

## CHAPTER 4\*

### **Effect of long-term phosphorus desorption using dialysis membrane tubes filled with hydrous iron oxide on phosphorus fractions**

#### **4.1 INTRODUCTION**

The application of phosphorus (P) as either fertilizers or manures in excess of plant requirements causes a build up of P in the soil. However, some of this accumulated P may not be readily plant available (Myres, et al., 2005).

Presently conventional soil P tests, which consist of single extraction procedure, are used to estimate fertilizer requirements and represent an index of plant available P. Since available P in soil is not a single entity, a “complete account or budget” of the P forms present in the soil have to be obtained in order to determine the fate of applied P fertilizers (Solomon et al., 2002). This can be achieved by characterizing both labile and less labile inorganic and organic P pools.

Plant P availability of residual P in soils can be quantified by successive cropping experiments carried out in field or green house studies, where P is taken up until P deficiency occurs or a response to added P is measured (Indiati, 2000). To deplete the soil P in this approach, however, takes many years. For example, Johnston and Poulton (1976) showed that a Batcombe clay loam soil (Typic Hapludalf), which had received no manure since 1901 took in excess of 50 yr to deplete Olsen P concentrations via crop removal from approximately 65 mg kg<sup>-1</sup> to the minimum

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concentration required for optimal crop growth. McCollum (1991) estimated that with out further P fertilizer additions, it would take about 14 yr of maize (*Zea mays*. L) or soybean (*Glycine max* (L.) Merr.) production to deplete Melich-3 extractable P concentration of a Portsmouth fine sandy loam (mixed thermic Typic Umbraquult) from 100 mg kg<sup>-1</sup> to an agronomic threshold of 20 mg kg<sup>-1</sup>. As estimating residual P by this approach is time consuming and very expensive, it would be useful to have a laboratory method that would allow an estimate of phosphate desorption from the soil over time and the subsequent changes on the P dynamics that would result from successive P desorption.

Several methods can be used to estimate plant available P in soils called ion sink tests that employ a P adsorbing surface. Some of these P sink methods such as anion exchange resin /FeO-coated paper strips are used for a short term desorption studies while others such as dialysis membrane tubes filled with hydrous ferric oxide solution (DMT-HFO) can be used for long-term desorption studies (Freese et al., 1995; Lookman et al., 1995). These P testing methods have an advantage over conventional chemical extractants such as Bray-1P, Olsen-P and Melich-3P because the ion sink methods function similarly to a plant-root surface adsorbing available P ions from the *in situ* labile P pool in soil (Menon et al., 1989). In contrast, the use of single extractants in chemical tests for soil P may solubilize non-labile P more tightly bound to Al, Fe, and Ca complexes, which may not be plant available. When this occurs, accurate interpretation of test results becomes more difficult (Myres et al., 2005).

Ion sinks have advantages over typical chemical extractants, as they do not react with the soil, but only sorb the chemical entering the soil solution. Hence, they can be

favorably employed to estimate plant-available P for soils with large variations in physical and chemical properties (Sarkar and O'Connor, 2001). Furthermore, as extraction with these P-sink methods is a mild process conservating the chemical structure of soil, it has been possible, by this way, to make a series of extractions from one soil sample (Indiati and Sharpley, 1996). Depletion of soil P artificially using these methods therefore could simulate the action of P removal by crops in successive cropping experiment, which would normally take many years to realize. Consecutive extraction procedures carried out by these ion sink methods (McKean and Warner, 1996) combined with subsequent fractionation procedure (Tiessen and Moir, 1993) may, therefore, constitute a convenient laboratory method to characterize the P supplying capacity of a soil and to understand which P pools are involved in replenishing the soil solution P.

Successive desorption of P by DMT-HFO followed by subsequent fractionation method as described by Hedley et al., (1982) or Tiessen and Moir (1993) have been recently employed in South Africa to study the P dynamics of incubated soils. De Jager (2002) investigated the desorption kinetics of residual and applied phosphate to red sandy clay soils. It was found that the total amount of phosphate desorbed during a 56 day period of extraction was virtually equal to the decrease in the NaOH extractable inorganic phosphate fraction that was ascribed to the active contribution of NaOH (moderately labile) fraction in the desorption process. Ochwoh et al. (2005) also studied the chemical changes of applied and residual phosphorus (P) in to different pools in two soils [Alfisols], a red sandy clay soil [Haplo-Palcustafs] and a red sandy loam soil [Pale-Xerults] after P application and incubation. They found that between 30-60% of the added P was transformed to the less labile P pools in 1 day

and 80-90% of the added P after 60 days of incubation. A major portion of the P was transformed to the NaOH-extractable P pool. In the same study, Ochwoh (2002) attempted to determine the P desorption rates by successive DMT-HFO extractions followed by sequential extraction for the same soils. The results revealed that the so-called un-labile soil P pools contributed to the labile P pool by different proportions. However, information regarding the effectiveness of this modified method on soils which have a long term fertilization history is limited. On top of this, there is still a lack of information trying to relate such information with plant yield parameters. The objectives of this research were: 1) to study the changes in labile, non-labile and residual P using successive P desorption by DMT-HFO followed by a subsequent fractionation method and 2) to investigate which P pools contribute to the P requirements of maize for some soils with a long term fertilization history.

## **4.2 MATERIALS AND METHODS**

### **4.2.1 Fertilization history and soil analyses**

The sampling procedure and experimental site history of the soil samples used in this experiment are detailed in Sections 3.2.1 and 3.2.2. Table 3.1 shows some selected physical and chemical properties of the different treatments.

### **4.2.2 Long-term desorption study**

A long term desorption study was carried out using dialysis membrane tubes filled with hydrous ferric oxides similar to that described by Freese et al. (1995). Detail of this particular step was also documented in Section 3.2.3.

### 4.2.3 Fractionation procedure

Soil samples were sequentially extracted for P using Tiessen and Moir (1993) method with a slight modification made on the first step where by the resin in the Tiessen and Moir (1993) procedure was replaced by the DMT-HFO (De Jager & Claassens 2005; Ochwoh et al. 2005). The P fractionation procedure used consists of the following steps: 1.0 g soil sample in 80 ml 2 mM CaCl<sub>2</sub> and 0.3 mM KCl solution was successively extracted for soluble P with dialysis membrane tube filled with ferric hydrous solution for different periods (1, 7, 14, 21, 28, 42 & 56 days). This was followed by sequential extractions in the order: (i) 0.5M NaHCO<sub>3</sub> at pH 8.5, extracts weakly adsorbed P<sub>i</sub> (Hedley et al., 1982) and easily hydrolysable organic P (P<sub>o</sub>)-compounds like ribonucleic acids and glycerophosphate (Bowman and Cole, 1978) (labile-P<sub>i</sub> and P<sub>o</sub>), (ii) 0.1M NaOH, extracts P<sub>i</sub> associated with amorphous and crystalline Al and Fe (oxy) hydroxides and clay minerals and P<sub>o</sub> associated with organic compounds (fulvic and humic acids). This is designated as slow labile P<sub>i</sub> and P<sub>o</sub>, (iii) 1.0M HCl extracts P<sub>i</sub> associated with apatite or octacalcium P (Frossard et al., 1995) and this represents slow-labile P<sub>i</sub>, (iv) Hot concentrated HCl extracts P<sub>i</sub> and P<sub>o</sub> from more stable pools. Organic P extracted by concentrated HCl may also come from particulate organic matter (Tiessen and Moir, 1993). This represents occluded /recalcitrant/lattice fixed P<sub>i</sub> and P<sub>o</sub>, (v) 5ml of concentrated H<sub>2</sub>SO<sub>4</sub> (approx. 18M) and 2-3 ml of H<sub>2</sub>O<sub>2</sub> represents the very recalcitrant P<sub>i</sub> and P<sub>o</sub> which is considered as a residual P. A separate soil sample (0.5 g) was analyzed for total P content by means of concentrated H<sub>2</sub>SO<sub>4</sub> digestion to verify the total soil P determined by summation of all fractions as described by Schmidt et al., (1997). The extracted P was determined in solution according to the colorimetric method described by Murphy and Riley (1962).

#### 4.2.4 Field data

Maize (*Zea mays* L.) was grown in summer (November to March) since the establishment of the long-term experiment (1939). Field data for grain yield ( $\text{t ha}^{-1}$ ) was collected from the experimental station. Since there was no plant analysis to evaluate plant P uptake, soil analysis data was correlated to dry grain yield (12% moisture content) grown in the same and subsequent years as the soil analysis.

#### 4.2.5 Data analysis

The data obtained were statistically analyzed by using statistical Analysis System (SAS Institute 2004). Analysis of variance was done using the General Linear Model (GLM) procedure. The Tukey test was used to determine significant differences at  $\alpha = 0.05$ . The percent P extracted by each fraction was calculated by dividing the P extracted by the respective extractants with the total P obtained by direct determination of P and multiplying the ratio by 100%. Correlation with the plant yield parameter was done using Pearson linear correlation, PROC CORR (SAS Institute 2004).

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 P recovery and distribution

The total P ( $\sum P_i + \sum P_o$ ) extracted using this fractionation method was compared with the total P obtained by direct method. In the first case average of the total P obtained for day1 and 56 days of extraction was considered. The results showed that treatments

NK, NPK, MNK and MNPK extracted about 102.55, 107.31, 104.32 and 104.51 percent of the total P determined by direct method (Table 4.1).

