CHAPTER 1

GENERAL INTRODUCTION

Phosphorus is commonly a limiting nutrient for plant growth in many soils arround the world (McDowell and Stewart, 2006). The amount of available soil P has been more frequently evaluated than the rate of its release when studying the P nutrition of plants. The availability of a nutrient to plants depends, among others, on the rate at which it is released to replenish the soil solution (Raven and Hossner ,1994). There can be a significant residual effect due to desorption of phosphate from the soil of long term fertilization history and this can lead to an underestimation of the benefit of phosphate fertilizer if not taken in to account (Mckean and Warren, 1996).

Soil tests for plant available P are used world wide to determine the current P status of soils so as to estimate fertilizer P requirements for specific yield goals. The current P status is due to indigenous (native) P present in the soil and P from previous fertilizer P application (residual P) (Indiati, 2000). Since the actual plant available P is composed of solution P plus P that enters the solution as the result of desorption/dissolution from a solid phase, the conventional soil test methods have been unsatisfactory in predicting the plant P uptake (Beck and Sanchez, 1994).

Plant P availability of residual P in soils can be reliably estimated by successive cropping experiments carried out in field or green house conditions, where P is taken up until P deficiency occurs or a response to added P is measured (Indiati, 2000). As this approach is very expensive and time consuming, soil extractions with P sink methods have been proposed to estimate residual P. Contrary to the conventional soil

P test methods , these P-sink methods may be considered nondestructive methods as they do not react with soil and have minimal effect on the soil physicochemical properties that influence the release of P. Furthermore, extraction with these sink methods prevents solution P from increasing to levels where further P release is prohbited and hence one can make a series of extractions from a soil sample (Indiati, 1998, Mckean and Warren, 1996). Consecutive extraction of soils by these methods may therefore be a convenient laboratory method to characterize the capacity of soil to supply P, and to investigate the kinetics of residual P release. Such methods use anion exchange resins (Abrams and Jarrel, 1992), iron oxide impregnated paper strips (Indiati, 2000) or dialysis membrane filled with hydrous ferric oxide solution (DMT-HFO) (Freese et al., 1995; Lookman et al., 1995; Koopmans et al., 2001) Characterizing the residual P by employing these methods could solve the time frame by which these residual P become available for plant use in a reasonably short time but lacks to indicate which P pools involve in replenishing the labile P pool.

The sequential extraction procedure developed by Hedley et al. (1982) and modified by Tiessen and Moir (1993) has been applied to determine the different forms of P in the soil. Characterizing the residual P by making use of this method could solve the problem of identifying which P pool involves in replenishing the P uptake by plants but doesn’t indicate the time frame by which these residual P become available for plant use. The problems mentioned in this and the above paragraph could be alleviated if the two methods mentioned above are combined. Thus, successive extraction procedures carried out by these ion sink methods combined with subsequent fractionation procedure (Hedley et al. 1982; Tiessen and Moir, 1993) hereafter termed as a *combined method* may, therefore, constitute a convenient laboratory method to investigate the kinetics of residual P release and to understand the dynamics of soil P. This combined method simulates the successive cropping experiment carried out either in the field or green house conditions. In addition to this, it indicates which P pool serves as a major source for buffering the solution P depleted as the result of continuous desorption.

This combined method has been recently employed in South Africa to study the desorption kinetics and P dynamics of incubated soils. De Jager and Claassens (2005) investigated the desorption kinetics of residual and applied phosphate to red sandy clay soils. They reported that no desorption maximum was reached after 56 days of shaking revealing that desorption could possibly continue for a longer period. They also reported that application of P increased the desorption rate of P from the labile pool (SP_A) where as the P applied had less impact on the desorption rate of P from the less available pool (SP_B). In the same study De Jager (2002) reported that the total amount of phosphate desorbed during a 56-day period of extraction was virtually equal to the decrease in the NaOH extractable inorganic phosphate fraction. Ochwoh et al. (2005) also studied the chemical changes of applied and residual phosphorus (P) in to different pools in two soils [Alfisols], a red sandy clay soil [Haplo-Palcustafs] and a red sandy loam soil [Pale-Xerults] after P application and incubation using the same procedure. They found that between 30-60 % of the added P was transformed to the less labile P pools in 1 day and 80-90 % of the added P after 60 days of incubation. A major portion of the P was transformed to the NaOH-extractable P pool.

However, there is little information on the relationship between kinetics of P release using this new method and plant P uptake for soils with long-term fertilization history.

Methods like this follow the procedure of shaking for a long period of time there by exploiting the whole volume of soil. However plants exploit only a limited amount of the soil volume ranging from 3-4 % (Kamper and Claassens 2005). The other problem with regard to this is its impracticality to use it for a routine soil analysis, as it is very expensive and time consuming. Accordingly, the objectives of this study were:

i) To determine the desorption characteristics of soils of long-term fertilization history using successive DMT-HFO extraction method

ii) To assess how the information gained from P desorption kinetic data relate to plant growth at green house and field trials

iii) To study the changes in labile, non-labile and residual P using successive P desorption by DMT-HFO followed by a subsequent fractionation method (combined method)

iv) To investigate the effect of varying shaking time on DMT-HFO extractable P.

v) To propose a short cut approach to the combined method.

CHAPTER 2

2. LITERATURE REVIEW

Phosphorus deficiency in soils is a wide spread problem in the world (Harrison 1987). It is believed to be the second most important soil fertility problem through out the world next to nitrogen (Warren 1992) and often the first limiting element in acid tropical soils (Buehler et.al., 2002).

Also in the Sub-Saharan Africa, P is a limiting nutrient in many soils of the semi-arid tropics and in acid, highly weathered soils of the sub-humid and humid tropics (Buresh et al., 1997). Oxisols and andisols are major soils in the sub-humid and humid tropics of Africa (Deckers, 1993) and are characterized by low total and available P content and high P retention capacity (Friesen et al.,1997). In addition, andepts and oxisols have a high P fixation capacity (Sanchez and Uehera, 1980).

In acid soils, P is fixed in to slightly soluble forms of precipitation and sorption reaction with Fe and Al compounds as well as crystalline and amorphous colloids (Sanchez and Uehera, 1980). Phosphorus sorption was highly correlated with the clay and total free Fe-oxide contents extracted by Dithionite-Citrate-Bicarbonate (DCB) in ultisols and alfisols derived from the savanna and rainforest zones of West Africa (Juo and Fox, 1977). Arudino et al., (1993) found that sorption capacity of acidic alfisols from South Africa were highly correlated with the DCB extractable iron oxides and with amorphous Fe and Al oxide content (Oxalate extractable). Based on P sorption isotherms for 200 soils from West, East and South Africa, Warren (1992) concluded that fertilizer requirements tend to follow the order andisols> oxisols> ultisols>

alfisols> entisols. With the exception of andisols, there is, in general, a direct relationship between P sorption by soils and the surface area of Fe and Al oxides. Clay content in soils also affects P sorption. For example, millet producing soils of West Africa in the Sudano-Sahellian agro-ecological zone are generally sandy in texture, have a low sorption capacity and only need low to medium inputs of P to maintain an adequate pool of labile P (Manu et al., 1991).

In calcareous alkaline soils, solid-phase $CaCO_3$ is the dominant factor affecting P availability. Data for 19 soils from different agricultural areas of West Asia and North Africa showed that $CaCO_3$, Fe-oxides, amount and reactivity of silicate clays as well as P fertilizer addition rate and time after application affect the availability of P in calcareous soils (Afif et al., 1993). Iron oxides particularly the more reactive forms have a modifying influence on P fractions in calcareous soils, despite the dominant influence of $CaCO_3$ (Ryan et al., 1985). With 20 calcareous soils in the USA, Sharpley et al., (1984) found a negative correlation between labile P and $CaCO_3$ content after six months of incubation.

2.1 Sorption and desorption of phosphorus

Phosphorus sorption is the removal of labile P from the soil solution, due to the adsorption on, and absorption into the solid phases of the soil, mainly on to surfaces of more crystalline clay compounds, oxihydroxides, or carbonates (Hollford and Mattingly, 1975). The term “labile P” is commonly used to represent mobile P, which is available (or rapidly becomes available by reactions with fast kinetics) as a nutrient for plant growth, including soluble P and that which has been deposited by the slow reaction (which is not readily available) (McGechan and Lewis, 2002). Although soil P sorption has been studied intensively, relatively less has been done on the P desorption in soils and sediments. Desorption refers to the release of P from the solid phase in to the solution phase. Desorption occurs in soils when plant uptake depletes soluble P concentrations to very low levels, or in an aquatic system when sediment – bound P interacts with natural waters with low P concentrations (Pierzynski et al., 1994). Interest in P desorption studies are rising due to the importance of P on soil fertility and pollution (Sharpley, 1985). Intensive animal husbandry in Europe has led to the production of large amounts of animal manures, and the disposal of manures on the agricultural land have led to increased soil P tests (Gerke, 1992). Many soils have become saturated and contributed to surface water eutrophication (Sharpley, 1985; Mozaffari and Sims, 1994; Penn et al., 1995; Sharpley, 1996; Pote et al., 1998). Similar problems also occur where sewage sludges has been disposed on land (Gerke, 1992; Sharpley and Sisak, 1997).

