

**Characterizing phosphate desorption kinetics from soil: An approach
to predicting plant available phosphorus**

by

Abi Taddesse Mengesha

**Submitted in partial fulfillment of the requirements for the
degree Doctor of Philosophy: Soil Science in the Faculty of
Natural and Agricultural Science University of Pretoria
Pretoria**

May 2008

TABLE OF CONTENTS

List of tables	vii
List of figures	x
Declaration	xii
Acknowledgements	xiii
Abstract	xvi
Chapter 1	
General introduction	1
Chapter 2	
Literature review	5
2.1 Sorption and desorption of phosphorus	6
2.2 Phosphorus sorption and desorption rates	7
2.3 Phosphorus status of South African soils	8
2.4 Chemical extractants	11
2.5 The sequential extraction of phosphorus	15
2.6 Methods to investigate and describe phosphorus desorption	17
2.6.1 Use of P free solutions	17
2.6.2 Use of materials that bind phosphate	19
Chapter 3	
Kinetics of phosphate desorption from long-term fertilized soils of South Africa and its relationship with maize grain yield	
3.1 Introduction	25
3.1.1 Theory	27
3.2 Materials and methods	29
3.2.1 Sampling procedure and experimental site history	29



3.2.2 Soil characterization	30
3.2.3 Long term desorption study	33
3.2.4 Field data	33
3.2.5 Data analysis	34
3.3 Results and discussion	34
3.3.1 DMT-HFO extractable P	34
3.3.2 Plant growth as related to phosphorus desorption kinetics	41
3.4 Conclusion	45
Chapter 4	
Effect of long-term phosphorus desorption using dialysis membrane tubes filled with hydrous iron oxide on phosphorus fractions	
4.1 Introduction	47
4.2 Materials and methods	50
4.2.1 Fertilization history and soil analyses	50
4.2.2 Long term desorption study	50
4.2.3 Fractionation procedure	51
4.2.4 Field data	52
4.2.5 Data analysis	52
4.3 Results and discussion	52
4.3.1 P recovery and distribution	52
4.3.2 Effect of P level and extraction time on the labile P (DMT-HFO-P _i + HCO ₃ -P _i +P _o) fraction	54
4.3.2.1 DMT-HFO extractable P _i	54
4.3.2.2 0.5M NaHCO ₃ -extractable P _i	58
4.3.2.3 0.5M NaHCO ₃ -extractable P _o	59

4.3.3 Effect of P level and extraction time on the less labile	
P (0.1M NaOH-P _i + 0.1M NaOH-P _o +1M HCl-P _i) fraction	61
4.3.3.1 0.1M NaOH-extractable P _i	61
4.3.3.2 0.1M NaOH-extractable P _o	63
4.3.3.3 1M HCl-extractable P _i	65
4.3.4 Effect of P level and extraction time on the stable	
P [(C/HCl-P _i + C/HCl-P _o +(C/H ₂ SO ₄ +H ₂ O ₂ -P)] fraction	66
4.3.4.1 C/HCl- extractable P _i	66
4.3.4.2 C/HCl- extractable P _o	67
4.3.4.3 C/H ₂ SO ₄ + H ₂ O ₂ - extractable P	68
4.3.5 Plant growth as related to phosphorus fractions	69
4.4 Conclusion	72
Chapter 5	
Effect of shaking time on long term phosphorus desorption using dialysis membrane tubes filled with hydrous iron oxide	
5.1 Introduction	73
5.2 Materials and methods	75
5.2.1 Long term phosphate desorption experiment	75
5.2.2 Modification of the shaking time	75
5.2.3 Field data	77
5.2.4 Data analysis	77
5.3 Results and discussion	77
5.3.1 DMT-HFO-P _i	77



5.3.2 Plant growth as related to phosphorus desorption kinetics	83
5.4 Conclusion	87
Chapter 6	
Short cut approach alternative to the step-by-step conventional soil phosphorus fractionation method	
6.1 Introduction	89
6.2 Materials and methods	93
6.2.1 Long-term desorption study	93
6.2.2 Fractionation procedure	94
6.2.3 Short cut approach to a modified fractionation procedure	94
6.2.4 Field data	95
6.2.5 Data analysis	95
6.3 Results and discussion	95
6.3.1 Modifications made on the C/HCl step of Tiessen and Moir (1993) method	95
6.3.2 DMT-HFO-extractable P_i	99
6.3.3 C/HCl extractable P_i	100
6.3.4 Plant growth as related to phosphorus extracts by DMT-HFO and C/HCl	105
6.4 Conclusion	107

