CHAPTER 8 [*]

Phosphate desorption kinetics study for Avalon soils and its relationship with plant growth

8.1 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 span of time. Thus, kinetic information is required to properly characterize the P supplying capacity of soils, to design fertilizer-P 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 study is to obtain information on reaction mechanisms (Skopp, 1986).

In order to assess long-term P desorption kinetics, it is necessary to sufficiently suppress the back ward resorption reaction. Introducing effective P sink into the system can serve the purpose. 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

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chemical extractants in estimating available soil P (Sharply, 1996). However, this method was found to be not well applicable 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 DMT-HFO in place of resin/Fe-oxide paper strips for studying long-term P dynamics has been proposed (De Jager and Claassens, 2005; Ochwoh et al. 2005).

However, relatively little information is available on 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 (1600hrs). Research was also done which linked short-term soil P tests to long-term soil P kinetics (Koopmans et al., 2001; Maguire et al., 2001). Recently, studies were also made on some South African soils using DMT-HFO method as a phosphate sink. De Jager and Claassens (2005) investigated the desorption kinetics of residual and applied P to an 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 kinetics of phosphorus release using this new method and plant yield parameter. The objective of this research was to relate the kinetic data generated using the DMT-HFO method to maize yield at the green house level.

8.2 MATERIALS AND METHODS

The sampling procedure and experimental site history of the soil samples used in this experiment are detailed in Section 7.2. Table 7.2 shows some selected physical and chemical properties of the different treatments.

8.2.1 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) the detail of which is presented in Section 3.2.3. We followed the same procedure for these samples too.

8.2.2 Greenhouse experiment

The detail of this particular experiment is as detailed in Section 7.2.4.

8.2.3 Data analysis

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

8.3 RESULTS AND DISCUSSION

8.3.1 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 although the difference of this fraction was not significant between P_1L_1 and the control (Table 7.3). The cumulative P desorbed was higher in the P_2L_1 treatment (0.72-5.71 mg kg^{-1}) and lower in the control (0.06-1.67 mg kg^{-1}) 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 with in the first two weeks (14 days), followed by a slower release that was still continuing after 56 days of extraction (Figure 8.1).
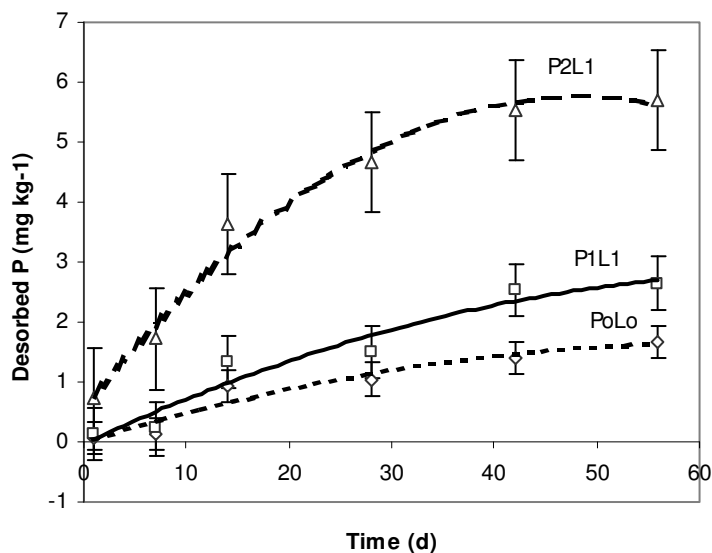

Figure 8.1. Cumulative P desorbed over time, extracted using DMT-HFO for the

different treatments; error bars represent standard errors of the mean.

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 from the surface of Fe and Al oxides, followed by relatively slow diffusion in to the matrix of sesiquioxides (Pavlatou and Polyzopoulos, 1988). No desorption maximum was reached by the end of the 56 day (1344h) period analogous to the result documented in section 2.3.1 for the long-term fertilized soils collected from the University of Pretoria. Similar reports have also been reported by other researchers (Lookman et al., 1995; Maguire et al., 2001; Koopmans et al., 2001; De Jager and Claassens, 2005; Ochwoh et al., 2005).

