Chapter 1

1) Introduction

Phosphorus deficiency is one of the major soil fertility problems that limit optimum crop production in most parts of the world, especially in the tropical and sub-tropical regions (McKean & Warren, 1996). In South Africa P deficiencies are also widely experienced, especially under extensive farming conditions. According to Bainbridge, Miles & Praan (1995), this can be attributed to the low natural P status of the soils and the fast rate at which applied phosphate fertiliser becomes unavailable for plants.

The main reasons for the low plant availability of phosphate are:

- **Presence of Ferric (Fe(III)) - and aluminium (Al) oxy- hydroxides.**

  Fe(III)- and Al oxy-hydroxides have a high affinity for phosphate and adsorbs phosphate strongly (chemisorbed). The phosphate sorption capacity of Fe(III)- and Al oxy-hydroxides also increases with decreasing pH due to the development of positive surface charge on the Fe(III)- and Al oxy-hydroxides surfaces (Sposito, 1989, Bainbridge *et al*, 1995). In a phosphate sorption study on 29 Natal soils Bainbridge *et al.* (1995), found that more than half of the studied soils fell in the medium (100 – 500 mg P.kg^{-1}) to very high (> 1000 mg P.kg^{-1}) phosphate sorption capacity category. This means that a soil with a phosphate sorption capacity of 500mg P.kg^{-1} will require approximately 1112.5 kg P.ha^{-1} (estimated at 2.225×10^{6} kg soil. ha^{-1}) to saturate the phosphate adsorption sites in the top 15 cm. Due to the cost of phosphate fertiliser this would not be economically viable;

- **Low organic material content of South African soils.** The low organic material content of soils under cultivation is the result of both farming practices and the high decomposition rate of organic material in the soil. In South Africa it is common practice to utilise the plant material, left after harvesting, as cattle feed during the winter. Only a fraction of the organic material is therefore returned to the soil. The little organic material that is returned to the soil, is quickly decomposed, and the mineralised P is readily sorbed by the soil. Generally, the addition of organic

material decreases the phosphate sorption capacity of a soil. The reduction of phosphate sorption capacity is mainly due to two factors; firstly, organic anions such as oxalates, citrates, humates ect,. form stable complexes in solution with Fe^{3+} and Al^{3+}, this complex formation decreases the Fe^{3+} and Al^{3+} activity in solution, which increases the solubility of Fe(III)- and Al oxy-hydroxides. The decrease in Fe^{3+} and Al^{3+} activity also increases the solubility of aluminium and ferric phosphates; secondly, organic compounds can also compete with phosphate for the adsorption sites, decreasing the phosphate adsorption capacity of the soil. Organic material is also an important source of P for plants (Appelt, Coleman & Pratt, 1975, Stevenson, 1982, Iyamuremye & Dick, 1996, Baldock & Skjemstad, 1999).

1.2) Phosphate dynamics in the soil

The P concentration in the soil solution is controlled by both chemical and biological reactions, of which chemical reactions are dominant. Soil P is often divided into pools according to potential plant availability (Barrow & Shaw 1975(a), 1975(b):

$$\text{Organic P} \leftrightarrows \text{P in solution} \leftrightarrows \text{Labile P} \leftrightarrows \text{Non-labile P} \qquad (1.1)$$
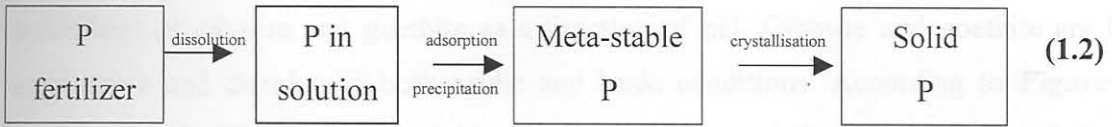
Equation 1.1 is an oversimplification of the real P dynamics in the soil because well-defined P pools do not exist in the soil. (Barrow & Shaw 1975(a), 1975(b), Mattingly, 1975, Orlov, 1992, Iyamuremye & Dick, 1996).

1.3) Phosphate dynamics in acid soils

It is accepted that the two major reactions responsible for phosphate sorption in acid soils are phosphate adsorption by Fe(III)- and Al oxy-hydroxides and the precipitation of aluminium and ferric phosphates. These two phenomena are interrelated and it is commonly accepted that with time adsorbed phosphate will be transformed to aluminium phosphates (variscite) and ferric phosphates (strengite) if the adsorbed phosphate does
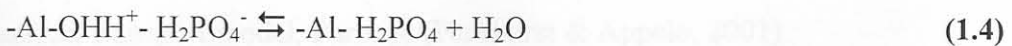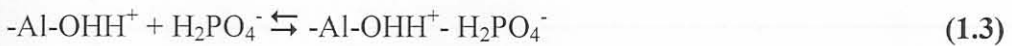
not desorb. Devine, Grunary & Larsen (1968) illustrated the fate of P fertiliser and also the interrelation between phosphate adsorption and phosphate precipitation as follows:

$$\boxed{\begin{array}{c}P \\ \text{fertilizer}\end{array}} \xrightarrow{\text{dissolution}} \boxed{\begin{array}{c}P \text{ in} \\ \text{solution}\end{array}} \xrightarrow[\text{precipitation}]{\text{adsorption}} \boxed{\begin{array}{c}\text{Meta-stable} \\ P\end{array}} \xrightarrow{\text{crystallisation}} \boxed{\begin{array}{c}\text{Solid} \\ P\end{array}} \quad (1.2)$$

1.3.1) Phosphate adsorption by 1:1 and 2:1 clay minerals

1:1 Clay minerals have a higher phosphate adsorption capacity than 2:1 clay minerals because of the higher content of exposed Al-OH groups (Tan, 1998).

