

**SURFACE CHARGE CHARACTERISTICS  
AND PHOSPHORUS AVAILABILITY IN  
SELECTED OXISOLS AND ULTISOLS OF KERALA**

**BY**

**SREEKALA S.**

**THESIS**

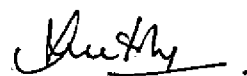
**SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT  
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**1993**

## DECLARATION

I hereby declare that this thesis entitled "Surface Charge Characteristics and Phosphorus availability in selected Oxisols and Ultisols of Kerala" is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me any degree, diploma, associateship, fellowship or other similar title at any other university or society.



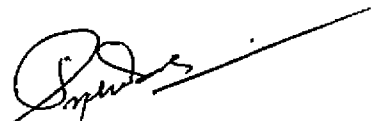
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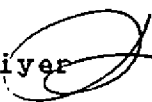
  
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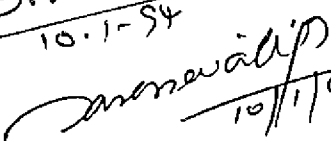
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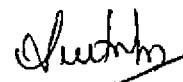
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A handwritten signature in black ink, appearing to be 'Shubh' or similar, written in a cursive style.

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# **INTRODUCTION**

## INTRODUCTION

With the advent of modern cultivation practices and due to the popularisation of high yielding varieties of crops, food production has increased at a slightly faster rate than the rate of growth of population in food deficient countries of the tropics (Sanchez and Cochrane 1980). However this marginal increase in food production is no way sufficient to feed the starving stomachs of the thousands and millions of cattle and people of the region. Dulal (1980) estimated that agricultural production in the tropics must increase by 60 per cent by 2000 AD in order to meet future food requirements at the present rate of population growth. Further increase in food production in the future must come from intensification of agriculture in these areas which are dominated mostly by impoverished highly weathered variable charge soils viz. Alfisols, Oxisols and Ultisols (Kang and Spain 1984). These soils characterized as Low Activity Clay (LAC) soils accounts to nearly 70 per cent of the total geographical area of the humid tropics (NAS 1982). To meet the goal of increased food production in areas dominated by LAC soils through the development of efficient crop production systems, it is essential that appropriate

soil management technology be practiced to alleviate specific physical and chemical soil related constraints.

Sanchez and Cochrane (1980) in reviewing the management problems of LAC soils in humid and sub-humid tropics, compiled a long list of soil related constraints in which wide spread deficiency of phosphorus and moderate to high 'P' fixation, coupled with low nutrient holding capacity was identified as the major items. These soils with wide spread deficiencies of 'P' are known to vary widely in their 'P' supplying power to crops mainly due to differences in the content and dynamics of its transformation which are guided by fixation reactions in one direction and release characteristics in the opposite direction (Mahendran 1979). The low nutrient retention capacity of LAC soils is related to low specific surface, low surface charge density or a combination of both (Uehara 1980). Since the product of the specific surface and surface charge density is the cation exchange capacity (CEC), the rejuvenation of these impoverished variable charge soils involve increasing one or both these surface parameters.

For the soils with variable charge the CEC may be increased by raising soil pH through liming or by lowering the zero point of charge (ZPC) (Uehara 1980). The ZPC of

variable charge minerals may be altered by phosphate fertilizers, soluble silicates or organic matter. Laboratory and field studies by Wann and Uehara (1978) and by Gillman and Fox (1980) in highly weathered soils showed that application of soluble silicates and phosphates have considerably improved the cation exchange capacity of these soils, increased the cation retention and lowered the ZPC. Although phosphates and silicates are not mobile elements, the combined effects of tillage and leaching helps to distribute these ions to lower layers and hence the associated increase in exchange properties give better protection of cations from leaching (Rajan 1976).

When the chemical soil constraints are eliminated by liming and application of the necessary amounts of fertilizers, the productivity of these Oxisols and Ultisols are among the highest in the world. This elimination of soil constraints by application of the necessary amounts of fertilizers and amendments are considered high input soil management technology. On the otherhand the basic concept of low input soil management technology is to make the most efficient use of the scarce purchased inputs but does not attempt to eliminate the use of fertilizers or amendments.

The relatively high cost of phosphatic fertilizers coupled with the widespread deficiency and fixation

constraints require the development of low input technology that can make most efficient use of applied phosphorus in these Oxisols and Ultisols (Sanchez and Salinas 1984). A major component of low input strategy suggested for sound phosphorus management, is to decrease the phosphorus fixation capacity of these soils by applying amendments such as lime and silicate. The strategy of using lime to eliminate the soil acidity constraints by increasing the soil pH to near neutrality does not work in most Oxisol-Ultisol regions because of the different chemistry of low activity clay minerals, which often result in yield reduction if such soils are limed to neutrality (Kamprath 1970). The effect of lime on 'P' availability may depend on the extent to which the phosphorus is fixed by the adsorbing surfaces or by reactions with exchangeable aluminium (Smyth and Sanchez 1980). Several studies have showed that when exchangeable aluminium was neutralized by liming, 'P' fixation decreased (Haynes 1984).

Work of Smyth and Sanchez (1980) has proved that application of agronomically relevant rates of lime, silicate and mixtures of lime and silicate, decreased 'P' fixation by about 20-30 per cent in treatments that did not receive 'P'. The use of soluble silicates for releasing fixed phosphorus without causing a change in surface charge

was reported by many workers. The specific adsorption of silicates and phosphates and its influence on exchange properties have been studied by Obihara and Russell (1972), Gillman and Fox (1980) and Hingston et al (1972). Parks and de Bruyn (1962) also reported this effect of specific anion retention leading to cation protection and increase in negative charge.

In most of the underutilized red and laterite soils of Kerala which occupy nearly 70 per cent of the total geographical area included under Oxisol and Ultisol, the above mentioned soil constraints and management technologies appear to be theoretically sound and equally applicable. Practically no work has been attempted so far in these highly weathered Oxisols and Ultisols of Kerala to study the effectiveness of low grade soluble silicates in releasing the fixed phosphorus by anion proxying. The reported by-product effect of the application of low grade phosphates and silicates in exercising better cation protection by an enhancement of CEC of the LAC soils needs to be tested in the similar variable charge soils of Kerala through experimentation.

In the light of the aforementioned reports the following main objectives were set for the programme.

1. To have a deeper insight into electro-chemical properties of two selected LAC soils.

2. To study the adsorption characteristics of selected Oxisol and Ultisol with respect to application of silicate and phosphate.
3. To study the magnitude of increase in negative charge (CEC) of variable charge soils consequent to specific adsorption of anions namely silicates and phosphates as predicted by surface chemical reactions involving ligand exchange.
4. To study the role of soluble silicates in releasing strongly adsorbed or fixed phosphorus by proxying the phosphate anion and thus without causing a decrease in the cation exchange capacity.
5. To study the amendment effect of phosphates and silicates in cation protection.
6. To study the effect of graded levels of silicate on the availability of soil 'P' through Neubauer's experiment.



# REVIEW OF LITERATURE

## REVIEW OF LITERATURE

Oxisols and Ultisols with high "specific surface area oxides" are well known for their good physical properties and poor chemical properties. These soils have low cation exchange capacity and moderate to high phosphate fixing capacity. The low nutrient retention capacity of these soils is related to low specific surface, low surface charge density or a combination of both. Hence simultaneous correction of nutrient deficiency and low surface charge can lead to deep seated long lasting beneficial changes in the fertility of these soils. (Uehara 1980).

An overview of the literature on the charge characteristics and fertility aspects of these soils are presented below.

### 1. Theoretical orientation to variable charge soils of the Tropics

Parks and de Bruyn (1962) distinguished two types of electrical double layer on the basis of the mechanisms by

which free charges are distributed across a solid solution interface. The constant potential model having reversible double layer applied to soil minerals such as oxides and hydrous oxides of iron and aluminium with surface charges controlled by the electrolyte concentration and counterion valence of the equilibrating solution, while the constant charge model with a completely polarisable double layer applied to layer silicate minerals such as smectite and vermiculite which have permanent negative charge due to isomorphous substitution.

It is customary to refer to the activities of the potential determining ions in calculating the surface potential of variable charge systems. This means that the pH of the solution should be considered if  $H^+$  and  $OH^-$  are the potential determining ions. (Morais et al, 1976, Uehara and Gillman 1980). When  $H^+$  and  $OH^-$  ions are the potential determining ions, the surface potential is related to  $H^+$  concentration by a Nernst type equation.

$$\begin{aligned}\psi_0 &= \frac{RT}{F} \ln \frac{H^+}{H^+ ZPC} \\ &= 59 (ZPC - pH) \\ &= 59 \Delta pH. \quad \text{mv at } 25^\circ\text{C}\end{aligned}$$

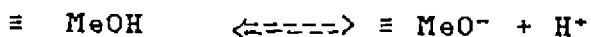
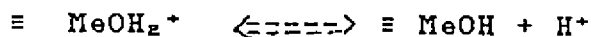
Thus it is possible to calculate the double layer potential at any pH if ZPC is known (van Raij and Peech 1972).

The highly weathered soils of the tropics are characterised by an accumulation of iron and aluminium oxides and hydrous oxides. Studies by van Raij and Peech (1972) revealed that organic matter, Kaolinite, gibbsite and iron oxides are the major components in these soils. Works by many workers (Morais et al. 1976, Keng and Uehara 1974, Gallez et al. 1976) have confirmed that the charge properties of highly weathered soils of the humid tropics are similar to those exhibited by constant surface potential colloids.

Manrique (1985) reported that the tropical soils generally contain clay minerals with constant surface potential with surface charge derived through protonation and deprotonation of hydroxyl groups in the lattice surface.

### 1.1 Oxides

van Raij <sup>and Peech</sup> (1972) and Rajendran (1992) reported that iron and aluminium oxides which dominate the clay fraction of the tropics when in contact with electrolyte solutions, behave like constant potential type colloids. The variable or pH dependent charges on the surface of hydrous oxides of Al, Fe and Si are originated by proton transfer at the amphoteric surface of these oxides.



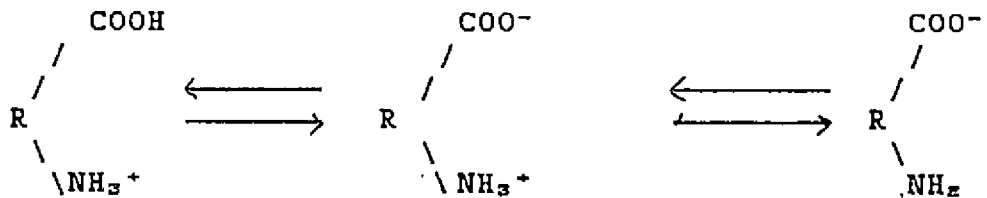
Oxides such as  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  have a ZPC at higher values while  $\text{SiO}_2$  and acidic oxides have lower ZPC values. The reported values of ZPC for the various oxides are 9.5 for gibbsite, 8.1 for goethite, 7.5 for hematite, 6.9 for ferrihydrite and 2.0 for hydrated  $\text{SiO}_2$  (Juo and Adams 1984).

## 1.2 Clay Minerals:

Most prominent clay mineral found in tropical soils is kaolinite which has a small specific surface, small CEC and positive charge (Gallez *et al.* 1976, Morais *et al.* 1976, Rajendran 1992).

## 1.3 Organic matter

The organic matter bear a variable charge, and these charges develop due to protolysis of functional amino and carboxyl groups on organic surface.



Organic matter is considered the main source of negative charge in highly weathered soils of the tropics. Taking into account the contribution of negative charge from

this source, which is vital for the retention of cations, it is of prime importance to conserve or even increase the organic matter content of these soils (Gillman and Bell 1976, Rajendran 1992).

## 2. Charge characteristics of Oxisol and Ultisol

A major feature of Oxisol and Ultisol soil is the dominance of variable charge colloids such as Kaolinite, iron and aluminium oxides (Clark et al. 1966) and hydroxides in their clay fraction. These variable charged colloids are bearing a constant potential where the net charge depends on the concentration of potential determining ions (van Raij and Peech 1972, Rajendran 1992).

### 2.1 Zero point of charge

Of the various attributes, Zero Point of Charge (ZPC) is considered the most important to represent the essential surface charge characteristics of variable charge systems (Uehara and Gillman 1980).

Parks (1967) has defined the Zero Point of Charge (ZPC) or  $pH_0$  as the pH value of the soil solution at which there is no net surface charge on the solid particles. The ZPC and the surface charge of soils and oxide systems is determined by potentiometric titration as a function of pH

and electrolyte concentration or by measuring the counter ion retention using an indifferent electrolyte such as NaCl and NaNO<sub>3</sub> (Schofield 1949, van Raij 1972, Rajendran 1992).

van Raij and Peech (1972) while studying the electro-chemical properties of some Oxisols and Alfisols of Brazil determined the ZPC and found that the values varied from 2.1 to 6.16. The estimated values of ZPC increased with depth. They attributed the higher ZPC values of the subsoils to the presence of large amounts of Fe and Al oxides, while the lower ZPC values of the surface samples to the presence of clay minerals with permanent negative charge as well as organic matter. Thus ZPC reflects the overall mineralogical composition as well as organic matter content of the soil. Keng and Uehara (1974) observed that the ZPC of some Oxisols and Ultisols from Hawaii generally falls between 4 to 6 and  $\overline{\text{ZPC}}$  is higher in Oxisols than Ultisols.

Gallez et al. (1976) attributed the relatively low ZPC of highly weathered soils to large amounts of kaolinite and silica present in these soils.

Hendershot and Lavkulich (1978) and Dolui and Dey (1990) pointed out that ZPC can be used as a measure of pedogenic development. They observed that with increased pedogenic development the ZPC became more clearly defined

and approached the natural pH of the soil and there was a decrease in the relative significance of pH dependent charge.

Several workers have (van Raij and Peech 1972, Keng and Uehara 1974, Gallez et al 1976) indicated that most low activity clay soils have ZPC values between pH 4 and 6, whereas the ZPC of the Fe and Al oxides and hydrous oxides occur between pH 7 and 9.

Sakurai et al. (1990) found that the iron oxide that accumulated in the strongly weathered soils increased the ZPC value and enlarged the specific surface area but the increase in surface area did not always result in an increase in CEC. In contrast the CEC was reduced through the ZPC shift towards a higher pH value. The degree of chemical weathering particularly the degree of desilication also is indicated in the ZPC as highly leached ferruginous soils low in organic matter generally showed higher ZPC values (Raman 1986).

Many workers have (van Raij and Peech 1972, Uehara and Gillman 1980, Anne Lewis 1991) suggested the direct measurement of adsorption of potential determining ions by potentiometric titrations as the best method for ZPC



determination. It also permits the estimation of the values of net charge on the surface at different ionic strength and pH values.