The different fractions/pools of P were grouped according to Tiessen and Moir (1993) as labile ( $\text{DMT-HFO-P}_i + \text{NaHCO}_3\text{-P}_i + \text{NaHCO}_3\text{-P}_o$ ), less labile ( $\text{NaOH-P}_i + \text{NaOH-P}_o + \text{D/HCl-P}_i$ ) and stable P pools ( $\text{C/HCl-P}_i + \text{C/HCl-P}_o + \text{C/H}_2\text{SO}_4\text{-P}$ ). Accordingly, the percentage contributions of labile, less labile and stable fractions varied between 3.02-25.11, 13.58-39.45 and 39.42-82.61 of the total soil P respectively. These results showed that the largest portion of the total soil P, for all treatments, was the stable P fraction. These results concur positively with the results of du Preez and Claassens (1999) for Avalon and Clovelly soils and Ochwoh et al. (2005) for a red sandy clay soil [Haplo-Palcustafs] and a red sandy loam soil [Pale-Xerults] of South Africa. According to Table 4.1, the relative proportion of the stable fraction was largest in the control (NK) and least in the high P treated soil (MNPK). This indicated that over 65 years of continuous cropping resulted in the depletion of the more labile pools in the control (NK) and what is left is predominantly stable in nature. The fact that there was a small decline of P in the stable P pool after the 56-day extraction period indicated that the stable P pool must have contributed to the extracted P. Long-term application of P in the form of fertilizer or manure therefore changed the distribution of P in the P treated soils compared to the control. Hence, the labile and less labile fractions increased relative to the stable form. However, the stable P pool also increased indicating that some of the excess applied P was transformed to the stable P pool.

Comparison of the gain/loss (difference) between day1 and 56 days of extraction for each fraction and all treatments are presented in Table 4.1. The gain/loss was

calculated by subtracting the value of day 1 from day 56 for each fraction. The fact that there was a small difference in the total P extracted on day 1 and 56 can be attributed to experimental error. On average, however, more than 96% of the variation could be resulted from P redistribution due to continuous P extraction by DMT-HFO.

#### **4.3.2 Effect of P application level and extraction time on the labile P (DMT-HFO- $P_i$ + $HCO_3^-$ - $P_i$ + $P_o$ ) fraction**

##### **4.3.2.1 DMT-HFO-extractable $P_i$**

The amount of  $P_i$  extracted by DMT-HFO was significantly influenced ( $P \leq 0.05$ ) both by the levels of P applied and extraction time (Table 4.2). Temporal change of this fraction, however, was not significant for the control. The cumulative P desorbed was higher in the MNPK treated soil (19.83-103.46 mg kg<sup>-1</sup>) and lower in the control NK (0.08-1.13 mg kg<sup>-1</sup>) at all levels of extraction time (1 –56 days). In this study, NPK (4.87 – 19.34 mg kg<sup>-1</sup>) and MNK (5.85 – 18.76 mg kg<sup>-1</sup>) treated soils resulted in a comparable amount of extracted P at all levels of extraction time despite the different source of applied P. This is possibly because P might have been accumulated in inorganic forms in preference to organic forms (Sharpley, et al., 1993; Koopmans et al., 2003). This is evidenced by having nearly similar amount of Bray 1P and total P for both NPK and MNK treated soils (Table 3.1). The P source therefore seemed not to influence the amount of P extracted from both types of treatments. Cumulative P released with time followed, in general, the same pattern for all treatments, with an initial rapid release of P, roughly within the first two weeks (14 days), followed by a slower release that was still continuing after 56 days of extraction as depicted in



Figure 4.1a though the degree of increment was more pronounced for the high P treatments than the others. This is attributed to the presence of two distinct pools of soil P, one with rapid release kinetics and the other with slower desorption kinetics (Lookman et al., 1995, De Jager and Claassens, 2005). This can be explained by P desorbing quickly on to the surface of Fe and Al oxides, followed by relatively slow diffusion in to the matrix of sesquioxides (Pavlatou and Polyzopoulos, 1988).

The percentage distribution of DMT-HFO- $P_i$  fraction ranged from 0.02 –0.30, 0.77 – 3.18, 0.89 – 3.07 and 2.24 – 11.84 for NK, NPK, MNK and MNPK treated soils respectively from day 1 to 56 days of extraction time (calculated from Table 4.1). The percent P extracted in all cases was very low as compared to the total P. Similar results have also been reported by other researchers where the proportion of P extracted by DMT-HFO method was low compared to the large amounts of P initially present in the soils investigated (Koopmans et al., 2001; De Jager and Claassens, 2005; Ochwoh et al., 2005).

**Table 4.1.** Phosphorus content (mg kg<sup>-1</sup>) in different inorganic (P<sub>i</sub>) and organic (P<sub>o</sub>) fractions for the differentially P treated soils

P fractions	NK <sup>†</sup>			NPK			MNK			MNPk		
	Day 1	Day 56	Difference <sup>§</sup>	Day 1	Day 56	Difference	Day 1	Day 56	Difference	Day 1	Day 56	Difference
DMT-HFO	0.08 <sup>†</sup>	1.13	1.05	4.87	19.34	14.47	5.85	18.76	12.91	19.83	103.46	83.63
HCO <sub>3</sub> Pi	6.33	0.9	-5.43	77	52.72	-24.28	66.48	46.78	-19.7	108.5	70.17	-38.33
HCO <sub>3</sub> Po	8.04	9.23	1.19	21.11	15.49	-5.62	23.19	36.77	13.58	54.87	45.65	-9.22
Labile	14.45	11.26		102.98	87.59		95.52	102.31		183.2	219.28	
<b>%Labile</b>	<b>3.80</b>	<b>3.02</b>		<b>15.87</b>	<b>13.71</b>		<b>14.53</b>	<b>15.83</b>		<b>20.73</b>	<b>25.11</b>	
OH-Pi	17.75	11.09	-6.66	116.03	110.67	-5.35	122.82	100.28	-22.54	167.83	145.14	-22.62
OH-Po	28.32	47.36	19.04	51.14	77.31	26.17	74.07	96.17	22.1	80	119.76	39.76
1M HCl-Pi	5.65	2.29	-3.36	41.75	25.67	-16.08	29.99	23.33	-6.66	100.72	44.58	-56.14
Less-labile	51.68	60.67		208.92	213.84		226.88	219.78		348.55	309.55	
<b>%Less-labile</b>	<b>13.58</b>	<b>16.28</b>		<b>32.20</b>	<b>33.42</b>		<b>34.51</b>	<b>34.00</b>		<b>39.45</b>	<b>35.45</b>	
C/HCl-Pi	52.03	42.63	-9.4	110.9	67.69	-33.76	96.9	61.16	-35.74	106.7	72.75	-27.25
C/HCl-Po	25.22	22.98	-2.24	36	46.22	-9.15	38.31	46.22	7.61	69.32	53.22	-16.1
C/H <sub>2</sub> SO <sub>4</sub> -P	237	235	-2	190	223.65	43.65	196.7	216.93	17.42	201.11	215.64	14.53
Stable	314.25	300.61		336.9	337.56		331.91	324.31		377.13	341.61	
<b>%Stable</b>	<b>82.61</b>	<b>80.68</b>		<b>51.92</b>	<b>52.83</b>		<b>50.95</b>	<b>50.17</b>		<b>41.49</b>	<b>39.24</b>	
∑P <sub>i</sub> +P <sub>o</sub>	380.42	372.61	-7.81	648.8	638.85	9.95	654.31	646.4	-7.91	908.88	870.44	-38.48
*P <sub>total</sub>	367.16			600			623.43			851.22		
(∑P <sub>i</sub> +P <sub>o</sub> )/P <sub>total</sub> (%)	103.61	101.48	-2.13	108.13	106.48	-1.65	104.95	103.68	-1.26	106.77	102.25	-4.52
Average	102.55			107.31			104.32			104.51		

<sup>§</sup> Values are cumulative P differences between 56 days and 1 day of extractions for the different P fractions (mg kg<sup>-1</sup>), total P extracted (mg kg<sup>-1</sup>) and percent P recovered, negative values signify decreases and positives, increases

<sup>†</sup> Mean values of three replicates <sup>‡</sup> Plots treated with different amount of P \* Total P obtained by direct determination of P

**Table 4.2** Effect of P levels and extraction time on soil P desorption

P fractions (mg kg <sup>-1</sup> )	Treatments	Extraction time (days)				
		1	7	14	28	56
HFO-P <sub>i</sub>	NK	<sup>‡</sup> x 0.08 <sup>†</sup> a <sup>§</sup>	x1.05a	x1.07a	x1.08a	x1.13a
	NPK	x4.87a	y9.29a	y11.84ab	y13.5ab	y19.34b
	MNK	x5.85a	y10.46ab	y11.91ab	y12.91ab	y18.76b
	MNPK	y19.83a	z60.72b	z73.33c	z87.62d	Z103.47e
HCO <sub>3</sub> -P <sub>i</sub>	NK	x6.33a	x4.11a	x5.46a	x2.29a	x0.88a
	NPK	z77.00a	z69.4ab	y65.92b	y55.73c	y52.72c
	MNK	y66.53a	y55.86b	y58.46ab	y51.51bc	y46.78c
	MNPK	w108.5a	w97.84b	z91.25b	z85.9c	z70.17d
HCO <sub>3</sub> -Po	NK	x8.04a	x8.66a	x8.99a	x8.55a	x9.23a
	NPK	y21.11b	y31.09a	y12.32c	y16.75bc	Y15.49bc
	MNK	y23.19b	y23.87a	y18.89b	z35.88a	z36.77a
	MNPK	z54.87a	z49.90ab	z45.35b	w44.88b	W45.65b
NaOH-P <sub>i</sub>	NK	x17.75a	x16.58a	x15.68a	x14.47a	x11.09a
	NPK	y116.03a	y117.03a	y105.88a	xy114.17a	Y110.67a
	MNK	y122.82a	y121.80a	y116.59ab	y106.6b	Y100.28b
	MNPK	z167.83a	z160.03a	z154.60b	z150.80b	Z145.14b
NaOH-Po	NK	x28.37a	x25.71a	x26.26a	x31.06a	x47.98a
	NPK	xy51.14ab	y44.4b	y55.79ab	y82.73a	y77.31a
	MNK	yz74.1b	y61.62b	y71.41 ab	y76.32ab	yz96.17a
	MNPK	z80.42bc	y57.97c	y69.46bc	y86.58b	Z119.76a
1M HCl-P <sub>i</sub>	NK	x5.65a	x6.33a	x3.64a	x3.64a	x2.29a
	NPK	z41.75a	z37.97a	y32.86ab	y26.67b	y25.67b
	MNK	y29.99a	y26.23a	y25.76a	y24.69a	y23.33a
	MNPK	w100.72a	w81.62b	z73.33bc	z65.65c	z44.58d
C/HCl-P <sub>i</sub>	NK	x52.3a	x49.78a	x50.31a	x44.48a	x42.63a
	NPK	z110.9a	z93.7b	yz78.90c	yz73.07c	yz67.78c
	MNK	y96.9a	y75.19b	y68.84b	y62.48bc	y61.6c
	MNPK	yz106.7a	z95.31ab	z85.87b	z75.72bc	z72.54c
C/HCl-Po	NK	x25.22a	x17.75a	x11.66a	x18.89a	x22.98a
	NPK	xy36.31a	x16.55c	x21.51b	y33.31bc	y46.22a
	MNK	y38.31 ab	y34.39bc	x25.52c	y33.31bc	y46.22a
	MNPK	z69.32a	z47.77b	x32.54c	y35.54c	y53.23b
Residual P	NK	x237.1a	x232.93a	x225a	x239.03a	x235a
	NPK	x190.02a	x211.1a	x227.96a	x217.78a	x223.65a
	MNK	x196a	x203.53a	x203.53a	x241.18a	x216.93a
	MNPK	x200.73a	x202.68a	x202.69a	x222.14a	x215.64a

