A phosphate sorption and desorption study on an acid sandy clay soil

by

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Abstract

The desorption kinetics of residual and applied phosphate to an acid sandy clay soil were investigated over a 56-day period using hydrous ferric oxide in dialysis tubes as a specific phosphate sink, followed by a sequential phosphate fractionation. The long-term phosphate desorption kinetics were describe with a two component first order model. The assumptions made were that two discrete phosphate "pools", with different exchangeability, participated in the desorption process and that the two phosphate pools follows first order kinetics. The desorption kinetics of the soil were describe relatively well according to the determination coefficients (R^2) ($R^2 = 0.9730$ for the control and $R^2 = 0.9528$ and $R^2 = 0.9870$ for the phosphate treatments of 75 and 150 mg kg^{-1} respectively) with the two component first order model. The more exchangeable pool (pool A) of the different treatments were depleted within the 56 day period. Extrapolation of the data showed that in the long term, desorption kinetics are controlled by the less exchangeable pool B. The total of mount phosphate desorbed in the 56-day period were virtually equal to the decrease in the NaOH extractable inorganic phosphate fraction (OH-Pi fraction) of the different treatments indicating that the OH-Pi fraction or "pool" is quite labile and actively involved in the desorption process. The $NaHCO_3$ extractable inorganic fraction (HCO_3-Pi fraction) of the different treatments were virtually depleted in the 56-day period but contributed considerably less to the total phosphate desorbed than the OH-Pi fraction. The calculated total extractable phosphate of the different treatments were ± 54% of the day 1 values of the OH-Pi fractions and ± 50% of the day 1 values of the HCO_3-Pi + OH-Pi fractions. If the hydrous ferric oxide simulates phosphate uptake by plants then the calculated total exchangeable phosphate represents the long-term plant available phosphate. For this particular soil it seems that half of the phosphate extracted with NaOH (24 hours) gives a good estimation of the long-term plant availability of the solid phase phosphate in the soil.

Keywords: Desorption maximum, hydrous ferric oxide, phosphate desorption kinetics, two component first order model, sequential phosphate fractionation, NaOH extractable inorganic phosphate, $NaHCO_3$ extractable inorganic fraction.

Table of Contents

Index of Figures

Index of Tables

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):

$$\textbf{Organic P} \leftrightarrows \textbf{P in solution} \leftrightarrows \textbf{Labile P} \leftrightarrows \textbf{Non-labile P} \qquad \textbf{(1.1)}$$

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:

$$\boxed{\text{P fertilizer}} \xrightarrow{\text{dissolution}} \boxed{\text{P in solution}} \underset{\text{precipitation}}{\xrightarrow{\text{adsorption}}} \boxed{\text{Meta-stable P}} \xrightarrow{\text{crystallisation}} \boxed{\text{Solid P}} \tag{1.2}$$

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.

$$\text{-Al-OHH}^{+} + \text{H}_2\text{PO}_4^{-} \leftrightarrows \text{-Al-OHH}^{+}\text{- H}_2\text{PO}_4^{-} \tag{1.3}$$

$$\text{-Al-OHH}^{+}\text{- H}_2\text{PO}_4^{-} \leftrightarrows \text{-Al- H}_2\text{PO}_4 + \text{H}_2\text{O} \tag{1.4}$$

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.

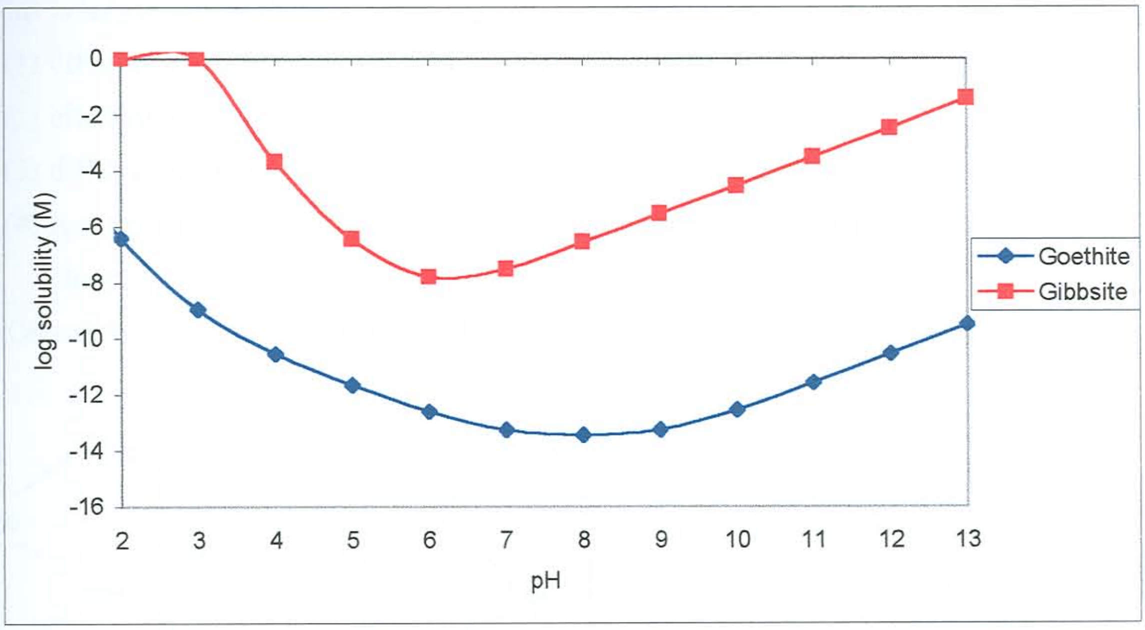


Figure 1.1. Solubilities of goethite and gibbsite as functions of pH calculated with the geochemical transport model, Phreeqc (Parkhurst & Appelo, 2001).

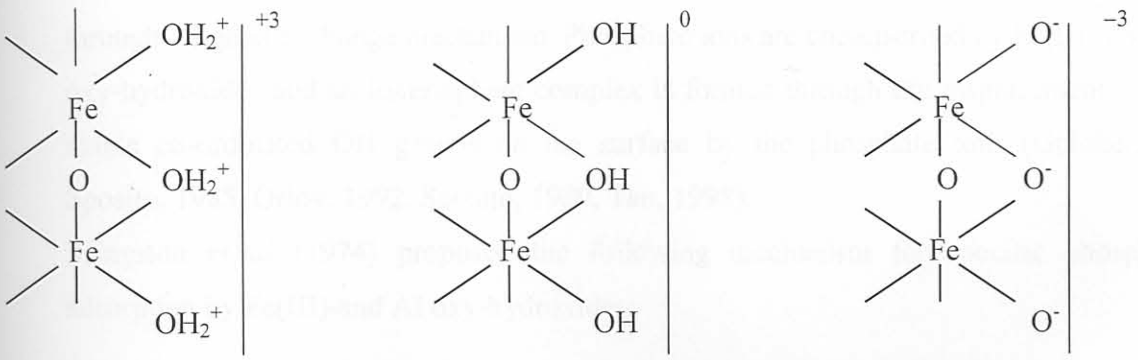
Amorphous Fe(III)-and Al oxy-hydroxides also occur in the soil. The specific surface area of amorphous Fe(III)-and Al oxy-hydroxides can be as high as 800 $m^2.g^{-1}$ and therefore has a much higher phosphate adsorption capacity than goethite or gibbsite. The presence of amorphous Fe(III)-and Al oxy-hydroxides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

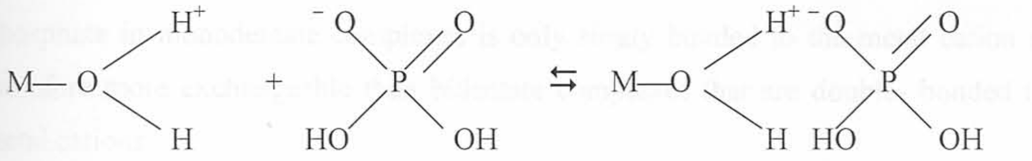
Figure 1.2. Illustration of the pH dependent charges at a ferric oxy-hydroxide surface (Gangaiya & Morrison, 1987).

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).

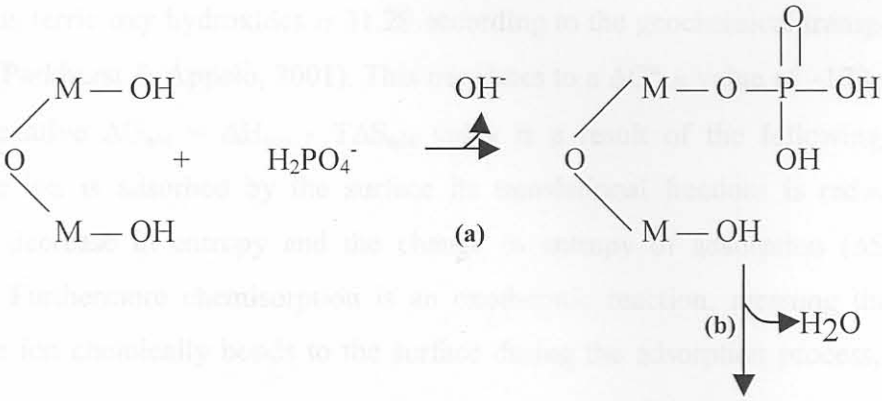


(1.6)

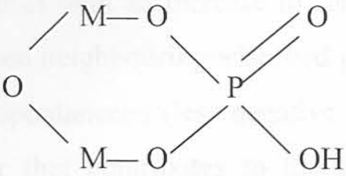
Specific adsorption

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:



(1.7)



(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 ΔG°_{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:

$$[P_{tot}] = [H_3PO_4^{0}] + [H_2PO_4^{-}] + [HPO_4^{2-}] + [PO_4^{3-}] + [FeH_2PO_4^{2+}] + [FeHPO_4^{+}] \tag{1.11}$$

And the phosphate concentration in solution governed by the solubility equilibria of gibbsite and that of variscite can be represented by the following equation:

$$[P_{tot}] = [H_3PO_4^{0}] + [H_2PO_4^{-}] + [HPO_4^{2-}] + [PO_4^{3-}] + [AlH_2PO_4^{2+}] + [AlHPO_4^{+}] \tag{1.12}$$

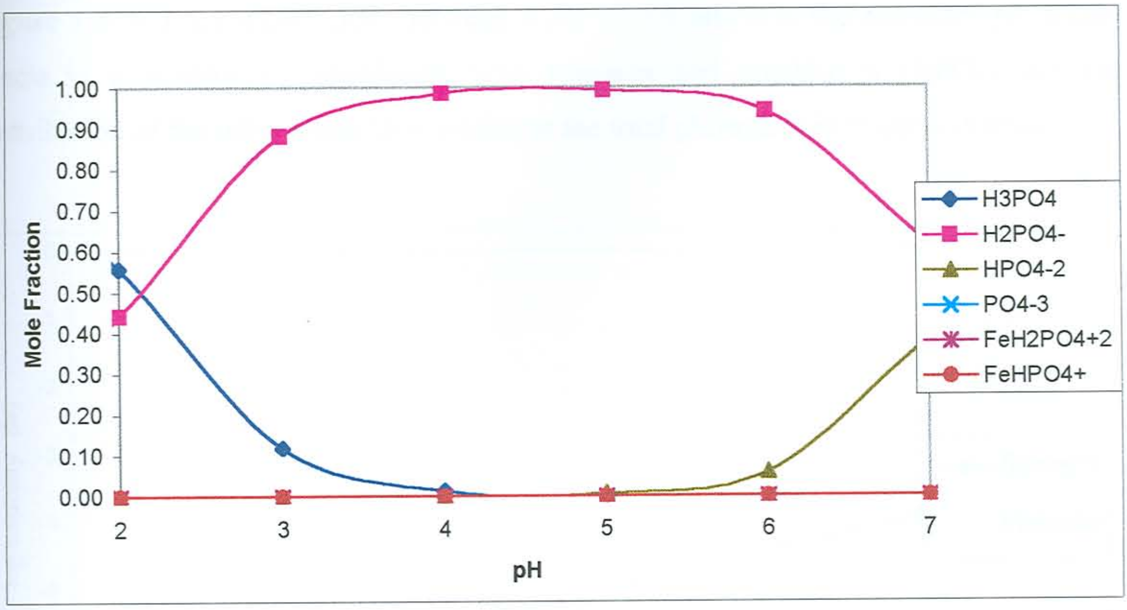


Figure 1.3. The mole fraction distribution of soluble phosphate species in equilibrium with strengite and goethite.

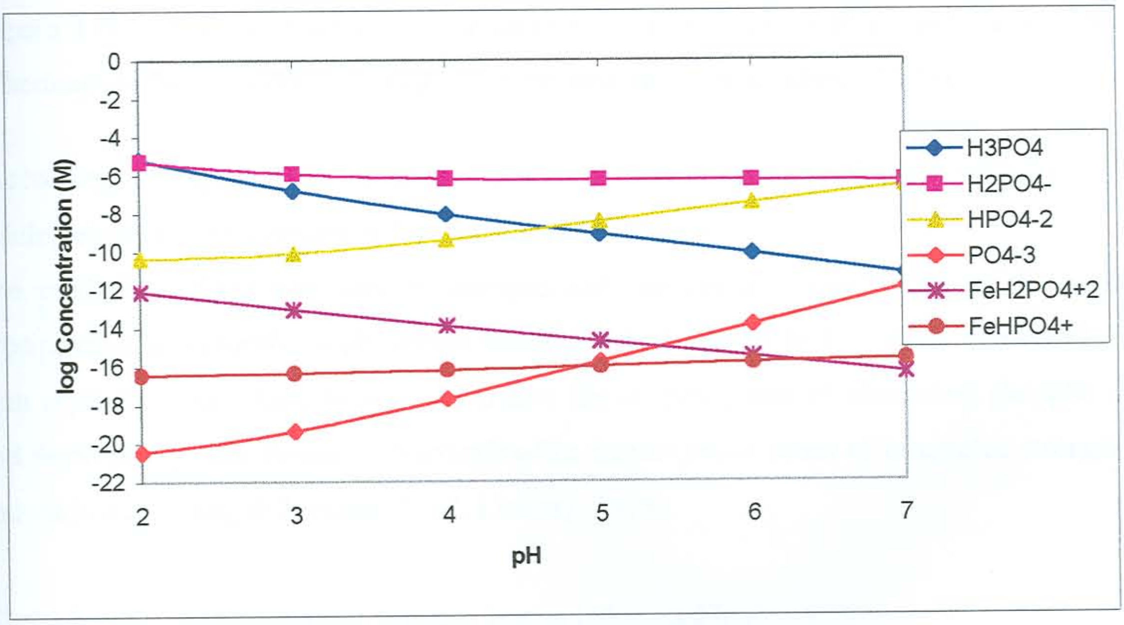


Figure 1.4. Soluble phosphate species in equilibrium with strengite and goethite, calculated with the geochemical transport model, Phreeqc (Parkhurst & Appelo, 2001).

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.

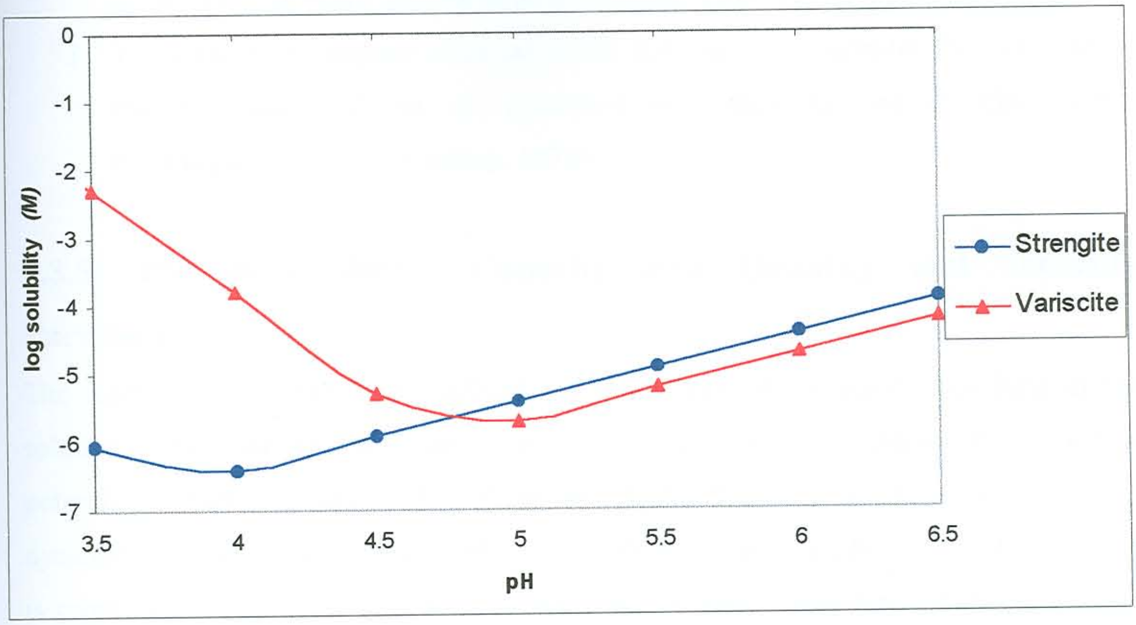


Figure 1.5. Solubility of strengite and variscite in equilibrium with goethite and gibbsite. (Thermodynamic equilibrium constants where obtained from Lindsay, (1979).