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 (Koopmans et al., 2001; De Jager and Claassens, 2005; Ochwoh et al. 2005). In this study the last time the soils received any P was in the season 1979/80, which means the soils were incubated on average for nearly 25 years. Cropping did continue after P application was 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 labile P would be lower.

8.3.2 Plant growth as related to phosphorus desorption kinetics

Correlations between the rate coefficients k_A and k_B (day^{-1}) with yield parameters such as shoot dry matter yield and plant P uptake were made as illustrated in Table 8.1. 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 $P_oL_o>P_1L_1>P_2L_1$ 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 desorption 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

Table 8.1 Correlation between the kinetic parameter k (day [-1])(Rate coefficient) shoot

dry matter yield and P uptake; N=3

	Dry matter Yield	P-uptake
	mg kg^{-1}	
k_A	-0.994[**]	-0.982[**]
k_B	-0.856[*]	-0.893[*]
k_A+k_B	-0.999[**]	-0.994[**]

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

reactive surfaces that is in direct contact with the aqueous phase. This pool is presumed to be easily available to plants in a reasonably short period of time (Lookman et al., 1995). The 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 will be available only over a long period of time and that is probably why the correlation was lower. Although the P pools are theoretically grouped in to these two discrete pools for the sake of convenience, the fact that both pools involve simultaneously in the uptake process indicates that one should take in to account the effect of both when such correlations are made. Thus, the sum of the rate constants (k_A+k_B) showed a highly significant correlation with both shoots dry matter yield (r = -0.999**) and P uptake (r = -0.994**).

Table 8.2. Correlations between the cumulative P desorbed over a 56-day period, shoot dry matter yield, P uptake and Bray 1P; N=3

P extracted	Dry matter yield	P uptake	Bray 1P
		mg kg^{-1}	
HFO-Pi	0.997**	0.999**	0.982**
Bray 1P	0.965**	0.982**	-

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

The cumulative amount of P extracted by the DMT-HFO over a 56-day period was also correlated with yield and Bray 1P as shown in Table 8.2. The correlation between the cumulative P extracted and maize yield was highly significant. The correlation between Bray 1P and maize yield was also highly significant. 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. This is contrary to the results obtained for the other long-term soil samples carried out at the field level as documented in Section 3.3.2. In the later case it was only the rate coefficient parameter that showed a significant correlation with the yield. The reason for this disparity could be that experiments conducted at the field level are difficult to control and plant response could be influenced by several interacting soil, plant and climatic factors besides P content.

8.4 CONCLUSIONS

According to this study, cumulative P released with time followed the same pattern for all P treated soils, with an initial rapid release of P with in the first two weeks (14 days), followed by a slower release that was still continuing after 56 days of extraction. Desorption maximum was not reached during the entire period of extraction time, indicating that desorption can continue for a longer period 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. However, data from a wider range of soils is also necessary to evaluate the universality of this method.

CHAPTER 9

General conclusions and recommendations

9.1 Kinetics of phosphorus desorption and its relationship with plant growth

The kinetics of phosphate desorption was done using DMT-HFO method. The cumulative P released with time followed the same pattern for both soils from UP (University of Pretoria) and Ermelo, Mpumalanga; with an initial rapid release of P followed by a slower release that was still continuing after 56 days of extraction. No desorption plateau was reached on both cases during the entire period of extraction time, indicating that desorption can continue for a longer period than 56 days. The rate coefficients were in the range of 0.0059 - 0.104 day $^{-1}$ for the UP soils and 0.2294 - 0.1313 day^{-1} for Ermelo soils. The P desorption rate was higher for Ermelo soils than the UP soils. These variations could be ascribed to the differences in the physical properties of the two soils. The clay content of the UP soils was about three times higher than the Ermelo soils and hence the lower rate of release. Nonetheless, the cumulative desorbed P was consistent with the total P content of the soils (UP>>Ermelo). The other notable difference observed on these two long-term trials was that in the case of UP soils the rate coefficient increased with increased P content of the different treatments hence the control being the least in its P content, resulted in the lowest rate of P release. However, the rate of P release declined with increased P content for Ermelo soils. The contribution made by SP_A was found to be higher than SP_B in the 56 days of extraction. However, the degree of increment with time showed that it is the less exchangeable pool (SP_B) that will control the release kinetics of the soil in the long term.

