CHAPTER III

MOBILITY AND ADSORPTION BEHAVIOUR OF AMMONIUM ORTHO- AND PYROPHOSPHATES IN CONTRASTING INDIAN SOILS
A. INTRODUCTION AND REVIEW OF LITERATURE

A.1. Mobility and diffusion of ortho- and pyrophosphates in soils

Studies on the mobility and diffusion of ortho- and pyrophosphate anions of applied phosphatic fertilizers broadcast on the soil surface or placed as a band in the soils are necessary to understand their concentration at different depths in soils in relation to the availability of phosphorus to plant roots.

There is sufficient evidence that the downward movement of orthophosphate when applied as a top-dressing is very slow. Brown (1935) observed that the movement of orthophosphate below 2.5 inches on permanent pasture plots which were fertilised for 16 years with superphosphate at the rate of 65 lbs P$_{2}$O$_{5}$ every 2 years did not occur in that soil. Similarly, Sell and Olsen (1947) found no detectable movement below one inch in a sandy loam soil during a period of 3 years when 80 lbs P$_{2}$O$_{5}$ as superphosphate was applied as a top dressing and with heavier soils, silt loam and clay loams, the movement was even slower. Likewise, Roy and Thomas (1951) reported that none of the phosphate had moved down to more than 8 inches from the surface of pasture land soil which had received dressings of 700 lb/Acre in the forms of basic slag and superphosphate at three-year intervals for nearly fifty years.

Mobility of phosphate ions in soils is controlled mainly by three factors, namely, (i) mass flow arising from leaching by rain and surface water; (ii) diffusion due to thermal movement of molecules or ions (along the concentration gradient), and (iii) mechanical mixing.
due to the action of soil organisms, disturbances of soil by wind and rain and cultivation (Russel and Shone, 1963). Gunary et al. (1964b) have pointed out that the mobility of ions will depend upon the concentration gradient of the ions, porosity, moisture content and the tendency for soil to adsorb the particular ion. Barber (1962) has drawn a distinction between the ions in the solution and those closely associated with soil particles. The mass flow and diffusion process was predominant for translocating ions in solution whereas ions retained on soil particles could only move by exchange diffusion on the electrically charged surfaces. Moreover, it was also pointed out that in the soils studied, mass flow could account for only a small fraction of phosphorus taken up by the plants. Similarly, phosphorus is not normally considered to be lost by leaching although some loss may occur over a geological time. The movement by mass flow may become relatively important when the phosphorus concentration is higher. Ozanne et al. (1961) have reported that phosphorus can leach in soils of extremely low phosphorus adsorption capacity. Similarly, Larsen and Sutton (1966) while conducting the experiment in the glasshouse, have shown that considerable phosphorus movement can take place in soil when adsorption complex has been satisfied by heavy phosphorus applications. The phosphorus concentration in the soil solution may also be raised by the activity of organisms. As Hannapel et al. (1964) have pointed out, this may account for the large body of evidence which shows that phosphorus penetration is greater in soils which have received manure rather than inorganic phosphorus fertilizer.
Diffusion process occurs due to the transportation of molecules or ions from one system to another as a result of their thermal movement and this will not exist in a medium where the system is in equilibrium. However, the diffusion process operates on account of differences in concentration, charges, porosity etc. and transport of phosphorus through soil will cause several physical and chemical changes to occur both in liquid and solid phases, thus causing difficulties in the measurement of diffusion coefficient. These problems can be overcome by using carrier free $^{32}P$ which permits the measurement to be done in the absence of a concentration gradient. Lewis and Quirk (1965) have suggested the term

$$D_e = D_p \times \frac{\text{solution } ^{32}P}{\text{total } ^{32}P}$$

where $D_p$ is the diffusion coefficient which would have been obtained if $^{32}P$ had not been adsorbed onto the solid phase and $D_e$ is the observed (apparent) diffusion coefficient. In a given soil, the term solution $\frac{^{32}P}{\text{total } ^{32}P}$ will increase with increasing degree of saturation of the phosphorus adsorption system. Thus, they showed that $D_e$ was directly related to the amount of added phosphate.