The mechanisms of phosphate adsorption by 1:1 clay minerals are (a) electrostatic adsorption (non-specific adsorption) of phosphate by protonated hydroxyl groups (**equation 1.3**) in acid conditions. Phosphate adsorbed non-specifically has a high exchangeability and desorbs readily if the surface charges become less positive with increasing pH; (b) specific adsorption which occurs through the replacement of structural OH groups through ligand exchange, (**equation 1.4**). According to Bohn, McNeal & O'Connor (1979), both specific and non-specific adsorption occur simultaneously, and generally specifically adsorbed phosphate has a low exchangeability; (c) the integration of phosphate in the crystal structure, which is a very slow reaction, taking place over weeks and even months.

$$-Al\text{-}OHH^+ + H_2PO_4^- \leftrightarrows -Al\text{-}OHH^+\text{-} H_2PO_4^- \qquad (1.3)$$

$$-Al\text{-}OHH^+\text{-} H_2PO_4^- \leftrightarrows -Al\text{-} H_2PO_4 + H_2O \qquad (1.4)$$

Due to their structure, 2:1 clay minerals can only adsorb small amounts of phosphate on exposed OH groups at their edges at very low pH values. In the case of montmorillonite, phosphate can also move into the interlayer space and precipitates as insoluble $AlPO_4.nH_2O$ (Orlov, 1992).

1.3.2) Phosphate adsorption by Fe(III)-and Al oxy-hydroxides

Goethite (α-FeOOH) and gibbsite (γ– Al(OH)$_3$) are the most common Fe(III)-and Al oxy-hydroxides in the soil and are important surfaces at which phosphate adsorption occurs (Lindsay, 1979, Stucki & Bamwart, 1979, Sposito, 1989,). **Figure 1.1** show the solubilities of gibbsite and goethite as a function of pH. Gibbsite and goethite are both amphoteric and dissolve in both acidic and basic conditions. According to **Figure 1.1** goethite is significantly less soluble than gibbsite especially below a pH of 5, this indicating that goethite possibly plays a more important role in phosphate adsorption than gibbsite in acid soils.
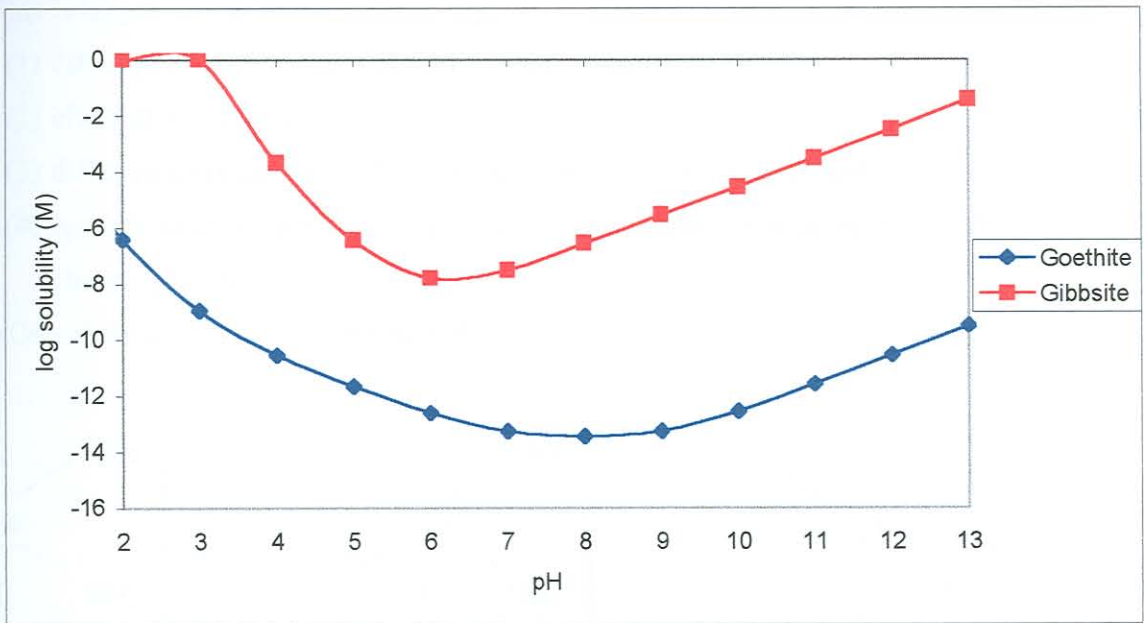

Figure 1.1. Solubilities of goethite and gibbsite as functions of pH calculated with the geochemical transport model, Phreeqc (Parkhurst & Appelo, 2001).

Amorphous Fe(III)-and Al oxy-hydroxides also occur in the soil. The specific surface area of amorphous Fe(III)-and Al oxy-hydroxides can be as high as 800 m^2.g^{-1} and therefore has a much higher phosphate adsorption capacity than goethite or gibbsite. The presence of amorphous Fe(III)-and Al oxy-hydroxides enhances the phosphate adsorption capacity of a soil. Amorphous Fe(III)-and Al oxy-hydroxides are however meta stable

and with time transform to the more stable goethite or gibbsite (Lindsay, 1979, Lookman, Freese, Merckx, Vlassak &Riemsdijk, 1995,).

The variable charge on Fe(III)-and Al oxy-hydroxides surfaces play an important role in phosphate sorption in soils. The surface charge arises from the association and dissociation of protons, which is a function of the pH and the ionic strength of the soil solution. The pH dependency of the variably charged surfaces is illustrated in **Figure 1.2.**

The point of zero charge, (pH at which the surface charge is zero) can vary substantially. This is largely due to the:

(1) different hydration states of the oxy-hydroxide surfaces;
(2) effect of impurities;
(3) different co-ordinations of the hydroxyl groups to the cations and;
(4) specific adsorption of certain ions causing a decrease or increase in the point of zero charge (p.z.c.).
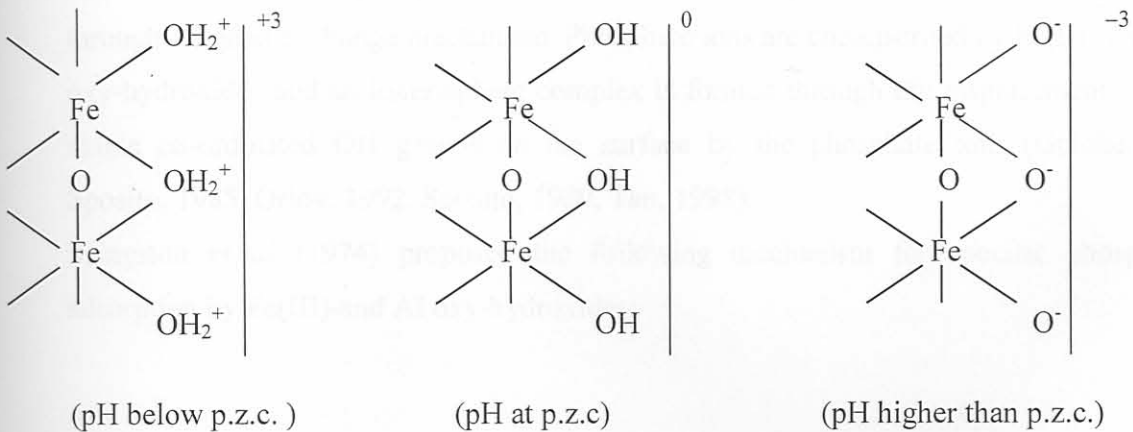
(Greenland & Mott, 1978, White, 1980).