## 2.2 Enhancement in CEC

Many have reported on the usefulness of the application of soluble phosphates, organic matter and silicates in the variable charge soils to improve the CEC and for lowering the ZPC.

Works of Ayres and Hagihara (1953) illustrated that leaching losses of potassium could be measurably reduced by prior application of phosphate fertilizer to the soil. This was consistent with the calculated charge reversal in soil materials to which phosphorus was added. Barlett and Mc.Intosh (1969) observed that treatment of acid soil samples with increasing levels of  $\text{CaCO}_3$ ,  $\text{CaSiO}_3$ ,  $\text{CaF}_2$  and  $\text{CaHPO}_4$  markedly raised CEC along with pH and lowered the activity of K and exchangeable aluminium. They hypothesised that hydroxyl, phosphate or flouride ions neutralised positive charges on aluminium. This freed the negatively charged exchange sites and thereby raised the CEC. With increased CEC, the percentage saturation of the exchange complex with K and therefore availability of potassium was increased compared to untreated soil.

Schalscha et al (1972) suggested two mechanisms to explain the effect of  $H_2PO_4$  ion in increasing CEC. These include (a) the formation of complex Al-Phosphates and Fe-phosphates which adsorbs  $K^+$  and  $Na^+$ , from which  $NH_4^+$  replaces these two cations and (b) neutralisation of positive charges by reaction with phosphate and the simultaneous release of negative charges that are free to adsorb a  $K^+$  or  $Na^+$ . The authors favoured the second mechanism and suggested that the positive charge neutralised by phosphate is largely associated with the partially neutralised hydroxy Al-polymers,  $AlOH^+$  exposed on surfaces of allophane and the aluminium complexed by organic matter.

According to Wann and Uehara (1978) adsorbed 'P' increases the surface charge density by lowering the zero point by charge, thus making CEC a large value. They observed that CEC and extractable bases increased with increased 'P' levels and the quantity of divalent cations extracted decreased. They attributed the high affinity of the surface for divalent ions where 'P' was added to the excess calcium adsorption in the Stern layer. The authors cited 3 causes for phosphate or other anion induced CEC of the variable charge soils.

- (1) Shift in the ZPC to lower pH
- (2) Neutralisation of the positive charge and
- (3) Electrolyte imbibition.

Gillman and Fox (1980) also obtained agronomically significant increases in CEC of the surface horizons of some soils in Hawaii, with increasing superphosphate application.

Greenhouse and lab experiments conducted by Smyth and Sanchez (1980) in some Kaolinitic soils of Brazil showed that  $\text{CaCO}_3$ ,  $\text{CaSiO}_3$  and previous 'P' application decreased 'P' fixation and improved cation retention properties. Also found that application of 'P' and soil amendments to these soils increased the negative charge and decreased the positive charge. They concluded that application of both phosphates and amendments made a major improvement in cation retention against leaching but may increase anion leaching.

Panjaitan and Kosasih (1986) recommended the usage of phosphate prior to urea, KCl and Keiserite application to reduce nutrient losses.

Philips et al (1988) studied the effect of lime and phosphate addition and subsequent leaching on CEC of some variable charge soils in Newzealand. They observed that incorporation of amendments increased the CEC and the magnitude of increase was related to the rate of addition, levels of organic matter and exchangeable aluminium in the samples.

### 3. Problems of Oxisols and Ultisols

The major soil related constraints of low base status Ultisols and Oxisols are chemical rather than physical (Sanchez and Uehara 1980). Although phosphorus is generally a limiting element, deficiencies of N, K, S, Ca, Mg and Zn are common. In addition Al toxicity is almost universal and Mn toxicity is often limiting, especially in Ultisols.

Phosphorus deficiency is the most widespread soil constraint in Oxisol and Ultisol. This deficiency problem is compounded by the widespread phosphorus fixation capacity. These soils generally possess low CEC and frequently require a large initial dose of phosphate fertilizer to obtain acceptable crop yields (Sanchez and Salinas 1984).

#### 3.1 Phosphorus fixation

Phosphorus applied to the tropical acid soils is readily rendered unavailable to plants because of the high phosphorus fixing power of these soils. Two mechanisms, chemical adsorption and phosphorus fixation are considered to be responsible for this non availability of the applied phosphorus (Udo and Uzu 1972).

Paho Hsu (1964) while studying the mechanism of fixation in slightly acid soils recognised two adsorption reactions operating at two different rates. The one taking place rapidly was believed to be due to the surface adsorption of phosphate on the iron and aluminium oxides already present in the soil. The other a much slower reaction was attributed to surface adsorption on similar amorphous oxides and hydroxides produced from the structural silicates.

The relative amounts of the added 'P' retained by clay and silt and the amount converted to different chemical forms in the soils were determined by Koshy and Britomuthunayagam (1961) in an investigation on the behaviour of 'P' in acid soils. The results favoured the chemical precipitation theory of 'P' fixation in soils, but did not exclude the possibility of adsorption by clay minerals as well.

Frageria and Barbosa (1987) studied the phosphorus fixation in the Oxisols of Brazil and revealed that it may take values between 77 and 90% depending on the levels of 'P' applied.

Juo and Fox (1977) as well as Sanchez and Uehara (1980) had reported that these Oxisols and Ultisols have high to moderate 'P' fixation capacities.

Lopes and Cox (1977) reported that among Oxisols and Ultisols phosphorus fixation generally increases with clay content because of its direct relationship with surface area where the iron and Al-oxides and hydroxides largely responsible for 'P'-fixation are located.

### 3.2 Aluminium toxicity

Oxisols and Ultisols being the products of acid weathering, accumulation of more soluble forms of mineral aluminium is usually encountered (Kamprath 1978). A major characteristic of Al toxicity is inhibition of the uptake and translocation of 'P' by plants. Thus in acid soils, effects of Al-toxicity and 'P' deficiency are often difficult to separate. Liming can increase plant 'P' uptake by decreasing Al-toxicity rather than having a direct effect on 'P'-availability (Haynes 1984).

As Al is often the predominant phytotoxic soluble and exchangeable cation in acid soils, an index of its concentration is often used as an indication of lime requirement (Kamprath 1970).

Neutralisation of aluminium increased the effectiveness of a given rate of fertilizer 'P' in increasing plant growth on Oxisols. (Mendez and Kamprath 1978). Friezen et al (1980) found that increased 'P' uptake

when exchangeable Al was neutralised correlated with increased root growth in an Ultisol.

#### 4. Anion adsorption in Oxisols and Ultisols

As colloids of the constant potential type can under acid conditions acquire net positive charge, anion adsorption become a particularly important feature in soils containing these colloids (Mekaru and Uehara 1972). In low activity clay soils such as Oxisols and Ultisols, adsorption of phosphates and silicates deserve special attention. The former bears special importance in soil fertility management, whereas the latter provides useful information on degree of weathering and surface reactivity of Fe and Al oxides in soils.

Works of Ayres and Hagihara (1953) suggested that specifically adsorbed anions render colloid surface more negative and therefore retain cations more tentatively. They observed that 'K' applied as KCl leached rapidly from the soil compared to 'K' added as sulphate or phosphate.

Gallez et al (1976) reported that presence of small amounts of specifically adsorbed silicon, magnesium, iron etc. on oxides contributed to low ZPC of the soils of Nigeria. Bolal and Barrow (1984) and Barrow (1985) described the effects of the amount of anion adsorption on

the change in surface charge. They found that charge conveyed to the surface by each increment of phosphate, differed from that of previous increment, because each successive increment reacted with a surface with a different net charge. Bowden et al (1980) found that specific adsorption of phosphate makes the surface more negative at all pH values and shifts ZPC to a lower value. Naidu et al (1990) reported that adsorption of phosphate reduced positive charge at low pH and increased the negative charge.

#### 4.2 Phosphate Adsorption Isotherms

The adsorption isotherms obtained by a plot of adsorbed phosphate against phosphate remaining in solution has been used by many workers to measure the phosphate adsorption capacity of soils (Fox and Kamprath 1970, Rajan and Fox 1975, Udo and Uzu 1972).

Several workers have proposed that the phosphate requirements of soils can be estimated using this Quantity: Intensity plots (Q:I), ie phosphate adsorption isotherms (Barrow 1985). The fertilizer requirement is usually estimated as the quantity of phosphate required to raise solution phosphate concentration to an arbitrary standard concentration which is often set at 0.2  $\mu\text{g/ml}$ .



#### 4.3 Silica Adsorption Isotherms

Both the content of soluble silica in soil solution and the capacity of soils to adsorb added soluble silica are useful criteria for soil characterisation (Gallez et al 1977, Herbillon et al 1977). It is well known that silica adsorption by oxides and clay minerals is dependant upon pH. Silicate adsorption generally increases with pH up to pH 9.0 which equals the pK for silicate dissociation (Parfitt 1978). For pure oxides such as gibbsite, hematite and goethite, the maximum of the silicate sorption curves occur at about pH 9.2 (Hingston et al 1972). Mc.Keague and Cline (1963) studied this phenomena for clay minerals and soils. Therefore Si adsorption data is determined at pH 9.2. The silica adsorption capacity of the minerals follow the order gibbsite > goethite > kaolinite (Gallez et al 1977).

#### 4.4 Silica Loss

Desilication is among the important process of tropical soil weathering. Both the content of soluble silica in the soil solution and the capacity of soils to adsorb soluble silica determined at pH 9.2 provide a good measure of the type of surface in soils as well as degree of desilication of the soils. (Gallez et al 1977).

They proposed two easily measured parameters namely Index of silica reaction (ISR) and Index of silica saturation (ISS). The ISR which is the ratio of the amount of soluble silica that a soil releases when equilibrated with salt solution and the amount of silica adsorbed at pH 9.2 can be used to describe the pedogenic environments of weathering and soil formation.

#### 4.5 Ligand adsorption

Phosphate is considered to be adsorbed specifically by metal hydrous oxides by affecting a ligand exchange displacing  $\text{OH}_2^-$  or  $\text{OH}^-$  that are co-ordinated to metal ions at the surface.

Works of Parfitt et al (1975) have established that the adsorption process of phosphate on synthetic iron oxides is ligand exchange where pairs of FeOH react with Phosphate to give a binuclear bridging,  $\text{FeOP}(\text{O}_2)\text{OFe}$  complex.

Studies with gibbsite,  $\text{Al}(\text{OH})_3$  and kaolinite by many workers (Hingston et al 1972, Obihara and Russell 1972, Rajan 1976) have shown that phosphate is strongly adsorbed on edge  $\text{Al}(\text{OH})\text{H}_2\text{O}$  groups and the resulting complex is probably a binuclear bridging form  $\text{AlO P}(\text{O}_2)\text{OAl}$ , although the bidentate  $\text{OAlO PO}_2$  complex could also be present.

Atkinson et al (1972) used infrared spectroscopy for studying dried samples of phosphated goethite and concluded that phosphate was adsorbed as a binuclear bridging complex.

Hingston et al (1972) showed that anions of incompletely dissociated acids such as phosphate could be adsorbed beyond the neutralisation of positive surface sites and even on a surface having a net negative charge. For this process they proposed a mechanism, where protonated anions are adsorbed on to a negatively charged surface after dissociation of their protons, which then react with surface hydroxyls to form water molecules that in turn can be readily replaced by the anions.

Alvarez et al (1976) in a preliminary study of phosphate adsorption on gibbsite using Raman spectroscopy found evidences for specific interaction of phosphate ions with surface hydroxyl groups.

Mott (1988) stated that unlike non specifically adsorbed ions, ligand exchanged ions do not have adsorption and desorption isotherms that are identical kinetically, and for ligand exchanged ions desorption at constant pH is a much slower process than adsorption. This kind of irreversibility has been shown to be the case of phosphate.

Goldburg and Sposito (1985) gave sufficient evidences pointing to ligand exchange as the mechanism of the phosphate-surface hydroxyl reaction. The evidences included the kinetics of adsorption and desorption, hydroxyl ion release infrared spectroscopic and stereochemical calculations.

#### 4.6 Mechanism of specific anion fixation:

Anions are considered to be adsorbed specifically by metal hydrous oxides by affecting a ligand exchange displacing  $\text{OH}_2^+$  or  $\text{OH}^-$  that are coordinated to metal ions at the surface. (Juo and Adams 1984). For the oxide rich LAC soils, the affinity of anions followed the order.

Phosphate > arsenate>selenite> =Molybdate =

flouride>sulfate = silicate >chloride>Nitrate

Hingston et al (1972) studied the adsorption of  $\text{SO}_4^{2-}$ ,  $\text{H}_3\text{SiO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{MoO}_4^{2-}$ , and  $\text{SiO}_3^{2-}$  on goethite and gibbsite and showed that these anions were adsorbed on by ligand exchange with surface  $\text{OH}^-$  or  $\text{OH}_2^+$ . He further reported that  $\text{SO}_4^{2-}$  is adsorbed only on the acid side of the ZPC, and its adsorption decreased with increase in pH up to 8 and beyond this value no adsorption occurred.

Mekaru and Uehara (1972) found that in Oxisols and Ultisols, negative adsorption of nitrate occur as soon as sulphate is added substantiating the view that specifically adsorbed anions increase negative charge. Their studies have further shown that for variable charge soils adsorption of sulphate decreased with increased pH and that the iron oxides were the chief carriers of hydroxyl groups capable of ligand exchange with sulphate in the Oxisol (Zhang and Zhang 1989, Zhang et al 1991).

#### 5. Silicate application and phosphorus availability:

There are various schools of thought regarding the influence of silicon on the availability of phosphorus and much work has been carried out on this aspect.

Wolff and Kreuzhage (1884) were perhaps the first to recognize the importance of Si-P relationship. They observed that silica application produced effects similar to phosphorus treatments.

Lemmerman and Weismann (1922) argued that silicon could perform in the plants some functions of phosphorus.

Birch (1953) reported that sodium silicate applied to a very acid heavy clay soil produced growth without phosphate fertilizers, almost equal to that on the phosphate

reactions being probably simultaneous.

✓ Mariakulandai (1954) in his study on the effects of sodium silicate, superphosphate and silicophosphate, with and without lime and green manure on lateritic soils of Nilgiris concluded that silicophosphate treated soils showed nearly double the available phosphate when compared to those treated with superphosphate.

✓ Hosoda and Takata (1957) found that in a soil with a low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio the availability of phosphorus in the soil and phosphorus in the plant were higher in calcium silicate plot than in calcium carbonate applied plot.

Jones and Handreck (1967) reported that increase in 'P' availability by various crops after application of silicate to the soil can be more thoroughly interpreted in the light of the expected competition between silicon and phosphorus on the adsorption sites in the clay fraction. They also expected that silicate could lower the activity of  $\text{Al}^{3+}$  in the soil solution and so prevent it from precipitating phosphate.