The rate of phosphorus diffusion is governed by the amount of phosphorus present at the surface (Rennie and Bole, 1968), soil water content (Lawton and Vomocil, 1954), chemical reaction with the soil (Lehr et al., 1959) and soil bulk density (Mira and Singh, 1977). Porter et al. (1960) have discussed the major factors like porosity, moisture content, concentration of soil solution and electric charges in relation to the mobility of ions in soils.
Nye (1966) has noted that ions other than phosphate may influence the rate of phosphorus diffusion. In his development of the theory of self diffusion and bulk diffusion in soils he observed that a small extent phosphorus diffusion takes place along the surface of the solid phase.

Gunary (1963, 1964a) and Gunary et al. (1964b) conducted studies on phosphorus diffusion in soil crumbs and the results obtained are relevant to natural conditions. They reported that the rate of diffusion was related to the degree of saturation of the phosphorus adsorption capacity. Gunary et al. (1964b) observed the mobility of phosphate in both natural soil crumbs and in soil models, by following the movement of $^{32}\text{P}$. They reported that more phosphate was sorbed by the crumbs in the presence of highly hydrated iron oxide when montmorillonite was present rather than kaolinite.

Fox and Kamprath (1971) reported that soluble phosphorus fertilizer was readily leached from an organic soil and high organic matter sandy soil which contained no inorganic colloids. They found that addition of $\text{AlCl}_3$ resulted in large amounts of exchangeable $\text{Al}$ which almost completely stopped leaching of phosphorus.

Logan and Mclean (1973) studied the movement of $^{32}\text{P}$ labelled monocalcium phosphate in columns of three soils of Rossmoyne, Toledo and Wauseon from Ohio, U.S.A. and reported that leaching of phosphorus increased with phosphorus application rate and intensity of leaching; constant head leaching resulted in greater movement of $^{32}\text{P}$ out of the surface layer with greater accumulation in the leachate compared to
intermittent leaching. They recovered $^{32}\text{P}$ in the nonionic form in the leachate and obtained significant amounts of $^{32}\text{P}$ in the leachate of sandy loam soil at the highest phosphorus application rate.

Rao and Datta (1979) studied the movement of monocalcium orthophosphate applied in labelled form (200 kg/ha) to the surface of a column of laterite soil from Kharagpur, India and found that the total quantity of phosphorus moved out of surface and subsequently retained in successive layers up to 25 cm was 77 per cent in constant head as against 66 per cent under intermittent leaching and there was no tangible accumulation of $^{32}\text{P}$ in the leachate in either case.

Recently, Hira and Singh (1978) studied the rate of phosphorus diffusion from fertilizer applied at the soil surface using Fick's law of diffusion and determined the diffusion coefficient of phosphorus from a knowledge of the tortuosity factor and phosphorus adsorption isotherm. They found that phosphorus diffusion coefficient calculated from Nye's equation (1968) did not prove suitable at very low or high concentration of phosphorus at the soil surface but phosphorus diffusion coefficient calculated from the experimental data increased linearly with the square root of phosphorus concentration applied as the source.

Limited data are available on the relative rates of movement and diffusion of ortho- and pyrophosphate anions in different soils. Gunary (1966) studied these parameters using labelled ortho- and pyrophosphate anions ($\text{NaH}_2^{32}\text{PO}_4$ and $\text{Na}_2\text{H}_2^{32}\text{P}_2\text{O}_7$) in two British agricultural soils (soil characteristics not indicated by the authors) and reported that the total quantity of phosphate moved beyond the basal section of
one of the soils was greater with orthophosphate than with pyrophosphate, whether the movement was by mass flow or diffusion; but for the other soil, the mass flow rates were similar for the two forms of phosphate although the diffusion of orthophosphate was greater than that of pyrophosphate. Hashimoto and Lehr (1973) examined the mobility of ortho-, pyro-, tripoly-, longchain polyphosphates of ammonium and cyclic tri- and tetrametaphosphates of ammonium applied to surface columns of soil from Alabama, U.S.A. These authors reported that the total distance of movement and distribution patterns of water-soluble phosphorus were similar for all the phosphates tested but the tri- and long chain polyphosphates differed markedly in the degree of immobilization of phosphorus and differed significantly in the positions of maximum retention of phosphorus in the soil columns. Similarly, Khasawneh et al. (1974) studied the mobility of orthophosphate as well as pyrophosphate by using diammonium orthophosphate (DAP), triammonium pyrophosphate (TPP) and ammonium polyphosphate (APP) in columns of Hartsells fine sandy loam, U.S.A. for 4 weeks under water movement and found that the extent of phosphorus movement from all three sources was generally similar; comparatively, the maximum mobility range of DAP was up to 3 cm whereas those of TPP and APP were up to 2 cm.

