sorption was evaluated by allowing the gel suspension to settle for 1.5 hr at the end of the shaking period. A 10-ml aliquot was then taken from a constant depth below the surface, made up to a final volume of 50 ml with distilled water, and the transmittance % read at 700 nm in a 1-cm cell immediately after shaking the flask.

5.3 Results and Discussion

5.3.1 Effect of pH on Mo sorption

Isotherms for the sorption of Mo by Fe gel at pH 5.0, 6.2, and 7.4 are shown in Fig. 5.1. Isotherms at pH 5.0 and 6.2 were similar in shape, both being H-type, with appreciably more Mo being sorbed at pH 5.0 at any one final Mo concentration. Considerably more Mo was sorbed at low concentrations ($< 1 \mu\text{mol l}^{-1}$) at pH 5.0 than at pH 6.2, whereas at concentrations greater than $1 \mu\text{mol l}^{-1}$, the two isotherms were similar in shape. The isotherm at pH 7.4 differed markedly from those at lower pH values, being L-type with very small amounts of Mo sorbed at low final solution concentrations. A gradual increase in Mo sorbed over the whole concentration range ($0\text{-}100 \mu\text{mol l}^{-1}$) was obtained. The shape of the isotherm also differed significantly from that obtained by Ryden et al. (1977a) for P sorption by Fe gel

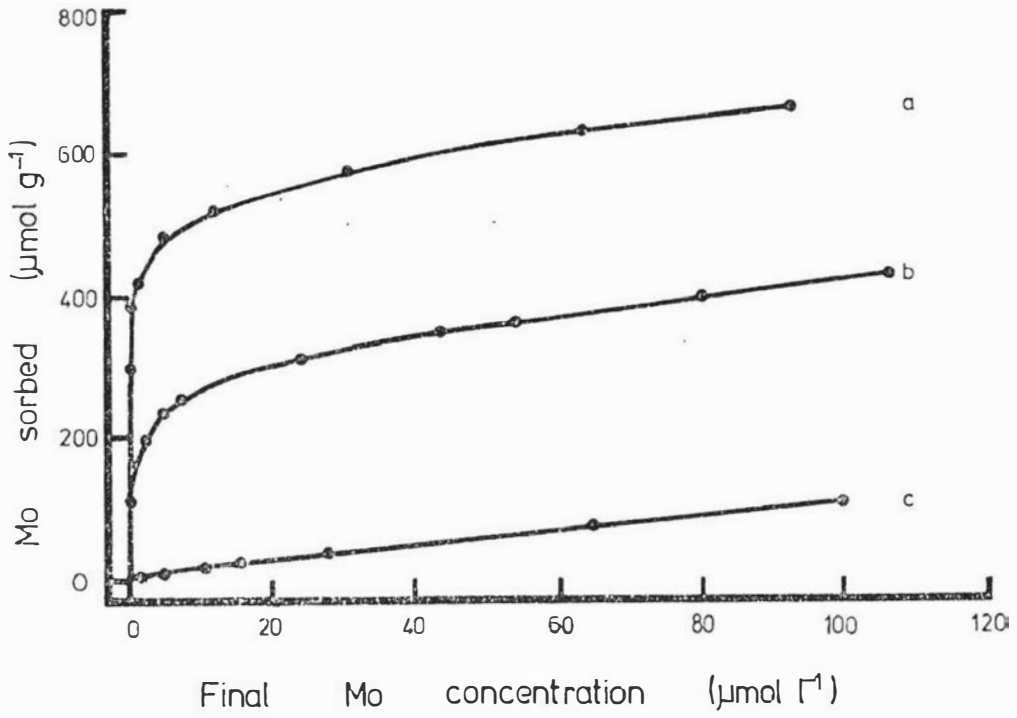


Fig. 5.1 Isotherms for the sorption of Mo by Fe gel from 10^{-1}M NaCl during 40 hr at three different pH values. a = pH 5.0, b = pH 6.0, and c = pH 7.4.

at pH 7.2. The P sorption isotherm at this pH was markedly H-type.

Test of isotherm data for fit to the Langmuir equation was carried out and at pH 5.0 and 6.2, three regions were obtained, each being described by a separate Langmuir equation. At pH 7.4, only two regions were obtained. The b , k , and ΔG values at each pH are given in Table 5.1. The two regions found at pH 7.4 had k and ΔG values that were of the same order as the k and ΔG values for regions II and III of the isotherms at other pH values, and consequently the two regions at pH 7.4 were ascribed to region II and III.

For each region, the ΔG values were very similar at different pH values, indicating that the sorption reactions were similar at the different pH values. The exception was region I, in which sorption did not occur at pH 7.4. Comparison of ΔG values for sorption by Fe gel in region I (Table 5.1) with those for soils (Table 3.3) indicates that ΔG values for Fe gel were higher than those for soils. Because they were still of the same order of magnitude, the chemical reactions occurring, and hence $\Delta G_{\text{chem.}}$ must be the same, because $\Delta G_{\text{chem.}}$ appears to dominate the overall ΔG (Chapter 3). The differences in ΔG values between soils and Fe gel in region I would, therefore, appear to be due to a greater $\Delta G_{\text{Coul.}}$, i.e., greater coulombic interactions. As $\Delta G_{\text{Coul.}}$ depends on the electrical potential (ψ_d), it would appear that the well-defined Fe gel surface has a greater ψ_d than the soil surfaces. The fact that ΔG_I for Mo sorption by Fe gel at pH 5.0 is greater than that at pH 6.2 confirms that the increase in ΔG is due to coulombic interactions. The surface charge of oxide surfaces is more positive at lower pH values (Parks and de Bruyn, 1962) and hence ψ_d is greater. Thus,

Table 5.1 Sorption maxima (b), sorption energy constants (k), and free energies of sorption (ΔG) for Mo sorption by Fe gel from 10^{-1} M NaCl during 40 hr at pH 5.0, 6.2, and 7.4

pH	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}	ΔG_I	ΔG_{II}	ΔG_{III}
	$\mu\text{mol g}^{-1}$			$l \mu\text{mol}^{-1}$			kJ mol^{-1}		
5.0	289	211	444	384	1.44	0.0065	-48.6	-34.9	-21.6
6.2	112	149	435	135	0.60	0.0059	-46.1	-32.8	-21.4
7.4	-	6.7	500	-	0.096	0.0024	-	-28.2	-19.4

ΔG_{coul} would also be greater at lower pH values.

The extent of each sorption reaction, as indicated by the respective b values, differed markedly at each pH. Sorption in region I decreased with increasing pH. In region II, sorption also decreased with increasing pH and at pH 7.4, the sorption maxima in region II was very small, compared to that at lower pH values. The decreasing amounts of chemisorbed Mo with increasing pH, therefore, explains the decrease in H-type character of the isotherms with pH (Fig. 5.1). Sorption in region III was only slightly affected by pH changes; the b values for region III did not decrease between pH 5.0 and 6.2, and increased at pH 7.4. Over the concentration range of 0-100 $\mu\text{mol l}^{-1}$, the amount of Mo sorbed in region III, calculated from b and k values, decreased slightly as the pH increased. For example, at $c = 50 \mu\text{mol l}^{-1}$, 107, 94, and 50 $\mu\text{mol g}^{-1}$ was sorbed in region III at pH 5.0, 6.2, and 7.4, respectively. Thus, although the number of sites available for sorption (indicated by the sorption maximum) did not decrease with increasing pH, the amount of Mo sorbed at any one final concentration decreased because of a decrease in k values, indicating a decreasing driving force of the reaction, with increasing pH. The pH at the point of zero charge (pH(p.z.c.)) of the Fe gel was not determined. For Fe gels prepared in a similar manner, pH (p.z.c.) prior to sorption is in the range 8.0 to 8.4 (J.R. McLaughlin, pers. comm.). This implies that the limited chemisorption of Mo by Fe gel at pH 7.4 is not because the gel surface has a net negative charge at that pH. For P sorption, considerable chemisorption has been reported (Ryden et al., 1977a) at pH 9.0, indicating that Fe gel is capable of sorbing some anions at pH values greater than pH (p.z.c.). Hence, the almost non-existent chemisorption of Mo at pH 7.4 would seem to be primarily a function of the Mo anion,

rather than of the Fe gel surface.

5.3.2 Mo sorption by Fe gel from 10^{-4} M NaCl

5.3.2.1 Sorption isotherms

Isotherms for the sorption of Mo from 10^{-1} M and 10^{-4} M NaCl during 40 hr are shown in Fig. 5.2. The pH of the gel suspension in 10^{-1} M NaCl was 5.0 and the pH in 10^{-4} M NaCl was 4.9. Both isotherms had the same shape, i.e., H-type, with large amounts of Mo being sorbed at $C < 1 \mu\text{mol l}^{-1}$. At concentrations greater than $1 \mu\text{mol l}^{-1}$, the isotherms in 10^{-4} M NaCl levelled off and the increase in Mo sorbed, relative to that sorbed at $C < 1 \mu\text{mol l}^{-1}$, was much less in 10^{-4} M NaCl than in 10^{-1} M NaCl. In 10^{-4} M NaCl, the increase in Mo sorbed in the concentration range of 50 - 100 $\mu\text{mol l}^{-1}$ was negligible.

The sorption constants obtained for sorption from 10^{-1} M and 10^{-4} M NaCl are shown in Table 5.2. For sorption from 10^{-4} M NaCl, two linear regions of the overall isotherm, each being described by a distinct Langmuir equation, were obtained. From the k and ΔG values obtained, these two regions corresponded to regions I and II of the sorption isotherms in 10^{-1} M NaCl systems. There was no sorption in region III from 10^{-4} M NaCl. Sorption maxima for sorption in regions I and II were smaller than the corresponding values for sorption from 10^{-1} M NaCl. No direct comparison of b values can be made, however, because ionic strength affects the kinetics of Mo sorption (Chapter 3.3) and at 40 hr, the systems are not at equilibrium. It is of interest that the value of b_I for Mo sorption from 10^{-4} M NaCl was similar to that obtained by Ryden et al. (1977a) for P sorption by Fe gel which was prepared by the same method as the gel in this study, and for sorption during the same time period and at approximately the same pH; this is in contrast to the b values obtained for Mo and P

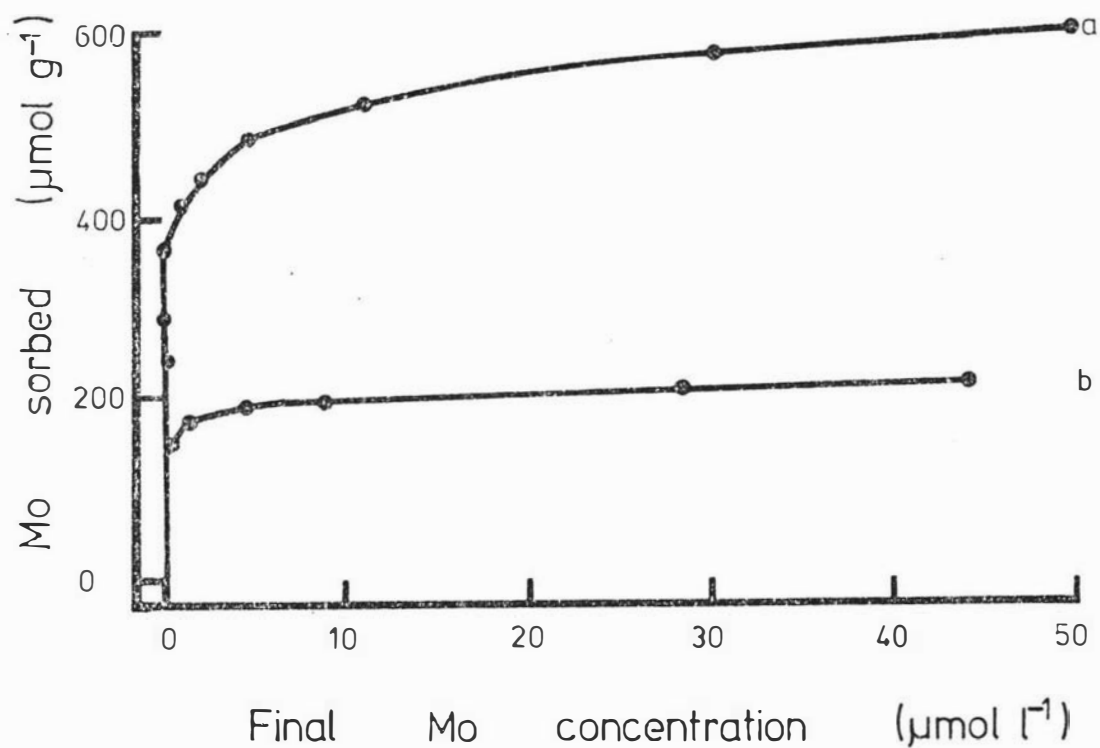


Fig. 5.2 Isotherms for the sorption of Mo by Fe gel from solutions of different ionic strength, but essentially the same pH, during 40 hr. a = 10^{-1} M NaCl, pH 5.0, and b = 10^{-4} M NaCl, pH 4.9.

Table 5.2 Sorption maxima (b), sorption energy constants (k), and free energies of sorption (ΔG) for Mo sorption by Fe gel from $10^{-1}M$ and $10^{-4}M$ NaCl during 40 hr

Ionic strength	pH*	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}	ΔG_I	ΔG_{II}	ΔG_{III}
		$\mu\text{ mol g}^{-1}$			$l \mu\text{ mol}^{-1}$			kJ mol^{-1}		
$10^{-1}M$	5.0	289	211	444	384	1.44	0.0065	-48.6	-34.9	-21.6
$10^{-4}M$	4.9	175	50	-	26	0.095	-	-42.0	-28.2	-

* in the absence of added Mo.

sorption from 10^{-1} M NaCl (Chapters 3 and 4).

The free energies of sorption for regions I and II in 10^{-4} M NaCl are noticeably smaller than those for the corresponding values in 10^{-1} M NaCl, although the value for region I in 10^{-4} M NaCl is still much greater than the ΔG value obtained for region II in 10^{-1} M NaCl. At higher ionic strengths, the net surface charge, and hence the electrical potential of the double layer, on oxide surfaces is greater (Parks and de Bruyn, 1962). The coulombic free energy term of equation (3.4) would, therefore, make a greater contribution to the overall free energy at higher ionic strengths. Given this fact, the data of Table 5.2 appear to indicate that the same chemical reactions occur in regions I and II in different ionic strength media.

5.3.2.2 Charge and pH relationships

The pH and flocculation data (measured by transmittance %) for Fe gel suspensions subsequent to Mo sorption from 10^{-4} M NaCl are shown in Fig. 5.3, as a function of the amount of Mo sorbed. Point a corresponds to near saturation of region I (95% b_I) and a very low saturation of region II (5% b_{II}). These saturation values were calculated using the b and k values for each region.

Values for pH subsequent to sorption increased as the amount of Mo sorbed increased. Because sorption in region II was not significant until point a, it appears that sorption in region I caused an increase in the pH of the solution. At sorption values beyond point a, pH continued to increase, indicating that sorption in region II also caused an increase in pH. Initial studies showed that pH increases were not due to ionization of MoO_4^{2-} , but were a result of Mo sorption.

Changes in the degree of flocculation of Fe gel reflected changes in the diffuse layer potential (ψ_d), as a result of changes in the

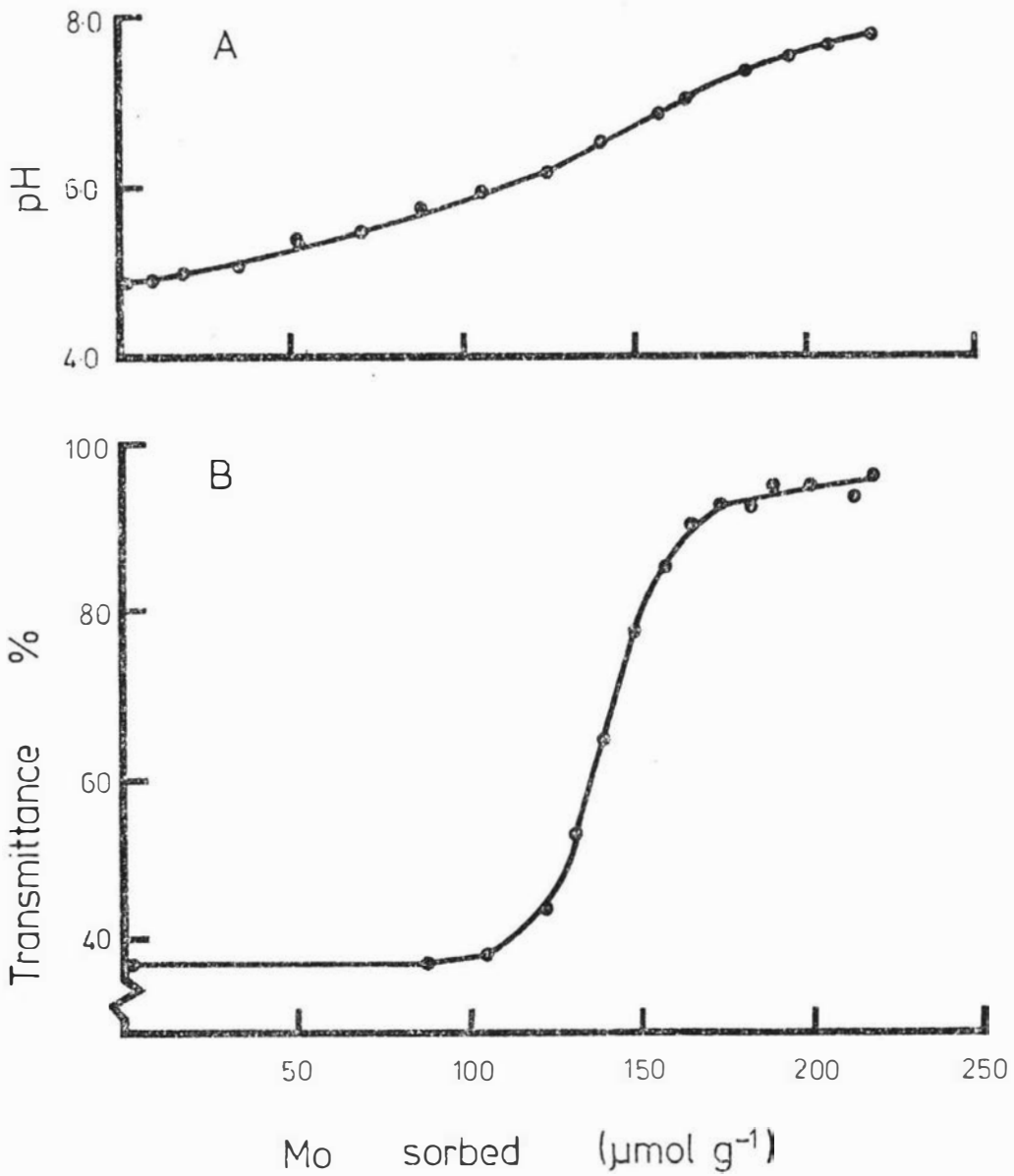


Fig. 5.3 Data for pH (A) and transmittance % (B) of Fe gel suspensions subsequent to Mo sorption from 10^{-4}M NaCl during 40 hr, as a function of the amount of Mo sorbed. For point a, refer to text.

surface charge, because changes in the ionic strength of the medium were not sufficient to cause flocculation changes. Fig. 5.3 indicates that as region I reached saturation, the degree of flocculation increased, i.e., the surface charge of the gel was being neutralised because of Mo sorption in region I. At point a, the surface charge of the gel had been neutralised. Sorption in region II did not result in further changes in surface charge because the gel remained flocculated as the extent of saturation of region II increased. The fact that after point a was reached, increasing Mo sorption did not result in the dispersion of the gel indicates that sorption in region II was not causing changes in the diffuse layer potential, which would be expected if Mo was sorbed at the inner Helmholtz plane (Fig. 1.2A) and superequivalent sorption resulted (Fig. 1.2B), i.e., Mo sorption in region II must involve exchange with surface groups and not result in changes in surface charge.

5.3.3 Acid consumption to maintain constant pH during Mo sorption

The acid required to maintain constant pH during Mo sorption by Fe gel during 4 hr is plotted against Mo sorbed in Fig. 5.4. It was not possible to determine whether the acid was used to maintain constant pH as a result of OH^- release resulting from Mo sorption or by H^+ uptake during Mo sorption. Point a indicates where Mo was detected in solution and shows that Mo sorption caused a pH increase over the whole concentration range ($0 - 100 \mu\text{mol l}^{-1}$). For any experimental data point, the mole ratio of H^+ consumed to Mo sorbed (R) was greater than 1.0 and less than 1.5, with the ratio being slightly greater at low final solution concentrations ($< 1 \mu\text{mol l}^{-1}$).