(pH below p.z.c.)   (pH at p.z.c)   (pH higher than p.z.c.)

Figure 1.2. Illustration of the pH dependent charges at a ferric oxy-hydroxide surface (Gangaiya & Morrison, 1987).

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1.3.2.1) Reaction mechanisms of phosphate adsorption

Phosphate adsorption at the surfaces of oxy-hydroxide can be specific and/or non-specific.

Non-specific adsorption

Oxy-hydroxide surfaces are positively charged at pH levels below the p.z.c because of the protonation of the surfaces. The negative charged phosphate ions are attracted by the positively charged surface of the oxy-hydroxide. This type of adsorption is weak and highly pH dependant (Hingston, Posner & Quirk, 1974, White, 1980).

$$(1.6)$$
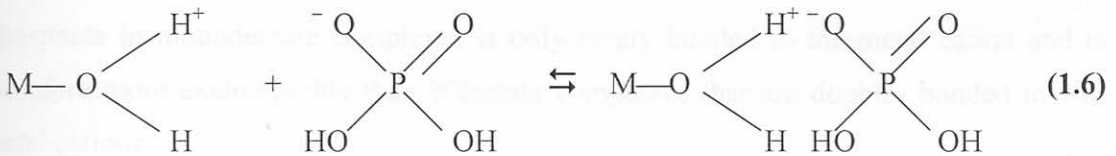
Specific adsorption

Specific adsorption of phosphate on the surface of Fe(III)-and Al oxy-hydroxides occurs through a ligand exchange mechanism. Phosphate ions are chemisorbed by Fe(III)-and Al oxy-hydroxides and an inner-sphere complex is formed through the displacement of the single co-ordinated OH groups on the surface by the phosphate ions (Goldberg & Sposito, 1985, Orlov, 1992, Sposito, 1989, Tan, 1998).

Hingston *et al* (1974) proposed the following mechanism for specific phosphate adsorption by Fe(III)-and Al oxy-hydroxides:

$$
\begin{array}{c}
\text{M--O} \qquad \text{O} \\
\text{O} \qquad \text{P} \\
\text{M--O} \qquad \text{OH}
\end{array}
$$
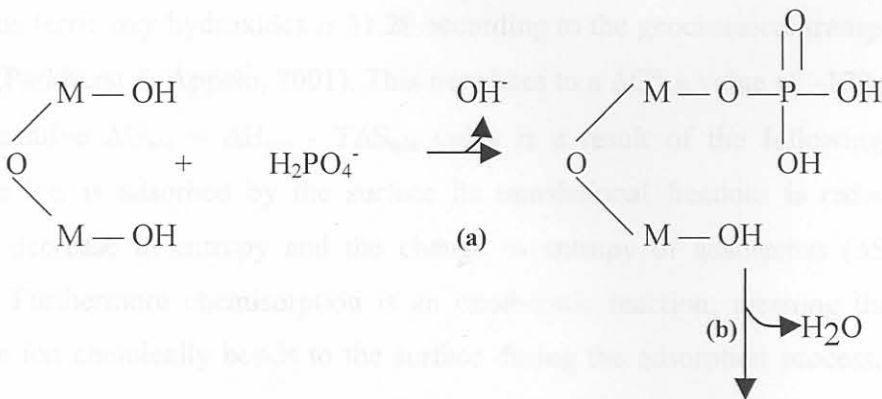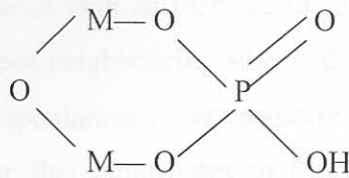
(a) $H_2PO_4^-$ exchanges with single co-ordinated hydroxyl on the hydrous
     oxide surface and a monodentate complex forms;

(b) A second ligand exchange occurs and a bidentate complex is formed,
     resulting in the release of H_2O.

Phosphate in monodentate complexes is only singly bonded to the metal cation and is therefore more exchangeable than bidentate complexes that are double- bonded to two metal cations

Infrared spectroscopy (IR) and other studies confirmed that the amount of phosphate fixed in bidentate complexes usually exceeds the amount of phosphate fixed in monodentate complexes at low surface coverage However, with increasing surface coverage, the mole fraction monodentate complex on the surface increases as the number of vacant sites decreases (Atkinson, Parfitt & Smart, 1974, Parfitt, 1978, Goldberg & Sposito, 1985).

1.3.2.2) Thermodynamics of phosphate adsorption

Phosphate adsorption is a spontaneous process and requires that the change in Gibbs free energy (ΔG_{ads}) must be negative. The intrinsic log K value for phosphate adsorption on amorphous ferric oxy hydroxides is 31.29 according to the geochemical transport model, Phreeqc (Parkhurst & Appelo, 2001). This translates to a $\Delta G°_{ads}$ value of -178.64 kJ mol^{-1}. The negative $\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$ value is a result of the following: When a phosphate ion is adsorbed by the surface its translational freedom is reduced which causes a decrease in entropy and the change in entropy of adsorption (ΔS_{ads}) to be negative. Furthermore chemisorption is an exothermic reaction, meaning that when a phosphate ion chemically bonds to the surface during the adsorption process, energy is

released to the surroundings in the form of heat, the enthalpy change due to adsorption (ΔH_{ads}) is therefore also negative. ΔH_{ads} increases with an increase in surface coverage, this is mainly due to steric interferences between neighbouring adsorbed phosphate ions. Phosphate adsorption therefore becomes less spontaneous (less negative ΔG_{ads}) with an increase in surface coverage. Another factor that contributes to the increase in the enthalpy of adsorption and the subsequent less negative ΔG_{ads} is the fact that the phosphate affinity of the adsorption sites is not homogeneous. Phosphate adsorption initially occurs at the energetically most favourable sites (reaction is more spontaneous at these sites). With an increase in surface coverage, phosphate adsorption occurs at adsorption sites with lower affinity resulting in less spontaneous adsorption reactions and less negative ΔG_{ads} (White, 1980, Sposito, 1989, Schulthess & Sparks, 1991, Atkins, 1999).