A.2. Adsorption behaviour of ammonium ortho- and pyrophosphates in soils

Attention has already been directed to the fact that the molecular forces at the surface of a liquid or a solid are in a state of unbalance or unsaturation. As a result of the unsaturation, solid and liquid surfaces tend to satisfy their residual forces by attracting onto
and retaining on their surfaces gases or dissolved substances with which they come in contact. This phenomenon of concentration of a substance on the surface of a solid or a liquid is called adsorption. The substance thus attracted to a surface is said to be the adsorbed phase, while the substance to which it is attached is the adsorbent. In case of absorption, a substance is not only retained on the surface but also passes through the surface to become distributed throughout the body of solid or liquid (Maron and Prutton, 1961). The reverse process, namely, the movement of the substance from the solid phase to the solution, is conveniently called desorption (Wiklander, 1950).

Because of soil complexity, most studies on the mechanism of phosphorus sorption have been conducted with individual soil minerals such as pure clays (Low and Black, 1950; Hsu and Rennie, 1962; Bache, 1964; Juo and Fox, 1977). Phosphate is adsorbed on the clay surface as well as on fine particles of minerals including colloidal forms of iron and aluminium. Phosphorus adsorption behaviour has been frequently used to characterize the phosphorus supplying power of soil (Dean, 1949; Olsen, 1953; Hamwell, 1957; Fried and Broeshart, 1967). Rajan et al. (1974) observed that at low phosphate adsorption corresponding to low phosphate concentration, adsorption on hydrous alumina took place mainly by dissolving aquo-groups (Al-H₂O) with increase in phosphate concentration hydroxyl groups (Al-OH) become predominantly the sites of adsorption. At still higher concentration of phosphate the hydroxyl bridge linking aluminium atoms (Al-OH-Al) were broken creating new sites which were responsible for additional adsorption of phosphate.
Rajan and Fox (1975) reported that phosphate adsorption in tropical acid soils increases at higher pH, followed by preferential concentration but silicate is released throughout the adsorption reaction. At higher concentration, adsorbed phosphate is capable of displacing the structural silicate ions of clays. Moreover, the phenomenon becomes complicated by the pH of the system, clay co-ion presence, and absence of organic matter and nonsilicate iron compounds (Hayman, 1975).

Fox and Kamprath (1971) reported that soils with organic colloids have generally very low adsorption capacity. However, according to Adrikhin and Vokora (1967) such adsorption is inversely related to the soil moisture content.

Muljadi et al. (1966) investigated phosphorus-adsorption on two aluminium oxides (gibbsite and boehmite) and clay (kaolinite) over a pH range from 3 to 10 with phosphorus concentrations from $10^{-5}$ to $10^{-1}$ M. They found three distinct adsorption regions, namely, (a) at low concentration of phosphorus ($10^{-4}$ M), (b) at intermediate concentrations of phosphorus ($10^{-4}$ to $10^{-1}$ M) and (c) at medium to high concentrations of phosphorus ($10^{-3}$ to $10^{-1}$ M). They suggested that the reaction sites in the regions (a) and (b) were responsible for adsorption due to aluminium atoms located on the edge face of the crystal lattice and that the region (c) was responsible for the linear adsorption isotherm.

