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NATURE AND TRANSFORMATION OF CRYSTALLINE
PHOSPHATES PRODUCED BY INTERACTION OF
PHOSPHATE FERTILIZERS WITH SLIGHTLY ACID
AND ALKALINE SOILS.**

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NATURE AND TRANSFORMATION OF CRYSTALLINE PHOSPHATES
PRODUCED BY INTERACTION OF PHOSPHATE FERTILIZERS WITH SLIGHTLY
ACID AND ALKALINE SOILS

by

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INTRODUCTION

Of the major elements applied to soil as fertilizers, phosphorus is the least efficiently absorbed from the soil by plants, and hence the chemistry of phosphorus-soil interaction is a topic of major importance in soil fertility. When water-soluble phosphate fertilizers are added to soils, the fertilizers quickly dissolve and react with the soil. The nature of the products of the reaction is influenced by the chemical composition of both fertilizer and soil. Because the transformation of the original fertilizer phosphate to new and chemically different phosphates in the soil takes place in far less time than that required to grow crop plants from seed to harvest, the value of a soluble phosphate fertilizer as a source of phosphorus for plants depends to a large extent on the availability of the phosphorus in the newly formed soil phosphates.

A review of the literature indicates that the crystalline products of reaction of water-soluble phosphate fertilizers with soils are predominantly iron and aluminum phosphates in acid soils and calcium phosphates in alkaline soils. Dibasic calcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) has been identified as an important initial reaction product. This compound is sparingly soluble and, in vitro, has been observed to undergo transformation to octacalcium phosphate [$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$] in slightly acid and alkaline solutions. The latter compound, in turn, has been observed to undergo transformation to hydroxyapatite [$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$]. The solubility of the compounds decreases with each succeeding transformation.

There is some evidence that transformations of calcium phosphates observed in vitro occur also in soils, thereby decreasing the availability of phosphorus to plants. Information on the initial products formed in soils and on the transformations that may occur there with time is limited, however, perhaps because the properties of the phosphate products that might otherwise be measured by X-ray diffraction, petrographic analysis, and other techniques are masked by the large excess of nonphosphatic material normally present.

The investigation reported in this thesis was designed to overcome some of the problems of identification and hence to allow better definition of the factors affecting the formation and transformation of products of reactions of phosphate fertilizers with slightly acid and alkaline soils. The investigation was conducted in two parts.

Part I had two prime objectives. The first objective was to develop techniques for direct identification of crystalline phosphates produced in slightly acid and alkaline soils treated with soluble phosphate fertilizers. The second objective was to use these techniques to determine the effect of various factors on the nature and transformations of the crystalline phosphates formed in the initial reaction between fertilizer and soil.

Part II of the investigation was designed to complement Part I. The objectives of Part II were (i) to develop techniques for obtaining qualitative and quantitative data on the transformations of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ added to slightly acid and alkaline soils and (ii) to use these techniques to investigate the factors affecting these transformations.

REVIEW OF LITERATURE

The reactions of water-soluble phosphate fertilizers in acid soils appear to be dominated by iron and aluminum. In alkaline soils, however, precipitation of relatively insoluble calcium phosphates is favored by the higher pH and the greater content of reactive calcium. This calcium is present in the exchangeable form and often in carbonate form as well (Tisdale and Nelson, 1966).

The reactions of the slightly soluble calcium phosphates are complex, even in pure systems, and a review of the known properties of these phosphates is necessary in understanding their formation and transformation in soils.

Chemistry of the Slightly Soluble Calcium Phosphates

Only four of the slightly soluble calcium phosphates are definitely known to precipitate from aqueous solution in the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ system. They are dibasic calcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), anhydrous dibasic calcium phosphate (CaHPO_4), octacalcium phosphate [$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$], and hydroxyapatite [$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$] (Mooney and Aia, 1961; Brown, 1964). Beta-tribasic calcium phosphate [$\beta\text{-Ca}_3(\text{PO}_4)_2$] is also precipitated from aqueous solutions, but only in the presence of magnesium or smaller ions (Hayek and Neuesely, 1958). This compound is found in nature as the mineral whitlockite (Fleisch and Neuman, 1960) and in pathological calcifications (Tovborg Jensen and Rowles, 1957). The other well-established slightly soluble calcium phosphates, alpha-tribasic calcium phosphate [$\alpha\text{-Ca}_3(\text{PO}_4)_2$]

and tetrabasic calcium phosphate $[\text{Ca}_4\text{O}(\text{PO}_4)_2]$ are high temperature products and have not been found in precipitates from aqueous solutions (Mooney and Aia, 1961; Brown, 1964).

Brown (1964) stated that, of the salts listed in the preceding paragraph, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is the most soluble and has been found the easiest to precipitate in good crystalline form and with the correct composition. This salt, although metastable with respect to CaHPO_4 , can persist in dilute aqueous solutions for a long time. At high temperatures, or in concentrated solutions, its transformation to the anhydrous form is rapid.

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ has been shown to hydrolyze to more basic calcium phosphates under certain conditions. Moreno et al. (1960a) investigated the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at 25°C . in water and dilute phosphoric acid solutions in the absence of carbon dioxide. They found that this salt hydrolyzed to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ when the pH of the solution was 6.38 or higher. The extent of the hydrolysis increased with an increase in the initial pH of the solution. Rowles (1958) found that crystals of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were formed on the surface of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ by the action of water. Development of these crystals was inhibited or delayed by the presence of 10^{-5}M copper ions or 10^{-3} magnesium ions.

By adding $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to distilled water with continuous stirring at 85°C ., Brown et al. (1962) were able to detect $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ crystals within 5 minutes. These crystals grew at the expense of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ for about 15 minutes until all the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ had disappeared. At about this time, aggregates of fine acicular crystals of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ were first observed. These aggregates developed slowly at the expense of the

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, which dissolved. After the mixture had been allowed to cool and stand overnight, the remaining $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was found to have been converted to $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. A transformation from $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ is thought to occur in dental calculus (Brown et al., 1957). $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ can also form a more basic phosphate by reaction with dilute fluoride solutions to produce fluorapatite $[\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6]$ (Kurmies, 1953).

Brown (1964) stated that CaHPO_4 , in contrast to the dihydrate, is difficult to prepare in good crystalline form and with stoichiometric composition. At room temperature, the dihydrate will usually precipitate in preference to the anhydrous form, but the latter is preferred at high temperatures, in concentrated solutions, or after longer periods of reaction. At high temperatures and concentrations, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ also is likely to be a stable phase. The composition of the solution will determine whether CaHPO_4 or $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ is the more stable phase.

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was described long ago by Berzelius (1845) and Warrington (1866), but its existence as a distinct crystalline species was not established until recently. Carlström (1955) and Neuman and Neuman (1958) questioned the existence of the species, but X-ray studies by Brown et al. (1957) and Bjerrum (1958) established $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ as a unique compound. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ has frequently been found in systems more basic than dicalcium phosphate (Arnold, 1950; Tovborg Jensen and Hansen, 1957; Hayek et al., 1960; Bjerrum, 1949), and it is now known that dental calculus contains this phosphate (Tovborg Jensen and Hansen, 1957; Rowles, 1958; MacGregor and Brown, 1965; Saxton, 1968).

A number of investigators have shown that $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ will hydrolyze to form $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. Arnold (1950) found that a solid of approximately $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ composition transformed slowly at room temperature to a solid with composition approximating $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. MacGregor and Brown (1965) obtained evidence to support their view that, in children, bone mineral is first formed as $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and that an aging process or hydrolysis converts the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ into $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ in adult bone. Recent work by Simpson (1966) showed that initially precipitated $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was converted to $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ in a solution of pH 10.4 at 25°C . High partial pressures of carbon dioxide, however, were found to favor the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ over apatite when calcite was reacted with a solution of sodium phosphate. In the presence of fluoride, apatite formed even under high carbon dioxide concentration. Presumably the final product in this case was fluorapatite, although the author did not state so.

At higher than room temperatures, particularly above 50°C ., $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ has been shown to hydrolyze readily to $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ (Brown et al., 1962). Working with a single crystal of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, Brown et al. found that the Weissenberg pattern of the crystal showed reflections for both $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ after it had been boiled in water for 6 hours. After 72 hours the Weissenberg pattern indicated that the product was essentially all $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$.

The hydrolysis of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ is inhibited by magnesium at concentrations as low as 0.001N. The inhibition is a result of the formation of a magnesium complex on the terminal edges of the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$

crystals (Brown et al., 1962). In contrast, fluoride is known to induce the hydrolysis of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ (Farr et al., 1962), and this reaction proceeds much faster than that between $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ and fluoride (Brown et al., 1962).

$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ is the most basic calcium phosphate that can precipitate from aqueous solution (Brown, 1964). Bassett (1917) stated that it is the only calcium phosphate which is not decomposed by water. However, in aqueous solutions containing low concentrations of fluoride ion, $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ is the most stable calcium phosphate (Farr et al., 1962). The replacement of hydroxyl in $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ by fluoride to form $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ nonetheless occurs very slowly (Russell, 1961; and Brown et al., 1962).

Many investigators have observed that precipitated calcium phosphates which give apatitic X-ray patterns often have mole ratios of calcium to phosphorus less than that in $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ (Arnold, 1950; Carlström, 1955; Eisenberger et al., 1940; Neuman and Neuman, 1958; Posner et al., 1960; Stutman et al., 1962; Winand and Dallemagne, 1962). Suggestions by these investigators as to the reason for this apparent anomaly include (a) solid solutions among different phosphates with varying ratios of calcium to phosphorus, (b) defect-apatite structures, (c) isomorphous replacement of calcium ions of apatite by hydronium ions, and (d) solids with compositions that have been altered by adsorption or by other changes in the calcium to phosphorus ratio on the surface.

Brown et al. (1962) stated that none of these explanations offered is entirely satisfactory. Brown et al. conducted X-ray and petrographic in-

vestigations of basic calcium phosphates, of which the mole ratios of calcium to phosphorus ranged from 1.33 [that in $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$] to 1.67 [that in $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$]. They obtained evidence to support the suggestion of Brown et al. (1957) that $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ form crystalline interlayered or lamellar mixtures, analogous in this respect to clays. Both $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ have a layer-type structure (Taves, 1963; Brown, 1962), and the similarity of part of the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ structure to that of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ allows epitaxial overgrowths of one compound on the other (Brown, 1962). Preparations with ratios of calcium to phosphorus intermediate between those of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were found by Brown et al. (1962) to give X-ray powder diffraction patterns with lines for both compounds. The relative intensities of the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ lines generally decreased, and those of the $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ lines increased, as the ratio of calcium to phosphorus increased.

Reaction of Water-Soluble Phosphate Fertilizers with Soils

Monobasic calcium phosphate monohydrate $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$, the main phosphatic constituent of superphosphate, is one of the most widely used water-soluble phosphates, and hence the interaction of this salt with soils has been studied extensively (Huffman, 1962). Of the other water-soluble phosphate fertilizers in use, monobasic ammonium phosphate $(\text{NH}_4\text{H}_2\text{PO}_4)$ and dibasic ammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$ are the most important (Lindsay and Taylor, 1960).

Fertilizer dissolution process

Lehr et al. (1959) studied the dissolution process in some detail. When a water-soluble salt such as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, or $(\text{NH}_4)_2\text{HPO}_4$ is placed in a moist soil, water vapor moves from the surrounding soil into the fertilizer to form an almost saturated solution. This concentrated solution is removed from the granule by the capillary action of the soil. The process of inward movement of water and outward movement of solution continues until the concentration of the solution is decreased by dilution or precipitation of the phosphate to a level at which no osmotic gradient remains.

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ does not dissolve congruently in water but hydrolyzes to form phosphoric acid and dicalcium phosphate (Farr, 1950). Lindsay and Stephenson (1959a) showed that shaking excess $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ with water at room temperature resulted in the formation of a solution which was in metastable equilibrium with freshly precipitated $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and undissolved $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. After 24 hours the composition of this so-called metastable triple-point solution changed to that of the stable triple-point solution as the more stable CaHPO_4 slowly precipitated out and the initially formed $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ dissolved. The metastable triple-point solution was found to have a pH of 1.48 and to be 3.98 M in phosphorus and 1.44 M in calcium. The triple-point solution had a pH of 1.01 and was 4.50 M in phosphorus and 1.34 M in calcium. Lindsay and Stephenson investigated the dissolution of a band of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ in soil and found that the solution moving out of the band approximated very closely the metastable triple-point solution.

According to Brown and Lehr (1959), the composition of the solution leaving a $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ granule is independent of the composition of the surrounding soil. Using phase rule data, they calculated the quantity of dicalcium phosphate that should remain as residual material at the site of the original $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ source. They estimated that 28% of the phosphorus would be precipitated if only CaHPO_4 formed, whereas 21% of the phosphorus would be precipitated if only $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ formed. Residues from pellets of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ allowed to dissolve in four soils kept at 0.5 moisture equivalent were found to contain between 27% and 30% of the original phosphorus. Hinman et al. (1962) found that the mean amount of phosphorus remaining at $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ granule sites in soil at four temperatures and two water levels was 20.2%.

The effect of associated nonphosphatic salts on the transformation of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was investigated by Bouldin et al. (1960). They found that the fraction of added phosphorus that remained as a residue at the granule site varied from 92% when CaCO_3 was mixed with the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, to only 2% when ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ was added.

The ratio of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to CaHPO_4 remaining as residues of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ dissolution varies with moisture and temperature. Lehr et al. (1959) and Bouldin et al. (1960) found that high soil moisture and low temperatures favored the dihydrate over the anhydrous form. High soil temperatures in conjunction with high moisture, however, favored the dihydrate.

Of interest here is the finding by Bouldin et al. (1960) that when CaCO_3 was mixed with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ in soil, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ formed as a

major phase in addition to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ formed extensively as concretionary deposits upon residual calcite crystals during the 3-week incubation period. Lehr and Brown (1958) isolated the residues of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ from soils which had been cropped for approximately 4 months. In three acid soils the residues were identified as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 , the latter representing approximately 5% of the residue in each soil. In two basic soils to which $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ had been added, only a few crystals of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were detected, the main phase in the residue being $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$.

Unlike $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ dissolve congruently in water with no hydrolysis or precipitation of new phases. The saturated solution produced by $\text{NH}_4\text{H}_2\text{PO}_4$ has a pH of 3.47 and is 2.87 M in phosphorus and ammonium, whereas $(\text{NH}_4)_2\text{HPO}_4$ produces a saturated solution of pH 7.98 and is 3.82 M in phosphorus and 7.64 M in ammonium (Lindsay et al., 1962). The pH and the cation contents of the saturated solutions of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ are so different that some diversity is to be expected in the nature of the crystalline phosphates formed when these solutions interact with a given soil.

Identification of reaction products

<p><u>Identification after isolation from soil</u></p>	<p>Some success in identifying</p>
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the crystalline phosphates produced in soils treated with soluble phosphate salts has been achieved by probing small quantities of the phosphates from the soil and examining the isolated substances in one way or another.

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 residues left after the dissolution of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ granules in soil have been isolated and subsequently identified with relative ease. The coarsely crystalline residues have been separated from the soil by "handpicking" under a microscope (Lehr and Brown, 1958; Lehr et al., 1959) or by use of the vacuum procedure described by Bouldin and Sample (1958). The nature of these residues and the factors affecting their composition have been discussed previously.

Hinman et al. (1962) were able to probe small amounts of reaction products from the soil immediately surrounding the site of a $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ pellet which had reacted with a calcareous very fine sandy loam for 2 weeks. Collection of the phosphate was facilitated by the accumulation of relatively coarse crystals in the form of Liesegang rings (or periodic precipitates). After being washed with acetone, the crystals were identified by their optical properties as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 , the former being the most prevalent phase.

Racz and Soper (1967) used X-ray diffraction analysis to identify the crystalline phosphates produced in two calcareous soils treated with pellets of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$. The compounds probed from the soil to which $\text{NH}_4\text{H}_2\text{PO}_4$ had been added were identified as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and dibasic magnesium phosphate trihydrate $[\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}]$. Only $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was formed in the soil having a ratio of 2.12 moles of water-soluble calcium to 1 of water-soluble magnesium, whereas both $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were formed in the soil with a ratio of 0.69 mole of water-soluble calcium to 1 of water-soluble magnesium. Both soils reacted with $(\text{NH}_4)_2\text{HPO}_4$ to form only $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$.

Nagelschmidt and Nixon (1944) identified the phosphate coating on chalk fragments isolated from a field to which superphosphate had been added for over 100 years. Removal of the calcium carbonate by heating the chalk to 800°C . and extracting the resulting calcium oxide with a carbon dioxide-free sucrose solution left a residue which gave the X-ray powder pattern of an apatite.

Of relevance here are the investigations designed to detect the transformations of calcium phosphates with time after their precipitation in soil. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is an important initial soil-fertilizer reaction product in the vicinity of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{NH}_4\text{H}_2\text{PO}_4$ fertilizer (Lindsay *et al.*, 1959; Lindsay and Taylor, 1960; Racz and Soper, 1967). Above pH 5, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is theoretically unstable with respect to CaHPO_4 , $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, and $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ (Moreno *et al.*, 1960b).

Lehr and Brown (1958) investigated the possible transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ added to a number of acid and alkaline soils which were cropped for approximately 4 months. The phosphate residues were carefully isolated from the soils and subjected to petrographic and X-ray examination. Lehr and Brown found that in acid soils the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was unaltered, whereas in three alkaline soils it had changed extensively to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and possibly $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. In a fine sandy loam limed to pH 5.4, 6.6, 7.2, and 7.5, the amount of alteration to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ increased from pH 6.6 to 7.5, no alteration being observed at pH 5.4. In conjunction with these experiments, Lehr and Brown also added CaHPO_4 , $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, and $\text{Ca}_3(\text{PO}_4)_2$ to the same range of acid and alkaline soils. However, none of these compounds appeared to have changed physically or

chemically during the 4-month experiment.

Larsen et al. (1964) added $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to both acid and alkaline soils and, after 26 months, were able to recover from 0% to 20% of the original phosphate in granules separated from the soil. X-ray examination showed only $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to be present in the residues. Similar results were obtained by Racz and Soper (1967), who incubated $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in four alkaline soils (containing from 0.17% to 25.20% carbonate) and in CaCO_3 and MgCO_3 . After 1, 3, and 6 months, samples of the phosphate were recovered and subjected to X-ray analysis. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was formed after 1 month when $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was incubated in CaCO_3 ; however no alteration product was detected in the MgCO_3 or any of the four soils, even after 6 months.

Inference from phosphates precipitating from fertilizer-solution extracts of soil Lindsay and Stephenson (1959b), being aware of the difficulties involved in isolating small quantities of crystalline reaction products from soils treated with phosphate fertilizers, developed a new approach to the problem. These investigators devised a technique to simulate a sampling of the reacting solution in the soil surrounding a 5-mesh fertilizer granule at distances of 0.2, 0.4, 0.6, ..., 2.0 mm. from the granule. The crystalline phosphates that formed when the solutions were allowed to stand were presumed to be the same as the crystalline phosphates that would have formed in soil around the hypothetical granule, but the components could be identified with comparative ease because of the absence of soil.

The details of the method of Lindsay and Stephenson are as follows.

Three hundred and fifty grams of air-dry soil were shaken with 700 ml. of saturated $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ solution for periods of 1 to 16 hours. The suspension was filtered, a quantity of the filtrate was set aside, and the remainder of the filtrate was shaken with a smaller quantity of soil, maintaining the ratio of 1 gram of soil to 2 ml. of solution as before. This sequence of operations was repeated until ten quantities of soil had been equilibrated successively with the solution. The pH of each solution was measured, the content of phosphorus, iron, aluminum, manganese, and calcium was determined, and the portion of the solution not used for these analyses was allowed to stand in a stoppered flask for 3 months. The solids that precipitated were washed with water and acetone and then examined by X-ray and petrographic methods.

Using this technique Lindsay et al. (1959) reacted the metastable triple-point solution (the solution saturated with respect to $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) with a slightly calcareous loam. Analysis of the successive filtrates showed that appreciable amounts of aluminum, iron, manganese, and calcium were dissolved or exchanged from the soil. The solution gradually became supersaturated with respect to calcium, iron, and aluminum phosphates, and, as the pH rose above 2.3, precipitation of phosphate was observed. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was identified as a precipitated phase in each of the ten filtrates. Only a small amount of CaHPO_4 was found, and this was mainly in the more acid filtrates which had contacted only one or two batches of soil. The only crystalline compound found in the filtrates in addition to the calcium phosphates was potassium taranakite $[\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}]$.

Investigations by Lindsay and Stephenson (1959a) had shown that the soil nearest a granule of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is repeatedly contacted by fresh emerging metastable triple-point solution as long as any $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ remains undissolved. Moreover, water vapor continues to move into the reaction zone, where it condenses and dilutes the concentrated salt solution. In an attempt to simulate this changing chemical environment surrounding a $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ source, Lindsay and Stephenson (1959c) repeatedly reacted a slightly calcareous soil with the metastable triple-point solution and later with water. Soil repeatedly contacted by the saturated solution became more acid and showed continued loss of iron and aluminum to the solution. Precipitates identified in the filtrates which had stood 1 year consisted of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4) \cdot 18\text{H}_2\text{O}$, a potassium aluminum iron phosphate $[\text{H}_8\text{K}(\text{Al},\text{Fe})_3(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}]$ and a trace of CaHPO_4 . Addition of water to the soil residues increased the pH and caused further precipitation of phosphate from solution. Analysis of the filtrates after 1 year showed the presence of $\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$, $\text{H}_8\text{K}(\text{Al},\text{Fe})_3(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$, and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

A comprehensive study of the reactions of the saturated solutions of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ with soils and common soil constituents was conducted by Lindsay et al. (1962). Addition of CaCO_3 , magnesium oxide $[\text{MgO}]$, or dolomite $[\text{CaMg}(\text{CO}_3)_2]$, to the metastable triple-point solution resulted in the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 . With large additions of MgO , $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ also formed. Addition of aluminum hydroxide $[\text{Al}(\text{OH})_3]$ caused the formation of two calcium aluminum phosphates, $\text{CaAlH}(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaAl}_6\text{H}_4(\text{PO}_4)_8 \cdot 20\text{H}_2\text{O}$. Calcium ferric phosphate

$[\text{CaFe}_2(\text{HPO}_4)_4 \cdot 8\text{H}_2\text{O}]$ and a colloidal hydrated iron phosphate $[(\text{Fe}, \text{X})\text{PO}_4 \cdot n\text{H}_2\text{O}]$ were formed on addition of ferric oxide $[\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}]$. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was formed in larger quantities than any other reaction product. The excess of this substance over the others was greatest in calcareous soils.

Reaction of an acid fine sandy loam with a saturated solution of $\text{NH}_4\text{H}_2\text{PO}_4$ yielded an ammonium taranakite $[(\text{NH}_4)_3\text{Al}_5\text{H}_6(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}]$ as a reaction product. A calcareous loam reacted to form CaHPO_4 and struvite $[\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}]$. A variety of substances was produced when pure compounds were added to the $\text{NH}_4\text{H}_2\text{PO}_4$ solution. $\text{Al}(\text{OH})_3$ produced $(\text{NH}_4)_3\text{Al}_5\text{H}_6(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ formed an ammonium ferric phosphate $[\text{NH}_4\text{Fe}(\text{HPO}_4)_2]$, and $\text{Al}(\text{OH})_3$ and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ together gave $(\text{NH}_4)_3\text{Al}_5\text{H}_6(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$ and colloidal $(\text{Fe}, \text{Al}, \text{X})\text{PO}_4 \cdot n\text{H}_2\text{O}$. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was the main product of CaCO_3 addition, whereas $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ formed when $\text{CaMg}(\text{CO}_3)_2$ was added. Small amounts of MgO reacted with the $\text{NH}_4\text{H}_2\text{PO}_4$ solution to form $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ as transient phases, with hannayite $[\text{Mg}_3(\text{NH}_4)_2(\text{HPO}_4)_4 \cdot 8\text{H}_2\text{O}]$ as the persisting phase. Larger amounts of MgO produced only $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

Lindsay *et al.* found that the acid fine sandy loam reacted with the alkaline $(\text{NH}_4)_2\text{HPO}_4$ solution to form $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and a basic aluminum phosphate $[\text{NH}_4\text{Al}_2(\text{PO}_4)_2\text{OH} \cdot 8\text{H}_2\text{O}]$. Filtrates from the reaction of $(\text{NH}_4)_2\text{HPO}_4$ solution with the calcareous loam also yielded $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in addition to a calcium ammonium phosphate $[\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}]$, originally reported as $\text{Ca}_2(\text{NH}_4)_2(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$. The correct formula was given by Frazier *et al.* (1964).

When small amounts of CaCO_3 were added to the $(\text{NH}_4)_2\text{HPO}_4$ solution, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and, later, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were formed. With larger

additions of CaCO_3 , $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ appeared first but later dissolved to form mainly a calcium ammonium phosphate $[\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}]$ with lesser amounts of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. $\text{CaMg}(\text{CO}_3)_2$ formed the same reaction products as the calcareous loam, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. $\text{Al}(\text{OH})_3$ reacted with the $(\text{NH}_4)_2\text{HPO}_4$ solution to produce $\text{NH}_4\text{Al}_2(\text{PO}_4)_2\text{OH} \cdot 8\text{H}_2\text{O}$, as did the acid fine sandy loam. No crystalline reaction product was produced upon addition of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Following this comprehensive study by Lindsay et al., a number of investigators have obtained similar results using the same technique. Beaton et al. (1963) reacted a calcareous fine sandy loam with saturated solutions of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$. Infra-red analysis of the reaction products led the authors to the conclusion that $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ were the major initial reaction products obtained with $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$, respectively. Similar results were obtained by Larsen and Widdowson (1966). The reaction of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ with a calcareous clay produced $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, respectively. When the fertilizer solutions contained pyrophosphate, however, neither $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ nor $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ was formed. The authors suggested that the pyrophosphate inhibited the formation of these calcium phosphates by preventing either nucleation or crystal growth.

The ratio of water-soluble calcium to water-soluble magnesium in soil was found by Racz and Soper (1967) to be related to the types of crystalline phosphates formed when the soils interact with solutions of phosphate fertilizers. A calcareous soil with a ratio of 0.69 moles of water-soluble calcium to 1 mole of water-soluble magnesium reacted with

$\text{NH}_4\text{H}_2\text{PO}_4$ to form $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. Only $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was produced, however, when $\text{NH}_4\text{H}_2\text{PO}_4$ reacted with a calcareous soil having a ratio of 2.12 moles of water-soluble calcium to 1 mole of water-soluble magnesium. Both soils reacted with $(\text{NH}_4)_2\text{HPO}_4$ to form $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ as the only product.

It is apparent from the investigations discussed previously that a large number and variety of reaction products have been identified by the use of the technique of Lindsay and Stephenson (1959b). This is in contrast to the relatively small number of reaction products identified by direct isolation from soil. The difference between the two methods may or may not be due to the fact that the direct isolation method lacks the sensitivity of the Lindsay and Stephenson technique.

The latter method involves the repeated contact of a saturated fertilizer solution with air-dry soil. This causes a relatively slow dilution of the saturated solution with soil water during the repeated extractions. In agricultural soils in which the water content is somewhat higher than that in the air-dry state, the saturated fertilizer solution would be expected to become progressively diluted more rapidly as it moves into the surrounding soil. Accompanying the decreases in concentration of phosphate should be changes in pH and differences in dissolution of soil constituents, all of which might have some effect on the nature of the crystalline phosphates produced and the distance at which they are produced from the source. Another possibility is that some of the substances identified by Lindsay and Stephenson have been overlooked by persons attempting physical isolation of the products from the soil because certain of the reaction products occur only in a thin layer of soil immediately

adjacent to the fertilizer.

Inference from composition of aqueous extracts of soil This method involves comparing the solubility product constants for known phosphates with the ion-activity products calculated for solutions in equilibrium with soils. A plot of $\frac{1}{2} pCa + pH_2PO_4$ (phosphate potential) against $pH - \frac{1}{2} pCa$ (lime potential) for solutions in equilibrium with a given calcium phosphate yields a straight line characteristic for that phosphate species. The p's refer to the negative logarithms and the ion symbols to the ion activities. The values of $\frac{1}{2} pCa + pH_2PO_4$ and $pH - \frac{1}{2} pCa$ are computed for the solution in equilibrium with a given soil, and the values are plotted as a point on the solubility diagram. If an experimentally determined point falls on one of the lines representing the solubility of a given calcium phosphate, the implication is that the solution is in equilibrium with this compound and that the compound must be present in the soil.

Only limited success has been achieved by the use of this method to identify the reaction products of phosphate fertilizers and alkaline soils. Aslyng (1954) measured the lime and phosphate potentials of a number of Rothamsted soils. In neutral and calcareous soils which had received regular applications of superphosphate, Aslyng found the phosphate was more soluble than $Ca_{10}(OH)_2(PO_4)_6$ and less soluble than $CaHPO_4 \cdot 2H_2O$ and appeared to approach $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ in composition. Weir and Soper (1963) found that the solubility points for fertilized and unfertilized calcareous soils from Manitoba did not correspond to any definite compound but fell between the solubility lines of $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ and $Ca_{10}(OH)_2(PO_4)_6$. Similar results were obtained by Larsen and Court (1961) on a number of

fertilized acid and alkaline soils. The solubility values obtained exhibited no particular tendency to follow the solubility line for any of the calcium phosphates.

Hagin and Hadas (1962) applied the solubility product principle to five calcareous soils to which various quantities of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ had been added. The ion activity product increased from a value corresponding approximately to a saturated solution of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in the control soil to a value indicating supersaturation with respect to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at the highest phosphate application. The authors concluded that either no calcium phosphate compounds having a well-defined structure were formed or, more probably, that an equilibrium between the solid phase and solution was not reached. Essentially similar results were obtained by Withee and Ellis (1965) when they added various quantities of phosphorus to two calcareous soils.

The apparent supersaturation with respect to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ found by Hagin and Hadas and Withee and Ellis may be explained by the findings of Moreno et al. (1960), who investigated the equilibration of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and soil. These investigators found that solubilized soil organic matter complexed calcium ions in appreciable quantities above pH 6, introducing apparent supersaturation conditions with respect to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The rate of precipitation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, expected to form at pH values above pH 6.4 in solutions saturated with $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, was reduced by the organic matter.

One of the major complications with the solubility product method is that solutions in contact with $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ may remain supersaturated with respect to these species for a long time (Bjerrum, 1949; Wier, 1968). This behavior is probably reflected in most of the investigations discussed.

PART I. REACTION OF MONOBASIC CALCIUM PHOSPHATE MONOHYDRATE,
MONOBASIC AMMONIUM PHOSPHATE, AND DIBASIC AMMONIUM
PHOSPHATE WITH SLIGHTLY ACID AND ALKALINE SOILS

MATERIALS, APPARATUS, AND METHODS

Materials

Soils

The pH and source of the six untreated soils used in this investigation are shown in Table 1. Each soil was a surface sample and, except for the Harpster silty clay loam II, had not received fertilizer. A small amount of potassium chloride (KCl) had been applied to the Harpster silty clay loam II. The soils were air-dried, crushed to pass a 2 mm. sieve, thoroughly mixed, and stored in polyethylene bags until used. Certain physical properties of the soils are shown in Table 2.

Quantities of each of the three acid soils were adjusted to different pH values as described in the section on methods. The adjustment of the pH values of the two Harpster soils and the addition of CaCO_3 to the Norfolk, Lloyd, and Webster soils is also described in that section. Certain chemical properties of the natural and adjusted soils are listed in Table 3.

Phosphates

The three phosphates used in this investigation, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$, were reagent-grade quality. The phosphate crystals were sieved, and the 40- to 60-mesh fraction was washed with acetone, dried under vacuum, and stored in tightly sealed glass containers until used.

Polyethylene film

The low-density polyethylene film (Polyfilm 114) employed as a water vapor seal on top of the soil columns was obtained from the Dow Chemical

Table 1. The pH and source of the untreated soil samples

Soil type	Reference number	pH ^a	Source
Norfolk loamy sand	U.S.D.A. 51652	5.78	North Carolina
Lloyd clay loam	U.S.D.A. 51633	6.09	Georgia
Webster silty clay loam	F 2984	5.74	Control plot, N.E. corner of Agronomy and Agricultural Engineering Field Research Center, Iowa State University
Harpster silty clay loam I	F 2871	7.23	Plot 1114, Old Agronomy Farm, Iowa State University
Harpster silty clay loam II	F2874	7.40	Plot 1215, Old Agronomy Farm, Iowa State University
Darling Downs clay	--	7.80	Queensland, Australia

^apH determined on a suspension of 1 part soil to 2 parts 0.01 M CaCl₂ by weight with a Beckman pH meter.

Company, Chicago, Illinois. The film was 1 ml (0.00254 cm.) thick.

Miscellaneous

The white massive calcite (chalk) used to make the CaCO₃ chips originated in Dover, England, and was obtained from Ward's Natural Science Establishment, Rochester, New York.

The glass-fiber filter paper used in this investigation was Whatman brand, number GF-83, having a weight of 55g. per m² and a thickness of

Table 2. Certain physical properties of soils used

Soil	Water content by weight		Particle size distribution							Dominant clay mineral
	Retained at matric suction of 0.3 bar, %	Retained at field capacity, %	by weight, %							
			<2 μ	2-4 μ	4-8 μ	8-16 μ	16-31 μ	31-62 μ	>62 μ	
Norfolk loamy sand	3.5	11.9	3.3	0.2	0.2	1.5	1.1	4.8	89.0	Vermiculite
Lloyd clay loam	21.6	21.8	18.0	3.7	4.3	6.2	6.1	4.8	57.0	Kaolinite
Webster silty clay loam	32.6	27.4	33.6	4.7	7.5	12.4	13.5	7.7	20.6	Montmorillonite
Harpster silty clay loam I	31.3	27.3	32.2	4.4	7.3	10.2	13.7	9.4	22.8	Montmorillonite
Harpster silty clay loam II	31.6	27.8	38.6	4.9	10.3	10.3	12.1	7.3	16.4	Montmorillonite
Darling Downs clay	56.5	51.1	48.9	13.8	10.5	8.2	7.5	4.6	6.6	Montmorillonite

Table 3. Certain chemical properties of the natural and adjusted soils

Soil type	pH ^a in water	pH ^b in CaCl ₂	Organic carbon, %	Calcium carbonate equivalent, %	Cation ex- change capa- city/100g., m.e.	Exchangeable calcium/100g., m.e.	Exchangeable magnesium/100g. m.e.
Norfolk	7.10	6.41	0.41	0.00	10.9	1.52	0.97
loamy	7.52	6.87	0.41	0.00	10.9	1.62	0.70
sand	8.41	7.91	0.41	0.00	10.9	2.52	0.42
	8.52	7.91	0.40	9.09	9.2	6.02	0.70
	9.64	8.70	0.41	0.00	10.9	0.79	0.55
Lloyd	6.62	6.21	4.43	0.00	21.0	4.96	1.02
clay	7.18	6.81	4.43	0.00	21.0	7.32	0.85
loam	7.84	7.49	4.43	0.00	21.0	9.13	0.49
	7.94	7.51	3.99	9.09	19.1	10.10	0.47
Webster	6.88	6.53	3.59	0.00	34.0	21.3	4.81
silty	7.39	7.04	3.59	0.00	34.0	25.8	4.77
clay	8.00	7.71	3.59	0.00	34.0	29.2	3.51
loam	8.05	7.75	3.23	9.09	30.9	25.0	2.42
Harpster	8.03	7.51	4.16	2.99	35.4	27.1	1.97
silty clay loam I							
Harpster	8.03	7.52	4.13	21.7	39.9	33.1	1.75
silty clay loam II							
Darling	8.55	7.80	3.82	4.01	53.6	38.4	11.8
Downs clay							

^a pH determined on a suspension of 1 part soil to 2.5 parts water by weight.

^b pH determined on a suspension of 1 part soil to 2 parts 0.01M CaCl₂ by weight.

0.26 mm.

The certified refractive index liquids employed covered the index range from 1.460 to 1.700 in intervals of 0.010 and were obtained from Ward's Natural Science Establishment, Rochester, New York.

Apparatus

The columns fabricated to contain the soil-fertilizer system under investigation were constructed as follows. A section 10 cm. long was cut from a cylinder of Plexiglas (an acrylic plastic) with an outside diameter of 4.45 cm. and a wall thickness of 0.32 cm. The section was then cut longitudinally to produce two mirror-image halves. The halves were cemented back together to form a cylinder using white silicone rubber seal marketed by the General Electric Co. The ends of the cylinder were closed with sheets of Plexiglas 5 cm. by 5 cm. by 0.63 cm. Each sheet had a hole drilled in each corner to permit use of bolts to hold the assembly together. One sheet was solid, except for the corner holes, and the other had a central hole 2.54 cm. in diameter. The sheet with the central hole was cemented to the cylinder with silicone rubber before the column was filled with soil. The other sheet was not cemented in place until the column had been filled.

Pellet press for mounting CaCO_3 chips

The embedding of a CaCO_3 chip in a pellet of cornstarch for X-ray analysis was performed using the apparatus illustrated in Figure 1.

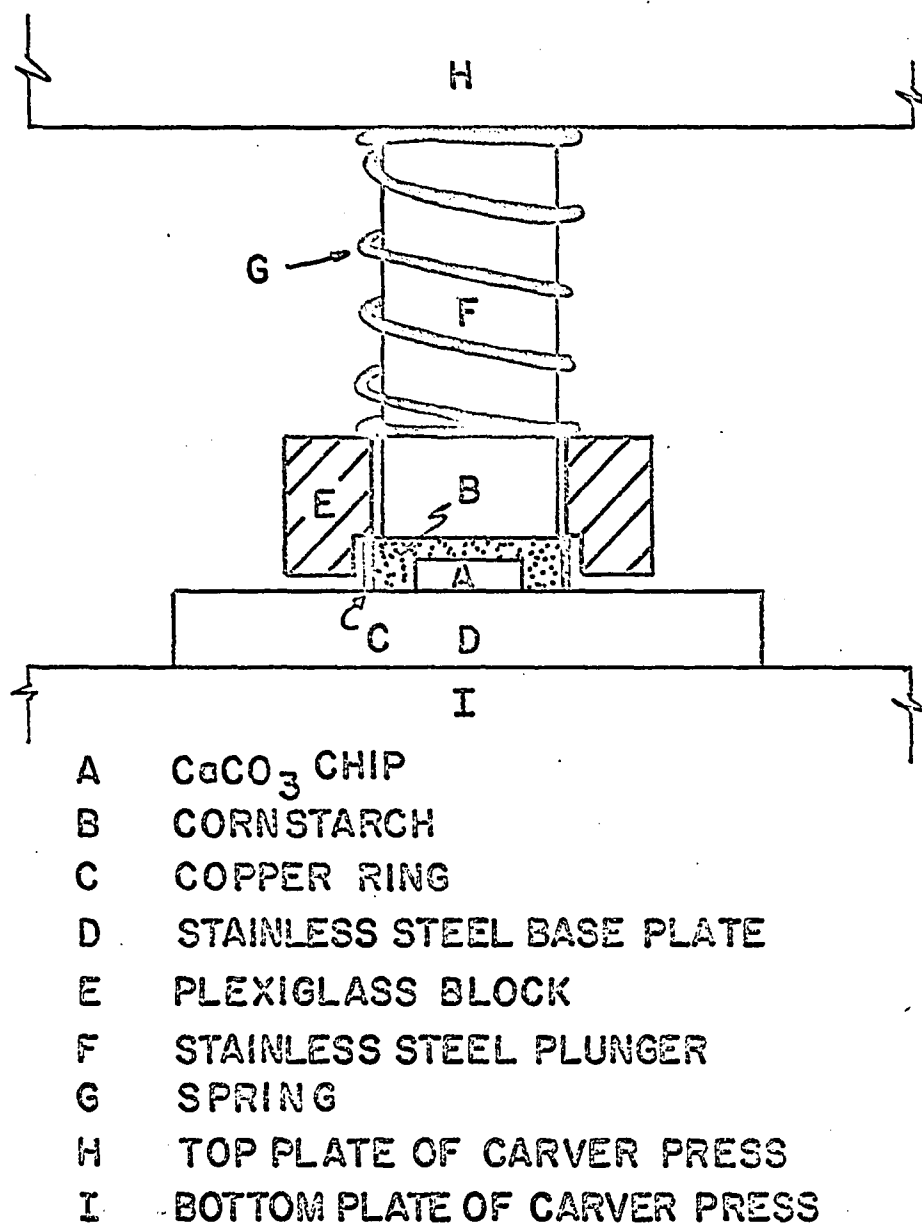


Figure 1. Cross-section diagram (actual size) of pellet press for mounting a CaCO_3 chip for X-ray diffraction analysis.

Miscellaneous

The X-ray analysis of samples was conducted with a General Electric XRD6 X-ray diffraction unit. A copper tube and nickel filter were used.

The binocular microscope used in this investigation had a maximum magnifying power of 60 (X20 eyepiece and X3 objective) and was made by the American Optical Company, Buffalo, New York. The polarizing microscope was a Polarstar Series 2300 having a maximum magnifying power of approximately 970 (X10 eyepiece and X97 objective). This microscope also was manufactured by the American Optical Company, Buffalo, New York.

Methods

Adjustment of soil properties

Quantities of Norfolk loamy sand, Lloyd clay loam, and Webster silty clay loam were adjusted to different pH values with calcium oxide (CaO) on the basis of preliminary trials as follows. Enough CaO was added to 20g. of soil to theoretically neutralize 25, 50, 100, 150, 200, and 300% of the exchange acidity (Peech, 1965a) of the soil. pH determinations were made on the samples after they had incubated for 2 to 4 weeks at a water content of approximately 1.5 times that at field capacity. From a plot of pH versus amount of CaO added, the amount of CaO needed to adjust the pH of bulk samples of soil to a given value was calculated.

The amount of CaO required for the bulk samples was mixed with approximately 500 g. of the soil to be treated. This mixture was then sprinkled over the surface of the bulk soil (4000 to 6000 g.) which had been spread on a flexible plastic sheet to a depth of approximately 3 cm. The soil

was mixed on the plastic and then put through a sample splitter ten times to ensure complete mixing. Each bulk sample of soil was placed in a polyethylene bag, and enough deionized water was added to give the soil a water content of 1.5 times that at field capacity. The bags were sealed and placed in the dark in a constant temperature room at 25°C. After 4 weeks, a small sample was taken from each bag for a pH determination. Some of the pH values were different from the predicted values. The development of somewhat anaerobic conditions during the incubation appeared to be responsible for these discrepancies. In some treatments, however, it was obvious that the amount of CaO required had been underestimated.

The problems were alleviated in the following way. Incubation was ceased and each soil sample was slowly air-dried. Additional CaO was added in the manner described previously to those soil samples requiring it. To prevent development of anaerobic conditions, the soil samples were incubated at 25°C. in quantities of approximately 500 g. at a water content varying from 1.3 to 1.4 times that at field capacity. The pH values obtained on the samples after 4 weeks were very close to the predicted values, and so the incubation was ceased. The soils were air-dried, crushed to pass a 2 mm. sieve, thoroughly mixed, and stored in thick polyethylene bags until used.

To investigate the effect of CaCO₃, three calcareous soils were prepared by addition of CaCO₃ to the Norfolk loamy sand, Lloyd clay loam, and Webster silty clay loam. Ten grams of CaCO₃ per 100 g. of oven-dry soil were added to (and incubated with) those soil samples which had been selected for treatment with the highest amount of CaO in the procedure

described previously. It was estimated that sufficient CaO had been added in these treatments to allow the formation of a very small amount of CaCO_3 (<0.50%) after neutralization of the soil acidity. The pH of a nonsodic soil in equilibrium with CaCO_3 is constant at a given partial pressure of carbon dioxide (CO_2). Hence, it was assumed that the addition of the large amount of CaCO_3 should not significantly alter the pH. The pH values of the adjusted soils shown in Table 3 attest to the validity of this assumption.

The maximum pH obtainable in nonsodic soils in equilibrium with CaCO_3 at the partial pressure of CO_2 in the atmosphere is generally less than 8.5 (Russell, 1961). To obtain soil samples with somewhat higher pH values, sodium carbonate (Na_2CO_3) was added to the Norfolk loamy sand and Webster silty clay loam in the manner described previously for the CaO additions.

