# The Mechanism of Phosphorus Fixation in Soils and the Nature of Retained Phosphates

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Extensive studies have been carried out on the mechanism of phosphorus fixation in soils and the nature of retained phosphates. Nevertheless, this still remains a controversial subject.

There are two widely accepted theories regarding the mechanism of phosphorus fixation in soils, viz., (i) adsorption theory, and (ii) chemical precipitation theory. Various other hypotheses have also been proposed but they have received little support.

According to the adsorption concept, within certain ranges of reaction, phosphate retained is adsorbed on the surface of colloidal clay particles. Doughty (1929) considered that phosphate fixed by the soil even after removing iron and aluminium by leaching with dilute hydrochloric acid was due to physical adsorption. Kurtz *et al* (1946) found the relatiohship between phosphate retention and phosphate concentration to comply with the Freundlich adsorption isotherm and regarded the phosphate replaced by ammonium fluoride to be adsorptively held. Hibbard (1935) studied phosphate retention with different soil fractions and presented evidence that retention was greatest with the finest fraction and decreased as the particle size increased. Scarseth (1935), Davis (1935) and Owen (1947) have also contributed important papers supporting this view.

Several workers, on the other hand, favour the chemical precipitation hypothesis of phosphate fixation. In acid soils containing appreciable amounts of active iron and aluminium, soluble phosphates are believed to be reverted to insoluble phosphates of these elements. This view is supported by four types of evidence, viz .,

(i) Correlations have been obtained between phosphate sorption and the amounts of iron and aluminium in soils (Metzger, 1941; Raychaudhuri *et al*, 1941).

(ii) Removal of iron and aluminium from soil colloids has been found to reduce the magnitude of phosphate fixation (Ghani, 1943; Kelley *et al*, 1943; Metzger, 1940).

(iii) Addition of iron and aluminium compounds to soils has been shown to enhance phosphate fixation (Davis, 1943; Scarseth, 1935).

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(iv) Compounds formed during phosphate sorption have been identified by comparing the effect of pH on the solubility of iron and aluminium phosphates (Doughty, 1929; Scarseth, 1935).

More conclusive evidence that phosphorus fixation is a precipitation mechanism has been furnished by the fractionation studies of Ghani and Islam (1946) on the acid soils of India. When moist soils mixed with phosphate fertilisers were fractionated periodically they observed that reversion took place mainly to iron and aluminium phosphates, very little phosphate being fixed as calcium phosphate. Cole and Jackson (1950a, 1950b) using X-ray and electron diffraction techniques have shown that the compounds formed in the soil by the reaction of soluble phosphates with iron and aluminium are crystalline and possibly members of the variscite-barrandite-strengite isomorphous series. Haseman *et al* (1950) and Kittrick and Jackson (1955a, 1955b, 1955c, 1956) have also confirmed the formation of oxy- and hydroxyphosphates of iron and aluminium in the soil.

The aim of the present investigation was to clarify the behaviour of phosphates in the soil with a view to giving a clearer understanding of the mechanism of phosphorus fixation in soils and the nature of retained phosphates. Two lines of investigation indicated below were adopted:

(i) Amounts of native phosphate present in association with the clay and silt fractions of soils were determined. The soils were then brought to equilibrium with known amounts of soluble phosphate and the phosphate fixed by clay and silt was again estimated. Thus the added phosphate retained per gram of clay and silt was calculated. Obviously, if phosphate fixation is an adsorptive process, larger proportion of phosphate should be retained by the clay fraction which consists of smaller particles than silt.

(ii) Known amounts of phosphate were brought to equilibrium with soils and the treated samples chemically fractionated into different forms of phosphorus. By comparing these fractionation values with those of the untreated samples, the chemical form to which the added phosphate is converted was ascertained.

## Materials and Methods

Eight surface soils covering a wide pH range of 4.4 — 8.2 were used in this study. The chemical characteristics of these soils are shown in Table 1.

