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Implications of Soil Chemical Interactions on the Management of Fertilizers in Oxisols

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Implications of soil chemical interactions on the management of fertilizers in oxisols

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Sumário

Resumo

A agricultura no Brasil é praticada predominantemente em latossolos, solos que encontram-se em estágio avançado de intemperismo, com predominância de óxidos de ferro e alumínio. A maioria desses solos são ácidos, pobres em nutrientes minerais (P, K, Ca e Mg) e de permeabilidade elevada. Além disso esses solos possuem baixa capacidade de troca catiônica, portanto os insumos aplicados na forma de sais solúveis são, em parte, perdidos por lixiviação, que é mais elevada no período chuvoso, quando as atividades agrícolas são mais intensas, visto que no Brasil predomina a agricultura de sequeiro.

O foco desse capítulo é uma abordagem sobre o manejo racional do emprego de fertilizantes em sistemas de produção agrícola enfatizando os aspectos e as interações físico-química dos latossolos.

Abstract

The Brazilian agriculture is predominantly established in Oxisols, soils that are in an advanced stage of weathering, with a predominance of Fe and Al oxides. The majority of these soils are acidic, poor in chemical nutrients (P, K, Ca and Mg) and with high permeability. In addition, these soils are characterized by low cation exchange capacity, and as such, fertilizers applied as soluble salts are, in part, lost by leaching, which is higher during the raining season, when the agricultural activities are more intense, as in Brazil predominates the non-irrigated agriculture.
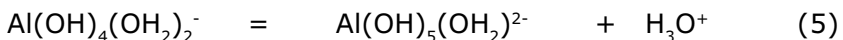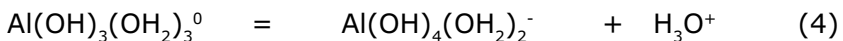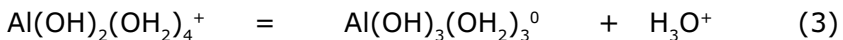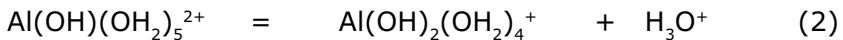
The focus of this chapter is an approach about the racional management of fertilizers in crop production systems emphasizing physico-chemical aspects and interaction of Oxisols.

1. Introduction

In Brazil, Oxisols occupy an area estimated to be of approximately 100 million hectares (Malavolta and Kliemann, 1985). The weathering sequence that generated these soils have as necessary reagents, H_2O and H^+ and as products dissolved silica and cations that are leached (Garrels and Christ, 1965). The result is that the granulometric clay fraction of Oxisols is dominated by Fe and Al oxides and hydroxides, and kaolinite.

These soils are characterized by acidic pH, high Al, low CEC (cation exchange capacity), low base saturation and high fixation capacity of oxyanions such as phosphate and sulfate. Malavolta and Kliemann (1985) show Oxisols data implying that these soils are like "a great nutritional desorder that requires a lot of limestone and fertilizers, particularly phosphorus to be corrected".

The acidity of Oxisols is intimately linked to the solution chemistry of Al, which is toxic to plants. Al is present in solution in a solvation shell of 6 water molecules. The species hydrolyses in various degrees depending on the pH (Bohn et al., 1979):

$$Al(OH_2)_6^{3+} \quad = \quad Al(OH)(OH_2)_5^{2+} \quad + \quad H_3O^+ \qquad (1)$$

$$Al(OH)(OH_2)_5^{2+} \quad = \quad Al(OH)_2(OH_2)_4^+ \quad + \quad H_3O^+ \qquad (2)$$

$$Al(OH)_2(OH_2)_4^+ \quad = \quad Al(OH)_3(OH_2)_3^0 \quad + \quad H_3O^+ \qquad (3)$$

$$Al(OH)_3(OH_2)_3^0 \quad = \quad Al(OH)_4(OH_2)_2^- \quad + \quad H_3O^+ \qquad (4)$$