Sorption data were tested for fit to the Langmuir equation. Three

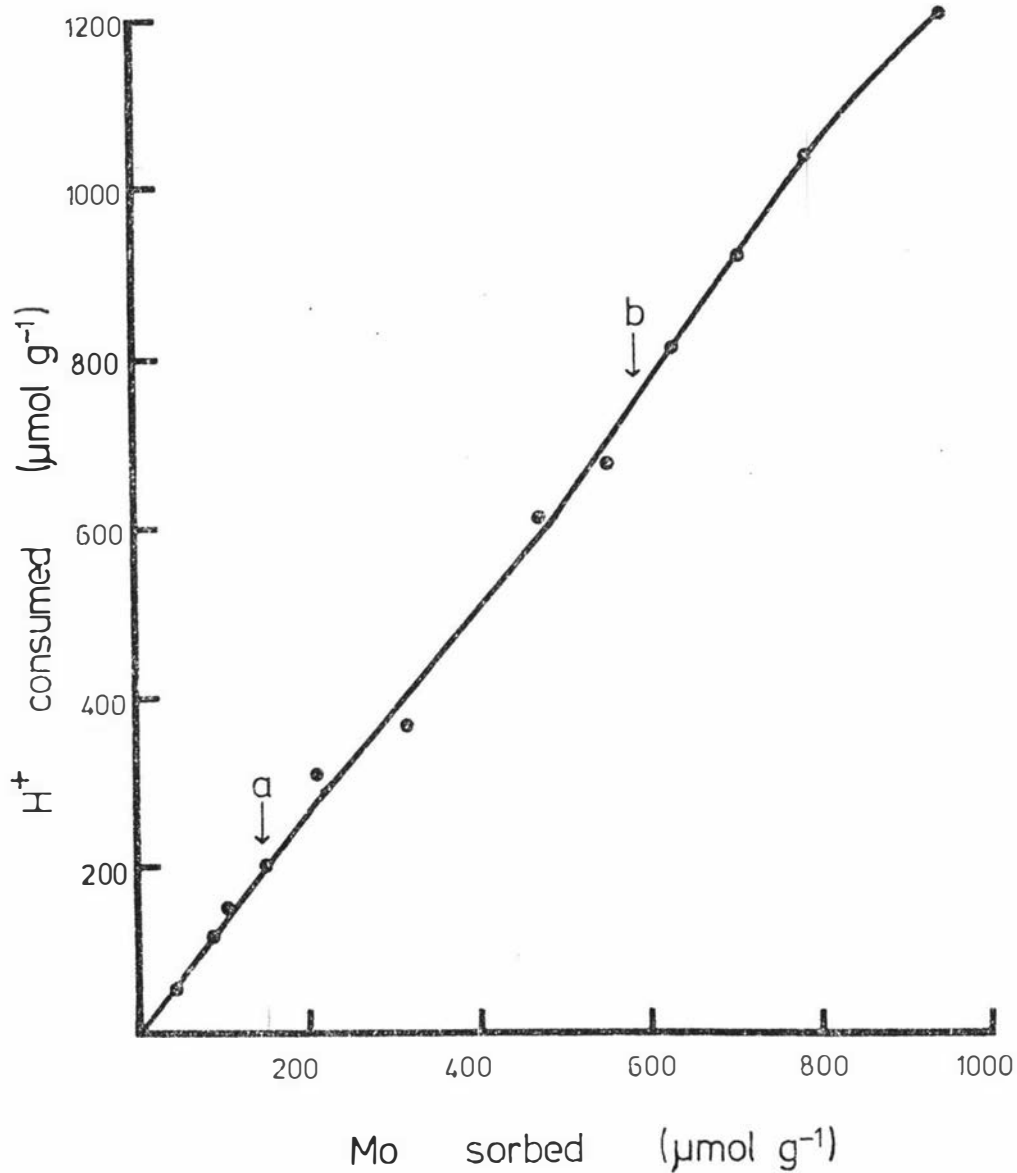
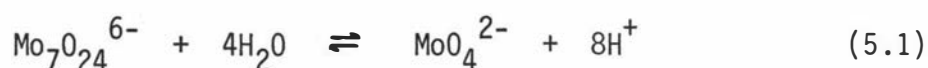


Fig. 5.4 Acid consumed to maintain constant pH (pH 6.0) during Mo sorption by Fe gel from 10^{-1}M NaCl during 4 hr, as a function of the amount of Mo sorbed. For points a and b, refer to text.

regions, each conforming to a distinct Langmuir equation, were again obtained. Point a in Fig. 5.4 indicates where saturation of region I was almost complete and saturation of region II became significant; point b indicates where saturation of region III became significant. There did not appear to be any marked change in acid consumption as sorption in the different regions began to dominate overall sorption and Mo sorption appeared to cause pH increases in each region of sorption.

The ratio (R) was not an exact integer at any one concentration, as might be expected for simple charge relationships. There appeared to be several factors that influenced this ratio, in addition to the back titration to pH 6.0. As will be discussed later, sorption of Mo appears to involve ligand-exchange with surface groups and consequently, may affect the surface charge of the hydrous oxide. The increase in pH subsequent to Mo sorption, and the possibility of a change in surface charge, suggest that some of the H^+ added subsequently may be sorbed at the surface as potential determining H^+ when the pH is returned to 6.0, in accord with surface charge-pH relationships of oxide surfaces (Fig. 1.3). The effect of this on the amount of H^+ consumed to maintain constant pH would be to over-estimate the ratio, R. Also, hydrous oxide surfaces are known to have a limited buffer capacity (Parks and de Bruyn, 1962) and this would affect the quantity of H^+ consumed. For high concentrations of added Mo, it is possible that the added Mo solutions would contain polymerised Mo anions at pH 6.0 (Cotton and Wilkinson, 1966). Common polymeric anions, e.g., $Mo_7O_{24}^{6-}$, dissociate according to equation (5.1) (Aveston et al., 1964):



Assuming that Mo sorbs as a monomeric anion (Reyes and Jurinak, 1967), then sorption of Mo would displace equation (5.1) to the right, resulting in the release of H^+ , which would affect the amount of H^+ measured to maintain constant pH. Each region of the overall sorption isotherm may also correspond to a different reaction, with different stoichiometry for OH^- release or H^+ consumption. This would mean that, at concentrations where sorption in different regions overlapped, the ratio (R) would have values intermediate between the extremes. All these factors would combine to give R values that would be non-integral. It does appear, however, that at least one mole of H^+ is required to maintain constant pH for every mole of Mo sorbed over all three regions of sorption.

5.3.4 The mechanism of Mo sorption

Any mechanism proposed must accommodate all the experimental data. These include the three different regions of sorption, each with a different free energy of sorption, which describe overall Mo sorption; the effects of pH and ionic strength on sorption in each of these three regions; the charge relationships and pH changes subsequent to Mo sorption; and the similarities and dissimilarities between Mo and P sorption.

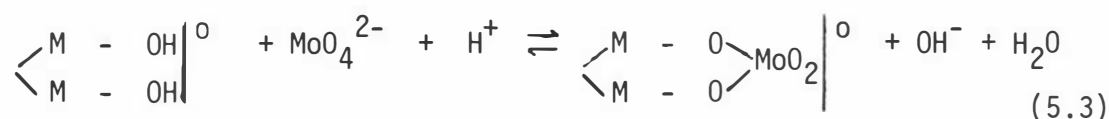
The sorbing surface is taken to be a hydrous oxide of Fe or Al, which has been shown in Chapter 1 to be important in anion sorption.

Such surfaces may be represented as: $\begin{matrix} < M - OH_2^+ \\ < M - OH \end{matrix} \Bigg| ^+$ (Parks and de Bruyn, 1962),

where $-OH_2^+$ and $-OH$ groups are singly-coordinated species that are adjacent in one plane (Russell et al., 1974). The proportion of $-OH_2^+$ to $-OH$ is governed by pH (Parks and de Bruyn, 1962; Yopps and Fuerstenau, 1964). The $-OH_2^+$ and $-OH$ species are considered to be

part of the hydrous metal oxide surface and replacement of these species by sorbing anions is a ligand-exchange process, which can be considered as a chemisorption reaction, with a new bond being formed between the surface and the anion.

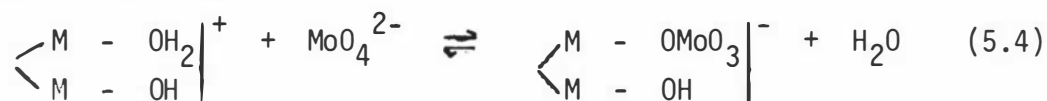
The mechanisms proposed lead to the formation of bidentate complexes by ligand-exchange of MoO_4^{2-} with surface $-\text{OH}_2^+$ and $-\text{OH}$ groups. Equation (5.2) is proposed to describe the sorption of Mo in region I, and equation (5.3) to describe sorption of Mo in region II, at pH values where MoO_4^{2-} is the predominant Mo species in solution ($\text{pH} > 5$):



The protons involved in equation (5.2) and (5.3) may be derived from solution, or at pH values where the species HMoO_4^- dominates ($\text{pH} < 5$), may be donated from this anion.

The reaction described by equation (5.2), involving ligand-exchange sorption at a positively-charged site, would have a higher free energy than the reaction described by equation (5.3) because of the greater electrostatic attraction, and would correspond to sorption in region I. Equation (5.2) would be influenced by pH, which would affect both the number of positively-charged surface sites, and the concentration of H^+ . The fact that sorption in region I did not occur at pH 7.4 (Table 5.1), even though some positive sites might be expected to exist at this pH, is almost certainly a consequence of H^+ limiting the extent of the reaction. Equation (5.2) would result in a reduction of the surface charge from a positive to a zero value, which is in agreement

with the flocculation data (Fig. 5.3). Formation of a monodentate bond with the surface (equation (5.4)) would result in the formation of a negatively-charged surface:



Because equation (5.4) results in replacement of one positive charge with one negative charge, the net surface charge would equal zero when the sum of the non-exchanged $-\text{OH}_2^+$ sites equalled the sum of the exchanged $-\text{OMoO}_3^-$ sites, i.e., at 50% saturation of the $-\text{OH}_2^+$ sites. Consequently, flocculation data would be expected to show a maximum at 50% b_I , with further saturation of region I resulting in a build up of negative charge and a resulting dispersed gel system. Detailed infrared studies of phosphated Fe oxides have shown that at low solution concentrations, P is bonded as a bidentate ligand to two Fe atoms by replacement of adjacent A-type hydroxyls (Russell et al., 1974; Parfitt et al., 1975; Parfitt and Atkinson, 1976). Recent infrared absorption studies have shown that Mo may also be bonded as a bidentate ligand at low solution concentrations (R.J. Parfitt, pers. comm.). Equation (5.4) is not in accord with the observation that sorption in region I requires the addition of H^+ to maintain constant pH (Fig. 5.4). The fact that equation (5.2) appears to describe Mo sorption in region I, rather than equation (5.4), is possibly because the bidentate complex formed in equation (5.2) would result in formation of a more stable uncharged complex than the charged monodentate complex formed in equation (5.4). Also, displacement of two ligand groups by MoO_4^{2-} would result in an overall increase in the entropy of the system and hence, would result in a greater decrease in the overall free energy of the system.

It is proposed that the consumption of H^+ rather than the release of OH^- explains the observed pH increase (Fig.5.3) and the quantity of acid consumed to maintain constant pH (Fig. 5.4), subsequent to Mo sorption in region I. Equation (5.2) would result in a decrease in surface charge and therefore, may result in H^+ sorption during back titration, as discussed in Section 5.3.3. As sorption in region I affects surface charge, it may be regarded as a potential-determining sorption. Such reactions are expected to be affected by ionic strength (Parks and de Bruyn, 1962) and the absence of such effects for Mo sorption by soils in region I may be due to the buffering capacity of other soil components, e.g., organic matter.

Sorption of Mo in region II (equation (5.3)) does not affect the surface charge and consequently would not be affected by ionic strength. Also, sorption according to equation (5.3) would not affect the degree of flocculation of Fe gel, as observed in Fig. 5.3. The extent of reaction (5.3) would be affected by pH because pH affects the concentration of H^+ available for the reaction. Reaction (5.3) would also result in a pH increase because of both H^+ consumption and OH^- release. The large reduction in the sorption maximum of region II with increases in pH (Table 5.1) can, therefore, be explained. The fact that small amounts of Mo appear to be sorbed in region II at pH 7.4 (Table 5.1) indicates that some Mo may be sorbed without the involvement of H^+ , probably by equation (5.5):



Such a reaction appears to be unfavourable because very little sorption occurs in region II at pH 7.4, implying that H^+ is necessary. This probably results from the fact that displacement of the second $-OH$

group to form the favourable bidentate complex is aided by H^+ weakening the second M-OH bond. The high free energy of sorption indicates that the driving force of the reaction must be sufficiently great to overcome the limitation of no free reactant H^+ . The dependence of sorption in region II on pH, however, indicates that equation (5.5) is of limited importance at pH values less than 7.0.

Both equations (5.2) and (5.3) involve ligand-displacement at the oxide surface and the formation of new chemical bonds. As such, they may be regarded as chemisorption reactions. Both reactions also appear to involve the formation of stable bidentate complexes, which would result in a decreased enthalpy of the system and an increased entropy of the system and hence, greater negative free energies of sorption. Therefore, equations (5.2) and (5.3) would have high free energies of sorption. Such high ΔG values were obtained for regions I and II. Sorption in regions I and II would, therefore, probably result in a chemisorbed layer that would be similar to a ferric molybdate surface of one molecular layer thickness.

It is proposed that sorption in region III occurs in a plane at some distance from the surface, approximating the Stern layer in simple double layer models. Such sorption would not involve ligand-exchange with surface groups and could occur with or without the presence of chemisorbed Mo. The Mo anion would not necessarily be held as a bidentate ligand, but such Mo could be considered "specifically sorbed"; i.e., the forces resulting in sorption are not only coulombic but also include chemical interactions (Breeuwsma and Lyklema, 1973). The chemical attractive energies, which operate over only short distances, would be less than those involved in the chemisorption of Mo. Thus, sorption in region III would be of a more-physical sorption type than

regions I and II. Because the anion would be held by both chemical and coulombic attraction, sorption in region III can be classed as intermediate between chemisorption and physical sorption.

Of the components of the total free energy of sorption, the chemical free energy is independent of pH, whereas the coulombic free energy depends on pH. As discussed previously, the fact that ΔG did not vary with the amount of Mo sorbed, or with pH, indicates that the chemical free energy must dominate the overall free energy for region III, and the sorption reaction cannot be classified as "true" physical sorption.

Because more-physical sorption in region III would not involve exchange with surface groups, and because H^+ would not be involved in the sorption reaction, the extent of sorption in region III would be expected to be independent of pH, as reported in Table 5.1. The sorption maxima would depend on the surface area and nature of the sorbent, rather than pH parameters. Sorption at the Stern layer, however, would depend on ionic strength, as obtained for sorption in region III (Chapter 3 and Table 5.2). This dependence on ionic strength arises because the potential at the Stern layer (ψ_d) depends on ionic strength. From theoretical double layer equations, it can be shown that increasing ionic strength reduces the magnitude of this potential, and also reduces the distance the potential extends from the surface, i.e., it suppresses the "thickness" of the double layer. Decreasing ψ_d results in a greater sorption density of potential-determining H^+ (Parks and de Bruyn, 1962). This would result in larger amounts of Mo being sorbed. Decreasing the thickness of the double layer also allows a greater concentration of ions at close distances to the surface, where chemical interactions become important, and hence, the sorption of more-physically sorbed Mo would increase.

At very low ionic strengths, increased thickness of the double layer would result in insignificant amounts of Mo approaching sufficiently close to the surface for chemical attractive forces to operate, and consequently, sorption in region III would be negligible. This was observed for Mo sorption by Fe gel from 10^{-4} M NaCl (Table 5.2).

Sorption in region III does not require the presence of chemisorbed Mo, as sorption in region III still occurred at pH 7.4 when very little chemisorbed Mo was present (Table 5.1). When such a chemisorbed layer does occur, however, sorption in region III may be considered as more-physical sorption at the chemisorbed layer. Adamson (1967) has stated that such sorption may result in sorption being described by multiple Langmuir equations, as reported for Mo sorption by soils and soil components in this study (Chapter 3). The free energies of sorption obtained from these Langmuir equations are in agreement with the proposed mechanisms. Ligand-exchange reactions would have higher free energies than long-range chemical attractions. Consequently, the smaller free energies of sorption for region III are in accord with the proposed mechanism.

It is well established that polymeric forms of the Mo anion can exist in solution under appropriate conditions (Cotton and Wilkinson, 1966). In the present study, however, the existence of polymeric Mo anions in final solutions is considered unlikely because at $\text{pH} > 5.0$, and for Mo concentrations less than $100 \mu\text{mol l}^{-1}$, polymeric anions do not occur in solution (Chojnacki, 1963; Aveston et al., 1964). Such concentrations were rarely exceeded in the present study. By comparing observed and calculated sorption maximum values, Reyes and Jurinak (1967) have concluded that sorption of polymeric Mo species did not occur up to final concentrations of $550 \mu\text{mol l}^{-1}$.

The proposed mechanisms for sorption of Mo in regions I, II, and III explain the observed differences between Mo and P sorption. Sorption mechanisms proposed for P commonly involve ligand exchange with surface $-OH_2^+$ and $-OH$ groups (Breeuwsma and Lyklema, 1973; Rajan, 1975; Ryden et al., 1977a). The difference between Mo and P sorption is that free H^+ is not required in P sorption mechanisms because the anionic species ($H_2PO_4^-$ and HPO_4^{2-}) contain H^+ that can react with surface $-OH$, enabling formation of the favoured bidentate complex. Hence, the chemisorption of P would only be limited by the effect of pH on surface charge, whereas the chemisorption of Mo would be limited by solution H^+ concentration. The fact that Fe gel sorbed similar amounts of Mo and P from $10^{-4}M$ NaCl in region I at pH 4.9 (Section 5.3.1), whereas at pH 6.0 much more P was sorbed than Mo (Chapter 4), confirms the suggested effect of H^+ concentration on Mo sorption. At pH 4.9, the dominant Mo sorbing species would be $HMoO_4^-$, and the extent of chemisorption would not be limited by the concentration of free H^+ . This also explains the fact that the sorption maximum for Mo occurs at or near the pKa (Jones, 1957; Tuev, 1969; Theng, 1971; Hingston et al., 1972). At this pH, the concentration of reactants is not limiting sorption.

The proposed mechanisms for Mo sorption in regions I and II are similar to those that have been proposed for P sorption, and appear to validate the common assumption that Mo and P sorption are similar (Barrow, 1970; Theng, 1971; Gonzalez et al., 1974), with the limitation of pH effects as discussed above. The proposed three-step mechanism for Mo sorption is similar to that proposed by Ryden et al. (1977a) for P and lends evidence to the argument that anion sorption by soils occurs by a common mechanism. The classification of sorbed

Mo and P into chemisorbed and more-physically sorbed types indicates that a similar mechanism may operate for other anions, with the distribution between the two types explaining differences and/or similarities between anion sorption behaviour. The Mo sorption models proposed here have features which are common to, and also different from, general anion mechanisms that have been proposed by others (Hingston et al., 1967, 1968b; Bowden et al., 1973, 1974, 1977). In agreement with Hingston et al. (1967, 1968b), it is proposed that the chemisorption of Mo involves ligand-exchange with surface $-OH_2^+$ and $-OH$, although the requirement that surface negative charge increases subsequent to Mo sorption, proposed by Hingston et al., has been shown to be invalid for Mo sorption in region II. It is proposed that sorption of Mo in region III does not change surface charge, per se, but results in an overall increase in double layer negative charge. This increase in charge is believed to occur on the solution side of the interface, rather than at the surface. Sorption in region III is, in fact, similar to that proposed by Bowden et al. (1973, 1974) for anion sorption. These authors did not propose any mechanism involving ligand-exchange, however, as proposed in the present study for Mo sorption in regions I and II.

The model for Mo sorption proposed in this Chapter states that two types of sorption occur, namely, chemisorption involving ligand-exchange and a more-physical sorption type. This classification may be useful in explaining other observed Mo sorption properties, such as time-dependent sorption and competitive sorption with other anions.

CHAPTER 6

COMPETITIVE SORPTION OF MOLYBDATE AND PHOSPHATE

6.1 Introduction

In previous Chapters it has been concluded that the sorption reactions between Mo and the surface of the soil components are similar to those between P and the same surfaces. It is possible that competitive sorption studies can give further insight into the reactions of these two anions at sorbing surfaces.

A Langmuir-type equation can be derived for competitive sorption (Brunauer, 1945) and this has been applied to the competitive sorption of P and Se or As by synthetic soil components (Hingston et al., 1971). There has been no detailed study of P-Mo competition, although Gorlach et al. (1969) have shown that the competition of these two anions is affected by pH. In this Chapter, the applicability of a Langmuir competitive sorption equation is tested and isotherms are obtained in an attempt to rationalise the competitive sorption of Mo and P in terms of sorption in each particular region of sorption. Competitive sorption in each of these regions is discussed in terms of the mechanisms proposed for Mo and P sorption.

6.2 Methods

Okaihau, Ramiha, and Tokomaru topsoils, Tokomaru subsoil, and Fe gel were used.

Isotherms for the sorption of P by the soils and Fe gel from

10^{-1} M NaCl were obtained during 40 hr. Using the appropriate sorption constants obtained from the three Langmuir equations describing these P sorption isotherms, additions of P were calculated which gave known saturations of the P sorption complex, corresponding to 90% of region I, 50% of region II, and 20% of region III for all soils and Fe gel. Additions leading to saturation of 50% of region I were calculated for Ramiha topsoil, Tokomaru subsoil, and Fe gel, and additions leading to 40% saturation of region III were calculated for Okaihau and Tokomaru topsoils.

For each level of added P, additions of Mo were made simultaneously in order to obtain Mo sorption isotherms over the final Mo concentration range of 0 - 100 $\mu\text{mol l}^{-1}$, i.e., for each level of P, between ten and fifteen Mo additions were made. Sorption isotherms for Mo were obtained in 10^{-1} M NaCl during 40 hr. Solution:solid ratios for isotherm determinations were 40:1 and 800:1 for the soils and Fe gel, respectively.

6.3 Results and Discussion

6.3.1 Mo sorption isotherms

The simultaneous addition of P with Mo decreased the extent of Mo sorption by both soils and Fe gel, the reduction in Mo sorption being greater at higher additions of P. Fig. 6.1 illustrates the effect of P on Mo sorption for Okaihau and Tokomaru topsoils. Increasing P additions decreased the H-type character of the isotherms. As illustrated by Fig. 6.1, the effect of P on the shape of the Mo sorption isotherm was greater for Okaihau topsoil than for Tokomaru topsoil. This effect was most pronounced for Mo sorption by Fe gel.

