The Retention of Phosphate by Soil. A Review

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THE scope of the present review is limited to the evidence for, and the nature of, the retention of phosphate by soil. It does not include the numerous experiments that have purported to measure the availability to plants of the retained phosphate. The literature up to 1932 has been surveyed by Weiser (157) and some of the more recent literature by Midgley (95).

The following terminology will be adopted:—

'Phosphate' refers to the anions which are formed from the dissociation of orthophosphoric acid or any of its salts.

'Phosphate sorption' and 'phosphate retention' are used synonymously and are taken to mean the removal of phosphate from solution by soil or by a soil constituent. No particular mechanism is implied. 'Phosphate adsorption' and 'phosphate absorption' are taken to mean the retention of phosphate at a surface and within a solid phase, respectively.

'Phosphate fixation' is used to describe any change that the phosphate undergoes in contact with the soil, which reduces the amount that plant roots can absorb. It is understood that plant roots active in nutrient absorption can penetrate into the locality of the phosphate, that is, the phosphate is not positionally unavailable to the roots.

There is, unfortunately, a general lack of agreement on the meanings that should be associated with these terms, especially with 'phosphate fixation', which is more commonly taken to mean the retention of phosphate from solution. As the retention of phosphate by soil and its decreased availability to plants are two processes that have quite different implications in agriculture, and in addition probably differ chemically, it is desirable to distinguish between them. This is done by using the above terminology.

GENERAL

The retention of phosphate by soil seems to have been first demonstrated by Way (153) in 1850, though Liebig (71) had anticipated the results 10 years earlier. Liebig stated, with regard to soluble phosphates, that 'in a few seconds the free acids unite with the bases contained in the earth, and a neutral salt is formed in a very fine state of division.' Way (153) found that the whole of the phosphate was retained when solutions of sodium phosphate in water, and guano in dilute sulphuric acid, were poured over a layer of calcareous soil. He thus found that a solution of phosphate differed from solutions of nitrate, chloride, and sulphate which passed through the soil with their concentrations unchanged. Way suggested that an insoluble calcium phosphate was formed. The importance of his observation was that water-soluble phosphate, as in the fertilizer superphosphate which was then coming into use, was retained by soil and not leached out in the drainage

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water. This was confirmed by Way when he carried out analyses of drainage water and found only small amounts of phosphate (155). In three of the seven samples he examined the amount was too small to determine. Subsequently, many similar determinations have been carried out and in general they yield the same results.

Some losses have, however, been reported. Robinson and Jones (119) carried out analyses of 6 soil profiles 10 years after the soils had been given a broadcast application of basic slag (200 lb. P_2O_5 per acre.) They could find little trace of the phosphate and concluded that it had been washed out of the top 18 inches of the soil by the heavy rainfall (35 – 75 inches per annum at the 6 centres) within 6 to 10 years after application. Some workers have reported losses from sandy soils (34, 81, 102), and others from soils receiving unusually heavy phosphate applications (61). Glentworth (53), observing that total phosphate is lowest and acetic acid soluble phosphate is highest in the gley horizon of poorly drained soils, suggests there might be a loss of phosphate in the ground water of poorly drained soils. Loss of phosphate may be serious where there is much run-off water (8, 64, 120, 127).

Apart from these special circumstances most of the phosphate remains in the soil. Its distribution within the soil is, however, of importance, because the phosphate should penetrate into the root zone of plants if it is to be of any value for crop growth. Way (154) and Voelcker (147) assumed that the water solubility of superphosphate should ensure not only the formation of a finely divided precipitate in soil, but also its adequate distribution within the soil. It has, however, been shown by a number of workers (8, 23, 24, 55, 58, 90, 104, 146, 150), that movement of phosphate within the soil is sometimes limited to as little as 2 or 3 inches, though it varies according to soil texture, amount of phosphate applied, rainfall, &c. Dyer (39) analysed the continuous wheat plots at Rothamsted and found that most of the phosphate that had been applied, and had not been removed in crops, was still present in the top 9 inches of soil. The penetration was greater when other fertilizer salts of farmyard manure had been used in conjunction with the superphosphate. This effect of organic matter has also been observed by others (43, 47, 91). Stephenson and Chapman (136) found evidence for the penetration of phosphate below the first foot in medium textured and light soils, but for practically no penetration below 6 inches in heavy soils. Phosphate that has been broadcast on a soil growing grass seems to move only very slowly from the surface (12, 94, 128, 132, 160, 162), though Doak (35) found appreciable penetration to 4 inches.

According to Weaver (156) some plants such as cereals and swedes may not send many roots into the top inch or two of soil. It is therefore not surprising that under some conditions at least the smallness of the movement of phosphate within the soil is responsible for the low response of crops to a phosphate application (24, 60, 94).