The rate coefficients showed significant correlations with plant yield parameters for both cases. The rate coefficient, therefore, appeared to be a good index of plant availability. The correlations between the cumulative amount of P desorbed and plant yield parameters however were not similar. Correlation between the cumulative P extracted and maize yield was not significant for soils collected from UP where as significant difference was observed for soils collected from Ermelo. The reason for this contrasting result could be attributed to the difference in the actual approach in making such a comparison. In the case of UP soils, the treatments were from a field trial where as in the case of Ermelo soils it was done in a pot trial. Experiments carried out at the field level are in general less controlled compared to what it would be when the same experiments were to be done at the green house level. The result from UP soils indicates that the plant response is probably influenced by several interacting soil, plant, and climatic factors besides P deficiency. However, in this research correlation with other plant yield parameters such us 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 to validate the above results especially under field condition. Besides, data from a wider range of soils is also needed to evaluate the universality of this method.

9.2 The dynamics of phosphorus and the relationship between different pools and plant growth

The use of successive desorption of P by DMT-HFO followed by subsequent fractionation as described by Hedley et al., (1982) or Tiessen and Moir (1993) was

employed to study the P dynamics of long-term fertilized soils from South Africa. The effect of P levels and extraction time was found to be statistically significant for all P fractions except the residual P pool in both soils. Almost all the inorganic P fractions decreased with increased time of extraction by DMT-HFO. The only inorganic fraction that showed an increasing trend was the $OH-P_i$ fraction from Ermelo. All the organic fractions in general increased with increased time of extraction for both cases that is attributed to the microbial immobilization of P (Stewart and Tiessen, 1987). Therefore, the contribution of the labile and non-labile Pi fractions in replenishing the solution Pi was significant where as the contribution by organic fractions was limited in replenishing the soil solution P for the desorption periods considered in this study.

The amount of P extracted by the different extractants (including total P) was correlated with dry matter yield and plant P uptake. This comparison was made between the different P extracts after 56 days of extraction by DMT-HFO and maize grain yield for UP soils and plant yield parameters such as shoot dry matter yield and P uptake for Ermelo Soils. Significant correlations were observed between maize grain yield and all the P pools and the total P except $DMT-HFO-P_i$ and HCO_3-P_o for the UP soils where as in the case of Ermelo soils, significant correlations were observed between the different P pools and plant yield except HCO_3-P_o, $C/HCl-P_o$ and P_t.

The decreasing trend in the inorganic fractions with time revealed their different contributions to the soil solution P extracted with DMT-HFO. In the case of UP soils, $NaHCO_3-Pi$, $NaOH-P_i$ and $C/HCl-Pi$ were the most important fractions that contributed in replenishing the soil solution P. Among the inorganic fractions, $C/HCl-P_i$ was the major contributor. This suggests that this fraction may be a buffer to the

more labile P fractions. The $C/HCl-P_i$ was also the fraction that decreased most for the Ermelo soil especially for the high P treatments indicating the importance of this fraction in replenishing the more labile P fractions.

9.3 Effect of varying shaking time on phosphorus desorption

The DMT-HFO method, similar to other soil P tests, exploits 100 percent of the soil sample volume, which is, much more than the percent root exploitation of plants. Therefore, exploiting the whole volume of the soil by continuous shaking may not represent 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. In this case an attempt to investigate the effect of varying the shaking periods was done. Four shaking options were considred. Continous shaking for 1, 7, 14 ,28, and 56 days, which is the usual approach, was assumed to be a conventional approach (option 1). Option 2 referred to a continous shaking for 75% of option 1. Option 3 referred to a continous shaking for 50 % of option 1 and option 4 referred to a continous shaking equivalent to 25% of option 1. The effect of varying shaking options on the extractable DMT-HFO-Pi for the different P treatments showed significant difference only for treatment that received the highest P (MNPK). 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 for shaking options 1, 2, 3, and 4 respectively. The only rate coefficient from the less labile pool, k_B , which showed a significant but moderate correlation ($r = 0.78^{*}$) with maize grain yield, was $k_{B1.}$ 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. However, the higher correlations observed between the sum of the rate coefficients and plant parameters as illustrated in the previous chapters indicates that this pool could contribute in replenishing the solution P over long periods and it appears that this approach to simulate the plants mode of action is not ideal.