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.

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$$\mathrm{A} \leftrightarrows \mathrm{B} \qquad \textbf{(1.13)}$$

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:

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

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

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.

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

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

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.

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

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:

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

Equation 1.17 can be integrated as follows

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

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

$$ln\ A_t - ln\ A_0 = -kt \qquad \textbf{(1.20)}$$

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

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.

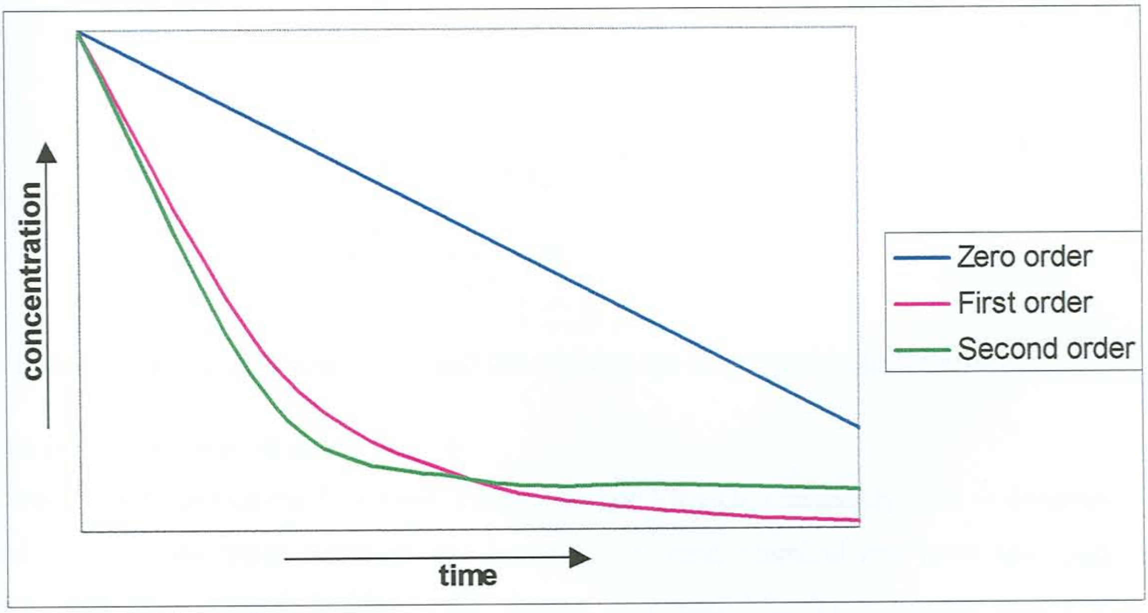


Figure 1.6. Theoretical zero, first and second order reactions.

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.

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

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

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

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

Equation (1.22) can be integrated as follows

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

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

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

A linear relationship between $\frac{1}{(A)}$ 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

$$\text{Organic P} \underset{\text{immobilisation}}{\overset{\text{mineralisation}}{\rightleftharpoons}} \text{Inorganic P} \qquad \textbf{(1.25)}$$

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.

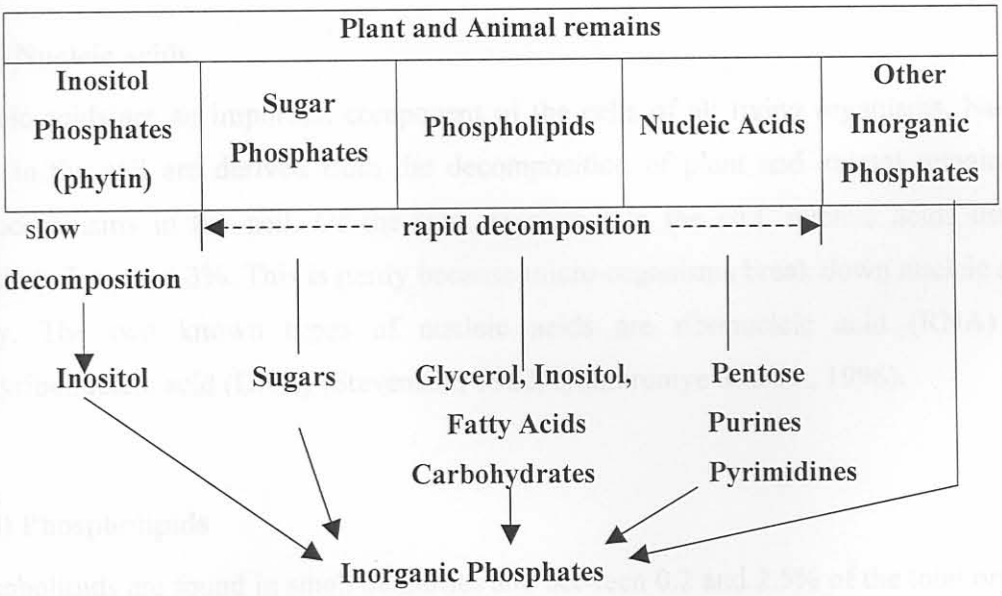


Figure 1.7 Mineralisation of organic phosphate in the soil. (Stevenson, 1982).

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.

Chapter 2

2) Materials and Methods

2.1) The soil used in the study

The soil used was a red sandy clay soil that came from Piet Retief, Mpumalanga. Selected chemical and physical properties in of the studied soil are given in **Table 2.1** and **2.2**. According to Turner & Laker, (1999), clay and sandy clay Hutton soil forms from this region originated from the Piet Retief biotite granite. This particular soil was chosen because it is known that red clay and red sandy clay soil have a high phosphate sorption capacity (Bainbridge *et al,* 1995). The high sorption capacity of the studied soil is also illustrated in **Table 2.3**. The high phosphate sorption capacity can mainly be contributed to two factors; firstly, the dominant clay mineral in these soils is kaolinite, which has a pH dependable charge on the edges of the 1:1 clay mineral; and secondly, the precipitation of Fe(III) oxy-hydroxide on the planar surfaces of these clay mineral increases the pH dependable charge of the clay mineral and greatly enhances the phosphate adsorption capacity.

Table 2.1. Selected chemical properties of the soil used in the study.

pH (H$_2$0)	Bray 1 P (mg kg^{-1})	Total^{a} P (mg kg^{-1})	CEC (cmol$_c$ kg^{-1})	C content (%)	Oxalate extractable Fe (mg kg^{-1})	Oxalate extractable Al (mg kg^{-1})
4.1	1.16	161.09	7.2	0.87	1516	1300

a) H_2SO_4 digestion

Table 2.2. Texture of soil used in the study

Sand (%)	Clay (%)	Silt (%)
59	39	2

Table 2.3. Phosphate sorption capacity of the studied soil

Phosphate added ($\mu g.g^{-1}$)	Phosphate in solution ($\mu g.g^{-1}$) after 72 hour shaking with 0.02M KCl	Phosphate sorbed ($\mu g.g^{-1}$)
0	1.92	0
250	7.46	242.54.
10000	8370.17	1629.83
1000 (and incubated for a month)	2.49	997.51

2.2) The different soil treatments

Two 250g soil samples were wetted to field capacity with a KH_2PO_4 solution with phosphate concentration equivalent to 75 and 150mg P $.kg^{-1}$ soil respectively. The soil samples were then thoroughly mixed and incubated for 5 months at ± 21 °C, while the soils were kept at field capacity. Along with the two samples that were incubated with 75mg.kg^{-1} (R75) and 150mg kg^{-1} (R150) phosphate, a third samples was also wetted to field capacity with deionised water and incubated for 5 months as the control (R).

2.3) The preparation of the DMT-HFO.

Reagents

200 g $Fe(NO_3)_3$,

4 *M* NaOH

1 *M* HCl

Preparation

HFO was prepared by a precipitation reaction. The increase in pH of a acidic ferric (III) solution causes the precipitation of a red brown gelatinous polymer $Fe_2O_3.xH_2O$ (usually written as $Fe(OH)_3$).

$$Fe^{3+} + 3OH^- \leftrightarrows Fe(OH)_3(s)\ (amorph) \qquad \mathbf{(2.1)}$$

Amorphous ferri oxy-hyroxide ($Fe(OH)_{3(am)}$) is sparingly soluble with a solubility product (K_{sp}) of 2.6×10^{-39} (McMurry & Fay, 1995, Shriver &Atkins, 1999).

Two hundred grams (0.83 moles) of ferric nitrate nonahydrate was dissolved in 2 ℓ of deionised water, and 4 *M* NaOH was added drop wise to the solution until a pH of 7 - 8 was obtained, because maximum precipitation occurs at this pH according to **Figure 2.1**. The suspension was then decanted in centrifuge tubes and centrifuged to separate the $Fe(OH)_{3(am)}$ from the Na^+ and NO_3^- containing solution. After the solution was decanted, the remaining $Fe(OH)_{3(am)}$ in the centrifuge tubes was re-suspended in deionised water and centrifuged again. This procedure was repeated three times to thoroughly clean the $Fe(OH)_{3(s)(am)}$. Finally, the pH was adjusted to more or less the pH of the soil with 1*M* HCl. The $Fe(OH)_{3(am)}$ was re-suspended in deionised water to obtain a volume of 4 ℓ with a total ferric iron concentration of $10^{-0.68}$ *M*. **Figure 2.1** shows that when pH ≤ 2, all the ferric iron (or $10^{-0.68}$ *M*) will be in solution, and when the pH is increased to 4.1 the total Fe^{3+}concentration in solution drops to $10^{-4.77}$ *M* which means that, at this pH, 99.99% of the ferric iron will precipitated out.

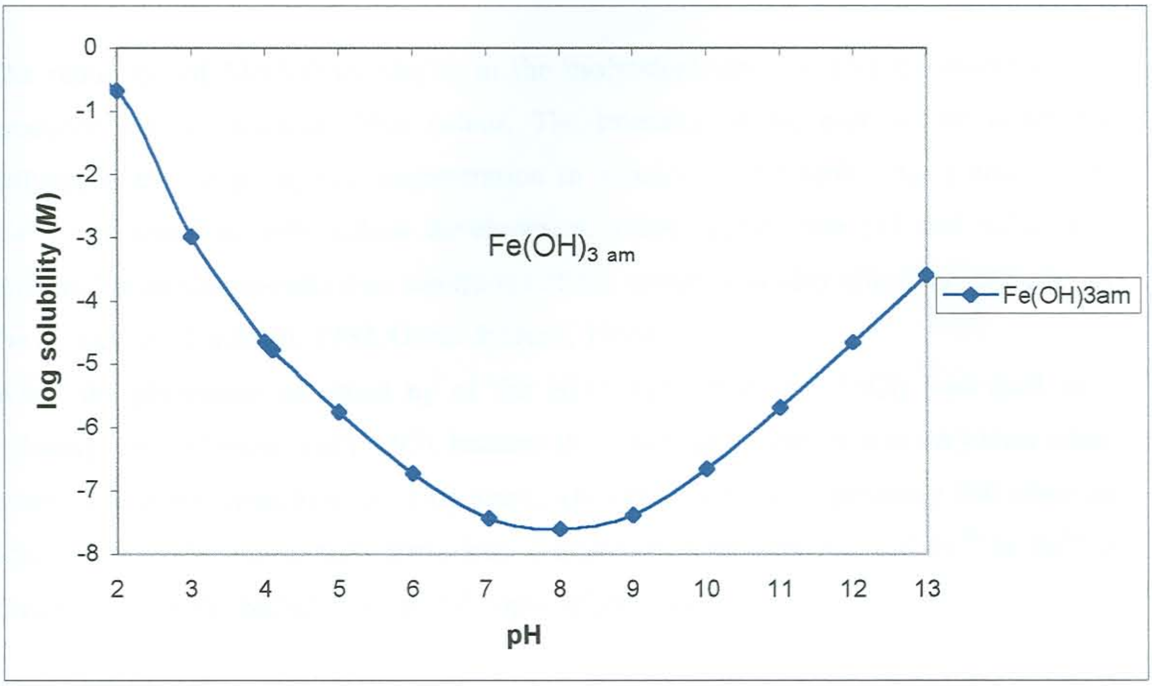


Figure 2.1. Solubility of amorphous $Fe(OH)_3$ calculated with the geochemical transport model, Phreeqc (Parkhurst & Appelo, 2001).

Fifteen centimetre length DMT (diameter of 14.3 mm, approximate pore size 2.5 – 5 nm; membrane thickness 3 μm obtained from Medicell International Ltd) were boiled twice for 5 minutes each in deionised water and thoroughly rinsed. Each dialysis tube was filled with 10 ml HFO, containing ± 2.07 *mmol* $Fe(OH)_{3(am)}$. The ends of each DMT were folded tightly and closed with household plastic clips to ensure that no HFO would leak into the soil solution during the period of shaking.

2.4) Determination of phosphate in the extracts

Total phosphate and inorganic phosphate were determined colourimetrically with the method of Murphy & Riley (1962). This method is based on the principle that a heteropoly molybdophosphoric acid complex forms when phosphate is added to an acid molybdate solution:

$$H_3PO_4 + 12\ H_2MoO_4 \leftrightarrows H_3(PO_4MoO_{10})_4 + 12H_2O \qquad \textbf{(2.2)}$$

The reduction of Mo(VI) to Mo(V) in the molybdophosphoric acid by ascorbic acid produces the characteristic blue colour. The intensity of the blue colour is mainly influenced by the phosphate concentration in solution, but arsenic (As^{5+}) and silicon (Si^{4+}) can interfere with colour development. Other factors like pH and substances influencing oxidation-reduction conditions of the system can also affect the intensity of the blue colour (Jackson, 1962, Olsen & Dean, 1965).

When the phosphate adsorbed by of the HFO was determine, $SnCl_2$ was used as a reducing agent (Freese *et al* (1995), because the colour development was very slow when ascorbic acid was used as a reducing agent. The reason for this is probably that when an acid solution also has a high ferric iron concentration the reduction of Fe^{3+} to Fe^{2+} is favoured above the reduction of molybdophosphoric acid.

Reagents

0.25 M H_2SO_4

4 M NaOH

Paranitrophenol (indicator)

The following reagens were the **colour developing reagents**
0.032 M $(NH_4)_6 Mo_7O_{24}.4H_2O$ (ammonium molybdate)

0.3 M $C_6H_8O_6$ (ascorbic acid) solution.

0.01 M $K(SbO)C_4H_4O_6.0.5H_2O$ (potassium antimonyl tartrate hemihydrate)

$SnCl_2$ (reducing agent used for determination of phosphate adsorbed by of the HFO)

Method

A suitable aliquot was pipetted into a 50 cm^3 volumetric flask, and a drop of the indicator, paranitrophenol was added. The pH of the aliquot was adjusted to ± 5.6, first by adding 4 M NaOH until the indicator turned yellow and then 0.25 M H_2SO_4 until the indicator just turned clear again. Alkaline extractions were only acidified untill the indicator turned clear, 8 ml of the colour developing solution was added, made up to volume, shaken and the colour intensity was read after 10 minutes on a spectrophotometer at 712 nm.