Several workers have found that an increase in acidity increased the amount of phosphate adsorbed by soils and clay systems (Muljadi et al., 1966; Syers et al., 1973; Anderson et al., 1974) whereas
Reeve and Summer (1970) found that liming of oxisols failed to reduce phosphate fixation.

A number of attempts have been made in the past to provide theoretical support to experimental data pertaining to quantitative descriptions of short term reaction between soils and orthophosphate. Freundlich and Langmuir equations (Olsen and Watanabe, 1957; Gunary, 1970) were derived to describe the adsorption of materials on solids and have provided a common way of describing mathematically phosphorus sorption by soils. The Freundlich equation is given as follows:

\[ Y = aC^b \quad \text{or} \quad \log Y = \log a + b \log C \]

where \( Y \) is the amount of phosphorus adsorbed per unit weight of soil, \( C \) is the concentration of phosphorus in solution and \( a \) and \( b \) are constants varying with soils. This adsorption isotherm is purely empirical and the constants have no physical meaning. The Freundlich equation has been used to describe the adsorption of phosphate by soils (Russel and Prescott, 1916; Low and Black, 1950).

The Langmuir equation modified by Olsen and Watanabe (1957) for the determining the adsorption maxima of phosphorus concentration is given by

\[ \frac{C}{Y} = \frac{C}{S} + \frac{1}{kS} \]

where \( C \) is the equilibrium concentration of phosphate in solution (\( \mu g \ P/ml \)), \( Y \) is the quantity of phosphate adsorbed (\( \mu g \ P/g \ soil \)), \( k \) is a constant, and \( S \) is the phosphate adsorption maximum (\( \mu g \ P/g \ soil \)). From this equation \( S \) can be obtained if the plot of \( \frac{C}{Y} \) against
C is linear since then the slope is equal to \( \frac{1}{S} \). The Langmuir equation has the advantage of providing estimates of parameters that indicate the bonding energy between phosphorus and the surfaces of the particles and capacity of these surfaces to sorb phosphorus, if the conditions described by Langmuir (1918) are fulfilled. Olsen and Watanabe (1957) reported that adsorption of phosphorus by soils from dilute solution showed a closer agreement with the Langmuir isotherm than with the Freundlich isotherm.

Gunary (1970) noted a curvilinear trend in the Langmuir plot of phosphorus sorption by soils and proposed the addition of a quadratic term to the Langmuir equation as follows:

\[
\frac{C}{Y} = A + BC + D / C \quad \text{or} \quad \frac{1}{Y} = B + \frac{A}{C} + \frac{D}{\sqrt{C}}
\]

where \( A, B \) and \( D \) are constants, \( Y \) is the adsorbed phosphate, \( C \) is the equilibrium concentration of phosphate in solution. As the values of \( C \) increase to infinity, the \( Y \) approaches \( S \), the phosphate adsorption maxima and is equal to \( \frac{1}{B} \). In this equation the square root term is added to describe the curvature observed when \( \frac{C}{Y} \) is plotted against \( C \). He interpreted this curvature as meaning that the soil would adsorb a small amount of phosphate firmly, a slightly greater amount less firmly and so on.

The adsorption maxima calculated from the Langmuir equation were generally found to be higher for pyrophosphate than for orthophosphate, even when allowance was made for the fact that one pyrophosphate
ion contains two phosphorus atoms (Sutton and Larsen, 1964; Gunary, 1966). Similarly, Blancher and Hossner (1969b) reported that the phosphorus adsorption capacities for orthophosphate (NaH$_2$PO$_4$$ \cdot $H$_2$O), pyrophosphate (Na$_4$P$_2$O$_7$$ \cdot $10H$_2$O) and tripolyphosphate (Na$_5$P$_3$O$_{10}$) were 462, 965 and 706 μg P/g soil, respectively, whereas trimetaphosphate (Na$_3$P$_3$O$_4$) was not appreciably adsorbed by this soil.

