

## Long-term kinetics of phosphate desorption from soil and its relationship with plant growth

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Accepted 20 April 2008

Knowledge on the availability of residual P in soils is of great importance for fertilization management. The use of dialysis membrane tubes filled with hydrous ferric oxide solution has recently been reported as an effective way to characterize P desorption over long-term laboratory studies. However, there is relatively little information relating the desorption indices of this method to plant parameters. The objective of this research was to relate the kinetic data generated using the DMT-HFO method to shoot dry matter yield of maize grown under greenhouse conditions. Accordingly, the labile pool rate coefficient ( $k_A$ ) showed a highly significant correlation with both shoot dry matter yield ( $r = -0.994^{**}$ ) and plant P uptake ( $r = -0.982^{**}$ ). The less labile rate coefficient ( $k_B$ ) also showed a significant correlation with both shoot dry matter yield ( $r = -0.856^*$ ) and P uptake ( $r = -0.893^*$ ). The correlation between the cumulative P extracted and shoot dry matter yield was highly significant. A strongly significant correlation was also observed between Bray 1P and shoot dry matter yield. Judging from the r-values, both the kinetic parameters and the cumulative amount of P desorbed could serve as reliable indices of plant available P revealing the effectiveness of this method in estimating the availability of residual P in soils. However, assessment of the reliability of this method at field level is important. Data from a wider range of soils is necessary to evaluate the universality of this method.

**Keywords:** Desorption of P, dialysis membrane tubes, hydrous ferric oxide solutions, phosphorus release rate, soil test methods

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### Introduction

The kinetics of P desorption is a subject of importance in soil and environmental sciences primarily because P uptake by plants occurs over a period of time. Thus, kinetic information is required to properly characterize the P supplying capacity of soils, to design P-fertilizer management to optimize efficiency, to reduce environmental pollution, and to develop guidelines for the disposal of P-rich wastes onto the land (Skopp, 1986). Another reason for kinetic studies is to obtain information on reaction mechanisms.

In order to assess long-term P desorption kinetics, it is necessary to sufficiently suppress the backward resorption reaction. This can be done by introducing effective P sink into the system. Van der Zee *et al.* (1987) proposed the use of Fe-oxide impregnated filter paper strips (Fe-oxide strips) as a promising method to study the P release kinetics of soils. Acting as a sink for P, the Fe-oxide strips have a sounder theoretical basis than the chemical extractants in estimating available soil P (Sharples, 1996). However, this method was not found to be suitable for long-term desorption studies as it may lead to errors due to adhesion of fine P-rich particles to the paper strips and due to the mechanical instability of the paper when used for long desorption studies (Freese *et al.*, 1995; Lookman *et al.*, 1995). Recently, use of dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO) in place of resin/Fe-oxide paper strips for studying long-term P dynamics has been proposed (De Jager & Claassens, 2005; Ochwoh *et al.*, 2005). Nonetheless, relatively little information is available in the literature in relation to the use of this method. Lookman *et al.* (1995) studied the kinetics of P desorption using this procedure. They concluded that P desorption could be well described by a two component first order model. They also reported that no desorption maximum was

reached in the entire period of desorption (1600 h). Research was also done which linked short-term soil P tests to long-term soil P kinetics (Koopmans *et al.*, 2001; Maguire *et al.*, 2001). Recently, studies were also made on some South African soils using the DMT-HFO method as a phosphate sink. De Jager and Claassens (2005) investigated the desorption kinetics of residual and applied P to acid sandy clay soils from Mpumalanga, South Africa. They reported that no desorption maximum was reached after 56 days of shaking. However, there is still a paucity of information on the relationship between the kinetics of phosphorus release using this new method and plant yield parameters. The objective of this research was to relate the kinetic data generated using the DMT-HFO method to maize yield.

### Theory

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



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

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

$$\begin{aligned} P_{R(t)} &= SP_{A0} - SP_{A(t)} + SP_{B0} - SP_{B(t)} \\ &= SP_{A0} - SP_{A0} e^{-k_A t} + SP_{B0} - SP_{B0} e^{-k_B t} \\ &= SP_{A0} (1 - e^{-k_A t}) + SP_{B0} (1 - e^{-k_B t}) \end{aligned} \quad (2)$$

It was assumed that the rate constant of P release from the soil

was equal to the rate constant of P adsorption ( $k_A$ ) by the DMT-HFO. The rate constant of P adsorption ( $k_A$ ) by the DMT-HFO was obtained from a plot of the natural logarithm ( $\ln$ ) of the P adsorbed by the DMT-HFO against time with the slope as  $k_A$ . In this work the rate constants  $k_A$ ,  $k_B$  and cumulative amount of P desorbed were correlated with maize yield. Lookman *et al.*, (1995) and De Jager and Claassens (2005) have provided details of the mathematical derivation and the assumptions behind this approach.