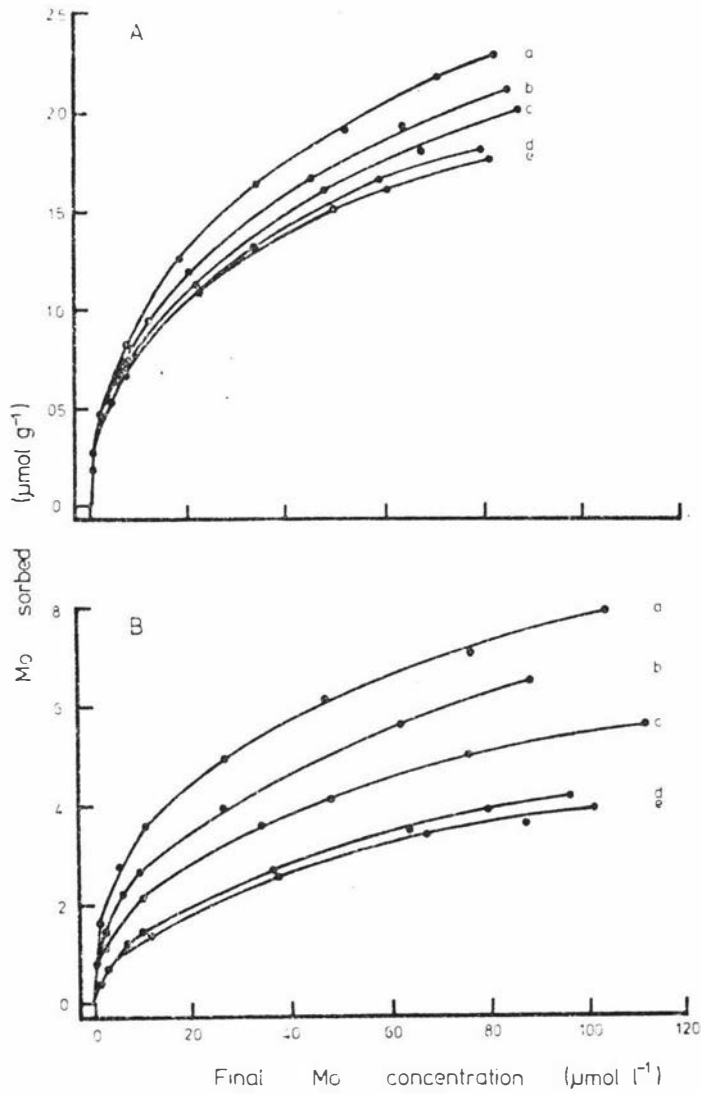


Fig. 6.1 Isotherms for the sorption of Mo by Tokomaru topsoil (A) and Okaihau topsoil (B) from 10^{-1}M NaCl during 40 hr in the presence of added P. Levels of P added to give saturations of the P sorption complex corresponding to a = 0, b = 90% of b_{I} , c = 50% of b_{II} , d = 20% of b_{III} , and e = 40% of b_{III} .

6.3.2 Evaluation of Mo sorption isotherms

6.3.2.1 Use of the competitive Langmuir equation

For competitive sorption of two species at common sorption sites, an equation based on Langmuir theory can be derived (Brunauer, 1945). The surface is assumed to consist of a certain number of sites (S), of which S_1 are occupied by species 1, S_2 by species 2, and $S - (S_1 + S_2)$ are unoccupied. Because the rate of sorption equals the rate of desorption at equilibrium, for species 1 :

$$k_{d1}S_1 = k_{a1}c_1(S - (S_1 + S_2)) \quad (6.1)$$

and for species 2 :

$$k_{d2}S_2 = k_{a2}c_2(S - (S_1 + S_2)) \quad (6.2)$$

where k_d = rate constant for desorption of species 1 or 2, k_a = rate constant for sorption of species 1 or 2, and c_1 and c_2 = the concentrations of the species in solution. The fractional surface coverages, θ_1 and θ_2 , equal $\frac{S_1}{S}$ and $\frac{S_2}{S}$, respectively. After substitution solving equations (6.1) and (6.2) simultaneously gives :

$$\theta_1 = \frac{k_1c}{1 + k_1c + k_2c} \quad (6.3)$$

where $k_1 = \frac{k_{a1}}{k_{d1}}$ and $k_2 = \frac{k_{a2}}{k_{d2}}$. The amount of any one species sorbed (x),

is given by equation (6.4) :

$$x = \frac{k_1b_1c}{1 + k_1c_1 + k_2c_2} \quad (6.4)$$

where b_1 = the sorption maxima for species 1. k and b for any single species are the same as k and b in the absence of any competing anion. For Mo and P, the amount of Mo sorbed in any one region would be affected by the amount of P sorbed in that region, i.e.,

$$x_I^{\text{Mo}} = \frac{k_I^{\text{Mo}} b_I^{\text{Mo}} c^{\text{Mo}}}{1 + k_I^{\text{Mo}} c^{\text{Mo}} + k_I^{\text{P}} c^{\text{P}}} \quad (6.5)$$

where x_I^{Mo} = amount of Mo sorbed in region I and k_I^{Mo} and b_I^{Mo} are the sorption constants for Mo sorption in region I in the absence of P, and similarly for k_I^{P} . Similar equations can be written for x_{II}^{Mo} and x_{III}^{Mo} .

Using the k and b values obtained for sorption in the absence of competition, Mo sorption isotherms can be calculated for each region and then combined to give a predicted overall isotherm. These are shown in Fig. 6.2 for Mo sorption by Fe gel at two levels of added P. Similar results were obtained for the soils. In all cases, the amounts of sorbed Mo, predicted from equation (6.4), exceeded the experimentally-obtained results, i.e., Mo sorption in the presence of P did not obey the competitive Langmuir equation. This is probably not surprising as the derivation of equations (6.4) and (6.5) assumes that the surface available for sorption of both Mo and P is the same. In the case of Mo and P sorption, however, the surface available for P sorption is much greater than that for Mo sorption (as reflected in the b values for sorption in the absence of a competing anion). Thus, the fractional surface coverage of a given anion will be greater for sites occupied by Mo than for similar types of sites occupied by P. Considering the rates of sorption and desorption to be equal, as above, equations (6.6) and (6.7) can be derived :

$$k_d^{\text{Mo}} = k_a^{\text{Mo}} c^{\text{Mo}} (S - (S_{\text{Mo}} + S_{\text{P}})) \quad (6.6)$$

and

$$k_d^{\text{P}} = k_a^{\text{P}} c^{\text{P}} (S^1 - (S_{\text{Mo}} + S_{\text{P}})) \quad (6.7)$$

where S and S^1 are the total number of sites available for sorption of Mo and P, respectively. Hence, there are four fractional surface

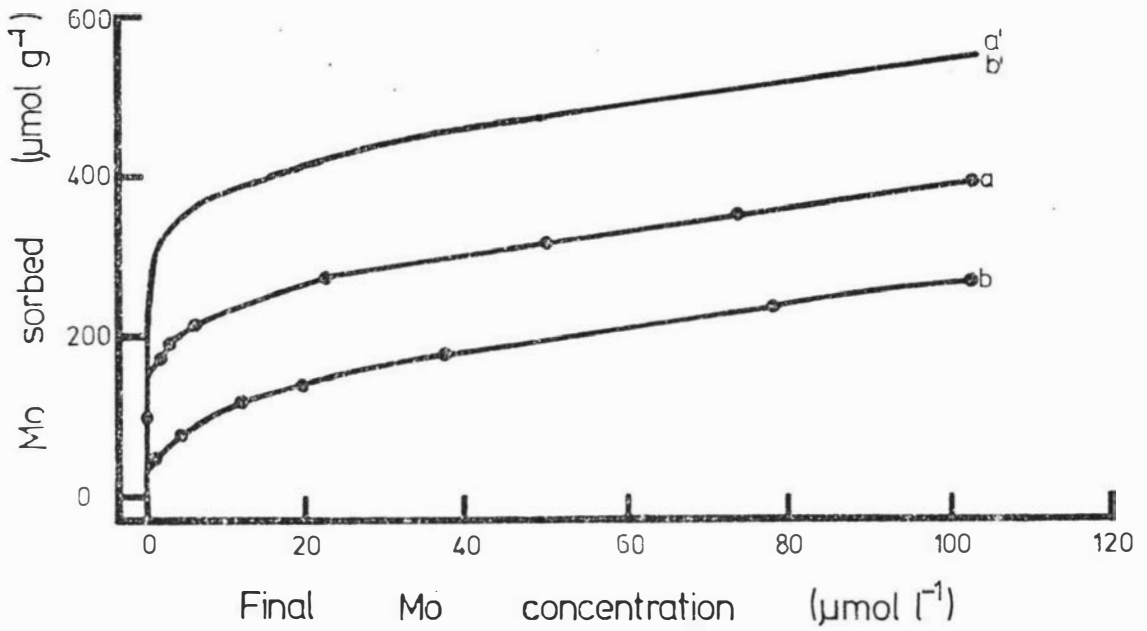


Fig. 6.2 Isotherms for the sorption of Mo by Fe gel from 10^{-1} M NaCl during 40 hr at two levels of added P, $a = 50\%$ of b_I , and $b = 90\%$ of b_{II} . ' ' refers to isotherms calculated using the competitive Langmuir equation.

coverages : $\theta_{\text{Mo}} = S_{\text{Mo}}/S$, $\theta_{\text{P}} = S_{\text{P}}/S$, $\theta_{\text{Mo}}^1 = S_{\text{Mo}}/S^1$, and $\theta_{\text{P}}^1 = S_{\text{P}}/S^1$, and a simple equation cannot be derived. The amounts of the lowest sorbing species sorbed (Mo in this case), as estimated by equation (6.4) would be overestimated because the fractional surface coverage of the competing anion would be higher than that used to derive equation (6.4).

6.3.2.2 Use of the simple Langmuir equation

Using the method of successive approximations (Table 3.2), which enabled resolution of Mo sorption isotherms in the absence of P into three regions of sorption (Chapter 3), data for Mo sorption in the presence of P were tested for fit to the Langmuir equation. For all soils and Fe gel, at all levels of added P, sorption isotherms for Mo could be described by three simple Langmuir equations, each with distinct b and k values. As was the case for Mo sorption in the absence of P, overall sorption was dominated by region I over the range of $0 - 0.5 \mu\text{mol Mo l}^{-1}$, by region II over the range of $1 - 10 \mu\text{mol Mo l}^{-1}$ and by region III over the range of $20 - 100 \mu\text{mol Mo l}^{-1}$.

The sorption maxima (b) and sorption energy constants (k) were determined for each region of sorption. In the presence of P, these values of b and k are empirical, i.e., there is no theoretical reason why sorption should conform to simple Langmuir equations, and to relate k , in this case, to the free energy of sorption would appear to be an oversimplification. Values of b and k for the four soils and Fe gel corresponding to a known saturation of the P sorption complex (in the absence of Mo) are given in Tables 6.1, 6.2, 6.3, 6.4, and 6.5.

Isotherms for sorption of Mo in each region were obtained from the b and k values and these individual isotherms were summed to give a regenerated isotherm. Fig. 6.3 compares experimental and regenerated

Table 6.1 Sorption constants for the sorption of Mo from 10^{-1} M NaCl during 40 hr by Okaihau topsoil in the presence of varying levels of added P

Saturation of P-sorption complex	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}
	$\mu\text{mol g}^{-1}$			$l \mu\text{mol}^{-1}$		
0	0.71	3.13	10.53	14.43	0.311	0.0060
90% b_I	0.74	3.03	10.0	5.87	0.135	0.0061
50% b_{II}	0.42	2.22	6.25	8.91	0.169	0.0081
20% b_{III}	0.27	1.20	4.00	6.07	0.253	0.0119
40% b_{III}	0.20	1.14	3.70	6.08	0.208	0.0162

Table 6.2 Sorption constants for the sorption of Mo from 10^{-1} M NaCl during 40 hr by Ramiha topsoil in the presence of varying levels of added P

Saturation of P-sorption complex	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}
	$\mu\text{mol g}^{-1}$			l	μmol^{-1}	
0	0.47	2.56	11.24	6.52	0.283	0.0079
50% b_I	0.46	2.63	11.24	4.08	0.232	0.0068
90% b_I	0.39	2.27	11.11	3.49	0.183	0.0052
50% b_{II}	0.37	1.79	8.70	1.96	0.147	0.0055
20% b_{III}	0.10	1.30	6.06	4.90	0.201	0.0065

Table 6.3 Sorption constants for the sorption of Mo from 10^{-1} M NaCl during 40 hr by Tokomaru topsoil in the presence of varying levels of added P

Saturation of P-sorption complex	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}
	$\mu\text{mol g}^{-1}$			$l \mu\text{mol}^{-1}$		
0	0.131	0.99	2.94	10.0	0.206	0.0080 ✓
90% b_I	0.139	0.98	2.70	8.05	0.123	0.0074
50% b_{II}	0.139	0.91	2.38	9.00	0.106	0.0090
20% b_{III}	0.139	0.98	1.85	8.57	0.099	0.0099
40% b_{III}	0.131	1.04	1.72	7.66	0.111	0.0078

Table 6.4 Sorption constants for the sorption of Mo from 10^{-1} M NaCl during 40 hr by Tokomaru subsoil in the presence of varying levels of added P

Saturation of P-sorption complex	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}
	$\mu\text{mol g}^{-1}$			$\text{l } \mu\text{mol}^{-1}$		
0	0.53	1.23	15.63	34.54	1.17	0.0086
50% b_I	0.49	1.11	15.38	21.24	0.825	0.0092
90% b_I	0.50	0.56	15.38	11.52	0.741	0.0094
50% b_{II}	0.40	0.51	15.15	8.60	0.456	0.0091
20% b_{III}	0.31	0.52	14.29	5.36	0.312	0.0085

Table 6.5 Sorption constants for the sorption of Mo from 10^{-1} M NaCl during 40 hr by Fe gel in the presence of varying levels of added P

Saturation of P-sorption complex	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}
	$\mu\text{mol g}^{-1}$			$l \mu\text{mol}^{-1}$		
0	265	115	556	58.5	0.503	0.0043
50% b_I	93	135	556	49.8	0.740	0.0039
90% b_I	23.0	102	526	16.2	0.212	0.0033
50% b_{II}	1.9	35.1	476	6.6	0.259	0.0044
20% b_{III}	0.51	6.8	625	2.2	0.164	0.0023

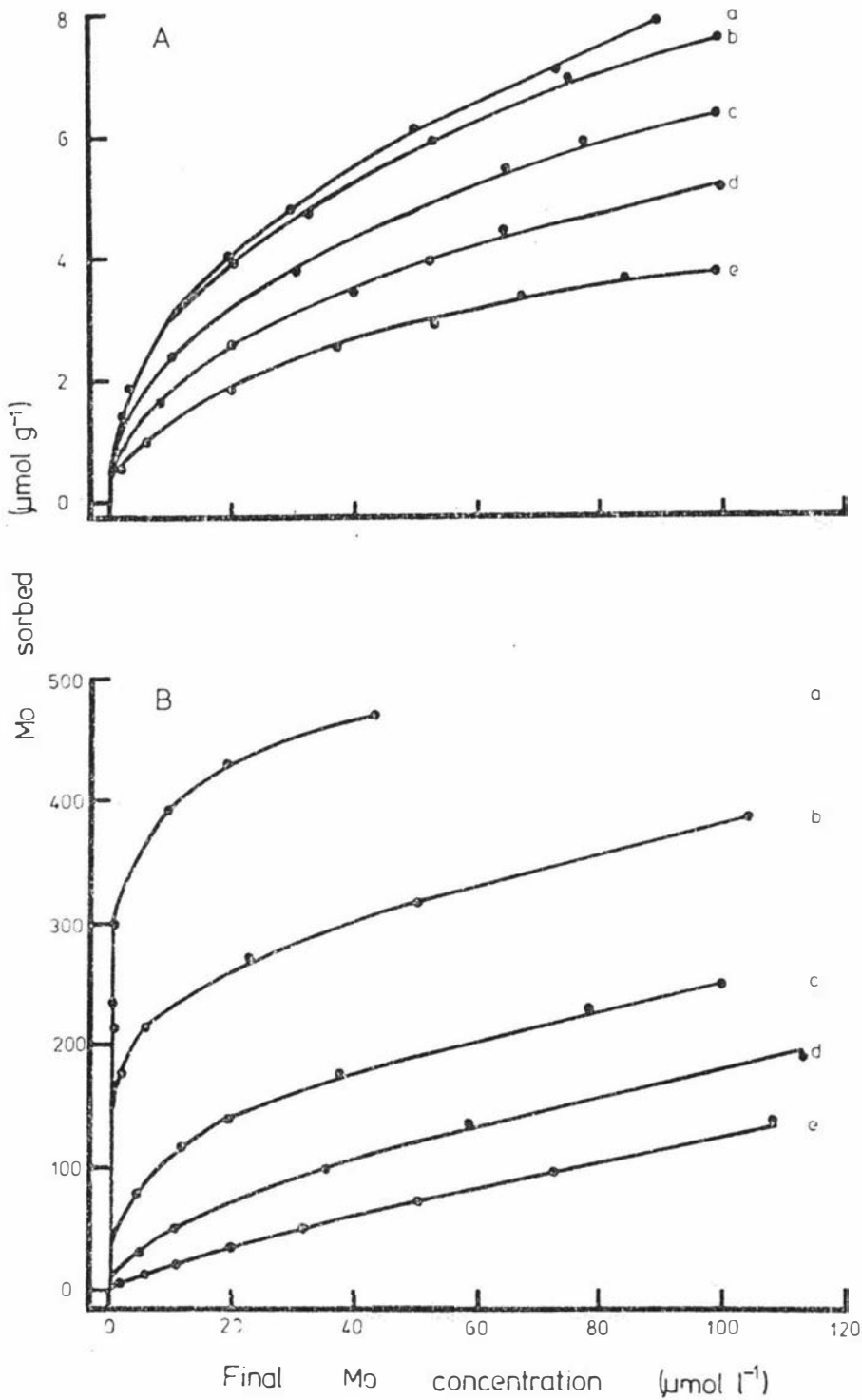


Fig. 6.3 Regenerated isotherms for the sorption of Mo by Ramiha topsoil (A) and Fe gel (B) from 10^{-1} M NaCl during 40 hr in the presence of added P, calculated from the simple Langmuir equation. Data points are from experimentally-obtained isotherms. Levels of added P are: a = 0, b = 50% of b_I , c = 90% of b_I , d = 50% of b_{II} , and e = 20% of b_{III} .

overall sorption isotherms for Ramiha topsoil and Fe gel. The closeness of fit of the experimental data to the theoretical isotherm (variation < 2% over the range of 0 - 100 $\mu\text{mol l}^{-1}$) indicates that the use of a three-term Langmuir expression successfully accounted for Mo sorption in the presence of added P. Similar results were obtained for the other soils.

There is no obvious explanation as to why Mo sorption in the presence of P can be described by simple Langmuir equations. Because the sorption data obey the Langmuir equation, it would appear that after 40 hr, the two anions can be regarded as sorbing at different fractions of the sorbing surface; not necessarily at different types of sites, but on different fractions of the total number of one type of site. The fact that the simple Langmuir equation was obeyed may be rationalised as follows. The maximum surface covered by Mo (at high final solution Mo concentrations) is considered as the surface available for Mo sorption, the rest of the surface that was formerly available for Mo sorption being blocked by added P. At Mo concentrations less than that required to give maximum surface coverage, some of these surface sites would be covered by P, but only in proportion to the solution Mo concentration. Consequently, the new surface area available for sorption is proportional only to the solution Mo concentration, because increases in Mo sorbed are considered to be unaffected by P in solution. Thus, the rate of sorption is proportional to $(1 - \theta)c_{\text{Mo}}$, where θ is the fractional coverage by Mo of the new reduced surface, rather than being proportional to $(1 - \theta - \theta_{\text{P}})c_{\text{Mo}}$, where θ_{P} is the fractional coverage by P of the surface available for Mo sorption. A simple Langmuir equation is then obeyed for Mo sorption at the reduced surface area, with the b and k values obtained referring to this surface.

6.3.3 Effect of added P on sorbed Mo

Examination of the b values in Tables 6.1 to 6.5 indicates that there was competition between P and Mo for sorption sites in each region of sorption, but that the effect of P depended on both the sorbent and the region of sorption. Additions of P to Tokomaru topsoil had a negligible effect on the Mo sorption maxima in both regions I and II (i.e., the chemisorption sites), whereas P additions to the other sorbents reduced the sorption maxima for both these regions. This explains the different effect of P on the shape of the sorption isotherms for Okaihau and Tokomaru topsoils (Fig. 6.1). For Tokomaru subsoil, the saturation of region I by native P was less than that for the topsoil. Because the b values for Tokomaru subsoil only decreased by small amounts for P additions up to 90% saturation of b_I , it appears that the small effect of simultaneously added P on Mo sorption by Tokomaru topsoil was not only due to the high saturation of region I by native P. Both Tokomaru topsoil and subsoil sorbed almost equal amounts of Mo and P when added separately (Figs. 2.1 to 2.4), which must therefore influence the competitive effect of P on Mo sorption. Before further conclusions could be drawn, isotherms for sorption of P by Tokomaru soils in the presence of added Mo would need to be determined.

For P additions leading to a 50% saturation of region II with P and 20% of region III with P, the region I P sorption complex would be saturated for all sorbents, in the absence of Mo. A small amount of Mo was still sorbed in region I at these P additions. This suggests that small amounts of Mo are able to compete successfully with P for sites in region I, as would be expected from the similarity in ΔG values for the two anions. The b_{III} values for Mo were unaffected at low P additions, because at these levels of addition, only small amounts of P

would be sorbed in region III. For higher P additions, where P sorption in region III became important, the b values for Mo sorption decreased as the P additions increased. The decrease in the sorption maxima for Mo in region III was less than the amount of P expected to be sorbed in region III, implying that either P and Mo together can be sorbed in greater amounts than each of the anions alone, or that Mo decreased the amount of P sorbed and thus, not all the added P that was calculated to be sorbed in region III was, in fact, sorbed in the presence of Mo. Initial studies showed that some P was displaced in the presence of Mo (data not presented). The complexity of the problem, however, which would involve determining P sorption isotherms at each Mo level, prevented further examination of the effect.