$$Al(OH)_4(OH_2)_2^- \quad = \quad Al(OH)_5(OH_2)^{2-} \quad + \quad H_3O^+ \qquad (5)$$
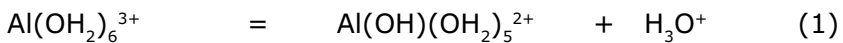
The $Al(OH)(OH_2)_5^{2+}$ form is of minor importance because it occurs only at a narrow pH range. The $Al(OH)_5(OH_2)^{2-}$ occurs at pH values above those of soils. $Al(OH_2)_6^{3+}$ is predominant below pH 4.7, and is preferred over other cations with less charge at the exchangeable site of colloids, promoting the leaching of Ca, Mg, K and trace metals. $Al(OH)_2(OH_2)_4^+$ is the predominant form

between pH 4.7 and 6.5. $Al(OH)_3(OH_2)_3^0$ is the predominant form between 6.5 and 8.0. $Al(OH)_4(OH_2)_2^-$ is predominant above pH 8.

Solid phase $Al(OH)_3$ precipitates when its solubility product is exceeded, which is the rational behind the strategy to raise the pH above a value of 5.5 to make the Al unavailable to plants. Thus a common fundamental practice in the management of Oxisols is the application of limestone which provides Ca and hydroxyls:

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^- \qquad (6)$$

The hydroxyl ions produced neutralize soil acidity, raise the soil pH, which in turn promotes Al precipitation and increases the CEC of the soil.

Liming, however, may be effective only to the layer in which it was applied and consequently the rizosphere is restricted to that layer. One strategy to control Al availability in deeper layers is to apply gypsum (Reeve and Sumner, 1972; Ritchey et al., 1980; Pavan et al., 1984). The transport of Ca^{2+} downwards is promoted by SO_4^{2-} as the accompanying ligand, forming the complex ion $CaSO_4^0$ which is leached and dissociates. The Ca^{2+} exchanges with surface complexed Al^{3+} which in turn complexes in solution with SO_4^{2-} forming the non toxic $AlSO_4^+$ species.

It is important to note that application of gypsum does not alter the soil pH. Also, Ca^{2+} ions may displace K^+ and Mg^{2+} from the exchangeable sites. Malavolta and Kliemann (1985) call attention for the possibility of applying limestone and gypsum in combination to avoid these potential losses.

Manganese and Iron toxicities should also be of concern for crop production in Oxisols. Manganese occurs in the soil in three valence states: Mn^{2+} , Mn^{3+} (as Mn_2O_3) and Mn^{4+} (a very stable oxide). The level of Mn^{2+} in the soil solution, available for plants depends on the pH, oxidation-reduction and microbiology of the soil. Mn toxicity may occur with decreased aeration due to compaction and floding, promoting an excess of the Mn^{2+} form. Same conditions that lead to Mn toxicity may lead to Fe toxicity as well. Liming acid soils usually control both Al and Mn toxicities.

2. Surface charge

At the edges, the constituent metal ions are unable to complete their coordination pattern existing in the bulk of the crystal. The result is unsatisfied bonds. In this case, the metal ion coordinates with OH groups, producing an hydroxylated surface which may accept or donate protons depending on the pH of the solution. An excess of protons will render the surface positive while the dissociation of surface hydroxyls will render the surface negative. Hence, protons and hydroxyls are referred as potential determining ions (PDI) and the surface charge depends on the pH of the environment, and as such referred as variable charge. Usually, Oxisols have a pH close to the Point of Zero Charge (PZC), which was referred as isoelectric weathering (Mattson, 1932), and thus their net surface charge is close to zero.

3. Phosphate fixation

One of the main restrictions of crop production systems in Oxisols is the management of phosphate fertilizers, because phosphate is highly sorbed by Fe-Al oxides and becomes unavailable for plant uptake.

Infrared spectroscopic techniques were used to obtain a structural model for the surface reaction between iron oxides and phosphate ions (Parfitt, 1975). Results indicated that the principal mode of adsorption on all of the iron oxides studied was via a strongly bonded binuclear complex, in which two of the oxygen atoms of the phosphate ion are coordinated each to different Fe^{3+} ions on the surface. In this process, two surface hydroxyl ions or water molecules are replaced by one phosphate ion (ligand exchange). The changes in infrared spectra of surface OH^- groups and of phosphate ions, which are due to the coordination to Fe^{3+}, were contrasted with the absence of spectral changes for adsorption of nitrate or chloride.