A. FACTORS AFFECTING PHOSPHATE RETENTION

1. Mechanical composition of soil.

It is generally accepted that most of the retaining power of soil for phosphate lies in its finer mechanical fractions, especially clay. Hibbard (59) found that the retention of phosphate by the three fractions that were retained on 1-mm., 40-mesh, and 100-mesh sieves and the fraction that passed through a 100-mesh sieve was greatest with the finest fraction and decreased as the particle size increased. Perkins, Wagoner, and King (106) divided a soil sample into six mechanical fractions (average diameter 0.06, 0.034, 0.016, 0.006, 0.003, and $<$0.003 mm.) and found that on a weight basis phosphate retention increased with decreasing particle size, though on a surface area basis the reverse held. The phosphate was added as monocalcium phosphate. Owen (104) found a fairly close relationship between phosphate retention and clay percentage that could be described by the regression equation

$$\log y = a + b \log m,$$

where y = percentage retention, m = percentage clay, and a and b are constants. Other workers have found a similar relationship (7, 103). Coleman (20) found that the fine ($< 0.2\ \mu$) kaolinitic and montmorillonitic clay fractions of two soils sorbed over twice as much phosphate per gm. of clay as the corresponding coarse ($2 - 0.2\ \mu$) fractions. Using the minerals quartz, hematite, muscovite, phlogophite, biotite, pyro-phyllite, talc, montmorillonite, and kaolinite, Perkins and King (108) showed that the retention of phosphate increased with their fineness of grinding.

The effect of the chemical composition of the colloid fractions of soil is discussed later.

2. Phosphate concentration.

Russell and Prescott (123), Hibbard (59), Davis (27), Kurtz, De Turk and Bray (67), and Owen (104) have shown that the greater the ratio of phosphate to soil, the greater is the retention of phosphate. Laatsch (68) found that this also applies to NH_4^+ permutite. The relationship between phosphate retention and phosphate concentration has been shown to comply with the Freundlich adsorption isotherm (27, 67, 104, 123). Fisher (42) has pointed out that this does not necessarily imply an adsorption process, as precipitation processes also give results which fit the Freundlich adsorption isotherm.

3. Time and temperature.

Retention of phosphate differs from the retention of cations in that the reaction comes to completion only very slowly, if at all. It has been shown that with soil and with soil clay the initial stages of the reaction proceed rapidly, but the reaction, although getting slower, continues for many weeks (19, 27, 59, 67). A similar effect of time has been observed with kaolinite by Black (10), and with muscovite, montmorillo-nite, hematite, and limonite by Perkins (110). Black (10), Coleman (19), and Perkins (110) have shown that the amount of phosphate sorbed by the clay minerals increases much more with time at pH 3 – 4 than at pH 6 – 7. Scarseth and Tidmore (124), on the other hand, reported practically no difference in the amount of phosphate ' fixed ' after 1 hour and after 20 days. They used 0.05 normal and 0.1 normal sulphuric acid to measure ' fixation '.

The solubility in dilute acids of phosphate that has been added to soil has been shown to decrease with time. This has been demonstrated with 1 and 2 per cent. acetic acid and CO_2-saturated water (4), with 0.002 normal sulphuric acid (59, 97, 125), with 0.01 normal sulphuric acid (104), and with dilute acetic acid (50). Williams and Stewart (159) found a very rapid decrease in solubility in calcium lactate, magnesium bicarbonate, acetic acid, potassium bisulphate, citric acid, and sodium hydroxide solutions.

Under sterile conditions phosphate retention increases only slightly as the temperature is increased from 25°C to 35°C (158). If the temperature is increased up to 100°C the reaction proceeds much more rapidly (7, 57), though there is no evidence that the total amount of phosphate that can be retained is increased. If clay or soil is heated to much higher temperatures the hydrous minerals lose water and hydroxyl groups and their capacity to retain phosphate is decreased, though this does not apply to the hydrous aluminium oxides

(44, 66). The effect of temperature on the retention of phosphate under non-sterile conditions would be expected to depend on the relative rates of mineralization of soil organic matter, thus allowing release of phosphate, and on the absorption of phosphate by microorganisms. Consideration of these factors is, however, outside the scope of the present review.

4. Effect of salts.

According to Liebig (72) sodium chloride, sodium nitrate, and ammonium salts increase the water solubility of calcium phosphate. Liebig argued that this increased solubility would still be exerted in the presence of soil and hence these salts would increase the diffusion of phosphatic fertilizers through the soil. Dyer (39) carried out analyses of the soil from the continuous wheat plots at Rothamsted and found that the salts potassium, sodium and magnesium sulphates had permitted greater penetration of the phosphate that had been applied as superphosphate. The phosphate that was retained was more easily soluble in 1 per cent. citric acid than on the plots not receiving these salts.

McGeorge and Breazeale (75) found that all the neutral salts that they tried decreased the solubility of rock phosphate and soil phosphate. Greaves (54) found that potassium chloride, sodium chloride, calcium chloride, calcium nitrate and calcium sulphate decreased the solubility of the phosphate of these two materials, but sodium nitrate, potassium sulphate and ammonium sulphate increased the solubility. Midgley (94) reported that potassium sulphate and ammonium sulphate slightly decreased and calcium hydroxide considerably decreased the penetration of superphosphate through a slightly acid silt loam, whereas the penetration was considerably greater in the presence of sodium nitrate.