The fact that P was able to displace large amounts of Mo, yet only small amounts of P appeared to be displaced by Mo, cannot be explained in terms of the different affinities of the anions for the surface, as the respective ΔG values for any one region were very similar (Chapter 4). The small amount of data for the Tokomaru soils showed that Mo was able to cause considerable increases in P solution concentration (up to 10%). The fact that the Tokomaru soils sorbed comparable amounts of Mo and P in the absence of competing anions would indicate that the large effect of P on Mo sorption observed with the other soils and Fe gel was because greater amounts of P were sorbed. Gorlach et al. (1969) showed that, for competitive sorption, the ratio of P sorbed:Mo sorbed decreased with decreasing pH, as did the ratio of P sorbed:Mo sorbed for sorption in the absence of a competing anion. Because it is considered that pH does not affect the mechanism of Mo or P sorption, but only the extent of sorption (Chapter 5), the effectiveness of each anion in competing for common sites is primarily affected by

the extent of sorption. This is, of course, in agreement with the Law of Mass Action (Moore, 1962).

The effect of added P on Mo sorption in any particular region is illustrated by Figures 6.4 and 6.5, which show the regenerated isotherms for Mo sorption by Okaihau topsoil and Fe gel, respectively, in each region. The plots for Okaihau soil illustrate that at low solution Mo concentrations, the amounts of Mo sorbed were reduced by added P, even though the overall sorption maxima for Mo was unaffected. That is, at high final solution concentrations, Mo was more competitive with P, possibly because the rate of Mo sorption would be greater. Additions of P resulting in near saturation of region I had a greater effect on Mo sorption in region I by Fe gel than by the soils and conversely, had less effect on Mo sorption in regions II and III. The points in Fig. 6.4 marked A_1 etc., B_1 etc., and C_1 etc., and in Fig. 6.5 marked D_1 etc., and E_1 etc., correspond to a common Mo addition (for each letter) at various additions of P. These data show that although increasing amounts of P resulted in decreased amounts of Mo sorbed in region I, increased amounts of Mo sorbed in regions II and III, relative to the zero P addition, could result. For a common Mo addition leading to a low saturation of region II in the absence of P (points A, C, and D), the amounts of Mo sorbed in region II increased with increasing P additions until the P saturation of region II became relatively high. For a common Mo addition, leading to near saturation of region II with Mo in the absence of P (points B), increasing P additions decreased the amounts of Mo sorbed in region II. Similar results were obtained for Mo sorption in region III. This shows that merely measuring the change in overall Mo sorption does not accurately reflect changes in the amount of Mo sorbed in one particular region and that significant changes in the Mo bond type can occur with very little decrease in overall Mo sorption.

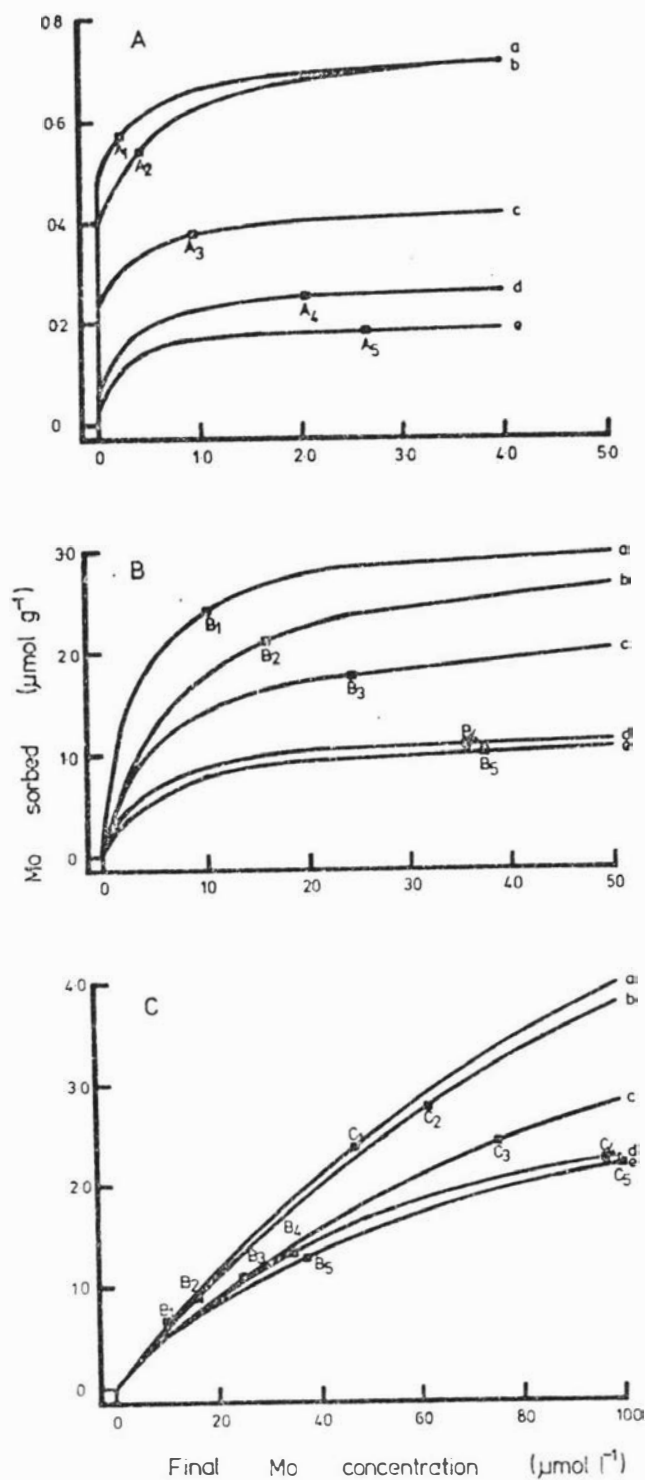


Fig. 6.4 Isotherms for the sorption of Mo by Okaihau topsoil from 10^{-1} M NaCl in region I (A), region II (B), and region III (C), in the presence of varying levels of added P, during 40 hr. Levels of added P to give known saturation of the P sorption complex are: a = 0, b = 90% of b_I , c = 50% of b_{II} , d = 20% of b_{III} , and e = 40% of b_{III} . A_1, A_2 , etc. = common Mo addition of $0.8 \mu\text{mol g}^{-1}$, B_1, B_2 , etc. = common Mo addition of $4.0 \mu\text{mol g}^{-1}$, C_1, C_2 etc. = common Mo addition of $8.0 \mu\text{mol g}^{-1}$.

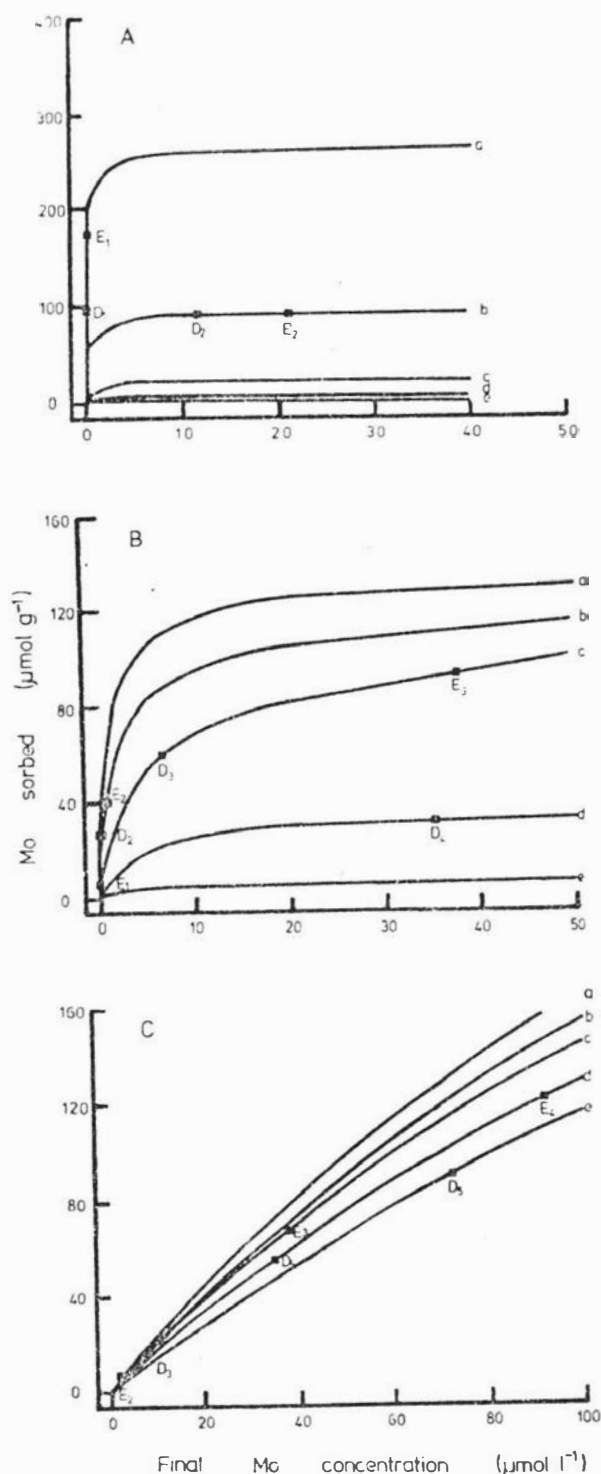


Fig. 6.5 Isotherms for the sorption of Mo by Fe gel from 10^{-1} M NaCl in region I (A), region II (B), and region III (C), in the presence of varying levels of added P, during 40 hr. Levels of added P to give known saturation of the P sorption complex are: a = 0, b = 50% of b_I , c = 90% of b_I , d = 50% of b_{II} , and e = 20% of b_{III} . D_1, D_2 , etc. = common Mo addition of $98 \mu\text{mol g}^{-1}$, E_1, E_2 , etc. = common Mo addition of $176 \mu\text{mol g}^{-1}$.

Because the rate of sorption was greater at higher concentrations for both anions, the anion which had the greatest initial solution concentration would be sorbed to a greater extent by the highest energy sites. Larger amounts of P than Mo were usually added, even at P additions leading to saturation of 50% of region I for P, and consequently, more P would be sorbed at the high energy sites, with Mo being sorbed at the less energetically favourable sites. This effect would increase with increasing level of P addition and would result in decreasing amounts of Mo being sorbed in region I, and then in region II, as observed in Figures 6.4 and 6.5, and Tables 6.1 to 6.5.

A classification of surface sites into those which are common to both sorbing species, and those common to one species only, as proposed by Hingston et al. (1971), could lead to the erroneous conclusion that P and Mo do not sorb at the same type of site and by the same mechanism. Hingston et al. assumed that the amount of anion desorbed by its competitor could be equated with the value for the amount of anion sorbed at common sites. This approach does not appear to be valid, however, as it assumes the presence of only one type of site. In the case of P and Mo, Mo could be prevented from sorbing in region I, but still could sorb in region II or III, and the change in solution Mo concentration would not reflect the changes on the surface.

The fact that increasing P additions competitively displaced Mo from all three regions (Figs. 6.4 and 6.5) is good evidence that P and Mo are bonded to similar surface sites and by similar sorption mechanisms. The fact that not all Mo was displaced from region I by large additions of P which would be expected to saturate region I is not evidence that P and Mo bond at different sites, but rather that, because of the high affinity of the surface for Mo in region I, the rate of reaction between

the surface and added Mo was sufficiently great to allow small amounts of Mo to be retained.

The amounts of P sorbed differ from the amounts of Mo sorbed because of pH effects and the different capacity of some soil components to sorb P or Mo, as discussed in Chapters 4 and 5. The greater extent of P sorption, therefore, resulted in P sorption at more sites than were occupied by Mo and resulted in P being more competitive than Mo for sorption by the soils and Fe gel. For sorbents where the sorption of the two anions in the absence of competitors was equal, Mo appeared to be competitive with simultaneously added P. To draw any further conclusions, P sorption isotherms in the presence of many added levels of Mo, plus isotherms for the sorption of Mo in the presence of P by sorbents where the ratio of P sorbed:Mo sorbed (in the absence of competitors) could be varied, e.g., Fe gel at different pH values, would need to be evaluated. Only then could the investigations into competitive sorption be conclusive.

CHAPTER 7

DESORPTION AND EXTRACTION OF SORBED MOLYBDATE
AS INFLUENCED BY ADDED PHOSPHATE AND
TIME AFTER MOLYBDATE ADDITION

7.1 Introduction

The amounts of Mo added to soils in the field situation are very small compared to those of P, an average Mo addition being between 50 and 150 g $\text{Na}_2\text{MoO}_4 \text{ ha}^{-1}$, whereas an average P addition is usually between 20 and 50 kg P ha^{-1} . The effect of large additions of P on sorbed Mo in the soil is poorly understood.

It is known that Mo can be extracted by P (Gorlach et al., 1969; Gonzalez et al., 1974). It is also known that extractability of sorbed Mo decreases with time after addition (Gorlach et al., 1969; Barrow, 1973), but there is little information available on which form of sorbed Mo is extracted by P. In previous chapters it has been shown that Mo is strongly sorbed at surfaces of soil components, with the free energies of sorption being sufficiently high to suggest that Mo would not easily be removed from the surface. In this Chapter, the extractability of sorbed Mo in several reagents, including P solution, is investigated as a function of time after Mo addition. In an attempt to relate the findings to the field situation, extraction studies were conducted on several soils which had received added Mo in fertilizer trails conducted under field conditions.

It has been shown in previous Chapters that both Mo and P are retained by soil components by a sorption reaction (Chapters 3, 4, and 5). Also, it has been shown that Mo and P compete for the same surface sites (Chapter 6). Consequently, in this Chapter the extraction of sorbed Mo

by P (and less strongly-held anions such as Cl) will be referred to as desorption; the removal of sorbed Mo by 10^{-1} M NaOH and the CDB reagent will be referred to as extraction.

7.2 Methods

7.2.1 Desorption and extraction of Mo added to soils in the laboratory

7.2.1.1 Mo sorbed during short-time periods

In the study of the desorption of Mo sorbed during 40 hr, Okaihau, Ramiha, and Tokomaru topsoils (hereafter referred to as soils) were used. Samples (1-g) of soil were shaken with varying amounts of added Mo in 40 ml of 10^{-1} M NaCl during 40 hr. The suspensions were then centrifuged and the supernatants recovered by Millipore ($<0.45\mu\text{m}$) filtration. The polycarbonate tube plus remaining soil suspension was then weighed to determine the volume of entrapped solution and 10^{-1} M NaCl was added to make the final volume up to 40 ml. To investigate the effect of P solutions on the desorption of sorbed Mo, aliquots of P in 10^{-1} M NaCl were added to the soil suspension remaining after centrifugation, and the final volume made up to 40 ml with 10^{-1} M NaCl. The suspensions were then shaken for the required length of time, centrifuged, and the supernatant solutions recovered by filtration.

7.2.1.2 Mo sorbed during long-time periods

Okaihau and Ramiha topsoils (hereafter referred to as soils) were used in this study. Solutions of Mo in water were sprayed onto air-dry soil with an atomiser spray, the volume being added such that the final moisture content of each soil corresponded to -50 cm suction. The gravimetric moisture contents at this suction were 46 and 55% for Okaihau and Ramiha soils, respectively. Two levels of added Mo were

made to each soil: 1.0 and 3.0 $\mu\text{mol Mo g}^{-1}$ (on an air-dry basis) to Okaihau soil, and 0.2 and 1.5 $\mu\text{mol Mo g}^{-1}$ to Ramiha soil. Controls for each soil (with no added Mo) were also moistened to -50 cm suction. Although the Mo additions were large compared to those made in the field situation, analytical detection limits required that the lowest Mo addition was, of necessity, relatively high. Levels of addition were chosen which gave approximate equilibrium concentrations of 0.05 and 1.00 $\mu\text{mol Mo l}^{-1}$ for the low and high additions, respectively, to each soil. Equilibrium concentrations were obtained from equilibrium isotherms determined in 10^{-1}M NaCl (Chapter 3). Each treatment with added Mo was made in duplicate. The soils plus added Mo were incubated in loosely-covered containers at 100% relative humidity. A constant water content was maintained by periodic checking and water addition as required.

At various times, between 1 and 100 days, after addition of Mo, duplicate 1-g subsamples of the incubated soil were taken and shaken with 40 ml of various extractants over a period of 16 hr. The extracting solutions were: 10^{-1}M NaCl alone; 10^{-1}M NaCl containing a low and a high P concentration; and 10^{-1}M NaOH . The low P solutions gave a solution P concentration of approximately 1.0 $\mu\text{mol P l}^{-1}$ at the end of the 16-hr period, and the high P solutions a solution P concentration of approximately 50 $\mu\text{mol P l}^{-1}$. Solution additions of P were 6.0 and 25.0 $\mu\text{mol P g}^{-1}$ (air-dry basis) to Okaihau soil, and 10.0 and 40.0 $\mu\text{mol P g}^{-1}$ to Ramiha soil. Non-occluded (or surface-bound) Mo was removed by extraction with 10^{-1}M NaOH , by analogy with P (Williams et al., 1967). Subsequent to extraction with 10^{-1}M NaOH , the soil residue was extracted with citrate-dithionite-bicarbonate (CDB) reagent at 75°C (Jackson, 1956) after washing with 1M NaCl. By analogy with P, CDB reagent is expected

to remove Mo occluded within free Fe and Al oxides and hydrous oxides (Williams et al., 1967; Smith and Leeper, 1969).

Aliquots of the NaCl and the NaCl + P extracts were evaporated to dryness, oxidised with H_2O_2 and H_2SO_4 , and analyzed for Mo. Aliquots of the NaOH extracts were acidified, centrifuged to remove humic acids, and a further aliquot taken and evaporated to dryness. After ignition at 550°C for 4 hr to remove organic matter, Mo was determined in the residue after digestion in H_2SO_4 at 60°C . The CDB extracts were evaporated to dryness, oxidised with $\text{HNO}_3/\text{H}_2\text{SO}_4$, and ignited at 550°C for 4 hr to remove citrate, and analyzed for Mo. Recovery of Mo added to NaOH and CDB extracts was found to be very good (95 - 102%).

7.2.2 Desorption and extraction of Mo added to soils in the field

To investigate the extractability of Mo from soils which had received realistic amounts of added Mo in fertilizer trials, three soils from a Mo response trial near Dunedin, New Zealand, were used. The soils were Warepa silt loam, Waipari silt loam, and Kaiwera silt loam. Each soil had received different Mo and lime treatments, namely: 1 = control, 2 = $140\text{g Na}_2\text{MoO}_4 \text{ ha}^{-1} \text{ yr}^{-1}$ for 3 years, 3 = $2500 \text{ kg lime ha}^{-1}$, 3 yr prior to collection of soil samples, and 4 = $140 \text{ g Na}_2\text{MoO}_4 \text{ ha}^{-1} \text{ yr}^{-1}$ for 3 years plus $2500 \text{ kg lime ha}^{-1}$, 3 yr prior to collection of soil samples.

Samples (1-g) of air-dried soil were shaken with the following reagents for 16 hr : 10^{-1}M NaCl , 10^{-1}M NaCl containing two levels of added P, and 10^{-1}M NaOH . The two P solution additions were 5.0 and $15.0 \mu\text{mol P g}^{-1}$, which corresponded to the P added in 375 and 1125 kg superphosphate ha^{-1} (2 cm depth) $^{-1}$, respectively. Total Mo was determined on a ground sample (<120 mesh) by digestion in HF in

"Teflon" beakers following prior digestion of organic matter with a mixture of concentrated HClO_4 and HNO_3 .

7.3 Results and Discussion

7.3.1 Desorption and extraction of Mo added to soils in the laboratory

7.3.1.1 Desorption by Cl of Mo sorbed during short-time periods

The amount of sorbed Mo desorbed by Cl depended on the time of desorption, following a 40-hr sorption period. As shown in Fig. 7.1, the concentration of Mo in the desorbing solution increased during 1 hr, and then reached a steady state between 4 and 24 hr. At desorption times >24 hr, solution Mo concentration slowly decreased (data not presented). Similar patterns were observed for all three soils. Because the results showed that resorption of Mo was not significant until times greater than 24 hr, further desorption experiments were carried out at a single desorption time of 16 hr.

