CHAPTER 1

GENERAL INTRODUCTION

Background

Phosphorus deficiency in plants is believed to constitute the second most important soil fertility problem throughout the world (Sanchez and Salinas, 1981; Lindsay, Vlek and Chien, 1989). Sanchez (1976), Pushparajah and Bachik (1987), Sattell and Morris (1992), and Doula, Ioannou and Dimirkou (1996) have all indicated that phosphorus was the second most limiting element in the Alfisols, Oxisols, and Ultisols of tropical Africa, Asia, and South America. Phosphorus deficiency in such soils is often exacerbated by a high capacity to fix phosphates in different ways making P less available to crops. Most of these soils are often rich in Fe and Al oxihydroxides that form strong bonds with phosphate anions. Other soil characteristics such as pH, clay and organic matter content, exchangeable cations, ionic strength, redox potential, and temperature may also influence P-sorption (Quang et al., 1996). As phosphate fertilizer is one of the most expensive inputs, it is essential not only to know the most cost effective phosphate application rates but also the long-term effects of the added phosphate in the soil. Therefore, the acquisition of precise information concerning soil phosphate availability is a prerequisite to ensure sustainable management of soil.

The P fractionation procedure to characterize different P fractions in fertility studies was used by Chang and Jackson (1957). Only inorganic P was characterized, due to the lack of proper methodologies to identify organic P fractionations at the time. The progressive importance given to the organic P fraction made it necessary to look for more comprehensive fractionation procedures. A procedure was thus, proposed which allowed for a more complete characterization of soil P than the previous procedures (Hedley, Steward and Chauhan, 1982). This procedure has been used in different soils to study the transformations and distribution of inorganic and organic P forms (Vazquez, Noellemyer and Coremberg, 1991). Tiessen and Moir (1993)

regrouped the P fractions based on the rates of their recovery or transformations into different inorganic P pools. This allowed for the development of a more dynamic picture of P transformations in the soils.

There could be a significant residual effect due to the possible desorption of phosphate from the different soil components and when this benefit is ignored it could lead to unnecessarily high P applications (Quang et al., 1996). The residual plant-available P in soils can be quantified by successive cropping experiments carried out in field or greenhouse conditions. This approach, however, is very expensive and time consuming, and methods that approximate a biological measure can be very useful analytical tools in P fertility studies in soils (Indiati, 1998).

The conventional routine chemical extractants cannot be used to assess the potential desorption rates of P, because they disrupt the chemical structure of soils. Some soil test methods that have limited effects on the soil system that include isotopic exchange techniques, anion exchange resins, iron oxide-impregnated paper strips, and dialysis membrane tubes filled with hydrous ferric oxides (DMT-HFO) have been proposed (Amer et al., 1955; Dalal, 1985; Menon et al., 1990; Freese et al., 1995). These methods extract more of the "plant-available P" than the chemical procedures. Successive extractions carried out by any of these methods may constitute a convenient laboratory method to characterize the capacity of soil to supply P, and to investigate the rates of P release from original and P fertilized soils over a period of time (Indiati, 1998).

Phosphorus status of South African soils

In South Africa, P deficiencies due to P sorptions are widespread especially in highly weathered soils in the high rainfall areas (Reeve and Sumner, 1970; Mcgee, 1972; Bainbridge, Miles and Praan, 1995). Within such areas P deficiency is reported to be the most common and economically important nutritional deficiency. The studies of Reeve and Sumner (1970) revealed a wide variation in the P sorption capacities of some Oxisols in Kwazulu-Natal Province. Similarly Mcgee (1972), in evaluating P

sorptions in soils of Gauteng, Mpumalanga, Northwest, and Free State Provinces found considerable variations in their sorption capacities. Bainbridge et al., (1995) in an effort to quantify the P sorption capacities of soils in Kwazulu-Natal Province determined the P-sorption isotherms of 50 soil samples from a number of localities in the province. They found that the amounts of P sorbed ranged from 5 - 1174 mg kg^{-1} and that the highest sorptions occurred in the highly weathered red and yellow-brown clay soils with a high organic carbon contents in the A horizon (Inanda, Kranskop and Magwa forms). This agrees with the findings of Haynes (1984) who had indicated that ferric and aluminium ions complexed with organic matter provide additional sites for P sorption.

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 (Johnson, Miles and Thiabau, 1991). It has been shown further that, soils with predominantly 1:1 type clay materials (i.e. highly weathered red and yellow-brown clay soils) sorb far much more P than the soils with predominantly 2:1 type clays. Johnson et al., (1991) also conducted various studies on soils from 54 sites on a wide range of soils in Kwazulu-Natal Province to calculate P requirements and to establish how much P must be applied to overcome any buffering effects and raise the extractable P content to desired levels. In a long-term experiment (over 15 years) on yellowish brown sandy clay loam (Avalon) and a red sandy clay (Clovelly) soil in Ermelo, Mpumalanga 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.

Phosphorus sorption and desorption characteristics

Phosphorus sorption is the removal of labile P from the soil solution, due to adsorption on, and absorption into the solid phases of the soil, mainly onto surfaces of more crystalline clay compounds, oxihydroxides, or carbonates (Holford and Mattingly, 1975). The labile P forms are also referred to as readily available or plant-available P_i (Hedley et al., 1982). Many highly weathered tropical and subtropical

soils can absorb large amounts of phosphates applied as fertilizers, which reduces the nutrient use efficiency of the applied P. Sorption of P is greatest in soils containing Fe- and Al- oxihydroxides, and allophanic clays, followed by kaolinitic and lastly montmorillonitic clays (Sanchez, Palm and Szoth, 1991). Although soil P sorption has been studied intensively relatively less has been done on the P desorptions in soils and sediments. Interests in P desorption studies are rising due to the importance of P on soil fertility and pollution (Sharpley et al., 1985). Intensive animal husbandry in Europe has led to the production of large amounts of animal manures, and the disposals of the manures on agricultural land have led to increased soil P contents (Gerke, 1992). Many soils have become saturated and contributed to surface water eutrophication (Sharpley et al., 1985; Mozaffari and Sims, 1994; Penn et al., 1995; Sharpley, 1996; Pote et al., 1998). Similar problems also occur where sewage sludge has been disposed on land (Gerke, 1992; Sharpley and Sisak, 1997).

P sorption and desorption rates

The rates of P sorptions have received considerable attention over the past years (Freese et al., 1995; Bowman, Rodrignez and Self, 1998). 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 into the soil aggregates (Willet, Chartres and Nguyen, 1988), or due to the slow formation of P containing minerals (van Riemsdijk et al., 1984; Lookman et al., 1995).

The P desorption rates in soils are of particular interests in respects to the bio-availability 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; Pautler and Sims, 2000). Theoretically, all adsorbed P present in the soil should be desorbable, but in practice, part of the soil P is so strongly bound that it is considered irreversibly fixed (Ryden, McLaughlin and Seyers, 1977; Bowman et al., 1998). A study of the P desorption rates of soil may give more insight to the nature of the plant availability of soil P pools (Lookman et al., 1995).

According to Lookman et al. (1995) little information has been availed on P desorption rates, especially on the long-term. This is due to several practical problems that complicate such long-term studies. In their studies, they classified desorption kinetics into a fast and slow desorbing pools. The fast P pool presumably represents primarily P bound to the reactive surfaces, which are in direct contact with the aqueous phase (Hingston, Posner and Quirk, 1974; Madrid and Posner, 1979). Other possible contributions to the fast desorbing pool may be the less soluble P salts originating from recent fertilizer applications that are not yet in equilibrium with reactive hydrous oxides. Complexed P with organic material may also be part of the fast desorbing pool (Gerke, 1992). The slow P release rates from the second pool are either a result of slow dissolution rates or from slow diffusion from interior sites inside oxihydroxide particles. The sum of the fast and slow pools as defined can be represented by an oxalate extract (P_{ox}) and is an estimate of the total inorganic P in soils that have received a high load of fertilizer (van der Zee, and van Riemsdijk, 1988; Lookman et al., 1995).

The sequential extractions of inorganic-P (P_i) and organic-P (P_o) pools

The applicability of the traditional soil P test procedures that were developed for use in fertilizer application recommendations, especially in agricultural systems with no or low fertilizer P inputs proved inadequate particularly in highly weathered soils (Sanchez et al., 1991). These procedures are basically empirical and yield responses can vary considerably. The sequential P extraction procedures by Chang and Jackson (1957), Hedley et al. (1982), and Tiessen and Moir (1993) have been proposed to improve the estimation of plant-available P. These are methods that use increasingly harsher treatments to extract P pools that are believed to be increasingly less available to plants.

The use of sequential extraction procedures allows different soil P pools to be separated and characterized (extractions by different methods, such as extractions by an anion exchange resin, or dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO), and P soluble in alkali and acids of varying strengths). This

fractionation procedure gives separate soil P pools, which vary in the extent of their availability to the growing plants (Hedley et al., 1982; Tiessen and Moir, 1993).

Classification of P fractions (pools)

(a). The dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO) or resin-extractable inorganic P (P_i) has been identified as solution P pool, which is readily available for plants;

(b). Extraction with 0.5M $NaHCO_3$ dissolves labile P_i and P_o absorbed on the soil particle surfaces, including a small amount of microbial P (P_o) and represents a fairly labile P pool;

(c). Extraction with 0.1M NaOH dissolves P_i held more strongly due to chemisorption by Fe- and Al- components and moderately labile organic P (P_o). The P_i extracted from these oxihydroxide surfaces, is characterized as moderately labile P_i.

(d). Extraction with 1M HCl dissolves P_i from apatite-type minerals. These are the calcium bound P_i, which exist mainly as hydroxy apatites ($Ca_5(PO_4)_3OH$), fluorapatite ($Ca_5(PO_4)_3F$), and also as dicalcium $Ca(H_2PO_4)_2$ (brushite), $CaHPO_4$ (monetite), tricalcium ($Ca_3(PO_4)_2$), and octacalcium ($Ca_8H_2(PO_4)_6.5H_2O$) phosphates that exist in small amounts as transitional Ca-P forms. The 1M HCl-P_i is thus clearly defined as Ca- associated P_i, as organic phosphorus (P_o) is rarely found in this extract.

(e). Hot concentrated HCl extract has been found useful in distinguishing P_i and P_o in very stable residual pools. However, P_o extracted in this step may also come from particulate organic matter that is not alkali extractable, but readily bio-available. The P_i is mainly from the occluded and recalcitrant (insoluble) P pools. The occluded P has been described as sparingly soluble and is enveloped (occluded) by ferric and aluminium oxihydroxides (Chang and Jackson, 1957, Bowman et al., 1998). The

recalcitrant P pool is defined as the resistant or residual P pool, sometimes termed insoluble, immobile, or fixed P and forms part of the lattice P, and may originate from fertilizer P that underwent chemical changes in the soil (Chang and Jackson, 1957; Udo and Ogunwale, 1977).

(f). Hot concentrated H_2SO_4 plus H_2O_2 extract residual P, which contains only highly retained or recalcitrant P_i (such as lattice P) and chemically stable P_o (humus and residual microbial cells) that is strongly retained or fixed P, and is regarded as completely unavailable to plants. This more chemically stable P_o and relatively insoluble P_i forms are dissolved by acid digestion and oxidation with H_2SO_4 and H_2O_2 (Tiessen and Moir, 1993).

The overall advantage of the fractionation of soil phosphates 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 fertilizers (Hedley et al., 1982, Tiessen and Moir, 1993). Hedley et al., (1982) used this procedure to study the transformations and distribution of P within the soil P pools after incubating the soils. They concluded that the sequential P fractionation procedure could be used to record some transformations in soil P that occur during short-term incubation experiments.

Approaches to characterization of plant-available phosphorus in soils

The plant-available P in soils is a functional concept rather than a measurable quantity, since no simple direct measurements are available. Plant-available P is defined as all the P that can be taken up by a plant during a specific period, such as a cropping season, year or growth cycle. The advantage of using sequential extraction procedures is that P that becomes available slowly over a longer-term can now also be evaluated (Hedley et al., 1982, Tiessen and Moir, 1993).

While P extraction methods for fertility indices have been well established, methods to distinguish and quantify labile and non-labile P such as the occluded and residual

P are less well established (Bowman et al., 1998). Some issues concerning methodology, timeliness and reproducibility of the sequential extraction procedures have not yet been completely resolved. For example, whether the unavailability of the extractable "non-labile P" is the same regardless of the methods of extraction used such as proposed by the sequential extraction methods of Chang and Jackson (1957), Hedley et al. (1982), and Tiessen and Moir (1993). Although such comparisons may not yet have been done, similarities of the results have indicated that some of this so-called non-labile P can be available. Bowman et al. (1998) concluded that reactive surfaces such as oxihydroxides of Fe and Al, and $CaCO_3$ play important roles in the transformations of P in soils from available to unavailable forms or vice versa.

Assessment of P desorption rates in soils

Phosphorus desorption curves are used to evaluate the P desorption rates in soils. It is prepared by using several methods, such as: successive extractions with water or dilute salt solutions (Fox and Kamprath, 1970); extractions of sub-samples with several soil/water ratios (Brewster, Gancheva and Nye, 1975; Barrow, 1979); anion-exchange resin as a P sink (Brewster et al., 1975; Bache and Ireland, 1980; Raven and Hossner, 1994); dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO) as a P sink (Freese et al., 1995; Lookman et al., 1995; Bowman et al., 1998).

Thus, several experimental techniques have been used to study soil P desorption behaviour. The simplest procedure is to use a solution which is initially free of P to induce desorption (Kafkafi et al., 1967; Hingston et al., 1974; Barrow, 1979; Reddy et al., 1980; Barrow, 1983). In general, it can be expected that only a very small fraction will be desorbed, until equilibrium with the soil solution is reached. The processes can in principle be repeated to desorb more P. However, experimental (analytical) errors tend to accumulate and only a small percentage of the P present in the sample can be desorbed in this way.

Leaching of soil columns with a P-free solution is another option to study P desorption (Sawhney, 1977; Stuanes and Enfield, 1984; Nagpal, 1986; van der Zee and Gjaltema, 1992). This is an effective method for soils with relatively high P concentrations but not for soils with low P concentrations, due to the strong non-linearity of the phosphate desorption 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.

Desorption can also be studied by adding materials that bind phosphate strongly, keeping the solution concentration low so that 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. Anion-exchange resins were originally used for this purpose (Amer et al., 1955; Cooke and Hislop, 1963; Bache and Ireland, 1980; Dalal, 1985; Sayin et al., 1990; Abrams and Jarrell, 1992; Yang and Skogley, 1992).

The resin approach was thought to be more effective when studying the plant available P in the soils, because: (i) anion -exchange resin imitated the general action of plant roots to remove P from the soil solution; (ii) P extracted by anion-exchange resin correlated well with the P absorbed by plants, even when considering soils of quite variable properties (Sibbesen, 1983; van der Zee and van Riemsdijk, 1988). However, the use of anion-exchange resins to desorb P from soil was later found to have some serious drawbacks: (i) the non-specific desorption of different adsorbed anions, (ii) the difficulty in separating the soil from the resin after each desorption step, and (iii) the incapacity of the resin to maintain low P concentrations and to act as an infinite sink (Amer et al., 1955; Barrow and Shaw, 1977; Skogley et al., 1990).

The use of anion-exchange resin membranes proposed by Cooperband and Logan, (1994) provided a major improvement on the point of separability of P sink and soil suspension, however, the disadvantage of using it as a P sink still remained. Apart from the drawbacks mentioned above, the capacity of an anion-exchange resin to

extract desorbable P was found to depend on the chemical form of the resin, e.g., Cl^-, HCO_3^-, or OH^- (Sibbesen, 1978; Bache and Ireland, 1980). In practice, however, the bicarbonate form of the resin is the one mainly used, which generally leads to an increase in the pH of the soil suspension, making HPO_4^{2-} species the dominant P ion in soil solution (Abrams and Jarrell, 1992). The use of a strong acid anion-exchange resin for phosphate in a moderately 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 resin method, although often used to assess plant-available phosphorus, is not ideal for studying P desorption of acid soils (Amer et al., 1955; Cooke and Hislop, 1963; Abrams and Jarrell, 1992; Yang and Skogley, 1992).

To overcome these problems, a method for the assessment of long-term P desorption kinetics of soils using a synthetic ferrihydrite suspension or hydrous ferric oxide (HFO) in dialysis membrane tubes (DMT) as a P sink, has been proposed by Freese et al. (1995). The applicability of dialysis membranes to separate P source and P sink was tested for monophosphate solutions and water extracts of several soils. The system was reported to be mechanically stable for long reaction periods. The pH of the soil solution during desorption remained almost constant. After the desired time of contact between soil suspension and P sink, the sink could easily be separated from the soil suspension with practically no loss of soil material. As such, this technique had important advantages over the previous methods. The system was capable of maintaining a constant low P activity in solution, necessary to study long-term P desorption kinetics of soils.

Conventional routine soil P tests

Conventional routine soil tests are used to monitor the phosphate status of soils in terms of plant availability and fertilizer requirements for optimum plant growth. 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). They further

contended that, conventional soil tests used to monitor the phosphate status of soil lacks sensitivity. Many tests are designed for routine soil testing making them quick and simple to perform, but they indicate little about the phosphate release rate characteristics of a soil.

According to Tiessen and Moir (1993) it is difficult to describe methods for the determination of soil-available P for two basic reasons: (a) Methods for the determination of available P in an agronomic context never measure the quantity of P available to crop, but measure a pool of soil P that is somehow related to the portion of soil P, which is plant available; (b) P availability needs to be defined with respect to an external sink, i.e. a plant, or plant community (crop). Plants differ in their ability to extract P from soils due to differences in rooting systems, mycorrhizal associations, and growth rates. Since any "immediately available" soil P pool is constantly replenished through reactions of dissolution or desorption of "less available" P, and through the mineralization of organic P, the pool size of "total available" P is strongly time dependent.

Contributions of organic P (P_o) to labile P pools

Previous work by Walker and Syers (1976) and Tiessen et al. (1984), had shown that in highly weathered soils, organic P (P_o) forms may be important in supplying extractable resin inorganic P (P_i). Sharpley (1985) reported that mineralization of P_o in calcareous and slightly weathered unfertilised soils of the Southern Plains of the U.S.A. could contribute the equivalent of between 10 to 37 kg P ha^{-1} yr^{-1}. The absolute and relative amounts of P_o mineralised, however, are generally greater for more weathered soils. For example in Ghana, Adepetu and Corey (1976) measured P_o mineralization rates of 91 and 123 kg P ha^{-1} yr^{-1} for a sandy loam soil under cocoa and a savannah bush respectively. While in Nigeria, Cunningham (1963) found P_o mineralization rates of 141 to 393 kg P ha^{-1} yr^{-1} for a fine sandy loam soil cleared of tropical rainforest.

Thus, according to Tiessen et al. (1984) the available P was found to be largely controlled by the mineralization of P_o and up to 80 % of the resin extracted P_i has been accounted for by variations in bicarbonate P_o pool in some highly weathered soils. The more stable NaOH extractable P_o pool appeared to act as a sink since most of this P fraction was associated with P that could not be extracted with a resin P_i contents. Moderately labile P_i pools also contribute to the plant available resin P_i but their contribution was only significant in a small number of the cases analysed. However, in a long-term experiment (over 15 years) on Avalon and Clovelly soils in Ermelo, Mpumalanga Province, du Preez and Claassens (1999), found that the NaOH-extractable P (moderately adsorbed P) was mainly responsible for the replenishment of the labile soil P pool. The importance of P_o for plant nutrition in more weathered soils may help to explain observations by Haas et al. (1961) that P_o was reduced by 42 % during 30 to 40 years of cropping in southern U.S. soils but only by 27 % in northern soils.