Kafkafi and Bar Yosef (1969) investigated the relationship between phosphorus and silicon adsorption on kaolinite and reported that when silica was adsorbed on kaolinite equal amounts of phosphate was desorbed which suggested silicate adsorption to occur on the same sites. Obihara and Russel (1972) found that silicate adsorption followed the Langmuir equation and decreased in the presence of phosphate.

Parfitt (1978) also reported that phosphate and humus can reduce silicate adsorption which suggested the involvement of the same sites in the adsorption process.

Kundu et al (1988) reported that the presence of silicate and flouride anions resulted in increased recovery of phosphorus and that the effects of silicate and flouride ions in reducing 'P' fixation was found to decrease with time.

Domning and Amberger (1989) in their model experiments to study the influence of silicates on the availability of soil and fertilizer phosphate observed that the availability of water soluble phosphate was increased by the addition of sodium and calcium silicates. They attributed this effect to both a rise in soil pH and high values of water soluble 'P'. Both silicates decreased the sorption of phosphorus.

Subramaniam and Gopaldaswamy (1991) studied the effect of moisture, organic matter and silicate on the availability of silicon and phosphorus in rice soils and found that addition of silicate significantly increased the availability of silica in all soils, and phosphorus in acid soils. Anderson et al 1992 observed significant yield increase of sugarcane and rice in Florida, USA by the application of soluble silicate as calcium silicate slag.

#### 6. Phosphorus management in Oxisol and Ultisol:

Phosphorus is perhaps the most expensive purchased input in Oxisol and Ultisol. The relatively high unit cost of phosphorus fertilizers coupled with widespread deficiency and fixation constraints in these soils, require the development of low input technology that can make most efficient use of the scarce and expensive purchased input through a series of practices. Liming, soluble silica application, use of less soluble 'P'-sources, selection of varieties tolerant to low levels of available soil phosphorus etc are some of the physico-chemical methods suggested for phosphorus management in these soils.

##### 6.1 Liming:

Considerable controversy exists as to whether liming decreases phosphorus fixation or not. Several



studies in acid soils show that when exchangeable Al was neutralised by liming, 'P'-fixation decreased. Liming has little or no effect in decreasing 'P'-fixation in soils with pH values of 5-6 (Haynes 1983). The effect of lime on 'P'-fixation depends on pH levels (Sanchez and Uehara 1980). Parfitt (1980) reported that liming variable charge soils from pH 5 to 6 can cause an increase in their effective CEC of about 50 per cent. Smyth and Sanchez (1980) found that the effect of applied phosphate was greater when soils were simultaneously limed.

#### 6.2 Silicate application:

There are various reports that silicate application can markedly decrease phosphorus requirements. (Jones and Handreck 1967, Kundu et al 1988, Domning and Amburger 1989).

Smyth and Sanchez (1980) found that silicate application decreased the 'P' fixation by 20 - 30% . It is also reported that the silica effect is not to reduce the formation of insoluble calcium phosphates, but rather to reduce the adsorption of 'P' by the freshly precipitated Fe and Al hydroxides (Mc Keague and Cline 1963). There are numerous works recommending the use of silicate as an amendment on acid tropical soils which may provide

protection against the hazard of overliming and may improve the 'P' economy, in addition to the useful benefits derived from its liming effect.

### 6.3 Use of less soluble Phosphate sources:

Rhenania phosphate and rock phosphate are found to be as effective or more effective than superphosphate in high P fixing Oxisol and Ultisol. It is reported that Rhenania Phosphate obtained by fusing rock phosphate of low citrate solubility with silica and soda ash is a potential 'P' fertilizer for tropical acid soils with relatively high 'P' retention, provided its cost can be justified. (Sanchez and Salinas 1984).

# **MATERIALS AND METHODS**

## MATERIALS AND METHODS

To investigate the charge characteristics and its relation to phosphorus availability, the following five experiments were conducted in two selected soils representing Oxisol and Ultisol. Bulk samples collected from the red soils of Pachalloor and highly weathered upland soils of the NARP Special station, Kottarakkara represented the Oxisol and Ultisol respectively.

1. A laboratory study to assess the important electro-chemical properties, available phosphorus and silica status and the phosphate and silicate fixation capacity.
2. A laboratory incubation experiment to study the effect of added silicates in releasing unavailable soil phosphorus.
3. A laboratory experiment to study the adsorption desorption pattern with respect to graded addition levels of soluble phosphates and silicates.

4. Soil column studies to ascertain the reported enhancement of cation exchange capacity consequent to the addition of soluble silicates and phosphates in, highly weathered low activity clay soils.
5. Neubauer's experiment to study the effect of graded levels of silicate in combination with lime on the availability of soil phosphorus.

1. Basic laboratory investigations on soils.

- 1.1 Collection and preparation of samples :

Bulk samples of surface soil (0-6") typical of the Oxisol (Haplustox) and Ultisol (Kandiustult) were collected from Pachalloor and NARP special station, Kottarakkara respectively. The two soil samples collected were spread on polythene sheets and allowed to dry in air for one week. The airdried samples were then powdered gently with a wooden mallet and sieved through a 2mm sieve and stored in two polythene bags. These samples were then used for subsequent analyses and experiments.

- 1.2 Soil analysis :

The two soil samples were subjected to the following physico-chemical analyses using standard analytical procedures.

### 1.2.1 Mechanical analysis :

Mechanical components like coarse sand, fine sand, silt and clay were determined by the International Pipette Method (Piper 1966).

### 1.2.2 pH :

pH of the soil samples were measured in a 1:2.5 soil-water suspension, 1:2.5 soil-N KCl suspension and 1:50 Soil-N sodium fluoride suspension, using a pH meter.

### 1.2.3 Electrical conductivity (EC) :

The EC of the samples were determined in a 1:2.5 soil water suspension as per procedure outlined by Jackson (1973).

### 1.2.4 Organic Carbon:

Organic carbon was determined by the Chromic acid wet digestion method of Walkley and Black as given by Jackson (1973).

### 1.2.5 Available Phosphorus:

Available phosphorus was determined colorimetrically by Bray and Kurtz method as described by Jackson (1973) employing flouride ion to displace phosphate ion.

#### 1.2.6 Available silica:

Available silica was determined in both water extract and dilute HCl extract. The silica was determined by silicomolybdate method modified by Murthy et al (1965). A suitable aliquot of 5 ml. was treated with 2 ml. of 1:1 HCl, followed by 2ml of 10% ammonium molybdate. Interference of ferric iron was subdued by the previous addition of 0.5ml. solution of hydroxylamine hydrochloride and of phosphorus by the addition of 1ml. of 10% Oxalic acid. The silicomolybdate formed was then reduced by the addition of 1-2 ml. of 0.5% ascorbic acid. The mixture, allowed to stand for 15-20 minutes to complete reduction was made upto the volume and the blue colour intensity was read using a red filter in a Klett Summerson photoelectric colorimeter.

#### 1.2.7 Total phosphorus:

Total phosphorus was determined in perchloric-nitric acid system by vanadomolybdate yellow colour method as described by Jackson (1973).

#### 1.2.8 Total iron:

Total iron was determined in the hydrochloric acid extract of the samples, using Atomic Absorption spectrophotometer (PE 3030).

#### 1.2.9 Dithionite extractable iron ( $Fe_d$ ):

To 1g of soil sample added 10 ml. of 0.3M sodium citrate 1 ml. of 1M.  $NaHCO_3$  and 1 g solid  $Na_2S_2O_4$ , stirred for 15 minutes and added 2.5ml NaCl solution and 2.5 ml. acetone. One ml of this dithionite citrate bicarbonate extract of the soil was made upto 100 ml. and fed to an Atomic Absorption Spectrophotometer. The iron determined was expressed as percentage of oxides (Kunze and Dixon 1986).

#### 1.2.10 Oxalate extractable iron ( $Fe_o$ ):

2 g soil was shaken with 200 ml of 0.2M ammonium oxalate, centrifuged and supernatant fed to an Atomic Absorption Spectrophotometer for the determination of iron.

#### 1.2.11 KCl extractable aluminium:

10 g soil was extracted with 50 ml of 1 N KCl, fed to an Atomic Absorption spectrophotometer and the aluminium content determined (Black 1965 ).

#### 1.2.12 Total sesquioxides : ( $R_2O_3$ )

The sesquioxide in the hydrochloric acid extract was precipitated with excess of ammonium hydroxide in presence of ammonium chloride, dried in an oven and ignited



in a muffle furnace to constant weight. The sesquioxide content was reported as percentage of soil on oven dry basis (Piper 1966).

#### 1.2.13 Cation exchange capacity : (CEC)

The cation exchange capacity was determined using neutral normal ammonium acetate as described by Jackson (1973).

#### 1.2.14 Anion exchange capacity:

Anion exchange capacity was determined by Mehlich's method as described by Hesse (1971).

#### 1.2.15 Phosphorus fixation capacity:

Phosphorus fixation capacity of the soil was determined by the method described by Hesse (1971). One gram soil was shaken with 20 ml of standard phosphate solution for 2 hours centrifuged and the phosphate determined in the supernatant. From the change in phosphate concentration of the standard solution, fixation capacity was calculated.

#### 1.2.16 Silica fixation capacity:

Silica fixation capacity was determined as per the procedure described by Gallez et al (1977).

### 1.2.17 -Zero point of charge (ZPC):

The procedure described by van Raij and Peech (1972) was used. A series of 4 g H-saturated soil samples was equilibrated with known amounts of acid (HCl) and base (NaOH) in various concentrations of NaCl for 3 days. The pH of the supernatant solution was determined using a pH meter. The amount of  $H^+$  and  $OH^-$  ions absorbed at a given pH value was taken as equal to the amount of HCl and NaOH added to the suspension minus the amount of acid or base required to bring the same volume of electrolyte solution without soil to the same pH value. The ZPC of the soil is taken as the pH value where the charge pH curves measured in different electrolyte concentrations intersect one another.

### 2. Incubation experiment:

A laboratory incubation experiment was conducted using the two soils to study the effect of added silicates in releasing the unavailable soil phosphorus. The study was programmed in CRD with the treatments replicated thrice for each soil. The treatment schedule included liming at two levels,  $L_0$  and  $L_1$  representing unlimed soil and soil limed to near neutrality, and silicate application at 4 levels (0, 200, 400 and 800 ppm).

5 g of both limed and unlimed soil samples were treated with silicate in the form of sodium silicate as per the treatment schedule. The treated soils were then equilibrated at field capacity and kept for incubation in plastic containers of 100ml capacity at room temperature upto 40 days. Sufficient number of replication was provided to represent 3 samples per treatment per sampling. Water loss was made up every day so as to maintain the soil at field capacity. Periodically soil samples were withdrawn on the 1st, 5th, 10th, 20th, and 40th day of incubation. The available phosphorus in these samples were then estimated by Bray and Kurtz method (Jackson 1973).

### 3. Adsorption Isotherms

#### 3.1 Phosphate adsorption Isotherms:

Data for plotting phosphate adsorption isotherms were obtained by equilibrating 3 g samples of soil for 6 days at room temperature in 30 ml of 0.01 N  $\text{CaCl}_2$  containing various amounts of  $\text{KH}_2\text{PO}_4$ . Equilibration was carried out in 50 ml plastic centrifuge tubes by shaking the sample in a reciprocating shaker for 30 minutes daily. After centrifugation in a superspeed centrifuge phosphorus was determined in the supernatant. Phosphorus which disappeared from solution was considered to have been

adsorbed. Phosphorus adsorbed was plotted against phosphorus in the supernatant solution to get the adsorption isotherms. (Fox and Kamprath, 1970).

### 3.2 Silicate adsorption Isotherms :

Silicate adsorption isotherms were made as described by Gallez et al (1977). A series of 20ml of 0.05 N NaCl solution containing various amounts of soluble silicate (sodium silicate) were allowed to equilibrate with 4g of soil in polyethylene bottles. After 7 days of incubation at room temperature the soil was centrifuged and the supernatant solution was analysed colorimetrically for soluble silicate. The amount of silicate disappearing from the solution was taken as silicate sorbed by the soil. The sorbed silicate was then plotted against silicate in the supernatant, to get the adsorption isotherms.

### 4. Soil column study :

A soil column study was conducted to ascertain the reported enhancement in cation exchange capacity, consequent to treatment with graded levels of soluble silicates and phosphates.

Sections of glass cylinders with a diameter of 5 cm. and length of 50 cm packed with soils were used as

columns for the study. The lower end of the tubes were covered by Whatman No.42 filter paper and then with muslin cloth over it. The airdried soil samples were slowly filled in the columns with fairly good packing. Then about 500 ml of phosphate and silicate solutions in the form of superphosphate and sodium silicate respectively at two levels of 500 and 1000 ppm were used for leaching the columns. After transferring the solution completely into the columns, the columns were left undisturbed for four days. The whole process was repeated 3 times and the soil was allowed to drain completely after the last leaching. Small increments of soils were removed from the top, middle and bottom portion of the columns. Each section of soil was dried separately and the CEC determined using neutral normal ammonium acetate as described by Jackson (1973).

#### 5. Neubauer's Experiment :

Modified Neubauer's experiments were conducted to study the effect of graded levels of silicate on the availability of soil phosphorus.

Tapioca and Cowpea were used as test crops for the study in two separate Neubauer's experiments. Single noded cuttings of uniform weight (20 g) and bold grain cowpea seeds (culture 9) were used as planting materials. The

experiments were conducted in CRD with 3 replications. The treatments used were as follows :

- L<sub>1</sub> - Limed to neutrality
- L<sub>0</sub> - Unlimed
- S<sub>0</sub> - No silicate
- S<sub>1</sub> - 400 ppm silicate
- P<sub>0</sub> - No phosphate
- P<sub>1</sub> - Phosphate added as per recommendation for the crops.

250 and 500 g of unlimed and limed soil samples were weighed into plastic containers and mixed with varying amounts of phosphate and silicate in accordance with the treatment schedule. Tapioca cuttings were then planted in containers with 500 g soil and cowpea in containers with 250 g soil. Nitrogen and Potash were applied as per the usual recommendations. The plants were uprooted at the flowering and 3 months stage for cowpea and tapioca respectively. After removing the soil particles adhering to the roots the plants were washed in a gentle flow of tap water, wiped clean and kept for drying. The whole plant dry weight was recorded and 'P' determined in the triple acid extract of the plant samples.

## **RESULTS**

## RESULTS

### 1. Basic laboratory investigation on samples

The results of the basic laboratory studies made on the two samples collected are summarised in Table 1.

#### 1.1. Mechanical composition

The mechanical analysis of the samples revealed that the clay content of the Haplustox of Pachalloor was about 7.5% while that of the Kandiustult of Kottarakara was 35%. The silt content of the two soils were 17.5% and 15% respectively. The coarse sand and fine sand contents were 51.2% and 18% for the Haplustox and 44% and 5% for the Kandiustult respectively.