Chapter 7

Long-term phosphorus desorption using dialysis membrane tubes filled with hydrous iron oxide and its effect on phosphorus pools for Avalon soils

7.1 Introduction	109
7.2 Materials and methods	111
7.2.1 Fertilization history and soil analysis	111
7.2.2 Long term desorption study	112
7.2.3 Fractionation procedure	113
7.2.4 Green house experiment	113
7.2.5 Data analysis	114
7.3 Results and discussion	114
7.3.1 Percent P distribution	114
7.3.2 Changes in inorganic P	117
7.3.2.1 DMT-HFO extractable P _i	117
7.3.2.2 0.5M NaHCO ₃ -extractable P _i	119
7.3.2.3 0.1M NaOH-extractable P _i	120
7.3.2.4 1M HCl-extractable P _i	123
7.3.2.5 C/HCl extractable P _i	124
7.3.3 Changes in organic P	125
7.3.3.1 0.5M NaHCO ₃ -extractable P _o	125
7.3.3.2 0.1M NaOH- extractable P _o	127
7.3.3.3 C/HCl- extractable P _o	128
7.3.4 C/H ₂ SO ₄ +H ₂ O ₂ - extractable P	129
7.3.5 Plant growth as related to phosphorus fractions	129
7.4 Conclusion	131



Chapter 8

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

8.1 Introduction	133
8.2 Materials and methods	135
8.2.1 Long term desorption study	135
8.2.2 Green house experiment	135
8.2.3 Data analysis	135
8.3 Results and discussion	136
8.3.1 Long term desorption study of P	136
8.3.2 Plant growth as related to phosphorus desorption kinetics	137
8.4 Conclusion	140

Chapter 9

General conclusions and recommendations

9.1 Kinetics of phosphorus desorption and its relationship with plant growth	141
9.2 The dynamics of phosphorus and the relationship between fractional pools and plant growth	143
9.3 Effect of varying shaking time on phosphorus desorption	144
9.4 Short cut to the combined method	146
9.5 General remarks	147
9.6 Research needs	148
References	149

LIST OF TABLES

Table 3.1 Selected physical and chemical properties of the soil samples studied	31
Table 3.2 N, P, K and manure (kg ha^{-1}) applied for treatments NK, NPK, MNK and MNPK	32
Table 3.3 Effect of P levels and extraction time on soil P desorption	35
Table 3.4 Correlation between maize grain yield (t ha^{-1}) and kinetic parameters k (day^{-1}) (rate coefficient) of the DMT-HFO method	42
Table 3.5 Correlation between cumulative amounts of P (mg kg^{-1}) extracted by the DMT-HFO and Bray 1P (mg kg^{-1}) with maize grain yield (t ha^{-1})	43
Table 4.1 Phosphorus content (mg kg^{-1}) in different inorganic (P_i) and organic (P_o) fractions for the differentially P treated soils	56
Table 4.2 Effect of P levels and extraction time on soil P desorption	57
Table 4.3 Correlations between the cumulative P desorbed over 56 day period, the subsequent fractions, Bray 1P(mg kg^{-1}) and maize grain yield (t ha^{-1}), $N=4$	70
Table 5.1 The different shaking patterns according to the conventional and modified approaches	76
Table 5.2 The effect of different shaking options on the extractable DMT-HFO- P_i for the different P levels	79

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	85
Table 5.4 Pearson correlations between the cumulative DMT-HFO- P_i (mg kg^{-1}) and the change in DMT-HFO- P_i (mg kg^{-1}) with dry maize grain yield, N=4	86
Table 6.1 Amount of C/HCl extracted P_i (mg kg^{-1}) for the different treatments according to the modified and the conventional approach of Tiessen and Moir (1993)	97
Table 6.2 Effect of P level and extraction time on soil P extracted by DMT-HFO	100
Table 6.3 Effect of P level and DMT-HFO extraction time on soil P extracted by C/HCl using the short cut approach and the conventional approach	101
Table 6.4 Comparison of the sum of inorganic P fractions extracted by Tiessen and Moir (1993) method and the short cut approach	104
Table 6.5 Correlations between cumulative DMT-HFO- P_i and C/HCl- P_i (mg kg^{-1}) with maize grain yield (t ha^{-1}) both for the method of Tiessen and Moir (1993) and the short cut approach N=4	107
Table 7.1 Selected physical and chemical properties of the soil samples studied	116
Table 7.2 Phosphorus content (mg kg^{-1}) in different inorganic (P_i) and organic (P_o) fractions for the differentially P treated soils	118