2.5) The sequence of the phosphate fractionations

2.5.1 DMT-HFO extraction

The sequence of the fractionation is illustrated in **Figure 2.2.** After the DMT-HFO was prepared, it was immersed in glass flasks containing 40 cm^3 of deionised water and 1g of soil. The flasks were placed in a constant temperature room on a horizontal shaker and shaken for 56 days. On days 1, 7, 14, 21, 28, 35,42 and 56, the DMT-HFO's were replaced with new DMT-HFO. With each replacement four of the DMT's were removed from the flasks, cut open and the HFO was washed out of the tubes into a glass beaker. The HFO suspension was then dissolved with 5 cm^3 5.4 *M* H_2SO_4 and the phosphate concentration was determined colorimetrically with the molybdophosphoric blue method using $SnCl_2$ as reductant. A standard series was prepared with the same background Fe and H_2SO_4 concentrations. After the DMT-HFO was removed the soil suspensions in the glass flasks were transferred to centrifuge tubes and centrifuged to separate the soil and the solution. The supernatant solution was discarded and the soil was sequentially extracted for phosphate according to the flow chart in **Figure 2.2.**

2.5.1) $NaHCO_3$ extraction

The $NaHCO_3$ - extraction is based on the method of Olsen & Dean (1965). The $NaHCO_3$ -extraction is used on a wide range of acid and calcareous soils. In calcareous soils the addition of $NaHCO_3$ changes the equilibrium between $CaCO_3$ and calcium phosphate. The increased CO_3 concentration in solution will favour the dissolution of calcium phosphate due to the precipitation of $CaCO_3$. In acid soils the increase in pH increases the solubility of ferric-and aluminium phosphates as illustrated in **Figure 1.5**. As explained earlier the excess of CO_3 in solution favours the precipitation of $CaCO_3$ and prevents the precipitation of calcium phosphate. Therefore the phosphate that goes into solution because of the dissolution of ferric and aluminium phosphates will not re-precipitate as calcium phosphate (Olsen & Dean, 1965, Hesse, 1971, Lindsay, 1979, Tiessen & Moir, 1993).

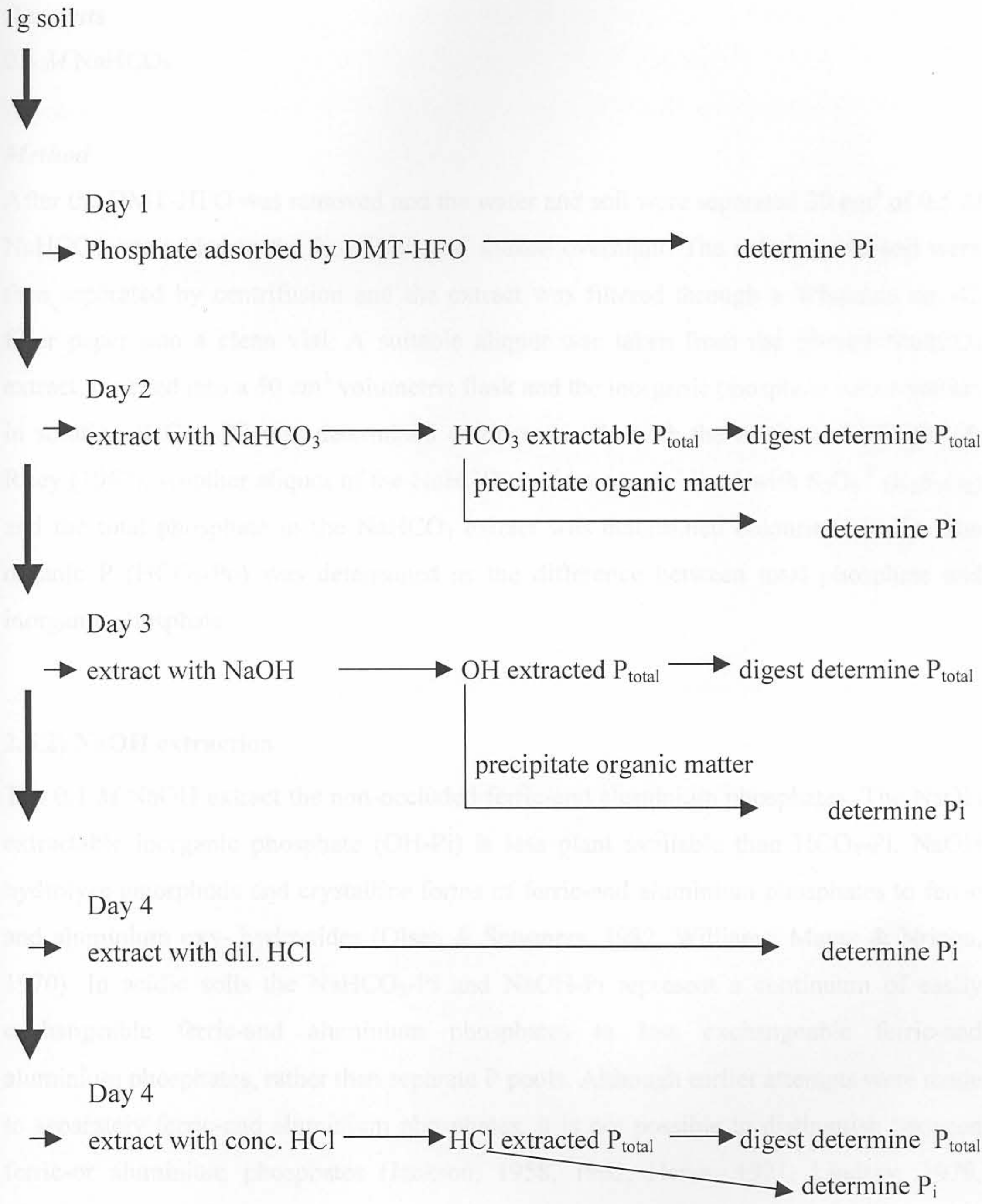


Figure 2.2. Flow chart of the sequential P extraction method

Reagents

0.5 *M* $NaHCO_3$

Method

After the DMT-HFO was removed and the water and soil were separated 30 cm^3 of 0.5 *M* $NaHCO_3$ was added to the 1g of soil and shaken overnight. The solution and soil were then separated by centrifusion and the extract was filtered through a Whatman no. 42 filter paper into a clean vial. A suitable aliquot was taken from the filtered $NaHCO_3$ extract, pipetted into a 50 cm^3 volumetric flask and the inorganic phosphate concentration in solution (HCO_3-Pi) was determined colorimetrically with the method of Murphy & Riley (1962). Another aliquot of the $NaHCO_3$ extract was oxidised with $S_2O_8^{-2}$ ($K_2S_2O_8$) and the total phosphate in the $NaHCO_3$ extract was determined colourimetrically. The organic P (HCO_3-Po) was determined as the difference between total phosphate and inorganic phosphate.

2.5.2) NaOH extraction

The 0.1 *M* NaOH extract the non-occluded ferric-and aluminium phosphates. The NaOH extractable inorganic phosphate (OH-Pi) is less plant available than HCO_3-Pi. NaOH hydrolyse amorphous and crystalline forms of ferric-and aluminium phosphates to ferric and aluminium oxy- hydroxides (Olsen & Summers, 1982, Williams, Mayer & Nriagu, 1970). In acidic soils the $NaHCO_3$-Pi and NaOH-Pi represent a continuum of easily exchangeable ferric-and aluminium phosphates to less exchangeable ferric-and aluminium phosphates, rather than separate P pools. Although earlier attempts were made to separately ferric-and aluminium phosphates, it is not possible to distinguish between ferric-or aluminium phosphates (Jackson, 1958, 1962, Hesse, 1971, Lindsay, 1979, Tiessen & Moir, 1993).

According to Anderson (1975), NaOH is also the most effective extractant for soil organic phosphate. NaOH hydrolyses the organic P esters in the soil, releasing it in solution. Because the nature of a large part of the organic phosphate compounds in the soil are still unknown, it is not yet possible to determine exactly which organic phosphate was extracted (Anderson, 1975). According to Tiessen & Moir (1993), the organic phosphate extracted with $NaHCO_3$ ($NaHCO_3$-Po) and NaOH (NaOH-Po) probably also represents the same organic phosphate pool.

Reagents

0.1 *M* NaOH

Method

30 cm^3 of 0.1 *M* NaOH was added to the 1g of soil that was brought over from the $NaHCO_3$ extraction and shaken overnight. The solution and soil were then separated by centrifusion and the extract was filtered through a Whatman no. 42 filter paper into a clean vial. A suitable aliquot was taken from the filtered NaOH extract, pipetted into a 50 cm^3 volumetric flask and the inorganic phosphate concentration (OH-Pi) in solution was determined colorimetrically with the method of Murphy & Riley, (1962). Another aliquot of the NaOH extract was oxidised with $S_2O_8^{-2}$ ($K_2S_2O_8$) and the total phosphate in the NaOH extract was determined colorimetrically. The organic phosphate (OH-Po) was determined as the difference between total phosphate and inorganic phosphate.

2.5.3) 1 *M* HCl extraction

1 *M* HCl is very effective in extracting phosphate associated with calcium phosphates, from dicalcium phosphate ($CaHPO_4$) dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$), octacalcium phosphate [$Ca_8H(PO_4)_6.5H_2O$] to the least soluble calcium phosphate, namely fluorapatite [$Ca_5(PO_4)_3F$] (Lindsay, 1979, Williams, Syers, Harris & Armstrong, 1970). Organic phosphate is seldom present in this fraction (Tiessen & Moir, 1993). When the pH of this soil is considered it is unlikely, that calcium phosphate would have precipitated in this soil. If calcium phosphate was present in the soil it was most probably trace amounts of residual phosphate fertilizer. In this study it is more likely that the 1 *M* HCl extracted aluminium- and ferric phosphates not extracted with 0.1 *M* NaOH.

Reagents

1 *M* HCl

Method

30 cm^3 of 1 *M* HCl was added to the 1g of soil that was brought over from the NaOH extraction and shaken overnight. The solution and soil were then separated by centrifusion and the extract was filtered through a Whatman no. 42 filter paper into a clean vial. A suitable aliquot was taken from the filtered 1 *M* HCl extract, pipetted into a 50 cm^3 volumetric flask and the inorganic phosphate (1*M* HCl-Pi) concentration in solution was determined colorimetrically with the method of Murphy & Riley (1962).

2.5.4) Hot concentrated HCl extraction

Hot concentrated HCl extract most of the residual organic and inorganic P left in the soil and represents the very stable organic and inorganic P pools. The organic P extracted with concentrated HCl could also represent plant available P that is not alkali soluble (Tiessen & Moir, 1993).

Reagents

Concentrated HCl (11.3 *M*)

Method

10 cm^3 concentrated HCl was added to the 1 g soil brought over from the 1 *M* HCl extraction and heated on a water bath at 80°C for 10 minutes. After 10 minutes the samples were removed, 5 ml concentrated HCl was added and left at room temperature for one hour. The extract was then centrifuged and decanted into a clean vial. The soil residue was washed twice with deionised water, centrifuged and the extract was filtered through a Whatman no. 42 filter paper into a clean vial. A suitable aliquot was taken from the HCl extract, pipetted into a 50 cm^3 volumetric flask and inorganic phosphate (HCl-Pi) concentration in solution was determined colorimetrically with the method of Murphy & Riley,(1962). Another aliquot of the concentrated HCl extract was oxidised with $S_2O_8^{-2}$ ($K_2S_2O_8$) and the total P in the concentrated HCl extract was also determined

colorimetrically. The organic P (HCl-Po) was determined as the difference between total phosphate and inorganic phosphate.

2.6 Statistical analysis

An analysis of variance (Anova) of the data was done on the statistical program SAS. The Tukey test was used to determine significant differences at $\alpha = 0.05$.

Chapter 3

Results and Discussion

3.1) Inorganic phosphate fractions

3.1.1) DMT-HFO fraction

The role of the DMT-HFO is to act as a phosphate sink simulating a plant root in the soil. This will cause the equilibrium to shift to the phosphate sink, resulting in the mobilisation of solid phase phosphate to replenish the depleted phosphate in solution.

The origin of phosphate in solution can be de-adsorbed phosphate, phosphate from phosphate minerals and mineralised phosphate. It is however important to note that it is not possible to distinguish from which source the phosphate in solution originated. The fractional composition of the soil solution and the expected change in composition over time is at best an educated guess based on the facts that the release kinetics of some sources are slower or faster than that of others.

According to **Table 3.1** approximately the same amount of phosphate desorbed from the different phosphate treatments after 24 hours, indicating that the phosphate released from R, R75 and R150 after 24 hours, originated from the same solid phase with approximately the same release kinetics. Freese *et al*, (1995), found that for more or less 50 hours the phosphate release rate of 6 Belgium soils with a high phosphate saturation was higher than the transport rate through the DMT causing phosphate backup. In this study the amount of phosphate desorbed after 24 hours from all the treatments, were considerably less than that reported by Freese *et al.*, (1995), the amount of phosphate released from the different treatments in the first 24 hours varied form 2.06 –2.83 mg kg $^{-1}$ compared to 27 to 130 mg kg $^{-1}$ reported by Freese *et al.*, (1995). The rate constants of phosphate release of all the treatments were also lower that the rate constant of phosphate transport through the DMT reported. Therefore it is unlikely that phosphate "backup" occurred in this study.

Table 3.1. The effects of the different phosphate treatments on the amount of phosphate extracted with DMT-HFO over time.

Day	R (mg P kg^{-1})	R75 (mg P kg^{-1})	R150 (mg P kg^{-1})
1	x[1]2.06 **ab**[2]	x 2.83 **b**	x 2.80 **b**
7	x 2.89 **b**	y 6.09 **a**	z 7.64 **a**
14	x 2.87 **b**	x 2.50 **bc**	y 8.20 **a**
21	x 2.05 **ab**	xy 1.31 **c**	y 0.85 **b**
28	x 1.00 **a**	xy 1.52 **bc**	y 1.52 **b**
35	x 1.07 **a**	x 1.66 **bc**	x1.21 **b**
42	x 1.26 **a**	x 1.47 **bc**	x 1.74 **b**
56	x 0.93 **a**	y 2.23 **bc**	y 2.81 **b**

1 Mean values in rows with different letters x y z are significantly different ($\alpha = 0.05$).

2 Mean values in columns with different letters a, b, c, d, e and f are significantly different ($\alpha = 0.05$)

Figure 3.1 describes the cumulative phosphate desorbed over the 56-day period for the different treatments. After 56 days, a total of 24, 16.8 and 12.1 mg P kg^{-1} were released from R150, R75 and R respectively.

Although about twice as much phosphate was released from R150 than from the control (R) treatment, it represented only 8 % of the phosphate applied to R150 and 6 % of R75.

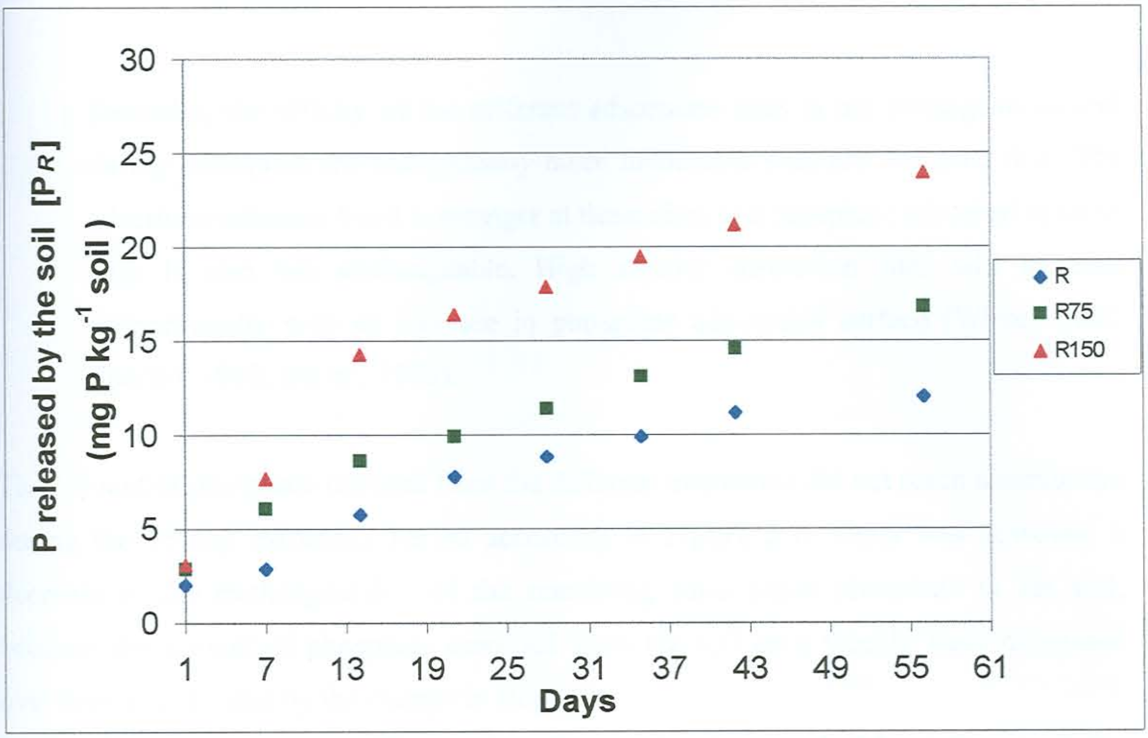


Figure 3.1. Cumulative P released from R, R75 and R150 over time.