#### 1.2. Soil reaction (pH)

Both the soil samples were acidic in reaction with a pH of 5 and 4.4 for the Haplustox of Pachalloor and the Kandiustult of Kottarakara. The delta pH values obtained by subtracting pH water from pH KCl were -1.1 and -0.9 for the Haplustox and Kandiustult respectively.



### 1.3. Electrical Conductivity (EC)

Both the samples had negligibly low values for the EC, showing only traces of soluble salts in the surface soils.

### 1.4. Organic carbon

Organic carbon content of the soil samples were found to be 0.36 and 1.32% respectively for the samples taken from Pachalloor and Kottarakara.

### 1.5. Available phosphorus ( $P_2O_5$ )

The available phosphorus were at the rate of 22.4 kg/ha for the Haplustox and 11 kg/ha for the Kandiustult, both rated as low with respect to phosphorus availability.

### 1.6. Available silica

The water extractable silicate was 5 and 8.5 ppm while HCl extractable available silica was 90 and 106 ppm for the Haplustox of Pachalloor and Kandiustult of Kottarakara respectively.

### 1.7. Total phosphorus

In the two soils, the total phosphorus contents were 262.5 ppm and 331 ppm for the Haplustox of Pachalloor and the Kandiustult of Kottarakara respectively.

Table 1. Physico chemical and electro - chemical properties of soil samples.

Parameters	Haplustox	Kandiustult
<b>Mechanical analysis</b>		
Coarsse Sand	51.2%	44.0%
Fine sand	18.0%	5.0%
Silt	17.5%	15.0%
Clay	7.5%	35.0%
pH		
Water (1:2.5)	5.0	4.4
KCl (1:2.5)	3.9	3.5
NaF (1:50)	8.0	9.0
Delta pH	-1.1	-0.9
Electrical conductivity	<0.05	<0.05
Organic Carbon	0.36%	1.32%
Available P	5.0ppm	2.5ppm
Total P	262.5ppm	331.0ppm
<b>Available silica</b>		
Water extractable	5.0ppm	8.5ppm
Dil. HCl extractable	90.0ppm	106.0ppm
Total sesginoxide	16.6%	27.5%
Total iron	3.37%	4.83%
DCB extractable iron	1.7%	2.1%
Oxalate extractable iron	0.24%	0.56%
KCl extractable aluminium	0.30 $\text{cmol}(p^+) \text{kg}^{-1}$	1.37 $\text{cmol}(p^+) \text{kg}^{-1}$
CEC	3.24 $\text{cmol}(p^+) \text{kg}^{-1}$	5.7 $\text{cmol}(p^+) \text{kg}^{-1}$
AEC	0.31 $\text{cmol}(e^-) \text{kg}^{-1}$	0.62 $\text{cmol}(e^-) \text{kg}^{-1}$
P fixation capacity	57.2%	99.0%
Silicate fixation capacity	31.2%	40.7%
ZPC	3.0	3.5
ECEC	0.99 $\text{cmol}(p^+) \text{kg}^{-1}$	1.62 $\text{cmol}(p^+) \text{kg}^{-1}$

### 1.13. Cation exchange capacity (CEC)

The cation exchange capacity as determined by the neutral normal ammonium acetate method were 3.24  $\text{cmol}(\text{p}^+)\text{kg}^{-1}$  and 5.7  $\text{cmol}(\text{p}^+)\text{kg}^{-1}$  for the Haplustox and Kandiustult respectively.

### 1.14. Anion exchange capacity (AEC)

The anion exchange capacity was found to be 0.31  $\text{cmol}(\text{é})\text{Kg}^{-1}$  for the Kaplustox and 0.62  $\text{cmol}(\text{é})\text{Kg}^{-1}$  for the Kandiustult.

### 1.15. Phosphorus fixation capacity

The phosphorus fixation capacity of the two samples were found to be very high. The Haplustox of Pachalloor fixed 57.2% of the added 'P' while the Kandiustult of Kottarakara fixed almost 99% of the 'P' added.

### 1.16. Silicate fixation capacity

The Haplustox of Pachalloor fixed 31.2% of the added silicate while the Kandiustult of Kottarakara fixed 40.7% of the added silicate.

### 1.17. Zero point of charge (ZPC)

The zero point of charge of the soils as determined from the cross over points of potentiometric titration curves were 3.0 and 3.5 respectively for Haplustox and Kandiustult.

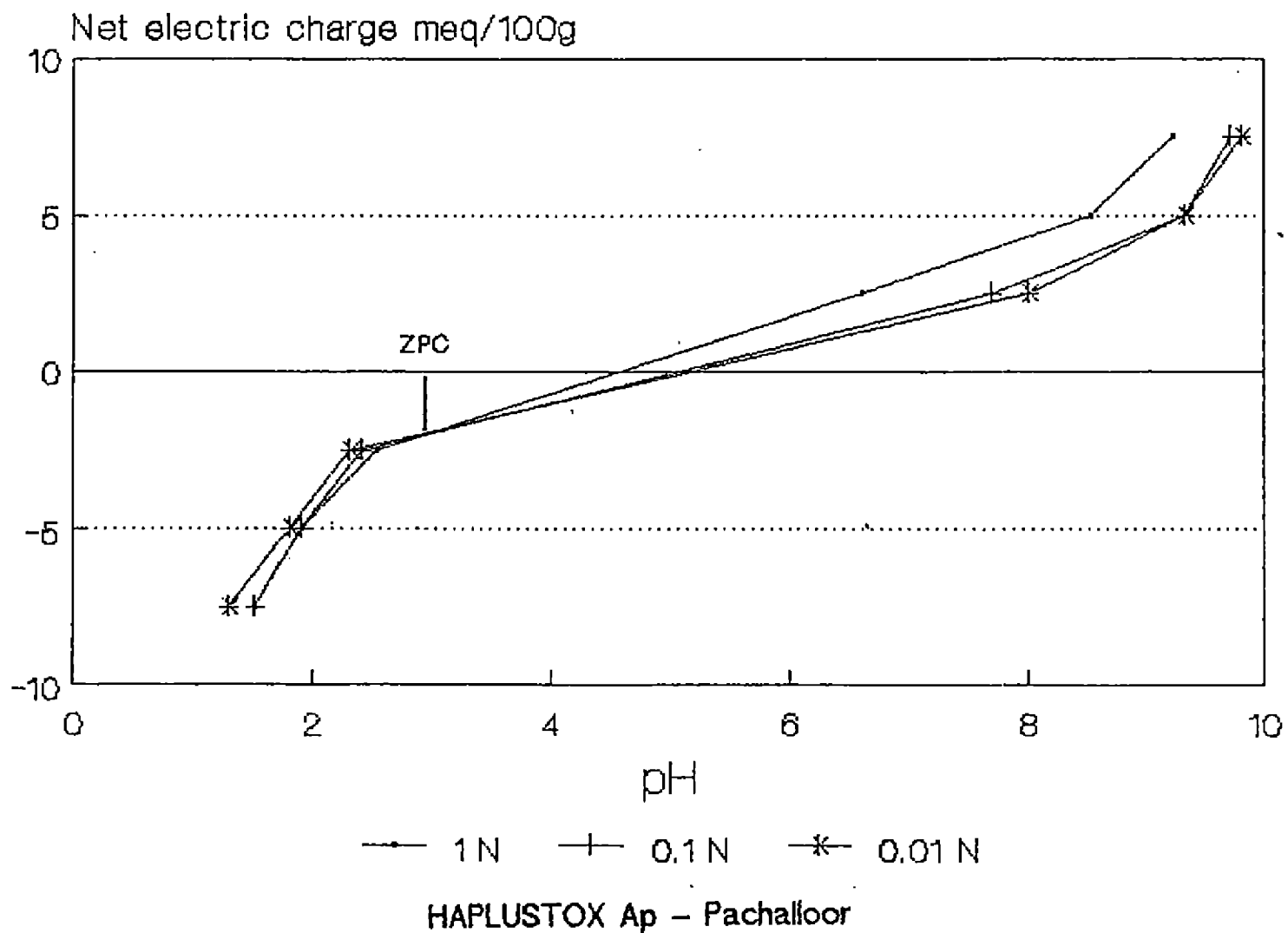
## 2. Incubation experiment

Data on the incubation experiment conducted are presented in Tables 2 and 3. This represent the observed increase in available phosphorus from 5g soil incubated over a period of 40 days consequent to treatment with silicate in limed and unlimed samples.

Liming is found to have no significant effect on the release of 'P' in the Haplustox of Pachalloor, whereas the Kandiustult of Kottarakara showed significant increase in the available 'P'.

Silicate application registered significant effect on the release of phosphorus from both the soils. In the case of Oxisol, silicate application @ 200 and 400 ppm were statistically not significant but the highest level of 800 ppm gave the maximum effect. In the case of the Kandiustult of Kottarakara the untreated soil differed significantly from the silicate treated samples. Here also silicate application at 800 ppm recorded the maximum effect on release of 'P'.

**Fig 1 Net electric charge as a function of pH and concentration of NaCl**





In both the soils, the period of incubation showed highly significant effect on the release of phosphorus. For the Haplustox the second and the third observations on the 5th and the 10th day of incubation had the same result. The 4th observation on the 20th day recorded the highest value for available phosphorus which thereafter, on the 40th day representing the 5th observation registered a lower value. The Kandiustult of Kottarakara recorded the maximum value of available 'P' on the 20th day and subsequently showed a slight decline towards the last observation on the 40th day of incubation.

### 3. Adsorption studies

#### 3.1. Phosphorus adsorption isotherms

Adsorption isotherms for phosphorus on the Haplustox of Pachalloor and Kandiustult of Kottarakara showed high affinity for adsorption at higher solution concentrations. The Haplustox of Pachalloor adsorbed nearly 68.7 per cent of the added phosphate whereas the Kandiustult of Kottarakara adsorbed almost 88 percent at the highest addition rate of 2000 ppm. In the case of the Haplustox, a larger proportion of the added phosphorus was observed in the solution phase after equilibration. The Haplustox with lower AEC ( $0.31 \text{ cmol(e-)}\text{kg}^{-1}$ ) lower organic matter content

Table 2. Effect of silicate application on available phosphorus in the Haplustox of Pachalloor

Treatments	Observation means (P ppm)				
	1st day	5th day	10th day	20th day	40th day
a <sub>1</sub> b <sub>1</sub>	4.0	8.0	8.5	10.5	9.0
a <sub>1</sub> b <sub>2</sub>	4.5	9.5	9.0	10.5	9.5
a <sub>1</sub> b <sub>3</sub>	4.2	10.0	9.5	10.0	10.5
a <sub>1</sub> b <sub>4</sub>	5.0	11.0	9.5	12.0	12.0
a <sub>2</sub> b <sub>1</sub>	4.7	7.5	8.0	10.0	9.5
a <sub>2</sub> b <sub>2</sub>	4.7	8.5	9.0	11.0	10.0
a <sub>2</sub> b <sub>3</sub>	5.0	8.5	9.5	11.5	10.5
a <sub>2</sub> b <sub>4</sub>	5.5	10.5	10.5	12.5	11.0

a<sub>1</sub> = Unlimed  
 a<sub>2</sub> = Limed to neutrality  
 b<sub>1</sub> = Without silicate  
 b<sub>2</sub> = 200 ppm silicate  
 b<sub>3</sub> = 400 ppm silicate  
 b<sub>4</sub> = 800 ppm silicate

Table 3. Effect of silicate on available P in the Kandiustult of Kottarakara

Treatments	Observation means (P ppm)				
	1st day	5th day	10th day	20th day	40th day
a <sub>1</sub> b <sub>1</sub>	2.75	2.50	2.55	3.75	3.00
a <sub>1</sub> b <sub>2</sub>	3.00	3.25	2.75	4.75	4.00
a <sub>1</sub> b <sub>3</sub>	3.25	2.75	3.00	8.00	3.00
a <sub>1</sub> b <sub>4</sub>	3.75	2.75	3.25	8.00	4.00
a <sub>2</sub> b <sub>1</sub>	2.50	2.00	1.63	4.25	3.75
a <sub>2</sub> b <sub>2</sub>	2.85	2.75	2.55	5.50	4.00
a <sub>2</sub> b <sub>3</sub>	3.25	3.00	3.50	9.00	4.75
a <sub>2</sub> b <sub>4</sub>	3.75	3.50	3.75	9.50	5.25



and sesquioxide content had lesser amounts of phosphate adsorbed after equilibration. This is evidenced by the flattened curve obtained for the adsorption isotherms of the Oxisol. A steeper slope for the the curve was observed for the Kandiustult of Kottarakkara having a higher AEC and sesquioxide content.

### 3.2. Silica adsorption isotherms

Silica adsorption isotherms of these two soils also showed a similar trend as that of phosphate adsorption isotherms. The Haplustox showed lesser adsorption of silicate than the Kandiustult.

## 4. Soil column study

The results of the column study conducted to ascertain the reported enhancement in the cation exchange power of soils following treatment with soluble phosphate and silicate are shown in Table 6.

The cation exchange capacity of the two soils increased markedly on treatment with phosphate and silicate. The phosphate treatment was found to be superior to silicate treatment in the present study.

The upper layers of the column showed maximum enhancement in CEC consequent to treatment effects. With

Table 4. Quantities of P in the equilibrium solution and adsorbed by the Haplustox and Kandiustult at different addition levels.

