PHOSPHORUS SORPTION STUDIES IN THREE TYPICAL SOILS OF NIGERIA

BY

EDWARD O. UYOVBISERE
[BSc, MSc]

A Thesis Submitted to the Postgraduate School in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

in the

Department of Soil Science
Faculty of Agriculture
Ahmadu Bello University, Zaria
Nigeria

November, 1994

DECLARATION

I hereby declare that the concepts presented in this thesis are original in content, and are products of my imagination and execution. Where otherwise, the sources have been acknowledged by references. The subject matter has not been presented in any previous application for a higher degree at the Ahmadu Bello University, or any other University.

30/9/94

Edward O. Uyovbisere

Confirmed by

15/12/94

Dr. V. O. Chude,
Chairman, Supervisory Committee.

AHMADU BELLO UNIVERSITY
POST GRADUATE SCHOOL
ZARIA

CERTIFICATION

This thesis titled: "Phosphorus Sorption Studies in Three Typical Soils of Nigeria", by Edward Oniovosa UYOVBISERE, meets the regulations governing the award of the degree of Doctor of Philosophy for which it was presented. The thesis is acceptable in form and content, and is approved after an oral examination of the candidate, for its contribution to knowledge and literary presentation.

Dr. V. O. Chude
Chairman, Supervisory Committee

Dr V.O. Chude 15/12/95

Professor Dr. J. J. Owonubi
Member, Supervisory committee and
Head of Department

23/3/95

Dean, Postgraduate School

9/1/96

ACKNOWLEDGEMENT

This project was jointly funded by the University Board of Research (UBR), A.B.U., Zaria, and the Danish Land Development Service (DLDS), Denmark, courtesy of the ABU-DLDS Linkage Project, and carried out in the laboratories of the Department of Soil Science, ABU, Zaria, and the Department of Plant Nutrition, The Royal Veterinary and Agricultural University, Copenhagen, Denmark. These awards are gratefully acknowledged.

I thank Dr V. O. Chude for supervising the work, and along with members of the supervisory committee - Professor J. J. Owonubi and Dr. Y. Yusuf- for seeing the project to completion. I also thank Professor G. Lombin for his role in securing funds from the UBR, ABU, Zaria.

My appreciation also goes to Dr. A Bationo of IFDC-ICRISAT, Niamey, Dr. H Christian of RVAU, Denmark and Dr. A. A. Ramalan of the Department of Agric. Engineering, A.B.U. for their invaluable suggestions and assistance. The difference diffractograms were done with the assistance of Dr. H Christian, and Dr. A. A. Ramalan allowed liberal access and use of the computing facility used to compile this work. It was also a great honour to work with Professor N. E. Nielsen and Dr. S. O. Gahoonia of RVAU, Denmark, using their method on the thin slicing technique in the rhizosphere study presented here. I also thank Fian Sadri for her collegial contributions especially in the analysis of the sorption data and Dr. J. O. Agbenin for the useful discussions and relevant references.

My very deep thanks goes to Mr. Augustine Chiemeke and Lotte Gronagar for their technical assistance, and to all members of the Department of Soil Science for being so understanding during the course of this study. I also thank Professor O. A. Ogungbile and Dr. J. Olukosi for their constant encouragement and concern.

Lastly, I thank the Almighty God for giving me the strength to complete this work, and to my family - my wife and children - for their patience, understanding, concern and assistance.

ABSTRACT

Phosphorus deficiency is widespread in tropical soils due to intense weathering. Soil solution phosphates are often low because Fe and Al oxides sorb P strongly. Phosphorus availability can be improved by good management practices, but requires good understanding of soil phosphate reaction processes. A study was initiated to test the application of phosphorus sorption isotherms for evaluating the phosphorus requirement and supplying capacity of soils, and the lability of P fractions. The objective was to generate prediction indices, and determine the influence of OM on P sorption and release to plants.

The study was carried out using three soils on basement complex from Nigeria (two savanna Alfisols and a forest Oxisol), some Fe oxide modified soils and two Danish soils. The soils were acid to neutral in reaction and kaolinitic.

The first section considered P sorption reactions and relationships with soil properties. Total P (P_T) content of the surface soils ranged from 251 - 737 yg P/g with P_0 constituting 25 - 40 % of P_T. Phosphate reactions were largely controlled by amounts and forms of soil oxides and OM. Though OM seemed to enhance adsorption in amorphous systems, the effect of Fe_{ox} was greater than OM by 72 % to 30 % relative effects. P sorbed decreased with OM and oxide crystallinity.

The Freundlich equation was superior, and modelled the sorption data better over the P concentration range tested. The Langmuir equation was however effective at low solution P levels. The standard phosphate requirement (SPR) of the soils ranged from 2 - 693 yg/g. The Alfisols sorbed less P, and

were very low - medium sorbing, relative to the Oxisol (which was medium - high sorbing).

The second section examined plant response to adjusted solution P levels and the efficiency of the soil test methods in the greenhouse. The usefulness of adsorption isotherm for determining the P needs of soils was demonstrated. Critical P levels for 95 % yield maximum ranged from 0.45 - 1.00 yg/ml, and was in excess of the standard concept of 0.2 yg/ml. OM enhanced yield, and the efficiency of P utilization was 2.5 times higher in soils with crystalline Fe oxide dominant.

The efficiency of the soil-test methods was influenced by the buffer index. The resin method correlated best with plant uptake and yield and was superior to other methods tested. The critical and threshold soil-test P values are suggested.

The third section considered the depletion profiles and the lability of the Hedley P fractions. The P depletion zone exceeded 5.00 mm, and most of the P depleted at distances in excess of 3.00 mm from the root was the P_o fraction. The P acquisitive power of rape was greater than maize and both plants seemed to differ in fractions preferentially depleted under conditions of P stress. The results also confirmed the high lability of the bicarbonate fraction, and P availability in P deficient soils was dictated by the P_o fraction.

The study reveals that most of the tropical soils from Nigerian are low to medium sorbing, implying plant response to moderate amounts of applied P. Organic matter management is fundamental to improving the availability of P in the highly weathered tropical soils, and estimating P needs of the soils should be based on the Q/I concept.

TABLE OF CONTENTS

Page

CHAPTER 1 1

INTRODUCTION 1

CHAPTER 2 6

LITERATURE REVIEW 6

2.1 Nigerian Soils, their Nature and Basic Properties 6

2.2 Soil Oxides and Hydrous Oxides of Fe and Al . . . 8

2.2.1 Forms and pedogenetic distributions . . . 8

2.2.2 Surface area and particle size 10

2.2.3 Iron oxide coating on mineral surfaces . . 10

2.3 Soil Organic Matter and its Interactions with Inorganic Soil Constituents 11

2.3.1 Nature and properties of soil OM 11

2.3.2 Interactions of humic substances with inorganic soil constituents 13

2.3.3 Complexes with metal oxides and hydroxides 13

2.4 Soil Phosphorus and Availability 14

2.4.1 Amounts and forms of phosphorus in the soil 15

2.4.2. Phosphorus reactions in soils 17

2.4.2.1. Reaction with inorganic colloids . 17

2.4.2.2. Reactions with organic matter . . . 19

2.4.3. Soil phosphorus fractionation 21

2.4.4. Phosphorus adsorption and desorption . . . 23

2.4.4.1. Phosphorus adsorption 23

2.4.4.2. Properties affecting phosphorus adsorption 28

2.4.4.4. Phosphorus desorption 30

2.4.5. Phosphorus availability indices 32

2.6. Rhizosphere Processes: Turnover and Transport of Phosphorus 36

CHAPTER 3 41

MATERIALS AND METHODS 41
3.1. Site Selection and Main Features of the Areas . . 41
3.2. Soil Sampling and Sample Preparation 42
3.3. Characterization of Study Soils 43
3.3.1. Routine determinations 43
3.3.2. Specific surface area determination . . . 44
3.3.3. Determination of surface charge characteristics 45
3.3.4. Mineralogical analysis 47
3.3.4.1. Separation of sand, silt and clay for mineralogical analysis 47
3.3.4.2. Mineralogy of the size separates 48
3.3.4.3 Difference diffractogram analysis 50
3.3.5 Organic matter extraction and fractionation 50
3.4 Preparation of The Special Soils 51
3.4.1 Preparation of the iron and aluminium oxide-soil systems 52
3.4.1.1 Removal of OM 52
3.4.1.2. Preparation of the Fe and Al oxide coated soil particle 53
3.4.1.3. Crystallization of oxide coatings on particle surfaces 55
3.5. Phosphate Studies 56
3.5.1. Forms of phosphorus 56
3.5.2 Adsorption studies 57
3.5.2.1 Soil P x time interaction 57
3.5.2.2 Phosphorus adsorption isotherms . . 58
3.5.2.3 Determination of soil P adsorption

indices 58
3.5.3. Phosphorus desorption studies 59
3.5.4. Soil test methods 60
3.5.5. Determination of relative fertility index (FI) for selected soils 61
3.5.6. Phosphate determination in solution extracts 61
3.6 Greenhouse Study 62
3.6.1 *Greenhouse experiment on maize in P adjusted* soils 62
3.6.1.1. Greenhouse procedure 62
3.6.1.2 Chemical analysis of the plant and soil samples. 63
3.6.2. Growth chamber studies on maize and rape 64
3.6.2.1 Phosphorus depletion and turn-over in the rhizosphere. 64
3.6.2.2. The pre-experimental set up . . . 64
3.6.2.3. The experimental set up 66
3.6.2.4. Slicing the soil 68
3.8 Statistical Analysis 68

CHAPTER 4 70

RESULTS AND DISCUSSION 70
4.1. Properties of the Soils 70
4.1.1. Soil characteristics 71
4.1.1.1. Properties of the profiles 71
4.1.1.2. Selected properties of the special soils 77
4.1.1.3 Some properties of the soils for studies of the rhizosphere 81
4.1.2. *Fe and Al oxide fractions of the soils* . 82
4.1.2.1. *Fe and Al oxide fractions of the* profiles 82
4.1.2.2 Fe and Al oxide fractions of the special soils. 86

4.1.3. Organic matter fractions of the profile soils 88
4.1.4. Mineralogical analysis of the soils . . . 89
4.1.4.1 Mineralogical analysis of the profile soils 89
4.1.4.2. Mineralogy of the Special Soils. 96
4.2. Phosphorus Status and Relationships 101
4.2.1. Native phosphate status of the profiles 101
4.2.2. Hedley phosphate fractions of the rhizosphere study soils 105
4.2.3. Phosphorus extractable by chemical soil tests 106
4.2.4. Soil phosphate relationships 111
4.2.4.1. Relationship between soil properties and P forms 111
4.2.4.2 Relationship between soil oxides and soil phosphate forms 112
4.2.4.3. Relationship between soil test-P, phosphate forms and soil oxides. . . 116
4.3. Adsorption of Added Phosphorus 120
4.3.1 Phosphorus vs time interaction 120
4.3.2. Description of adsorption isotherms for the profiles 122
4.3.3. Description of P adsorption isotherms for the special soils 125
4.3.3. Comparison of adsorption equations. . . 129
4.3.3.1 Profile soils 129
4.3.3.2. Special soils 135
4.3.4 Phosphorus sorption parameters and buffer indices. 138
4.3.4.1. Profile soils 138
4.3.4.2. Special soils 141
4.3.5 Soil properties affecting phosphate sorption 143
4.3.5.1. Profile soils 143

4.3.5.2 Special soils 149
4.4. *Phosphorus Desorption* 157
4.4.1. Phosphorus desorption isotherms and hysteresis 157
4.4.2. Adsorption - desorption relationships and critical P 161
4.5. *Greenhouse Evaluation of Maize in P Adjusted Soils* 164
4.5.1. Soils and fertilization 164
4.5.2. Response to phosphate application. . . 164
4.5.2.1 Response models for the soils. . 166
4.5.2.2 Response model for treatment effects. 173
4.5.3. Effects of selected soil properties on yield and uptake. 179
4.5.4.1. Effects of treatments on extractable P values 181
4.5.4.2 Total P uptake and efficiency of soil tests methods. 184
4.5.4.3. Relationship between soil tests P and yield. 188
4.5.5. Soil test calibration for yield level estimation. 191
4.6. Phosphorus Depletion and Turnover in the Rhizosphere 195
4.6.1. *Relative fertility of the selected soils* 195
4.6.2. Crop yield and plant parameters 197
4.6.3 Mobilization of P in the soils by the growing plants 199
4.6.4. *Phosphate depletion Profiles.* 208
4.6.4.1. Depletion of $NaHCO_3$ P_i 209
4.6.4.2 Depletion of $NaHCO_3$ P_o 211
4.6.4.3. Depletion of NaOH P_i and Po, HCl and Residual fractions. 211
4.6.5. *Turnover and transport of P in the* rhizosphere 214

4.6.5.1 *Turnover of P in the rhizosphere* 215
4.6.5.2. Transport of P in the rhizosphere. 218
4.6.6. Lability of P forms in soil. 219

CHAPTER 5 224

SUMMARY AND CONCLUSION 224

REFERENCES 231

APPENDIX 259

LIST OF TABLES

Table — Page

3.1. Volumes of NaCl, 0.1 N HCl, 0.1 N NaOH and water required to obtain a titration curve for the determination of ZPC depending on pH and ΔpH of soil. 46

3.2. Selected properties of the natural soils used for the special studies 53

3.3. P solution concentration used for the desorption experiment in the various soils. 60

3.4: P added to each soil before equilibration to attain the desired levels of solution P for the greenhouse cropping. 63

3.5: Nutrient concentration in the maintenance solution A and B and the basic nutrient solution C (pH 5.5). 66

4.1.1 Some selected features of the sites and classification of the profiles 71

4.1.2. Selected physical and chemical properties of the soil profiles. 72

4.1.3. Correlation matrix of selected properties of the soil profiles. 76

4.1.4: Some selected chemical properties of the special soils. 77

4.1.5: Some selected chemical properties of the special soils: Mean values with respect to treatments. . . . 79

4.1.6: Correlation matrix of selected soil properties and

oxide fractions for the special soils. 80

4.1.7: Some chemical and physical properties of the test soils. 82

4.1.8. Dithionite, oxalate and pyrophosphate extractable iron and aluminium fractions, active Fe and Al, and dithionite Fe/clay ratios. 83

4.1.9: Iron and aluminium oxide fractions of the special soils. 87

4.1.10: Iron and aluminium oxide fractions of the special soils: Mean values with respect to treatments. 87

4.1.11: Humic and fulvic acid fractions and total organic matter contents of the soil profiles. Percentage of organic matter in parenthesis. 89

4.1.12: Mineralogical composition of the sand fraction of the profiles: X-ray diffraction and petrographic study. . 92

4.1.13: Mineralogical composition of the silt fraction of profiles. 92

4.2.1: Distribution of inorganic phosphate fractions (P_i), P_o and P_T in the profiles, and OC/P_o ratio. 101

4.2.2: Percentage contribution of the various phosphate forms to P_T in the soil profiles. 103

4.2.3: Distribution of Hedley P fractions in the unplanted (Control) test soils. 106

4.2.4: Phosphorus extractable by some chemical soil tests, and resin-P (Q)/water (I) ratio. 107

4.2.5: Phosphorus extractable by chemical soil tests expressed as percent of total P. 108

4.2.6: Correlation coefficients of selected soil properties and Fe and Al oxide fractions and phosphate forms of the profile soils. 112

4.2.8: Correlation matrix of Al and Fe oxide fractions, clay and surface area for the profile soils. 116

4.2.9: Correlation matrix of phosphate forms and phosphorus extractable by chemical soil tests. 119

4.3.1. Buffer capacity and affinity constants of the respective special soils obtained from graphic plots at the dilute range of solution P (0 - 10 µg/g P), and P sorbed at 0.6 µg/g equilibrium phosphate concentration. 127

4.3.2: The R^2 and root mean square error (RMSE) for the comparison of the adsorption models for the description of P adsorption by the soils fitted by non-linear regression models. 130

4.3.3: Comparative effectiveness of the linear and non-linear models of the sorption equations in describing the P sorption data for the soils as shown by the R^2 values. 130

4.3.4: The R^2 and root mean square error (RMSE) for the comparison of the adsorption models for the description of P adsorption by the natural and artificial soils fitted by non-linear regression models. 136

4.3.5: The R^2 linear and non-linear regressions for the adsorption models fitted to the P sorption data for the natural and artificial soils. 137

4.3.6. Phosphorus adsorption indices estimated from the Langmuir adsorption models for the soils at the whole range of P concentrations used. 139

4.3.7: Estimates of phosphate sorption indices for the soils calculated from the linearized model at 0 - 10 µg/ml equilibrium solution P concentration. 140

4.3.8: Phosphorus adsorption indices estimated from the Langmuir models for the prepared and natural soils for the entire range of P added. 143

4.3.9: Phosphate adsorption indices for the special soils at equilibrium solution P less than 10 µg P/ml (Calculated from the Langmuir equation). 143

4.3.10: Phosphate adsorption indices for equilibrium solution P less than 10 µg P calculated from the Langmuir equation: Mean values with respect to treatments. . 143

4.3.11: Correlation coefficients of selected soil properties and P sorption indices for the profile soils. . . . 145

4.3.12: Multiple regression equations for estimating the P adsorption indices from soil properties. 148

4.3.13: Correlation coefficients of phosphate forms, extractable P and P sorption indices for the profile soils. 149

4.3.14: Correlation matrix of selected soil properties and phosphate sorption indices for the special soils combined. 150

4.3.15: Correlation matrix of selected soil properties and phosphate sorption indices for the artificial soils.

. 151

4.3.16: Correlation matrix of selected soil properties and phosphate sorption indices for the natural soils. . 151

4.3.17: Relationship between Fe and Al oxide fractions and phosphorus adsorption indices and selected soil properties for the soils as influenced by treatments. 152

4.3.18: Multiple regression equations for estimating the P adsorption indices from properties of the special soils. 156

4.4.1: Relationship between P dosorbed (y) and P adsorbed (x) expressed in simple linear regression. Estimates of critical P (P_{crit}) and % of P assumed to be physically sorbed ($P_{max}-P_{crit}$) were calculated from the expression. 162

4.5.1: Analysis of variance table for the response of some agronomic parameters as function of treatment effects in the greenhouse. 165

4.5.2: Agronomic response to varying rates of phosphate amendments in relation to soil type, oxide form and OM interaction: Dry matter yield and plant height at 3 weeks. 167

4.5.3. Response surface analysis of maize dry matter to adjusted solution P levels. Yield prediction equation, R^2 , RMSE, point of maximum response, and yield estimate at 0.20 ug P/ml equilibrium solution concentration for the special soils. 169

4.5.4: Response surface analysis for maize response to adjusted solution P levels. Yield prediction equations,

R^2 , RMSE, point of maximum response and yield estimate at 0.20 g P/ml: mean interaction effect of OM and state of soil oxides forms. 174

4.5.5: The relationship between dry matter yield (y) and P uptake (x) in maize expressed in simple linear regression. 179

4.5.6. Correlation relationships between dry matter yield, P uptake and phosphate sorption parameters and soil oxide fractions for all soils. 180

4.5.7: Analysis of variance table for extractable P values as affected by treatment effects: P extracted from P amended soils prior to cropping. 182

4.5.8: Effect of type*, crystallinity and depth interaction on P extractable by the various soil tests methods for P adjusted and incubated soils before cropping. . . . 183

4.5.9: Analysis of variance table for difference in extractable P levels by the various soil tests due to cropping (Test-P pre minus Test-P post), and for P uptake by the maize plant. 186

4.5.10. Effects of type, crystallinity and depth interaction on P loss estimated by the various soil tests due to cropping, and total P uptake by the maize plant. . . 187

4.5.11. Relationship between P uptake and P extractable at 0.6 µg P/ml equilibrium solution P adjusted and the difference in extractable P due to cropping. . . 188

4.5.12: Correlation relationships between dry matter yield and the various estimates of extractable P as influenced by organic matter and soil type. 190

4.5.13: Soil test calibration for yield level estimation based on regression models. Predicted critical and threshold yield response points and corresponding 'sufficient' and deficient levels for the soil test methods for the test soils. 192

4.6.1: Regression relationship between soil solution P concentration and solution:soil ratio, solution P concentration at particle surface, and relative fertility indices for the soils. 196

4.6.2: Dry matter yield, plant nutrient concentration and uptake for maize and rape at 7 and 14 day growth periods in the growth chamber. 198

4.6.3: Total P_i and P_o depleted in each soil as a function of proximity to the root mat for rape and maize plants. 200

4.6.4: Relative contributions of the inorganic and organic phosphate forms to the phosphate pool depleted by the plants. 206

4.6.5: Percentage contributions of the inorganic and residual factions to total P_i depleted in 5 mm of rhizosphere soil. 220

4.6.6: Comparative net lability of the organic P forms (bicarbonate P_o and NaOH P_o) as shown by the relative amounts depleted or accumulated in 5 mm of rhizosphere soil, after 7 and 14 days of growth of maize and rape in the growth chamber. 222

LIST OF FIGURES

Figure — Page

3.1. Flow chart for the extraction and fractionation of Humic substances in soil. 52

3.2: Flow chart for the sequencial extraction of phosphorus by the modified Hedley et al., (1982) method. 57

3.3. Illustrations of the plant-growing technique. Pre-experimental (I) and experimental set-up (II) 65

4.1.1: Surface charge characteristics for the soil profiles. Pedon 1 - Acquic Kanhaplustalf (Samaru). 73

4.1.2: Surface charge characteristics of the artificial soils. 78

4.1.3: Relationship between the organic matter and the oxide forms. 85

4.1.4: X-ray diffraction analysis for the sand fraction of selected horizons of the profiles. 90

4.1.5: Random powder X-ray diffraction analysis of the silt fraction for selected horizons of the pedons 93

4.1.6: Random powder X-ray diffraction pattern of the Mg - saturated clay samples of the pedons 94

4.1.7: X-ray diffractograms for the Mg saturated clay samples for the top and sub-soils of the pedons. 95

4.1.8: Powder X-ray diffractograms for the special soils; silt and clay fractions superimposed 97

4.1.9: Difference diffractograms for the natural soils . . 98

4.1.10: Difference diffractograms for the artificial soils 99

4.2.7: Correlation coefficients of selected soil properties and P extractable by some soil tests methods. (Profile samples). 113

4.2.1: Regression relationship between Al-P and Fe-P with organic matter 114

4.2.2: Relationships between oxide fractions and some P forms 117

4.3.1: Equilibrium solution concentration with time of reaction in days of some natural and artificial soils and pedon 1 (0-15cm). 121

4.3.2: Phosphorus adsorption isotherms for the soils of the profiles. 123

4.3.3: Phosphorus adsorption isotherms for the special soils 126

4.3.4: Langmuir plots of the sorption data for the soils profiles. 131

4.3.5: Freundlich isotherms for the soils - log x vs log C. 133

4.3.6: Temkin adsorption isotherms (x vs log C). 134

4.3.10. Curve fit to the Langmuir prediction model for ArtAmB 138

4.3.11: Relationship between standard phosphate requirement (SPR) and Fe_d . Estimation equations for some phosphate parameters are given as foot notes. 146

4.3.12: The relationship between P adsorption maximum and Fe_{ox} in all soils. 155

4.4.1: Phosphorus desorption isotherms for the natural soils. 158

4.4.2: Phosphorus desorption isotherms for the artificial soils. 159

4.4.3: Phosphate retention potentials of the soils as affected by treatments. 163

4.5.1: Response curves for yield and plant height at 3-weeks in relation to adjusted solution P levels. 171

4.5.2: Relative yield advantage in relation to equilibrium solution P for the soils. 172

4.5.3: Effects of 'soil type X OM interaction' on the response of maize to adjusted solution P levels. . . 176

4.5.4: Yield response in relation to 'soil type X crystallinity' 177

4.5.5: Yield response in relation to 'depth X crystallinity' for DM yield and plant height. 177

4.5.6: Mean response of maize to adjusted solution P levels in the natural and artificial soils 178

4.5.7: Mean response of maize to adjusted solution P levels as influenced by organic matter. 178

4.5.8: The relationship between P sorption capacity with yield 185

4.6.1: Total depletion of phosphate fractions by rape as

function of proximity to root surface at 7 and 14 days in selected soils. 202

4.6.2: Total depletion of phosphate fractions by maize as function of proximity to root surface at 7 and 14 days in selected soils. 204

4.6.3: Bicarbonate P_i depletion profiles of the soils. . 210

4.6.4: Bicarbonate P_o depletion/accumulation profiles of the soils. 212

4.6.5: Phosphate depletion profiles for NaOH P_i and P_o, HCl and residual fractions in two tropical soils 213

4.6.6: Percentage depletion of the various fractions as function of proximity to the root surface in 5 mm of rhizosphere soil: Rape. 216

4.6.7: Percentage depletion of the various fractions as function of proximity to the root surface in 5 mm of rhizosphere soil: Maize. 217

ABBREVIATIONS

P_t	-	Total phosphorus.
P_o	-	Organic phosphorus.
OM	-	Organic matter.
OC	-	Organic carbon.
B_iP_i	-	Bicarbonate inorganic P.
B_iP_o	-	Bicarbonate organic P.
P_i	-	Inorganic phosphorus.
ZPC	-	Zero point of charge.
S	-	Siemens (unit of conductivity)
SAREA	-	Specific surface area.

CHAPTER 1

INTRODUCTION

Phosphorus applied to the highly weathered soils of the tropics are readily rendered unavailable because of the high retentive capacity of the soils (Udo and Uzu, 1972; Bates and Baker, 1960; Jones and Wild, 1975). Consequently, soil solution P concentrations are often low, and insufficient to meet crop demands. Phosphorus limitations to crop production could attain acute levels such that plant growth ceases as soon as the phosphorus stored in the seed is exhausted (Mokwunye, et al., 1986).

Phosphorus moves to the roots of plants largely by diffusion, and uptake by plants is mainly governed by the concentration of P in solution (Barber, 1962, Lewis and Quirk, 1967). The various reaction processes which control nutrient dynamics and availability take place largely in the rhizosphere (Jungk, 1991). Williams (1967) discussed and classified these factors as intensity (P in solution), quantity (labile P, i.e. P exchangeable on particle surfaces), capacity (P release potential) and mobility (rate of P supply) factors. These factors are related to the nature and preponderance of surface active inorganic and organic colloids.

Aluminium and iron oxides are the most important phosphate adsorbents in soils (Parfitt, 1978; Borggaard, 1986; Udo and Uzu, 1972). Interactions are known to occur between organic matter and these oxides, inhibiting their

crystallization, and thereby increasing their phosphate adsorption capacity (McLaughlin et al., 1981; Schwertmann et al., 1986). Positive correlation between organic matter content and phosphate sorption have been reported (Lupez-Hernandez and Burnham, 1974), implying possible direct adsorption of P by soil organic matter. On the contrary, Apelt et al. (1975) and Borggaard (1983) found no effect of organic matter on phosphate adsorption; while Sibanda and Young (1986), observed that organic matter in solution significantly decreased P adsorbed onto aluminium and iron oxides, and onto soils.