## Material and methods

Topsoil samples (0-250 mm) were collected from the long-term fertilizer trial initiated in 1976 by the Nooitgedacht Agricultural Development Center in Ermelo, Mpumalanga, South Africa in March 2005. This trial was conducted on an Avalon soil type. Soil samples were collected from selected P treatments. The samples were cored from three sites on each plot and three replications at each site. The samples were air-dried and ground to pass through a 2 mm sieve. Composite samples were used for the subsequent analyses. The soil samples collected were treated with different levels of P. The control  $P_0L_0$  received no P since the inception of the trial. The  $P_1L_1$  and  $P_2L_1$  treatments respectively received 35 and 69 kg P ha<sup>-1</sup> in years 1977/78 and 1979/80. Potassium was band placed annually at a rate of 50 kg K ha<sup>-1</sup> year<sup>-1</sup> as potassium chloride (KCl). Limestone ammonium nitrate was applied annually at rates determined by the climatic conditions of the season. Since then no P has been applied to these soils despite the continuous maize production for more than 20 years. All the treatments except the control considered here were also limed to ensure the pH of the soil at an acceptable range (pH  $\geq$  6) for maize production. Du Preez and Claassens (1999) provided a detailed fertilization history of these soils. Table 1 shows some selected physicochemical properties of the soils for different treatments. The pH (KCl) of the samples was determined by dispersing 20 g of dried soil in 50 ml of 1M KCl. After 2 h of end-over-end shaking at 20 rpm, the pH was determined in the soil suspension (Freese *et al.*, 1995). Particle size analysis was done using the hydrometer method after dispersion of the soil with sodium hexametaphosphate. Organic C was determined by the dichromate oxidation technique while exchangeable Ca, Mg and K were determined by neutral 1 M ammonium acetate extraction. Total soil P ( $P_T$ ) was determined on sub-samples of 0.5 mg soil by the addition of 5 ml concentrated H<sub>2</sub>SO<sub>4</sub> and heating to 360°C on a diges-

tion block with subsequent stepwise (0.5 ml) additions of H<sub>2</sub>O<sub>2</sub> until the solution was clear (Thomas *et al.*, 1967). The available phosphorus was determined using Bray and Kurtz (Bray-1P) method (0.03 M NH<sub>4</sub>F + 0.025 M HCl). Details of analytical methods are described in Kuo (1996) and The Non-Affiliated Soil Analysis Work Committee (1990).

## Long-term desorption study

A long-term desorption study was carried out using 0.15 m DMT strips (Medicell International Ltd., London; dialysis tubing: Visking, size 3 20/32 inches, approximate pore size 2.5-5.0 nm; membrane thickness 3  $\mu$ m) filled with 10 ml hydrous ferric oxide solution similar to that described by Freese *et al.* (1995). The dialysis membrane tubes, filled with hydrous ferric oxide, were placed in a 200 ml plastic bottle with 1g of soil and 80 ml of 2 mM CaCl<sub>2</sub> and 0.3 mM KCl solution. All the treatments were performed in triplicate. The plastic bottles were continuously shaken for 56 days on an end-over-end shaker at a speed of 120 oscillations per minute (opm). On days 1, 7, 14, 21, 28 and 42 the DMT-HFO was replaced with new DMT-HFO. When it was replaced, a glass rod was used to rub off the soil material adhering to the DMT. At each time interval, three of the tubes were cut open and the contents transferred to glass bottles. The suspension was then dissolved in 1 ml of concentrated sulfuric acid. The hydrous ferric oxide was analysed for P colorimetrically with the molybdate blue method using ascorbic acid as a reductant (Murphy & Riley, 1962). A standard series and blank were prepared with the same background Fe and sulfuric acid.

## Greenhouse experiment

A greenhouse experiment was carried out to investigate the relationship between dry matter yield and P uptake using the same soil-P level combinations tested in the laboratory. Three replicates of each treatment were prepared by planting six maize seeds into 4 L pots containing 6 kg of soil each, to which 50 mg kg<sup>-1</sup> N had been applied prior to planting. One week after planting seedlings were thinned to four plants per pot and two weeks after planting 50 mg kg<sup>-1</sup> N was applied. Shoot dry matter yield was determined at harvest, after drying fresh samples at 68°C for 48 h in an oven. The P content of shoot dry matter was determined on 0.5 mg samples by the addition of 5 ml concentrated H<sub>2</sub>SO<sub>4</sub> and heating to 360°C on a digestion block with subsequent stepwise (0.5 ml) additions of H<sub>2</sub>O<sub>2</sub> until the solution was clear (Thomas *et al.*, 1967).