The analysis of P data based on acceptable concepts of the soil P cycle shows clearly that available P, and therefore the agronomically important P, in highly weathered soils is closely related to the organic P fractions. This may explain the many difficulties encountered in the testing of P fertility in tropical and subtropical soils and indicates that the study of labile forms of P_o might contribute to advances in soil test procedures (Tiessen et al., 1984).

Transformations and distribution of the added P into different soil P pools

Soluble P added to a soil becomes rapidly insoluble. Several possible mechanisms have been proposed to explain P adsorption in acid soils, where the Fe-, Mn-, and Al-P forms are predominant (Hingston et al., 1974; Symith and Sanchez, 1980). Bramley and Barrow (1992) indicated that low pH values encourage reactions between $H_2PO_2^-$ and Fe, Al, Mn, and silicate minerals. While at neutral to high pH values both the $H_2PO_4^-$ and HPO_4^{-2} ions would be found and the main reaction for P fixation would be as calcium phosphate ($Ca_3(PO_4)_2$) (Brady, 1990; Doula et al., 1996). In calcareous soils, solid phase $CaCO_3$ is believed to govern P reactions.

However, the reactivity of $CaCO_3$ is dependent on specific surface that is related to particle size distribution, rather than to total $CaCO_3$ (Holford and Mattingly, 1975).

The organic matter on the other hand form complexes with Fe, Al ions, and the oxihydroxides thereby preventing these materials from reacting with applied fertilizer P. Several workers have noted positive correlations between soil organic matter and P adsorption capacity. However, according to Doula et al. (1996) it seems more likely that this is indicative of soils with adsorption sites suitable for both P and organic anions, rather than of adsorption of P by the organic matter. Thus, P held in organic form can occur under appropriate conditions, be released into the soil solution, and then become subject to uptake by plants or fixed into some insoluble form (Doula et al., 1996).

Bramley and Barrow (1992) reported that as the initially added P concentration increased, the percentage of P sorped decreased. They explained that at low P concentration, available and easily reached sorption sites are immediately occupied, while at higher P concentrations, the more difficult sorption sites are also reached but the percentage P complexed become less as the sites become occupied.

The effects of incubation on desorption rates of applied P from different P pools

In a study to find a more general method for describing P desorption that was applicable after both short and long periods of contact between soil and P prior to desorption, Barrow (1979) found that after short periods of incubation (1 hour-20 days), the amount of P desorbed in dilute $CaCl_2$ solutions increased rapidly at first but then net re-adsorption occurred. After long periods of incubation (62-240 days), desorption was slower and there was no net re-adsorption.

Mckean and Warren (1996) found that time and temperature of incubation affected the amount of added P that can be recovered both at first extraction and the ultimate amount. In different soils, there were different responses to the incubation treatments. By comparing the different incubation times and temperatures, the initial

amount of P recovered by successive resin extractions was found to decrease with an increase in either time or temperature of incubation. This was in agreement with the work of Barrow and Shaw (1975b), who reported that the ultimate amount of P that could be recovered was almost always less than or little different from the amount of P added. Where recovery was in excess of 100 %, a possible explanation was that the addition of inorganic P caused an increase in the mineralization of organic P as reported by Dalal (1977). Increasing incubation time from 2–55 days generally lowered the ultimate amount of P that could be recovered, suggesting that after incubation for a long time, the slow P adsorption reaction had reduced the amount of readily desorbable P (Barrow and Shaw, 1975c).

Determinations of the residual effects of applied fertilizer P

The rate of P sorption by soils is initially fast and then continues slowly for a long time with no apparent end (Amer et al., 1955; Munns and Fox, 1976; Bramley and Barrow, 1992; Mckean and Warren, 1996). Barrow and Shaw (1975a) described the P adsorption and desorption reactions using a three compartment model: A ←→ B ←→ C. Compartment A represented the phosphate in the soil solution, the equilibrium between A and B was rapid and this reaction determined the initial adsorption of added phosphate, and therefore, its initial effectiveness. The transfer of phosphate between compartments B and C was slower and the phosphate was held more firmly in compartment C. The extent to which this slow adsorption reaction was then reversible (desorption) was fundamental in determining the residual effectiveness of added P (Barrow and Shaw, 1975b).

Mckean and Warren (1996) using successive resin extractions showed differences between treatments that were similar in the initial amounts of added P. In some soils, the desorption curves reached a plateau by the eighth extraction or before where no more P could be recovered, while others continued to release P slowly. This property could be relevant for the crop in the field with respect to the residual effect of added fertilizer P. Thus a knowledge of the type of desorption curve that the soil has, i.e.

whether it reaches a plateau or whether it continues to release phosphate could be important in the economical management of fertilizer applications.

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 (Amer et al., 1955; Cooke, 1966; Williams et al., 1967; Barber, 1984). Dalal and Hallsworth (1976) reported that the rate of soil P release to anion-exchange resin could be correlated with P uptake at relatively early plant growth stages. Parameters related to the P desorption kinetics from soils, such as calculated rate constants, have shown significant correlation with plant uptake (Cooke, 1966; Onken and Matheson, 1982). However, these relationships are difficult to interpret since the rate constant of each kinetic model has a unique characteristic (Raven and Hossner, 1994).

The residual plant-available P in soils could also be quantified by successive cropping experiments carried out in field or greenhouse conditions. In such experiments, plant-available P is removed until P deficiency occurs or a response to added P is measured (Mckean and Warren, 1996; du Preez and Claassens, 1999; Kamprath, 1999). This approach, however, is very expensive and time consuming, and methods that approximate a biological measure could represent very useful analytical tools in P fertility and effectiveness of P fertilizer in soils (Indiati, 1998).

Use of successive DMT-HFO-P extractions to simulate mechanism of P sorption by plant roots

The soil test methods that have limited effects on the soil system are isotopic exchange techniques (Amer et al., 1955); anion-exchange resins (Amer et al., 1955; Hedley et al., 1982; Dalal, 1985; van Raij et al., 1986); iron oxide-impregnated paper strips (Menon et al., 1990; Tiessen and Moir, 1993); and DMT-HFO (Freese et al., 1995; Lookman et al., 1995). These methods extract more of the "available P" than the chemical procedures. They estimate the labile P pools and are good indicators of plant available P, more closely reflecting processes involved in P uptake by plant

roots in soil. In fact, resin, Fe oxide-coated paper strips, and DMT-HFO serve as a sink for released P, preventing solution P built up to levels where further P release is inhibited.

The applicability of dialysis membranes to separate P source and P sink was tested for monophosphate solutions and water extracts of several soils. The system was reported to be mechanically stable for long reaction periods (Freese et al., 1995; Lookman et al., 1995). The pH of the soil solution during desorption remained almost constant. After the desired time of contact between soil suspension and P sink, the sink could easily be separated from the soil suspension with practically no loss of soil material. As such, this technique had important advantages over the resin, and Fe oxide-coated paper strips, methods. The system was capable of maintaining a constant low P activity in solution, necessary to study long-term P desorption kinetics of soils. Successive extractions carried out by this method may constitute a convenient laboratory method to characterize the capacity of soil to supply P, and to investigate the rates of P release from original and P fertilized soils ((Freese et al., 1995; Lookman et al., 1995); Indiati, 1998).

The research objectives were:

(1) To study the transformations and distribution of the initial and the added P into the different P pools by use of the successive DMT-HFO and the sequential P extractions, after different incubation periods;

(2) How added P changed the equilibrium between the different P pools and the desorption rates of P after incubation periods; and

(3) To determine which P pools were supplying the P to the successive DMT-HFO-P extractions and at what rates.

It was hypothesized:

(1) That the initial and applied fertilizer P are adsorbed or fixed to varied degrees by the Hutton soils of Rustenburg and Loskop experimental

farms and thus become unavailable to plants;

(2) That the fate of the applied fertilizer P may be predicted by the use of sequential P fractionation procedures to determine the P adsorption and desorption characteristics of these soils;

(3) That the sequential P fractionation procedures could be used to determine some transformations in the initial and applied P and the distribution of P within the different P pools of the two soils during the incubation periods.

(4) That by successive P extractions using the DMT-HFO procedure it is possible to simulate P absorption by plant roots;

(5) That it is possible to determine the release rates of the adsorbed or fixed P, over time by successive extractions of plant-available P and the sequential P extractions to determine the P pool supplying the labile P.

CHAPTER 2

A STUDY ON THE CHANGES AND DISTRIBUTION OF THE INITIAL AND APPLIED P INTO THE DIFFERENT P POOLS IN HIGH AND LOW P FIXING SOILS AFTER DIFFERENT INCUBATION PERIODS

INTRODUCTION

Phosphorus deficiency in plants is believed to constitute the second most important soil fertility problem throughout the world (Lindsay et al., 1989). Sattell and Morris (1992) stated that phosphorus was the second most limiting element in the Alfisols of tropical Asia, Africa, and South America. The acquisition of precise information concerning soil phosphate availability is a prerequisite to ensure sustainable management of soil. Thus, the characterization of soil phosphate availability has been the focus of numerous studies.

The P fractionation procedure to characterize different inorganic P fractions in fertility studies was used by Chang and Jackson (1957). The progressive importance given to the organic P fraction made it necessary to look for more comprehensive fractionation procedures like that proposed by Hedley et al. (1982). This procedure has been used in different soils to study the transformations and distribution of inorganic and organic P forms (Vazquez et al., 1991). Tiessen and Moir (1993) regrouped the P fractions based on the rates of their renovations or transformations into the different P pools. This allowed for the development of a more dynamic picture of P transformations in the soils.

The overall advantage of the fractionation of soil P into the different P categories is that it permits the determination of the chemical status of the residual and applied P. Thus, Hedley et al. (1982) reported that the sequential fractionation procedure they

proposed could be used to record changes in soil P that occur during short-term incubation experiments.

Recently, a methodology for the assessment of long-term P desorption kinetics of soils using hydrous ferric oxide in dialysis membrane tubes (DMT-HFO) as a P sink, was proposed (Freese et al., 1995). The ability of dialysis membrane tubes (DMT) to separate the P source in the soil and the P sink (HFO in the DMT tube) was tested for phosphate solutions and water extracts of several soils. The system was reported to be mechanically stable for long reaction periods, while the pH of the soil solution during desorption remained almost constant. After the desired time of contact between the soil suspension and P sink, the sink could easily be separated from the soil suspension with practically no loss of soil material. This new technique has thus important advantages over the previously used resin methods. The system was capable of maintaining a constant low P activity in solution, necessary to study long-term P desorption kinetics of soils for over 500 hours.

Soils of Rustenburg and Loskop experimental farms with high and low P fixing capacities respectively

(a) Rustenburg soil

The soils of the formerly Tobacco and Cotton Research Institute (ARC-TCRI) now renamed ARC-Institute for Industrial Crops (ARC–IIC), at Rustenburg were previously surveyed by Botha et al. (1968), and five different soil types were identified. The "dark reddish brown sandy clay soils", classified as Hutton form, and Ventersdop family according to the Soil Classification Working Group (1991) was selected for this research. This is equivalent to Ferric Luvisols of the FAO/UNESCO System (1974), or Alfisols (Haplo-Palcustalfs) of the USDA System (1975). It is a structure-less, deep red soil, and varies considerably in texture. The clay fraction was found to contain mainly kaolinitic clays (52 %). The soil has a relatively high water holding capacity due to its high fine sand and clay contents. Chemical analysis

showed medium to high N, low to medium organic carbon, and low plant available P, and a pH near neutrality (6.0-7.2) (Table 1).

Some trials carried out on this soil reportedly showed a high P fixing capacity. Crops tested especially tobacco showed severe P deficiency symptoms. Several trails to correct the deficiency by applications of different sources of P (e.g. triple super phosphates, single super phosphates, mono-ammonium and di-ammonium P), liming, and incorporations of mycorrhiza failed to produce satisfactory results. The trials with cotton also showed clear signs of P deficiencies (i.e. stunted growth, smallish dark leaves, low boll survival rates, and the characteristic leaf reddening symptoms of late-season P deficiency).

(b) Loskop soils

A similar soil type was identified at Loskop experimental farm near Groblersdal. The soil was identified as "dark reddish brown sandy loam" (Botha et al., 1968). It also falls under the Hutton form but to the Shorrocks family. This is equivalent to Ferric Acrisols (FAO/UNESCO System, 1974) or Alfisols (Pale-Xerults) (USDA System, 1975). Its chemical, mineralogical, and physical data are also shown in Table 1. However, the Loskop soil shows only low to moderate P sorption capacities.

It was therefore hypothesized that the added fertilizer P in both soils could be adsorbed to varied degrees by Al- and Fe- oxihydroxides, soil organic matter, and layered silicate clay crystals, or precipitated as Ca and Mg compounds depending on the pH that ranges near neutrality. Due to the limited P uptake in the Rustenburg soil by both the tobacco and cotton plants, it was found necessary to investigate the fate of both the initial and the applied P in the high P fixing Rustenburg and the low P fixing Loskop soils by use of the sequential P fractionation procedures after different P treatments and incubation experiments.

MATERIALS AND METHODS

1: MATERIALS

1.1: Soils

The soils for this research were obtained from ARC – Institute for Industrial Crops, Rustenburg and the affiliated experimental station at Loskop near Groblersdal. These areas are situated at 25.7 ^{0}S / 27.3 ^{0}E (North West Province), and 25.2 ^{0}S / 29.4 ^{0}E (Mpumalanga Province) respectively, in the Republic of South Africa. These two soils (Rustenburg and Lokop) have already been described in details on pages 19 and 20.

1.2: Incubation materials

-1 000 cm^3 glass jars
- Cardboard boxes, - to hold 12 glass jars
- KH_2PO_4
- Climate room (20^0 C; + or – 2^0 C)

2: SOIL INCUBATION TRIALS

2.1: Soil samples

Soils from Rustenburg and Loskop were used in the trials. Bulk samples of 200 kg each were collected from the fields. Both soils have been under cropping for the last 5 years, and fertilized as recommended for different crops. The soil samples were dried in a forced air oven at 40 ^{0}C, and ground to pass a 2 mm sieve. Each bulk sample was then thoroughly mixed and stored at room temperature.

2.2: P-Treatments

Potassium dihydrogen phosphate (KH_2PO_4) was used as the P source. The calculated values equivalent to 0, 5, 10, 20, 25, 50, 75, 100, 125, 150, 175, 200, 225, and 250 mg P kg^{-1} were weighed out and made up as stock solutions. To each 500 g soil sample weighed out into a 1 000 cm^3 glass jar, the calculated volume of the stock solution was added, mixed thoroughly with the soil, and brought to field capacity before starting the incubation processes.

2.3: Incubation

Five (5) incubation periods (1, 60, 120, 180, and 240 days) were applied on each P treatment. Each treatment combination was then replicated three times. The samples were put in boxes and placed randomly in a climatic room where they were incubated at a temperature of 20 ^{0}C (+ or - 2 ^{0}C). After each incubation period, the replicated samples of each P treatment were withdrawn and forced air dried before they were used for the sequential P extractions.

3: SOIL ANALYSES

3.1: Routine chemical, physical, and mineralogical analyses

Before commencing the incubation treatments, each soil was selectively analysed for pH, N, organic carbon (O.C.), P (Bray 1 and 2), Total P, exchangeable K, Ca, Mg, texture and clay mineralogy according to Black et al. (1965) methods.

3.2: Sequential P extractions

The sequential P extractions were carried out as described by Tiessen and Moir (1993) with one modification. The resin strips were replaced by dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO), as described by Freese et al. (1995).

3.2.1: Materials

- pH metre
- Horizontal shaker
- Centrifuge
- Spectrophotometer
- Water bath
- Digestion rack
- DMT- Dialysis membrane tube strips
- Medi - clips (clips)
- Extran, - phosphate free washing reagent
- **HCl**: Conc (11.3M), 0.5M, and 1.0M
- 0.5M $NaHCO_3$
- **NaOH**: 4M, 1M, and 0.1M
- **H_2O_2**: 30%
- **H_2SO_4**: Conc (18M), 2.5M, 0.9M, and 0.25M

- **Ammonium molybdate**: Dissolve 40.0 g in 1000 cm^3 of deionized water.
- **Ascorbic acid**: Dissolve 26.4 g in 500 cm^3 of deionized water.
- **Antimony potassium tartrate**: Dissolve 1.454 g in 500 cm^3 of deionized water.

- **Solution A**: Add 75 cm^3 ammonium molybdate, 50 cm^3 ascorbic acid and 25 cm^3 of antimony potassium tartrate solutions to 250 cm^3 of 2.5M H_2SO_4, and dilute to a final volume of 500 cm^3 with deionized water in a volumetric flask.

- **Hydrous ferric oxide (HFO) suspension**: Dissolve 200 g of ferric nitrate nonahydrate in 2 000 cm^3 of deionized water. Add drop wise 1M NaOH until a pH of 7 to 8 is obtained. The suspension is then centrifuged for 10 minutes, decanted, and re-suspended in deionized water. This procedure is repeated at least two times. Finally, the hydrous ferric oxide (HFO) is suspended in

deionized water to obtain a volume of 4 000 cm^3 and adjusted with 0.5M HCl to pH 6.5 (i.e. close to the pH of the soils under study). This suspension is stable for two weeks.

-Dialysis membrane tubes (DMT): Fifteen cm-lengths of the dialysis membrane tubes (DMT) are boiled twice in deionised water for 5 minutes at a time. After each boiling period the tubes are rinsed thoroughly. Each dialysis tube is then closed at one end with a clip and filled with 10 cm^3 of HFO suspension (approximately 0.05M Fe per DMT tube), and the open end also closed with a clip. While filling the tubes, the HFO suspension is stirred vigorously to obtain a homogeneous suspension.

3.2.2: P determinations by Murphy - Riley (1962) method

This method is used to determine directly the P extracted from the DMT-HFO, the dilute and concentrated HCl, and the conc. $H_2SO_4 + H_2O_2$ extracts.

Pipette 10 cm^3 aliquot into a 100 cm^3 volumetric flask. Add two drops of the paranitrophenol as an indicator and adjust the pH. If the extract is too acidic, adjust the pH with 4M NaOH to yellow and then with 0.25 M H_2SO_4 until the indicator just turns clear. For alkaline extracts just acidify.

Add 8 cm^3 of Solution A, fill up to the volume, shake, and read on the spectrophotometer at 772 nm after 10 minutes (colour is stable for 24 hours).

3.2.3: Determination of the inorganic P (P_i) in the dilute and conc. HCl (D/HCl-P_i and C/HCl-P_i) and $H_2SO_4 + H_2O_2$ (H_2SO_4-P_i) extracts

Pipette 10 cm^3 aliquot into a 100 cm^3 volumetric flask and determine the P according to Murphy–Riley (1962) method.

3.2.4: Determination of the inorganic P in the 0.5M $NaHCO_3$ (-HCO_3-P_i) and 0.1M NaOH (-OH-P_i) extracts

- Pipette 10 cm^3 of the extract into a 50 cm^3 centrifuge tube.
- Acidify the 0.5M $NaHCO_3$ extract by adding 6 cm^3 of the 0.9M H_2SO_4 solution and the 0.1M NaOH extracts with 1.6 cm^3 of the same solution, and then cool them down in a cold room for 30 minutes.
- Centrifuge at 2 500 RPM for 10 minutes.
- Decant the supernatant into a 100 cm^3 volumetric flask.
- Rinse the tubes carefully (without disturbing the precipitated organic material) with 2–3 cm^3 of acidified water.
- Adjust the pH and measure the P content as described in (3.2.2).