On the other hand, Brown (12) showed that sodium nitrate or ammonium sulphate when added to a slightly acid subsoil in a laboratory percolation experiment resulted in practically no increase in the penetration of phosphate that could be detected by the method of Truog and Meyer (144). Also, Hibbard (59) found that calcium sulphate and calcium and magnesium carbonates considerably depressed the water solubility of the phosphate that had been applied to four soils, but sodium sulphate and ammonium sulphate had practically no effect and potassium and magnesium sulphates had only a slight depressive action.

Eriksson (40, 41), working with acidic Swedish soils, showed that the solubility and availability of phosphate are considerably lowered by the presence of potassium chloride. The effect increased with an increase in the salt concentration. A similar effect on phosphate solubility has been reported by Kurtz *et al.* (67).

There is, as yet, insufficient knowledge to explain these apparently contradictory results. In soils in which calcium phosphate is formed, the addition of a calcium salt which involves no change in pH would be expected to decrease phosphate solubility by the common ion effect, and other neutral salts would be expected to increase the solubility by lowering the activities of the phosphate and calcium ions. This latter effect is well known in analytical chemistry.

Cameron and Hurst (14) found that neutral salts depressed the solubility of aluminium phosphate. Similar observations were made by Karlsson and Mattson (65) with an aluminium phosphate precipitate at pH values above its iso-electric point (pH 5). At lower pH values the effect was reversed. This might explain the observations that have been made by Eriksson (40, 41) and by Kurtz and his co-workers (67).

Cameron and Hurst (14) reported that the solubility of ferric phosphate was decreased by potassium chloride and sodium nitrate, but slightly increased by potassium sulphate.

B. THE NATURE OF THE RETAINED PHOSPHATE

1. Iron and aluminium compounds.

Voelcker (147), in 1863, showed that a sample of clay soil containing only a small percentage of calcium carbonate was active in phosphate sorption. He concluded that this was due to the formation of insoluble compounds with the hydrous iron and aluminium oxides that were known to be present, and to the consequent precipitation of calcium phosphate. A few years later Warington (151) found that artificially prepared hydrous ferric oxide and alumina retained considerable amounts of phosphate from solution, even in the presence of carbon dioxide. He determined (152) the retention of phosphate by two soils which had been treated with dilute acetic acid to remove calcium, and found that the soil with the greater amount of iron and aluminium soluble in hydrochloric acid retained the greater amount of phosphate. He thought that ' in all soils containing a sufficient amount of oxide of iron or alumina, the phosphoric acid will be found in combination with these bases, and not as alkaline or alkaline-earthy phosphate '.

As it became known that the water-solubility of the phosphate in superphosphate was reduced by the presence of iron and aluminium compounds, so was it inferred that in soils also, which were known to contain these compounds, phosphate reacted to form insoluble iron and aluminium phosphates. Thus, Dehérain (30) thought that iron and aluminium phosphates were gradually formed in the unmanured experimental plots at Grignon. In 10 years there was a loss of 800 kilograms per hectare of P_2O_5 which was soluble in dilute acetic acid. Gerlach (48) shook samples of a soil in 1 per cent. acetic acid for periods of 3 hours, 24 hours, and 14 days, and found that 0.0103, 0.0079, and 0.0024 gm. P_2O_5 was dissolved. He attributed this diminution in the amount of phosphate extracted to a gradual sorption of the phosphate by iron or aluminium hydroxide after it had been dissolved from the more soluble phosphates. Similar observations were made by Russel and Prescott (123) in more exhaustive work.

In the last 30 years an intensive study has been made of the reactions that take place between soil and phosphate ions, and much of this work has been directed to elucidating the part played by iron and aluminium. These elements are found, in most soils at least, concentrated in the clay fraction. They both occur in the clay minerals themselves in octahedral linkage, and aluminium is found also in tetrahedral linkage. They can both occur as free hydroxides and oxides, aluminium as gibbsite $Al(OH)_3$ (1), and iron as hematite Fe_2O_3, geothite and limonite $FeO(OH)$ (100), and as magnetite Fe_3O_4 (15). Except in acid soils the amount of each in the soil solution is small. Magistad (82) found that the concentration of aluminium in soil solutions is only likely to be greater than 3 p.p.m. outside the pH range 4.5—8.0. Aluminium ions are considered by some workers to be present as exchangeable cations as it is known that aluminium comes into solution when an acid soil is leached with a neutral salt (105). Iron is present in soil organic matter (149), and aluminium probably occurs similarly.

