Another mechanism for the sorption of phosphate by soils and hydrous ferric oxide gels is through chemisorption at protonated ($-OH_2^+$) sites (Figure 7).
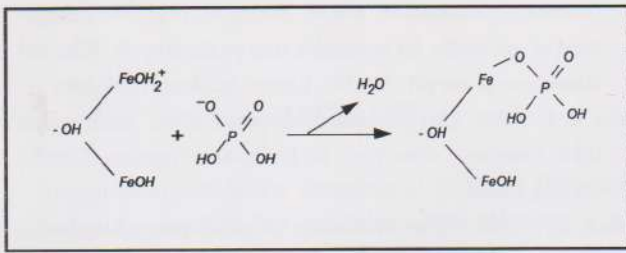

Figure 7. Mechanism for the sorption of phosphate by soils and hydrous ferric oxide gels is through chemisorption at protonated ($-OH_2^+$) sites

Figure 8 shows that very little phosphorus was retained by the Haplustoll soil. The Gibsihumox soil, consisting primarily of well-crystallized iron and aluminum oxides, gibbsite, goethite, and hematite, had considerably more phosphorus retention capacity. Greatest phosphorus fixation occurred with the Hydrandept soil composed principally of X-ray amorphous colloids and finely divided gibbsite and goethite (Kawai, 1980; Tisdale et al., 1985; Prasad and Power, 1997; Barreal et al., 2001).
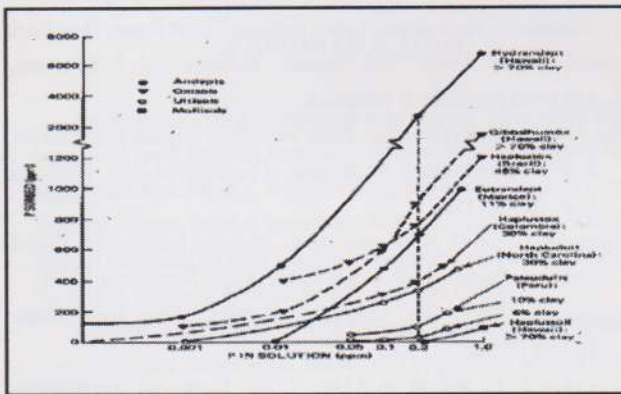

Figure 8. Examples of phosphorus sorption isotherms determined by the method of Fox and Kamprath (Tisdale et al., 1985).

Figure 9 illustrates the importance of pH in governing fixation reactions and thereby the availability of phosphates to plants. Miller and Donahue (1995) reported that phosphorus is most available near pH 6.5 for mineral soils and pH 5.5 for organic ones. Aluminum and Fe hydrous oxides sorb more P with decreasing pH (McDowell et al., 2001).
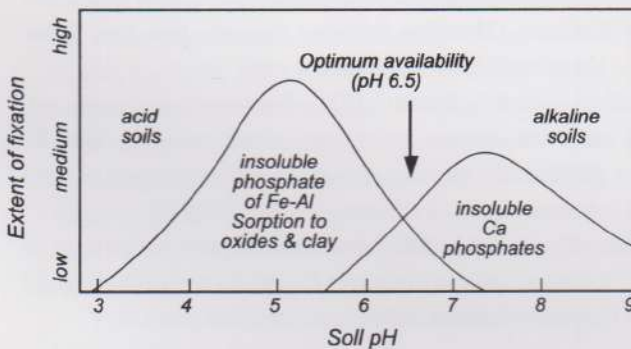

Figure. 9. Effect of pH on phosphate forms and extent of P fixation in soil (Stevenson and Cole, 1999)

Parfitt (1989) reported that the adsorption followed the order hematite < natural goethite < ferrihydrite < allophane which is the order of the calculated specific surface areas (Figure 10). The adsorption curve for 1 to 30 days, are presented in Figure 11. The increase with time followed the order goethite < ferrihydrite, hematite < allophane (Figure 12).
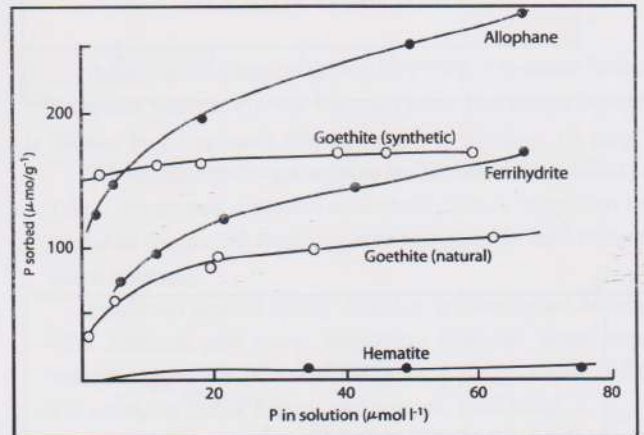