The procedure adopted for the various determinations is given below:

(i) *Relative amounts of phosphate retained by clay and silt*

10 g of the soil was weighed into a tall 600 ml beaker and treated with sodium hypobromite solution for the oxidation of organic matter as in Troell's method (1931) After treatment the excess hypobromite and washings were collected together with the soil washings and kept aside. The soil was then transferred to a tall-cylinder, the suspension made up to 500 ml, shaken well and pipetted for the clay and silt fractions into two weighed 100 ml Erlenmeyer flasks. The two fractions were evaporated to dryness and their weights determined. The amounts of clay and silt were thus obtained The residues were then digested with 20 ml

## TABLE  I

Chemical  character of soils

| Locality | pH | Sesquioxides per cent | CaO per cent | $P_2O_5$ per cent |
|----------|-----|----------------------|--------------|-------------------|
| Vazhappally | 4.4 | 15.22 | trace | 0.024 |
| Karaikkal | 5.5 | 27.30 | ,, | 0.078 |
| Kaviyoor | 6.4 | 26.30 | ,, | 0.093 |
| Vallamkulam | 6.8 | 35.26 | ,, | 0.256 |
| Ayikudi | 8.0 | 15.33 | 2.91 | 0.204 |
| Sampurvadakarai | 8.1 | 6.73 | 0.42 | 0.034 |
| Thiruppathisaram | 7.9 | 18.66 | 5.32 | 0.082 |
| Ponnamkulam | 8.2 | 5.70 | 1.36 | 0.028 |

1:1 HCl, filtered, made up to 100 ml and the phosphate in each determined. From this the phosphate retained by the clay and silt fractions was calculated. Only very small amounts of phosphate were released by the hypobromite treatment followed by the washings. The amount of phosphate associated with larger particles than silt was obtained by difference, but this too was an insignificant fraction. The percentages of clay and silt and the amounts of phosphate associated with these fractions are given in Table II.

## TABLE  II

Native  phosphate associated  with clay and silt

| Sl. No. | | Clay per cent | Silt per cent | $P_2O_5$ associated with clay mg | $P_2O_5$ associated with silt  mg | $P_2O_5/$ g of clay mg | $P_2O_5/$ g of silt mg |
|---------|---|---------------|---------------|------------------|------------------|--------|--------|
| 1. | Vazhappally | 33 | 19 | 10 | 7 | 0.30 | 0.37 |
| 2. | Karikkal | 39 | 32 | 18 | 20 | 0.46 | 0.63 |
| 3. | Kaviyoor | 15 | 23 | 2k | 44 | 1.73 | 1.91 |
| 4. | Vallamkulam | 28 | 36 | 110 | 112 | 3.93 | 3.11 |
| 5. | Ayikudi | 48 | 14 | 133 | 24 | 2.77 | 1.71 |
| 6. | Sampurvadakarai | 28 | 6 | 20 | 7 | 0.71 | 1.17 |
| 7. | Thiruppathisaram | 56 | 9 | 48 | 17 | 0.86 | 1.88 |
| 8. | Ponnamkulam | 17 | 20 | 8 | 13 | 0.47 | 0.65 |

10 g of the soil was then treated with 10 mg $P_2O_5$ as $KH_2PO_4$ in 100 ml solution and the suspension slowly boiled to dryness. The treated sample was fractionated and the phosphate in association with clay and silt determined. The amounts of added $P_2O_5$ retained in these two fractions were calculated by difference. The results are shown in Table III.