In Indian soils, Gaikwad and Patnaik (1969) and Singh (1973) reported that the relation between phosphate retention and equilibrium phosphate concentration complied with the Freundlich equation. Subramanian (1965) observed that the phosphate adsorption by some Indian soils and clays would be defined by Langmuir's equation. Bahl and Sinha (1971) and Vig and Dev (1975) also found their data on phosphorus adsorption to fit the Langmuir equation, in spite of the fact that the adsorption sites are localised and are not uniform and there is interaction between the adsorbate molecules. Gupta et al. (1977) and Narasinha et al. (1979) while working with some soils of Haryana and Andhra Pradesh, respectively, also found that phosphorus adsorption by those soils could be described by the Langmuir equation. Recently, Savant and Tambe (1979) noted positive linear relationships between orthophosphate and pyrophosphate sorption maxima computed using Langmuir equation and amounts of anhydrous NH$_3$ on noncalcareous, calcareous and laterite soils from Maharashtra, India. They further reported that indices of bonding energy of orthophosphate and pyrophosphate increased exponentially as ammoniation level of the soils increased from 33 to 100% of ammonia retention capacity.

Syers et al. (1973) interpreted the curvilinear shape of a Langmuir plot of phosphorus sorption of soils as indicating the presence
of two or three types of sorption sites. Similarly, other workers (Holford et al., 1974; Holford and Mattingly, 1975; 1976b; Rajan, 1975a, 1975b; Rajan and Fox, 1975) used Langmuir equations with terms of two surfaces with differing affinity and maxima terms. Ryden et al. (1977) used equations with terms for three surfaces.

The electrostatic effect was included in the equations of Bowden (1973a) and Bowden et al. (1973b, 1977) while considering the decreasing affinity of surface of soil with increasing adsorption. The model of their equations is a complex one decreasing not only the effects on adsorption of changes in concentration but also effects of changes in pH and in the concentration of supporting electrolyte.

Recently, Harter and Baker (1977) critically examined the Langmuir adsorption equation for the estimation of parameters of adsorption maxima of phosphate and bonding energy and reported that the equation can be used to obtain a calculated phosphate adsorption maximum for comparison to other adsorbent properties but not for the adsorption dynamics and bonding energy, due to the neglect of the effect of desorbed ions in the equilibrium solution obtained for the curvilinear nature of the C/Y/m vs C plots (where C is the equilibrium phosphorus concentration, Y/m is the amount of phosphorus adsorbed per unit mass adsorbent).

Using the proposed equation by Langmuir for adsorption on more than one surface of adsorbent, Holford et al. (1974) obtained near-perfect fits to phosphate adsorption isotherm data for 41 widely varying soils from Britain and Australia. Holford and Mattingly (1976a)
have suggested that the Langmuir parameters may also be used to calculate the phosphate buffer capacity which integrates the intensity and capacity aspects of adsorption into one parameter.

Recently, Barrow (1978) attempted to compare the various adsorption equations (Langmuir, Freundlich, Gunary, Double-Langmuir) using one of the criteria for goodness of fit such as the residual sums of squares as the basis on a Western Australian soil and found that these equations generated very similar curves plotting phosphate adsorbed (μg P/g soil) vs phosphate concentration in solution (μg P/ml).

In summary, it is evident that there are divergent views regarding the computations and significance of bonding energy of phosphate in soils based on the original Langmuir equation or its modifications described above. However, there is general agreement in literature that the values of phosphate adsorption maxima of soils derived from Langmuir equation (Olsen and Watanabe, 1957) or modified Langmuir equation (Gunary, 1970) form a valid basis for describing the comparative adsorption behaviour of different adsorbates (phosphate ions) in soils. This approach has been used in the present investigation as described in the following Sections.

Despite the emphasis on the magnitude, extent and description of phosphorus sorption by soils, relatively few studies have been directed towards relating phosphorus sorption characteristics of soils with their capacities to supply phosphorus to another sorbing surface such as a plant root. Woodruff and Kasprath (1965) enriched soils with phosphorus on the basis of their adsorption maxima and measured crop...
growth on these soils. They reported generally increasing yields of dry matter with increasing degrees of saturation of the sorption maxima although both the magnitude of sorption maxima and the degree of saturation affected the accumulation of phosphorus by plants. Similarly, Fox and Kamprath (1970) used phosphorus sorption isotherms to estimate the quantity of phosphorus sorbed by soils in order to be in equilibrium with a solution of phosphorus concentration of 0.2 μg/ml; although this estimate of phosphorus requirement generally agreed well with plant accumulation of phosphorus, it sometimes failed to evaluate the phosphorus supplying capabilities of widely differing soils.