Figure. 10. Sorption curves for phosphate on 1 g of mineral (25 °C, 16 h shaking, 0.002 M $CaCl_2$)

The amount of inorganic P sorbed by a range of Fe- and Al- containing components varied appreciable and decreased in the order allophane > fresh Al gel > Fe gel pseudoboehmite > aged Al gel > dried Fe gel > Fe-coated kaolinite > haematite > goethite > akaganeite > gibbsite = ground kaolinite > dispersed kaolinite as shown in Figure 13 (McLaughlin et al., 1981).

MANAGING SOIL PHOSPHORUS

An effort to minimize phosphorus adsorption and to maximize phosphorus efficiency are as follows: maintain the soil pH between 6.0 and 7.0; promote as much relatively fresh organic matter in the soil; band phosphorus fertilizers for row crops; and anticipate less root absorption of phosphorus in cold weather.
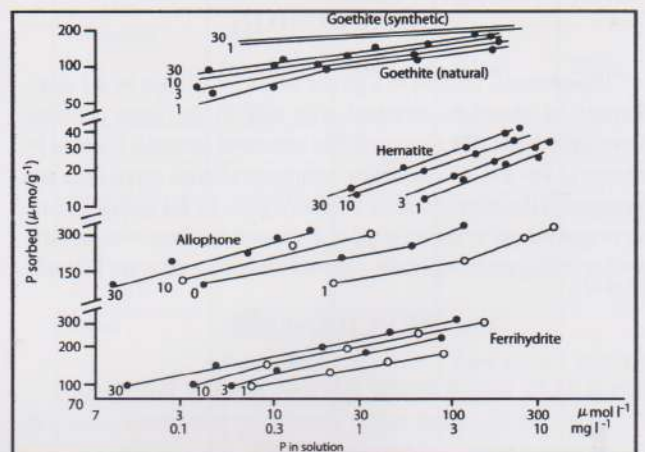

Figure. 11. Sorption curves for phosphate on 1 g of mineral with minimal shaking for 1-30 d
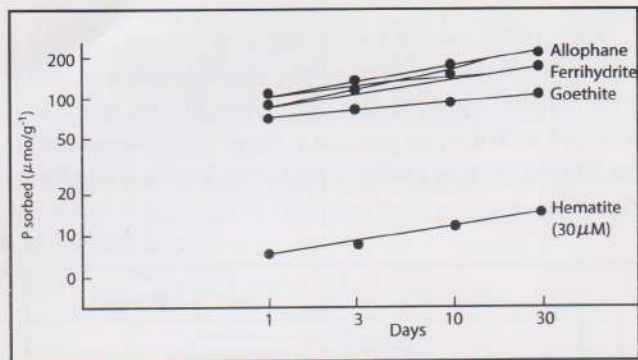
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Figure 12. Sorption of phosphate with time on 1 g of mineral at 10 umol P/l final solution concentration
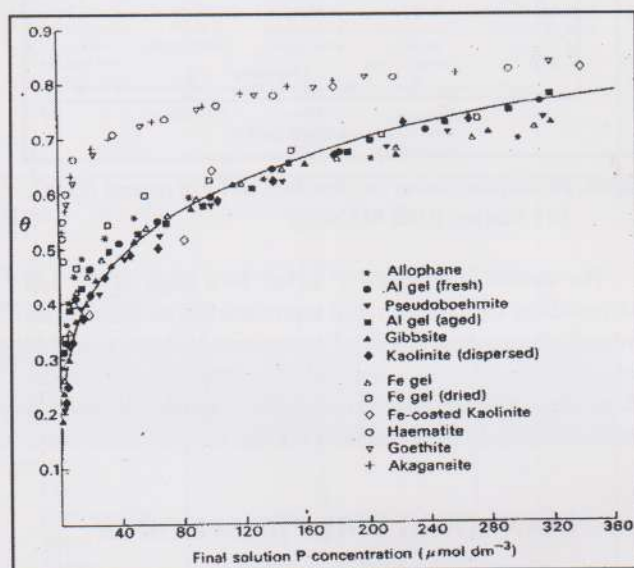

Figure. 13. Isotherms for the sorption of P by the sorbents indicated plotted as the fractional saturation of the sorption maximum () for each sorbent against final solution P concentration at 168 h.