The Mo sorbed during 40 hr was not reversible to Cl, i.e., the sorption and desorption isotherms showed hysteresis, as illustrated in Fig. 7.2 for Okaihau soil. Ryden and Syers (1977) have shown that for P, this hysteresis is due to non-equilibrium conditions, i.e., sorption and desorption isotherms obtained at equilibrium would be coincident. Given the similar time-dependent sorption and desorption behaviour of Mo and P, a similar explanation is possible for Mo. Ryden and Syers (1977) have also shown that P sorbed in region III was reversible. To test if Mo sorbed in region III was reversible to solution Mo concentration, the amount of Mo desorbed at any one level of Mo addition was subtracted from the amount sorbed in region III at that addition prior to desorption. The resulting value was then plotted

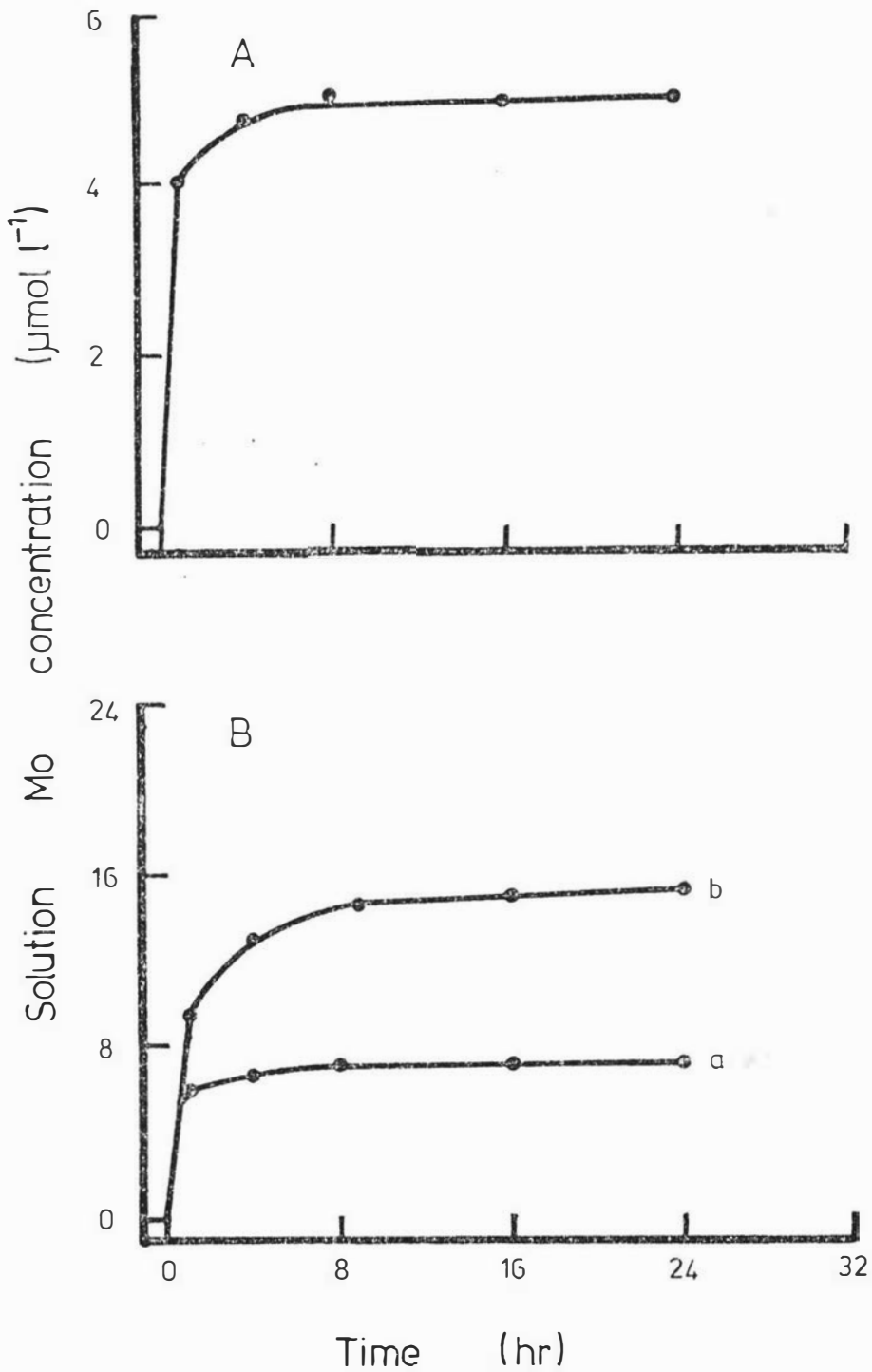


Fig. 7.1 Relationship between Mo concentration maintained in solution during desorption from Ramiha soil of Mo sorbed (during 40 hr) and the time allowed for desorption. Added Mo = $2.0 \mu\text{mol g}^{-1}$. A = desorption in 10^{-1}M NaCl and B = desorption in 10^{-1}M NaCl plus $5.0 \mu\text{mol P g}^{-1}$ (a) and $45 \mu\text{mol P g}^{-1}$ (b).

against the desorption solution concentration, as illustrated in Fig. 7.2. For all three soils, the data points did not fall on the regenerated isotherm for region III, showing that Mo sorbed in region III was not completely reversible to solution Mo concentration. This is in contradiction to the results reported for P (Ryden and Syers, 1977), although close examination of the data of these workers indicates that P sorbed in region III may not have been completely reversible. Examination of ΔG values for sorption of Mo and P in region III indicates that ΔG values for Mo are slightly more negative than those for P. This appears to be a result of greater coulombic energy contributions to the overall free energy in the case of Mo, as discussed in Chapter 4. The differences in magnitude of ΔG for Mo and P must, therefore, be sufficient to cause differences in the desorption of each anion. Because the Mo sorbed in region III was not completely reversible to solution Mo concentration, sorption of Mo in regions I and II would be very much less reversible, because of the higher ΔG values in these regions.

7.3.1.2 Desorption by P of Mo sorbed during short-time periods

Desorption of sorbed Mo by solution P was investigated during a desorption time of 16 hr, after initial studies showed that a constant Mo solution concentration was reached between 8 and 24 hr, as illustrated for Ramiha soil in Fig. 7.1B. These initial studies also showed that resorption of desorbed Mo did not occur during the 16-hr desorption period.

Comparison of the data in Fig. 7.1A and 7.1B shows that solution P increased the desorption of Mo relative to that desorbed by Cl alone. Table 7.2 shows the amounts of Mo desorbed by solution P from Okaihau, Ramiha, and Tokomaru soils, at two levels of added Mo and two solution P levels which resulted in final solution P concentrations of approximately

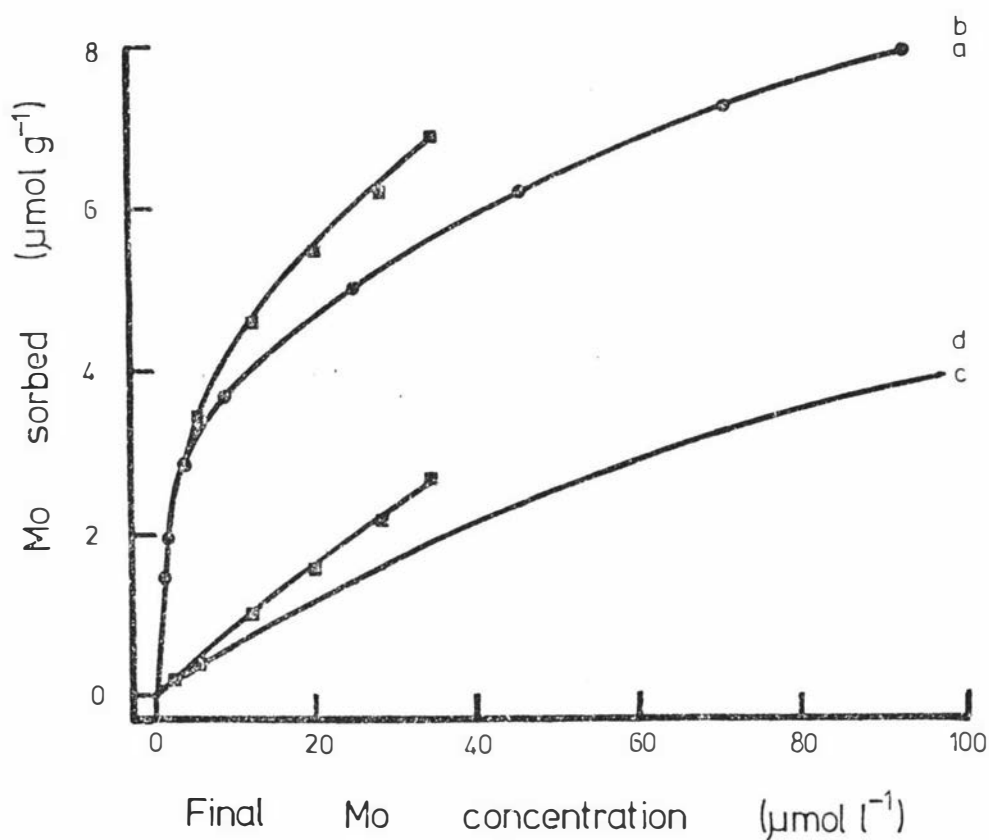


Fig. 7.2 Isotherms for the sorption by, and desorption from, Okaihau soil of added Mo, using a matrix solution of 10^{-1} M NaCl in both steps. ● = sorption data and ◻ = desorption data. a = 40-hr sorption isotherm, b = 16-hr desorption isotherm following 40-hr sorption, c = region III isotherm, and d = 16-hr region III desorption isotherm (assuming all Mo desorbed is from region III).

0.4 and 60 $\mu\text{mol P l}^{-1}$ after 16 hr. The data in Table 7.2 show that, although increasing P additions desorbed greater amounts of Mo, a large percentage of the added Mo was not desorbed by P. Even at high additions of P, where the ratio of P added in solution to Mo sorbed was high, P did not displace all the sorbed Mo, i.e., the exchange of Mo for P is not a simple reaction, but must involve ligand-displacement of sorbed Mo, which would not only depend on P concentrations but also on the ease of desorption of sorbed Mo. This is in accord with the concept of the chemisorption of Mo.

For each addition, the amounts of Mo sorbed in each region prior to desorption could be calculated (Chapter 3). These are given in Table 7.1. There was no obvious relationship between the amounts of Mo desorbed by P and the amounts of sorbed Mo in any particular region, i.e., solution P did not desorb Mo from a particular region. Because the amount of Mo desorbed was sometimes greater than that sorbed in region III for each soil, added P must desorb some chemisorbed Mo. If it is assumed that the more-weakly bound Mo (region III) is desorbed preferentially, however, then the fraction of chemisorbed Mo desorbed by solution P was always small. For example, the data of Table 7.1 show that, assuming that the highest P additions displaced all the Mo sorbed in region III, the percentage of chemisorbed Mo (regions I and II) that was desorbed by the highest solution P addition to all soils was between 10 and 15%.

7.3.1.3 Desorption and extraction of Mo sorbed during long-time periods

All results reported in this section are the mean of two additions of Mo for each level of addition. The variation in extractable Mo between duplicate additions in incubated systems was always less than 5%.

Table 7.1 Total Mo sorbed, Mo sorbed in each region (x), and Mo desorbed by solution P, at two levels of sorbed Mo, for Okaihau, Ramiha, and Tokomaru soils

Total Mo sorbed $\mu\text{mol g}^{-1}$	x_I	x_{II}	x_{III}	Mo desorbed ($\mu\text{mol g}^{-1}$) by solution P ($\mu\text{mol g}^{-1}$)			
	$\mu\text{mol g}^{-1}$			P:			
			Okaihau	P:	0	4	28
2.74	0.70	1.54	0.40		0.18	0.28	0.73 (14.6)
6.22	0.71	3.01	2.50		1.30	1.70	2.98 (12.9)
			Ramiha	P:	0	5	45
0.75	0.29	0.35	0.12		0.043	0.066	0.20 (12.5)
1.75	0.33	1.01	0.41		0.18	0.26	0.60 (14.2)
			Tokomaru	P:	0	0.2	6.0
0.18	0.11	0.08	0.01		0.019	0.023	0.037 (14.2)
0.59	0.13	0.33	0.12		0.12	0.14	0.19 (15.2)

Percentage of ($x_I + x_{II}$) desorbed by highest P addition, assuming all x_{III} is desorbed, are given in parentheses.

The amounts of Mo extracted by NaCl alone (denoted as 0 P), NaCl containing two solution P levels, 10^{-1} M NaOH and the CDB reagent following a 10^{-1} M NaOH extraction, from Okaihau and Ramiha soils, after various times of incubation, are given in Tables 7.2 and 7.3. The data show that, for each soil, the amounts of Mo desorbed by P increased as the concentration of solution P increased, but that the proportion of added Mo desorbed by P was never greater than 30%. This percentage decreased with increasing time of incubation. The proportion of added Mo desorbed by P was greater at the high Mo additions for both soils, in contrast to the constant proportion of extractable Mo found by Barrow (1973).

Comparison of the data for the amounts of Mo desorbed from the two soils highlights the fact that the amounts of Mo desorbed by NaCl alone from both soils at the low levels of Mo addition, and from both soils at the high levels of Mo addition, were almost exactly the same after long periods of incubation, although there were quite considerable differences at short-time intervals. This appears to justify the use of equilibrium isotherms to predict Mo additions which would lead to similar solution Mo concentrations, and its corollary of similar saturations of each region of sorption.

Over the whole period of incubation for Ramiha soil, and at times less than 40 days for Okaihau soil, 10^{-1} M NaOH extracted almost all the added Mo (94-100%). After long periods of incubation, the percentage of added Mo extracted by NaOH decreased slightly for Okaihau soil. The amounts of Mo removed by a subsequent CDB extraction were, at all times, very small relative to the amount of added Mo. For Ramiha soil, these amounts of CDB-extractable Mo remained relatively constant over the incubation period. There was a small increase in the amounts of

Table 7.2 Amounts of Mo desorbed and extracted by various reagents from Okaihau soil incubated with two levels of added Mo, after various times of incubation

Added Mo $\mu\text{mol g}^{-1}$	Time of Incubation days	Mo desorbed ($\mu\text{mol g}^{-1}$) by solution P ($\mu\text{mol g}^{-1}$)			Mo extracted ($\mu\text{mol g}^{-1}$) by	
		0	6.0	25.0	10^{-1}M NaOH	CDB*
1.0	1	0.032 (3.2)	0.077 (7.7)	0.16 (16.0)	0.92 (92)	0.006 (0.6)
	7	0.018 (1.8)	0.043 (4.3)	0.12 (12.0)	1.00 (100)	0.011 (1.1)
	13	0.009 (0.9)	0.035 (3.5)	0.10 (10.0)	1.02 (102)	0.010 (1.0)
	48	0.004 (0.4)	0.012 (1.2)	0.050 (5.0)	0.93 (93)	0.019 (1.9)
	85	0.001 (0.1)	0.006 (0.6)	0.032 (3.2)	0.90 (90)	0.021 (2.1)
	104	0.001 (0.1)	0.005 (0.5)	0.026 (2.6)	0.89 (89)	0.021 (2.1)
3.0	1	0.23 (7.7)	0.40 (13.0)	0.73 (24.0)	2.76 (92)	0.014 (0.5)
	7	0.14 (4.6)	0.26 (8.7)	0.56 (19.0)	3.00 (100)	0.040 (1.3)
	13	0.11 (3.7)	0.21 (7.0)	0.48 (16.0)	3.05 (102)	0.048 (1.6)
	48	0.046 (1.5)	0.11 (3.7)	0.28 (9.3)	2.89 (96)	0.067 (2.2)
	85	0.024 (0.8)	0.072 (2.4)	0.22 (7.3)	2.88 (96)	0.073 (2.4)
	104	0.015 (0.5)	0.066 (2.2)	0.21 (7.0)	2.67 (89)	0.080 (2.6)

Amounts of Mo desorbed, as a % of Mo added, given in parentheses.

* Subsequent to extraction by 10^{-1}M NaOH .

Table 7.3 Amounts of Mo desorbed and extracted by various reagents from Ramiha soil incubated with two levels of added Mo, after various times of incubation

Added Mo $\mu\text{mol g}^{-1}$	Time of Incubation days	Mo desorbed ($\mu\text{mol g}^{-1}$) by solution P ($\mu\text{mol g}^{-1}$)			Mo extracted ($\mu\text{mol g}^{-1}$) by	
		0	10	40	10^{-1}M NaOH	CDB*
0.2	1	0.004 (2.0)	0.011 (5.5)	0.029 (15.0)	0.19 (95)	0 (-)
	7	0.003 (1.5)	0.006 (3.0)	0.025 (13.0)	0.19 (95)	0.003 (1.5)
	15	0.002 (1.0)	0.004 (2.0)	0.016 (8.0)	0.20 (100)	0.003 (1.5)
	49	0.001 (0.5)	0.003 (1.5)	0.007 (3.5)	0.20 (100)	0.003 (1.5)
	85	0 (0)	0.001 (0.5)	0.004 (2.0)	0.19 (95)	0.002 (1.0)
1.5	1	0.16 (11.0)	0.25 (17.0)	0.45 (30.0)	1.43 (95)	0.004 (0.3)
	7	0.12 (8.0)	0.23 (15.0)	0.42 (28.0)	1.51 (101)	0.010 (0.7)
	15	0.10 (6.7)	0.20 (13.0)	0.35 (23.0)	1.58 (105)	0.010 (0.7)
	49	0.047 (3.1)	0.098 (6.5)	0.21 (14.0)	1.49 (99)	0.009 (0.6)
	85	0.016 (1.1)	0.048 (3.2)	0.11 (7.3)	1.48 (99)	0.016 (1.1)

Amount of Mo desorbed as a % of Mo added given in parentheses.

* Subsequent to extraction by 10^{-1}M NaOH .

CDB-extractable Mo for Okaihau soil with increasing time, these amounts being greater in magnitude at the higher Mo addition, but not greater as a percentage of added Mo.

The relative change in the ease of desorption of Mo with time are illustrated in Fig. 7.3 for both soils. The y-ordinate represents the amount of Mo desorbed by P alone, i.e., $(P + NaCl) - (NaCl)$, expressed as a fraction of Mo extracted by P alone at $t = 1$ day. The plots show the marked decrease with time of the amounts of Mo desorbed by P, the rate of decrease being greater at short times of incubation and falling at times greater than approximately 60 days. With the high Mo additions to Ramiha soil ($1.5 \mu\text{mol g}^{-1}$), there was no decrease in the fractional amount of Mo desorbed by P over the period of 0 to 7 days, for both low and high P solutions. This behaviour was not observed for the low Mo addition to Ramiha soil, nor for the desorption of Mo by P from Okaihau soil.

The data obtained for the two soils show several similar features, namely (1) the lower the Mo addition, the faster was the rate of decrease in the amount of Mo which could be desorbed; (2) the higher the solution P level used for desorption, for a constant Mo addition, the slower the rate of decrease in the amount of Mo which could be desorbed; (3) it would appear that for times greater than those used in this study, the amount of Mo desorbed by P would continue to decrease, although at a reduced rate. For example, after 85 to 100 days, equilibrium was not reached.

The decrease in the amounts of Mo desorbed by P with increasing time suggests that Mo was being converted to a form which was not replaceable by P. Given the magnitude of the additions of Mo, and the rapid sorption of added Mo over short-time periods (Chapter 3), it seems

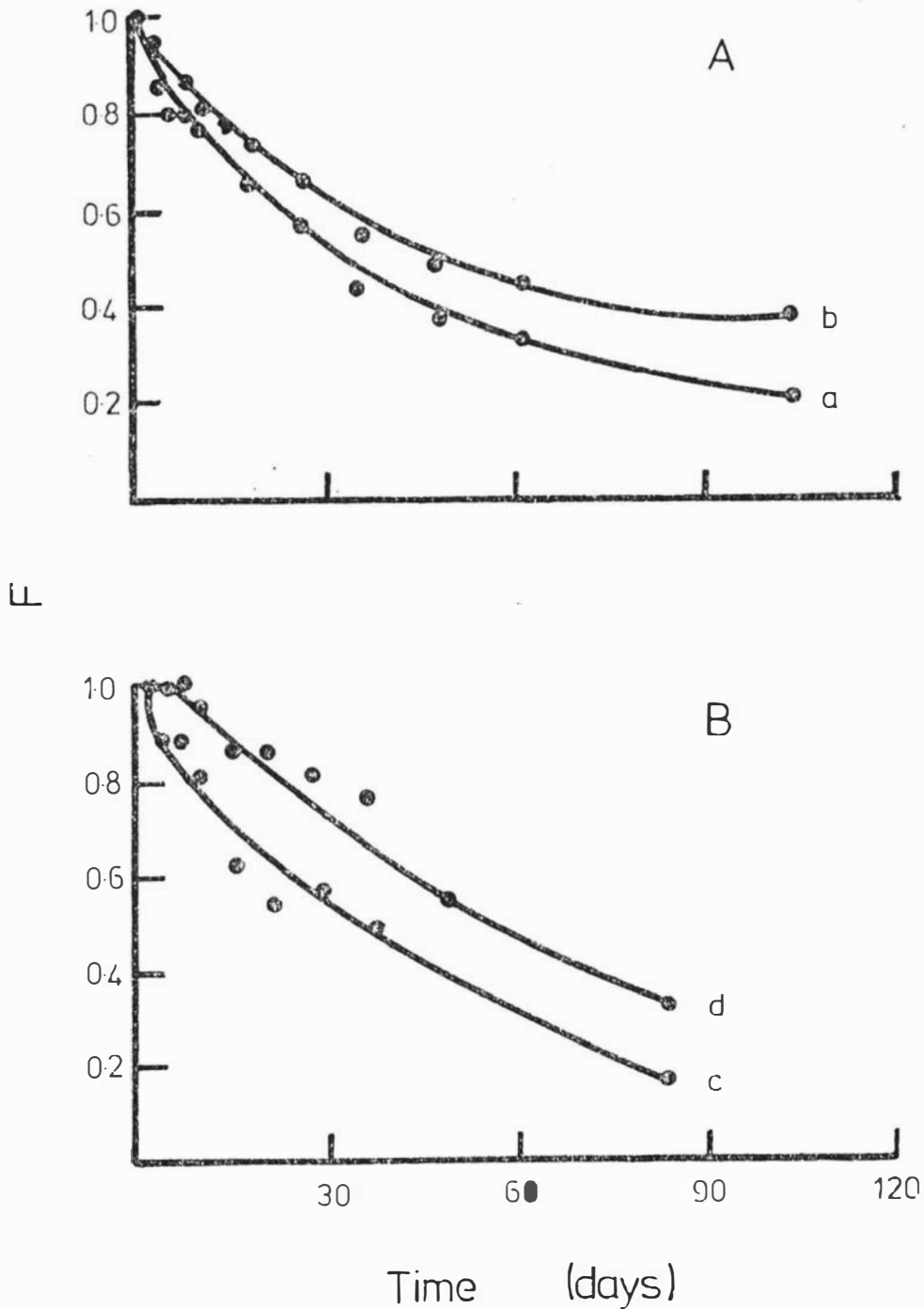


Fig. 7.3 Relationship between the fractional amount of Mo desorbed by P alone (F) (NaCl + P minus NaCl alone, expressed as a fraction of that desorbed after incubation for 1 day) and time of incubation, for two levels of Mo added to Okaihau (A) and Ramiha (B) topsoils.