1.3.3) Desorption of adsorbed phosphate

In recent years the emphasis in research on phosphorus dynamics in soils has changed. Previously the emphasis was on the components, processes and kinetics responsible for phosphate immobilisation. Recently more emphasis has been placed on quantifying phosphate release rates and the factors influencing it in different soil types (Brewster Gancheva & Nye, 1975, Barrow & Shaw, 1977, Cabrera, De Abrambarri, Madrid & Toca, 1981, Raven & Hossner, 1994, Garcia-Rodeja & Gil-Sotres, 1995, Lookman, Freese, Merckx, Vlassak & Riemsdijk, 1995. McKean & Warren, 1996, Myers, Pierzynski & Thien, 1997). The phosphate mobilisation kinetics of soils are generally much slower than phosphate immobilisation kinetics and differ dramatically from soil to soil, making it difficult to predict plant available phosphate accurately (Holford, 1991; Lookman et al., 1995).

Phosphate adsorbed by Fe(III)-and Al oxy-hydroxides has a low exchangeability because of the strong binuclear complexes that form. The ΔG of phosphate de-adsorption from amorphous ferric oxy hydroxide surfaces is positive (+178.64 kJ mol^{-1} according to Parkhurst & Appelo, 2001) and is not a spontaneous process. Because of above-

mentioned facts Hingston *et al.* (1974), concluded that adsorbed phosphate is to a certain degree "kinetically irreversible".

Furthermore, it seems that phosphate de-adsorption becomes even less spontaneous with an increase in soil temperature. Both Doula, Ioannou & Dimirkou, (1996) and McKean & Warren (1996), found that desorption decreases with increasing temperature. Doula *et al*, (1996), found that phosphate de-adsorption rates of entisols and alfisols were at a maximum at 5°C and at a minimum at 50°C. In vertisols and inceptisols the de-adsorption rates were at a maximum at 25°C and at a minimum at 50°C.

1.3.4) Precipitation and dissolution of phosphate minerals.

As a rule the first row *d*-block elements as well as aluminium form insoluble solids with phosphate. It is commonly accepted that strengite ($FePO_4.2H_2O$) and variscite ($AlPO_4.2H_2O$) are the predominant phosphate minerals present in acid soils with a pH below 6.5. Above this pH, calcium phosphates like $Ca_5(PO4)_3OH$ and $Ca_5(PO4)_3F$ are less soluble and control phosphate in solution (Lindsay,1979, Shriver &Atkins, 1999).

The phosphate concentration in solution governed by the solubility equilibria of goethite and that of strengite can be represented by the following equation:

$$[P_{tot}] = [H_3PO_4^0] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [FeH_2PO_4^{2+}] + [FeHPO_4^+]$$

(1.11)
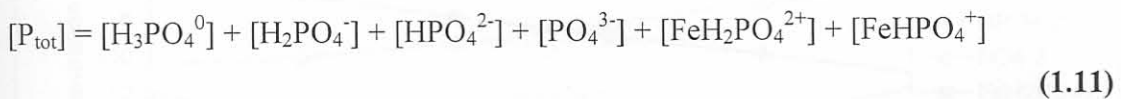
And the phosphate concentration in solution governed by the solubility equilibria of gibbsite and that of variscite can be represented by the following equation:
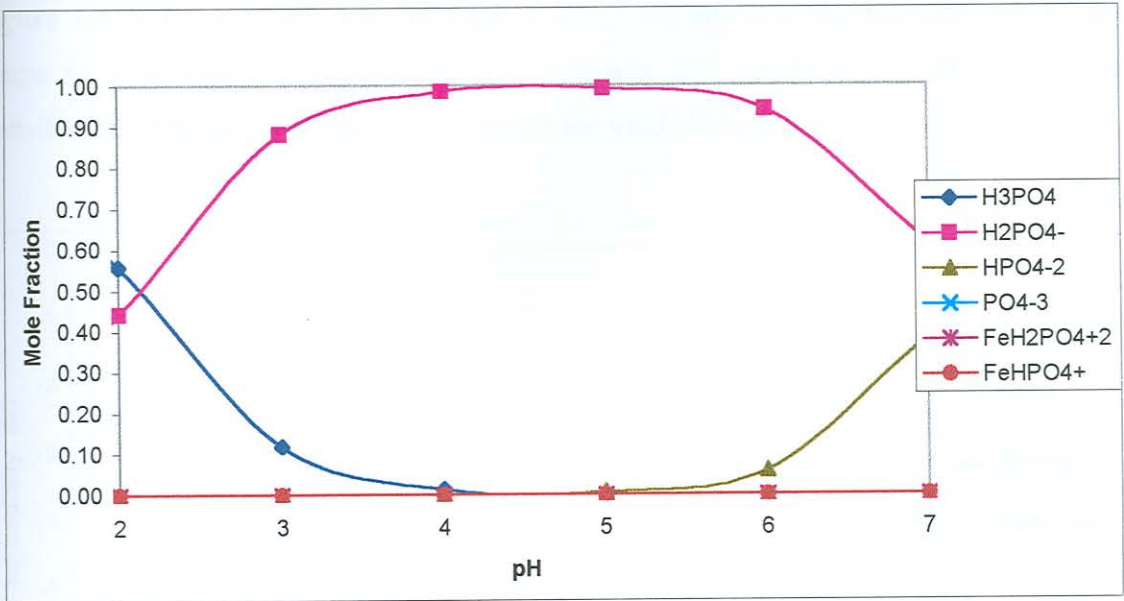
$$[P_{tot}] = [H_3PO_4^0] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [AlH_2PO_4^{2+}] + [AlHPO_4^+]$$