CONCLUSION

Phosphorus is retained to a greater extent by 1:1 than by 2:1 clays. Sorption of phosphate increased with time in the order goethite< ferrihydrite, hematite < allophane. The amount of inorganic P sorbed by a range of Fe- and Al- containing components varied appreciable and decreased in the order allophane > fresh Al gel > Fe gel pseudoboehmite > aged Al gel > dried Fe gel > Fe-coated kaolinite > hematite > goethite > akaganeite > gibbsite = ground kaolinite > dispersed kaolinite.

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CLAY MINERALS AS A FACTOR THAT INFLUENCE PHOSPHORUS RETENTION IN SOILS

Ali Jamil

ABSTRAK

Tanah-tanah tropik masam, yang termasuk kedalam kelompok Ordo Ultisol dan Oksisol adalah tanah-tanah melapuk lanjut, mengandung dalam jumlah banyak koloid liat bermuatan variable , mempunyai pH tanah (tanah:air = 1:1) lebih rendah dari 5,0 dan mempunyai kapasitas tukar kation (KTK) rendah (biasanya lebih kecil dari 10 cmol(+)kg^{-1}) dengan kandungan kejenuhan basa yang rendah dan kejenuhan aluminium (Al) yang sangat tinggi, dengan banyak nilai diatas 80%. Fosfor tersedia bagi tanaman rendah, seperti halnya juga kandungan kalium, kalsium, dan magnesium dapat dipertukarkan. Pada tanah-tanah masam, reaksi antara fosfat dan komponen-komponen non biologi tanah melibatkan permukaan aktif dari atom-atom Fe dan Al. Mineral-mineral tanah seperti allofan, ferrihidrit dan gutit, hematite dan kaolinit adalah jenis yang sangat reaktif. Mineral-mineral tersebut bersama dengan kompleks humus-Al merupakan komponen yang mungkin paling aktif bereaksi dengan fosfat dalam tanah-tanah masam. Kapasitas penjerapan fosfor (P) oleh mineral-mineral liat tergantung kepada banyak faktor; antara lain proporsi luas permukaan yang ditempatinya. Sebenarnya, kaolinit (liat 1:1) menjerap lebih banyak P per unit luas permukaan dibandingkan dengan mineral liat 2:1. Tanah-tanah dengan kandungan andik seperti Andisol memiliki kapasitas retensi anion yang tinggi, berhubungan dengan kandungan senyawa Al dan Fe yang tinggi. Retensi senyawa PO4 oleh mineral-mineral tanah bervariasi meningkat dengan urutan: hematite < gutit alam < ferrihidrit < allofan. Jumlah P-anorganik yang dijerap oleh senyawa-senyawa yang mengandung Fe dan Al bervariasi dan menurun dengan urutan : allofan > gel Al segar > gel pseodobumit Fe > gel Al tua > gel Fe kering > Fe terikat kaolinit > hematir > gutit > akaganit > gibsit = kaolinit > kaolinit terdispersi. Gel Al menjerap P sebanyak 30 sampai 70 kali lebih banyak dari gibsit, dan gel Fe menjerap sekitar 10 kali lebih banyak dari bentuk mineral kristalin yang sama (hematite, gutit, dan akagenit).

Kata kunci : Minereal liat, mempengaruhi, fosfor, retensi

INTRODUCTION

Acid tropical soils, which belong to the orders Ultisol and Oxisols, they are highly weathered, contain large amounts of variable charge colloids, have a soil pH (1:1) below 5.0, have a low CEC (usually < 10 cmol(+)kg^{-1}) with low base saturation and very high aluminum saturation (Edwards et al., 1991).

Some of the phosphate added to soils in fertilizers is frequently converted to an insoluble form and fixed in soil. Such fixation can be due to the formation of insoluble salts of iron, aluminum, or alkaline earths. Aluminum in the form of silicate, hydrous oxide, and oxide minerals is an abundant soil constituent that reacts strongly with orthophosphate. Kaolinite or possibility halloysite, has the highest power of all the clay minerals for phosphate fixation (Grim, 1968; Veith and Sposito, 1977; Roy and De Datta, 1985; Miller and Donahue, 1995).