It is now established that iron and aluminium hydrous oxides can sorb phosphate under the conditions that normally exist in soils. This has been demonstrated with hydrogels (51, 70, 76, 96, 98), with ferric hydroxide (66), and with soluble iron and aluminium (46, 84, 98, 114, 139, 141). Ford (44) showed that goethite and bauxite, but not hematite, retained phosphate from solution and the phosphate retained by geothite had a very low solubility in 0.002 normal sulphuric acid. Perkins and King (109) found that limonite and one sample of hematite sorbed about 1 per cent. of their own weight of phosphoric acid, but another sample of hematite and magnetite sorbed practically no phosphate. Weiser (157) also reported that hematite sorbed no phosphate and thus differed from the hydrous oxides of iron such as limonite and goethite.

Thus, on *a priori* grounds the formation of iron and aluminium phosphate in soil would be expected. Support for this conclusion comes from four types of evidence.

(*a*) Correlations have been established between phosphate sorption and the amounts of iron and aluminium in soils.

Phosphate sorption has been shown to vary inversely as the SiO_2 $(Fe_2O_3+Al_2O_3)$ ratio of soil colloids (83, 87, 124, 142). Gaarder and Grahl-Nielsen (47) showed that the phosphate sorption capacity of forty-three soils increased with the ratio of basoids to acidoids. Gile (52) found in a pot experiment that the efficiency of superphosphate decreased as the SiO_2 $(Fe_2O_3+Al_2O_3)$ ratio of the soil colloids decreased.

The amount of iron and aluminium which is soluble in acids and the amount of phosphate that the soils sorbed have been correlated (3, 45, 118).

A correlation between the amounts of iron and aluminium and phosphate dissolved by dilute acids has also been established (19, 104, 148).

Metzger (93), using forty-two soil samples, found a significant correlation between total Al_3O_3, Fe_2O_3 $(Al_2O_3 + Fe_2O_3)$ and phosphate sorption. He also found that the reduction in phosphate sorption capacity, due to extraction with 0.002 normal sulphuric acid, when expressed as a percentage of the original sorption capacity was correlated with the amount of iron that was soluble in the extracting reagent. He established a correlation between the percentage of total Fe_2O_3 that dissolved in 0.002 normal sulphuric acid and the percentage reduction in the phosphate sorption capacity that resulted from acid extraction. A similar correlation was not found with aluminium.

(*b*) Iron and aluminium have been removed from soils soil colloids and the effect on phosphate sorption has been studied.

Toth (142, 143) and Kelly and Midgley (66) used the hydrogen sulphide method of Drosdoff and Truog (38) to show that the removal of iron and aluminium oxides from soil colloid reduced phosphate sorption. The effect varied with colloid under investigation. A similar result has been reported by a number of workers (10, 17, 18, 20, 92) after the iron and aluminium had been removed by a slightly modified hydrogen sulphide method (145). However, it has never been proved that the clay minerals remain unaffected by the reagents used to extract iron and aluminium oxides and, in fact, Toth (143) and Dion (33) have reported evidence of such decomposition. Romine and Metzger (121) showed that the phosphate sorption capacity of soil was lower after extraction with 0.002 normal H_2SO_4.

Ghani (49) found that the addition of 8-hydroxyquinoline to soil reduced the sorption of phosphate under acid conditions. As 8-hydroxyquinoline was thought to block active iron and aluminium, this was taken as evidence for the formation of iron and aluminium phosphates.

(*c*) Iron and aluminium compounds have been added to soils and soil colloids and the effect on phosphate sorption has been studied.

Wolkoff (161) found that the addition of ferric chloride to a soil treated with rock phosphate reduced the amount of phosphate dissolved by 0.2 normal nitric acid. Aluminium chloride had no effect. Doughty (36) saturated a peat soil with iron and aluminium ions by leaching with solutions of ferric chloride and aluminium chloride. He found that both the iron and aluminium caused a considerable increase in phosphate sorption. The maximum sorption was at pH 2.5 following the ferric chloride treatment, and at pH 4.0 after leaching with aluminium chloride. Scarseth (126) found that a low-iron bentonite sorbed much more phosphate in the pH range 3.0—7.0 after being treated with a ferric chloride solution.

Davis (25, 26) reported that ferric chloride and aluminium chloride that had been added to soil-Ca $(OH)_2$-H_2O-air systems increased phosphate sorption especially at low pH values. In the sample treated with ferric chloride retention against 0.002 normal sulphuric acid and 0.1 normal sulphuric acid was also increased. He concluded that only at pH values lower than 4.5 are appreciable amounts of iron and aluminium phosphates formed that are insoluble in 0.002 normal sulphuric acid.

(*d*) Compounds formed during phosphate sorption have been identified by comparing the effect of pH on phosphate sorption with the known effect of pH on the solubility of iron and aluminium phosphates.

The effect of pH on the precipitation of iron and aluminium phosphates has been studied by Teakle (141). With iron, precipitation of phosphate was greatest at pH 3.0, and with aluminium, at pH 6.8.