**Table 1** Selected physical and chemical properties of the soil samples studied

Sample types	pH (KCl)	$P_{total}$	Bray-1P	Ca <sup>‡</sup>	Mg <sup>‡</sup>	K <sup>‡</sup>	Particle size distribution (%)				Organic C (%)
							Clay	Silt	Sand	Sand	
$P_0L_0$	3.90	303.47	2.54	73	23	89	5.8	9.3	83.0	0.48	
$P_1L_1$	5.40	333.83	2.26	423	74	163	9.0	6.0	82.2	0.63	
$P_2L_1$	5.24	363.98	13.71	452	80	138	5.8	9.3	82.8	0.67	

§  $P_0L_0$  = received no phosphorus and lime since the inception of the trial and served as a control;  $P_1L_1$  = treated with 35 kg P ha<sup>-1</sup> P and lime and  $P_2L_1$  = treated with 69 kg ha<sup>-1</sup> P and lime

‡Extractable Ca, Mg and K: Determined using 1 M ammonium acetate at pH 7

## Data analysis

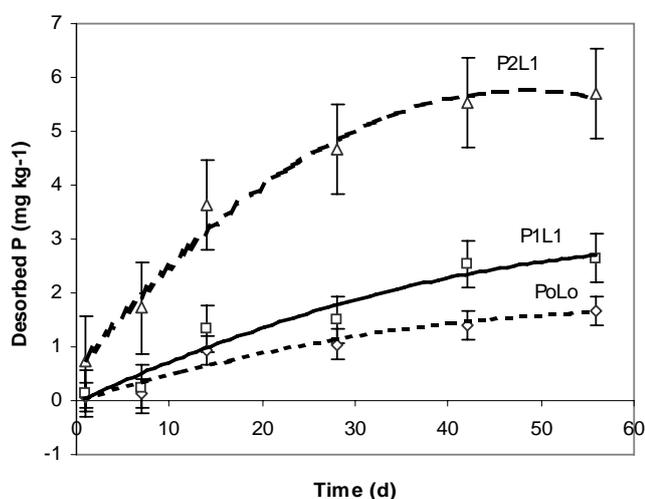
The data obtained were statistically analysed using Statistical Analysis System (SAS Institute 2004). Analysis of variance was done using the General Linear Model (GLM) procedure. The Tukey test was used to determine significant differences at  $\alpha = 0.05$ . Correlations of the rate parameters and the cumulative amount of P released with plant yield were done using Pearson linear correlation, PROC CORR (SAS Institute, 2004).

## Results and discussion

### Long-term desorption of P

The amount of  $P_i$  extracted by DMT-HFO was significantly influenced ( $P \leq 0.05$ ) both by the P content and extraction time. The change of this fraction, however, was not significant between  $P_1L_1$  and the control (data not shown). The cumulative P desorbed was higher in the  $P_2L_1$  treatment (0.72-5.71 mg kg<sup>-1</sup>) and lower in the control (0.06-1.67 mg kg<sup>-1</sup>) at all levels of extraction time (1–56 days). 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 though the degree of increment was not pronounced (Figure 1). This was 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 & Claassens, 2005). This can be explained by P desorbing quickly from the surface of Fe and Al oxides, followed by relatively slow diffusion into the matrix of sesquioxides (Pavlatou & Polyzopoulos, 1988). No desorption maximum was reached after 56 days. Similar results have also been reported by other researchers (Lookman *et al.*, 1995; Maguire *et al.*, 2001; Koopmans *et al.*, 2001; De Jager & Claassens, 2005; Ochwoh *et al.*, 2005).

The percentage of P extracted in all cases was very low as compared to the total P (data not shown). Similar results have also been reported by other researchers (Koopmans *et al.*,



**Figure 1** Cumulative desorbable P with time, extracted using iron oxide filled dialysis membrane tubes for the different treatments; error bars represent standard errors of the mean.

2001; De Jager & Claassens, 2005; Ochwoh *et al.*, 2005). In this study the last time the soils received any P was in the 1979/80 season, which means the soils were incubated on average for nearly 25 years. Cropping continued after P application discontinued, which means, at the same time, that P in the soil was also depleted. It was therefore expected that, as a result of the longer equilibration time and P depletion, the easily available P would be lower.