The small amount of phosphate recovered from the treated soil is the result of the low exchangeability of sorbed phosphate from this soil.

1. Strengite and variscite are the predominant phosphate minerals present in acid soils and have a low solubility that decrease with a decrease in pH as illustrated in **Figure 1.5**. Because of the low solubility of strengite and variscite it will take a long time to replenish the phosphate removed from solution.
2. Phosphate adsorbed by aluminium and ferric oxy hydroxides also has a low exchangeability because of the strong bonded binuclear complexes that form with aluminium and ferric oxy hydroxides. The recovery of added phosphate also decreases with an increase in the adsorption surface of a soil. This is due to two factors; firstly, with an increase in saturation of the adsorption surface steric interference increases between neighbouring adsorbed species, which increase the exchangeability of these adsorbed species. Therefore the larger the adsorption surface the more phosphate can adsorbed before steric interference will occur.

Secondly, the affinity of the different adsorption sites is not homogeneous and during adsorption the energetically more favourable sites are occupied first. The adsorbate-substrate bond is stronger at these sites and phosphate adsorbed at these sites is also less exchangeable. High affinity adsorption sites will increase proportionally with an increase in phosphate adsorption surface (White, 1980, Sposito, 1989, Atkins, 1999).

The amount of phosphate released from the different treatments did not reach a maximum during the 56-day extraction period according to **Figure 3.1.** There was however, a decrease in the exchangeability of the remaining solid phase phosphate in the soil, because the amount of phosphate desorbed from the soil on a weekly basis decreased over time as indicated by the change in slope.

Figure 3.1 shows that two different phosphate pools, distinguished by different release kinetics participated in the desorption process of R75 and R150. A more labile phosphate pool (pool A), characterised by the higher phosphate release rate compared to the second phosphate pool (pool B), dominated the phosphate release kinetics during the first 14 days. The desorption rate of the control treatment decreased more gradually over time and did not show the distinct change in the phosphate release kinetics that R75 and R150 showed.

An explanation why the release kinetics of the control treatment did not show the same distinct change could be that the control treatment contained very little adsorbed phosphate. According to Hingston *et al.* (1974), and Lookman *et al.*, (1995), the faster release kinetics is usually associated with the desorption of adsorbed phosphate directly in contact with the soil solution.

The amount of phosphate released from R150 after 14 days was more than double (111%) the amount of phosphate released by the control treatment, while 49% more phosphate desorbed from R75. After ±14 days a less exchangeable phosphate pool (pool B) became more dominant, which lead to a decrease in the phosphate release rates of R R75 and R150. The slower release kinetics of Pool B is probably the result of slow dissolution kinetics of phosphate minerals (such as strengite and variscite) and/or the slow diffusion kinetics of phosphate from interior adsorption sites inside sequi-oxides (Lookman *et al.* 1995).

3.1.1.1) Kinetics of phosphate desorption.

In this study, first order kinetics was used to describe the phosphate release kinetics of the soil. It is however important to note that, in a heterogeneous system like soil, the phosphate release kinetics would not necessarily follow first order kinetics exactly because of the different solid phases with different release kinetics which are responsible for the phosphate released in solution. It is therefore more correct to refer to it as pseudo first order kinetics.

As discussed earlier, **Figure 3.1** showed two different phosphate pools, distinguished by different release kinetics indicated by the change in the slopes of curves. The transition between the two phosphate pools were probably a more gradual process, with both phosphate pools participating from the start of the experiment. However because the release rate of pool A was higher than that of pool B, it dominated the release kinetics in the first 14 days and as the pool A became depleted Pool B became more dominant. To obtain one kinetic equation that describes simultaneous phosphate release from two phosphate pools with different release kinetics a two-component first order model was used.

The mass balance equation for the total exchangeable solid phase phosphate (SP_{total}) in the soil at time t = 0 is

$$SP_{total_0} = SP_{A_0} + SP_{B_0} \qquad \textbf{(3.1)}$$

where SP_{A_0} = Initial amount of phosphate in Pool A
SP_{B_0} = Initial amount of phosphate in Pool B

The mass balance equation at time *t* will therefore be:

$$SP_{total(t)} = SP_{A(t)} + SP_{B(t)} \qquad \textbf{(3.2)}$$

If the decrease in the different phosphate solid phases over time follow first order kinetics, the integrated rate laws for Pool A and B will be:

$$SP_{A(t)} = SP_{A_0}\, e^{-k_1 t} \tag{3.3}$$

where k_1 = conditional first order rate constant (day^{-1}) for phosphate desorption from Pool A.

$$SP_{B(t)} = SP_{B_0}\, e^{-k_2 t} \tag{3.4}$$

where k_2 = conditional first order rate constant (day^{-1}) for phosphate desorption form Pool B.

The total solid phase phosphate ($SP_{total(t)}$) left in the soil at time ***t*** will be given by:

$$SP_{total(t)} = SP_{A_0}\, e^{-k_1 t} + SP_{B_0}\, e^{-k_2 t} \tag{3.5}$$

The amount of phosphate **released** at time ***t*** will be the difference between initial amount of phosphate in the respective pools and amount of phosphate in the pools at time ***t:***

$$P_{R(t)} = SP_0 - SP_0\, e^{-k\,t} \tag{3.6}$$

The total amount of phosphate released at time *t* can therefore be expressed as:

$$\begin{aligned} P_{R(t)} &= SP_{A_0} - SP_{A_0}\, e^{-k_1 t} + SP_{B_0} - SP_{B_0}\, e^{-k_2 t} \\ &= SP_{A_0}\,(1 - e^{-k_1 t}) + SP_{B_0}\,(1 - e^{-k_2 t}) \end{aligned} \tag{3.7}$$

(Snoeyink & Jenkins, 1980, Olson & Shuman, 1985, Freese *et al*, 1995, Lookman *et al*, 1995, Atkins, 1999).

Using mass balance principles the contribution of SP_A and SP_B to $P_{R(t)}$ as a function of time can be represented as follows:

Contribution of SP_B to $P_{R(t)}$ as a function of time:

$$\alpha_A = \frac{\left(1 - e^{k_1 t}\right) SP_{A_0}}{P_{R(t)}} \tag{3.8}$$

$$SP_{A(t)} = \alpha_A \, P_{R(t)} \tag{3.9}$$

Contribution of SP_B to $P_{R(t)}$ as a function of time:

$$\alpha_B = \frac{\left(1 - e^{k_2 t}\right) SP_{B_0}}{PR_{total(t)}}. \tag{3.10}$$

$$SP_{B(t)} = \alpha_B \, P_{R(t)} \tag{3.11}$$

The release kinetics of the soil under the influence of the DMT-HFO can be represented as follows:

$$SP \xrightarrow{k_R} P_{sol} \xrightarrow{k_T} P_{HFO} \tag{3.12}$$

Where SP = Solid phase phosphate

P_{sol} = phosphate in solution

P_{HFO} = phosphate adsorbed by HFO

k_T = rate constant of phosphate transport through the membrane (0.09 ± 0.01 h^{-1}, Freese *et al*, 1995)

k_R = is the rate constant of phosphate release

In this study the rate constant of phosphate release *(k_R)* was lower than the rate constant of phosphate transport across the dialysis membrane *(k_T),* therefore phosphate release was the rate-determining step. It was therefore assumed that the rate constant of phosphate release from the soil was equal to the rate constant of phosphate adsorption *(k_A)* by the DMT-HFO.

The rate constant of phosphate adsorption *(k_A)* by the DMT-HFO was obtained from a plot of the natural logarithm (*ln*) of the phosphate adsorption by the DMT-HFO over time (with the slope as k_A), this is illustrated in **Figures, 3.2, 3.3** and **3.4**. The desorption data was split into two parts to obtain the rate constants of the different pools. The desorption data of the control treatment was also divided at day 14 for the sake of comparison.

The SP_{A_0} of R, R75 and R150 were taken as the amount of P adsorbed (by the HFO) after 14 days. The SP_{B_0} of R, R75 and R150 were then obtained by solving **Equation 3.7** in terms of SP_{B_0} because it was the only unknown left in the equation.

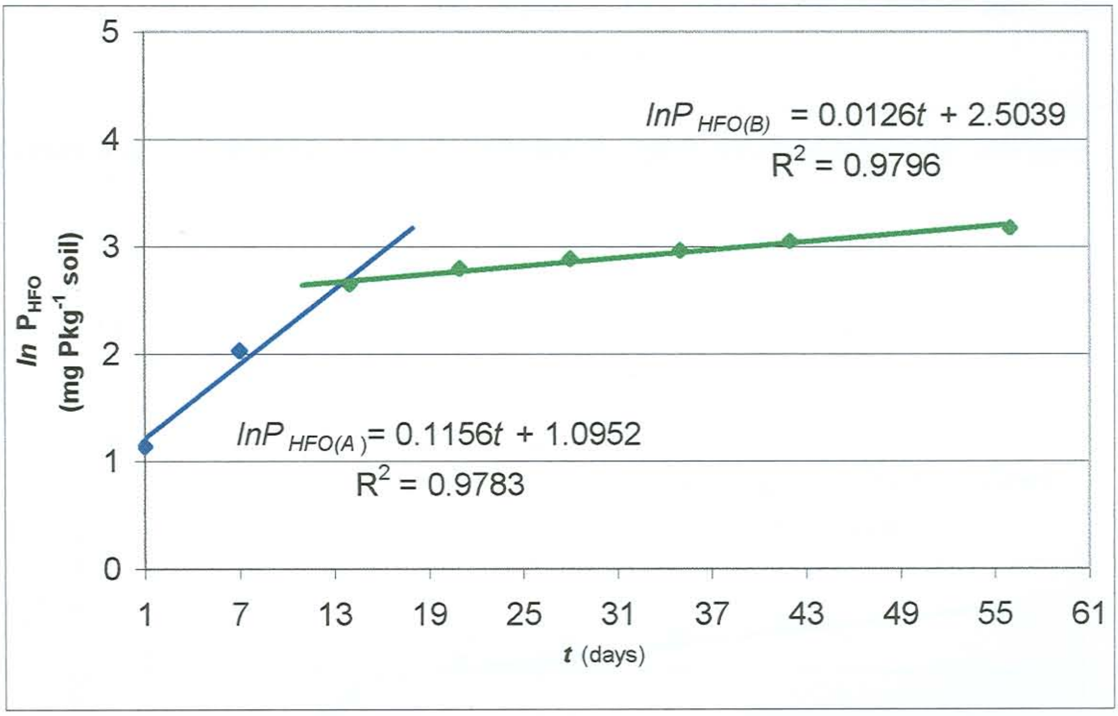


Figure 3.2. The natural logarithm (ln) of the phosphate released from R150 over time

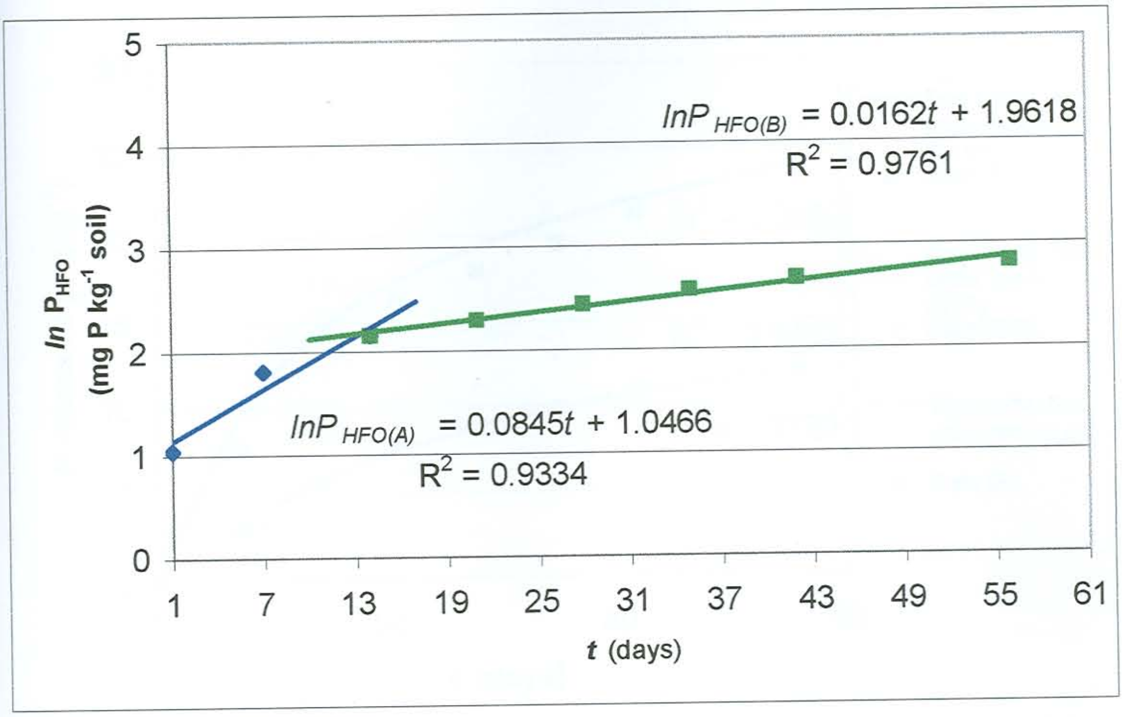


Figure 3.3. The natural logarithm (ln) of the phosphate released from R75 over time

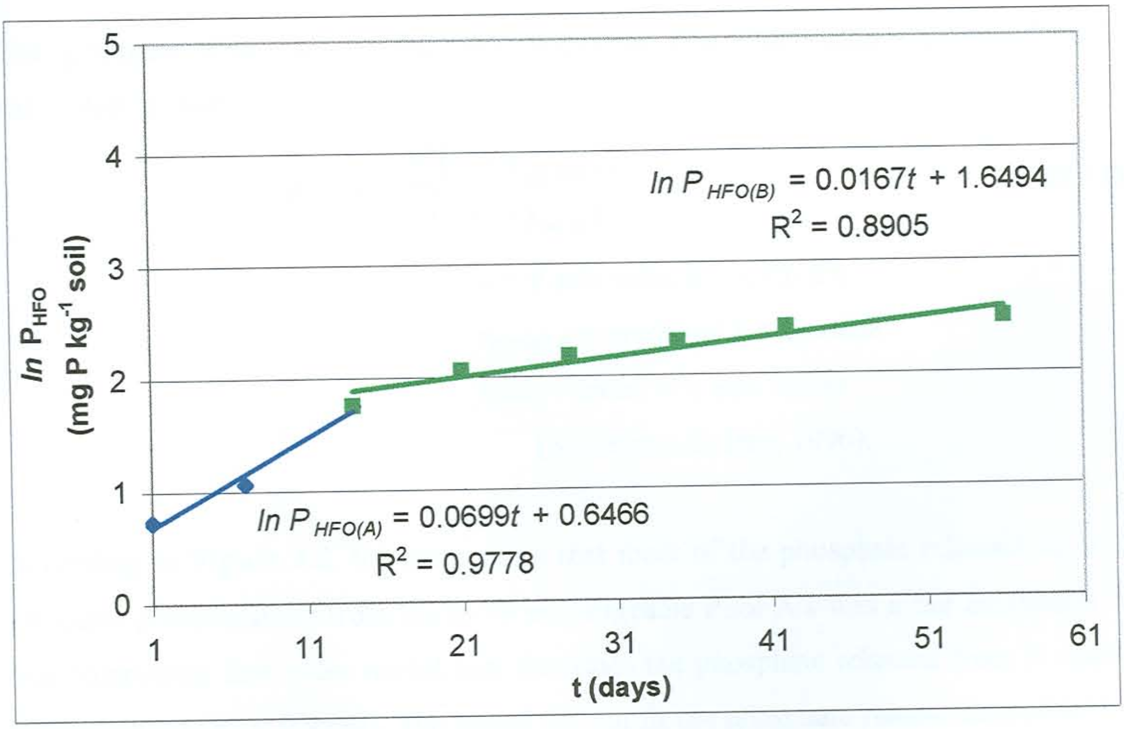


Figure 3.4. The natural logarithm (ln) of the phosphate released from R over time