Soil sample	ppm added	Quantity in equilibrium solution		Quantity adsorbed	
		ppm	% of added	ppm	% of added
Haplustox of Pachalloor	200	12	6.0	188	94.0
	400	71	17.7	329	82.2
	600	173	28.8	427	71.2
	800	299	37.3	501	62.6
	1000	364	36.4	636	63.6
	1200	483	40.2	716	59.6
	1400	516	36.8	884	73.6
	1600	625	39.0	975	60.9
	1800	650	36.1	1150	63.9
	2000	632	31.6	1374	68.7
Kandiustult of Kottarakara	200	0	0	200	100.0
	400	4.7	1.17	395	98.5
	600	7.1	1.18	593	98.8
	800	14.2	1.77	785	98.1
	1000	16.6	1.66	983	98.3
	1200	27.5	2.29	1172	97.6
	1400	32.5	2.32	1367	97.6
	1600	47.5	2.96	1552	97.0
	1800	135.0	7.50	1665	92.5
2000	237.0	11.85	1762	88.0	

Fig. 3

### Phosphate adsorption isotherms of Halplustox and Kandiustult

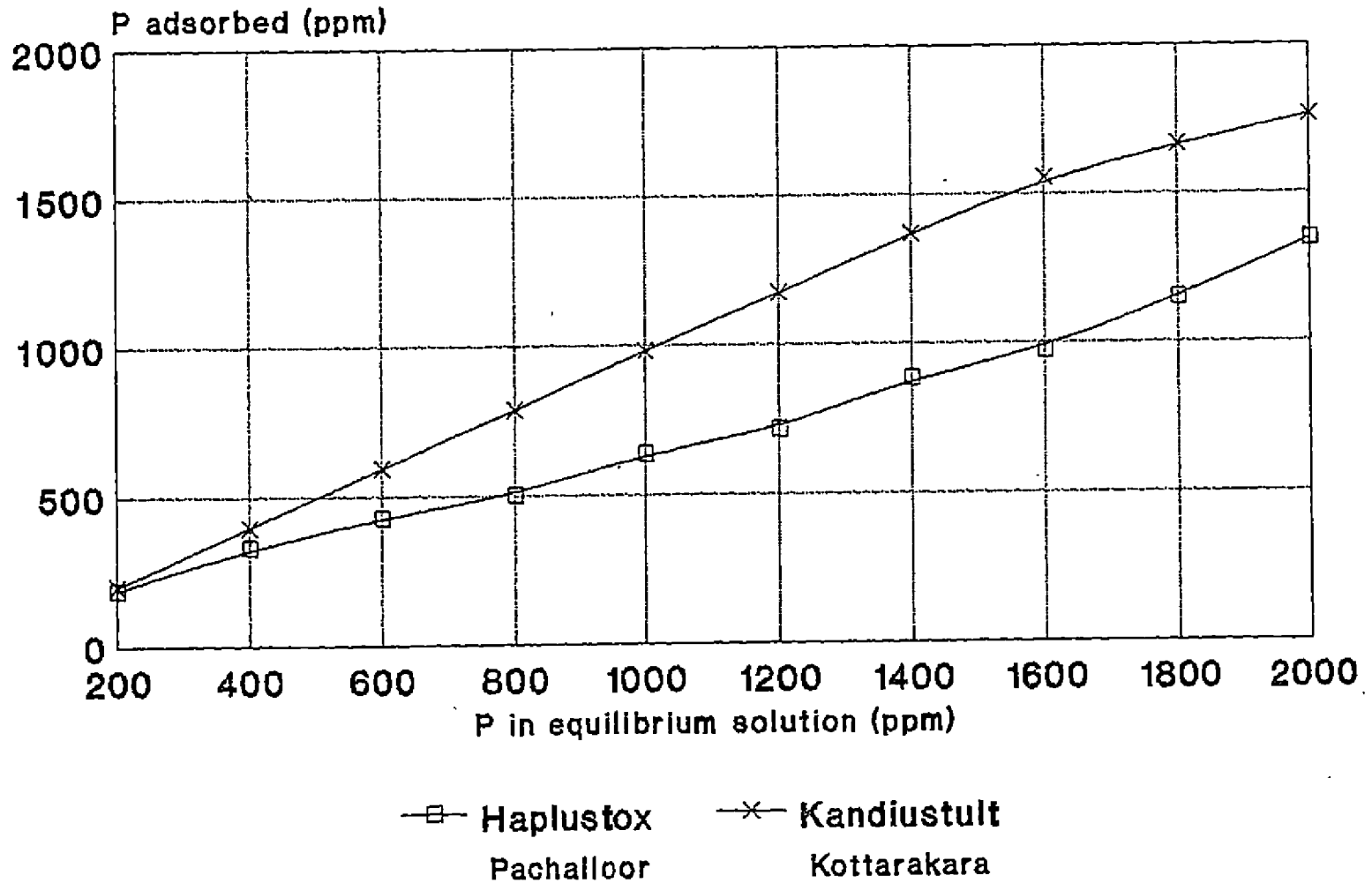
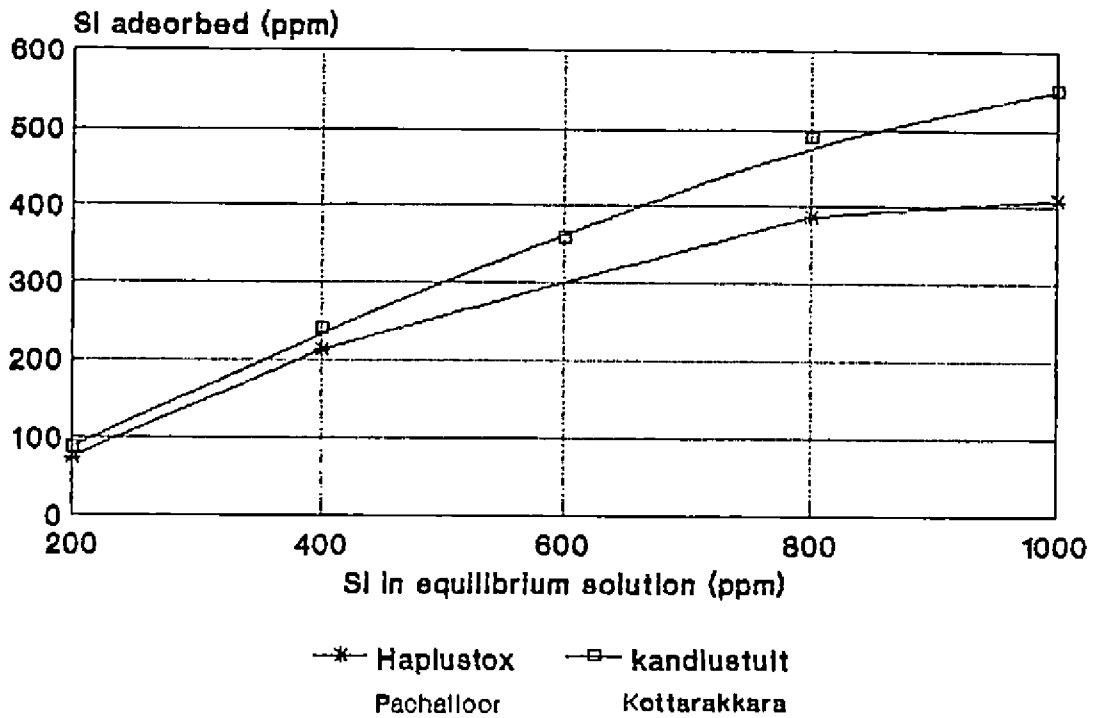


Table 5. Quantities of Si in the equilibrium solution and adsorbed by the Haplustox and Kandiuistult at different addition levels.

Element	Soil type	ppm added	Quantity in equilibrium solution		Quantity adsorbed	
			ppm	% of added	ppm	% of added
Silicon	Haplustox of Pachalloor	200	125	62.50	75	37.5
		400	187	46.75	213	53.2
		600	262	43.66	237	39.5
		800	412	51.50	388	48.5
		1000	590	59.00	410	41.0
Silicon	Kandiuistult of Kottarakara	200	112.5	56.2	87.5	43.7
		400	160.0	40.0	240.0	60.0
		600	240.0	40.0	360.0	60.0
		800	310.0	38.7	490.0	61.2
		1000	450.0	45.0	550.0	55.0

Fig. 4

**Silicate adsorption isotherms of  
Haplustox and Kandlustult**

Increasing depths the cation retention was found to be poor as evidenced from lower values of the CEC. The Haplustox of Pachalloor which had an original CEC of  $3.24 \text{ cmol(p}^+)\text{kg}^{-1}$  on leaching with phosphate solution at a concentration of 500 ppm enhanced the CEC to  $4.4 \text{ cmol(p}^+)\text{kg}^{-1}$ . The samples taken from a depth of 15 cm showed a decrease in CEC to  $3.0 \text{ cmol(p}^+)\text{kg}^{-1}$  and the third depth of 25 cm recorded a further decrease to  $2.9 \text{ cmol(p}^+)\text{kg}^{-1}$ . At a concentration of 1000 ppm, the CEC values were 4.76, 3.76 and  $3.24 \text{ cmol(p}^+)\text{kg}^{-1}$  for the first, second and third depth respectively.

The Kandiustult of Kottarakkara also showed a similar trend. On leaching with phosphate at 500 ppm, the soil which had an original CEC of  $5.7 \text{ cmol(p}^+)\text{kg}^{-1}$  recorded an increase in the CEC through the entire depth of the column, the values being 8.08, 6.16 and  $5.72 \text{ cmol(p}^+)\text{kg}^{-1}$  for the surface, second and third layers respectively. Leaching with 1000 ppm phosphate solutions showed further increase in the cation exchange capacity of the surface, the values being 8.16, 5.88 and  $6.12 \text{ cmol(p}^+)\text{kg}^{-1}$  respectively for the three depths from the surface downwards.

Leaching the soil columns with silicate at the two levels of 500 and 1000 ppm in both Haplustox and Kandiustult recorded a significant increase in CEC of the surface layers. The subsequent lower layers registered a decrease

Table 6. Effect of phosphate and silicate treatment on the cation exchange capacity of the Haplustox and the Kandiustult.

Depth of the column (cm)	Cation Exchange Capacity $\text{cmol}(\text{p}^+) \text{Kg}^{-1}$							
	Haplustox				Kandiustult			
	Phosphate		Silicate		Phosphate		Silicate	
	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
0 - 5	4.4	4.76	3.56	4.80	8.08	8.16	7.40	7.40
15	3.0	3.76	2.84	3.04	6.16	5.88	6.00	6.40
25	2.9	3.24	2.84	3.08	5.72	6.12	6.12	6.12

**Fig 5 Variation of CEC with depth at different levels of silicate and phosphate (Haplustox Ap - Pachalloor)**

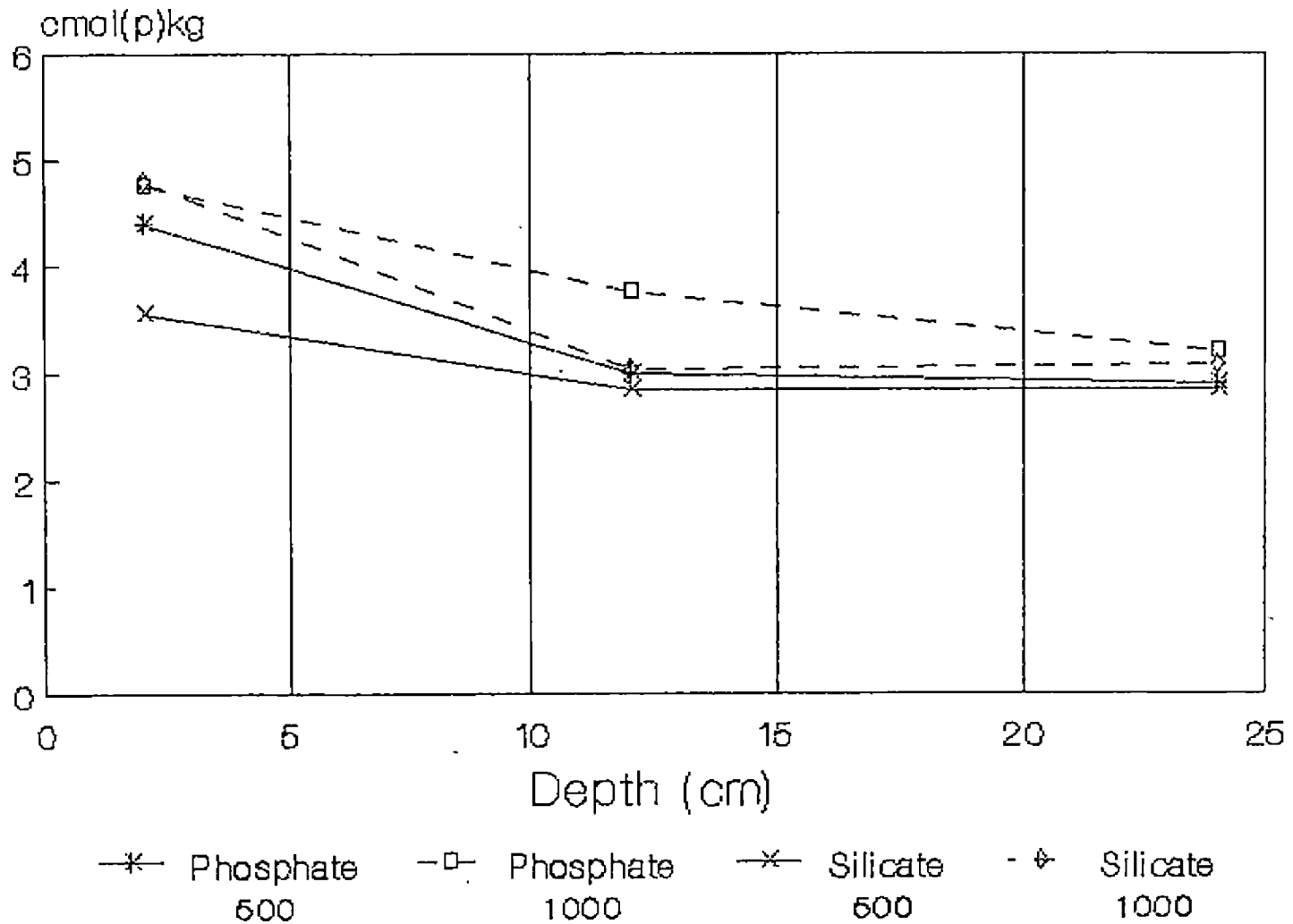
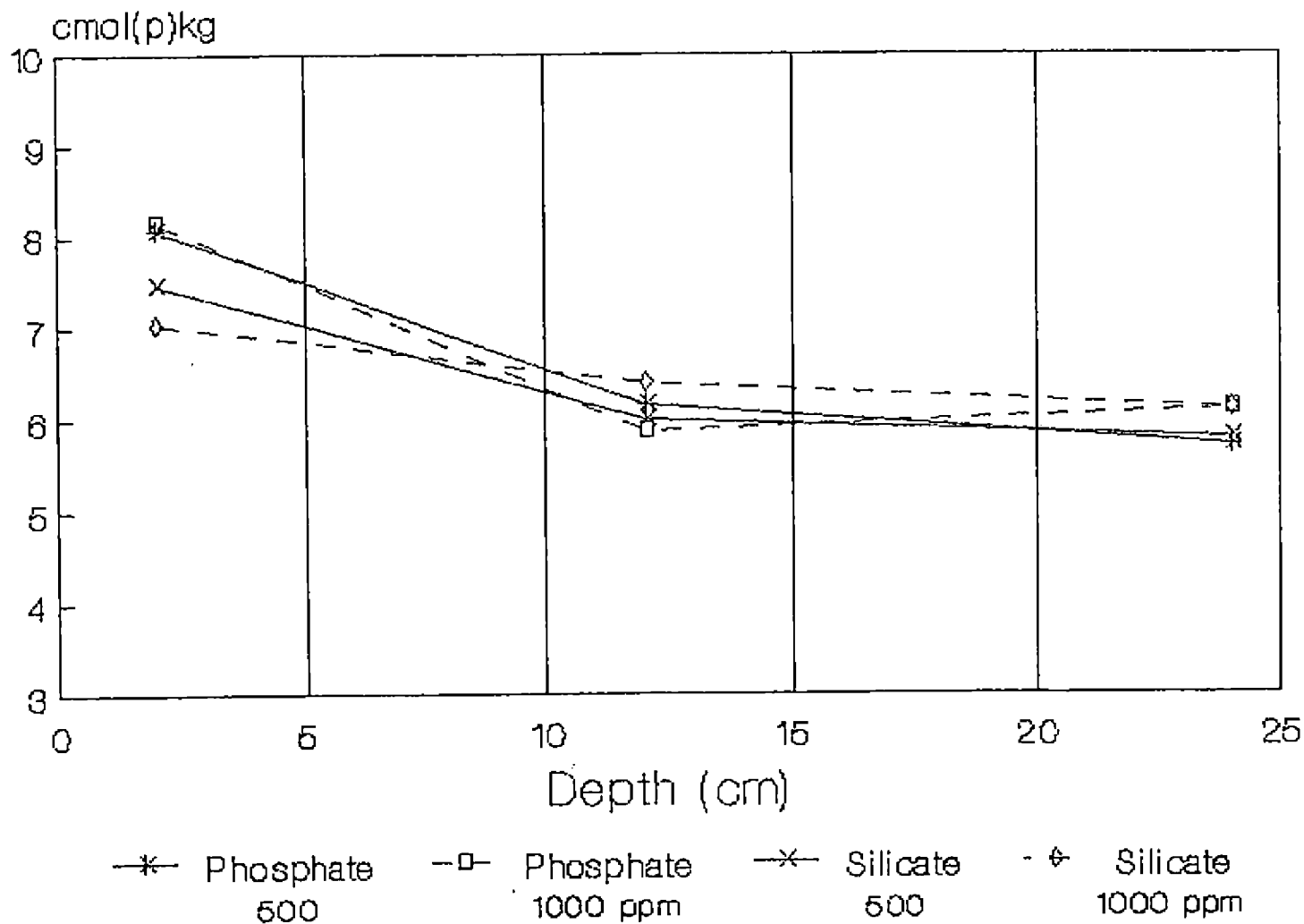




Fig 6 Variation of CEC with depth at different levels of silicate and phosphate (Kandiustult Ap-KOTTARAKKARA)



in the CEC than the original value for the Haplustox of Pachalloor. However in the case of the Kandiustult of Kottarakkara the CEC values recorded for the lower layers was higher than the original value.