3.2.5: Determination of the total P in the 0.5M $NaHCO_3$ (-HCO_3-P_t), 0.1M NaOH (-OH-P_t), and conc. HCl (C/HCl-P_t) extracts

- Pipette 5 cm^3 of the extract into 100 cm^3 volumetric flasks.
- To the 0.5M $NaHCO_3$ extract add 0.5 g ammonium persulfate and 10 cm^3 0.9M H_2SO_4.
-To the 0.1M NaOH extract add 0.6 g ammonium persulfate and 10 cm^3 0.9M H_2SO_4.
- To the conc. HCl extract add 0.4 g ammonium persulfate and 10 cm^3 deionized water.
- Cover with tin foil (double layer for conc. HCl) and heat very slowly on a hot plate, the $NaHCO_3$ and HCl extracts for 60 minutes, and the NaOH extract for 90 minutes.
- Adjust the pH and measure the P content as described in Section 3.2.2.

3.2.6: Procedures for the P sequential extractions

Day 1: Weigh out 1.00 g of soil into 100 cm^3 polyethylene flasks. Add 80 cm^3 of a solution containing 0.002 M $CaCl_2$ and 0.0003 M KCl.

Place the 15 cm DMT tubes filled with 10 cm^3 HFO in the soil suspension and shake gently for 16 hours.

Day 2: Prior to removing the DMT-HFO tube, the soil material adhering to it is rubbed off with a glass rod to minimize loss of soil material from the suspension and then rinsed with deionized water to remove any remaining traces of adhering soil material. The DMT-HFO tube is then transferred to a conical flask where it is opened and 1 cm^3 of conc. H_2SO_4 is added to the extract to dissolve the HFO before the empty DMT is removed. Determine the DMT-HFO-P_i as described in Section 3.2.2.

Centrifuge the soil suspension at 2 500 RPM for 10 minutes, filter through millipore filter (pore size 0.45µm) and then wash the soil from the filter back into the centrifuge tube with 30 cm^3 of 0.5M $NaHCO_3$ solution and then shake the suspension overnight (16 hours). Ensure that all the soil is in suspension before starting to shake.

Day 3: Centrifuge the soil suspension at 2 500 RPM for 10 minutes. Filter the $NaHCO_3$ extract through a millipore filter into a 50 cm^3 volumetric flask. Determine the inorganic P_i (HCO_3-P_i) and total P_t (HCO_3-P_t) on the bicarbonate extract as described in sections 3.2.4 and 3.2.5 respectively. Wash all the soil from the filter back into the tube with 30 cm^3 0.1M NaOH and shake the suspension overnight.

Day 4: Centrifuge the suspension at 2 500 RPM for 10 minutes. Decant the NaOH extract through a millipore filter into a 50 cm^3 volumetric flask. Determine inorganic P_i (OH-P_i) and total P_t (OH-P_t) in the NaOH extract as described in Sections 3.2.4 and 3.2.5 respectively. Wash all the soil from the filter back into the tube with 30 cm^3 of 1M HCl and shake the suspension overnight.

Day 5: Centrifuge the soil suspension at 2 500 RPM for 10 minutes. Decant the HCl

extract through a millipore filter into a 50 cm^3 volumetric flask. Determine the inorganic P (HCl-P_i) in the HCl extract.

Wash the soil from the filter back into the centrifuge tube with 10 cm^3 conc. HCl. Heat the soil sample on a water bath at 80°C for 10 minutes. Suspend the soil sample in the HCl by vortex before heating the suspension for approximately 10 minutes to come to temperature, add a further 5 cm^3 conc. HCl, vortex, and let it stay at room temperature for 1 hour (vortex every 15 minutes). Centrifuge at 2 500 RPM for 10 minutes and decant supernatant into a 100 cm^3 volumetric flask. Wash the soil with 10 cm^3 H_2O and centrifuge. Add the supernatant together with the test solution, make to 100 cm^3, and determine the inorganic P_i (HCl-P_i) and total P_t (HCl-P_t) in HCl solution as described in Sections 3.2.4 and 3.2.5 respectively.

Add 10 cm^3 of deionized water to the soil residue and vortex to disperse the soil. Transfer the suspension into a 75 cm^3 digestion tubes (use the minimum amount of water possible to transfer all the soil residue), add 5 cm^3 conc. H_2SO_4 and one boiling chip (Hengar granules), vortex, and put on a cold digestion block. Raise the temperature very slowly to evaporate water and when 360 °C is reached H_2O_2 is added as follows: remove the tubes from the digestion block and let them cool to hand-warm; add 0.5 cm^3 of H_2O_2; reheat for 30 minutes to evaporate H_2O_2. Repeat the H_2O_2 additions until the liquid is clear (usually about 5 - 10 times to decompose the H_2O_2). Make sure there is adequate heating after the final H_2O_2 addition, since residual H_2O_2 interferes with the P determination. Cool, make up to volume, shake, and allow residue to settle out overnight. Determine P_i (H_2SO_4-P_i) in the extracted solution according to the Murphy- Riley (1962) method.

3.2.4: P–standards

The P concentrations were determined according to the method of Murphy-Riley (1962). The concentrations were determined by comparing the colour

developed with a standard range. The standard solutions for the different P extractions were prepared with the same extraction reagent and concentrations as in the unknown sample solutions.

A standard stock solution containing 250 mg P dm^{-3} was prepared by weighing accurately 1.0982 gm of oven-dry Analar KH_2PO_4 into a clean $1dm^3$ volumetric flask, dissolved in deionised water and then filled to the mark.

A standard range was prepared by pipetting into 11 clean 100 cm^3 volumetric flasks, 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 cm^3 of the stock solution. An equal amount of one of the extracting solutions (e.g. $NaHCO_3$) was added to each of the volumetric flasks and then 8 cm^3 of the colour reagent was added and filled up to the mark with deionised water

After the colour had developed for 1 hour, the blue colour intensities of the solutions were determined by a spectrophotometer, at a wavelength of 772 nm. The P concentrations of the extracts were then read off from the standard P curves.

Procedure	P - Fractions/Functional roles
1.0 g soil	
↓	
Extraction with DMT-HFO in water	soluble - available P_i
↓	
Extraction with 0.5M $NaHCO_3$	labile - P_i and P_o
↓	
Extraction with 0.1M NaOH	Al-, Fe-hydrous oxide bound-P slow - labile - P_i and P_o
↓	
Extraction with dil. 1.0M HCl	Ca - bound - P slow - labile - P_i
↓	
Extraction with conc. HCl	occluded/recalcitrant - P fixed/unavailable P_i and P_o
↓	
Extraction with conc.$H_2SO_4 + H_2O_2$	residual/recalcitrant/lattice - P fixed/unavailable P_i and P_o

Fig. 1: Flow chart of the sequential P extractions

4: STATISTICAL ANALYSIS

The data from the experiments were analysed statistically using a "Genstat 5 (1995) computer programme. The programme involved the Analysis of Variance (ANOVA) to determine whether F values were statistically different between or among the treatments. The Least Significant Differences (LSDs) were determined by the LSD Fisher tests at 5% confidence level. The correlation coefficients were determined as well as the regression equations for the exponential fits of the graphs.

The graphs for the extracted P and percent P recovered are presented as smooth curves constructed through different regression fits using 'Microsoft Excel' (1995) programmes: Where linear: $y = mx + b$ (where m is the slope and b is the intercept); logarithmic: $y = c\ln x + b$ (where c and b are constants, and ln is the natural logarithm function); polynomial: $y = b + c_1x + c_2x^2$ (where b, c_1 and c_2 are constants); exponential $y = ce^{bx}$ (where c and b are constants, and e is the natural logarithm; and power: $y = cx^b$ (where c and b are constants) to produce the best fits for each set of data. The graphs are accompanied by regression equations and the correlation coefficient (R^2) values.

To calculate the percentage recovery of the added P the amount of the initial soil P extracted was subtracted from the amount recovered after incubation under the same conditions with the added P, thereby correcting for the effect of the initial P during incubation. Thus % P recovered = (P*x*–P*o*)/P1*100; where P*x* was P in the *x*th fraction of the P treatment, and P*o* was P in the *o*th fraction of the initial no P (P0) treatment, while P1 was the applied P level (Sattell and Morris, 1992; Doula et al., 1996).

RESULTS AND DISCUSSION

1. Chemical, physical, and mineralogical characteristics of Rustenburg and Loskop soils

Some selected properties of the two soils (Table 1) under study show that the Rustenburg soil is a sandy-clay while the Loskop soil is a sandy-loam. Kaolinite is the dominant clay mineral in both soils. The pH (H_2O: 1:2.5 suspension) values show that the soils are near neutral. The organic carbon content is low for both soils although it is a little bit higher in the Rustenburg soil (Black et al., 1965). Initial P contents (Bray 1) were generally low for both soils. According to Sharpley (1996), Bray 1 gave the best indications of labile P in the slightly to highly weathered soils.

2. Sequential fractionations of soil P into various inorganic-P (P_i), and organic-P (P_o) pools

The sequential P extractions were carried out as outlined by Tiessen and Moir (1993) with a slight modification, where the resin strips were replaced by dialysis membrane tubes filled with hydrous ferric oxides (DMT-HFO), as described by Freese et al., (1995). The procedures used are summarized in the flow chart in Figure 1.

The summaries of the results of the sequentially extracted P and percent P recoveries of the added P as influenced by added P and incubation periods are presented in Tables 2-3.

Table 1: Some chemical, physical, and mineralogical characteristics of Rustenburg (R) and Loskop (L) soils

Soil Samples	R	R	R	L	L
Depths (cm)	30	60	90	30	60
Soil Texture (%)					
Sand	42	38	34	81	72
Silt	7	7	9	0	1
Clay	51	55	57	19	27
Textural Class	Sandy-clay	Clay	Clay	Sandy-loam	Sandy clay-loam
Clay Mineralogy (%)					
Kaolinite	52	54	40	37	26
Quartz	29	35	18	52	74
pH H_2O (1:2.5)	6.87	6.82	6.60	6.84	6.47
Total N (mg kg^{-1})	486	419	347	206	163
O.C. „	6700	5800	4400	4100	3900
P (Bray 1) „	5.0	3.0	0.0	12.5	1.0
P (Bray 2) „	8.0	4.5	0.5	16.5	1.0
Total P „	265.0	202.0	95.8	152.8	97.5
K „	250	178	83	198	100
Ca „	910	853	690	640	720
Mg „	683	720	830	200	240

Tables 4-8 show the transformations and distribution of the sequentially extracted-P fractions with the various rates of added P and incubation period as percentages of the total soil P pools for Rustenburg and Loskop soils. Figures 2-10 show the regression equation curves. The analyses of variances (ANOVA) and the tables of means are presented in Appendices I Nos. 1-24. In general the ANOVA tables show that there were highly significant changes (P = 0.01) in the sequentially extracted-P fractions with all the rates of the added P, the incubation period, and their interactions (Rustenburg, Appendices I Nos. 1-12; Loskop, Appendices I Nos. 13-24). Figures 2-10 present the regression equations with the best-fitted linear, exponential, logarithmic, polynomial, and power functions. The R^2 values indicated very good correlations in most cases.

3. The effects of P and incubation treatments on the sequentially extracted inorganic P (P_i), organic P (P_o), percentage P recovered, and P distribution into different P pools

According to their relative availabilities to plants in the soils, the results of the sequentially extracted P have been classified into three groups:

(a) Plant-available P: comprising solution or freely available P (DMT–HFO-P_i extracts) and labile P (0.5M $NaHCO_3$-P_i and P_o);

(b) Adsorbed P: consisting of adsorbed or slow labile P (0.1M NaOH-P_i plus P_o, and 1.0M HCl-P_i extracts);

(c) Occluded and residual P: consisting of occluded and recalcitrant P (conc. HCl-P_i and P_o extracts), and residual, fixed or lattice P (conc. H_2SO_4 + H_2O_2-P_i and P_o extracts);

The organic P (P_o) that falls within each group is regarded as having comparable availabilities to the P_i (Hedley et al., 1982; Tiessen and Moir, 1993).

3a: The effects of the added P and incubation time on the extractable plant-available P - [solution P (DMT-HFO-P_i) and labile P (0.5M $NaHCO_3$-P_i and P_o)]

3a: (i). The effects of the added P and the incubation period on DMT-HFO-P_i

The results of the extractable and percent recoveries of the added P are presented in Tables 2-3. While Figures 2a and b show the regression curves. The analyses of variances (ANOVA) and the tables of means are presented in Appendices I Nos. 1 and 13 respectively for Rustenburg and Loskop soils. The ANOVA tables showed highly significant differences (P = 0.01) in the DMT-HFO extracted-P fraction with the levels of added P, incubation periods, and their interactions in both soils. The data in Tables 2-3 shows that, the extracted DMT-HFO-P_i fraction increased with increasing levels of the added P. However, the amounts extracted for each level of added P decreased with increasing incubation time. This would tend to agree with Doula et al. (1996), who reported that soluble P added to a soil is usually adsorbed and precipitated rapidly but the concentrations in solution continue to decline slowly over a period of months.

The DMT-HFO-P_i extracts of Rustenburg soil were low and ranged from 2.50-40.09 mg kg^{-1} after 1 day to only 2.79-12.59 mg kg^{-1} after 240 days of incubation from 0-200 mg kg^{-1} of applied P. This represented percent P recoveries of 28.92-18.80 % after 1 day to only 7.36-4.90 % after 240 days from the lowest and the highest added P respectively (Table 2). According to Freese et al. (1995), this is well below the capacity of the DMT to diffuse P across the membrane in 16 hours. Tables 4a and 8a showed that the DMT-HFO-P_i extracted only a small fraction of the total soil P pool. The proportion varied from 1.35-10.75 % after one day to only 1.31-3.00 % after 240 days.

The corresponding values for Loskop soil showed the same trend but differed in that more P was extracted than from the Rustenburg soil. Table 3 shows that the values varied from 5.40–64.78 (1 day) to 4.54-16.75 mg kg^{-1} (240 days) between 0 and 200

mg kg^{-1} added P. These represent percent P recoveries of 21.08-29.69 % (1 day) and 7.68-6.11 % (240 days) from 25-200 mg kg^{-1} added P respectively. The proportion of the DMT-HFO extracted P_i after 16 hours extraction time also constituted only a small fraction of the total soil P pool, although relatively higher than for the Rustenburg soil. They ranged from 3.83-19.50 % (1 day) and 2.83-4.65 % after 240 days of incubation with 25-200 mg kg^{-1} added P respectively (Tables 4b-8b).

Figures 2a and b show the effects of the applied P and the incubation periods on the DMT-HFO-P_i extracts from (a) Rustenburg and (b) Loskop soils respectively between 1 and 240 days of incubation. The graphs show that for both soils DMT-HFO- extracted P_i increased with the increasing P levels, but were greatly reduced by the number of days they were under incubation. Thus, increasing incubation period from 1-240 days reduced the amount of P_i that can be extracted with DMT-HFO significantly suggesting that during the incubation processes the slow adsorption reaction reduces the amounts of the solution (DMT-HFO-P_i) phosphates (Doula et al., 1996).

Rustenburg soil shows a big difference in extractable P between 1 day and 60 days, where after only limited DMT-HFO-P_i remained available for extraction. It should be noted that the greater the distances between the lines of the fitted curves of the labile P (DMT-HFO- and $-HCO_3$-P extracts), the greater the P-fixation capacity of the soil and the shorter the time it takes to fix the added P (e.g. 1 day vis-à-vis 60 days in Figs. 2 and 3) (Sattell and Morris, 1992; Doula et al., 1996).

In contrast, the Loskop soil took longer to reach equilibrium because it was only after 120 days that the distances between the lines became small indicating little fixation thereafter. In general more DMT-HFO-P_i was extracted from Loskop than from Rustenburg soil from all the added P levels throughout the incubation period, indicating that the Rustenburg soil has the capacity to fix P faster than the Loskop soil. However, after 120 days both soils were able to equally fix most of the applied P because the percentages recovered after longer periods of incubation were relatively low and more or less the same.

Table 2: The effects of the added P and incubation period on the sequentially extracted inorganic P, organic P, and percent P recovered from Rustenburg soil.

Incubation period (days)	1							60							120						
Added P ($mg\ kg^{-1}$)	0	25	50	100	150	200	Average-P	0	25	50	100	150	200	Average-P	0	25	50	100	150	200	Average-P
HFO-P_i	2.50	9.73	17.10	30.59	33.12	40.09	22.19	2.87	6.08	6.92	12.00	16.92	19.58	10.73	2.75	5.65	6.17	9.17	13.23	15.17	8.69
% P recovered		28.92	29.20	28.09	20.41	18.80	25.08		12.84	8.10	9.13	9.37	8.36	9.56		11.60	6.84	6.42	6.99	6.21	7.61
HCO_3-P_i	6.30	17.42	25.99	32.00	41.89	67.13	31.79	6.00	7.58	13.75	18.08	24.08	31.25	16.79	4.20	5.17	8.08	12.50	20.33	23.58	12.31
% P recovered		44.48	39.38	25.70	23.73	30.42	32.74		6.32	15.50	12.08	12.05	12.63	11.72		3.88	7.76	8.30	10.75	9.69	8.08
OH-P_i	30.00	35.80	39.37	61.03	68.20	82.53	52.82	34.33	42.00	52.08	68.33	83.67	94.42	62.47	43.42	48.25	54.17	72.00	85.25	98.00	66.85
% P recovered		23.20	18.74	31.03	25.47	26.27	24.94		30.68	35.50	34.00	32.89	30.05	32.62		19.32	21.50	28.58	27.89	27.29	24.92
D/HCl-P_i	6.73	7.14	9.76	13.40	14.05	15.07	11.03	6.92	9.42	12.33	15.08	17.58	19.92	13.54	7.25	10.17	13.21	16.08	18.92	22.04	14.61
% P recovered		1.64	6.06	6.67	4.88	4.17	4.68		10.00	10.82	8.16	7.11	6.50	8.52		11.68	11.92	8.83	7.78	7.40	9.52
C/HCl-P_i	50.93	51.60	53.83	56.93	60.97	63.73	56.33	58.00	60.00	62.33	65.67	70.33	75.33	65.28	58.33	61.33	65.00	76.00	80.67	93.00	72.39
% P recovered		2.68	5.80	6.00	6.69	6.40	5.51		8.00	8.66	7.67	8.22	8.67	8.24		12.00	13.34	17.67	14.89	17.34	15.05
$H_2SO_4P_i$	55.27	56.17	56.83	57.33	59.50	61.67	57.80	55.73	56.67	59.00	65.22	72.38	80.47	64.91	56.50	58.83	65.67	74.17	80.17	89.50	70.81
% P recovered		3.60	3.12	2.06	2.82	3.20	2.96		3.76	6.54	9.49	11.10	12.37	8.65		9.32	18.34	17.67	15.78	16.50	15.52
HCO_3-P_o	10.00	10.47	10.72	11.37	11.77	12.90	11.21	10.00	14.75	18.17	22.67	24.00	26.17	19.29	11.00	15.00	17.67	19.33	21.50	23.00	17.92
% P recovered		1.88	1.44	1.37	1.18	1.45	1.46		19.00	16.34	12.67	9.33	8.09	13.09		16.00	13.34	8.33	7.00	6.00	10.13
OH-P_o	13.80	14.47	14.97	15.10	15.90	15.97	15.04	14.17	16.34	20.63	24.25	25.92	26.79	21.35	15.21	17.25	22.33	25.58	26.88	28.08	22.56
% P recovered		2.68	2.34	1.30	1.40	1.09	1.76		8.68	12.92	10.08	7.83	6.31	9.16		8.16	14.24	10.37	7.78	6.44	9.40
C/HCl-P_o	9.67	9.73	10.10	10.50	13.65	13.80	11.24	11.75	12.17	13.50	16.25	17.93	19.25	15.14	12.83	13.17	15.00	18.50	19.00	20.67	16.53
% P recovered		0.24	0.86	0.83	2.65	2.07	1.33		1.68	3.50	4.50	4.12	3.75	3.51		1.36	4.34	5.67	4.11	3.92	3.88
Total P extracted	185.20	212.53	238.67	288.25	319.05	372.89	269.43	199.77	225.01	258.71	307.55	352.81	393.18	289.51	211.49	234.82	267.30	323.33	365.95	413.04	302.66
Total % P recovered		109.32	106.94	103.05	89.23	93.85	100.48		100.96	117.88	107.78	102.03	96.71	105.07		93.32	111.62	111.84	102.97	100.78	104.11