With equivalent amounts of Fe . . . and PO'_4'', Doughty (36) found that the greatest precipitation was at pH 3.5-4.5 and Gaarder (46) at pH 2.0-3.0. Both workers reported that precipitation takes place up to at least pH 8 in the presence of a considerable excess of iron. With equivalent amounts of Al . . . and PO'_4'', Doughty found greatest phosphate precipitation at pH 6.8, and Gaarder at pH 3.6-4.0, but with an excess of aluminium Doughty found the pH range of greatest precipitation became 6.5-8.5, and Gaarder 4.5-6.5. Rathje (116) found that the greatest precipitation of phosphate by excess iron was at pH 3, and at pH 4 with excess aluminium.

Results from similar experiments have been obtained by Murphy (98) using ferric chloride and an iron hydrosol, and by Perkins and King (109) with limonite and hematite. McGeorge and Breazeale (76) and Stelly and Pierre (135) have reported results of the effect of pH on the solubility of iron and aluminium phosphate minerals. Stelly and Pierre found that the lowest solubility of the aluminium phosphate minerals wavellite and variscite was in the pH range 4.5-7.0, and of the iron phosphate minerals vivianite and dufrenite was in the pH ranges 6.0-7.0 and 3.0-6.0 respectively.

The first experiment to be reported that accurately related phosphate sorption of soil to the pH value was that of Roszmann (122). He found that the greatest sorption with the electrodialysed clay fraction of Putnam silt loam was at pH 3.0-4.0, with little sorption above pH 10.

Doughty (36) studied the retention of phosphate by a peat soil over the pH range 3-10 and attributed the retention at low pH values to iron and aluminium. Scarseth (126) found that the greatest retention of phosphate by an electrodialysed bentonite titrated with sodium hydroxide was at pH 6-7, which he thought was due to a reaction of the phosphate with the aluminium of the clay mineral. Allison (2) found a similar maximum at pH 6 with three soil colloids titrated with sodium hydroxide. He found another peak in the phosphate sorption pH curve at pH 3.0-3.5 which he attributed to the presence of iron and aluminium hydrous oxides, especially the former.

Black (10) working with Cecil Clay, found a maximum in the phosphate-sorption curve at pH 3-4, which he thought was due to hydrous iron oxide. He found that the amount of phosphate that was sorbed at this maximum was reduced by the removal of the free iron oxide, but it still remained appreciable. He also concluded that the maximum in the phosphate-sorption curve at pH 6-7, which he found with a sample of 2/μ kaolinite, was due to adsorption by free aluminium hydroxide. The aluminium was thought to come slowly into solution, especially under more acid conditions, because after 30 days' shaking the maximum had shifted to pH 5-6.

Coleman (18, 20) using montmorillonitic and kaolinitic clays showed that most sorption of phosphate took place at pH 3.0, but after removal of free iron oxides the sorption was reduced so to be about the same at pH 3.0, 7.0, and 9.5.

Mechanism of the reaction with iron and aluminium. Reference has already been made to the work of Russel and Prescott (123). These workers found that if soils were extracted with acids of low concentration (N/20 to N/10) the amount of phosphate that was extracted decreased with an increase in the time of the extraction. The action of dilute acids thus seemed to consist of two parts:

1. A direct solvent action of the acid on the phosphorus compounds of the soil that depended only on the concentration of the acid, and not on its nature.
2. A retention of the liberated phosphate that was greatest in the presence of mineral acids such as nitric and hydrochloric acids and least in the presence of organic acids such as citric and oxalic acids.

They argued that the retention of phosphate was more likely to be due to adsorption than to precipitation as the reaction was found to follow the Freundlich adsorption isotherm. Also, they found that there was no precipitation of phosphate by a soil extract that would have contained any soluble compounds capable of precipitating the phosphate, and they also assumed that the concentration of acid they employed would prevent the precipitation of insoluble phosphates. Their argument has been criticized by Fisher (42) and Comber (21). Fisher pointed out that compliance with the Freundlich equation is not restricted to adsorption reactions, whilst Comber showed that the strengths of acid used by Russel and Prescott were not sufficient to prevent the precipitation of phosphate. Murphy (98) objected to the precipitation theory on the grounds that only under conditions of extreme acidity is sufficient iron or aluminium present in the soil solution to cause rapid precipitation, though for this criticism to be valid it would be necessary to show that the soil solution cannot be rapidly renewed by dissolution of iron or aluminium from the solid phase.

It has already been pointed out that numerous workers have shown that iron and aluminium hydroxides and hydrous oxides can sorb phosphate. It has therefore been postulated that there is an exchange reaction between phosphate ions (mainly $H_2PO'_4$ HPO''_4) and the hydroxyl ions present in these compounds (56, 86, 87, 115). Kelly and Midgley (66) found an increase in pH value when ferric hydroxide and a phosphate solution at the same pH value were mixed. Ford (44) and Kelly and Midgley (66) showed that only iron oxide that is hydrated will retain phosphate and the substance loses this property if it is strongly heated. Heck (56) believed that in Hawaiian soils, which are known to fix phosphate very strongly, a basic ferric phosphate is formed, i.e., not all the hydroxyl groups are replaced. Swenson, Cole, and Sieling (139) have claimed that not more than one of the hydroxyl ions of iron and aluminium hydroxides can be replaced.