Jurinak (1966) visualized the replacement or exchange of each surface OH by the H_2PO_4 anion as being accomplished by the tip of the apial oxygen of the PO_4 tetrahedron with the two protons associated with the 3 basal oxygens that are oriented parallel to the surface. The product is then a surface having an increased OH density with the central coordinating ion now being P instead of Fe. Because the OH population would essentially double based upon the proposed mechanism, and because the amount of adsorbed water molecules did not vary in samples of hematite treated with P, the author concluded that the physically adsorbed water is H-bonded to only one proton of the H_2PO_4 group. The tenacity with which the second proton of this group is held to the surface was manifested in the high temperature required to remove the traces of the OH water. Jurinak (1966) showed that the surface area of hematite was increased from 9.9 m^2/g to 11.1 m^2/g upon P adsorption.

Due to the high phosphate sorption capacity of Oxisols, one strategy for crop production in this soil is a massive application

of broadcast P fertilizers in the first cropping year, followed by successive band applications at subsequent years (Yost et al., 1979). The good results achieved with this management result from the initial saturation of the strongly adsorbing phosphate surface sites so that subsequent additions will provide a more available phosphorus for crop production. Thus, a feature of crop production systems in the savanna regions of Brazil and in many parts of the world is that agricultural inputs are made in a soil previously fertilized with phosphorus. The management of P have consequences on the CEC and on the retention and mobility of other chemical species.

4. Effect of phosphate fertilization on surface charge

The net surface charge becomes more negative when phosphate reacts with variable charge soils (Mekaru and Uehara, 1972; Fey and Le Roux, 1976; Wann and Uehara, 1978a; Bolan and Barrow, 1984). In this case, the ion is no longer acting as an exchangeable counter ion but rather as a PDI.

Hingston (1970) concluded that the values for the average change in surface charge per unit amount of anion adsorbed were characteristic of the anion and the surface, but did not vary with amount of anion adsorbed. In contrast, Rajan (1976) reported that the negative charge added to the surface per unit amount of anion adsorbed decreased with phosphate adsorption, and this decrease was followed by an abrupt increase and then remained constant at higher levels of phosphate adsorption. At low surface coverage, phosphate is adsorbed at positive sites displacing aquo-groups with a rapid neutralization of charge. At higher surface coverage, phosphate is adsorbed at neutral sites displacing hydroxyl ions, with little change in surface charge. The abrupt change in net surface charge at high levels of phosphate adsorption was interpreted as disruption of hydrous-alumina polymers creating new surface sites; and with the fresh surface thus exposed, extra phosphate is adsorbed. Ryden et al. (1977) observed that the surface negative charge increased linearly for the initial levels of adsorption, it remained constant at intermediate levels of adsorption, and there was a linear increase at high levels of adsorption. Their model for phosphate adsorption contained three distinct regions and they postulated different reaction mechanisms in each region, which was criticized in other studies (Posner and Bowden, 1980; Sposito, 1982; White, 1980).

Bolan and Barrow (1984) used the model of Bowden et al. (1973, 1974) to describe the effects of anion adsorbed on the change in surface charge upon P adsorption. The authors claimed that the ligand exchange reactions with aquo-groups and hydroxyl-groups are not sufficient to explain the fact that there is always