	180							240						
Added P ($mg\ kg^{-1}$)	0	25	50	100	150	200	Average-P	0	25	50	100	150	200	Average-P
HFO-P_i	2.58	5.08	5.57	8.42	9.58	14.00	7.54	2.79	4.63	5.79	8.39	9.49	12.59	7.28
% P recovered		10.00	5.98	5.84	4.67	5.71	6.44		7.36	6.00	5.60	4.47	4.90	5.67
HCO_3-P_i	3.17	4.67	5.92	9.92	15.58	20.92	10.03	2.90	4.42	5.63	9.71	15.38	19.25	9.55
% P recovered		6.00	5.50	6.75	8.27	8.88	7.08		6.08	5.46	6.81	8.32	8.18	6.97
OH-P_i	44.08	52.17	60.00	78.67	87.17	103.00	70.85	46.70	53.67	63.33	80.00	93.00	104.00	73.45
% P recovered		32.36	31.84	34.59	28.73	29.46	31.40		27.88	33.26	33.30	30.87	28.65	30.79
D/HCl-P_i	8.00	12.33	15.17	18.17	21.83	24.83	16.72	8.85	13.33	16.92	20.33	23.75	27.17	18.39
% P recovered		17.32	14.34	10.17	9.22	8.42	11.89		17.92	16.14	11.48	9.93	9.16	12.93
C/HCl-P_i	59.00	62.33	68.67	78.67	86.00	98.00	75.45	59.60	64.62	70.67	80.10	89.96	100.54	77.58
% P recovered		13.32	19.34	19.67	18.00	19.50	17.97		20.08	22.14	20.50	20.24	20.47	20.69
$H_2SO_4P_i$	60.67	62.00	67.67	73.67	86.67	93.33	74.00	61.83	65.67	70.17	78.58	89.67	99.17	77.52
% P recovered		5.32	14.00	13.00	17.33	16.33	13.20		15.36	16.68	16.75	18.56	18.67	17.20
HCO_3-P_o	5.08	6.92	7.33	8.33	8.67	10.08	7.74	4.86	6.00	6.46	6.88	7.29	9.00	6.75
% P recovered		7.36	4.50	3.25	2.39	2.50	4.00		4.56	3.20	2.02	1.62	2.07	2.69
OH-P_o	13.33	16.67	20.00	22.33	24.50	26.17	20.50	12.42	15.00	17.08	20.33	23.17	24.83	18.81
% P recovered		13.36	13.34	9.00	7.45	6.42	9.91		10.32	9.32	7.91	7.17	6.21	8.18
C/HCl-P_o	13.33	14.60	16.40	18.67	20.00	21.33	17.39	13.52	16.71	19.21	20.52	21.75	23.67	19.23
% P recovered		5.08	6.14	5.34	4.45	4.00	5.00		12.76	11.38	7.00	5.49	5.08	8.34
Total P extracted	209.24	236.77	266.73	316.85	360.00	411.66	300.21	213.47	244.05	275.26	324.84	373.46	420.22	308.55
Total % P recovered		110.12	114.98	107.61	100.51	101.21	106.89		122.32	123.58	111.37	106.66	103.38	113.46

Table 3: The effects of the added P and incubation period on the sequentially extracted inorganic P, organic P, and percent P recovered from Loskop soil.

Incubation period (days)			1							60								120						
Added P (mg kg^{-1})	0	25	50	100	150	200	Average-P		0	25	50	100	150	200	Average-P		0	25	50	100	150	200	Average-P
HFO-P_i	5.40	10.67	18.56	39.33	49.89	64.78	31.44		5.25	7.50	10.71	22.08	28.33	33.58	17.91		5.35	7.09	7.96	15.58	19.00	23.08	13.01
% P recovered		21.08	26.32	33.93	29.66	29.69	28.14			9.00	10.92	16.83	15.39	14.17	13.26			6.96	5.22	10.23	9.10	8.87	8.08
HCO_3-P_i	12.83	17.76	30.08	45.12	59.29	74.95	40.01		8.11	10.92	15.42	28.83	40.28	49.03	25.43		6.89	9.67	13.42	25.21	33.46	41.75	21.73
% P recovered		19.72	34.50	32.29	30.97	31.06	29.71			11.24	14.62	20.72	21.45	20.46	17.70			11.12	13.06	18.32	17.71	17.43	15.53
OH-P_i	21.43	27.10	39.43	45.57	54.80	62.23	41.76		26.42	32.17	46.33	52.83	65.83	73.25	49.47		31.17	37.50	50.33	62.17	73.33	84.67	56.53
% P recovered		22.68	36.00	24.14	22.25	20.40	25.09			23.00	39.82	26.41	26.27	23.42	27.78			25.32	38.32	31.00	28.11	26.75	29.90
D/HCl-P_i	5.97	7.50	8.00	9.28	9.93	10.43	8.52		5.99	8.95	9.13	10.14	10.63	11.96	9.47		6.17	9.43	10.22	11.70	12.13	13.25	10.48
% P recovered		6.12	4.06	3.31	2.64	2.23	3.67			11.64	6.28	4.15	3.09	2.99	5.67			13.04	8.10	5.53	3.97	3.54	6.84
C/HCl-P_i	29.33	32.27	35.30	37.67	38.53	39.87	35.50		31.50	33.00	35.08	41.58	42.17	48.42	38.63		31.92	38.58	40.50	47.75	55.25	60.58	45.76
% P recovered		11.76	11.94	8.34	6.13	5.27	8.69			6.00	7.16	10.08	7.11	8.46	7.76			26.64	17.16	15.83	15.55	14.33	17.90
H_2SO_4-P_i	39.83	40.00	40.50	41.00	42.50	45.67	41.58		40.67	41.76	41.92	52.03	57.35	66.17	49.98		41.38	41.80	45.13	52.25	59.69	70.48	51.79
% P recovered		0.68	1.34	1.17	1.78	2.92	1.58			4.36	2.50	11.36	11.12	12.75	8.42			1.68	7.50	10.87	12.21	14.55	9.36
HCO_3-P_o	9.55	10.28	10.54	11.33	11.35	12.18	10.87		10.00	11.42	12.88	16.08	17.30	20.30	14.66		10.25	12.48	13.55	16.25	17.92	18.84	14.88
% P recovered		2.92	1.98	1.78	1.20	1.32	1.84			5.68	5.76	6.08	4.87	5.15	5.51			8.92	6.60	6.00	5.11	4.30	6.19
OH-P_o	7.38	8.48	8.85	10.12	10.30	10.35	9.25		9.81	11.96	13.00	13.71	15.71	16.13	13.39		10.17	13.50	14.71	16.42	18.33	19.83	15.49
% P recovered		4.40	2.94	2.74	1.95	1.49	2.70			8.60	6.38	3.90	3.93	3.16	5.19			13.32	9.08	8.25	5.44	4.83	7.78
C/HCl-P_o	9.20	9.96	10.00	10.18	10.71	11.78	10.31		8.78	10.11	10.78	11.61	14.50	15.05	11.81		9.94	11.25	11.78	13.72	14.06	15.89	12.77
% P recovered		3.04	1.60	0.98	1.01	1.29	1.58			5.32	4.00	2.83	3.81	3.14	3.82			5.24	3.68	3.78	2.75	2.98	3.68
Total P extracted	140.92	164.02	201.26	249.60	287.30	332.24	229.22		146.53	167.79	195.25	248.89	292.10	333.89	230.74		153.24	181.30	207.60	261.05	303.17	348.37	242.46
Total % P recovered		92.40	120.68	108.68	97.59	95.66	103.00			85.04	97.44	102.36	97.05	93.68	95.11			112.24	108.72	107.81	99.95	97.57	105.26

Incubation period (days)			180							240						
Added P (mg kg^{-1})	0	25	50	100	150	200	Average-P		0	25	50	100	150	200	Average-P
HFO-P_i	4.92	6.84	8.92	14.33	17.75	19.58	12.06		4.54	6.46	7.21	11.50	15.57	16.75	10.34
% P recovered		7.68	8.00	9.41	8.55	7.33	8.19			7.68	5.34	6.96	7.35	6.11	6.69
HCO_3-P_i	6.00	7.62	8.13	16.00	22.00	28.92	14.78		5.56	6.89	7.67	13.17	18.83	23.17	12.55
% P recovered		6.48	4.26	10.00	10.67	11.46	8.57			5.32	4.22	7.61	8.85	8.81	6.96
OH-P_i	34.92	40.17	53.50	72.58	83.17	89.50	62.31		37.83	45.33	59.50	78.58	87.83	96.07	67.52
% P recovered		21.00	37.16	37.66	32.17	27.29	31.06			30.00	43.34	40.75	33.33	29.12	35.31
D/HCl-P_i	6.25	10.15	11.18	12.06	14.58	14.67	11.48		6.08	11.33	11.67	12.92	16.07	16.42	12.42
% P recovered		15.60	9.86	5.81	5.55	4.21	8.21			21.00	11.18	6.84	6.66	5.17	10.17
C/HCl-P_i	32.33	40.42	42.17	53.67	60.25	65.63	49.08		34.83	39.42	44.67	55.08	64.33	71.08	51.57
% P recovered		32.36	19.68	21.34	18.61	16.65	21.73			18.36	19.68	20.25	19.87	18.13	19.22
H_2SO_4-P_i	41.97	42.36	46.13	57.59	61.15	71.45	53.44		42.59	44.27	50.78	60.16	71.40	79.82	58.17
% P recovered		1.56	8.32	15.62	12.79	14.74	10.61			6.72	16.38	17.57	19.21	18.62	15.70
HCO_3-P_o	8.50	10.21	11.75	13.79	15.09	15.88	12.54		7.83	8.83	10.92	12.25	14.00	15.67	11.58
% P recovered		6.84	6.50	5.29	4.39	3.69	5.34			4.00	8.18	4.42	4.11	3.92	4.53
OH-P_o	11.38	13.57	14.86	17.40	18.92	20.67	16.13		11.58	13.18	14.50	16.13	17.13	19.09	15.27
% P recovered		8.76	6.96	6.02	5.03	4.65	6.28			6.40	5.84	4.55	3.70	3.76	4.85
C/HCl-P_o	9.28	11.89	13.11	14.22	15.38	16.89	13.46		9.39	13.39	15.94	20.05	21.22	22.28	17.05
% P recovered		10.44	7.66	4.94	4.07	3.81	6.18			16.00	13.10	10.66	7.89	6.45	10.82
Total P extracted	155.55	183.23	209.75	271.64	308.29	343.19	245.28		160.23	189.10	222.86	279.84	326.38	360.35	256.46
Total % P recovered		110.72	108.40	116.09	101.83	93.82	106.17			115.48	125.26	119.61	110.77	100.06	114.24

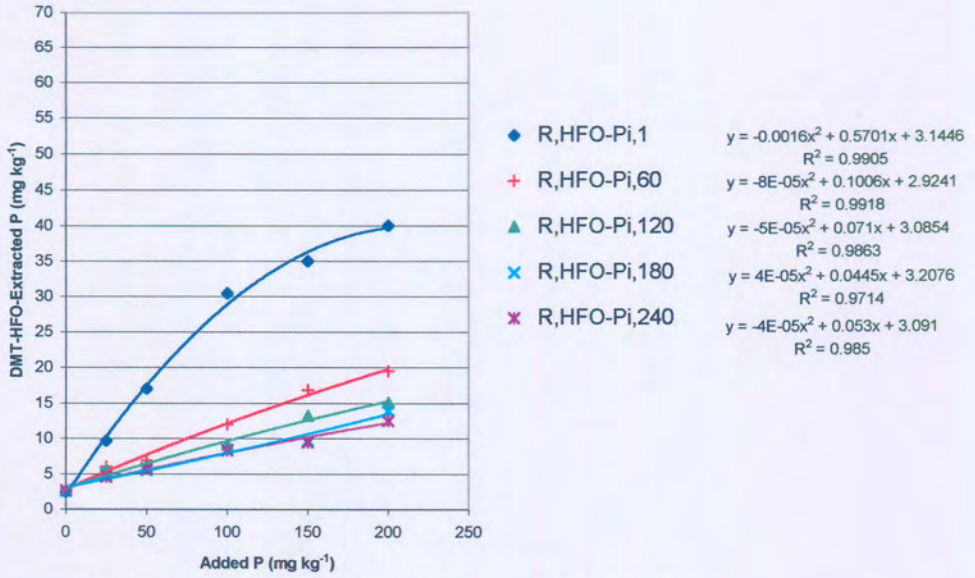

Fig. 2a. The effects of the added P and incubation time on the DMT-HFO extracted inorganic P (P_i) from the Rustenburg soil.

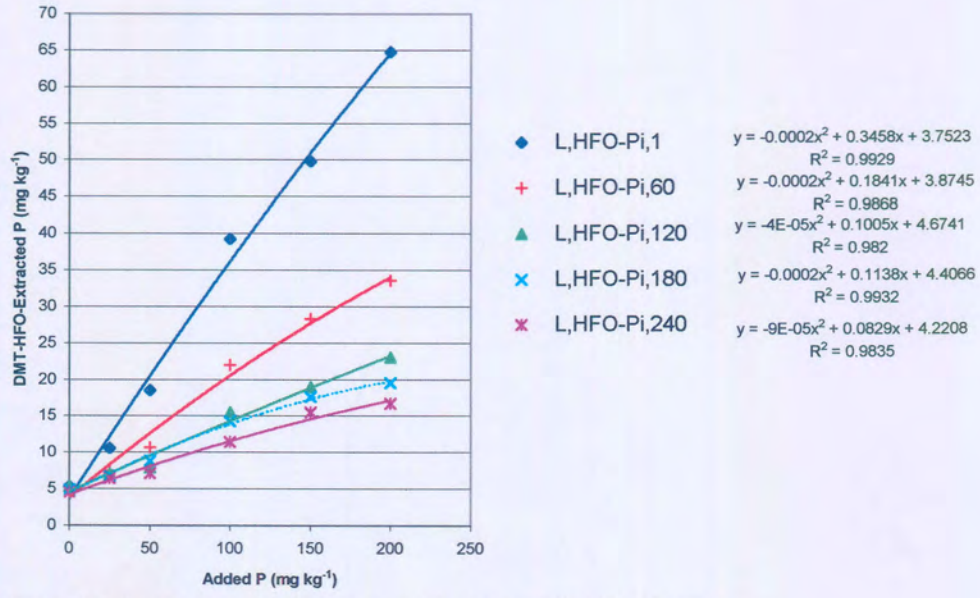

Fig. 2b. The effects of the added P and incubation time on the DMT-HFO extracted inorganic P (P_i) from the Loskop soil.

The proportion of DMT-HFO-P_i as a fraction of the extracted total soil P pool was generally low for Rustenburg but relatively higher for Loskop soil. The proportions increased with the added P levels but were markedly reduced during the incubation period (Tables 4-8). For example, the Rustenburg soil had 1.35-10.75 % after 1 day (Table 4a) but only 1.31-3.00 % after 240 days (Table 8a) of incubation from 0-200 mg kg^{-1} of added P. Meanwhile the Loskop soil had 3.83-19.50 % after 1 day (Table 4b) but only 2.83-4.65 % after 240 days (Table 8b) of incubation. The changes in the distribution of soil P could have resulted from the chemical changes brought about during the moist incubation period, which could have altered the extractability of soil P pools. The changes could also have resulted from the conversion of P through microbial activities even in the control sample, which was subsequently released to the soil on deaths of the cells (Chauhan et al., 1981).

The differences in the DMT-HFO extractable P_i, percent recoveries of the applied P, and the distribution as fractions of the extracted total soil P pools in the two soils could be due to the differences in the clay contents and types, and organic matter contents. Rustenburg soil had more clay and organic matter than the Loskop soil (Table 1). The clay contents (Rustenburg, 51%; Loskop, 19%), coupled with the higher amounts of the kaolinites (Rustenburg, 52 %; Loskop, 37%) could have been the major reasons for the lower percent recovery of the added P from the Rustenburg soil with the prolonged incubation periods (Dalal 1973; Loganathan et al., 1987; Sanchez et al., 1991).

The solution P recoveries of a soil have also been reported to be dependent on the conditions under which the soil and P are allowed to react. In their study, Raven and Hossner (1994) reported that a relatively high proportion of the added P (67 to 85 %) was desorbed by anion-exchange resin (equivalent to DMT-HFO) after 31 days of incubation. Sharpley, et al. (1984) on the other hand, reported that in 78 soils of the US treated to 0-120 mg P kg^{-1}, incubated at field capacity for six months, and subjected to three wetting and drying cycles, only 7-74 % of the added P was extracted by the anion-exchange resin. The high recoveries in the Raven and Hossner

(1994) study were probably due to the relatively short incubation time (31 days) and the absence of wetting and drying cycles.

Both soils showed that as more P was added, the percent recoveries stayed more or less the same within each incubation period, and thus not correspondingly more solution-P_i was made available (Tables 2 and 3). Earlier, Kafkafi et al. (1967) had reported that when P is added to a soil, some of it is converted directly into the fixed form (insoluble and residual P). This could have affected the percent P recovered as noted in this experiment.

3a: (ii). The effects of the added P and incubation period on the 0.5M $NaHCO_3$-extracted P (P_i and P_o)

0.5M $NaHCO_3$-extracted P_i:

The results of the different P and incubation treatments are presented in Tables 2 and 3, 4-8, Figures 3a and b, and Appendices I Nos. 2, and 14 respectively for Rustenburg and Loskop soils. The extracted $-HCO_3$-P_i fraction significantly increased ($P = 0.01$) with increasing levels of added P for both the Rustenburg and Loskop soils (Appendices I Nos. 2, and 14). However, the amounts extracted for each level of added P decreased significantly with the increasing days of incubation as can be seen by the reduction in the percent P recovered (Tables 2 and 3). The trend however, was similar to the HFO-P_i extracts for both soils.

For the Rustenburg soil the amounts of $-HCO_3$-P_i extracted varied between 6.30 and 67.13 (1 day) and 2.90-19.25 mg kg^{-1} (240 days) from the lowest to the highest P applications (Table 2). This represented a percent P recovery of approximately 30 % after one day, but the P recovered reduced to approximately 10 % after 60 days of incubation. For the longer incubation periods the percent P recovered tended to increase with higher P applications but the amount of P extracted were lower. This tendency indicates that whereas for the DMT-HFO extracts the percent P recoveries

decreased there were corresponding increases with the $-HCO_3$-extract, showing that some soluble P was transferred to the $-HCO_3$-extractable P pool.

For the Loskop soil however, the changes in the percent P recoveries were more gradual up to 180 days of incubation. This again clearly shows the differences between the two soils. For the Rustenburg soil, most of the added P was transformed between the first and 60 days of incubation, after which only small amounts of $-HCO_3$-P_i could be extracted. However, for the Loskop soil, the transformation was slower, and fairly large percentage of the applied P was bicarbonate extractable up to 180 days of incubation (Table 3 and Fig. 3b). Here again it was evident that some of the DMT-HFO-P_i was transferred to the $-HCO_3$-extractable P pool.