## TABLE III

Added phosphate retained by clay and silt

| Sl. No. | Locality | Clay per cent | Silt per cent | $P_2O_5$ associated with clay mg | $P_2O_5$ associated with silt mg | $P_2O_5/$ % of clay mg | $P_2O_5/$ g of silt mg |
|---|---|---|---|---|---|---|---|
| 1. | Vazhappally | 33 | 19 | 45 | 56 | 1.37 | 2.97 |
| 2. | Karaikkal | 39 | 32 | 40 | 45 | 1.03 | 1.41 |
| 1 | Kaviyoor | 15 | 23 | 34 | 31 | 2.27 | 1.35 |
| 4. | Vallamkulam | 28 | 36 | 5 | 80 | 0.18 | 2.22 |
| X | Ayikudi | 48 | 14 | 7 | 76 | 0.14 | 0.54 |
| 6. | Sampurvadakarai | 28 | 6 | 75 | 8 | 2.68 | 1.33 |
| 7. | Thiruppathisaram | 56 | 9 | 82 | 3 | 1.46 | 0.33 |
| 8. | Ponnamkulam | 17 | 20 | 67 | 15 | 3.97 | 0.75 |

(ii) *Relative amounts of added phosphate reverted to different forms of soil phosphorus*

To 5 g portions of the soil 50 ml lots of $KH_2PO_4$ solution containing 1 mg and *1* mg respectively of $P_2O_5$ were added. This would correspond to 20 and 40 mg respectively of $P_2O_5$ per 100 g soil. Two of the soils which contained very high amounts of native phosphorus were treated with 100 mg $P_2O_5$ per 100 g soil. The mixture of soil and solution was gently boiled to dryness, then moistened with distilled water and finally air-dried. 2 g of the treated sample was chemically fractionated into different forms of phosphorus by the method proposed by Dean (1938) and modified by Brito—Mutunayagam and Koshy (1951). From the fractionation values of the treated and untreated samples added phosphate retained by each fraction was obtained. The results are presented in Tables IV and V.

## TABLE IV

Chemical forms of soil phosphorus before and after addition of phosphate (mg. $P_2 O_5$ per 100 g. of soil)

| Sl. No. | Locality | Phosphate added | Acetic acid soluble | Alkali soluble in-organic | Organic | 2N. $H_2 SO_4$ Soluble | Inso-luble | Total |
|---|---|---|---|---|---|---|---|---|
| 1. | Vazhappally | 0.0 | 0.3 | 8.5 | 5.0 | 1.5 | 7.7 | 23.0 |
| | | 20.0 | 1.0 | 27.7 | 4.8 | 1.7 | 7.4 | 42.6 |
| | | 40.0 | 2.4 | 46.5 | 5.3 | 1.9 | 7.4 | 63.5 |
| 2. | Karaikkal | 0.0 * | .. | 22.9 | 17.2 | 10.7 | 28.0 | 78.8 |
| | | 20.0 | 0.2 | 42.0 | 17.1 | 10.8 | 28.8 | 989 |
| | | 40.0 | 0.4 | 62.2 | 17.0 | 10 0 | 28.4 | 118.0 |
| 3. | Kaviyoor | 0.0 | 0.1 | 36.4 | 10.9 | 8.1 | 40.1 | 95.6 |
| | | 20.0 | 0.5 | 52.5 | 10.9 | 9.8 | 40.1 | 113.8 |
| | | 40.0 | 1.5 | 72.0 | 11.0 | 10.5 | 40.1 | 135.1 |
| 4. | Vallamkulam | 0.0 | 0,6 | 86.4 | 86.4 | 25.5 | 64.0 | 262.9 |
| | | 100.0 | 3.0 | 176.0 | 86.8 | 34.5 | 64.0 | 364.3 |
| 5. | Ayikudi | 0.0 | 65.0 | 52.1 | 4.5 | 66.6 | 19.3 | 207.5 |
| | | 100.0 | 110.0 | 62.5 | 4.5 | 92.0 | 38.0 | 307.0 |
| 6. | Sampurvadakarai | 0.0 | 4.0 | 3.9 | 6.0 | 4.2 | 13.9 | 32.0 |
| | | 20.0 | 14.0 | 7.8 | 5.8 | 11.6 | 14.0 | 53.2 |
| | | 40.0 | 25.0 | 10.4 | 5.8 | 17.0 | 14.0 | 72.2 |
| 7. | Thiruppathisaram | 0.0 | 16.0 | 3.9 | 1.7 | 33.8 | 24.9 | 80.3 |
| | | 20.0 | 26.3 | 6.4 | 1.7 | 41.6 | 24.5 | 100.5 |
| | | 40.0 | 36.9 | 8.0 | 2.0 | 48.0 | 24.9 | 119.8 |
| 8. | Ponnamkulam | 0.0 | 1.7 | 3.8 | 0.4 | 11.3 | 7.5 | 24.7 |
| | | 20.0 | 12.5 | 3.8 | 0.5 | 19.0 | 7.8 | 43.6 |
| | | 40.0 | 23.8 | 3.8 | 0.4 | 29.0 | 7.5 | 64.5 |