some negative charge conveyed to the surface and the amount
is always less than the charge on the phosphate anion adsorbed.
A theory involving the balance of surface charge by the ions that
constitute the background electrolyte, and the position these ions
occupy in the double layer (Bolan and Barrow, 1984), was invoked
to explain all the above observations. The theory states that at
pH values below the PZC the surface is positively charged. In the
absence of P adsorption, this positive charge on the surface is
balanced by electrolyte anions. At low adsorption of P, the negative
charge on the adsorbed P is largely balanced by displacing these
electrolyte anions. Therefore, the decrease in positive charge on
the surface would be rapid initially. With increased P adsorption
there are fewer electrolyte anions to be displaced and greater
tendency for the negative charge on the adsorbed phosphate to
be balanced by adsorption of H^+ (or release of OH^-) onto the
surface plane. The net charge conveyed to the surface is therefore
smaller and the change in surface charge with P adsorption
flattens. When the surface becomes negative (at pH values above
the PZC or at high levels of P adsorption), the charge on the
adsorbed P can be balanced by the adsorption of electrolyte cations
and the balancing of the charge moves increasingly to the region
outside the boundary of the surface. The result is an increase in
charge conveyed to the surface at high levels of P. The conflict
with the conclusion (Rajan, 1976) that at high levels of adsorption,
phosphate promotes disruption of particles producing new sites
is obvious. The above theory (Bolan and Barrow, 1984) associated
with the model of Bowden et al. (1977) also explains why the
negative charge added to the surface per mole of sulfate adsorbed
onto gibbsite (Hingston, 1981) is greater than that added by
phosphate adsorption: sulfate has a less intimate degree of
complexation with the surface as compared to phosphate, thus
the mean plane for adsorption of sulfate is further from the surface
relative to phosphate. In this case, the charge balance on sulfate
adsorption is further from the surface as compared to the balance
on phosphate. The further the adsorbed ion is from the surface,
the more likely the balance of surface charge will be effected by
the background electrolyte. Hence the induced background
electrolyte charge will be larger. On the other hand, the closer
the adsorbed ion is to the surface, the more likely the ligand
exchange process will occur and the charge conveyed to the
surface will be smaller. Bolan and Barrow (1984) also showed

that increasing the ionic strength of the system, by increasing the concentration of the background electrolyte, resulted in an increased availability of electrolyte ions, which caused the balance of charge, upon adsorption, to move outside the boundary of the surface. So, the charge conveyed to the surface at high ionic strength is greater.

The amount of negative charge conveyed to the surface upon phosphate adsorption should be less than the charge on the phosphate anion adsorbed (Bolan and Barrow, 1984). Melamed (1993) found that -1.1 and -0.7 mmolc were added to the surface per each mmol of phosphate added as estimated by potentiometric titration and ion adsorption, respectively, which are in close agreement to those of Mekaru and Uehara (1972) who found that -0.8 mmolc were added per mmol of phosphate adsorbed.

The effect of the phosphate ion on the surface charge character of an Oxisol of the Central Plateau of Brazil was to shift the PZC to lower pH values, and to make the net negative surface charge more negative at any pH value above the corresponding PZC. The presence of phosphate had a stronger impact on CEC and AEC of this Oxisol than would be expected from the variation in pH alone. CEC was significantly increased, i.e., the negative charge at a given pH became more negative in the presence of phosphate. By the same token, AEC was lowered, or, the positive charge decreased as the levels of phosphate treatment increased (Melamed, 1993).

5. Interactions of phosphate sorption and soil pH

Hingston et al. (1972) showed that there was a general trend for phosphate adsorption to decrease as the pH increased. Barrow (1987) points out that there were bends in the curves near some of the pK values of the relevant acid and that a particular characteristic of anion adsorption is that a well defined adsorption maximum can be specified. These bends in the slopes of phosphate adsorption envelopes were also noted by Obihara and Russel (1972).

For anions that protonate, such as HPO_4^{2-}, an increase in pH produces an "adsorption envelope" that reflects the competition between the surface site and anion for the decreasing presence of the proton as well as increasing anion repulsion (Sposito, 1989).

Another possible reaction that contributes to the reduction of anion adsorption with increasing pH involves the competition of OH^- for a site containing a complexed anion:

$$S\text{-}OH_2^+(s) + A^-(aq) = SA^0(s) + H_2O \tag{7}$$

$$SA^0(s) + OH^-(aq) = S\text{-}OH^0(s) + A^-(aq) \tag{8}$$

$$S\text{-}OH^0(s) + OH^-(aq) = S\text{-}O^-(s) + H_2O \tag{9}$$
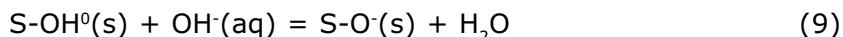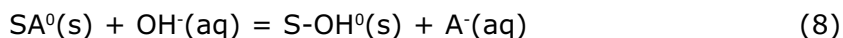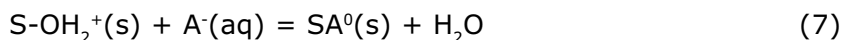
where

SOH_2^+ is the positive site,

SOH^0 is the neutral site,

A- is the specifically adsorbed anion.