Here again the differences in the $-HCO_3$ extractable P_i and the percent P recoveries of the two soils could be due to the differences in the clay and organic matter contents and types. As it was stated earlier in relation to the DMT-HFO-P_i extracts, the clay content coupled with the high amounts of the kaolinites and possibly Fe and Al oxihydroxides could have contributed to the lower percent P recoveries from the Rustenburg soil because more P was transformed to less bicarbonate extractable P (Dalal 1973; Loganathan et al., 1987; Sanchez et al., 1991).

Furthermore, the noted differences in the amounts extracted and the percent P recovered could also have been influenced by the mineralization of P from the readily decomposable soil organic matter and the deaths of microbial cells during the incubation period. According to Tables 2 and 3 the percent P recoveries were higher at the lower P than the higher P application rates and more from the Rustenburg soil that had relatively higher organic matter content. Tiessen et al. (1984) had shown that the available (labile) P was largely contributed to by the mineralization of the bicarbonate P_o.

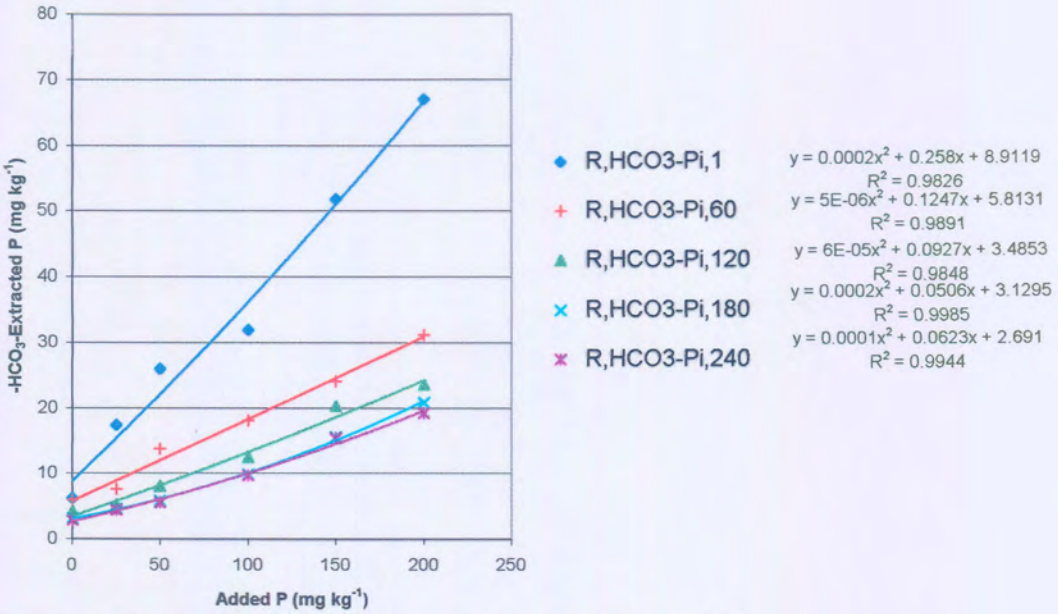

Fig. 3a. The effects of the added P and incubation time on the bicarbonate (-HCO_3) extracted inorganic P (P_i) from the Rustenburg soil.

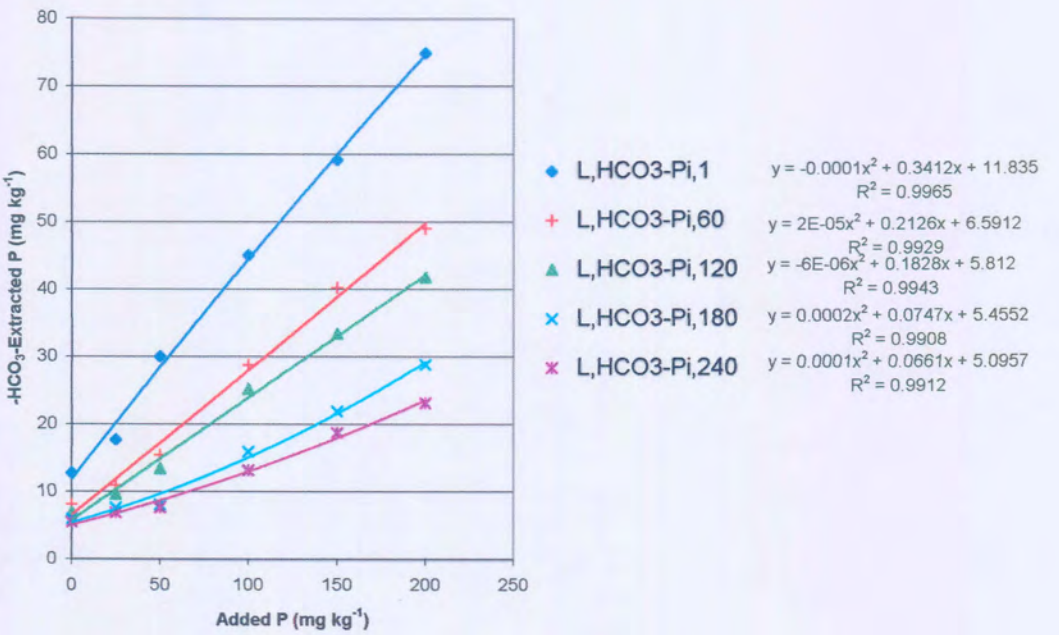

Fig. 3b. The effects of the added P and incubation time on the bicarbonate (-HCO_3) extracted inorganic P (P_i) from the Loskop soil.

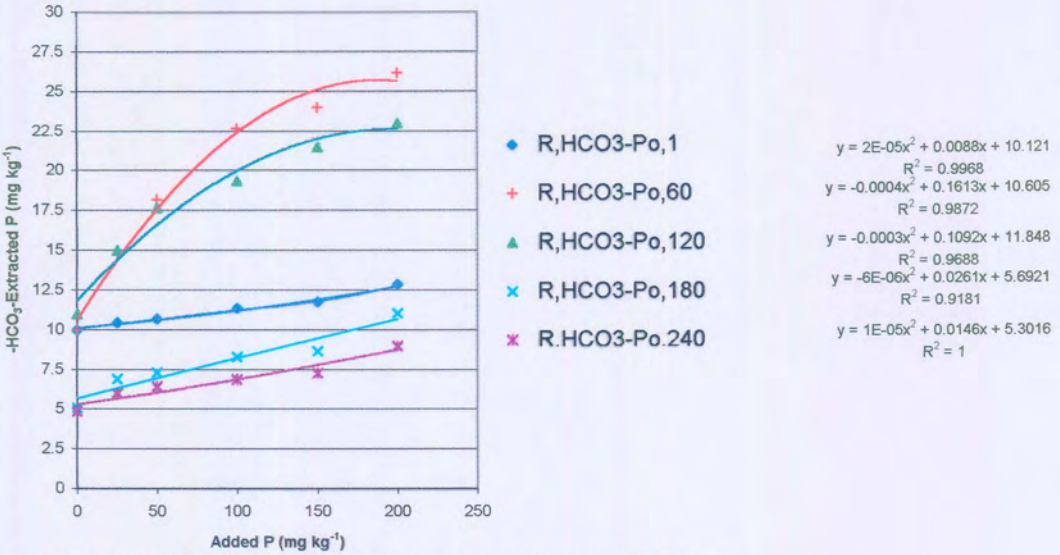

Fig. 4a. The effects of the added P and incubation time on the bicarbonate ($-HCO_3$) extracted organic P (P_o) from the Rustenburg soil.

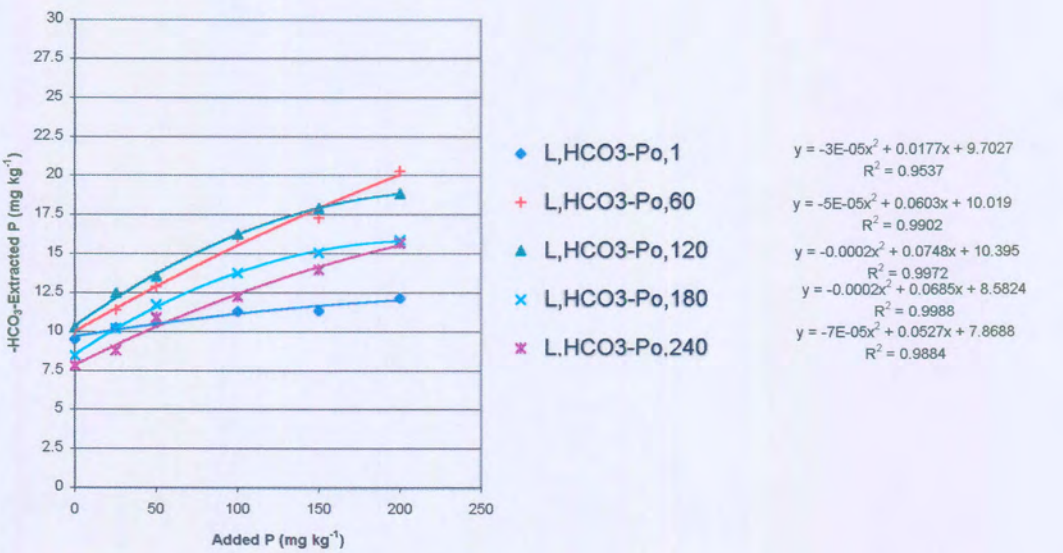

Fig. 4b. The effects of the added P and incubation time on the bicarbonate ($-HCO_3$) extracted organic P (P_o) from the Loskop soil.

The contributions of $-HCO_3$-P_i extracts to the extracted total soil P pool were initially relatively lower for the Rustenburg compared to the Loskop soil. The contributions increased with the increasing levels of the added P but were markedly reduced by increasing incubation periods. Thus, for Rustenburg soil the contributions ranged from 3.40-18.00 % (1 day, Table 4a) to 1.36-4.58 % (240 days, Table 8a). While for Loskop soil the contributions varied from 9.10-22.56 % (1 day, Table 4b) to 3.47-6.43 % (240 days, Table 8b) between the lowest and the highest applied P respectively. This also indicated that both soils lost large proportions of $-HCO_3$-P_i to stable P pools during the incubation period.

As the $NaHCO_3$-P_i is classified as labile P fraction, it is recognized along with DMT-HFO-P_i (solution P_i) as the most readily available for plant uptake and growth. It is therefore expected that they would reflect seasonal short-term changes in plant available P, and consistent with this, the largest proportion of P lost from the individual P pools would occur from these two pools (Hedley et al., 1982; Bowman et al., 1998). Thus, prolonging incubation periods from 1-240 days generally reduced the availability of labile P, due to different adsorption and fixation reactions similar to the solution DMT-HFO-P_i shown earlier. The reductions were however, noticeably more gradual for Loskop soil that is a relatively light soil with less clay and soil organic matter (Oades and Ladd, 1977; Dalal, 1977).

0.5M $NaHCO_3$-extracted P_o:

The amounts of the bicarbonate organic P ($-HCO_3$-P_o) extracted from all the added P levels were slightly higher for Rustenburg than for Loskop soil between 1 and 120 days of incubation (Tables 2 and 3; Figs. 4a and b). For longer incubation periods the extractable P_o became very low indicating that the organic P was mineralised within 120 days where after it became depleted especially in the Rustenburg soil. In the Loskop soil this fraction did not become as depleted as in the Rustenburg soil. The noted differences in the amounts extracted and the percent P recovered could have been due to the increased microbial populations and activities during the incubation period.

The contributions of $-HCO_3$-P_o to the total soil P pool were also low for both soils. The fractions remained stable although slight decreases were noticeable with increased P levels and the incubation periods, indicating possible enhancement of P_o mineralization in both cases (Tables 4a,b-8a and b; Figs. 4a and b). Thus the extracted -HCO_3-P_o (highest and lowest values) varied from 6.66 % (60 days) to 2.19 % (240 days), as fraction of the total soil P pool in the Rustenburg soil, while in the Loskop soil, -HCO_3-P_o accounted for 6.35 % (60 days) to 4.48 % (240 days) highest and lowest values respectively. In related long-term field trials in Mpumalanga, du Preez and Claassens (1999) working with Avalon and Clovelly soils found the values ranged from 5.20-8.75 %, and 1.70-3.40 % respectively. Although Tiessen, et al. (1984) had shown that 80 % of the availability in resin P (equivalent to DMT-HFO-P_i) was accounted for by variations in the bicarbonate P_o, but our results show that the contribution of the bicarbonate P_o is marginal in both soils.

Total plant-available P (DMT–HFO-P and $NaHCO_3$-P extracts)

According to the data in Tables 4a, b - 8a, b the immediately plant-available P_i (HFO-P_i + -HCO_3-P_i) of Rustenburg soil accounted for 4.75 % of the total soil P pool where no P was added and 28.75 % where 200 mg P kg^{-1} was added after 1 day of incubation. These values decreased to 2.67 % and 7.58 % after 240 days of incubation respectively.

While for the Loskop soil the values were 12.93 % of the total soil P pool where no P was applied and increased to 42.06 % where 200 mg kg^{-1} was added after 1 day of incubation, but decreased to 6.30 % and 11.08 % after 240 days of incubation respectively. The plant-available P_i thus accounted for progressively smaller fractions of the extracted total soil P pools as incubation progressed from 1 to 240 days.

Table 4a. The effects of the added P on the changes and distribution of P into different P pools after 1 day of incubation of Rustenburg soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	2.50	6.30	30.00	6.73	50.93	55.27	10.00	13.80	9.67	33.47	151.73	185.20	185.20
	% of Total P	1.35	3.40	16.20	3.63	27.50	29.84	5.40	7.45	5.22	18.07	81.93	100.00	
25	Extracted P	9.73	17.42	35.80	7.14	51.60	56.17	10.47	14.47	9.73	34.67	177.86	212.53	210.20
	% of Total P	4.58	8.20	16.84	3.36	24.28	26.43	4.93	6.81	4.58	16.31	83.69	101.11	
50	Extracted P	17.10	25.99	39.37	9.76	53.83	56.83	10.72	14.97	10.10	35.79	202.88	238.67	235.20
	% of Total P	7.16	10.89	16.50	4.09	22.55	23.81	4.49	6.27	4.23	15.00	85.00	101.48	
100	Extracted P	30.59	32.00	61.03	13.40	56.93	57.33	11.37	15.10	10.50	36.97	251.28	288.25	285.20
	% of Total P	10.61	11.10	21.17	4.65	19.75	19.89	3.94	5.24	3.64	12.83	87.17	101.07	
150	Extracted P	33.12	41.89	68.20	14.05	60.97	59.50	11.77	15.90	13.65	41.32	277.73	319.05	335.20
	% of Total P	10.38	13.13	21.38	4.40	19.11	18.65	3.69	4.98	4.28	12.95	87.05	95.18	
200	Extracted P	40.09	67.13	82.53	15.07	63.73	61.67	12.90	15.97	13.80	42.67	330.22	372.89	385.20
	% of Total P	10.75	18.00	22.13	4.04	17.09	16.54	3.46	4.28	3.70	11.44	88.56	96.80	
Average	Extracted P	22.19	31.79	52.82	11.03	56.33	57.80	11.21	15.04	11.24	37.48	231.95	269.43	272.70
Average	% of Total P	7.47	10.79	19.04	4.03	21.71	22.53	4.32	5.84	4.28	14.43	85.57	99.27	

Table 4b. The effects of the added P on the changes and distribution of P into different P pools after 1 day of incubation of Loskop soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	5.40	12.83	21.43	5.97	29.33	39.83	9.55	7.38	9.20	26.13	114.79	140.92	140.92
	% of Total P	3.83	9.10	15.21	4.24	20.81	28.26	6.78	5.24	6.53	18.54	81.46	100.00	
25	Extracted P	10.67	17.76	27.10	7.50	32.27	40.00	10.28	8.48	9.96	28.72	135.30	164.02	165.92
	% of Total P	6.51	10.83	16.52	4.57	19.67	24.39	6.27	5.17	6.07	17.51	82.49	98.85	
50	Extracted P	18.56	30.08	39.43	8.00	35.30	40.50	10.54	8.85	10.00	29.39	171.87	201.26	190.92
	% of Total P	9.22	14.95	19.59	3.97	17.54	20.12	5.24	4.40	4.97	14.60	85.40	105.42	
100	Extracted P	39.33	45.12	45.57	9.28	37.67	41.00	11.33	10.12	10.18	31.63	217.97	249.60	240.92
	% of Total P	15.76	18.08	18.26	3.72	15.09	16.43	4.54	4.05	4.08	12.67	87.33	103.60	
150	Extracted P	49.89	59.29	54.80	9.93	38.53	42.50	11.35	10.30	10.71	32.36	254.94	287.30	290.92
	% of Total P	17.37	20.64	19.07	3.46	13.41	14.79	3.95	3.59	3.73	11.26	88.74	98.76	
200	Extracted P	64.78	74.95	62.23	10.43	39.87	45.67	12.18	10.35	11.78	34.31	297.93	332.24	340.92
	% of Total P	19.50	22.56	18.73	3.14	12.00	13.75	3.67	3.12	3.55	10.33	89.67	97.45	
Average	Extracted P	31.44	40.01	41.76	8.52	35.50	41.58	10.87	9.25	10.31	30.42	198.80	229.22	228.42
Average	% of Total P	12.03	16.03	17.90	3.85	16.42	19.62	5.07	4.26	4.82	14.15	85.85	100.68	

Table 5a. The effects of the added P on the changes and distribution of P into different P pools after 60 days of incubation of Rustenburg soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	2.87	6.00	34.33	6.92	58.00	55.73	10.00	14.17	11.75	35.92	163.85	199.77	199.77
	% of Total P	1.44	3.00	17.18	3.46	29.03	27.90	5.01	7.09	5.88	17.98	82.02	100.00	
25	Extracted P	6.08	7.58	42.00	9.42	60.00	56.67	14.75	16.34	12.17	43.26	181.75	225.01	224.77
	% of Total P	2.70	3.37	18.67	4.19	26.67	25.19	6.56	7.26	5.41	19.23	80.77	100.11	
50	Extracted P	6.92	13.75	52.08	12.33	62.33	59.00	18.17	20.63	13.50	52.30	206.41	258.71	249.77
	% of Total P	2.67	5.31	20.13	4.77	24.09	22.81	7.02	7.97	5.22	20.22	79.78	103.58	
100	Extracted P	12.00	18.08	68.33	15.08	65.67	65.22	22.67	24.25	16.25	63.17	244.38	307.55	299.77
	% of Total P	3.90	5.88	22.22	4.90	21.35	21.21	7.37	7.88	5.28	20.54	79.46	102.60	
150	Extracted P	16.92	24.08	83.67	17.58	70.33	72.38	24.00	25.92	17.93	67.85	284.96	352.81	349.77
	% of Total P	4.80	6.83	23.72	4.98	19.93	20.52	6.80	7.35	5.08	19.23	80.77	100.87	
200	Extracted P	19.58	31.25	94.42	19.92	75.33	80.47	26.17	26.79	19.25	72.21	320.97	393.18	399.77
	% of Total P	4.98	7.95	24.01	5.07	19.16	20.47	6.66	6.81	4.90	18.37	81.63	98.35	
Average	Extracted P	10.73	16.79	62.47	13.54	65.28	64.91	19.29	21.35	15.14	55.79	233.72	289.51	287.27
Average	% of Total P	3.42	5.39	20.99	4.56	23.37	23.01	6.57	7.40	5.30	19.26	80.74	100.92	