A = desorption of Mo from soil incubated with $1.0 \mu\text{mol Mo g}^{-1}$ (a) and $3.0 \mu\text{mol Mo g}^{-1}$ (b) by a P solution of $25 \mu\text{mol P g}^{-1}$; B = desorption of Mo from soil incubated with $0.2 \mu\text{mol Mo g}^{-1}$ (a) and $1.5 \mu\text{mol Mo g}^{-1}$ (b) by a P solution of $40 \mu\text{mol P g}^{-1}$.

reasonable to assume that more than 95% of added Mo was sorbed by the soil at $t = 1$ day. Immobilization of added Mo by microorganisms is not expected to be significant, as Barrow (1970) has stated that the formation of 1 g of microbial tissue immobilizes only 0.0001 μmol Mo. The amount of sorbed Mo, indicated by 10^{-1}M NaOH-extractable Mo, remained constant for Ramiha soil and decreased only slightly for Okaihau soil. Thus, the change in the ease of desorption of Mo by P appears to reflect changes in the nature of the bond of Mo to the surface, rather than changes in the amounts of Mo held at the surface. From the sorption isotherms obtained during 40 hr and at equilibrium, the amounts of Mo sorbed in each region were calculated (Chapter 3). These values are given in Table 7.4 for the two Mo additions to each soil, at equilibrium and 40 hr. Even though the sorption isotherms were obtained from 10^{-1}M NaCl at a solution:solid ratio of 40:1, the qualitative features that they illustrate would still be the same for the incubation experiment. Table 7.4 shows that, between 40 hr and equilibrium, there was a decrease in the amounts of Mo sorbed in regions II and III and an increase in the amounts sorbed in region I, i.e., a conversion from the more-weakly bound to the more-strongly bound Mo. This implies that, with increasing time of incubation, it would be more difficult to desorb Mo, in accord with the observed results. By analogy with P, at times less than equilibrium, a greater amount of Mo would be sorbed at a narrower solution:solid ratio (White, 1966). Thus, the data in Table 7.4 probably overestimate the amount of Mo sorbed in regions II and III for the incubated soil samples at times less than equilibrium. Hence, comparison of the data in Tables 7.2 and 7.3 with that in Table 7.4 indicates that some of the chemisorbed Mo (regions I and II) was desorbed by P. The fact that the amounts of Mo desorbed decreased with time implies

Table 7.4 Amounts of Mo sorbed (x) during 40 hr and at equilibrium by Okaihau and Ramiha soils in each region of sorption, calculated from isotherms for sorption of Mo from 10^{-1} M NaCl at a solution:solid ratio of 40:1

Mo addition $\mu\text{mol g}^{-1}$	Time of sorption	x_I	x_{II}	x_{III}
		$\mu\text{mol g}^{-1}$		
Okaihau				
1.00	Equilibrium	0.84	0.14	0.01
	40 hr	0.61	0.36	0.03
3.0	Equilibrium	1.40	1.43	0.17
	40 hr	0.70	1.85	0.29
Ramiha				
0.20	Equilibrium	0.154	0.044	0.007
	40 hr	0.135	0.055	0.014
1.50	Equilibrium	0.73	0.64	0.10
	40 hr	0.32	0.81	0.25

that the chemisorbed Mo which was desorbed by P was primarily from region II, because the extent of Mo sorption in region I increased with time.

The slower decrease in extractable Mo with time for the higher Mo additions to each soil would reflect the greater percentage of added Mo held in the less-tightly bound forms, even at longer-time periods. The apparently constant fraction of Mo desorbed by P for the high Mo addition to Ramiha soil (Fig. 7.3) indicates that the conversion of sorbed Mo to a more tightly-held form in this allophanic soil was initially slow, i.e., kinetically controlled. This is in agreement with the results obtained in Chapter 3 for the sorption of Mo by synthetic allophane, where it was concluded that the negatively-charged silica core of allophane slows the rate of chemisorption of added Mo.

Similar decreases in the amount of Mo desorbed by P with time have been reported by Gorlach et al. (1969) and Barrow (1973). Because Barrow (1973) used 1M P solutions to displace sorbed Mo, it is possible that such high concentrations caused disruption of the sorbing surface (Rajan, 1975) and hence, the results found by Barrow are of more theoretical, than practical interest. Barrow (1973), however, did suggest that the decrease in P-extractable Mo with time was due to a change in the nature of the bond between Mo and the surface.

Because Mo is sorbed with large negative free energies of sorption, the activation energy for desorption of Mo would be expected to be high (Giles et al., 1974) and it would be expected that little Mo would be desorbed by P. That P was able to desorb Mo appears to be a result of several factors. First, because the rate of the desorption reaction would depend on P concentration, the high solution P concentrations would increase the rate of desorption. Second, the large amounts of P sorbed by the soil would result in a considerable increase in surface

negative charge (Ryden et al., 1977a). This increase in negative charge would be expected to cause desorption of the more-physically sorbed Mo (region III), the extent of this sorption being dependent on the potential of the sorbing surface. Desorption of chemisorbed Mo would not be affected by changes in surface charge. Third, small increases in pH are observed subsequent to P sorption (Rajan et al., 1974; Ryden et al., 1977a) and because Mo sorption is very dependent on pH (Chapter 5), this could be a factor causing the desorption of chemisorbed Mo.

The non-existent (for Ramiha) or very small (for Okaihau) decrease in 10^{-1} M NaOH-extractable Mo with time contrasts with the observation of Smith and Leeper (1969) for several Australian soils. These authors, however, did find that the extent of the decrease in NaOH-extractable Mo varied greatly between soils. For Ramiha soil, where the primary mineral component is allophane (Chapter 2), NaOH extraction would probably cause dissolution of the aluminosilicate gel and hence, changes in the form of sorbed Mo would not be reflected in changes in NaOH-extractable Mo for this soil. Also, the relatively large amounts of added Mo used may have masked small changes in NaOH-extractable Mo.

The increases observed in the amount of Mo extracted by CDB from Okaihau soil, although small in terms of the percentage of sorbed Mo, were not inconsiderable. This increase in CDB-extractable Mo has been postulated by Smith and Leeper (1969) to indicate a change in the nature of bonding at the surface. Such Mo, however, would be expected to be extracted by 10^{-1} M NaOH. Ryden et al. (1977b) have concluded that the observed increases in CDB-extractable P with time were a result of diffusion of P both into surface defects of particles and into short-range order materials (e.g., Fe gel) which are thought to be "structurally

porous". Such movement into materials can be regarded as an absorption reaction. This explanation for the increase in CDB-extractable Mo appears more plausible than a change in the nature of the bond to the surface. Significant increases in CDB-extractable P with time for Okaihau soil have been observed by Ryden et al. (1977b). It can probably be assumed that the large amounts of native sorbed P (3.51 and 1.39 $\mu\text{mol P g}^{-1}$ for Ramiha and Okaihau soil, respectively) are sorbed at sites in region I and consequently, would be able to diffuse into short-range order materials. Presumably, such P would compete with chemisorbed Mo for the absorption reaction. At equilibrium, the amounts of native sorbed P would be greater than the amounts of Mo sorbed in region I, except for the highest Mo addition to Okaihau soil, and therefore, the diffusive movement of P would be favoured over that of Mo. This would be the case because according to Ficks First Law of Diffusion, diffusive flux is proportional to the concentration gradient (Olsen and Kemper, 1968).

A change in the nature of the bond between Mo and the surface with time, however, provides a possible explanation for the decrease in the amount of Mo desorbed by P with increasing time, as this decrease was much greater than the increase in CDB-extractable Mo for Okaihau soil; the decrease in Mo desorbed by P occurs in Ramiha soil with no increase in CDB-extractable Mo. A shift of Mo from more-physically sorbed Mo to chemisorbed Mo is also in accord with the three compartment model for Mo sorption proposed by Barrow and Shaw (1975c), who postulated that weakly-held Mo was converted to more strongly-held Mo which is not plant available. Such strongly-held Mo would correspond to chemisorbed Mo, as defined in this study, although it would appear that some of the chemisorbed Mo may be desorbed by P.

7.3.2 Desorption and extraction of Mo added to soils in the field

Although the P solutions used for desorption corresponded to considerable P fertilizer additions ($375 \text{ kg ha}^{-1} (2\text{cm})^{-1}$ and $1125 \text{ kg ha}^{-1} (2\text{cm})^{-1}$ superphosphate) for all three soils, no Mo was detected following desorption with P solution for a 16-hr shaking time. This implies that either, no Mo was desorbed or that the amount desorbed was so small as to be undetected. Resorption of desorbed Mo was not found to occur during a 16-hr shaking time in Section 7.3.1. It is not possible to conclude that solution P did not desorb Mo, but as a percentage of the added Mo, the amount would be small. A more sensitive method of detecting changes in solution Mo concentrations, such as plant uptake, could possibly detect changes after shaking with P solutions. Additions of P have been found to increase Mo levels in plants in some studies (Stout et al., 1951; Podzolkina, 1966). In contrast, Gupta and Cutcliffe (1968) found that superphosphate additions decreased Mo uptake by plants. Changes in Mo uptake by plants are not clear indications of changes in Mo concentration in the soil solution, however, because competition and interaction within the plant-root zone can influence uptake results (Stout et al., 1951).

The results of Section 7.3.1 showed that the amount of Mo desorbed by P decreased with time after application of Mo. Because added Mo levels are very small in the field situation, compared to the levels used in laboratory studies ($140 \text{ g Na}_2\text{MoO}_4 \text{ ha}^{-1} (2\text{cm})^{-1}$ corresponds to approximately $0.003 \mu\text{mol g}^{-1}$), the levels of Mo desorbed by P would be expected to be at the lowest limits of detection, and these levels would decrease with time.

The amounts of Mo extracted by 10^{-1} M NaOH and of total Mo for the three soils are given in Table 7.5. Levels of NaOH-extractable Mo were

Table 7.5 Amounts of Mo extracted by 10^{-1} M NaOH and total amounts of Mo for three soils which had received various treatments of added Mo and lime

Soil	Treatment*	10^{-1} M NaOH-extractable Mo $\mu\text{mol g}^{-1}$	Total Mo $\mu\text{mol g}^{-1}$
Warepa	1	b.d.	0.0192
	2	b.d.	0.0219
	3	b.d.	0.0195
	4	b.d.	0.0215
Waipari	1	b.d.	0.0188
	2	b.d.	0.0209
	3	b.d.	0.0178
	4	0.0005	0.0192
Kaiwera	1	0.0005	0.0097
	2	0.0005	0.0104
	3	0.0005	0.0097
	4	0.0010	0.0111

b.d. : below detection limit, i.e., $< 0.0005 \mu\text{mol g}^{-1}$.

*

1 = Control.

2 = $140 \text{ g Na}_2\text{MoO}_4 \text{ ha}^{-1} \text{ yr}^{-1}$.

3 = $2500 \text{ kg lime ha}^{-1}$ applied 3 yr prior to sampling.

4 = $140 \text{ g Na}_2\text{MoO}_4 \text{ ha}^{-1} \text{ yr}^{-1}$ plus $2500 \text{ kg lime ha}^{-1}$ applied 3 yr prior to sampling.

at or below the lowest limits of detection, except for the lime plus Mo treatment to Kaiwera soil. The low amounts extracted make generalisations difficult. The increase in NaOH-extractable Mo for both Waipari and Kaiwera soils treated with lime plus Mo, compared to those soils treated with Mo alone, however, indicates that lime treatment increases the amount of Mo sorbed at the surface. Diffusion of chemisorbed Mo into soil components, which is thought to occur to a limited degree for Mo at very low levels of addition, could account for a significant proportion of added Mo. Increasing the pH decreases chemisorbed Mo (Chapter 5) and would consequently decrease the absorption reaction, resulting in greater amounts of Mo being retained at the surface and thus extractable by 10^{-1} M NaOH. ①

For each soil, total Mo levels were greater for treatments with added Mo than those for treatments that had not received Mo. The differences in total Mo between treatments with added Mo and treatments without Mo, however, do not account for all the added Mo, i.e., total Mo of treatment 2 minus total Mo of treatment 1 was less than total added Mo. The soil samples were taken over a 10-cm depth, whereas the amount of added Mo was calculated over a 2-cm depth; also a bulk density of 1.0 g cm^{-3} was assumed. Bulk densities greater than 1.0 and calculation of addition levels on a 10-cm depth basis would reduce the calculated levels of addition. For two of the soils (Warepa and Waipari), the field trial was essentially a grazing trial with two herbage cuts taken annually, with the clippings removed. In the case of the trial on Kaiwera soil, herbage cuts were made throughout and the clippings removed. If the levels of Mo differed in the herbage, for the different Mo treatments, then loss of added Mo may have occurred through removal by grazing animals or in herbage clippings. No data ②

are available, however, to ascertain whether losses of added Mo may have occurred in this manner.

The differences in total Mo for each soil, with and without added Mo, indicate that much of the added Mo had not been lost. Several investigators (Jones and Belling, 1967; quoted by Smith and Leeper, 1969) have concluded that a large proportion of added Mo is lost by leaching because of the limited response to Mo in years subsequent to addition. Jones and Belling (1967) also showed that approximately 80% of added Mo was leached out by water equivalent to 450 mm of rainfall. Their data, however, were for soils of pH greater than 7.0; for two soils of pH 5.5 leaching of added Mo was very small. This is qualitatively in agreement with the data of Chapter 5; at pH values greater than 7.0, chemisorption of Mo would be minimal and the more-physically sorbed Mo would more easily be lost by leaching. At pH 5.5, chemisorption of Mo would occur and this Mo would be less likely to be leached out. Smith and Leeper (1969) and Jones and Smith (1972) concluded that the decreased availability of Mo with increasing time was due to conversion of Mo to less-soluble forms. The data of Section 7.3.1.3 demonstrated the conversion of sorbed Mo to chemisorbed forms and the possible absorption of this adsorbed form. Data for the differences in total Mo levels (Table 7.5) suggest that some sorbed Mo had been converted to a form which was not extractable by 10^{-1} M NaOH. Because organic immobilization is not expected to be large (Barrow, 1970), absorption by porous components is probably significant. Because P and Mo appear to be sorbed by similar sorption mechanisms (Chapter 4), previous P additions would be expected to affect the amounts of subsequently added Mo that are chemisorbed. With large previous P additions, significant proportions of the added Mo could be held by a

more-physical sorption mechanism and hence, this form of Mo would be more easily leached. With time, however, absorption of previously added P would result in regeneration of chemisorption sites (Ryden et al., 1977b), and the amounts of more-weakly held Mo would decrease as this form of Mo was converted to chemisorbed forms. After an appreciable period of time, the amount of extractable Mo would be very small. The specific effects of previously added P on the sorbed form of added Mo will be investigated in the next Chapter.

The results of this Section show that Mo added to soils is strongly held and that, because of the shift to chemisorbed forms, the extractability of sorbed Mo decreases with time. Additions of fertilizer P, even at high levels, would not cause desorption of significant amounts of this added Mo.

CHAPTER 8

THE EFFECT OF PREVIOUS ADDITIONS OF
PHOSPHATE AND LIME ON MOLYBDATE SORPTION

8.1 Introduction

In previous Chapters, it has been shown that the sorption energies of P and Mo are very similar and it has been proposed that the two anions are sorbed by the same types of sorption reactions (Chapter 5). It was also shown that Mo and P compete for sorption sites on soils and soil components (Chapter 6); this was taken as further evidence that P and Mo sorb at the same surface sites. Consequently, the sorption of Mo would be expected to be altered by previous additions of P.

Large additions of fertilizer P are made annually to many soils in New Zealand, resulting in different saturations of the soil sorption complex. This would be expected to affect the extractability and plant availability of subsequently added Mo.

Similarly, additions of lime are known to affect the availability of both native and subsequently added Mo (Cullen, 1955; During et al., 1960; Hagstrom and Berger, 1963; During, 1970). It is also known that soil pH affects the sorption of Mo by soils (Barrow, 1970; Theng, 1971). There has been little quantitative investigation, however, of the effect of lime on the sorption of Mo.

Recent work has suggested that sorbed P can be divided into two distinct forms, namely chemisorbed and more-physically sorbed forms (Ryden et al., 1977a). In the present study, soils were saturated to different degrees of the chemisorption and more-physical sorption maxima for P, and the effect of these P additions on the subsequent sorption of Mo investigated. To examine the effect of previous P fertilizer and lime additions on Mo sorption, a comparison of Mo

sorption by a soil with known, differing fertilizer P and lime histories was also made.

In order to obtain similar saturations of corresponding regions of sorption for different soils at, or near, equilibrium, isotherms at equilibrium must be obtained. Incubation of added P with soils is, however, carried out at solution:soil ratios which are much narrower than those usually used, and P sorption isotherms obtained at different solution:soil ratios differ (Larsen and Court, 1960; Fordham, 1963). Prior investigation of the effect of solution:soil ratio on P sorption was carried out so that equilibrium isotherms could be obtained at solution:soil ratios that were experimentally practical, and yet were relevant to soils incubated with added P.

8.2 Methods

8.2.1 Effect of solution:soil ratio on P sorption

Ramiha, Dannevirke, and Tokomaru topsoils (hereafter referred to as soils) were used in this study.

Sorption isotherms for P were obtained in 10^{-1} M NaCl during 40 hr at solution:soil ratios varying from 1:1 (except for Ramiha soil) to 40:1. To prevent microbial activity, $368 \mu\text{mol HgCl}_2 \text{ l}^{-1}$ was added to each system.

For subsequent kinetic studies, appropriate amounts of P were added in aliquots of 10^{-1} M NaCl at times of 0, 24, 48, and 72 hr after commencing to shake samples with 10^{-1} M NaCl. Shaking was continued for 74 hr, thus ensuring that the total time of shaking for each system was the same, but the times of contact between soil and added P were 74, 98, 122, and 144 hr. Solution:soil ratios, after the addition of the P aliquot, were again varied within the range 1:1 to 40:1.

To determine the effect of solution:soil ratio at equilibrium, without determining actual equilibrium isotherms, the levels of P addition were, of necessity, different for each ratio used. The rationale upon which P additions were based is given in Table 8.1. For a given amount of P sorbed (x), the same equilibrium P concentration (y) will be maintained in solution if the equilibrium isotherms are coincident. When equilibrium solution P concentration is expressed on a $\mu\text{mol P g}^{-1}$ of soil basis, then the required amount of added P (sum of x plus y terms) is greater at a ratio of 40:1 than at a ratio of 1:1. Similar calculations can be made for the other ratios used. After shaking, suspensions were centrifuged, filtered, and analyzed for P. The solution P concentrations obtained at the experimental times were used to estimate equilibrium P concentration by extrapolating the linear relationship between solution P concentration and the reciprocal of time to $1/t = 0$, i.e., $t = \infty$ (Ryden and Syers, 1975).

8.2.2 Effect of previously added P on Mo sorption

Ramiha, Dannevirke and Tokomaru topsoils (hereafter referred to as soils) were used. By extrapolation of the linear relationship between solution P concentration and the reciprocal of time to $1/t = 0$, for times between 75 and 150 hr, equilibrium P sorption isotherms were constructed for the soils. Between ten and twelve P additions were made in order to obtain an equilibrium isotherm over the final P concentration range of 0 - 300 $\mu\text{mol l}^{-1}$ at a solution:soil ratio of 40:1 in 10^{-1}M NaCl . From the three Langmuir equations which described P sorption, determined as described in Chapter 4, P additions were calculated for all soils which corresponded to a known saturation of the sorption maximum of a particular region of sorption.

Table 8.1 Outline of the calculations to determine the required amount of P and initial solution P concentration at different solution:soil ratios in kinetic studies based on the assumption that equilibrium sorption is independent of the solution:soil ratio used.

Solution:soil ratio	Amount of P sorbed at equilibrium $\mu\text{mol g}^{-1}$	Equilibrium solution P concentration		Amount of added P required $\mu\text{mol g}^{-1}$	Initial solution P concentration $\mu\text{mol l}^{-1}$
		$\mu\text{mol l}^{-1}$	$\mu\text{mol g}^{-1}$		
1:1	x	y	$y/1000$	$x + y/1000$	$x + y/1000$
40:1	x	y	$40y/1000$	$x + 40y/1000$	$x/40 + y/1000$

Two levels of added P, plus a zero addition, were made to each soil; the additions corresponded to 20% and 50%, respectively, of the sorption maximum of region II at equilibrium. The P additions were 13.27 and 32.00 $\mu\text{mol P g}^{-1}$ (Ramiha), 3.75 and 10.56 $\mu\text{mol P g}^{-1}$ (Dannevirke), and 0.58 and 3.20 $\mu\text{mol P g}^{-1}$ (Tokomaru). Additions of P were made in sufficient water such that the resulting moisture contents of the soil corresponded to 0.60 bar suction. The gravimetric moisture contents at this suction were 26.0, 20.0, and 13.7 for Ramiha, Dannevirke, and Tokomaru, respectively. Mercuric chloride was also added at a level of 1.85 $\mu\text{mol g}^{-1}$. The P solutions were applied with an atomiser spray. The moist soils were stored in loosely-covered jars, which were placed in containers above a free-water surface and stored at 25°C. Moisture contents were checked periodically and water added as required.

After an incubation period of 12 months, the soils were removed and air-dried. Isotherms for sorption of Mo were then determined on the air-dried samples. Isotherms were determined in 10^{-1}M NaCl during 40 hr at a solution:soil ratio of 40:1. Between twelve and fifteen additions of Mo were made to give final Mo concentrations in the range of 0 - 100 $\mu\text{mol Mo l}^{-1}$.

The amount of 10^{-1}M NaOH -extractable P was determined on soils before and after the incubation period. Samples (1-g) of moist soil were shaken overnight with 40 ml of 10^{-1}M NaOH . Following centrifugation, an aliquot of the supernatant was acidified to precipitate organic matter, and analyzed for P.

8.2.3 Effect of previous fertilizer P and lime additions on Mo sorption

The soil used in this study was Papatoetoe silt loam; the depth of

sampling was 0 - 5 cm. The experimental site was located at the New Zealand Fertilizer Manufacturers' Research Association, Otara. Four samples which had different fertilizer P and lime histories were used : treatment 1 was a control, with no fertilizer and lime additions; treatment 2 was 34 kg P ha⁻¹ applied annually as superphosphate for 22 yr; treatment 3 was 1 tonne of lime ha⁻¹ applied annually for 22 yr; and treatment 4 was 34 kg P ha⁻¹ as superphosphate plus 1 tonne lime ha⁻¹ applied annually for 22 yr.