Soils in Nigeria are highly varied, with diverse properties that change with the climatic and vegetation zones, from the humid tropical forest soils in the south (high in organic matter) to the dry savanna soils in the north with low organic matter content (Enwezor and Moore, 1966; Jones and Wild, 1975). The nature of iron and aluminium oxide forms have a strong influence on the behaviour of P in these soils. The amorphous oxides have a greater propensity to adsorb P than the more crystalline forms (Udo and Uzu, 1972; Wada and Kunjigake, 1979; Schwertmann, 1966). The ability to retain phosphorus is also influenced by the prevailing soil moisture regime (Reeve and Summers, 1970). The Fe and Al oxide components of the drier savanna soils of northern Nigeria, exist more in the crystalline state (Jones and Wild, 1975), while in the humid southern forest soils, the percentage of the amorphous oxide forms could be high (Greenland, 1972). Therefore P reactions in soils with properties that differ

appreciably in OM content and amount and forms of soil oxides are expected to differ accordingly.

Soil phosphate availability indices as obtained with chemical extractants (Oteng and Acquaye, 1971) or theoretical concepts of intensity and capacity factors (Ozanne and Shaw, 1968) are often poorly correlated with actual plant uptake and yield, because vital factors important for the acquisition of nutrients by plants from soil are often not fully considered. Despite some inadequacies observed in the use of P adsorption equations (Posner and Bowden, 1980; Harter, 1984), they are still considered useful for empirical description of data, and for phosphorus fertilizer recommendations in the highly weathered soils of the tropics. The classical sorption equations of Langmuir, Freundlich and Temkin (Bache and Williams, 1971) will be used as tools to assess the mechanisms by which P react in the soils, and to better quantify P requirements of the soils.

Two study soils sampled from different climatic and vegetation zones were selected to provide appreciable differences in the forms of soil oxides and organic matter (OM) content. These were: (i) a Kanhaplic Haplustalf from the Northern Guinea savanna, found to be high in crystalline iron oxides, and (ii) a Kandiustalfic Eustrustox which contain a higher amounts of the amorphous oxides from the southern forest zone. The third soil, an Acquic Kanhaplustalf was obtained from an area of fluvial deposition in the Northern Guinea savanna. The first two soils were the natural soils. Through some chemical treatments, the third soil was made to

simulate properties of the natural soils, in OM content and forms of soil oxides, and formed the bases for comparison between the natural and artificial systems. By this modification, it was possible to isolate those soil reactions that could be attributed solely to differences in the nature of soil organic matter and iron oxides, as well as their interactions in soils. The genetic differences of the soils in their natural state could therefore be assessed and the effects of variability due to the peculiar nature and parent materials of the natural soils could, in effect, be eliminated to an extent. By comparing the reaction of these three soils, we expect to get a reasonably clear picture of the sorption property of the soils, and the effects of the interaction between surface active inorganic colloids (Fe and Al oxides) and organic matter on P retention.

Attempts were also made to look at the rhizosphere with greater resolution. Phosphorus acquisition by diffusion is limited to 1.5 mm from the root surface, and this is influenced by soil properties, such as the organic matter and the inorganic colloidal content of soil. Under controlled conditions, P depletion profiles can be described, and the nature of P availability can be further elucidated. By employing the principle of regeneration of Nielsen (1984) to regulate the soil pH of circulating nutrient solution and to produce healthy plants, the plant growing technique of Gahoonia and Nielsen (1991) and the P fractionation scheme of Hedley et al. (1982), it might be possible to assess the soil

phosphate status, the lability of the P forms and quantify the turn-over and transport of P in the rhizosphere.

The study therefore has the following objectives:

1. To characterize the phosphorus sorption property of three typical soil of Nigeria, and study the effects of the interaction between organic matter and forms of Fe and Al oxides on phosphate sorption and release in the soils.
2. To evaluate the effects of such interaction on the efficiency of selected soil test methods in predicting phosphate requirements in the soils.
3. To study the application of phosphorus sorption isotherms for evaluating the phosphorus needs of an index plant in the greenhouse.
4. To study the depletion of the various phosphate fractions in the rhizosphere of rape and maize as influenced by organic matter and soil oxide interaction.
5. To characterize the P depletion profile in soils, and the effect of plant species on P transformation and transport in the soils.

CHAPTER 2

LITERATURE REVIEW

2.1 Nigerian Soils, their Nature and Basic Properties

Deriving from the generalized soil map of West Africa (based on D'Hoore, 1964) much of the Nigerian soils (as classified under the French system) are Ferralitic in the humid southern forest vegetation zones, and Tropical Ferruginous in the drier northern savannas (Jones and Wild, 1975). Subsequent reviews by D'Hoore (Moss, 1968) placed the Ferralilic soils in the Oxisol order of the USDA system, and also regarded Ferrisols, while having a structural B horizon, as Oxisols. The USDA soil map of the world (Ackerson et al., 1968) classified most of Nigerian soils on Basement Complex as Alfisols, and on sandstones as Ultisols, a position also favoured by subsequent workers (Harpstead, 1974). This generalized groupings may tend to suggest basic similarities in the soil reaction processes with reaction intensities and/or minor variations only modified by climatic and vegetation differences. However, a closer scrutiny reveal significant differences in the chemical nature of the soil components that control the reaction processes in the soils (Greenland, 1981).

In common with most of the soils of the humid tropics (Greenland, 1981) and with the savanna soils (Jones and Wild, 1975), koalinite is dominant in the clay fraction (Gallez et al., 1975; Jungerius and Levelt, 1964; Ojanuga, 1979). This is considered a common phenomenon in tropical soils (Soil

Survey Staff, 1975, Hughes, 1981). Kaolinite and Fe-oxyhydroxides are shown to form 80 - 90% of the constitution of the clay fraction of the Nigerian soils (Moberg and Esu, 1991). This basic characteristic has far reaching implications on the fertility and crop production potentials of the soils. The soils are highly weathered, coarse textured, low in organic matter content and cation exchange capacity, are generally acidic and poorly buffered with respect to most nutrients (Jones and Wild, 1975; Heathcote and Stockinger, 1970, Greenland, 1981). Consequently, the soil chemical balance remain delicate and are generally deficient in nitrogen and phosphorus (Mokwunye and Vlek, 1988). The highest P containing soils are formed on basic rocks relatively high in P, while soils formed on sedimentary deposits have low values (Udo and Ogunwale, 1977). Variation in the soil reaction processes across the country, from the southern to the northern latitudes are linked with the nature of the surface active inorganic colloids. Generally, the crystalline oxide fractions are dominant in the well drained profiles of the tropics, but there is the tendency for the oxides to be less crystalline in the more humid environments, as could be found in soils of the rain forest. The potentials of the soil to fix phosphorus and their P supplying power to growing plants should vary accordingly with the state of crystallinity of Fe and Al oxides in soils.

2.2 Soil Oxides and Hydrous Oxides of Fe and Al

The oxides (for brevity, used here on a group name for all compounds of $Fe_2O_3.H_2O$ and $Al_2O_3.H_2O$ systems, that is, including the oxyhydroxides and hydrous oxides) of Fe and Al are found in almost all soils as constituents of clays, and occur as discrete particles or as coatings on other minerals (Brown et al. 1978; Davidtz and Summer, 1965, Roth et al., 1967). Despite the relatively small amounts in which they are found in soils, their effects on soil properties are important to soil fertility management.

The trivalent cations of Al and Fe formed by hydrolysis have important effects on the physico-chemical properties of soils such as aggregation and flocculation, soil pH and surface charge on soil particles (Brown et al., 1978; Roth et al., 1968, Tweneboah et al., 1967). Iron and aluminum oxides react with soil phosphate and modify the availability of applied phosphate fertilizers to plants (Parfitt, 1978; Borggaard, 1983; van der Zee and Riemsdijk, 1986; Juo and Fox, 1977).

2.2.1 Forms and pedogenetic distributions

The iron and aluminum oxides are readily differentiated into three fractions by a process of selective dissolution. Total free iron and aluminum oxides are extracted by the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960). An estimate of the amorphous fraction (Fe_{ox} and Al_{ox}) is extracted by the acid ammonium oxalate method (Tamm, 1922; Schwertmann, 1964), while the Fe and Al oxides in

organic complexes (Fe_{py} and Al_{py}) are assumed to be extracted by sodium pyrophosphate (Aleksandrova, 1960; McKeague, 1967). Several workers have found these methods useful for the differentiation of the oxides especially iron oxides (Bascomb, 1968; McKeague et al., 1971 and Juo et al., 1974).

The profile distribution of the various forms of Fe and Al oxides are useful criteria for the interpretation of pedogenetic processes (Mckeague and Day, 1966; Blume and Schwertmann, 1971; Juo et al., 1974). The presence of amorphous oxides may have significant influence on soil properties, such as phosphate retention and soil aggregation (Sherman et al., 1964; Greenland and Oades, 1968). However, the Alfisols and Ultisols derived from acidic parent rocks in West Africa contain small amounts of amorphous iron oxides (Juo et al., 1974). Detailed studies in some benchmark soils in West Africa (Greenland, 1981) have revealed:

(a) decreasing active iron ratio (Fe_{ox}/Fe_{d}) down the profile indicating high proportion of crystalline oxides in the subsoil;

(b) Increasing values of Fe_{d} to clay ratio with depth in Alfisols and Ultisols suggest the downward co-migration of iron oxides and clay.

(c) In the Alfisols, the oxalate iron is significantly higher than the pyrophosphate-iron, and the reverse is true for Ultisols. This phenomenon was explained as due to better conditions for the formation of organo-iron complexes in Ultisols.

2.2.2 Surface area and particle size

Iron and aluminium oxides in the clay fractions formed from basic parent rocks (i.e. basalt) exist mostly as very fine, discrete electron dense particles showing little association with the kaolin particles, whereas the oxides formed from acidic parent materials (granite, sandstone) show strong interaction with kaolinite (Greenland et al. 1968; Hughes, 1978). This strong interaction results in the reduction of specific surface area which is much higher for the more basic soils. Though more work is needed to draw conclusions from, it seemed probable that it is the surface reactivity of iron oxides, rather than the total amount present in soil that is crucial in influencing the chemical and physical properties of the soils (Greenland and Moth, 1978; Quirk, 1971; Juo, 1978; Udo and Uzu, 1972; Hughes, 1978; Juo and Fox, 1977).

2.2.3 Iron oxide coating on mineral surfaces

The iron and aluminum oxides have been shown to exist as coatings on silicate surfaces (Follett, 1965; de Villiers and Jackson, 1967; Habibullah, 1971). Habibullah (1971) also observed that only amorphous iron oxides form coatings and only under reducing or flooded conditions in soils. Fordham and Norrish (1979) reported evidence of coatings of iron oxides and finely divided clay minerals on larger clay particles in Australian soils. Iron oxide coatings can be precipitated onto kaolinite, illite and bentonite clays under suitable laboratory conditions, leading to an increased net

positive charge on the clay surface and a change in surface properties (Greenland and Moth, 1978; Kavanagh and Quirk, 1978; Rengasamy and Oades, 1979; Wilding et al., 1982; Parfitt, 1980).

2.3 Soil Organic Matter and its Interactions with Inorganic Soil Constituents

Soil organic matter (OM) is the heterogeneous mixture of products resulting from microbial and chemical transformation (humification) of organic debris and are known to have beneficial effects on soil conditions and fertility. The chemistry of soil OM and its constituents (humic substances) has been reviewed extensively by several authors (Dubach and Mehta, 1963; Kononova, 1966, Stevenson and Butler, 1969; Schnitzer and Khan, 1972; Hayes and Swift, 1978). Basically, organic matter consists of (i) amorphous, polymeric, brown coloured humic substances which are differentiated on the bases of solubility properties into humic acid, fulvic acids and humins; and (ii) compounds belonging to recognizable classes, such as polysaccharides, polypeptides and altered lignins to name a few (Kononova, 1966, 1975). The first group constitute the most important organic reactants in soil.

2.3.1 Nature and properties of soil OM

The decomposition products of plant and animal tissue constitute the principal carbon source for humus formation. Plants contribute large amounts of structural and non-

structural carbohydrates, which along with other organic materials are deposited in the soil. These are readily metabolized by soil micro-organisms and are removed from the system. The more resistant lignins and polyphenols change slowly and limit the overall turnover rate of soil carbon (Minderman, 1968). This later fraction constitute the partially decomposed OM.

The non-humic substances consists of organic compounds, such as carbohydrates, lipids, organic acids and amino acids. They occur in small but variable amounts in all soils and are normally associated with recognizable plant, animal and microbial structures. Some of these substances are incorporated into humic substances (Tate and Theng, 1980).

Soil humic substances are classically divided into humic acid, fulvic acid and humin according to their solubilities, or otherwise, in either alkali or acid (Goh, 1980). Though this fractionation scheme has met with some criticisms as regards discrete group of substances extracted by the reagents (Kibblewhite and Tinsley, 1979), it is still widely used for studies on humic substances (Tate and Theng, 1980). The observation that humic substances from different soils yield essentially similar materials, led Schnitzer (1978) to suggest that benzene carboxylic and phenolic acids make up the principal structural units of humus. The difference between classical fractions lies in the range of their molecular weights. The polyanionic character of humic and fulvic acids are attributed to individual molecules being joined by weak bonds, such as hydrogen bonds and van der Waals interactions

(Schnitzer and Khan, 1972, Schnitzer, 1978). The effects of organic matter in soil chemical processes could therefore be, essentially, the functions of the amounts present in the soil.

2.3.2 Interactions of humic substances with inorganic soil constituents

In aqueous solutions above pH 3, humic and fulvic acids exist and behave as negatively charged polyelectrolytes due to the dissociations of carboxyl (3 < pH > 9) and phenolic hydroxyls (pH > 9) groups in the molecule (Posner, 1964). Below pH 3, the dissociation of these functional groups is suppressed and the molecule behave as an uncharged polymer. Generally at the pH of normal productive agricultural soils, humic acids have a CEC of about 300 meq/100g (300 cmol+/kg soil) and a surface area of about 1250 m^2/g (Flaig et al., 1975; Tate and Theng, 1980). The contributory effects of organic matter to soil fertility could therefore be tremendous.

2.3.3 Complexes with metal oxides and hydroxides

The polyfunctional anionic character of humic substances also account for the propensity of these materials for forming complexes with metal ions in solution (Schnitzer and Khan, 1972; Jacquin, et al., 1978). The stability and water solubility of the complexes depend on the nature of the metal ion, the size of the humic polymer, the metal/polymer ratio, pH and ionic strength. The trivalent Fe^{3+} and Al^{3+} complexes were more stable than the divalent complexes of Mg^{2+} and Ca^{2+}

(Schnitzer and Hansen, 1970). In the reaction of organic polymer with soil oxides, the anionic group of the polymer may penetrate the coordination layer (inner Helmholtz plane) of the Fe and Al hydroxides and so become incorporated in the surface hydroxyl sheet (Greenland, 1971), in a mode of bonding referred to as ligand exchange or specific adsorption (Hingston et al., 1967). This reaction process increases the negative charge on the oxide surface, therefore lowers the ZPC (zero point of charge) of the oxides and also lowers the soil pH. Metal humates are resistant to microbial degradation due to possible toxicity of the metal component to the micro-organism (Juste et al., 1975). The organic component of the complex is known to be physically and sterically inaccessible to microbial enzymes (Sen, 1961; Jacquin et al., 1978). Organo-metallic interactions play a part in the development of many tropical soils (Wada and Aomine, 1973; Schwertmann, 1971; Herbillon, 1980).

2.4 Soil Phosphorus and Availability

Phosphorus deficiency is prevalent in the highly weathered tropical acid soils of West Africa. In some soils, the deficiency is so acute that plant growth virtually stops as soon as the seed reserves of phosphate has been used up (Jones and Wild, 1975; Mokwunye, et al., 1986). Soil solution P concentrations are often low because of the high fixing power of the soils, and applied P readily gets immobilized (Uzo and Uzu, 1972; Juo and Fox, 1977). Predicting the P requirements of the soils will always remain a matter of

conjecture if the reaction processes that control its availability is not looked at systematically. Predictive measures, in most instances, fail to correlate with actual crop yields because factors which are important for the acquisition of nutrients from soil are not all considered.

Several factors determine the flux of P to plant roots. There is a general consensus of opinion by workers in the field of the significance of the use of the intensity, quantity, capacity and mobility factors for the description of P availability in soil and the acquisition of P by plants (Williams, 1967; Fox and Kamprath, 1970). The various soil P reaction processes and availability concepts will be the subject of this section.

2.4.1 Amounts and forms of phosphorus in the soil

Phosphorus in soil consists of organic and inorganic forms. Amounts in soil are influenced by the parent material, vegetation and past management history (Jones and Wild, 1975; Enwezor and Moore, 1966). Soils formed on crystalline acid rocks are much lower in P than soils developed on basic rocks such as basalt (Klinkenberg and Higgins, 1968, Nye and Bertheux, 1957; Udo and Ogunwale, 1977).

Quite a sizeable volume of information can be found on the phosphorus content of the soils of the West African Savanna (Jones and Wild, 1975; Anonymous, 1964; Tyley, 1972; Tpinmidum, 1974; Uyovbisere, 1979; Goldworthy and Heathcote, 1963; Nye and Bertheux, 1957), and for the derived savanna and forest soils (Juo, 1981; Uzu et al., 1975; Adepetu and Corey,

1975; Omotosho, 1971). Total P contents of the savanna soils were found to vary from as low as 13 µg/g to 630 µg/g, with an average at 143 µg/g. The vertisols and hydromorphic soils contained more P, of which 21 to 45% was found to exist in the organic fraction. Values for the forest soils varied from 150 - 1500 with a mean of about 200 µg/g. Organic P generally constitute about 25 - 75% of total P in these soils, with an average at 50%. Bray P for most soils of the savanna is less than 10 µg/g (Singh et al., 1983 a,b,c), and only slightly more in the forest soils. Total P content generally decreased with depth (Juo, 1981). In comparison with the P content of most temperate soils (420 - 700 µg/g, Cooke, 1958; Lauclette, 1971), the average value of 140 - 360 µg/g P found in tropical soils of basement complex origin is low (Wild, 1958; Nye and Bertheux, 1957).

Studies on the inorganic P distribution in some Nigerian and tropical soils have given indications as to the relative abundance of the various fractions in the soils (Jones and Wild, 1975; Enwezor, 1977; Uyovbisere, 1979). Generally, calcium phosphate (Ca-P) is least abundant because it is highly soluble in the predominantly acid soils, and easily reverts to less soluble Fe and Al phosphates (Chang and Jackson, 1957; Enwezor, 1977). On the other hand, iron phosphate (Fe-P) is most abundant of the active fractions because it is least soluble, and tends to accumulate at the expense of Ca-P and aluminium phosphate (Al-P) in the soil (Basco and Bohorquez, 1968; Enwezor and Moore, 1966; Nye and Bertheux, 1957). Al-P is intermediate in solubility. The

relative abundance of the fractions in soil is therefore a reflection of the inverse function of their solubility. Much of the inorganic P in the soils exist as residual P occluded in Fe and Al oxide films (Chang and Jackson, 1957; Jones and Wild, 1975).

The amounts of organic P often represents a significant fraction of total P in the upper horizons (Jones and Wild, 1975; Enwezor, 1977; Barrow, 1961; Chater and Mattingly, 1980; Hedley, et al. 1982; Lan et al. 1981), and exist largely as compounds of humic and fulvic acids (Levesque and Schnitzer, 1967; Shinha, 1971). The presence of iron and aluminium complexed humic and fulvic acids leads to the formation of stable and undissociated complex organo-metallic phosphate which have profound influence on soil-P availability and plant nutrition (Stevenson, 1967; Fox and Kamprath, 1970). It is therefore imperative to understand the nature of the forms and the reaction of P in the soil so as to make effective use of the limited phosphate resource in the soil.

2.4.2. Phosphorus reactions in soils

2.4.2.1. Reaction with inorganic colloids

Quite a few approaches have been used to describe the reactions of P in soils. The use of thermodynamic criteria (Ryden et al., 1977) and the solubility product principle (Lindsay and Moreno, 1960) have been used to explain phosphate reactions. The formation of insoluble iron and aluminium phosphate is generally inferred in nearly all cases. Heseman et al., (1950) have shown the formation of crystalline

phosphates of Al and Fe when clays of Al and Fe oxides reacted with phosphorus solution. During the process of dissolution of monocalcium phosphate in soil, Fe and Al phosphates first dissolve and later precipitate in the form of complex crystalline compounds of the taranakite type, such as $H_6KAl_5(PO_4)_8.18H_2O$ (taranakite), and $H_6(HN_4)Al_5(PO_4)_8.18H_2O$ (ammonium taranakite), along with dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$), (Lindsay and Stevenson, 1959; Lindsay and Moreno, 1960, Wada, 1959).

It is well established that phosphate adsorption in tropical and subtropical soils is affected mainly by the clay content, and Fe and Al oxides (Saunders, 1965; Williams et al., 1958). This in turn is dependent on the soil reaction conditions as described by the pH and ionic strength of the soil solution, organic carbon content and soil mineralogy (Nye and Bertheux, 1957, Udo and Ogunwale, 1977; Juo and Fox, 1977; Borggaard, 1983).

Two mechanisms, chemical adsorption and precipitation are considered to be responsible for P fixation, although Kittrick and Jackson (1956), and Hsu (1964), regard both mechanisms as resulting from the same chemical force. Several workers in different studies have tried to elucidate P reaction mechanisms in soils (Muljadi et al., 1966; Hingston et al., 1972; Breeuwsma and Lyklema, 1973; Chien et al., 1973; Kuo and Lotse, 1974; Rajan and Fox, 1975). Based on effects of pH (Hingston et al., 1972) and on the release of hydroxyl ions during P sorption (Rajan and Fox, 1975), several P sorption mechanisms have been proposed. These mechanisms have

invariably involved ligand exchange reactions at the hydrated oxide surfaces, implying chemisorption of P. As evidence for physical adsorption of P, White (1981) observed that the activation energy of the initial fast reaction was low, which strongly favours physical adsorption. Increasing temperature reportedly increases P adsorption, suggesting endothermic reaction (Griffin and Jurinak, 1973; Barrow, 1974; White and Taylor, 1977). Working with iron oxides systems, as well as on soils, Ryden et al., (1977) arrived at three mechanism for P sorption by soil. These were described as (i) chemisorption at protonated surface sites (ii) chemisorption by replacement of surface hydroxyls and (iii) a more physical sorption of P as a potential-determining (pd) ion. A more plausible reaction mechanism was put forward by Russel et al., (1974) and Parfitt et al., (1975) which provided spectroscopic evidence favouring the ligand exchange mechanism. Parfitt et al., (1975) in their explanation stated that two surface hydroxyl ions (or water molecules) are replaced by one phosphate ion. Two of the oxygen atoms of the phosphate ion are co-ordinated each to a different Fe^{3+} ion, resulting in a binuclear surface complex of the type $Fe\text{-}O\text{-}P(O_2)\text{-}O\text{-}Fe$. This coordination structure was substantiated in their study using various hydrous oxides and amorphous gels.

2.4.2.2. Reactions with organic matter

Interactions are known to occur between organic matter and soil oxides, inhibiting their crystallization and thereby increasing their phosphate adsorption capacity (McLaughlin et

al., 1981; Huang and Violante, 1986; Schwertmann et al., 1986). On the other hand, its been observed that humic and fulvic acids and low molecular weight organic acids may block sites on soil materials and thus reduce P adsorption (Nagarajah et al., 1968, 1970; Lopez-Hernandez et al., 1986; Sibanda and Young, 1986; Kafkafi et al., 1988). Simple organic acids in soils may be released by decay of plant, animal and microbial tissues or as root exudates (Rovira, 1969). The amount of organic matter in the soil could therefore strongly influence the supply of P to plants by the presence of organic ligands in the rhizosphere (Nagarajah, et al., 1968, 1970; Earl et al., 1979; Kafkafi et al., 1988). Kwong and Huang (1981) and Violante and Huang (1989), found that the amounts, the nature, and the size of organic ligands co-precipitated with Al, as well as the surface charge properties of the organo-mineral complex, strongly influence P adsorption. Competition between organic matter and phosphate for adsorption sites in soils is thought to be due the chelating ability of hydroxyl-carboxyl ligands found in soil organic matter (Levesque and Schnitzer, 1967; Reddy et al., 1980; Parfitt, 1979). It has also been found that acids with short chain length and high carboxyl density, derived extensively from transient organic acids of microbial and root exudate origin, compete with phosphate most effectively (Struthers and Sieling, 1950), and Nagarajah et al., (1970), linked the proton buffering nature of the acid with its competitive ability. Organic compounds are said to be effective in desorbing phosphate only when their pKa values

are less than the pH of the soil solution (Bache and Williams, 1971). Organic acids are fully dissociated at pH above 6.5 or pH 7-8 for phenolic hydroxyls, therefore their capacity for releasing phosphate could be negligible at high pH values (Lopez-Hernandez et al., 1979). Harter (1969) observed in his study that organic matter and phosphate were not adsorbed in soil by the same mechanism, and suggested that phosphate may be bonded directly to organic matter in which the phosphate anion replaces the organic hydroxyls. This view was supported by Lopez-Hanandez and Burnham (1974).

2.4.3. Soil phosphorus fractionation

Various chemical fractionation schemes have been developed in an effort to characterize the forms of P in soils and sediments (Fraps, 1906; Dean, 1938; Ghani, 1943; Williams, 1950; Chang and Jackson, 1957; Khin and Leeper, 1960, Peterson and Corey, 1966, Williams et al., 1967, 1971, 1980). The schemes evolved from the assumption that certain reagents can preferentially extract discrete chemical forms (or pools) of P in a given geological material. Although the assumption and procedures have been criticized in connection with the effects of the reagents on pure compounds and mineral associations (Fife, 1959, 1963; Smith, 1965; Bromfield, 1967; Larson, 1967; Hooker et al., 1980), the Chang and Jackson (1957) procedure which distinguishes four main groups: Ca-P, Al-P, Fe-P and reductant soluble-P, have been used widely in recent times to characterize soil phosphate forms (Udo and Ogunwale, 1977; Lekwa and Whiteside, 1986; Day et al., 1987). One major

problem in the chemical extractants used was the possibility of resorption of P by soil when a series of extractants are applied sequentially (Williams and Walker, 1969). Consequently several modifications of the Chang and Jackson scheme have been made in an effort to eliminate the enumerated problems (Peterson and Corey, 1966; Williams and Walker, 1969). Reasonable estimates of the P fractions of the Nigerian soils were obtained using the Chang and Jackson modified methods (Jones and Wild, 1975, Enwezor, 1977; Udo and Ogunwale, 1977; Uyovbisere, 1979, Lekwa and Whiteside, 1986).