### Plant growth as related to phosphorus desorption kinetics

Correlations between the rate coefficients  $k_A$  and  $k_B$  (day<sup>-1</sup>) with yield parameters such as shoot dry matter yield and plant P uptake were made as shown in Table 2. The correlation between the rate coefficients and plant yield was negative in all cases because of the decreased rate of P release with increased cumulative P content of the soils considered. The rate of P release followed the order  $P_0L_0 > P_1L_1 > P_2L_1$  whereas the cumulative P released followed the reverse order. The plant yield obtained was also in accordance with the total P content of the treatments. The labile pool rate coefficient  $k_A$  showed a highly significant correlation with both shoot dry matter yield ( $r = -0.994^{**}$ ) and P uptake ( $r = -0.982^{**}$ ). This pool represents the P pool with fast release kinetics that comprises presumably primarily P bound to the reactive surfaces that are in direct contact with the aqueous phase. This pool is presumed to be easily available to plants in a short period of time (Lookman *et al.*, 1995). The less labile rate coefficient  $k_B$  also showed a significant correlation with both shoot dry matter yield ( $r = -0.856^*$ ) and P uptake ( $r = -0.893^*$ ). 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 would be available only over a long period of time and that is probably why the correlation was weaker. Although the P pools are theoretically grouped into these two discrete pools for the sake of convenience, the fact that both pools are simultaneously involved in the uptake process indicates that one should take the effect of both into account when such a correlation is made. Thus, the sum of the rate constants ( $k_A + k_B$ ) showed a strongly significant correlation with both shoot dry matter yield ( $r = -0.999^{**}$ ) and P uptake ( $r = -0.994^{**}$ ). The rate coefficient for the labile fraction,  $k_A$ , strongly correlated ( $r = 0.997^{**}$ ) with the sum of  $k_A$  and  $k_B$  ( $k_A + k_B$ ) unlike the less labile fraction,  $k_B$  ( $r = 0.840^*$ ) revealing the larger contribution of the labile P fraction in replenishing the soil solution P than the less labile fraction for the extraction period considered in this study.

The cumulative amount of P extracted by the DMT-HFO

**Table 2** Correlation between the rate coefficients ( $k_A$  and  $k_B$ , day<sup>-1</sup>) shoot dry matter yield and P uptake ( $n = 3$ )

	Dry matter yield	P-uptake	$k_A + k_B$
$k_A$	-0.994 <sup>**</sup>	-0.982 <sup>**</sup>	0.997 <sup>**</sup>
$k_B$	-0.856 <sup>*</sup>	-0.893 <sup>*</sup>	0.840 <sup>*</sup>
$k_A + k_B$	-0.999 <sup>**</sup>	-0.994 <sup>**</sup>	-

<sup>\*\*</sup>Significant at 0.01 probability level.

<sup>\*</sup>Significant at 0.05 probability level

**Table 3** Correlation between the cumulative P desorbed over the 56-day period and plant parameters (n = 3)

P extracted	Dry matter yield	P uptake	Bray-1P
mg kg <sup>-1</sup>			
HFO-Pi	0.997**	0.999**	0.982**
Bray-1P	0.965**	0.982**	-

\*\*Significant at 0.01 probability level.

\*Significant at 0.05 probability level

over the 56-day period was also correlated with shoot dry matter yield and Bray-1P (Table 3). The correlation between the cumulative P extracted and shoot dry matter yield was highly significant. The Bray-1P also showed strong correlation with shoot dry matter yield. Based on the r-values, both the kinetic parameters and the cumulative amount of P desorbed could serve as reliable indices of plant available P, suggesting the importance of the DMT-HFO method in predicting the availability of P in long-term desorption studies.

### Conclusions

According to this study, cumulative P released with time followed the same pattern for all P treated soils, with an initial rapid release of P, approximately within the first two weeks, followed by a slower release that was still continuing after 56 days of extraction. Desorption maximum was not reached during the period of extraction, indicating that desorption can continue for a period longer than 56 days. Both the kinetic parameters and the amount of P extracted showed highly significant correlations with yield parameters and hence could be reliable indices of plant available P. The present study suggests that the DMT-HFO method can serve as analytical tool to assess the availability of residual P in soils. However, assessment of the reliability of this method at field level is important. Data from a wider range of soils are necessary to evaluate the universality of this method.

### Acknowledgments

The authors would like to thank the University of Haramaya (Agricultural Research and Training Program), Ethiopia for granting financial assistance and the Nooitgedacht Agricultural Development Centre in Ermelo, Mpumalanga, South Africa for allowing us to use their long-term fertilizer trial.

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