The two Harpster soils were chosen because they had similar properties with the exception of the CaCO_3 equivalent (2.99% versus 21.71%). It was anticipated that the two soils would be useful for determining the effect of CaCO_3 in this investigation. The Harpster silty clay loam I had been fertilized with KCl, and it was considered desirable to leach the sample with water to remove any excess salt. A preliminary experiment in which 100 g. of both the Harpster soils were leached with deionized water showed that the pH of the Harpster I soil in 0.01 M CaCl_2 rose from 7.23 to 7.52 and that the pH of the Harpster II soil rose from 7.40 to 7.52. As it was a distinct advantage to have the two soils with nearly identical pH values, bulk lots of both soils were leached with deionized water until their pH values approached the equilibrium value of 7.5. The soils were leached in

the following way. Approximately 2500 g. of air-dry soil was placed in a double-walled ceramic pot similar to that described previously by Richards (1941). The inner wall was porous, and the construction of the pot was such that a vacuum could be applied to the space between the walls. Approximately 28 liters of deionized water was allowed to pass through the soil under vacuum at a constant rate of 10 ml. per minute. A 2 cm. head of water was maintained on top of the soil during the leaching process. After the leaching was completed, the soil was air-dried, crushed to pass a 2 mm. sieve, mixed, and stored in polyethylene bags until required.

Preparation of CaCO_3 -coated plastic strips

A sheet of Plexiglas 0.15 cm. thick was cut into pieces 6 cm. long and 2.5 cm. wide. (The dimensions of the strip were dictated by the size of the sample holder in the X-ray diffraction unit.) A thin layer of the Plexiglas on one side of the strip was dissolved by brushing on a small amount of ethylene dichloride. After the surface had become tacky, a large excess of reagent grade CaCO_3 was added and pressed onto the strip with a spatula. When the Plexiglas had solidified (about 12 hours), the strip was turned over, and the process was repeated on the other side. After the strip was thoroughly dry, the excess CaCO_3 was brushed off, and both sides of the strip were gently smoothed with very fine carbonundum paper. A soft camel-hair brush was then used to brush away any loose CaCO_3 . The strips were examined by X-ray diffraction, and the resulting pattern showed only the peaks for CaCO_3 .

Preparation of CaCO_3 chips

With the aid of a hacksaw and very fine carborundum paper, chips 1.5 cm. long, 1.0 cm. wide, and 0.4 cm. thick were fashioned from large massive fragments of chalk. X-ray analysis of the chips produced a diffraction pattern exhibiting only the peaks for CaCO_3 .

Preparation of soil columns for incubation

Filling of the columns with soil A standard filling technique was employed for all soils. Each column, as described previously, was filled in an inverted position with the base plate absent. A circular piece of 40-mesh stainless steel gauze 3.7 cm. in diameter was placed in the Plexiglas cylinder on the end piece with the central hole. A disc of glass-fiber filter paper 3.7 cm. in diameter was placed on the gauze. A predetermined weight of air-dry soil was transferred to the column through a funnel with a long stem. To limit segregation of the soil, the lower end of the funnel stem was kept just above the surface of the soil in the column.

The soil was packed by dropping the column ten times on a wood table top from a height of 2.5 cm. Any soil that would not go into the column prior to packing was added during the packing process. Preliminary experiments had shown that each soil packed quickly to a "natural" bulk density and that this value increased only slightly as more drastic packing procedures were adopted.

The bulk density value of a given soil in columns containing inclusions such as glass-fiber paper strips, CaCO_3 -coated strips, or CaCO_3 chips was kept the same as the value for the soil in columns without these inclusions.

Table 4 lists the bulk density values employed for the various soils. It can be seen that the bulk density values of the soils to which CaCO_3 was added are slightly higher than the values for the untreated soils. This effect is probably due in part to the filling of some of the larger pores of the soil by the small crystals of CaCO_3 . The bulk density values of soils to which Na_2CO_3 had been added were slightly lower than those of the untreated soils, perhaps because of the effect of the sodium ion on the dispersion of the soil colloids..

Table 4. Bulk density values of soils in Plexiglas columns

Soil	pH	Soil treatment	Bulk density g. per cm^3
Norfolk loamy sand	6.41	CaO	1.70
	6.87	CaO	1.70
	7.91	CaO	1.70
	7.91	CaO+ CaCO_3	1.75
	8.70	Na_2CO_3	1.68
Lloyd clay loam	6.21	CaO	1.09
	6.81	CaO	1.09
	7.49	CaO	1.09
	7.51	CaO+ CaCO_3	1.14
Webster silty clay loam	6.53	CaO	1.10
	7.04	CaO	1.10
	7.71	CaO	1.10
	7.75	CaO+ CaCO_3	1.12
	8.81	Na_2CO_3	1.07
Harpster silty clay loam I	7.51	-	1.05
Harpster silty clay loam II	7.52	-	1.02
Darling Downs clay	7.80	-	0.95

Addition of glass-fiber paper strips One of the techniques conceived for the isolation and identification of phosphate reaction products formed at different distances from a fertilizer source involved the positioning of a strip of glass-fiber filter paper 9.7 cm. long and 2.2 cm. wide in the soil columns perpendicular to the fertilizer band. It was anticipated that, as the fertilizer moved into the soil, precipitation of phosphate would occur in the interstices of the filter paper as well as in the pores of the soil. The strip could then be removed from the soil and X-rayed with little soil contamination to mask the properties of the precipitated phosphate.

The soil columns containing the glass-fiber paper strips were filled in the same manner as described in the preceding section. Before the soil was added, however, the strip was inserted into the column so that the short axis of the strip was in the same plane as the two vertical seams of the column. The strip was held in position by a specially constructed wire holder which was slowly raised as the column was filled.

Addition of CaCO_3 -coated plastic strips As a possible aid in identifying the crystalline phosphates produced in calcareous soils, a flat strip of CaCO_3 -coated Plexiglas was positioned in the soil column in a manner similar to that described in the preceding section for the strip of filter paper. It was supposed that precipitation of phosphate would occur on the CaCO_3 attached to the strip of Plexiglas as well as on the soil CaCO_3 . After removal from the soil, the CaCO_3 -coated strip of Plexiglas could be examined directly by X-ray diffraction with relatively little interference from soil.

Addition of CaCO_3 chips

In some calcareous soils, CaCO_3 occurs as relatively large pieces. Although these pieces can be isolated from soil, it is not easy to identify the surface coating of phosphate by the use of X-ray diffraction because of the generally irregular nature of the CaCO_3 surface. To circumvent this difficulty, small, flat, rectangular-shaped chips of CaCO_3 , fashioned from chalk fragments as described previously, were placed in columns of calcareous soil at various distances from the fertilizer band. Three such chips were arranged in an echelon in each soil column, with their ends overlapping slightly and with their large plane surface perpendicular to the end of the column. The chips had the advantage that they could be mounted in a specially constructed holder which permitted their plane surfaces to be X-rayed.

Addition of water

The water contents of the soils at field capacity and at a matric suction of 0.3 bar are shown in Table 2. The Norfolk loamy sand felt dry at 0.3 bar and contained only 3.5% water. The water content of the soil at field capacity was significantly higher (11.9%). The difference between the water contents determined by the two methods for the other soils was not nearly as marked. In the light of these observations, it was decided to wet all the soils to field capacity. The volume of water added to each column included an allowance, where relevant, for the water held by a glass-fiber paper strip, a CaCO_3 -coated plastic strip, or three CaCO_3 chips.

The following method was used to add water to the soil columns. One end of a 50 cm. length of Tygon plastic tubing (0.63 cm. internal diameter) was attached to the tip of a 50 ml. clamped burette, and the other end was

attached to a 5 cm. piece of glass tubing. A hole was drilled in a No. 6 neoprene rubber stopper to accommodate one end of the glass tubing, and the tubing was inserted to the depth of the stopper. After the burette and tubing had been filled with deionized water, the rubber stopper was inserted into the central hole in the Plexiglas sheet at the bottom of the soil column. The burette was raised or lowered to provide a head of 10 to 20 cm. of water above the bottom of the soil column. After the predetermined volume of water had been slowly run into the soil from the burette, the tubing was clamped and the column was allowed to stand for 30 to 45 minutes. During this time the soil wetted up to within a few centimeters of the upper surface, and those soils which exhibited swelling tendencies had expanded to leave the predetermined 0.2 cm. space at the open end of the column for fertilizer addition.

During the addition of water to the Webster silty clay loam which had been adjusted to pH 8.81 with Na_2CO_3 , the soil swelled to such an extent that it became impervious to water. Various other methods of wetting the soil to a given water content also failed and so this soil treatment was discarded.

Addition of fertilizer The quantity of phosphate salt to supply 0.6143 g. of phosphorus was sieved onto the soil through a 20-mesh sieve 2.8 cm. in diameter. A spatula was used to spread the phosphate fertilizer evenly over the surface of the soil, and the fertilizer was gently pressed down flush with the top of the column by the use of a flat sheet of Plexiglas.

The quantity of fertilizer salts used was enough to produce extensive precipitation zones containing relatively large quantities of reaction products for isolation and identification. At the same time, the extremes of concentration of added phosphate contacting the soil, i.e., zero and a saturated solution of the fertilizer salt, would be the same as those encountered whenever the salt in question is added as a solid.

The fertilizer salts were added in quantities to supply 0.0536 g. of phosphorus per square centimeter of soil. The thickness of the layer of salt was about 2 mm., which is of the same order of magnitude as the thickness of bands of fertilizer often applied for row crops. A direct comparison of the applications made in the laboratory with those made per unit of land area in the field cannot be made because of differences in geometric factors affecting movement of phosphorus from the fertilizer into the soil.

Sealing of the columns and incubation After the fertilizer had been added, the solid Plexiglas sheet was sealed to the ends of the Plexiglas column by silicone rubber. After the silicone rubber had cured for 10 minutes, each column was inverted so that the fertilizer was now at the base. A square of polyethylene film 3.3 cm. by 3.3 cm. was placed over the hole in the top plate of each column and secured with four 5 cm. strips of transparent adhesive cellulose tape 1.27 cm. in width.

In this investigation, it was considered desirable to keep the soil water content constant during incubation so that other soil factors could be investigated. The main purpose of the polyethylene seal was to restrict water vapor movement out of the soil columns and yet to prevent the de-

velopment of anaerobic conditions by allowing the inward diffusion of oxygen and the outward diffusion of carbon dioxide. Many films were considered for this purpose, but the one selected appeared to have the best combination of desirable properties.

After being sealed, each column was transferred to a cabinet in a constant temperature room at 25°C. or to an incubator at 35°C. To slow down the rate of water vapor loss through the polyethylene seals, moist air was passed over the columns throughout the incubation period. The continuous passage of air through the incubation containers also ensured that the oxygen and carbon dioxide levels around the soil columns remained unchanged. Incubation times of 4, 16, and 48 weeks were employed.

Examination of soil columns after incubation

Opening of column . After being incubated for the designated period, each column was opened for examination. The end plates were removed by cutting the rubber seals with a razor blade. The circular pieces of stainless steel gauze and glass-fiber paper were also removed from the top of the column.

At the base of soil columns to which $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ had been added, a residue of phosphate remained, and this was carefully removed for future analysis. In most soils to which $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ had been added, a crust of phosphate 1.5 to 2.0 mm. thick had formed in the soil adjacent to the fertilizer. This crust was also carefully removed for future examination. In the $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ treatments no fertilizer residue remained, but often a thin layer of precipitated phosphate was observed in the first few millimeters soil adjacent to the original fertilizer. Thus it was

decided to remove, for future analysis, the first 2 millimeters of soil.

Each column was then split into two identical halves. This was achieved by first cutting the two longitudinal silicone rubber seals with a razor blade. The soil core was then cut in halves with a sharpened spatula, care being taken not to damage any inclusions present. Any inclusions such as glass-fiber paper strips, CaCO_3 -coated plastic slides, or CaCO_3 chips present in the column were isolated, air-dried, brushed lightly to remove excess soil, and placed in stoppered vials for future examination.

Determination of the fertilizer-phosphorus distribution The distance moved by the fertilizer phosphorus was determined by the use of a modification of the rapid, nondestructible method described by Sample and Taylor (1964). A strip of Whatman 40 filter paper 2.5 cm. wide and approximately 13 cm. long was impregnated with a solution of ammonium molybdate in hydrochloric acid [$0.0024 \text{ M } (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 0.7 M HCl]. The excess solution was removed by blotting the strip on a large piece of filter paper. The strip was then placed on the surface of one half of a soil column, the surface having been smoothed off previously with a spatula. A flat spatula was gently run across the surface of the filter paper to ensure good contact with the soil. After approximately 30 seconds the paper was removed and sprayed with a stannous chloride solution ($0.05 \text{ M SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 0.02 N HCl) to develop the blue color. (Sample and Taylor used a solution consisting of $0.0019 \text{ M SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 0.013 N HCl to develop the color, but the solution used here produced a more stable color with the soils used in this investigation.) The distance moved by the fertilizer phosphorus was indicated on the strip of filter paper by the length of the

dark blue band. Three separate determinations of the phosphorus movement in each column were made. The length of the blue section on each of the three filter paper strips was measured, and the average value was taken as the distance moved by the fertilizer phosphorus.

Microscopic examination of soil columns After the phosphorus distribution had been determined on one half of each soil column, a layer of soil 2 to 3 mm. thick was removed from the surface contacted by the molybdate-impregnated filter paper. This freshly exposed longitudinal section of each column was then examined under a binocular microscope, and the distribution of any crystalline reaction products was recorded.

pH determinations on soil segments One half of each soil column was cut crosswise into 1 cm. segments. The segments were placed in pre-weighed 50 ml. beakers and air-dried by placing the samples in a forced draft oven at 30°C. for 24 hours. The beakers were then weighed, and the weight of air-dry soil in each beaker was calculated. Enough 0.01 M CaCl_2 was added to each sample to keep a constant ratio of 1 g. of soil to 2 ml. of CaCl_2 . The pH value of each sample was then determined by the method of Peech (1965b) using a Beckman Model G pH meter with a glass electrode and saturated calomel reference electrode.

Examination of soil segments The remaining one half of each soil column was cut crosswise into 1 cm. segments for microscopic, petrographic, and X-ray analyses. Each segment was placed on a watch glass and examined under a binocular microscope. Crystalline reaction products were isolated

from the soil for petrographic analysis with a pair of extra-fine pointed stainless steel forceps or with a mounted needle.

The crystals of the reaction products were placed in a drop of refractive index liquid on a glass microscope slide, a glass coverslip was placed over the liquid, and the sample was examined under the petrographic microscope. The average refractive index of the crystals was determined by trial and error with a range of refractive index liquids using the Becke line method (Bloss, 1961). The average refractive index value of the crystals, together with the additional properties of morphology and birefringence, generally allowed a positive identification of the phosphate to be made. The optical data on pure phosphates listed by Lehr et al. (1967) were used in the identification process.

In some instances, enough crystals of phosphate were probed from the soil to permit X-ray diffraction analysis. The crystals were ground in an agate mortar, and the powder was smeared onto a piece of cellophane tape with adhesive on both sides. The tape had been previously mounted on a glass microscope slide. The slide was placed in the holder of the X-ray diffraction unit and scanned with copper K α radiation using a nickel filter, 1° beam slit, medium resolution soller slit, and 0.2° detector slit. Various settings of the time-constant and counts-per-second controls were used, depending on the nature of the sample. The X-ray diffraction data obtained on the sample were compared with the data for pure phosphates listed by Lehr et al. (1967).

Samples of the soil segments were also X-rayed. These samples were mounted for analysis by pressing the soil into brass washers (2.54 cm.

internal diameter) using a Carver press and a pressure of 1680 kg. per cm.²

Examination of glass-fiber paper strips The glass-fiber paper strips were examined under a binocular microscope, and the presence and distribution of any crystalline phosphate species were noted. In some instances the optical properties of crystals probed from the strips were determined with the petrographic microscope. After microscopic examination, each strip was cut into two sections, each section being stuck to a separate glass microscope slide with the aid of cellophane tape with adhesive on both sides. The strip sections were then X-rayed at 0.5 cm. intervals along their entire length. (The strips were analyzed in two pieces because they would not fit into the sample holder of the X-ray diffraction unit in one piece.)

Examination of CaCO₃-coated plastic strips The strips were examined under a binocular microscope, and the presence and distribution of any surface precipitates were noted. In many instances, crystals were probed from the surface of the CaCO₃, and their optical properties were determined under the petrographic microscope. X-ray diffraction analysis of each slide was made at 0.5 cm. intervals along its length.

Examination of CaCO₃ chips Each chip was examined under the binocular microscope, and the optical properties of crystals probed from the surface were determined under the petrographic microscope. The chips were prepared for X-ray analysis as follows. A chip was placed inside a copper ring on a steel base plate. Cornstarch was poured around and on the chip,

and, with the aid of the apparatus described previously, a pellet was formed by applying a pressure of 1680 kg. per cm.² The pellet containing the CaCO₃ chip, together with the surrounding copper ring, was transferred to the sample holder of the X-ray diffraction unit. The pellet was positioned so that the exposed plane surface of the chip was flush with the front of the sample holder. The exposed surface of the chip was then X-rayed.

Soil physical and chemical analyses

The water content of the soils at field capacity was determined by the method of Kirkham and Powers (1965). A pressure membrane apparatus was used to determine the water content of the soils at a matric suction of 0.3 bar in the manner described by Richards (1965). Particle-size analysis was conducted by the pipette method using the particle-size divisions of Wentworth (1935).

Carbonate (reported as CaCO₃ equivalent) was determined by the vacuum-distillation and titration method (Allison and Moodie, 1965). Organic carbon analysis was performed by the wet oxidation method of Mebius (1960). The barium chloride-triethanolamine method described by Peech (1965a) was used for the determination of exchange acidity. The cation exchange capacity of the soils was determined by sodium saturation as described by Chapman (1965). Exchangeable calcium and magnesium were determined by extracting the cations with 1 N sodium acetate (pH 8.2) and determining the calcium and magnesium in the extract by using a Perkin-Elmer Model 303 atomic absorption spectrophotometer as described by the Perkin-Elmer

Staff (1966).

All soil analyses reported are on an oven-dry basis unless otherwise stated. The water content was determined from the loss in weight of a soil sample after drying at 110°C. for 18 to 24 hours.

RESULTS AND DISCUSSION

Distance Moved by Fertilizer Phosphorus

The distribution of reaction products in a soil in contact with water-soluble phosphate fertilizers will depend, in part, on the distance the fertilizer phosphorus moves into the soil. Table 5 shows the distance to which the fertilizer phosphorus moved in soils in contact with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ for 4, 16, and 48 weeks. It was intended that the phosphorus added would be insufficient to diffuse the complete length of the column. In some treatments, however, particularly those involving Norfolk loamy sand, the fertilizer phosphorus did move the entire length of the soil column (9.7 cm.).

It can be seen from Table 5 that the distance moved by phosphorus in a given time was greatest with $(\text{NH}_4)_2\text{HPO}_4$, intermediate with $\text{NH}_4\text{H}_2\text{PO}_4$, and least with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. This order held true for all soil types, pH values, and times of contact. The difference in the distance of phosphorus movement among fertilizers is related to the properties of the fertilizers. The pH values of the saturated solutions of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ are 1.48, 3.47, and 7.98, respectively (Lindsay *et al.*, 1962). The most acid solution would be expected to react the most rapidly with soil constituents, resulting in a relatively fast precipitation of phosphate compounds and a smaller distance of movement by the fertilizer phosphorus. In addition to the fact that $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ produces the most acid solution, approximately one-fifth of the phosphorus in the salt is left as a residue of dicalcium phosphates at the site of dissolution. All

Table 5. Distance of movement of phosphorus from monobasic calcium phosphate monohydrate, monobasic ammonium phosphate, and dibasic ammonium phosphate into different soils in 4, 16, and 48 weeks

Original pH of soil	Calcium carbonate equivalent in soil, %	Fertilizer added	Distance of phosphorus movement, cm. ^a		
			4 weeks	16 weeks	48 weeks
<u>Norfolk loamy sand (25°C.)^b</u>					
6.41	0	MCP ^c	8.9	9.7	9.7
		MAP ^d	9.7	9.7	9.7
		DAP ^e	9.7	9.7	9.7
6.87	0	MCP	8.8	9.7	9.7
		MAP	9.7	9.7	9.7
		DAP	9.7	9.7	9.7
7.91	0	MCP	7.3	9.7	9.7
		MAP	9.7	9.7	9.7
		DAP	9.7	9.7	9.7
7.91	9.1	MCP	3.7	2.4	4.2
		MAP	7.1	9.7	9.7
		DAP	9.7	9.7	9.7
8.70	0	MCP	9.7	9.7	9.7
		MAP	9.7	9.7	9.7
		DAP	9.7	9.7	9.7
<u>Lloyd clay loam (25°C.)</u>					
6.21	0	MCP	4.5	5.5	7.0
		MAP	5.7	9.7	9.7
		DAP	6.5	9.7	9.7
6.81	0	MCP	4.6	6.0	6.7
		MAP	5.8	9.7	9.7
		DAP	6.6	9.7	9.7
7.49	0	MCP	3.8	5.2	5.4
		MAP	4.9	9.7	9.7
		DAP	6.5	9.7	9.7
7.51	9.1	MCP	2.0	2.5	3.4
		MAP	4.7	5.7	6.3
		DAP	5.4	7.4	9.7

^aEqual amounts of phosphorus were added to all soils in all fertilizers.

^bTemperature of incubation.

^c $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

^d $\text{NH}_4\text{H}_2\text{PO}_4$.

^e $(\text{NH}_4)_2\text{HPO}_4$.

Table 5. (Continued)

Original pH of soil	Calcium carbonate equivalent in soil, %	Fertilizer added	Distance of phosphorus movement, cm. ^a		
			4 weeks	16 weeks	48 weeks
<u>Webster silty clay loam (25°C.)</u>					
6.53	0	MCP	4.4	6.2	7.7
		MAP	5.7	8.0	9.7
		DAP	5.9	8.5	9.7
7.04	0	MCP	4.2	5.7	6.5
		MAP	5.4	8.1	9.7
		DAP	5.5	8.1	9.7
7.71	0	MCP	3.2	4.6	5.1
		MAP	4.6	6.7	9.7
		DAP	4.7	7.0	9.7
7.75	9.1	MCP	2.4	3.1	3.7
		MAP	3.9	5.1	-f
		DAP	4.4	6.0	-f
<u>Webster silty clay loam (35°C.)</u>					
6.53	0	MCP	4.6	6.0	5.2
		MAP	5.8	8.1	8.0
		DAP	6.3	7.5	9.7
7.04	0	MCP	4.3	5.4	6.0
		MAP	5.5	8.0	9.7
		DAP	5.9	7.4	9.7
7.71	0	MCP	3.7	4.5	4.2
		MAP	4.7	7.9	9.7
		DAP	5.0	6.0	9.7
7.75	9.1	MCP	2.5	2.7	3.3
		MAP	4.2	4.3	-f
		DAP	5.0	6.5	-f
<u>Harpster silty clay loam I (25°C.)</u>					
7.51	3.0	MCP	2.9	4.9	-f
		MAP	4.7	5.6	-f
		DAP	5.0	5.7	-f
<u>Harpster silty clay loam II (25°C.)</u>					
7.52	21.7	MCP	1.7	2.2	2.6
		MAP	3.5	3.6	-f
		DAP	5.1	5.3	-f
<u>Darling Downs clay (25°C.)</u>					
7.80	4.0	MCP	3.2	4.1	4.5
		MAP	4.3	4.7	-f
		DAP	4.4	5.2	-f

^f Boundary indistinct; the distance of movement could not be determined precisely.

of the phosphorus of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ is available for movement into the soil because these salts do not leave a phosphate residue at the site of dissolution.

In almost all instances in which the fertilizer did not move the full length of the column in the first 4 weeks, further movement took place with time. The distance of movement between 4 and 48 weeks usually did not exceed the distance of movement in the first 4 weeks.

There was an inverse relationship between the distance moved by the phosphorus and the amount of reactive material in a soil in the form of exchangeable bases and carbonate. Comparison of the results obtained with the noncalcareous samples of Norfolk loamy sand, Lloyd clay loam, and Webster silty clay loam shows that the phosphorus movement from a given fertilizer at a given pH and time interval was greatest with the Norfolk soil and smallest with the Webster soil, the Lloyd soil being intermediate. The cation exchange capacities and contents of exchangeable calcium were in the reverse order, Norfolk < Lloyd < Webster. The effect of carbonate content on the phosphorus movement may be seen in a comparison of the two Harpster silty clay loams which have approximately similar cation exchange capacities. The phosphorus movement from a given fertilizer during each time interval was smaller in the Harpster silty clay loam II containing 21.7% CaCO_3 equivalent than in the Harpster silty clay loam I containing 3.0% CaCO_3 equivalent.

In each soil investigated after adjustment to different pH values with CaO , the movement of phosphorus decreased with increasing pH, presumably as a result of the increase in exchangeable calcium. The sample of Norfolk

loamy sand adjusted to pH 8.70 with Na_2CO_3 , however, had the lowest exchangeable calcium content of all samples of this soil, and hence the phosphorus movement was extensive.

The effect of temperature may be observed by comparing results obtained with samples of Webster silty clay loam incubated at 25°C . and 35°C . After 4 weeks, the phosphorus movement was greater at 35°C . than at 25°C . This behavior might be explained on the basis that the rate of diffusion of solutes in water increases with increasing temperature. At the end of 16 and 48 weeks, however, the distance of movement of the phosphorus was greater at 25°C . than at 35°C . Perhaps this reversal with time was a consequence of a greater rate of reaction of the fertilizer phosphorus with the soil at the higher temperature.

Crystalline Reaction Products Formed in Soils in Contact with Phosphate Fertilizers

The crystalline reaction products were identified by petrographic and X-ray analysis of crystals isolated directly from the soil and by analysis of crystals precipitated on such inclusions as glass-fiber paper strips, CaCO_3 -coated strips, and CaCO_3 chips. The results obtained using the more direct method will be discussed first. These findings will then be compared with those obtained by the analysis of the various inclusions.

Reaction of monobasic calcium phosphate monohydrate with soils

Analysis of residues Observation of the soil columns indicated that the incongruent dissolution of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ had been completed in all soils in less than 2 weeks. The nature of the phosphate residues re-

maining after the dissolution of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is shown in Table 6.

In all soils incubated at 25°C ., the dominant phosphate residue identified after 4 and 16 weeks was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The other phosphate phase, CaHPO_4 , occurred in trace to minor amounts. By the end of 48 weeks, substantial transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to CaHPO_4 had occurred in Norfolk loamy sand, Lloyd clay loam, and Webster silty clay loam, but only slight transformation had occurred in the Darling Downs clay and Harpster silty clay loams.

The transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to the anhydrous salt increases with increasing concentration of phosphate in the surrounding solution (Brown, 1964). The concentration of phosphorus in the solution contacting the dicalcium phosphate residues would be lower in those soils which react rapidly with phosphorus. Such soils would include those containing carbonate or having a high content of exchangeable calcium. These facts might explain the results observed with the Harpster silty clay loams and Darling Downs clay. These soils contain carbonate as well as having a high content of exchangeable calcium. In Webster silty clay loam (25°C .), the ratio of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to CaHPO_4 at 48 weeks increased with increasing pH (and hence increasing exchangeable calcium) and was greatest in the soil containing CaCO_3 . Norfolk loamy sand and Lloyd clay loam had much smaller cation exchange capacities and hence smaller amounts of exchangeable calcium than the other soils, and this was reflected in the low ratio of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to CaHPO_4 observed after 48 weeks. The effect of CaCO_3 in restricting this transformation is obvious in the Norfolk loamy sand.

When Webster silty clay loam was incubated at 35°C ., the phosphate residues were essentially all CaHPO_4 , even after 4 weeks. This effect of

Table 6. Nature of phosphate residues at the site of placement of mono-basic calcium phosphate monohydrate 4, 16, and 48 weeks after addition of the salt to different soils

Soil pH before incuba- tion	Soil treat- ment	Phosphate compound identified			
		Species	Relative amounts ^a		
			4 weeks	16 weeks	48 weeks
<u>Lloyd clay loam (25°C.)^b</u>					
6.21	--	CaHPO ₄ ·2H ₂ O	***	***	*
		CaHPO ₄	*	*	***
6.81	--	CaHPO ₄ ·2H ₂ O	***	***	*
		CaHPO ₄	*	*	***
7.49	--	CaHPO ₄ ·2H ₂ O	***	***	*
		CaHPO ₄	*	*	***
7.51	CaCO ₃	CaHPO ₄ ·2H ₂ O	***	***	*
		CaHPO ₄	T	*	***
<u>Norfolk loamy sand (25°C.)</u>					
6.41	--	CaHPO ₄ ·2H ₂ O	***	***	*
		CaHPO ₄	*	*	***
6.87	--	CaHPO ₄ ·2H ₂ O	***	***	T
		CaHPO ₄	*	*	***
7.91	--	CaHPO ₄ ·2H ₂ O	***	***	T
		CaHPO ₄	*	*	***
7.91	CaCO ₃	CaHPO ₄ ·2H ₂ O	***	***	**
		CaHPO ₄	*	*	**
8.70	--	CaHPO ₄ ·2H ₂ O	***	***	*
		CaHPO ₄	*	*	***
<u>Webster silty clay loam (25°C.)</u>					
6.53	--	CaHPO ₄ ·2H ₂ O	***	***	*
		CaHPO ₄	T	*	***
7.04	--	CaHPO ₄ ·2H ₂ O	***	***	**
		CaHPO ₄	*	*	**
7.71	--	CaHPO ₄ ·2H ₂ O	***	***	**
		CaHPO ₄	*	*	**
7.75	--	CaHPO ₄ ·2H ₂ O	***	***	***
		CaHPO ₄	*	*	*

^a*** = major phase, ** = similar amounts of both phases, * = minor phase, T = trace, and 0 = none detected.

^bTemperature of incubation.

Table 6. (Continued)

Soil pH before incuba- tion	Soil treat- ment	Phosphate compound identified			
		Species	Relative amounts ^a		
			4 weeks	16 weeks	48 weeks

<u>Webster silty clay loam (35°C.)</u>					
6.53	--	CaHPO ₄ ·2H ₂ O	T	T	0
		CaHPO ₄	***	***	***
7.04	--	CaHPO ₄ ·2H ₂ O	T	0	0
		CaHPO ₄	***	***	***
7.71	--	CaHPO ₄ ·2H ₂ O	T	0	0
		CaHPO ₄	***	***	***
7.75	CaCO ₃	CaHPO ₄ ·2H ₂ O	T	T	*
		CaHPO ₄	***	***	***
<u>Harpster silty clay loam I (25°C.)</u>					
7.51	--	CaHPO ₄ ·2H ₂ O	***	***	***
		CaHPO ₄	T	*	*
<u>Harpster silty clay loam II (25°C.)</u>					
7.52	--	CaHPO ₄ ·2H ₂ O	***	***	***
		CaHPO ₄	T	*	*
<u>Darling Downs clay (25°C.)</u>					
7.80	--	CaHPO ₄ ·2H ₂ O	***	***	***
		CaHPO ₄	T	*	*

elevated temperatures on the formation of CaHPO_4 is well known (Lehr et al., 1959).

Reaction products identified in soils The crystalline reaction products produced by the interaction of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ with Norfolk loamy sand after 4, 16, and 48 weeks are shown in Table 7. The only reaction products identified (by petrographic and X-ray diffraction analysis) were $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 , the latter being found as trace amounts in the 2 mm.

Table 7. Crystalline phosphates identified in fertilizer residue and soil after incubation of mono-basic calcium phosphate monohydrate with Norfolk loamy sand for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.41</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	*
				CaHPO ₄	*	*	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
				CaHPO ₄	T	T	+
0-2-1.0	2.83	3.48	4.08	CaHPO ₄ ·2H ₂ O	T	T	T
1.0-2.0	3.11	3.56	4.12	CaHPO ₄ ·2H ₂ O	T	T	0
2.0-3.0	3.16	}3.62	4.20	CaHPO ₄ ·2H ₂ O	T	T	T
3.0-4.0	3.55		4.41	CaHPO ₄ ·2H ₂ O	T	T	T
4.0-5.0	}4.63	}3.70	}4.50	CaHPO ₄ ·2H ₂ O	T	T	T
5.0-6.0				CaHPO ₄ ·2H ₂ O	T	T	T
6.0-7.0	}5.52	}4.11	}4.71	CaHPO ₄ ·2H ₂ O	T	T	T
7.0-8.0				CaHPO ₄ ·2H ₂ O	T	T	T
8.0-9.7	6.29	4.30	5.24	CaHPO ₄ ·2H ₂ O	—0—	T	T ^b

^aFor the fertilizer residue, *** = major phase, ** = similar amounts of both phases, * = minor phase, and T = trace. For the soil, ++++ = very large amount, +++ = large amount, ++ = moderate amount, + = small amount, T = trace, and 0 = none detected. (Here and throughout other tables.)

^bLine denotes the distance to which fertilizer phosphorus moved in the time intervals indicated. (Here and throughout other tables.)

Table 7. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.87</u>							
0 (fertilizer residue)	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	***	***	T
				CaHPO_4	*	*	***
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	+++
				CaHPO_4	T	+	T
0.2-1.0	2.92	3.52	4.18	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
1.0-2.0	3.02	3.60	4.30	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
2.0-3.0	3.21	} 3.81	} 4.38	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
3.0-4.0	3.68			$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
4.0-5.0	} 4.62	} 4.04	} 4.48	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
5.0-6.0				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
6.0-7.0	} 5.70	} 4.13	} 4.52	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
7.0-8.0				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
8.0-9.7	6.42	4.30	4.52	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
<u>Initial soil pH 7.91</u>							
0 (fertilizer residue)	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	***	***	T
				CaHPO_4	*	*	***
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	+++
				CaHPO_4	0	T	T
0.2-1.0	2.91	3.69	4.90	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	+	T
1.0-2.0	3.30	4.07	4.52	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
2.0-3.0	4.00	} 4.12	} 4.59	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
3.0-4.0	4.40			$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
4.0-5.0	} 5.20	} 4.27	} 4.80	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
5.0-6.0				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
6.0-7.0	} 6.90	} 4.45	} 4.94	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
7.0-8.0				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
8.0-9.7	7.84	4.63	5.44	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T

Table 7. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.91 (9.1% CaCO₃ added)</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	**
				CaHPO ₄	*	*	**
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	+++
				CaHPO ₄	T	T	T
0.2-1.0	5.93	6.42	6.82	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	6.32	6.71	6.99	None	0	0	0
2.0-3.0	6.74	7.06	7.01	"	0	0	0
3.0-4.0	7.34	7.25	7.26	"	0	0	0
4.0-5.0	7.63	} 7.51	7.39	"	0	0	0
5.0-6.0	7.76		7.45	"	0	0	0
6.0-7.0	} 7.89	} 7.69	} 7.50	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.89	7.86	7.63	"	0	0	0
<u>Initial soil pH 8.70</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	*
				CaHPO ₄	*	*	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
				CaHPO ₄	T	T	T
0.2-1.0	--	3.96	--	CaHPO ₄ ·2H ₂ O	0	T	T
1.0-2.0	--	4.08	--	CaHPO ₄ ·2H ₂ O	T	T	T
2.0-3.0	--	} 4.18	--	CaHPO ₄ ·2H ₂ O	T	T	T
3.0-4.0	--		--	CaHPO ₄ ·2H ₂ O	T	T	T
4.0-5.0	--	} 4.66	--	CaHPO ₄ ·2H ₂ O	T	T	T
5.0-6.0	--		--	CaHPO ₄ ·2H ₂ O	T	T	T
6.0-7.0	--	} 5.29	--	CaHPO ₄ ·2H ₂ O	T	T	T
7.0-8.0	--		--	CaHPO ₄ ·2H ₂ O	T	T	T
8.0-9.7	--	5.62	--	CaHPO ₄ ·2H ₂ O	T	0	0

of soil adjacent to the fertilizer residue. In all samples, the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (as clusters of needle-shaped crystals) was most extensive in the 0- to 2-mm. zone. The distribution and extent of this phosphate were similar for each of the non-calcareous samples and reflect the low content of reactive calcium in the soil. The samples containing CaCO_3 reacted rapidly with the acid solution derived from the fertilizer and produced a dense precipitate of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the first 1 cm., with little evidence of precipitation of the salt past this point.

It is apparent that the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was essentially complete at 4 weeks because little change in amount or distribution of this salt was evident in examinations made at the end of 16 and 48 weeks.

Table 8 shows the reaction products formed by the interaction of $\text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$ with Lloyd clay loam. The major product identified was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, the amount decreasing with distance from the fertilizer source. The amount and distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were essentially the same at 4, 16, and 48 weeks, indicating that the precipitation of the phosphate after 4 weeks was slight in spite of the fact that the fertilizer phosphorus continued to move out into the soil. The distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was essentially the same for each of the noncalcareous samples. The presence of CaCO_3 at pH 7.51, however, shortened the precipitation zone and resulted in a more extensive precipitate of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ from 0 to 1 cm.

As shown in Table 9, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was the major reaction product identified in Webster silty clay loam incubated at 25°C. and 35°C. The precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was greatest in the soil adjacent to the fertilizer source and decreased with distance from the source. Little precipitation of the phosphate appeared to occur after

Table 8. Crystalline phosphates identified in fertilizer residue and soil after incubation of mono-basic calcium phosphate monohydrate with Lloyd clay loam for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4	16	48		Relative amounts ^a		
					4	16	48
	weeks	weeks	weeks		weeks	weeks	weeks
<u>Initial soil pH 6.21</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	*
				CaHPO ₄	*	*	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	T	T
0.2-1.0	3.46	3.99	4.52	CaHPO ₄ ·2H ₂ O	++	++	++
1.0-2.0	3.99	4.16	4.78	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	4.79	4.50	4.98	CaHPO ₄ ·2H ₂ O	+	++	+
3.0-4.0	5.53	4.98	5.10	CaHPO ₄ ·2H ₂ O	0	T	T
4.0-5.0	6.07	5.12	5.17	None	0	0	0
5.0-6.0	6.02	5.40	5.39	"	0	0	0
6.0-7.0	} 6.05	} 5.64	} 5.59	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.09	5.71	5.80	"	0	0	0

Table 8. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.81</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	*
				CaHPO ₄	*	*	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	T	T
0.2-1.0	3.66	4.18	4.50	CaHPO ₄ ·2H ₂ O	++	++	++
1.0-2.0	4.04	4.37	4.72	CaHPO ₄ ·2H ₂ O	+	++	++
2.0-3.0	4.87	4.58	5.02	CaHPO ₄ ·2H ₂ O	T	++	+
3.0-4.0	6.02	5.00	5.20	CaHPO ₄ ·2H ₂ O	0	T	T
4.0-5.0	6.81	} 5.46	5.64	None	0	0	0
5.0-6.0	6.90		5.92	"	0	0	0
6.0-7.0	} 6.88	} 6.51	} 6.40	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.89	6.58	6.48	"	0	0	0
<u>Initial soil pH 7.49</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	*
				CaHPO ₄	*	*	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	+	T
0.2-1.0	3.70	4.16	4.63	CaHPO ₄ ·2H ₂ O	++	++	++
1.0-2.0	4.32	4.37	4.90	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.37	4.70	5.30	CaHPO ₄ ·2H ₂ O	+	+	+
3.0-4.0	7.16	5.18	5.63	CaHPO ₄ ·2H ₂ O	0	T	+
4.0-5.0	7.40	5.82	6.22	None	0	0	0
5.0-6.0	7.52	6.93	7.22	"	0	0	0
6.0-7.0	} 7.52	7.41	} 7.49	"	0	0	0
7.0-8.0		7.47		"	0	0	
8.0-9.7	7.52	7.46	7.49	"	0	0	0

Table 8. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4	16	48		Relative amounts ^a		
					4	16	48
	weeks	weeks	weeks		weeks	weeks	weeks

<u>Initial soil pH 7.51 (9.1% CaCO₃ added)</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	*
				CaHPO ₄	T	*	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	+	T
0.2-1.0	5.28	5.10	5.70	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	6.70	5.92	6.22	None	0	0	0
2.0-3.0	7.65	6.86	6.96	"	0	0	0
3.0-4.0	7.62	7.41	7.50	"	0	0	0
4.0-5.0	} 7.61	} 7.48	} 7.58	"	0	0	0
5.0-6.0				"	0	0	0
6.0-7.0		} 7.47	} 7.57	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7		7.46	7.58	"	0	0	0

Table 9. Crystalline phosphates identified in fertilizer residue and soil after incubation of mono-basic calcium phosphate monohydrate with Webster silty clay loam for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.53 (25°C.)^b</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	*
				CaHPO ₄	T	*	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	+	T
0.2-1.0	4.05	4.39	4.73	CaHPO ₄ ·2H ₂ O	++	+++	++
1.0-2.0	4.57	4.80	4.96	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.00	5.10	5.04	CaHPO ₄ ·2H ₂ O	+	+	+
3.0-4.0	5.66	5.35	5.32	CaHPO ₄ ·2H ₂ O	T	T	T
4.0-5.0	6.11	5.67	5.62	None	0	0	0
5.0-6.0	6.45	5.89	5.82	"	0	0	0
6.0-7.0	} 6.49	} 6.15	} 6.08	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.49	6.29	6.22	"	0	0	0
<u>Initial soil pH 6.53 (35°C.)</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	T	T	0
				CaHPO ₄	***	***	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	+	T
0.2-1.0	4.42	4.69	4.80	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	5.06	5.11	5.11	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.53	5.30	5.21	CaHPO ₄ ·2H ₂ O	+	+	+
3.0-4.0	5.90	5.40	5.36	None	0	0	0
4.0-5.0	6.34	} 5.77	5.58	"	0	0	0
5.0-6.0	6.47		5.75	"	0	0	0
6.0-7.0	} 6.47	} 6.08	} 5.91	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.47	6.21	6.05	"	0	0	0

^bTemperature of incubation. (Here and in following tables.)