#### 5. Neubauer's Experiment

The average effect of silicate lime and phosphate application on phosphorus uptake by plants was determined on both the soil types by conducting a modified Neubauer's experiment using cowpea and tapioca plants grown in these samples. The Haplustox of Pachalloor showed no significant effect for the added silicate, and lime on phosphorus uptake. In the Kandiustult of Kottarakkara though there was no significant effect observed for silicate application and liming, the added phosphate showed significant results.

The mean values of the phosphorus content of the cowpea plants grown in the Haplustox did not differ significantly for the silicated (581 ppm) and non-silicated (486.8 ppm) samples. The effect of lime treatment also was not significant. The mean "P" content of the limed plant samples was 539 ppm while that of unlimed was 528 ppm. The average effect of phosphate application on 'P' uptake on these samples also was found to be non-significant. It was 564.7 ppm for phosphated sample and 503 ppm for the control.

Table 7. Effect of silicate, phosphate and lime application on P uptake by cowpea in the Haplustox of Pachalloor

Treatment	Observation mean (P ppm)
s <sub>0</sub> l <sub>0</sub> p <sub>0</sub>	481.2
s <sub>0</sub> l <sub>0</sub> p <sub>1</sub>	598.7
s <sub>0</sub> l <sub>1</sub> p <sub>0</sub>	493.9
s <sub>0</sub> l <sub>1</sub> p <sub>1</sub>	373.7
s <sub>1</sub> l <sub>0</sub> p <sub>0</sub>	435.5
s <sub>1</sub> l <sub>0</sub> p <sub>1</sub>	598.5
s <sub>1</sub> l <sub>1</sub> p <sub>0</sub>	602.0
s <sub>1</sub> l <sub>1</sub> p <sub>1</sub>	688.0
CD	148.36

Table 8. Effect of silicate, lime and phosphate on P uptake by cowpea in the Kandiustult

Treatment	Observation mean (P ppm)
s <sub>0</sub> l <sub>0</sub> p <sub>0</sub>	678.7
s <sub>0</sub> l <sub>0</sub> p <sub>1</sub>	1861.5
s <sub>0</sub> l <sub>1</sub> p <sub>0</sub>	1036.1
s <sub>0</sub> l <sub>1</sub> p <sub>1</sub>	1960.5
s <sub>1</sub> l <sub>0</sub> p <sub>0</sub>	570.0
s <sub>1</sub> l <sub>0</sub> p <sub>1</sub>	1610.0
s <sub>1</sub> l <sub>1</sub> p <sub>0</sub>	1247.0
s <sub>1</sub> l <sub>1</sub> p <sub>1</sub>	1718.3
CD	1164.4

Table 9. Effect of silicate, lime and phosphate on, P uptake by tapioca in the Haplustox of Pachalloor

Treatment	Mean P content (P ppm)
s <sub>0</sub> l <sub>0</sub> p <sub>0</sub>	1450.0
s <sub>0</sub> l <sub>0</sub> p <sub>1</sub>	1685.0
s <sub>0</sub> l <sub>1</sub> p <sub>0</sub>	1773.7
s <sub>0</sub> l <sub>1</sub> p <sub>1</sub>	2180.0
s <sub>1</sub> l <sub>0</sub> p <sub>0</sub>	2070.0
s <sub>1</sub> l <sub>0</sub> p <sub>1</sub>	3007.5
s <sub>1</sub> l <sub>1</sub> p <sub>0</sub>	2775.0
s <sub>1</sub> l <sub>1</sub> p <sub>1</sub>	3362.5
CD	1264.22

Table 10. Effect of silicate, lime and phosphate treatment on P uptake by tapioca in the Kandiustult of Kottarakara

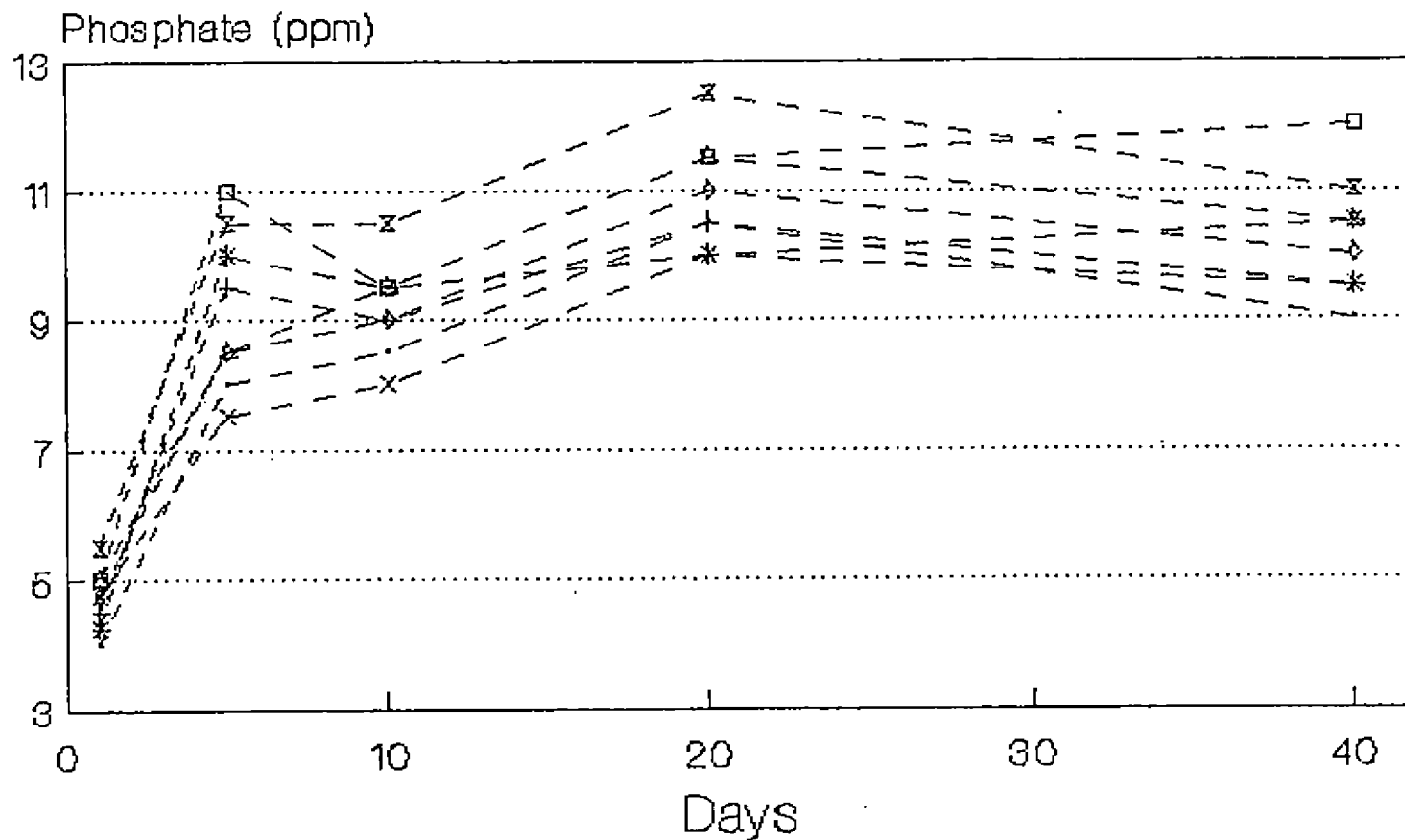
Treatments	P content in the plant sample (ppm)
s <sub>0</sub> l <sub>0</sub> p <sub>0</sub>	2200.00
s <sub>0</sub> l <sub>0</sub> p <sub>1</sub>	2650.00
s <sub>0</sub> l <sub>1</sub> p <sub>0</sub>	2050.00
s <sub>0</sub> l <sub>1</sub> p <sub>1</sub>	3676.00
s <sub>1</sub> l <sub>0</sub> p <sub>0</sub>	1587.50
s <sub>1</sub> l <sub>0</sub> p <sub>1</sub>	2880.00
s <sub>1</sub> l <sub>1</sub> p <sub>0</sub>	2755.00
s <sub>1</sub> l <sub>1</sub> p <sub>1</sub>	2795.00
CD	722.90

The cowpea samples of Kandiustult also registered non-significant effect for silicate and lime applications, but showed significant results for phosphate treatment.

The chemical analysis of the tapioca plant samples also revealed a similar trend for the two soil types. Phosphate content of the samples of the Haplustox of Pachalloor which received silicate treatment was 2803.7 ppm, while that of the controls samples was 1772.1 ppm. The mean value of phosphate content of the tapioca samples from the Kandiustult also indicated a non significant effect for the silicate and lime treatments. The average value of 'P' content in silicate applied samples was 2504 ppm and that of the control plants was 2644 ppm. The average phosphate content of tapioca samples which received phosphate treatments was 3000 ppm and that of the control was 2146.1 ppm, the difference being significant statistically.

**Fig 7 Release of P at different levels  
of silicate application with time**

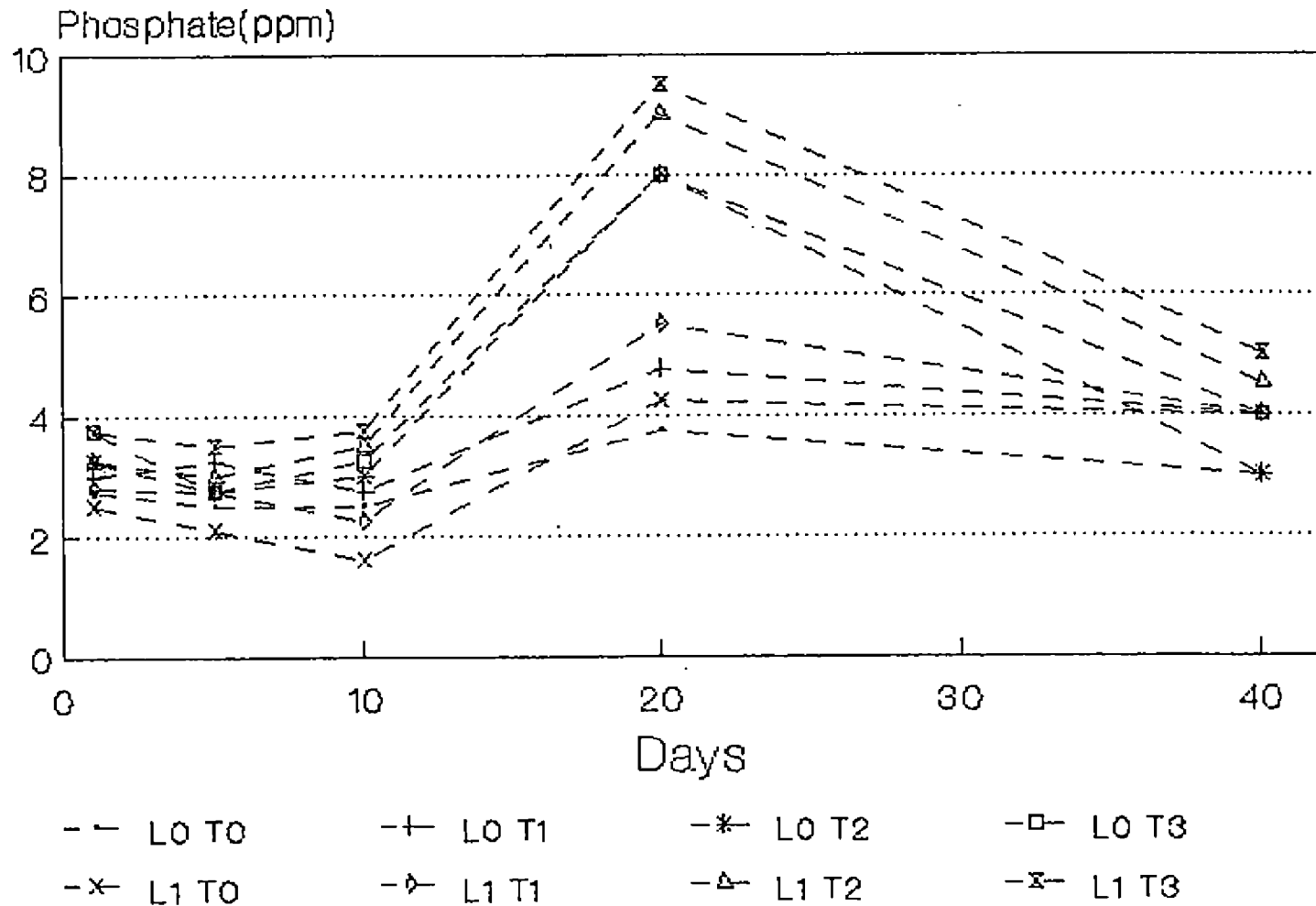
(Haplustox Ap - Pachalloor)