Mattson and Karlsson (89) and Karlsson and Mattson (65) studied the effect of salts on the retention of phosphate by aluminum hydroxide and concluded that phosphate ions may be ' saloid-bound ' or ' colloid-bound ', that is, be ' gegen-ionen ' or be chemo-sorbed. The phosphate is predominantly ' saloid-bound ' when the precipitate has a positive charge, as it has at low pH values. Both Mattson (83) and Schofield (130) attributed the retention of chloride and sulphate ions by clay at low pH values to the presence of free hydrous iron and aluminium oxides, especially the former.

Although there is good evidence that either iron or aluminium, or both, can react with phosphate under the conditions that exist in soil, it cannot be stated with certainty whether these ions come from the clay minerals or from the free hydrous oxides. There seems no reason why they should not come from both. Further, there is uncertainty on the mechanism of the reaction. The distinction between precipitation on the one hand, and adsorption with the formation of chemical bonds (chemo-sorption) on the other, is a fine one, and will be difficult to resolve.

2. Calcium and magnesium compounds.

Both Way (154) and Voelcker (147) supposed that an insoluble calcium phosphate is formed when a soluble phosphate is mixed with soil containing calcium carbonate. This insoluble phosphate was assumed to be either dicalcium phosphate or tricalcium phosphate (48, 62, 129, 137), though tricalcium phosphate was thought to be produced in all soils containing more than a trace of calcium carbonate. Bassett (6), however, after a phase-rule study of the system $CaO-P_2O_5-H_2O$ concluded that a more basic compound such as hydroxy-apatite would be formed in neutral and calcareous soils. McGeorge and Breazeale (75) later postulated the formation of carbonate-apatite in soils containing a high percentage of calcium carbonate.

Dean (28) fractionated the phosphorus contained in the slightly calcareous soil at Rothamsted and concluded that the phosphorous which had been applied as superphosphate had been retained as tricalcium phosphate or apatite. Direct evidence for the formation of a fluorine-containing apatite on this soil was later obtained by Nagelschmidt and Nixon (101) from examination of the chalk fragments by an X-ray diffraction technique and chemical analysis. This confirmed an earlier suggestion by MacIntire and Hatcher (80) that fluorapatite is formed in calcareous soils.

There is also evidence that phosphate ions can be retained through exchangeable calcium. Naftel (99) thought that this type of adsorption could take place up to about pH 6.5, but that at higher pH values tricalcium phosphate or apatite is precipitated. Other workers have postulated that exchangeable calcium can retain phosphate at pH values as low as 4.0 (2, 5, 126) or below (111). Phosphate is not precipitated from solution by Ca^{++} ions at pH values lower than about 5.0 (9, 46). Boischot, Coppenet, and Hebert (11) have recently put forward the suggestion that in calcareous soils the initial reaction is an adsorption on to the surface of calcium carbonate particles rather than to precipitation of an insoluble phosphate.

Perkins (111) found that up to pH 4.5, Mg^{++} ions that had been added to 100-mesh koalin were about as effective as an equivalent amount of Ca^{++} ions in precipitating phosphate, but at higher pH values they were far less effective. He concluded that precipitation of phosphate by magnesium is not likely to be of importance in ordinary agricultural soils. Not only is the final product important, but it is also important to know the rate at which the various forms of calcium phosphate are formed. Mac Intire and his co-workers (77, 78, 79) showed that dicalcium phosphate when mixed with calcium carbonate and distilled water and kept under laboratory conditions undergoes only slow transformation to tricalcium phosphate. Thirty per cent. of the dicalcium phosphate was converted to the triphosphate in the first week, but after 12 months 40 per cent. of the dicalcium phosphate remained unchanged. They suggested (80) that the dicalcium phosphate probably persists in moderately limed soils for a considerable period. In most calcareous soils the calcium carbonate: calcium phosphate ratio is much wider than they employed, and the rate of transformation might therefore be expected to be more rapid.

The size of the apatite particles that are formed is not known, but MacIntire and Hatcher (80) suggest that compared with finely ground rock phosphate they are of ' infinitesimal fineness '. This fineness of division is one of the factors that determines the availability of the apatite to plants.

3. Compounds with clay minerals.

Montmorillonite. Scarseth (126) working with low-iron bentonite that had been electrodialysed found that the greatest sorption of phosphate by the Na-clay was at about pH 6.5. He thought that there was an exchange between PO_4''' and $3OH'$ groups which dissociated from aluminium ions present at the surface of the aluminosilicate. Murphy (98) found that bentonite sorbed only half as much phosphate as did kaolinite, but he did not report the relative fineness of the two minerals. Similarly, Stout (138) reported a sorption at pH 7 of 11 milli-equivalents of phosphate per 100 gm. bentonite, whereas with ball-milled kaolinite, under similar conditions 172 milli-equivalents of phosphate were sorbed. Maximum sorption with the bentonite occurred at pH 6.