2.2 P sorption and desorption rates

Phosphorus sorption capacity is an important soil characteristic that affects the rate and plant response to P fertilizer application. (Fox and Kamprath, 1970; Hollford and Mattingly, 1975). Phosphorus sorption by soils is usually rapid at first but then slows with time (Dimirkou et al., 1993). The initial fast P sorption rates are presumably due to reaction with surface sites of metal oxides or hydroxide particles that are exposed to the solution phase. Slow P sorption that continues after the initially rapid sorption is ascribed to the slow diffusion in to the soil aggregates (Willet et al., 1988), or due to the slow formation of P containing minerals (Van Riemsdijk et al., 1984; Lookman et al., 1995; McGechan and Lewis, 2002).

The P desorption rate in the soils are of particular interests in respect to the bioavailability and the pollution risk as a result of P translocation to deeper layers and by surface runoffs (Pote et al., 1996; Li et al., 1999; Paulter and Sims, 2000). Desorption kinetics can also be classified in to fast and slow rates (Munns and Fox, 1976). The fast P pool presumably represents primarily P bound to the reactive surfaces that are in direct contact with the aqueous phase (Hingston et al., 1974, Madrid and Posner, 1979). The relatively higher surface coverage of soil with P and thus, easy replacement of the adsorbed phosphate may be attributed to a higher initial P desorption from the soil (McGechan and Lewis 2002). Other possible contribution to the fast desorbing pool may be the less soluble P salts originating from recent fertilizers applications that are not yet in equilibrium with reactive hydrous oxides (Lookman et al., 1995). Complexed P with organic material may also be part of the fast desorbing pool (Gerke, 1992). The slow P release rate from the second pool is either the result of slow dissolution rates or from slow diffusion from interior sites inside oxyhydroxide particle (McDowell and Sharpley, 2003). The extent to which this slow reaction is then reversible (desorption) is fundamental in determining the residual effectiveness of added phosphate.

2.3 Phosphorus status of South African soils

Phosphorus deficiency is the most widespread and economically important nutrient deficiency in the higher rainfall areas of South Africa. The problem of satisfying the P requirements of plants is twofold. Firstly the soils are severely deficient in P and secondly, the plant availability of applied fertilizer P tends to be rapidly reduced through reactions with soil components (Bainbridge et al., 1995). The main reasons for the low plant availability of phosphate are presence of ferric Fe (III) - and aluminum (Al) oxyhydroxides (Sposito, 1989; Bainbridge et al., 1995) and low organic material content of South African soils (Applet et al., 1975; Stevenson, 1982; Iyamuremye and Dick, 1996; Baldock and Skjemstad, 1999).

The studies of Reeve and Sumner (1970) revealed a wide variation in the P sorption capacities of some oxisols in Kwa-Zulu-Natal province. Similarly McGee (1972), in evaluating P sorption in soils of Guateng, Mpumalanga, North West and Free State provinces found considerable variation in their sorption capacities. Bainbridge et al., (1995) determined the P-sorption isotherms of 50 soil samples from a number of localities in the Kwa-Zulu-Natal province. They reported that the amount of P sorbed ranged from 5-1174 mg kg $^{-1}$ and that the highest sorption occurred in the highly weathered red and yellow-brown clay soils with a high organic carbon content in the A horizons (Inanda, Kranskshop and Mgwa forms). This agrees with the findings of Haynes (1984) who had indicated that ferric and aluminum ions complexed with organic matter provide additional sites for P sorption. In an effort to identify soil properties responsible for P sorption, Henry and Smith (2002) constructed phosphorus isotherms for 21 selected soils from the Republic of South Africa and reached to the conclusion that the citrate bicarbonate dithionite- Al to be an important factor in P sorption although other soil constituents such as clay percentage, organic matter, citrate bicarbonate dithionite-Fe and Bray II P content also contributed to P sorption characteristics of the soils. Estimates of the phosphorus requirement of 20 selected soils of the South African tobacco industry were interpolated from phosphorus sorption isotherms and the results showed that the phosphorus required varied widely and is influenced by both the level of Bray II P content and the P fixation capacity of the soil (Henry and Smith, 2003). Although P sorption has been found to increase with increasing soil clay content, a considerable variation in sorption capacities have been obtained in different soils with similar clay contents (Johnston et al., 1991). It has been shown further that, soils with predominantly 1:1 type clay material (i.e. highly weathered red and yellow brown clay soils) sorp much more P than the soils with predominantly 2:1 type clays.

Van Zyl and Du Preez (1997 I) have tried to study the effect of farming practices such as tillage, fertilization and liming on the phosphorus fractions in soils from the summer rainfall area (25^0-30^0S; 24^0-30^0E) in South Africa by comparing the phosphorus level of selected virgin and cultivated areas. They found that P_T(total P) increased in the case of cultivation, which is attributed to use of fertilization as opposed to the virgin land. They also reported the influence of cultivation on the phosphorus fraction of the same soils and found that most of the inorganic fractions increased as the result of cultivation although the effect was not significant for the residual P_i fraction. $NaHCO_3$-P_O was found the most depleting organic fraction due to cultivation ascribing its easily minerlizable property as opposed to the other organic fractions (Van Zyl and Du Preez, 1997II). In a long-term experiment (>15 years) on yellowish brown sandy clay loam (Avalon) and a red sandy clay (Clovelly) soil in Ermelo, Mapumalanga province, Du Preez and Claassens (1999), concluded that the NaOH-extractable P (moderately adsorbed P) was mainly responsible for the replenishment of the labile soil P pool.

Relatively little information is available on areas pertaining to the long-term P desorption studies. Recently, studies related to the desorption kinetics of residual and applied phosphate to an acid sandy clay soils of Piet Retief, Mpumalanga were carried out over a 56-day period using hydrous ferric oxide in dialysis tubes (DMT-HFO) as a specific phosphate sink, followed by a sequential phosphate extraction. The total amount of phosphate desorbed during the stated period was reported to be virtually equal to the decrease in the NaOH (moderately labile) extractable inorganic phosphate fraction revealing the active participation of this fraction in the desorption process (De Jager, 2002). In an endeavor to investigate the fate of the applied P in soils, Ochwoh et al., (2005) also carried out the same experiment for sandy clayey soil (Ferric Luvisols) from Rustenberg (high P fixing) and a red sandy loam soil (Ferric Acrisols) from Loskop (low P fixing). The results showed that 30-60 % of the added P was transformed into the less labile P pools with in one day and 80-90% after 60 days. In the same study made by Ochwoh (2002), an attempt was made to determine the P desorption rates by successive DMT-HFO extractions after the transformation of the applied P followed by sequential extraction. They observed the transformation and redistribution of the applied P during incubation periods and proved that all the so-called unlabile soil P pools contributed to the labile P pool by different proportions.

2.4 Chemical extractants

Soil phosphate testing is used to predict plant yield from the amount of P already present in soil. This requires knowledge of the relationship between plant yield and soil P test values, where the yield measured later on in a season is related to soil P test values measured on soil samples collected earlier in season (Kumar et al., 1992). Soil testing for P is done using a chemical extractant. A large number of extractants have been suggested by various researchers (Tan, 1996) and the choice of appropriate soil test reagent depends on many factors, among which are the following:

- The soil and extractant type (Kleinman et al., 2001)
- The nature of the crop (Ibrikci et al., 1992) and
- The fertilizer type (Indiati et al., 2002).

The suitability of a specific soil P tests for soils is dependent on the pedogenic properties of the soils. For instance, Bray-1, Melich-1, and to a lesser extent, Melich-3, are not considered suitable for calcareous soils because soluble P may be precipitated by CaF_2, a product of the reaction between NH_4F and $CaCO_3$. Generally, acid extractants provide inconsistent measures of soil P in calcareous soils. Some extraction methods, however, such as Olsen, are considered suitable over a wide range of soils, from acidic to calcareous (Kleinman et al., 2001). Dilute acidic extractants such as Melich-1 (M-1) have been used on acidic soils. Investigations involving the M-1 test in Florida's acidic soils suggested excessive P recommendations for other crops such as watermelon [*Citrus lanathus Thunb*]. The M-1 dissolves Ca-P compounds in soils containing apatite and predicts high P values (Ibricki et. al., 1992). The Mehlich-3 (M-3) extractant was developed to predict nutrient requirements of plants over a wide range of soil chemical characteristics for macro- and micronutrients. The M-3 contains fluorides, which enhances the extraction of Al-phosphate through complexation reaction. According to Menon et al. (1990), acid extractants used in Bray-1 and 2 procedures, may extract more P from soils than the amount accumulated by plants. Acid extractants are capable to dissolve aluminum phosphate and calcium phosphate (Leal et al., 1994) giving high P values that do not reflect the level of available P. In general, acidic extractants have been found very effective in estimating available P in acidic soils. The same methods may not be appropriate when used in calcareous soils because of neutralization by the soil carbonates. In addition, acidic solutions may overestimate P from soils fertilized with water-insoluble fertilizer P such as phosphate rock (PR), by dissolving more P from PR than the plant could use.