Table 5b. The effects of the added P on the changes and distribution of P into different P pools after 60 days of incubation of Loskop soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	5.25	8.11	26.42	5.99	31.50	40.67	10.00	9.81	8.78	28.59	117.94	146.53	146.53
	% of Total P	3.58	5.53	18.03	4.09	21.50	27.76	6.82	6.69	5.99	19.51	80.49	100.00	
25	Extracted P	7.50	10.92	32.17	8.95	33.00	41.76	11.42	11.96	10.11	33.49	134.30	167.79	171.53
	% of Total P	4.47	6.51	19.17	5.33	19.67	24.89	6.81	7.13	6.03	19.96	80.04	97.82	
50	Extracted P	10.71	15.42	46.33	9.13	35.08	41.92	12.88	13.00	10.78	36.66	158.59	195.25	196.53
	% of Total P	5.49	7.90	23.73	4.68	17.97	21.47	6.60	6.66	5.52	18.78	81.22	99.35	
100	Extracted P	22.08	28.83	52.83	10.14	41.58	52.03	16.08	13.71	11.61	41.40	207.49	248.89	246.53
	% of Total P	8.87	11.58	21.23	4.07	16.71	20.90	6.46	5.51	4.66	16.63	83.37	100.96	
150	Extracted P	28.33	40.28	65.83	10.63	42.17	57.35	17.30	15.71	14.50	47.51	244.59	292.10	296.53
	% of Total P	9.70	13.79	22.54	3.64	14.44	19.63	5.92	5.38	4.96	16.26	83.74	98.51	
200	Extracted P	33.58	49.03	73.25	11.96	48.42	66.17	20.30	16.13	15.05	51.48	282.41	333.89	346.53
	% of Total P	10.06	14.68	21.94	3.58	14.50	19.82	6.08	4.83	4.51	15.42	84.58	96.35	
Average	Extracted P	17.91	25.43	49.47	9.47	38.63	49.98	14.66	13.39	11.81	39.86	190.89	230.74	234.03
Average	% of Total P	7.03	10.00	21.11	4.23	17.46	22.41	6.45	6.03	5.28	17.76	82.24	98.83	

Table 6a. The effects of the added P on the changes and distribution of P into different P pools after 120 days of incubation of Rustenburg soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	2.75	4.20	43.42	7.25	58.33	56.50	11.00	15.21	12.83	39.04	172.45	211.49	211.49
	% of Total P	1.30	1.99	20.53	3.43	27.58	26.72	5.20	7.19	6.07	18.46	81.54	100.00	
25	Extracted P	5.65	5.17	48.25	10.17	61.33	58.83	15.00	17.25	13.17	45.42	189.40	234.82	236.49
	% of Total P	2.41	2.20	20.55	4.33	26.12	25.05	6.39	7.35	5.61	19.34	80.66	99.29	
50	Extracted P	6.17	8.08	54.17	13.21	65.00	65.67	17.67	22.33	15.00	55.00	212.30	267.30	261.49
	% of Total P	2.31	3.02	20.27	4.94	24.32	24.57	6.61	8.35	5.61	20.58	79.42	102.22	
100	Extracted P	9.17	12.50	72.00	16.08	76.00	74.17	19.33	25.58	18.50	63.41	259.92	323.33	311.49
	% of Total P	2.84	3.87	22.27	4.97	23.51	22.94	5.98	7.91	5.72	19.61	80.39	103.80	
150	Extracted P	13.23	20.33	85.25	18.92	80.67	80.17	21.50	26.88	19.00	67.38	298.57	365.95	361.49
	% of Total P	3.62	5.56	23.30	5.17	22.04	21.91	5.88	7.35	5.19	18.41	81.59	101.23	
200	Extracted P	15.17	23.58	98.00	22.04	93.00	89.50	23.00	28.08	20.67	71.75	341.29	413.04	411.49
	% of Total P	3.67	5.71	23.73	5.34	22.52	21.67	5.57	6.80	5.00	17.37	82.63	100.38	
Average	Extracted P	8.69	12.31	66.85	14.61	72.39	70.81	17.92	22.56	16.53	57.00	245.66	302.66	298.99
Average	% of Total P	2.69	3.72	21.77	4.70	24.35	23.81	5.94	7.49	5.53	18.96	81.04	101.15	

Table 6b. The effects of the added P on the changes and distribution of P into different P pools after 120 days of incubation of Loskop soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	5.35	6.89	31.17	6.17	31.92	41.38	10.25	10.17	9.94	30.36	122.88	153.24	153.24
	% of Total P	3.49	4.50	20.34	4.03	20.83	27.00	6.69	6.64	6.49	19.81	80.19	100.00	
25	Extracted P	7.09	9.67	37.50	9.43	38.58	41.35	12.48	13.50	11.25	37.23	143.62	180.85	178.24
	% of Total P	3.92	5.35	20.74	5.21	21.33	22.86	6.90	7.46	6.22	20.59	79.41	101.46	
50	Extracted P	7.96	13.42	50.33	10.22	40.50	45.13	13.55	14.71	11.78	40.04	167.56	207.60	203.24
	% of Total P	3.83	6.46	24.24	4.92	19.51	21.74	6.53	7.09	5.67	19.29	80.71	102.15	
100	Extracted P	15.58	25.21	62.17	11.70	47.75	52.25	16.25	16.42	13.72	46.39	214.66	261.05	253.24
	% of Total P	5.97	9.66	23.82	4.48	18.29	20.02	6.22	6.29	5.26	17.77	82.23	103.08	
150	Extracted P	19.00	33.46	73.33	12.13	55.25	59.69	17.92	18.33	14.06	50.31	252.86	303.17	303.24
	% of Total P	6.27	11.04	24.19	4.00	18.22	19.69	5.91	6.05	4.64	16.59	83.41	99.98	
200	Extracted P	23.08	41.75	84.67	13.25	60.58	70.48	18.84	19.83	15.89	54.56	293.81	348.37	353.24
	% of Total P	6.63	11.98	24.30	3.80	17.39	20.23	5.41	5.69	4.56	15.66	84.34	98.62	
Average	Extracted P	13.01	21.73	56.53	10.48	45.76	51.71	14.88	15.49	12.77	43.15	199.23	242.38	240.74
Average	% of Total P	5.02	8.16	22.94	4.41	19.26	21.92	6.28	6.54	5.47	18.29	81.71	100.88	

Table 7a. The effects of the added P on the changes and distribution of P into different P pools after 180 days of incubation of Rustenburg soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	2.58	3.17	44.08	8.00	59.00	60.67	5.08	13.33	13.33	31.74	177.50	209.24	209.24
	% of Total P	1.23	1.52	21.07	3.82	28.20	29.00	2.43	6.37	6.37	15.17	84.83	100.00	
25	Extracted P	5.08	4.67	52.17	12.33	62.33	62.00	6.92	16.67	14.60	38.19	198.58	236.77	234.24
	% of Total P	2.15	1.97	22.03	5.21	26.33	26.19	2.92	7.04	6.17	16.13	83.87	101.08	
50	Extracted P	5.57	5.92	60.00	15.17	68.67	67.67	7.33	20.00	16.40	43.73	223.00	266.73	259.24
	% of Total P	2.09	2.22	22.49	5.69	25.75	25.37	2.75	7.50	6.15	16.39	83.61	102.89	
100	Extracted P	8.42	9.92	78.67	18.17	78.67	73.67	8.33	22.33	18.67	49.33	267.52	316.85	309.24
	% of Total P	2.66	3.13	24.83	5.73	24.83	23.25	2.63	7.05	5.89	15.57	84.43	102.46	
150	Extracted P	9.58	15.58	87.17	21.83	86.00	86.67	8.67	24.50	20.00	53.17	306.83	360.00	359.24
	% of Total P	2.66	4.33	24.21	6.06	23.89	24.08	2.41	6.81	5.56	14.77	85.23	100.21	
200	Extracted P	14.00	20.92	103.00	24.83	98.00	93.33	13.08	26.17	21.33	60.58	354.08	414.66	409.24
	% of Total P	3.38	5.05	24.84	5.99	23.63	22.51	3.15	6.31	5.14	14.61	85.39	101.32	
Average	Extracted P	7.54	10.03	70.85	16.72	75.45	74.00	8.24	20.50	17.39	46.12	254.59	300.71	296.74
Average	% of Total P	2.36	3.04	23.25	5.42	25.44	25.06	2.72	6.85	5.88	15.44	84.56	101.33	

Table 7b. The effects of the added P on the changes and distribution of P into different P pools after 180 days of incubation of Loskop soil.

Added P (mg kg^{-1})	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	4.92	6.00	34.92	6.25	32.33	41.97	8.50	11.38	9.28	29.16	126.39	155.55	155.55
	% of Total P	3.16	3.86	22.45	4.02	20.78	26.98	5.46	7.32	5.97	18.75	81.25	100.00	
25	Extracted P	6.84	7.62	40.17	10.15	40.42	42.36	10.21	13.57	11.89	35.67	147.56	183.23	180.55
	% of Total P	3.73	4.16	21.92	5.54	22.06	23.12	5.57	7.41	6.49	19.47	80.53	101.48	
50	Extracted P	8.92	8.13	53.50	11.18	42.17	46.13	11.75	14.86	13.11	39.72	170.03	209.75	205.55
	% of Total P	4.25	3.88	25.51	5.33	20.10	21.99	5.60	7.08	6.25	18.94	81.06	102.04	
100	Extracted P	14.33	16.00	72.58	12.06	53.67	57.59	13.79	17.40	14.22	45.41	226.23	271.64	255.55
	% of Total P	5.28	5.89	26.72	4.44	19.76	21.20	5.08	6.41	5.23	16.72	83.28	106.30	
150	Extracted P	17.75	22.00	83.17	14.58	60.25	61.15	15.09	18.92	15.38	49.39	258.90	308.29	305.55
	% of Total P	5.76	7.14	26.98	4.73	19.54	19.84	4.89	6.14	4.99	16.02	83.98	100.90	
200	Extracted P	19.58	28.92	89.50	14.67	65.63	71.45	15.88	20.67	16.89	53.44	289.75	343.19	355.55
	% of Total P	5.71	8.43	26.08	4.27	19.12	20.82	4.63	6.02	4.92	15.57	84.43	96.52	
Average	Extracted P	12.06	14.78	62.31	11.48	49.08	53.44	12.54	16.13	13.46	42.13	203.14	245.28	243.05
Average	% of Total P	4.65	5.56	24.94	4.72	20.23	22.32	5.21	6.73	5.64	17.58	82.42	101.21	

Table 8a. The effects of the added P on the changes and distribution of P into different P pools after 240 days of incubation of Rustenburg soil.

Added P ($mg\ kg^{-1}$)	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	2.79	2.90	46.70	8.85	59.60	61.83	4.86	12.42	13.52	30.80	182.67	213.47	213.47
	% of Total P	1.31	1.36	21.88	4.15	27.92	28.96	2.28	5.82	6.33	14.43	85.57	100.00	
25	Extracted P	4.63	4.42	53.67	13.33	64.62	65.67	6.00	15.00	16.71	37.71	206.34	244.05	238.47
	% of Total P	1.90	1.81	21.99	5.46	26.48	26.91	2.46	6.15	6.85	15.45	84.55	102.34	
50	Extracted P	5.79	5.63	63.33	16.92	70.67	70.17	6.46	17.08	19.21	42.75	232.51	275.26	263.47
	% of Total P	2.10	2.05	23.01	6.15	25.67	25.49	2.35	6.21	6.98	15.53	84.47	104.47	
100	Extracted P	8.39	9.71	80.00	20.33	80.10	78.58	6.88	20.33	20.52	47.73	277.11	324.84	313.47
	% of Total P	2.58	2.99	24.63	6.26	24.66	24.19	2.12	6.26	6.32	14.69	85.31	103.63	
150	Extracted P	9.49	15.38	93.00	23.75	89.96	89.67	7.29	23.17	21.75	52.21	321.25	373.46	363.47
	% of Total P	2.54	4.12	24.90	6.36	24.09	24.01	1.95	6.20	5.82	13.98	86.02	102.75	
200	Extracted P	12.59	19.25	104.00	27.17	100.54	99.17	9.00	24.83	23.67	57.50	362.72	420.22	413.47
	% of Total P	3.00	4.58	24.75	6.47	23.93	23.60	2.14	5.91	5.63	13.68	86.32	101.63	
Average	Extracted P	7.28	9.55	73.45	18.39	77.58	77.52	6.75	18.81	19.23	44.78	263.77	308.55	300.97
Average	% of Total P	2.24	2.82	23.53	5.81	25.46	25.53	2.22	6.09	6.32	14.63	85.37	102.47	

Table 8b. The effects of the added P on the changes and distribution of P into different P pools after 240 days of incubation of Loskop soil.

Added P ($mg\ kg^{-1}$)	P Recovered	HFO-P_i	HCO_3-P_i	OH-P_i	D/HCl-P_i	C/HCl-P_i	H_2SO_4-P_i	HCO_3-P_o	OH-P_o	C/HCl-P_o	TOT-P_o	TOT-P_i	Extracted TOT-P	Expected TOT-P
0	Extracted P	4.54	5.56	37.83	6.08	34.83	42.59	7.83	11.58	9.39	28.80	131.43	160.23	160.23
	% of Total P	2.83	3.47	23.61	3.79	21.74	26.58	4.89	7.23	5.86	17.97	82.03	100.00	
25	Extracted P	6.46	6.89	45.33	11.33	39.42	44.27	8.83	13.18	13.39	35.40	153.70	189.10	185.23
	% of Total P	3.42	3.64	23.97	5.99	20.85	23.41	4.67	6.97	7.08	18.72	81.28	102.09	
50	Extracted P	7.21	7.67	59.50	11.67	44.67	50.78	10.92	14.50	15.94	41.36	181.50	222.86	210.23
	% of Total P	3.24	3.44	26.70	5.24	20.04	22.79	4.90	6.51	7.15	18.56	81.44	106.01	
100	Extracted P	11.50	13.17	78.58	12.92	55.08	60.16	12.25	16.13	20.05	48.43	231.41	279.84	260.23
	% of Total P	4.11	4.71	28.08	4.62	19.68	21.50	4.38	5.76	7.16	17.31	82.69	107.54	
150	Extracted P	15.57	18.83	87.83	16.07	64.33	71.40	14.00	17.13	21.22	52.35	274.03	326.38	310.23
	% of Total P	4.77	5.77	26.91	4.92	19.71	21.88	4.29	5.25	6.50	16.04	83.96	105.21	
200	Extracted P	16.75	23.17	96.07	16.42	71.08	79.82	15.67	19.09	22.28	57.04	303.31	360.35	360.23
	% of Total P	4.65	6.43	26.66	4.56	19.73	22.15	4.35	5.30	6.18	15.83	84.17	100.03	
Average	Extracted P	10.34	12.55	67.52	12.42	51.57	58.17	11.58	15.27	17.05	43.90	212.56	256.46	247.73
Average	% of Total P	3.84	4.58	25.99	4.85	20.29	23.05	4.58	6.17	6.66	17.40	82.60	103.48	

3b: The effects of the added P and the incubation periods on the adsorbed P: Al- Fe-oxihydroxide P, and Ca-bound-P (0.1M NaOH- and 1.0M HCl-P)

3b: (i). The effects of the added P and the incubation period on the 0.1M NaOH-extractable P_i and P_o

0.1M NaOH-extracted P_i:

As it has already been indicated, 0.1M NaOH extracts mainly P_i and P_o held more strongly by chemisorption onto the surfaces of iron and aluminium oxihydroxides. According to Tables 2 and 3 the extracted P_i from this fraction increased highly significantly (P = 0.01) (Appendices I Nos. 4 and 5) with the increased P additions and the increasing incubation time.

For the Rustenburg soil increases were from 30.00–82.53 (1 day) to 46.70-104.00 mg kg^{-1} (240 days) between 0 and 200 mg kg^{-1} added P. This represented an average percent P recovery of 24.94 % after one day. The percent P recovery increased to an average of 32.62 % after 60 days of incubation. However, longer incubation periods did not increase the percent P recovery significantly, they remained relatively stable at around 30 % in average (Table 2; Fig. 5a). According to Figure 5a, -OH- extracted P increased between 1 and 60 days and thereafter there were no more significant increases in the extracted P. This showed that equilibrium was reached after 60 days of incubation with all the levels of applied P. The contributions to the extracted total soil P pool also remained relatively constant after 60 days, with average values of 21.77-23.53 % between 120-240 days of incubation (Tables 4a and 8a).

The OH extractable P values for Loskop soil varied from 21.43–62.23 (1 day) to 37.83-96.07 mg kg^{-1} (240 days) between 0 and 200 mg kg^{-1} added P. However, for the Loskop soil, again the changes in extractable P were more gradual up to 240 days of incubation (Table 3; Fig. 5b). The fact that the percent P recoveries between the two soils were relatively close indicates that the transformation reactions of the P were similar but only the amounts involved were different.

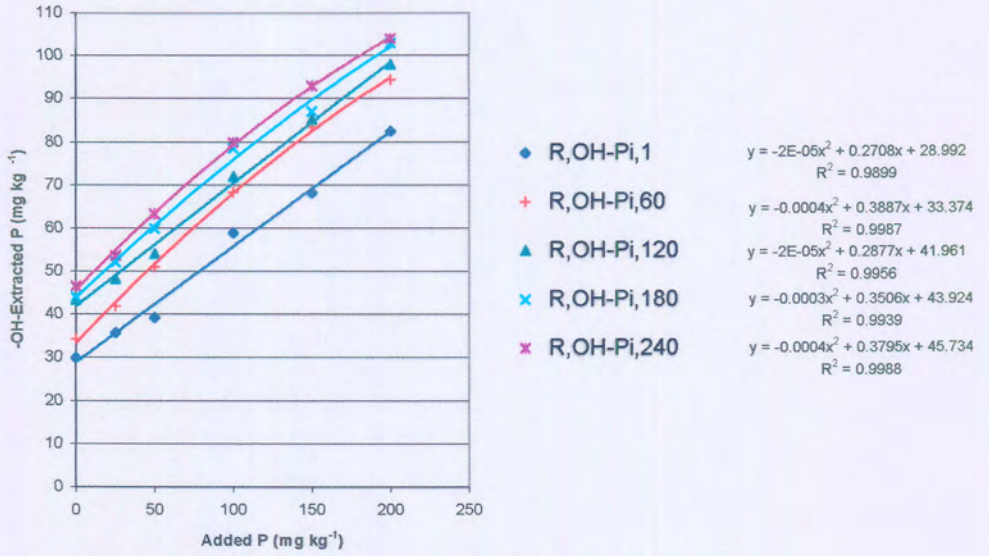

Fig. 5a. The effects of the added P and incubation time on the hydroxide (-OH) extracted inorganic P (P_i) from the Rustenburg soil.

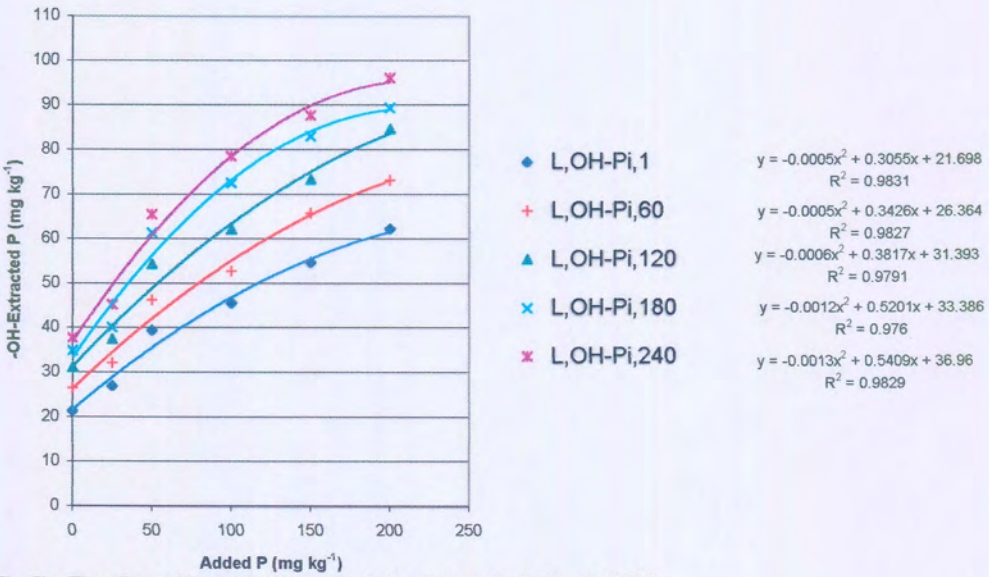

Fig. 5b. The effects of the added P and incubation time on the hydroxide (-OH) extracted inorganic P (P_i) from the Loskop soil.