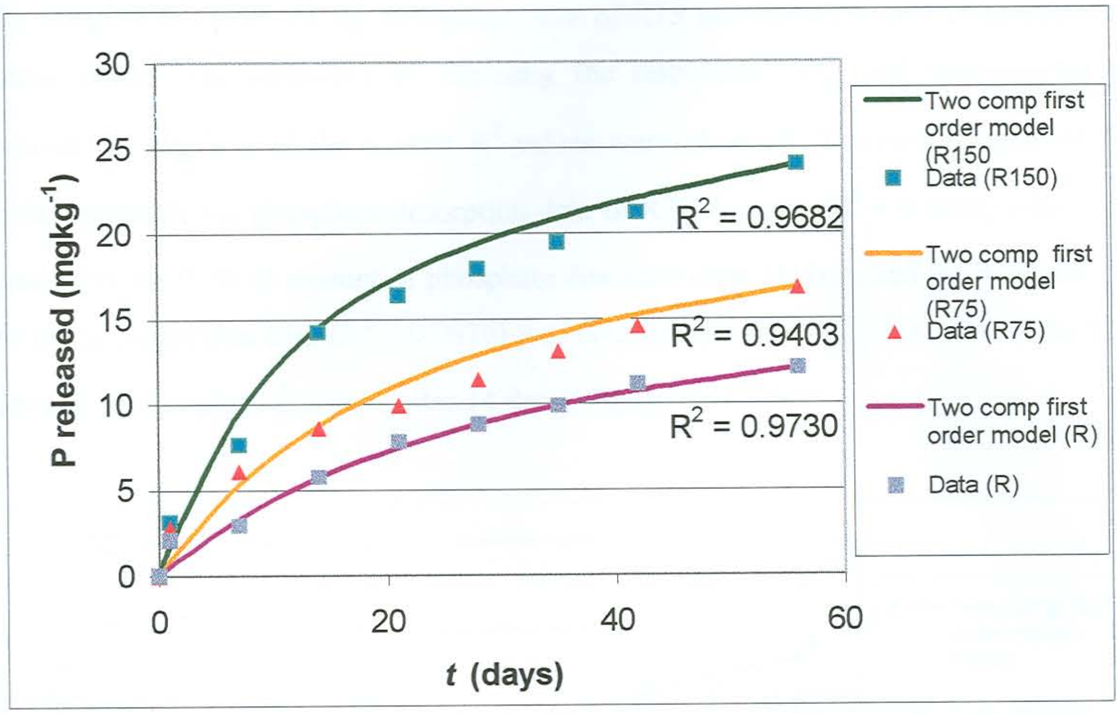


Figure 3.5. Comparison of the desorption data of the different treatments over time with the two-component first model

The goodness-of-fit (R^2) of the two-component first order model to the data, was calculated as follows:

$$R^2 = 1 - \frac{\sum (y_i - y_{predicted})^2}{\sum (y_i - y_{mean})^2} \qquad \textbf{(3.13)}$$

y_i = y axis value at the *i*th day

$y_{predicted}$ = predicted y axis value

y_{mean} = mean of y axis values

(Schulthess & Dey, 1996).

According to **Figure 3.5**, the assumption that most of the phosphate released up to day 14, came predominantly from the more exchangeable Pool A's was a fair estimation. The two-component first order model best describes the phosphate released from R over the 56-day period ($R^2 = 0.9730$). The model did not fit the phosphate release data of R75 and R150 that well ($R^2 = 0.9403$ and $R^2 = 0.9682$ for R75 and R150 respectively).

To obtain a fit better for the desorption data of R75 and R150 the two component first order model was optimised by adjusting the respective SP_{A_0} and recalculating the respective SP_{B_0}'s until the highest R^2 values were obtained. The two component first order model fit the phosphate desorption data of R75 the best (R^2 = 0.9528) when SP_{A_0} was taken as 78 % of amount of phosphate desorbed after 14 days, and for R150 the best fit to the desorption data (R^2 = 0.9870) was obtained of when SP_{A_0} was taken as 86 % of amount of phosphate desorbed after 14 days (**Figure 3.6**).

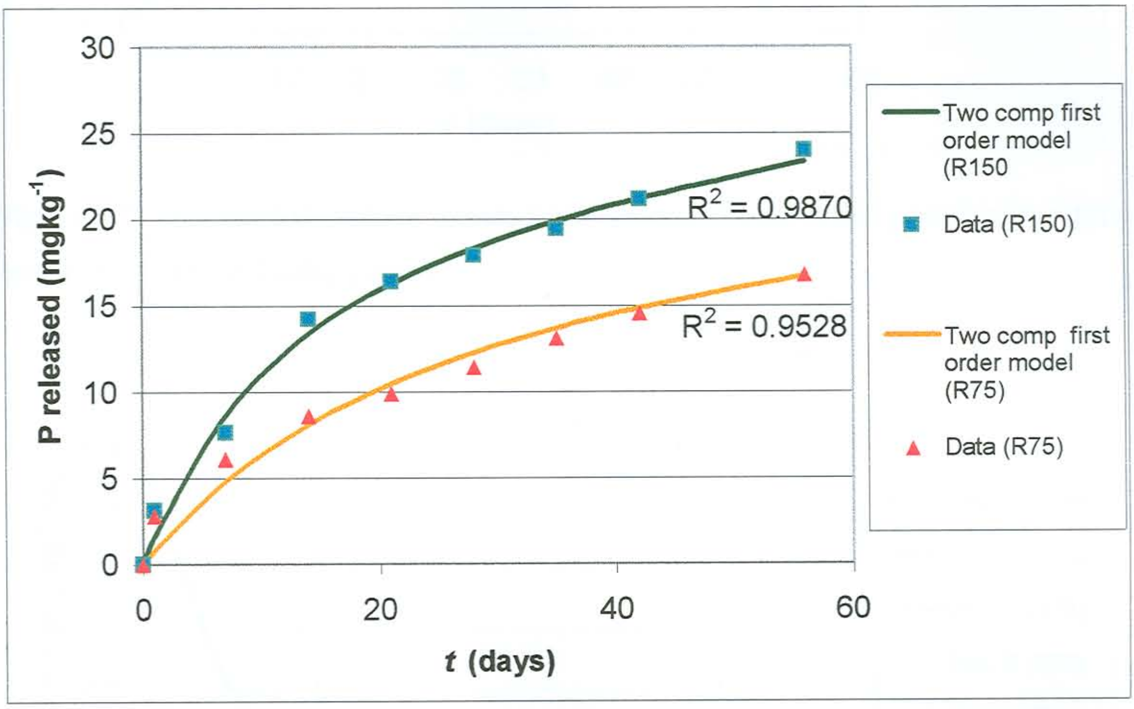


Figure 3.6. Comparison of the desorption data of R75 and R150 over time with the two-component first model using the second estimation of the respective pool A's.

In **Figure 3.7,** using **equations 3.9** and **3.11,** the release kinetics of the two phosphate pools of the different treatments were plotted separately to show the different release kinetics of each pool over the 56-day period. In **Figure 3.8** the desorption rates of the two phosphate pools of the different treatments were plotted as a function of time.

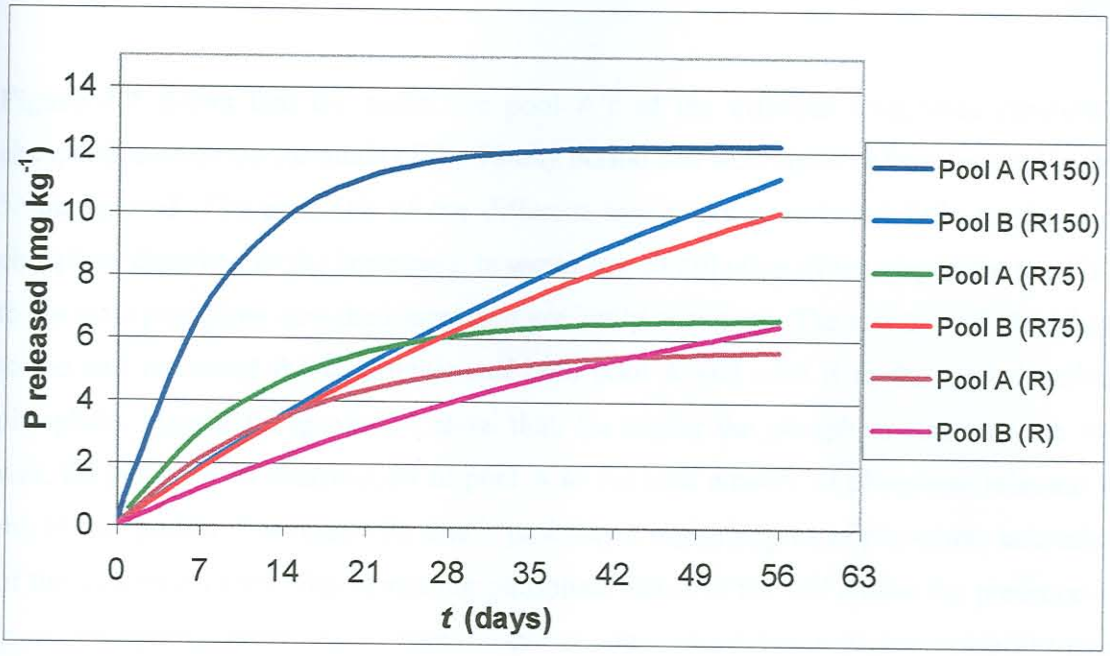


Figure 3.7. Simulated phosphate release from respective pool A and pool B of the different treatments over the 56-day period.

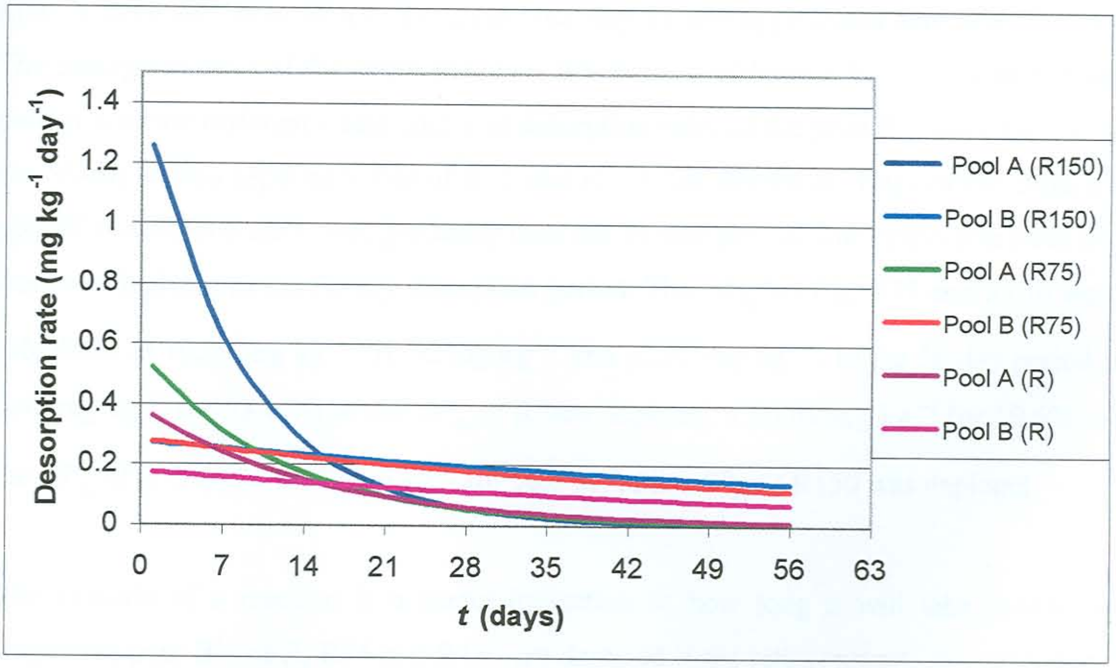


Figure 3.8. Desorption rates of the respective pool A's and pool B's of the different treatments over the 56-day period.

Figure 3.7 shows that the respective pool A's of the different treatments controlled phosphate desorption for much of the 56-day period and were more or less depleted in the 56-day period. The pool B's of the different treatments contributed little to the total phosphate desorbed in the beginning, however the contribution of the respective pool B's to the total phosphate desorbed increased gradually over time. The addition of phosphate to the soil increased the contribution of both pool A and pool B to the total desorbed phosphate. However **Figures 3.7** show that, the higher the phosphate status of the soil was, the greater was contribution of pool A to the total amount of phosphate released in the 56-day period. The reason for this is probably a higher degree of phosphate saturation of the adsorption sites with increasing phosphate status of the soil and/or the presence of more amorphous ferric and aluminium phosphates, which has a higher solubility than crystalline ferric and aluminium phosphates. **Figure 3.8** shows that the desorption rate of the pool A of R150 was initially higher than the desorption rates of the pool A's of the other treatments. The desorption rates of the respective pool A's decreased rapidly in the first 14 days and were almost the same after day 21 and approaches zero after day 35. The desorption rates of the respective pool B's were considerably lower than that of the pool A's of the different treatments The desorption rates of the pool B's were similar in the 56-day period especially that of R75 and R150, the desorption rates of the different pool B's decreased also more gradually over the 56-day period. The respective Pool B's were not depleted in the 56-day desorption period. The SP_{B_0}'s of R, R75 and R150 were calculated at 10.60 mg kg $^{-1}$ 16.92 mg kg $^{-1}$ and 22.07 mg kg $^{-1}$. In the 56-day period ± 6.44 mg kg $^{-1}$ (or 53.1 %) of the SP_{B_0} of R was depleted, ± 10.09 mg kg $^{-1}$ (or 59.6%) of the SP_{B_0} of R75 and ± 11.17 mg kg $^{-1}$ (or 50.6 %) of the SP_{B_0} of R150 was depleted.

The half-life of a reaction is a useful indication of how long it will take before the respective pool B's of R, R75 and R150 are depleted if the rate constants do not change. The half-life for a reaction, following first order kinetics is derived as follows.

At $t_{1/2}$ of the respective pool B's:

$$SP_{B_{(t)}} = \frac{1}{2} SP_{B_0} \qquad \textbf{(3. 14)}$$

Using the integrated rate law of a first order reaction (**Equation 1.21**), **Equation 3.14** can be rewritten as follows:

$$\ln\left(\frac{\frac{1}{2}SP_{B_0}}{SP_{B_0}}\right) = -k_2\, t_{1/2}$$

$$\ln\left(\frac{1}{2}\right) = -k_2\, t_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k_2} \qquad \textbf{(3. 15)}$$

(Snoeyink & Jenkins, 1980, Atkins, 1999).

Using **equation 3. 15** the half-lives of the pool B's were calculated at ± 41.5 days for R, ± 43 days for R75 and that of R150 at ± 55 days. The addition of 75 mg kg^{-1} prolonged the half-life of Pool B of the studied soil only slightly. The 150 mg kg^{-1} treatment however prolonged the half-life of Pool B of the studied soil with ± 13.5 days. Although it will take only 55 days for pool B of R150 to halve it would take ± 1500 days or 4 year before the pool B of R150 is depleted at the current rate constant of phosphate release for the pool B of R150!

Figure 3.9 shows the release kinetics of the two phosphate pools extrapolated over a 600-day period, the critical assumptions here were that the rate constants do not change over time and no phosphate is added to the soil.