Selection of appropriate soil test reagent also depends on the crop type. Crop species are known in their efficiency for utilization of nutrients from the soil. For instance, peanut [*Arachis hypogia L*] has been shown not to respond to phosphorus even in the soils testing low in Olsen extractable P where as wheat grown on the same field shown marked responses to residual as well as direct P application. Total P removed by peanut and wheat was comparable. It was, therefore, postulated that peanut perhaps taps some of the reserve P-fractions in the soil that are not readily available to other crops like wheat and mustard as the result of long-term fertilizer P application (Pasricha et al., 2002). A similar report was obtained on some soils of western Quebec (Canada), which were brought in to cultivation in the 1940s for some forage grasses. Grass grown on fine textured soils of the area did not respond to P fertilizer during the first two growing seasons during a 3-year *in situ* study (Ziadi et al., 2001). These soils initially had low Melich-3 extractable P contents and very high clay contents. Some studies using chemical extractions reported that the Melich-3 soil test might underestimate the P availability in clay soils (Cox, 1994). The lack of response of forage grass to P fertilizers suggests a significant contribution of the P reserves, which was not predicted by the Melich-3 extractant.

Identification of appropriate soil testing method is also influenced by the fertilization history of the soil that is whether the nature of fertilizer employed is consistent or not. Soil P testing has been developed for soluble P fertilizers, such as superphosphates and ammonium phosphate fertilizers. Recently, however, reactive rock phosphate (PR) and partially acidulated rock phosphate (PAPR), fertilizers are being advocated as alternative P fertilizers for super phosphate principally due to

i) Per kilogram of P, PR is usually the cheapest fertilizer and

ii) PRs can be more efficient than soluble fertilizers in terms of recovery of phosphate by plants, even from short-term crops in soils where soluble P is readily leached, as in sandy soils and possibly for long-term crops in other soils (Indiati et al., 2002).

Partially acidulated rock phosphates (PAPR) are prepared by treating the phosphate rock (PR) with less acid than would be required to convert the entire P content into superphospates (Menon et al., 1991). Application of the above fertilizers resulted in an increase in different soil P fractions. Phosphate rock fertilization resulted in an increase in the H_2SO_4- soluble Ca-P fraction (Steffens, 1994). After applying different P fertilizers there are still problems with soil testing methods in analyzing P availability for a P fertilizer recommendation. This is especially true after PR or PAPR fertilization. Acid extraction methods such as double lactate overestimate P and CAL method underestimates the plant availability of apatite P. This occurs because the soil test methods do not consider the release of adsorbed P or the dissolution of apatitic P in the soil (Steffens, 1994).

The information on proper fertilizer use emanating from the soil testing laboratories is primarily based on critical soil fertility limits of different nutrient elements and soils

(Sonar, 2002). However these soil tests give only a relative index of available P that can be supplied by the soil for plant growth, but do not measure actual available P quantitatively (Hedley et al., 1982; Tiessen and Moir, 1993). Plant available P is all P that is taken up by a plant during a specific period, such as a cropping season, year, or growth cycle (Tiessen and Moir, 1993). Since the actual plant available P is composed of solution P plus P that enters the solution as the result of desorption/dissolution from a solid phase, the conventional soil test methods have been unsatisfactory in predicting the plant P uptake. A possible explanation is that P from the less labile pools not measured by the common soil tests also contribute to plant uptake (Stevenson, 1986; Tiessen and Moir, 1993) as these fractions are in equilibrium with the P fractions extracted by the soil P tests.

2.5 The sequential extraction of phosphorus

The sequential extraction procedure of Chang and Jackson (1957) extracts various inorganic P pools and is widely used to study transformations of applied phosphate (Nurwakera 1991) and native phosphate forms (Williams et al., 1967). However this method extracts predominantly strongly retained P and is not appropriate for studying soil P dynamics that influence uptake by plants (Beck and Sanchez, 1994). The extraction procedure introduced by Hedley et al. (1982) fractionates the soil P into five inorganic P (P_i) pools, three organic P (P_o) pools, and one residual P pool. Sequential fractionation procedures are based on the assumption that chemical extractants selectively dissolve discrete groups of P compounds, and such operationally defined soil P fractions are subject to broad interpretations. Nevertheless, the information obtained from P fractionation schemes has been useful for interpretation of soil development (Cross and Schlinsinger, 1995) as well as plant availability of P (Tiessen and Moir, 1993). The overall advantage of the fractionation of soil phosphate into discrete chemical forms permits the quantification of different P pools, their chemical status in native or cultivated soils, and to study the fate of the applied P fertilizer (Hedley et al., 1982, Tiessen and Moir, 1993).

In the fractionation procedure developed by Hedley et al., (1982) and modified by Tiessen and Moir (1993), the P fractions (in order of extractions) are interpreted as follows. Resin –P_i represents inorganic P (P_i) either from the soil solution or weakly adsorbed on (oxy) hydroxides or carbonates (Mattingly, 1975). Sodium bicarbonate 0.5 M at pH 8.5 also extracts weakly adsorbed P_i (Hedley, 1982) and easily hydrolysable organic P (P_o) (Buehler et al., 2002). Sodium hydroxide 0.5 M extracts P_i associated with amorphous and crystalline Al and Fe (oxy) hydroxides and clay minerals and P_o associated with organic compounds (fulvic and humic acids). Hydrochloric acid 1M extracts P_i associated with apatite or octacalcium P. Hot conc. HCl extracts P_i and P_o from more stable pools. Organic P extracted by conc. HCl may also come from particulate organic matter (Tiessen and Moir, 1993). The residue left from the HCl extraction is dissolved in hot concentrated H_2SO_4 plus H_2O_2 and assumed to be composed of occluded P_i associated with the remaining inorganic minerals, and non-extractable P_o (Tiessen and Moir, 1993).

2.6 Methods used to investigate and describe phosphorus desorption

2.6.1 Use of P-free solution

Among the many methods that have been used to examine the kinetics of P release is the use of water or P-free solutions such as $CaCl_2$ to induce desorption. Some researchers equilibrated soil or mineral samples with water at soil/water ratios ranging from 1:10 to 1:1000, and measured the P concentration in the equilibrating solution after given reaction periods to calculate the amount of P desorbed (Dimirkou et al., 1993). Other researchers have studied P desorption kinetics in a similar way using dilute solutions such as 0.01M $CaCl_2$ (which is designed to simulate soil solutions) instead of water as desorptioin media with soil /solution ratios in the range of 1:5 to 1:200 in single (Munns and Fox, 1976) or successive extractions (Hooda et al., 2000). The 0.01M $CaCl_2$ as a universal soil extractant was recommended by Houba et al., (1986). The advantage is that the other nutrients also could be measured in this extractant. The disadvantages are the analytical difficulties raised by some soils because of low levels of desorbed P. In earlier studies, significant relationship has been obtained between the 0.01M $CaCl_2$ desorbed P and P fertilizer dose and between $CaCl_2$-P and the estimated P balance (Jaszbereni and Loch, 1996). They also reported the importance of 0.01M $CaCl_2$ in predicting the P supply potential using the soil samples of long-term fertilization experiments. The result of the desorption investigations showed that beside characterizing the actual supply, the single time extraction P values in 0.01 M $CaCl_2$ can also express the P supply potentials. Not only plant available, labile soil-P can be characterized by the 0.01M $CaCl_2$ extractable P but also the excessive and environmentally undesirable P levels. Recent investigations on the use of 0.01 $CaCl_2$ have also revealed that this extractant can be used to characterize the potentially available P and the P in solution (McDowell and Sharpley, 2003). The disadvantage of these methods however is, they release small concentrations of P because the increase in solution concentration leads to the establishment of equilibrium. The process can, in principle, be repeated to desorb more P; however, experimental (analytical) errors tend to accumulate and still only a small percentage of the P present in the sample can be desorbed in this way (Freese et al., 1995). They also suggest that true release kinetics might be masked due to the resorption of P.