In this sense, the OH$^-$ species is an effective competing ion in addition of being a potential determining ion. The decreasing adsorption of anions with increasing pH indicates the overriding importance of the H$^+$/OH$^-$ ion couple with regards to soil functional groups.

Because adsorption of phosphate involves ligand exchange it is expected that P additions to suspensions should increase the pH of the soil solution. However, Lutz and Haque (1975) found that only higher rates of phosphate treated kaolinite affected the suspension pH. H_3PO_4 treatment to the clays decreased their pH and $CaH_4(PO_4)_2$ treatment increased the pH of kaolinite. Both sources of P increased the zeta potential and hydration of the clays although these increases were irregular.

Rajan and Fox (1975) showed that the adsorption of P increased the solution pH up to a point and then either remained constant for one soil or decreased for another soil.

Treatments of 16.2, 32.4 and 48.6 mmol P/kg of Oxisol increased the equilibrium column pH from 5.5 to 5.8, 6.0 and 6.5, respectively (Melamed et al., 1995).

6. The effect of phosphate fertilization on the availability of other nutrients

The effect of phosphate on the electrical properties of soil surfaces is important in agricultural systems because it can alter the retention and mobility of chemical species. Phosphate can effectively increase the mobility of anions that form inner-sphere surface complexes, such as sulfate (Chao et al. 1962), and of anions that form outer-sphere surface complexes, such as nitrate (Mekaru and Uehara, 1972; Kinjo and Pratt, 1971; Wann and Uehara, 1978b) and decrease the leaching of Ca and K.

6.1 Anionic species

Studies by Chao et al. (1962), indicated only slight effects of P on sulfate movement on a Aiken soil with 57% clay and 6.84% Fe_2O_3, while in Willamette soil with 29% clay and 2.37% Fe_2O_3, P had an appreciable effect on S-SO_4^{2-} movement, increasing its activity in the leachate. The leaching loss of sulfate ranged from 17% with no P applied to 28% at the lowest level of P. At higher rates no further increase in sulfate movement was observed.

Decreases in the adsorption of anions such as SO_4^{2-} in the presence of phosphate were also reported (Ryden et al., 1987). Bolan et al. (1988) have demonstrated that incubation of soils with P resulted in an increase in net negative charge and a decrease in sulfate adsorption in batch experiments and early BTC of sulfate in column studies.

Adsorption studies on a Brazilian Oxisol (Kinjo and Pratt, 1971) showed that negative adsorption of NO_3^- occured when $H_2PO_4^-$ exceeded certain concentration levels. Mekaru and Uehara (1972) found negative adsorption of nitrate when phosphate was added to soil colloidal suspensions which were initially positively charged.

Negative adsorption has been shown to be an important phenomena in considering the movement of anions through soil (Bond et al., 1982; Krupp et al., 1972; James and Rubin, 1986; Thomas and Swoboda, 1970). Negative adsorption, preferably termed anion exclusion in solute transport theory, refers to the repulsion of anions at a negatively charged soil surface (Schofield, 1947). The phenomena gives rise to a local deficit of anions in the vicinity of negatively charged particles and an excess of anions in the bulk solution (De Haan and Bolt, 1963). The importance of anion exclusion is that anions are removed from the relative immobile water associated with the diffuse double layer and positioned in the faster moving pore water. The result is that the average velocity of the anion is greater than the average pore water velocity (Smith, 1972). The volume of water immediately adjacent to the clay surfaces does not hold anions, does not participate in the leaching reaction and so, the larger the anion exclusion volume, the greater the mobility of salt at a given soil water content and water application (Thomas and Swoboda, 1970).