Table 7.3 Effect of P level and extraction time on soil P desorption	122
Table 7.4 Correlations between the cumulative P desorbed over 56 day period, the subsequent fractions, shoot dry matter yield, P uptake and Bray 1 P, N=4	130
Table 8.1 Correlation between the kinetic parameter k (day ⁻¹) (rate coefficient) shoot dry matter yield and P uptake, N=3	138
Table 8.2 Correlations between the cumulative P desorbed over 56 day period, shoot dry matter yield and P uptake, N=3	139

LIST OF FIGURES

Figure 3.1 Cumulative desorption data of the different P treated soils fitted to a two component first order model	37
Figure 3.2 Simulated P desorption from pool A (SP_A) of the different treatments over 56 days	38
Figure 3.3 Simulated P desorption from pool B (SP_B) of the different treatments over 56 days	40
Figure 3.4 Desorption rates for the different P treatments over 56 days	41
Figure 4.1 (a-b) Changes in the cumulative DMT-HFO- P_i (a) and HCO_3 - P_i (b) fractions over time. The values in the figure are means of three replicates. Vertical bars represent the standard error	59
Figure 4.2 (a-b) Changes in the HCO_3 -Po (a) and NaOH-Po (b) fractions over time. The values in the figure are means of three replicates. Vertical bars represent the standard error	61
Figure 4.3 (a-b) Changes in the 0.1M NaOH- P_i (a) and D/HCl- P_i (b) fractions over time. The values in the figure are means of three replicates. Vertical bars represent the standard error	64
Figure 4.4 (a-b) Changes in the C/HCl- P_i (a) and C/HCl-Po (b) fractions over time. The values in the figure are means of three replicates. Vertical bars represent the standard error	67
Figure 5.1 (a-d) Simulated P desorption from pool A (SP_A) of the different treatments and shaking options	81
Figure 5.2 (a-d) Simulated P desorption from pool B (SP_B) of the different treatments and shaking options	82

- Figure 6.1** (a-b) Simple linear correlation between the conventional approach and short cut with (a) modified C/HCl extraction and (b) conventional C/HCl extraction 98
- Figure 6.2** (a-b) Simple linear correlation between the conventional approach and short cut with (a) modified C/HCl extraction and (b) conventional C/HCl extraction for the whole triplicates of trial 1. 98
- Figure 6.3** (a-b) Changes in the C/HCl extractable P_i with time. The values in the figure are means of three replicates. Vertical bars represent the standard error 103
- Figure 6.4** (a-d) Simple linear correlations between the Tiessen and Moir (1993) method and the short cut approach for the sum of P_i over different periods of extraction 106
- Figure 7.1** (a-b) The changes in extractable (a) HCO_3 -Po and (b) C/HCl-Po over time. The values in the figures are means of three replicates. Vertical bars represent the standard error 126
- Figure 8.1** Cumulative desorbable P with time extracted using DMT-HFO for the different treatments; error bars represent standard errors of the mean 136



Declaration

I, Abi Tadesse Mengesha, hereby declare that this dissertation for a PhD degree at the University of Pretoria is my own work and has never been previously submitted by myself at any other university

Abi Tadesse Mengesha

May 2008

Acknowledgements

First and foremost, I would like to praise the Almighty God; the governor, the cherisher and the sustainer of this world, for his mercy and for providing me the strength required to complete this study.

I should like to express my deep appreciation to my promoter Professor A.S Claassens for his patience, inspiration, consistent encouragement and invaluable advice that he offered me not only during the preparation of this manuscript but ever since I came here to the University of Pretoria.

Especial thanks should goes to Mr. P.C. De Jager for his persistent encouragement and constructive advice he provided me during the laboratory works.

I am deeply indebted to Professor H.S Hammes for allowing me to use soil samples from one of the oldest long-term fertilizer trial in South Africa.

Immense appreciation should goes to Dr. J.H.Van Der Waals for standing by my side and helping me overcome all my ups and downs that I encountered during my stay in South Africa. His concern in comforting international students like me especially at time when one feels so lonely (Christmas celebrations and other holidays) is unforgettable.