PHOSPHORUS IN THE SOIL

Phosphorus is the second key plant nutrient, it is the second most often deficient nutrient. A phosphorus cycle is shown in Figure 1 (Miller and Donahue, 1995).

Phosphorus in solution is present as primary or secondary orthophosphate ions ($H_2PO_4^-$ or HPO_4^{2-}) both of which are capable of direct absorption by plant roots. Phosphorus is needed for favorable seed formation, root development, strength of straw in cereal crops, and crop maturity. P requirements of plant as given in Table 1.

Factors that influence of phosphorus availability in soil: soil pH, texture, clay mineral, organic matter content, soil moisture, and temperature (Chavarria, 1982). Stevenson and Cole (1999) reported that much of the P applied to soils is converted to one of many insoluble or complex forms (Figure 2).

CLAY MINERALS IN SOIL

Silicate clay minerals

Silicate clay minerals groups are the **kandites** (1:1 layer silicates), the **smectites** (2:1 layer silicates), and chlorite (2:1:1 layer silicate) (Sposito,1989; Singer and Munns, 1996). Layer silicate minerals are differentiated into 5 different types (Bohn et al, 1979) and it is shown in Table 2.

Non silicate clay minerals

Some soils contain an abundance of clay-sized minerals that have some of properties of silicate clays but they do not have Si as the main building block. These are **sesquioxides or hydrous oxides** of iron and aluminum. The amorphous mineral are given the general name **allophane**.
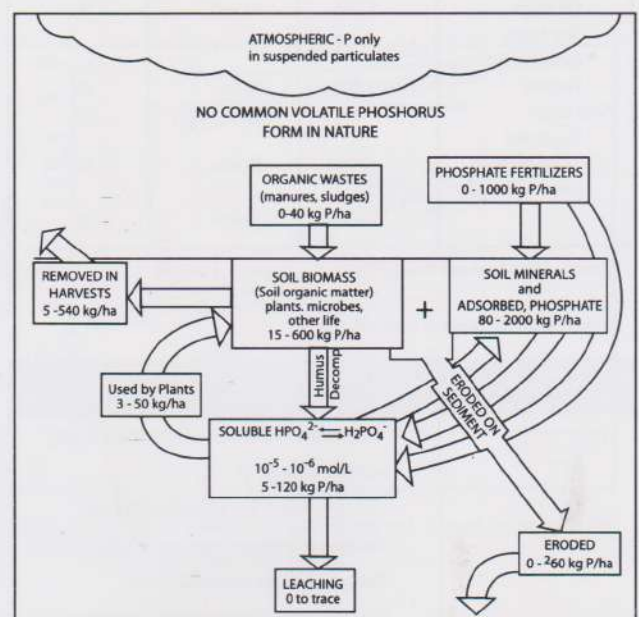

Figure 1. The phosphorus cycle showing gains, losses, and transformations in the soil

These minerals have a variable charge or a pH dependent charge, because the charge changes greatly depending on the H^+ concentration and also at the broken edge of the crystal or on the surfaces of amorphous particles, exposed –AlOH or –FeOH groups have an amphoteric character being able to accept or

lose hydrogen ions depending on the pH of the solution with which they are in contact (Figure 3 and 4). The lines to the Al indicate that it is part of an octahedral sheet.
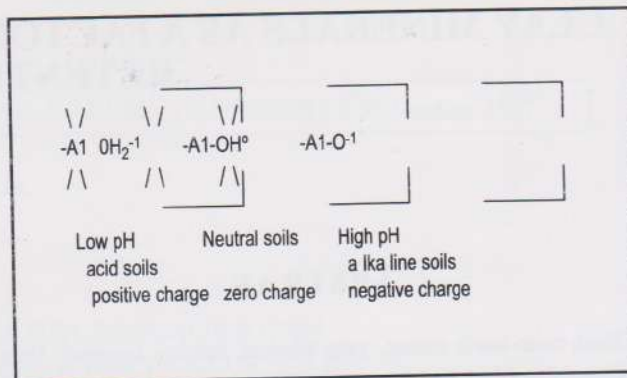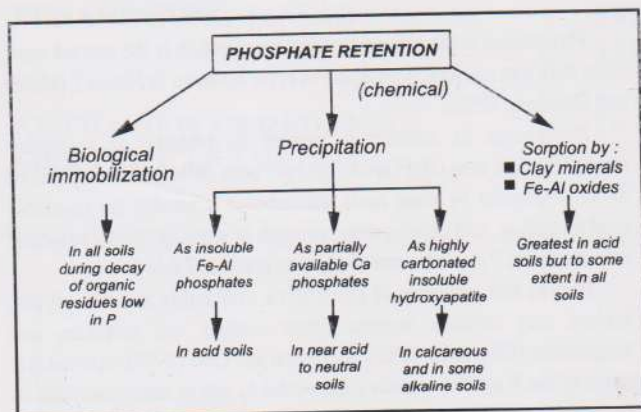