Table 9. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.04 (25°C.)</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	**
				CaHPO ₄	*	*	**
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	+	+
0.2-1.0	4.12	4.59	4.70	CaHPO ₄ ·2H ₂ O	++	+++	+++
1.0-2.0	4.62	4.87	5.00	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.13	5.12	5.17	CaHPO ₄ ·2H ₂ O	+	++	++
3.0-4.0	5.99	5.49	5.52	CaHPO ₄ ·2H ₂ O	T	+	+
4.0-5.0	} 7.01	6.01	5.89	None	0	0	0
5.0-6.0		6.40	6.24	"	0	0	0
6.0-7.0	} 7.02	} 6.58	} 6.62	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.01	6.88	6.78	"	0	0	0
<u>Initial soil pH 7.04 (35°C.)</u>							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	T	T	0
				CaHPO ₄	***	***	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	+	+	+
0.2-1.0	4.58	4.69	4.95	CaHPO ₄ ·2H ₂ O	++	+++	++
1.0-2.0	5.09	5.04	5.20	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.60	5.25	5.38	CaHPO ₄ ·2H ₂ O	+	+	+
3.0-4.0	6.40	5.58	5.67	None	0	0	0
4.0-5.0	6.86	} 6.16	} 6.01	"	0	0	0
5.0-6.0	6.86			"	0	0	0
6.0-7.0	} 6.82	} 6.67	} 6.40	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.89	6.72	6.58	"	0	0	0

Table 9. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.71 (25°C.)</u>							
0 (fertilizer residue)	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	***	***	**
0-0.2	--	--	--	CaHPO_4	*	*	**
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++++	++++	++++
				CaHPO_4	T	+	T
0.2-1.0	4.18	4.51	4.82	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	+++	+++
1.0-2.0	5.00	4.94	5.12	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	++
2.0-3.0	6.45	5.39	5.42	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	+
3.0-4.0	7.70	6.21	6.05	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
4.0-5.0	7.76	6.97	6.69	None	0	0	0
5.0-6.0	7.77	7.37	7.30	"	0	0	0
6.0-7.0	} 7.78	} 7.50	} 7.51	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.72	7.63	7.62	"	0	0	0
<u>Initial soil pH 7.71 (35°C.)</u>							
0 (fertilizer residue)	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	0	0
0-0.2	--	--	--	CaHPO_4	***	***	***
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++++	++++	+++
				CaHPO_4	+	+	++
0.2-1.0	4.29	4.83	5.00	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	+++	+++
1.0-2.0	5.08	5.36	5.50	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	++
2.0-3.0	6.19	5.80	5.92	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	+
3.0-4.0	7.28	6.52	6.70	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
4.0-5.0	7.58	7.02	7.27	None	0	0	0
5.0-6.0	7.61	7.38	7.40	"	0	0	0
6.0-7.0	} 7.68	} 7.49	} 7.40	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.0	7.69	7.50	7.43	"	0	0	0

Table 9. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks

Initial soil pH 7.75 (9.1% CaCO ₃ added, 25°C.)							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	***	***	***
				CaHPO ₄	*	*	*
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
				CaHPO ₄	T	T	T
0.2-1.0	5.02	5.21	5.45	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	6.02	5.91	6.00	CaHPO ₄ ·2H ₂ O	+	T	+
2.0-3.0	7.31	6.72	6.61	CaHPO ₄ ·2H ₂ O	0	0	T
3.0-4.0	7.64	7.32	7.04	None	0	0	0
4.0-5.0	7.69	} 7.53	7.38	"	0	0	0
5.0-6.0	7.72		7.43	"	0	0	0
6.0-7.0	} 7.72	} 7.61	7.54	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.71	7.61	7.52	"	0	0	0

Initial soil pH 7.75 (9.1% CaCO ₃ added, 35°C.)							
0 (fertilizer residue)	--	--	--	CaHPO ₄ ·2H ₂ O	T	T	*
				CaHPO ₄	***	***	***
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
				CaHPO ₄	+	+	+
0.2-1.0	5.30	5.40	5.44	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	6.58	6.20	5.97	CaHPO ₄ ·2H ₂ O	T	+	+
2.0-3.0	7.50	6.79	6.72	CaHPO ₄ ·2H ₂ O	0	T	T
3.0-4.0	7.72	7.28	7.22	None	0	0	0
4.0-5.0	7.79	} 7.39	7.35	"	0	0	0
5.0-6.0	7.80		7.32	"	0	0	0
6.0-7.0	} 7.79	} 7.41	7.39	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.80	7.47	7.38	"	0	0	0

4 weeks even though the fertilizer phosphorus continued to diffuse into previously unaffected soil. The distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the non-calcareous samples incubated at a given temperature varied little with the initial soil pH. The presence of CaCO_3 , however, had an effect similar to that described for Norfolk loamy sand and Lloyd clay loam.

Temperature appeared to have only a slight effect on the amount and distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Webster silty clay loam. In the samples with initial pH values of 6.53 and 7.04, the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ occurred to a slightly greater distance from the fertilizer source at 25°C. than at 35°C. Temperature appeared to have no effect in the samples with initial pH values of 7.71 and 7.75.

The reaction of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ with Harpster silty clay loams I and II and Darling Downs clay (Table 10) followed the same pattern as described for the Norfolk, Lloyd, and Webster soils. Harpster silty clay loams I and II each had essentially the same pH but contained carbonate equivalent to 3.0% and 21.7% CaCO_3 , respectively. The greater content of carbonate in the Harpster silty clay loam II resulted in a more narrow precipitation-zone. The precipitate of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was concentrated closer to the source in Harpster silty clay loam II than in Harpster silty clay loam I presumably because of the higher carbonate content of the former soil. The distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Darling Downs clay (4.0% CaCO_3 equivalent) was similar to that observed in Harpster silty clay loam I.

As may be observed from Tables 7, 8, 9, and 10, the acid solution (saturated solution pH of 1.48) from $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ depressed the soil pH to various degrees, depending on the buffering capacity of the soil. This

Table 10. Crystalline phosphates identified in fertilizer residue and soil after incubation of monobasic calcium phosphate monohydrate with Harpster silty clay loams I and II and Darling Downs clay for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Harpster silty clay loam I (pH 7.51)</u>							
0 (fertilizer residue)	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	***	***	***
				CaHPO_4	T	*	*
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++++	++++	++++
				CaHPO_4	T	T	T
0.2-1.0	4.25	4.74	5.01	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	+++
1.0-2.0	5.25	5.25	5.48	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	++
2.0-3.0	6.31	5.72	5.79	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	+	+
3.0-4.0	7.43	6.31	6.20	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	0	T
4.0-5.0	7.50	7.06	6.59	None	0	0	0
5.0-6.0	7.45		7.03	"	0	0	0
6.0-7.0	7.47	7.31	7.38	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.47	7.32	7.41	"	0	0	0
<u>Harpster silty clay loam II (pH 7.52)</u>							
0 (fertilizer residue)	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	***	***	***
				CaHPO_4	T	T	*
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++++	++++	++++
				CaHPO_4	T	0	+
0.2-1.0	6.09	6.30	6.50	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	+++
1.0-2.0	7.24	6.79	7.20	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
2.0-3.0	7.49	7.26	7.50	None	0	0	0
3.0-4.0	7.52	7.30	7.55	"	0	0	0
4.0-5.0	7.50	7.37	7.53	"	0	0	0
5.0-6.0				"	0	0	0
6.0-7.0		7.39	7.52	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7		7.40	7.57	"	0	0	0

Table 10. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks

<u>Darling Downs clay (pH 7.80)</u>							
0 (fertilizer residue)	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	***	***	***
				CaHPO_4	T	*	*
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++++	++++	++++
				CaHPO_4	0	0	T
0.2-1.0	4.98	5.24	5.69	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	+++
1.0-2.0	5.70	5.88	6.33	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	++
2.0-3.0	6.67	6.38	6.99	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	+
3.0-4.0	7.42	6.77	7.38	None	0	0	0
4.0-5.0	7.60	7.24	7.52	"	0	0	0
5.0-6.0	7.60	7.56	7.65	"	0	0	0
6.0-7.0	} 7.60	} 7.52	} 7.70	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7				7.64	7.52	7.77	"

capacity increased with increasing content of exchangeable bases and carbonate. $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ depressed the pH of noncalcareous Norfolk loamy sand (0.79 to 2.52 meq. of exchangeable Ca/100g.) to a greater extent than in noncalcareous Lloyd clay loam (4.96 to 9.13 meq. exchangeable Ca/100g.). Similarly, the depression of pH values in noncalcareous Lloyd clay loam was greater than that observed in noncalcareous Webster silty clay loam (21.3 to 29.2 meq. of exchangeable Ca/100g.).

The pH values of the soil in which $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitated ranged from 2.83 in Norfolk loamy sand to 6.67 in Darling Downs clay. Although the pH values of soil containing precipitated $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ did increase with time, the values rarely exceeded pH 6.5. The transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was found in Part II to occur only at pH values greater than about 7.0 at 25°C. and at values greater than about 6.5 at 35°C. Thus it is obvious why $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was not detected as a hydrolysis product of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in this particular investigation.

Reaction of monobasic ammonium phosphate with soils

$\text{NH}_4\text{H}_2\text{PO}_4$ dissolves congruently to produce a saturated solution having a pH of 3.47 and containing 2.87 moles of phosphorus and ammonium per liter (Lindsay *et al.*, 1962). With one exception, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was the only reaction product identified in soils which had reacted with $\text{NH}_4\text{H}_2\text{PO}_4$. In Darling Downs clay, $\text{Mg NH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was found as a reaction product in addition to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. In all soils, the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ invariably precipitated as small clusters of blade-like crystals, whereas $\text{Mg NH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ generally occurred as single prismatic crystals.

The amount and distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ produced in Norfolk loamy sand by reaction with $\text{NH}_4\text{H}_2\text{PO}_4$ are shown in Table 11. It is obvious that most of the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ occurred in 4 weeks because little change in the amount and distribution of the phosphate compound was observed at 16 or 48 weeks. Only trace to small amounts of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were formed in the segments of the samples adjusted to pH values of 6.41, 6.87, and 7.91 (minus CaCO_3), presumable because of the low content of exchangeable calcium in the soil. Because the fertilizer is devoid of calcium, the quantity of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitated would be expected to be dependent on the content of reactive calcium in the soil. In addition to exchangeable calcium, CaCO_3 can be a source of reactive calcium, as can be seen from the intensity of the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Norfolk loamy sand at pH 7.91 with and without CaCO_3 . The failure to detect $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ or other crystalline phosphates in the Norfolk loamy sand adjusted to pH 8.70 with Na_2CO_3 probably resulted in part from the low content of exchangeable calcium.

As shown in Table 12, the pattern of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitation in Lloyd clay loam was similar to that observed in Norfolk loamy sand. The amounts of the compound precipitated in segments of samples of comparable initial pH were greater in the Lloyd soil than in the Norfolk soil probably because of the greater content of exchangeable calcium in the Lloyd soil.

The amount and distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Webster silty loam after reaction with $\text{NH}_4\text{H}_2\text{PO}_4$ at 25°C . and 35°C . are shown in Table 13. There appears to be little or no difference in the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at the two temperatures. The extent of the precipitation zone of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (approximately 0 to 4.0 cm.) in noncalcareous Webster silty clay loam varied

Table 11. Crystalline phosphates identified after incubation of monobasic ammonium phosphate with Norfolk loamy sand for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.41</u>							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	T	O	O
0.2-1.0	4.96	} 5.27	5.09	CaHPO ₄ ·2H ₂ O	T	T	T
1.0-2.0	5.10		5.22	CaHPO ₄ ·2H ₂ O	T	T	T
2.0-3.0	5.16	} 5.30	} 5.36	CaHPO ₄ ·2H ₂ O	T	T	T
3.0-4.0	5.15			CaHPO ₄ ·2H ₂ O	T	T	T
4.0-5.0	} 5.10	} 5.18	} 5.30	CaHPO ₄ ·2H ₂ O	O	T	T
5.0-6.0				CaHPO ₄ ·2H ₂ O	O	T	T
6.0-7.0	} 4.97	} 5.16	} 5.32	None	O	O	O
7.0-8.0				"	O	O	O
8.0-9.0	5.21	5.28	5.20	"	O	O	O
<u>Initial soil pH 6.87</u>							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	O	O	O
0.2-1.0	4.98	} 5.32	5.02	CaHPO ₄ ·2H ₂ O	T	T	T
1.0-2.0	5.13		5.14	CaHPO ₄ ·2H ₂ O	T	T	T
2.0-3.0	5.20	} 5.30	} 5.27	CaHPO ₄ ·2H ₂ O	+	T	T
3.0-4.0	5.25			CaHPO ₄ ·2H ₂ O	+	T	T
4.0-5.0	} 5.36	} 5.31	} 5.27	CaHPO ₄ ·2H ₂ O	T	T	T
5.0-6.0				CaHPO ₄ ·2H ₂ O	T	T	T
6.0-7.0	} 5.36	} 5.31	} 5.30	None	O	O	O
7.0-8.0				"	O	O	O
8.0-9.7	5.61	5.32	5.23	"	O	O	O

Table 11. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.91</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	0
0.2-1.0	4.97	} 5.31	5.00	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	T	T
1.0-2.0	5.18		5.21	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	T
2.0-3.0	5.27	} 5.33	} 5.29	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	T
3.0-4.0	5.33			$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	T
4.0-5.0	} 5.45	} 5.38	} 5.38	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
5.0-6.0				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
6.0-7.0	} 5.31	} 5.30	} 5.38	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
7.0-8.0				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
8.0-9.7	5.91	5.29	5.20	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	0	T
<u>Initial soil pH 7.91 (9.1% CaCO_3 added)</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	++
0.2-1.0	6.95	} 6.42	6.20	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	++	+
1.0-2.0	6.82		6.02	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	+
2.0-3.0	6.81	} 6.27	} 6.05	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	0
3.0-4.0	6.56			None	0	0	0
4.0-5.0	6.18	} 6.31	} 6.00	"	0	0	0
5.0-6.0	6.17			"	0	0	0
6.0-7.0	} 6.15	} 6.24	} 6.04	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.84	6.02	--	"	0	0	0
<u>Initial soil pH 8.70</u>							
0-0.2	--	--	--	None	0	0	0
0.2-2.0	--	5.93	--	"	0	0	0
2.0-4.0	--	6.09	--	"	0	0	0
4.0-6.0	--	6.09	--	"	0	0	0
6.0-8.0	--	6.07	--	"	0	0	0
8.0-9.7	--	6.03	--	"	0	0	0

Table 12. Crystalline phosphates identified after incubation of monobasic ammonium phosphate with Lloyd clay loam for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks

<u>Initial soil pH 6.21</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	0	0
0.2-1.0	5.18	5.61	5.42	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	+	++
1.0-2.0	5.49		5.36	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	+	+
2.0-3.0	5.50	5.21	5.18	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	+
3.0-4.0	5.21		4.90	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	0
4.0-5.0	4.90	4.67	4.44	None	0	0	0
5.0-6.0	5.05			"	0	0	0
6.0-7.0	5.77	4.22	4.52	"	0	0	0
7.0-8.0	6.08			"	0	0	0
8.0-9.7	6.15	4.17	4.58	"	0	0	0

<u>Initial soil pH 6.81</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	0	0
0.2-1.0	5.30	5.57	5.40	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	+	+
1.0-2.0	5.62		5.35	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	+
2.0-3.0	5.57	5.11	5.26	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	+	+
3.0-4.0	5.32		5.09	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
4.0-5.0	5.12	4.67	4.79	None	0	0	0
5.0-6.0	5.60			"	0	0	0
6.0-7.0	6.53	4.34	4.70	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.70	4.30	4.63	"	0	0	0

Table 12. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.49</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	T	T
0.2-1.0	5.42	5.82	5.33	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	+
1.0-2.0	5.60		5.28	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	+	+
2.0-3.0	5.72	5.34	5.14	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	++	+
3.0-4.0	5.58		4.95	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	++	+
4.0-5.0	5.50	4.68	4.82	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
5.0-6.0	6.89			None	0	0	0
6.0-7.0	7.33	4.56	4.82	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.42	5.16	4.92	"	0	0	0
<u>Initial soil pH 7.51 (9.1% CaCO_3 added)</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	+
0.2-1.0	6.11	6.50	6.11	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	+
1.0-2.0	6.30	6.44	6.13	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	+
2.0-3.0	6.38	6.22	6.09	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	0	T
3.0-4.0	6.38	6.02	5.88	None	0	0	0
4.0-5.0	6.94	5.75	5.81	"	0	0	0
5.0-6.0	7.42		5.97	"	0	0	0
6.0-7.0	7.57	6.92	7.00	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7		7.02	7.09	"	0	0	0

Table 13. Crystalline phosphates identified after incubation of monobasic ammonium phosphate with Webster silty clay loam for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.53 (25°C.)^b</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	++
0.2-1.0	5.12	} 5.32	5.19	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	+++	+++
1.0-2.0	5.15		5.20	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	+++	++
2.0-3.0	5.08	} 5.19	5.19	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	++	++
3.0-4.0	5.24		5.05	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	+	+
4.0-5.0	5.41	} 4.70	} 4.62	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	0
5.0-6.0	5.83			None	0	0	0
6.0-7.0	} 6.42	} 4.55	} 4.60	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.56	4.59	4.53	"	0	0	0
<u>Initial soil pH 6.53 (35°C.)</u>							
0-0.2	--	--	--	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	++
0.2-1.0	5.49	} 5.93	5.09	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+++	+++	+++
1.0-2.0	5.58		5.09	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	++	++	+++
2.0-3.0	5.58	} 5.81	5.13	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	+	+	+
3.0-4.0	5.63		5.19	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	T	+	T
4.0-5.0	6.08	} 5.99	} 5.26	None	0	0	0
5.0-6.0	6.60			"	0	0	0
6.0-7.0	} 6.68	} 6.11	} 5.46	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.69	6.20	5.54	"	0	0	0

Table 13. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4	16	48		Relative amounts ^a		
	weeks	weeks	weeks		4	16	48
					weeks	weeks	weeks
Initial soil pH 7.04 (25°C.)							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
0.2-1.0	5.12	} 5.29	5.20	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	5.21		5.21	CaHPO ₄ ·2H ₂ O	++	+++	+++
2.0-3.0	5.09	} 5.01	5.12	CaHPO ₄ ·2H ₂ O	++	++	++
3.0-4.0	5.18		4.92	CaHPO ₄ ·2H ₂ O	+	+	+
4.0-5.0	5.41	} 4.54	} 4.71	None	0	0	0
5.0-6.0	6.32			"	0	0	0
6.0-7.0	} 7.03	} 4.54	} 4.70	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.05	4.81	4.68	"	0	0	0
Initial soil pH 7.04 (35°C.)							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
0.2-1.0	5.61	} 5.75	5.43	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	5.54		5.54	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.45	} 5.58	5.52	CaHPO ₄ ·2H ₂ O	+	+	+
3.0-4.0	5.52		5.49	CaHPO ₄ ·2H ₂ O	+	+	T
4.0-5.0	5.80	} 5.29	} 5.33	None	0	0	0
5.0-6.0	6.10			"	0	0	0
6.0-7.0	} 6.76	} 5.37	} 5.31	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	6.99	5.51	5.35	"	0	0	0
Initial soil pH 7.71 (25°C.)							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
0.2-1.0	5.21	} 5.32	5.08	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	5.31		5.12	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.10	} 5.08	5.03	CaHPO ₄ ·2H ₂ O	+	+	++
3.0-4.0	5.31		4.89	CaHPO ₄ ·2H ₂ O	T	T	+
4.0-5.0	5.75	} 4.91	} 4.80	CaHPO ₄ ·2H ₂ O	0	T	0
5.0-6.0	7.20			None	0	0	0
6.0-7.0	} 7.64	} 4.92	} 4.81	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.69	6.18	5.01	"	0	0	0

Table 13. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
Initial soil pH 7.71 (35°C.)							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
0.2-1.0	5.74	} 6.17	5.40	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	5.89		5.48	CaHPO ₄ ·2H ₂ O	++	++	++
2.0-3.0	5.91	} 6.19	5.55	CaHPO ₄ ·2H ₂ O	+	+	+
3.0-4.0	6.00		5.62	CaHPO ₄ ·2H ₂ O	T	+	T
4.0-5.0	6.62	} 6.50	} 5.55	None	0	0	0
5.0-6.0	7.36			"	0	0	0
6.0-7.0	} 7.56	} 7.03	} 5.31	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.69	7.59	5.40	"	0	0	0
Initial soil pH 7.75 (9.1% CaCO ₃ added, 25°C.)							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
0.2-1.0	6.50	} 6.12	5.99	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	6.62		6.02	CaHPO ₄ ·2H ₂ O	+	+	++
2.0-3.0	6.75	} 5.79	5.91	CaHPO ₄ ·2H ₂ O	0	+	+
3.0-4.0	7.18		5.91	None	0	+	+
4.0-5.0	7.53	} 6.15	6.51	"	0	0	0
5.0-6.0	7.56		7.11	"	0	0	0
6.0-7.0	} 7.72	} 7.18	} 7.20	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.72	7.26	7.20	"	0	0	0
Initial soil pH 7.75 (9.1% CaCO ₃ added, 35°C.)							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
0.2-1.0	6.67	} 6.90	6.10	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	6.79		6.16	CaHPO ₄ ·2H ₂ O	T	T	T
2.0-3.0	6.88	} 6.98	6.30	CaHPO ₄ ·2H ₂ O	0	0	T
3.0-4.0	7.01		6.91	None	0	0	0
4.0-5.0	7.52	} 7.12	7.21	"	0	0	0
5.0-6.0	7.52		7.28	"	0	0	0
6.0-7.0	} 7.65	} 7.35	-	"	0	0	0
7.0-8.0			-	"	0	0	0
8.0-9.7	7.70	7.48	-	"	0	0	0

little with the initial soil pH and was of magnitude similar to that observed in noncalcareous Lloyd clay loam. The amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitated in each soil segment, however, was much greater than that observed in comparable segments of Lloyd clay loam. The more extensive precipitation in Webster silty clay loam was associated with its higher content of exchangeable calcium. The addition of CaCO_3 to the Webster soil shortened the precipitation zone of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

The influence of carbonate on the amount and distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Harpster silty clay loam may be observed in Table 14. The precipitation zone of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was longer in Harpster silty clay loam I (3.0% CaCO_3 equivalent) than in Harpster silty clay loam II (21.7% CaCO_3 equivalent).

When $\text{NH}_4\text{H}_2\text{PO}_4$ reacted with Darling Downs clay, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was identified as a reaction product in addition to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Table 14). The $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals observed in this soil after 4 weeks were in the form of hemimorphic pyramidal prisms up to 1 mm. in length (Figure 2). The X-ray diffraction pattern, the refractive index, and the morphology of the crystals all agreed with those given for $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ by Lehr et al. (1967).

$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is reported to form in irrigation ditches when ammonium phosphate fertilizers are dissolved in alkaline water (Lehr et al., 1967), and this salt has also been identified in the precipitates formed when MgO or $\text{CaMg}(\text{CO}_3)_2$ is added to saturated solutions of $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ (Lindsay et al., 1962). Aside from the report by Lehr et al., however, no account of formation of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in soil was encountered in the literature. It is apparent that Darling Downs clay contained a sufficiently high content of reactive magnesium to permit precipitation of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

Table 14. Crystalline phosphates identified after incubation of monobasic ammonium phosphate with Harpster silty clay loam I and II and Darling Downs clay for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species.	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Harpster silty clay loam I (pH 7.51)</u>							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
0.2-1.0	6.12	6.31	5.69	CaHPO ₄ ·2H ₂ O	+++	+++	+++
1.0-2.0	6.49	6.31	5.80	CaHPO ₄ ·2H ₂ O	++	+++	+++
2.0-3.0	6.36	5.83	5.79	CaHPO ₄ ·2H ₂ O	+	++	++
3.0-4.0	6.02	5.60	5.72	CaHPO ₄ ·2H ₂ O	T	+	+
4.0-5.0	6.80	5.58	5.73	None	0	0	0
5.0-6.0	7.48	5.65	5.71	"	0	0	0
6.0-7.0	} 7.46 }	} 6.65 }	} 6.21 }	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7				7.51	7.13	7.13	"
<u>Harpster silty clay loam II (pH 7.52)</u>							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	++++	++++	++++
0.2-1.0	6.99	6.80	6.72	CaHPO ₄ ·2H ₂ O	++	+++	+++
1.0-2.0	7.37	6.85	7.18	CaHPO ₄ ·2H ₂ O	0	+	0
2.0-3.0	7.25	6.84	7.16	None	0	0	0
3.0-4.0	7.56	6.84	7.19	"	0	0	0
4.0-5.0	7.58	} 7.11 }	} 7.29 }	"	0	0	0
5.0-6.0	7.53			"	0	0	0
6.0-7.0	} 7.52 }			} 7.26 }	} 7.31 }	"	0
7.0-8.0		"	0			0	0
8.0-9.7		7.51	7.28			7.38	"

^bBroken line indicates distance of movement could not be determined precisely by method used. (Here and throughout other tables.)

Table 14. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4	16	48		Relative amounts ^a		
					4	16	48
	weeks	weeks	weeks		weeks	weeks	weeks
<u>Darling Downs clay (pH 7.80)</u>							
0-0.2	--	--	--	CaHPO ₄ ·2H ₂ O	+++	+++	+++
				MgNH ₄ PO ₄ ·6H ₂ O	T	0	0
0.2-1.0	6.22	6.45	5.82	CaHPO ₄ ·2H ₂ O	+++	++	+++
				MgNH ₄ PO ₄ ·6H ₂ O	+++	+++	+
1.0-2.0	6.34	6.49	5.98	CaHPO ₄ ·2H ₂ O	++	++	++
				MgNH ₄ PO ₄ ·6H ₂ O	++	++	T
2.0-3.0	6.27	6.30	6.09	CaHPO ₄ ·2H ₂ O	+	+	++
				MgNH ₄ PO ₄ ·6H ₂ O	T	+	T
3.0-4.0	6.40	6.31	6.08	CaHPO ₄ ·2H ₂ O	T	T	T
				MgNH ₄ PO ₄ ·6H ₂ O	0	T	0
4.0-5.0	7.00	6.44	6.03	None	0	0	0
5.0-6.0	7.56	6.96	6.01	"	0	0	0
6.0-7.0	} 7.60	} 7.32	} 6.88	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7				"	0	0	0



Figure 2. Magnesium ammonium phosphate hexahydrate found in a column of Darling Downs clay 16 weeks after addition of a band of monobasic ammonium phosphate (X/5). The crystals were from soil 0.5 to 1.0 cm. from the fertilizer band.

As may be seen from Table 14, only a trace of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was identified in the 0 to 0.2 cm. soil segment at 4 weeks. The precipitation of this compound quickly reached a peak in the 0.2 to 1.0 cm. segment and then decreased with distance to about 3.0 cm. The initial contact of the acid fertilizer solution with the first few millimeters of soil probably provided an environment too acid for precipitation of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

After 16 weeks, some of the $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals showed a small amount of pitting, indicating that dissolution was occurring. Only a small quantity of the compound remained after 48 weeks. The remaining crystals were only fragments of the original crystals observed at 4 weeks. A white powder was observed on the surface of the residual crystals, but the amount was too small for X-ray diffraction analysis, and identification by the optical properties was not successful. It is known, however, that $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ will dissolve incongruently in water to form a magnesium phosphate of composition $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$. It is conceivable, then, that the white powdery material observed on the $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals at 48 weeks was $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$.

The $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ formed in Darling Downs clay occurred as small clusters of blade-shaped crystals, as in the other soils. The amount of the phosphate compound identified decreased with distance from the source of $\text{NH}_4\text{H}_2\text{PO}_4$, and the major portion of the precipitation appeared to have been completed in 4 weeks.

Because $\text{NH}_4\text{H}_2\text{PO}_4$ does not produce a solution as acid as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, the pH values of the soils in contact with the former salt were higher than in comparative segments of soils which had reacted with the latter

salt. In the soils which reacted with $\text{NH}_4\text{H}_2\text{PO}_4$, however, the conversion of NH_4^+ to NO_3^- (nitrification) with time resulted in a slight decrease in pH from 4 to 48 weeks.

In the soils reacted with $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was found from pH 4.96 to pH 6.99. This range is smaller than that observed in the case of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (2.83 to 6.67), and the upper and lower limits are higher. The pH values were still too low, however, to promote the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$.

Reaction of dibasic ammonium phosphate with soils

Like $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ dissolves congruently, leaving no solid residue. The saturated solution produced by the dissolution of $(\text{NH}_4)_2\text{HPO}_4$, however, is alkaline (pH 7.98), in contrast to the acid solution (pH 3.47) produced by $\text{NH}_4\text{H}_2\text{PO}_4$. The saturated solution of $(\text{NH}_4)_2\text{HPO}_4$ contains 3.82 moles of phosphorus and 7.64 moles of ammonium per liter (Lindsay et al., 1962).

Table 15 shows the reaction products identified after the reaction of $(\text{NH}_4)_2\text{HPO}_4$ with Norfolk loamy sand for 4, 16, and 48 weeks. After 4 weeks, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (dimorph B) was identified in each of the soils adjusted to various pH values. This compound was observed under the binocular microscope as white lath-like structures on the surface of the soil particles. When these structures were examined under the petrographic microscope, each was found to consist of hundreds of parallel rods. (The morphology of these crystals may be seen in Figure 3 which occurs at a later stage and which contains a photomicrograph of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$)

Table 15. Crystalline phosphates identified after incubation of dibasic ammonium phosphate with Norfolk loamy sand for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.41</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	T	0	0
0.2-1.0	7.06	} 6.88	5.58	None	0	0	0
1.0-2.0	7.00		5.72	"	0	0	0
2.0-3.0	7.02	} 6.92	} 5.80	"	0	0	0
3.0-4.0	6.75			"	0	0	0
4.0-6.0	6.42	6.82	5.90	"	0	0	0
6.0-8.0	5.91	6.97	5.88	"	0	0	0
8.0-9.7	5.72	6.80	5.78	"	0	0	0
<u>Initial soil pH 6.87</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	T	0	0
0.2-1.0	7.01	} 6.88	5.90	None	0	0	0
1.0-2.0	6.74		5.71	"	0	0	0
2.0-3.0	6.81	} 6.84	} 5.92	"	0	0	0
3.0-4.0	6.78			"	0	0	0
4.0-6.0	6.56	6.82	5.92	"	0	0	0
6.0-8.0	6.10	6.80	5.92	"	0	0	0
8.0-9.7	5.90	6.72	5.76	"	0	0	0

Table 15. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.91</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	+	T	0
0.2-1.0	6.92	6.97	5.80	None	0	0	0
1.0-2.0	6.80		5.81	"	0	0	0
2.0-3.0	6.69	7.01	6.00	"	0	0	0
3.0-4.0	6.30			"	0	0	0
4.0-6.0	6.01	6.93	6.02	"	0	0	0
6.0-8.0	6.10	6.94	5.89	"	0	0	0
8.0-9.7	6.04	6.91	5.89	"	0	0	0
<u>Initial pH 7.91 (9.1% CaCO_3 added)</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	+++	T	0
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	+	+
0.2-1.0	6.91	6.83	5.98	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	+	0	0
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	T	T
1.0-2.0	6.67	7.15	5.79	None	0	0	0
2.0-3.0	6.76		6.01	"	0	0	0
3.0-4.0	6.49			"	0	0	0
5.0-6.0	5.96	6.87	5.97	"	0	0	0
6.0-8.0	6.13	6.88	6.00	"	0	0	0
8.0-9.7	6.90	6.86	5.55	"	0	0	0
<u>Initial pH 8.70</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	T	0	0
0.2-1.0	--	7.04	--	None	0	0	0
1.0-2.0	--		--	"	0	0	0
2.0-3.0	--	7.02	--	"	0	0	0
3.0-4.0	--		--	"	0	0	0
4.0-6.0	--	7.03	--	"	0	0	0
6.0-8.0	--	6.99	--	"	0	0	0
8.0-9.7	--	7.09	--	"	0	0	0

crystals isolated from Harpster silty clay loam I.) The compound had an average refractive index of 1.51 which agreed with the data given by Lehr *et al.* (1967) for $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ ($\alpha = 1.506$, $\beta = 1.510$, $\gamma = 1.511$). The X-ray diffraction data obtained on the compound also agreed with those given for $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ by Lehr *et al.*

In the noncalcareous samples of Norfolk loamy sand, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was identified at 4 weeks in trace to small amounts only in the first 2 mm. adjacent to the $(\text{NH}_4)_2\text{HPO}_4$ source. The initial precipitation of the compound in the sample treated with CaCO_3 was more extensive but still did not occur more than 5 mm. away from the fertilizer source.

With increasing time, the $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ slowly dissolved. At 48 weeks, the compound could not be detected in any of the Norfolk samples. In the calcareous sample, however, it was possible to detect a white powdery residue of the originally dense precipitate of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$. Under the petrographic microscope, the residue was observed as very small (about 1μ in diameter) crystals roughly circular in shape. The refractive index of these crystals was difficult to determine but was in the range 1.55 to 1.56. *In vitro* studies have shown that $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ can alter to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Frazier *et al.*, 1964). This latter compound has refractive indexes of 1.540 (α), 1.545 (β) and 1.551 (γ). It is conceivable, therefore, that the residue was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. Unfortunately, the residue produced no X-ray diffraction peaks, so that a positive identification could not be made with this method.

As shown in Table 16, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was also identified in Lloyd clay loam. The amounts were higher than in Norfolk loamy sand, presumably because of the higher content of reactive calcium in the Lloyd

Table 16. Crystalline phosphates identified after incubation of dibasic ammonium phosphate with Lloyd clay loam for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.21</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	T	0	0
0.2-1.0	6.00	} 6.68	6.18	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	T	0	0
1.0-2.0	6.18		6.28	None	0	0	0
2.0-3.0	6.21	} 6.53	6.25	"	0	0	0
3.0-4.0	6.30		6.01	"	0	0	0
4.0-5.0	6.18	} 6.44	} 6.04	"	0	0	0
5.0-6.0	5.92			"	0	0	0
6.0-7.0	5.20	} 6.02	} 6.03	"	0	0	0
7.0-8.0	5.28			"	0	0	0
8.0-9.7	5.89	4.80	5.84	"	0	0	0
<u>Initial soil pH 6.81</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	+	0	0
0.2-1.0	6.19	} 6.60	5.65	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	+	0	0
1.0-2.0	6.29		5.98	None	0	0	0
2.0-3.0	6.28	} 6.51	5.91	"	0	0	0
3.0-4.0	6.40		6.11	"	0	0	0
4.0-5.0	6.38	} 6.37	} 6.21	"	0	0	0
5.0-6.0	6.48			"	0	0	0
6.0-7.0	6.48	} 5.91	} 6.31	"	0	0	0
7.0-8.0	6.22			"	0	0	0
8.0-9.7	6.32	--	--	"	0	0	0

Table 16. (Continued).

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.49</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	++	T	0
0.2-1.0	6.00	} 6.72	6.20	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	+	T	0
1.0-2.0	6.21		6.28	None	0	0	0
2.0-3.0	6.32	} 6.72	6.23	"	0	0	0
3.0-4.0	6.45		6.09	"	0	0	0
4.0-5.0	6.36	} 6.70	} 6.13	"	0	0	0
5.0-6.0	6.72			"	0	0	0
6.0-7.0	6.82	} 6.66	} 5.93	"	0	0	0
7.0-8.0	7.33			"	0	0	0
8.0-9.7	7.37	6.48	5.70	"	0	0	0
<u>Initial soil pH 7.51 (9.1% CaCO_3 added)</u>							
0-0.2	--	--	--	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	++++	+++	T
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	0	+
0.2-1.0	6.25	6.61	6.37	$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$	++	+	T
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0	0	T
1.0-2.0	6.29	6.52	6.41	None	0	0	0
2.0-3.0	6.31	6.58	6.28	"	0	0	0
3.0-4.0	6.33	6.50	6.21	"	0	0	0
4.0-5.0	6.47	} 6.41	} 6.31	"	0	0	0
5.0-6.0	7.11			"	0	0	0
6.0-7.0	7.39	} 6.26	} 6.12	"	0	0	0
7.0-8.0	7.48			"	0	0	0
8.0-9.7	7.50	6.49	6.12	"	0	0	0

soil. The precipitation of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ generally occurred in the first few millimeters of soil, and only in the samples treated with CaCO_3 did it extend as far as 5 mm. from the fertilizer source. The amount of the compound formed at 4 weeks increased with the initial pH and content of reactive calcium in the soil.

By the end of 16 weeks, the crystals of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ had lost their characteristic lath-like shape and had formed a white powdery material. The powdery material was still present at the end of 48 weeks, and the presence of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was identified in it by X-ray diffraction.

The nature of the reaction products identified after the reaction of $(\text{NH}_4)_2\text{HPO}_4$ with Webster silty clay loam at 25°C . and 35°C . is shown in Table 17. $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was identified in all samples at the end of 4 weeks. The precipitation of this compound followed the same pattern as that described for Lloyd clay loam. The amount of the compound formed in Webster silty clay loam, however, was generally larger than that formed in Lloyd clay loam at the same temperature and comparable soil pH, presumably as a result of the higher content of exchangeable calcium in the former soil. At 35°C ., the precipitation of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was in all instances less than in comparable samples at 25°C .

At 16 and 48 weeks, a tan colored powdery residue of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was found in Webster silty clay loam adjusted to pH values of 7.71 and 7.75. The residue had optical properties similar to those of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

In Webster silty clay loam, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was identified as an important reaction product at 4 weeks and, in noncalcareous soil, extended from 0 to

Table 17. Crystalline phosphates identified after incubation of dibasic ammonium phosphate with Webster silty clay loam for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 6.53 (25°C)</u>							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	++	0	0
				CaHPO ₄ ·2H ₂ O	T	++	++
0.2-1.0	6.52	6.90	6.30	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	T	0	0
				CaHPO ₄ ·2H ₂ O	T	++	++
1.0-2.0	6.52	6.40	6.27	CaHPO ₄ ·2H ₂ O	+	+	++
2.0-3.0	6.70		5.68	CaHPO ₄ ·2H ₂ O	+	+	++
3.0-4.0	6.52	6.91	5.28	CaHPO ₄ ·2H ₂ O	+	++	++
4.0-5.0	5.68		4.94	CaHPO ₄ ·2H ₂ O	T	++	0
5.0-6.0	5.73	4.91	4.89	None	0	0	0
6.0-7.0	6.23			"	0	0	0
7.0-8.0	6.50	4.69	4.92	"	0	0	0
8.0-9.7	6.79			"	0	0	0
<u>Initial soil pH 6.53 (35°C.)</u>							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	+	0	0
				CaHPO ₄ ·2H ₂ O	+	++	++
0.2-1.0	6.60	--	6.29	CaHPO ₄ ·2H ₂ O	T	++	+
1.0-2.0	6.74	--	6.20	CaHPO ₄ ·2H ₂ O	+	T	0
2.0-3.0	6.79	--	6.00	CaHPO ₄ ·2H ₂ O	+	++	+
3.0-4.0	6.89	--	5.82	CaHPO ₄ ·2H ₂ O	+	++	+++
4.0-5.0	6.99	--	5.50	CaHPO ₄ ·2H ₂ O	T	0	T
5.0-6.0	6.82	--		None	0	0	0
6.0-7.0	6.73	--	5.38	"	0	0	0
7.0-8.0	6.59	--		"	0	0	0
8.0-9.7	6.76	--	5.32	"	0	0	0

Table 17. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
<u>Initial soil pH 7.04 (25°C.)</u>							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	++	0	0
				CaHPO ₄ ·2H ₂ O	T	++	++
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T
0.2-1.0	6.32	6.90	6.35	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	T	0	0
				CaHPO ₄ ·2H ₂ O	T	+	+
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T
1.0-2.0	6.53	6.22	6.31	CaHPO ₄ ·2H ₂ O	+	+	++
2.0-3.0	6.54		5.72	CaHPO ₄ ·2H ₂ O	+	+	++
3.0-4.0	6.62		5.32	CaHPO ₄ ·2H ₂ O	+	++	++
4.0-5.0	5.80	4.81	5.10	None	0	0	0
5.0-6.0	6.28			"	0	0	0
6.0-7.0	6.74			"	0	0	0
7.0-8.0	7.04	4.68	5.02	"	0	0	0
8.0-9.7	7.06	4.77	5.15	"	0	0	0
<u>Initial soil pH 7.04 (35°C.)</u>							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	+	0	0
				CaHPO ₄ ·2H ₂ O	++	++	+
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T
0.2-1.0	6.48	7.07	5.98	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	T	0	0
				CaHPO ₄ ·2H ₂ O	+	+	T
				CaHPO ₄ ·2H ₂ O	+	0	0
1.0-2.0	6.67	6.90	6.01	CaHPO ₄ ·2H ₂ O	+	+	++
2.0-3.0	6.64		5.98	CaHPO ₄ ·2H ₂ O	+	++	++
3.0-4.0	6.85		5.72	CaHPO ₄ ·2H ₂ O	0	+	+
4.0-5.0	6.60	6.52	5.48	CaHPO ₄ ·2H ₂ O	0	0	0
5.0-6.0	6.32			"	0	0	0
6.0-7.0	6.70			6.12	5.42	"	0
7.0-8.0		"	0			0	0
8.0-9.7	6.98	6.09	5.40	"	0	0	0

Table 17. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
Initial soil pH 7.71 (25°C.)							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	+++	T	0
				CaHPO ₄ ·2H ₂ O	0	++	++
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T
0.2-1.0	6.40	6.88	6.41	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	+	0	0
				CaHPO ₄ ·2H ₂ O	0	+	+
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	0
1.0-2.0	6.55	6.18	6.30	CaHPO ₄ ·2H ₂ O	T	T	T
2.0-3.0	6.58			CaHPO ₄ ·2H ₂ O	T	T	T
3.0-4.0	6.47			CaHPO ₄ ·2H ₂ O	T	++	++
4.0-5.0	5.58	5.17	5.10	CaHPO ₄ ·2H ₂ O	0	T	0
5.0-6.0	6.51		5.19	None	0	0	0
6.0-7.0	7.55	4.94	5.38	"	0	0	0
7.0-8.0					"	0	0
8.0-9.7	7.64	5.55	5.70	"	0	0	0
Initial soil pH 7.71 (35°C.)							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	T	T	0
				CaHPO ₄ ·2H ₂ O	++	++	++
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T
0.2-1.0	6.71	7.11	6.25	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	T	0	0
				CaHPO ₄ ·2H ₂ O	0	T	+
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	0	T
1.0-2.0	6.82	7.02	6.28	CaHPO ₄ ·2H ₂ O	T	T	T
2.0-3.0	7.00			CaHPO ₄ ·2H ₂ O	T	T	T
3.0-4.0	7.18			CaHPO ₄ ·2H ₂ O	T	T	+
4.0-5.0	7.80	7.10	6.13	CaHPO ₄ ·2H ₂ O	T	0	T
5.0-6.0	--		5.98	None	0	0	0
6.0-7.0	--	7.22	5.58	"	0	0	0
7.0-8.0	--				"	0	0
8.0-9.7	7.80	7.21	5.42	"	0	0	0

Table 17. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
Initial soil pH 7.75 (9.1% CaCO ₃ added, 25°C.)							
0-0.2	--	--	--	Ca(NH ₄) ₂ HPO ₄) ₂ ·H ₂ OB	++++	++	+
				CaHPO ₄ ·2H ₂ O	0	+	+
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T
0.2-1.0	6.57	7.06	6.52	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	+	0	0
				CaHPO ₄ ·2H ₂ O	0	T	T
1.0-2.0	6.73	6.65	6.53	CaHPO ₄ ·2H ₂ O	0	0	0
2.0-3.0	6.78		6.48	CaHPO ₄ ·2H ₂ O	0	0	T
3.0-4.0	6.91		6.38	CaHPO ₄ ·2H ₂ O	0	0	T
4.0-5.0	7.23	5.89	6.35	None	0	0	0
5.0-6.0	7.55		6.62	"	0	0	0
6.0-7.0	7.53	6.89	7.04	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.76	7.12	7.10	"	0	0	0
Initial soil pH 7.75 (9.1% CaCO ₃ added, 35°C.)							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	+++	+	0
				CaHPO ₄ ·2H ₂ O	T	T	+
0.2-1.0	6.60	7.10	6.23	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	T	0	0
				CaHPO ₄ ·2H ₂ O	T	T	T
1.0-2.0	6.80	7.02	6.37	CaHPO ₄ ·2H ₂ O	0	0	0
2.0-3.0	6.82		6.46	CaHPO ₄ ·2H ₂ O	0	0	T
3.0-4.0	6.95		6.55	CaHPO ₄ ·2H ₂ O	0	0	T
4.0-5.0	7.24	7.15	6.49	None	0	0	0
5.0-6.0	7.96		6.39	"	0	0	0
6.0-7.0	8.00	7.36	6.89	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.93	7.49	6.99	"	0	0	0

4-5 cm. The pattern of precipitation of this compound was the same at 25°C. and 35°C. except in the first few millimeters of soil adjacent to the $(\text{NH}_4)_2\text{HPO}_4$ source. In this zone, there was a definite tendency for the amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to be higher at 35°C. than at 25°C. (the reverse situation was observed with $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$). The $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ referred to here was in the form of well-crystallized, small to medium-size crystals. These crystals were distinct from the powdery residue of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$, which also was thought to be $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. At pH 7.04, 7.71, and 7.75, traces of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were found after 16 weeks on this well-crystallized $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The formation appeared greater at 35°C. than at 25°C.

The amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitated in a given segment of soil was smaller the higher the initial pH, and this amount increased with time. It is apparent that the precipitation of this compound was not favored by the environment encountered when the alkaline $(\text{NH}_4)_2\text{HPO}_4$ solution first reacted with the soil. Presumably the calcium concentration was too low. As the NH_4^+ was converted to NO_3^- with passage of time, the pH of all samples dropped, and more $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was formed.

It is of interest at this point to observe the lack of identification of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ as an initial phase in Lloyd clay loam and Norfolk loamy sand. The exchangeable calcium content of these soils was low in comparison with that in Webster silty clay loam, and this may have been the reason why $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was not detected as an initial crystalline product in these soils.