It is very pleasant to express thanks to all the people from the Department of Plant Production and Soil Science, Microbiology department, UP farm management and Nooitgedacht Agricultural Development Centre, Ermelo, Mpumalanga, South Africa

for providing me with the various technical help and suggestions that I needed in the entire period of this work.

Much gratitude is expressed to all my friends (Ethiopians and other citizens) that make my stay in South Africa pleasant and especially the Pretoria congregation for making me feel at home away from home.

Especial thank should also goes to the University of Haramaya for providing me this opportunity and in particular to ARTP Project for availing financial assistance.

The last but not least, I would like to extend my special thanks to my whole family for their profound love and unreserved support through out the entire period of the study.



DEDICATION

To my wife, Rahel, with much love, admiration and appreciation.

Characterizing phosphate desorption kinetics from soil: An approach to predicting plant available phosphorus

By

Abi Tadesse Mengesha

Supervisor: Prof. A.S. Claassens

Department: Plant Production and Soil Science

Degree: Ph D (Soil Science)

ABSTRACT

Many agricultural fields that have received long-term applications of P often contain levels of P exceeding those required for optimal crop production. Knowledge of the effect of the P remaining in the soil (residual effect) is of great importance for fertilization management. In order to characterize P forms in soils, a wide variety of methods have been proposed. The use of dialysis membrane tubes filled with hydrous ferric oxide (DMT-HFO) has recently been reported as an effective way to characterize P desorption over a long-term in laboratory studies. However, there is little information on the relationship between kinetics of P release using this new method and plant P uptake. This method consists of a procedure of shaking a sample for a long period of time thereby exploiting the whole volume of the soil which is in contrast to the actual plant mode of uptake. This method has also practical limitations in employing it for a routine soil analysis, as it is very expensive and time consuming. The objectives of this study were (i) to study the changes in labile, non-labile and residual P using successive P desorption by DMT-HFO followed by a subsequent fractionation method (combined method) (ii) to assess how the information gained from P desorption kinetic data relates to plant growth at green house and field trials

- (iii) to investigate the effect of varying shaking time on DMT-HFO extractable P and
- (iv) to propose a short cut approach to the combined method.

The release kinetics of the plots from long term fertilizer trials at the University of Pretoria and Ermelo were studied. P desorption kinetics were described relatively well by a two-component first-order model ($R^2 = 0.947, 0.918, \& 0.993$ for NPK, MNK, & MNPK treatments respectively). The relative contributions of both the labile pool (SP_A) and the less labile pool (SP_B) to the total P extracted increased with increased P supply levels. Significant correlations were observed between the rate coefficients and maize grain yield for both soil types. The correlation between the cumulative P extracted and maize yield ($r = 0.997^{**}$) however was highly significant for Ermelo soils.

This method was also used to determine the changes in the different P pools and to relate these P fractions with maize yield. Highly significant correlations were observed between maize grain yield and the different P fractions including total P. In both soil types the contribution of both the labile and non-labile inorganic P fractions in replenishing the solution P_i was significant where as the contributions from the organic fractions were limited. The C/HCl- P_i is the fraction that decreased most in both cases as well.

Investigation was carried out to evaluate the effect of varying shaking periods on the extractable DMT-HFO- P_i for UP soils of varying P levels. Four shaking options were applied. Significant difference was observed for the treatment of high P application. Shaking option 2 seemed relatively better than the others since it showed the strongest correlation. Thus for soils with high releasing kinetics and high total P content,

provided that the P release from the soil is a rate limiting step, reducing the length of shaking time could shorten the duration one needs to complete the experiment without influencing the predicting capacity of the methodology.

The other objective of this thesis was also to present a short cut method alternative to the combined fractionation method. 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 a conventional step-by-step method with the sum of DMT-HFO-P_i and a single C/HCl-P_i extraction as a short cut approach for all extraction periods resulted in strong and significant correlations. The C/HCl-P_i fraction extracted by both methods was correlated with maize grain yield and it was found to be highly significant. This study revealed that this 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 in replenishing the labile portion of P is already identified.

The method employed here therefore could act as an analytical tool to approximate successive cropping experiments carried out under green house or field condition. However, data from a wider range of soils is needed to evaluate the universality of this method. More work is also required in relating desorption indices of this method with yield parameters especially at field level.

Key words: desorption of P, dialysis membrane tubes, phosphorus, phosphorus dynamics, phosphorus fractionation, phosphorus release rate, shaking time optimization, short cut methodology, soil test methods, successive desorption of P, two component first order model