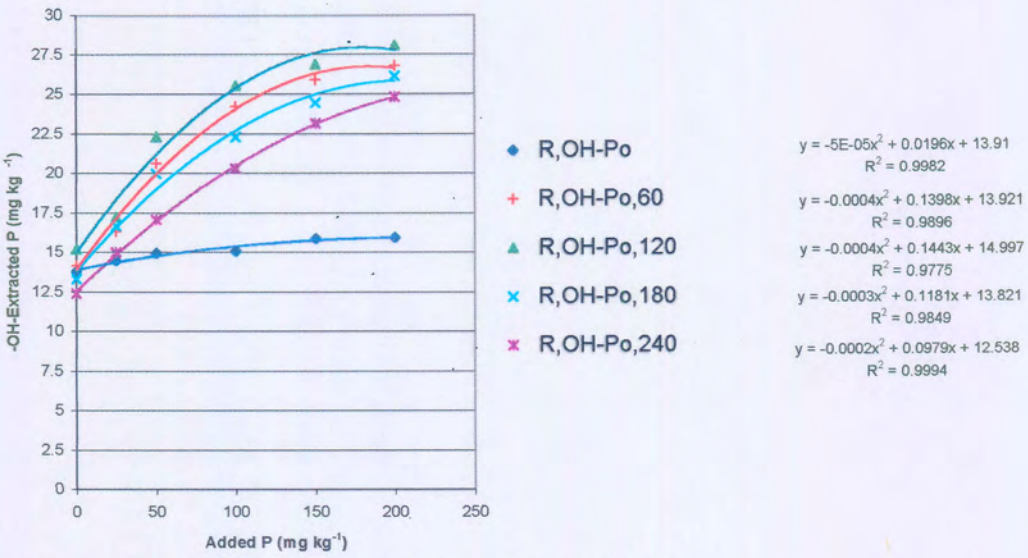

Fig. 6a. The effects of the added P and incubation time on the hydroxide (-OH) extracted organic P (P_o) from the Rustenburg soil.

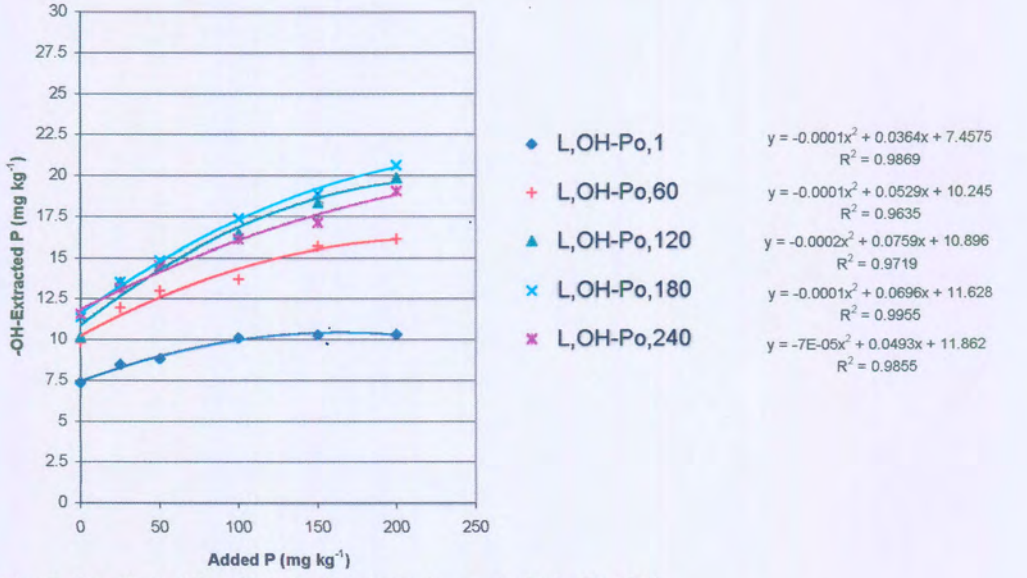

Fig. 6b. The effects of the added P and incubation time on the hydroxide (-OH) extracted organic P (P_o) from the Loskop soil.

The results further showed that both the –OH-P_i extracts and the percent P recoveries each contributed to approximately 25 % of the extracted total soil P pool, and thus the highest contributions to the extracted P_i pools in the two soils (Tables 2-3; 4-8). This would indicate that both soils gained more or less equal amounts of –OH-P_i from the different added P rates during the incubation period. Thus, the contribution of the –OH fraction the total soil P pool was affected in two main ways, by increasing P application rates as well as time of incubation, which increased contributions to the total soil P pool. This may indicate similar abilities of the two soils to transform the applied P to the –OH extractable P pool during the incubation period.

However, the noted differences in the –OH-extractable P_i and the percent P recoveries of the two soils could also be attributed to the differences in the clay contents and the types and to a less extent the organic matter contents. It has already been indicated in earlier discussions that the Rustenburg soil had more clay and organic matter than the Loskop soil (Table 1). The clay content plus the high amount of the kaolinites and to a less extent the mineralization of organic P could have contributed to the higher –OH-extractable P_i, in the Rustenburg soil (Dalal, 1973; Loganathan et al., 1987; Sanchez et al., 1991).

According to Figure 5b it can be concluded that the Loskop soil reached equilibrium with the higher P application rates (> 100 mg kg^{-1}) because of the curve-linear nature of the fitted lines in the graph. It could further show that the soil became saturated with –OH P fraction as more P was applied.

0.1M NaOH-extracted P_o:

According to the values given in the ANOVA (Appendices I Nos. 5 and 17) the –OH-extracted P_o was also significantly influenced by the applied P and incubation periods.

But according to Tables 4-8 the actual contributions of this P fraction to the total P Pool were relatively small (5-7 % for Rustenburg and 4-6 % for Loskop soil). Here again the P_o content increased with increasing incubation time and added P. The incubation time caused increased mineralization of P_o. This became well marked after 120 days when it started to decline in the Rustenburg soil showing that the soil organic matter was becoming depleted. This depletion was not so obvious in the Loskop soil (Tables 2-3; 4-8; Figs. 6a and b). In long-term field trials du Preez and Claassens (1999) found -OH-P_o made up 3.10-9.00% (Avalon) and 4.60-8.60% (Clovelly) of the total soil P pools, while Hedley et al. (1982) found -OH-P_o made up in average 15 % of the total soil P pool (from long-term wheat rotation experiment).

There seemed to have been a stimulation effect of –OH extracted P_o by the mineral P added, which could not be easily explained. The problem could have arisen during the differentiation of the P_i and P_o. There might be some problem in the methodology used, where the P_o may be over estimated at the expense of P_i (Tiessen and Moir, 1993).

3b: (ii). The effects of the added P and incubation periods on the 1.0M HCl-extracted P (P_i)

The variations of the P extracted with 1M HCl were significantly (P = 0. 01) influenced by the P application rate and incubation time (Appendices I Nos. 6 and 18).

The amounts of dilute acid (D/HCl-P_i) extracts for Rustenburg soil ranged from 6.73–15.07 (1 day) to 8.85-27.17 mg kg^{-1} (240 days) between 0 and 200 mg kg^{-1} of added P (Table 2). Of significance is the fact that at the early stages of incubation the percent recovery was small but after 180 days of incubation there was a significant increase in P extracted and percent recovery. The percent P recovered however decreased with increased applied P rates. This indicates that the transformation of added P into Ca-bound-P_i was relatively low (Table 2; Fig. 7a).

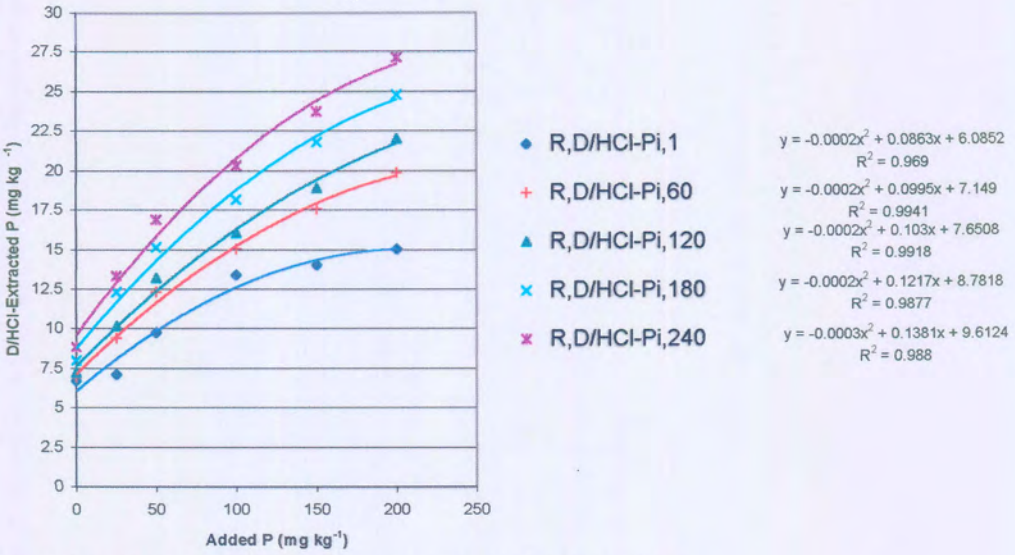

Fig. 7a. The effects of the added P and incubation time on the dilute hydrochloric acid (D/HCl) extracted inorganic P (P_i) from the Rustenburg soil.

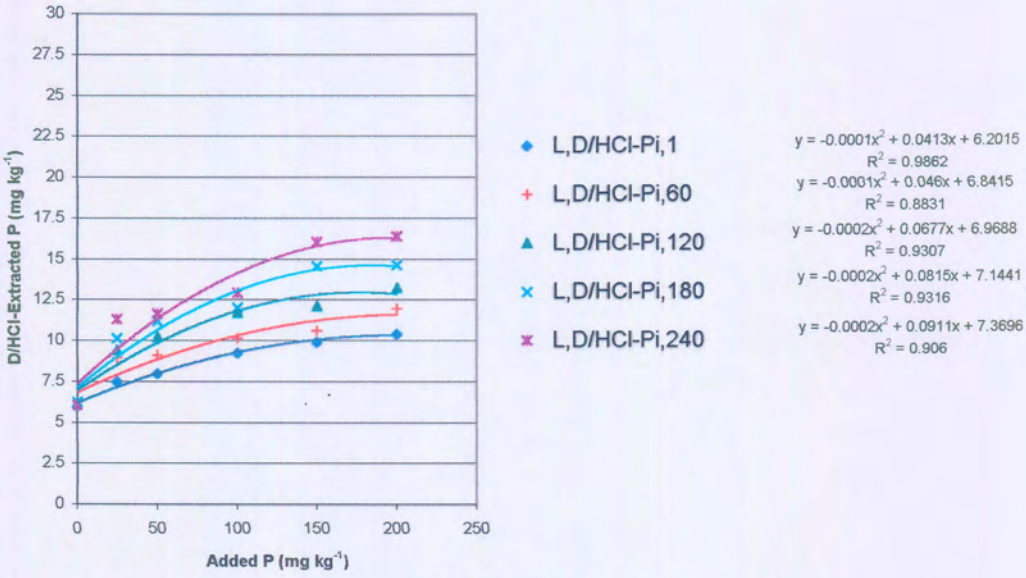

Fig. 7b. The effects of the added P and incubation time on the dilute hydrochloric acid (D/HCl) extracted inorganic P (P_i) from the Loskop soil.

Meanwhile for the Loskop soil, both the amounts of the D/HCl-P_i extracted and the percent P recoveries were lower than for the Rustenburg soil, although there were noted increases in both soils with the increased rates of added P and incubation times (Tables 2 and 3; Figs. 7a and b). Furthermore, the amounts extracted and the percent P recovered followed similar trends as those of the -OH-P_i for both soils. The only differences were in the quantities of the extracts and the tendencies towards equilibria that were more marked for the Loskop soil. The fact that in both soils, but especially the Loskop soil the graphs tended to level off indicates that this fraction becomes easily saturated with higher rates of the applied P (Figs. 7a and b).

The percent recoveries of the added P were also relatively higher for Rustenburg soil, and increased with the days of incubation (Tables 2 and 3). However, in general both the gains (percent P recovered) and the contributions to the total soil P pool were noticeably low for both soils, although were slightly higher for the Rustenburg soil (Tables 2-3; Tables 4-8). Accordingly, Sattell and Morris (1992) found an average of 8 %, and Hedley et al. (1982) found an average of 7 % of the total extracted soil P pool. But, du Preez and Claassens (1999) reported that this fraction contributed less than 1 % of the total soil P pool in the Clovelly soil. The changes in D/HCl-P_i with time and cultivation were small indicating that this fraction was of little importance.

The noted differences in the D/HCl-P_i extracted from Rustenburg and Loskop soils could possibly be attributed to the differences in the clay content and especially the amounts of Ca and Mg, which were relatively higher for the former than for the latter (Table 1). This high Ca and Mg could have resulted in the higher degree of precipitation of the applied P as Ca-P and possibly also as Mg-P. Both these P forms are relatively less available than Al-P or Fe-P (Chang and Jackson, 1957; Loganathan and Sutton, 1987). This may in part also explain why the P applied in the Rustenburg soil remains relatively more unavailable to crop plants than in the Loskop soils.

It has previously been shown that at neutral to higher pH values both the $H_2PO_4^-$ and HPO_4^{-2} ions are found and the main reaction for P adsorption or precipitation (fixation) would be as calcium phosphate (Brady, 1990; Doula, et al., 1996). The

reaction can be presented as: $Ca(H_2PO_4)_2.\ H_2O + 2CaCO_3 ====> Ca_3(PO_4)_2 + 2CO_2 + 2H_20$. Chang and Jackson (1957), Thomas and Peaslee (1973), and Loganathan and Sutton (1987), have all indicated that the degree of availability of the adsorbed P_i decreased in the order of Al-P, >Fe- P, >Ca-P, >Mg-P.

Total adsorbed or slow labile P (0.1M NaOH-P_i; and 1.0M HCl-P_i extracts)

The slow or moderately available P (–OH-P_i and D/HCl-P_i) fraction of the total soil P pool accounted for the second largest proportion of P with the Rustenburg soil averaging 23.07 % (1 day) and 29.34 % after 240 days, and for Loskop soil the average values were from 21.75 % (1 day) and 30.84 % after 240 days of incubation.

Thus, there were roughly equal increases in the moderately plant-available P (-OH-P_i and D/HCl-P_i) in both soils. These increases could have been the results of the formations of P associated with Fe-, Al-, Ca-, and Mg- compounds, which form at low to medium soil pH, as was the case in both soils (Loganathan et al., 1987). However, according to Hedley et al. (1982), during crop growth, specific root processes, such as the release of H^+ ions could be responsible for solubilizing the relatively insoluble 1M HCl P_i.

3c: The effects of the added P and incubation period on the occluded and residual P (conc. HCl- and $H_2SO_4 + H_2O_2$ –extracted P

3c: (i). The effects of the added P and incubation periods on the conc. HCl-extracted P (C/HCl-P_i and P_o)

Concentrated HCl extracted significantly different amounts of P from the different added P rates and the incubation times at P = 0.01 (Appendices I Nos. 7, 8, 19, and 20).

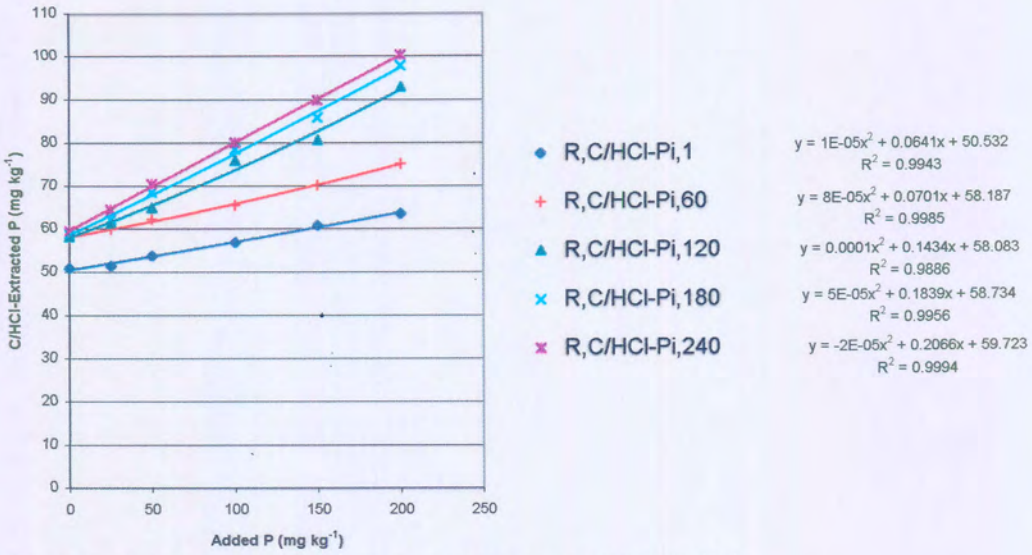

Fig. 8a. The effects of the added P and incubation time on the concentrated hydrochloric acid (C/HCl) extracted inorganic P (P_i) from the Rustenburg soil.

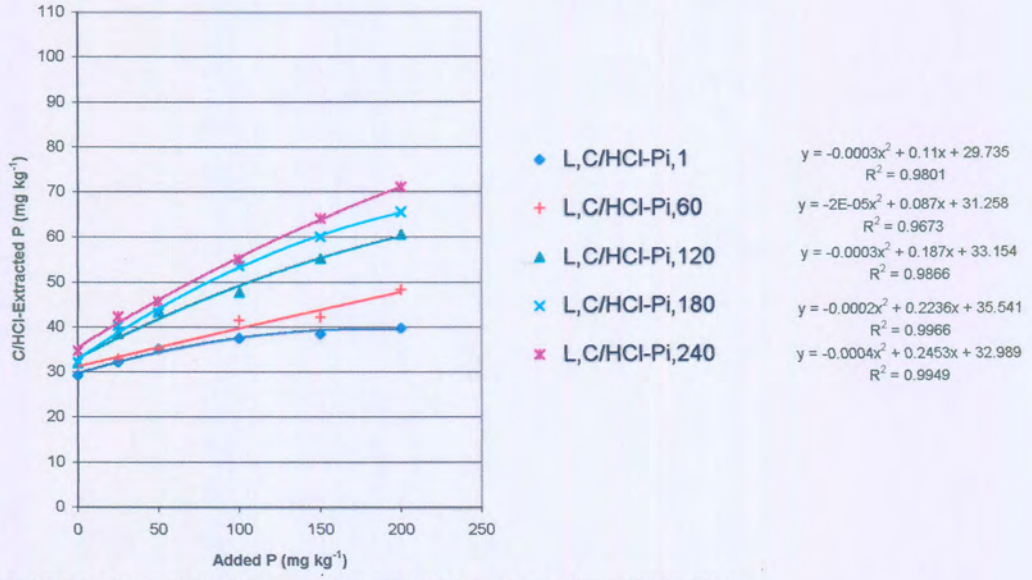

Fig. 8b. The effects of the added P and incubation time on the concentrated hydrochloric acid (C/HCl) extracted inorganic P (P_i) from the Loskop soil.