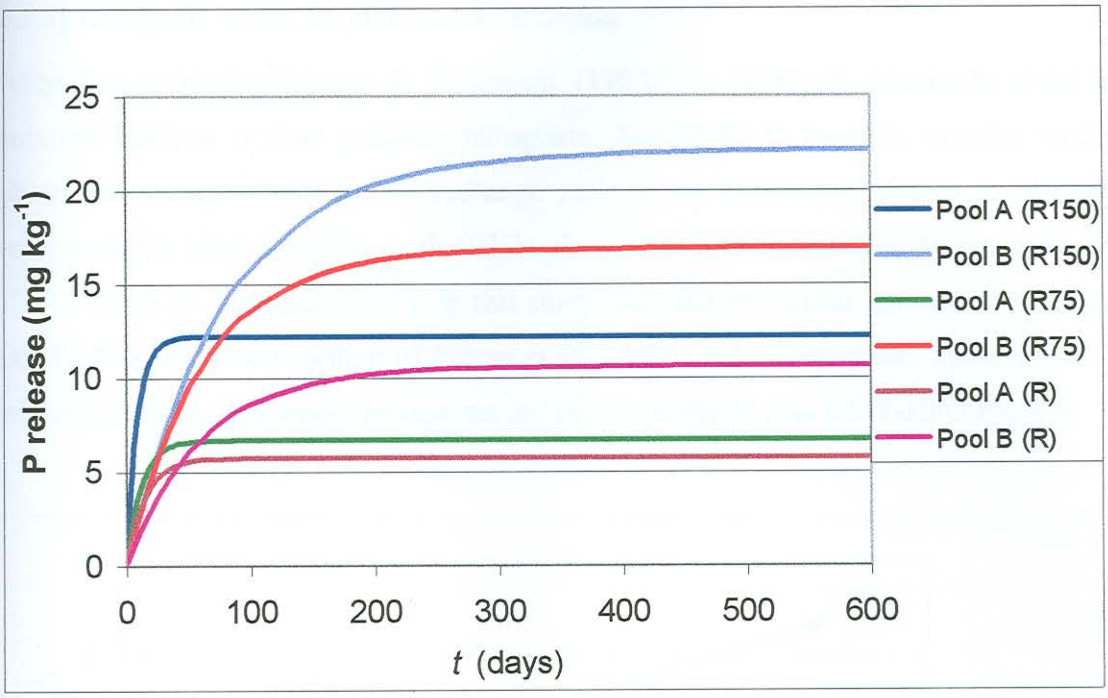


Figure 3.9. Simulated phosphate release from respective pool A and pool B of the different treatments extrapolated over a 600-day period.

Figure 3.9 shows the importance of the less exchangeable pool B in the long term (>56 days) phosphate desorption kinetics of the studied soil, eventually the less exchangeable pool B will control phosphate desorption kinetics. In the 56-day window, the effect of the addition of phosphate on the desorption kinetics of the less exchangeable pool B were not that evident, extrapolating the desorption kinetics to 600 days gave an indication of the long term effect of applied phosphate on the desorption kinetics of the pool B of the studied soil.

If the assumption is true that pool A represents predominantly adsorbed phosphate and pool B represents predominantly mineral phosphate and phosphate that diffused into occluded adsorption sites, then this study also gives an insight into the rates at which added phosphate diffuses into occluded adsorption sites and transforms into strengite and variscite in this particular soil. During the five-month incubation 73.9 mg kg^{-1} P (or 98.6%) of the 75 mg kg^{-1} phosphate applied and 143.4 mg kg^{-1} (or 95.6%) of the 150 mg kg^{-1} phosphate was transformed to mineral P or diffused into occluded adsorption sites

3.1.2) Inorganic $NaHCO_3$ (HCO_3-Pi) fraction

According to Hedley Stewart & Chaunhan, (1982), the HCO_3-Pi reflects the short-term seasonal changes in plant available phosphate. The HCO_3-Pi fraction, together with the phosphate extracted with anion exchange resin in the method of Hedley *et al* (1982), represents the plant available or the labile phosphate forms in the soil (Bowman & Cole, 1978 , Olsen & Watanabe 1957). In this study the resin extraction was substituted by the DMT-HFO extraction method of Freese *et al* (1995), and it is therefore assumed that the labile phosphate pool would be represented by the HCO_3-Pi plus DMT-HFO fraction.

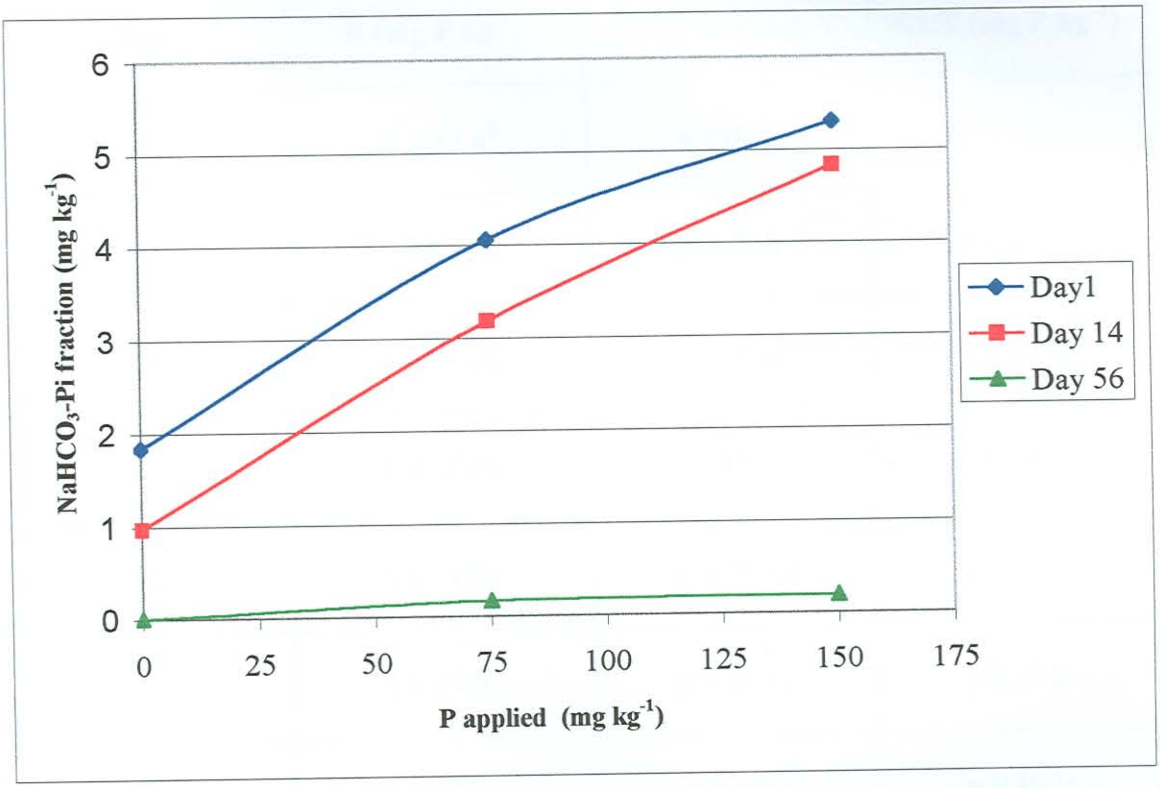


Figure 3.10. The change in the HCO_3-Pi fraction as influenced by phosphate application and DMT-HFO extraction as a function of time.

There was an increase in the HCO_3-Pi fraction of the soil with an increase in the amount of phosphate applied. According to **Figure 3.10,** the 75 mg P kg^{-1} and 150 mg P kg^{-1} treatments increased the HCO_3-Pi fraction of this soil by 120 % and 187% respectively (day 1 values).

The difference between the control and the different treatments was significant according to **Table 3.2**, however, the difference between the HCO_3-Pi fractions of R75 and R150 was never significant over the 56-day period. Under the influence of the DMT-HFO the HCO_3-Pi fractions of the different treatments were virtually depleted after 56 days.

Table 3.2. The influence of the DMT-HFO extraction on the HCO_3-Pi fractions of R, R75 and R150.

Day	**R (mg P kg^{-1})**	**R75 (mg P kg^{-1})**	**R150 (mg P kg^{-1})**
1	**x**[1] 1.84 **a**[2]	**y** 4.06 **a**	**y** 5.30 **a**
7	**x** 1.56 **ad**	**y** 2.49 **b**	**y** 4.25 **a**
14	**x** 0.97 **ad**	**y** 3.18 **ab**	**y** 4.83 **a**
21	**x** 0.42 **bc**	**y** 0 **c**	**y** 0 **b**
28	**x** 0.21 **bc**	**xy** 0.83 **cd**	**y** 0.97 **b**
42	**x** 0.13 **bc**	**y** 0.26 **cd**	**y** 0.32 **b**
56	**x** 0.0006**c**	**y** 0.17 **d**	**y** 0.19 **b**

1 Mean values in rows with different letters x y z are significantly different ($\alpha = 0.05$)

2 Mean values in columns with different letters a, b, c, d, e and f are significantly different ($\alpha = 0.05$)

The HCO_3-Pi fractions of R, R75 and R150 were very small compared to the other fractions, which are characteristic of highly weathered soils. Du Preez (1997), Cross & Schlesinger (1995) and Tiessen & Moir (1993), also found that the HCO_3-Pi fraction of highly weathered soils seldom exceed 10 mg P kg^{-1}.

This finding is surprising because it is expected that the increase of the soil suspension pH to 8.5 or even to 7 would significantly increase the solubility of strengite and variscite in highly weathered soils. Despite this little phosphate was extracted with 0.5M $NaHCO_3$. A possible explanation for the small amounts of phosphate usually extracted in highly weather soils is that the Point of Zero Charge (P.Z.C.) of ferric oxy hydroxide like goethite can be as high as 8-8.5 (the reason for this is that the surface groups of oxy hydroxide are weak Brønsted acids). It is also known that phosphate adsorption can take place even beyond the P.Z.C. of the adsorption surfaces because phosphate adsorption is predominantly a chemisorption process and not electrostatically adsorbed. It is therefore possible that phosphate that are extracted with HCO_3 because of the dissolution of strengite and variscite will be re-adsorbed by goethite and gibbsite or any other oxy hydroxide with high P.Z.C..

3.1.3) Inorganic NaOH (NaOH-Pi) fraction

A 0.1 *M* NaOH solution (pH = 13) is more basic than a 0.5 *M* $NaHCO_3$ and therefore a stronger extractant of solid phase phosphate for the following reasons:

1. The higher solubility of variscite and strengite at a pH of 13,
2. The excess OH^- in solution will displace all the remaining adsorbed phosphate in the soil after the 0.5 *M* $NaHCO_3$.
3. The increased dissolution of gibbsite and goethite (see **Figure 1.1)** exposes phosphate adsorbed in occluded adsorption sites. The subsequent decrease in adsorption surfaces further reduces the risk of possible re-adsorption of phosphate that comes in solution because of the dissolution of variscite and strengite.

At a pH of 4.1 according to **Figure 1.5,** strengite is less soluble than variscite and if variscite did form in this soil it would transform to strengite. Whether strengite or variscite is the predominate phosphate mineral depends on how long the pH of the soil was under 5 and the transformation rate of variscite to strengite.

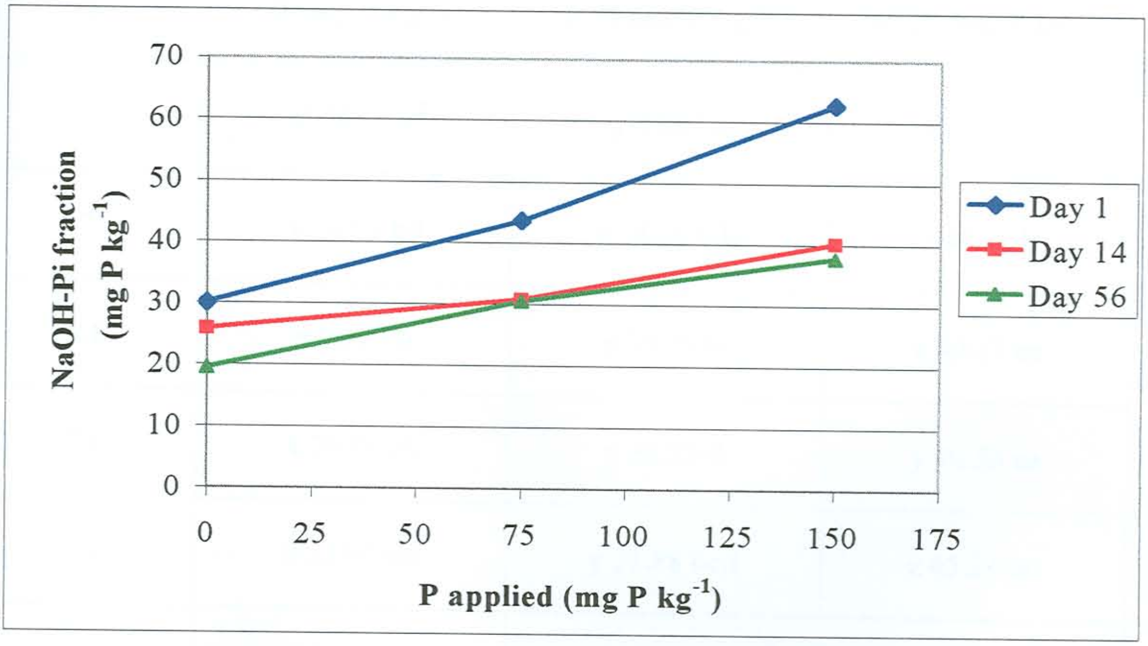


Figure 3.11: The change in the OH-Pi fraction as influenced by phosphate application and DMT-HFO extraction as a function of time.

According to **Figure 3.11,** the 75 mg P kg^{-1} and 150 mg P kg^{-1} treatments increased the OH-Pi fraction of this soil by 45% and 109% respectively (day 1 values) the difference between the different treatments were significant according to **Table 3.3.** From this data it can e concluded that more phosphate was transformed into less soluble NaOH extractable phosphate than to the more soluble $NaHCO_3$ extractable phosphate forms. The difference between the OH-Pi fraction of the control and the OH-Pi fraction of the treatments was greater than the difference between the HCO_3-Pi fraction of control treatment and the HCO_3-Pi fraction of the treatments. For every 1 mg P kg^{-1} the HCO_3-Pi fraction of R75 increased, the OH-Pi fraction increased by 6.16 mg P kg^{-1}. This ratio increased to 1:9.5 for R150.

Table 3.3. The influence of the DMT-HFO extraction on the OH-Pi fractions of R, R75 and R150.

Day	**R (mg P kg^{-1})**	**R75 (mg P kg^{-1})**	**R150 (mg P kg^{-1})**
1	x[1] 30.00 **a**[2]	y 43.63 **a**	z 62.74 **a**
7	x 24.54 **bd**	y 34.26 **bde**	z 49.82 **b**
14	x 25.75 **b**	y 30.75 **bc**	z 40.07 **ce**
21	x 26.54 **ab**	y 36.23 **d**	y 40.58 **ce**
28	x 23.96 **bd**	y 31.88 **bcd**	z 45.24 **bc**
42	x 21.53 **cd**	y 26.64 **c**	y 36.59 **de**
56	x 19.45 **c**	y 30.42 **ce**	z 37.72 **cd**

1 Mean values in rows with different letters x y z are significantly different (($\alpha = 0.05$)

3 Mean values in columns with different letters a, b, c, d, e and f are significantly different (($\alpha = 0.05$)

There was a general tendency for the OH-Pi fractions of R, R75 and R150 to decrease with increasing DMT-HFO extraction time and the OH-Pi fractions of the different treatments were significantly lower than the respective day 1 levels. The OH-Pi fraction of the different treatments showed the biggest decrease (18 – 20%) in the first 7 days. The sharp decrease in the first week cannot solely be contributed to the influence of the phosphate sink, because the phosphate solid phase in the soil was also trying to equilibrate with the volume of solution added.

3.1.4) Comparison between phosphate released and HCO-Pi and OH-Pi fractions of the different treatments.