B. MATERIALS AND METHODS

The soils selected for the study were a red sandy loam from Raigarh, Madhya Pradesh, a laterite from Ratnagiri, Maharashtra, a medium black clay loam from Trombay, Maharashtra and a deep black clay loam from Poona, Maharashtra. Description of the major characteristics of the red sandy loam, laterite and medium black clay loam soils used in the mobility and adsorption studies are given in Chapter II under Section B.3. The physicochemical indices of these soils are reported in Table 1 (Chapter II, Section B.3). The deep black clay soil (Pellustert) is clay to clay loam in structure, containing 2:1 layer type minerals (montmorillonite/illite), having high base exchange capacity, alkaline pH, high biological activity and deficient in phosphorus content. These soils were weighed and transferred to glass leaching containers so that after compaction it provided a depth of 15 cm (Fig. 7). The soils were packed into the leaching containers with a packing block similar to
Fig. 7. Schematic diagram of leaching container.
that described for measurement of hydrolytic conductivity (USDA, 1954). The soils were maintained at field capacity for a week and the $^{32}\text{P}$-labelled compounds, namely, ammonium dihydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), triammonium pyrophosphate monohydrate ($\text{(NH}_4)_3\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}$) and tetraammonium pyrophosphate ($\text{(NH}_4)_4\text{P}_2\text{O}_7$), each having a specific activity of 0.15 mCl $^{32}\text{P}$/g $\text{P}_2\text{O}_5$, were applied at the rate of 80 kg $\text{P}_2\text{O}_5$/ha to the smoothed top surface of the soil columns. Glasswool was packed on the surface to reduce the disturbances of soil when water was applied. Duplicate columns of the four soils were maintained at field capacity moisture status by replenishing daily the water lost through leaching and evaporation; between 25 and 50 cm of water was added to different soils over the duration of the experiment. For diffusion, another set of columns in duplicate, of two soils, namely, laterite and medium black clay loam were sealed after moistening to field capacity and phosphate addition; no further quantities of water were added throughout the experimental period. The columns were stored at $24 \pm 1^\circ\text{C}$ for 8 weeks, after which they were cut into segments 2.5 cm thick. Soil in each segment was air-dried and assayed for $^{32}\text{P}$ using a thin end-window G-M counter. The radioassay data were corrected for detector and unlabelled soil control background as well as for self absorption of $\beta$-radiation where applicable.

The adsorption maxima for the orthophosphate and the two pyrophosphates in the four experimental soils were determined by shaking 5 g samples of soil with 100 ml of 0.01 M CaCl$_2$ containing carrier free $\text{H}_3\text{PO}_4$ for 18 h at $24 \pm 1^\circ\text{C}$. The $E_{18h}$ value is the quantity of soil phosphate that exchanged with labelled phosphate
during the shaking period. The adsorption maxima were computed by the Langmuir equation used by Olsen and Watanabe (1957) as shown below:

\[ \frac{C}{Y} = \frac{C}{S} + \frac{1}{kS} \]  

(4)

The adsorption maxima were also computed by the Gunary's modified equation which includes a square-root term as given below:

\[ \frac{1}{Y} = B + \frac{A}{C} + \frac{D}{\sqrt{C}} \]  

(6)

The parameters involved in these equation (4) and (6) have been described in Section A.2 of this Chapter. As the values of C (Eqn. 6) increase to infinity, the Y approaches S, the phosphate adsorption maxima and is equal to \( \frac{1}{B} \).

C. RESULTS AND DISCUSSION

Data on the movement of tri- and tetrammonium pyrophosphates and ammonium orthophosphate in the red sandy loam and laterite soils under conditions of continuous replenishment of moisture are reported in Table 3. Corresponding data on medium black clay loam and deep black clay loam soils are presented in Table 4.