The nature of the reaction products identified after the reaction of $(\text{NH}_4)_2\text{HPO}_4$ with the Harpster silty clay loams I and II and Darling Downs

clay is shown in Table 18. The nature, amount, and distribution of the reaction products formed in Harpster silty clay loam I (pH 7.51) were essentially the same as those observed in Webster silty clay loam with a pH value of 7.71. This similarity would be expected because the two soils had similar contents of exchangeable calcium (the Harpster soil did, however, contain carbonate equivalent to 3.0% CaCO_3). The formation of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ on the surface of granules of Harpster silty clay loam I is shown in Figure 3 together with a photomicrograph of a sample of the $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ isolated from this soil.

When $(\text{NH}_4)_2\text{HPO}_4$ reacted with Harpster silty clay loam II, a white material was found coating most of the soil granules in the 2 to 3 mm. of soil adjacent to the fertilizer source (Figure 4). This material generally lacked any visible structure when it was observed under the low power binocular microscope. In a few instances, some lath-like structure was evident, but this was different from the structure exhibited by the $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ identified in the soils discussed previously. The compound appeared to be stable, the quantity and physical nature changing little from 4 to 48 weeks.

The X-ray diffraction pattern of the material from the soil incubated for 4, 16, or 48 weeks consisted of a broad peak of low intensity at approximately $32^\circ 2\theta$. This peak was resolved into two peaks characteristic of either $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ or $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. In addition to these two peaks, the sample from the 16-week incubation had a small peak at $4.75^\circ 2\theta$ (equivalent to a d spacing of 18.6\AA), which is characteristic for $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. Under the petrographic microscope, the material was

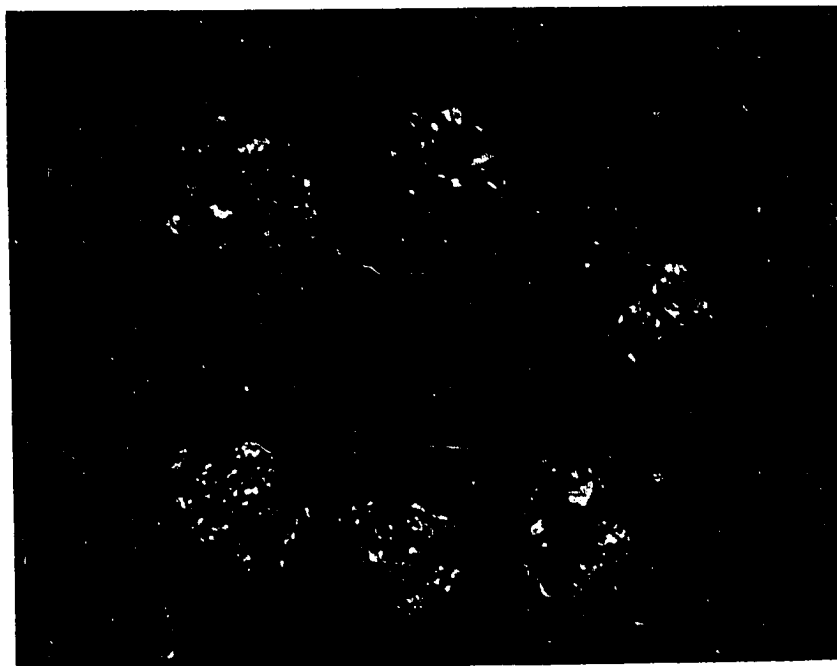
Table 18. Crystalline phosphates identified after incubation of dibasic ammonium phosphate with Harpster silty clay loams I and II and Darling Downs clay for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
					Relative amounts ^a		
	4 weeks	16 weeks	48 weeks		4 weeks	16 weeks	48 weeks
Harpster silty clay loam I (pH 7.51)							
0-0.2	--	--	--	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	+++	+	0
				CaHPO ₄ ·2H ₂ O	0	++	++
0.2-1.0	6.75	7.00	6.21	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	T	T	0
				CaHPO ₄ ·2H ₂ O	T	+	0
				Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	T	T	T
1.0-2.0	6.87	6.99	6.39	CaHPO ₄ ·2H ₂ O	T	T	T
2.0-3.0	6.99	6.80	6.28	CaHPO ₄ ·2H ₂ O	T	T	++
3.0-4.0	7.02	6.37	6.29	CaHPO ₄ ·2H ₂ O	T	T	++
4.0-5.0	7.08	5.91	6.17	CaHPO ₄ ·2H ₂ O	0	T	T
5.0-6.0	7.38	5.87	6.08	None	0	0	0
6.0-7.0	} 7.42	5.90	} 6.47	"	0	0	0
7.0-8.0		6.64		"	0	0	0
8.0-9.7	7.48	7.10	7.03	"	0	0	0
Harpster silty clay loam II (pH 7.52)							
0-0.2	--	--	--	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	+++	+++	+++
0.2-1.0	7.08	7.09	6.77	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	T	0	0
1.0-2.0	7.29	7.11	6.79	None	0	0	0
2.0-3.0	7.32	7.20	6.89	"	0	0	0
3.0-4.0	7.23	6.98	7.10	"	0	0	0
4.0-5.0	7.34	6.90	7.00	"	0	0	0
5.0-6.0	7.51		7.19	"	0	0	0
6.0-7.0	} 7.44	} 7.14	} 7.22	"	0	0	0
7.0-8.0				"	0	0	0
8.0-9.7	7.44	7.22	7.26	"	0	0	0

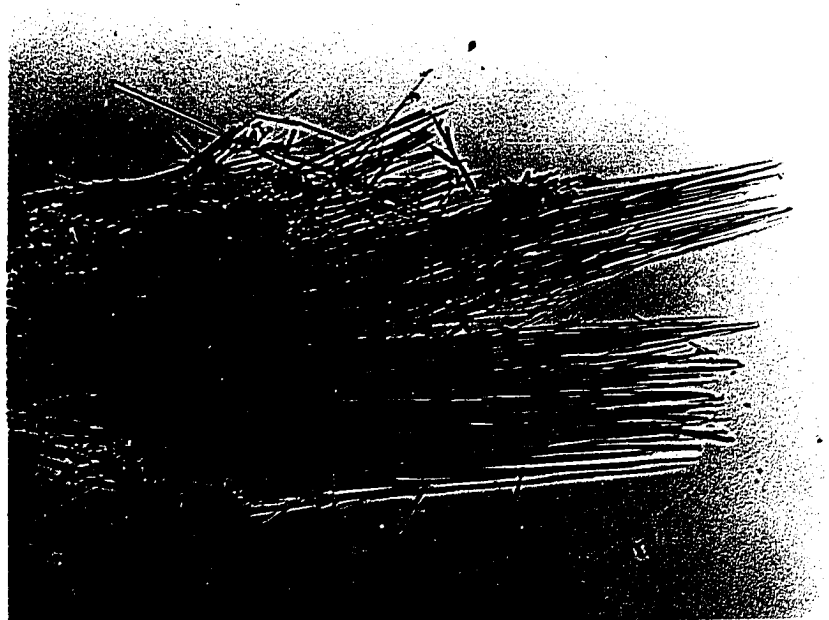
Table 18. (Continued)

Distance from fer- tilizer source, cm.	pH of soil			Species	Reaction products identified		
	4 weeks	16 weeks	48 weeks		Relative amounts ^a		
					4 weeks	16 weeks	48 weeks
<u>Darling Downs clay (pH 7.80)</u>							
0-0.2	--	--	--	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	+	+	+
				CaHPO ₄ ·2H ₂ O	T	T	T
0.2-1.0	6.79	7.52	6.72	CaHPO ₄ ·2H ₂ O	+++	+++	+++
				MgNH ₄ PO ₄ ·6H ₂ O	++	0	0
1.0-2.0	6.91	7.58	6.65	CaHPO ₄ ·2H ₂ O	++	+++	++
				MgNH ₄ PO ₄ ·6H ₂ O	++	0	0
2.0-3.0	7.08	7.47	6.55	CaHPO ₄ ·2H ₂ O	+	T	+
				MgNH ₄ PO ₄ ·6H ₂ O	+	++	T
3.0-4.0	7.31	7.50	6.53	CaHPO ₄ ·2H ₂ O	T	T	T
				MgNH ₄ PO ₄ ·6H ₂ O	T	T	0
4.0-5.0	7.73	7.36	6.64	MgNH ₄ PO ₄ ·6H ₂ O	0	T	0
				None	0	0	0
5.0-6.0	7.81	7.43	6.81	"	0	0	0
6.0-7.0	} 7.73	7.50	} 7.12	"	0	0	0
7.0-8.0		7.50		"	0	0	0
8.0-9.7		7.31		"	0	0	0

Figure 3. Photomicrographs of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ found in a column of Harpster silty clay loam I four weeks after addition of a band of dibasic ammonium phosphate at the end of the column. A. Granules of soil coated with $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ placed around a central granule from control soil that had not reacted with the fertilizer (X16). Coated granules were from soil within 3 mm. of the fertilizer band. B. Crystals of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ isolated from one of the granules in A (X 285).



A.



B.

Figure 4. Octacalcium phosphate found in a column of Harpster silty clay loam II four weeks after addition of a band of dibasic ammonium phosphate at the end of the column. A. Granules of soil coated with octacalcium phosphate placed around a central granule from control soil that had not reacted with the fertilizer (X16). Coated granules were from soil within 3 mm. of the fertilizer band. B. Crystals of octacalcium phosphate isolated from one of the granules in A (X 250).



A.



B.

observed as masses of very small irregularly shaped crystals which often merged into clusters of very thin, elongated, parallel crystals as shown in the photomicrograph in Figure 4. The characteristic X-ray diffraction peak at $4.75^\circ 2\theta$ exhibited by $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ arises from planes parallel to the platelike direction of the crystals, and the intensity of the peak would be expected to be low for very thin crystals (Brown et al., 1962).

The average refractive index of the crystals was 1.58, which agrees with the data given for $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ by Lehr et al. (1967) ($\alpha = 1.576$, $\beta = 1.583$, $\gamma = 1.585$). If the crystals had consisted of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ interlayered with some $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ (Brown et al., 1962), the observed refractive index should have been greater than 1.58 (in the case of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, $\omega = 1.647$ and $\epsilon = 1.640$). In the light of these observations, the reaction product was considered to be only $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$.

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was not found as a reaction product in Harpster silty clay loam II, probably because the pH was kept high by the action of the carbonate (21.7% as CaCO_3) in neutralizing the acidity produced by the nitrification of NH_4^+ .

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was also identified as a reaction product in Darling Downs clay. The refractive index of the thin, elongated, blade-like crystals was 1.58, and the X-ray diffraction pattern of the compound exhibited a broad peak at $32^\circ 2\theta$. The $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was found at 4, 16, and 48 weeks as a pinkish white coating on a few soil granules in the first few millimeters adjacent to the $(\text{NH}_4)_2\text{HPO}_4$ source. In addition, a slight trace of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was observed under the petrographic microscope to have formed on the surface of some of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals precipitated in the 0 to 0.2 cm. segment of soil. This $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, how-

ever, was probably formed by the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and not by direct precipitation.

Both $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ precipitated in Darling Downs clay in a manner similar to that observed when $\text{NH}_4\text{H}_2\text{PO}_4$ was the added salt. The precipitation of these two reaction products (as well as that of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) appeared to be essentially complete after 4 weeks. The $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals slowly disappeared after 4 weeks.

The amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ decreased with distance from 0 to 4 cm., but little change was noticed from 4 to 48 weeks. It might be expected that the amount of this compound would increase with time as the pH decreased as a result of the transformation of NH_4^+ to NO_3^- . The $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals looked very similar to small $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals, and often they could be distinguished only by isolating them from the soil and determining their refractive index. It is conceivable, therefore, that the relative amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ could have been overestimated at both 4 and 16 weeks in some segments.

Although $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was identified as a prominent product of reaction of $(\text{NH}_4)_2\text{HPO}_4$ with soil in this investigation, Lindsay *et al.* (1962) did not detect it as a precipitated crystalline phase in solutions of $(\text{NH}_4)_2\text{HPO}_4$ that had been allowed to react with an acid soil, an alkaline soil, and various soil components. Perhaps the difference in results is related to pH effects. In the investigation of Lindsay *et al.*, the pH of the solution of $(\text{NH}_4)_2\text{HPO}_4$ which had reacted with soils and soil components ranged from 7.51 to 8.17 after 10 days and this range may have been too high to allow precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. In the present investigation,

the pH values after 4 weeks were lower (5.58 to 6.99 in the soil segments in which $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ formed), presumably because of greater buffering by the soil and greater microbial production of NO_3^- from NH_4^+ .

Lindsay *et al.*, however, did identify $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$, and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ as reaction products of $(\text{NH}_4)_2\text{HPO}_4$ and soil and soil components. When they added a small amount of CaCO_3 to a saturated solution of $(\text{NH}_4)_2\text{HPO}_4$, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was formed; but, when large amounts of CaCO_3 were added, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was formed. These results agree with the observations in this thesis. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was found as a reaction product only in Harpster silty clay loam II containing carbonate equivalent to 21.7% CaCO_3 , whereas $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was formed in all the remaining soils. These soils (including Harpster silty clay I with carbonate equivalent to 3.0% CaCO_3) contained no CaCO_3 or significantly less CaCO_3 than the Harpster silty clay loam II. Lindsay *et al.* identified $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ as a reaction product of MgO or $\text{CaMg}(\text{CO}_3)_2$ and a saturated solution of $(\text{NH}_4)_2\text{HPO}_4$. This reaction product was also observed to form in extracts of an acid fine sandy loam which, like Darling Downs clay used in this thesis investigation, obviously contained a high amount of reactive magnesium.

Analysis of the glass-fiber paper strips

In a given soil column, the distance moved by the fertilizer phosphorus in the paper strip was found to be the same as the distance moved by the fertilizer phosphorus in the soil. Furthermore, the distances of

phosphorus movement were found to be essentially the same in columns with and without the paper strips.

The use of the paper strips to facilitate the detection and identification of the reaction products formed in soils achieved variable success. Table 19 shows the comparison of soil and paper strips in Webster silty clay loam with pH 7.71 at 16 weeks. The occurrence of a diffraction peak at $11.7^{\circ} 2\theta$ provides a qualitative test for the presence of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and the relative heights of the peaks provide some indication of the relative amounts of the substance present. As indicated by the distances from the source at which $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was identified, microscopic analysis was more sensitive than X-ray analysis in detecting $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in soil; however, there was little difference between the sensitivity of microscopic and X-ray analysis in the detection of this compound on the paper strip. The precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ on the paper strip appeared to mirror the precipitation of the compound in the soil because the precipitation zones (as determined by microscopic analysis) were of the same length on the paper strips as in the soil. The comparative sensitivities of direct microscopic examination of the soil, direct X-ray examination of the soil, microscopic examination of the paper strips, and X-ray examination of the paper strips were similar at 4 and 48 weeks with the Webster soil and at 4, 16, and 48 weeks with all the other soils except Darling Downs clay. Nearly all the paper strips in the soil were torn into small pieces by the swelling pressures developed in this soil during wetting.

One unanticipated advantage of the paper strips was that the strips gave some insight into the effect of the phosphate fertilizers on the soil

Table 19. Distribution of crystalline phosphates in Webster silty clay loam and in glass-fiber paper strips in the soil after reaction of the soil with monobasic calcium phosphate monohydrate, monobasic ammonium phosphate, and dibasic ammonium phosphate for 16 weeks

Analysis of soil				Analysis of paper strip			
Distance from fertilizer source, cm.	Crystalline phosphates identified	Relative amount by microscopic analysis	Height of X-ray dif-fraction peak ^b	Distance from fertilizer source, cm.	Crystalline phosphates identified	Micro-scopie analysis ^c	Height of X-ray dif-fraction peak
			<u>Ca(H₂PO₄)₂·H₂O</u>				
0-1	CaHPO ₄ ·2H ₂ O	+++	31	0.5	CaHPO ₄ ·2H ₂ O	*	7
				1.0	CaHPO ₄ ·2H ₂ O	*	14
1-2	CaHPO ₄ ·2H ₂ O	++	6	1.5	CaHPO ₄ ·2H ₂ O	*	29
				2.0	CaHPO ₄ ·2H ₂ O	*	26
2-3	CaHPO ₄ ·2H ₂ O	+	0	2.5	CaHPO ₄ ·2H ₂ O	*	16
				3.0	CaHPO ₄ ·2H ₂ O	*	2
3-4	CaHPO ₄ ·2H ₂ O	T	0	3.5	CaHPO ₄ ·2H ₂ O	*	0
				4.0	None	0	0
4-5	CaHPO ₄ ·2H ₂ O	0	0	4.5	"	0	0
				5.0	"	0	0
			<u>NH₄H₂PO₄</u>				
0-1	CaHPO ₄ ·2H ₂ O	+++	3	0.5	CaHPO ₄ ·2H ₂ O	*	20
				1.0	CaHPO ₄ ·2H ₂ O	*	41
1-2	CaHPO ₄ ·2H ₂ O	++	2	1.5	CaHPO ₄ ·2H ₂ O	*	29
				2.0	CaHPO ₄ ·2H ₂ O	*	32
2-3	CaHPO ₄ ·2H ₂ O	+	4	2.5	CaHPO ₄ ·2H ₂ O	*	40
				3.0	CaHPO ₄ ·2H ₂ O	*	32
3-4	CaHPO ₄ ·2H ₂ O	T	0	3.5	CaHPO ₄ ·2H ₂ O	*	14
				4.0	CaHPO ₄ ·2H ₂ O	*	3
4-5	CaHPO ₄ ·2H ₂ O	T	0	4.5	CaHPO ₄ ·2H ₂ O	*	0
				5.0	None	0	0
5-6	None	0	0	5.5	"	0	0
				6.0	"	0	0

^bValues are heights of the 11.7° 2θ peak for CaHPO₄·2H₂O in units of diffractometer chart divisions.

^c* = present and 0 = none detected.

Table 19. (Continued)

Analysis of soil				Analysis of paper strip			
Distance from fertilizer source, cm.	Crystalline phosphates identified			Distance from fertilizer source, cm.	Crystalline phosphates identified		
	Species	Relative ^a amount by microscopic analysis	Height of ^b X-ray dif-fraction peak		Species	Micro-scopic analysis ^c	Height of X-ray dif-fraction peak
<u>(NH₄)₂HPO₄</u>							
0-1	CaHPO ₄ ·2H ₂ O	+	0	0.5	CaHPO ₄ ·2H ₂ O	*	6
1-2	CaHPO ₄ ·2H ₂ O	T	0	1.0	CaHPO ₄ ·2H ₂ O	*	4
2-3	CaHPO ₄ ·2H ₂ O	T	0	1.5	CaHPO ₄ ·2H ₂ O	*	3
3-4	CaHPO ₄ ·2H ₂ O	++	0	2.0	CaHPO ₄ ·2H ₂ O	*	4
4-5	CaHPO ₄ ·2H ₂ O	T	0	2.5	CaHPO ₄ ·2H ₂ O	*	3
5-6	None	0	0	3.0	CaHPO ₄ ·2H ₂ O	*	2
				3.5	CaHPO ₄ ·2H ₂ O	*	3
				4.0	CaHPO ₄ ·2H ₂ O	*	2
				4.5	CaHPO ₄ ·2H ₂ O	*	0
				5.0	None	*	0
				5.5	"	*	0
				6.0	"	*	0

organic matter. Paper strips isolated from soils which had reacted with $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ were irregularly stained brown from the end near the fertilizer source to the outer limit of phosphorus movement where the staining was most intense and had the appearance of a band. For a given fertilizer, the brown stain was the least intense with Norfolk loamy sand (0.41% organic carbon), and the most intense with Harpster silty clay loam I and II (4.16 and 4.13% organic carbon, respectively). In a given soil, there was often a tendency for the stain to be more intense with $(\text{NH}_4)_2\text{HPO}_4$ than with $\text{NH}_4\text{H}_2\text{PO}_4$. Figure 5 is a photograph showing the stain on a paper strip isolated from Harpster silty clay loam II which had reacted with $\text{NH}_4\text{H}_2\text{PO}_4$ for 16 weeks.

No brown stain of any description was found in the paper strips isolated from soils which had reacted with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. It appears that the slightly acid solution of $\text{NH}_4\text{H}_2\text{PO}_4$ and the alkaline solution of $(\text{NH}_4)_2\text{HPO}_4$ dissolved some of the organic matter in the soil near the fertilizer. This organic matter was then precipitated at the outer margin of the precipitation of phosphate. The position of the organic matter band did not change from 4 to 48 weeks even though the fertilizer phosphorus continued to move out into the soil after 4 weeks.

Presumably, the ammonium phosphate fertilizers solubilized some of the soil organic matter by reacting with cations, such as Ca, Fe, and Al, which were attached to exchange sites on the organic matter and which kept the latter flocculated. At a certain distance in the soil, the precipitation of calcium and other phosphates ceased because of the reduction in the phosphate concentration in solution. At this point, the dispersed organic matter took up calcium and other flocculating cations (which could



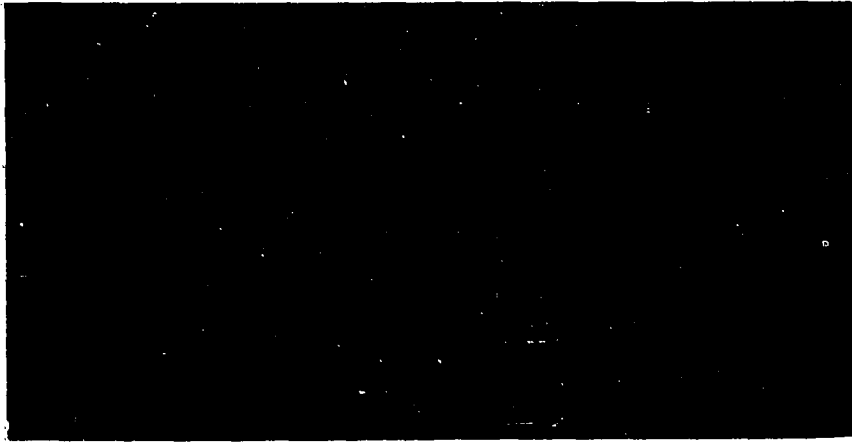
Figure 5. Interaction of monobasic ammonium phosphate with Harpster silty clay loam II. Phosphate from the fertilizer placed initially at the bottom of the column was allowed to move upward into the soil for 16 weeks. The strip of glass-fiber paper shown in the center was present in the soil column during the period of interaction. The brown stain is due to organic matter solubilized by the fertilizer and then precipitated near the maximum distance of movement of the phosphate in the soil. The blue stain on the strip of paper at the left shows the location of the zones of high phosphorus concentration in the soil as found at the end of the 16-week period.

no longer be removed by precipitation as phosphates) from the exchange complex of the soil.

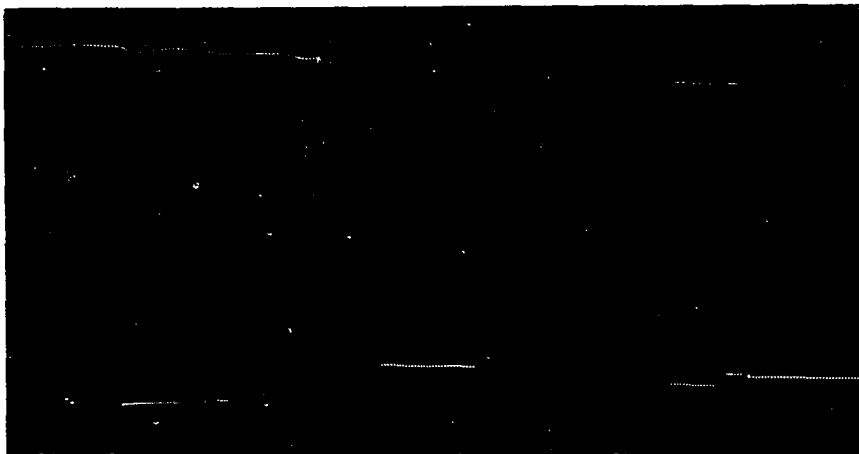
That the effect of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ on the soil organic matter was not an artifact of the paper strip is verified by Figure 6. This figure contains photographs of 0.01 M CaCl_2 extracts (1 part of soil to 2 parts of CaCl_2 solution) of Harpster silty clay loam I at different distances from sources of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ after 16 weeks. The photographs indicate that $(\text{NH}_4)_2\text{HPO}_4$ was more effective in solubilizing soil organic matter than $\text{NH}_4\text{H}_2\text{PO}_4$ whereas $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ did not appear to have any such effect.

The general conclusions reached in the comparison of the findings made by examination of the glass-fiber paper inclusions and the soil were the following. For purposes of identification and characterization of the crystalline phosphates produced throughout the full range of phosphorus movement into the soil from the fertilizers, direct microscopic examination of the soil was preferable to microscopic examination of the paper inclusions. To obtain a qualitative test for the presence of crystalline phosphates throughout the full range of phosphate movement into the soil, microscopic examinations of paper inclusions and soil were equally sensitive. Both were somewhat more sensitive than X-ray diffraction analysis of the paper, and this, in turn, was considerably more sensitive than X-ray diffraction analysis of the soil. X-ray diffraction analysis of the paper inclusions was much more rapid than were the microscopic examinations. None of the methods showed definitely the presence of crystalline phosphates to the full distance of movement of phosphorus from the fertilizers into some of the soils. To show the location of the zone of organic matter

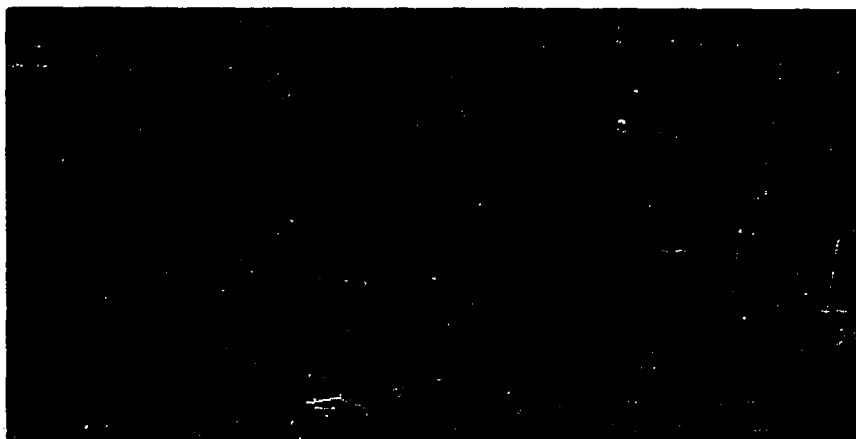
Figure 6. Photographs of 0.01-molar calcium chloride extracts of samples taken different distances from a band of each of three phosphate fertilizers in columns of Harpster silty clay loam I sixteen weeks after addition of the fertilizers. A. Monobasic calcium phosphate monohydrate. From left to right, the tubes contain extracts from samples 0 to 1, 1 to 2, 2 to 3, 3 to 4, 4 to 5, and 5 to 9.7 cm. from the fertilizer band. The fertilizer phosphorus moved to a distance of 4.9 cm., and detectable quantities of dibasic calcium phosphate dihydrate extended to a distance of 3.0 cm. from the fertilizer band. B. Monobasic ammonium phosphate. From left to right, the tubes contain extracts from samples 0 to 1, 1 to 2, ..., 7 to 8, and 8 to 9.7 cm. from the fertilizer band. The fertilizer phosphorus moved to a distance of 5.6 cm., and detectable quantities of dibasic calcium phosphate dihydrate extended to a distance of 4.0 cm. from the source. C. Dibasic ammonium phosphate. From left to right, the tubes contain extracts from samples 0 to 1, 1 to 2, ..., 7 to 8, and 8 to 9.7 cm. from the fertilizer band. The fertilizer phosphorus moved to a distance of 5.7 cm., and detectable quantities of dibasic calcium phosphate dihydrate extended to 5.0 cm. from the fertilizer band.



A.



B.



C.

precipitation, the glass fiber paper was valuable, and direct visual examination of most soils was not. An aqueous extract of the soil showed the location of the soluble organic matter, but in most instances direct visual examination of the soil did not. The paper was stained irregularly throughout the zone between the fertilizer and the terminal band in which staining was strong, providing some evidence for the zone of solubilization of organic matter.

Analysis of CaCO_3 -coated slides

Reaction with monobasic calcium phosphate monohydrate Table 20

shows the reaction products formed in calcareous soils and on CaCO_3 -coated slides in these soils during reaction with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ for 4, 16, and 48 weeks. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was the only reaction product identified on the slides and in the soils.

The distance from the source of fertilizer phosphorus to which $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ could be identified by microscopic examination was essentially the same on the CaCO_3 -coated slides as in the soil. Microscopic analysis (using a magnification of 20) was more sensitive than X-ray diffraction analysis in detecting the presence of this compound in the soil. With the CaCO_3 -coated slides, however, the sensitivity of X-ray diffraction analysis in detecting the presence of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was equal to or greater than that obtained using microscopic analysis. In many instances, it was difficult to determine the outer margin of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitation on the slide with the microscope because the creamy-white clusters of phosphate crystals blended into the white background of the CaCO_3 on the slide. To estimate qualitatively the distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in calcareous soils, X-ray

Table 20. Comparison of the crystalline phosphates formed in calcareous soils and on calcium carbonate-coated slides in calcareous soils that had been in contact with monobasic calcium phosphate monohydrate for 4, 16, and 48 weeks

Analysis of soil							
Distance from fer- tilizer source, cm.	Crystalline phosphates identified						
	Species	Microscopic analysis ^a			X-ray analysis ^a		
		4	16	48	4	16	48
		weeks	weeks	weeks	weeks	weeks	weeks
<u>Norfolk loamy sand (pH 7.91, 9.1% CaCO₃)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	*	*	*	0	*	0
2-3	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	0
3-4	None	0	0	0	0	0	0
<u>Lloyd clay loam (pH 7.51, 9.1% CaCO₃)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	*	*	0	0	0	0
2-3	None	0	0	0	0	0	0
<u>Webster silty clay loam (pH 7.75, 9.1% CaCO₃)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	0
2-3	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	0
3-4	None	0	0	0	0	0	0
<u>Harpster silty clay loam I (pH 7.51, 3.0% CaCO₃ equivalent)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	*	*	*	*	0	0
2-3	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	0
3-4	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	0
4-5	None	0	0	0	0	0	0

^a* = present and 0 = none. (Here and following tables.)

Analysis of CaCO ₃ -coated slide							
Distance from fer- tilizer source, cm.	Species	Crystalline phosphates identified					
		Microscopic analysis			X-ray analysis		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
Norfolk loamy sand (pH 7.91, 9.1% CaCO ₃)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2.0	CaHPO ₄ ·2H ₂ O	*	*	0	*	*	0
2.5	CaHPO ₄ ·2H ₂ O	0	*	0	0	*	0
3.0	CaHPO ₄ ·2H ₂ O	0	*	0	0	*	0
3.5	None	0	0	0	0	0	0
4.0	"	0	0	0	0	0	0
Lloyd clay loam (pH 7.51, 9.1% CaCO ₃)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	0	*	*	*	*	*
2.0	CaHPO ₄ ·2H ₂ O	0	*	0	*	*	0
2.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
3.0	None	0	0	0	0	0	0
Webster silty clay loam (pH 7.75, 9.1% CaCO ₃)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2.0	CaHPO ₄ ·2H ₂ O	0	*	0	0	*	*
2.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	*
3.0	None	0	0	0	0	0	0
3.5	"	0	0	0	0	0	0
4.0	"	0	0	0	0	0	0
Harpster silty clay loam I (pH 7.51, 3.0% CaCO ₃ equivalent)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2.5	CaHPO ₄ ·2H ₂ O	0	*	*	0	*	*
3.0	CaHPO ₄ ·2H ₂ O	0	*	*	0	*	*
3.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
4.0	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
4.5	None	0	0	0	0	0	0
5.0	"	0	0	0	0	0	0

Table 20. (Continued)

Distance from fer- tilizer source, cm.	Species	Analysis of soil					
		Crystalline phosphates identified					
		Microscopic analysis ^a			X-ray analysis ^a		
		4	16	48	4	16	48
		weeks	weeks	weeks	weeks	weeks	weeks
<u>Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	*
2-3	None	0	0	0	0	0	0
<u>Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	*	*	*	*	0	*
2-3	CaHPO ₄ ·2H ₂ O	0	*	*	0	0	0
3-4	None	0	0	0	0	0	0

Analysis of CaCO ₃ -coated slide							
Distance from fer- tilizer source, cm.	Species	Crystalline phosphates identified					
		Microscopic analysis			X-ray analysis		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks

Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)

0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	*
2.0	None	0	0	0	0	0	0
2.5	"	0	0	0	0	0	0
3.0	"	0	0	0	0	0	0

Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)

0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2.0	CaHPO ₄ ·2H ₂ O	*	*	*	0	*	*
2.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
3.0	None	0	0	0	0	0	0
3.5	"	0	0	0	0	0	0
4.0	"	0	0	0	0	0	0

diffraction analysis of the slides seems to be the best of the methods tried. It proved to be as sensitive as microscopic analysis of the soils in detecting this compound, but it is faster and more convenient.

Reaction with monobasic ammonium phosphate The reaction products identified in calcareous soils and on CaCO_3 -coated slides in the soils that had been in contact with $\text{NH}_4\text{H}_2\text{PO}_4$ for 4, 16, and 48 weeks are shown in Table 21. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was the only reaction product identified in most instances. It occurred both in the soil and on the CaCO_3 -coated slides. Both $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ were found in Darling Downs clay. These species occurred both in the soil and on the slides.

The precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ on the CaCO_3 -coated slides appeared to mirror the precipitation of these compounds in the soil. X-ray analysis of the slides was about as sensitive as microscopic analysis of the soil for determining the presence of a reaction product.

Reaction with dibasic ammonium phosphate The reaction products identified in calcareous soils and on CaCO_3 -coated slides in the soils in which $(\text{NH}_4)_2\text{HPO}_4$ was the reacting phosphate salt are shown in Table 22. In Norfolk loamy sand and Lloyd clay loam at 4 and 16 weeks, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_4 \cdot \text{H}_2\text{O}$ was identified in the soil and on the slides to equal distances from the fertilizer source. At 48 weeks, a white powdery

Table 21. Comparison of the crystalline phosphates formed in calcareous soils and on calcium carbonate-coated slides in calcareous soils that had been in contact with monobasic ammonium phosphate for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	Analysis of soil						
	Crystalline phosphates identified						
	Species	Microscopic analysis ^a			X-ray analysis ^a		
		4	16	48	4	16	48
		weeks	weeks	weeks	weeks	weeks	weeks
<u>Norfolk loamy sand (pH 7.91, 9.1% CaCO₃)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	0
2-3	None	0	0	0	0	0	0
<u>Lloyd clay loam (pH 7.51, 9.1% CaCO₃)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	0	*	*	0	0	0
2-3	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	0
3-4	None	0	0	0	0	0	0
<u>Webster silty clay loam (pH 7.71, 9.1% CaCO₃)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	*
2-3	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	0
3-4	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	0
4-5	None	0	0	0	0	0	0
<u>Harpster silty clay loam I (pH 7.51, 3.0% CaCO₃ equivalent)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	*
2-3	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	0
3-4	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	0
4-5	None	0	0	0	0	0	0

Analysis of CaCO ₃ -coated slide							
Distance from fer-tilizer source, cm.	Species	Crystalline phosphates identified					
		Microscopic analysis			X-ray analysis		
		4	16	48	4	16	48
		weeks	weeks	weeks	weeks	weeks	weeks
Norfolk loamy sand (pH 7.91, 9.1% CaCO ₃)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	0
2.0	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
2.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
3.0	None	0	0	0	0	0	0
Lloyd clay loam (pH 7.51, 9.1% CaCO ₃)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	*
2.0	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	*
2.5	None	0	0	0	0	0	0
3.0	"	0	0	0	0	0	0
3.5	"	0	0	0	0	0	0
4.0	"	0	0	0	0	0	0
Webster silty clay loam (pH 7.71, 9.1% CaCO ₃)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	*	0	*	*	*	*
2.0	CaHPO ₄ ·2H ₂ O	*	0	*	0	*	*
2.5	CaHPO ₄ ·2H ₂ O	*	0	*	0	*	0
3.0	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
3.5	None	0	0	0	0	0	0
4.0	"	0	0	0	0	0	0
4.5	"	0	0	0	0	0	0
5.0	"	0	0	0	0	0	0
Harpster silty clay loam I (pH 7.51, 3.0% CaCO ₃ equivalent)							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
3.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
3.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
4.0	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
4.5	None	0	0	0	0	0	0
5.0	"	0	0	0	0	0	0

Table 21. (Continued)

Analysis of soil							
Distance from fer- tilizer source, cm.	Species	Crystalline phosphates identified					
		Microscopic analysis ^a			X-ray analysis ^a		
		4	16	48	4	16	48
		weeks	weeks	weeks	weeks	weeks	weeks
<u>Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1-2	None	0	0	0	0	0	0
<u>Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)</u>							
0-1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	*	*	*	0
1-2	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	*	0	*	0
2-3	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	*
	MgNH ₄ ·PO ₄ ·6H ₂ O	*	*	*	0	0	0
3-4	CaHPO ₄ ·2H ₂ O	*	*	0	0	0	0
4-5	None	0	0	0	0	0	0

Table 21. (Continued)

Analysis of CaCO ₃ -coated slide							
Distance from fer- tilizer source, cm.	Species	Crystalline phosphates identified					
		Microscopic analysis ^a			X-ray analysis ^a		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
<u>Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)</u>							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
1.5	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
2.0	None	0	0	0	0	0	0
<u>Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)</u>							
0.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	0	*	*	0
1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	*	0	*	0
1.5	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·2H ₂ O	*	*	0	0	*	0
2.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·2H ₂ O	*	*	0	0	*	0
2.5	CaHPO ₄ ·2H ₂ O	*	*	*	0	*	*
3.0	CaHPO ₄ ·2H ₂ O	0	0	*	0	0	*
3.5	None	0	0	0	0	0	0
4.0	"	0	0	0	0	0	0
4.5	"	0	0	0	0	0	0
5.0	"	0	0	0	0	0	0

Table 22. Comparison of the crystalline phosphates formed in calcareous soils and on calcium carbonate-coated slides in calcareous soils that had been in contact with dibasic ammonium phosphate for 4, 16, and 48 weeks

Distance from fer- tilizer source, cm.	Analysis of soil						
	Crystalline phosphates identified						
	Species	Microscopic analysis ^a			X-ray analysis ^a		
		4	16	48	4	16	48
		weeks	weeks	weeks	Weeks	weeks	weeks
<u>Norfolk loamy sand (pH 7.91, 9.1% CaCO₃)</u>							
0-0.2	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	0	*	*	0
	CaHPO ₄ ·2H ₂ O	0	0	*	0	0	0
0.2-1.0	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	0	0	0	0
	CaHPO ₄ ·2H ₂ O	0	0	*	0	0	0
1.0-2.0	None	0	0	0	0	0	0
2.0-3.0	"	0	0	0	0	0	0
<u>Lloyd clay loam (pH 7.75, 9.1% CaCO₃)</u>							
0-0.2	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	*	*	*	0
	CaHPO ₄ ·2H ₂ O	0	0	*	0	0	*
0.2-1.0	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	*	*	*	0
	CaHPO ₄ ·2H ₂ O	0	0	*	0	0	0
1.0-2.0	None	0	0	0	0	0	0
<u>Webster silty clay loam (pH 7.75, 9.1% CaCO₃)</u>							
0-0.2	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	0	*	0	0
	CaHPO ₄ ·2H ₂ O	0	*	*	0	*	0
0.2-1.0	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	0	0	0	0
	CaHPO ₄ ·2H ₂ O	0	0	*	0	0	0
1.0-2.0	None	0	0	0	0	0	0
2.0-3.0	"	0	0	0	0	0	0
<u>Harpster silty clay loam I (pH 7.51, 3.0% CaCO₃ equivalent)</u>							
0-0.2	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	0	0	*	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	*	0	0	0	0
	CaHPO ₄ ·2H ₂ O	0	*	*	0	*	0
0.2-1.0	CaHPO ₄ ·2H ₂ O	0	*	0	0	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	*	0	0	0	0
1.0-2.0	None	0	0	0	0	0	0

^bThe compound formed may have been either Ca₈H₂(PO₄)₆·5H₂O or Ca₁₀(OH)₂(PO₄)₆.

Analysis of CaCO ₃ -coated slide							
Distance from fer- tilizer source, cm.	Species	Crystalline phosphates identified					
		Microscopic analysis ^a			X-ray analysis ^a		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
<u>Norfolk loamy sand (pH 7.91, 9.1% CaCO₃)</u>							
0.2	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	0	0	*	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	0	*	0	0	0
0.5	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	0	0	*	0	0
1.0	None	0	0	0	0	0	0
1.5	"	0	0	0	0	0	0
2.0	"	0	0	0	0	0	0
2.5	"	0	0	0	0	0	0
<u>Lloyd clay loam (pH 7.75, 9.1% CaCO₃)</u>							
0.2	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	0	*	0	0
	Ca ₈ H ₂ (PO ₄) ₅ ·5H ₂ O	0	0	*	0	0	0
0.5	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	*	0	*	0	0
1.0	None	0	0	0	0	0	0
1.5	"	0	0	0	0	0	0
<u>Webster silty clay loam (pH 7.75, 9.1% CaCO₃)</u>							
0.2	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	*	0	0	*	0	0
	CaHPO ₄ ·2H ₂ O	0	0	0	0	*	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	*	*	0	*	0
0.5	--b	0	0	0	0	0	*
1.0	--b	0	0	0	0	0	*
1.5	--b	0	0	0	0	0	*
2.0	--b	0	0	0	0	0	*
2.5	--b	0	0	0	0	0	*
3.0	None	0	0	0	0	0	0
<u>Harpster silty clay loam I (pH 7.51, 3.0% CaCO₃ equivalent)</u>							
0.2	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	0	0	*	0
0.5	None	0	0	0	0	0	0
1.0	"	0	0	0	0	0	0
1.5	"	0	0	0	0	0	0
2.0	"	0	0	0	0	0	0

Table 22. (Continued)

Analysis of soil							
Distance from fer- tilizer source, cm.	Crystalline phosphates identified						
	Species	Microscopic analysis ^a			X-ray analysis ^a		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
Harpster silty clay loam II (pH 7.52, 21.7% CaCO ₃ equivalent)							
0-0.2	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	*	*	*	*
0.2-1.0	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	0	0	0	0
1.0-2.0	None	0	0	0	0	0	0
Darling Downs clay (pH 7.80, 4.0% CaCO ₃ equivalent)							
0-0.2	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	*	0	*	0
	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·6H ₂ O	*	0	0	*	0	0
0.2-1.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	0	0	*	0	0
1.0-2.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	-	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	0	*	-	0
2.0-3.0	CaHPO ₄ ·2H ₂ O	*	*	*	*	-	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	0	*	-	0
3.0-4.0	CaHPO ₄ ·2H ₂ O	*	0	0	*	-	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	0	*	-	0
4.0-5.0	None	0	0	0	0	-	0

Analysis of CaCO ₃ -coated slide							
Distance from fer- tilizer source, cm.	Species	Crystalline phosphates identified					
		Microscopic analysis ^a			X-ray analysis ^a		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
<u>Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)</u>							
0.2	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	0	0	*	0
0.5	None	0	0	0	0	0	0
1.0	"	0	0	0	0	0	0
1.5	"	0	0	0	0	0	0
2.0	"	0	0	0	0	0	0
<u>Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)</u>							
0.2	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	0	0	0	0
	CaHPO ₄ ·2H ₂ O	*	*	0	*	*	0
0.5	CaHPO ₄ ·2H ₂ O	*	*	0	*	*	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	0	0	*	0	0
1.0	CaHPO ₄ ·2H ₂ O	*	*	0	0	*	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	0	0	0	0	0
	--b	0	0	*	0	0	*
1.5	CaHPO ₄ ·2H ₂ O	*	*	0	*	*	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	0	0	0	0	0
	--b	0	0	*	0	0	*
2.0	CaHPO ₄ ·2H ₂ O	*	*	0	*	*	0
	MgNH ₄ PO ₄ ·6H ₂ O	*	0	0	*	*	0
	--b	0	0	*	0	0	*
2.5	CaHPO ₄ ·2H ₂ O	*	0	0	0	0	0
	MgNH ₄ PO ₄ ·2H ₂ O	*	*	0	0	*	0
3.0	CaHPO ₄ ·2H ₂ O	*	0	0	0	0	0
	MgNH ₄ PO ₄ ·2H ₂ O	*	*	0	0	0	0
3.5	None	0	0	0	0	0	0
4.0	"	0	0	0	0	0	0

residue of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ (most probably $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was observed microscopically in the soils but was difficult to detect on the white slides. A zone of 2 to 3 mm. of white lath-shaped structures was observed at the ends of the slides nearest the $(\text{NH}_4)_2\text{HPO}_4$ source. Under the petrographic microscope, this material was observed to consist of masses of very thin elongated crystals having an average refractive index of 1.58, a description corresponding to that of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. This product was not found on the slides by X-ray analysis, and it was not found in the soil by either X-ray analysis or microscopic analysis.