Discreet phosphate pools do not exist in the soil and the phosphate extracted with different extractants represents a continuum of easily to less exchangeable phosphate rather than distinct phosphate pools. However, correlations have been found between $NaHCO_3$ extractable phosphate and plant available phosphate and, to a lesser extent between NaOH extractable phosphate and plant available phosphate in tropical soils. (Olsen & Watanabe 1957, Bowman & Cole, 1978 , Ball-Coelho, Salcedo, Tiessen & Stewart, (1993).In this section the total phosphate desorbed in the 56-day period from the different treatments were compared to the decrease in HCO_3-Pi and OH-Pi fractions to determine how important role these fractions played in the desorption process

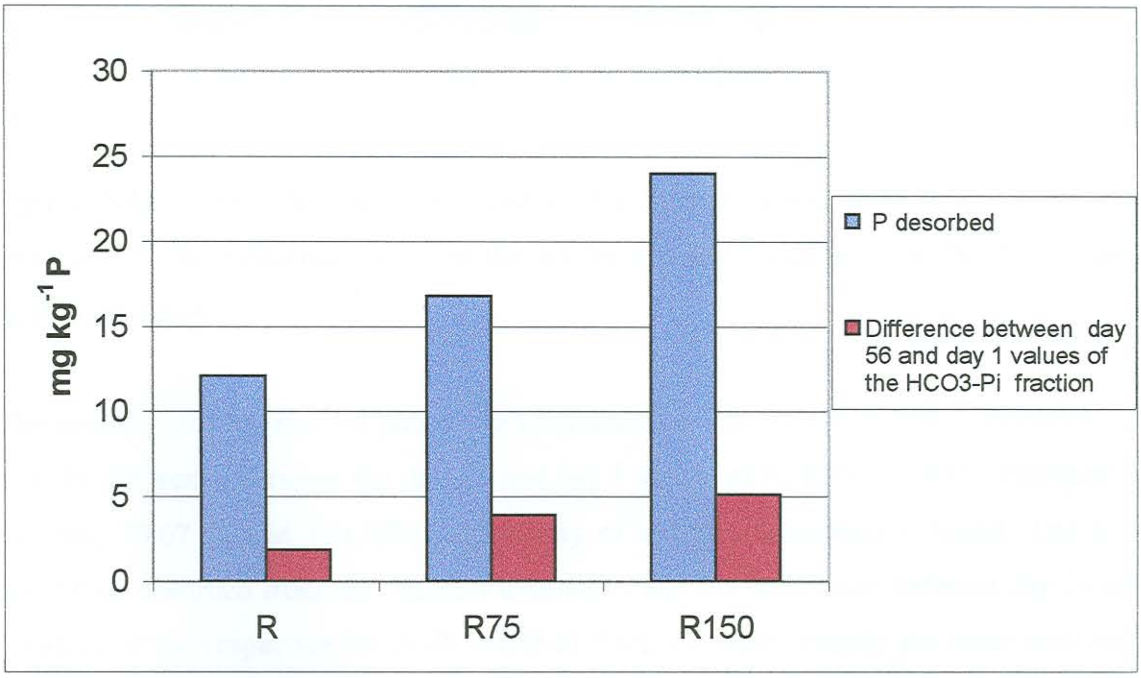


Figure 3.12. Total phosphate desorbed in the 56-day period from R, R75 and R150 compared to the differences between the day 56 and day 1 values of the HCO-Pi fraction of R, R75, and R150.

According to **Figure 3.12** very little of the desorbed phosphate originated from the HCO_3-Pi fractions of the different treatments. The decrease in the HCO_3-Pi fractions of

R, R75 and R150 represented only 15.27 %, 23.18 % and 21.31 % respectively of the total phosphate released from the soil.

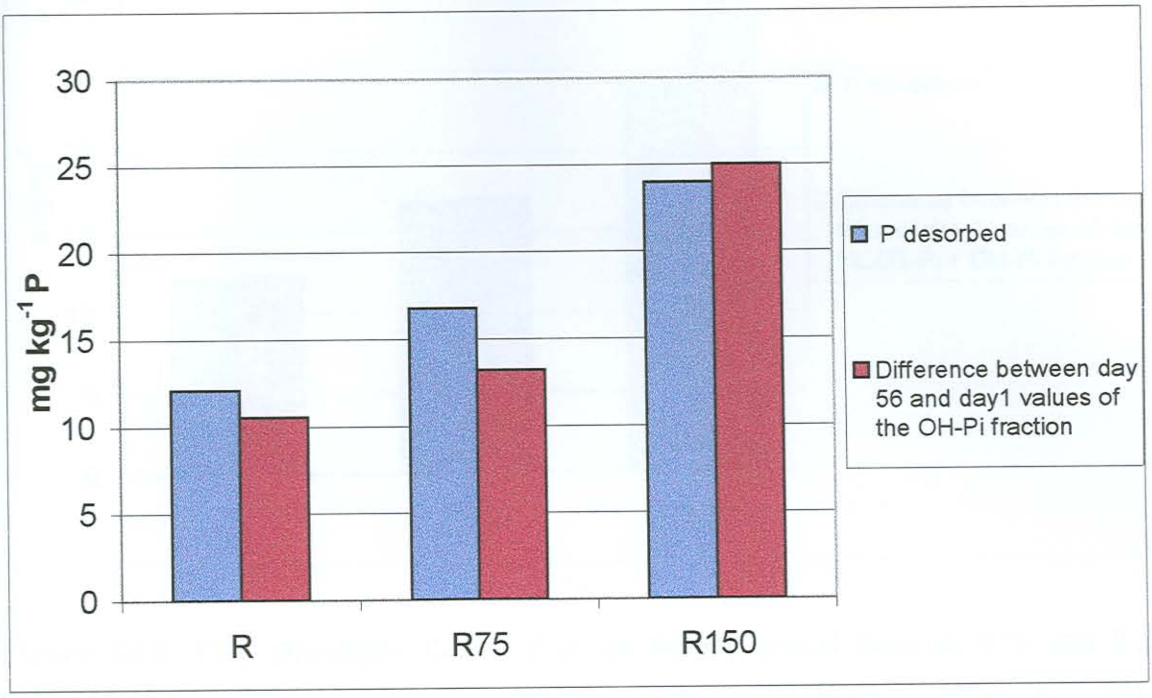


Figure 3.13. Total phosphate desorbed in the 56-day period from R, R75 and R150 compared to the differences between the day 56 and day 1 values of the OH-Pi fraction of R, R75, and R150.

The majority of the desorbed phosphate originated from the OH-Pi fraction (**Figure 3.13**) and the difference between the day 56 and day 1 values of R, R75 and R150 represented 87.38%, 78.67 % and 104.30% respectively of the total phosphate released. The total phosphate desorbed from the different treatments and the differences between day 56 and 1 values of the respective HCO_3-Pi + OH-Pi fractions were virtually the same according to **Figure 3.14.** The differences between the day 56 and day 1 values of the different treatments represented 102.66 %, 101.85 % and 125.61 % of the total phosphate released from R, R75 and R150 respectively.

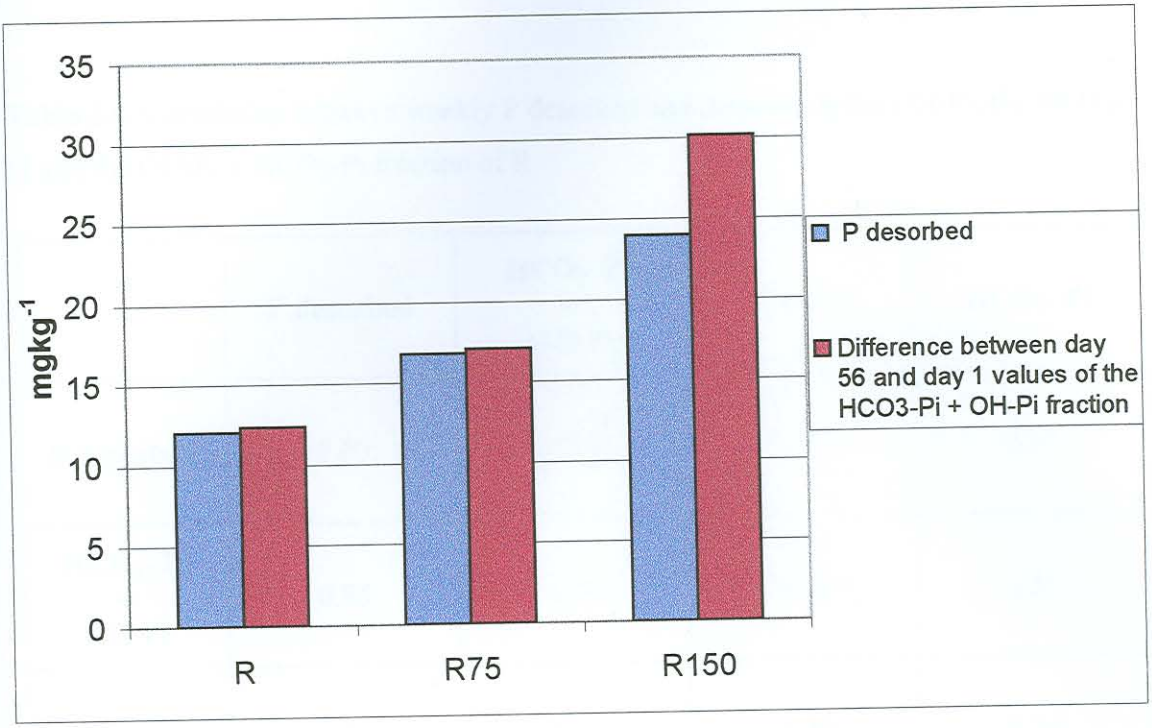


Figure 3.14. Total phosphate desorbed in the 56-day period from R, R75 and R150 compared to the differences between day 56 and day 1 values of the HCO_3-Pi + OH-Pi fraction of R, R75, and R150.

Determining the origin of the desorbed phosphate by comparing phosphate desorption data and decrease in the different fractions, was complicated by the fact that some phosphate that entered the solution, because the of the dissolution of phosphate minerals is probably re-adsorbed again by adsorption surfaces. This fact and experimental error was probably the reason why the phosphate released could not precisely be accounted for in the decrease of the HCO_3-Pi and OH-Pi fractions.

A correlation analysis was done with SAS to determine how strong the linear relationship was between the weekly phosphate desorbed from the different treatments and the weekly decrease in the OH-Pi, HCO3-Pi and OH-Pi + HCO3-Pi fractions of R, R75 and R150.

Table 3.4. Correlation between weekly P desorbed and decrease in the OH-Pi, the HCO_3-Pi and the OH-Pi + HCO_3-Pi fraction of R.

	P desorbed	**HCO_3- Pi + OH-Pi**	**OH-Pi**	**HCO_3- Pi**
P desorbed	1.00	0.85	0.80	0.57
HCO_3- Pi + OH-Pi	0.85	1.00	0.99	0.51
OH-Pi	0.80	0.99	1.00	0.34
HCO_3- Pi	0.57	0.51	0.34	1.00

There was a low correlation between the weekly decrease in the HCO_3-Pi fraction and the phosphate released from the different treatments according to **Tables 3.4, 3.5** and **3.6.** The correlation between the weekly decrease in the HCO_3-Pi fraction and the phosphate released from this soil, decreased from $r = 0.567$ (**Table 3.4)** for the control to $r = 0.376$ for R150 **(Tables 3.6)**. There was a higher correlation between the weekly change in the OH-Pi fractions and the phosphate desorbed from R, R75 and R150. The correlation between the weekly change in the OH-Pi fraction and phosphate desorbed increased from $r = 0.79$ for the control to $r = 0.915$ for R150.

Table 3.5. Correlation between weekly P desorbed and the decrease in the OH-Pi, the HCO_3-Pi and the OH-Pi + HCO_3-Pi fraction of R75.

	P desorbed	**HCO_3- Pi + OH-Pi**	**OH-Pi**	**HCO_3- Pi**
P desorbed	1.00	0.86	0.82	0.51
HCO_3- Pi + OH-Pi	0.86	1.00	0.98	0.54
OH-Pi	0.82	0.98	1.00	0.35
HCO_3- Pi	0.51	0.54	0.34	1.00

According to **Tables 3.4 and 3.5,** the weekly phosphate desorbed from R and R75 showed the highest correlation of $r = 0.85$ and $r = 0.86$ respectively with the weekly change in the OH-Pi + HCO_3-Pi fraction. In the case of R150, the correlation between the weekly change in the OH-Pi fraction and the weekly phosphate desorbed, and the correlation between the weekly change in the OH-Pi + HCO_3-Pi fraction and the weekly phosphate desorbed were the same

Table 3.6. Correlation between weekly P desorbed and the decrease in the OH-Pi, the HCO_3-Pi and the OH-Pi + HCO_3-Pi fraction of R150.

	P desorbed	**HCO_3- Pi + OH-Pi**	**OH-Pi**	**HCO_3- Pi**
P desorbed	1.00	0.91	0.92	0.38
HCO_3- Pi + OH-Pi	0.91	1.00	0.98	0.51
OH-Pi	0.92	0.98	1.00	0.34
HCO_3- Pi	0.38	0.51	0.34	1.00

The good correlation between the decrease in the OH-Pi fraction of the different treatments and phosphate desorbed shows that, although the OH-Pi fraction is less exchangeable than the HCO_3-Pi fraction, it could still be considered part of the labile phosphate pool of the studied soil. If the DMT-HFO simulated plant phosphate uptake, then the OH-Pi fraction is a better indicator of the plant-available phosphate over the longer term (± 2 months) than the HCO_3-Pi fraction. The decrease in the correlation between the weekly change in the HCO_3-Pi fraction and the phosphate desorbed, and the increase in the correlation between the change in the OH-Pi fraction and phosphate desorbed, also illustrated that applied phosphate transforms to less exchangeable NaOH extractable phosphate rather than $NaHCO_3$ extractable phosphate.

3.1.5) Inorganic 1 *M* HCl (1M HCl-Pi) fraction

According to Tiessen & Moir, (1993), 1 *M* HCl is very effective in extracting phosphate associated with calcium phosphates. Considering the pH of the studied soil, it is expected that the precipitation of aluminium and ferric phosphate would be favoured over that of calcium phosphate. It is therefore more likely that the phosphate extracted with 1 *M* HCl was aluminium and ferric phosphate that was left in the soil after the NaOH extraction.

Table 3.7. The influence of the DMT-HFO extraction on the 1M HCl-Pi fractions of R, R75 and R150.

Day	**R (mg P kg^{-1})**	**R75 (mg P kg^{-1})**	**R150 (mg P kg^{-1})**
1	**$x^1$1.10 a^2**	**xy 1.49 bc**	**y 1.90 cd**
7	**x 1.20 a**	**xy 1.58 bc**	**y 1.95 cd**
14	**x 1.08 a**	**x 1.17 ac**	**x 1.38 cd**
21	**x 1.35 a**	**x 1.46 bc**	**x 1.71 cd**
28	**x 1.40 a**	**x 1.60 bc**	**x 1.98 cd**
42	**x 1.15 a**	**x 0.94 c**	**x 1.048 d**
56	**x 1.20 a**	**x 2.13 bd**	**x 2.20 c**

1 Mean values in rows with different letters x y z are significantly different ($\alpha = 0.05$)

2. Mean values in columns with different letters a, b, c, d, e and f are significantly different ($\alpha = 0.05$)

There was no significant change in the 1 *M* HCl-Pi fraction of the different treatments over time (**Table 3.7**) and except for day 7 and 14, there also was no significant difference between R, R75 and R150.

3.1.5) Inorganic Concentrated HCl (con HCl-Pi) fraction

The concentrated HCl-Pi fraction represents the stable residual phosphate pool of the soil. This stable residual phosphate probably consists of: occluded phosphate; ferric and aluminium phosphates covered by a ferric oxy-hydroxides coating which protected the inner phosphate nucleus from solvent action, and maybe also stable apatite type minerals that could not be extracted with 1*M* HCl (Chang & Jackson, 1957, Lindsay, 1979). Most of the total phosphate extracted came from this fraction and it seems that the concentrated HCl-Pi fraction was the fate of most of the phosphate originally added to the soil.

Table 3.8. The influence of the DMT-HFO extraction on the concentrated HCl-Pi fractions of R, R75 and R150.

Day	**R (mg P kg^{-1})**	**R75 (mg P kg^{-1})**	**R150 (mg P kg^{-1})**
7	**x**[1] 104.62 **ac**[2]	**y** 116.04 **a**	**z** 136.11 **a**
14	**x** 116.07 **a**	**xy** 125.89 **a**	**y** 133.82 **a**
21	**x** 116.36 **a**	**x** 112.75 **a**	**x** 116.67 **a**
28	**x** 92.31 **c**	**xy**120.50 **a**	**y** 124.67 **a**
42	**x** 104.14 **ac**	**xy** 116.82 **a**	**y** 120.91 **a**
56	**x** 98.59 **ac**	**xy** 117.41 **a**	**y** 119.20 **a**

1 Mean values in rows with different letters x y z are significantly different ($\alpha = 0.05$)

2 Mean values in columns with different letters a, b, c, d, e and f are significantly different ($\alpha = 0.05$)

There was no significant change over time in the concentrated HCl-Pi fraction of the different treatments (**Table 3.8**). There was however a significant difference between concentrated HCl-Pi fraction of R150 and that of the control.

3.2) Organic phosphate fractions

Because of the low organic content of South African soils (especially soils under cultivation) organic P is not as an important source of phosphate than inorganic phosphate forms. It is important to note that the DMT-HFO cannot simulate the biochemical reactions involved in the mineralisation of organic P. Organic P mineralisation in the soil is usually faster in the presence of plant roots than in the absence of plant roots, the reason for this is the absence of the enzyme phosphatase which is vital for P mineralisation. This enzyme enhances the hydrolysis of phosphorus from the organic compounds, and the absence of phosphatase greatly reduces organic P mineralisation.
(Thompson & Black, 1970a, Islam & Ahmed, 1973, Campbell & Racz, 1975, Blair & Boland, 1978, Racz, 1979).