Hedley et al., 1982 developed a procedure to separate inorganic P (P_i) and organic P (P_o) into different bioavailable forms and chemical groupings. In the sequential extraction so developed, resin P_i and bicarbonate P_i were the labile fractions (more readily available to plants), while the dilute hydroxide P_i and P_o were moderately labile, and can buffer the more labile fractions. The acid extractable P_i is essentially calcium bound including apatite (Williams et al., 1980). Bicarbonate P_o is the most labile of the organically bound P (Bowman and Coles, 1978), while the hydroxide P_o is more stable and probably involved in long-term P transformation and turnover in soils (Batsula and Krivonosova, 1973). The residual fraction extractable with H_2SO_4 and H_2O_2 digest consists of occluded and non-extractable P, the nature of which is not clearly understood.

2.4.4. Phosphorus adsorption and desorption

2.4.4.1. Phosphorus adsorption

The behaviour of labile inorganic phosphate in soils is dominated by sorption and desorption processes (Bache and Williams, 1971), therefore the characterization of phosphate relationships in soils should reflect their sorption properties. The mechanism of P reactions with soil particles and organic matter was discussed in an earlier sections of this chapter (2.4.2).

The phenomenon of phosphorus sorption and desorption in soils is widespread because of its agricultural importance, and has been the subject of considerable study and controversy (Bache and Williams, 1971; Mead, 1981, Hsu and Rennie, 1962; Gunary, 1970; Syers, et al., 1973; Rajan et al., 1974; Juo and Fox, 1977; Barrow, 1978; Sposito, 1982; Hingston et al., 1986; Posner and Bowden, 1980). The amount of literature on the subject of phosphate sorption by soil and soil constituents is voluminous, therefore only basic concepts will be described here.

Williams (1960) classified the several factors which determine the flux of P to plant roots as intensity, quantity, capacity and mobility factors. Phosphate concentration in soil solution represents the intensity factor and it has been found that plants vary in this requirement. While 0.03 µg P/g continuously supplied in soil solution will maintain maximum growth for some plants, others require concentrations 25 times this amounts (Asher and Loneragan, 1967, Ozanne and Shaw, 1968). Beckwith (1965) suggested the use of 0.2 µg P/g as the

standard solution concentration for comparing soils. This was based on the assumption that successful growth of plants in soils would require a P concentration of approximately this magnitude in the soil solution. Beckwith recognized that the critical value will most certainly vary among crops and soils since soil moisture content influences diffusion to roots (Olsen and Wanatabe, 1966). But he did however suggest that phosphate sorption at the standard P concentration in solution would provide useful information about phosphate fertilizer requirements. Fox and Kamprath (1970) obtained 95% of maximum yield by using this level. Ozanne and Shaw (1968) used 0.3 µg/g as a standard to establish fertilizer rates for wheat. The amount of equilibrium solution P required to attain 95% of maximum yield which is generally referred to as the external P requirement, ESP (Fox et al., 1981) varies with crops and soils.

The quantity factor is the amount of labile P in soils. The quantity of P required to attain a standard P concentration in solution equilibrated with the soil is a useful statistic for comparing soils of widely varying properties. The capacity factor is described as the quantity of P retained at specific conditions of intensity. It indicates the phosphate buffering capacity of the soils and ability of the soil to maintain intensity during P depletion. This is a constant factor for soils which is described by the slope of the adsorption isotherm (Khasawneh, 1971; Mattingly, 1965; Ozanne and Shaw, 1968). Mobility includes a number of

rate factors involved in the transport of P to roots and the uptake of P by plants (Barber, 1962, Fox and Kamprath, 1970).

A sorption isotherm is a curve relating the amount of a substance sorbed at an interface to its concentrations at equilibrium in the medium in contact with the interface at a predetermined temperature condition. For soil phosphate, the situation is complex and reactions generally range from true adsorption to true precipitation (Hsu and Rennie, 1962; Muljadi et al., 1966). As stated by Barrow, (1978), the main objectives for using adsorption isotherms in studies of P sorption are to summarize many experimental sorption data using relatively few numbers, and also to gain understanding of the process. He however cautioned that only isotherms based on some physical model representing sorption of ionic solutes on charged surfaces are useful.

The Langmuir, Temkin and Freundlich equations are often used to describe the quantity/intensity relationships between solid and solution phosphates in soils (Olsen and Wanatabe, 1957; Hayward and Trapnell, 1964; Bache and Williams, 1971), but have been shown to fit sorption data only to a limited range of solution phosphate concentrations (Syers et al., 1973; Holford et al., 1974; Fitter and Sutton, 1975).

The Langmuir equation was for a while the most popular because it has the advantage of providing estimates of bonding energy and adsorption maximum if the conditions described by Langmuir (1918) have been fulfilled. It is based on the assumption that P is adsorbed on a monolayer, and the energy

of adsorption does not vary with surface coverage. This is normally written as:

$$x = \frac{KXmC}{1+KC} \qquad (3.1)$$

where x is the amount of adsorbed P(µg/g soil); K = adsorption / desorption equilibrium constant (ml/µg P), which is related to the bonding energy, and Xm = adsorption maximum (µg P/g soil), C = equilibrium solution P concentration (µg/ml). The parameters are usually derived by the linear transformation:

$$C/x = \frac{C}{Xm} + \frac{1}{KXm} \qquad (3.2)$$

A plot of C/x against C should give a straight line of slope 1/Xm and intercept 1/KXm from which the parameters can be calculated.

The Freundhich equation may be written as:

$$x = aC^{1/n} \qquad (3.3)$$

where a and n are constants. The linear form of the equation is written as:

$$\log x = \log a + \frac{1}{n} \log C \qquad (3.4)$$

This was first introduced as an empirical equation (Fitter and Sutton (1975), and implies that the energy of adsorption

decreases exponentially with increasing saturation of the surface. A plot of log x against log C should give a straight line. It has been suggested that the constants 'a' and 'n' correlate with adsorption capacity and intensity respectively (Van Bladel and Moreale, 1977).

The Temkin equation can be derived from the Langmuir equation by inserting the condition that the energy of adsorption decreases linearly with surface coverage. This equation is written as:

$$\frac{x}{Xm} = \frac{RT}{b} \ln(AC) \qquad (3.5)$$

where A and b are constants. A plot of x against log C should give a straight line.

The equations have been used to describe P with limited success in experiments covering wide P concentration ranges (Olsen and Wanatabe, 1957; Gunary, 1970; Bache and Williams, 1971; Syers et al., 1973; Holford et al., 1974) which has led to the use of extended modification of the equations, such as the 'double Langmuir' (Holford et al., 1974) and 'extended Freundlich' (Fitter and Sutton, 1975) equations.

Criticisms have been raised that question the validity of the Langmuir model as a physical model for P sorption by soil (Vieth and Sposito, 1977, 1982; Barrow, 1978;). On the other hand, the Freundlich isotherm previously considered empirical was shown to be capable of rigorous theoretical derivation (Sposito, 1980). It was also shown to be more in harmony with the process of P sorption by soils (Barrow, 1978). Generally,

the choice among equations is often predicted by the goodness of fit (which is commonly the linearity of the plots) obtained in a given case, along with a given equation simplicity of form. The two surface Langmuir has not been universally accepted and the futility of attempting to split the basic Langmuir isotherm has been discussed (Posner and Bowden, 1980). It is observed that despite its poor ability to predict adsorption maxima, the one surface Langmuir equation is useful for empirical description of data (Harter and Smith, 1981; Posner and Bowden, 1980; Harter, 1984).

2.4.4.2. Properties affecting phosphorus adsorption

Factors influencing P sorption in the soil are numerous and include P concentration in the soil solution and contact time, temperature, clay content, free Fe and Al oxides, pH, organic matter, redox potential, ionic strength of soil solution, soil mineralogy and consequently, parent material and surface area (Mokwunye, 1975; Muljadi et al., 1966; Syers et al., 1971, 1973; Kuo and Lotse, 1972; Juo and Fox, 1977; Roy and de Datta, 1985; Fageria and Filho, 1987). Because of the overlapping effect of these factors, it is difficult to evaluate each factor in isolation in a system as complex as the soil (Syers et al., 1971).

Ionic strength decreases the negative potential on the colloid surface, restricting the diffuse double layer and increasing the access of P to adsorption sites on clay edges and oxides surfaces, leading to increased adsorption and strong bonding (Bar-Yosef et al., 1988). Soil pH also affects

the surface chemistry through its variation in charge density in clay edges and oxides in soils as well as influence the ionic species of P in solution ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) which differ in their affinity for the surface and competition with OH^- for adsorption sites (Lindsay and Moreno, 1960; Bar Yosef et al., 1988; Syers et al., 1973). Many workers have found increasing P adsorption with increasing pH in many soils (Mokwunye, 1975; White and Taylor, 1977; Murrman and Peech, 1969; Anderson et al., 1974; Muljadi et al., 1966). Reeve and Summers (1970) found that liming has led to reduce P adsorption in oxisols. Hourigan et al., (1961) reported a depressing effect of lime on yield consistent with reduced phosphate availability.

The role of organic matter in increasing P adsorption is mainly related to the effect of the organically bound Al and Fe oxides rather than the organic matter per se, and on the inhibiting effects on Fe oxide crystallization (Kafkafi et al., 1988; Saunders, 1965). More detailed account has been presented in an earlier section of this chapter.

Mineralogy and clay content and type (1:1 or 2:1 layer silicates) affect P sorption capacity appreciably, and this has been shown to be due to the surface area (Udo and Uzu, 1972; Juo and Fox, 1977). The 1:1 layer silicates with variable charge surfaces sorb P extensively in comparison to the 2:1 layer silicates (Muljadi et al., 1966). Phosphate sorption capacity was more related to the dithionite extractable Fe as an effective P sink than oxalate Fe. In other conditions, oxalate Fe was found to be better correlated

with P sorption capacity than dithionite extractable Al (Singh et al., 1983a,b,c; Bahia Filho et al., 1983). On the contrary, amorphous Al has been shown to be more responsible for the high P fixation of some Brazilian soils (LeMare, 1982); and some Danish soils (Borggaard et al., 1990).

2.4.4.4. Phosphorus desorption

Because phosphate sorption and desorption processes are believed to primarily govern the behaviour of labile inorganic P in soils, a greater predictive understanding of P sorption and release characteristics of the highly weathered soils is necessary. Desorption or the release of P into soil solution constitutes the limiting step in the bioavailability of phosphorus (Cabrera et al., 1981). Generally, considerable hysteresis are observed between P sorption and desorption isotherms, resulting in most cases in an overestimation of the replenishing ability of soils to supply P to soil solution when estimates are based on sorption isotherms (Kafkafi et al., 1967; Fox and Kamprath, 1970; Okajima et al., 1982; Ryden and Syers, 1977; Bowman and Olsen, 1985; Sanyal et al., 1993). Hingston et al. (1974) suggested that the apparent irreversibility of adsorption is due to the rearrangement of P ions which involves the transformation from monodentate to a bidentate bonding. Kafkafi et al., (1977), observed in their study that P applied in small increments is converted directly into the fixed form, but in the presence of large concentration of P all applied phosphate become exchangeable. Taylor and Ellis (1978), proposed a two point attachment at

low P concentration and a one point attachment at high concentration. These observation may explain the lapses in the sorption and desorption isotherms. Considerable reduction in hysteresis is shown to occur with time as P adsorbed increases with time (Munns and Fox, 1976; Okajima et al., 1983).

Sanyal et al., (1993) reported that equilibrium and kinetic P parameters were closely correlated with clay and organic matter contents, and surface area of soils. The negative correlation between specific P adsorption by clay or organic matter, and clay and organic matter contents of the soils, may tend to suggest an association between the two colloidal components of the soils. This reduces the effective P sorbing surface area. Organic matter therefore could enhance P desorption in mineral soils. Okajima et al., (1983) observed characteristic difference in the types of hysteresis subloops suggesting that reversible and irreversible types of subloops have a specific role to play in P availability to plant, and in the residual effect of applied P.

Phosphorus can be desorbed from soil by solutions of constant pH and ionic strength, such as 0.01 M $CaCl_2$ and 0.1 M KCl (White and Beckett, 1964; White and Taylor, (1977). Isotopic dilution (^{32}P) techniques have also been employed to assess the quantity of adsorbed P in the exchange forms and this has been shown to represent conditions closest to the natural soil processes (Amer et al., 1955). However, since the estimates are only valid at equilibrium which is hardly attained in soils, the technique was considered unsuitable.

Consequently, Amer et al., (1955) proposed the use of anion resins to characterize the desorption capacity of soils. This was considered as an effective P sink analogous to roots and have been used extensively by other workers for similar characterizations (Gunary and Sutton, 1967; Hislop and Cooke, 1968; Vaidyanathan and Talibudeen, 1970).

The use of other chemical extractants attempts to simulate this property. The use of the plant itself as the ultimate test could be complicated by microbial uptake and immobilization (Bowman and Olsen, 1985b). Soil phosphate fractionation has also been employed as an effective tool to characterize desorbed P and to assess the quantity of the labile pool (Barrow, 1980; Fixen and Ludwick, 1982; Russel et al., 1988).

2.4.5. Phosphorus availability indices

Tropical acid soils high in Fe and Al oxide contents are often low in soil solution phosphate. Phosphorus deficiency therefore constitutes a major factor limiting crop growth in the region. It becomes relevant under such circumstance to attach importance to the assessment of soil phosphate availability. Attempts to find suitable availability index by quick extraction procedures have been rather unsuccessful (Nye and Bertheux, 1957, Dabin, 1963). The inadequacy of chemical extractants as availability indices have been demonstrated by numerous researchers, including Adepetu et al. (1979), for some Nigerian soils. Most often, correlation coefficients between extraction values and plant parameters are poor. The

unexplained variation in such instances may have resulted from the interplay of other soil factors not accounted for by the extractant.

Quite a number of techniques have been employed to characterize the available phosphorus fraction in attempts to estimate phosphorus fertilizer requirements. The most commonly used methods include the use of chemical extractants (Oteng and Acquaye, 1971; Sibbesen, 1983; Ryden and Syers, 1976; Olsen et al., 1954; Troug, 1930; Bray and Kurtz, 1945; Amer et al., 1955), P fractionation procedures (Chang and Jackson, 1957; Hedley et al., 1982), isotopic dilution techniques (Larsen, 1952, 1967; Ryden and Syers, 1976; Thiband et al., 1988; Gunnarson and Fredriksson, 1951; McAuliffe et al., 1947), sorption isotherm (Fox et al., 1968; Bache and Williams, 1971; Olsen and Wanatabe, 1957; Holford, 1979; Fox and Kamprath, 1970), phosphate potential (Schofield, 1955; LeMare, 1960), and biological methods (Lathwell, 1958; Williams and Knight, 1963). Schofield (1955) suggested that the chemical potential of phosphate is a suitable measure of availability of P to plants. However, White and Beckett (1964) considered this as valid only when soils of comparable calcium status are considered.

Labile P measurable only by isotopic dilution (Larson, 1967) was considered the pool of available P_i. Uptake of isotopically exchangeable P was negatively correlated to P buffer capacity and bonding energy (Holford and Mattingly, 1976, 1979). The phosphate fractions, just like the chemical extractants, is considered effective in characterizing the

available plant P, but are only able to account for part of the available P. The biological method, obtained by sequential and exhaustive cropping was considered the ultimate method by which the effectiveness of all other methods can be assessed (Bowman, et al., 1978), but immobilization in microbial biomas may complicate any valid assessment.

The mode of action of the extractants also determines how successful the extractants can predict P requirement (Bache and Williams, 1971). The isotopic exchange technique (Gunnarson and Frederiksson, 1951; Larsen, 1952; Olsen and Wanatabe, 1970) and the desorption method by anions exchange resin (Amer et al., 1955; Cooke and Hislop, 1963) are considered mild extractant and affect the soil property only slightly (Bowman et al., 1978). They are known to adequately estimate labile P pool and are excellent indicators of plant available P (Larson, 1952; Fried, 1957; Bekett and White, 1964; Dallal and Hallsworth, 1976).

Velayutham et al., (1981) presented a comprehensive list of chemical extractants commonly used for routine soil tests, and classified them as acid, acid-fluoride, natural (water and CO_2 saturated) and alkaline. In his assessment, the acid fluoride extractant was suitable for the neutral to acid soils and the alkaline extractants (NaOH and $NaHCO_3$) for calcareous soils. Sibbesen (1983) looked at the suitability of phosphate soil tests to assess the phosphate status of soils, and ranked them into three groups, with anions resin as best, water and alkali methods as intermediate, and all acid methods the worst.

There is a consensus of opinion that the most valid estimate of available P is the intensity factor and the description of available P must take into account the intensity, quantity, capacity and rate factors (Dalal and Hallsworth, 1976; Bache and Williams, 1971). As stated by Holford and Mattingly, (1979), a successful soil test can, at best, only give a measure or index value of the amount of phosphorus available to the plant during its growing period. It should therefore simulate the plant root system by extracting an amount of phosphate which is a direct function of the quantity of labile phosphate, but a negative function of the buffer capacity. This emphasizes the intensity factor and reduces the complexity to a simple Q/I relationship, which is the P buffer capacity, and which describes the slope of the adsorption - desorption isotherm. The soil buffer capacity has been shown to affect the critical level of most P extractants, such as the P extractable by 0.5 M $NaHCO_3$ (Heyler and Spencer, 1977). This parameter has been described for soils using different approaches such as buffering capacity (Beckett and White, 1964), maximum adsorption capacity (Olsen and Wanatabe, 1957), maximum buffer capacity (Holford and Mattingly, 1976b) sorption index (Bache and Williams, 1971) sorption capacity (Piper, 1942), sorption test (Ozanne and Shaw, 1967) and buffering index (Holford, 1979). Bowman and Olsen (1985) determined the P buffering capacity of their soils by the ratio of the change in resin-P (quantity factor)/change in water-P (intensity factor). The criterion

for selecting a suitable index should be determined by a combination of soil factors.

From the above discussion, it is apparent that indices for estimating plant-available P are typically based on the chemically extractable P_i. Few estimates take into account other P pools, notably the organic pool (P_o) which has been shown to contribute significantly to P nutrition in tropical soils (Ayodele and Agboola, 1983; Sharpley et al., 1987; Sattel and Morris, 1992). Recent studies have shown that soil tests that measure only P_i grossly underestimate plant available P, therefore the desirability of including other fractions have been advocated (Bowman and Cole, 1978, Abbott, 1978, Thien and Myers, 1992; Hedley et al., 1982). Readily mineralizable P_o (by soil microbes) as extracted by Olsen reagent (Olsen et al., 1954; Hedley et al., 1982; Molla et al., 1984; Bowman, 1978b) contribute significantly to the labile P fraction of tropical soils high in Fe and Al oxides where much of the P exist in the organic form (Adepetu and Corey, 1976; Anderson, 1980, Fuller and McGeorge, 1951).

2.6. Rhizosphere Processes: Turnover and Transport of Phosphorus

The various reaction processes which control nutrient dynamics and availability to plants take place largely in the rhizosphere. So far, predictive measures as characterized by chemical extraction techniques are often poorly correlated with actual plant uptake. This is because vital factors such

as spatial availability of nutrients as determined by root growth and mobility, and the mobilization and immobilization of mineral nutrients, that are important for the acquisition of nutrients from soil by plants are often not adequately considered.

Plants absorb nutrients from soil solution. Employing Bray's (1954) concept of mobility of nutrients in the soil, Barber (1962) observed that phosphate transport to the vicinity of plant roots is mainly by diffusion. Because of the high buffer power of phosphate in soil, its rate of diffusion is very low. This leads to rapid depletion of P in the immediate vicinity of roots (Hendriks et al., 1981; Bhat and Nye, 1973). The study of phosphate behaviour in the rhizosphere is therefore crucial to fully understand, determine and describe soil phosphate dynamics and availability in soil. Gahoonia and Nielsen (1991) described a plant growing technique by which rhizosphere processes can be studied under controlled nutrition of plants. By the thin slicing technique employed, phosphate concentration along a depletion profile was assessed with a high degree of resolution.

The solubility of mineral phosphate compounds in soil such as iron, aluminium and calcium phosphate compounds are pH related (Lindsay and Moreno, 1960). Calcium phosphate solubility increases with decrease in pH, while Al-P and Fe-P are solubilized essentially by ligand exchange, and with pH increase. The most important aluminium phosphate and iron

phosphate compounds in soils are variscite ($AlPO_4.2H_2O$) and strengite ($FePO_4.2H_2O$) with dissociation reactions as follows:

$$AlPO_4.2H_2O \rightleftharpoons Al^{3+} + H_2PO_4^- + 2OH^-$$

and

$$FePO_4.2H_2O \rightleftharpoons Fe^{3+} + H_2PO4^- + 2OH^-$$

(Bolt and Burggenwert, 1978).

The release of bicarbonate (HCO_3^-), which may dissociate into OH^- and CO_2 would release $H2PO4^-$ from the Fe and Al phosphate minerals. The pH of the soil rhizosphere was observed to differ considerably from that of the bulk solution (Marschner and Roenheld, 1983; Kuchenbuch, 1983), which consequently affect a number of rhizosphere processes (Marschner et al., 1986). The availability of P in soil may therefore vary with the predominant fraction of soil phosphates.

The various phosphate forms in soil are known to vary in the extent to which they are available to plants (Hedley et al., 1982; Chang and Jackson, 1957). The contributory effect of the organic P fraction to the labile phosphate pool is gaining greater importance (Heldey et al., 1982; Stevenson, 1982 p 120-134; Adepetu and Corey, 1976; Anderson, 1980; Tiessen et al., 1984; Enwezor and Moore, 1966). It is also shown to modify important soil parameters related to the sorption and transport of P in the rhizosphere (Helal and Dressler, 1989; Hedley et al., 1982). The use of sequential extraction techniques has allowed the fractionation of soil P and the assessment of the bioavailability of the various fractions.

The importance of organic P mineralization as a viable source of plant available P has been reported (Dormaar, 1972; Chater and Mattingly, 1980), and has been found to constitute upto 90% of the P in the rhizosphere soil solution, with a maximum just outside the root zone (Helal and Dressler, 1989). Phosphate transformation is therefore important in the description of the available P status of soils. The depletion profiles of inorganic phosphate in soils are influenced by the reaction processes in the rhizosphere (Gahoonia et al., 1992). The relationship between pH and phosphate mobilization in the rhizosphere of rape seedings has been much studied (Grinsted et al., 1982; Bekele et al., 1983; Hoffland et al., 1989 a,b). The pH change in the rhizosphere results from the unequal amounts of nutritive cations and anions taken up by plant roots (Bretele, 1973; Heldey et al, 1982) and by adjusting the ratio of NH_4^+ and NO_3^- in the nutrient solutions, an effective control of the pH can be achieved (Nielsen, 1984; Gahoonia and Nielsen, 1992). By employing the principle of regeneration of Nielsen (1984), the plant growing technique of Gahoonia and Nielsen, (1991), and the P fractionation technique of Hedley et al., (1982), it may be possible to assess the soil phosphate status, and quantify the turn-over and transport of P in the rhizosphere.

Modelling P transformations in the rhizosphere, Halm et al., (1972), as well as Cole et al., (1977), demonstrated that organic P interacted with almost all the inorganic P fractions. The microbial soil biomas was found to play a

central role in these interactions both as a sink and as a source of P (Cosgrove, 1977).

Evidence obtained from the work of Helal and Dressler (1979), showed that the rhizosphere is a key site for P transformation and considerable mobilization of P from non-exchangeable fractions. The organic and microbial P contribute to the labile P fraction, and modify the sorption and the transport of P in the rhizosphere.

CHAPTER 3

MATERIALS AND METHODS

3.1. Site Selection and Main Features of the Areas

Three pedons representing soils with properties that differed in Fe and Al oxides, but contained similar amounts of organic matter in the surface horizons were selected for description and sampling in the field. Two of these pedons were from the relatively dry Northern Guinea savanna and the third was obtained from the forest zone. Location, environmental features and field morphological descriptions of profiles are given in Appendix 3.1.

Pedons 1 and 2 were located at the Institute for Agricultural Research Station, at Samaru, with sample sites described by the map coordinates 11°10'N and 7°37'E. The main features of the sites were: average elevation of 680 m, annual rainfall of 1,090 mm, with a mono-modal rainy season (May to October), and a Northern Guinea Savanna vegetation of grass lands and woodlands. Geology is Basement complex of the Precambrian era, with some Quatenary aeolian deposits. Pedon 1 was poorly drained and with acquic soil moisture regime. The profile was situated on a footslope of gradient 1 - 2 % and it was an area of fluvial deposition. Pedon 2 was well drained, ustic soil moisture regime, and situated on a midslope of 2 - 3 % gradient. Pedon 3 was located at the outskirts of Isoya village, 10 km south of Ife town, with map coordinates 7°20'40'' N and 4°32'55''E. Average elevation of this site was 280 m above sea level. Mean annual rainfall was

1,375 mm with a 9-10 months bimodal rainy season. Usually, December and January are dry months but can change with the year. The vegetation was rain forest, and the geology was also Basement complex of the Precambrian era, with soils formed from amphibolite rich metasediments. Profile 3 was well drained with udic soil moisture regime. It was situated on a footslope of 3-4 % gradient.

3.2. Soil Sampling and Sample Preparation

At the study sites, profile pits were sunk and genetic horizons were marked and described. Samples were taken from each identified horizon presented in Appendix 3.1 for characterization and for special studies. Bulk samples were also taken from specified horizons for detailed studies on P reactions in soil.

In the forest soil, the Ap (0-30 cm) and the Bv1 (70-95 cm) horizons were bulk sampled. In the savanna soil (profile 2), the Ah (0-22 cm) and the Bt (55-100 cm) horizons were also bulk sampled. The tops and the subsoils were sampled in the two zones to obtain soils with and without organic matter in each case. The fluvial soil (Acquic Kanhaplustalf) was sampled to the depth of 0-15 cm to obtain soils with about the same organic matter content found in the surface soils of profiles 2 and 3 (soils 2 and 3). All profiles had little or no human influence in the past 5-10 years. The three profiles were used in the initial characterization of phosphate reactions in soils. The profile soils provided the required variation in OM. The natural soils for the detailed study

were the bulk samples of profiles 2 and 3. The 0-15 cm sample of profile 1 (soil 1) was used to prepare the artificial soils and by some chemical treatments, these soils acquired properties analogous to the natural soils.

The top soils of pedons 1 and 2, and the subsoils of pedons 2 and 3 were used to investigate the depletion of P in the rhizosphere of maize and rape plants in soils. For comparison with the tropical soils, two temperate top soils from Denmark were included. The soil samples were air dried, crushed in an agate mortar and passed through a 2 mm mesh sieve, and then stored for chemical analysis and experimentation.

3.3. Characterization of Study Soils

3.3.1. Routine determinations

Particle size distribution was determined by the pipette method (Andreason, 1939), and this required pretreatment with 30 % H_2O_2 to destroy the organic matter (OM). Soil pH was measured potentiometrically in 1:1 soil-water and 1:2.5 soil-0.01 M $CaCl_2$ suspension. Exchangeable Ca, Mg, K and Na extraction was carried out by the NH_4OAc method (Chapman, 1965) and by the 'compulsive' exchange method of Bascomb (1964) as modified by Gillman, (1979). The Ca and Mg contents of the extracts were determined by the AAS, and the K and Na by the flame photometer. Exchangeable Al and extractable acidity were determined by the 1 M KCl method (McLean et al., 1965). The ECEC was obtained by summation of the exchangeable bases and

extractable acidity. CEC by NH_4OAC saturation at pH 8.2 (Chapman, 1965) was also determined. OM content was estimated by the wet oxidation method of Walkley and Black (1965). The soil electrolyte activity was measured in 1:2 soil-water suspension using the Metrohn E587 conductometer. The micronutrients (Zn, Fe, Cu and Mn) were extracted in 0.1 N HCl, and determined by the AAS.