(1.12)
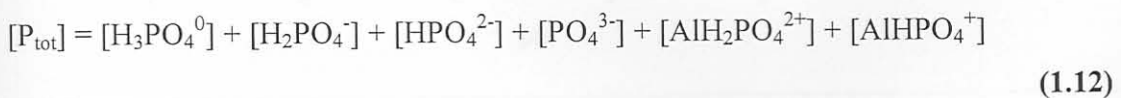
Figure 1.3. The mole fraction distribution of soluble phosphate species in equilibrium with strengite and goethite.
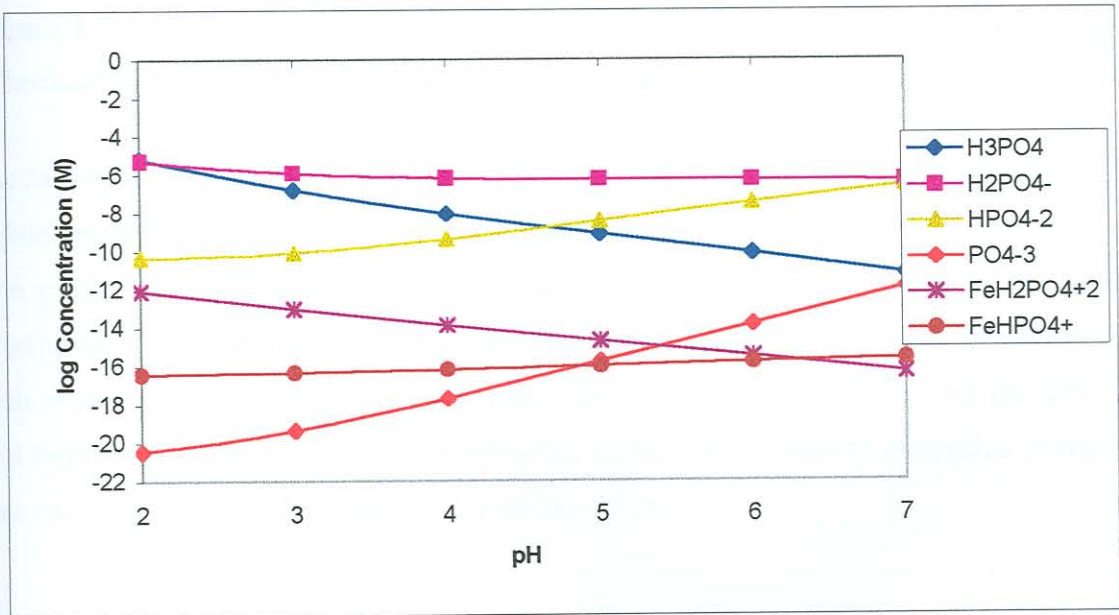

Figure 1.4. Soluble phosphate species in equilibrium with strengite and goethite, calculated with the geochemical transport model, Phreeqc (Parkhurst & Appelo, 2001).

Figure 1.3 and 1.4 shows that, between a pH of 3.5 and 6.5, the dominant phosphate specie in a solution in equilibrium with strengite and goethite is $H_2PO_4^-$, and the contribution of the other phosphate species to the total phosphate in solution is small.
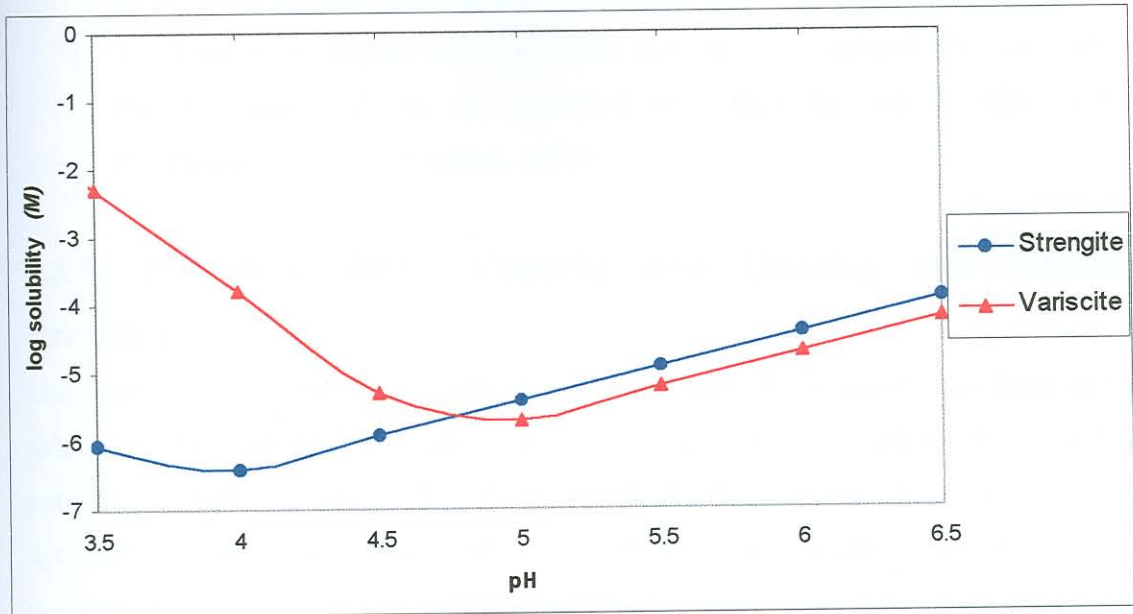

Figure 1.5. Solubility of strengite and variscite in equilibrium with goethite and gibbsite. (Thermodynamic equilibrium constants where obtained from Lindsay, (1979).

According to Figure 1.5., variscite is less soluble than strengite above a pH of ± 4.7, while below this pH strengite is less soluble than variscite.

The prediction of the solubility of strengite and variscite are complicated by the initial precipitation of amorphous phosphate minerals which are 10 to 100 times more soluble than crystalline phosphate minerals, and also the co-precipitate of aluminium phosphates and ferric phosphates forming a barrandite-like isomorphous series of integrated strengite and variscite (Chang & Jackson, 1957, Lindsay, 1979).

The solubility of strengite and variscite is also influenced by:

1. Waterlogging, which causes an increase in the pH of acidic soils, and a subsequent increase in the solubility of strengite and variscite. Anaerobic conditions also favour the formation of more soluble ferrous phosphate minerals such as vivianite;

2. The ionic strength of the soil solution. It is however not expected that the ionic strength of the soil solution will reach levels that will significantly increase the solubility of strengite and variscite in an open system where free drainage occurs;

3. The addition of organic material to the soil may also increase the solubility of strengite and variscite, as described previously (Savant & Ellis, 1964, Ponnamperuma, 1972, Lindsay, 1979).