- - L0 T0      - + L0 T1      - \* L0 T2      - □ L0 T3  
 - x L1 T0      - ○ L1 T1      - △ L1 T2      - x L1 T3



**Fig 8 Release of P at different levels  
of silicate application with time  
(Kandiustult Ap - KOTTARAKKARA)**



## **DISCUSSION**

## DISCUSSION

### 1. Physicochemical and electro-chemical properties of the soils

Results of the basic laboratory analysis pertaining to the important physical, chemical and electro-chemical properties of the soils used for the study are summarised in Table 1. A close scrutiny of the data reveals that the soil is depleted of bases with very low percentage base saturation, rich in sesquioxides and poor in organic matter status. Soil reaction is distinctly acidic with a pH 4.4 and 5 for the Kandiestult of Kottarakara and the Haplustox of Pachalloor respectively. The soil is texturally sandy loam and sandy clay in the case of Haplustox of Pachalloor and Kandiestult of Kottarakara respectively. Low values of clay at the surface samples clearly indicate downward migration of clay in both the soils. Kandiestult of Kottarakara however registered a comparatively higher value (35%) in respect of clay even at the surface. Delta pH values as obtained by subtracting pH-water from pH-KCl indicated negative values showing the predominance of organic fractions in the surface soils. (-1.1 and -0.9 for the Haplustox and Kandiestult

respectively). Nearly one unit change in pH was observed between pH-water and pH KCl. The interaction of the humus colloids with the inorganic soil components would have changed the exchange behaviour of the inorganic colloids, thus making the delta pH value negative. The silt and sand fractions did not vary significantly thus indicating greater vertical mobility for the clay fraction. Electrical conductivity (EC) values were negligibly low showing excessive leaching and downward movement of bases present in the soils. Further the tropical climate with heavy rainfall alternated with high temperatures would have enhanced the solute movement from the surface layers. The organic carbon content registered lower values for both soils amounting to 0.36 and 1.32 percent for samples taken from the Haplustox of Pachalloor and Kandiustult of Kottarakkara respectively. Slightly higher content of organic carbon observed in the Kandiustult of Kottarakkara may be due to the partially humified and undecomposed organic matter accumulated at the undisturbed surface layers. The impoverished nature of both the soils is clearly brought about by the very low available phosphorus content of  $22.4 \text{ kg ha}^{-1}$  and  $11 \text{ kg ha}^{-1}$  of  $\text{P}_2\text{O}_5$  for samples representing Haplustox and Kandiustult respectively. Total phosphorus content registered values as high as 262.5 ppm for the Haplustox of Pachalloor and 331 ppm for the Kandiustult of Kottarakkara. The extremely low

values of available 'P' with comparatively higher total 'P' in the soils studied indicated the significance of soil management for the release of 'P' by suitable low input management techniques.

Available silica status as extracted by water and diluted HCl (1:20) showed low values indicating the appreciable loss of soluble silicates from the surface soils. Extremely low values of soluble silicates in highly weathered tropical soils reported by many workers (Gallez et al 1977, Herbillon et al 1977) is thus in conformity with the present study.

Total sesquioxide content registered high values amounting to 16.6 and 27.5 percent respectively for Haplustox and Kandiustult. This clearly indicate chances of high phosphorus fixation in these soils. Further clay migration to lower layers would have enhanced a relative enrichment of surface layers with comparatively less soluble iron aluminium oxides. Low values for the dithionate extractable iron of 1.7 and 2.1 percent respectively for the Haplustox and Kandiustult indicate low amounts of crystalline iron forms present in these soils. The values observed for Oxalate extractable form of iron was found to be 0.24 and 0.56 percent for the Haplustox and Kandiustult respectively. The oxalate extractable form

represents chiefly the amorphous form of iron which is more reactive than the crystalline forms. Thus the active role of oxalate extractable iron and its reaction with soluble phosphate leading to 'P' fixation mechanisms is indicated.

Exchangeable aluminium as determined by normal KCl extraction indicated values, 1.37 and 0.30 cmol for Kandiuistult and Haplustox respectively. Thus the percentage aluminium saturation is 24 percent for the Kandiuistult and 9.25 percent for the Haplustox. Thus higher values of sesquioxides with comparatively lower values for total iron clearly indicate the predominance of aluminium oxides in both the soils studied. However this has not been reflected in the KCl extractable aluminium. This is obviously due to the existence of aluminium in the nonexchangeable stable oxide or insoluble forms, thus without appreciable effect in the fixation of soluble phosphates.

The electro-chemical properties of soils studied clearly showed that the inorganic components of soil is of variable charge type with low CEC values of 5.7 and 3.24  $\text{cmol}(\text{p}^+)\text{kg}^{-1}$  for the Kandiuistult and Haplustox respectively. The AEC values were 0.31  $\text{cmol}(\text{e}^-)\text{kg}^{-1}$  and 0.62  $\text{cmol}(\text{e}^-)\text{kg}^{-1}$  for the Haplustox and the Kandiuistult respectively. The values appeared to be lower for the surface soils mainly due to the dilution effect brought out

by the organic fraction. Interaction between the humus fraction and the clay inorganic complexes would have modified the exchange complex to the advantage of cation exchange thus registering very low AEC values (Determination of the AEC values of the lower layers of the soil had not been attempted.). The point of zero charge (ZPC) as determined from potentiometric titration curves registered values 3 and 3.5 respectively for the Haplustox and Kandiuult, the lower values thus obtained are due to the influence of organic fraction at the surface layer. Lower ZPC values observed for the surface soils by many authors (van Raij and Peech 1972, Keng and Uehara 1974) are thus in agreement with the present observation. Iron aluminium oxides, other oxidic materials and pure kaolinitic clay minerals generally exhibit extremely high values of ZPC (Gallez et al 1976, Juo and Adams 1984). Though the soils used for the study are rich in oxidic materials and kaolinitic type of clay minerals, the influence of the organic fraction would have subdued their effect in giving a comparatively higher ZPC values. Further interaction of organic matter with the inorganic fractions of the soil needs elaboration to have a deeper insight of the problem.

2. Incubation experiment to study the effect of added silicates in relation to the available phosphorus.

Table 2 and 3 and Appendix 1 and 2 present data on the incubation experiment conducted to study the effect of added silicates in releasing soil phosphorus. This represents the observed increase in available 'P' from 5 g of soil incubated over a period of 40 days consequent to silicate application in limed and unlimed samples. The results showed significant effect on the release of phosphorus from both the soils. However the effect of liming was not significant on the release of phosphorus in the Haplustox of Pachalloor. In the case of Kandiustult liming significantly increased the availability of phosphorus subsequent to silicate incorporation. In the Haplustox of Pachalloor silicate application at the rate of 200 and 400 ppm were statistically non significant and the highest level of 800 ppm alone recorded significant effect. It has to be realised that the increase in the available 'P' concentration was substantial at the maximum concentration of silicate application in both cases. The nonsignificant effect due to liming recorded for the Haplustox of Pachalloor is mainly due to higher initial starting pH of 5.0. The increase in 'P' availability is mainly attributed to the enhancement of available phosphorus consequent to release of 'P' by silicate proxying from unavailable



phosphate complexes through ligand exchange. Similar mechanisms are reported by many workers (Hingston et al 1972, Obihara and Russell 1972) to explain the increase in available 'P' content in highly weathered Oxisols and Ultisols. Further the efficiency of silicate anion to displace phosphate at higher pH values are also indicated in the study. Studies conducted by Smyth and Sanchez (1980), Obihara and Russell (1970) also support this view. A strongly increasing trend with time of incubation was observed in the case of Haplustox in silicate treated samples. Almost a doubling of the available 'P' concentration was observed from the 2nd observation onwards and stabilised to a value slightly less than the attainable maximum on the 40th day of incubation. In all the treatments the maximum available 'P' values were recorded in the case of the highest dose of silicate application.

In both the soils the period of incubation showed highly significant effect on the release of phosphorus. In the case of Haplustox the 2nd and the 3rd observations had the same result and the 4th observation on the 20th day recorded the highest value for available phosphorus. The Kandiustult of Kottarakara however showed lower values in all observations when compared to the first two observations of available 'P' in the Haplustox though the effect was

significant. This is attributed mainly to the low initial status of available 'P' and the high 'P' fixing capacity of the Kandiustult.

Similar studies reported by Subramaniam and Gopalaswamy (1991) in the 4 rice soils of Tamilnadu also confirm the enhancement of phosphorus availability consequent to silicate application. They have attributed this reported enhancement in available phosphorus status to ligand exchange reaction, which involve competition between phosphate and silicate for adsorption sites. The results of another study by Obihara and Russell (1972) is also in conformity with the present observations. They found silicate anions which are adsorbed more strongly at higher pH values could displace phosphate easily from complexes particularly near neutral pH.

Thus the beneficial effects of silicate application in releasing phosphorus is well documented. The reported information that liming to neutral pH leads to substantial improvement in phosphate availability needs further elaboration as the effect of liming in the present study is not statistically significant. However the trend indicated in majority of the samples, a slight increase in available phosphorus over unlimed samples. Further this is supposedly due to the effect of the associated cation of the

silicate source used, the highly mobile and alkaline sodium, thus directly raising the pH values in both soils. Consequently the liming effect of calcium was subdued by the more alkaline sodium.

As period of incubation progressed, in both soils the available 'P' increased, the highest values of 12.5 ppm and 9.5 ppm was recorded in the 4th observation for the Haplustox and the Kandiustult respectively. This observation indicates the influence of period of incubation on phosphate release by silicate application. Further the need for adjusting the time of application of silicate to synchronize with the 'P' requirement of the crop is also indicated in the present study.

Thus silicate application in low activity clay soils of high 'P' fixing capacity is a low input soil management <sup>e</sup>technology that can be recommended for alleviating 'P' deficiency. The beneficial effects depends primarily on the initial 'P' status, fixation capacity and the amount of silicate added. The other beneficial effects contributed from the added silicates through its acid neutralising capacity and the possible improvement in the physico-chemical and microbiological properties of the soils are to be studied separately.

4. Adsorption desorption pattern of soluble phosphates and silicates:

Table 4 summarises the data on adsorption of phosphates and silicates by the two soils studied. The adsorption isotherms of the data presented in Table 4 are given in Figures 3 and 4. From the data it is evident that the two soils have widely varying adsorption behaviour with respect to phosphate and silicate. The highest dose of addition of phosphate and silicate selected was far above the anion exchange capacity of the soils, since mechanisms other than mere physical adsorption is believed to operate in the retention of these anions. It was observed that nearly 68.7 percent and 94 percent of the added phosphate was retained at the exchanger by the Haplustox at addition rates of 2000 ppm and 200 ppm respectively. This clearly indicates that even at an addition rate of 2000 ppm the exchange complex is able to hold nearly 69 percent of the added phosphorus and is capable of continuing adsorption at still higher rates. Intermediate levels of phosphate addition from 400 to 1800 ppm is also indicative of this trend. The Kandlustult of Kottarak<sup>k</sup> however showed extremely high adsorption rates of 88percent and 100 percent at concentrations of 2000 and 200 ppm respectively. This is evident from the steeper slope of the curve. Such a high adsorption capacity of this soil is an indication of its

nigh phosphate fixing capacity. Between the two soils, intermediate concentrations of phosphate addition also reported a higher percentage of adsorbed 'P' in the Kandiustult. This clearly brings about the greater buffering effect of the solid phase in respect to phosphate for the Kandiustult of Kottarakkara. Though both the soils are of high 'P' fixation capacity, a more flattened curve observed for the Haplustox of Pachalloor is suggestive of a better 'P' availability when phosphate is added at equal doses. The statistical validity of the adsorption isotherms were not tested using any adsorption equation as the purpose of the study was to highlight the behaviour of added phosphorus in relation to 'P' availability.

In respect to silicate adsorption the trend observed was similar to phosphate adsorption. However the absolute values of adsorbed silicate corresponding to each concentration of added silicates decreased drastically thus indicating very poor affinity of the soil material for silicate retention. At equivalent addition rates, Kandiustult retained a higher percentage of added silicates than the Haplustox. This is further evidenced from the steeper slope of the silicate adsorption isotherm for the Kandiustult.

Among the two anions added, thus adsorption is maximum for phosphate in both the soils at all levels of addition. Silicates though is adsorbed in appreciable quantities was present in larger quantities in the equilibrium solution. This observation further points out the need for higher doses of silicate to be added for the displacement of even extremely low amounts of phosphate. This increased adsorption of phosphate in the exchanger under the humid tropical soils with high sesquioxides suggests its possible inactivation through fixation from soluble phosphates added. Appreciable loss of soluble silicates is also indicated from the poor affinity for the exchange sites with respect to silicates. Thus regulated, small but frequent applications of soluble phosphates depending upon the type of crop and uptake by the crop in question may be advocated for 'P' nutrition. Massive dose of soluble phosphates to saturate the 'P' fixation capacity is not a suitable proposition in such soils whereas, with respect to less soluble forms of 'P', exploiting the acidity factor, higher rates of application can be recommended. An equally sound proposition in continuously 'P' fertilized soils in this context is the use of high doses of soluble silicate at least for one season to partially mobilise the already fixed/adsorbed phosphate.

## 4. Soil column study:

Table 6 summarises data on the results of the column study conducted to ascertain the reported enhancement in the cation exchange power of soils consequent to the application of silicates and phosphates. Cation exchange capacity of soil materials of the surface from zero to a depth of 5cm of the Kandiyustult of Kottarakara<sup>K</sup> increased with increasing quantities of phosphate and silicate applied. The results showed significant effect on enhancement in CEC from 5.7 to 8.08  $\text{cmolp}^+\text{kg}^{-1}$  at addition rates of 500 ppm phosphate. The corresponding enhancement in the exchange properties consequent to silicate application was from 5.7 to 7.4  $\text{cmolp}^+\text{kg}^{-1}$  at the lower level of silicate application. With increasing depth at 15cm the enhancement in CEC was marginal to 6.16 and 5.88  $\text{cmolp}^+\text{kg}^{-1}$  respectively for phosphate at addition rates of 500 and 1000 ppm. The corresponding values due to silicate application at the same depth was 6 and 6.4  $\text{cmolp}^+\text{kg}^{-1}$  respectively at two levels of 500 and 1000 ppm. As the depth increased to 25 cm the values decreased drastically to 5.72 and 6.12 for phosphate and 6.12 for both the levels of silicate.