The soil Fe and Al oxide fractions were determined. The citrate-bicarbonate-dithionate (CBD) extractable Fe and Al were determined by the method of Mehra and Jackson, (1966), as described by Mckeaque et al., (1971). The oxalate extractable Al and Fe were determined by the photochemical extraction procedure as outlined by McKeaque and Day, (1966). The pyrophosphate extractable Al and Fe were determined by the method of McKeaque et al., (1971). The Fe contents of the extracts were estimated by the AAS, and the aluminium contents were estimated colorimetrically by the aluminon method (Hsu, 1963) after destroying the extracting solutions with aqua regia and removing the iron in solution.

3.3.2. Specific surface area determination

The specific surface area of the soils was determined by the ethylene glycol method as outlined by Mortland and Kemper, (1965). The OM was not destroyed in the soils before determination. The apparatus was not modified but consisted of a pyrex vacuum desiccator containing P_2O_5. This unit was attached to a vacuum pump. The culture chamber/glycol solvate - aluminium box assemblage which contained the samples was

maintained. Approximately 1.1 g soil was weighed out into the tarred aluminum boxes and dried to constant weight for about 6 hours over P_2O_5 in the evacuated desiccator. The soil was wetted with 1 ml of glycol before equilibrating over the $CaCl_2$-glycol solvate in the culture chamber. The equilibration time as specified in the procedure was adhered to and the change in weight was monitored periodically. When two consecutive weighings coincided or showed a slight loss, the equilibration was terminated and the amount of bound ethylene glycol was determined (ethylene glycol adsorbed as a monolayer on soil particle surfaces). The specific surface was then calculated from the relationship:

$$A = Wg/(W_s \times 0.00031) \qquad (3.1)$$

where A = specific surface in $m^2\ g^{-1}$

Wg = weight of glycol retained by the sample.

Ws = weight of P_2O_5 dried sample in g.

0.00031 = Dyal-Hendricks value for the amount of glycol required to form a monolayer on a m^2 of surface.

3.3.3. Determination of surface charge characteristics

A modification of the procedure as described by Van Raij and Peech, (1972), was used. To 5 g of the 2 mm soil sample (not pre-washed) in six 100 ml polypropylene bottles were added appropriate amounts of NaCl, and 0.1N HCl or 0.1N NaOH and water to achieve a final solution volume of 25ml. The amount of HCl and NaOH added depended on the soil pH and the

ΔpH value (pH KCl - pH H_2O, Table 3.1). The final concentration of NaCl in each set of 6 treatments were 5 N and 0.005 N, therefore the determination required two sets of 6 bottles for each soil. The bottles were tightly covered and shaken periodically by hand. After 3 days the pH of the suspension was measured. The amount of H^+ and OH^- adsorbed by

Table 3.1. Volumes of NaCl, 0.1 N HCl, 0.1 N NaOH and water required to obtain a titration curve for the determination of ZPC depending on pH and ΔpH of soil.

	Bottles					
Treatments	1	2	3	4	5	6
	-cm3-					
If pH (H_2O) > 5.5, and ΔpH is negative						
0.I N HCl	20	16	8	4	2	0
H_2O	0	4	12	16	18	20
NaCl*	5	5	5	5	5	5
If pH (H_2O) is <5.5, and ΔpH is negative						
0.I N HCl	12	8	4	2	0	0
0.I N NaOH	0	0	0	0	0	0
H_2O	8	12	16	18	20	18
NaCl*	5	5	5	5	5	5
If ΔpH is zero or negative						
0.I N HCl	4	2	0	0	0	0
0.I N NaOH	0	0	0	2	4	8
H_2O	16	18	20	18	16	12
NaCl*	5	5	5	5	5	5

* NaCl concentration in final solution was 5 N and 0.005 N.

the soil at any given pH value was taken as equal to the amount of HCl or NaOH added to the suspension minus the amount of acid or base required to bring the same volume and the same concentration of NaCl solution, without the sample to the same pH. The ZPC was taken as the common intersection point of the titration curves carried out in the presence of the two concentrations of NaCl.

3.3.4. Mineralogical analysis

3.3.4.1. Separation of sand, silt and clay for mineralogical analysis

The sand, silt and clay were separated by the method of Jackson (1956) with slight modifications. Fifty grams of 2 mm mesh soil was transferred to a dispersion cup, 400 ml of 0.002 M $Na_4P_2O_7$ was then added and stirred at high speed for 10 mins with an electrical stirrer. The silt + clay was separated from the sand by the principle of sedimentation by siphoning to a depth of 10 cm following the time/temperature schedule after transferring to a sedimentation bottle. This was repeated until the supernatant was clear. The silt + clay was then transferred to a dispersion cup with $Na_4P_2O_7$, and the process as described above was again repeated. The clay was separated from the silt by repeated sedimentation and siphoning in accordance with predetermined time schedule until the supernatant was clear.

The sand and silt fractions were washed thoroughly with distilled water by centrifugation and then air dried. The

clay fraction was flocculated with NaCl, and excess Cl^- was washed off repeatedly until the 0.1 M $AgNO_3$ test for Cl^- was low or absent. The soil was washed further with ethanol and dried. The sand fraction was further separated into 5 fractions using a row of sieves to give particle size fraction ranges of the following dimensions: 20-75 µm, 75-125 µm, 125-250 µm, 250-710 µm and 710 µm - 2mm. The sand size range of 125-250 µm was used for the mineralogical analysis of the sand fraction.

3.3.4.2. Mineralogy of the size separates

Sand and silt separates: The fine sand fraction (125-250 µm) was further separated into various magnetic fractions by means of an isomagnetic separator. The magnetic fractions were then examined under the petrographic microscope for the identification of the mineralogy of the sand grains. The procedure outlined by Cady (1965) was followed. The criteria for identification were the refractive index or birefringence, colour, shape, cleavage and crystal form.

The mineralogical composition of the non-mangnetic sand fraction and silt was determined by X-ray diffraction analysis using the procedure described by Jackson (1956). The samples were ground in an agate mortar to approximately 10 µm and directly mounted on a random powder wedge and X-rayed with a deffractometer operating at 50 kV and 30 mA using a copper radiation tube. Scanning speed was 2° 2θ/min and divergence slit was 1°. Scanning was done over the range of 9° 2θ to 50°

2θ to allow for the identification of quartz, microcline and feldspars.

The clay fraction was pretreated to remove organic matter (H_2O_2 treatment) and free oxides (CBD extraction: Mehra and Jackson, 1960) and then saturated with MgOAc. Excess MgOAc was removed by washing with ethanol. The oriented clay specimens for X-ray diffraction analysis were prepared by depositing clay suspensions on glass slides and evaporation. The oriented clay samples were scanned at 50 kV and 25 mA; range at 2×10^3, scanning speed at 1° 2θ/min., paper speed at 80 mm/min, divergence slit = 1/2°. Scanning range was 4° 2θ to 16° 2θ using a copper radiation tube.

For the random powder clay analysis, the rest of the sample was air dried and ground. X-ray diffraction analysis was carried out as described for the sand and silt random powder analysis, but in this case, the scanning range was 8° 2θ to 42° 2θ. Lattice distance or d spacing was calculated from Bragg's equation:

$$n\lambda = 2d \sin \theta \qquad (3.2)$$

where λ = wavelength of radiation (X-ray) tube,

d = interplaner distance

θ = angle of incidence of the monochromatic X-ray beam,

n = order of diffraction.

The λ value for the Cu radiation tube used was 1.542 and n was assumed to be 1. The d spacing were calculated in Amstrongs (Å).

3.3.4.3 *Difference diffractogram analysis*

The selected natural and artificial soils were examined to determine the nature of Fe oxides forms in the samples. The silt+clay fractions of the soils were separated from the sand fraction by the sedimentation technique based on Stoke's law, (1851). The soil particles were dispersed using double deionized water and over-night shaking on an end-over-end shaker. The suspension was then flocculated with $MgCl_2$ and washed with ethanol by centrifugation. The dried sample was crushed in a agate mortar and analyzed by powder X-ray diffraction.

Difference difractograms were produced by removing the free oxides by CBD treatment and analyzing the treated sample by powder X-ray diffraction as was done for the untreated samples, ensuring that the angles of diffractions were similar. The diffractograms of the treated and untreated samples were then subtracted to identify the oxide minerals present in the soil. This was done by scaling one of each pair of diffractograms until the quartz peaks disappeared or almost disappeared. Kaolinite peak was used to scale the NatAmB sample. The peaks discernable after the subtraction of the diffractogram of the treated soil from that of the untreated soil should give an indication of the mineralogy of the Fe and Al oxides of the study samples.

3.3.5 Organic matter extraction and fractionation

The soil organic matter contents of the A horizons of the profiles were extracted and fractionated as described by

Schnitzer (1982). Ten grams of air dry soil was transferred into a 200 ml polypropylene bottle, 100 ml of 0.1 M NaOH was added and the air displaced by N_2. The bottles was tightly covered and shaken longitudinally on an end-to-end shaker for 24 hours at room temperature. The dark coloured supernatant was separated from the residual soil by centrifugation (10,000 rpm for 10 min.), washed once with water and combined with the supernatant.

Fractionation and purification of the extract was carried out as follows: The alkaline extract was then acidified to pH 2 with 2 N HCl and allowed to stand at room temperature for 24 hours. The coagulated humic acid was then separated by centrifugation and washing. The fulvic acid fraction still in solution was further purified by repeated passing of the extract over cation exchange resin in the H^+ form (Schnitzer and Khan, 1978). The HA and FA fractions were then frozen and freeze dried and weighed. The humin fraction was taken as the original estimate of soil OM minus the estimates of the FA and HA fractions. The flow chart for the fractionation of OM is illustrated in Figure 3.1.

3.4 Preparation of The Special Soils

The bulk samples taken from the pedons were used for this section of studies. The natural soils; pedon 2 (Ah:0-22 and Bt: 60-100 cm) and pedon 3(AP:0-30 and Bv1:70-95 cm) were used. Three kg of soil from each selected horizon was washed twice with 0.001M $CaCl_2$ to remove easily soluble material and

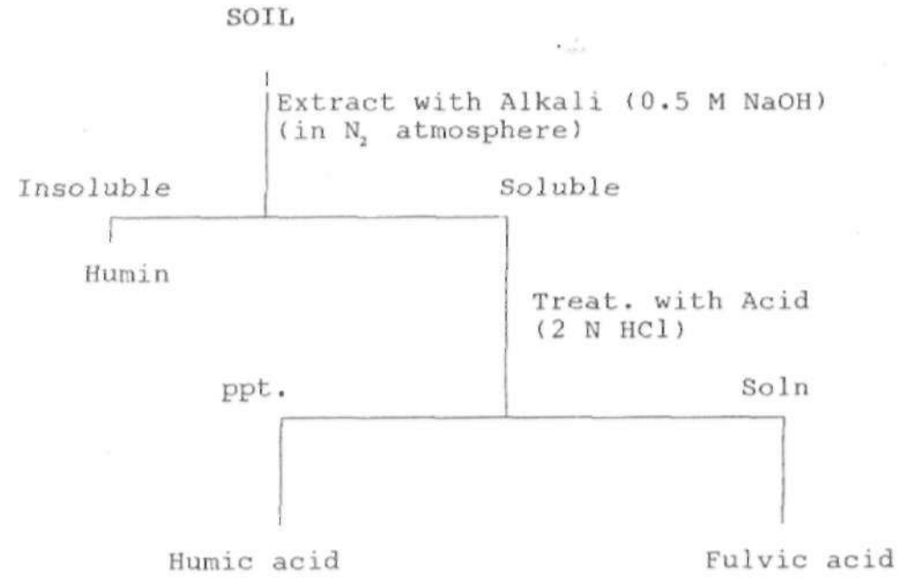


Fig. 3. 1. Flow chart for the extraction and fractionation of Humic substances in soil.

then air-dried. The bulk sample from pedon 1 (0-15 cm) was used for the preparation of the artificial soils.

Some selected chemical and physical properties of the natural soils are presented in Table 3.2.

3.4.1 Preparation of the iron and aluminium oxide-soil systems

3.4.1.1 Removal of OM

The bulk soil of pedon 1 (<2 mm, 0-15 cm) was used to prepare the artificial soils. The artificial soils were expected to have properties analogous to the natural soils selected for this section of study, which in this case was four.

Table 3.2. Selected properties of the natural soils used for the special studies

Pedon	Depth (cm)	pH H_2O	pH $CaCl_2$	Org.C	ECEC*	Tot. P	Bray P_i	Sand[a]	Silt	Clay	Texture[b]
				%	$Cmol_c\ kg^{-1}$	ppm	ppm		- % -		
1	0-15	4.44	3.84	2.79	14.8	294	21.9	25.6	18.6	55.8	C
2	0-22	6.80	6.43	2.22	11.7	313	23.6	77.5	7.7	14.8	Sl
2	60-100	6.42	5.62	0.30	11.1	118	0.70	54.6	8.1	37.4	Sc
3	0-30	5.90	5.46	2.40	15.2	840	8.40	25.6	18.8	55.6	Cl
3	70-95	6.10	6.02	0.20	7.7	678	0.30	15.0	11.4	73.5	C

* Compulsive exchange (Gillman, 1979)
a. Pipette method
b. C = Clay, S = Sand, L = loam

Eleven kilograms of the 0-15 cm soil of pedon 1 was weighed out and thoroughly mixed and split into 2 halves. The OM content of one half (5.5 kg) was removed by H_2O_2 treatment in a plastic bucket placed in a water bath pre-heated to 70 - 80°C. The H_2O_2 treatment was continued until there was no more reaction. The pH of the reacting suspension was maintained at above 4 with 2 N NH_3 solution when it dropped below this value. The soil was then centrifuged and washed twice with distilled water to remove excess reagent and soluble matter, and then air dried and stored for the next phase of treatments.

3.4.1.2. Preparation of the Fe and Al oxide coated soil particle

The reagents used for the preparation of the artificial soils were as follows:

a) 0.3M solution of both $AlCl_3$ and $FeCl_3$ were prepared separately. This was done by dissolving 40.05 g of $AlCl_3$ and 48.75 g of $FeCl_3$ separately in 1 litre of water.

b) 4 M KOH solution as the neutralizing reagent was prepared by dissolving 224 g of KOH pellet in 1 liter of water.

c) 10% Al containing Fe solution: To obtain a 10% Al containing Fe solution, 100 ml of $AlCl_3$ was added to 900 ml of $FeCl_3$. Because of the high oxidation rate of $FeCl_3$, a fresh solution of this reagent was prepared immediately before use.

The soils (dehumified and the humus soils) were introduced separately into polypropylene containers with the right amount of 0.275 M solutions of 10 % Al in Fe solution to give a 4 % Fe content of soil. The suspension was then stirred and allowed to stand for 10 mins. A predetermined volume of 4 M KOH was then added rapidly to neutralize the suspension to pH 7, stirring continuously. After 30 min, the pH was again checked and adjusted with KOH or HCl to pH 7. The suspension was shaken overnight and then allowed to stand for 24 hours on a hot water bath at 80°C, stirring periodically. The suspension was aged for 2 months, by allowing it to stand at room temperature and mixing properly every week. At the end of the aging period, the soil was separated from the solution by high speed centrifugation and washed once with distilled water, and air dried, ground and sieved through the 2 mm mesh screen.

The chemically treated soils, (humus and dehumified), were again split into two halves; one half was washed twice with 0.001M $CaCl_2$, air-dried and stored for further use. The second half was subjected to 10 cycles of crystallization process as described in the next section.

3.4.1.3. Crystallization of oxide coatings on particle surfaces

The soils for crystallization were transferred to small plastic containers of 7 cm diameter and 8 cm high with perforations at the base to allow for drainage. Filter papers were placed over the perforations before the soil was introduced. The soils in the containers were then wetted and placed in a water bath at 80°C for 2 days, and then subjected to 10 cycles of air drying, freezing (at -4°C), temperature equilibration at room temperature, oven drying at 40°C and rewetting (done subterrainially in the perforated cups with soil). Each step was for a duration of 24 hours and each cycle was completed in one week. At the end of the crystallization process (2½ months), the soils were ground and washed with 0.001M $CaCl_2$, air-dried and stored for characterization and experimentation.

To ensure that the oxide treatment was an integral part of the soil particle surface, the air-dried soil was further stored for another 6 months before use for the next phase of experiments.

All through the process of neutralization and crystallization, the pH, Al and Fe content of the ambient

solution were monitored. The prepared soils were characterized with respect to the following properties as described above: pH in water and $CaCl_2$, CEC by Gillman, specific surface, Fe and Al fractionation and X-ray diffraction analysis.

3.5. Phosphate Studies

3.5.1. Forms of phosphorus

Total phosphorus (P_T) was determined by the perchloric acid digestion method as described by Olsen and Sommers, (1982), and P in digest was estimated by the molybdenum blue colour method of Murphy and Riley, (1962). Organic phosphorus (P_o) was determined by the ignition method of Saunders and Williams, (1955), as modified by Walker and Adams (1958). P in solution was estimated colorimetrically as was done for P_T. Phosphate fractions of the soils were determined by two methods. Phosphate fractionation into the various inorganic phosphate forms (Al-P, Fe-P, Ca-P and the reductant soluble P) was carried out according to the method of Chang and Jackson (1957) as modified by Peterson and Corey (1966). The residual fraction was taken as P_T minus the sum of the chemical forms so determined. Phosphate distribution in the profile soils were determined by this method.

For the determination of the lability of phosphate P_i and P_o forms in the rhizosphere samples, the modified Hedley et al., (1982) method was used. The soils were extracted sequencially with 0.5 M $NaHCO_3$, 0.1 M NaOH and 1 M HCl

solutions, and the residual P determined by the H_2SO_4-H_2O_2 digest. Between extractions, the soil residue was washes twice with saturated solution of NaCl. The schematic flow chart of the modified Hedley method is given in Figure 3.2.

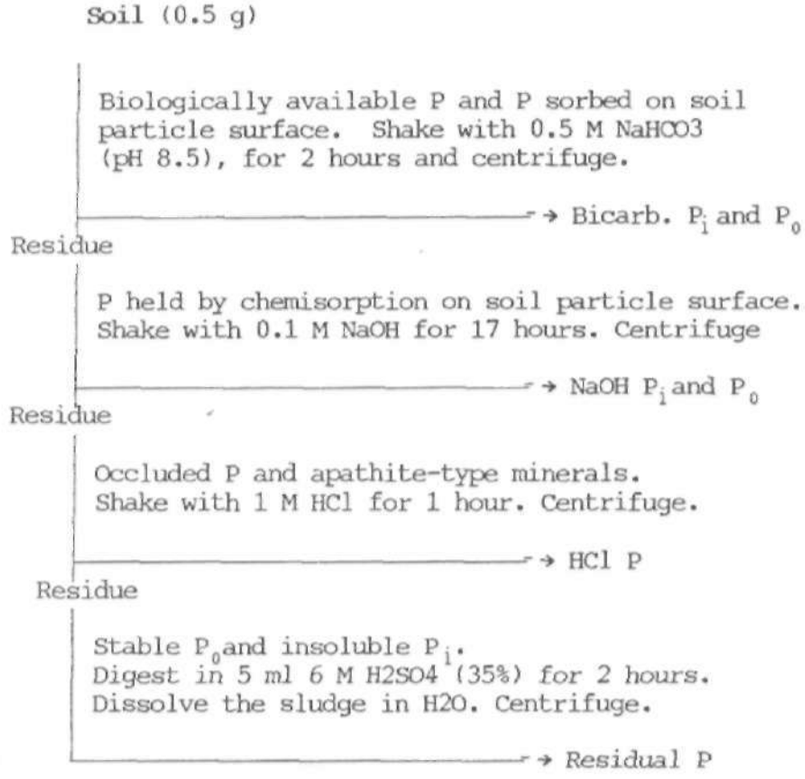


Figure 3.2: Flow chart for the sequencial extraction of phosphorus by the modified Hedley et al., (1982) method.

3.5.2 Adsorption studies

3.5.2.1 Soil P x time interaction

Equilibration time greatly influences P adsorption (Munns and Fox, 1976). A phosphorus sorption x time experiment was carried out on some selected soils. The selected natural soils were equilibrated with 300 µg P/g soil, while the

artificial soils were equilibrated with 1,500 µg P/g soil. Equilibration time ranged from 1 to 19 days after which the P in solution was determined. Phosphorus in solution was then plotted against time to obtain the effect of time on P sorption in both natural and artificial (prepared) soils.

3.5.2.2 Phosphorus adsorption isotherms

Phosphorus adsorption isotherms were determined as described by Fox and Kamprath, (1970). Three grams of soil (2mm) were placed in 50 ml centrifuge tubes and equilibrated with 30 ml of 0.01M $CaCl_2$ containing varying amounts of P (0-1500 µg P g^{-1} soil) as KH_2PO_4. Three drops of 3 mM $HgCl_2$ L^{-1} was added to each system to suppress microbial growth. The tubes were shaken twice daily for 30 mins longitudinally on an end-to-end shaker at room temperature for 6 days. At the end of the equilibration period, the soil suspension was centrifuged at high speed and P was determined in the supernatant solution by the method of Murphy and Riley (1962). Phosphorus which disappeared from solution was considered to have been adsorbed, and P sorbed was plotted against P concentration in the soil solution to obtain the adsorption isotherms from which soil adsorption parameters were determined.

3.5.2.3 Determination of soil P adsorption indices

The adsorption indices evaluated were adsorption maxima, P affinity and buffering capacity and the standard phosphate requirement (µg P/g soil sorbed at 0.2 µg solution P concentration).

To estimate the indices the adsorption data were fitted to the Langmuir model earlier presented. The Langmuir equation was used because of its simplicity in summarizing adsorption data, its predictive capability and the physical significance of the constants and correlative parameters for comparing soils (Barrow 1985; Sposito 1979, 1989). The data were also fitted to the Freundlich and Temkin models to further elucidate the behaviour of P in the soils. Non-Linear regression (NLIN) was used to fit the data directly into the equation and the parameter estimates determined by least-square iterative process (SAS Institute, 1987). The goodness of fit was determined by the R^2 value and the root mean square error (RMSE) defined as

$$RMSE = (RSS\ (o - p)^1)^{1/2} \qquad (3.3)$$

where 'RSS' is the residual sum of squares for the nonlinear regression, 'o' is the number of observations, and 'p' is the number of parameters in the model (Kinniburgh, 1986; Morris et al., 1992). The maximum buffer capacity (MBC) was calculated by the product of the adsorption maximum and the bonding energy or affinity index (Holford, 1979b). The standard P requirement was determined by interpolating adsorbed P at 0.2 µg P/ml equilibrium solution concentration.

3.5.3. Phosphorus desorption studies

To obtain data for the desorption isotherms for the special soils, the soils were equilibrated with P in 0.01 M $CaCl_2$ at 2 levels (Table 3.3) for 11 days as described by Fox

and Kamprath (1970). After the initial period of (11 days), 28 mls of the supernatant solution was replaced with 0.01M $CaCl_2$ and the soil again resuspended for 48 hours. The sample was again centrifuged, 28 ml of supernatant removed for P analysis and the cycle repeated 22 times. In calculating P desorbed, allowance was made for the 2 ml of supernatant carried over from each cycle (entrained solution).

Table 3.3. P solution concentration used for the desorption experiment in the various soils.

Special Soils	µg P g^{-1} soil	
	Low	High
NatCrA	50	100
NatCrB	50	100
NatAmA	150	700
NatAmB	700	1250
ArtCrA	900	2000
ArtCrB	1250	2000
ArtAmA	1500	2500
ArtAmB	1500	3000

3.5.4. Soil test methods

The available phosphate fractions were estimated by 4 chemical methods. These were Bray-P, Olsen-P, and Water-P and Resin-P as described by Olsen and Summers (1982). Specifically, Bray P_1 was measured in soil:solution ratio of 1:7, Olsen P: in 1:20, water-P in 3:30, and resin in 1:100, with 1 g resin-P (type Amberlite IRA in Cl^- form) in 60 mesh

soil-water suspension. Soil was washed off the resin and P desorbed with acidified NaCl solution.

3.5.5. Determination of relative fertility index (FI) for selected soils

The fertility coefficient or soil solution P at soil particle surface of selected soils was determine in 0.01M $CaCl_2$ solution. 5 g of soils were equilibrated in 10, 20, 30, 80, and 160 ml of $CaCl_2$ solution for 10 days. The suspension was shaken every day by hand. Two drops of toluene were added to each unit to suppress microbial growth. At the end of the equilibration time, a portion of solution was obtained by centrifugation and analyzed for solution P.

The resulting soil:solution ratio was calculated and regressed against the estimated P in solution. Interpolation to zero soil:solution ratio would give an estimate of P concentration at particle surface. The FI were calculated from the reciprocal of the regression coefficients.

3.5.6. Phosphate determination in solution extracts

Inorganic phosphate (P_i) in aliquots of solution extracts was determined by the blue colour method of Murphy and Riley (1962). Organic P contents of extracts was estimated from 5 ml aliquot digest at 110° C with $K_2S_2O_8$ in NaOH solution in an autoclave (EPA 1971), and P in neutralized digest was determined by the blue colour method of Murphy and Riley (1962). This gave an estimate of the total P from which the organic P was obtained by the difference.

3.6 Greenhouse Study

3.6.1 Greenhouse experiment on maize in P adjusted soils

3.6.1.1. Greenhouse procedure

The selected natural and artificial soils (special soils) earlier described were used in this section of the greenhouse studies. One hundred gram of soil was weighed out into plastic bottles with wide neck. Six levels of P were established in each soil by adding P as indicated by the appropriate sorption curve to give soil solution concentration of 0, 0.02, 0.06, 0.20, 0.60, 1.50 µg/g P. The amount of P added to attain this level of solution P are presented in Table 3.4. P was added as KH_2PO_4 solution and mixed with the soil after which soil water was adjusted to 80 % field capacity and equilibrated for 21 days, mixing occasionally. Because of the high content of clay in these soils, a preliminary trial cropping was carried out. To improve aeration for proper root growth in the limited volume of soil proposed, 50 g of acid washed sand (pH 7) was added to each plastic bottle containing the incubated soil, and mixed thoroughly at the right moisture content.

Finally, blanket treatments of N, K and S, and micro-nutrient were mixed with the soil as given in Appendix 3.2. The treatments were replicated three times in a randomized complete block design. Three pre-germinated maize seeds (test crop) were planted in each pot and soil moisture was maintained by irrigating twice daily throughout the duration of the experiment. The plants were harvested 23 days after. Agronomic parameters measured included plant height, leaf

Table 3.4: P added to each soil before equilibration to attain the desired levels of solution P for the greenhouse cropping.