Leaching of soil columns with a P free solution is another option to study desorption (Van der Zee and Gjaltema, 1992). This is an excellent method for soils with relatively high P concentrations. Soils with low P concentrations however, require impractically high numbers of pore volumes due the strong non- linearity of the phosphate adsorption isotherm. Another disadvantage is that the experimental set up required is more complicated and rather expensive. This technique is, therefore, not very suitable to study large numbers of soil samples (Freese et al., 1995). The soil column leaching method, however, was found to be advantageous in experiments, which involve the stability of soil aggregates. It prevented the break up of soil aggregates resulting from the various shaking required by the other methods. Leaching soil columns also permitted the removal of desorbable P with time, which simulates nutrient removal by plant uptake more closely than batch equilibrations (Wang et al., 2001).

2.6.2 Use of materials that bind phosphate

Desorption can also be studied by adding materials that bind phosphate strongly, keeping the solution activity low so that the desorption from the soil particles can continue. The added material should have a high capacity to bind P. Another requirement is the possibility of separating the phosphate "sink" from the soil suspension in order to be able to assess the amount of P desorbed from the soil particles (Freese et al., 1995). Anion exchange resins (AER) have often been used for this purpose (Abrams and Jarrel, 1992; Sen Tran et al., 1992; Yang and Skogley, 1992).

Ion exchange materials can be viewed as competitive exchangers with those soil solids that are in dynamic equilibrium with the soil solution. In the case of P at a relatively acid pH range (4.3-5.0), $H_2PO_4^-$ is transferred via the soil solution from the soil solid phase to the ion exchange material. The reaction is simple exchange of adsorbed Cl^- for other anions in solution. In contrast, the equilibrium reaction of $H_2PO_4^-$ with metal-oxide-coated resin can be characterized as surface precipitation and adsorption via ligand exchange (Menon et al., 1990). This reaction is essentially irreversible, although anions like selenate, arsenate, and organic acids have been shown to compete with phosphate sorbed to Fe- and Al- oxyhydroxides (Traina et al., 1986). The resultant functional model for exchange resins relates to soil solution P dynamics. Since the mechanism for resin materials is ion exchange, there will be competition between $H_2PO_4^-$ and other anions at the resin sorption surface, particularly if other anion activities are high.

According to Cooperband and Logan (1994), over time, anion exchange materials will behave as either sinks or exchangers for P depending on: (i) the intrinsic anion exchange capacity of the resin material; (ii) the amount of time in contact with the soil; and (iii) the soil's P retention capacity. Throughout the literature, resin materials are described as infinite- sinks, probably because their exchange capacities remain large across the study period or the soil's P retention capacities are low enough to minimize competition for P between the resin and soil solid phase. In general, then, most anion-exchange resins react rapidly with $H_2PO_4^-$, and the rate of sorption is limited by the rate of desorption or dissolution in the case of agitated systems, and by pore and film diffusion in the case of *in situ* resin placement. Resin can be used to estimate instantaneous soil solution $H_2PO_4^-$ concentration by regression analysis. Resin-membrane-extractable P could also be calibrated with the labile P component of soils with differing P retention capacities. Once this relationship is established resin materials can be used in the field with time to estimate changes in net labile soil P (Cooperband and Logan, 1994). The resin extraction method is considered superior compared to chemical based soil tests for assessment of nutrient availability (Ibrikci et al., 1992).

Various researchers have modified this method using different soil/resin/solution ratios, equilibration times, forms of resins, and means to separate the resin beads from the soil after extraction (Yang et al., 1991). However, all the AER bead methods have disadvantage in that the soil must be finely ground so that it can be separated from the resin beads after extraction. Also, analytical errors can arise when fine roots and soil particles are trapped in the cloth, nylon, or polyester-netting bags often used to facilitate the separation process. Furthermore, the sealed edges of the bags may rapture through normal wear and tear resulting in the loss of resin beads into the soil suspension (Lee and Doolittle, 2002). The other problems with regard to the use of AER are their non-specific adsorption desorption of different anions and the incapacity of the resin to maintain low P concentrations and to act as infinite sink especially in the long-term studies (Freese et al., 1995)

The use of anion exchange resin membranes (Cooperband and Logan, 1994) provides a major improvement on the point of separability of P sink and soil suspension, the other disadvantages of the use of anion exchange resins as a P sink, however, remain. Apart from the drawbacks mentioned above, the capacity of an anion exchange resin to fix desorbing P depends on the chemical forms of the resin, e.g., Cl^-, HCO_3^-, or OH^- (Freese et al., 1995). Bacha and Ireland (1980) stated that the HCO_3^- form is better than the Cl^- form because the HCO_3^- form of the resin extracts a constant proportion of the isotopically exchangeable P from acid and calcareous soils. Besides, it stabilizes the extraction system in such a way that the resin type and soil/ water ratio only slightly affect the quantities of extracted P and the pH of the suspension (Sibbesen, 1978). The P extracted by HCO_3^- saturated resin is also better correlated with plant growth, apparently because it resembles the chemistry of the rhizosphere due to HCO_3^- accumulation in the medium (Sibbesen, 1978). Use of the bicarbonate form however, generally leads to an increase in the pH of the soil solution (Abrams and Jarrel, 1992), rendering HPO_4^{2-} species the dominant P ion in solution. The relatively weak specificity of a strong acid anion exchange resin for phosphate in an acid pH range of about 5 to 6 is based solely on the fact that a bivalent ion is preferred over monovalent ions in the ion exchange process. For these reasons the anion exchange method, although often used to assess plant available phosphorus, is not very suitable for studying P desorption of acid soil under conditions of natural pH.

Despite these disadvantages, anion exchange membranes (AEM) however are used as extracting agents. Saggar et al., (1990) reported that the AEM behaves similarly to AER beads and give an equally good estimate of soil phosphate. Schoenou and Haung (1991) reported that similar trends in predicting relative P availability were observed for AEM-extractable P, water extractable-P, bicarbonate extractable total P, and bicarbonate extractable organic P. Therefore, the AEM is well suited for routine soil P analysis. It is also low cost, simple, and consistent across all soil types. Lee and Doolittle (2002) showed that the AEM extracted more P than the AER from the soil-solution systems and the amount of soils phosphorus extracted by AEM and AER was significantly correlated in all the soil types tested.

Desorption studies of soil using Fe or Fe-Al oxide impregnated filter paper as a P sink, (P_i) became a better option than the resin approaches (Sharpley, 1991; Bramley and Roe, 1993; Sharpley, 1993). The two major drawbacks of this method however made it unsuitable for studying long-term P desorption from the soils. First, the paper strips are mechanically unstable during longer desorption times (weeks), leading to relatively large losses of the P sink in to the soil sample. Moreover, filter paper traps part of the soil material during every desorption step, affecting particularly the fine size fraction (Freese et al., 1995). These results in an overestimation of the amount of P desorbed, since any P associated with these particles is accounted for as desorbed after analyzing the filter paper.

Some investigations also reported on the use of cation anion exchange resin membranes (CAERM) (McKean and Warren, 1996; Indiati, 2000; Delgado and Torrent, 2000, and Delgado and Torrent, 2001) for extraction of soil P. The reports revealed that this method is in general effective in extracting more amounts of P than the other methods. The relative effectiveness of CAER method is probably due to promoted dissolution of metal phosphates. The cation exchange resin reduces cation activity in solution, thus decreasing the ionic activity product and favoring metal phosphate dissolution (Delgado and Torrent, 2000).

Recently, a new desorption technique has been developed that is also based up on the use of hydrous ferric oxide (HFO) as a sink for P (Freese et al., 1995). Instead of being impregnated in filter paper, the HFO is present inside dialysis tubing. Separation of P sink from the soil suspension thus becomes possible without extracting soil particles. This new system is found to be mechanically stable for very long reaction periods, provided that a microbial inhibitor, e.g., chloroform, is added to the soil suspension to prevent hydrolysis of the membrane. The pH of the soil solution during desorption remain almost constant. As such this technique has important advantages to the Fe- oxide impregnated filter paper extraction method. The system is capable of maintaining low P activity in solution necessary to study long term desorption kinetics of soils (Freese et al., 1995; Lookman et al., 1995; Koopmans et al., 2001; De Jager and Claassens 2005; Ochwoh et al., 2005). The disadvantage of using dialysis tubing is that P diffusion kinetics through the membrane may affect the soil P release kinetics. This is, however, only the case for the initial stage of desorption where the P release is relatively rapid. The DMT-HFO technique is therefore not as such useful to study short-term desorption kinetics (Lookman et al., 1995).

In summary, soil tests for plant available P are used world wide to determine the current P status of soils so as to estimate fertilizer P requirements for specific yield goals. The current P status is due to indigenous (native) P present in the soil and P from previous fertilizer P application (residual P). Plant P availability of residual P in soils can be reliably estimated by successive cropping experiments carried out in field or green house conditions, where P is taken up until P deficiency occurs or a response to added P is measured (Sahrawat et al., 2003). As this approach is very expensive and time consuming, soil extractions with P sink methods have been proposed to estimate residual P. Thus consecutive extraction of soils by these methods may be a convenient laboratory method to characterize the capacity of soil to supply P, and to investigate the kinetics of residual P release. Such methods use anion exchange resins (Abrams and Jarrel, 1992), iron oxide impregnated paper strips (Indiati, 2000) and DMT-HFO (Freese et al., 1995; Lookman et al., 1995; Koopmans et al., 2001; De Jager & Claassens, 2005; Ochwoh et al., 2005). This study focuses on the assessment of the efectiveness of succssive P desorption followed by subsequent extraction, termed as combined methodology, which is used to investigate the long-term desorption study of soils under green house and field trials.