<sup>§</sup>Mean values in rows with different letters a, b, c, d and e are significantly different ( $\alpha = 0.05$ )

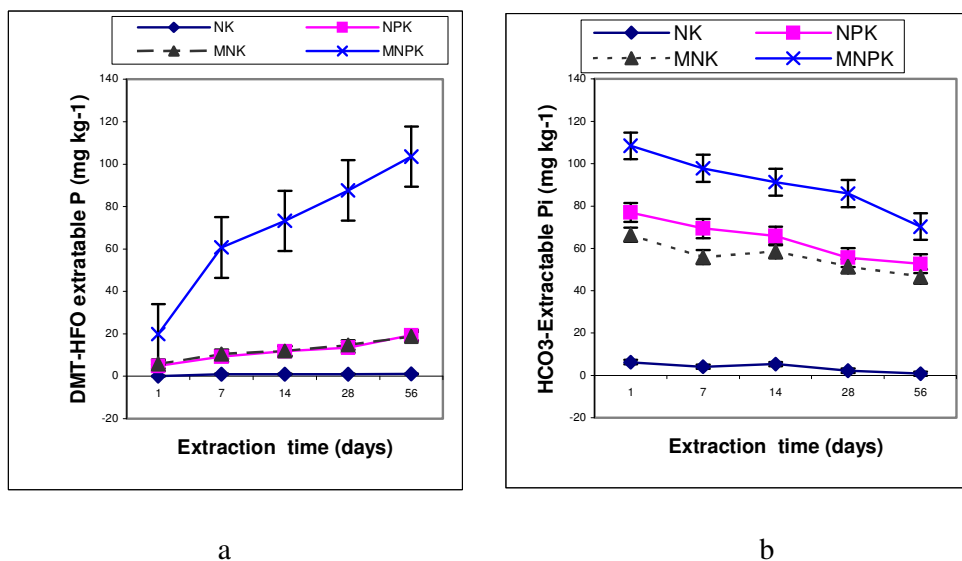
<sup>†</sup>Mean values of three replicates

<sup>‡</sup>Mean values in columns with different letters x, y, z and w are significantly different ( $\alpha = 0.05$ ).

#### 4.3.2.2 0.5M NaHCO<sub>3</sub>- Extractable P<sub>i</sub>

The temporal change of the 0.5M NaHCO<sub>3</sub> extractable P<sub>i</sub> due to continuous DMT-HFO extraction was significant ( $P \leq 0.05$ ) for all P treated soils as shown in Table 4.2. The amount of this fraction (Table 4.2) ranged from 6.33 – 0.88, 77.0 – 52.72, 66.53 – 46.71 and 118.44 – 72.33 mg kg<sup>-1</sup> respectively between 1 and 56 days of extraction for NK, NPK, MNK and MNPK treatments respectively. In general the HCO<sub>3</sub>-P<sub>i</sub> decreased in the order MNPK > NPK > MNK > NK. The bicarbonate extractable P<sub>i</sub> decreased with increasing time of extraction revealing the contribution of this fraction to the solution P depleted by DMT-HFO as shown in Figure 4.1b. Ochwoh (2002) and De Jager and Claassens (2002) also reported similar results for some South African soils, which have been incubated for 6 months and subjected to the same successive extraction by DMT-HFO from 1 to 56 days. However, the amounts extracted are relatively low in both cases as compared to our results possibly due to the low amount of total P in their soils ( $\cong 400$ mg/kg) compared to this study ( $\cong 800$  mg/kg).

The percentage distribution of this fraction was 1.68 – 0.23, 12.26 – 8.67, 10.12 – 7.03, and 12.27 – 8.06 for treatments NK, NPK, MNK, and MNPK respectively. As an average of all extraction time, the P treated soils extracted 11(NPK), 9(MNK) and 10.7(MNPK) times as much phosphate extracted from the control. The application of P in the form of fertilizer or manure, therefore, increased the NaHCO<sub>3</sub>-P<sub>i</sub>.



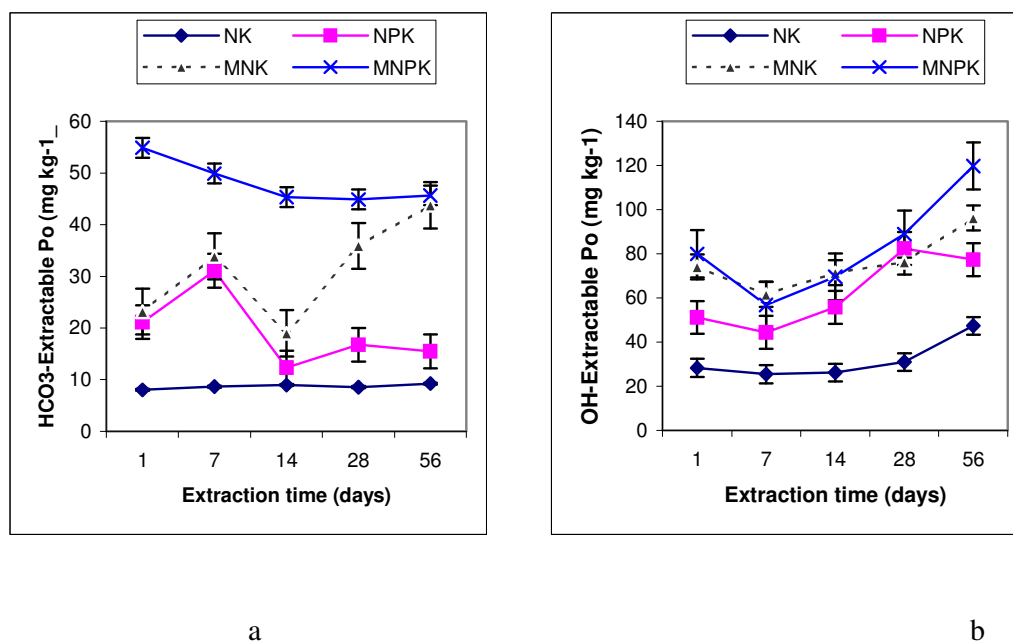
**Figure 4.1(a-b)** Changes in the cumulative DMT-HFO-P<sub>i</sub> (a) and HCO<sub>3</sub>-extractable P<sub>i</sub> (b) fractions over time. The values in the figures are means of three replicates. Vertical bars represent the standard error

#### 4.3.2.3 0.5M HCO<sub>3</sub>-Extractable P<sub>o</sub>

The change in the 0.5M NaHCO<sub>3</sub>-extractable organic P after successive DMT-HFO extraction was significant for all P treated soils ( $P \leq 0.05$ ) (Table 4.2). The amount of HCO<sub>3</sub>-P<sub>o</sub> extracted for the respective treatments was NK (8.04-9.23 mg kg<sup>-1</sup>), NPK (21.11-15.49 mg k<sup>-1</sup>), MNK (23.19-36.77 mg kg<sup>-1</sup>), and MNPK (54.57-45.39 mg kg<sup>-1</sup>) after 1 day and 56 days of extraction. In general the amount of this fraction followed the order MNPK>MNK>NPK>NK. The change in 0.5MHCO<sub>3</sub>-extractable P<sub>o</sub> with time showed a different pattern for the different treatments (Figure 4.2a). The control showed little variation with time. This clearly indicated that the organic material content of the soil was very low and probably no P<sub>o</sub> was extracted during extraction with DMT-HFO. For the NPK treatment the P<sub>o</sub> extracted was relatively

lower than MNK treatments. This is because this treatment received only inorganic P and the DMT-HFO extraction did not influence the extractable  $P_o$  significantly especially after 14 days of extraction. The  $P_o$  extracted from the MNK treatment was higher than the NPK treatment obviously due to the long history of applied  $P_o$  in the form of manure (Table 3.1). The reason for the increased amount of this fraction with time could be due to microbial immobilization of P (Stewart and Tiessen, 1987). MNPK treated plots showed a reduction in  $0.5M\text{HCO}_3$ -extractable  $P_o$  until the 14<sup>th</sup> day and remained constant afterwards. The observed general decline in  $0.5M\text{HCO}_3$ -extractable  $P_o$  for soils with MNPK treatment might be due to the relatively high amount of P extracted by the DMT-HFO compared to others. In all other cases, the amount of P extracted by DMT-HFO was less than the Bray-1P except the MNPK treated plots. The involvement of  $0.5M\text{HCO}_3$ -extractable  $P_o$  for MNPK treated soils, therefore, could be to replenish at least in part the P removed by the DMT-HFO (Tables 4.2 and 3.1).