Treatment	Equil. Soln. P conc.	NatCrA	NatCrB	NatAmA	NatAmB
	µg/ml		----------µg/g soil---------		
Natural soils					
1	0	0	0	0	0
2	0.02	0.50	110.00	20.00	370.00
3	0.06	1.00	127.00	58.00	490.00
4	0.20	5.00	145.00	100.00	615.00
5	0.60	25.00	230.00	280.00	765.00
6	1.50	43.00	307.50	435.00	958.00
Prepared soils					
	Equil. soln. P conc.	ArtCrA	ArtCrB	ArtAmA	ArtAmB
1	0	0	0	0	0
2	0.02	145.00	500.00	680.00	780.00
3	0.06	260.00	625.00	870.00	950.00
4	0.20	425.00	800.00	1065.00	1320.00
5	0.60	775.00	1160.00	1440.00	1780.00
6	1.50	1130.00	1495.00	1870.00	2270.00

Moisture content adjusted to 80% field capacity.

length and leaf width, number of stands and leaf stage, all at 2 and 3 weeks after planting. At harvest, the plant tops were removed and oven dried at 60°C, ground and stored for analysis.

3.6.1.2 *Chemical analysis of the plant and soil samples.*

Plant tissue samples were digested in triple acid mixture (H_2SO_4, HNO_3 and $HClO_4$) and analyzed for total P by the method

of Murphy and Riley (1962); Ca, Mg, Zn, Na and K by the AAS and flame photometer for the divalent and monovalent cations respectively, fitted with the right filters and lamps, and total N by the kjeldahl digest and distillation method (Bremner, 1965). The pre-cropped and cropped soils were analyzed for extractable P by the Bray-P, Resin-P, Olsen-P and Water-P methods as described in section 3.4.4.

3.6.2. Growth chamber studies on maize and rape

3.6.2.1 Phosphorus depletion and turn-over in the rhizosphere.

The tropical top soils of pedons 1 and 2 and the bulk sub-soil of pedons 2 and 3, as well as the two temperate soils from Denmark that differed in fertility status, were used in this investigation.

The special techniques of Gahoonia and Nielsen (1991) to study rhizosphere processes in thin soil layers of different proximity to the root surface was used. This incorporated the principle of regeneration of Nielsen (1984) to regulate the pH of the medium. The experimental set-ups from which the rhizosphere soils were generated are shown in Fig.3.3. These were composed of the pre-experimental set up (I), and experimental set up (II). Test crops were maize (Zea mays L.C. Trak) and rape (Brassica napus, var. globel).

3.6.2.2. The pre-experimental set up

A piece of fine-mesh nylon cloth impervious to roots was glued to the bottom opening of a PVC tube (Fig 3.3, I). Two wicks, made of glassfiber (TBA FORTAG LASS L14) were placed

along the inner sides of each tube which was then filled with pre-treated vermiculite. The water conductivity of the wicks was 5 mL h^{-1} at 20 cm water tension. Uniform germinated maize and rape seeds were transplanted in the vermiculite. The tubes were than placed on a sand bath and supplied (continuously circulated) via the wicks with a basic nutrient solution C (Table 3.5) which was maintained at an electrical conductivity of 0.63 mS cm^{-1} by daily addition of maintenance solution A or B (Table 3.5). The nutrient ratios in these

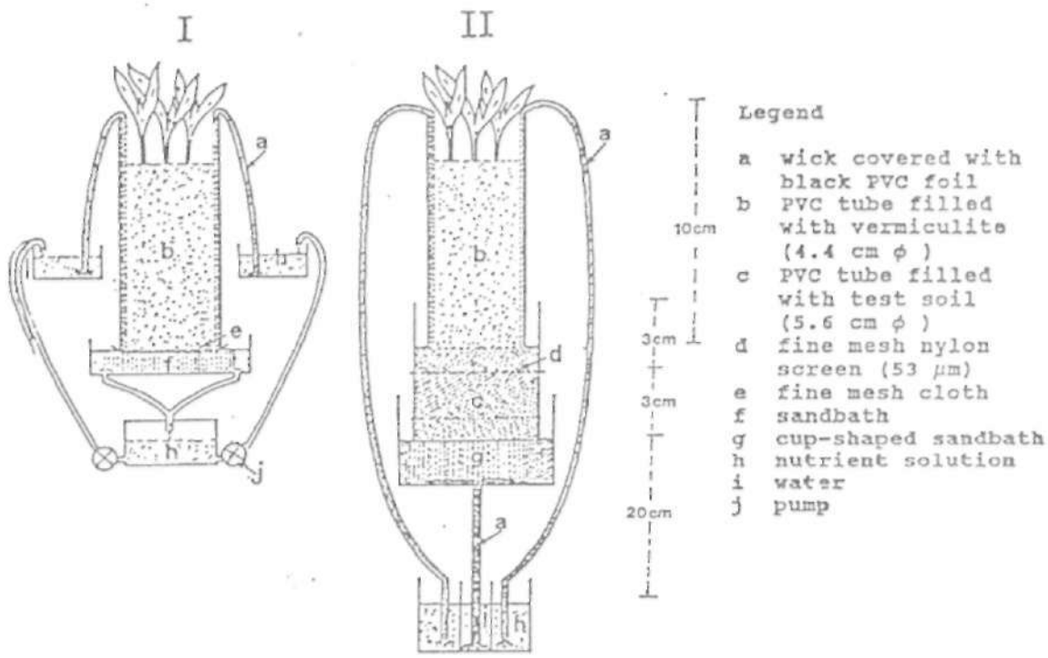


Fig. 3.3. Illustrations of the plant-growing technique. Pre-experimental (I) and experimental set-up (II)

Table 3.5: Nutrient concentration in the maintenance solution A and B and the basic nutrient solution C (pH 5.5).

	NO_3	NH_4	K	Ca	Mg	Na	P	S	Cl	Fe[a]	Mn	Zn	Cu	B	Mo
	mM									μM					
A	83.5	5.05	35.8	20	8.1	1.2	6.1	2	2	76	61	26	4.4	52	0.73
B	95.8	17.8	35.8	20	8.1	1.2	6.1	2	2	76	61	26	4.4	52	0.73
C	5	0	0.59	1.92	0.75	0	0.05	0.43	90	90	7	0.7	0.7	2	0.7

[a] - Was added as Fotopur (iron (III) Ethylenedinitrilotetra-acetic acid).

solutions were chosen according to their absorption by the plants. To control solution pH, the ratio of ammonium and nitrate was adjusted according to the principle of regeneration (Nielsen, 1984). Solution A was added to the system when the pH of circulating nutrient solution dropped below a standard value, and solution B when the pH rose above the value. The pre-experimental stage lasted for 9 days during which a uniform root mat was formed on the nylon cloth.

3.6.2.3. The experimental set up

The experimental set-up (Fig. 3.3 II) used to create rhizosphere soil samples consisted of two PVC tubes placed upon each other. The lower tube consisted of two rings of 2-cm and 1-cm length, respectively, and the former had and axial cut. A 53-μm-meshed nylon screen (PE 53) was glued on the top opening of the 2-cm ring of the lower tube. The upper tube was glued loosely to the lower tube so that the tubes were separated by the screen. The lower tube was filled with a

test soil packed to a uniform density (1.1 - 1.3 g cm^{-3}) with a vibrator depending on the soil property. The upper tube contained 1 cm of the test soil having the same bulk density as the packed soil in the lower tube. The soils in the upper and lower tubes was then saturated with water and adjusted to a water tension of 20 cm. To maintain a defined moisture content in the soil, the lower tube was placed on a small sand bath fitted with a wick from the base dipping into a reservoir of distilled water.

The PVC tubes with their plants from the pre-experimental set-up (Fig. 3.3 I) were placed on the 1-cm soil layer in the 3 cm upper tube of the experimental sept-up (Fig. 3.3 II). The supply of the nutrient solution through the two wicks in the vermiculite was continued. However, the concentration of nutrients in this solution was adjusted to the estimated demand of the plants based on the adjustments made at the pre-experimental stage. This was done by adjusting the basic nutrient solution C with solution A or B. Final nutrient solutions used for the rape and maize experiments are given in Appendix 3.3. The roots grew quickly into the 1-cm soil layer and formed a new root mat over the screen covering the test soil column. Root hairs were, however, able to penetrate this screen.

Plants were harvested at 7 days and 14 days of growth on the test soil column for each crop. The water tension of the experimental set-up was maintained at 20 cm by adjusting the supply solution level and the water level in the conical flask, which partially met the moisture requirement of the

plant through the test soil column. The daily supply of nutrient solution and water were recorded to determine the water flux to the plant, and the nutrient uptake by the plant.

3.6.2.4. Slicing the soil

At the end of the experiment, the root mat over the screen was separated carefully from the screen with a sharp knife. The soil column with PVC rings and intact screen was held tightly with screw clamps between two small metal plates and quickly frozen in liquid nitrogen for 30 seconds. The screen and the 2-cm long PVC ring were removed, and with the 1-cm ring, the frozen soil block was held tightly in a refrigerated microtome (Leitz 1512). The frozen (-25°C) soil column was then sliced perpendicular to the root mat into thin layer of 0.2 mm distance. The soil samples were collected in small glass bottles and air-dried, ground in an agate mortar and analyzed for Hedley et al., (1982) P fractions. The treatments were replicated 4 times but combined to two replicates while generating the rhizosphere samples. Twelve successive samples of the following distances from the root mat were obtained: 0.1, 0.3, 0.5, 0.7, 0.9, 1.19, 1.56, 1.95, 2.39, 2.87, 3.62 and 4.62 mm.

The rhizosphere samples so generated were analysed for Hedley P fractions.

3.8 Statistical Analysis

General relationships between estimated soil parameter were calculated by simple correlation analysis, and the

effects of soil properties on phosphate parameters were evaluated by simple linear regression analysis. Multiple regression analysis was used to determine the combination of soil properties for estimating P availability and adsorption indices. Response surface regression analysis was used to estimate the response patterns and the point of maximum response of agronomic parameters to adjusted P levels.

The adsorption data were fitted to the sorption equations by the NLIN regression procedure (METHOD =DUD). The parameters were estimated by the least square iterative process until the least square deviation was at the minimum to produce the best fit. The models were ranked based on the goodness of fit evaluated by the R^2 values and RMSE. Parameter estimates from the linearized sorption equations were done by simple linear regression. All calculation were done using the SAS statistical package (SAS Institute, 1987).

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Properties of the Soils

The classification of the soils and main features of the locations of the study soils are presented in Table 4.1.1. Based on field description (Appendix 3.1) and laboratory data (which will be discussed subsequently), the soils were classified as clayey, kaolinitic Acquic Kanhaplustalf, clayey, kaolinitic Kanhaplic Haplustalf and clayey, kaolinitic Kandiustalfic Eustrustox for pedons 1, 2 and 3 respectively. There were evidence of an argillic or kandic horizons in the savanna soils. The savanna soils from Samaru were both Alfisols and the rain forest soil from Isoya was an Oxisol as shown by the classifications.

The special soils (selected natural and artificial soils), were used for detailed studies in the laboratory and greenhouse on P reactions and response. The artificial soils were made to simulate the natural soils for purposes of comparison between the two systems. By the treatments, the artificial soils subjected through the processes of crystallization simulated the savanna soils, while the non-crystallized portion simulated properties of the forest Oxisol. In this study, the prefixes 'Nat' and 'Art' denote natural and artificial respectively, while the suffix 'Cr' and `Am' denote the crystalline and amorphous properties of the soils. The additional terms 'A' and 'B' denote top- and sub-soil respectively, signifying presence or absence of OM. The

Table 4.1.1 Some selected features of the sites and classification of the profiles

Profile	Location	Classification (USDA)	Parent Material	Rainfall	
				Amount (mm)	Duration (months)
Pedon 1	Samaru	Acquic Kanhaplustalf	Fluvial deposits from metasediments of the Basement Complex	1090	5
Pedon 2	Samaru	Kanhaplic Haplustalf	Metaigeneous rocks and aeolian deposits on Basement Complex	1090	5
Pedon 3	Isoya	Kandiustalfic Eustrustox	Amphibolite rich metasediments of the Basement complex	1375	10

special soils were considered reasonably homogenous, more so with the artificial soils formed from the same natural bulk soil, which makes it possible to isolate the effects of the treatments.

For studies on P depletion in the rhizosphere, the tropical subsoils of pedons 1 and 2 and subsoils of pedons 2 and 3, as well as the Danish soils were used as test soils.

4.1.1. Soil characteristics

4.1.1.1. Properties of the profiles

The selected physical and chemical properties of the profiles are given in Table 4.1.2. The soils were all deeply weathered and clayey with the clay content decreasing consistently with depth in both soils from the savanna, and

increasing with depth in the rain forest Oxisol (pedon 3). The textural classes of the hydromorphic (pedon 1) and upland (pedon 2) soils of the savanna varied from clay and sandy clayloam respectively in the surface, to sandy clay loam at about 50-100 cm depth in both profiles. Because the soils had developed under different drainage and soil moisture conditions, and from varied parent materials and natural influences, their nature and reactions are expected to differ.

Table 4.1.2. Selected physical and chemical properties of the soil profiles.

Profile	Depth	Sand	Silt	Clay	Org.C	ECEC	ECe	B.S	pH H_2O	ZPC*	SS area	Texture
	(cm)	%				$Cmol_c\ kg^{-1}$	$dS\ m^{-1}$	%			$m^2\ g^{-1}$	
Pedon 1	0-4	9	21.1	69.6	6.02	14.28	0.18	76	4.84	2.94	132.1	c
	10-20	31	17.3	50.7	1.61	9.46	0.11	46	4.30	2.18	60.6	c
	20-40	27	18.6	54.2	0.89	6.08	0.11	84	4.80	2.52	65.6	c
	40-90	59	13.0	28.1	0.24	4.14	0.04	75	5.32	2.98	48.9	scl
Pedon 2	0-22	77	7.6	14.6	2.20	9.13	0.17	93	6.77	2.20	24.4	sl
	22-55	51	7.7	41.1	0.40	6.36	0.04	93	6.55	2.53	47.7	sc
	55-100	54	8.0	37.1	0.29	5.41	0.04	92	6.41	2.85	63.0	scl
	100-120	58	9.6	31.0	0.28	5.37	0.03	92	6.42	3.84	61.3	scl
Pedon 3	0-30	26	18.5	55.6	2.41	8.60	0.16	96	5.91	3.15	75.0	c
	30-55	17	12.5	70.2	0.89	5.09	0.07	92	5.95	4.12	75.1	c
	55-70	16	11.5	72.3	0.34	4.04	0.04	91	5.95	3.95	65.2	c
	70-95	15	11.4	73.3	0.19	3.78	0.03	90	6.10	3.57	62.4	c
	95-130	18	11.2	70.9	0.18	3.70	0.03	89	5.72	3.22	60.4	c

* Zero point of charge

c = clay, sc = sandy clay, sl = sandy loam, scl = sandy clay loam.

Pedon 3 had a uniform clay texture through out the profile, though the surface soil was slightly lower in clay.

The soils of the poorly drained profile (pedon 1) were acidic, whereas soils of the well drained pedons (2 and 3), were acidic to slightly acidic in reaction. The surface charge characteristics of the respective soils are illustrated in Figure 4.1.1. The ZPC values (Table 4.1.2) indicate that the soils should normally be negatively charged under normal field conditions. The ZPC values were higher for the Oxisol apparently due to the higher content of the soil oxides in the soil. Clay content and dithionite extractable Fe (Fe_d) were

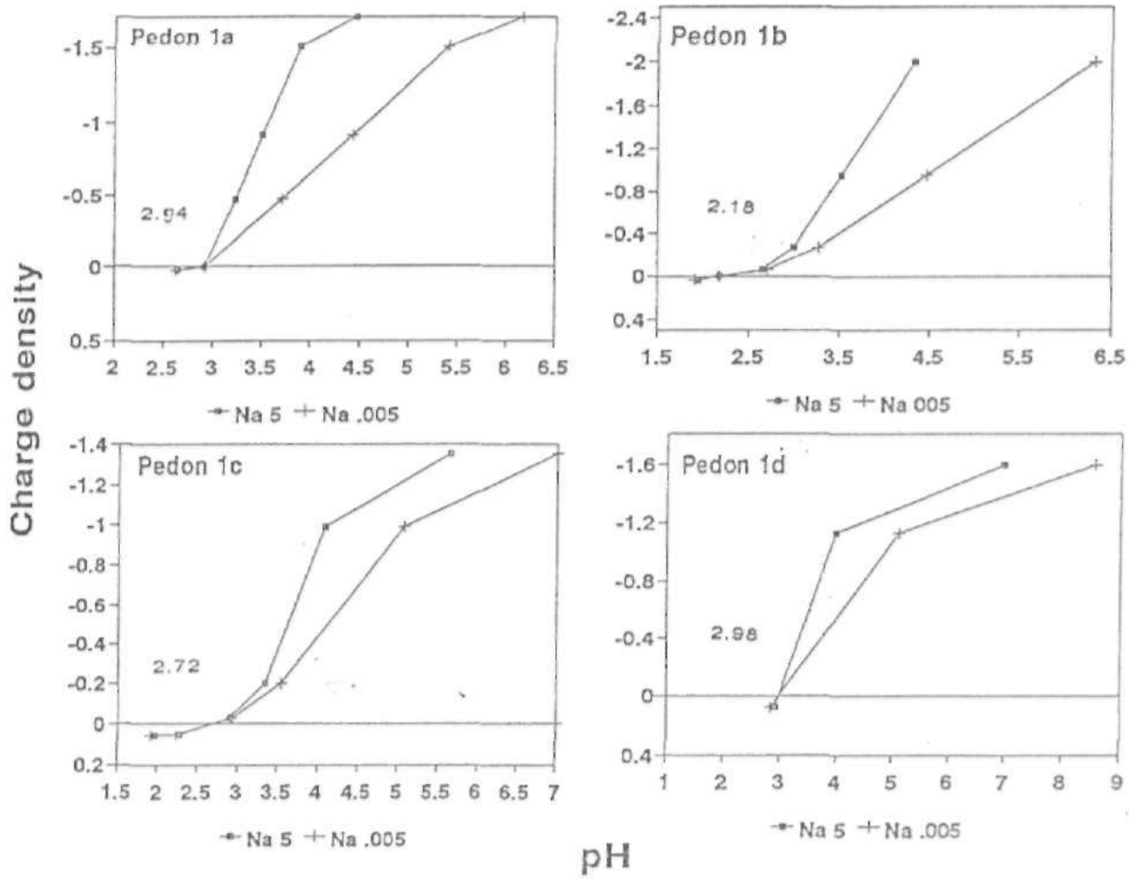


Figure 4.1.1: Surface charge characteristics for the soil profiles. Pedon 1 - Acquic Kanhaplustalf (Samaru).

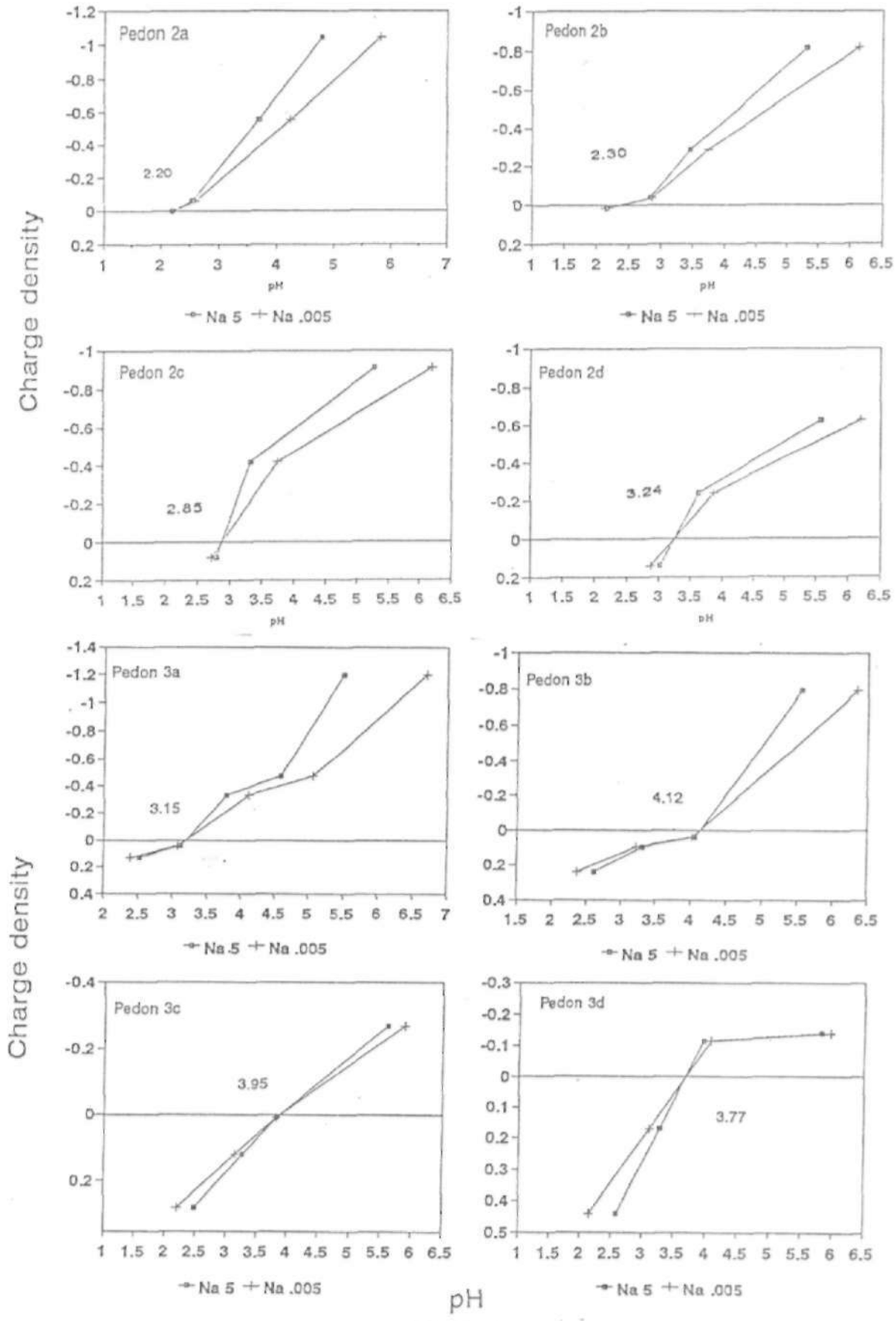


Figure 4.1.1 continues. Pedons 2 - Kanhaplic Haplustalf, and Pedon 3 - Kandiustalfic Eustrustox.

the major factors that influenced the pattern of variation as shown by the relationships between ZPC and clay (r=65)**, and Fe_d (r=79**) in Table 4.1.3. These were essentially the crystalline components of the soil colloidal fraction. Al_d is known to be associated more with the amorphous phase (Borggaard et al.,1990).

The organic C content was high in all surface soils, but decreased appreciably with depth in all cases. The variation in ECEC reflected the variation in organic C (r=0.93**) which also decreased consistently with depth. Values were low in all soils (< 10 Cmol$^+$ Kg^{-1}) with the exception of the surface soil of pedon 1 where the ECEC was 14.28 Cmol$^+$ Kg^{-1}. The organic carbon content was as high as 6.02 % in this soil. The result suggests that the constituting clay fraction was of low reactivity, consistent with the report of Greenland, (1981) on some Nigerian soils.

The specific surface area as measured by the ethylene glycol method increased with depth in pedon 2, but was the inverse in pedon 3. The trend was not consistent in pedon 1. Soil texture, organic carbon content and the amorphous fractions of the soil Fe and Al oxides seemed to have had significant influence on the specific surface area in the soils (Table 4.1.3). The significance of this observation rests in the fact that the difference in the properties of the organic matter due to the source and influencing climatic factors may impart different modifying effects on soil reactions (Stevenson, 1982). Absolute specific surface values for the surface soils were 132.4, 24.4 and 75.0 m^2/g soils for

Table 4.1.3. Correlation matrix of selected properties of the soil profiles.

Factors	Clay	Silt	Sand	Org. C	$pH(H_2O)$	pH ($CaCl_2$)	Acid-ity	ECEC	Fe_d	Fe_{ox}	Fe_{py}	Al_d	Al_{ox}	Al_{py}	SAREA	XPC
Clay	1.00	0.46	-0.98	0.16	-0.34	-0.11	-0.09	-0.04	0.66	0.74	0.26	0.16	0.65	-0.21	0.63	0.65
Silt		1.00	-0.61	0.63	-0.83	-0.75	0.58	0.56	-0.05	0.79	0.82	0.43	0.53	0.16	0.70	-0.04
Sand			1.00	-0.27	0.48	0.25	0.21	-0.07	-0.58	-0.82	-0.41	-0.23	-0.68	0.14	-0.70	-0.57
Org. C				1.00	-0.37	-0.32	0.52	0.93	-0.38	0.34	0.93	0.45	0.42	0.19	0.70	-0.21
$pH(H_2O)$					1.00	0.94	-0.79	-0.39	0.21	-0.68	-0.61	-0.25	-0.29	-0.29	-0.48	0.19
$pH(CaCl_2)$						1.00	-0.76	-0.38	0.41	0.47	-0.55	-0.22	-0.08	-0.42	-0.41	0.31
Acidity							1.00	0.65	-0.51	0.29	0.66	0.07	0.19	0.39	0.37	-0.45
ECEC								1.00	-0.59	0.19	0.90	0.40	0.28	0.26	0.53	-0.47
Fe_d									1.00	0.39	-0.36	-0.15	0.34	-0.44	0.04	0.79
Fe_{ox}										1.00	0.50	0.41	0.57	-0.10	0.56	0.22
Fe_{py}											1.00	0.46	0.51	0.25	0.77	-0.25
Al_d												1.00	0.26	-0.20	0.23	-0.12
Al_{ox}													1.00	-0.12	0.53	0.19
Al_{py}														1.00	0.25	-0.23
SAREA															1.00	0.29
XPC																1.00

ns < 0.40, 0.40 - 0.50 = sig. at 5 %, > 0.50 = sig. at 1 % level of probability. more with the amorphous phase (Borggaard et al., 1990).

pedon 1, 2 and 3 respectively. The corresponding electrical conductivity values were 0.11, 0.07 and 0.07 dS m^{-1}. The soils were therefore non-sodic or saline (Landon, 1984).

4.1.1.2. Selected properties of the special soils

Some chemical properties of the special soils are presented in Table 4.1.4. All the soils were weakly acidic to neutral in reaction. The pH in water and $CaCl_2$ were lower in the soils containing the OM fraction. The ΔpH values (pH $CaCl_2$ - pH H_2O) were negative for all soils indicating that the soils, including the artificial soils, were negatively charged at the ambient solution pH of the soils. The magnitude of the charge density (ΔpH) increased in the subsoil in the natural soils, but decreased in the prepared soils. This may tend to

Table 4.1.4: Some selected chemical properties of the special soils.