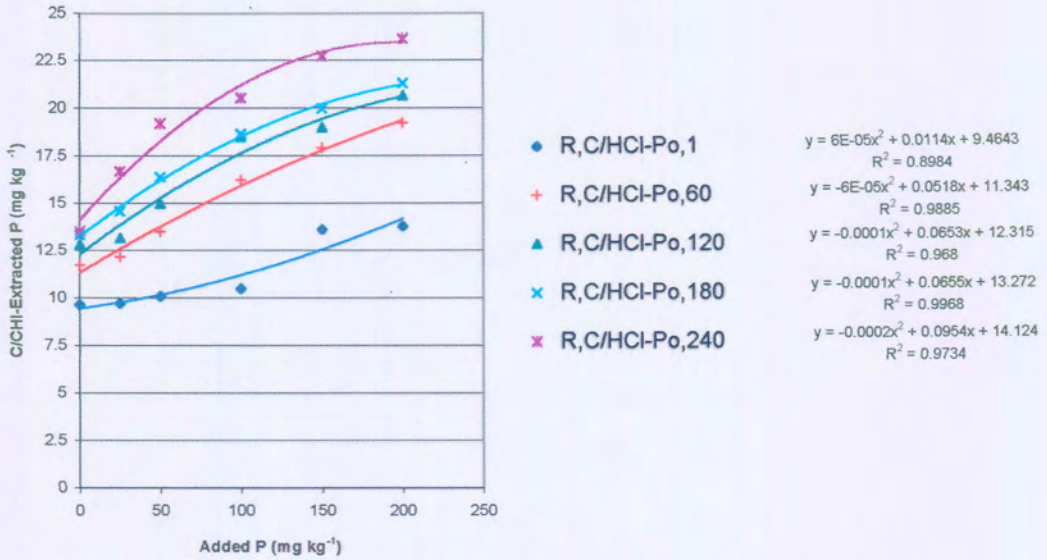

Fig. 9a. The effects of the added P and incubation time on the concentrated hydrochloric acid (C/HCl) extracted organic P (P_o) from the Rustenburg soil.

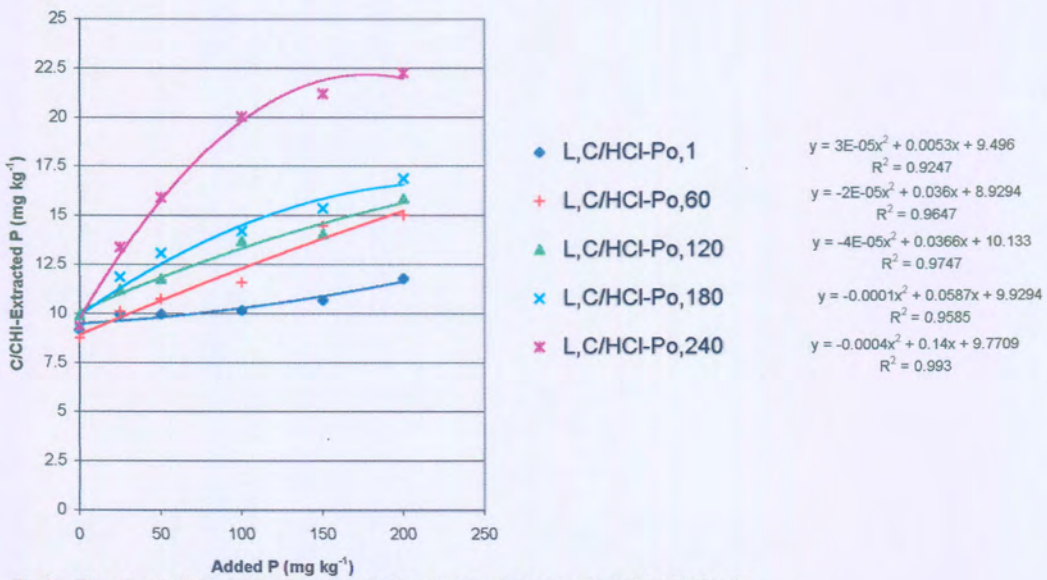

Fig.9b. The effects of the added P and incubation time on the concentrated hydrochloric acid (C/HCl) extracted organic P (P_o) from the Loskop soil.

C/HCl- extracted P_i:

The amounts of the C/HCl-P_i extracts from the Rustenburg soil were high throughout the incubation period and increased with the higher rates of applied P and the incubation period (Table 2; Fig. 8a). The amounts ranged from 50.93–63.73 after 1 day and 59.60-100.54 mg kg^{-1} after 240 days from the lowest and highest P applied. These represented average P recovery of 5.51 % after one day and 20.69 % after 240 days of incubation. The conc. HCl extracts also represent an average of more than 20 % of the total extractable soil P pool (Tables 4a-8a).

The corresponding values for the Loskop soil were lower ranging from 29.33–39.87 (1 day) to 34.83-71.08 mg kg^{-1} (240 days) for 0-200 mg kg^{-1} added P. The average P recovered was 8.69 % after 1 day and 19.22 % after 240 days of incubation. The conc. HCl-P_i extracts represent in average about 20 % of the total extractable P pool, which are roughly identical to those of the Rustenburg soil (Tables 4b-8b).

These values are relatively lower than those of Tiessen and Moir (1993) who found values of 193 mg kg^{-1} conc. HCl-P_i extracts for Chernozem (mollisol) from native prairie, and 140 mg kg^{-1} from similar soil after 65 years cultivation in Canada. But the values are higher than those of du Preez and Claassens (1999) with a highly weathered Clovelly soil that remained unchanged between about 45.3-51.5 mg P kg^{-1} after 15 years of cultivation. But, with another highly weathered Avalon soil, they found relatively very low values (19.30-7.55 mg P kg^{-1}).

The graphs in Figures 8a and b also show that for both soils C/HCl-extracted P_i increased with the increases of the added P and the increasing incubation time. The fact that these regression equation graphs were straight lines indicates that no equilibrium was reached, but longer incubation time would be required to fix sufficient amounts of the added P into this pool. The marginal changes recorded between the first and 60 days of incubation further confirms that this fraction consists of mainly the occluded and the recalcitrant P that requires some time to form.

C/HCl-extracted P_o:

According to the ANOVA in the Appendices I Nos. 8 and 20 there were significant differences in the extractable C/HCl-P_o due to the treatments applied. Here again this fraction contributed just a small part of the total soil P pool (Tables 4-8). In this P_o fraction the extractable P_o kept on increasing with increasing incubation time (Tables 2 and 3; Figs. 9a and b). This indicates that some of the added P (P_i) was evaluated with the P_o, which again may have been an experimental error in the differentiation of P_i and P_o as explained by Tiessen and Moir (1993).

3c: (ii). The effects of added P and the incubation periods on the conc. H_2SO_4 + H_2O_2 –extracted P

The data for the residual P (conc. H_2SO_4 + H_2O_2-P_i) extracts of Rustenburg and Loskop soils show that the changes with different P and incubation treatments were also highly significant at 0.01 % level (Appendices I Nos. 9 and 21).

The H_2SO_4-P_i extracts of Rustenburg soil were very high and varied in values from 55.27–61.67 (1 day) to 61.83-99.17 mg kg^{-1} (240 days) between 0 and 200 mg kg^{-1} of added P. The average P recoveries were 2.96 % after one day and 17.20 % after 240 days of incubation (Table 2). This fraction represented approximately 20-25 % of the total soil P pool during the incubation period (Tables 4a-8a).

Corresponding values for the Loskop soil were lower and ranged from 39.83-45.67 (1 day) and 42.59-79.82 mg kg^{-1} (240 days) with 0-200 mg kg^{-1} added P. The average percent P recovered were 1.58 % after one day and 15.70 % after 240 days of incubation (Table 3). This fraction represented approximately 20 % of the total extracted soil P pool throughout the incubation period (Tables 4b-8b).

The graphs in Figures 10a and b are very similar to Figures 8a and b of the conc. HCl-P_i extracts. These graphs show that for both soils H_2SO_4-P_i extracts increased steadily with the increasing P additions and incubation times. Both soils showed that

a fair amount of transformation to this fraction took place within 60 days. It is also evident that this pool can be a major sink for applied P because in both soils there were steady increases in this pool with increased incubation times.

The contributions of H_2SO_4-P_i extracts to the total extracted soil P pool were as high as those from the –OH-P_i and the conc. HCl-P_i fractions for both soils. However, they also decreased with the added P levels like the conc. HCl-P_i (indicating that transformations of the added P into the pool was low) and similarly increased with the increasing days of incubation (Tables 4-8). These tables also show that both soils gained more or less equal amounts of H_2SO_4-P_i with the added P levels throughout the incubation period.

These findings are comparable to those of Bowman et al. (1998) who also found an average of about 26 % of the total soil P pool was resistant P. But the more weathered soils from the tropics contained about 50 % resistant P or residual P. Similarly du Preez and Claassens (1999) also reported that the H_2SO_4-P_i fraction represented 44.1-48.6 % (Avalon) and 51.1-59.4 % (Clovelly) of the total soil P pool.

Chang and Jackson (1957) had reported that the residual fraction consisted mainly of Fe-and Al-P, and the proportions of each depended on pH, total amounts of P, ages of soils, and degrees of weathering. The amounts of residual P were highest in the samples from the oldest soils that were studied. Further, Oades and Ladd (1977) reported that as much as one quarter of P in the bacterial cells were non-extractable from soil. They concluded that it was possible that during the incubation processes the bacterial population increased, and that could have resulted in the slow accumulation of residual P.

Further they suggested that the majority of P_o forms in the residual P_o (H_2SO_4-extracts) are of larger molecular weights that correspond to the humic and fulvic acid fractions, which are stable, and not subject to much mineralization over time. Dalal (1977) had also reported that phosphorus held in organic form could be fixed into some insoluble form and become occluded or residual.

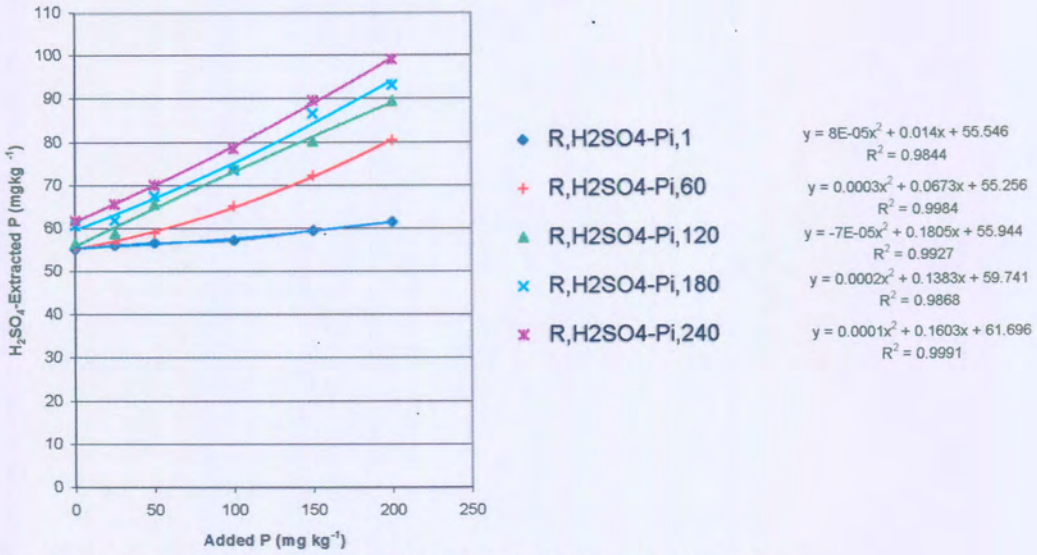

Fig. 10a. The effects of the added P and incubation time on the concentrated sulphuric acid (H_2SO_4) extracted residual P (P_i) from the Rustenburg soil.

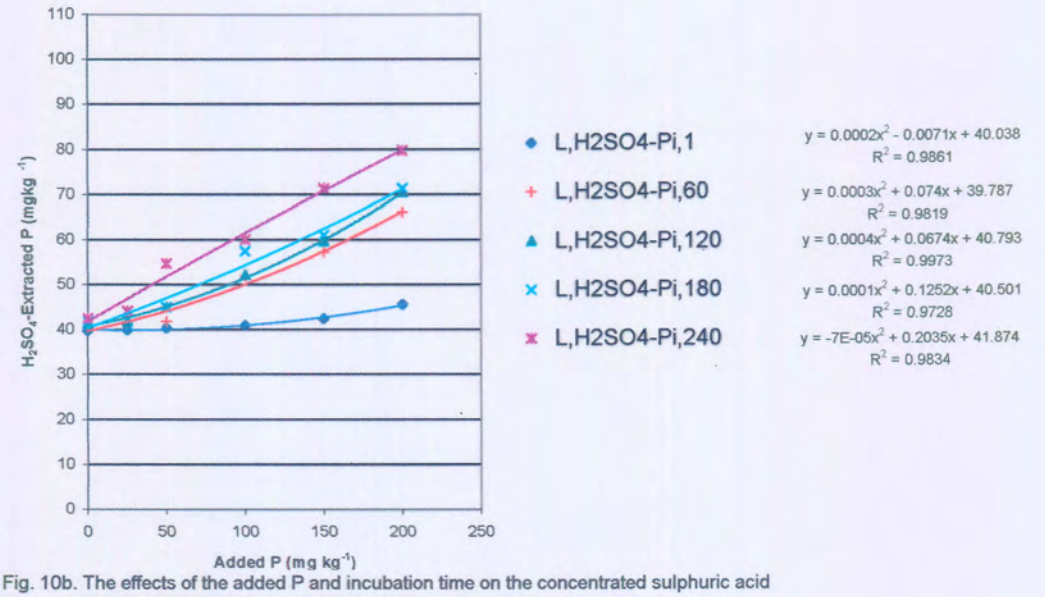

Fig. 10b. The effects of the added P and incubation time on the concentrated sulphuric acid (H_2SO_4) extracted residual P (P_i) from the Loskop soil.

Total insoluble P: Occluded and residual P (conc. HCl- and H_2SO_4 + H_2O_2-P_i –extracts)

The proportion of the total soil P extracted in the insoluble P (C/HCl-P_i + H_2SO_4-P_i) pool represented 44.24 % (1 day) and 51 % (240 days) for Rustenburg, and 36 % (1 day) and 43.34 % (240 days) for Loskop soil (Tables 4-8). These results show that the largest proportion of the total soil P pools in both soils consists mainly of relatively insoluble P_i (occluded and residual P) forms and stable humus and humic acids. The effects of incubation on the applied P of both soils resulted in accumulation of P in pool.

4. The effectiveness and limitations of the methodologies used

The resin strips technique in the Tiessen and Moir (1993) method was replaced by a new desorption technique developed by Freese et al. (1995) that is based upon the use of hydrous ferric oxide (HFO) as a sink for P. Instead of being impregnated in filter paper, the HFO is present inside dialysis membrane tubing (DMT). The membrane seemed to have provided excellent means to separate the soil suspension from the P sink. The DMT-HFO system was mechanically stable during the course of the experiments, and practically no HFO passed through the membrane. After each desorption step, the sink was easily separated from the soil suspension with very minimal or no loss of soil materials. As such, the new technique showed important advantages over the resin strips method.

However, since the P_o extracted as –HCO_3-P and –OH-P were determined by the difference between P_t and P_i in each extract, there was an inherent source of error. The P_i was determined in the supernatant after precipitation of organic matter with acid, and any P_i that precipitated along with the organic matter could have caused an error in the calculation of P_o (P_t-P_i). This is reported to occur with P_i associated with Fe and Al oxihydroxides, which are soluble at high, but insoluble at low pH. It has so far not been possible to quantify the P_o overestimation. This could have resulted in the relatively higher levels of P_o extracted from the Rustenburg and Loskop soils.

However, this fractionation approach is reported to be currently the only one that can be used with moderate success for the evaluation of available P_o. According to Tiessen and Moir (1993), the original fractionation of Hedley et al. (1982) left between 20 and 60 % of the P in the soil un-extracted. This residue often contained significant amounts of P_o that sometimes participated in relatively short-term transformations. As a whole the sequential P extraction procedures proved very effective. The amounts extracted varied from 96-107 % and 95-104 % of the expected total P from Loskop and Rustenburg soils respectively.

CONCLUSIONS

In a study to investigate the fate of the applied P to two soils, a red-sandy clayey soil (Ferric Luvisols) from Rustenburg (high P fixing) and a red-sandy loam soil (Ferric Acrisols) from Loskop (low P fixing), a DMT-HFO extraction procedure was used to extract P from the treated soils. The subsequent sequential fractionations to determine the P content of the different P pools gave an indication as to which pool the applied P was transformed into. The two soils were treated to different P rates (0, 25, 50, 100, 150, and 200 mg kg^{-1}), and incubated for 1, 60, 120, 180, and 240 days under a laboratory conditions. The sequential P fractionation procedure determined, (a) plant-available P: DMT-HFO-P (solution P_i) and 0.5M $NaHCO_3$-P (labile P_i and P_o); (b) adsorbed P: 0.1M NaOH-P (Al-, Fe- oxihydroxide-P_i and P_o) and 1.0M HCl-P (apatite/Ca-bound-P_i); (c) insoluble and residual P: conc. HCl-P (occluded/insoluble-P_i and P_o) and conc. H_2SO_4 + H_2O_2-P (residual/lattice-P_i and P_o) soil P pools.

The sequential P extractions identified the P quantities in the different P pools after different incubation periods, and how much of the added P could be recovered. In total nearly 100 % of the added P could be extracted through the different extractions. The percent P in each fraction changed with time of incubation. Between 20 and 30 %, and 20 and 35 % of the P could be extracted with DMT-HFO while between 20 and 40 %, and 20 and 35 % with the $-HCO_3$ extract after one day of

incubation from Rustenburg and Loskop soils respectively. This indicates that approximately 30 to 60 % of the added P were transformed into less labile form after 1 day. Within 60 days 80-90 % of the added P was transformed to the less labile P pools. This transformation was faster in the Rustenburg than the Loskop soil showing a higher P fixation capacity. A major part of the P transformation was to the –OH-P. The recovery from this pool was fairly constant for the different incubation periods (approximately 30 %). The percentage recoveries in the other pools increased up to 60 or 120 days where after the increases were less for longer incubation periods.

Thus, while solution and labile P decreased with time of incubation, there were corresponding increases in adsorbed, occluded and residual P. The Loskop soil had more marked increases in solution and labile P than the Rustenburg soil, while the Rustenburg soil showed higher values for the adsorbed, occluded and residual P forms. The noted differences could explain the reportedly higher levels of P fixation (adsorption and/or precipitation) by the Rustenburg soil than by the Loskop soil. It should also be noted that increasing levels of applied P did not correspondingly increase the percent recovery of labile P in both soils.

It may also be noted that the changes of P in soils are complex, and although the added fertilizer P is transformed to more stable (immobile) P forms, it could be seen as long-term residual P pools for plants. Thus, having determined the extent of P fixations by the two soils, it became necessary to establish how much of this transformed or fixed P can become available to plants over time and at what rate. This therefore, formed the basis for the experiments reported in Chapter 3.

To maximize fertilizer P efficiency especially in the Rustenburg soil, band placement at planting time should be recommended, as the findings show that after 1 day of incubation 60 % of the added P was transformed into less labile P. When band placed the soil in the vicinity of the band will be saturated with P and some P will remain in more labile form and thus available for a longer period of time. The use of plants with well-developed root systems could also be recommended to ensure that it explores the soil volume more effectively.