Data in Table 3 indicate that in the red sandy loam where approximately 50 cm of water was leached through the soil column, a small fraction of the applied phosphate (10 per cent of the orthophosphate and 5-8 per cent of the pyrophosphates) moved out of the top 2.5 cm layer to which the compounds were applied; these quantities were transported to the 2.5 - 5.0 cm deep segment of the soil column. It is also
### Table 3

Movement of pyro- and orthophosphates through red sandy loam and laterite soils under conditions of continuous replenishment of moisture

**Duration of experiment:** 56 days

<table>
<thead>
<tr>
<th>Depth of soil column</th>
<th>Distribution of applied phosphate in soil column (% of total)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Red sandy loam (NH₄)₃P₂O₇·H₂O (NH₄)₄P₂O₇ NH₄H₂PO₄</td>
</tr>
<tr>
<td>0 - 2.5 cm</td>
<td>92.0 94.6 90.4</td>
</tr>
<tr>
<td>2.5 - 5.0 cm</td>
<td>8.0 5.40 9.6</td>
</tr>
<tr>
<td>5.0 - 7.5 cm</td>
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<tr>
<td>7.5 - 10.0 cm</td>
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</tbody>
</table>
Table 4

Movement of pyro- and orthophosphates through medium black clay loam and deep black clay loam soils under conditions of continuous replenishment of moisture

Duration of experiment: 56 days

<table>
<thead>
<tr>
<th>Depth of soil column</th>
<th>Distribution of applied phosphate in soil column (% of total)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Medium black clay loam</td>
</tr>
<tr>
<td></td>
<td>(NH₄)₃HP₂O₇·H₂O</td>
</tr>
<tr>
<td>0 - 2.5 cm</td>
<td>100.0</td>
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<td>2.5 - 5.0 cm</td>
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<td>5.0 - 7.5 cm</td>
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evident (Tables 3 and 4) that in the laterite columns, through which about 50 cm of water was leached, as well as in the medium black clay loam and deep black clay loam columns, which were leached with nearly 25 cm of water, all the pyro- and orthophosphates were retained in the top 2.5 cm soil layer.

Table 5 reports data on the mobility of phosphates in the laterite and medium black clay loam under conditions where phosphate movement was, in the main, by the diffusion process. Data show that no detectable quantities of either the pyrophosphates or the orthophosphate moved out of the top 2.5 cm segment to which the phosphates were applied in the two soils.

Studies of Philen and Lehr (1967) and Cate and Gurney (unpublished TVA data) on the reactions of several clays and other soil minerals with ammonium pyrophosphates indicated that over periods up to 200 days little precipitation of the phosphate occurred. This effect, which is in marked contrast to the reactions of the orthophosphate, was attributed to the sequestering action of pyrophosphates on cations associated with the clays and the iron and aluminium oxides in the soil minerals, and led these authors to suggest that water-soluble pyrophosphates would move further through the soil than water-soluble orthophosphate.

However, under conditions of the present study, the mobility of the tri- and tetraammonium pyrophosphates was similar to that of ammonium orthophosphate in soils of widely different characteristics. Recent work of Hashimoto and Lehr (1973) on a Hartsells fine sandy loam
Table 5

Movement of pyro- and orthophosphates through laterite and medium black clay loam soils under diffusion conditions.

Duration of experiment: 56 days

<table>
<thead>
<tr>
<th>Depth of soil column</th>
<th>Distribution of applied phosphate in soil column (% of total)</th>
<th>Laterite</th>
<th>Medium black clay loam</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(NH₄)₃HP₂O₇·H₂O</td>
<td>(NH₄)₂P₂O₇</td>
<td>NH₄H₂PO₄</td>
</tr>
<tr>
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<td>7.5 - 10.0 cm</td>
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</table>

*Soil columns wetted to field capacity and sealed.
from Alabama, United States of America, which is the only report available in the literature on comparative movement of ammonium ortho- and pyrophosphates in soil columns, also indicates that gross movement of the ortho- and pyrophosphates over a period of 4 weeks was remarkably similar.