The percentage distribution of  $\text{HCO}_3$ -extractable  $P_o$  was 2.13-2.45, 3.36-2.55, 3.53-5.69 and 6.17- 5.23 for NK, NPK, MNK and MNPK respectively between 1 day and 56 days of extraction. The addition of fertilization in the form of fertilizer or manure therefore increased the  $0.5M\text{NaHCO}_3$ - $P_o$  compared with the unfertilized control (NK). As an average of all extraction time and P levels, the percent  $0.5M\text{NaHCO}_3$ -extractable  $P_o$  was about 3.89. Hence, the percentage contribution of this fraction to the total P was generally very low and in consonant with the results of Du Preez and Claassens (1999) and Ochwoh et al. (2005).



**Figure 4.2(a-b)** Changes in the HCO<sub>3</sub>-extractable Po(a) and NaOH-extractable P<sub>o</sub>(b) fractions over time. The values in the figures are means of three replicates. Vertical bars represent the standard error

#### 4.3.3 Effect of P level and extraction time on the less labile P (0.1MNaOH-P<sub>i</sub>+0.1M NaOH-P<sub>o</sub>+1M HCl-P<sub>i</sub>) fraction

##### 4.3.3.1 0.1M NaOH- Extractable P<sub>i</sub>

The changes in 0.1M NaOH extractable P<sub>i</sub> after the successive DMT-HFO extraction showed significant difference ( $P \leq 0.05$ ) due to the influence of applied P (Table 4.2). The decline of this fraction with time (Figure 4.3a) indicated that this fraction contributed to the soil solution P depleted as the result of extraction by DMT- HFO. The extractable P<sub>i</sub> for the NPK and MNK treatments was nearly similar and

significantly better than the control. The highest  $P_i$  was extracted from the MNPK treatment. The  $P_i$  extracted from the control did not significantly alter due to the extraction time with DMT-HFO, indicating that very little DMT-HFO extractable P was available in this fraction. In soil from the MNPK treatment there was a steady decline in the NaOH- $P_i$  indicating that some of this fraction was extracted with DMT-HFO over the 56-day period. The same tendency was observed for the MNK treatment but to a lesser extent. 0.1M NaOH extractable  $P_i$  ranged from 13.94- 11.09, 116.03-110.00, 122.82-100.28 and 167.83- 145.21  $\text{mg kg}^{-1}$  for NK, NPK, MNK and MNPK respectively between 1 day and 56 days of extraction. This fraction is therefore the second largest fraction of all the P fractions.

As an average of all extraction time, the percent NaOH- $P_i$  contributed 3.33, 18.85, 17.10 and 17.81 for NK, NPK, MNK, and MNPK treated soils respectively. The result of this study was comparable with the results from previous reports especially for the P treated soils. De Jager (2002) reported that the 0.1M NaOH extractable  $P_i$  was ranged from approximately 15-16% of the total P for control and the high P treated soils after 1 day and 56 days of extraction by DMT-HFO. In a similar work done by Ochwoh (2002), the percentage of this fraction ranged from 12-14% after 1 day and 56 days of extraction by DMT HFO for the control and high P incubated soil. The lower fractional contribution of the control in this study could be the inherently lower inorganic fractions due to P depletion over time.

As compared to the control, on average, about 5.5 times more phosphate was extracted from P treated soils. The addition of fertilization in the form of fertilizer or manure, therefore, increased the 0.1M NaOH extractable  $P_i$  on the P treated plots.

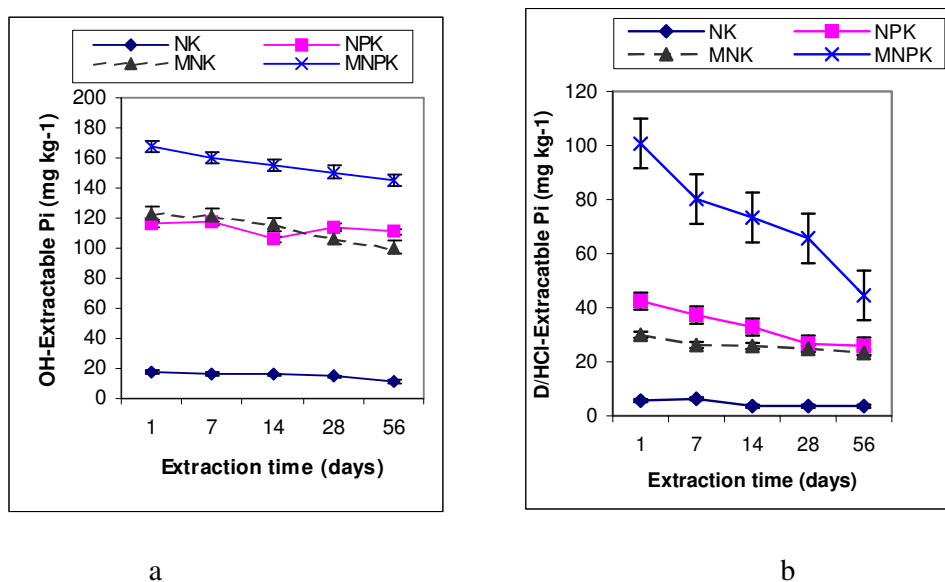


#### 4.3.3.2 0.1M NaOH-Extractable $P_o$

The change in the 0.1M NaOH-extractable  $P_o$  showed a significant difference ( $P \leq 0.05$ ) with respect to changes in P levels and extraction time (Table 4.2). The amount of this fraction ranged from 28.32- 47.36, 51.14-77.31, 74.07-96.17, and 80.42-119.76 mg kg<sup>-1</sup> for NK, NPK, MNK, and MNPK respectively after 1 day and 56 days of extraction by DMT-HFO. There were significant increases in extractable NaOH  $P_o$  due to increasing of P application compared to the control. The increased  $P_o$  extracted from the NPK treatment that did not received any organic P could be due to the higher yields obtained from this treatment compared to the control and the subsequent higher additions of organic material including P from the crops roots. The amount of extractable OH- $P_o$  followed the order NK<NPK<MNK<MNPK. In all treatments the OH- $P_o$  extracted increased with time of extraction (Figure 4.2b). The reason for the increased amount of this fraction could be due to microbial immobilization of P (Stewart and Tiessen, 1987) or possibly due to the removal of NaOH- $P_i$  and the subsequent dissolution of  $P_o$  that could be extracted with NaOH.

Soil  $P_o$  has been recognized as a significant source of available P particularly for grassland and forest soils (Gracia-Mounteil et al., 2000) where as for soil with a long-term fertilization history the contribution of  $P_o$  to the crop-available P pool seems rather limited. Examining the ratio of NaHCO<sub>3</sub>- $P_o$  to NaOH- $P_o$  served as a means to determine whether the  $P_o$  can be a source for available P (Kuo et al, 2005). Where  $P_o$  was an important source of available P for crops (Hedley et al., 1982; Tiessen et al., 1984; Zhang and Mackenzie 1997b), the ratio of NaHCO<sub>3</sub>- $P_o$  to NaOH- $P_o$  was high

(25.23%). Where the ratio is <10%, the contribution of  $P_o$  to plant available P could presumably be less important (Schmidt et al. 1997; Kuo et al. 2005). Based on this, the ratio was found to be >30% for this study and the contribution of  $P_o$  to plant available P could, therefore, be important especially in the long-term when the current inorganic P gets exhausted to induce  $P_o$  mineralization.



**Figure 4.3(a-b)** Changes in the 0.1M NaOH-extractable  $P_i$  and D/HCl-extractable  $P_i$  fractions over time. The values in the figures are means of three replicates. Vertical bars represent the standard error

As an average of all extraction time, the percent NaOH- $P_o$  contributed 10.03, 10.43, 13.06 and 11.44 of the total P for NK, NPK, MNK, and MNPK treated soils respectively. The percentage distribution of OH- $P_o$  therefore followed the order: MNK>MNPK>NPK>NK. However, there seemed to be no big difference on the percent recovery of this fraction from P treated soils as compared to the control.

#### 4.3.3.3 1M HCl- Extractable P<sub>i</sub>

This fraction also showed a significant difference ( $P \leq 0.05$ ) with respect to variations in P levels and extraction time with DMT-HFO (Table 4.2). However extraction time did not influence the extractable P<sub>i</sub> for the NK and MNK treatments significantly. In both these treatments it was obvious that it did not contribute to the P<sub>i</sub> extracted with DMT-HFO. The NPK and MNPK treatments contributed significantly to the DMT-HFO extractable P. In all treatments the 1M HCl-extractable P<sub>i</sub> decreased with time of successive extraction by DMT-HFO and the effect of time on the extractability of this fraction was much more pronounced on the P received plots than the control as depicted in Figure 4.3b. The amount of extracted 1M HCl-P<sub>i</sub> was in the range from 5.79-2.29, 41.75-25.67, 29.99-23.33, and 100.71-44.58 mg kg<sup>-1</sup> for the plots treated in NK, NPK, MNK, and MNPK respectively after 1 day and 56 days of extraction.

The P<sub>i</sub> extracted by this extractant from P received plots is 5.08, 3.82, and 7.71 times as much compared to the control for NPK, MNK and MNPK respectively. The addition of fertilization in the form of commercial fertilizer or manure therefore significantly increased this fraction as compared with the unfertilized control. The contribution of this fraction was on average 6% for all P treated soils. Du Preez and Claassens (1999) reported <1% of contribution to the total P of this fraction for the Clovelly soil. While other similar studies revealed 5-8% contribution of this fraction to the total P (Hedley et al., 1982; Sattel and Morris, 1992; Ochwoh et al., 2005).