Onken et al. (1977) pointed out that both bromide and chloride could be used as an indicator of nitrate movement due to their similar interaction with the soil surface, and neither bromide or chloride are subjected to biological transformations as is the nitrate ion. The usefulness of the Br anion as a tracer for nitrate in column studies was demonstrated by Smith and Davis (1974). Br is used in preference over the Cl anion, due to its low concentration in soils and waters and because its ionic radii resembles that of nitrate more closely than does the ionic radii of Cl^-. Melamed et al. (1994) showed that the presence of phosphate at surface sites induced a faster movement of Br^- through Oxisol soil columns. Analysis of their breakthrough curves (BTC) indicated that Br^- movement was actually retarded in the non-treated Oxisol soil column. As the levels of phosphate treatment increased, Br^- mobility progressively increased as reflected by the shifts in BTCs to the left. The extent of the effect of phosphate on the mobility of Br^- in this soil resulted in retardation factors less than 1 implying anion exclusion of Br^-. This was especially noted at the two higher phosphate treatment levels. These results are corroborated by batch adsorption experiments (Kinjo and Pratt, 1971) that demonstrated Oxisols are able to adsorb anions that form outer-sphere surface complex, that these soils showed a slight

preference for Cl^- adsorption over NO_3^- adsorption, and that negative adsorption of NO_3^- occured when sulfate or phosphate exceeded certain concentration levels.

6.2 Cationic species

Wann and Uehara (1978b) showed that the position of K-BTCs from an Oxisol depended on the anion accompanying the K tracer. The K concentration in the effluent attained one-half of the influent concentration at 4.25 pore volumes when the accompanying anion was Cl^-, while it took 8.20 pore volumes when the accompanying anion was $H_2PO_4^-$. They attributed the marked differences in the shape and position of BTC to changes in CEC associated with anion adsorption. The shifts in the K-BTCs to the right were significantly related to a lowering of the PZC, which was in turn related to levels of applied phosphorus. Phosphate additions to soils have also been shown to increase the adsorption of cations such as Ca^{2+} (Ryden and Syers, 1976).

Helyar et al. (1976) postulated a surface complex consisting of two adjacent adsorbed phosphate ions and a central divalent cation of appropriate size such as Ca, charge and coordinating properties. These conclusions were later criticized by Barrow and Shaw (1979b), because their results show an inverse relation between the ability of a salt to induce desorption of phosphate and its ability to displace Ca. Barrow and Shaw (1979b) concluded that the identity and concentration of the cation had a large effect on the desorption of phosphate and that the escaping tendency of phosphate was decreased when the cations which balance the negative charge on the adsorbed phosphate were close to the surface.

Ryden and Syers (1976) found that retained Ca was essentially recovered in 1M KCl washings in contrast to the fractional recovery of sorbed phosphate. The retention of Ca in response to phosphate sorption was attributed to a decrease in negative charge associated to phosphate adsorption rather than a precipitation reaction of calcium phosphate.

7. Conclusion

There are many key processes involved in the management of fertilizers for crop production in Oxisols. An integrated system which includes soil chemistry and fertility, plant physiology and genetics, organic matter, alternative fertilizers, tillage and irrigation practices is of fundamental importance.

This paper addresses important physicho-chemical aspects that affect the management of nutrients in Oxisols with emphasis on soil acidity, surface charge, P fertiliztion and pH interactions.

The complexity of the chemistry of phosphate in Oxisols and the understanding of its behaviour and interactions with other soil parameters makes the management of phosphorus fertilization one of the main strategies for good plant growth and development in these soils.

References

Barrow, N.J. 1987. Reactions with variable-charge soils. Developments in Plant and soil sciences. Martinus Nijhoff Publishers, Dordrecht/Boston/Lancaster.

Barrow, N.J., and T.C. Shaw. 1979b. Effects of ionic strength and nature of the cation on desorption of phosphate from soil. J. Soil Sci. 30:53-65.

Bohn, H.L., McNeal, B.L. and O´Connor, G.A. 1979. Soil Chemistry. John Wiley & Sons

Bolan, N.S., and N.J. Barrow. 1984. Modelling the effect of adsorption of phosphate and other anions on the surface charge of variable charge oxides. J. Soil Sci. 35:273-281.