Soil	Depth simulatio	pH H_2O	pH $CaCl_2$	ΔpH	ECEC	Org C	%PC	SAREA
					cmol$_c$ kg^{-1}	%		m^2/g
NatCrA	Top	6.58	6.30	-0.28	11.76	1.71	2.20	24.4
ArtCrA	Top	6.37	5.47	-0.90	18.80	2.77	3.32	107.3
NatCrB	Sub	6.46	5.45	-1.01	11.14	0.24	2.85	63.0
ArtCrB	Sub	6.86	6.15	-0.71	18.60	0.45	3.55	107.3
NatAmA	Top	5.92	5.50	-0.42	15.21	1.88	3.15	75.0
ArtAmA	Top	6.46	5.61	-0.85	20.10	3.18	3.46	113.4
NatAmB	Sub	6.15	5.58	-0.57	7.72	0.15	3.57	62.4
ArtAmB	Sub	7.00	6.45	-0.55	16.20	0.42	4.01	124.0

reflect the extent of reactivity of soils towards phosphate and other anions. The surface charge characteristic of the artificial soils are presented in Figure 4.1.2. The titration curves for the amorphous soils were somewhat different from the crystallized soils as shown by the data in the Figure.

The ZPC values (Table 4.1.4) indicate clearly that the soils were negatively charged, with values consistently lower in the top soils where OM was higher. It is common to observe in variable charge soils, that the presence of hydroxides of iron and aluminium increase ZPC towards the high pH values,

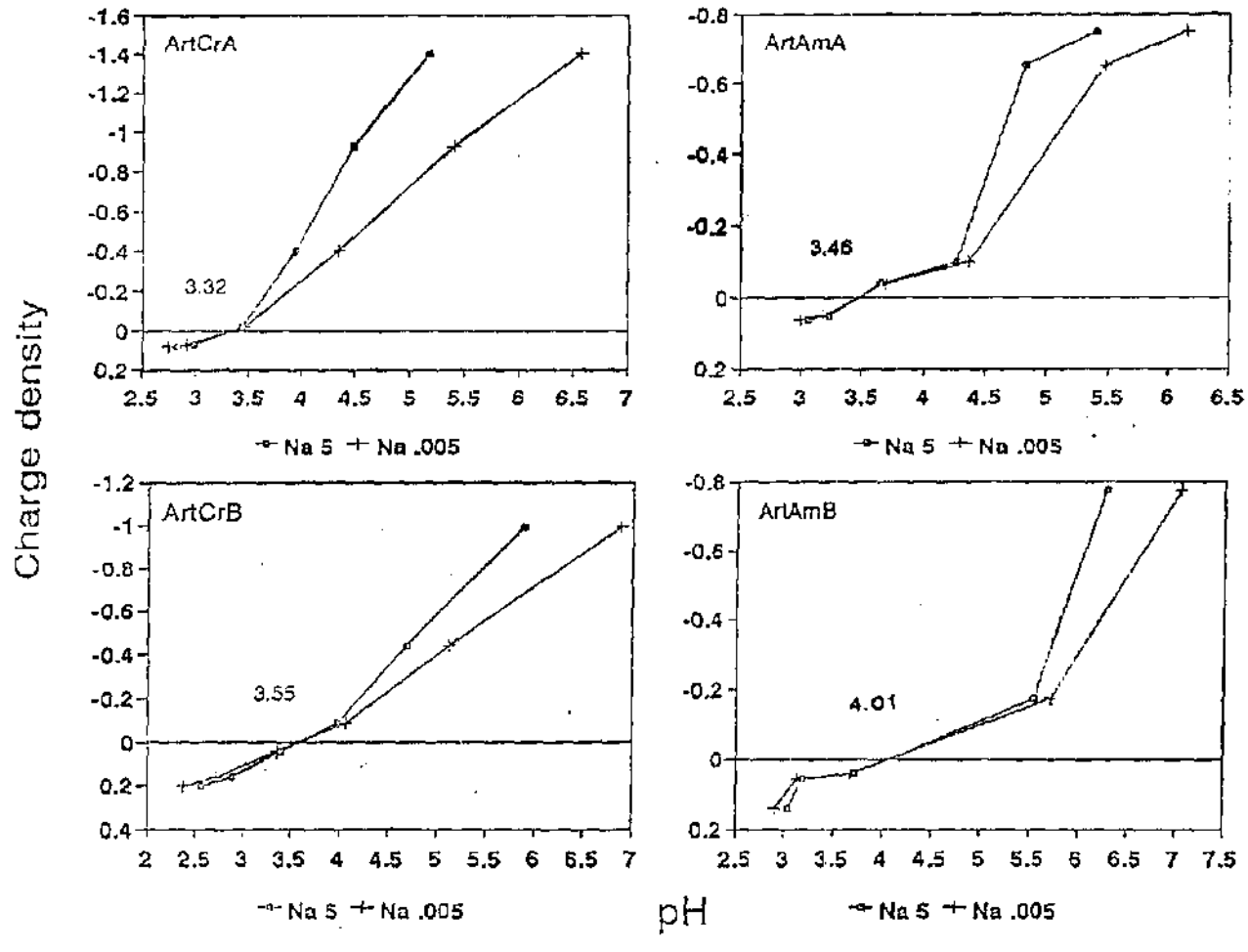


Figure 4.1.2: Surface charge characteristics of the artificial soils.

whereas the presence of clay with permanent negative charge, as well as OM, shift the ZPC to lower pH values (Dolui et al., 1987; Van Raij and Peech, 1972; Sposito, 1981). In the study presented here, ZPC was high in the artificial soils, and also in the subsoils (Table 4.1.5).

The ECEC was estimated by the compulsive exchange method of Gillman, (1979). This method was found suitable in an earlier assessment and was the only valid choice in view of the fact that the soils had been taken through series of treatments which altered the original cation contents. ECEC values ranged from 7.72 to 15.21 with a mean of 11.4 $cmol_c\ kg^{-1}$ for the natural soils, and 16.20 to 20.10 with a mean of 18.4 $cmol_c\ kg^{-1}$ for the artificial soils. The pattern of variation in both sets of soils were perfectly similar in trend. The largely amorphous Fe dominant subsoils had the least values in each case, while the amorphous Fe dominant topsoils had the highest values.

Table 4.1.5: Some selected chemical properties of the special soils: Mean values with respect to treatments.

Treatment	pH H_2O	pH $CaCl_2$	ΔpH	ECEC	Org C	ZPC	SAREA
				$Cmol_c\ kg^{-1}$	%		m^2/g
Top soil	6.33	5.72	-0.61	16.4	2.38	3.03	80.0
Sub soil	6.62	5.98	-0.64	13.4	0.31	3.49	89.2
Artificial	6.67	5.92	-0.75	18.4	1.71	3.58	113.0
Natural	6.27	5.78	-0.49	11.4	0.99	2.94	56.2

Table 4.1.6: Correlation matrix of selected soil properties and oxide fractions for the special soils.

	pH H_2O	pH $CaCl_2$	ECEC	Org C	ZPC	SAREA	Fe_d	Fe_{ox}	Fe_{py}	Al_d	Al_{ox}	Al_{py}
pH H_2O	1.00	0.71**	0.32	-0.29	0.26	0.38	-0.35	0.56*	-0.29	-0.21	-0.49	-0.60
pH $CaCl_2$		1.00	-0.08	-0.42	0.13	-0.01	-0.15	0.18	0.45	0.10	-0.28	-0.28
ECEC			1.00	0.61*	0.35	0.75**	-0.04	0.85**	0.73**	-0.35	0.18	0.05
Org C				1.00	-0.19	0.18	-0.05	0.33	0.87**	-0.36	0.27	0.61**
ZPC					1.00	0.83**	0.68**	0.65**	0.15	-0.19	0.19	-0.45
SAREA						1.00	0.35	0.88**	0.45	-0.38	0.21	-0.32
Fe_d							1.00	0.20	0.12	0.02	0.21	-0.14
Fe_{ox}								1.00	0.44	-0.40	-0.05	-0.34
Fe_{py}									1.00	-0.42	0.52*	0.57
Al_d										1.00	0.26	0.07
Al_{ox}											1.00	0.61*
Al_{py}												1.00

The OM content was little modified by the preparation methods. OM content of the dehumified soils were less than 0.5 % OC. Surface soil had an average of 2.38 % OC while the subsoils averaged 0.31 % OC. This variation in organic matter content influenced P reactions in soils differently.

The specific surface area of the surface bulk soil from which the artificial soil were prepared was 92.73 m^2 g^{-1}. Table 4.1.5 shows that there was increase in surface area as a result of the 10% Al containing 4% Fe oxide treatment used in this study. Mean values for the artificial soil was 113 m^2 g^{-1}. Borggaard et al., (1990) and Borggaard (1986) reported values for poorly crystallized and well crystallized Fe oxides determined in some soil to be 691 and 238 m^2 g^{-1} Fe respectively. The higher surface area of the amorphous Fe dominant soil over the crystallized Fe dominant soil of the artificial soil system may be attributed solely to the effects of the crystallization process, which indicates positive results of the treatments, and that the artificial soils fairly well simulated the natural soils.

4.1.1.3 Some properties of the soils for studies of the rhizosphere

The chemical and physical properties of the soils are presented in Table 4.1.7. The two Danish soils which were introduced at this phase of the experiment for purposes of comparison with the tropical soils, had comparable texture, but differed in fertility levels. The CEC and $NaHCO_3$ extractable P values for Danish I and II were 21.1 and 0.13

Table 4.1.7: Some chemical and physical properties of the test soils.

Soil	Particle size distribution			pH $CaCl_2$	CEC*	Org. C
	Clay	Silt	Sand			
		%			$cmol_c\ kg^{-1}$	%
NatCrA	15	10	75	6.43	10.7	2.18
NatCrB	41	10	49	5.80	10.0	0.40
NatAmA	70	13	17	5.58	14.2	0.90
Pedon 1	70	20	10	4.22	20.6	2.50
Danish I	15	16	68	6.70	21.1	1.16
Danish II	13	14	71	6.30	13.1	1.40

* - CEC by NH_4^+ saturation (tropical soils at pH = 8.4, Danish soils at pH = 7.0)

$cmol_c\ kg^{-1}$ soil, and 20 and 55 µg/g P respectively. The organic C content of the surface soils ranged from 1.16 to 2.50 %, but the subsoils values were less than 1.00 %. The CEC by NH_4^+ did not indicate the trend in fertility of the soils, as Danish II with higher extractable P value, was comparably low in CEC. The pH values showed that the soils were acid to slightly acid in reaction. On the average, the tropical soils were much higher in % clay.

4.1.2. Fe and Al oxide fractions of the soils

4.1.2.1. Fe and Al oxide fractions of the profiles

The distribution of the various forms of Fe and Al oxides in soils influence the physico-chemical properties of soils such as aggregate formation and phosphate sorption (Greenland and Oades, 1968). Understanding the nature of the

distribution is pertinent in the study of soil reactions. Table 4.1.8 shows the amount and forms of Al and Fe oxides in the respective profiles, and the active ratios (Fe_{ox}/Fe_{d}, Al_{ox}/Al_{d}). The lower the active ratio the greater the amounts of the crystallized oxides content of the profile (Juo et al.,1974).

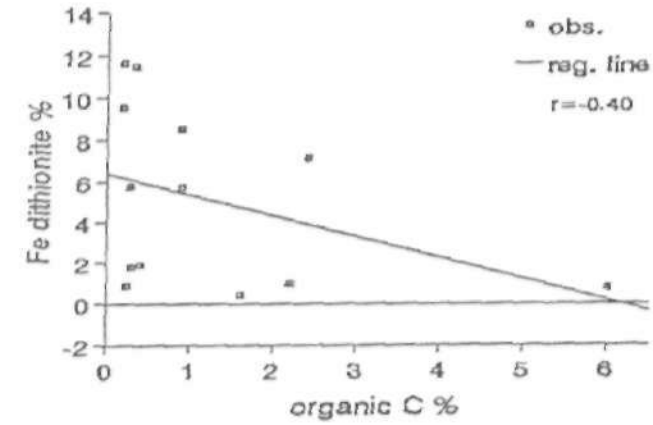
Table 4.1.8. Dithionite, oxalate and pyrophosphate extractable iron and aluminium fractions, active Fe and Al, and dithionite Fe/clay ratios.

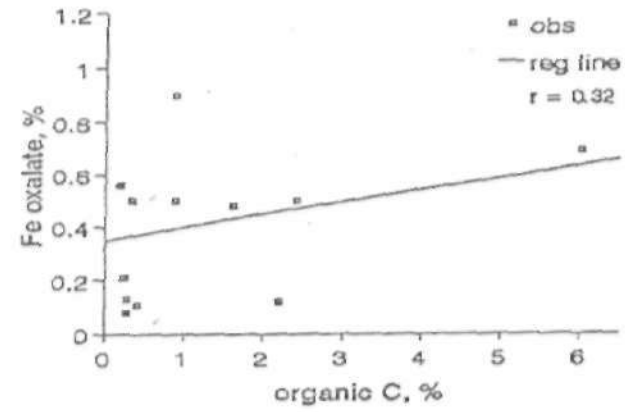
Profile	Depth	Fe_d	Fe_{ox}	Fe_{py}	Al_d	Al_{ox}	Al_{py}	Fe_{ox}/Fe_d	Al_{ox}/Al_d	Fe_d/clay
	(cm)	---------- % ----------						------- ratio x 10^2 -------		
Pedon 1	0-4	0.79	0.69	0.73	1.78	0.034	0.211	87.3	1.9	1.6
	10-20	0.44	0.48	0.32	1.28	0.028	0.208	109.0	2.2	1.2
	20-40	5.75	0.90	0.21	1.81	0.026	0.157	15.6	1.4	15.1
	40-90	0.89	0.21	0.03	1.50	0.015	0.181	23.6	1.0	4.5
Pedon 2	0-22	0.90	0.12	0.09	1.56	0.020	0.120	13.3	1.3	8.8
	22-55	1.93	0.11	0.02	1.68	0.020	0.115	5.7	1.2	6.7
	55-100	1.81	0.08	0.02	1.24	0.026	0.219	4.4	2.1	6.9
	100-120	5.80	0.13	0.34	0.77	0.017	0.207	2.2	2.2	26.7
Pedon 3	0-30	7.15	0.50	0.05	1.72	0.037	0.116	6.9	2.1	18.3
	30-55	8.50	0.50	0.02	1.43	0.020	0.143	5.9	1.4	17.3
	55-70	11.50	0.50	0.01	1.53	0.030	0.114	4.3	1.9	22.7
	70-95	11.70	0.56	0.01	1.30	0.030	0.103	4.8	2.3	22.3
	95-130	9.56	0.56	0.01	1.09	0.032	0.085	5.9	2.9	19.2

Active forms = oxalate/dithionite ratios

The distribution of Fe oxides in the well drained profiles showed that Fe_d increased and Fe_{py} decreased down the soil profile. The Fe_{ox} remained constant with depth in both profiles. The results show that the soils are highly weathered and the various oxide forms could have attained some quasi-equilibrium. The Fe_d was considerably greater than the Fe_{ox} and Fe_{py} forms indicating a much larger amount of crystalline Fe oxides in the soils (Schwertmann et al., 1982, Borggaard et al., 1990). The amount of the total free oxides in the soil is influenced by the mineralogy (Juo, 1981). The amount of Fe_d in the Oxisol (pedon 3) formed from amphibolite rich metasediments was considerably higher than those of the savanna soils (pedons 1 and 2) formed from fluvial sediments and acidic crystalline parent rocks respectively. In pedon 1, the forms were equal in amounts in the surface soils indicating that extractable Fe existed essentially in the amorphous state, possibly due to poor drainage (reduced) conditions or inhibition of the crystallization of the oxide by organic matter (Schwertmann et al., 1986; Huang and Violante, 1986). The crystalline form was dominant in the lower horizons of this profile.

The Fe_d and Fe_{ox} seemed to have influence the clay and silt fractions appreciably (Table 4.1.3). Fe in organic complexes extracted with pyrophosphate (McKeague, 1967), was strongly correlated with organic C (0.93**) as expected. Figure 4.1.3 shows the regression relationships between forms of Fe and organic C. Results in this study show that though all Fe_{py} could be amorphous, not all the amorphous Fe is tied





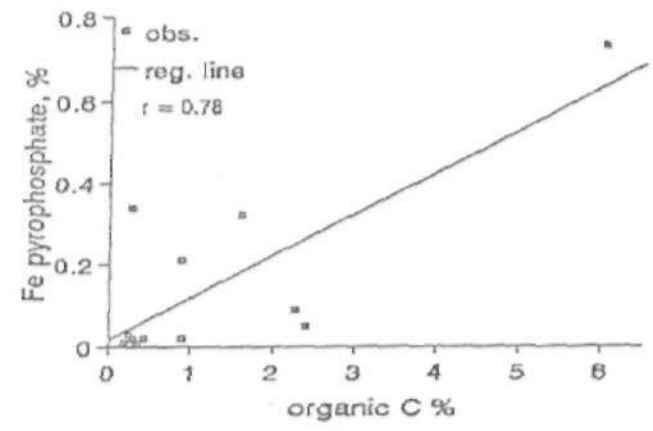


Figure 4.1.3: Relationship between the organic matter and the oxide forms.

to organic matter. Active Fe decreased with depth in all profiles indicating the increasing dominance of the crystalline forms in the subsoil. This was less apparent in the Oxisol in which the amorphous fractions was more evenly distributed down the profile.

The Al_d was considerably higher than both Al_{ox} and Al_{py} fractions in all profiles, but did not exhibit any clear pattern. Al_{ox} was least in all profiles. Organic C was significantly correlated with Al_d and Al_{ox} but not to Al_{py} as expected. This further lends supports to the criticism that the reagents are less successful in partitioning discrete chemical forms of Al oxides (Bascomb, 1968; McKeague, 1971; Juo et al., 1974). Al_d and Al_{ox} were significantly correlated with the amorphous Fe fractions and organic C, clearly suggesting that Al exists mainly in the amorphous or poorly ordered forms in these soils.

4.1.2.2 Fe and Al oxide fractions of the special soils.

The Fe and Al oxide fractions of the special soils are shown in Table 4.1.9. The mean values are presented in Table 4.1.10. The active ratios (Fe_{ox}/Fe_d and Al_{ox}/Al_d) are also shown. The properties of the bulk soil from which the artificial soils were prepared are presented in Appendix 4.1.1.

The oxide fractions of the natural soils were discussed earlier in the previous section. In the artificial soil system, the Fe_d content of the bulk soil was increased accordingly as a result of the treatment, much of which seemed

to exist in the amorphous state. Only about 11 - 20 % appeared to occur in the crystalline forms. Ryden et al., (1977), reported no observable X-ray diffraction peak of Fe gel prepared in their laboratory. It may be pertinent to note that much of the prepared oxides in the crystallized treatments, could have existed largely in the micro-crystalline state not distinguishable by chemical analysis or

Table 4.1.9: Iron and aluminium oxide fractions of the special soils.

Soil	Depth Simulation	Fe_d	Fe_{ox}	Fe_{py}	Al_d	Al_{ox}	Al_{py}	Fe_{ox}/Fe_d	Al_d/Fe_{ox}
				%				Ratio	
NatCrA	Top	1.21	0.17	0.12	0.96	0.02	0.85	0.14	0.79
ArtCrA	Top	4.84	4.05	0.36	0.94	0.19	0.57	0.84	0.19
NatCrB	Sub	2.20	0.09	0.07	0.81	0.01	0.48	0.04	0.37
ArtCrB	Sub	4.83	4.30	0.14	1.05	0.05	0.38	0.89	0.22
NatAmA	Top	5.11	0.42	0.44	1.05	0.51	1.05	0.08	0.20
ArtAmA	Top	5.62	4.57	0.54	0.84	0.11	0.74	0.81	0.15
NatAmB	Sub	8.77	0.51	0.03	1.00	0.10	0.53	0.06	0.11
ArtAmB	Sub	4.45	4.20	0.18	0.75	0.18	0.50	0.94	0.17

Table 4.1.10: Iron and aluminium oxide fractions of the special soils: Mean values with respect to treatments.

Treatment	Fe_d	Feox	Fe_{py}	Al_d	Al_{ox}	Al_{py}	Fe_{ox}/Fe_d
			%				Ratio
Top soil	4.19	2.30	0.36	0.84	0.21	0.82	0.55
Sub soil	5.06	2.27	0.11	0.90	0.08	0.47	0.44
Artificial	4.94	4.28	0.31	0.79	0.13	0.57	0.86
Natural	4.32	0.29	0.17	0.95	0.16	0.72	0.07

X-ray, but the reaction may indicate some extent of crystallization revealed in this instance, by the slightly improved surface area of the amorphous soils. The pyrophosphate Fe content was only slightly affected by the treatment. Results show that applied Fe oxide was redistributed into the various fractions. The total Al oxide added were equally redistributed in the various Al fractions, but largely in the oxalate extractable fraction. In effect, the active Fe ratios of the artificial soils were substantially greater than the natural soils signifying the high capacity of the soils to react. The Al_d/Fe_d ratios were higher for the natural soils indicating that much of the reactions observed with the homogenous artificial soils can be rightly ascribed to the Fe content introduced by the treatments. On the contrary, the natural soils represented the heterogenous system haven been derived from different parent materials.

4.1.3. Organic matter fractions of the profile soils

Table 4.1.11 shows the distribution of the humic fractions in the surface soil of the pedons. In the acidic poorly drained hydromorphic soil (pedon 1), humic acid constituted the greater proportion of the humic substances. On the contrary, the fulvic acid fraction was dominant in the well drained profiles of the savanna (pedon 2) and the rain forest Oxisol (pedon 3) where a steady state of turnover of the fractions must have been attained. The fulvic acid fraction constituted 74 % and 67 % respectively of total

Table 4.1.11: Humic and fulvic acid fractions and total organic matter contents of the soil profiles. Percentage of organic matter in parenthesis.

Pedon	Humic acid	Fulvic acid	Total OM
	- % of soil -		
1	8.10 (67.2)	2.41(20.0)	12.04
2	0.59 (13.4)	3.26(74.1)	4.40
3	1.32 (27.4)	3.25(67.4)	4.82

organic matter in these soils. Considering the pH of the soils (Table 4.1.2), the humic acids should exist as negatively charged poly-electrolytes due to the dissociation of the carboxyl groups in the molecule (Posner, 1964; Tate and Theng, 1980). Information in literature reveal that fulvic acid is of lower molecular weight and it is higher in oxygen containing functional groups, which are characteristics for high reactivity (Stevenson, 1982). It is apparent from the results that the reactivity of OM should be higher in the well drained profiles.

4.1.4. Mineralogical analysis of the soils

4.1.4.1 Mineralogical analysis of the profile soils

The random powder X-ray diffractogram (XRD) of the non-magnetic sand-sized separates of selected horizons of the profiles are presented in Figure 4.1.4. A comprehensive

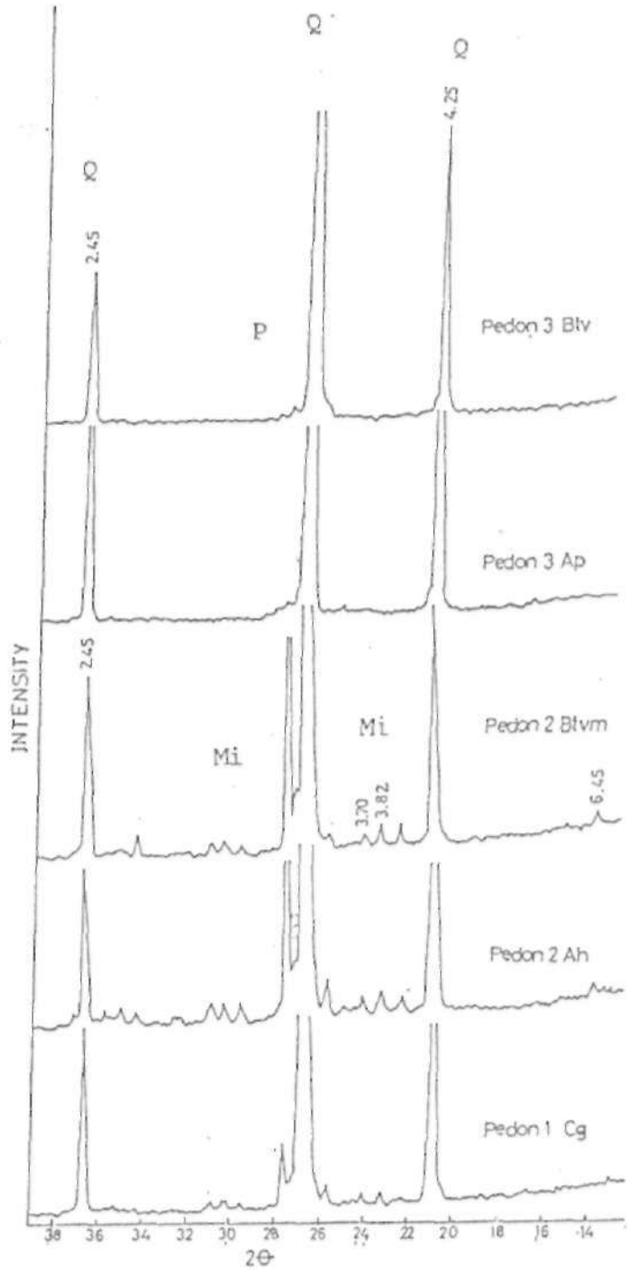


Figure 4.1.4: X-ray diffraction analysis for the sand fraction of selected horizons of the profiles. Q = quartz, P = plagioclase, Mi = microcline.

compilation of containing minerals, including results of petrographic examination of the magnetic fraction is shown in Table 4.1.12. Quartz and feldspar constituted the dominant mineralogy of the soils. Microcline (K-feldspar) was absent in the forest Oxisol (pedon 3) which contained plagioclase (Ca-feldspar). Common accessory minerals in all profiles included goethite, haematite, magnetite and ilmenite. Surfaces of mineral particles from the savanna were highly pitted, rough and dull in colour indicating a more highly weathered state of the savanna soil in comparison to the forest Oxisol where particle surfaces were more rounded and polished.

The mineralogy of the silt-size fraction varied somewhat among soils. The powder XRD for the profiles are presented in Figure 4.1.5. Quartz, feldspars and kaolinite were the dominant silt mineralogy. A qualitative compilation of the silt mineralogy is presented in Table 4.1.13. Accessory minerals included possible ferrihydrite (poorly ordered goethite) in pedon 1, haematite and goethite in pedon 2 and haematite, goethite and magnetite in pedon 3. Microcline was absent in the silt fraction of pedon 3.

Kaolinite was the dominant mineralogy of the clay fraction of the profiles (Figure 4.1.6). The XRD of oriented clay (Figure 4.1.7) clearly confirms this. Kaolinite and Fe-oxyhydroxides have been shown to constitute 80 % of the clay fraction of these soils (Ojanuga, 1979; Moberg and Esu, 1991).