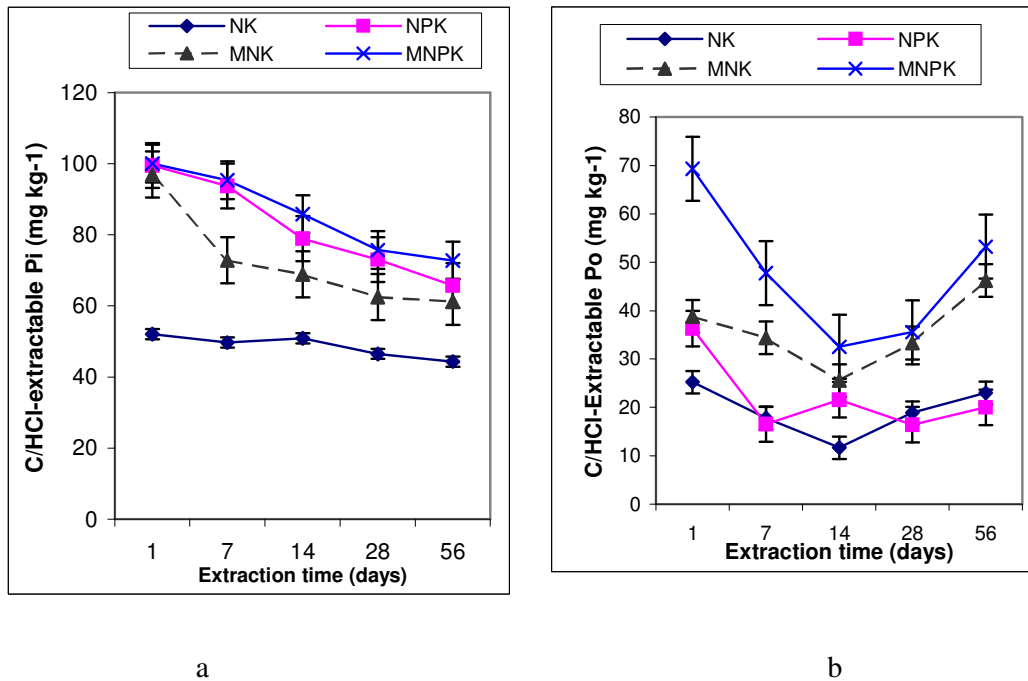
#### 4.3.4 Effect of P level and extraction time on the stable P (C/HCl-P<sub>i</sub> +C/HCl

##### P<sub>o</sub>+C/H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> -P) fraction

##### 4.3.4.1 C/HCl-Extractable P<sub>i</sub>

The change in concentrated HCl extractable P<sub>i</sub> after successive DMT-HFO-extraction showed a significant difference ( $P \leq 0.05$ ) both with respect to applied P levels and extraction time (Table 4.2). The amount extracted by this extractant ( $\text{mg kg}^{-1}$ ) varied from 52.30-42.62, 110.90-67.78, 96.90-61.60 and 106.69-72.54 for treatments NK, NPK, MNK and MNPk respectively after day 1 and 56 days of extraction. This fraction is the third largest fraction of all. Besides, the decrease in this fraction (Figure 4.4a) with increased time of extraction by DMT-HFO was the largest of all both for the control and the P treated soils. This clearly indicated that this fraction contributed significantly to the P extracted by DMT-HFO. This also suggests that this fraction may be a buffer to more labile P fractions in the long-term.

Averaged over all extraction time, the percent C/HCl-P<sub>i</sub> constituted 12.63, 14.40, 12.12 and 10.19 for NK, NPK, MNK, and MNPk treated soils respectively. The contribution of this fraction is on average 12.33% for all soils. Ochwoh (2002) reported between 15-25% contribution of this fraction to the total P for Loskop and Rustenburg soils of South Africa.



**Figure 4.4 (a-b)** Changes in the C/HCl-Extractable P<sub>i</sub> and C/HCl-Extractable P<sub>o</sub>.

fractions over time. The values in the figures are means of three replicates. Vertical bars represent the standard error

#### 4.3.4.2 C/HCl-Extractable P<sub>o</sub>

The change in concentrated HCl extractable P<sub>o</sub> as the result of successive DMT-HFO-extraction showed a significant difference ( $P \leq 0.05$ ) with respect to P levels and extraction time (Table 4.2). The amount extracted by this extractant (mg kg<sup>-1</sup>) varied from 25.22-22.98, 36.31-20.03, 38.31-46.22, and 69.32- 53.23 for treatments NK, NPK, MNK and MNPK respectively after 1 day and 56 days of extraction. The C/HCl-P<sub>o</sub> showed a decreasing tendency until 14 days of extraction followed by slight increment as the days of extraction increased as shown in Figure 4.4b. The reason for

a slight increment of  $C/HCl-P_0$  at the later days of extraction could be attributed to microbial immobilization of P (Stewart and Tiessen, 1987).

As an average of all extraction time, the percent of this fraction constituted 6.41, 4.45, 6.49 and 4.58 for NK, NPK, MNK, and MNPK treated soils respectively. Averaged over all extraction time and treatments, the contribution of this fraction to the total P was 4.23%, which is nearly comparable to the reports made by other researchers. Ochwoh (2002) reported 2-4% contribution of this fraction to the total P. Du Preez and Claassens (1999) reported 6.4-8.5% and 1.6-3.4% contribution to the total P for Avelon and Clovelly soils respectively. The  $C/HCl-P_0$  extracted by Hedley et al. (1982) was also found to be 3%. Bashour et al., (1985) however reported that the contribution made by this fraction ranged from 0-26.7%.

#### **4.3.4.3 $C/H_2SO_4 + H_2O_2$ extractable P**

This fraction showed no statistically significant differences for both extraction time and P level (Table 4.2). The fact that no significant decrease in extractable P took place after extraction with DMT-HFO over the 56-day period indicated that it contributed very little to the available P pool. This fraction was the largest fraction of all fractions for both the control and P treated soils. Similar reports have been made by Santos et al., (2006) on the study made on Cerrado soils. They observed that on average terms, the residual fraction corresponded to half of the recovered total P in all soils regardless of the source of applied P and method of applications.

Averaged over all extraction time, the percentage distribution of this fraction was 66.34, 33.40, 31.68 and 23.53 for NK, NPK, MNK and MNPK respectively. The P treated soils therefore showed less proportion (20-30%) of this fraction than the control where more than 60% of the pool was  $C/H_2SO_4 + H_2O_2$  extractable P. In this regard, the result of this study concurs with the result of Ocwoh et al. (2005), as the contribution of this fraction ranged between 20-25% to the total P pool for the P treated soils they investigated.

#### **4.3.5 Plant growth as related to phosphorus fractions**

The amount of P extracted by the different extractants (including total P) was also correlated with yield as illustrated in Table 4.3. This comparison was made between the cumulative DMT-HFO extractable P, the subsequent fractions and maize yield. The same kind of comparison was also made between Bray1P and maize yield. Significant correlations were observed between maize grain yield and all the P pools and the total P except DMT-HFO- $P_i$  ( $r=0.58$ ) and  $HCO_3-P_o$  ( $r=0.77$ ). A significant correlation was also observed between maize grain yield and Bray1P ( $r = 0.84^*$ ). Cajuste et al., (1994) reported highly significant correlations between Bray-1P and the different P fractions for oxisol and alfisol soils they studied under laboratory conditions. Unlike the correlation between DMT-HFO- $P_i$  and yield, the correlation of the former with Bray-1P was found to be highly significant ( $r = 0.95^{**}$ ). This observation probably indicates the ability of these extractants to extract the labile P. A possible explanation for the observed difference between extractants DMT-HFO and Bray-1P could be obtained by comparing the amount of P extracted by both extractants as depicted in Table 3.1. NK and MNPK treated soils released roughly

similar amount of P by both extractants where as NPK and MNK desorbed a DMT-HFO-P<sub>i</sub> extract, which was nearly half extracted by Bray-1P. The relatively lower amount of P desorbed by these treatments could be a possible reason for the poor correlation observed between DMT-HFO-P<sub>i</sub> and maize grain yield.

**Table 4.3.** Correlations among the cumulative P desorbed over 56 day period, the subsequent fractions, Bray 1P(mg kg<sup>-1</sup>) and maize grain yield (t ha<sup>-1</sup>), N=4

P extracts (mg kg <sup>-1</sup> )	Yield (t ha <sup>-1</sup> )	Bray 1P (mg kg <sup>-1</sup> )	Change in P fraction(mg kg <sup>-1</sup> )	Yield (t ha <sup>-1</sup> )
HFO-P <sub>i</sub>	0.58	0.92**	ΔHFO-P <sub>i</sub>	0.59
HCO <sub>3</sub> -P <sub>i</sub>	0.96**	0.95**	ΔHCO <sub>3</sub> -P <sub>i</sub>	-0.85**
HCO <sub>3</sub> -P <sub>o</sub>	0.76*	0.83**	ΔHCO <sub>3</sub> -P <sub>o</sub>	-0.08
OH-P <sub>i</sub>	0.96**	0.95**	ΔOH-P <sub>i</sub>	-0.62
OH-P <sub>o</sub>	0.88**	0.95**	ΔOH-P <sub>o</sub>	0.62
D/HCl-P <sub>i</sub>	0.88**	0.99**	ΔD/HCl-P <sub>i</sub>	-0.54
C/HCl-P <sub>i</sub>	0.95**	0.93**	ΔC/HCl-P <sub>i</sub>	-0.92**
C/HCl-P <sub>o</sub>	0.98**	0.92**	ΔC/HCl-P <sub>o</sub>	-0.21
Total P	0.88**	0.99**		
Bray-1P	0.84*	-		