Figure 2. Phosphate fixation reaction in soil

Table 1. Approximate amounts of P removed from the soil per season by specific crops

Crop	Yield		P removed (kg/ha)
	kg/ha	units/acre	
Grains			
Corn			
Grain sorghum	12,544	200 bu	152
Wheat	8,064	8,000 lb	54
Barley	5,376	80 bu	34
Oats	5,376	100 bu	28
Rice	3,584	100 bu	22
Forage crops	7,280	145 bu	25
Alfalfa			
Clovers	12,544	6 tons	35
Grasses (general)	8,064	4 tons	20
Oil crops	8,064	4 tons	20
Soy beans			
(beans only)			
Peanuts	3,360	50 bu	25
Fiber crops	3,360	3,000 lb	22
Sugarcane			
Sugar beets	67,200	30 tons	19
(roots and tops)			
	67,200	30 tons	28

Source : Stevenson and Cole (1999)

Table 2. Differentiation of layer silicates

Number	Items
1	The number and sequence of tetrahedral and octahedral sheets
2	The layer charge per unit cell of structure
3	The type of interayer bond and interlayer cations
4	The cations in the octahedral sheets
5	The type of stacking along the c-dimenstion

Source: Bohn et al. (1979)

2

Figure 4. The development of charge (Rowell, 1994)

CLAY MINERALS AS A FACTOR THAT INFLUENCE PHOSPHORUS RETENTION IN SOILS

Phosphorus is retained to a greater extent by 1:1 than by 2:1 clays. Kaolinitic clays will retain larger quantities of added phosphorus than those containing the 2:1 type due to the higher amounts of hydrated oxides of iron and aluminum associated with kaolinitic clays and also kaolinite with a low SiO_2/R_2O_3 ratio will fix larger quantities of phosphorus than clays with a high ratio. P retention by kaolinite increased with time is as shown in Figure 5 (Prasad and Power, 1997).
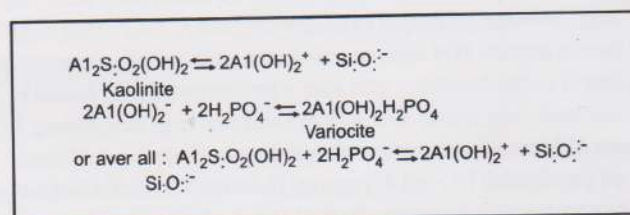

Figure 5. The reaction between Kaolinite and phosphate

Adsorption of phosphate at hydrous oxide surfaces through a ligand binding mechanism (replacement of H2O and/or OH) is one of the important processes affecting phosphate availability to plants (Figure 6) (Tan, 1994; Sui and Thompson, 2000; De Cristofaro, 200); Zhou and Li, 2001).
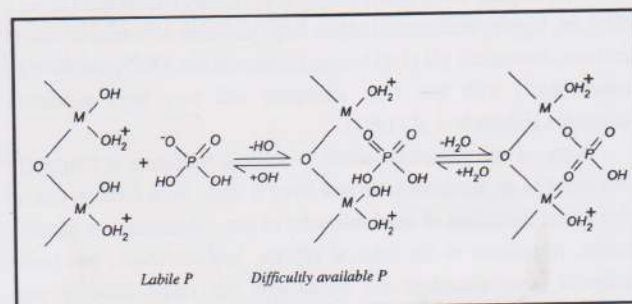

Figgure 6. Adsorption of phosphate at hydrous oxide surfaces through a ligand binding mechanism (replacement of H_2O and/or OH)