The reaction products formed in soil and on slides in Webster silty clay loam were similar to those observed with the Norfolk and Lloyd soils. At 4 weeks, a zone of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was observed in the soil and on the slides within a distance of 2 to 3 mm. from the fertilizer source. At 16 and 48 weeks, a white powdery residue of this compound was found both in the soil and on the slide. The presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ on the first few millimeters of the end of the slide at 16 and 48 weeks was confirmed by petrographic and X-ray analysis. This compound was not identified in the soil. At 48 weeks, a broad peak at about $32^\circ 2\theta$ was observed in the X-ray diffraction patterns of the slide from 0.5 to 2.5 cm. from the fertilizer source. This peak could indicate the presence of either $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ or $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. Petrographic analysis of samples isolated from the surface of the slide was inconclusive, perhaps because some of the soil organic matter solubilized by the $(\text{NH}_4)_2\text{HPO}_4$ had coated the surface of the CaCO_3 .

In Harpster silty clay loam I, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was the only reaction product detected (by X-ray and microscopic analysis) on the slide whereas

in the soil $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were also identified. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was the only reaction product identified in Harpster silty clay loam II, the compound being found on the slide and in the soil for 2 to 3 mm. from the fertilizer source.

The dominant reaction products in Darling Downs clay, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, were found on the slide and in the soil, the lengths of the precipitation zones in each case being the same. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified by petrographic analysis in the 2 mm. of the slide and soil adjacent to the fertilizer source. After 48 weeks, a broad peak at approximately $32^\circ 2\theta$ was observed in the X-ray diffraction pattern of the slide at 1.0, 1.5, and 2.0 cm. from the source of $(\text{NH}_4)_2\text{HPO}_4$. This peak could indicate the presence of either $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ or $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. Petrographic analysis of the slide in this region was hampered by precipitated soil organic matter.

In the treatments involving the reaction of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ with calcareous soils, the reaction products precipitated on the CaCO_3 -coated slides were the same as those identified in the soil. When $(\text{NH}_4)_2\text{HPO}_4$ was the added salt, however, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was often identified on the slides but not in the soil. In Norfolk loamy sand, Lloyd clay loam, and Webster silty clay loam, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified as a reaction product on the slides at 16 and 48 weeks but not at 4 weeks. This compound was not detected in the soil at 4, 16, or 48 weeks. The reason for this may have been that the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was covered by a layer of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ at 4 weeks, and that as the latter compound dissolved (it is more soluble than $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) it exposed the underlying

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. The precipitation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ close to the surface of the CaCO_3 would be favored by the higher concentration of calcium. It is also conceivable that $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ formed as $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ dissolved. Lindsay et al. (1962) found that the addition of CaCO_3 to a saturated solution of $(\text{NH}_4)_2\text{HPO}_4$ produced $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ which disappeared with time, resulting in the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$.

Interpretation The use of CaCO_3 -coated slides to estimate qualitatively the distribution of crystalline phosphate species in calcareous soils was found to be a valid technique when the reacting fertilizer was $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{NH}_4\text{H}_2\text{PO}_4$. The precipitation of phosphates on the slides appeared to mirror the precipitation of the compounds in the soil. X-ray diffraction of the slides was about as sensitive as microscopic analysis of soil in detecting the presence of a reaction product.

The differences between the crystalline phosphate species identified by examination of the CaCO_3 -coated slides and soil indicate invalidity of the findings made on the slides as a reflection of the character of the crystalline phosphates formed when $(\text{NH}_4)_2\text{HPO}_4$ interacts with calcareous soils. In particular, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ were occasionally found in the soils but not on the slides. Failure to find a species on the slides that is identified in the soil is clearly a deficiency of the slide technique for providing information on species formed in soil. Identification of a species on the slides that is not found in the soils, however, is another matter. The species may not be present in the soil, in which case the appearance of the compound on the slide would be viewed

as an artifact. On the other hand, soils are not homogeneous, and, if the species found on the slide is one that might be expected to form on the surface of carbonate particles in the soil, one may suspect the species is present in the soil but that it has not been identified. The slides provide a flat, uniform surface that can be examined by both microscopic and X-ray methods with little interference from substances other than carbonates. Because the species sometimes identified on the slides but not in the soil was $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, which has a higher ratio of calcium to phosphorus than the two species found in soil but not on the slides, it seems reasonable to suspect that this species was present on carbonate particles in the soil even though it was not identified in an examination of the soil as a whole. Examination of CaCO_3 -coated slides, therefore, may provide information on the character of crystalline phosphates formed in calcareous soil that supplements the findings made by direct examination of the soil.

Analysis of CaCO_3 chips

The reaction products identified on CaCO_3 chips isolated from calcareous soils which had reacted with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ are shown in Tables 23, 24, and 25, respectively. The reaction products identified in the soil were the same as those given in connection with CaCO_3 -coated slides (Tables 20, 21, and 22). For the purpose of comparing the reaction products identified on CaCO_3 chips with the products found in the soil, the position of the chips relative to the fertilizer source is given as follows. Chips 1, 2, and 3 extended from 0 to 1.5 cm., 1.3 to 2.8 cm., and 2.6 to 4.1 cm., respectively, from the fertilizer source.

Reaction with monobasic calcium phosphate monohydrate The only reaction product identified on CaCO_3 chips isolated from calcareous soils which had reacted with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Table 23). This reaction product was observed on the CaCO_3 chips only when it was also observed in the soil at the corresponding distance from the fertilizer source.

Reaction with monobasic ammonium phosphate Table 24 shows the reaction products formed on CaCO_3 chips isolated from calcareous soils which had reacted with $\text{NH}_4\text{H}_2\text{PO}_4$. In all soils, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was identified by petrographic and X-ray analysis on CaCO_3 chips and in the soil. Traces of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were observed on crystals of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ probed from the surface of the CaCO_3 chips isolated from each soil. Little evidence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ formation on $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals isolated from the soil, was observed except possibly in the case of Harpster silty clay loam II, which contained more carbonate than any of the other soils (21.7% CaCO_3 equivalent). In Harpster silty clay loam II, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ appeared to have formed on some $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals at 48 weeks, but the amount was so slight that a definite conclusion could not be made.

In addition to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was identified in the soil and on chips in Darling Downs clay. With time, the $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ disappeared.

Reaction with dibasic ammonium phosphate The reaction products identified on CaCO_3 chips isolated from calcareous soils which had reacted with $(\text{NH}_4)_2\text{HPO}_4$ are shown in Table 25. At 4 and 16 weeks, the reaction products on the chips were confined almost exclusively to the first 5 mm.

Table 23. Crystalline phosphates identified on CaCO_3 chips isolated from calcareous soils which had been in contact with monobasic calcium phosphate monohydrate for 4, 16, and 48 weeks

		Crystalline phosphates identified ^a					
Number ^b	Species	Petrographic analysis			X-ray analysis		
of chip		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
<u>Norfolk loamy sand (pH 7.91, 9.1% CaCO₃)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
<u>Lloyd clay loam (pH 7.51, 9.1% CaCO₃)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2	CaHPO ₄ ·2H ₂ O	*	*	0	0	*	0
3	None	0	0	0	0	0	0
<u>Webster silty clay loam (pH 7.75, 9.1% CaCO₃)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
3	None	0	0	0	0	0	0
<u>Harpster silty clay loam I (pH 7.51, 3.0% CaCO₃ equivalent)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2	CaHPO ₄ ·2H ₂ O	0	*	*	0	*	*
2	None	0	0	0	0	0	0
<u>Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
<u>Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
2	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	0
3	None	0	0	0	0	0	0

^a* = present and 0 = none detected.

^bThe chips were arranged in an echelon, chip number 1 being closest to fertilizer source.

Table 24. Crystalline phosphates identified on CaCO_3 chips isolated from calcareous soils which had been in contact with monobasic ammonium phosphate for 4, 16, and 48 weeks

Crystalline phosphates identified ^a							
Number ^b of chip	Species	Petrographic analysis			X-ray analysis		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
<u>Norfolk loamy sand (pH 7.91, 9.1% CaCO₃)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	0	0
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
<u>Lloyd clay loam (pH 7.51, 9.1% CaCO₃)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	0	0
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
<u>Webster silty clay loam (pH 7.71, 9.1% CaCO₃)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	0	0
2	CaHPO ₄ ·2H ₂ O	*	*	*	0	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	0	0
3	None	0	0	0	0	0	0
<u>Harpster silty clay loam I (pH 7.51, 3.0% CaCO₃ equivalent)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	0	0
2	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	0	0
3	None	0	0	0	0	0	0

^a* = present and 0 = none detected.

^bThe chips were arranged in an echelon, chip number 1 being closest to fertilizer source.

Table 24. (Continued)

Number ^b of chip	Species	Crystalline phosphates identified ^a					
		Petrographic analysis			X-ray analysis		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
<u>Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	0	0
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
<u>Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)</u>							
1	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	*	*	*	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T			
2	CaHPO ₄ ·2H ₂ O	*	*	*	*	*	*
	MgNH ₄ PO ₄ ·6H ₂ O	*	*	0	*	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	T	T	0	*	*
3	None	0	0	0	0	0	0

Table 25. Crystalline phosphates identified on CaCO_3 chips isolated from calcareous soils which had been in contact with dibasic ammonium phosphate for 4, 16, and 48 weeks

Number ^b of chip	Species	Crystalline phosphates identified ^a					
		Petrographic analysis			X-ray analysis		
		4 weeks	16 weeks	48 weeks	4 weeks	16 weeks	48 weeks
Norfolk loamy sand (pH 7.91, 9.1% CaCO ₃)							
1	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	*	0	0	0	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	*	*	0	*	C
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
Lloyd clay loam (pH 7.51, 9.1% CaCO ₃)							
1	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	*	*	*	*	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	*	*	0	0	C
2	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	0	0	0	0	C
3	None	0	0	0	0	0	0
Webster silty clay loam (pH 7.71, 9.1% CaCO ₃)							
1	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	*	0	0	0	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	*	*	0	0	C
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
Harpster silty clay loam I (pH 7.51, 3.0% CaCO ₃ equivalent)							
1	Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ OB	*	0	0	0	0	0
	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	*	0	*	C
2	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	0	0	0	0	0	C
3	None	0	0	0	0	0	0

^a* = present, 0 = none detected, C means compound formed may have been either $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ or $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$.

^bThe chips were arranged in an echelon, chip number 1 being closest to fertilizer source.

Table 25. (Continued)

Number ^b of chip	Species	Crystalline phosphates identified ^a					
		Petrographic analysis			X-ray analysis		
		4	16	48	4	16	48
		weeks	weeks	weeks	weeks	weeks	weeks
<u>Harpster silty clay loam II (pH 7.52, 21.7% CaCO₃ equivalent)</u>							
1	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	0	*	0	C
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0
<u>Darling Downs clay (pH 7.80, 4.0% CaCO₃ equivalent)</u>							
1	Ca ₈ H ₂ (PO ₄) ₆ ·5H ₂ O	*	*	*	*	0	C
2	None	0	0	0	0	0	0
3	"	0	0	0	0	0	0

of the chip nearest the fertilizer source. Similarly, in each soil, the reaction products identified occurred in the 0 to 5 mm. zone nearest the fertilizer.

In Norfolk loamy sand, Lloyd clay loam, and Webster silty clay loam, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was identified on the chips and in the soil at 4 weeks. (The extensive precipitation of this compound on the CaCO_3 chip isolated from Lloyd clay loam is shown in Figure 7.) With time, the $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ on the chips apparently dissolved, and, at 16 and 48 weeks, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified in the region previously occupied by $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$. It is uncertain whether the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ had been formed underneath the $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ (the macroscopic features of these compounds are similar) or whether it had formed as the latter compound dissolved. The $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ initially identified in the soil at 4 weeks also dissolved with time, but no $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was observed at 16 or 48 weeks.

In Harpster silty clay loam I at 4 weeks, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified as white blade-like crystals on the first chip on the plane facing the fertilizer source, whereas white lathlike crystals of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ were observed for 2 to 3 mm. along the sides of the chip. At 16 and 48 weeks, the latter compound had disappeared, but the former compound persisted. $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was the only reaction product identified in the soil.

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified in the soil and on the CaCO_3 chips in Harpster silty clay loam II and Darling Downs clay. In each case, the compound occurred on the first chip on the plane facing the fertilizer source.



Figure 7. $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ found on a calcium carbonate chip in a column of Lloyd clay loam 4 weeks after addition of a band of dibasic ammonium phosphate. The crystals are evident only on the end of the chip nearest the fertilizer. Scale divisions on the left are 1 mm. each.

Figure 8 is a photograph showing the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ on the chip isolated from Harpster silty clay loam II after 16 weeks.

Most of the previous discussion has revolved around the reaction products formed on the portion of the first chip closest to the $(\text{NH}_4)_2\text{HPO}_4$ source. At 48 weeks, however, some evidence was obtained in all soils for formation of a reaction product over a large portion of the first chip and often the second chip. X-ray diffraction analysis of the larger surfaces of the chips from all soils at 4 and 16 weeks did not detect any reaction product. (The $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ formed on the edges of the chip nearest the fertilizer source were identified by scraping off the compounds and X-raying them on a glass microscope slide.) At 48 weeks, the X-ray diffraction patterns of the larger surfaces of the chips revealed a broad peak at approximately $32^\circ 2\theta$, similar to that observed in the X-ray analysis of CaCO_3 -coated slides at 48 weeks. This peak could be due to either $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ or $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. Microscopic analysis (X20) of the portions of the chips giving rise to this X-ray diffraction peak did not reveal the presence of a precipitate on the CaCO_3 surface. Petrographic analyses of samples isolated from these areas were inconclusive perhaps due to the presence of precipitated soil organic matter. No peak at $32^\circ 2\theta$ was observed in X-ray diffraction patterns of corresponding soil segments at 48 weeks.

Interpretation The interpretation of findings made with the chips of CaCO_3 embedded in the soil is similar to the interpretation made previously of the results obtained with the CaCO_3 -coated slides. The use of CaCO_3 chips to determine the nature of the crystalline phosphate species in



Figure 8. Octacalcium phosphate found on a calcium carbonate chip in a column of Harpster silty clay loam II sixteen weeks after addition of a band of dibasic ammonium phosphate ($X/2$). The chip was positioned 0 to 1.5 cm. from the band, and the octacalcium phosphate was found only on approximately 2 mm. of the end of the chip nearest the fertilizer.

calcareous soils that had reacted with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ appeared to be a valid technique in that the phosphate species identified on the CaCO_3 chips and in the soil were the same.

In the instances where $(\text{NH}_4)_2\text{HPO}_4$ was the added fertilizer, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was often identified on CaCO_3 chips when this compound was not identified in the soil. The surface of the CaCO_3 seemed to provide a high-calcium environment that favored formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. In at least one instance, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, a compound with a low ratio of calcium to phosphorus, was found in the soil but was not detected on the CaCO_3 chips. Examination of CaCO_3 chips embedded in calcareous soil thus cannot substitute for examination of the soil.

Examination of the CaCO_3 chips would seem to supplement the examination of the soil by showing the phosphates that might form on carbonate surfaces in soil. The validity of this inference, however, remains to be determined. Much of the CaCO_3 in some calcareous soils is finely divided and is present in a matrix of noncarbonate material. Conditions at the surface of this naturally occurring CaCO_3 may be sufficiently different from those presented by an extensive surface that is all CaCO_3 to prevent the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ often observed on the CaCO_3 -coated slides and CaCO_3 chips that are not detected in the adjacent soil, therefore, might be formed on naturally occurring soil carbonate only if the particles are above some critical size.

SUMMARY AND CONCLUSIONS

The objectives of the work described in Part I of this dissertation were (a) to develop techniques for direct identification of crystalline phosphates produced in slightly acid and alkaline soils treated with soluble phosphate fertilizers and (b) to use these techniques to determine the effect of various factors on the nature and transformations of the crystalline phosphates formed in the initial reaction between fertilizer and soil.

The most sensitive and direct technique used for the detection and identification of crystalline reaction products was that involving petrographic and X-ray diffraction analysis of crystals which had been isolated from the soil with the aid of a low-power microscope.

The use of glass-fiber paper strips to facilitate the detection and identification of reaction products in soil appeared to be a valid technique in that the precipitation of a reaction product in the paper strips mirrored the precipitation of the product in the soil. X-ray diffraction analysis of the paper strips was far more sensitive than X-ray diffraction analysis of the soil in detecting the presence of a reaction product. Furthermore, analysis of the paper strips by X-ray diffraction was almost as sensitive as microscopic analysis of the soil but had the advantages of speed and convenience. The paper strips had an additional advantage of providing visual evidence of the effect of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ in dispersing soil organic matter.

In calcareous soils, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ often formed on the surface of inclusions of CaCO_3 -coated slides and CaCO_3 chips but was not always detected in the soil. The CaCO_3 inclusions thus may provide supplemental

information on reaction products that form on the surface of native soil carbonate.

In the portion of the work on factors affecting the nature and transformations of crystalline phosphates formed in soils from interaction with phosphate fertilizers, a layer of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, or $(\text{NH}_4)_2\text{HPO}_4$ was placed at one end of a column of soil that was kept moist continuously. Various soils were used, some with various treatments. The columns were examined for crystalline phosphates after 4, 16, and 48 weeks of incubation, in most instances at 25°C.

In columns treated with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at 25°C., a residue of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ with a minor amount of CaHPO_4 was found at the site of the fertilizer at the end of 4 weeks. The ratio of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to CaHPO_4 decreased from 4 to 48 weeks, at which time CaHPO_4 had become the major phase in most soils. The transformation of the dihydrate to the anhydrous form appeared to be slower in soils with a high content of reactive calcium than in those with a low content. At 35°C. the residue was essentially all CaHPO_4 at 4, 16, and 48 weeks.

The only reaction product identified in soils which had reacted with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The precipitation of this product appeared to be essentially complete in 4 weeks, and little change in the amount and distribution of the product was observed from 4 to 48 weeks, even though the fertilizer phosphorus continued to diffuse into previously uncontacted soil. The amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ formed in the soils increased with the amount of reactive calcium in the exchangeable and carbonate forms. The amount and distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Webster silty clay loam were

essentially the same at 25°C. and 35°C.

With one exception, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was the only reaction product identified in soils which had reacted with $\text{NH}_4\text{H}_2\text{PO}_4$. The precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in all soils appeared to be complete in 4 weeks because very little change in the amount and distribution of the compound was observed from 4 to 48 weeks. The relationship between the quantity of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitated and the amount of reactive calcium in exchangeable and carbonate forms in the soil was more pronounced than in the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ treatments. In Webster silty clay loam, little difference was observed in the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at 25°C. and 35°C.

In Darling Downs clay, which contained more reactive magnesium than the other soils, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was found in addition to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The precipitation of this compound was essentially complete at 4 weeks, and the quantity of the compound decreased thereafter, until at 48 weeks, only a trace remained. The transformation product observed on the residual $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals at 48 weeks appeared to be $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$.

In soils which had reacted with $(\text{NH}_4)_2\text{HPO}_4$, the reaction products identified were $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were detected as initial reaction products only in the few millimeters of soil first contacted by the concentrated fertilizer solution. The precipitation zones of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ were more extensive, extending several centimeters away from the fertilizer source.

In all soils except Harpster silty clay loam II and Darling Downs clay, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{OB}$ was identified as a reaction product after 4 weeks, the quantity increasing with the amount of reactive calcium in the soil.

This product was unstable and had essentially disappeared by the end of 16 weeks, leaving a residue of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. In Webster silty clay loam, the quantity of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ precipitated was less at 35°C . than at 25°C . $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified after 4 weeks in Harpster silty clay loam II, presumably because of the very high content of reactive calcium in this soil (21.7% CaCO_3 equivalent). The same phosphate was also identified on the surface of CaCO_3 -coated slides and CaCO_3 chips in all soils. Seemingly therefore, $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was the dominant reaction product below a certain concentration of reactive calcium, and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was the dominant product above it.

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was found as an initial reaction product only in Webster silty clay loam, Harpster silty clay loam I, and Darling Downs clay. In samples of Webster silty clay loam adjusted to various pH values, the amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ precipitated in the soil decreased with an increase in initial pH, and increased with time. Apparently the precipitation of this compound was not favored by the environment encountered when the alkaline $(\text{NH}_4)_2\text{HPO}_4$ solution first reacted with the soil. With the passage of time, the microbial conversion of NH_4^+ to NO_3^- caused the pH to drop, and more $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was formed. There was little or no difference in the precipitation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Webster silty clay loam at 25°C . and 35°C . $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was not found in Harpster silty clay loam II and the calcareous samples of Norfolk loamy sand and Lloyd clay loam, presumably because the pH was too high, whereas the absence of this compound from noncalcareous samples of the Norfolk and Lloyd soils was probably due to their low content of exchangeable calcium.

$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was identified after 4 weeks in Darling Downs clay treated with $(\text{NH}_4)_2\text{HPO}_4$. The compound dissolved with the passage of time, and at 48 weeks only traces of the compound remained.

PART II. TRANSFORMATIONS OF DIBASIC CALCIUM PHOSPHATE DIHYDRATE AND
OCTACALCIUM PHOSPHATE ADDED TO SLIGHTLY ACID AND ALKALINE
SOILS

MATERIALS, APPARATUS, AND METHODS

Materials

Soils

The soils used in this investigation were the same as those used in Part I. Certain physical and chemical properties of these soils are shown in Table 2 and Table 3, respectively. Three additional soil treatments, however, were added in this investigation. These treatments involved the addition of calcium fluoride (CaF_2), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and a calcium pyrophosphate ($\text{CaH}_2\text{P}_2\text{O}_7$) to selected soils.

Sufficient CaF_2 to supply 0.1% fluoride by weight was added to samples of the Norfolk loamy sand adjusted to pH values of 6.41, 7.91, and 8.70 and to samples of Webster silty clay loam adjusted to pH values of 6.53 and 7.71. [The fluoride content of soils ranges from 0.001% to 0.1% by weight (Mitchell, 1964).] The reagent grade CaF_2 was mixed with the soils in a manner similar to that described previously for CaO .

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was added to a sample of the Norfolk loamy sand with a pH of 7.91 and to a sample of the Webster silty clay loam with a pH of 7.71. The number of milliequivalents of magnesium added per 100 g. of each soil was equal to the cation exchange capacity of that soil in milliequivalents per 100 g.

The pyrophosphate treatments involved the addition of 0.5 g. of $\text{CaH}_2\text{P}_2\text{O}_7$ per 100 g. of soil to the Norfolk loamy sand (pH 7.91) and Webster silty clay loam (pH 7.71).

Phosphates

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ This phosphate was prepared by the method of Moreno et al. (1960a) because commercial preparations contain variable amounts of CaHPO_4 . Approximately 1 liter of metastable triple-point solution was prepared by adding 140 ml. of deionized water to 200 g. of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ in each of eight 250 ml. erlenmeyer flasks and shaking the mixture for 3 hours. The metastable triple-point solution was collected by filtering the suspension through a Whatman 42 filter paper under suction. A current of ammonia was passed through the filtered solution to raise the pH and precipitate the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The precipitate was washed by successive quick sedimentations until the pH of the supernatant liquid increased to approximately 6.2. The $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was then transferred to a sintered glass funnel, washed ten times with acetone, and dried under moderate suction for about 30 minutes. Each batch of phosphate was checked by X-ray and petrographic analysis. Both analyses indicated $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to be the only compound present. The salt was sieved, and the 105- to 210-micron size fraction was collected and stored in a refrigerator until needed. This size fraction was used for the preparation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and for the experiments involving the addition of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to soils.

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ This phosphate was prepared by the slow hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in a 0.5M solution of sodium acetate as basically described by Brown et al. (1957). Additional details of this method of preparation were supplied by Lehr.¹ Five grams of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were

¹Lehr, J.R., Fundamental Research Branch, Tennessee Valley Authority. Preparation of octacalcium phosphate. Private communication. 1966.

placed in a cylindrical 4 oz. sample bottle, and 100 ml. of 0.5M sodium acetate buffer were added. The bottle was placed in a water bath at 35°C. to a depth of about 2.5 cm. The slight thermal gradient in the solution column provided convection stirring. The mixture was equilibrated 3 to 4 days, during which time $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ dissolved and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ slowly precipitated as a surface crust until the pH dropped to about 6.2. The supernatant solution was then carefully decanted and replaced by fresh buffer solution, and the process was repeated four to five times.

The $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was crushed, filtered, and washed to remove residual sodium acetate by resuspending the salt in approximately 4 liters of deionized water and stirring the mixture overnight. The suspension was filtered through a sintered glass funnel, washed thoroughly with acetone, and dried under a moderate vacuum. X-ray analysis showed $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to be the only phase present. Petrographic analysis showed the presence of a slight trace of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

$\text{CaH}_2\text{P}_2\text{O}_7$ This compound was prepared by the method described by Lehr *et al.* (1967). A 250 ml. volume of reagent grade 85% orthophosphoric acid (H_3PO_4) was heated rapidly to 210°C. with vigorous stirring. $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was added at a rate of approximately 1 g. per minute until the first crystals of $\text{CaH}_2\text{P}_2\text{O}_7$ appeared; thereafter the rate of addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was decreased to about 0.2 g. per minute and continued until a relatively thick suspension of solids was obtained. The hot mixture was filtered immediately by suction on a fritted-glass filter. When cool, the crystals were thoroughly washed with acetone and air dried.

Miscellaneous

The glass-fiber filter paper used to prepare the envelopes containing $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was Whatman brand, number GF-81. This paper had a weight of 53 g. per m^2 . and a thickness of 0.25 mm.

The polyethylene film used as a seal on the soil columns in this investigation was the same as that used in Part I and is described therein.

The certified refractive index liquids employed were described in Part I.

Apparatus

Plexiglas columns

The units constructed to contain the soil-phosphate system under investigation were basically the same as those used in Part I and are described therein. The columns used in this investigation, however, were different from those used in Part I in that both end plates of each column had a central hole 2.54 cm. in diameter. As in Part I, one end plate was not sealed onto the column until after the latter had been filled with soil.

Miscellaneous

The binocular and petrographic microscopes and X-ray diffraction unit used in this investigation were described in Part I.

A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used for the determination of calcium in the acid digests of the calcium phosphates isolated from soils.

Methods

To determine whether the sequence $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ that seems to occur in vitro occurs also in soil, and to obtain quantitative data on the extent of the transformations, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were incubated in soil under different conditions. To ensure that the residues could be isolated for determination of calcium and phosphorus without contamination by soil particles, the phosphate salts were enclosed in envelopes of glass-fiber filter paper. To determine whether the alterations that occurred in the phosphate salts in the envelopes were similar to those that occurred in the same salts in direct contact with the soil, X-ray and petrographic analyses were made on phosphate residues isolated from the envelopes and from residues that had been in direct contact with the soil.

Preparation of envelopes containing $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$

A disc of glass-fiber filter paper 3 cm. in diameter was laid on a sheet of glass, and a piece of glass tubing 2.74 cm. in diameter and 2.5 cm. long was placed on the paper disc to leave a uniform margin of approximately 0.3 cm. outside the tubing. The weighed amount of phosphate (0.200 g. of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ or 0.130 g. of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) was poured onto the disc of paper through the glass tube. A thin layer of epoxy resin cement was then applied to the 0.3 cm. margin of the paper disc exposed beyond the walls of the glass tube. The glass tube was carefully removed, and another disc of glass-fiber filter paper 3 cm. in diameter was sealed onto the bottom disc to form an envelope. The epoxy resin was allowed to

dry 24 hours. The envelope was then placed on a glass sheet and gently pressed with another sheet of glass to spread the phosphate within the envelope into a thin, uniform layer. The average thickness of each envelope was approximately 0.12 cm. of which 0.07 cm. was phosphate. Envelopes containing $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were stored in a refrigerator until needed, but no special precautions were observed with the envelopes containing $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$.

Preparation of soil columns for incubation

Preliminary experiments involving the positioning of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in soil columns with and without envelopes had shown that the pH and phosphorus concentration of the soil generally was affected for only a few millimeters on either side of the phosphate source. It was found convenient, therefore, to place four phosphate treatments in each column. The four treatments involved the placement in the soil of 0.200 g. of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ with and without an envelope and of 0.130 g. of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ with and without an envelope. The longitudinal axis of each column was divided into quarters, and one treatment was placed at the midpoint of each quarter. The relative position of the four treatments in each column was determined by the use of a set of random numbers. Two replicates of each column were prepared.

Filling of the columns with soil The soils in this investigation were packed to the same bulk density values as the corresponding soils in Part I. These values are listed in Table 4.

A standard filling technique was used for all soils. Each column,

minus one end plate, was filled in a standing position. First, a circular piece of 40-mesh stainless steel gauze and then a circle of glass-fiber filter paper (both 3.7 cm. in diameter) were placed in the base of each column. A predetermined weight of air-dry soil was transferred in increments to each column through a long-stem funnel. The soil was added to each column in five steps to fill the column to depths of approximately 1.25, 3.75, 6.25, 8.75, and 10.0 cm. After addition of each increment of soil, the column was dropped on a wood table five times from a height of approximately 1 cm. The surface of the soil was then smoothed, and a phosphate application was made. Where the phosphate compounds were added without an envelope, a glass tube 2.74 cm. in diameter was placed on top of the soil in the column, and the phosphate was added through the tube to produce a uniform layer of phosphate on the soil. This method ensured that a layer of phosphate in direct contact with the soil occupied the same area and was of the same thickness as a layer of the same phosphate in an envelope.

Addition of water The water content of the soil in each column was adjusted to field capacity in a manner similar to that described in Part I. Preliminary experiments had shown that to obtain a constant moisture content throughout each column the required amount of water had to be added in two equal portions, one portion to each end of the column. (In the case of the Norfolk loamy sand, however, the water had to be added in five equal portions during the filling of each column with soil.) The first portion of water was added to each column through the hole in the base, as described previously. The second portion was added directly to

the top of the soil column from a burette.

Sealing of columns and incubation After 20 to 30 minutes had been allowed for the soil in each column to become wet, a circle of glass-fiber filter paper and then a circle of stainless steel gauze were added to the soil at the top of each column. The 5 cm. by 5 cm. Plexiglas end plate was then sealed onto each column with silicone rubber, and the polyethylene seals were placed over both ends in the manner described in Part I.

The columns were incubated for 4, 16, or 44 weeks under the same conditions as described in the previous investigation. Each column, however, was incubated with its long axis in a horizontal position. The advantages of this method were twofold. Firstly, the water content of the soil was kept more uniform from one end of the column to the other, and secondly, the oxygen and carbon dioxide levels should be more nearly uniform from end to end as a result of the diffusion of these gases through the polyethylene seals at both ends of the column.

Examination of soil columns after incubation

Isolation of phosphate After being incubated for the designated period, each column was opened by cutting the silicone rubber seals at the ends and along the sides of the column. The upper half of the Plexiglas cylinder was removed to expose the solid soil core. The envelopes containing $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were carefully removed with forceps, washed with acetone to remove soil particles, and partially dried on a sintered glass membrane under vacuum. Each envelope was opened by removing a circle of glass-fiber filter paper about 2.5 cm. in diameter from one side. The envelope was transferred to a sintered glass membrane, and

the exposed phosphate crystals were washed thoroughly with acetone and dried under a vacuum. The phosphate was carefully removed and transferred to a tightly stoppered vial. The vials containing $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ residues were placed in a refrigerator to ensure that the phosphate salt did not change to the anhydrous form before a detailed examination of the product could be made.

The phosphate placed in direct contact with the soil was treated similarly. The phosphate was carefully isolated from the soil with a spatula, washed with acetone, dried under vacuum, and placed in stoppered vials for future examination.

pH determinations on soil In selected columns, soil segments from 2 to 5 mm. wide were collected at various positions for pH determinations to ascertain the effect of incubation on the soil pH. The determinations were conducted using 0.01 M CaCl_2 in the manner described in Part I.

Calcium and phosphorus analyses The phosphate isolated from the glass-fiber filter paper envelopes was analyzed for calcium and phosphorus as follows. Approximately 0.05 g. of phosphate was accurately weighed into a 100 ml. beaker on an analytical balance. The phosphate was dissolved by adding 30 ml. of 3N HCl and heating on a steam plate for 30 minutes. The digest was quantitatively transferred to a 500 ml. volumetric flask and brought to volume with deionized water.

For calcium analyses, a 10 ml. aliquot was transferred to a 50 ml. volumetric flask, 10 ml. of a 5% solution of lanthanum as lanthanum chloride was added, and the volume was made to 50 ml. with deionized water. The lanthanum was added to prevent interference from phosphate in the

subsequent absorption measurements. Calcium standards containing the same lanthanum and acid concentrations as the samples were prepared to cover the range from 0 to 10 μg . of calcium per ml. The calcium content of the unknown samples was determined by comparing the absorption values of the samples and standards obtained with a Perkin-Elmer Model 303 atomic absorption spectrophotometer as described by the Perkin-Elmer Staff (1966).

Phosphorus determinations were made on 10 ml. aliquots of the phosphate solutions using the vanadomolybdophosphoric yellow color method (nitric acid system) described by Jackson (1958). The transmittancy of the yellow solutions was determined on an Evelyn photoelectric colorimeter equipped with a 420 m μ filter.

Petrographic and X-ray analysis Both the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ samples were examined under a petrographic microscope to determine the possible presence of new phases. Samples of phosphate were prepared for X-ray analysis by grinding them in an agate mortar and smearing the powder onto a piece of cellophane tape with adhesive on both sides. The tape had previously been mounted on a glass microscope slide. The samples were X-rayed in the manner described in Part I. The optical and X-ray diffraction data obtained on the samples were compared with the data for pure phosphates listed by Lehr et al. (1967).

RESULTS AND DISCUSSION

Transformations of Dibasic Calcium Phosphate Dihydrate

Alteration to octacalcium phosphate

The results of the microscopic and X-ray diffraction analyses of the residues from the incubation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in soils for 4, 16, and 44 weeks are shown in Tables 26, 27, and 28, respectively. After 4 weeks, the presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ as a new phase was definitely confirmed in Norfolk loamy sand and Webster silty clay loam (35°C.) at the higher pH values irrespective of whether the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ had been contained in an envelope or had been in direct contact with the soil. After 16 and 44 weeks, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was also detected in the phosphate isolated from each of the other soil types used in the investigation.

The new phase was positively identified as $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ by X-ray diffraction data which agreed with those given for the pure compound by Lehr *et al.* (1967). Under the petrographic microscope, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was observed as clusters of blade-like crystals on the surface of the rectangular $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals. Detection of the new phase was facilitated by observing the incubated phosphate crystals in a medium with a refractive index equal to the average refractive index of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (1.55). In this medium, the outline of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals almost completely disappeared, and any $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ crystals (average refractive index of 1.58) present stood out as dark-colored blades. The exact refractive indexes of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and other calcium phosphates of interest here are given in Table 31 (Appendix). Figure 9 contains photomicrographs showing $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ on the surface of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals isolated from Webster silty clay

Table 26. Ratio of calcium to phosphorus and presence of octacalcium phosphate in residues from dibasic calcium phosphate dihydrate incubated for 4 weeks in glass fiber paper envelopes in various soils and presence of octacalcium phosphate in residues incubated in direct contact with the soils

Average pH of soil during in- cubation	Soil treat- ment	Repli- cate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$			
				in envelope		in contact with soil	
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ Petrographic microscope ^a	X-ray dif- fraction ^b	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ Petrographic microscope ^b	X-ray dif- fraction ^b
Norfolk loamy sand (25°C.) ^c							
6.47	-	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.49	CaF_2	1	0.99	0	0	0	0
		2	1.00	0	0	0	0
6.69	$\text{CaH}_2\text{P}_2\text{O}_7$	1	0.99	0	0	0	0
		2	0.99	0	0	0	0
6.89	-	1	1.00	0	0	0	0
		2	0.99	0	0	0	0
7.87	-	1	1.02	T	0	*	0
		2	1.01	0	0	0	0
7.89	CaF_2	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.85	MgCl_2	1	0.98	0	0	0	0
		2	-	-	-	-	-
7.93	CaCO_3	1	1.00	T	0	*	0
		2	1.00	0	0	0	0
8.71	-	1	1.07	++	*	*	*
		2	1.08	++	*	*	*
8.73	CaF_2	1	1.08	++	*	*	*
		2	1.08	++	*	*	*

^a0 = none detected, T = trace, + = small, ++ = moderate, +++ = abundant, and ++++ = very abundant amounts, (here and in following tables).

^b0 = none detected and * = present, (here and in following tables).

^cTemperature of incubation, (here and in following tables).

Table 26. (Continued)

Average pH of soil during in- cubation	Soil treat- ment	Repli- cate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$			
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in envelope		$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in contact with soil	
				Petrographic microscope ^a	X-ray dif- fraction ^b	Petrographic microscope ^b	X-ray dif- fraction ^b
<u>Lloyd clay loam (25°C.)</u>							
6.19	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.87	--	1	0.99	0	0	0	0
		2	0.99	0	0	0	0
7.53	--	1	0.99	0	0	0	0
		2	0.99	0	0	0	0
7.57	CaCO_3	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
<u>Webster silty clay loam (25°C.)</u>							
6.56	--	1	1.00	0	0	0	0
		2	-	-	-	-	-
6.56	CaF_2	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.08	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.77	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.78	CaF_2	1	1.01	0	0	0	0
		2	1.01	0	0	0	0
7.79	CaCO_3	1	1.01	0	0	0	0
		2	1.00	0	0	0	0

Table 26. (Continued)

Average pH of soil during incubation	Soil treatment	Repligate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$		Petrographic microscope ^b	X-ray dif-fraction ^b
				CaHPO ₄ ·2H ₂ O in envelope	CaHPO ₄ ·2H ₂ O in contact with soil		
				Petrographic microscope ^a	X-ray dif-fraction ^b		
<u>Webster silty clay loam (35°C.)</u>							
6.53	--	1	1.00	0	0	0	0
		2	--	-	-	-	-
6.52	CaF ₂	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.06	--	1	0.99	0	0	0	0
		2	1.00	0	0	0	0
7.35	CaH ₂ P ₂ O ₇	1	0.99	0	0	0	0
		2	0.98	0	0	0	0
7.63	MgCl ₂	1	1.03	T	0	*	0
		2	1.01	T	0	*	0
7.71	--	1	1.02	T	0	*	0
		2	0.99	0	0	0	0
7.72	CaF ₂	1	1.03	T	0	*	0
		2	1.03	T	0	*	0
7.75	CaCO ₃	1	1.01	T	0	*	0
		2	1.03	T	0	*	0
<u>Harpster silty clay loam I (25°C.)</u>							
7.49	--	1	0.99	0	0	0	0
		2	0.99	0	0	0	0
<u>Harpster silty clay loam II (35°C.)</u>							
7.51	--	1	0.99	0	0	0	0
		2	0.98	0	0	0	0
<u>Darling Downs clay (25°C.)</u>							
7.80	--	1	0.99	0	0	0	0
		2	0.99	0	0	0	0

Table. 27. Ratio of calcium to phosphorus and presence of octacalcium phosphate in residues from dibasic calcium phosphate dihydrate incubated for 16 weeks in glass fiber paper envelopes in various soils and presence of octacalcium phosphate in residues incubated in direct contact with the soils

Average pH of soil during incubation	Soil treatment	Repliate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$			
				CaHPO ₄ ·2H ₂ O in envelope		CaHPO ₄ ·2H ₂ O in contact with soil	
				Petrographic microscope ^a	X-ray dif-fraction ^b	Petrographic microscope ^b	X-ray dif-fraction ^b
<u>Norfolk loamy sand (25°C.)^c</u>							
5.79	CaH ₂ P ₂ O ₇	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.43	--	1	1.00	0	0	0	0
		2	0.99	0	0	0	0
6.39	CaF ₂	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.83	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.76	--	1	1.08	++	*	*	0
		2	1.02	+	0	*	0
7.71	CaF ₂	1	1.12	++	*	*	0
		2	1.14	++	*	*	0
7.77	MgCl ₂	1	1.00	T	0	*	0
		2	1.00	T	0	*	0
7.81	CaCO ₃	1	1.04	++	*	*	0
		2	1.07	++	*	*	0
8.71	--	1	1.14	++++	*	*	*
		2	1.12	++++	*	*	*
8.71	CaF ₂	1	1.14	++++	*	*	*
		2	1.12	++++	*	*	*
<u>Lloyd clay loam (25°C.)</u>							
6.15	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.78	--	1	1.00	0	0	0	0
		2	0.99	0	0	0	0
7.49	--	1	1.00	T	0	*	0
		2	1.00	T	0	*	0
7.51	--	1	1.00	T	0	*	0
		2	1.00	T	0	*	0

Table 27. (Continued)

Average pH of soil during in- cubation	Soil treat- ment	Repli- cate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$			
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in envelope		$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in contact with soil	
				Petrographic microscope ^a	X-ray dif- fraction ^b	Petrographic microscope ^b	X-ray dif- fraction ^b
<u>Webster silty clay loam (25°C.)</u>							
6.51	--	1	1.00	0	0	0	0
		2	-	-	-	-	-
6.48	CaF_2	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.03	--	1	1.00	0	0	0	0
		2	-	-	-	-	-
7.68	--	1	1.03	+	0	*	0
		2	1.01	T	0	*	0
7.67	CaF_2	1	1.01	T	0	*	0
		2	1.01	+	0	*	0
7.71	CaCO_3	1	1.02	+	0	*	0
		2	1.02	+	0	*	0
<u>Webster silty clay loam (35°C.)</u>							
6.47	--	1	1.00	0	0	0	0
		2	-	-	-	-	-
6.41	CaF_2	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.98	--	1	1.00	T	0	*	0
		2	1.00	T	0	*	0
6.97	$\text{CaH}_2\text{P}_2\text{O}_7$	1	1.00	T	0	*	0
		2	1.00	T	0	*	0
7.54	MgCl_2	1	1.06	+	0	*	0
		2	1.11	+	0	*	0
7.63	--	1	1.08	++	*	*	0
		2	1.05	++	0	*	0
7.61	CaF_2	1	1.08	++	*	*	0
		2	1.10	++	*	*	0
7.65	CaCO_3	1	1.08	++	*	*	0
		2	1.06	++	0	*	0

Table 27. (Continued)

Average pH of soil during in- cubation	Soil treat- ment	Repli- cate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$			
				$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in envelope		$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in contact with soil	
				Petrographic microscope ^a	X-ray dif- fraction ^b	Petrographic microscope ^b	X-ray dif- fraction ^b
<u>Harpster silty clay loam I (25°C.)</u>							
7.51	--	1	1.00	T	0	*	0
		2	1.00	T	0	*	0
<u>Harpster silty clay loam II (25°C.)</u>							
7.52	--	1	1.00	T	0	*	0
		2	1.00	T	0	*	0
<u>Darling Downs clay (25°C.)</u>							
7.80	--	1	1.00	T	0	*	0
		2	1.01	T	0	*	0

Table 28. Ratio of calcium to phosphorus and presence of octacalcium phosphate in residues from dibasic calcium phosphate dihydrate incubated for 44 weeks in glass fiber paper envelopes in various soils and presence of octacalcium phosphate in residues incubated in direct contact with the soils

Average pH of soil during incubation	Soil treatment	Repligate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$			
				in envelope		in contact with soil	
				Petrographic microscope ^a	X-ray dif-fraction ^b	Petrographic microscope ^b	X-ray dif-fraction ^b
<u>Norfolk loamy sand (25°C.)^c</u>							
5.62	$\text{CaH}_2\text{P}_2\text{O}_7$	1	1.00	0	0	0	0
		2	0.99	0	0	0	0
6.33	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.37	CaF_2	1	1.03	0	0	0	0
		2	1.02	0	0	0	0
6.81	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.68	--	1	1.06	++	0	*	*
		2	1.04	++	0	*	*
7.61	CaF_2	1	1.04	++	0	*	*
		2	1.04	++	0	*	*
7.65	MgCl_2	1	1.01	T	0	*	0
		2	1.00	T	0	*	0
7.61	CaCO_3	1	1.07	+++	*	*	*
		2	1.18	+++	*	*	*
8.71	--	1	1.14	++++	*	*	*
		2	1.18	++++	*	*	0
8.71	CaF_2	1	1.17	++++	*	*	*
		2	1.16	++++	*	*	*
<u>Lloyd clay loam (25°C.)</u>							
6.09	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.67	--	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
7.48	--	1	1.03	++	0	*	0
		2	1.01	+	0	*	0
7.51	CaCO_3	1	1.00	+	0	*	0
		2	1.00	+	0	*	0

Table 28. (Continued)

Average pH of soil during in- cubation	Soil treat- ment	Repli- cate	Mole ratio of calcium to phosphorus (envelopes)	Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$			
				in envelope		in contact with soil	
				Petrographic microscope ^a	X-ray dif- fraction ^b	Petrographic microscope ^b	X-ray dif- fraction ^b
<u>Webster silty clay loam (25°C.)</u>							
6.46	--	1	1.00	0	0	0	0
		2	1.01	0	0	0	0
6.47	CaF_2	1	1.00	0	0	0	0
		2	1.00	0	0	0	0
6.94	--	1	1.00	T	0	*	0
		2	1.00	T	0	*	0
7.65	--	1	1.04	+	0	*	0
		2	1.04	+	0	*	*
7.63	CaF_2	1	1.09	++	*	*	*
		2	1.08	++	*	*	0
7.69	CaCO_3	1	1.07	++	*	*	*
		2	1.07	++	*	*	*
<u>Webster silty clay loam (35°C.)</u>							
6.39	--	1	1.00	0	0	0	0
		2	1.01	0	0	0	0
6.37	CaF_2	1	1.04	T	0	*	0
		2	1.05	T	0	*	0
6.84	--	1	1.04	+	0	*	0
		2	1.03	+	0	*	0
6.81	$\text{CaH}_2\text{P}_2\text{O}_7$	1	1.02	+	0	*	0
		2	1.03	+	0	*	0
7.51	MgCl_2	1	1.17	++	0	*	0
		2	1.17	++	0	*	0
7.56	--	1	1.24	++++	*	*	*
		2	1.13	+++	*	*	0
7.56	CaF_2	1	1.24	++++	*	*	*
		2	1.18	+++	*	*	*
7.60	CaCO_3	1	1.07	++	*	*	0
		2	1.13	+++	*	*	*

Table 28. (Continued)

Average pH of soil during in- cubation	Soil treat- ment	Repli- cate	Mole ratio of		Presence of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$		
			calcium to phosphorus (envelopes)	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in envelope		$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in contact with soil	
				Petrographic microscope ^a	X-ray dif- fraction ^b	Petrographic microscope ^b	X-ray dif- fraction ^b
<u>Harpster silty clay loam I (25°C.)</u>							
7.46	--	1	1.01	+	0	*	0
		2	1.01	+	0	*	0
<u>Harpster silty clay loam II (25°C.)</u>							
7.50	--	1	1.05	++	0	*	0
		2	1.07	+++	*	*	0
<u>Darling Downs clay (25°C.)</u>							
7.71	--	1	1.02	+	0	*	0
		2	1.01	T	0	*	0

Figure 9. Photomicrographs illustrating the formation of octacalcium phosphate on crystals of dibasic calcium phosphate dihydrate incubated in soil.