CHAPTER 3

Kinetics of phosphate desorption from long-term fertilized soils of South Africa and its relationship with maize grain yield

3.1 INTRODUCTION

The amount of P removed from a field by crops in general varies from 3-33% of applied P fertilizer (Aulakh & Pasricha, 1991; Linquist et al., 1998; Csatho et al., 2002; Aulakh et al., 2003; Pheave et al. 2003; Zhang et al., 2004; Kamper & Claassens, 2005). Soils receiving successive applications of fertilizer P or manure over a long-term, therefore, can accumulate large amounts of residual P. This represents not only an uneconomic practice but also the risk of potential for P loss to surface waters via overland or subsurface flow and intern accelerate freshwater eutrophication (McDowell & Sharpley, 2002).

The P availability for plants is usually done using single chemical extraction methods. However, it is accepted that the plant acquires its P from the soil solution that has to be replenished over the growth period. The availability of P to plants therefore depends, among other things, on the rate at which it is released to replenish the soil solution (Raven and Hossner, 1994). Due to P build up in soils over a long period, a significant residual effect can be expected and this can lead to an underestimation of the available P if not taken in to account.

Plant P availability of residual P in soils can be reliably estimated by successive cropping experiments carried out in field or green house conditions, where P is taken up until P deficiency occurs or a response to added P is measured (Indiati, 2000). This approach, however, takes many years to realize which makes it very expensive and time consuming. Therefore, instead of attempting to tap the residual P by continually cropping till the plant responds, more rapid soil test methods that can approximate this biological measure have been designed. According to these methods, a given soil is subjected to successive P desorptions using materials that can act as P sinks. By employing these methods, one can study the P release rate of a given soil and for how long a given soil can supply P. This intern enables to know for how long it will take for soil P to deplete to a concentration where manure or fertilizer P can again be applied.

Recently, successive extraction procedure employing hydrous ferric oxide in dialysis membrane tubes (DMT-HFO) as a phosphate sink, has been used in assessing long-term phosphate desorption (Freese et.al., 1995). This method is similar to Fe-oxide impregnated filter paper strips but in this case the HFO is placed in a dialysis membrane tube instead of being impregnated in the filter paper.The fact that this system is capable of maintaining low P activity in solution for longer period of time, and its mechanical stabilty makes it appropriate for long-term studies (Freese et al., 1995). However, relatively little information is available on the literature related to the use of this method. Lookman et al. (1995) studied the kinetics of P desorption using this procedure. They concluded that P desorption could be well described by a two component first order model: $P_{R(t)} = SP_{Ao} (1- e^{-kAt}) + SP_{Bo} (1- e^{-kBt})$, with SP_{AO} and $SP_{BO,}$ the amounts of P initially present in the labile pool A and strongly fixed pool B respectively. They also reported that no desorption maximum was reached in the entire period of desorption (1600h). Research was also done which linked short-term soil P tests to long-term soil P kinetics (Koopmans et al., 2001; Maguire et al., 2001). Recently, studies were also made on some South African soils using DMT-HFO method as a phosphate sink. De Jager and Claassens (2005) investigated the desorption kinetics of residual and applied P to acid sandy clay soils from Mpumalanga, South Africa. They reported that no desorption maximum was reached after 56 days of shaking. They also reported that application of P increased desorption rate of P from the labile pool (SP_A) where as the P applied had less impact on the desorption rate of P from the less available pool (SP_B). However, there is still a paucity of information on the relationship between kinetics of phosphorus release using this new method and plant yield parameters for soils that received fertilizers over a long-term. The objectives of this research were 1) to study desorption of residual P from soils with a long-term fertilization history using successive P extractions by DMT-HFO and 2) to relate the kinetic data generated to maize grain yield.

3.1.1 Theory

Desorption kinetics of soil as determined by DMT-HFO can be schematically represented as

$$SP \xrightarrow{k_R} P_{sol} \xrightarrow{k_T} P_{HFO} \qquad (1)$$

Where SP is solid phase P, P_{sol} is P in solution, P_{HFO} is P adsorbed by HFO, k_T is the rate constant of P transport through the membrane ($0.09 \underline{+} 0.01 h^{-1}$) (Freese et al., (1995) and k_R is the rate constant of P release (De Jager & Claassens (2005)).

The presence of two pools is assumed: the pool with the fast release kinetics is pool A (SP_A) and the pool with the slow release kinetics is pool B (SP_B). With this assumption, the mass balance equation for the total exchangeable solid phase soil P (SP_{total}) at time t = 0 is:

$$SP_{total\ 0} = SP_{A0} + SP_{B0} \qquad (2)$$

Where SP_{A0} is initial amount of P in pool A and SP_{B0} is initial amount of P in pool B.

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

$$SP_{total\ (t)} = SP_{A(t)} + SP_{B\ (t)} \qquad (3)$$

Assuming the decrease in SP_A and SP_B follow first order kinetics, the integrated rate laws for the decrease of SP_A and SP_B will be:

$$SP_{A(t)} = SP_{A0}\, e^{-k_A t} \quad \text{and} \quad SP_{B(t)} = SP_{B0}\, e^{-k_B t} \qquad (4)$$

Where k_A and k_B are conditional first order rate constants (day^{-1}) for P desorption from pools A and B respectively.

The total solid phase soil P ($SP_{total\ (t)}$) remaining at time t will be given by:

$$SP_{total\ (t)} = SP_{A0}\, e^{-k_A t} + SP_{B0}\, e^{-k_B t} \qquad (5)$$

The total amount of P released at time t is expressed as:

$$\begin{aligned} P_{R(t)} &= SP_{A0} - SP_{A\,(t)} + SP_{B0} - SP_{B\,(t)} \\ &= SP_{A0} - SP_{A0}\, e^{-k_A\, t} + SP_{B0} - SP_{B0}\, e^{-k_B\, t} \\ &= SP_{A0}\,(1 - e^{-k_A\, t}) + SP_{B0}\,(1 - e^{-k_B\, t}) \qquad (6) \end{aligned}$$

It was further assumed that the rate constant of P release from the soil was equal to the rate constant of P adsorption (k_A) by the DMT-HFO. The rate constant of P adsorption (k_A) by the DMT-HFO was obtained from a plot of the natural logarithm (*ln*) of the P adsorbed by the DMT-HFO against time with the slope as k_A (De Jager and Claassens, 2005).

3.2 MATERIALS AND METHODS

3.2.1 Sampling procedure and experimental site history

Surface soil samples (0-20cm) were collected from one of the oldest long-term fertilizer trial in South Africa established in 1939. According to the USDA Soil Taxonomy System (Soil Survey Staff, 1990), the soil is a loamy, mixed, thermic Rhodic Kandiudalf. The soils were air-dried and ground to pass through a 2 mm sieve. Soil samples were collected from selected P treated plots. The samples were cored from three sites on each plot and four replications at each site. The samples were mixed and composite samples were used for the subsequent analyses.

The soil samples collected had the following fertilization history. The NK treatment received only N (ammonium sulphate) and K (KCl) fertilizers since the inception of the trial and acted as a control. The NPK and MNK treatments served as medium P level samples. They have nearly similar P contents (Table 3.1) but received different sources of P. The P source of the NPK treatment was inorganic (superphosphate) where as MNK treatment received a mixture of cattle dung and compost, here in this paper referred to as manure, as a P source. The MNPK treatment received both inorganic and organic P fertilizer and was considered as high P soils relative to the others. The inorganic P was applied from 1939 to 1985 and discontinued since 1985. Application of P in the form of manure was applied from 1939 to1990 and discontinued after 1990. The reason for discontinuing P application in both cases was due to the build up of P resulted from previous excessive application. Nel et al. (1996) has provided a detailed fertilization history (1939 to 1991) of these soils. Since then the plots received 125 and 80 kg ha $^{-1}$ year $^{-1}$ N and K respectively. Table 3.2 shows the fertilization history of the selected treatments.