1.3.5) Phosphate Buffer Capacity and Quantity and Intensity Parameters

The intensity parameter (I) is defined as the activity of inorganic phosphate in the solution, while the quantity parameter (Q) is the amount of phosphate, which is potentially plant available. The Phosphate Buffer Capacity (P.B.C.) describes the dynamic relationship between phosphate in solution and the phosphate in solid phase, and is given by the slope of a Q/I curve. Quantity and Intensity parameters of phosphate give information about the equilibrium between the solution and the solid phases phosphate, or in other words the fixing and releasing characteristics of soils. The higher the P.B.C., the lower the rate at which phosphate in the solid phase, supplements phosphate in solution (Holford, 1991, Raven & Hossner, 1994, Moody & Bolland, 1999).

The P.B.C and Q/I relationships of a soil can be obtained from either sorption or desorption isotherms. Phosphate sorption isotherms have more often been used to determine phosphate requirements for crops than desorption isotherms. However, according to Raven & Hossner (1994), a specific Q parameter from a phosphate desorption isotherm is more useful than any parameter from a phosphate sorption isotherm. There is some controversy about the use of P.B.C. to determine plant available phosphate. The reason for this is that the P.B.C. of a soil is not a constant characteristic and is influenced by a number of factors such as:

(a) The addition of phosphate fertilisers lowers the P.B.C of a soil (Barrow, 1974);

(b) The strong hysteresis between phosphate desorption and sorption isotherms which results in different P.B.C.'s for the same soil depending on whether a phosphate sorption- or a phosphate desorption isotherms is used. P.B.C determined from the sorption approach is only valid if there is no hysteresis (Raven & Hossner, 1994);

(c) The mobilisation of non-labile phosphate not included in the initial Q/I curve makes it difficult to predict the replenishment of P in solution with P.B.C.;

(d) The application of P.B.C. becomes difficult when the chemical equilibrium is disturbed as a result of waterlogging;

(e) Mineralised phosphate can be absorbed directly by the plants without prior equilibration with the inorganic sorption sites, thus short-circuiting the inorganic phosphate sorption system in the soil. The P.B.C. is therefore difficult to apply in soils where organic phosphate provides a substantial amount of the P to plants,

(f) Micro-organisms like *Aspergillus niger, Penicillium simplicissimum, Pseudomonas* sp. and root exudates can solubilize calcium - and aluminium phosphates. Their presence can lower the P.B.C. to some extent in the rhizosphere (Holford & Patrick, 1981, Ilmer, Barbato & Schinner, 1995).

1.3.6) Kinetics of phosphate dynamics in the soil

1.3.6.1) Differential and Integrated Rate Laws

The phosphate sorption and desorption rates are functions of the phosphate activity in solution and change as activity decreases or increases. In order to characterise the kinetic behaviour of these reactions, the change in the rates of the reactions must be determined as the respective reactions progress.

$$A \leftrightarrows B \tag{1.13}$$

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The law of mass action states that the rate of a reaction is proportional to the rate of change in the concentration of the reactants or products. The rate of the forward reaction of **Equation 1.12** can be written as follows:

$$\frac{d(A)}{dt} = - k\,(A)^n \qquad\qquad (1.14)$$

$$\frac{d(B)}{dt} = k\,(B)^m \qquad\qquad (1.15)$$

where k = rate constant of the forward reaction

n = the order of the reaction with respect to A

m = the order of the reaction with respect to B

Rate laws can take on many forms, however, most chemical reactions follow zero order, first order or second order kinetics.

1.3.6.1.1) Zero order reaction kinetics

The rate of a zero order reaction is constant as the reaction progresses **(Figure 1.6)**, the reaction stops abruptly when the limiting reactant is depleted. A characteristic linear plot is obtained with a concentration versus time plot, with slope k.

$$\frac{d(A)}{dt} = -k_f\,(A)^0$$

$$\frac{d(A)}{dt} = -k_f \qquad\qquad (1.16)$$

1.3.6.1.2) First order reaction kinetics

The rate of a first order reaction is directly proportional to the concentration of the limiting reactant. **Figure 1.6** shows that the rate of a reaction following first order kinetics is not constant and decreases gradually as the reaction progresses and the limiting reactant is depleted.

$$\frac{d(A)}{dt} = -k\,(A)^1 \qquad\qquad (1.17)$$

Equation 1.16 is the differential rate law because a rate of a reaction is always a derived function obtained from the original function by differentiation. In order to obtain the original function, the first order differential equation has to be integrated

When **equation 1.16** is rearranged:

$$\frac{d(A)}{(A)} = -kdt \qquad (1.18)$$

Equation 1.17 can be integrated as follows

$$\int_{A_{(0)}}^{A_t} \frac{1}{(A)} d(A) = -k \int_0^t dt \qquad (1.19)$$

$$ln\, A_t + c - (ln\, A_0 + c) = -kt$$

$$ln\, A_t - ln\, A_0 = -kt \qquad (1.20)$$

$$\text{or } A_t = A_0\, e^{-kt} \qquad (1.21)$$

where A_t is the concentration of the limiting reagent at time t, A_0 is the initial concentration of the limiting reagent and c is the arbitrary constant of the integration on the left side.
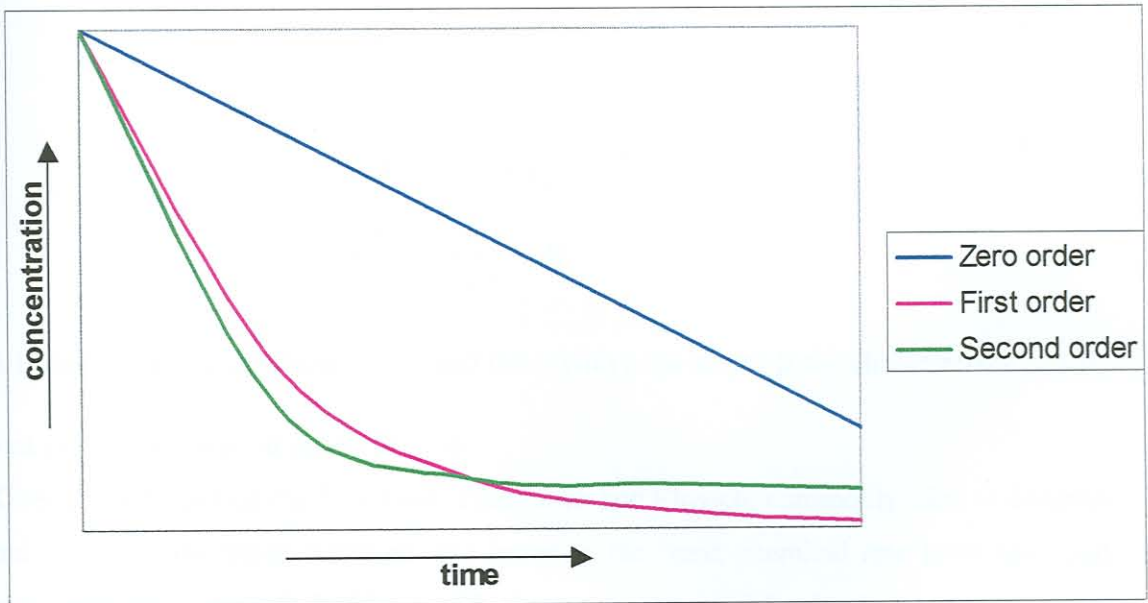
Figure 1.6. Theoretical zero, first and second order reactions.

A linear relationship between the natural logarithm (*ln*) of the concentration and time (with k the slope) is the characteristic kinetic plot or test for a first order reaction.

1.3.6.1.3) Second order reaction kinetics.

The rate of a second order reaction is directly proportional to the square of the concentration of the limiting reactant. **Figure 1.6** shows that a reaction following second order kinetics initially decreases faster than both zero and first order reactions, and decreases more gradually than a first order reaction as the reaction progresses and the limiting reactant is consumed.

$$\frac{d(A)}{dt} = -k(A)^2 \qquad (1.22)$$

The integrated rate law of equation (1.21) is obtained as follows:

When **equation (1.21)** is rearranged:

$$\frac{d(A)}{(A)^2} = -kdt \qquad (1.23)$$

Equation (1.22) can be integrated as follows

$$\int_{A_{(0)}}^{A_{(t)}} \frac{1}{(A)^2} d(A) = k \int_0^t dt \qquad (1.24)$$

$$\frac{1}{(A)} + c - \left(\frac{1}{(A_0)} + c \right) = -kt \qquad (1.25)$$

$$\frac{1}{(A)} - \frac{1}{(A_0)} = -kt$$

A linear relationship between $\dfrac{1}{(A)}$ and time (with k the slope) is the characteristic kinetic plot or test for a second order reaction

Kinetic equations like the Langmuir, Freundlich and Elovich, commonly used to describe and quantify adsorption reactions, are based in the basic chemical rate laws described previously (Snoeyink & Jenkins, 1980, Freese, Lookman, Merckx & Riemsdijk, 1995, Atkins, 1999).

1.4) Organic phosphate dynamics in the soil

In most soils organic phosphate can play an important role in replenishing the inorganic P in the soil. The organic P dynamics in the soil can be presented as follows

$$\text{Organic P} \underset{\text{immobilisation}}{\overset{\text{mineralisation}}{\rightleftharpoons}} \text{Inorganic P} \qquad (1.25)$$
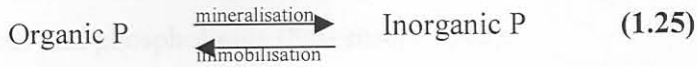
The mineralisation of organic phosphate is a biological process during which organic material is decompose by micro-organisms and inorganic phosphate is released in the solution. Immobilisation is the reverse reaction of mineralisation as illustrated in **Equation (1.25)** (Stevenson, 1982, Iyamuremye & Dick, 1996).

Phosphate mineralisation is influenced by temperature, moisture content and energy supply of the soil. However, little is known about the mechanisms involved in the immobilisation of phosphate by plants and micro-organisms, and most of the mechanisms are based on theories (Tan, 1998). High soil temperatures increase decomposition of organic material, thus increasing organic phosphate turnover. Because the end product of mineralisation, orthophosphate is readily adsorbed by the soil, it is difficult to determine the net rate of the mineralisation/immobilisation process.
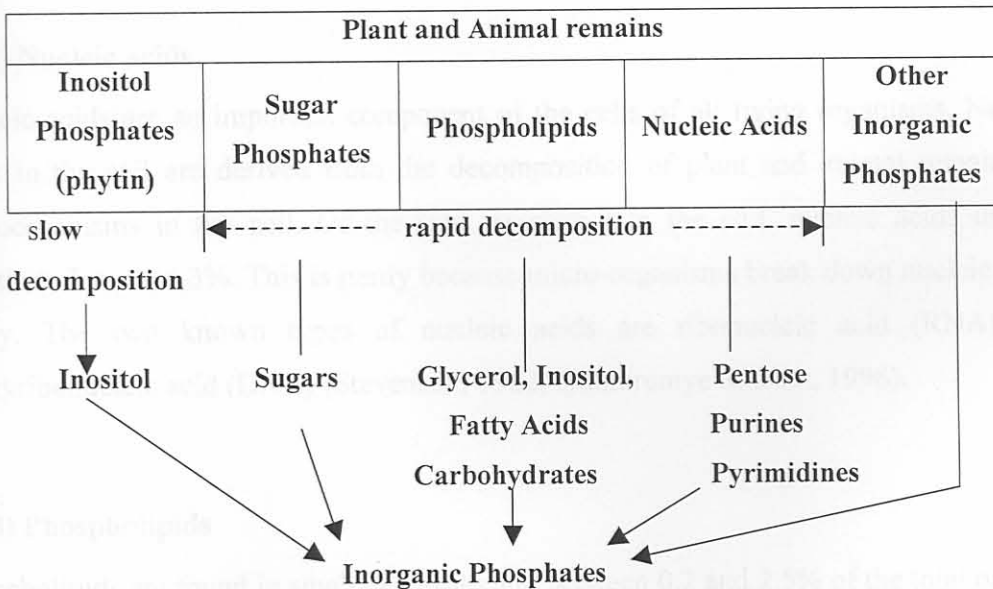

Figure 1.7 Mineralisation of organic phosphate in the soil. (Stevenson, 1982).