\*Significant at 0.05 probability level

\*\*Significant at 0.01 probability level

Correlation between P fraction decrease and maize grain yield was also done. The change in P fraction can be calculated as the difference between day1 and 56 days of DMT- HFO-P extraction (Table 4.1). The correlation between the change in P of each



fraction and dry maize grain yield was also made as illustrated in Table 4.3. The only two fractions that showed strong and highly significant correlation with grain yield were  $\text{HCO}_3\text{-P}_i$  ( $r = -0.85^{**}$ ) and  $\text{C/HCl-P}_i$  ( $r = -0.92^{**}$ ). All the other fractions were not significant. Changes in the inorganic fractions with time revealed the decreasing tendency of these fractions with time as depicted in Figures 4.1b – 4.3b and 4.4a although the degree of contribution differed from one fraction to the other. The values in Table 4.3 indicate the importance of the inorganic fractions especially  $\text{NaHCO}_3\text{-P}_i$ ,  $\text{NaOH-P}_i$  and  $\text{C/HCl-P}_i$  in replenishing the soil solution P than the organic fractions. From the inorganic fractions,  $\text{C/HCl-P}_i$  was the fraction that decreased most suggesting that this fraction may be the major P source to buffer the more labile P fractions. The P sources that act as a buffer for soil available P varied from soil to soil and include: organic P (Zhang and Mackenzi, 1997b),  $\text{NaOH-P}_i$  for soils receiving repeat applications from fertilizer and/or manure (Schmidt et al., 1996; Zhang and Mackenzi, 1997b; Guo et al., 2000) and  $\text{HCl-P}$  and/or residual P (Guo et al., 2000). Most studies made on highly weathered tropical soils revealed the importance of  $\text{NaOH-P}_i$  in replenishing the labile P fractions (Du Preez and Claassens, 1999; Ochwoh and Claassens, 2005; De Jager and Claassens, 2005). The present investigation positively concurs with the report of Araujo et al., (2003). The latter researchers reported the importance of acid P (equivalent to  $\text{C/HCl-P}$  in our study) in replenishing the labile P fractions for Latosols.

#### 4.4 CONCLUSIONS

In this study the involvement of the labile and non-labile  $P_i$  fractions in replenishing the solution  $P_i$  was significant except the residual fraction. The organic fraction appeared to have limited contribution in replenishing the soil solution P at this stage. They could act as a source of P only in the very long term when the inorganic P becomes too low to induce  $P_o$  mineralization. The amount of P extracted by the different fractions in general followed the order  $MNPK > NPK > NPK > NK$  for inorganic fractions whereas for the organic fraction the order appeared to be  $MNPK > MNK > NPK > NK$ . Highly significant correlations were observed between maize grain yield and the different P fractions including total P. The correlation between the change in P of each fraction and maize grain yield was highly significant for the fractions  $HCO_3-P_i$  ( $r = -0.85^{**}$ ) and  $C/HCl-P_i$  ( $r = -0.92^{**}$ ). From the inorganic fractions,  $C/HCl-P_i$  was the fraction that decreased most suggesting the importance of this fraction in replenishing the labile P fractions.

## CHAPTER 5\*

### **Effect of shaking time on long-term phosphorus desorption using dialysis membrane tubes filled with hydrous iron oxide**

#### **5.1 INTRODUCTION**

Several investigators showed that continuous application of phosphorus (P) either in the form of fertilizer or manure over a long-term can accumulate large amounts of residual P. This is principally due to the low amount of P removed from a field by crops, which in general varies from 3-33% of applied P fertilizer (Bolland & Gilkes, 1998; Csatho et al., 2002; Aulakh et al., 2003; Kamper & Claassens, 2005).

Plant P availability of residual P in soils can be quantified by successive cropping experiments carried out in field or green house studies, where P is taken up until P deficiency occurs or a response to added P is measured (Indiati, 2000). As depletion of the soil can take many years to study in the field or green house studies, which makes it very expensive and time consuming, more rapid soil extractions methods are required to assess the effect of P addition on the rate of P decrease in available soil P. One promising method uses ion sinks such as Fe-oxide impregnated filter paper strips that can act as infinite sinks for soil P release (Sharpley, 1996; McDowell and Sharpley, 2002). The Fe-oxide strips have a better theoretical basis for estimating plant available P in different soil types than chemical extractants (Sarkar and O'Connor, 2001; Hosseinpur and Ghane, 2006). This method however has two major drawbacks making it unsuitable for studying long-term P desorption from soils. First,

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the paper strips are mechanically unstable during longer desorption times (weeks), leading to relatively large losses of the P sink to the soil sample. Second, fine P rich particle adhere to the filter paper during every desorption step resulting in an overestimation of the amount of P desorbed, since any P associated with these particles is accounted for as desorbed after analyzing the filter paper (Freese et al., 1995; Lookman et al., 1995).

The use of dialysis membrane tubes filled with hydrous ferric oxide has recently been reported as an effective way to characterize long-term P desorption (Freese et.al., 1995). This method is similar to Fe-oxide impregnated filter paper strips but in this case the HFO is placed in a dialysis membrane tube instead of being impregnated in the filter paper. This has the advantage of not allowing strong chemicals to come in to contact with the soil. This system is mechanically stable and capable of maintaining low P activity in solution for longer period of time ,and, therefore, P release over long periods of time can be measured in a more natural environment than a routine soil tests (Freese et al., 1995; Lookman et al., 1995).

In studies to relate extraction methods with plant availability, the study of root systems especially in connection with the percent exploitation of the soil volume is important. Recent works related to the percent root exploitation of the soil volume revealed that 3-4% of the top soil volume was exploited at full maturity of a maize crop. The value was as low as 1% during the first two weeks, when most P uptake was anticipated to occur (Smethurst, 2000; Kamper & Claassens, 2005). However, the DMT-HFO method, similar to other soil tests, exploits 100 percent of the sample volume that is much more than the percent root exploitation of plants. Therefore,

exploiting the whole volume of the soil by continuous shaking, as has been done in this technique, may not simulate the plant mode of action very well. One possible solution to simulate the root P uptake could be by modifying the shaking procedure using different shaking periods. The objectives of this paper were to investigate the influence of shaking time variation on the P desorbed by DMT-HFO and to relate the desorption indices generated with maize yield.

## **5.2 MATERIALS AND METHODS**

The sampling procedure and experimental site history of the soil samples used in this experiment are detailed in Sections 3.2.1 and 3.2.2. Table 3.2 shows some selected physical and chemical properties of the different treatments.

### **5.2.1 Long-term Phosphate desorption experiment**

The procedure in this section is also detailed in Section 3.2.3.

### **5.2.2 Modification of the shaking time**

The shaking period was adjusted to investigate the influence of the different shaking periods on the amount of P extracted and to identify which shaking option better mimics the plant mode of action. This was done by comparing the conventional approach which served as a control with the modified approaches. Continuous shaking for 1, 7, 14, 28, and 56 days, which is the usual approach, was assumed to be a conventional approach. The modification was then carried out by reducing the length of shaking time by certain percentages such as 25%, 50% and 75% of the control. For example, if the shaking period is shortened by 25%, then the shaking procedure will

assume a different pattern. So instead of shaking for 1, 7, 14, 28 and 56 days continuously it will be shaken for  $\frac{3}{4}$ ,  $5\frac{1}{4}$ ,  $10\frac{1}{2}$ , 21 and 42 days continuously. This is equivalent to 75% of the respective shaking times of the control. The following shaking options were considered. Option 1 was the conventional approach which served as a control. Options 2, 3 and 4 are the modified approaches continuously shaken for 75%, 50% and 25% of the control respectively. Table 5.1 indicates the different possibilities one can obtain by considering the different shaking options.

**Table 5.1** The different shaking patterns according to the conventional and modified approaches

Shaking time (days) <sup>§</sup> Conventional approach	Shaking time (days) <sup>‡</sup> Modified approach		
Option1 Control	Option2 75%	Option3 50%	Option4 25%
1	0.75	0.5	0.25
7	5.25	3.5	1.75
14	10.5	7	3.5
28	21	14	7
56	42	28	14

<sup>§</sup>Conventional approach is the continuous shaking time for 1, 7, 14, 28, & 56 days; control

<sup>‡</sup>Modified approach is a continuous shaking for 75%, 50%, & 25% of the conventional approach for the shaking options 2, 3, and 4 respectively.

### 5.2.3 Field data

Maize (*Zea mays* L.) was grown in summer (November to March) since the establishment of the long-term experiment (1939). Field data for grain yield ( $\text{t ha}^{-1}$ ) was collected from the experimental station. Since there was no plant analysis to evaluate plant P uptake, soil analysis data was correlated to dry grain yield (12% moisture content).

### 5.2.4 Data Analysis

The data obtained were analyzed by using Statistical Analysis System Program (SAS Institute 2004). Analysis of variance was done using the General Linear Model (GLM) procedure. The Tukey test was used to determine significant differences at  $\alpha = 0.05$ . The rate constants  $k_A$  and  $k_B$  values were determined from equation [6] described in section 2.1.1 by splitting the solid phase P in to two pools: labile pool, Pool A and the less labile pool, Pool B as described by Lookman et al. (1995). Correlation with the plant yield parameter was done using Pearson linear correlation, PROC CORR (SAS Institute 2004).

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 DMT-HFO- $P_i$

The effect of varying shaking options on the extractable DMT-HFO- $P_i$  for each treatment is illustrated on Table 5.2. No statistically significant differences were observed for all treatments amongst the different shaking options except treatment MNPK. These treatments received high P and resulted in relatively large amount of P

at all extraction periods. The relatively high releasing capacity of these soils might have contributed to the difference shown on these treatments. The amount of P extracted was found to be consistent with the time of extraction for all treatments in all four shaking options. Thus, in general the pattern of release followed the order: option1>option 2> option3>option 4, consistent with the general expectation that the amount of P extracted by a given extractant increases with increasing time of extraction (Damodar et al., 1999; Pasricha et al., 2002).