Sorption isotherms for Mo were determined using air-dried samples (<2 mm) of these soils. Isotherms were determined in 10⁻¹M NaCl during 40 hr at a solution:soil ratio of 40:1. Between twelve and fifteen additions of Mo were made so that final solution Mo concentrations were in the range of 0 - 100 μmol l⁻¹.

The amounts of P and Mo extracted by 10⁻¹M NaOH were used as estimates of native sorbed P and Mo, respectively.

8.3 Results and Discussion

8.3.1 Effect of solution:soil ratio on P sorption

Isotherms obtained for the sorption of added P by the three soils during a 40-hr shaking period showed a dependence on solution:soil ratio. This is illustrated by the data for Ramiha soil (Fig. 8.1); similar data were obtained for the other two soils (not presented). Analytical errors were large for the Ramiha soil at a ratio of 1:1, because of the very low levels of P sustained in solution, and the data are not presented. Above a final solution P concentration of approximately 1 μmol P l⁻¹, more P was sorbed at a solution:soil ratio of 5:1 than at a ratio of 40:1 for a given level of P in solution. It has been shown (Ryden and Syers, 1975), however, that soil systems to which P has been added are not

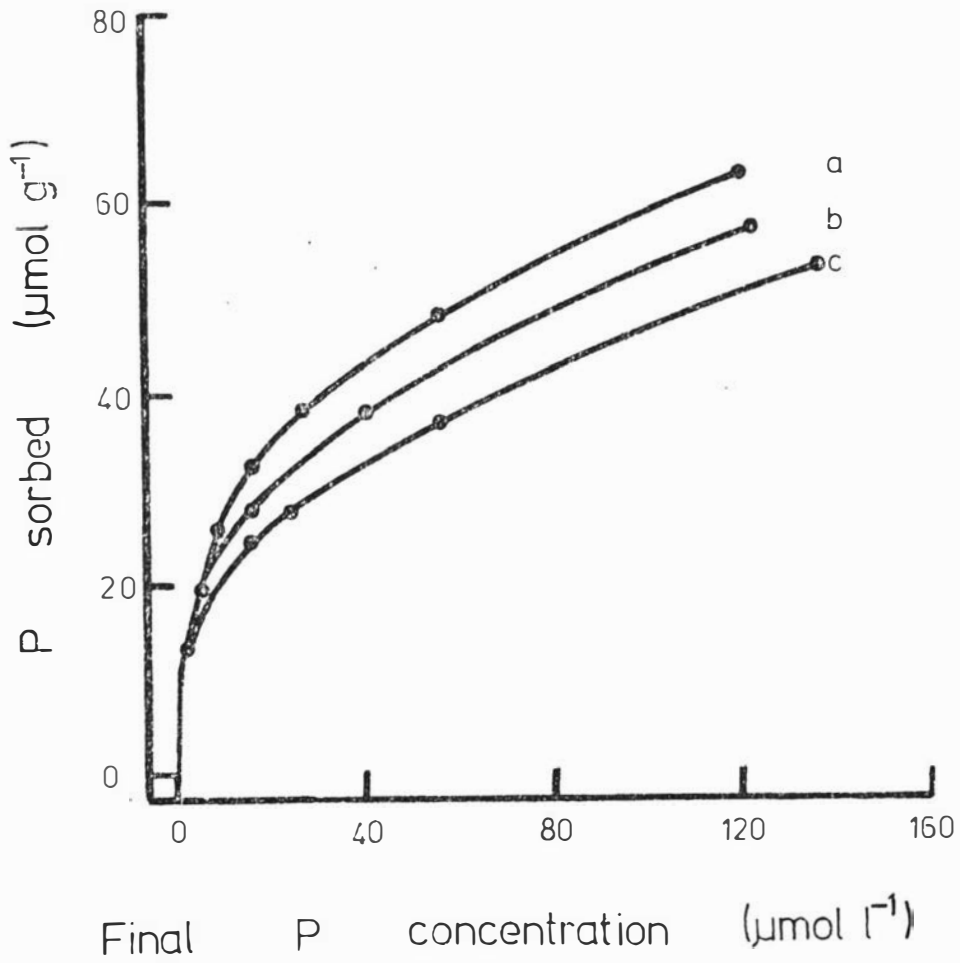


Fig. 8.1 Isotherms for the sorption of added P from 10^{-1} M NaCl during 40 hr by Ramiha soil at three solution:soil ratios: a = 5:1, b = 10:1, and c = 40:1.

at equilibrium after a 40-hr shaking period. Consequently, the kinetics of P sorption were evaluated in order to estimate the solution P concentration at longer time intervals.

The data for Ramiha soil in Fig. 8.2 demonstrate that the effect of solution:soil ratio on P sorption, evaluated by the change in solution P concentration as a function of time, was kinetically controlled. The data in Fig. 8.2 also indicate that, at a given time before equilibrium was reached, soil suspensions having a narrow solution:soil ratio were closer to equilibrium than those at a wider ratio. Solution P concentrations at equilibrium appeared to be coincident for each ratio at the high and low levels of added P used. Similar findings were obtained for the other two soils and the data are summarized in Table 8.2. The data in Table 8.2 indicate that the concentrations of P in solution at equilibrium, as determined by extrapolation, are not always exactly equal at varying solution:soil ratios. Within the limits of experimental error, and of the extrapolation technique used, however, the conclusion that solution P concentrations at equilibrium at different solution:soil ratios are coincident appears to be valid.

Comparison of the data for P remaining in solution at 40 hr and equilibrium (Table 8.2) indicates that at the lower level of P addition, solution:soil ratio had less influence than at higher levels of P addition. At equilibrium, however, for both low and high levels of P addition, solution P concentrations were independent of solution:soil ratio. This was assumed in choosing the initial levels of added P, and the initial assumption is therefore justified.

The results obtained for the sorption of P at different solution:soil ratios demonstrate that this ratio affects only the rate at which P is removed from solution (Fig. 8.2). This indicates that sorption

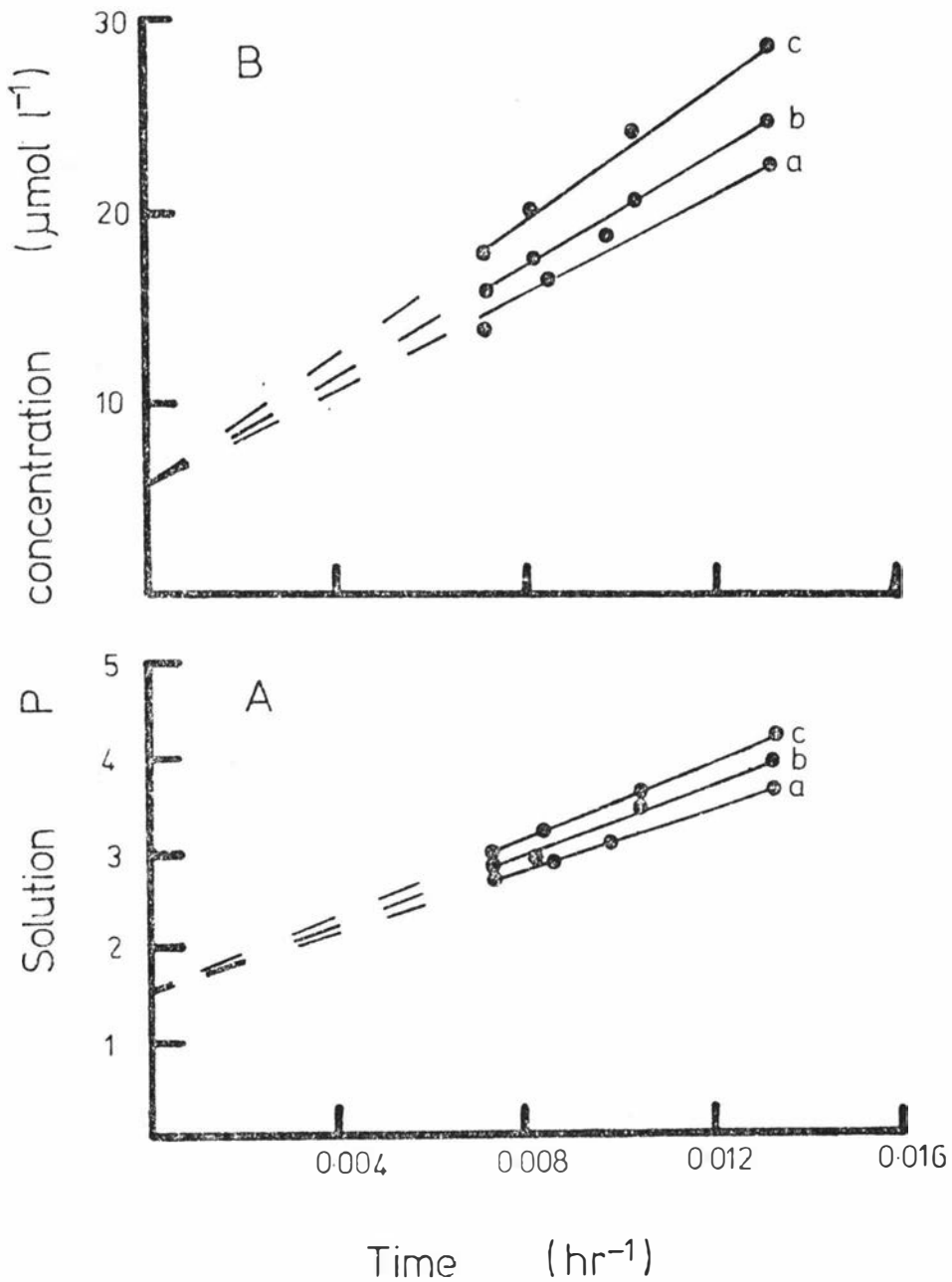


Fig. 8.2 Relationship between solution P concentration and reciprocal of time during sorption of P by Ramiha soil for three solution:soil ratios at high (A) and low (B) levels of P addition; dashed lines used to extrapolate the data to the ordinate, i.e. $1/t = 0$, $t = \infty$, to estimate equilibrium P concentration. Solution:soil ratios are $a = 5:1$, $b = 10:1$, and $c = 40:1$.

Table 8.2 Inorganic P remaining in solution at times indicated for three soils at varying solution:soil ratios

Soil	Added P level [*]	Inorganic P in solution at ratios and times indicated ($\mu\text{mol l}^{-1}$)							
		1:1		5:1		10:1		40:1	
		40 hr	Equilibrium	40 hr	Equilibrium	40 hr	Equilibrium	40 hr	Equilibrium
Tokomaru	low	5.81	2.36	5.81	2.45	6.78	2.55	6.78	2.45
	high	73.0	17.4	85.6	17.4	94.9	18.1	143.6	18.7
Dannevirke	low	3.22	1.65	3.23	1.55	5.87	1.68	3.87	1.65
	high	26.2	6.14	27.1	5.17	32.3	4.84	44.9	4.84
Ramiha	low	n.d.	n.d.	4.84	1.65	7.10	1.55	9.04	1.58
	high	n.d.	n.d.	27.1	5.81	32.0	5.81	51.7	6.00

* Amounts of added P not given because these differed for each solution:soil ratio, as discussed in the text.

n.d. = not determined.

isotherms would be coincident at equilibrium, irrespective of the ratio used and demonstrates a kinetic origin for the effect of solution:soil ratio on P sorption at times less than that required to reach equilibrium. The use of mercuric chloride as a sterilant in the present study would tend to negate the suggestion (Larsen and Widdowson, 1964) that increased microbial activity with increasing soil mass is responsible for the effect of solution:soil ratio on P solution concentration. At narrower solution:soil ratios, the initial solution P concentration is higher, as indicated in Table 8.1. Also, the greater mass of soil at a narrower ratio implies a greater concentration of P-sorbing sites. These factors, coupled with the dependence of the kinetics of P sorption on solution P concentration (Ryden and Syers, 1975) would account for the observation that, at times less than equilibrium, the narrower ratio systems are closer to equilibrium.

Most previous studies of the effect of solution:soil ratio on solution P concentration have been concerned with the desorption of P (Aslyng, 1954; Wild, 1959; Larsen and Court, 1960). It is unlikely, however, that the systems investigated in these studies were at equilibrium. The work of White and Beckett (1964) and White (1966), however, is directly relevant to the present study. Their work showed that the observed effects of solution:soil ratio on P sorption could be eliminated if the soil and added P were allowed to equilibrate for 2 to 3 months. From the data in Fig. 8.2, it is apparent that after 2 to 3 months, the solution P concentration is essentially the same at the different solution:soil ratios studied.

The results obtained indicated that the equilibrium isotherms estimated in laboratory studies at wide solution:soil ratios can be used to describe systems where P is incubated with soil at solution:soil ratios

less than unity and that, after time periods of three months or longer, such systems would be at, or near, equilibrium.

8.3.2 Effect of previously added P on Mo sorption

Incubating the soil with P prior to Mo sorption decreased the extent of sorption of Mo, as illustrated in Fig. 8.3 for Ramiha soil. Similar results were obtained for the other two soils. Increasing the amount of added P decreased the H-type character of the isotherm, indicating a reduction in the number of high-affinity sites available for Mo sorption.

Isotherms for sorption of Mo by all three soils, at all levels of added P, could be described by three Langmuir equations, each with widely differing k values and distinct b values. Values for b , k , and ΔG for each region of sorption for the three soils are summarized in Table 8.3.

Increasing the amounts of previously added P increased the k values for region I, but did not significantly alter k values for regions II and III, except for the highest P addition to Tokomaru soil. When k values were converted to ΔG values (equation 3.1), increases in ΔG for any one particular region were small compared to the differences in ΔG between different regions of the sorption isotherm, i.e., the presence of previously added P did not appear to change the mechanism of Mo sorption.

The decrease in the extent of Mo sorption after P additions was reflected in changes in b values. The low P addition to all three soils had little effect on b_{III} , but reduced both b_I and b_{II} values, the reduction in the sorption maxima being greatest for Ramiha soil and least for Tokomaru soil. The high P addition had less effect on sorption maxima in region I, but considerably reduced the extent of sorption

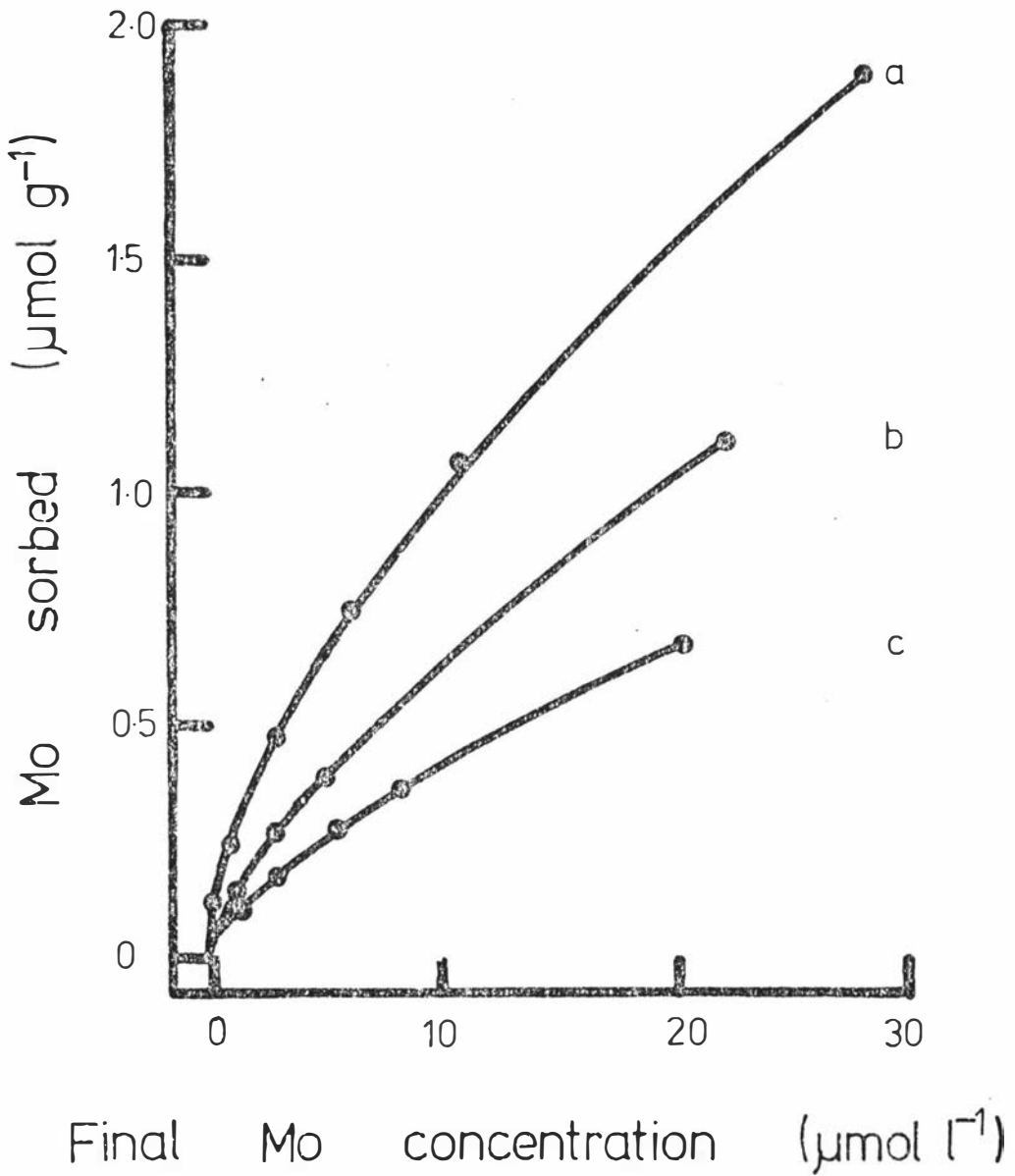


Fig. 8.3 Isotherms for the sorption of Mo from 10^{-1} M NaCl during 40 hr by Ramiha soil which had previously been incubated with three levels of added P. Levels of added P are a = 0, b = $13.27 \mu\text{mol P g}^{-1}$, and c = $32.0 \mu\text{mol P g}^{-1}$, which correspond to 0, 20%, and 50%, respectively, saturation of the sorption maximum of region II at equilibrium.

Table 8.3 Sorption constants for Mo sorption by three soils incubated with different levels of added P for 12 months

P added	b_I	b_{II}	b_{III}	k_I	k_{II}	k_{III}	ΔG_I	ΔG_{II}	ΔG_{III}
$\mu\text{mol P g}^{-1}$	$\mu\text{mol Mo g}^{-1}$			$l (\mu\text{mol Mo})^{-1}$			kJ mol^{-1}		
Rami ha									
0	0.12	1.35	7.14	12.3	0.10	0.0041	-40.1	-28.4	-20.5
13.27	0.052	0.67	7.14	26.9	0.14	0.0038	-42.1	-29.1	-20.3
32.00	0.023	0.56	4.35	87.8	0.11	0.0038	-45.0	-28.5	-20.3
Dannevirke									
0	0.024	0.200	1.75	18.10	0.15	0.0042	-41.4	-29.3	-20.5
3.75	0.015	0.092	1.47	30.0	0.23	0.0042	-42.4	-30.4	-20.5
10.56	0.013	0.054	1.05	33.1	0.17	0.0071	-42.6	-29.6	-21.8
Tokomaru									
0	0.028	0.22	1.04	6.82	0.18	0.0088	-38.7	-29.7	-22.4
0.58	0.020	0.16	1.00	14.6	0.21	0.0103	-40.6	-30.1	-22.7
3.20	0.012	0.031	0.59	14.2	0.74	0.035	-40.5	-33.3	-25.8

in regions II and III.