## TABLE V

Chemical forms to which added phosphate is reverted in soils
(mg $P_2 O_5$ per 100 g of soil)

| Sl. No. | Locality | Phospha-te added | Added phosphate retained as | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | Acetic acid soluble | Alkali soluble inorganic | orga-nic | 2N $H_2$ $SO_4$ soluble | Insolu-ble | Total (sum) |
| 1. | Vazhappally | 20.0 | 0.7 | 19.2 | -0.2 | 0.2 | -0.3 | 19.6 |
| | | 40.0 | 2.1 | 38.0 | 0.3 | 0.4 | -0.3 | 40.5 |
| 2. | Karaikkal | 20.0 | 0.2 | 19.1 | -0.1 | 0.1 | 0.8 | 20.1 |
| | | 40.0 | 0.4 | 39.3 | -0.2 | -0.7 | 0.4 | 39.2 |
| 3. | Kaviyoor | 20.0 | 0.4 | 16.1 | 0.0 | 1.7 | 0.0 | 18.2 |
| fe | | 40.0 | 1.4 | 35.6 | 0.1 | 2.4 | 0.0 | 39.5 |
| 4. | Vallamkulam | 100.0 | 2.4 | 89.1 | 0.4 | 9.0 | 0.0 | 101.4 |
| 5. | Ayikudi | 100.0 | 45.0 | 10.4 | 0.0 | 25.4 | 18.7 | 99.5 |
| 6. | Sampurvadakarai | 20.0 | 10.0 | 3.9 | -0.2 | 7.4 | 0.1 | 21.2 |
| | | 40.0 | 21.0 | 6.5 | -0.2 | 12.8 | 0.1 | 40.2 |
| 7. | Thiruppathisaram | 20.0 | 10.3 | 2.5 | 0.0 | 7.8 | -0.4 | 20.2 |
| | | 40.0 | 20.9 | 4.1 | 0.3 | 14.2 | 0.0 | 39.5 |
| 8. | Ponnamkulam | 20.0 | 10.8 | 0.0 | (VI | 7.7 | 0.3 | 18.9 |
| | | 40.0 | 22.1 | 0.0 | 0.0 | 17.7 | 0.0 | 39.8 |

## Results and Discussion

The data in Table II reveal that more phosphate is fixed per gram of clay than per gram of silt only in two of the eight soils studied. In all the other soils, phosphate associated with one gram of silt is greater than the phosphate associated with one gram of clay. When the soils are treated with phosphate (Table III), in four of the samples, added phosphate shows a tendency to be fixed in greater proportions in the clay fraction, while ia the remaining samples phosphate is retained in greater proportions in the silt fraction. These findings are quite inconsistent with the hypothesis that phosphate retention is due to adsorption. No consideration has been given here to the chemical and electrochemical character of the clay and silt fractions. It is probable that the hypobromite treatment to which the soil was subjected may have affected to some extent the amounts of phosphate in association with clay and silt. Nevertheless, since clay particles are on an average only ©ne-tenth the size of silt particles, if surface adsorption is the true mechanism of phosphate fixation, a larger proportion of