3.2.2 Soil characterization

The pH (KCl) of the samples was determined by dispersing 20g of dried soil in 50 mL of 1*M* KCl. After 2 h of end-over-end shaking at 20 rpm, the pH was determined in the soil suspension (Freese et al., 1995). Particle size distribution of the soils was determined using a hydrometer method after dispersion of the soil with sodium hexametaphosphate. Organic C was determined by dichromate oxidation technique while extractable Ca, Mg and K were determined by extraction with neutral ammonium acetate solution (1*M*). Total soil P (P_T) was determined on sub samples of

Table 3.1 Selected physical and chemical properties of the soil samples studied

Sample Types[§]	pH (KCl)	P_{total}	Bray-1P	Ca[‡]	Mg[‡]	K[‡]	Texture			Organic C
		mg kg^{-1}					%Clay	%Silt	%Sand	%
NK	5.36	367.16	1.35	453.28	148.17	110.67	23.70	6.30	66.90	0.69
NPK	4.85	600.00	51.37	405.41	122.47	91.42	24.65	7.65	64.75	0.84
MNK	5.04	623.43	45.10	551.52	140.25	93.94	21.15	10.65	66.20	1.14
MNPK	4.81	851.22	100.01	535.19	135.25	98.81	21.45	9.30	66.30	1.04

[§] NK= received only inorganic Nitrogen and Potassium, used as a control; NPK= Inorganic N, P K fertilizers applied to these soil types; MNK= the source of P is organic (cattle dung and compost) and MNPK= the source of P is both inorganic fertilizer and Cattle manure

[‡] Extractable Ca, Mg and K: Determined using 1 *M* Ammonium acetate at pH 7

0.5mg soil with the addition of 5 ml concentrated H_2SO_4 and heating to 360 ^{0}C on a digestion block with subsequent stepwise (0.5 ml) additions of H_2O_2 until the solution was clear (Thomas et al., 1967). The available phosphorus was determined using Bray and Kurtz (Bray- 1P) method (0.03 *M* NH_4F + 0.025 *M* HCl). Details of analytical methods are described in Kuo (1996) and the Handbook of Standard Soil Testing Methods for Advisory Purposes (The Non-Affiliated Soil Analysis Work Committee, 1990). Table 3.1 shows some selected physical and chemical properties of these treatments.

Table 3.2 N, P, K and manure (kg ha^{-1} y^{-1}) applied to NK, NPK, MNK and MNPK treatments

Year	N	P	K	Manure (dry)
1939-1966	42.5	34	31.5	4470
1966-1972	85	68	63	8940
1973-1983	205	100	100	8940
1984	205	0	100	8940
1985-1990	125+125[a]	0	80+100[b]	8940[c]
1991-2003	125	0	80	0

[a] Additional N topdresssed on NPK treatments

[b] Additional K applied to NPK treatments

[c] Applied annually up to year 1990

3.2.3 Long-term desorption study

A long-term desorption study was carried out using dialysis membrane tubes filled with hydrous ferric oxides as described by Freese et al. (1995). The hydrous ferric oxide-dialysis membrane tubes were placed in 200 ml polyethylene containers with 1g of soil and 80 ml of 2 *mM* $CaCl_2$ and 0.3 *mM* KCl solution. All the experiments were executed in triplicates. The polyethylene containers were continuously shaken for 56 days on an end-over-end shaker at 120 oscillations per minute (*opm*). It was found in a preliminary investigation (data not shown) that shaking at 120 *opm* created the required perturbance yet the tubes could be shaken for 14 days without physically damaging the dialysis tubes. On days of 1, 7, 14, 21, 28 and 42 days, the DMT-HFOs were replaced with new DMT-HFO. When they were replaced, a glass rod was used to remove any attached soil from the dialysis membrane tubes. At each time interval, three of the tubes were removed, opened and the contents transferred to glass bottles. The suspension was then dissolved by adding 1ml concentrated (98%) sulfuric acid. P in solution was colorimetrically determined with the molybdophosphoric blue (Murphy and Riley, 1962) method using ascorbic acid as a reductant. A standard series and blank were prepared with the same background Fe and sulfuric acid.

3.2.4 Field data

Maize (*Zea mays* L.) was grown in summer since the establishment of the experiment (1939). Field data for maize grain yield (t ha^{-1}) was collected from the experimental station. Since there was no similar data on the plant P uptake, the correlation was restricted only to dry (12% moisture content) maize grain yield.

3.2.5 Data analysis

The data obtained were statistically analyzed using Statistical Analysis System (SAS Institute 2004). Analysis of variance was done using the General Linear Model (GLM) procedure. The Tukey test was used to determine significant differences at $\alpha = 0.05$. The regression equations and correlation coefficients were determined with the exponential fits of the graph. k_A and k_B values of equation [6] were determined by splitting the respective pools in to two pools (Pool A and Pool B), taking in to account the pattern of P released with time, and plotting the natural log of the P desorbed against time. Correlation of k_A, k_B and the total amount of P released with plant yield parameter (Maize grain yield) was done using Pearson linear correlation, PROC CORR (SAS Institute 2004).

3.3 RESULTS AND DISCUSSION

3.3.1 DMT-HFO extractable P

The amount of P_i extracted by DMT-HFO was significantly influenced ($P \leq 0.05$) both by the levels of P applied and extraction time (Table 3.3). Temporal change of this fraction, however, was not significant for the control. The cumulative P desorbed was higher in the MNPK treated soil (19.83-103.46mg kg $^{-1}$) and lower in the NK (0.08-1.13 mg kg $^{-1}$) at all levels of extraction time (1 –56 days). In this study, NPK (4.87 – 19.34 mg kg $^{-1}$) and MNK (5.85 – 18.76 mg kg $^{-1}$) treated soils resulted in a comparable amount of extracted P at all levels of extraction time. This is possibly because in soils treated with large amounts of animal manure, like the case of MNK, P might have been accumulated in inorganic forms in preference to organic forms (Sharpley, et al., 1993; Koopmans et al., 2003; Turner and Leytem, 2004). This is evidenced by having nearly similar amount of Bray and total P for both NPK and MNK treated soils (Table 3.1). The P source therefore seemed not to influence the amount of P extracted from both types of treatments.

Table 3.3. Effect of P levels and extraction time on soil P desorption

Desorption time (days)	NK	NPK	MNK	MNPK
	(mg P kg $^{-1}$)			
1	[§]**x** 0.08[†] **a**[‡]	**x** 4.87 **a**	**x** 5.85 **a**	**y** 19.83 **a**
7	**x** 1.05 **a**	**y** 9.29 **a**	**y** 10.46 **ab**	**z** 60.72 **b**
14	**x** 1.07 **a**	**y** 11.84 **ab**	**y** 11.90 **ab**	**z** 73.33 **c**
28	**x** 1.08 **a**	**y** 13.50 **ab**	**y** 12.91 **ab**	**z** 87.62 **d**
42	**x** 1.11 **a**	**y** 15.65 **ab**	**y** 14.74 **b**	**z** 93.12 **d**
56	**x** 1.15 **a**	**y** 19.34 **b**	**y** 18.76 **b**	**z** 103.47 **e**

[§] Mean values in rows with different letters x, y, and z are significantly different ($\alpha = 0.05$)

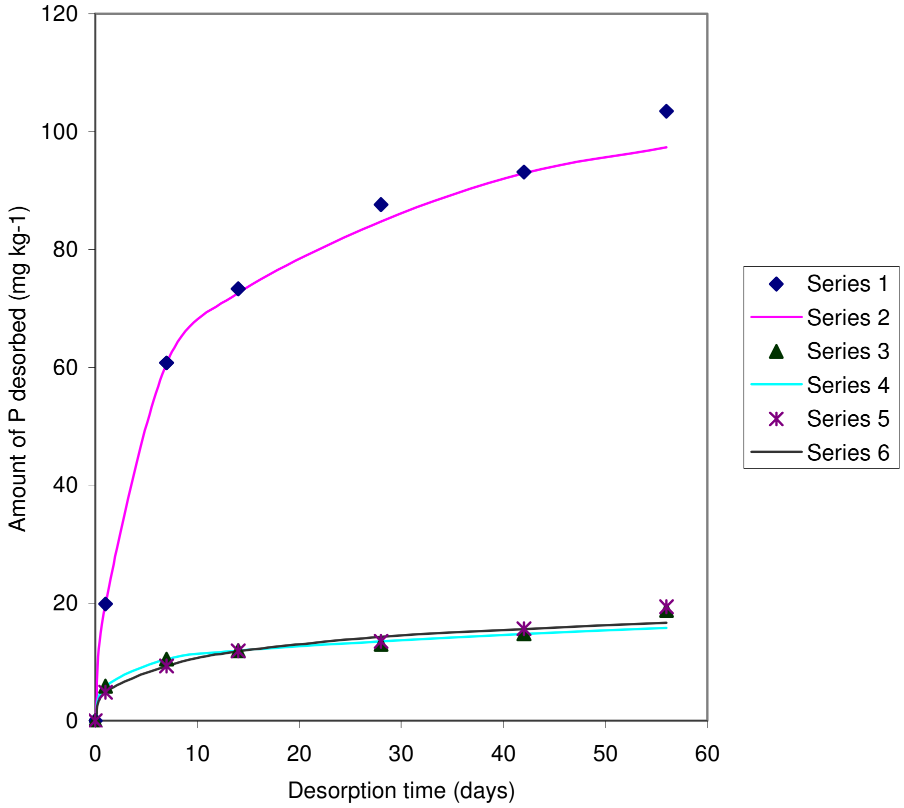
[†] Mean values of three replicates

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

When expressed as a percentage of the total P (Table 3.1), the percentage distribution of DMT-HFO-P_i fraction ranges from 0.02 –0.40, 0.81 – 3.22, 0.93 – 3.01 and 2.33 –

12.15 for NK, NPK, MNK and MNPK treated soils respectively from day 1 to 56 days of extraction time respectively. The percent P extracted was very low compared to the total P. Similar results were reported by other researchers (Koopmans et al., 2001; De Jager and Claassens, 2005; Ochwoh et al., 2005). Treatment MNPK however resulted in a relatively larger percent of extractable DMT-HFO-Pi especially at the latter time of extraction. This could be ascribed to the higher Bray and total P of this treatment (Table 3.1).