Differing from this work is that of Black (10), Coleman (18, 19), Perkins and King (108) and Perkins (110), who have shown that sorption of phosphate by montmorillonite can be at least as great as by kaolinite if minerals of similar fineness of grinding are used. Black (10) found the greatest retention by bentonite ($< 2/\mu$) at pH 5-6.

Kaolinite. Both Murphy (98) and Stout (138) studied phosphate sorption by the mineral kaolinite after it had been ball-milled. They found that sorption was high and that it increased as the pH value decreased to 3.0, the lowest value investigated. Black (10) showed that ball-milled kaolinite sorbed many times more phosphate than coarse ($< 2\mu$) kaolinite, but thought that the difference was due to the kaolinite crystals having been 'split and disorganized' during ball-milling. He found one maximum in the pH-phosphate sorption curve at pH 3.5-4.0 which he attributed to the replacement of the hydroxyl ions of the lattice layers of the kaolinite. With the coarse kaolinite there was another maximum at pH 6-7 which he thought was due to the formation of aluminium phosphate on the surface of hydrous aluminium oxides.

Cooke (22), Midgley (95), and Raychaudhuri and Mukherjee (118) reported that unground kaolinite sorbs little phosphate. On the other hand, Perkins (112), using kaolinite that had been ground to pass a 100-mesh sieve, found that almost 40 per cent. of the phosphate that had been supplied at the rate of 0.355 gm. H_3PO_4 per 100 gm. clay was retained in a few hours' shaking.

It is doubtful whether the experiments using ball-milled kaolinite give results at all analogous with those of soil clay because there is evidence that prolonged ball-milling induces changes in the crystalline structure of kaolinite. Sieling (133) found that the constituent of ball-milled kaolinite that was active in phosphate sorption could be extracted by 0.1 normal hydrochloric acid or 0.1 molar tartaric acid and believed it to be a form of hydrous alumina such as γ-AlOOH. Laws and Page (69) adduced evidence for the formation of a new permutite-like mineral when kaolinite is ball-milled for a long period. Perkins (112) has also given evidence that grinding causes a disruption of the kaolinite lattice that was manifested by a release of Al_2O_3, and water.

Stout (138) and Black (10) have reported that halloysite, which has a crystalline structure similar to that of kaolinite, can sorb a large amount of phosphate. Stout showed that halloysite sorbed slightly more phosphate than kaolinite over the pH range 3-10 and found greatest phosphate sorption by both minerals at pH 3, the values being 1,290 and 1,170 m.e. phosphate per 100 gm. mineral, respectively. Each mineral had been ball-milled. Black (10) reported that the maximum sorption by 60-mesh halloysite was at pH 4-5 from a solution of 1 p.p.m. phosphorus and at Hp 3.1 from a solution of 100 p.p.m. phosphorus.

Mica. Black (10) reported that a sample of illite which contained free iron oxides sorbed up to 10 per cent. of the phosphate in 48 hours from a solution of 100 p.p.m. phosphorus. The maximum from a solution of 1 p.p.m. phosphorus was at pH 5-6, and from a solution of 100 p.p.m. phosphorus at pH 3.

Perkins and King (107, 108) found that the micas muscovite, biotite, and margarite sorb large amounts of phosphate, which they attributed to the replacement of lattice silicon by aluminium.

There seems to have been no study made of the phosphate-retaining properties of the hydrous micas.

Mechanism of the reaction with clay minerals. There are two types of reaction by which phosphate ions might be retained by the clay minerals: by the formation of chemical bonds with lattice ions, and by adsorption as gegen ions.

Iron and aluminium are the only lattice ions that are likely to undergo a reaction with phosphate ions. The phosphate ions may be retained by an exchange reaction with the hydroxyl ions that are normally linked with the iron and aluminium ions. Alternatively the iron and aluminium may acquire a positive charge by the transfer of a proton from an H_3O^+ ion to an oxygen, as has been suggested by Schofield (130) for hydrous iron oxide. The former suggestion has been made by a number of workers (10, 29, 86, 115, 117, 126, 138, 142). The most direct evidence to support this postulate was presented by Stout (138). He showed that after being phosphated, the minerals kaolinite and halloysite contained fewer hydroxyl ions, for they lost less water on heating. It must, however, be borne in mind that Stout used ball-milled minerals which might have contained degradation products (v. supra).

Perkins and King (107) compared the retention of phosphate by the minerals pyrophyllite $[Si_4O_{10}Al_2(OH)_2]$ and talc $[Si_4O_{10}Mg_3(OH)_2]$ muscovite $[KAlSi_3O_{10}Al_2(OH)_2]$ and phlogophite $[KAlSi_3O_{10}Mg_3(OH)_2]$. They claimed that the pH values at which they found greatest precipitation were those that would be expected by a reaction of the metal to which the hydroxyl ions were attached. This is not clearly revealed by their published results. Thus there is some evidence, though not conclusive, that phosphate ions can replace the hydroxyl ions which are attached to the lattice ions of the clay minerals.