Figure 1.7 shows the numerous potential sources of organic phosphate as well as the different decomposition rates of these organic compounds in the soil, however, a large proportion of the organic compounds in the soil are still unknown. It is commonly accepted that the three main sources of organic phosphate in the soil are inositol phosphate, nucleic acids and phospholipids (Stevenson, 1982).

1.4.1) Inositol P

Inositol P is the most abundant organic P in the soil, and up to 60 % of the organic P in the soil can be inositol P. The accumulation of inositol P in the soil is because of, (a) the ability thereof to form insoluble complexes with Fe and Al in acid soils and Ca in calcareous soil; and (b) the low solubility of inositol P in both acid and basic conditions. Inositol P is an ester of hexahydroxy benzene. The most common P containing ester in the soil is hexaphosphate.

For years it was believed that phytin in higher plants is the main source of inositol P in the soil, but according to Stevenson (1982), micro-organisms synthesize inositol P *in situ*, because certain stereoisomers of inositol P in the soil (e.g. *scyllo*-inositol) do not occur in plants (Stevenson, 1982, Taite, 1987, Iyamuremye & Dick, 1996).

1.4.2) Nucleic acids

Nucleic acids are an important component of the cells of all living organisms. Nucleic acids in the soil are derived from the decomposition of plant and animal remains by microorganisms in the soil. Of the total organic P in the soil, nucleic acids usually constitute less than 3%. This is partly because micro-organisms break down nucleic acids easily. The two known types of nucleic acids are ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) (Stevenson, 1982, Iyamuremye & Dick, 1996).

1.4.3) Phospholipids

Phospholipids are found in small quantities and between 0.2 and 2.5% of the total organic P in the soil constitutes of phospholipids (Tan, 1998). The most abundant phospholipid in

the soil is phosphatidyl choline (VII) a degraded product of many lipids (Anderson, 1975, Stevenson, 1982).

1.5) Methods to investigate and describe phosphate desorption

Various methods, involving different chemical extractants, have been used to investigate and describe P desorption over time (Ryden & Syers, 1977, Barrow, 1979, Jazberenyi & Loch 1996). The major problem with these methods is that the chemical extractants change the physical and chemical properties of the soil samples used. To overcome some of these problems, anion-exchange resin, Fe(III)-or Al oxide impregnated filter paper and more recently, anion exchange membranes have been used to determine plant available P in soils (Amer, Bouldin & Black, 1955, Abrams & Jarell, 1992, Cooperband & Logan, 1994, Freese, *et al.*, 1995, Myers *et al.*, 1997). The anion - exchange resin, Fe(III)-or Al oxide impregnated filter paper and anion exchange membranes act as a phosphate sink (like a plant root), absorbing phosphate from solution. The depletion of the phosphate in solution causes the desorption of labile inorganic phosphate and P from the more soluble organic P complexes. These methods are thought to be more representative of the interaction between plant roots and the soil, and also do not change the chemical and physical properties of the soil (Amer, *et al*, 1955, Barrow & Shaw, 1977, Brewster, Gancheva & Nye, 1975, Cabrera *et al*, 1981, Tiessen & Moir 1993, Garcia-Rodeja & Gil-Sotres, 1995, Raven & Hossner, 1994, Lookman, *et al*, 1995).

Above-mentioned methods were mainly used in short term desorption experiments, little research has been done on the long-term (>21 days) dynamics of P in the soils. This is mainly due to certain problems with anion exchange resin, anion exchange membranes and Fe(III)-or Al oxide impregnated filter, which make them unsuitable for long-term studies.

The main problems with anion exchange resin, anion exchange membranes and Fe(III)-or Al oxide impregnated filter are:

- Anion-exchange resin and anion exchange membranes do not have the same specific affinity for phosphate ions. Anion selectivity by anion exchange resin and anion exchange membrane are governed by ion size (and hydration), valence and activity

(Cooperband & Logan, 1994, Freese *et al.*, 1995, Tiessen & Moir 1993). Cooperband & Logan (1994) found that concentration of $10^{-3.3}$ M SO_4^{2-} decreased phosphate adsorption by 95% and concentrations of $10^{-3.1}$ M NO_3^{-} decreased phosphate adsorption by 50 %.

- The bicarbonate form of anion exchange resin is often used. The exchange of bicarbonate by phosphate ions may increase the pH of the soil solution and influence the accuracy of this method in acidic soils (Freese *et al.*, 1995 Tiessen & Moir 1993).

- The phosphate adsorption reaction by resin is usually complete within 20 hours and cannot maintain a constant low P concentration in solution crucial for long-term P dynamic studies (Freese *et al*, 1995, Tiessen & Moir 1993).

- On the other hand, although Al or Fe(III)-oxide impregnated filter paper has a high specific affinity for phosphate, it is not mechanically stable for long periods.

- Al or Fe(III)-oxide impregnated filter paper tends to trap some of the soil especially the fine fraction. This may lead to an overestimation of short-term and underestimate long-term phosphate desorption rates (Lookman *et al*, 1995).

Freese *et al.*, (1995), used dialysis membrane tubes (DMT) filled with a hydrous ferric oxide suspension (HFO) as an alternative to anion exchange resin, Fe(III)-or Al oxide impregnated filter paper to extract phosphate from the soil According to Freese *et al.*, (1995), the DMT-HFO does not pose the same problems experience with anion-exchange resin, Fe(III)-or Al oxide impregnated filter paper because of the stability of the DMT-HFO over long periods and the high specific affinity of the HFO for phosphate ions, which enable the DMT-HFO to maintain the low phosphate concentration in solution necessary for long-term phosphate desorption studies. The slow equilibration rate of phosphate diffusion through the dialysis membrane (>30 hours) makes this method also more suitable for long-term phosphate dynamic studies (Freese *et al.*, 1995).

1.6) Aim of the study

The aim of this study was to (1) quantify the long term phosphate desorption kinetics of an acid sandy clay soil using chemical rate laws; (2) determine the influence of added

phosphate on the desorption kinetics of the soil; (3) investigate the lability of the different phosphate fractions and determine which phosphate fractions contributed to the desorbed phosphate; (4) investigate the change and distribution of applied P to the soil.