Cumulative P released with time followed, in general, the same pattern for all P treated soils, with an initial rapid release of P within the first two weeks (14 days), followed by a slower release that was still continuing after 56 days as illustrated on Figure 3.1. This is attributed to the presence of two distinct pools of soil P, one with rapid release kinetics and the other with slower desorption kinetics (Lookman et al., 1995, De Jager and Claassens, 2005). The fast P pool presumably represents P bound to reactive surfaces, directly in contact with the aqueous phase (Hingston et al., 1974, Madrid and Posner, 1979). The slow P release rate from the second pool is either the result of slow dissolution and/or diffusion kinetics from interior sites inside oxyhydroxide particles (McDowell and Sharpley, 2003). The fact that the control had very little DMT-HFO extractable P might be the result of the low amount of available P. The amount of P extracted from the control during the 56 days of extraction was comparable with the Bray-1P. De Jager and Claassens (2005) however reported contrary to this, cumulative DMT-HFO extractable P extracted over 56 days was 10 times more than the Bray extractable P. The difference could be attributed to the types of soils used. De Jager and Claassens (2005) used incubated soils for 5 months at ± 28 ^{0}C. In this study the last time the soils received any P was in 1985 for NPK and 1990 for MNK, which means the soils were incubated on average for nearly 20 years. In addition to this, cropping did continue after P application discontinued, which means, at the same time, that P in the soil was also depleted. It was therefore expected that, as a result of the longer equilibration time and P depletion, the easily available P would be lower in this study.



Series 1: Data (MNPK)

Series 2: Two component first order model (MNPK) $R^2 = 0.993$

Series 3: Data (MNK)

Series 4: Two component first order model (MNK) $R^2 = 0.918$

Series 5: Data (NPK)

Series 6: Two component first order model (NPK) $R^2 = 0.947$

Figure 3.1. Cumulative desorption data of the different P treated soils fitted to a two component first order model

The rate of desorption has not reached maximum, indicating that desorption will continue for longer period than 56 days. The experimental data were fitted with a two-component first order model. The correlation coefficients were 0.947, 0.918 and 0.993 for NPK, MNK and MNPK treated soils respectively as shown in Figure 3.1. The control is not considered here, as the amount of P extracted was negligibly small albeit the rate of desorption followed the same trend like the P treated plots. The rate constants (0.0003-0.0043 h^{-1}) of P release from all treatments were lower than the rate constant of P transport through the DMT (0.09 h^{-1}) reported by Freese et al. (1995), indicating that it is the P release from the soil solid phase and not P diffusion through the DMT that was the rate limiting step. This result concurs positively with the results of De Jager and Claassens (2005) (0.0046-0.0064 h^{-1}).

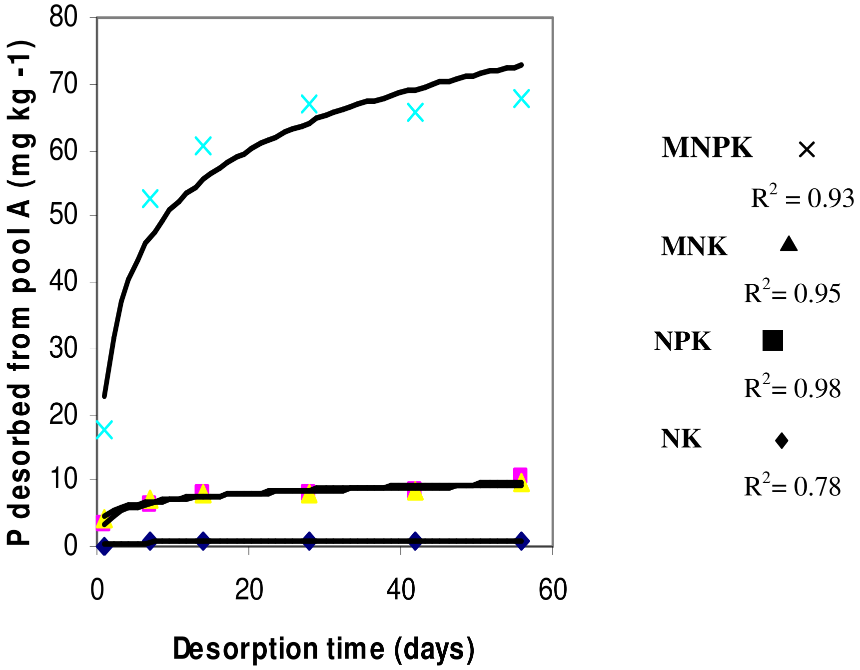


Figure 3.2. Simulated P desorption from pool A (SP_A) for the different treatments over 56 days

In Figures 3.2 and 3.3, the simulated P release from respective SP_A and SP_B pools were plotted against time to show the different release kinetics of each pool over 56 days. The contributions of SP_A and SP_B to $P_{R\,(t)}$ can therefore be calculated from the following equations (De Jager and Claassens, 2005).

$$SP_A\,(t) = \alpha_A\, P_{R(t)} \qquad \text{and} \qquad (7)$$

$$SP_B\,(t) = \alpha_B\, P_{R(t)} \qquad (8)$$

Where $\alpha_A = (1\text{-}e^{-KA\,t})\, SP_{A0}/\, P_{R(t)}$ and $\alpha_B = (1\text{-}e^{-KB\,t})\, SP_{B\,0}/\, P_{R(t)}$

The release kinetics of SP_A was faster in the first 14 days but declined with increasing time, where as the contribution made by SP_B increased with time, the increment being dominant especially with increasing time of extraction. The contributions of both SP_A and SP_B to the total P extracted varied among treatments following the order: MNPK>>MNK≈NPK>>NK. This is in accordance with the total P content of the plots (Table 3.1). The higher the P status of the soil, the greater was the contribution made by both SP_A and SP_B. This could be attributed to higher degree of P saturation of the adsorption sites with increasing P status of the soil (De Jager and Claassens, 2005). Toor and Bahl (1999) also reported the higher P desorption rate in fertilizer and manure treated soils. In their investigation, manure appeared to play significant role in enhancing the P desorption possibly due to complexation of Fe and Al ions.

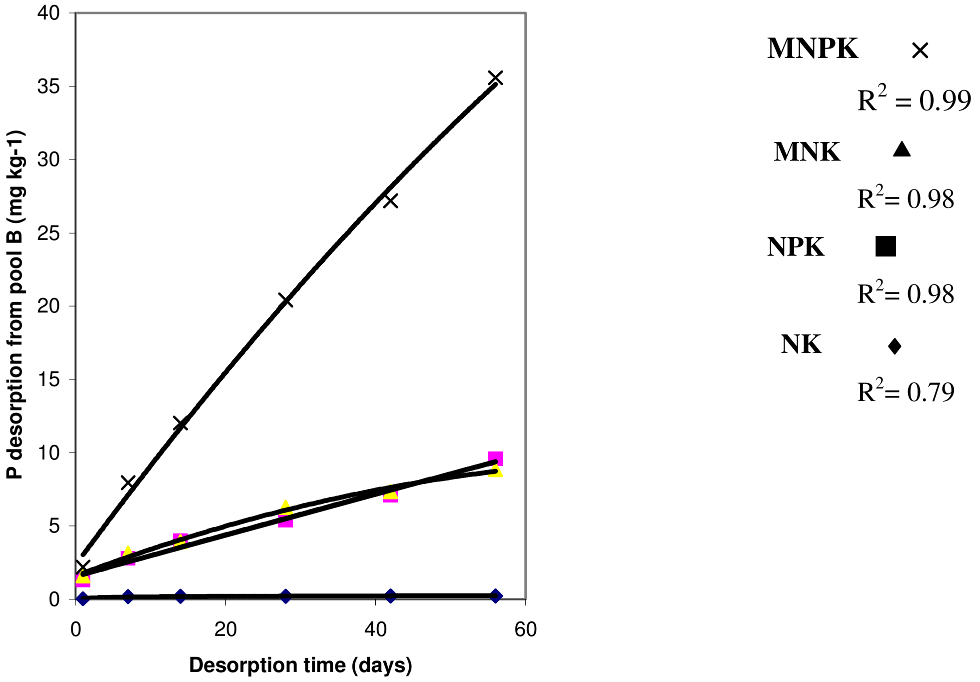


Figure 3.3. Simulated P desorption from pool B (SP_B) for the different treatments over 56 days