The plots of adsorption data of C/Y vs C according to Langmuir equation for ammonium ortho- and pyrophosphates in laterite and medium black clay loam soils as examples are shown in Fig. 8 and 9, respectively. It may be noted that the Langmuir plots for the medium black clay loam soil (Fig. 9) indicate a degree of curvature at the higher equilibrium concentration of both ortho- and pyrophosphates.

The adsorption maxima for pyro- and orthophosphates for four soils determined by the Langmuir equation used by Olsen and Watanabe (1957) are reported in Table 6. Data show that the adsorption maxima are higher for the pyrophosphates than for orthophosphate in the soils examined. Since the phosphate adsorption isotherms showed a small degree of curvature especially for the medium and deep black clay loam soils, the adsorption maxima were also computed using a modified equation suggested by Gunary (1970) and accounts for the variations due to curvature from the conventional Langmuir plots. Adsorption maxima derived by the modified equation which are included in Table 6 also indicate higher values for the pyrophosphates.

The values of adsorption maxima calculated according to Langmuir equation were in the range of 14.1 to 57.7 mg P/100 g soil for orthophosphate and 32.5 to 65.6 mg P/100 g soil for the pyrophosphates.
Fig. 9(a), 9(b). A plot of adsorption data for ammonium ortho- and pyrophosphates in the medium black clay loam soil according to Langmuir.
Fig. 9(a) and 9(b). A plot of adsorption data for ammonium ortho- and pyrophosphates in the laterite soil according to Langmuir.
According to Gunary (1970),

According to Olsen and Watanabe (1957)

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Modified</th>
<th>Langmuir Value</th>
<th>Langmuir Value</th>
<th>Langmuir Value</th>
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<td>Deep black clay loam</td>
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<td>665</td>
<td>362</td>
<td></td>
</tr>
<tr>
<td>Medium black clay loam</td>
<td>621</td>
<td>670</td>
<td>320</td>
<td>225</td>
</tr>
<tr>
<td>Laterite</td>
<td>690</td>
<td>683</td>
<td>640</td>
<td>550</td>
</tr>
<tr>
<td>Red sandy loam</td>
<td>642</td>
<td>655</td>
<td>467</td>
<td>151</td>
</tr>
</tbody>
</table>

Values in Soil Adsorption maxima for pyro- and orthophosphates in soils

Table 6
Sutton and Larsen (1964) on six English soils have reported the values in the range of 19.5 to 48.3 mg P/100 g soil for orthophosphate and 46.3 to 110.6 mg P/100 g soil for pyrophosphate. The values reported on four U.S.A. soils by Hashimoto et al. (1969) were in the range of 13.4 to 64.4 mg P/100 g soil for orthophosphate and 16.4 to 167 mg P/100 g soil for pyrophosphate. It is noteworthy that these values of ortho- and pyrophosphates adsorption maxima for the four tropical soils determined in the present study are broadly similar and of the same order of magnitude to the values of both ortho- and pyrophosphates for temperate soils reported in the literature.

The ortho- and pyrophosphate adsorption maxima of experimental soils (Table 6) could be arranged in the following order: laterite (Oxisol) > deep black clay loam (Pellustert) > medium black clay loam (Pellustert) > red sandy loam (Rhodustalf).

The above-mentioned results are in broad agreement with the data of Savant and Tambe (1979) who observed that the values of sorption maxima for orthophosphate (KH$_2$PO$_4$) and pyrophosphate (K$_4$P$_2$O$_7$), on three Indian soils were in the following order: laterite soil (Inceptisol) > calcareous soil (Vertisol) > noncalcareous soil (Vertisol).

The present findings on the mobility and adsorption behaviour of ortho- and pyrophosphates in major Indian soils suggest that although differences exist between the adsorption characteristics of the ortho- and pyrophosphates in the soils examined, these are not reflected in the relative mobility of the phosphates largely because of rapid hydrolytic
degradation of the pyrophosphates to orthophosphate forms in soils especially in the zone immediately below the surface layers to which the pyrophosphates were applied.