A different theory has been put forward by Low and Black (74). They showed that the addition of increasing amounts of phosphate to a sample of kaolinite at pH 4.5-4.7 brought increasing amounts of silica into solution. They took this as evidence for the disintegration of the surface layers of the kaolinite with the formation of insoluble aluminium phosphate and the release of silica. According to Mattson (87, 88) and Toth (142), silicate ions from artificial aluminium silicate and from some clays can be replaced by phosphate ions.

It is well established that the phosphate ions which are retained by clay particles can be replaced by other anions, at least partially. The order of replacing power of other anions depends not so much on their valency, as might be expected from the Hardy-Schulze valency rule, as on their chemical nature. Thus, it has been shown that citrate, tartrate, oxalate, arsenate, and fluoride have strong replacing properties whereas sulphate, thiocyanate, acetate, chloride, and nitrate have only weak replacing properties (29, 31, 32, 67, 123, 131). Swenson and his co-workers (139) have pointed out that the anions which are most effective in replacing phosphate can themselves form complexes with iron and aluminium.

There is no satisfactory evidence that the clay minerals have amphoteric properties and can therefore adsorb phosphate ions as gegen ions. Mattson (83) showed that if clay particles have a low $SiO_2/(Fe_2O_3+Al_2O_3)$ ratio they become positively charged at low pH values. The retention of chloride and sulphate ions increased as the positive charge increased, though there was a small retention of both ions when the particles had a small negative charge. Schofield (130) has also shown that at low pH values chloride ions can be retained by clay particles even though they have a net negative charge. Both these workers have attributed this manifestation of the amphoteric properties of the clay to the free iron oxide and not to the clay minerals.

The replacement of a small amount of the adsorbed phosphate by chloride ions has been attributed to a replacement of gegen ions (159). This phosphate is termed ' saloid-bound ' according to the terminology of Mattson and Karlsson (89). There is, however, no evidence to decide whether the clay minerals or the free hydrous iron and aluminium oxides are responsible for this type of adsorption.

4. Compounds with other inorganic soil constitutents.

Quartz. It has been found that a silica hydrogel can retain some of the phosphate from a solution of monocalcium phosphate (51, 134). This was explained by Ghosh and Bhattacharyya (51) as being due to adsorption of phosphate through the calcium ions which are held by the silica gel. Perkins and King (109) and Perkins (110) showed that the retention of phosphate by finely ground quartz is very small, but in another experiment (108) they found that ball-milled quartz sorbed a considerable amount of phosphate. It is possible that this sample of quartz had been contaminated in the ball-mill.

Manganese. Teakle (141) reported that phosphate was least soluble in the presence of manganese chloride at about pH 6.3. He suggests that $Mn_3 (PO_4)_2$ might form in soil at this and slightly lower pH values.

Titanium. According to Pugh (114) titanium chloride can precipitate phosphate at low pH values, but the precipitate hydrolyses at pH values above about 6. Perkins and King (109) found that 100-mesh rutile sorbed up to 0.29 gm. H_3PO_4 per 100 gm. The greatest sorption was in the pH range 3.5-5.0.

5. Compounds with organic matter.

The retention of phosphate by the non-living organic matter in soil is usually believed to be small (13, 113). Doughty gave evidence that such retention as there is, is due to a reaction of the phosphate with Fe^{+++}, Al^{+++}, and Ca^{++} ions which are associated with the organic matter (36, 37). Chaminade reported that humus forms a complex with phosphate ions which is not readily precipitated by Ca^{++} ions, even at high pH values (16). Other workers have shown that the humate ion can replace the phosphate ions that are adsorbed by clay minerals and by artificial alumino-silicates (85).

The part played by soil micro-organisms in retaining phosphate has never been thoroughly investigated. Lockett (73) has referred to some of the early literature. Pierre, in 1948, in a valuable review, suggested that micro-organisms may immobilize a large amount of phosphate when a source of nitrogen and energy is available (113). A year earlier Taylor (140) had published the results of some preliminary experiments which led him to the same conclusion. He found that the sorption of phosphate by a garden soil was substantially increased by the addition of peptone, urea, and blood meal. Sterilization of the soil by heat and by certain chemicals prevented this increase, but did not reduce the amount of phosphate retained when no organic supplements had been given. The author therefore concluded that inorganic phosphate is unlikely to be metabolized by micro-organisms unless phosphate is their limiting growth factor in the soil. At the same time, addition of substances which stimulate the growth of micro-organisms leads to an absorption by the micro-organisms which may be appreciable. In Finland, Kaila has recently shown that the carbon/organic phosphorus ratio in soils is roughly constant at 100-150, but if the ratio exceeds 200, inorganic phosphorus is liable to be biologically absorbed (63).

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(For list of 162 References see the original paper pages 235-238 in the *Journal of Soil Science*, Volume 1, Number 2, January, 1950.)