- A. Crystals of dibasic calcium phosphate dihydrate before addition to the soil. The crystals were photographed in a medium with a refractive index of 1.52 and at a magnification of 460. The dark body just below the center of the photomicrograph is a contaminant introduced during preparation of the mount.
- B. Crystals of octacalcium phosphate (dark) on the surface of crystals of dibasic calcium phosphate dihydrate (transparent) that had been incubated for 44 weeks in Webster silty clay loam at pH 7.71. To bring out the contrast between the species the crystals were photographed in a medium with a refractive index of 1.55 (magnification 365).



A.



B.

loam (pH 7.71) after 44 weeks incubation.

Where extensive alteration of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ had occurred, the phosphate crystals in the envelopes and in direct contact with the soil became loosely cemented together to form a crust. This phenomenon was also observed during the preparation of pure $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ by hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in a buffer solution.

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was the only new phase identified by petrographic and X-ray examination of residues of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ incubated in soils for up to 44 weeks. It is possible that a small amount of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ could have resulted from the hydrolysis of the newly formed $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. (There is little evidence available in the literature to suggest that $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ can form directly from $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The rate of this reaction at the temperatures and pH values used in this investigation, however, would be extremely slow. Furthermore, the results obtained from the addition of pure $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to soils (succeeding section) would suggest that little or no hydrolysis of the compound occurs, even after 44 weeks. A reaction of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ with fluoride to form $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ seems more likely; nevertheless, no $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ was positively identified by petrographic analysis or X-ray diffraction.

Tables 26, 27, and 28 show that $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was detected in the phosphate contained in envelopes only when it had also been detected in the phosphate which was in direct contact with the soil. It was not feasible to compare the extent of formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in the phosphate isolated from these two sources using the same scale because of the presence of soil contamination in the phosphate which had been in contact with the

soil. The extent of hydrolysis of individual crystals of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, however, appeared to be the same, irrespective of the source of the phosphate.

The fact that $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were the only species identified makes possible an estimate of the proportions of the components of the residues on the basis of their chemical composition. The residues in the envelope could be recovered without contamination by particles of soil; therefore, these residues were used for analysis. Because the results of petrographic and X-ray examination of the residues in the envelopes corresponded to the results obtained on residues in direct contact with soil, the quantitative transformations estimated from the composition of the residues may be similar to the quantitative transformations that occurred in the residues in direct contact with soil.

The theoretical calcium and phosphorus percentages in $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and its possible transformation products are shown in Table 29. If $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ alters to a more basic calcium phosphate, it is obvious that the calcium percentage and the ratio of calcium to phosphorus in the mixture will increase, the magnitude depending on the transformation product (or products) and the extent of the transformation. Because such a small sample (0.05 g.) of phosphate was used for calcium and phosphorus analyses, a small error in weighing would cause a relatively large error in the calcium and phosphorus percentages. Moreover, although inclusion of some glass fibers from the envelopes would not bias the results in favor of either calcium or phosphorus, the fibers would dilute the phosphates and would result in low values for both calcium and phosphorus. The ratio of calcium to

Table 29. Theoretical calcium and phosphorus percentages and mole ratio of calcium to phosphorus in dibasic calcium phosphate dihydrate, octacalcium phosphate, hydroxyapatite, and fluorapatite

Compound	Calcium content, %	Phosphorus content, %	Mole ratio of calcium to phosphorus
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	23.3	18.0	1.00
$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	32.6	18.9	1.33
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	39.9	18.5	1.67
$\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$	39.8	18.4	1.67

phosphorus, however, is insensitive to any error in the weight of the phosphate and thus was used as a measure of the extent of hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. In describing the transformations of calcium phosphates, the mole ratio of calcium to phosphorus is conventionally used in preference to the weight ratio and so mole ratios will be used throughout this discussion.

The relationship between the relative amounts of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in a mixture of the two and the mole ratio of calcium to phosphorus in the mixture is shown in Figure 10. The mole ratios of calcium to phosphorus in residues from dibasic calcium phosphate dihydrate incubated in soil for 4, 16, and 44 weeks are listed in Tables 26, 27, and 28, respectively.

Table 32 (Appendix) contains the calcium and phosphorus percentages from which these ratios were calculated. As is evident from Tables 26, 27, and 28, an increase in the ratio of calcium to phosphorus above the value of unity characteristic of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was accompanied by an increase in the

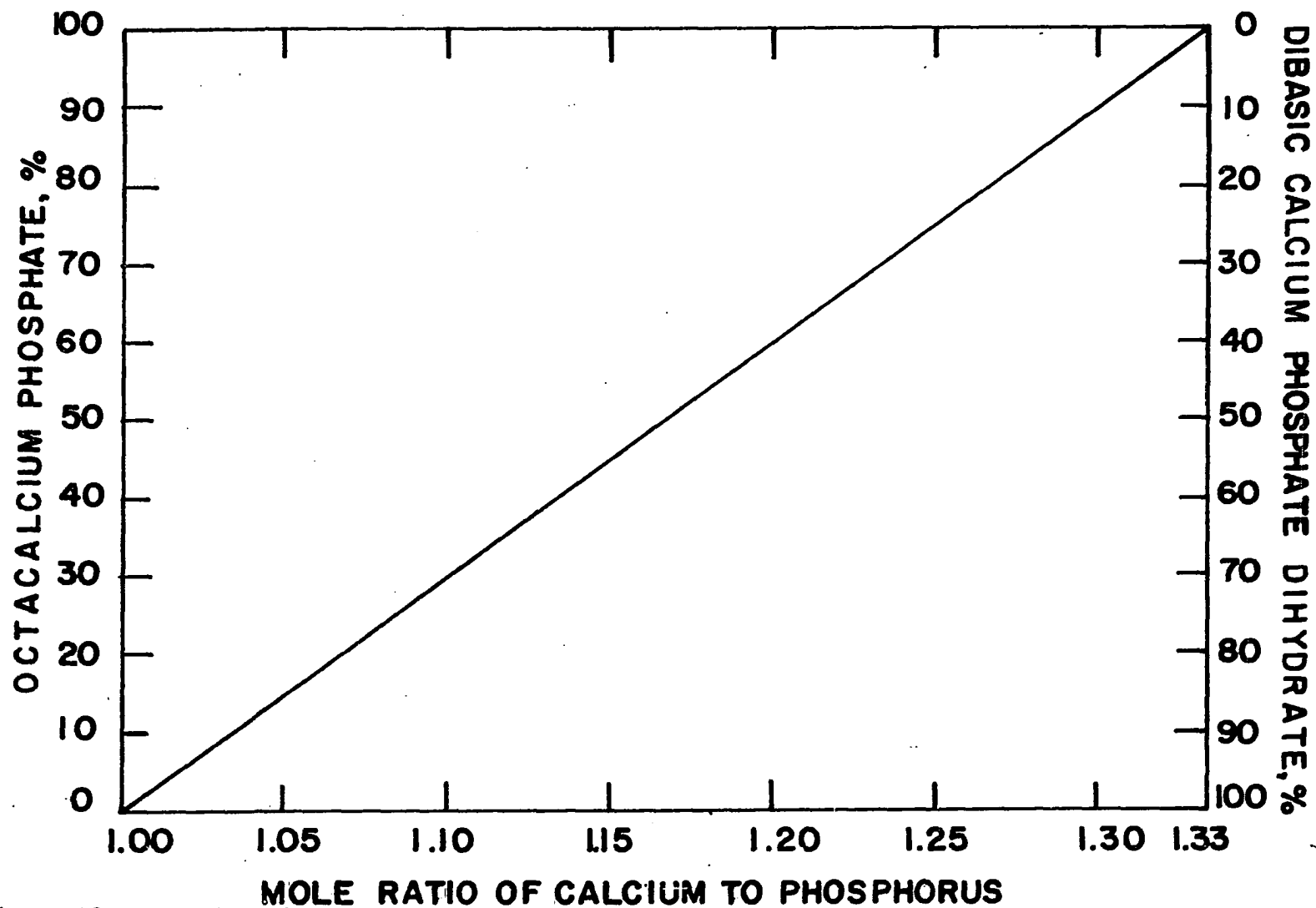


Figure 10. Relationship between the percentages of octacalcium phosphate and dibasic calcium phosphate dihydrate in a mixture of the two compounds and the mole ratio of calcium to phosphorus in the mixture.

proportion of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ found by petrographic analysis. The relationship may be seen more clearly in Figure 11.

Effect of carbonate

It is evident from Tables 26, 27, and 28 that at a given pH the mole ratios of calcium to phosphorus were not appreciably affected by additions of CaCO_3 . Accordingly, the CaCO_3 treatments are ignored in the next section, and the values obtained are plotted according to the soil pH, which seemed to be the controlling factor.

Effect of soil pH

The average pH values of the soils during incubation for 4, 16, and 44 weeks are shown in Table 33 in the Appendix. The trend with soil pH of the mole ratio of calcium to phosphorus in the phosphate residues of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ incubated in samples of Norfolk loamy sand adjusted to different pH values for 4, 16, and 44 weeks is shown in Figure 12. After 4 weeks, the ratio of calcium to phosphorus remained unchanged from a value of 1.00, characteristic of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, for pH values below about 8.0. The average ratio of the phosphate from the soil with pH 8.7 had increased significantly in this time, and petrographic analysis of the phosphate showed a moderate amount of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ on the surface of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals. At 16 and 44 weeks, the ratio of calcium to phosphorus remained unchanged below a pH value of about 7.0 but increased above this value, the increase being greater the higher the pH and the longer the incubation period. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was positively identified in all samples isolated at 16 and 44 weeks from soil with a pH value greater than 7.0. The maximum mole ratios attained

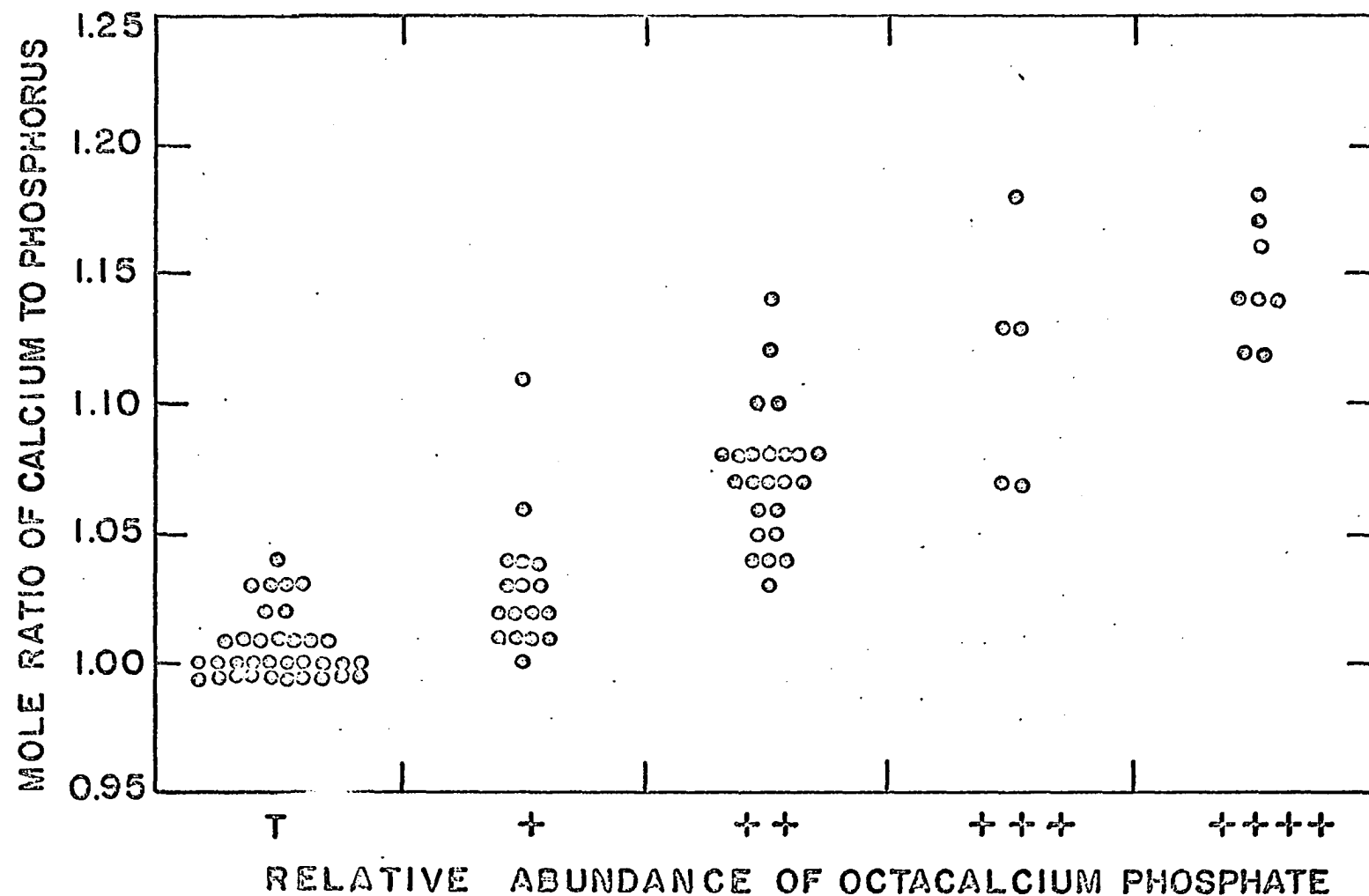


Figure 11. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate in glass-fiber paper envelopes in soils for 4, 16, and 44 weeks versus relative abundance of octacalcium phosphate in the residues as estimated from microscopic examination. Legend for relative amounts of octacalcium phosphate: T=Trace, +=small amount, ++=moderate amount, +++=large amount, and +++++=very large amount.

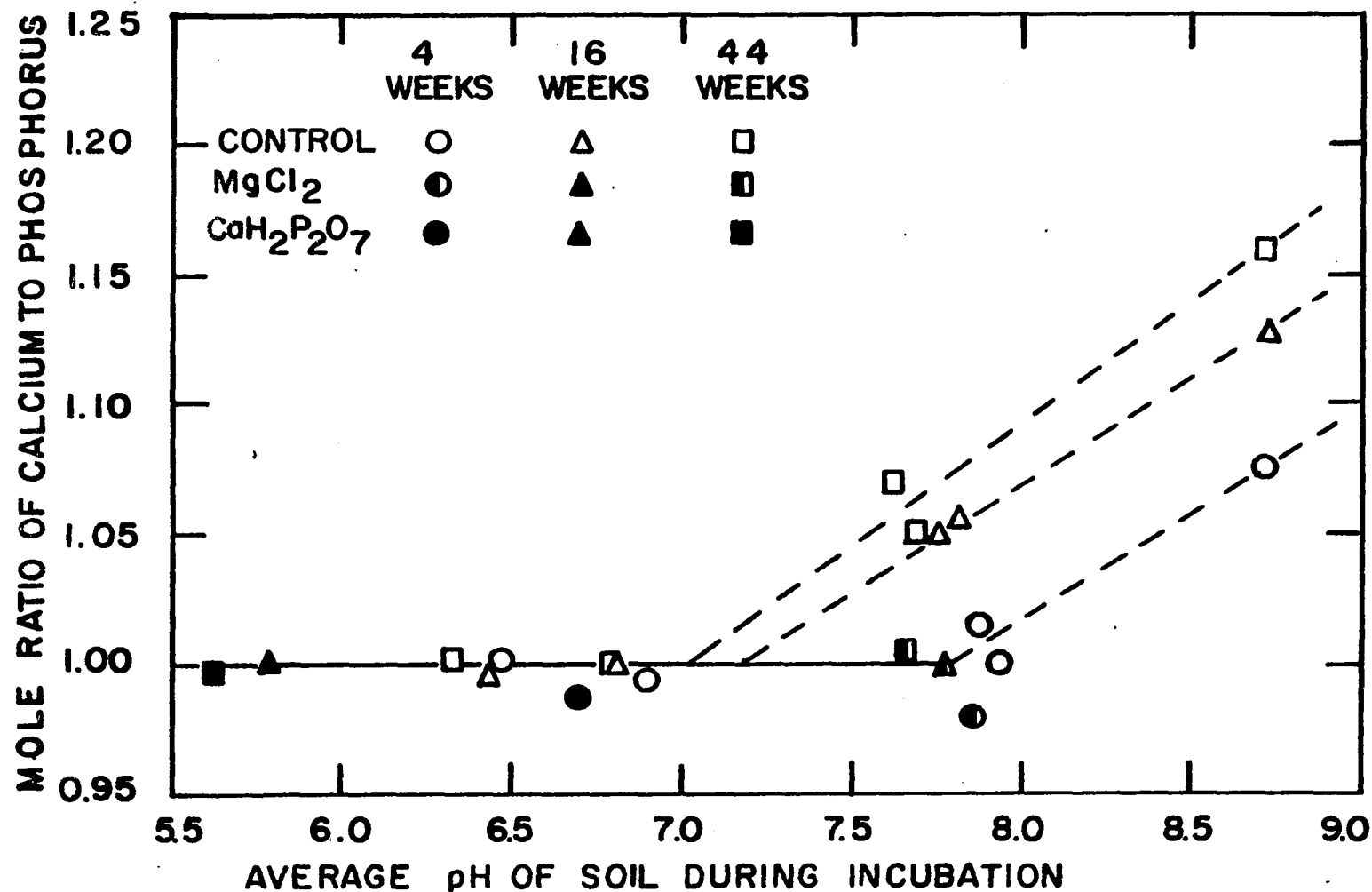


Figure 12. Mole ratio of calcium to phosphorus in residues from the incubation of dibasic calcium phosphate dihydrate at 25°C. in glass-fiber paper envelopes in Norfolk loamy sand for 4, 16, and 44 weeks versus the average pH of the soil during incubation. Magnesium chloride or calcium hydrogen pyrophosphate had been added to some samples. Each point represents the average of analyses on two replicates.

(at pH 8.70) after 4, 16, and 44 weeks corresponded to the presence of 24, 42, and 54% of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, respectively.

A similar trend in ratios of calcium to phosphorus with pH was observed with Lloyd clay loam at 25°C. and Webster silty clay loam at 25°C. and 35°C. The trend in the mole ratios with pH in samples incubated in Webster silty clay loam at 35°C. is shown in Figure 13.

The effect of pH on the mole ratios of calcium to phosphorus in residues of dibasic calcium phosphate dihydrate incubated at 25°C. with all soils used in this investigation is shown in Figures 14, 15, and 16. Irrespective of the soil type, the same general trend with pH was observed at each incubation period. After 4 weeks, the mole ratios increased above a pH value of about 7.8, indicating that transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ had occurred above this pH. After 16 weeks, the mole ratios had increased above pH 7.6. At the end of 44 weeks, increases in the ratios had occurred at pH values as low as 7.45.

In vitro studies have shown that the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ can occur above a pH of about 6.38, and it is conceivable that this transformation would have been observed at lower pH values if the incubation periods had been longer. It is of interest to note that, in Webster silty clay loam incubated at 35°C., $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified by the end of 44 weeks at a pH value as low as 6.8.

Effect of time

The effect of time on the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ incubated in Norfolk loamy sand is shown in Figure 17. The mole ratio of calcium to phosphorus did not change with time at pH values less than about 7. Above this pH the

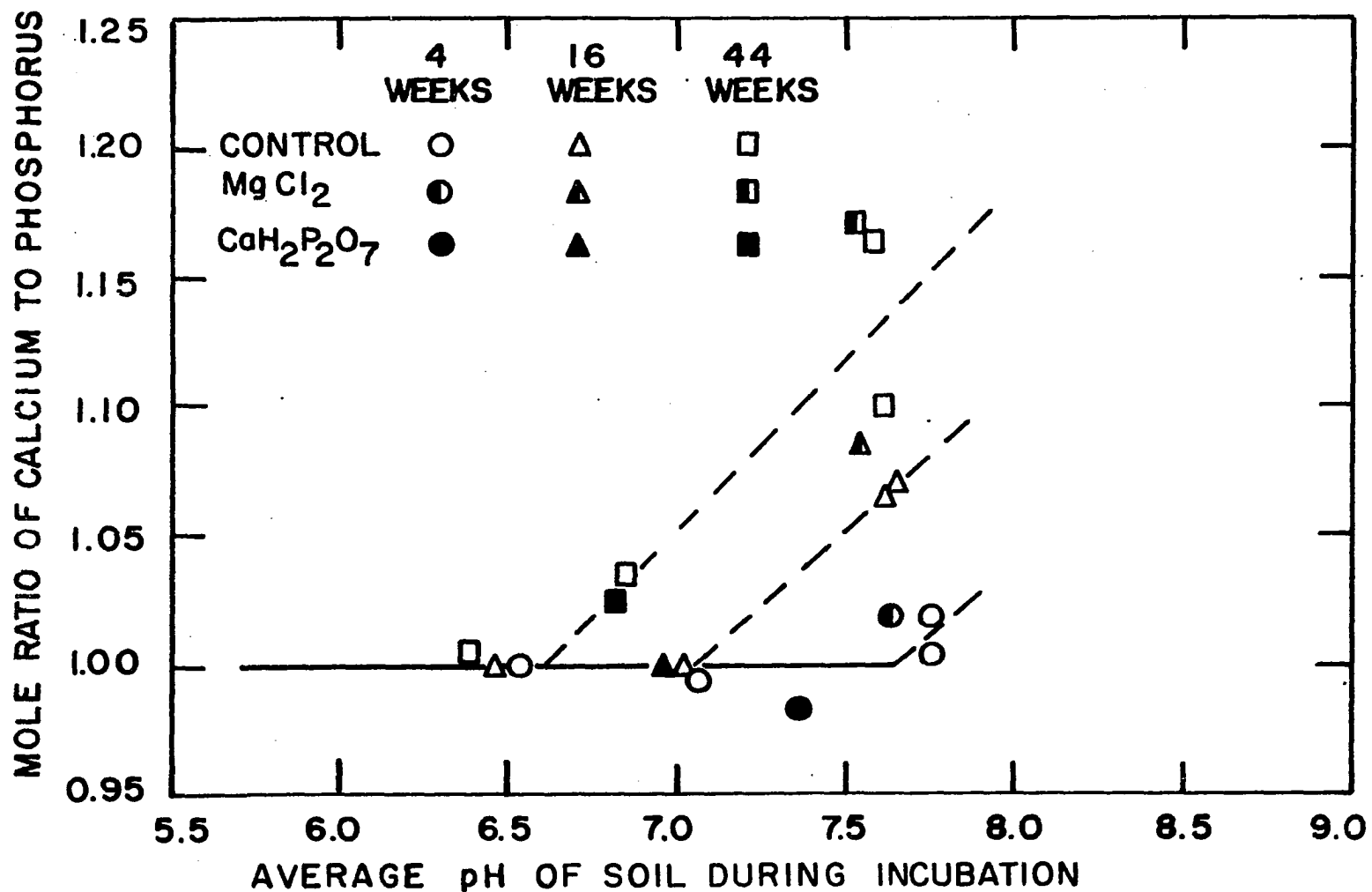


Figure 13. Mole ratio of calcium to phosphorus in residues from the incubation of dibasic calcium phosphate dihydrate at 35°C. in glass-fiber paper envelopes in Webster silty clay loam for 4, 16, and 44 weeks versus the average pH of the soil during incubation. Magnesium chloride or calcium hydrogen pyrophosphate had been added to some soil samples. Each point represents the average of analyses on two replicates.

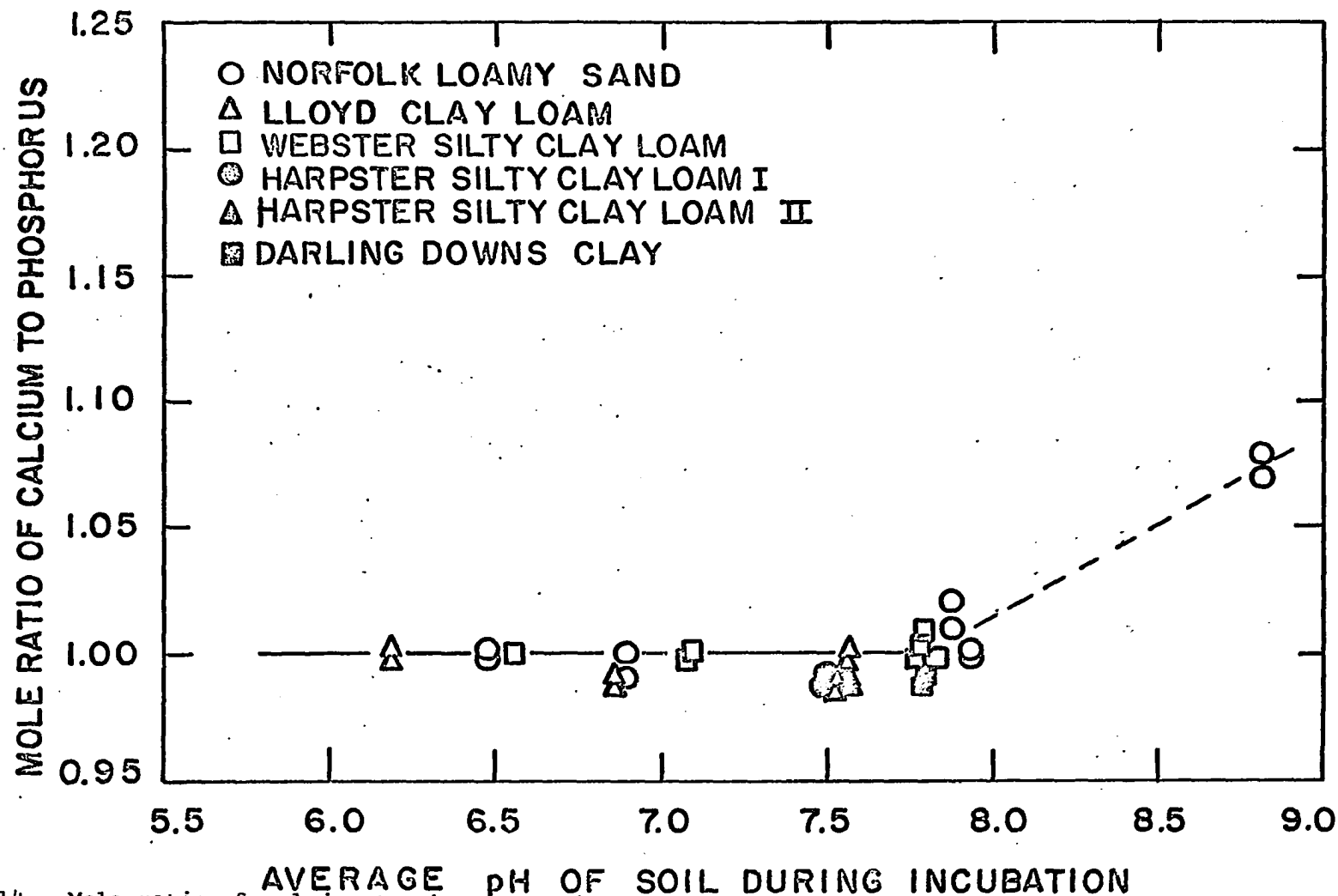


Figure 14. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate at 25°C. in glass-fiber paper envelopes in soils for 4 weeks versus the average pH of the soils during incubation. The points represent analyses on two individual replicates.

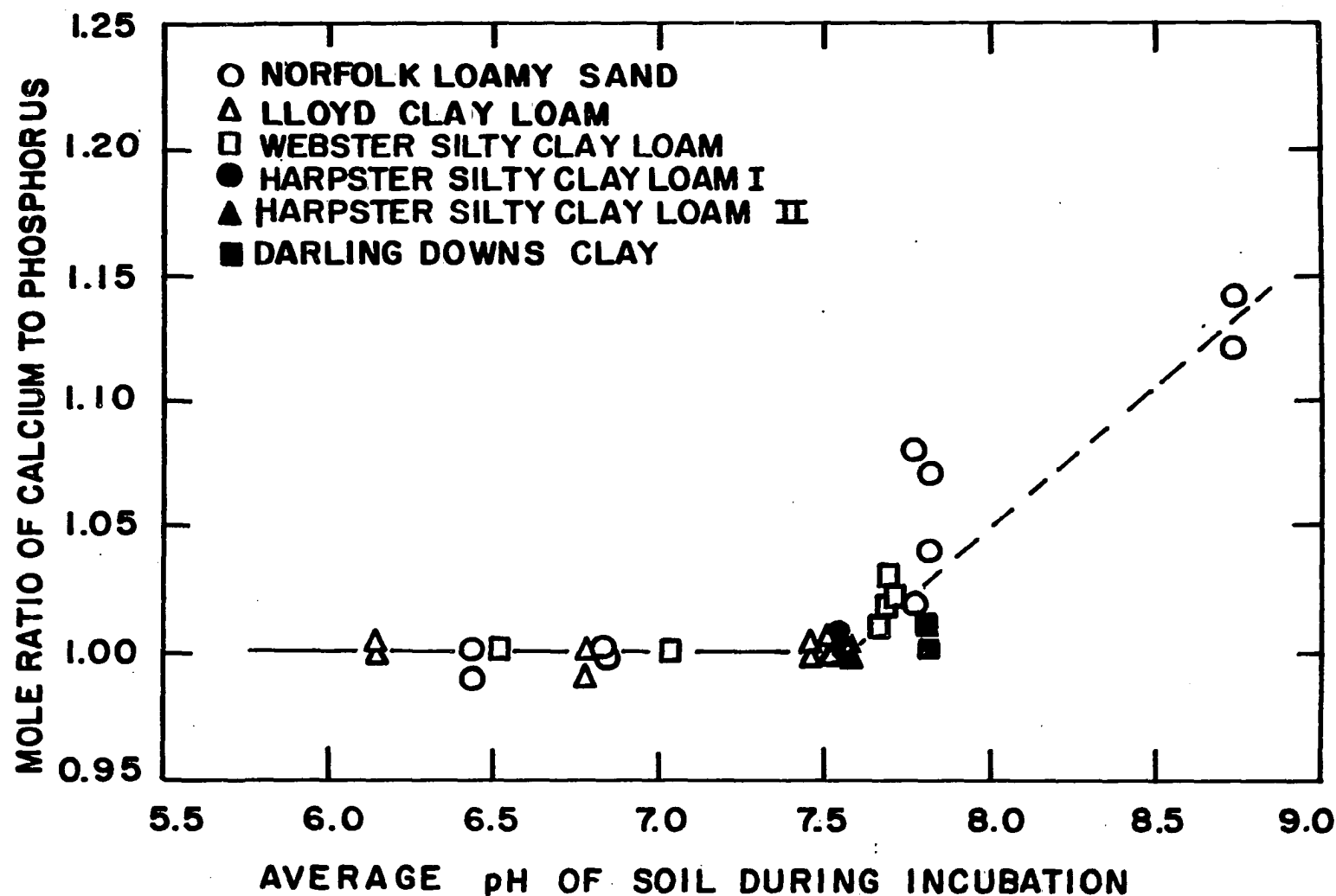


Figure 15. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate at 25°C. in glass-fiber paper envelopes in soils for 16 weeks versus the average pH of the soils during incubation. The points represent analysis on two individual replicates.

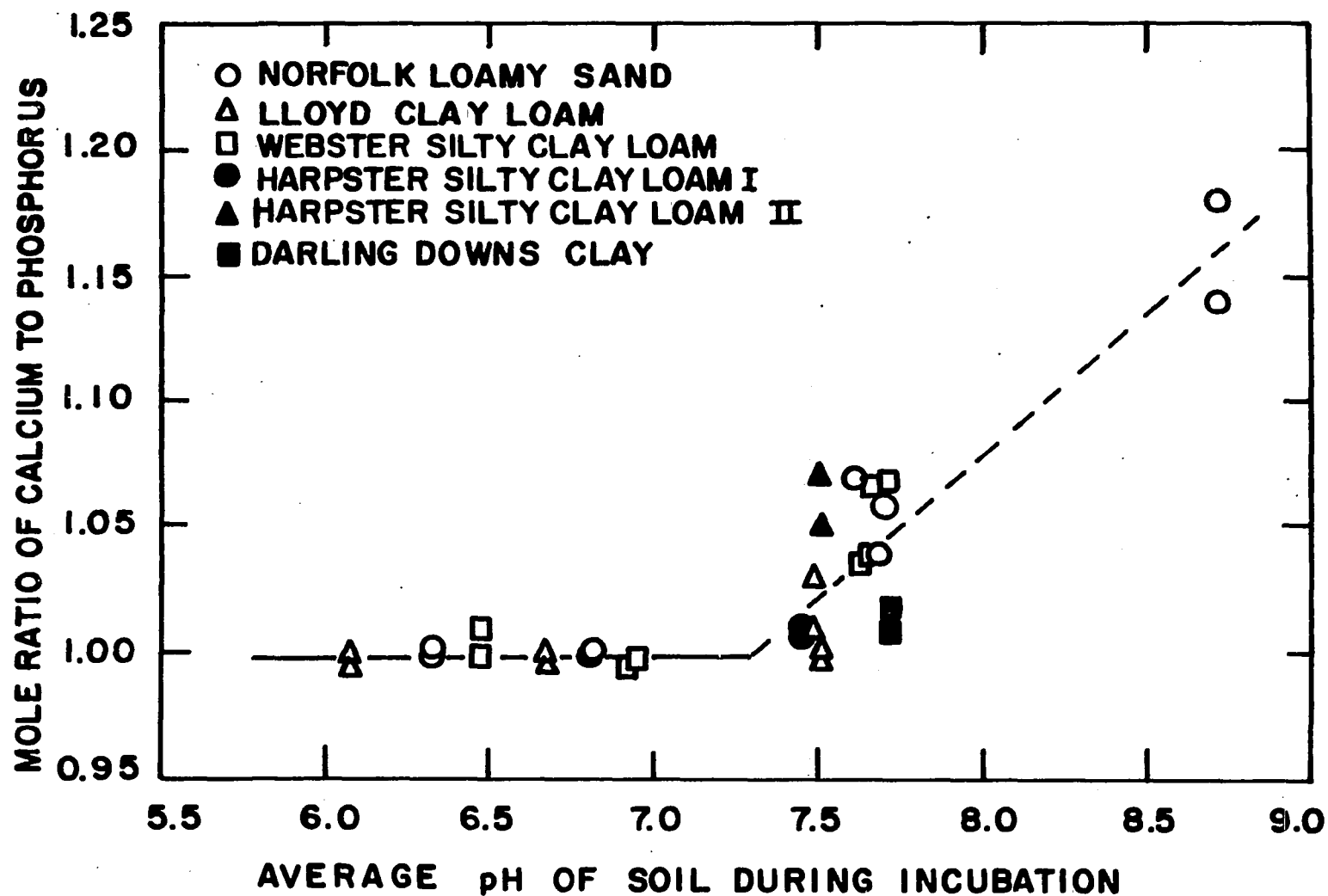


Figure 16. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate at 25°C. in glass-fiber paper envelopes in soils for 44 weeks versus the average pH of the soils during incubation. The points represent analyses on two individual replicates.

mole ratio increased with time, but the rate of increase also decreased with time. Similar trends were observed with the other soils.

If the pH was favorable, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ crystals grew on the surface of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals until, in many instances, the entire surface of the latter crystals was coated with $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. As the exposed surface area of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals decreases, so too should the rate of formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. This surface area effect might explain why the rate of increase in the mole ratio of calcium to phosphorus decreases with time.

Effect of temperature

Webster silty clay loam was the only soil incubated at 35°C . in addition to 25°C . Figures 18, 19, and 20 show the effect of temperature on the mole ratio of calcium to phosphorus in the phosphate residues after incubation for 4, 16, and 44 weeks, respectively. After 4 weeks, the mole ratio in the soil incubated at 35°C . exceeded that in soil incubated at 25°C . at pH values of 7.6 to 7.8 but not at pH values below 7.1. The same effect was observed after 16 weeks, but the difference between the mole ratios at 25°C . and 35°C . at pH values of 7.6 to 7.8 was more marked. After 44 weeks, the calcium to phosphorus ratios at 35°C . exceeded those at 25°C . at pH values greater than 6.8.

Effect of magnesium

The influence of added magnesium on the mole ratio of calcium to phosphorus in the residues remaining after incubation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Norfolk loamy sand for 4, 16, and 44 weeks can be seen in Figure 12. At a given pH,

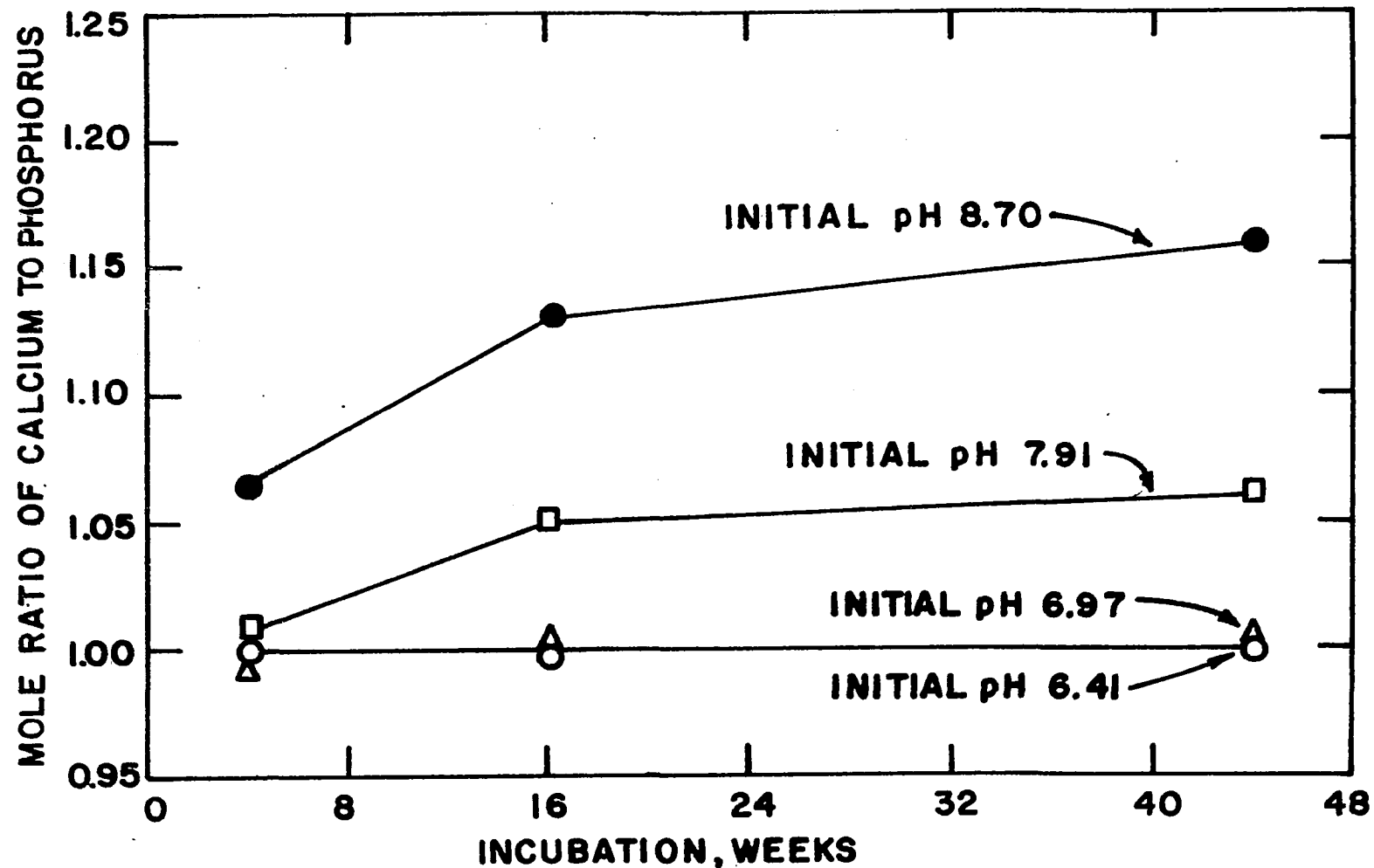


Figure 17. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate at 25°C. in glass-fiber paper envelopes in Norfolk loamy sand versus the time of incubation. Each point represents the average of analyses on two replicates.