the added phosphate must be retained by the clay fraction because it has greater surface area. Coleman (1944) found that fine kaolinite and montmorillonite clay fractions of two soils sorbed more than twice as much phosphate per gram of clay ($0.2 \mu$) as the corresponding coarse fractions ($0.2\mu$-$1.0\mu$). But in his studies the different size fractions were separated and fixation determined, whereas in the present investigation the soil was allowed to fix phosphorus and then fractionated. Raychaudhuri and Mukherjee (1941) have reported that unground kaolinite sorbs little phosphate and that the sorption capacity greatly increases when kaolinite is ball-milled. In this case, other factors like change in crystalline structure, etc., induced by ball-milling are probably involved and have contributed to enhanced fixation. It has to be borne in mind that fineness of division of reactants is an important factor which accelerates any type of chemical reaction. The view that phosphate fixed by soils from which free oxides of iron and aluminium have been removed by acid treatment is in the adsorbed state has been contradicted by Metzger (1940). He treated soil samples freed from iron and aluminium oxides with phosphate, then leached out the water-soluble phosphate and estimated the fixed phosphate that was replaced by the oxalate ion. It was found that only very small amounts of phosphate were replaced, thereby, indicating very little adsorption. It is important to note that the mere fact that the relation between phosphate concentration in solution and the retention of phosphate can be represented by the Freundlich adsorption isotherm does not necessarily imply an adsorption process because as pointed out by Fisher (1922) many precipitation reactions

also give results which fit the Freundlich isotherm.

The results of chemical fractionation studies, on the other hand, are far more conclusive and definite. The figures in Tables IV and V clearly indicate the transformation undergone by added soluble phosphate in the soil. The soils used in this study vary widely in reaction. Nos. 1—4 are acidic with large amounts of sesquioxides and only traces of calcium, whereas Nos. 5 – 8 are alkaline with appreciable amounts of calcinm carbonate. In all the acid soils the amount of added phosphate dissolved by acetic acid is very small ranging from $0.2 — 1.1$ mg when the rate of application is 20 mg $P_2 O_5$ per 100 g soil and $0.4 — 2.4$ mg for the higher dose of 40 mg $P_2 O_5$. In the alkaline soils, on the contrary, the major part of the added phosphate is recovered in the acetic acid soluble fraction. As acetic acid dissolves mono—, di—, and tri-calcium phosphates it is evident that in acid soils very little of the added phosphate is retained as calcium phosphates while in alkaline soils fixation is mainly as phosphates of this element. It will also be observed that the alkali soluble inorganic fraction comprising iron and aluminium phosphates is the major fraction to which reversion takes place in acid soils. In the alkaline soils, on the other hand, the amounts of phosphate reverted to this form are insignificant. The obvious conclusion is that in acid soils fixation is primarily due to the formation of insoluble phosphates of iron and aluminium whereas in alkaline and calcareous soils fixation is mainly in the form of apatite phosphates. As expected, there is practically no reversion of added phosphate to the organic and insoluble forms.

In the light of the evidence presented here the authors are of opinion that the dominant role in the fixation of phosphorus in soils must be assigned to chemical precipitation. The results do not, however, totally exclude the possibility that some of the precipitated compounds can also be adsorbed by the clay minerals of the soil by van der Waals' forces.

## Summary

An attempt has been made to clarify the behaviour of phosphates in the soil in order to give a clearer understanding of the mechanism of phosphorus fixation in soils and the nature of retained phosphates. The relative amounts of phosphate reverted to different chemical forms of soil phosphorus were determined.

The results obtained are inconsistent with the adsorption theory of phosphorus fixation which implies a far greater retention by the clay than by the silt. The evidence presented here is in favour of the chemical precipation theory, but does not, however, totally exclude the possibility of some adsorption by the clay minerals of the soil

## Acknowledgement

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