The cumulative amount of P ( $\text{mg kg}^{-1}$ ) desorbed over a 56-day period of extraction ranged from 1.74-1.57(NK), 23.61- 15.69 (NPK), 21.48- 15.7 (MNK) and 132.81-103.97 (MNPK) for shaking options 1 to 4 (Table 5.2). Cumulative P released with time followed, in general, the same pattern for all shaking options and in all P treatments, with an initial rapid release of P that continued up until 14 days of extraction (Option 1-3) and 7 days of extraction (option 4) followed by a slower release that was still continuing after the respective days of extraction. This is attributed to the presence of two distinct pools of soil P, one with rapid release kinetics and the other with slower desorption kinetics (Lookman et al., 1995, De Jager and Claassens, 2005). The fast P pool presumably represents primarily P bound to the reactive surfaces, which are in direct contact with the aqueous phase (Hingston et al., 1974, Madrid and Posner, 1979). The slow P release rate from the second pool is either the result of slow dissolution rates or from slow diffusion from interior sites inside oxyhydroxide particles (McDowell and Sharpley, 2003).



**Table 5.2.** The effect of different shaking options on the extractable DMT-HFO-Pi for different P levels

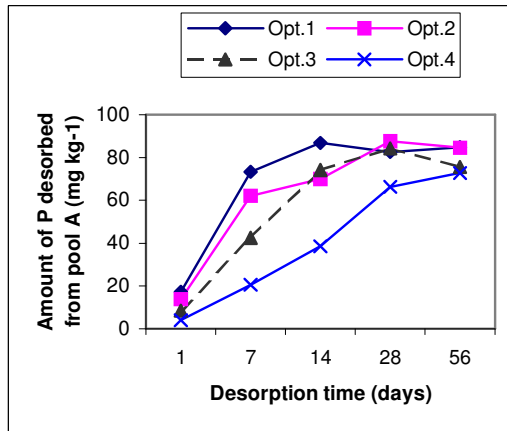
	Conventional approach	Percentages of continuous shaking			
		100% (Control)	75%	50%	25%
Treatment	Ext time	Opt1	Opt2	Opt3	Opt4
NK	1	<sup>s</sup> x1.47 <sup>†a‡</sup>	x1.41a	x1.36a	x1.28a
	7	x1.54a	x1.56a	x1.54a	x1.52a
	14	x1.57a	x1.57a	x1.54a	x1.54a
	28	x1.62a	x1.6a	x1.57a	x1.54a
	56	x1.74a	x1.69a	x1.62a	x1.57a
NPK	1	x4.59a	x3.03a	x2.19a	x1.8a
	7	x11.31a	x10.56a	x7.99a	x5.3a
	14	x15.69b	x11.73b	x11.31b	x7.99a
	28	x19.44b	x17.46bc	x15.69bc	x11.31b
	56	x23.61b	x21.37c	x21.37c	x15.69b
MNK	1	x6.15a	x3.18a	x3.18a	x1.98a
	7	x11.6a	x8.27ab	x9.46ab	x5.58a
	14	x15.76b	x13.39bc	x11.6bc	x9.47ab
	28	x17.55bc	x16.85c	x15.76bc	x11.6b
	56	x21.48c	x18.56c	x17.55c	x15.76b
MNPk	1	z18.87a	yz14.56a	xy8.97a	x4.52a
	7	w 85.8b	z67.21b	y46.01b	x24.03b
	14	z103.97c	y78.14c	y85.8c	x46.01c
	28	y108.85c	y105.17d	y103.97d	x85.80d
	56	z132.81d	y115.63e	x108.85d	x103.97e

<sup>s</sup>Mean values in rows with different letters x, y, z and w are significantly different ( $\alpha = 0.05$ )

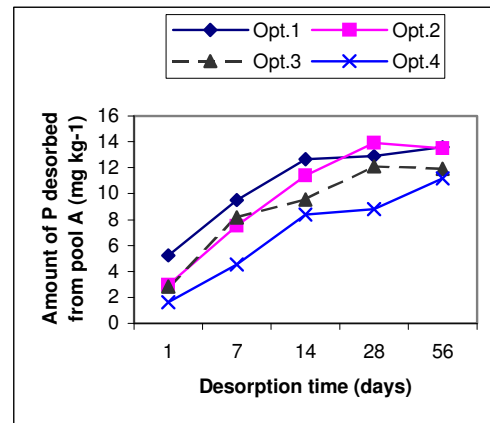
<sup>‡</sup>Mean values in columns with different letters a, b, c, d, and e are significantly different ( $\alpha = 0.05$ ).

<sup>†</sup>Mean values of three replicates

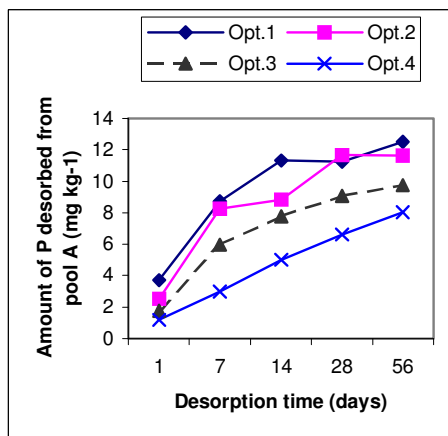
The contributions of both  $SP_A$  and  $SP_B$  to the total P extracted varied among treatments and shaking options following the order:  $MNPK \gg NPK \approx MNK \gg NK$  (Figure 5.1a-d for  $SP_A$  and Figure 5.2a-d for  $SP_B$ ). This is in accordance with the total P content of the treatments (Table 3.1). The higher the P status of the soil, the greater was the contribution made by both  $SP_A$  and  $SP_B$ . This could be attributed to higher degree of P saturation of the adsorption sites with increasing P status of the soil (De Jager and Claassens, 2005). Toor et al., (1999) also reported the higher P desorption rate in fertilizer and manure treated soils. In their investigation, manure appeared to play significant role in enhancing the P desorption possibly due to complexation of Fe and Al ions. The change of these pools with time in general varied in the same way. The contribution of  $SP_A$  increased with time for all P levels and shaking options as well. The only exception noted was for MNPK treated soils where by the contribution of  $SP_A$  consistently increased with time only for option 4 (note that the maximum period of extraction according to this option is only 14 days!) but started to decline for options 1-3 (Figure 5.1a-d). This indicates that the contribution of this pool is more pronounced only to short desorption period. On the other hand, the contribution made by the slowly released pool,  $SP_B$ , increased with time, the degree of increment being higher at the latter extraction time, revealing the predominant role played by this fraction in replenishing the soil solution P in long-term desorption studies (Figure 5.2a-d). The control resulted in negligible variation in this respect too for the reason reported previously.



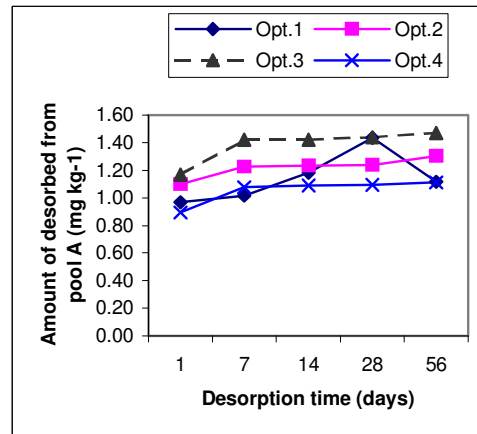
a) MNPK



b) MNK

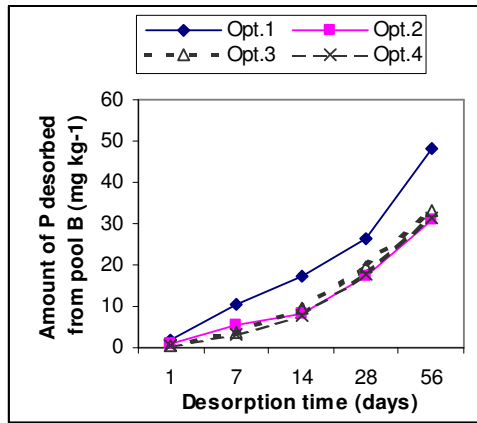


c) NPK

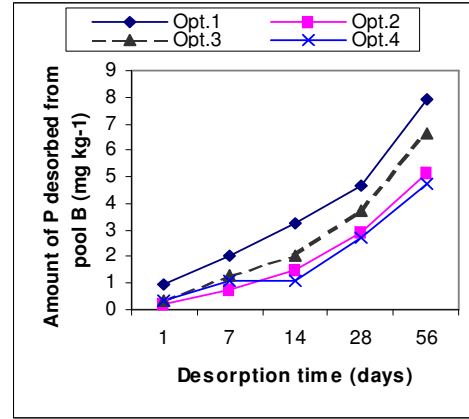


d) NK

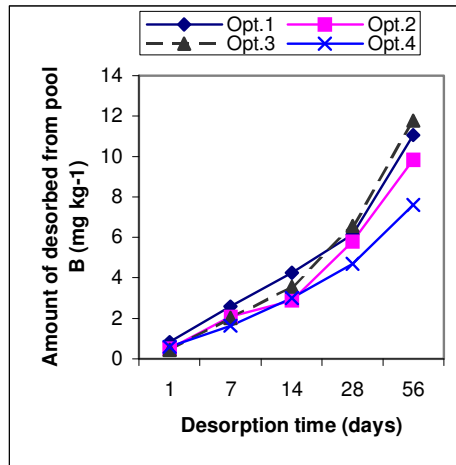
**Figure 5.1(a-d).** Simulated P desorption from pool A (SP<sub>A</sub>) of the different P treatments and shaking options



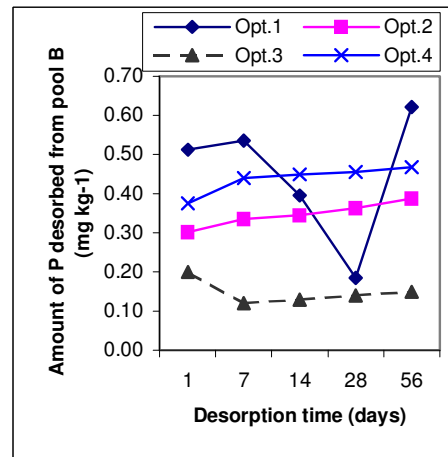
a) MNPK



b) MNK



c) NPK



d) NK

*Figure 5.2 (a-d).* Simulated P desorption from pool B ( $SP_B$ ) of the different P treatments and shaking options