The cumulative amount of P (mg kg^{-1}) extracted by DMT-HFO showed no statistically significant correlations with maize grain yield in all the options considered. Judging from the r-values, the rate coefficients appeared to be better indices of plant availability than the amount of P extracted by DMT-HFO. Option 2 seemed relatively better than the others since it showed the strongest correlation. So for soils with high releasing kinetics and high total P content, provided that the P release from the soil is the rate-limiting step, reducing the length of shaking time could shorten the duration one needs to complete the experiment with out influencing the predicting capacity of the methodology.

9.4 Short cut to the combined method

We employed a short cut combined method characterize the P supplying capacity of a soil and to understand the dynamics of soil P. The procedure used consecutive extraction of P from a soil sample, firstly by dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO) followed by subsequent P fractionation. However, this procedure is lengthy and time consuming and an approach to develop a way to shorten these P desorption studies in soils was important. The objective of chapter 6

was to propose a short cut method as an alternative to the conventional step-by-step method in understanding the P dynamics of long-term fertilized soils especially for soils where the P pool acting as a source in replenishing the labile P is already identified. The C/HCl-P_i was identified as a major source in replenishing the labile P pool from chapter 4. Comparison of the sum of DMT-HFO-P_i, NaHCO3-P_i, NaOH-P_i, D/HCl-P_i and C/HCl-P_i extracted by the modified Tiessen and Moir (1993) method with the sum of DMT-HFO-P_i and C/HCl-P_i extracted by the short cut approach, for all the extraction periods, resulted to very strong and significant correlations. Correlations between C/HCl-P_i and maize grain yield were also strongly significant for both methods. This study revealed that the short cut approach could be a simplified and economically viable option to study the P dynamics of soils especially for soils where the P pool acting as a source is already identified.

9.5 General remarks

Consecutive extraction procedures using dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO) followed by subsequent P fractionation procedure as described by De Jager and Claassens (2005) and Ochwoh et al., (2005) constitute a convenient laboratory method to investigate the kinetics of residual P release and to understand the dynamics of soil P. From the kinetic study, one can estimate the time frame of P release and the distribution of P between the labile and less labile forms. However, categorizing the P pools as labile and less labile P pools in the above way could be crude in the sense that it is not possible to identify which particular P pool involves in the replenishment of the P taken by the plants, which in this case was

approximated by using the DMT-HFO step. The importance of the subsequent fractionation would be to identify the principal less labile P fraction that acts as a major contributor to the more labile P pool. This combined method can approximate successive cropping experiments carried out either in the green house or field condition. The work done in this study focused on relating the P extracted by this method especially the DMT-HFO-P_i with plant yield parameter, to identify the P pools that served as a buffer in replenishing the labile P fractions, and to shorten the time required to carry out this kind of experiment. In general characterization of P using the combined method could be a more practical and environmentally responsible approach to P fertilizer recommendations. The DMT-HFO step has been regarded as a mild and nondestructive extractant influenced less by the soil's physicochemical properties making it suitable to study the fate of residual P. However, data from a wider range of soils is needed to evaluate the applicability of this method in this context.

9.6 Research needs

Use of successive extraction procedure employing hydrous ferric oxide in dialysis membrane tubes (DMT-HFO) as a phosphate sink is one of the promising methods to evaluate the fate of residual P especially for long-term fertilized soils. Only a limited research has been done since it was introduced for the first time about 12 years ago. One particular problem associated with this method is that it is lengthy and time consuming despite the attempt made in this study to shorten it to a certain extent. Besides, this methodology has not been done for soils of wider physical properties and documents relating the desorption indices of this method with plant yield

parameters are also scarce. More research in this regard is important to further the progress made so far. Little is also documented on the influences of soil type, pH, ionic strength and temperature on the labile and less labile rate constants and hence research related to these is also required.