More or less the same trend was observed for the Haplustox also though the individual values recorded were comparatively lower. It is clear from the above observation that the first increment of both phosphate and silicate increased cation exchange capacity more than the later increments. Same results were reported by Rajan (1976) who explained the mechanism of 'P' sorption of hydrous oxides in oxide rich soils consequent to the replacement of an aquo group resulting in a decrease in positive charge, with an increase in net negative charge. At low 'P' concentration he observed replacement of aquo groups to predominate and 'P' sorption has an appreciable effect on net surface charge. However replacement of hydroxyl group does not alter the surface charge. With respect to silicate the sorption process is highly pH dependent and at pH above neutrality (pH 9.2) the sorption increased drastically than it is at natural pH. However the effect of phosphates in altering the charge properties of oxidic soil materials is more pronounced, at lower pH than that of silicates. The proposed aquo exchange process in controlling the surface charge of oxidic soil materials has not been proved with respect to silicate adsorption (Gillman and Fox 1980). However the observed increase in cation exchange clearly indicates the existence of a similar mechanism in conjunction with ligand exchange (Hingston et al 1972).



Studies carried out by Gillman and Fox (1980) had shown that agronomically significant increases in CEC of surface horizons could be obtained with increased phosphate fertilization of soils. The effect with phosphate application was reported to be highly significant in soils with a natural pH below 5 and studies conducted by Gillman and Fox (1980) reported an increase of 5 or 6  $\text{cmol}(p^+)\text{kg}^{-1}$  in CEC for such a soil. This appears to be of very great practical significance in oxidic soils and soil materials which are continuously fertilized with low grade phosphates. Uehara (1980) also had reported that it is possible to increase cation retention by applying phosphate fertilizers or by the application of calcium silicate as a soil amendment. Laboratory incubation experiments by Wann and Uehara (1978) on soils treated with low grade phosphates observed retardation of K leaching at higher addition levels of phosphates. The observed enhancement in CEC consequent to the application of low grade silicates and phosphates, according to Uehara (1980) was due to a drastic reduction of the zero point of charge (ZPC) at the surface layers. The action of silicate and phosphate was believed to be similar to the action of humus in reducing the point of zero charge. Thus the present study highlights the amendment effect of phosphate and silicate in better cation protection through a clear enhancement of the CEC apart from its nutritional

effects in highly weathered soils. Even though economic constraints militate against using costly soluble phosphates and silicates, solely for this purpose, the use of low grade silicates and phosphates could be a better proposition to achieve this significant 'by product effect'.

#### 5. Neubauer's Experiment

Tables 7, 8, 9, 10 and Appendix 3 and 4 present data on the Neubauer's experiment conducted to determine the effect of silicate, lime and phosphate application on 'P' availability and uptake by test crops viz. cowpea and tapioca. Analysis of variance of the treatment and interaction effects of silicate, phosphate and lime on 'P' uptake by cowpea in the Haplustox of Pachalloor showed no significant results though treatments receiving phosphate and silicate in conjunction with lime gave the highest 'P' content. Treatment receiving silicate and phosphate with lime invariably resulted in a high 'P' content when compared to unlimed and control treatments of phosphate and silicate. This uniform trend though not significant is indicative of the beneficial effects of silicate application in releasing phosphate from soils. Highly significant positive effect as observed in the case of laboratory incubation experiment consequent to silicate application and liming with respect to 'P' availability was not reflected however in this

experiment. This probably is indicative of the possible reaction of the released soluble phosphorus with iron and aluminum compounds in the soil again, without being absorbed by the plant roots. Further the low requirement of phosphorus at the very early stages of the plant growth would have provided a substantial amount of released 'P' for reaction with soil components leading to fixation, particularly with a decline in silicate concentration. Thus release of soluble 'P' by silicates and its insitu fixation by the highly reactive, acidic, oxidic components of iron and aluminum needs further investigation. Had the absorption of the crop with respect to 'P' been sufficiently high, there would not have been such a greater chance for re-fixation and the effect would have been reflected in the 'P' uptake. This could be studied by further experimentation thus keeping the silicate concentration uniform over a long span of time so that the capacity of the plant roots to extract released 'P' attains considerable strength.

More or less the same trend was observed for tapioca also in the Haplustox of Pachalloor. Treatment  $s_0l_1p_1$  recorded the highest 'P' content followed by  $s_1l_0p_1$  and  $s_1l_1p_0$ . This also indicates the beneficial effect of silicate nutrition in 'P' availability. For confirmatory results further experimentation is required as the time span

of the experiment was very short and was not sufficient enough to bring about significant treatment effect in Cassava.

The Kandiustult of Kottarakara however showed significant treatment effect due to 'P' application for tapioca and recorded the highest value for 'P' content in the case of treatment  $s_0l_1p_1$ . Treatments  $s_1l_1p_1$  and  $s_1l_1p_0$  gave almost the same values. The significant effect observed consequent to 'P' application might be due to the high 'P' fixation capacity of the soil which have overshadowed the effect of silicates in releasing phosphorus. Significant interaction effects among lime, phosphate and silicate treatments have been observed in the case of tapioca which is suggestive of the beneficial effect of silicate nutrition. However confirmatory results needs further investigation by way of field experimentation.

In respect of cowpea significant effects was noticed in the Kandiustult for phosphate application and the individual and interaction effects of silicate and lime were totally non significant. The interaction effect of silicate, lime and phosphate also was found to be insignificant which indicated very poor treatment effect due to silicate application. All the 4 treatments of silicates were found to be less effective and the 4 treatments

receiving phosphate showed comparatively higher mean values for 'P' content in the plant. This observed non significant treatment effect might be due to the high 'P' fixation capacity of the soil, which rendered the already released soluble 'P' unavailable to the plant. However higher addition rates of silicates to counteract 'P' fixation and to maintain a 'high 'P' releasing capacity, could be a suitable proposition in these soils which has not been attempted here.

## **SUMMARY AND CONCLUSIONS**

## SUMMARY AND CONCLUSIONS

Most of the underutilized, potentially arable but impoverished uplands of Kerala classified under Oxisols and Ultisols are occupied by the highly weathered soils rich in variable charge minerals and oxides. The rejuvenation of these impoverished variable charge soils involve increasing the specific surface area or surface charge density or both the parameters. The cation exchange power of these variable charge soils can be increased by raising the soil pH through liming or lowering the zero point of charge (ZPC) of the soil by the application of phosphatic fertilizers, soluble silicates or organic matter. Hence it was felt necessary to get a deeper insight into the surface charge properties of the highly weathered upland soils of the state and its manipulation by the application of low grade soil amendments like soluble silicates and phosphates. Further, the relatively high cost of phosphatic fertilizers coupled with the widespread deficiency and fixation constraints require the development of low input technology that can make most efficient use of applied phosphorus in these Oxisol and Ultisol.

The studies were conducted in the form of suitable experiments in two soils representing two great groups, Haplustox and Kandlustult collected from Pachalloor and Kottarakkara respectively. The important observations and conclusions drawn from the investigations conducted are summarised below.

1. Results of the basic laboratory analysis revealed that the soils are distinctly acidic in nature, depleted of bases with very low percentage base saturation, rich in sesquioxides and poor in organic matter content. The delta pH value was negative for both the soils indicating the interaction of the humic colloids with the inorganic soil components. The electrical conductivity values were negligibly low showing leaching of bases to lower layers. Total phosphorus content was 262.5 and 331 ppm for the Haplustox and the Kandlustult respectively. The available P content was 5 ppm for the Haplustox and 2.5 ppm for the Kandlustult. The available silica status was low for both the soils indicating appreciable loss of soluble silicates from surface layers. Total sesquioxide content registered high values indicating chances of high phosphorus fixation.

The electro-chemical properties studied clearly showed that the inorganic components of the soils were of the variable charge with low CEC values of 5.70 and 3.24



$\text{cmol}(\text{p}^+)\text{kg}^{-1}$  for the Kandiustult and Haplustox respectively. The AEC values were 0.31 and 0.62 for the Haplustox and Kandiustult respectively. The point of zero charge (PZC) determined from potentiometric titration curves registered values 3 and 3.5 respectively for the Haplustox and Kandiustult. The data obtained for phosphorus fixation capacity was extremely high for both soils.

The physico-chemical characteristics, electro-chemical properties and specific anion fixing capacities of the two soils studied were indicative of low activity of these soils with very high phosphorus fixation capacity. Variable charge components namely iron-aluminium sesquioxides and hydrated oxides of iron and aluminium predominated in the inorganic fractions of the soil matrix.

2. Incubation experiment conducted to study the effect of added silicates in releasing soil phosphorus observed an increase in available P from both the soils. The highest level of application of 800 ppm recorded significant effect. This is mainly attributed to the enhancement of available P consequent to silicate proxying from unavailable phosphate complexes through ligand exchange. Almost a doubling of the available 'P' was observed by the second observation on the 20th day of incubation. Thus the beneficial effect of silicate application in releasing phosphorus is well documented.

3. The adsorption isotherms of the two soils studied gave widely varying adsorption behaviour with respect to phosphate and silicate. The adsorption pattern of phosphate in both the soil types indicated that they are having high phosphate fixing capacity. However adsorption pattern of added silicate indicated poor affinity of the soil materials for silicate retention compared to phosphate. Between the two soils studied Kandiyustult of Kottarakkara retained a higher percentage of added silicates.

4. Column study conducted to ascertain the reported enhancement in the cation exchange power consequent to low grade silicate and phosphate application showed significant effect. As the soil depth increased, the rate of enhancement decreased. The study showed that agronomically significant increases in CEC of surface horizons could be obtained with increased phosphate and silicate fertilization of soils.

5. The Neubauer's experiment conducted to determine the effect of silicate, lime and phosphate application on 'P' availability as well as uptake by the test crops did not show any significant result. However the trend was indicative of the beneficial effects of silicate application in increasing phosphorus release from the soil and 'P' uptake by the plant.

The present study thus enabled an assessment of the charge characteristics of two typical low activity clay soils of Kerala, and its relation to phosphorus management. The results of the present investigation and the review collected confirm the active role of soluble silicates in releasing strongly adsorbed soil phosphorus by proxying the phosphate anion and also the amendment effect of phosphates and silicates in better cation protection. However, the same effect on the uptake of 'P' by test crops need further experimentation, since it is not well documented by the present study.

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# APPENDICES

### APPENDIX I

ANOVA of the incubation experiment to study  
the effect of lime and silicate treatment on  
available P in the Haplustox of Pachalloor

Source	DF	MSS	F
Period	4	95.50	188.65** ✓
Lime	1	0.08	<u>1.31</u> ✓
Silicate	3	13.53	22.69** ✓
Lime x silicate	3	3.64	0.061
Lime x Period	4	0.54	1.06
Silicate x Period	12	1.33	2.62
Lime x Silicate x Period	12	0.45	0.89

CD (lime)	= 0.32
CD (silicate)	= 0.45
CD (period)	= 0.38

APPENDIX II

ANOVA of the incubation experiment to find the effect of lime and silicate on available P in the Kandiustult of Kottarakara

Source	DF	MSS -	F
Period	4	40.57	142.52**
Lime	1	2.26	6.28*
Silicate .	3	14.19	39.36**
Lime x silicate	3	1.15	3.18
Lime x Period	12	3.24	11.38**
Silicate x Period	4	1.21	4.26**
Lime x Silicate x Period	12	0.12	0.42

CD (lime) = 0.41<sub>v</sub>

CD (silicate) = 0.58

CD (period) = 0.51

### APPENDIX III

ANOVA of the Neubauer experiment to study the effect  
of silicate, phosphate and lime treatments  
on P uptake by cowpea in Haplustox

Source	DF	MSS	F
silicate	1	35438.5	2.14
Lime	1	479.5	0.29
Phosphate	1	15166.0	0.92
Silicate x lime	1	54803.0	3.31
Lime x phosphate	1	24774.5	1.49
Silicate x phosphate	1	15837.5	0.96
Silicate x lime x phosphate	1	6464.5	0.89

### APPENDIX IV

ANOVA on the effect of silicate, phosphate and lime  
treatments on P uptake by cowpea in Kandiustult

Source	DF	MSS	F
Silicate	1	383220	0.08
Lime	1	385332	0.79
Phosphate	1	3273388	6.79*
Silicate x lime	1	27058	0.056'
Lime x phosphate	1	170978	0.35
Silicate x phosphate	1	88800	0.18
Silicate x lime x phosphate	1	24108	0.50
CD		= 1164.4	

APPENDIX V

ANOVA on the effect of silicate, lime and phosphate applications on P uptake by tapioca in the Haplustox

Source	DF	MSS	F
silicate	1	4256480	3.54
Lime	1	882424	0.73
Phosphate	1	1173160	0.98
Silicate x lime	1	14552	0.012
Lime x phosphate	1	7984	0.006
Silicate x phosphate	1	195256	0.16
Silicate x lime x phosphate	1	67936	0.05
CD	= 1264.22		

APPENDIX VI

ANOVA on the effect of silicate, lime and phosphate applications on P uptake by tapioca in the Kandiustull

Source	DF	MSS	F
silicate	1	77984	0.19
Lime	1	958936	2.43
Phosphate	1	2904472	7.38*
Silicate x lime	1	10648	0.02
Lime x phosphate	1	1456	0.003
Silicate x phosphate	1	138192	0.35
Silicate x lime x phosphate	1	1474416	3.74*
CD	= 722.99		

**SURFACE CHARGE CHARACTERISTICS  
AND PHOSPHORUS AVAILABILITY IN  
SELECTED OXISOLS AND ULTISOLS OF KERALA**

BY

**J. REEKALA S.**

ABSTRACT OF A THESIS  
SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT  
FOR THE DEGREE  
MASTER OF SCIENCE IN AGRICULTURE  
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KERALA AGRICULTURAL UNIVERSITY

DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY  
COLLEGE OF AGRICULTURE  
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## ABSTRACT

To meet the goal of increased food production in areas dominated by LAC soils, it is essential to alleviate specific physical and chemical soil related constraints. A major constraint identified in the Oxisols and Ultisols is the widespread deficiency of phosphorus and moderate to high P-fixation coupled with low nutrient holding capacity. The use of low grade silicates and lime suggested as a low input strategy for sound phosphorus management in these soils is tested in the present study. In addition to this objective the by-product effect of the application of phosphate and silicate in exercising cation protection by enhancement of CEC is also tested in these selected soils. The results of the studies are summarised and appropriate conclusions drawn.

The electro-chemical properties of the two soils studied clearly showed that the inorganic components of the soils are of variable charge type. The results of the incubation experiment proved the beneficial effect of silicate application in enhancing the available 'P' status.

Adsorption studies of phosphate and silicate showed that the Kandiyustult of Kottarakkara exhibited extremely high adsorption capacity for 'P' indicating a higher 'P' fixing capacity than the Haplustox or Pachalloor.

The column study conducted revealed that it is possible to increase the retention of cations by applying phosphate and silicate as soil amendments.

Neubauer's experiment conducted to determine the effect of silicate lime and phosphate application on 'P' availability, did not show any significant result. However, the trend was indicative of the beneficial effect of silicate application in increasing the phosphate release from the soil. This aspect of the study needs further elaboration through field experiments.