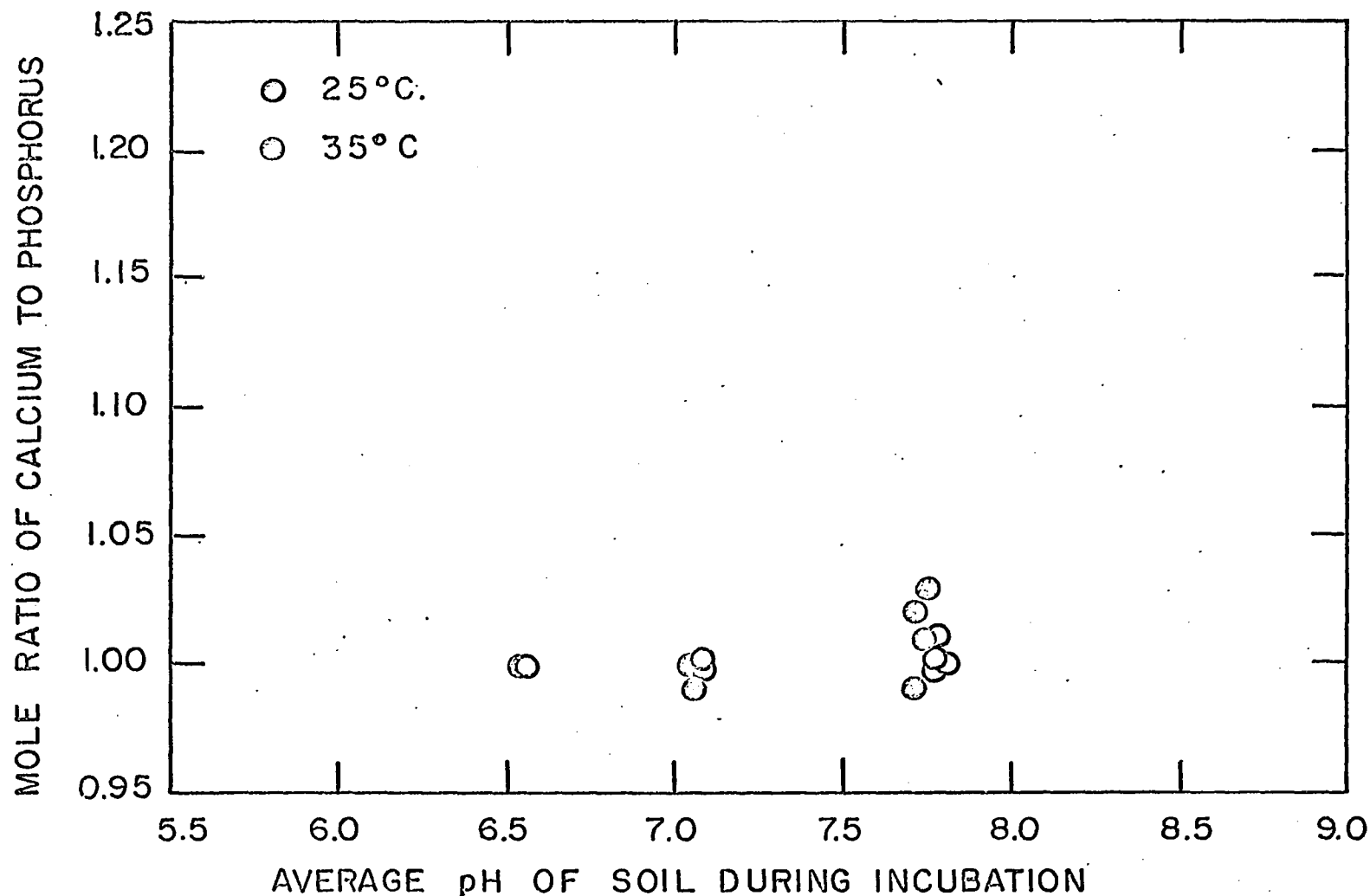


Figure 18. Mole ratio of calcium to phosphorus in residues from the incubation of dibasic calcium phosphate dihydrate in glass-fiber paper envelopes in Webster silty clay loam for 4 weeks at 25°C. and 35°C. versus the average pH of the soil during incubation. The points represent analyses on two individual replicates.

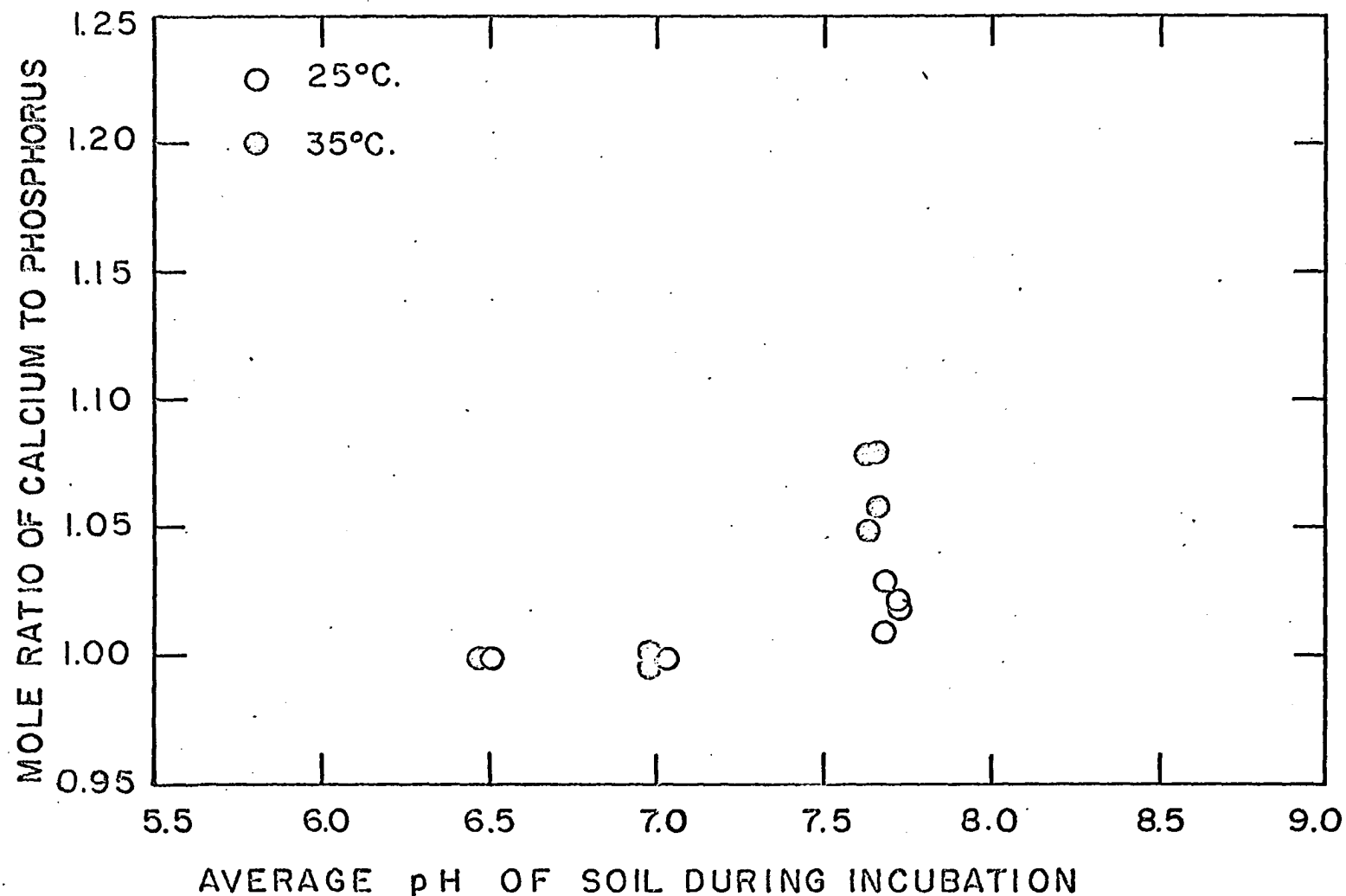


Figure 19. Mole ratio of calcium to phosphorus in residues from the incubation of dibasic calcium phosphate dihydrate in glass-fiber paper envelopes in Webster silty clay loam for 16 weeks at 25°C. and 35°C. versus the average pH of the soil during incubation. The points represent analyses on two individual replicates.

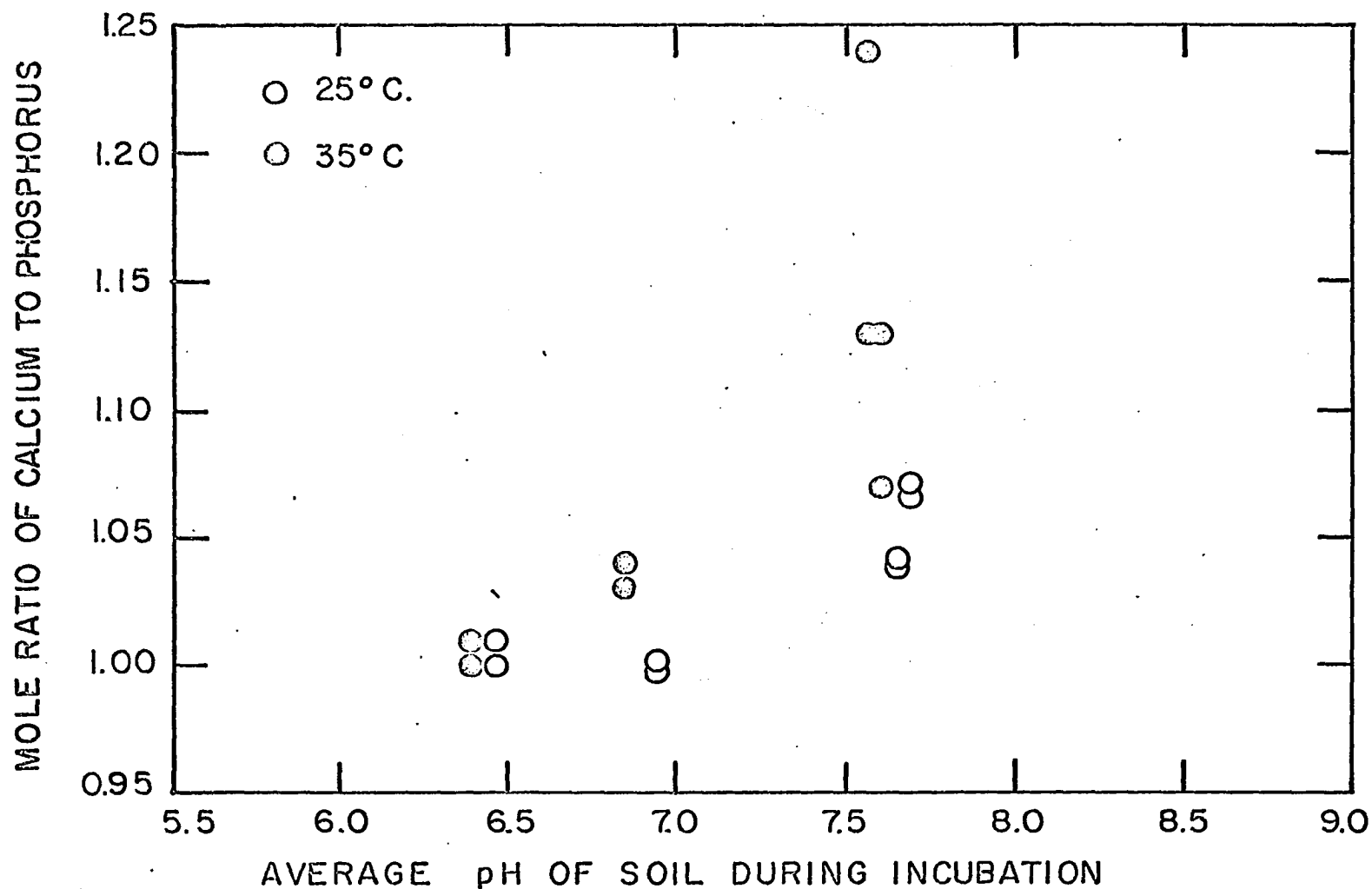


Figure 20. Mole ratio of calcium to phosphorus in residues from the incubation of dibasic calcium phosphate dihydrate in glass-fiber paper envelopes in Webster silty clay loam for 44 weeks at 25°C. and 35°C. versus the average pH of the soil during incubation. The points represent analyses on two individual replicates.

addition of magnesium consistently depressed the ratio of calcium to phosphorus at all periods of incubation, but the effect was most marked at 16 and 44 weeks. Further evidence of the depressive effect of magnesium on the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was obtained by petrographic examination of the residues. At 16 and 44 weeks (Tables 27 and 28, respectively), only traces of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were found in the soil receiving magnesium, whereas moderate amounts of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were identified in the phosphate isolated from the soil of similar pH but without added magnesium.

The effect of magnesium observed in Norfolk loamy sand may also explain the apparent depression in $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ formation in Darling Downs clay. The exchangeable magnesium in this soil is high (Table 3). The soil had a high pH (7.7 to 7.8), and, because of this, significant hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ would have been expected during even a relatively short incubation. After 16 weeks, however, only a trace of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was detected on the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals, and after 44 weeks the extent of the hydrolysis was still slight. These results confirm Rowles' (1958) observation that hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in vitro was inhibited or delayed by magnesium at a concentration of 10^{-3} moles per liter.

Figure 13 shows the influence of added magnesium on the mole ratio of calcium to phosphorus in the residues from the incubation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Webster silty clay loam at 35°C . At a given pH, the added magnesium appears to have had no appreciable effect on the mole ratio. Petrographic analyses at 4, 16, and 44 weeks (Tables 26, 27, and 28, respectively) indicated little, if any reduction in the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in the presence of the added magnesium.

Perhaps the higher temperature of incubation of the Webster soil overcame the inhibiting effect of magnesium on $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ formation. Alternatively, the concentration of magnesium ions in solution in this soil may have been lower than in Norfolk loamy sand or Darling Downs clay. (In both the Norfolk and Webster soils the additions of magnesium were equivalent to the cation exchange capacities.)

Effect of pyrophosphate

The effect of adding $\text{CaH}_2\text{P}_2\text{O}_7$ to Norfolk loamy sand on the composition of phosphates residues from the incubation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in this soil for 4, 16, and 44 weeks can be seen in Figure 12. The $\text{CaH}_2\text{P}_2\text{O}_7$ was added to a soil sample having a pH (7.91) at which $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ would be expected to form. Unfortunately, however, the hydrolysis of the pyrophosphate to orthophosphate caused the pH of the soil to drop to a value at which $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ did not form even in the soil to which $\text{CaH}_2\text{P}_2\text{O}_7$ was not added. Thus the effect of pyrophosphate on the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ could not be investigated in this soil.

When $\text{CaH}_2\text{P}_2\text{O}_7$ was added to Webster silty clay loam (initial pH = 7.71) incubated at 35°C. (Figure 13), the depression in pH was not as marked as in the Norfolk soil due to the greater buffering capacity of the former soil. After 44 weeks, the pyrophosphate addition had little effect, if any, in depressing the mole ratio of calcium to phosphorus in residues isolated from the soil at a pH of approximately 6.8. Petrographic analyses (Table 28) indicated that similar amounts of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ had formed at pH 6.8 irrespective of whether $\text{CaH}_2\text{P}_2\text{O}_7$ had been added to the soil or not. It is possible that the elevated temperature of incubation overcame any inhibit-

ing effect of the pyrophosphate. It is also conceivable that enough hydrolysis of the pyrophosphate occurred at the higher temperature (35°C.) to permit the transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to proceed.

These results do not confirm Larsen and Widdowson's (1966) observation that pyrophosphate inhibits formation of calcium orthophosphates; however, they cannot be said to contradict the observation. As mentioned previously, some of the conditions encountered in this work were unsuitable for testing the effect, and perhaps the others were as well. No examination of the soil was made to determine how long the pyrophosphate persisted.

Effect of fluoride

The effect of added fluoride on the mole ratio of calcium to phosphorus in the residues remaining after the incubation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in Norfolk loamy sand may be seen in Figure 21. With one exception, the ratios of calcium to phosphorus found in residues isolated from the soil samples containing added fluoride were equal to or greater than the corresponding ratios in the residues isolated from the control samples.

In the sample of Norfolk loamy sand containing added fluoride and adjusted to a pH of about 6.4, the ratios of calcium to phosphorus of the incubated phosphate after 44 weeks in replicate columns were 1.02 and 1.03 (Table 28). These values are considered significantly different from 1.00. Nevertheless, no $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was detected in these samples; furthermore, the formation of this compound at 25°C. was not detected in any of the soils used in this investigation below a pH value of about 7.4. Thus the observed increase in the mole ratios above the value characteristic for $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (1.00) may have been due to the formation of $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$. At the higher pH

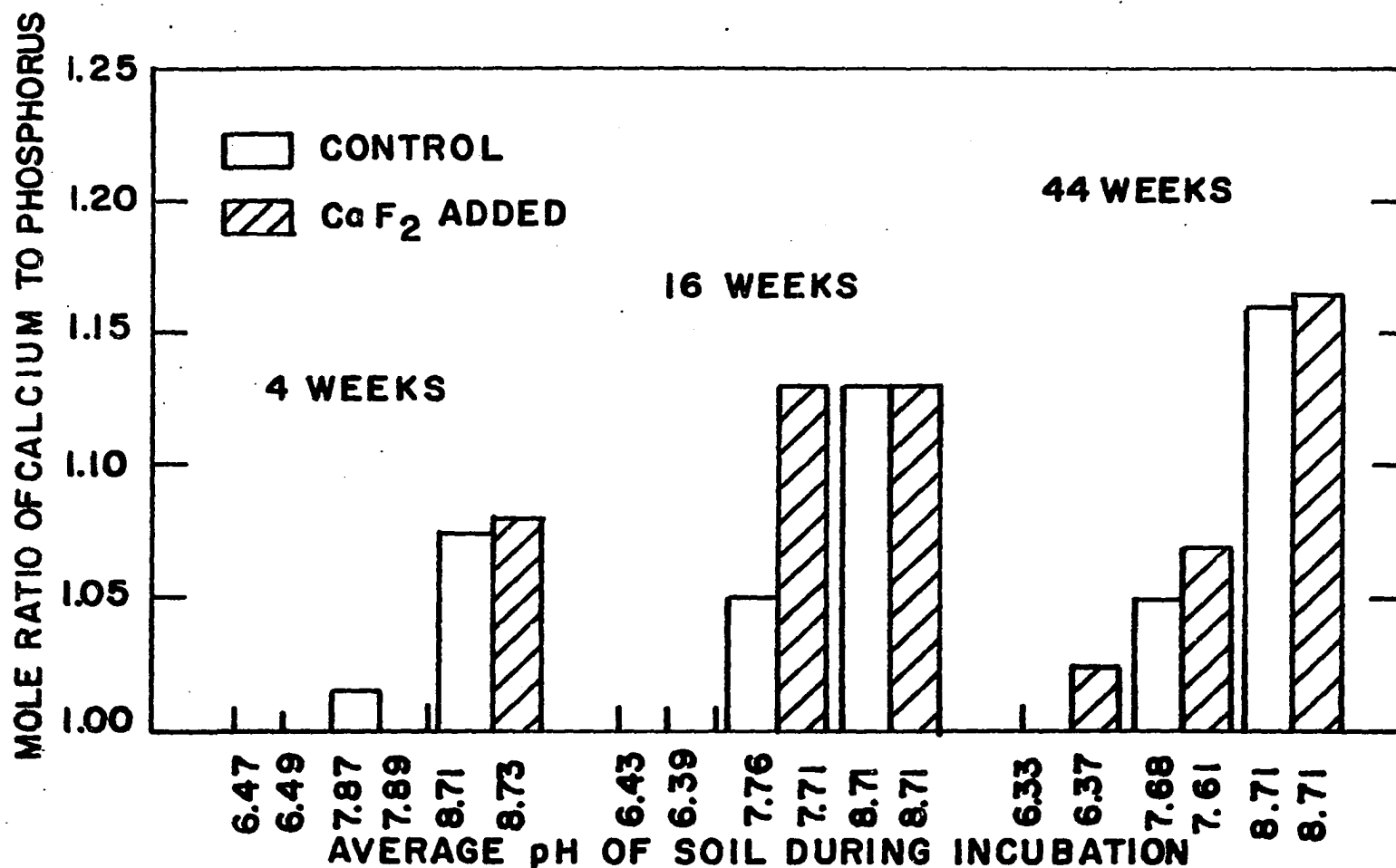


Figure 21. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate in Norfolk loamy sand at different pH values with and without added calcium fluoride for 4, 16, and 44 weeks at 25°C. The pH data are averages of initial and final values, and the histogram bars represent the average of analyses on two replicates.

values, $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ could have formed in addition to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$.

The effect of added fluoride on the mole ratio of calcium to phosphorus in $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ residues recovered from Webster silty clay loam incubated at 25°C. and 35°C. may be seen in Figures 22 and 23, respectively. At 35°C. the effect of fluoride appears to be more consistent than at 25°C. The calcium-to-phosphorus ratios of the phosphate incubated at 35°C. in soil containing added fluoride were equal to or greater than ratios of the phosphate incubated in the control soils at both pH levels after 4, 16, and 44 weeks. It is significant that only a trace of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was found in the phosphate incubated at 35°C. for 44 weeks in the soil samples with and without added fluoride at a pH of about 6.4. The mole ratio of phosphate incubated in the soil containing fluoride was much higher than one would expect if only a trace of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ had formed. It is conceivable, therefore, that the formation of $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ occurred at the lower pH and probably at the higher pH as well.

In vitro, $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ has been found to form by reaction of fluoride with either $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Kurmies, 1953) or $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ (Brown et al., 1962). Both reactions could have occurred in this investigation. There is evidence in the results obtained with Norfolk loamy sand at a pH of 6.4 that the transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ occurred without the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ as an intermediate compound. At higher pH values, $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ may have been formed by reaction of fluoride with either $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ or $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, but no definite conclusion could be made. It is of interest to note, however, that prepared $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ added to the same soils as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ did not appear to react with added fluoride to form $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ (succeeding section).

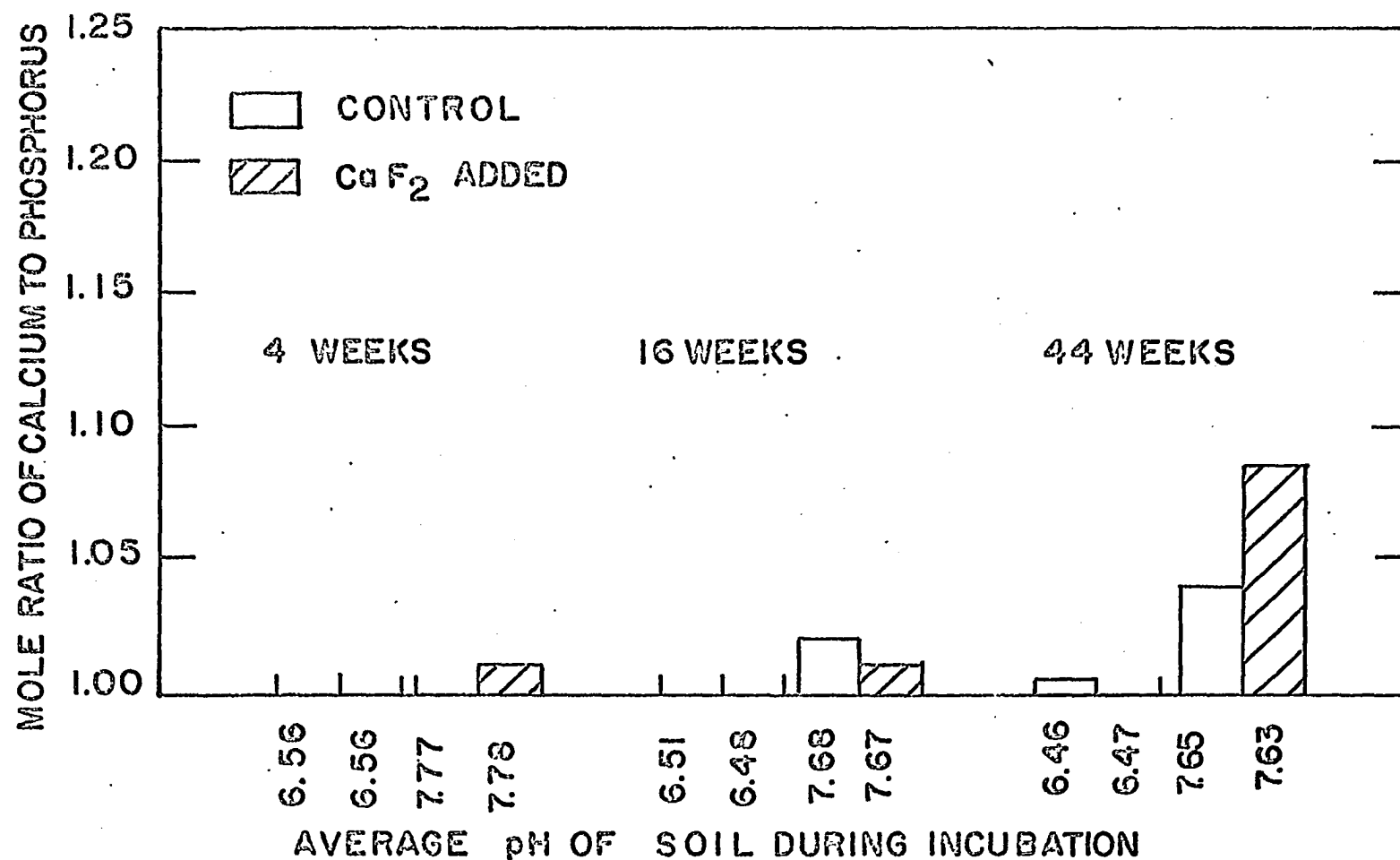


Figure 22. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate in Webster silty clay loam at different pH values with and without added calcium fluoride for 4, 16, and 44 weeks at 25°C. The pH data are averages of initial and final values, and the histogram bars represent the average of analyses on two replicates.

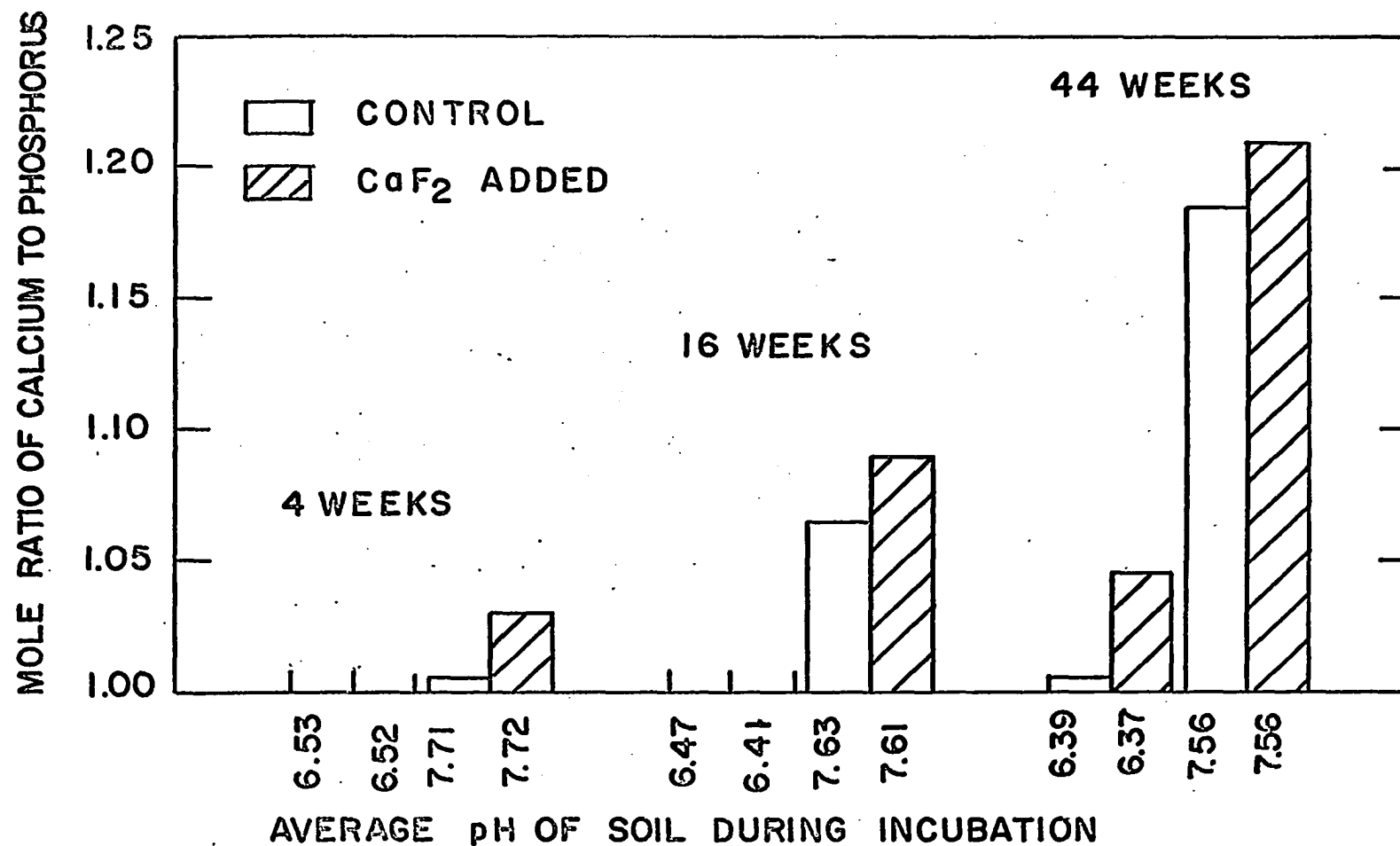


Figure 23. Mole ratio of calcium to phosphorus in residues from incubation of dibasic calcium phosphate dihydrate in Webster silty clay loam at different pH values with and without added calcium fluoride for 4, 16, and 44 weeks at 35°C. The pH data are averages of initial and final values, and the histogram bars represent the average of analyses on two replicates.

Transformations of Octacalcium Phosphate

Petrographic and X-ray diffraction analyses of the residues from $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ incubated in glass-fiber paper envelopes in soils and in direct contact with the soils for 4, 16, and 44 weeks failed to reveal the presence of a phosphate more basic than $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. It was not possible, therefore, to obtain a critical check on the validity of using the analysis of phosphate in envelopes as a substitute for the analysis of the phosphate in direct contact with soil. In the preceding section on the transformations of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, the use of the envelopes to eliminate contamination of the phosphate with soil was found to be a valid technique in that the nature and extent of the transformations were similar in $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in envelopes or in direct contact with the soil. There is no reason, therefore, to believe this technique is invalid in the case of the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ additions, and so the analysis of the phosphate in the envelopes will be used in this section as an indication of the transformations of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in direct contact with soil. The mole ratios of calcium to phosphorus in the phosphate will be used for the same reasons given previously in the section on the transformations of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

Before discussing the possible transformations of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in soils, it is necessary to consider the composition of the salt prepared for incubation in soil. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ is very difficult to prepare with the theoretical proportions of calcium and phosphorus (Bjerrum, 1958). Moreover, because of the peculiarities of the structure of this compound, the degree of hydration depends on the method of drying (Brown, 1962). The salt prepared for use in this investigation did not have the theoretic-

cal composition but it did not depart far from the theoretical values. The theoretical calcium and phosphorus contents of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ are 32.6% and 18.9%, respectively. The mole ratio of calcium to phosphorus is 1.33. Analysis of the prepared material yielded 32.0% calcium and 18.8% phosphorus, giving a ratio of 1.31 moles of calcium to 1 of phosphorus. The small depression in the mole ratio of the preparation from the theoretical value of 1.33 is apparently due to a low calcium content because the phosphorus content was close to the theoretical value of 18.9%. A trace of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was observed petrographically in the prepared $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, but the amount was too small to account for the difference between the theoretical and observed mole ratio of calcium to phosphorus (approximately 7% of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ would have to be present to account for this difference). It is apparent, therefore, that the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ prepared in this investigation was slightly deficient in calcium.

The calcium and phosphorus contents of the residues remaining after incubation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in envelopes in soils for 4, 16, and 44 weeks are shown in Table 34 (Appendix), and the corresponding mole ratios of calcium to phosphorus are shown in Table 30.

Effect of pH and time

The relationship between the mole ratio of calcium to phosphorus in residues from the incubation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in samples of Norfolk loamy sand and the pH of the soil is shown in Figure 24. After 4 weeks, the ratio was essentially unchanged from that of the prepared $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ (1.31) in the soil with a pH value of 6.47, whereas at all higher pH values (with the exception of pH 8.7) the ratio was very close to the theoretical value

Table 30. Mole ratios of calcium to phosphorus in residues from incubation of octacalcium phosphate in glass-fiber envelopes in soil at different pH values and with various treatments for 4, 16, and 44 weeks

Soil treat- ment	Repli- cate	4 weeks		16 weeks		44 weeks	
		Av. pH of soil during incubation	Mole ratio of calcium to phosphorus	Av. pH of soil during incubation	Mole ratio of calcium to phosphorus	Av. pH of soil during incubation	Mole ratio of calcium to phosphorus
Norfolk loamy sand (25°C.)							
CaH ₂ P ₂ O ₇	1	6.69	1.31	5.79	1.31	5.62	1.31
	2		1.31		1.32		1.29
-	1	6.47	1.31	6.43	1.33	6.33	1.34
	2		1.32		1.34		1.34
CaF ₂	1	6.49	1.33	6.39	1.34	6.37	1.37
	2		1.33		1.34		1.34
-	1	6.89	1.33	6.83	1.34	6.81	1.34
	2		1.34		1.34		1.34
-	1	7.87	1.34	7.76	1.35	7.68	1.34
	2		1.33		1.35		1.34
CaF ₂	1	7.89	1.35	7.71	1.34	7.61	1.34
	2		1.35		1.34		-
MgCl ₂	1	7.85	1.34	7.77	1.34	7.65	1.33
	2		--		1.34		1.34
CaCO ₃	1	7.93	1.33	7.81	1.34	7.61	1.32
	2		1.34		1.34		1.34
-	1	8.71	1.31	8.71	1.30	8.71	1.30
	2		1.31		1.33		1.30
CaF ₂	1	8.73	1.32	8.71	1.31	8.71	1.31
	2		1.31		1.32		1.32
Lloyd clay loam (25°C.)							
-	1	6.19	1.31	6.15	1.34	6.09	1.32
	2		1.33		1.34		1.32
-	1	6.87	1.34	6.78	1.34	6.67	1.33
	2		1.32		1.34		1.34
-	1	7.53	1.34	7.49	1.34	7.48	1.33
	2		1.34		1.34		1.31
CaCO ₃	1	7.57	1.34	7.51	1.34	7.51	1.32
	2		1.34		1.34		1.34

Table 30. (Continued)

Soil treat- ment	Repli- cate	4 weeks		16 weeks		44 weeks	
		Av. pH of soil during incubation	Mole ratio of calcium to phosphorus	Av. pH of soil during incubation	Mole ratio of calcium to phosphorus	Av. pH of soil during incubation	Mole ratio of calcium to phosphorus
Webster silty clay loam (25°C.)							
-	1	6.56	1.32	6.51	1.34	6.46	1.34
	2		-		-		1.33
CaF ₂	1	6.56	1.34	6.48	1.35	6.47	1.36
	2		1.33		1.34		1.36
-	1	7.08	1.34	7.03	1.34	6.94	1.34
	2		1.34		1.34		1.34
-	1	7.77	1.37	7.68	1.37	7.65	1.37
	2		1.36		1.37		1.38
CaF ₂	1	7.78	1.36	7.67	1.37	7.63	1.38
	2		1.36		1.36		1.38
CaCO ₃	1	7.79	1.38	7.71	1.34	7.69	1.40
	2		1.34		1.37		1.37
Webster silty clay loam (35°C.)							
-	1	6.53	1.31	6.47	1.35	6.39	1.33
	2		-		-		1.35
CaF ₂	1	6.52	1.34	6.41	1.36	6.37	1.36
	2		1.34		1.36		1.35
-	1	7.06	1.35	6.98	1.36	6.84	1.34
	2		1.35		1.34		1.35
CaH ₂ P ₂ O ₇	1	7.35	1.33	6.97	1.34	6.81	1.34
	2		1.32		1.34		1.36
MgCl ₂	1	7.63	1.35	7.54	1.37	7.51	1.36
	2		1.34		1.35		1.37
-	1	7.71	1.37	7.63	1.37	7.56	1.40
	2		1.38		1.37		1.39
CaF ₂	1	7.72	1.36	7.61	1.37	7.56	1.40
	2		1.36		1.40		1.41
CaCO ₃	1	7.75	1.37	7.65	1.41	7.60	1.40
	2		1.34		1.38		1.38

Table 30. (Continued)

Soil treat- ment	Repli- cate	Av. pH of soil during incubation	Mole ratio of calcium to phosphorus	Av. pH of soil during incubation	Mole ratio of calcium to phosphorus	Av. pH of soil during incubation	Mole ratio of calcium to phosphorus
<u>Harpster silty clay loam I (25°C.)</u>							
-	1	7.49	1.33	7.47	1.34	7.46	1.35
	2		-		1.34		1.34
<u>Harpster silty clay loam II (25°C.)</u>							
-	1	7.51	1.34	7.49	1.35	7.50	1.34
	2		-		1.33		-
<u>Darling Downs clay (25°C.)</u>							
-	1	7.80	1.34	7.72	1.35	7.71	1.36
	2		1.35		1.34		1.36

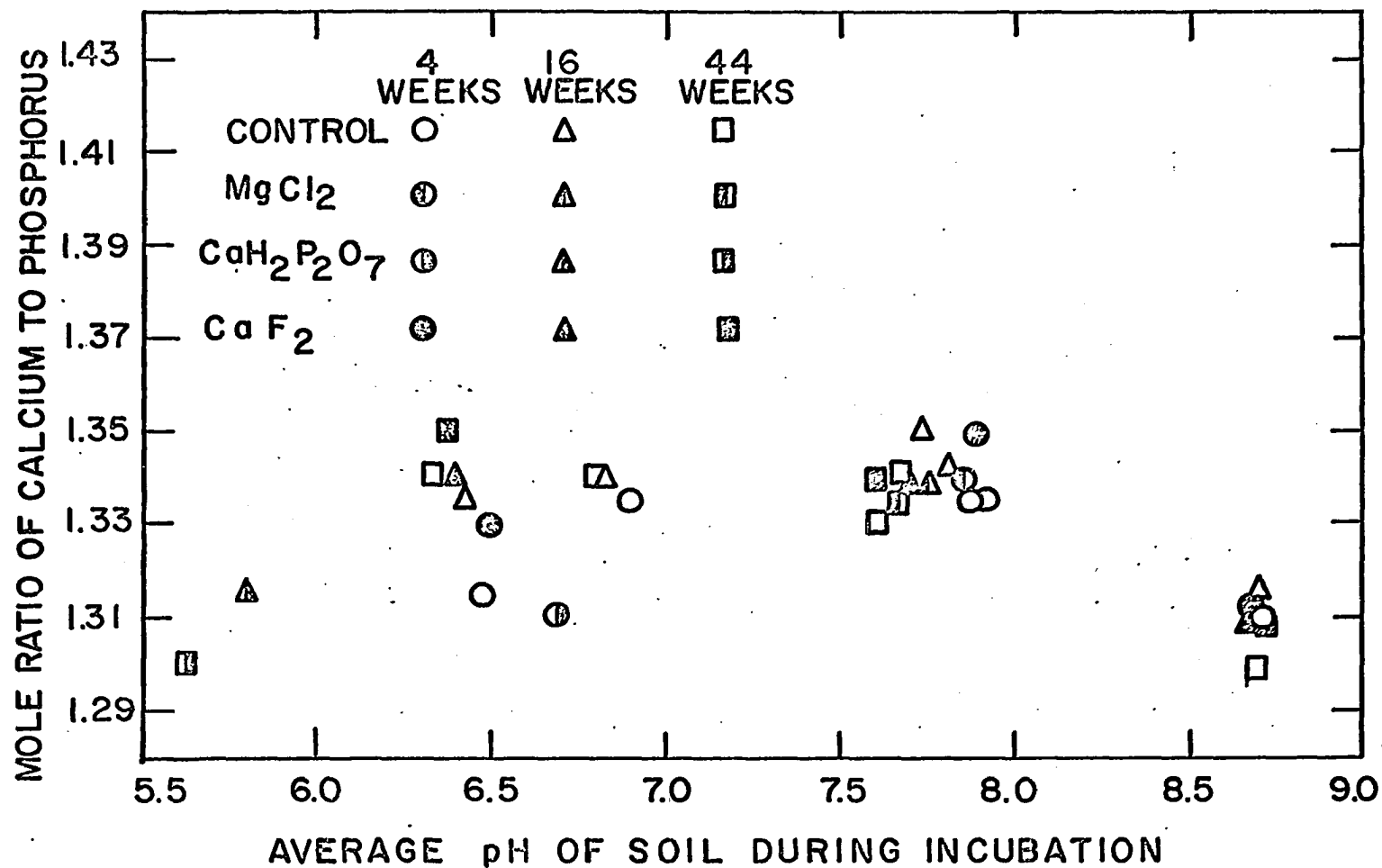


Figure 24. Mole ratio of calcium to phosphorus in residues from incubation of octacalcium phosphate at 25°C. for 4, 16, and 44 weeks in glass-fiber paper envelopes in Norfolk loamy sand to which various substances were added versus the average pH of the soil during incubation. The points represent the average of analyses on two replicates.

for this compound (1.33). After 16 and 44 weeks, the ratios were unchanged from those at 4 weeks except for the soil sample at pH 6.3 to 6.5 in which the ratio had increased to approximately 1.34. The phosphate from the soil samples with a pH value of 8.7 had calcium-to-phosphorus ratios equivalent to the prepared $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ (1.31) irrespective of the incubation period.

The increase in the mole ratio of calcium to phosphorus from 1.31 to a value of 1.33 to 1.34 at most pH values could indicate that transformation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ was occurring. (As shown in Table 29, the theoretical mole ratio of calcium to phosphorus in $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ is 1.67.) All other evidence, however, is against this possibility. The hydrolysis of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ is pH-dependent, and the extent of the hydrolysis should increase with increasing pH. At pH 8.7, however, essentially no change in the mole ratio was observed, even after 44 weeks. Consideration should also be given to the fact that there was little difference between the mole ratios at 4, 16, or 44 weeks. If the conditions were suitable for $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ formation, one would expect the amount to increase with time, resulting in a parallel increase in the calcium-to-phosphorus ratio. Finally, direct tests for $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ gave negative results. X-ray diffraction provided no evidence for the presence of crystalline species other than $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. Petrographic examination of the residues showed only $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ with a slight trace of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in many instances. A trace of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was present as an impurity in the starting material, and presumably some of this remained at the end.

It is apparent that there must be some other reason for the slight increase in the mole ratio of calcium to phosphorus noted at all pH values

except 8.7. The $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ used in this investigation was prepared by the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in a sodium acetate buffer solution. Analysis of the prepared $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ indicated a slight deficiency of calcium which was still evident in the phosphate after incubation in the soil adjusted to pH 8.7 with Na_2CO_3 . It seems reasonable to infer, therefore, that the slightly calcium-deficient salt added took up enough calcium from the soil solution to satisfy the theoretical ratio of calcium to phosphorus except where Na_2CO_3 was added. The Na_2CO_3 would produce a low concentration of calcium in the soil solution, and this might account for the persistent calcium deficiency observed in the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ at pH 8.7.

The analyses of phosphate residues isolated from samples of Lloyd clay loam after 4, 16, and 44 weeks (Table 30) showed little or no trend in the calcium-to-phosphorus ratio with pH or time. As in the case of Norfolk loamy sand, the incubated phosphate quickly attained mole ratios close to the theoretical value of 1.33 for $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. Petrographic and X-ray diffraction analyses showed no new phosphate phases.