The high content of haematite, goethite and magnetite/ilmenite in the sand fraction of the forest Oxisol

Table 4.1.12: Mineralogical composition of the sand fraction of the profiles: X-ray diffraction and petrographic study.

Sample (cm)	Q	Plg	Geo	He	Mag	il	Horn	Micro	Biot	Opal	Musc
Pedon 1											
0-4/10	x	-	x	x	x	x	-	-	x	-	x
Pedon 2											
0-22	x	-	x	x	x	x	x	x	-	-	-
60-100	x	-	-	x	x	x	x	x	-	-	-
110-120	x	-	x	x	x	x	x	x	-	-	-
Pedon 3											
0-30	x	x	-	-	x	x	x	-	-	x	-
55-70	x	-	-	x	x	x	-	-	x	x	-
95-130	x	x	x	x	x	x	x	-	-	x	x

Q = quartz, Plg = plagioclase, Goe = goethite, He = haematite, il = ilmenite, Horn = hornblende, Micro = microcline, Bio = biotite, Musc = muscovite.

Table 4.1.13: Mineralogical composition of the silt fraction of profiles.

Sample	Q	K	Goe	He	Il	Micro	plg
Pedon 1							
0-4/10	x	x	-	-	x	x	x
Pedon 2							
0-22	x	x	-	-	-	x	x
60-100	x	x	x	x	-	x	-
110-120	x	x	x	x	-	x	-
Pedon 3							
0-30	x	x	x	x	x	-	-
55-70	x	x	x	x	-	x	-
95-130	x	x	x	x	x	x	-

Q = quartz, K = kaolinite, Goe = goethite, He = haematite, Il = ilmenite, Micro = microcline, Plg = plagioclase.

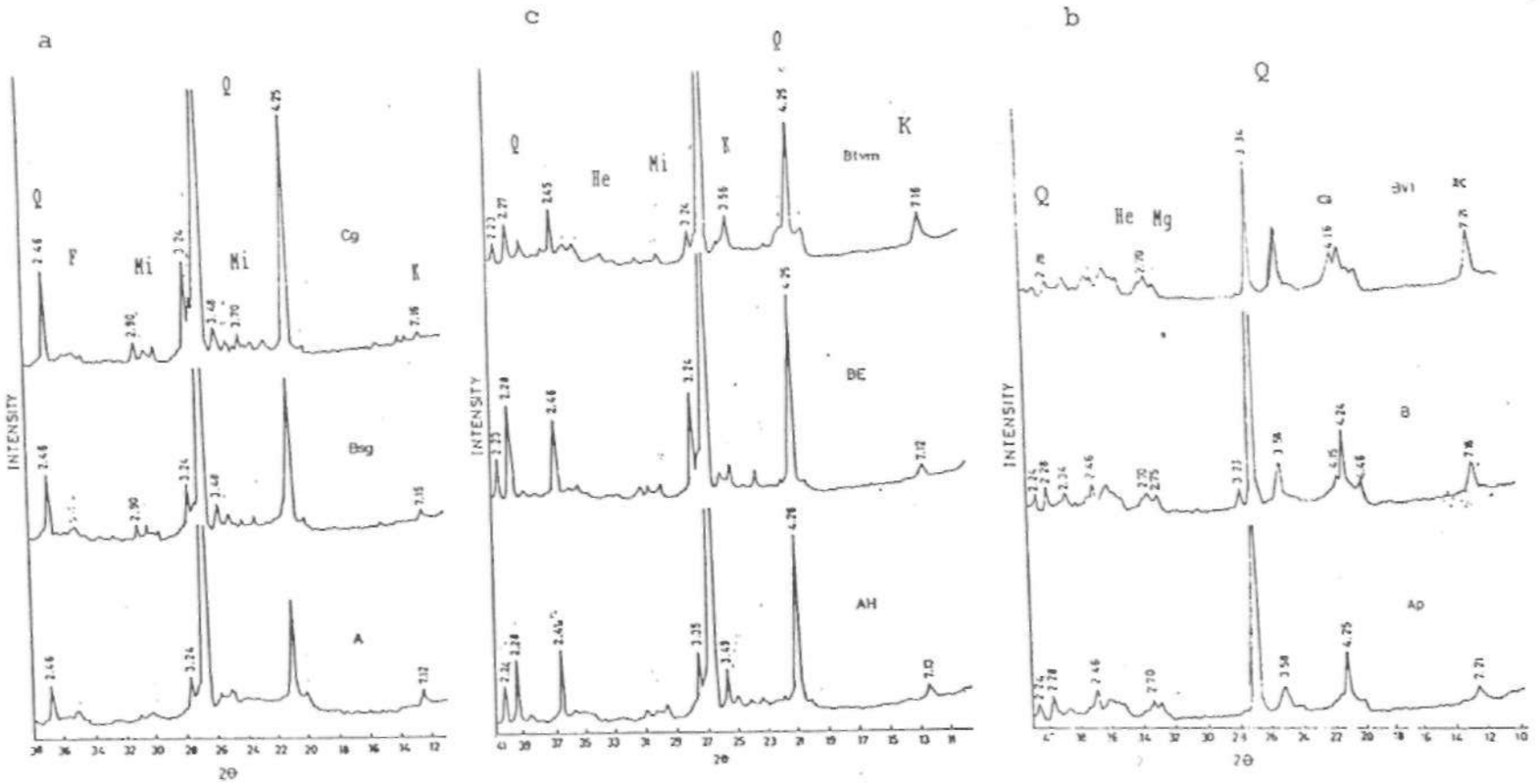


Figure 4.1.5: Random powder X-ray diffraction analysis of the silt fraction for selected horizons of the pedons; a - pedon 1, b - pedon 2 and c - pedon 3: Q = quartz, K = koalinite, Mi = microcline, F = ferihydrite, He = heamatite, Mg = magnetite.

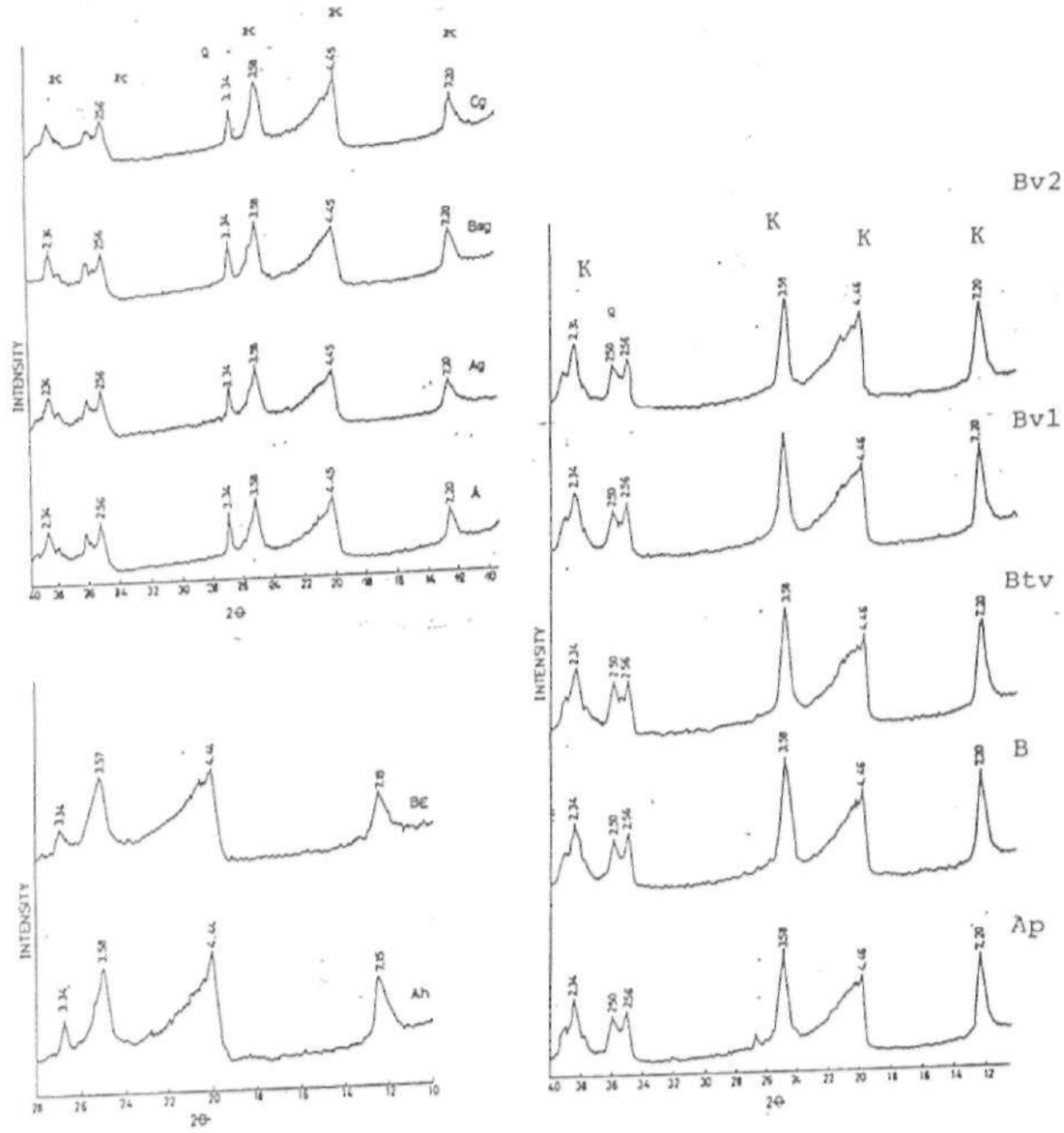


Figure 4.1.6: Random powder X-ray diffraction pattern of the Mg - saturated clay samples of the pedons; a - pedon 1, b - pedon 2 and c - pedon 3. Q = quartz, K = koalinite.

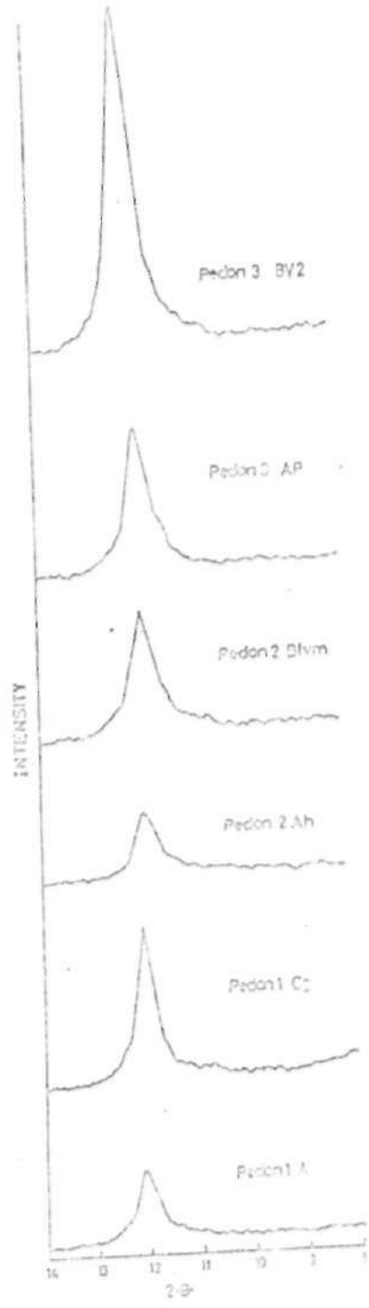


Figure 4.1.7: X-ray diffractograms for the Mg saturated clay samples for the top and sub-soils of the pedons.

is no doubt related to the Fe rich parent rock on which it is formed. The relatively high content of haematite and goethite in the lower horizons of the upland savanna Alfisol (pedon 2) was postulated to be the result of the influx of Fe in the groundwater which resulted in accumulation (Moberg and Esu, 1991). The low K status of the forest Oxisol (Appendices 4.1.1 and 4.1.3) was invariable due to the absence of microcline in the soil. The dominant kaolinite and high content of Fe and Al oxides in the clay fraction suggest the variable charge nature of the soils, implying that soil reaction processes should largely be pH dependent. The soils therefore are comparable in clay and silt mineralogy though differed in their parent material. A valid assessment of the effects of the interaction between organic matter and inorganic constituents on soil reactions can therefore be made in these soils.

4.1.4.2. Mineralogy of the Special Soils.

The X-ray diffractograms of the selected natural and artificial soils that constituted the special soils are presented in Figure 4.1.8. Goethite and haematite peaks were discernable in the natural soils but were not very evident in the prepared soils.

The difference diffractograms of the special soils, presented in Figures 4.1.9 and 4.1.10, clearly shows the presence of goethite and haematite in the natural soils. However, the diffractograms did not seem to indicate the presence of crystalline oxides in the artificial soils. This

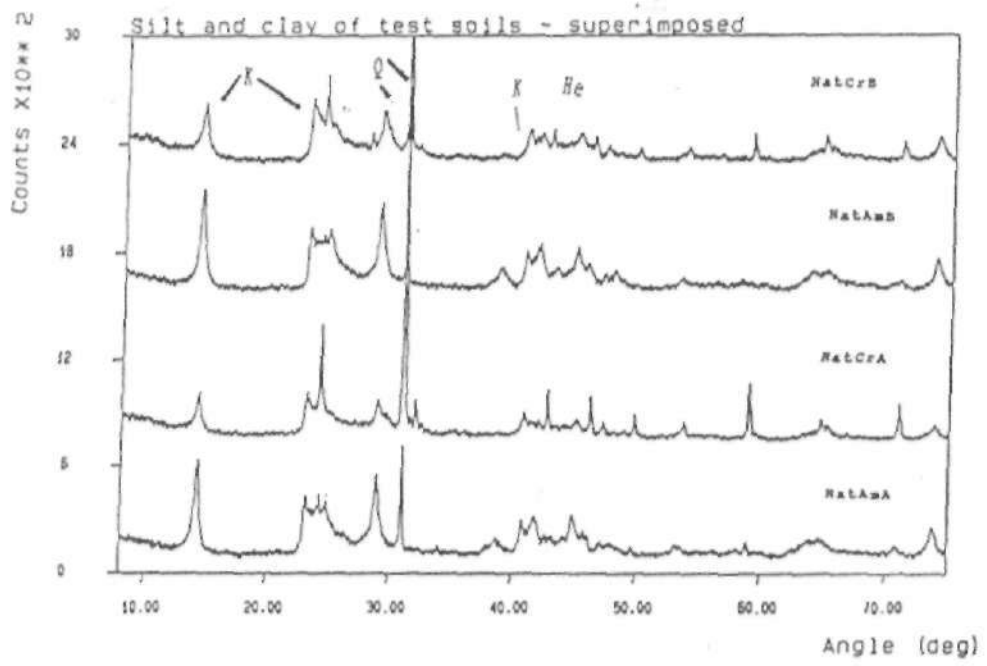


Figure 4.1.8: Powder X-ray diffractograms for the special soils; silt and clay fractions superimposed: a - natural soils, b - artificial soils.

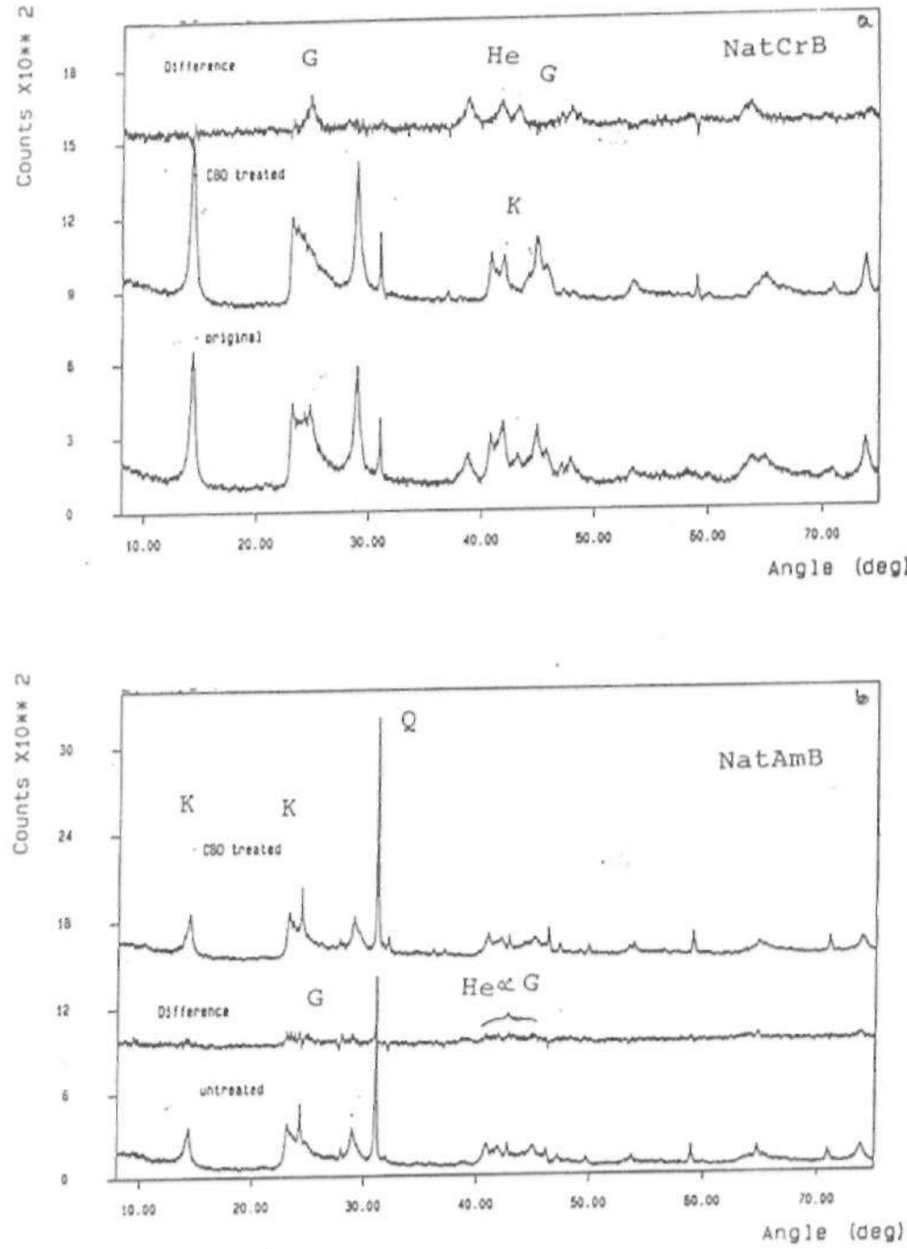


Figure 4.1.9: Difference diffractograms for the natural soils: a - NatAmB, b - NatCrB.

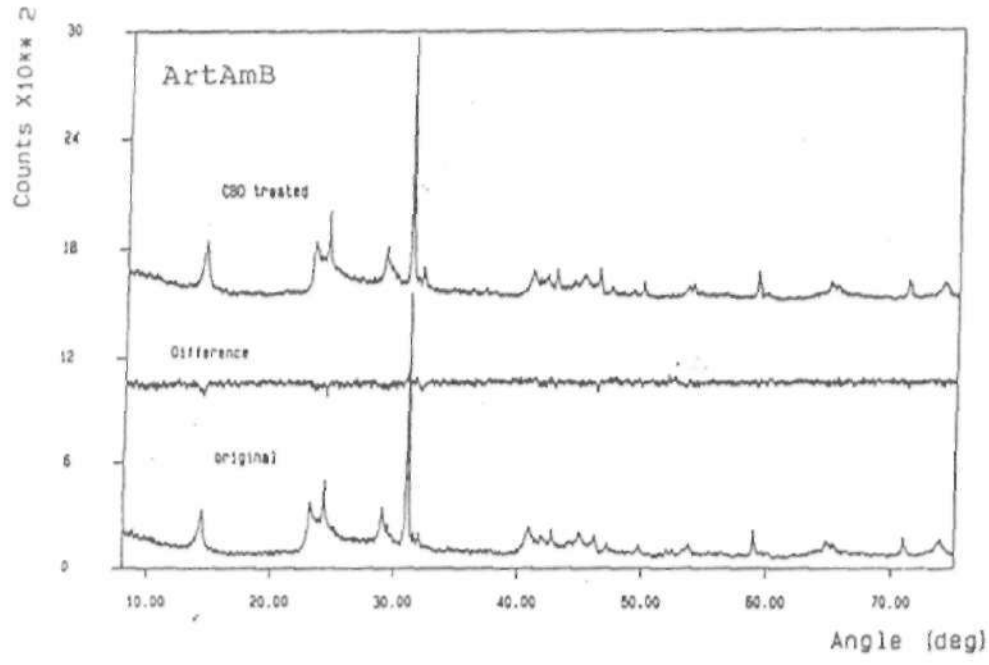


Figure 4.1.10: Difference diffractograms for the artificial soils: a - ArtAmB, b - ArtCrB.

may indicate that much of the Fe oxide introduced as treatment in the laboratory remained in the amorphous state, or possibly in the micro-crystalline state not detectable by the X-ray diffraction analysis (Ryden et al., (1977). The most probable iron oxide species in the prepared and natural soils were goethite (α-FeOOH), haematite (α-Fe_2O_3) and possibly ferrihydrite (α-$Fe_2O.nH_2O$) known to be associated with goethite and exists essentially in a more disorderly state (Schwertmann and Fischer, 1973). Working on some micaceous vermiculites, Roth et al., (1969), observed that the oxide coatings on this mineral were composed of Fe_2O with approximately 10 % by weight of Al_2O_3. The dominant oxide in the artificial soils as a result of the treatment was possibly haematite.

4.2. Phosphorus Status and Relationships

4.2.1. Native phosphate status of the profiles

The phosphorus status of the profiles and distribution in the various fractions are given in Table 4.2.1. Total P (P_T) for the soils were comparable to values commonly found for the Nigerian savanna Alfisol (Jones and Wild, 1975) and for the forest soils formed on Fe rich materials (Greenland, 1981). P_T

Table 4.2.1: Distribution of inorganic phosphate fractions (P_i), P_o and P_T in the profiles, and OC/P_o ratio.

Profile	Depth cm	P_T	Al-P	Fe-P	Ca-P	Red. Sol-P	Active-P	Org-P	Resid-P	$\sum P_i$	OC/P_o
						µg g^{-1}					ratio
Pedon 1	0-4	581.3	67.7	115.0	10.7	31.5	193.4	153.0	203.0	427.9	393
	10-20	171.8	19.5	29.0	2.5	16.7	51.0	68.8	35.3	103.1	234
	20-40	356.7	15.3	60.7	12.4	34.5	88.4	69.8	164.0	286.9	128
	40-90	131.2	18.0	16.7	2.5	25.5	37.2	42.4	26.1	88.8	56
Pedon 2	0-22	251.6	36.0	26.2	13.0	38.2	75.2	115.6	22.6	136.0	190
	22-55	148.1	14.0	12.5	4.7	13.5	30.7	43.7	40.2	84.4	92
	55-100	125.0	14.7	9.3	4.0	13.7	28.0	2.8	80.5	122.5	1036
	100-120	143.7	18.5	9.8	4.0	13.7	32.3	3.1	94.6	140.6	903
Pedon 3	0-30	737.5	26.5	59.5	18.4	44.0	104.4	281.3	307.6	456.0	86
	30-55	673.4	22.5	51.5	14.1	40.0	88.1	225.0	320.3	448.4	39
	55-70	668.7	20.5	89.5	21.1	55.5	131.1	45.9	436.2	622.8	74
	70-95	668.7	26.5	104.7	21.5	54.7	152.7	40.6	420.7	628.1	47
	95-130	668.7	25.3	104.2	23.0	62.0	152.5	28.1	426.1	640.6	64

content of the surface soils were 581, 251 and 737 µg/g for pedons 1, 2 and 3 respectively, and decreased with depth in the savanna soils, but was reasonably constant in pedon 3 with a slightly higher amount in the surface apparently due to OM. The high P content of the Oxisol (pedon 3) and the Bsg horizon of pedon 1 could be attributed to the high Fe oxide content of the horizons (Udo and Ogunwale, 1977; Table 4.1.8), probably with a relatively high amounts of the oxides in the micro-crystalline state. Deductively, we could infer that Fe oxide plays a significant role in the reactions and cycling of phosphorus in these soils.

The organic P (P_o) content of the soils were low, and decreased appreciably with depth along with the OM content down the profiles. Surface soil values were 153, 115 and 281 µg/g, constituting only 25, 46 and 38 % of P_t (Table 4.2.2) in the respective profiles (1, 2 and 3). These values are consistent with some previous studies on Nigerian soils (Jones and Wild, 1975; Udo and Ogunwale, 1977, Enwezor, 1977). The OC/P_o ratio (Table 4.2.1) indicate that P_o can be a relevant source of available P only in well drained profiles where ratios were less than 200 (Tisdal and Nelson, 1975). The OC/P_o values were considerably lower in the forest Oxisol which indicates high P content of the biomas and the ready availability of the P_o in the forest soil. The importance of P_o in tropical soils has been documented (Ayodele and Agboola, 1983; Adepetu and Corey, 1975; Lekwa and Whiteside, 1986).

The distribution of P in the various inorganic phosphate fractions in the profiles (Table 4.2.1) shows that the

Table 4.2.2: Percentage contribution of the various phosphate forms to P_T in the soil profiles.

Profile	Depth (cm)	Al-P	Fe-P	Ca-P	Active-P %	Red. Sol-P	Org.P	Resid.P	$\sum P_i$
					% of P_T				
Pedon 1	0-4	11.6	19.8	20.0	33.2	5.40	26.3	34.9	73.6
	10-20	11.3	16.9	1.4	29.6	9.7	40.0	20.5	60.0
	20-40	4.2	17.0	3.4	24.7	9.6	19.5	45.9	80.4
	40-90	13.7	12.7	2.0	28.3	19.4	32.3	10.0	67.6
Pedon 2	0-22	14.3	10.4	5.1	30.0	15.2	46.0	8.9	54.0
	22-55	9.5	8.4	2.8	20.7	9.1	29.5	27.1	57.0
	55-100	11.7	7.4	3.2	22.4	10.9	2.2	64.4	98.0
	100-120	12.8	6.8	2.8	22.4	9.5	2.2	65.8	97.8
Pedon 3	0-30	3.6	8.1	2.5	14.2	5.9	38.1	41.7	61.8
	30-55	3.3	7.6	2.1	13.8	5.9	33.4	47.5	66.6
	55-70	3.1	13.4	3.1	19.6	8.3	6.9	65.2	93.1
	70-95	3.9	15.6	3.2	22.8	8.1	6.0	62.9	93.9
	95-130	3.7	15.6	3.4	22.8	9.2	4.2	63.7	95.8

relative abundance of the various fractions were different among profiles that invariably differed in origin. The active fractions (Al-P, Fe-P and Ca-P) and the reductant soluble P (Fe oxide coated Fe-PO_4) decreased with depth in the savanna soils but increased in the forest Oxisol, though surface soil values in this profile was slightly higher due to the effects of OM. The Al-P values of the surface soils were 67.7, 36.0 and 26.5 µg/g for pedons 1, 2 and 3 respectively. The Fe-P values were 115.0, 26.2 and 59.5 µg/g, Ca-P values were 10.7, 3.0 and 18.4 µg/g while the reductant-soluble-P were 31.5,

38.2 and 41.0 µg/g respectively for the pedons.