Figure 3.4 indicates the desorption rate of the differentially P treated soils. The rate at which P desorbed from MNPK dropped faster up until 28 days and started to change slowly with progressive desorption time. The same trend was also observed for NPK and MNK treated soils although the rate of desorption declined faster up until 14 days and varied slowly afterwards. Moreover, the degree of variation was much less pronounced as compared to MNPK. The reason for such variation could be attributed to the difference in the amount of desorbable P, which is much greater for MNPK than either NPK or MNK treated plots. The control, however, showed almost negligible variation with time. These results are consonant with the reports made by De Jager and Claassens (2005). The reason for this could be ascribed to the very low P contents of the treatments that received no P and faster release kinetics are usually associated with desorption of adsorbed P directly in contact with the soil solution (Lookman et al. 1995).

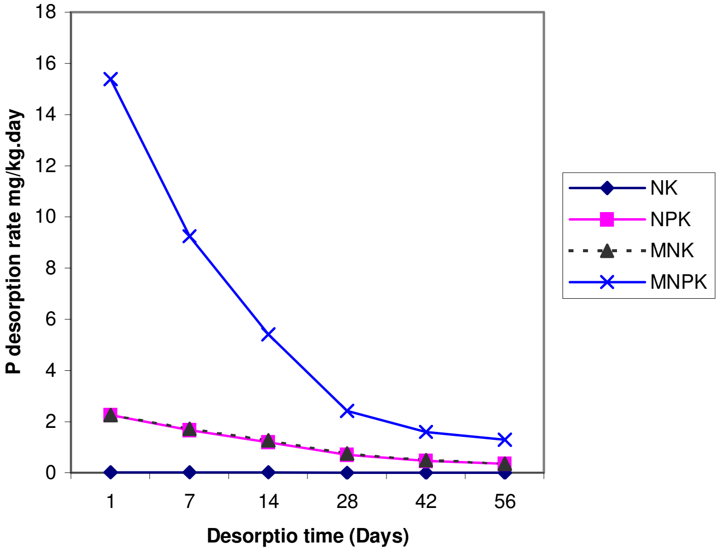


Figure 3.4. Desorption rates for the different P treatments over 56 days

2.3.2 Plant growth as related to phosphorus desorption kinetics

In this work, correlations between the rate coefficients k_A and k_B (day $^{-1}$) with maize grain yield (t ha $^{-1}$) were made as illustrated in Table 3.4. The grain yield considered for this comparison was the yield (four replications) obtained in the year of sampling. However, the yield obtained on the subsequent year was also comparable revealing the consistency of the data considered. A significant correlation was obtained between the labile pool rate coefficient k_A and maize grain yield ($r = 0.93^{**}$). This pool represents the P pool with fast release kinetics that comprises presumably primarily P bound to the reactive surfaces that is in direct contact with the aqueous phase. This pool is presumed to be easily available to plants in a reasonably short period of time (Lookman et al., 1995). The rate coefficient k_B also showed a significant but moderate correlation ($r = 0.78^*$) with maize grain yield. This pool represents the P pool with slow release kinetics that results from slow dissolution kinetics or from slow diffusion from the matrix of sesquioxide aggregates (Koopmans et al., 2004). This pool will be available only over a long period of time and that is probably why the correlation was not so strong.

Table 3.4. Correlation between maize grain yield (t ha^{-1}) and kinetic parameter k (day^{-1})(Rate coefficient) of the DMT-HFO method

	Yield	k_a	k_b	k_a+k_b
Yield	1.00			
k_A	0.93^{**}	1.00		
k_B	0.78^{*}	0.52	1.00	
k_A+k_B	0.97^{**}	0.99^{**}	0.62	1.000

**Significant at 0.01 probability level, *Significant at 0.05 probability level

Although the P pools are theoretically grouped in to these two discrete pools for the sake of convenience, the fact that both pools involve simultaneously in the uptake process indicates that one should take into account the effect of both when such a correlation is made. Thus, the sum of the rate constants (k_A+k_B) showed a significant correlation ($r = 0.97^{**}$) with maize grain yield, which is even stronger than the correlation with which each showed with maize grain yield. The rate coefficient for the labile fraction, k_A, strongly correlated ($r = 0.99^{**}$) with the sum of k_A and k_B (k_A+k_B) unlike the less labile fraction, k_B ($r = 0.62$) revealing the predominant contribution of the labile P fraction in replenishing the soil solution P than the less labile form for the extraction period considered in this study.

Table 3.5.Correlation between the cumulative amounts of P (mg kg^{-1}) extracted by the DMT-HFO and Bray 1 P (mg kg^{-1}) with maize grain yield (t ha^{-1})

P (mg kg^{-1})	Maize grain yield (t ha^{-1})	Bray 1P (mg kg^{-1})
DMT-HFO-P_i	0.58	0.92^{**}
Bray-1P	0.84^{*}	-

*Significant at 0.05 probability level **Significant at 0.01 probability level

The cumulative amount of P extracted by the DMT-HFO over a 56-day period was also correlated with yield and Bray 1P as depicted in Table 3.5. According to Sharpley (1996), Bray 1 provides the best indication of labile P in slightly to highly weathered soils. This extraction method is currently widely used as a soil P test method. Correlation between the cumulative P extracted and maize yield was not significant. However, the correlation between Bray 1P and maize grain yield was highly significant ($r = 0.84^{*}$). Unlike the correlation between DMT-HFO-P_i and yield, the correlation of the former with Bray-1P was found to be highly significant (r =

0.92^{**}). This observation probably indicates the ability of these extractants to extract the labile P. Although the correlation between DMT-HFO-P_i and Bray-1P was found to be highly significant, the correlation each showed with maize yield was apparently opposite, the former resulted in weak correlation, while the latter resulted in moderately strong and significant correlation with the yield parameter. A possible explanation for the observed difference between the two extractants could be obtained by comparing the amount of P extracted by both extractants as depicted in Table 3.1. NK and MNPK treated soils released roughly similar amount of P by both extractants where as NPK and MNK desorbed a DMT-HFO-P_i extract, which was nearly half extracted by Bray-1P. The relatively lower amount of P desorbed by these treatments could be a possible reason for the poor correlation observed between DMT-HFO-P_i and maize grain yield.

Judging from the r-values, the rate coefficient showed a better correlation with maize grain yield than the cumulative amount of P desorbed. The rate coefficient, therefore, appeared to be a good index to assess the P supplying capacity of the soils studied. The relatively weaker correlation of the amount of P released with maize grain yield is an indication of the need for further fine-tuning (optimization) of the existing approach. Moreover, correlation with other plant indices such as plant P uptake and relative plant response should also be included in the further assessment of this methodology.

3.4 CONCLUSIONS

According to this study, cumulative P released with time followed the same pattern for all P treated soils, with an initial rapid release of P with in the first two weeks (14 days), followed by a slower release that was still continuing after 56 days of extraction. No desorption plateau was reached during the entire period of extraction time, indicating that desorption can continue for a longer period than 56 days. P desorption kinetics were described relatively well by a two-component first-order model (R^2 = 0.947, 0.918, & 0.993 for NPK, MNK, & MNPK respectively). The contributions of both SP_A and SP_B to the total P extracted varied among treatments following the order: MNPK>>MNK≈NPK>>NK. The contribution made by SP_A was found to be higher than SP_B in the 56 days of extraction. However, the degree of increment with time showed that it is the less exchangeable pool (SP_B) that will control the release kinetics of the soil in the long term.

In this study the rate coefficient showed a better correlation with maize grain yield than the cumulative amount of P desorbed. The rate coefficient, therefore, appeared to be a good index of plant availability. However, in this research correlation with other plant yield parameters such as P uptake and relative plant response was not conducted due to lack of relevant data. More work relating these plant indices with desorption indices is therefore required. Data from a wider range of soils is also needed to evaluate the universality of this method. Besides, this method employed 100% exploitation of soil volume, which is in contrast to plants where the root exploitation is much less than this. Recent works related to the percent root exploitation of the soil volume revealed that 3-4% of the top soil volume was exploited at full maturity of a maize crop. This value was 1% during the first two weeks, when most P uptake was anticipated to occur (Kamper & Claassens, 2005). Therefore, exploiting the whole volume of the soil by continuous shaking, as has been done in this technique, may not well simulate the plant mode of action.