Bolan, N.S., J.K. Syers, R.W. Tillman, and D.R. Scotter. 1988. Effect of liming and phosphate additions on sulphate leaching in soils. J. Soil Sci. 39:493-504.

Bond, W.J., B.N. Gardiner and D.E. Smiles. 1982. Constant-flux absorption of a tritiated calcium chloride solution by a clay soil with anion exclusion. Soil Sci. Soc. Amer. J.   46:1133-1137.

Bowden, J.W., M.D.A. Bolland, A.M. Posner, and J.P. Quirk. 1973. Generalised model for anion and cation adsorption on oxide surfaces. Nature: Physical Sciences 245:81-83.

Bowden, J.W., A.M. Posner, and J.P. Quirk. 1974. A model for ion adsorption on variable charge surfaces. Transactions of 10th International Congress in Soil Science. Moscow. Vol. 11 pp. 29-36.

Bowden, J.W., A.M. Posner, and J.P. Quirk. 1977. Ionic adsorption on variable charge mineral surfaces: Theoretical-charge development and titration curves. Aust. J. Soil Res.   15:121-136.

Chao, T.T., M.E. Harward, and S.C. Fang. 1962. Movement of S^{35} tagged sulfate through soil columns. Soil Sci. Soc. Am. Proc. 26:27-32.

De Haan, F.A.M., and G.H. Bolt. 1963. Determination of anion adsorption by clays. Soil Sci. Soc. Am. Proc. 27:636-640.

Fey, M.V., and J. Le Roux. 1976. Electric charges on sesquioxidic soil clays. Soil Sci. Soc. Am. J. 40:359-364.

Garrels, R.M. and Christ, C.L. 1965. Solutions, Minerals, and Equilibria. Harper & Row Publishers, New York

Helyar, K.R., D.N. Munns, and R.G. Burau. 1976. Adsorption of phosphate by gibbsite. I. Effects of neutral chloride salts of calcium, magnesium, sodium, and potassium. J. Soil Sci. 27:307-314.

Hingston, F.J. 1970. Specific adsorption of anions on goethite and gibbsite. PhD dissertation, University of Western Australia.

Hingston, F.J. 1981. A review of anion adsorption. p. 51-90. *In* M.A. Anderson and A.J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science Publishers, Ann Arbor, MI.

Hingston, F.J., A.M. Posner, and J.P. Quirk. 1972. Anion adsorption by goethite and gibbsite: I. The role of the proton in determining adsorption envelopes. J. Soil Sci.23:177-192.

James, R.V. and J. Rubin. 1986. Transport of chloride ion in a water-unsaturated soil exhibiting anion exclusion. Soil Sci. Soc. Amer. J. 50:1142-1149.

Jurinak, J.J. 1966. Surface chemistry of hematite: anion penetration effect on water adsorption. Soil Sci. Soc. Am. Proc. 30:559-562.

Kinjo, T., and P.F. Pratt. 1971. Nitrate adsorption: II. In competition with chloride, sulfate, and phosphate. Soil Sci. Soc. Am. Proc. 35:725-728.

Krupp, H.K., J.W. Biggar, and D.R. Nielsen. 1972. Relative flow rates of salt and water in soil. Soil Sci. Soc. Am. Proc. 36:412-417.

Lutz, J.F., and I. Haque. 1975. Effects of phosphorus on some physical and chemical properties of clays. Soil Sci. Soc. Am. Proc. 39:33-36.

Malavolta, E. and Kliemann, H.J. 1985. Desordens Nutricionais no Cerrado. Associação Brasileira para Pesquisa da Potassa e do Fósforo

Mattson, S. 1932. The laws of soil colloidal behavior: IX. Amphoteric reactions and isoelectric weathering. Soil Sci. 34:209-240.

Mekaru, T., and G. Uehara. 1972. Anion adsorption in ferruginos tropical soils. Soil Sci. Soc. Amer. Proc. 36:296-300.

Melamed, R. 1993. Competitive adsorption of phosphate on the retention and mobility of anions. PhD dissertation. Utah State University.

Melamed, R., Jurinak, J.J. and Dudley, L.M. 1994. Anion exclusion-pore water velocity interaction affecting the transport of Br through an Oxisol. Soil Sci.Soc.Am. J. 58:1405-1410.