Phosphatase enzymes originate from two sources:

- Rhizosphere microorganisms. The highest concentration of phosphatase producing enzymes are found in the rhizosphere because of the higher carbon concentration in the rhizosphere due to root debris and also carbon-rich root exudates like glucose (Alexander, 1961 Greaves & Webley, 1965);
- Plant roots. Plant roots also produce and exudes phosphatase enzymes. (Szember, 1960b, Esterman & McLaren, 1961).

Because of these factors it is not expected that these experimental conditions accurately simulated the organic P dynamics that normally take place in the soil.

3.2.1) Organic $NaHCO_3$ (HCO_3-Po) fraction

The HCO_3-Po fraction consists of the portion of organic P forms (such as RNA nucleotides and glycerophosphates), which can easily be mineralised by biological processes (Bowman & Cole, 1978, McKercher & Tollefson, 1978, Tarafdar & Claassen, 1988).

Table 3.9: The influence of the DMT-HFO extraction on the $NaHCO_3$-Po fractions of R, R75 and R150.

Day	R (mg P kg^{-1})	R75 (mg P kg^{-1})	R150 (mg P kg^{-1})
1	x[1] 1.14 b[2]	y 4.00 b	y 5.43 b
7	x 6.62 a	y 8.57 c	z 10.52 a
14	x 2.14 b	y 11.11 d	y 11.43 a
21	x 1.39 b	x 0.0 a	x 0.71 c
28	x 3.08 ab	y 9.64 dc	y 9.11 a
42	x 2.78 ab	x 4.52 b	x 5.95 b
56	x 1.98 b	x 2.73 b	x 2.92 bc

1 Mean values in rows with different letters x y z are significantly different ($\alpha = 0.05$)

2 Mean values in columns with different letters a, b, c, d, e and f are significantly different ($\alpha = 0.05$)

According to **Table 3.9.** the HCO_3-Po fraction of the different treatments *increased* during the first two weeks. A possible explanation for this is that some of the phosphate that desorbed was immobilised again by microorganisms. There were a significant differences between the HCO_3-Po fraction of the different treatments up to day 28, indicating that some of the initially applied phosphate was immobilised by microorganisms. After day 28 there was no significant difference between the different treatments.

In this study the $NaHCO_3$ fraction was the only fraction where there was more $NaHCO_3$-Po than HCO_3-Pi. Armstrong & Helyar (1992) and Du Preez (1997), also found that the majority of the total HCO_3 extractable phosphate to consists of organic P. Cross & Schlesinger (1995), reported a general trend that the HCO_3-Po fraction increases with an increase in the degree of weathering of the soil.

3.2.2) Organic NaOH (OH-Po) fraction

The OH-Po fraction extracts the less labile alkali soluble organic P in the soil. Because the nature of a large part of organic P is still unknown, it is not possible to determine exactly which organic P compound was extracted (Anderson, 1975). According to Tiessen & Moir (1993), the organic P extracted with $NaHCO_3$ (HCO_3-Po) and the organic P extracted with NaOH probably represents the same organic P pool namely the alkali soluble organic P.

Table 3.10. The influence of the DMT-HFO extraction on the NaOH-Po fractions of R, R75 and R150.

Day	**R (mg P kg^{-1})**	**R75 (mg P kg^{-1})**	**R150 (mg P kg^{-1})**
1	x[1]22.73 **a**[2]	x 22.43 **a**	x 21.84 **a**
7	x 27.83 **a**	x 24.59 **a**	x 19.54 **a**
14	x 26.85 **b**	x 26.75 **a**	x 22.51 **a**
21	x 24.02 **a**	x 25.33 **a**	x 24.26 **a**
28	x 27.70 **a**	x 23.28 **a**	x 20.54 **a**
42	x 26.81 **a**	x 25.41 **a**	x 23.86 **a**
56	x 24.09 **a**	x 24.90 **a**	x 25.46 **a**

1 Mean values in rows with different letters x y z are significantly different ($\alpha = 0.05$)

2 Mean values in columns with different letters a, b, c, d, e and f are significantly different ($\alpha = 0.05$)

There was no significant change in the OH-Po fraction over the DMT-HFO extraction time (**Table 3.10**). The different phosphate levels the soil was incubated with caused no significant increase in the OH-Po fraction of this particular soil. It seems that no significant amount of P was mineralised from this fraction. This could probably be attributed to the absence of rhizosphere microorganisms responsible for the mineralisation of organic P.

3.2.3) Organic Concentrated HCl (con HCl-Po) fraction

The organic P extracted with concentrated HCl represents a very stable organic P pool or labile organic P that is not alkali soluble (Tiessen & Moir, 1993). The soil had a low organic material content and after the previous two extractions it seemed that virtually no organic P was left in the soil. There was little difference between the total P extracted with concentrated HCl (HCl-P_{tot}) and inorganic P extracted with concentrated HCl. In most instances there was no difference. Organic P extraction with concentrated HCl involved the most steps resulting in the end in the largest extrapolation factor to relate the determined values to mg P kg soil $^{-1}$. The small difference between the con HCl-Pi fraction and HCl-P_{tot} and the big difference between the extrapolation factors of concentrated HCl-Pi and concentrated HCl-P_{tot} meant that the slightest error in one of the four replications of the HCl-P_{tot} determination, magnified by the high extrapolation factor, could have resulted in the average of the con HCl-P_{tot} being dragged lower than that of the con HCl-Pi

Summary and Conclusion

The DMT-HFO method of Freese *et al.* (1995) is an effective method to study the phosphate desorption kinetics of soils and does not have the drawbacks of other methods. If the diffusive resistance through the dialysis membrane is brought in consideration, it seems that the method of Freese *et al*, (1995) will be more effective in investigating the phosphate release kinetics of soils with slow phosphate desorption rates (like most South African soils) than soils with relative high desorption rates, like the Belgium and German soils which Freese *et al*, (1995) and Lookman *et al*, (1995) tested it on. However, the method of Freese *et al*, (1995) has however two drawbacks:

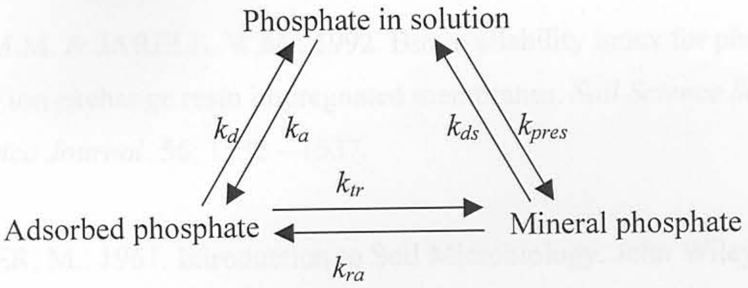
1. Some of the silt and clay fraction of the soil tend to accumulate on the plastic clips (from Medicell International Ltd) used by Freese *et al*, (1995) and Lookman *et al*, (1995) and has to be removed meticulously if the soil is used in conjunction with a phosphate fractionation method.
2. Because of the continuous shaking of the samples on the shaker, friction develops between the dialysis membrane and the soil when there is direct contact. This continuous friction weakens the dialysis membrane at this point of direct contact, and sometimes causing it to rupture, especially in the case of sandy soils.

This study supports findings by Armstrong & Helyar, (1992) and Ball-Coelho *et al*, (1993), who found that the participation of the presumably "less soluble fraction" OH-Pi fractions previously been underestimated. The fact that the correlation between the weekly decrease in the OH-Pi fraction and the phosphate desorbed was higher than the correlation between the HCO_3-Pi fraction and phosphate desorbed. The fact that most of the phosphate desorbed came from the OH-Pi fraction, indicated that the OH-Pi fraction was more actively involved in the desorption process. The weekly change in the OH-Pi + HCO_3-Pi fraction showed the best correlation with the weekly phosphate desorbed. The reason for this is that the OH-Pi fraction and the HCO_3-Pi fraction represent a continuum of easily extractable phosphate associated ferric and aluminium oxy hydroxides and ferric and aluminium phosphate to less extractable phosphate associated ferric and aluminium oxy hydroxides and ferric and aluminium phosphate rather than two separate phosphate pools (Tiessen & Moir, (1993).

No desorption maximum was reached, in this study on a soil with a relatively low phosphate status and high phosphate sorption capacity The desorption kinetics of the soil were describe relatively well (R^2 = 0.9730 for the control and R^2 = 0.9528 and R^2 = 0.9870 for R75 and R150 respectively) with the two component first order model. The more exchangeable pool A of the different treatments were depleted within the 56 day period, extrapolation of the data showed that in the long term, desorption kinetics is controlled by less exchangeable pool B. The extrapolation of the data showed that the 56-day desorption period represented only a small window on the long term desorption kinetics of studied soil, if the rate constants of the respective phosphate pools stay constant it will take ± 800 days before the cumulative desorption curve will reach a plato Using the two component first order model, the total exchangeable phosphate was calculated at 16.36 mg kg^{-1}, 23.62 mg kg^{-1} and 34.28 mg kg^{-1} for R, R75 and R150 respectively with two component first order model and the data obtained in this 56 day period. The calculated total exchangeable phosphate of R, R75 and R150 were ± 54% of the day 1 values of the OH-Pi fractions and roughly half of the day 1 values of the HCO_3-Pi + OH-Pi fractions. If the HFO-DMT simulates phosphate uptake by plants then the calculated total exchangeable phosphate represents the long-term plant available phosphate. For this particular soil it seems that roughly half the phosphate extracted with NaOH (24 hours) gives an estimate of the long-term plant availability of applied phosphate. However, the method of Freese *et al*, (1995) must still be extensively tested on different types of soil and crops to correlated it with plant uptake and desorption studies longer than 56 days also have to be conducted to verify the extrapolated desorption kinetics.

The phosphate desorption kinetics of a soil is also influenced by the experimental condition, and the rate constants obtained are therefore conditional rate constants. To obtain rate constants that are true for all conditions the influences of pH changes and ionic strength changes and temperature changes have to be quantified.

The inorganic phosphate dynamics in the soil can alternatively to **equation 1.1** be illustrated as follows:



Where k_a = rate constant of adsorption.
k_d = rate constant of desorption.
k_{ds} = rate constant of dissolution.
k_{pres} = rate constant of precipitation.
k_{tr} = rate constant of transformation of adsorbed phosphate to mineral phosphate.
k_{ra} = rate constant of re-adsorption of dissolved mineral phosphate.

Figure 3.15. An alternative representation of the inorganic phosphate dynamic in soils

The main difference between **equation 1.1** and **Figure 3.15** is that in **Figure 3.15** all the solid phases equilibrate directly with phosphate in solution; there is not an equilibration with an intermediate labile phosphate pool first, as in the case of **equation 1.1**.

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Appendix A

Table A1. ANOVA table for DMT-HFO extracts.

P sorption/desorption study

The ANOVA Procedure

Class Level Information

Class	Levels	Values
Plevels	3	1 2 3
Time	8	1 2 3 4 5 6 7 8

Number of observations 92

The ANOVA Procedure

Dependent Variable: v1

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	22	353.5050836	16.0684129	19.36	<.0001
Error	68	56.4390401	0.8299859		
Corrected Total	90	409.9441237			

R-Square	Coeff Var	Root MSE	v1 Mean
0.862325	34.99895	0.911036	2.603037

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Plevels	2	31.6969511	15.8484756	19.09	<.0001*
Time	7	217.7451769	31.1064538	37.48	<.0001*
Plevels*time	13	104.0629556	8.0048427	9.64	<.0001*

Table A2. ANOVA table for $NaHCO_3$- Pi extracts

P adsorption/desorption study

The ANOVA Procedure

Class Level Information

Class	Levels	Values
Plevels	3	1 2 3
Time	7	1 2 3 4 5 6 7

Number of observations 84

The ANOVA Procedure

Dependent Variable: v1

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	20	196.7145109	9.8357255	23.06	<.0001
Error	59	25.1635674	0.4265011		
Corrected Total	79	221.8780783			

R-Square	Coeff Var	Root MSE	v1 Mean
0.886588	33.60962	0.653071	1.943106

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Plevels	2	51.4249773	25.7124887	60.29	<.0001*
Time	6	115.6614249	19.2769042	45.20	<.0001*
Plevels*time	12	29.6281086	2.4690091	5.79	<.0001*

Table A3. ANOVA table for NaOH- Pi extracts

P adsorption/desorption study

The ANOVA Procedure

Class Level Information

Class	Levels	Values
Plevels	3	1 2 3
Time	7	1 2 3 4 5 6 7

Number of observations 84

The ANOVA Procedure

Dependent Variable: v1

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	20	7575.196291	378.759815	51.79	<.0001
Error	59	431.452492	7.312754		
Corrected Total	79	8006.648783			

R-Square	Coeff Var	Root MSE	v1 Mean
0.946113	7.961971	2.704210	33.96408

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Plevels	2	5068.589409	2534.294705	346.56	<.0001
Time	6	1845.538943	307.589824	42.06	<.0001
Plevels*time	12	661.067939	55.088995	7.53	<.0001

Table A4. ANOVA table for 1 *M* HCl extracts

P adsorption/desorption study

The ANOVA Procedure

Class Level. Information

Class	Levels	Values
Plevels	3	1 2 3
Time	7	1 2 3 4 5 6 7

Number of observations 84

The ANOVA Procedure

Dependent Variable: v1

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	20	10.89289279	0.54464464	4.64	<.0001
Error	57	6.69625129	0.11747809		
Corrected Total	77	17.58914408			

R-Square	Coeff Var	Root MSE	v1 Mean
0.619296	22.95507	0.342751	1.493137

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Plevels	2	3.87099534	1.93549767	16.48	<.0001*
Time	6	5.38353960	0.89725660	7.64	<.0001*
Plevels*time	12	1.63835785	0.13652982	1.16	0.3318

Table A5. ANOVA table for concentrated HCl –Pi extract.

1 **P adsorption/desorption study**

The ANOVA Procedure

Class Level Information

Class	Levels	Values
Plevels	3	1 2 3
Time	6	1 2 3 4 5 6

Number of observations 72

The ANOVA Procedure

Dependent Variable: v1

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	7958.64822	468.15578	7.85	<.0001
Error	52	3101.12584	59.63704		
Corrected Total	69	11059.77406			

R-Square	Coeff Var	Root MSE	v1 Mean
0.719603	6.633961	7.722502	116.4086

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Plevels	2	4545.803587	2272.901793	38.11	<.0001*
Time	5	1568.354278	313.670856	5.26	0.0006*
Plevels*time	10	1844.490356	184.449036	3.09	0.0037*

Table A6. ANOVA table for $NaHCO_3$ –Po extracts.

P adsorption/desorption study

The ANOVA Procedure

Class Level Information

Class	Levels	Values
Plevels	3	1 2 3
Time	7	1 2 3 4 5 6 7

Number of observations 84

The ANOVA Procedure

Dependent Variable: v1

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	20	1007.203425	50.360171	27.51	<.0001
Error	56	102.529090	1.830877		
Corrected Total	76	1109.732515			

R-Square	Coeff Var	Root MSE	v1 Mean
0.907609	26.37462	1.353099	5.130307

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Plevels	2	189.8393980	94.9196990	51.84	<.0001*
Time	6	622.7702720	103.7950453	56.69	<.0001*
Plevels*time	12	194.5937549	16.2161462	8.86	<.0001*

Table A7. ANOVA table for NaOH –Po extracts.

P adsorption/desorption study **15:00 Tuesday, February 5, 2002**

The ANOVA Procedure

Class	**Level**	**Information**
Class	**Levels**	**Values**
Plevels	**3**	**1 2 3**
Time	**7**	**1 2 3 4 5 6 7**

Number of observations 84

The ANOVA Procedure

Dependent Variable: v1

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	**20**	**388.456349**	**19.422817**	**0.91**	**0.5798**
Error	**59**	**1263.026464**	**21.407228**		
Corrected Total	**79**	**1651.482813**			

R-Square	Coeff Var	Root MSE	v1 Mean
0.235217	18.96445	4.626795	24.39720

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Plevels	2	149.0368277	74.5184138	3.48	0.0372
Time	6	69.3907049	11.5651175	0.54	0.7755
Plevels*time	12	170.0288166	14.1690680	0.66	0.7800