Although the sorption isotherms for Mo (Fig. 8.3) showed that incubating the soil with P decreased Mo sorption, they do not indicate which regions of Mo sorption were the most affected by P additions. From the sorption constants obtained, isotherms for sorption of Mo in each region were calculated. Such isotherms, illustrated in Fig. 8.4 for Ramiha soil, clearly indicate the effect of previously added P on Mo sorption. The low P addition (leading to 20% saturation of the P sorption maxima in region II) considerably reduced chemisorption of Mo (regions I and II) but had a very small effect on more-physically sorbed Mo (region III). A larger addition of P had a greater effect on Mo sorbed in region III, relative to the lower P addition. At the low P addition, P sorption in region III was small, but at the higher P addition, P sorption in region III became important. The fact that region III Mo was only reduced when P sorption in region III became important implies that sorption of both anions in region III occurs at similar surface locations. For a given Mo addition, increasing the amount of previously added P decreased the proportion of added Mo that was chemisorbed and increased the proportion of added Mo sorbed by a more-physical type mechanism. For example, for an addition of $0.004 \mu\text{mol Mo g}^{-1}$ to Ramiha soil incubated with no added P, 94% of the added Mo was chemisorbed and 2.5% was more-physically sorbed, whereas for the same Mo addition to Ramiha soil incubated with $32.0 \mu\text{mol P g}^{-1}$, 70% of added Mo was chemisorbed and 10% was more-physically sorbed. This observation could have implications to the field situation in New Zealand where large amounts of fertilizer P are frequently added annually. This may lead to a high percentage saturation of chemisorption sites. As a consequence, a higher proportion of subsequently added Mo would be less-strongly held

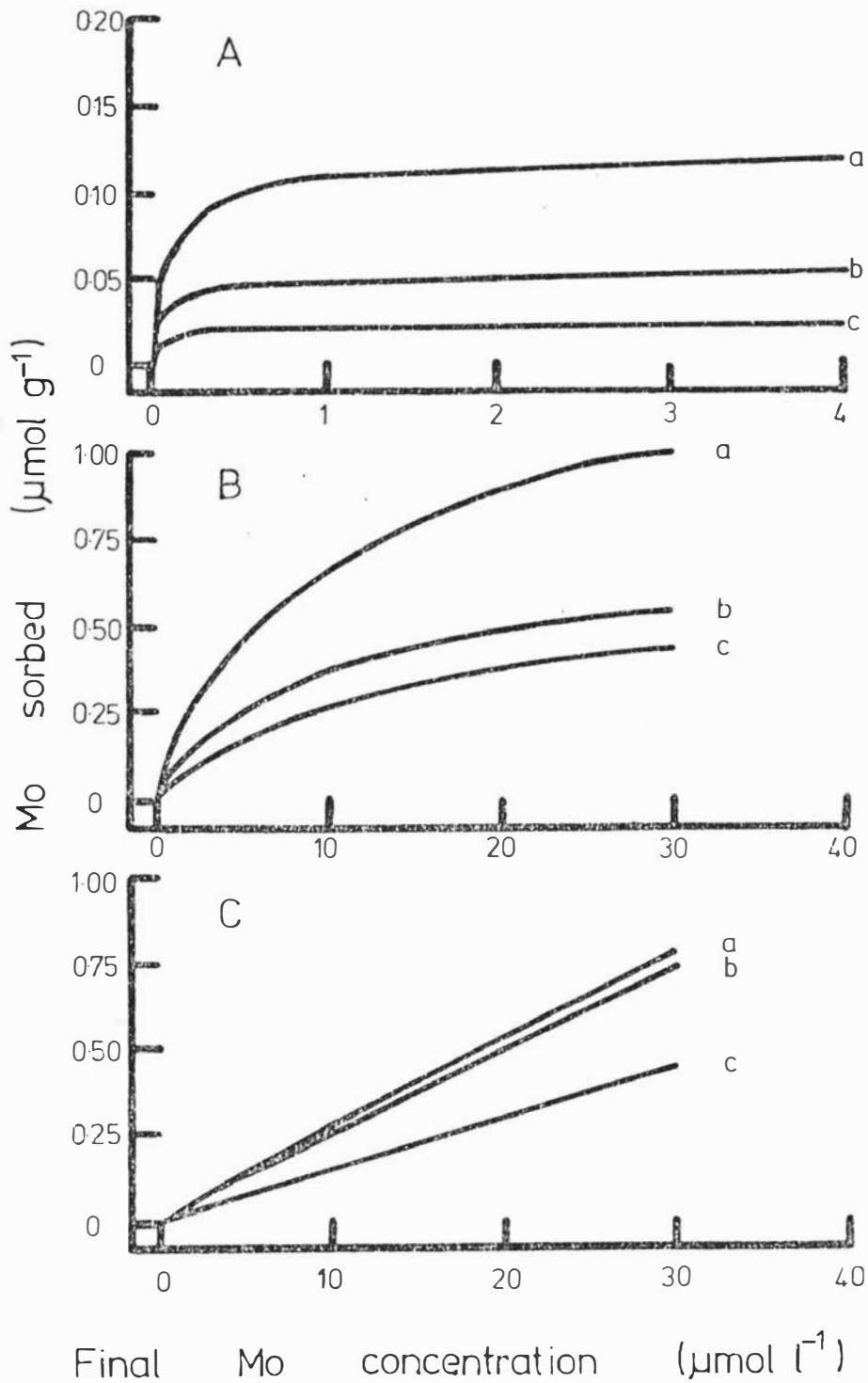


Fig. 8.4 Calculated isotherms for the sorption of Mo during 40 hr by Ramiha soil which had been incubated with three levels of added P prior to Mo sorption. Levels of added P are a = 0, b = $13.27 \mu\text{mol P g}^{-1}$, and c = $32.0 \mu\text{mol P g}^{-1}$, which correspond to 0, 20%, and 50% respectively, saturation of the sorption maximum of region II at equilibrium. A = Mo-region I, B = Mo-region II, and C = Mo-region III.

by a more-physical sorption mechanism and could possibly be lost more rapidly by leaching. This could lead to low responses to added Mo in years subsequent to addition. Absorption of adsorbed Mo (Chapter 7), however, could also lead to the same non-response.

Although the high P additions were sufficient to ensure complete saturation of sites for P in region I for each soil, Mo sorption still occurred in region I (Table 8.3). Because it has been concluded that P and Mo bond at similar surface sites (Chapters 4 and 6), no Mo sorption in region I would be expected. The fact that small amounts of Mo were sorbed in region I could arise for several reasons. It is possible that a small amount of chemisorbed P was desorbed during the 40-hr shaking period. This would enable a small amount of added Mo to be sorbed at sites previously occupied by P, i.e., the desorption of P, allowing sorption of subsequently added Mo, is probably an artefact of the laboratory procedure. It would be expected, however, that this desorption of P would be very small and would not account for all of the observed chemisorption of Mo in region I. The time-dependent sorption of P is believed to result from diffusion of chemisorbed P into both surface defects and short-range order materials (Ryden et al., 1977b) with consequent regeneration of surface chemisorption sites. At times less than that required to reach true equilibrium, regeneration of chemisorption sites would still be occurring. Such sites could be filled either by added Mo or by more-physically sorbed P, which shifts to chemisorbed forms (Ryden et al., 1977b). Evidence for absorption of surface-bound P during the incubation is presented in Table 8.4, which gives values for 10^{-1} M NaOH-extractable P before and after incubation of the soils with added P. The data show that for all soils at both levels of added P, the amounts of NaOH-extractable P decreased during the

Table 8.4 Added P extracted by 10^{-1} M NaOH from three soils immediately after addition of P and after a 12-month incubation period

Soil	Added P $\mu\text{mol g}^{-1}$	10^{-1} M NaOH-extractable P ($\mu\text{mol g}^{-1}$) after incubation for	
		0 months	12
Ramiha	13.27	13.25	12.34
	32.00	32.00	29.97
Dannevirke	3.75	3.75	3.26
	10.56	10.58	8.83
Tokomaru	0.58	0.60	0.47
	3.20	3.20	3.03

incubation period, i.e., the amounts of surface-bound P decreased during this period. Ryden et al. (1977b) have shown that the decrease in NaOH-extractable P, with increasing time after P addition, is commensurate with the increase in CDB-extractable P. The latter reagent is considered to extract the P present within the matrices of crystalline oxides and hydrous oxides of iron. Thus, the data in Table 8.4 suggest that surface-bound P was moving into short-range order materials. Such decreases in surface-bound P would lead to the regeneration of chemisorption sites at the surface. Whereas most of these chemisorption sites would subsequently be occupied by more-physically bound P, some could also be occupied by added Mo, thus resulting in the observed sorption of Mo in region I.

8.3.3 Effect of previous fertilizer P and lime additions on Mo sorption

Data for soil pH and native sorbed P for the different treatments of Papatoetoe soil are given in Table 8.5. The pH of the limed soils was one pH unit higher than that of the unlimed soils. Native sorbed P was considerably higher for the soils which had received superphosphate additions over 22 yr. Even the control treatments, however, contained large amounts of native sorbed P. Values for native P were slightly lower for the limed soils than for the unlimed soils for each P treatment. p 210.

There are good reasons to expect native sorbed P to be sorbed primarily at the sites of highest energy and hence, this would prevent the sorption of added Mo at such sites. From the P sorption data reported for the soil (Papatoetoe silt loam) by Ryden et al. (1977c), it appears that native sorbed P occupies approximately 35% of the chemisorption sites for P (regions I and II) for treatments 1 and 2, and approximately 80% of the chemisorption sites for P for treatments 3 and 4.

Table 8.5 pH and NaOH-extractable P values for Papatoetoe silt loam of different fertilizer treatment histories

Treatment	pH		10^{-1} M NaOH P $\mu\text{mol g}^{-1}$	
	H_2O^*	10^{-1} M NaCl ⁺		
1	5.8	5.9	8.8	<i>Control</i>
2	5.8	5.9	16.9	<i>P</i>
3	6.5	7.2	6.6	<i>L</i>
4	6.5	7.2	14.7	<i>PL</i>

* Solution:soil ratio = 2.5:1.

+ Solution:soil ratio = 40:1.

For treatments 3 and 4, therefore, region I sites would be completely occupied by native P. For treatments 1 and 2, saturation of region I by native P would also approach 100%. Given that P and Mo appear to be sorbed by similar mechanisms and at similar sites (Chapter 4), then no sorption of Mo in region I would be expected.

Both the superphosphate and lime treatments reduced Mo sorption, as shown in Fig. 8.5. Previous lime additions had a greater effect on Mo sorption than did previous P additions; that is, the effect of lime alone on Mo sorption was much greater than that of P alone.

By successive approximation of data points (Table 3.2), sorption isotherms for Mo for each of the four treatments were found to be described by two Langmuir equations, each equation having distinct b and k values. Table 8.6 summarises the b , k , and ΔG values for the two regions of Mo sorption for all four treatments. The ΔG values for the regions were very similar to those obtained for Mo sorption by unfertilized soils in regions II and III (Chapter 3) and consequently, the two regions of sorption for Papatoetoe silt loam were assigned to regions II and III, i.e., for all four treatments, there was no region I for Mo sorption.

The similarity of k and ΔG values for each respective region for all four treatments suggests that neither previous additions of fertilizer P nor of lime changed the mechanism of Mo sorption. For treatment 4, the free energy of sorption in region II increased, but the increase was not large enough to conclude that the Mo sorption mechanism was different. That previously added fertilizer P did not effect the mechanism of Mo sorption is in agreement with the results for soils incubated with added P in the laboratory (Section 8.3.2).

The extent of Mo sorption, indicated by the b values, was affected by both previous superphosphate and lime addition. Previous P addition

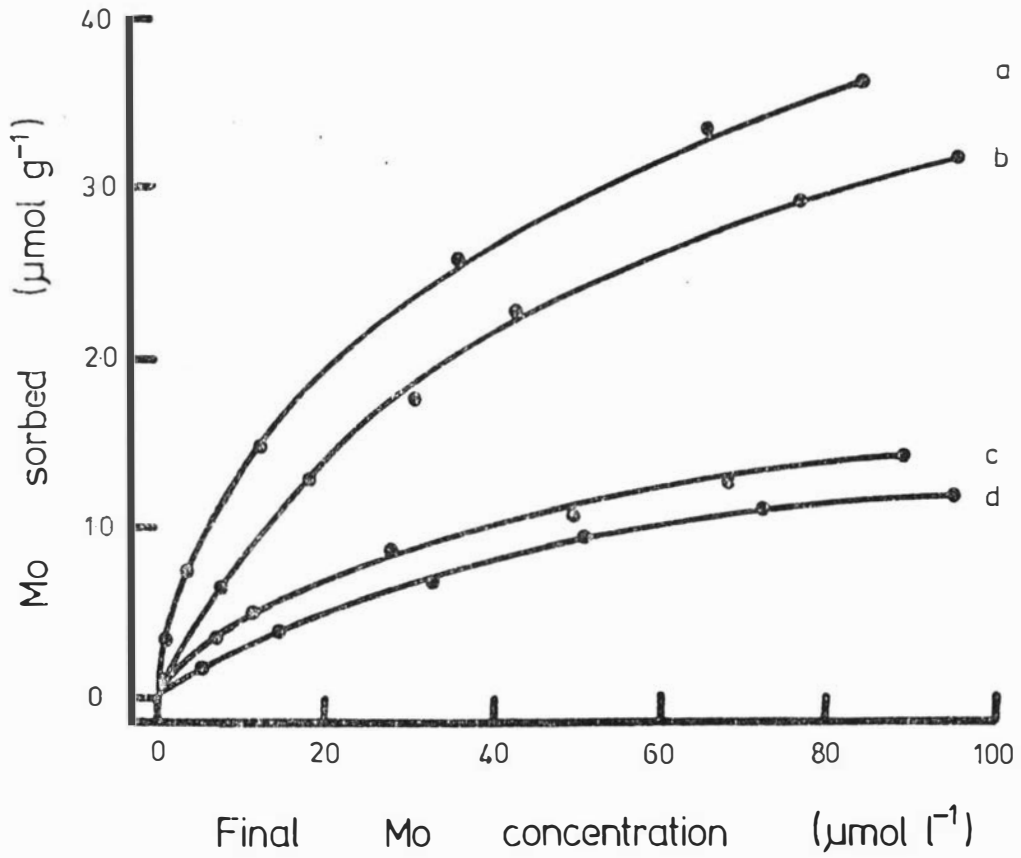


Fig. 8.5 Isotherms for the sorption of Mo from 10^{-1}M NaCl during 40 hr by Papatoetoe silt loam. a = treatment 1, b = treatment 2, c = treatment 3, and d = treatment 4.

Table 8.6 Sorption maxima (b), sorption energy constants (k), and free energies of sorption (ΔG) for Mo sorption from 10^{-1} M NaCl during 40 hr by Papatoetoe silt loam of different P fertilizer and lime histories

Treatment	b_{II} $\mu\text{mol g}^{-1}$	b_{III} $\mu\text{mol g}^{-1}$	k_{II} $l \mu\text{mol}^{-1}$	k_{III} $l \mu\text{mol}^{-1}$	ΔG_{II} kJ mol^{-1}	ΔG_{III} kJ mol^{-1}
1	1.49	4.17	0.132	0.0136	-29.0	-23.4
2	0.79	3.85	0.206	0.0168	-30.1	-23.9
3	0.23	1.92	0.261	0.0188	-30.7	-24.2
4	0.065	1.96	1.39	0.0155	-34.8	-23.7

(treatment 2) reduced Mo sorption in region II, but had little effect on Mo sorption in region III. Lime addition (treatment 3) had a greater effect on Mo sorption in region II than did P additions. Liming also decreased Mo sorption in region III, i.e., increasing the pH of the soil affected the extent of sorption in both regions II and III. The addition of both P plus lime to the soils further reduced Mo sorption in region II, but did not reduce sorption in region III, compared to the lime only addition.

The fact that Mo sorption in region I was not observed confirms the suggestion that large amounts of native sorbed P may prevent, or decrease, chemisorption of Mo. This result indicates that the chemisorption of added Mo would be greatly reduced in soils which had received heavy additions of fertilizer P. The finding that the soil from treatment 2 chemisorbed considerably less Mo than the control treatment (Table 8.6) confirms the observation that added P reduces the chemisorption of Mo. The fact that Mo sorption in region III was little affected by previous P additions to the soil in this study is not surprising. Ryden et al. (1977c) have shown that the sorption maximum for region III is only saturated to the extent of 5% by native sorbed P.

Although the amount of native sorbed P for treatment 3 was only approximately 50% of that for treatment 2 (Table 8.5), the value of b_{II} was less for treatment 2. This indicates that the effect of pH on sorption in region II was greater than the effect of previous additions of P. Similarly, b_{II} was much smaller for treatment 4 than for treatment 2. Therefore, pH must have a large effect on the sorption of Mo in region II. Similar conclusions were reached for Mo sorption by Fe gel in both regions I and II (Chapter 5). From the data in Table 8.6, it also appears that the sorption maximum for Mo in region III

was reduced by an increase in pH. This differs from the results reported by Ryden et al. (1977c) where it was found that the P sorption maxima for treatments 3 and 4 were almost equal. This indicates that the effect of lime addition on Mo sorption in region III was not due to a change in the nature of the sorbing surface, which would affect sorption of any anion, but was due to a chemical effect which was specific to Mo sorption. The effect of pH on Mo sorption in region III was found to be negligible for Mo sorption by Fe gel in Chapter 5. Because the ΔG values for region III are very similar for Mo sorption by both Fe gel and the limed soils in the present study, it would appear that increasing pH affects the kinetics, but not the mechanism, of Mo sorption by soils in region III. This could arise because increasing the pH of the soil would increase the overall negative charge of soil components (Chapter 1). This would reduce the coulombic attraction of the surface for the Mo anion, and hence, prevent the anion approaching positive sites at sufficiently close distances for strong chemical attractive forces to operate. A similar explanation was proposed for the low extent of chemisorption of Mo by allophane (Chapter 4). For Mo sorption by Fe gel, however, overall negative charges would not exist until pH values greater than pH (p.z.c.) (approximately 8.0 to 8.4, Chapter 5) and Mo sorption in region III would not be limited by kinetic charge effects.

The data obtained allow a more quantitative explanation to be given for the effect of pH on Mo sorption than has been given by other workers (Hingston et al. 1967, 1968b; Barrow, 1970; Theng, 1970). These workers have ascribed changes in Mo sorption with pH to changes in the distribution of the anions HMoO_4^- and MoO_4^{2-} . At the pH values of the soils used in this study, however, MoO_4^{2-} would be the predominant

species. Hence, changes in Mo sorption must be due to effects other than the distribution of anionic species. The mechanisms proposed for Mo sorption in the present study (Chapter 5) provide a more rational explanation for Mo sorption because they require the presence of free H^+ at pH values where only the fully-dissociated form of the Mo anion exists. The results obtained also help to explain the observation that liming increases the availability of Mo to plants on many soils (During, 1970). The Mo which is strongly held in regions I and II would be expected to be less available to plants than that which is more-weakly sorbed in region III. Increasing the pH decreases the amounts of Mo sorbed in regions I and II, and increases that sorbed in region III, thus increasing the availability of Mo to plants. Thus, the mechanisms proposed for Mo sorption allow both a qualitative and a quantitative explanation of Mo behaviour, both in the laboratory and the field situation.

SUMMARY

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

1. The literature relating to anion sorption by soils was reviewed and the soil components which are believed to be important in anion sorption established. The surface chemistry of these components was examined. Sorption of P and Mo by soils and soil components was considered in detail. Various topics requiring further research were identified.
2. Certain soil properties were examined for their importance in P and Mo sorption using four New Zealand soils. Soil properties which appeared to be important in the sorption of both P and Mo included pH, exchangeable Al, CDB-Al, oxalate Fe, and crystalline Fe. Allophane did not appear to be as important in the sorption of Mo as in the sorption of P.
3. Evaluation of the kinetics of Mo sorption by soils indicated that the initial removal of Mo from solution was extremely rapid, but that this was followed by a slow, continuing removal of Mo from solution. An estimate of equilibrium Mo concentration was obtained by extrapolation of the relationship between solution Mo and $1/t$ to $1/t = 0$, i.e. $t = \infty$. It was found that ionic strength affected Mo sorption at short-time periods but that this effect disappeared at equilibrium for equilibrium Mo concentrations less than $5 \mu\text{mol l}^{-1}$. In contrast, the effect of ionic strength on Mo sorption appeared to be absolute at high concentrations.

4. Isotherms for the sorption of Mo by both topsoils and subsoils, at equilibrium and 40 hr, could be described by three Langmuir equations. Each equation dominated overall sorption over definite concentration ranges (or regions). For both topsoils and subsoils, the free energies of sorption derived from the Langmuir equations were remarkably similar for each region of sorption. It was concluded that sorption in each region appeared to correspond to a distinct chemical reaction. Sorption maxima for each region described the extent of sorption of Mo for different soils.

5. Isotherms for the sorption of Mo by synthetic Fe gel and allophane could also be described by three distinct Langmuir equations. The free energies of sorption for each region of sorption were very similar to those obtained for soils. It was concluded that Fe gel is a satisfactory model for Mo sorption by soils. Although Mo sorption by allophane could also be described by three Langmuir equations, the amounts of Mo chemisorbed by allophane were much smaller than those chemisorbed by Fe gel.

6. Isotherms for the sorption of P by the four soils, Fe gel, and allophane could be described by three Langmuir equations. Comparison of P and Mo sorption indicated that the free energies of sorption for each region, for both anions, were very similar. Sites for sorption and the type of sorption reaction for both anions are, therefore, probably similar. Allophane chemisorbed much less Mo than P, relative to Fe gel, and this was attributed to kinetic charge effects.

7. Sorption of Mo by Fe gel in each region was affected in a different manner by changes in pH and ionic strength, and the charge

relationships of Mo sorption in each region also differed. These data, along with the calculated free energies of sorption, suggested that three distinct sorption reactions were involved in each of the three regions of sorption. Based on these data, plus the similarities between Mo and P sorption, equations were developed for the sorption of Mo. Sorption in regions I and II was considered to involve ligand-exchange chemisorption of MoO_4^{2-} for $-\text{OH}_2^+$ and $-\text{OH}$, respectively, resulting in the formation of a bidentate complex. Sorption in region III was considered to involve sorption at the Stern layer of the electrical double layer.

8. Studies of the competitive sorption of Mo and P indicated that the Langmuir equation developed to describe competitive sorption was not obeyed, but that the sorption of Mo, in the presence of P, could be described by three simple Langmuir equations. The effect of P on the nature of sorbed Mo was investigated and it was concluded that Mo and P compete for similar surface sites.

9. Solution P increased the amounts of sorbed Mo which were desorbed, relative to Cl, and also appeared to desorb both chemisorbed and more-physically sorbed Mo. Not all sorbed Mo, however, was desorbed by P.

10. The amounts of Mo desorbed by both Cl and P decreased with time after addition of Mo to soils. This was attributed to a shift of Mo from a more-physically sorbed form to chemisorbed forms. Results obtained for a chemical fractionation of sorbed Mo suggested that the absorption of adsorbed Mo was also occurring.

11. For several soils to which Mo had been added in the field, no Mo was extracted by P solutions. In addition, the fact that differences in total Mo between soils with and without added Mo could not be extracted with NaOH suggests the absorption of added Mo.

12. Solution:soil ratio affected solution P concentration during a 40-hr sorption period but this effect disappeared at equilibrium. This indicated that the solution:soil ratio affected only the rate at which P was removed from solution.

13. Incubating soil with P prior to the addition of Mo did not affect the mechanism of Mo sorption, but reduced both chemisorption (regions I and II) and more-physical sorption (region III) of Mo, depending on the amount of P added. Absorption of adsorbed P resulted in the further sorption of Mo, some of which became chemisorbed.

14. For a soil that had received annual additions of phosphate and lime for 22 yr, the chemisorption of added Mo was reduced by both fertilizer P and lime. The more-physical sorption maxima for Mo were not affected by P, but were reduced by lime additions. The results were explained in terms of the mechanisms of Mo sorption which had been developed, which enable a more rational explanation to be given than that possible using the mechanisms proposed by other workers.

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