Melamed, R., Jurinak, J.J. and Dudley, L.M. 1995. Effect of adsorbed phosphate on transport of arsenate through an Oxisol. Soil Sci. Soc. Am. J. 59:1289-1294.

Obihara, C.H., and E.W. Russel. 1972. Specific adsorption of silicate and phosphate by soils. J. Soil Sci. 23:105-117.

Onken, A.B., C.W. Wendt, R.S. Hargrove, and O.C. Wilke. 1977. Relative movement of bromide and nitrate in soils under three irrigation systems. Soil Sci. Soc. Am. J. 41:50-52.

Parfitt, R.L., R.J. Atkinson, and R.St.C. Smart. 1975. The Mechanism of phosphate fixation by iron oxides. Soil Sci. Soc. Amer. Proc. 39: 837-841.

Pavan, M.A., Bingham, F.T. and Pratt, P.F. 1984. Redistribution of Exchangeable Ca, Mg and Al following lime or gypsum application to a Brazilian Oxisol. Soil Sci. Soc. Amer. J.48(1): 33-38.

Posner, A.M., and J.W. Bowden. 1980. Adsorption isotherms. Should they be split? J. Soil Sci. 31:1-10.

Rajan, S.S.S. 1976. Changes in net surface charge of hydrous alumina with phosphate adsorption. Nature 262:45-46.

Rajan, S.S.S., and R.L. Fox. 1975. Phosphate adsorption by soils: II. Reactions in tropical acid soils. Soil Sci. Soc. Am. Proc. 39:846-851.

Reeve, N.G. and Sumner, M.E. 1972. Amelioration of subsoilacidity in Natal Oxisol by leaching of surface applied amendments. Agrochemophysica 4:1-6.

Ritchey, K.D., Souza, D.M.G., Lobato, E. and Correa, O. 1980. Ca leaching to increase rooting depth in a Brazilian savannah Oxisol. Agronomy 72:40-44.

Ryden, J.C., J.R. McLaughlin, and J.K. Syers. 1977. Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. J. Soil Sci. 28:72-92.

Ryden, J.C., and J.K. Syers. 1976. Calcium retention in response to phosphate sorption by soils. Soil Sci. Soc. Am. J. 40:845-846.

Ryden, J.C., J.K. Syers, and R.W. Tillman. 1987. Inorganic anion sorption and interactions with phosphate sorption by hydrous ferric oxide gel. J. Soil Sci. 38:211-217.

Schofield, R.K. 1947. Calculation of surface areas from measurement of negative adsorption. Nature. 160:408-410.

Smith, S.J. 1972. Relative rate of chloride movement in leaching of surface soils. Soil Sci. 114:259-263.

Smith, S.J., and R.J. Davis. 1974. Relative movement of bromide and nitrate through soils. J. Environ. Quality. 3:152-155.

Sposito, G. 1982. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena: II. The "two-surface" Langmuir equation. Soil Sci. Soc. Am. J. 46:1147-1152.

Sposito, G. 1989. The chemistry of soils. Oxford University Press, New York.

Thomas, G.W., and A.R. Swoboda. 1970. Anion exclusion effects on chloride movement in soils. Soil Sci. 110:163-166.

Wann, S.S., and G. Uehara. 1978a. Surface charge manipulation of constant surface potential soil colloids: I. Relation to sorbed phosphorus. Soil Sci. Soc. Am. J. 42:565-570.

Wann, S.S., and G. Uehara. 1978b. Surface charge manipulation of constant surface potential soil colloids: II. Effect on solute transport. Soil Sci. Soc. Am. J. 42:886-888.

White, R.E. 1980. Retention and release of phosphate by soil and soil constituents. p. 71-114. *In* P.B. Tinker (eds.) Soils and agriculture. Critical reports on applied chemistry volume 2, Society of Chemical Industry. Oxford: Blackwell Scientific Publications.

Yost, R.S., E.J. Kamprath, E. Lobato, and G.C. Naderman. 1979. Phosphorus response to of corn on an Oxisol as influenced by rates and placement. Soil Sci. Soc. Am. J. 43:338-343.