Figure 25 illustrates the relationship between the mole ratio of calcium to phosphorus and soil pH for Webster silty clay loam incubated 4, 16, and 44 weeks at 25°C. The trends in the mole ratio were the same as those discussed previously for Norfolk loamy sand with the exception of the treatments in which the soil pH was above 7.5. The calcium-to-phosphorus ratios of the phosphate from these latter treatments were significantly higher than those found in phosphate isolated from soil samples with pH values less than 7.5. Petrographic analysis of the phosphate from the soils with pH values greater than 7.5 showed that a new crystalline phase was present. This

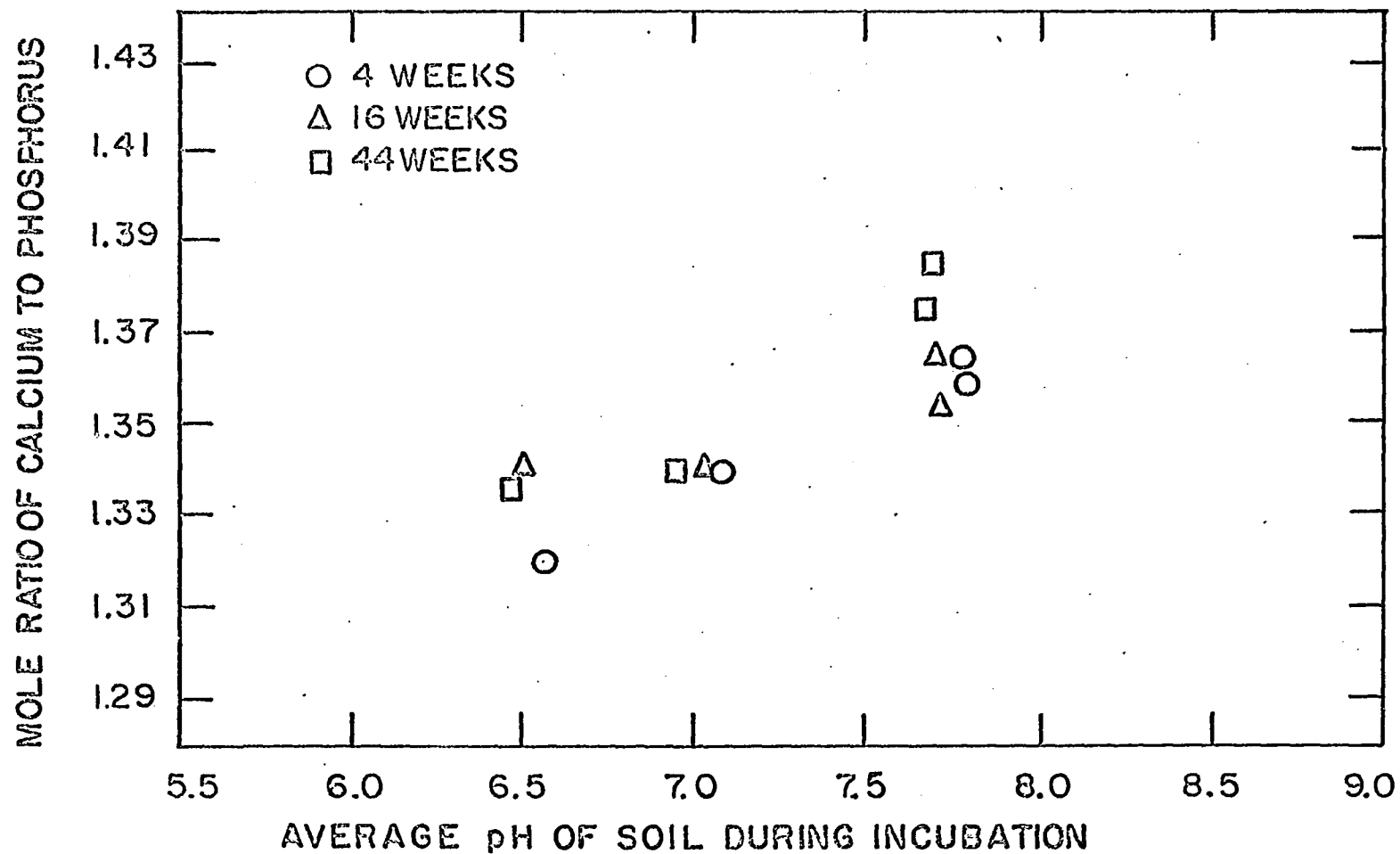


Figure 25. Mole ratio of calcium to phosphorus in residues from incubation of octacalcium phosphate in glass-fiber paper envelopes in Webster silty clay loam at 25°C. for 4, 16, and 44 weeks versus the average pH of the soil during incubation. Each point represents the average of analyses on two replicates.

phase was difficult to detect amid the clusters of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ crystals (Figure 26). It occurred as relatively large platy crystals, the refractive index of which varied from less than 1.50 to greater than 1.60. When viewed under crossed nicols, these crystals exhibited a wide range of interference colors (Figure 26), which indicated that they possessed two or more refractive indexes that were rather different. $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ has two refractive indexes that are very nearly equal in magnitude ($\omega = 1.647$ and $\epsilon = 1.640$), and thus the compound does not exhibit a great range in interference colors when viewed under crossed nicols. The optical properties of the new phase appeared to fit those of CaCO_3 ($\omega = 1.654$ and $\epsilon = 1.487$). A positive qualitative test for carbonate was obtained by locating crystals of the new phase in a microscope field and observing the production of gas when dilute hydrochloric acid was added at the side of the cover slip and allowed to move into the field. The presence of CaCO_3 would explain the high ratios of calcium to phosphorus in the phosphate isolated from the soil samples with pH values greater than 7.5.

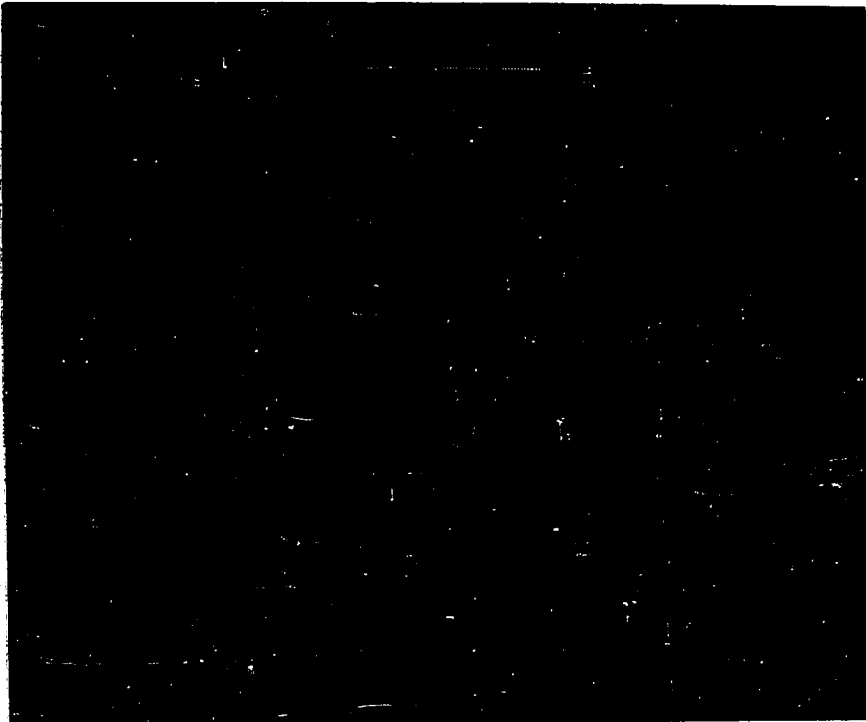
When Webster silty clay loam was incubated at 35°C . (Figure 27), the new crystalline phase identified as CaCO_3 was found in the residues of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ incubated in the soil samples with pH values greater than 7.5. The formation of this phase was reflected in the increase in mole ratios of calcium to phosphorus. At pH values below 7.5, the trend in the mole ratio was the same as that described previously for the Norfolk soil except that the ratio tended to attain a slightly higher ratio of 1.34 to 1.35.

The relationships between the mole ratios of calcium to phosphorus in residues from incubation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ at 25°C . and the pH of all the

Figure 26. Photomicrographs of the residue from incubation of octacalcium phosphate at 25°C. in a glass-fiber envelope in Webster silty clay loam (pH 7.7) for 44 weeks (X430). A. Needlelike octacalcium phosphate crystals with two large crystals of calcium carbonate barely visible as dark bodies near the center. The calcium carbonate formed during incubation. B. As in A except that the photograph was taken with polarized light (crossed nicols). The thin octacalcium phosphate crystals with their low birefringence fail to show, whereas the crystals of calcium carbonate, which are much thicker and have high birefringence (indicated by the interference colors), are easily seen.



A.



B.

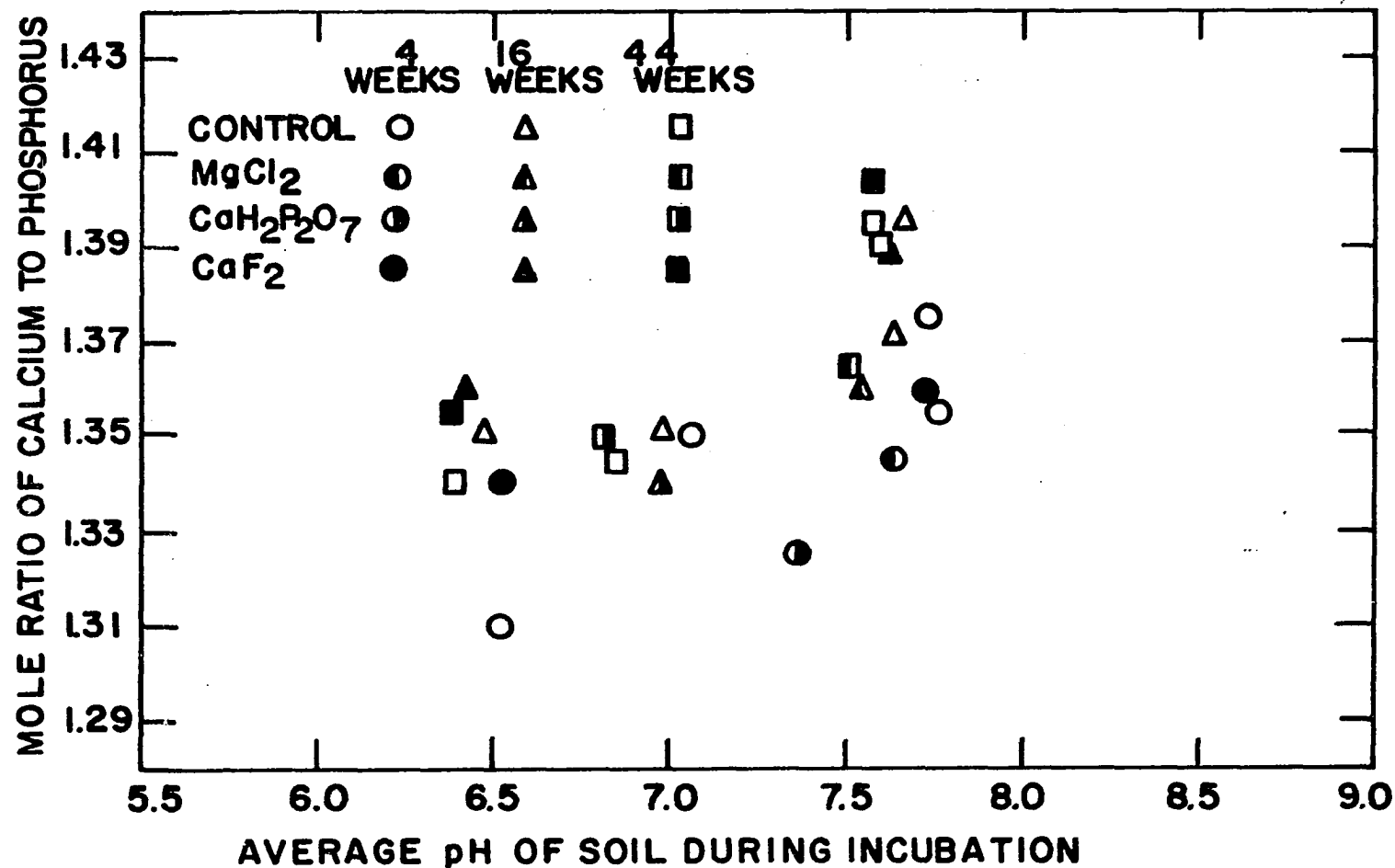


Figure 27. Mole ratio of calcium to phosphorus in residues from incubation of octacalcium phosphate at 35°C. for 4, 16, and 44 weeks in glass-fiber paper envelopes in Webster silty clay loam to which various substances were added versus the average pH of the soil during incubation. Each point represents the average of analyses on two replicates.

soils at 4, 16, and 44 weeks are shown in Figures 28, 29, and 30, respectively. Except for the anomalies in Webster silty clay loam above a pH value of 7.5 and in Norfolk loamy sand at pH 8.7, the relationship between the mole ratios of calcium to phosphorus and the pH is similar for all soils at 4, 16, and 44 weeks. After the calcium-deficient $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ took up sufficient calcium to produce a mole ratio of calcium to phosphorus approximating the theoretical ratio, the ratio stayed constant with increasing soil pH and period of incubation, indicating that little or no transformation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to more basic phosphates was occurring.

Effect of temperature

Webster silty clay loam was the only soil subjected to an incubation temperature of 35°C. as well as 25°C. There appeared to be little, if any, effect of temperature on the calcium-to-phosphorus ratios at a given pH after 4, 16, or 44 weeks (Table 30).

Effect of magnesium

In the sample of Norfolk loamy sand containing added magnesium, the ratio of calcium to phosphorus was essentially the same at 4, 16, and 44 weeks as that in the corresponding sample which had not received additions of magnesium (Figure 24). This result is to be expected because there was no evidence of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ formation in the soil at any pH value, even after 44 weeks.

In the work on Webster silty clay loam, magnesium was added only to the sample incubated at 35°C. (Figure 27). The added magnesium appears to have depressed the mole ratio of calcium to phosphorus at each period of

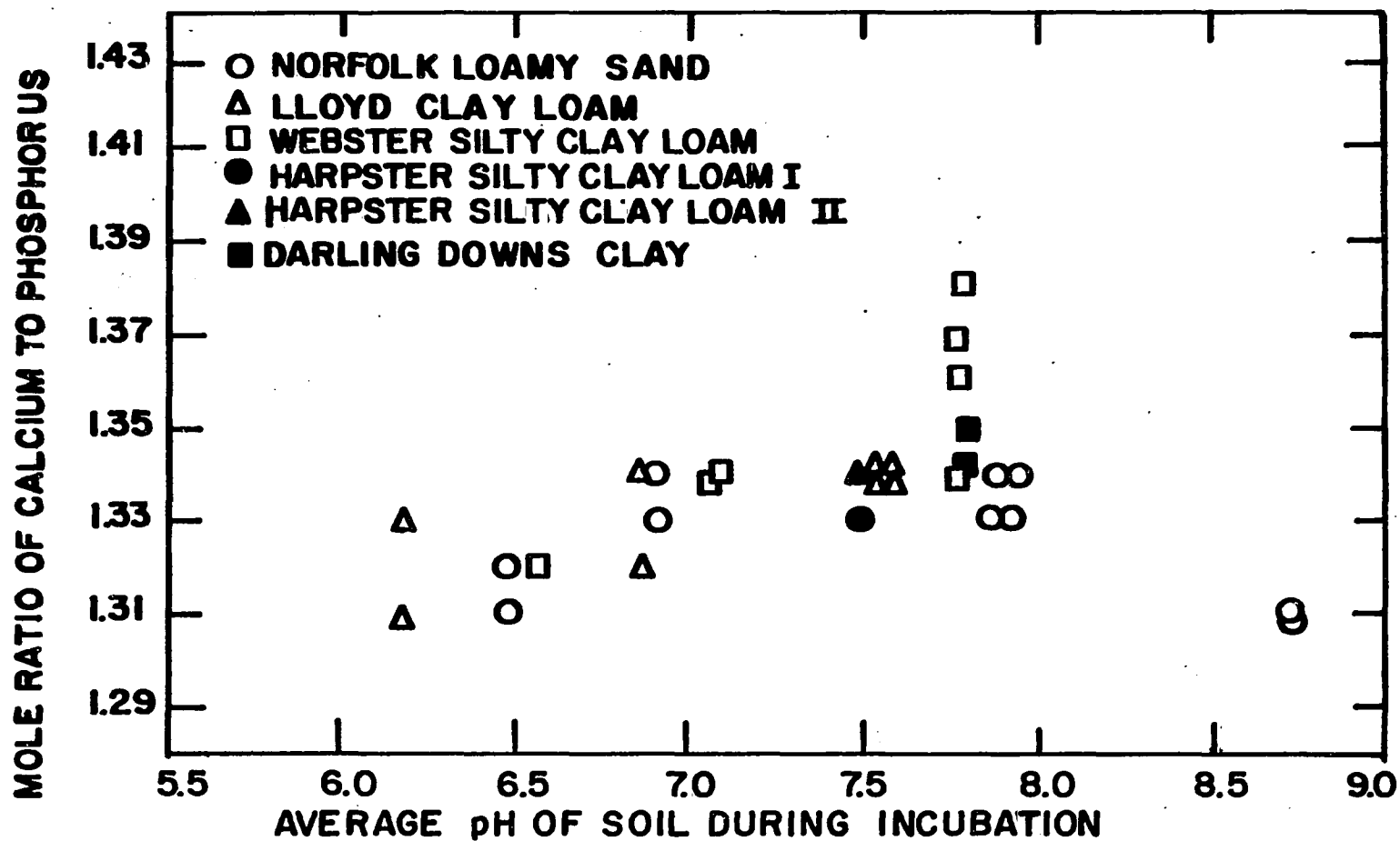


Figure 28. Mole ratio of calcium to phosphorus in residues from incubation of octacalcium phosphate in glass-fiber paper envelopes in soils at 25°C. for 4 weeks versus the average pH of the soils during incubation. The points represent analyses on two individual replicates.

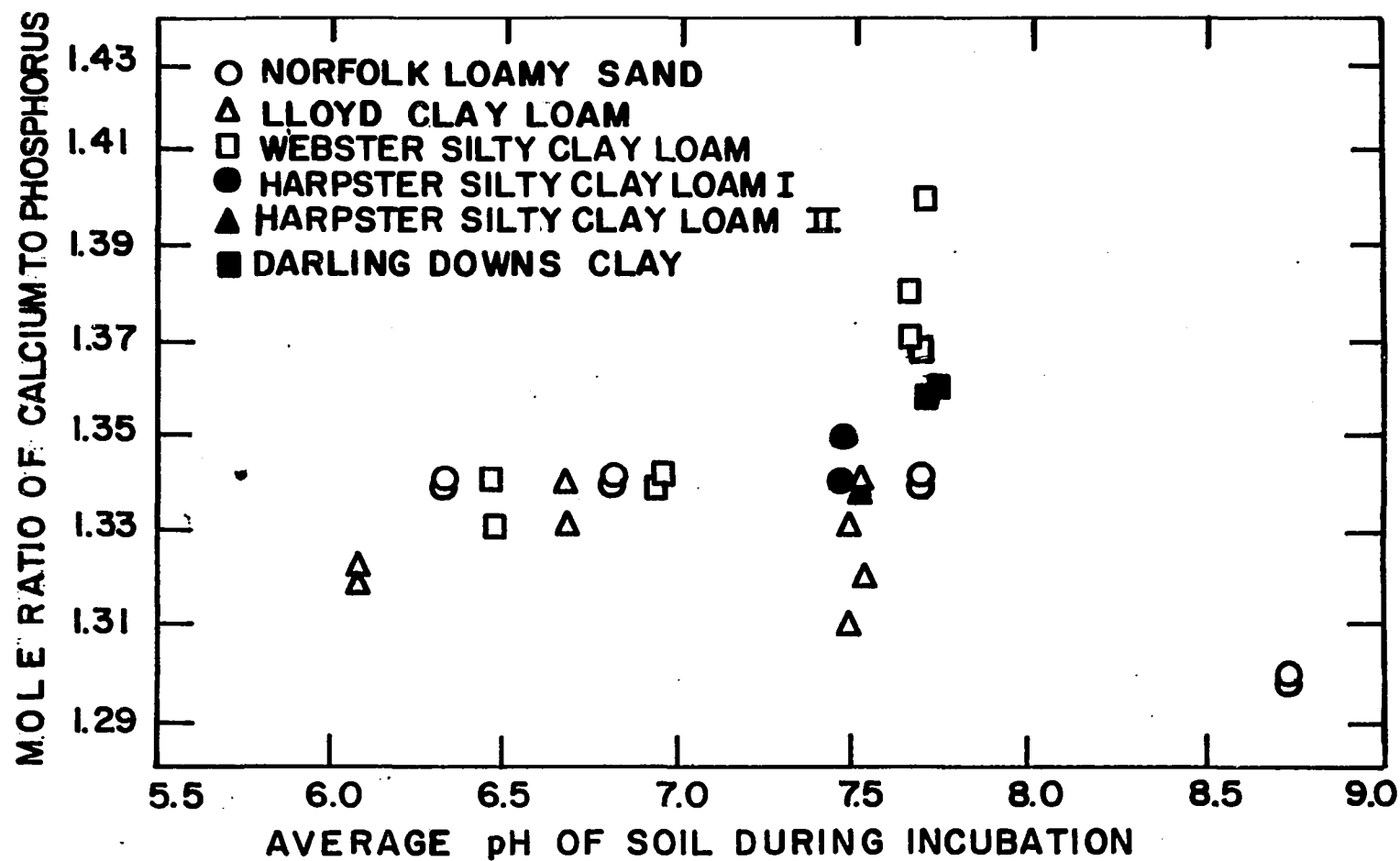


Figure 30. Mole ratio of calcium to phosphorus in residues from incubation of octacalcium phosphate in glass-fiber paper envelopes in soils at 25°C. for 44 weeks versus the average pH of the soils during incubation. The points represent analyses made on two individual replicates.

incubation. This effect may be attributed to the observed reduction in the formation of CaCO_3 as a new crystalline phase in the phosphate residues. The reduction could have been due to the lower pH produced in the soil samples containing added magnesium. It is also conceivable that the added magnesium directly affected the CaCO_3 formation in some manner.

No definite evidence for hydrolysis of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ was found in this work with soils. Consequently, the effect of magnesium in inhibiting the hydrolysis, observed by Brown et al. (1962) to take place in vitro, could not be checked.

Effect of pyrophosphate

The formation of calcium orthophosphates is known to be inhibited by pyrophosphate (Larsen and Widdowson, 1966). Pyrophosphate in the form of $\text{CaH}_2\text{P}_2\text{O}_7$ was added to a sample of Norfolk loamy sand (pH 7.91) and to a sample of Webster silty clay loam (pH 7.71) to see what effect it would have on the hydrolysis of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ in soil. Unfortunately, this specific effect could not be detected because no hydrolysis of the phosphate was observed in these or any other soils.

In Norfolk loamy sand, the pyrophosphate hydrolyzed and caused a marked drop in pH (Figure 24). The mole ratio of calcium to phosphorus of the phosphate incubated for 4, 16, and 44 weeks exhibited very little change from the ratio of the prepared $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. It is possible that the acid conditions, particularly at 16 and 44 weeks, were not favorable for the uptake of calcium by the calcium-deficient $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to produce the theoretical mole ratio of calcium to phosphorus of 1.33.

The pH of Webster silty clay loam containing added pyrophosphate did not decrease as markedly as that of Norfolk loamy sand, even though the former was incubated at 35°C. (Figure 2.7). At a given pH, there is little difference between the mole ratios observed with the soils containing added pyrophosphate and those not containing this compound.

Effect of fluoride

It is apparent from Figure 24 that the added fluoride had no significant effect on the ratio of calcium to phosphorus in the residues from $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ incubated in Norfolk loamy sand at acid or alkaline pH values, even after 44 weeks. Similar results were obtained with Webster silty clay loam incubated at 35°C. (Figure 27). Petrographic and X-ray diffraction analyses of the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ incubated in the fluoride treatments failed to show the presence of $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$. The reaction of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ with fluoride to form $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$, known to occur in vitro (Farr et al., 1962), thus did not occur under the conditions of this investigation or took place so slowly that it could not be detected in 44 weeks.

SUMMARY AND CONCLUSIONS

The objectives of Part II of this dissertation were (a) to develop techniques for obtaining qualitative and quantitative data on the transformations of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ added to slightly acid and alkaline soils and (b) to use these techniques to investigate the factors affecting these transformations.

Small quantities of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ were incubated in soil in glass-fiber paper envelopes and in direct contact with the soil. Petrographic and X-ray diffraction analyses showed that the nature and extent of the transformations which occurred in the phosphate were similar in residues in the envelopes and in residues in direct contact with the soil. The residues in the envelopes could be recovered without contamination by the soil particles, and the ratio of calcium to phosphorus in these residues gave a quantitative measure of the transformation to more basic phosphates under different conditions. For the detection of new phases, petrographic analysis was more sensitive than chemical analysis, which in turn was more sensitive than X-ray diffraction analysis.

To investigate the effect of various factors on the transformations of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, these phosphates were incubated in various soils for 4, 16, and 44 weeks, in most instances at 25°C . Some of the soils had been adjusted to different pH values and some contained added substances.

$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was positively identified as a transformation product of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in all soils. The transformation followed a similar pattern in each soil, being controlled primarily by the soil pH even though the

soils varied widely in chemical and physical properties. In general, the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ increased with increasing pH above a certain limiting pH value which depended on the duration and temperature of incubation. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified as a new phase after 4 weeks in the residues of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ which had been incubated at 25°C. in Norfolk loamy sand with a pH value of 8.7 and in the residues in Webster silty clay loam (pH 7.7) which had been incubated at 35°C. After 44 weeks, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was detected as a new phase in all soils incubated at 25°C. at pH values greater than 7.4. In Webster silty clay loam which had been incubated for 44 weeks at 35°C., $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was formed at pH values as low as 6.8.

The extent of the transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ increased with time, but the rate of the reaction decreased with time as the surface of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals became covered with the new phase.

In Webster silty clay loam, which was incubated at 25°C. and 35°C., the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was greater at 35°C. than at 25°C.

Addition of magnesium chloride to Norfolk loamy sand depressed the formation of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ at 4, 16, and 44 weeks. This depressive effect also occurred in Darling Downs clay, which contained a high content of natural magnesium. Addition of magnesium chloride to Webster silty clay loam incubated at 35°C., however, had little effect on the transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, presumably due either to a lower concentration of magnesium in the soil solution or to the effect of the higher temperature in overcoming the inhibiting effect of magnesium ions.

No definite conclusions could be reached about the effect of added pyrophosphate on the transformation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ because hydrolysis of

the pyrophosphate decreased the soil pH to a level at which $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was not found in corresponding soil treatments which had not received pyrophosphate.

In soils containing added fluoride, no new phase other than $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ was identified in residues of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ by petrographic and X-ray diffraction analysis. Calcium and phosphorus analyses of residues of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, however, indicated that the formation of a phosphate more basic than $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ had occurred. In vitro, fluoride has been shown to react with $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ to form $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$. In Norfolk loamy sand with a pH value of 6.4, evidence was obtained for the reaction of the added fluoride directly with $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to form $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$. In all the other instances in which fluoride was added, no definite conclusion could be made as to whether the $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ presumed to have formed had been produced by reaction of fluoride with $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, or both. The parallel investigation of the transformations of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ added to soils, however, indicated that this phosphate did not react with added fluoride to form $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$.

Petrographic and X-ray diffraction analyses of residues of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ incubated in soils did not detect the formation of any new phosphate phase. The $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ prepared for incubation in soil was slightly calcium-deficient and appeared to react quickly with calcium in the soil to produce a residue with a mole ratio of calcium to phosphorus close to the theoretical value of 1.33. With the exception of the phosphate in Webster silty clay loam at pH values greater than 7.5, the ratio of calcium to phosphorus in residues from $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ incubated in all soils remained essentially constant with increasing pH and time of incu-

bation and maintained a value close to the theoretical value for $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. The calcium-to-phosphorus ratios of residues in Webster silty clay loam at pH values greater than 7.5 were significantly higher than 1.33. In these instances, CaCO_3 was identified as a new phase intermixed with the $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$.

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APPENDIX

Table 31. Crystal system and refractive indexes of dibasic calcium phosphate dihydrate and some of its possible transformation products

Compound	Crystal system	Refractive indexes ^a
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Monoclinic	$\alpha = 1.540$ $\beta = 1.545$ $\gamma = 1.551$
$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	Triclinic	$\alpha = 1.576$ $\beta = 1.583$ $\gamma = 1.585$
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	Hexagonal	$\omega = 1.647$ $\epsilon = 1.640$
$\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$	Hexagonal	$\omega = 1.633$ $\epsilon = 1.629$

^aData from Lehr et al. (1967).

Table 32. Calcium and phosphorus contents of residues remaining after the incubation of dibasic calcium phosphate dihydrate^a in glass fiber paper envelopes in soils for 4, 16, and 44 weeks

pH of soil before in- cubation	Soil treat- ment	Repli- cate	Calcium content, %			Phosphorus content, %		
			4 weeks	16 weeks	44 weeks	4 weeks	16 weeks	44 weeks
Norfolk loamy sand (25°C.) ^b								
6.41	--	1	23.3	23.4	23.4	18.0	18.0	18.0
		2	23.4	23.2	23.4	18.1	18.2	18.1
6.41	CaF ₂	1	23.1	23.2	23.9	18.0	18.0	18.0
		2	23.2	23.3	23.6	17.8	18.0	18.0
6.87	--	1	23.3	23.3	23.5	17.9	18.0	18.0
		2	23.3	23.5	23.2	18.2	18.1	18.0
7.91	--	1	23.6	24.7	23.9	17.9	17.7	17.5
		2	23.5	23.7	23.8	18.0	17.9	17.8
7.91	CaF ₂	1	23.8	25.8	24.0	18.3	17.9	17.9
		2	23.4	26.3	25.3	18.2	17.8	17.8
7.91	MgCl ₂	1	23.0	23.0	22.7	18.1	17.7	17.3
		2	--	23.1	22.9	--	17.7	17.6
7.91	CaH ₂ P ₂ O ₇	1	23.4	23.3	23.3	18.3	18.1	18.0
		2	23.6	23.2	23.1	18.4	18.0	18.1
7.91	CaCO ₃	1	23.5	23.9	24.7	18.0	17.8	17.9
		2	23.6	24.7	27.5	18.2	17.9	17.9
8.70	--	1	24.8	25.5	24.0	17.8	17.3	16.3
		2	24.6	25.3	25.6	17.6	17.4	16.6
8.70	CaF ₂	1	24.5	25.5	25.9	17.6	17.3	17.1
		2	24.6	25.1	25.5	17.5	17.3	17.0

^a Experimentally determined calcium and phosphorus contents of CaHPO₄·2H₂O were 23.3% and 18.0%, respectively, in agreement with the theoretical contents.

^b Temperature of incubation.

Table 32. (Continued)

pH of soil before in- cubation	Soil treat- ment	Repli- cate	Calcium content, %			Phosphorus content, %		
			4 weeks	16 weeks	44 weeks	4 weeks	16 weeks	44 weeks
Lloyd clay loam (25°C.)								
6.21	--	1	23.1	23.1	23.4	18.0	18.0	17.9
		2	23.3	23.3	23.4	18.0	18.0	18.1
6.81	--	1	23.2	23.2	23.4	18.2	17.9	18.1
		2	23.1	23.2	23.3	18.0	18.0	18.1
7.49	--	1	23.3	23.3	23.7	18.2	18.0	17.8
		2	23.1	23.3	23.7	18.0	18.0	18.1
7.51	CaCO ₃	1	23.3	23.3	23.4	18.0	18.1	18.0
		2	23.2	23.4	23.9	17.9	18.0	18.2
Webster silty clay loam (25°C.)								
6.53	--	1	23.3	23.2	23.4	18.0	18.0	18.2
		2	--	--	23.4	--	--	17.9
6.53	CaF ₂	1	23.3	23.5	23.4	17.9	18.2	18.1
		2	23.2	23.4	23.4	18.0	18.0	18.1
7.04	--	1	23.4	23.2	23.5	18.0	18.0	18.0
		2	23.4	--	23.3	18.0	--	18.0
7.71	--	1	23.3	23.8	23.9	18.0	17.9	17.8
		2	23.3	23.4	24.0	18.1	17.9	18.0
7.71	CaF ₂	1	23.3	23.5	25.0	17.8	18.0	17.7
		2	23.6	23.3	24.5	18.0	17.9	17.5
7.75	CaCO ₃	1	23.5	23.6	24.9	17.9	17.9	18.0
		2	23.3	23.7	24.7	18.0	18.0	17.9

Table 32. (Continued)

pH of soil before in- cubation	Soil treat- ment	Repli- cate	Calcium content, %			Phosphorus content, %		
			4 weeks	16 weeks	44 weeks	4 weeks	16 weeks	44 weeks
<u>Webster silty clay loam (35°C.)</u>								
6.53	--	1	22.9	23.2	23.4	17.8	18.0	18.1
		2	—	—	23.6	—	—	18.0
6.53	CaF ₂	1	23.3	23.4	24.2	17.9	18.2	18.1
		2	23.2	23.5	24.7	18.2	18.1	18.1
7.04	--	1	23.4	23.3	24.1	18.3	18.1	18.0
		2	23.2	23.3	24.1	17.9	18.1	18.1
7.71	--	1	23.6	24.9	28.8	17.9	17.8	18.1
		2	23.1	24.3	26.6	18.1	17.9	18.2
7.71	CaF ₂	1	23.6	24.9	28.9	17.7	17.9	18.0
		2	23.6	25.7	27.8	17.8	18.1	18.2
7.71	MgCl ₂	1	22.7	23.3	23.3	17.4	17.0	15.3
		2	23.0	25.6	23.3	17.5	17.8	15.5
7.71	CaH ₂ P ₂ O ₇	1	23.2	23.2	23.9	18.2	18.0	18.1
		2	23.1	23.5	24.1	18.2	18.0	18.1
7.75	CaCO ₃	1	23.4	25.4	25.1	17.9	18.1	18.1
		2	24.0	24.8	26.5	18.1	18.1	18.1
<u>Harpster silty clay loam I (25°C.)</u>								
7.51		1	23.2	23.4	23.3	18.1	18.0	17.8
		2	23.2	23.4	23.6	18.1	18.0	18.0
<u>Harpster silty clay loam II (25°C.)</u>								
7.52		1	23.2	23.4	24.3	18.1	18.1	17.9
		2	23.1	23.0	25.0	18.1	18.1	17.9
<u>Darling Downs clay (25°C.)</u>								
7.80		1	22.8	23.3	23.7	17.9	18.1	17.9
		2	23.2	23.4	23.5	18.1	17.9	17.9

Table 33. pH values^a of soils before and after incubation for 4, 16, and 44 weeks with various treatments at different pH values produced by preliminary incubation of the soils with calcium oxide

Soil treat- ment	pH be- fore in- cubation	pH after incubation			Average pH during incubation		
		4 weeks	16 weeks	44 weeks	4 weeks	16 weeks	44 weeks
<u>Norfolk loamy sand (25°C.)</u>							
-	6.41	6.53	6.46	6.25	6.47	6.43	6.33
CaF ₂	6.41	6.57	6.38	6.32	6.49	6.39	6.37
-	6.87	6.92	6.78	6.75	6.89	6.83	6.81
-	7.91	7.84	7.61	7.45	7.87	7.76	7.68
CaF ₂	7.91	7.88	7.51	7.30	7.89	7.71	7.61
MgCl ₂	7.91	7.78	7.62	7.40	7.85	7.77	7.65
CaH ₂ P ₂ O ₇	7.91	5.48	5.54	5.52	6.69	5.79	5.62
CaCO ₃	7.91	7.95	7.70	7.32	7.93	7.81	7.61
-	8.70	8.72	8.72	8.72	8.71	8.71	8.71
CaF ₂	8.70	8.76	8.72	8.72	8.73	8.71	8.71
<u>Lloyd clay loam (25°C.)</u>							
-	6.21	6.17	6.10	5.98	6.19	6.15	6.09
-	6.81	6.93	6.75	6.53	6.87	6.78	6.67
-	7.49	7.56	7.50	7.47	7.53	7.49	7.48
CaCO ₃	7.51	7.63	7.50	7.51	7.57	7.51	7.51
<u>Webster silty clay loam (25°C.)</u>							
-	6.53	6.59	6.49	6.39	6.56	6.51	6.46
CaF ₂	6.53	6.59	6.42	6.40	6.56	6.48	6.47
-	7.04	7.12	7.01	6.84	7.08	7.03	6.94
-	7.71	7.83	7.65	7.58	7.77	7.68	7.65
CaF ₂	7.71	7.84	7.63	7.55	7.78	7.67	7.63
CaCO ₃	7.75	7.83	7.68	7.62	7.79	7.71	7.69

^aAll pH values were determined in 0.01 M CaCl₂.

Table 33. (Continued)

Soil treat- ment	pH be- fore in- cubation	pH after incubation			Average pH during incubation		
		4 weeks	16 weeks	44 weeks	4 weeks	16 weeks	44 weeks
<u>Webster silty clay loam (35°C.)</u>							
-	6.53	6.52	6.40	6.24	6.53	6.47	6.39
CaF ₂	6.53	6.50	6.28	6.20	6.52	6.41	6.37
-	7.04	7.08	6.92	6.70	7.06	6.98	6.84
-	7.71	7.71	7.56	7.41	7.71	7.63	7.56
CaF ₂	7.71	7.72	7.52	7.41	7.72	7.61	7.56
MgCl ₂	7.71	7.56	7.37	7.30	7.63	7.54	7.51
CaH ₂ P ₂ O ₇	7.71	6.99	6.76	6.70	7.35	6.97	6.81
CaCO ₃	7.75	7.75	7.56	7.45	7.75	7.65	7.60
<u>Harpster silty clay loam I (25°C.)</u>							
-	7.51	7.46	7.43	7.41	7.49	7.47	7.46
<u>Harpster silty clay loam II (25°C.)</u>							
-	7.52	7.50	7.45	7.48	7.51	7.49	7.50
<u>Darling Downs clay (25°C.)</u>							
-	7.80	7.80	7.64	7.62	7.80	7.72	7.71

Table 34. Calcium and phosphorus contents of residues from incubation of octacalcium phosphate^a in glass fiber paper envelopes in various soils at different pH values and with various treatments for 4, 16, and 44 weeks

pH of soil before in- cubation	Soil treat- ment	Repli- cate	Calcium content, %			Phosphorus content, %		
			4	16	44	4	16	44
			weeks	weeks	weeks	weeks	weeks	weeks
Norfolk loamy sand (25°C.)								
6.41	--	1	31.6	32.7	31.6	18.6	18.3	18.3
		2	32.1	32.6	32.3	18.7	18.8	18.5
6.41	CaF ₂	1	31.7	32.0	32.6	18.5	18.4	18.6
		2	32.1	32.5	32.8	18.7	18.7	18.5
6.87	--	1	32.1	32.2	32.3	18.6	18.6	18.6
		2	32.2	32.3	32.6	18.5	18.6	18.8
7.91	--	1	32.3	32.4	32.1	18.7	18.5	18.6
		2	32.0	32.5	31.9	18.6	18.4	18.4
7.91	CaF ₂	1	32.5	32.3	32.2	18.5	18.5	18.5
		2	32.6	32.4	--	18.7	18.6	--
7.91	MgCl ₂	1	32.1	31.9	31.7	18.5	18.5	18.4
		2	--	32.2	32.2	--	18.6	18.7
7.91	CaH ₂ P ₂ O ₇	1	32.5	32.2	31.7	19.2	19.0	18.8
		2	32.3	32.3	31.8	19.0	18.9	19.0
7.91	CaCO ₃	1	32.1	32.4	31.7	18.6	18.7	18.5
		2	32.2	32.3	32.2	18.6	18.6	18.6
8.70	--	1	30.6	31.1	30.5	18.0	18.5	18.1
		2	30.8	30.9	31.2	18.2	18.0	18.5
8.70	CaF ₂	1	31.1	31.3	31.3	18.2	18.3	18.4
		2	31.0	31.1	30.4	18.3	18.1	17.8

^aTheoretical calcium and phosphorus percentages of pure compound are 32.6% and 18.9%, respectively.

Table 34. (Continued)

pH of soil before in- cubation	Soil treat- ment	Repli- cate	Calcium content, %			Phosphorus content, %		
			4 weeks	16 weeks	44 weeks	4 weeks	16 weeks	44 weeks
<u>Lloyd clay loam (25°C.)</u>								
6.21	--	1	32.3	32.0	32.2	19.0	18.4	18.9
		2	32.2	31.9	31.9	18.7	18.4	18.7
6.81	--	1	32.6	32.3	32.1	18.8	18.7	18.6
		2	32.2	32.5	32.4	18.8	18.7	18.7
7.49	--	1	32.1	32.5	31.9	18.5	18.7	18.5
		2	32.3	32.3	31.8	18.6	18.6	18.8
7.51	CaCO ₃	1	32.5	32.5	31.8	18.8	18.7	18.6
		2	32.2	32.1	32.5	18.6	18.6	18.7
<u>Webster silty clay loam (25°C.)</u>								
6.53	--	1	32.4	32.7	32.5	19.0	18.8	18.7
		2	--	--	32.2	--	--	18.7
6.53	CaF ₂	1	32.6	32.8	32.5	18.8	18.7	18.5
		2	32.6	32.6	32.6	18.9	18.7	18.6
7.04	--	1	32.4	32.7	32.2	18.7	18.9	18.5
		2	32.8	32.4	32.1	19.0	18.6	18.4
7.71	--	1	32.3	32.5	32.6	18.3	18.5	18.2
		2	32.6	32.4	32.2	18.5	18.3	18.1
7.71	CaF ₂	1	32.3	32.7	32.4	18.4	18.5	18.1
		2	32.8	32.5	32.2	18.6	18.5	18.0
7.75	CaCO ₃	1	32.7	32.5	32.6	18.3	18.7	17.8
		2	32.3	32.8	32.3	18.6	18.5	18.3

Table 34. (Continued)

pH of soil before in- cubation	Soil treat- ment	Repli- cate	Calcium content, %			Phosphorus content, %		
			4 weeks	16 weeks	44 weeks	4 weeks	16 weeks	44 weeks
<u>Webster silty clay loam (35°C.)</u>								
6.53	--	1	32.3	32.5	32.2	19.0	18.6	18.7
		2	--	--	32.3	--	--	18.5
6.53	CaF ₂	1	32.6	32.6	32.6	18.7	18.5	18.5
		2	32.5	32.6	32.5	18.7	18.6	18.5
7.04	--	1	32.6	32.5	32.4	18.7	18.5	18.6
		2	32.6	32.5	32.1	18.7	18.8	18.3
7.71	--	1	32.7	32.2	32.4	18.4	18.1	17.9
		2	32.6	32.5	32.7	18.2	18.3	18.1
7.71	CaF ₂	1	32.7	32.2	32.5	18.5	18.2	17.9
		2	32.6	32.5	32.3	18.5	18.0	17.7
7.71	MgCl ₂	1	32.0	31.5	31.5	18.3	17.7	17.9
		2	32.4	31.5	31.0	18.8	18.0	17.4
7.71	CaH ₂ P ₂ O ₇	1	32.5	32.3	32.1	18.9	18.6	18.4
		2	32.4	32.4	32.1	18.9	18.7	18.2
7.75	CaCO ₃	1	32.7	32.5	32.4	18.5	17.9	17.9
		2	32.7	32.7	32.2	18.9	18.3	18.0
<u>Harpster silty clay loam I (25°C.)</u>								
7.51		1	--	32.5	32.2	--	18.6	18.3
		2	32.3	32.4	32.1	18.7	18.6	18.4
<u>Harpster silty clay loam II (25°C.)</u>								
7.52	--	1	--	32.6	32.4	--	18.6	18.7
		2	32.4	32.3	31.9	18.7	18.7	--
<u>Darling Downs clay (25°C.)</u>								
7.80	--	1	32.3	32.3	32.5	18.6	18.5	18.5
		2	32.5	32.1	32.6	18.6	18.6	18.5