### 5.3.2 Plant growth as related to phosphorus desorption kinetics

Correlations between the rate coefficients  $k_A$  and  $k_B$  ( $\text{day}^{-1}$ ) with maize grain yield ( $\text{t ha}^{-1}$ ) for the different shaking options were made and the results are presented in Table 5.3. The rate coefficients for the different shaking options are labeled as illustrated on Table 5.3. Significant correlations were obtained between the labile pool rate coefficients [ $k_{A1}$  ( $0.92^{**}$ ),  $k_{A2}$  ( $0.99^{**}$ ),  $k_{A3}$  ( $0.92^{**}$ ) and  $k_{A4}$  ( $0.92^{**}$ )] and maize grain yield. The labile pool represents the P pool with fast release kinetics that comprises presumably primarily P bound to the reactive surfaces that is in direct contact with the aqueous phase. This pool is presumed to be easily available to plants in a reasonably short period of time (Lookman et al., 1995). Comparing the values of the rate coefficients for this pool revealed that the rate coefficient for option 2 resulted in the best correlation with maize grain yield. The role of this pool in general enhanced with decreasing desorption time corroborating the pronounced contribution of this pool for short desorption studies. The only rate coefficient from the less labile pool,  $k_B$ , which showed a significant but moderate correlation ( $r = 0.78^*$ ) with corn grain yield, was only  $k_{B1}$ . This pool represents the P pool with slow release kinetics that results from slow dissolution kinetics or from slow diffusion from the matrix of sesquioxide aggregates (Koopmans et al., 2004). This pool will be available only over a long period of time and that is probably why the correlation was strong only in the case of option 1 which exhibited the longest desorption period. This evidenced that the role of this pool appeared to be much less pronounced with decreasing time of desorption.

Albeit the P pools are theoretically grouped in to these two discrete pools for the sake of convenience, they are presumed to involve simultaneously in the uptake process as reported previously. It is therefore important to take in to account the sum of the rate constants when such correlations are made. The sum of the rate constants ( $k_A+k_B$ ) in general showed significant correlations with maize grain yield in all shaking options considered as depicted on Table 5.3. The rate coefficient for the labile fraction,  $k_A$ , strongly correlated with the sum of  $k_A$  and  $k_B$  ( $k_A+k_B$ ) unlike the less labile fraction,  $k_B$ , revealing the predominant contribution of the labile P fraction in replenishing the soil solution P than the less labile form in all the options considered at least for the extraction period considered in the present study.

The cumulative amount of P extracted by the DMT-HFO was also correlated with yield and Bray 1P as depicted in Table 5.4. Both the cumulative amount of P ( $\text{mg kg}^{-1}$ ) extracted by DMT-HFO and the change in DMT-HFO- $P_i$  ( $\text{mg kg}^{-1}$ ) showed no statistically significant correlations with maize grain yield in all the options considered. However, option 2 seemed to correlate better in both cases as judged from their r-values. Statistically significant correlations were observed between DMT-HFO- $P_i$  and Bray-1P in all shaking options for both cases. This observation probably indicates the ability of these extractants to extract the labile P. Bray-1P has also showed a significant correlation with maize yield. Although the correlation between DMT-HFO- $P_i$  and Bray-1P was found to be very strong and statistically significant, the correlation each showed with maize yield was apparently opposite, the former resulted in no correlation for all the shaking procedures considered in the present study, while the latter resulted in moderately strong and significant correlation with the yield parameter.

**Table 5.3** Pearson correlations between the rate coefficients  $k_A$ ,  $k_B$ , and  $k_A + k_B$  with dry maize grain yield for the different options,  $N=4$

♦ Option1					Option2				
	Yield	$K_{A1}$	$K_{B1}$	$K_{A1}+K_{B1}$		Yield	$K_{A2}$	$K_{B2}$	$K_{A2}+K_{B2}$
$K_{A1}$	0.92**	-	0.73	0.99**	$K_{A2}$	0.99**	-	0.41	0.99**
$K_{B1}$	0.79*	0.73	-	0.76	$K_{B2}$	0.43	0.41	-	0.44
$K_{A1}+K_{B1}$	0.93**	0.99**	0.76	-	$K_{A1}+K_{B2}$	0.99**	0.99**	0.44	-
Option3					Option4				
	Yield	$K_{A3}$	$K_{B3}$	$K_{A3}+K_{B3}$		Yield	$K_{A4}$	$K_{B4}$	$K_{A4}+K_{B4}$
$K_{A3}$	0.92**	-	0.51	0.99**	$K_{A4}$	0.92**	-	0.40	0.99**
$K_{B3}$	0.59	0.51	-	0.55	$K_{B4}$	0.60	0.40	-	0.48
$K_{A3}+K_{B3}$	0.93**	0.99**	0.55	-	$K_{A4}+K_{B4}$	0.94**	0.99**	0.48	-

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

♦ Option 1 represents the control; Options 2, 3, and 4 represent continuous shaking for 75%, 50%, & 25% of the control.

A possible explanation for the observed difference between the two extractants could be obtained by comparing the amount of P extracted by both extractants as depicted in Table 3.1. NK and MNPK treated soils released roughly similar amount of P by both extractants where as NPK and MNK desorbed a DMT-HFO- $P_i$  extract, which was nearly half extracted by Bray-1P. The relatively lower amount of P desorbed by these treatments could be a possible reason for the poor correlation observed between DMT-HFO- $P_i$  and maize grain yield.

**Table 5.4** Pearson correlations between the cumulative DMT-HFO-P<sub>i</sub> (mg kg<sup>-1</sup>) and the change in DMT-HFO-P<sub>i</sub> (mg kg<sup>-1</sup>) with dry maize grain yield, N=4

§ Cumulative DMT-HFO-P <sub>i</sub> (mg kg <sup>-1</sup> )				‡ ΔDMT-HFO-P <sub>i</sub> (P max- P min)(mg kg <sup>-1</sup> )			
* Option 1				Option 1			
	Yield	DMT-HFO-P <sub>i</sub>	Bray-1P		Yield	DMT-HFO-P <sub>i</sub>	Bray-1P
DMT-HFO-P <sub>i</sub>	0.57	-	0.92**	DMT-HFO-P <sub>i</sub>	0.56	-	0.91**
Bray-1P	0.84*	0.92**	-	Bray-1P	0.84*	0.91**	-
Option 2				Option 2			
	Yield	DMT-HFO-P <sub>i</sub>	Bray-1P		Yield	DMT-HFO-P <sub>i</sub>	Bray-1P
DMT-HFO-P <sub>i</sub>	0.58	-	0.92**	DMT-HFO-P <sub>i</sub>	0.57	-	0.92**
Bray-1P	0.84*	0.92**	-	Bray-1P	0.84*	0.92**	-
Option 3				Option 3			
	Yield	DMT-HFO-P <sub>i</sub>	Bray-1P		Yield	DMT-HFO-P <sub>i</sub>	Bray-1P
DMT-HFO-P <sub>i</sub>	0.58	-	0.92**	DMT-HFO-P <sub>i</sub>	0.54	-	0.90**
Bray-1P	0.84*	0.92**	-	Bray-1P	0.84*	0.90**	-
Option 4				Option 4			
	Yield	DMT-HFO-P <sub>i</sub>	Bray-1P		Yield	DMT-HFO-P <sub>i</sub>	Bray-1P
DMT-HFO-P <sub>i</sub>	0.55	-	0.90**	DMT-HFO-P <sub>i</sub>	0.55	-	0.90*
Bray-1P	0.84*	0.90**	-	Bray-1P	0.84*	0.90*	-

\*Significant at 0.05 probability level

\*\*Significant at 0.01 probability level

\* Option 1 represents the control; Options 2, 3, and 4 represent continuous shaking for 75%, 50%, & 25% of the control.

§ Cumulative P extracted by DMT-HFO, which is the P extracted after 56, 42, 28 and 14 days of extraction for options 1,2,3 & 4 respectively.

‡ The change in P (ΔDMT-HFO-P<sub>i</sub>) calculated as the difference between the maximum and minimum extraction time for each options (56 vs.1, 42 vs. 0.75, 28 vs. 0.5 and 14 vs. 0.25 days).



In general, the correlation values among the rate coefficients and the cumulative P extracted by DMT-HFO with maize grain yield revealed that option 2 seemed relatively better than the other options. However, according to this study, the rate coefficients appeared to be better indices of plant availability than the amount of P extracted by DMT-HFO, as the latter showed no significant correlation with maize grain yield. In this research correlation with other plant yield parameters such as P uptake and relative plant response was not conducted due to lack of relevant data. More work relating these plant indices with desorption indices is therefore required. Data from a wider range of soils is also needed to evaluate the universality of this method.

#### **5.4 CONCLUSIONS**

The effect of varying shaking options on the extractable DMT-HFO- $P_i$  for each treatment showed no statistically significant difference for all treatments except the MNPK treated plots. The amount of P extracted was found to be consistent with the time of extraction for all treatments in all four options: option1>option2>option3>option 4 which is consistent with the general expectation that the amount of P extracted by a given extractant increases with increasing time of extraction.

From the results observed by relating rate coefficients and the cumulative P extracted by DMT-HFO with maize grain yield, the rate coefficients appeared to be better indices of plant availability than the amount of P extracted by DMT-HFO, as the former only showed significant correlation with maize grain yield. Thus, based on the r values, option 2 seemed relatively better than the others since it showed the strongest

correlation. In this research correlation with other plant yield parameters such as P uptake and relative plant response was not conducted due to lack of relevant data. More work relating these plant indices with desorption indices is therefore required. Besides, data from a wider range of soils is also needed to evaluate the universality of this method.