The relative contributions of the various fractions to total-P (Table 4.2.2) show that Al-P was quite important in the savanna profiles in contrast to the forest Oxisol. The low Al-P content of the pedon 3 suggests limited capacity of this soil to release P for plant use (Chang and Juo, 1962; Juo and Ellis, 1968; Chang and Jackson, 1958), a characteristic that describes strongly weathered soils (Westin and de Brito, 1969). The higher factional content of the less soluble Fe-P in this profile validates this concept. Ca-P was less important in these profiles though the constituting plagioclase (Ca-feldspar) in the mineralogy of pedon 3 increased the Ca-P content of this profile. From the results, we should expect a higher content of available P in the savanna soils.

The residual or non-extractable P values ranged from 9% in soils high in quartz sand, to 60% of P_T in the soils high in iron oxides (pedon 3 and lower horizon of pedon 2). Values of between 50-80 % of P_T have been observed in some Nigerian soils (Udo, 1976) and in other soils (Adams and Walker, 1975). The chemical nature of the residual fraction is suggested to be largely lattice P, with P proxying for Si in the tetrahedral unit of the clay mineral (Kurtz, 1953). It has also been suggested that all or part of residual P could exist as included apatite resistant to attack by strong acids (Syres et al., 1968). Despite the resistant nature of this fraction, studies have shown that it may be organic or inorganic (Adams et al., 1973; Walker and Syres, 1976; Syres et al., 1969).

38.2 and 41.0 µg/g respectively for the pedons.

The relative contributions of the various fractions to total-P (Table 4.2.2) show that Al-P was quite important in the savanna profiles in contrast to the forest Oxisol. The low Al-P content of the pedon 3 suggests limited capacity of this soil to release P for plant use (Chang and Juo, 1962; Juo and Ellis, 1968; Chang and Jackson, 1958), a characteristic that describes strongly weathered soils (Westin and de Brito, 1969). The higher factional content of the less soluble Fe-P in this profile validates this concept. Ca-P was less important in these profiles though the constituting plagioclase (Ca-feldspar) in the mineralogy of pedon 3 increased the Ca-P content of this profile. From the results, we should expect a higher content of available P in the savanna soils.

The residual or non-extractable P values ranged from 9% in soils high in quartz sand, to 60% of P_T in the soils high in iron oxides (pedon 3 and lower horizon of pedon 2). Values of between 50-80 % of P_T have been observed in some Nigerian soils (Udo, 1976) and in other soils (Adams and Walker, 1975). The chemical nature of the residual fraction is suggested to be largely lattice P, with P proxying for Si in the tetrahedral unit of the clay mineral (Kurtz, 1953). It has also been suggested that all or part of residual P could exist as included apatite resistant to attack by strong acids (Syres et al., 1968). Despite the resistant nature of this fraction, studies have shown that it may be organic or inorganic (Adams et al., 1973; Walker and Syres, 1976; Syres et al., 1969).

The soils studied had high content of residual P, which may indicate that they are strongly weathered soils, characteristic of the arable lands of the region.

4.2.2. Hedley phosphate fractions of the rhizosphere study soils

Phosphate fractions of the rhizosphere study soils were determined by the modified Hedley et al., (1982) fractionation scheme. The P_i and P_o fractions of the unplanted test soils are presented in Table 4.2.3.

Results indicate that the tropical soils (soils 1-4) and temperate soils (soils 5 and 6) differed in fertility status and distribution of the P fractions. The temperate soils were particularly rich in $NaHCO_3$ P, and HCl-P. The tropical top soils (Soils 1 and 4) were only moderately rich in $NaHCO_3$ P, a reflection of their fertility potential. Soil 4, was particularly high in NaOH extractable fractions (P_i and P_o) and $NaHCO_3$ P_o. The tropical subsurface soils, very low in OM, were poor in readily available NaHCO3 P_i, and contained no Ca-P (HCl-P). This is consistent with the report of Nye and Bertheux, (1957), that tropical soils are low in apatite, and that P is mostly bound to Fe and Al oxide surfaces in tropical soil systems (Parfitt, 1978). The HCl-P extracted from the tropical topsoils (Soils 1 & 4) were therefore artifacts, resulting from P reactions with the decomposition products of soil OM, or as a result of harmattern dust deposits known to be high in Ca minerals (Moberg and Esu, 1991). The Ca-P content of the tropical soils were therefore low, especially

Table 4.2.3: Distribution of Hedley P fractions in the unplanted (Control) test soils.

Soil	$NaHCO_3$		NaOH		HCl	H_2SO_4	TOTAL
	P_i	P_o	P_i	P_o	P_i	(P_i+P_o)*	
	µg/g						
1. NatCrA	7.2	11.20	19.74	29.6	11.30	133.80	219.24
2. NatCrB	1.35	5.10	10.41	27.55	0.0	127.46	169.27
3. NatAmB	0.61	9.73	32.06	85.73	0.0	517.70	645.83
4. Pedon 1	12.65	56.58	113.72	129.75	13.91	133.20	470.81
5. Danish I	28.4	12.65	41.49	33.26	108.15	225.4	449.35
6. Danish II	72.00	14.45	105.04	44.80	215.26	221.6	673.18

in the sub-soils, quite contrary to the situation in the temperate soils. Though tropical soil 3 and Danish Soil II were comparable in total P status, both soils differed in the distribution of P fractions which in all apparent terms, accounted for the differences in their fertility coefficients (to be discussed subsequently). The bicarbonate-P (Al-P) and NaOH-P (Fe-P) fractions were particularly low in the well drained profiles from the tropics.

4.2.3. Phosphorus extractable by chemical soil tests

The available phosphorus status of the soils was estimated by four chemical soil tests, namely Bray-P_1, water, Olsen and resin. The acid fluoride extractant of Bray and Kurtz (1945) extracted considerable amounts of P from the surface soils of the well drained pedons, but amounts extracted from the subsoils were negligible (Table 4.2.4). Surface soil values were 45.5, 23.6 and 8.4 µg/g representing 7.82, 9.38 and 1.13 % of P_T for pedons, 1,2 and 3 respectively

(Table 4.2.5). Though the NH_4F essentially prevents resorption of dissolved P by enhancing the dissolution of Al and Fe phosphates and complexing the metal ions (Bray and Kurtz, 1945), the relatively reduced efficiency of this reagent in the subsoils may be due to low OM content and stoichiometric or equivalent ratios of the reactants. The low free oxide content and high organic C of pedon 1 explained the high amount of extractable Bray-P_1 observed even for the subsoils, low in OM. In the Oxisol with a relatively higher content of

Table 4.2.4: Phosphorus extractable by some chemical soil tests, and resin-P (Q)/water (I) ratio.

Profile	Depth (cm)	Bray-P	Water-P	Olsen-P	Resin-P	Resin-P / Water-P
				$\mu g/g^{-1}$		ratio
Pedon 1	0 - 4	45.50	4.00	112.00	37.37	9.34
	10 - 20	13.30	1.02	14.50	12.53	12.28
	20 - 40	3.85	0.17	13.00	9.12	53.64
	40 - 90	0.70	0.27	4.50	8.32	30.81
Pedon 2	0 - 22	23.62	9.16	34.75	30.62	3.34
	22 - 55	0.70	0.13	4.30	8.12	62.46
	55 - 100	0.70	0.13	6.00	8.10	62.30
	100 - 120	0.05	0.13	3.75	8.50	65.38
Pedon 3	0 - 30	8.40	0.50	15.50	13.62	27.24
	30 - 55	0.70	0.12	8.00	8.00	66.67
	55 - 70	0.35	0.04	9.00	8.12	203.00
	70 - 95	0.30	0.10	9.20	9.62	96.20
	95 - 130	0.33	0.08	5.00	9.75	121.87

micro-crystalline oxides, extractable P was low. In the presence of OM, the capacity of the reagent to desorb P was enhanced.

Water extractable P was low in comparison to other extractants. Surface soil values were 4.00, 9.16 and 0.50 µg/g, (Table 4.2.4), representing 0.63, 3.64 and 0.06% of P_T respectively (Table 4.2.5). Calibration studies by Bingham (1947), and Martin and Mikkelsen (1960) indicate that response to fertilizer P may be unlikely if water extractable P is in excess of 0.13 µg/g. The results obtained in this study suggests the need for adequate field calibration for

Table 4.2.5: Phosphorus extractable by chemical soil tests expressed as percent of total P.

Profile	Depth	Bray-P	Water-P	Olsen-P	Resin-P
		%			
Pedon 1	0 - 4	7.82	0.69	19.26	6.42
	10 - 20	7.74	0.59	8.44	7.29
	20 - 40	1.07	0.04	3.64	2.55
	40 - 90	0.53	0.20	3.42	6.34
Pedon 2	0 - 22	9.38	3.64	13.81	12.17
	22 - 55	0.47	0.08	2.90	5.48
	55 - 100	0.56	0.10	4.80	6.48
	100 - 120	0.03	0.09	2.60	5.91
Pedon 3	0 - 30	1.13	0.06	2.10	1.84
	30 - 55	0.10	0.02	1.18	1.18
	55 - 70	0.05	0.01	1.34	1.21
	70 - 95	0.04	0.02	1.37	1.43
	95 - 130	0.04	0.01	0.74	1.45

meaningful interpretation of values. The highly weathered Oxisol was particularly low in water extractable P.

The Olsen-extractant (0.5 N $NaHCO_3$ at pH 8.5) extracted more P from the soils than other reagents. The Olsen-P values for the surface soils were 112.0, 34.8 and 15.5 µg/g respectively, which corresponds to 19.3, 13.8 and 2.1 % of P_T. This comparatively high efficiency of the reagent in the subsoil was derived from its capacity to precipitate Ca as $CaC0_3$ in the neutral soils, and promote the hydrolysis of Al and Fe phosphates in acid soils (Olsen et al., 1954; Menon et al., 1991; Lindsay and Moreno, 1960). In each case adsorbed P was released by exchange with HCO_3^- and OH^- in the extractant, and the concentration of Ca, Fe and Al in solution were kept low as a result. This extractant has been found suitable for acid soils (John, et al., 1967), and for neutral and acid soils (Williams and Knight, 1963; Walmsley and Cornfort, 1973).

The amount of P extracted by resin was inferior only to Olsen-P. The principle of reaction of the resin method is based on surface exchange of P through Cl^- or HCO_3^- on the resin without chemical reaction or pH change (Amer et al., 1955; Sibbesen, 1978). Surface soil values for resin-P were 37.4, 30.6 and 13.6 µg/g for pedons 1, 2 and 3 respectively, representing 6.42, 12.17 and 1.18% of P_T (Table 4.1.11). Compared to other soils, the relative desorptive capacity of the reagent down the profile differed considerably among soils, but was more related to the HCO_3^- (Olsen) reagent in these acid soils.

The amount of P extracted by all reagents decreased down the profile in all soils consistent with decrease in OM, and was particularly low in soils high in Fe oxides, especially in the forest Oxisol. Resin and water methods have been classified as suitable extractants for the evaluation of soil P-status. These reagents were considered less harsh on the soil (Olsen and Watanabe, 1970; Sibbesen, 1978) and extracted more of the available P than the chemical procedures of Bray and Olsen. However, Bray P_1 has been widely used in assessing the status of available phosphorus in Nigerian acid soils (Udo and Ogunwale, 1978).

The P availability indices by chemical extracts is a useful parameter to assess plant P uptake over relatively short periods (Bowman and Olsen, 1985c), but for an entire season, prediction accuracy is improved by considering the quantity (Q)/intensity (I) relationship, defined by the buffer capacity (Ozanne and Shaw, 1973). The resin-P (Q)/water-P (I) relationship, an estimate of the buffer index was calculated for the soils and shown in Table 4.1.10. Values increased consistently down the profile, implying that P concentration in solution should decrease consistently down the profile, along with decrease in OM, at the same level of labile P. As suggested by Holford (1980), an effective soil test should extract P only from the labile pool, and amounts extracted should reflect principally the intensity aspect of labile P.

4.2.4. Soil phosphate relationships

4.2.4.1. Relationship between soil properties and P forms

The correlation coefficients of selected soil properties and phosphate properties are given in Tables 4.2.6 and 4.2.7. Soil texture seem to play a major role in the amount and distribution of the various phosphate forms. The consistently negative correlation of the sand fraction with the P forms shows that most of the soil P was associated with the finer soil particles (clay and silt) which provide the sink for soil P. Al-P and P_o were the only two fractions that were not significantly related with clay. Total P (P_T) was significantly correlated with specific surface area and ZPC while P_o was related to organic C (OC) and ECEC.

With the active fractions, Al-P was highly correlated with OC (r=0.91*), ECEC (r=0.78**) and surface area (r=0.06**). The Fe-P fraction was highly correlated with surface area (r=0.61) but was weakly correlated at the 5% level of probability to ZPC and OC. Ca-P was less important in these soils and was only related to clay while the reductant soluble faction was significantly related only to ZPC and clay. The results suggest that OC and the extensiveness of the reactive surfaces were the two most important soil factors which controlled the availability of P in the soils. Al-P and Fe-P were significantly correlated with both factors. The relationship of both fractions to OC are illustrated in Figure 4.2.1.

Table 4.2.6: Correlation coefficients of selected soil properties and Fe and Al oxide fractions and phosphate forms of the profile soils.

Property	Al-P	Fe-P	Ca-P	Red-Sol-P	Active-P	Org-P	Total-P
Selected soil properties							
Clay	0.23	0.84**	0.52**	0.60**	0.75**	0.27	0.78**
Silt	0.45*	0.49*	0.24	0.15	0.43*	0.50**	0.29
Sand	-0.30	-0.84**	-0.52**	-0.56**	-0.75**	-0.35	-0.76**
Org C	0.91**	0.42*	0.06	0.02	0.44*	0.53**	0.27
pH(H_2O)	-0.21	-0.30	-0.21	0.04	-0.19	-0.11	0.03
pH($CaCl_2$)	-0.12	-0.05	0.03	0.30	0.06	0.01	0.28
Acidity	0.36	0.09	0.15	-0.31	0.01	0.03	-0.17
ECEC	0.78**	0.16	0.01	-0.21	0.20	0.43*	0.02
SAREA	0.66**	0.61**	0.08	0.08	0.53**	0.36	0.45*
ZPC	-0.02	0.46*	0.24	0.58*	0.47*	0.22	0.72**
Fe and Al oxide fractions							
Fe_d	-0.20	0.55**	0.47*	0.75**	0.55**	0.08	0.70**
Fe_{ox}	0.29	0.75*	0.47*	0.52**	0.69**	0.34	0.49*
Fe_{py}	0.77**	0.42*	0.08	-0.05	0.39	0.49*	0.21
Al_d	0.33	0.28	0.05	0.22	0.31	0.47*	0.17
Al_{ox}	0.36	0.70	0.51**	0.49*	0.67**	0.33	0.65**
Al_{py}	0.10	-0.25	-0.26	-0.63*	-0.33	-0.16	-0.38

*, ** = Significant at 5 and 1% levels of probability.

4.2.4.2 Relationship between soil oxides and soil phosphate forms

Iron and aluminum oxide fractions were correlated with phosphate forms (Tables 4.2.6 and 4.2.7). Interestingly, Fe_d and Fe_{ox} were highly correlated with all phosphate forms with

Table 4.2.7: Correlation coefficients of selected soil properties and P extractable by some soil tests methods. (Profile samples).

Property	Org C	Bray-P	Water-P	Olsen-P	Resin-P
Selected soil properties					
Clay	0.16	0.02	-0.42*	0.28	-0.08
Silt	0.64**	0.49*	-0.08	0.46*	0.32
Sand	-0.28	-0.12	0.39	-0.34	0.01
Org C	1.00	0.95**	0.54**	0.82**	0.89**
pH (H_2O)	-0.38	-0.33	0.17	-0.28	-0.12
pH ($CaCl_2$)	-0.31	-0.28	0.20	-0.22	-0.07
Acidity	0.53**	0.57*	0.15	0.39	0.39
ECEC	0.93**	0.92**	0.57**	0.69**	0.85**
SAREA	0.70**	0.54**	-0.14	0.67**	0.39
ZPC	-0.21	-0.35	-0.45*	0.00	-0.34
Fe and Al oxide fractions					
Fe_d	-0.38	-0.48*	-0.44	-0.16	-0.48*
Fe_{ox}	0.34	0.23	-0.17	0.34	0.12
Fe_{py}	0.94**	0.85**	0.29	0.74**	0.71**
Al_d	0.45*	0.38	0.23	0.36	0.35
Al_{ox}	0.42*	0.30	-0.07	0.37	0.23
Al_{py}	0.19	0.18	-0.02	0.11	0.11

*,** - Significant at 5 and 1 % probability levels.

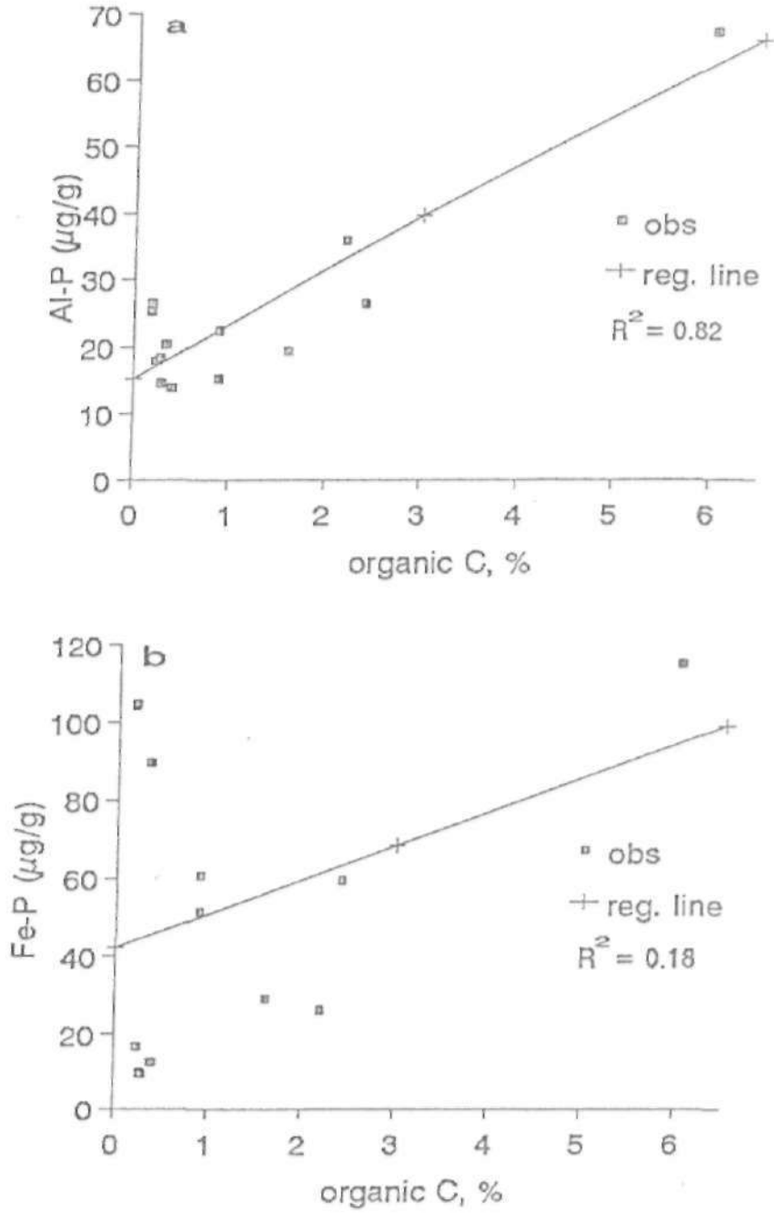


Figure 4.2.1: Regression relationship between Al-P and Fe-P with organic matter; a - Al-P and b - Fe-P.

the exception of Al-P and P_o. These later fractions were significantly correlated with Fe_{py} (Fe bound to OM) which suggests that Al-P and P_o fractions existed in organic complexes. This lends support to the significance of OM in rendering P available in the soils as Al-P has been shown to be more readily available to plants (Juo and Boyd, 1968; Tandon, 1987). Results obtained show that much of the Fe-P was amorphous as shown by the correlation coefficient (r) with Fe_{ox} (r=0.75**) and with Al_{ox} (r=0.70**). The high correlation of P_T, Fe-P and Red-P to Fe_d and the amorphous Fe and Al fractions show that P immobilization in the soils was largely controlled by the soil oxides especially in their amorphous states. This is in consonance with previous works on tropical soils (Udo and Uzu, 1972; Lekwa and Whiteside, 1986). P_T and the reductant soluble fractions were high in the soils with the crystalline oxide forms dominant.

The relationships of the phosphate forms and the Al oxide fractions were less consistent. The pyrophosphate reagent seemed to have extracted the fraction of Al more active in immobilizing P. As shown in Table 4.2.8, only the amorphous fractions of Fe and Al as well as Fe_{py} were significantly correlated with surface area, a factor considered important in the reaction of P in the soils. Reliably, it could be deduced that these oxide fractions and clay were the inorganic colloidal fraction that control phosphate sorption and release in these acid soils. The regression relationship between the oxide fractions and some P forms are illustrated in Figure 4.2.2.

Table 4.2.8: Correlation matrix of Al and Fe oxide fractions, clay and surface area for the profile soils.

Property	Fe_d	Fe_{ox}	Fe_{py}	Al_d	Al_{ox}	Al_{py}	SAREA	Clay
Fe_d	1.00	0.39	-0.36	-0.16	0.34	-0.04*	0.04	0.66**
Fe_{ox}		1.00	0.50	0.41*	0.57**	-0.10	0.56**	0.74**
Fe_{py}			1.00	0.45*	0.51	0.25	0.77**	0.26
Al_d				1.00	0.26	0.20	0.23	0.16
Al_{ox}					1.00	-0.12	0.53**	0.64**
Al_{py}						1.00	0.26	-0.21
SAREA							1.00	0.63**
Clay								1.00

**, * - Significant at 1 and 5% levels of Probability

4.2.4.3. Relationship between soil test-P, phosphate forms and soil oxides.

The correlation coefficients of soil test-P and soil properties are shown in Table 4.2.7. The results show that the influence of soil texture was less important in defining P extracted by the various extractants. Surface area, OC and ECEC were highly correlated with all soil test-P except water-P and resin-P that were not related to surface area. This result corroborates the earlier statement of the importance of these factors in describing available phosphorus in these soils. The fact that all soil test-P was highly correlated with Al-P only allows one to suggest that all the methods used extracted P from about the same phosphate pool (Table 4.2.9). The order of relationship to Al-P was Bray-P > Resin - P > Olsen - P > Water-P. Olsen-P was also significantly correlated to Fe-P. Since this method extracted more P than

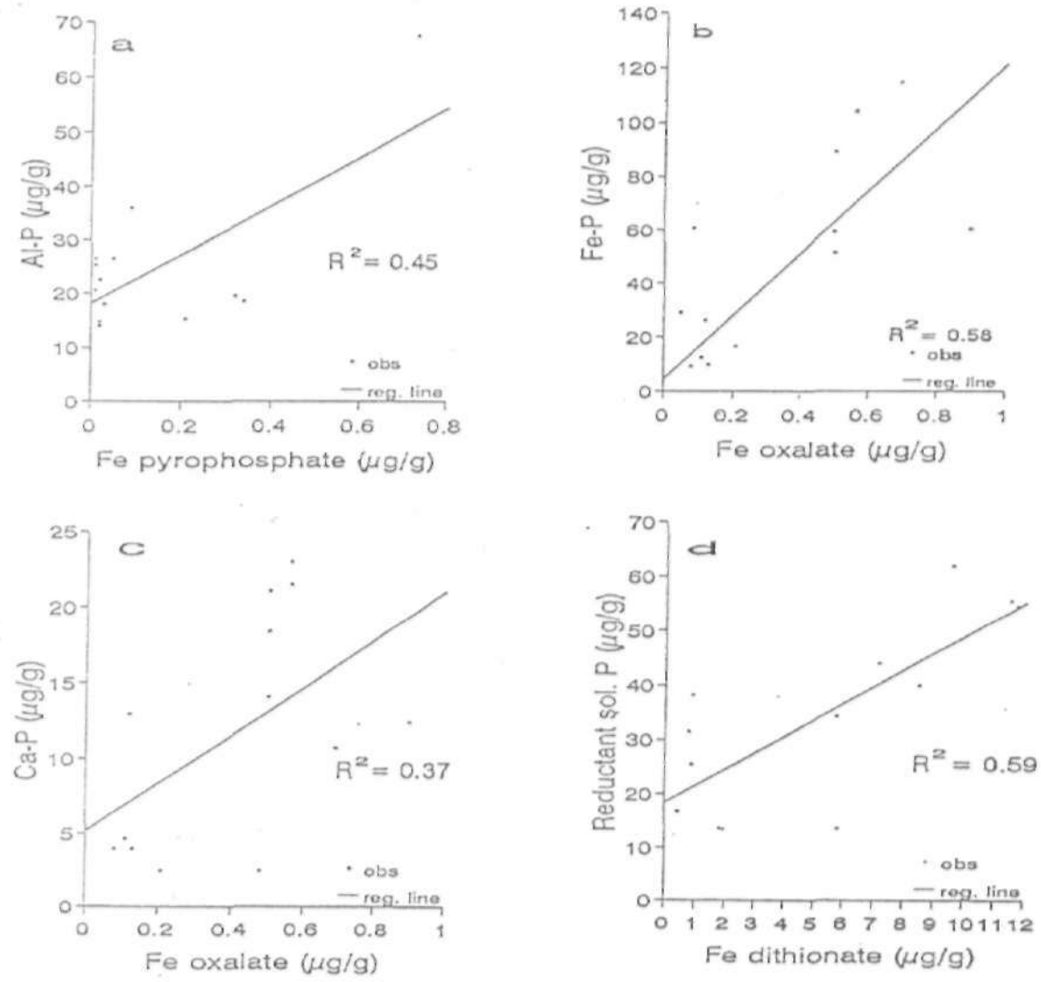


Figure 4.2.2: Relationships between oxide fractions and some P forms; a = Al-P vs Fe_{py}, b = Fe-P vs Fe_{ox}, c = Ca-P vs Fe_{ox}, and d = Red. soluble-P vs Fe_{d}.

the other methods (Table 4.2.4) much of the P extracted could be said to exist in difficulty available forms. Al-P has been commonly shown to be the more available form of the discrete chemical fractions (Juo and Boyd, 1968) implying that P extracted by these methods could be a reliable index of labile P, or more restrictively, P intensity (I). Phosphorus extracted by all soil tests were significantly interrelated.

Resin-P has often been shown to be closely related to plant available P (Menon et al., 1991; Dalal and Hallsworth, 1976; Bowman et al., 1978). The close relationship of the soil test-P to resin-P provides an indication of the predictive accuracy of these methods in describing plant available P. Following this guide, the soil test methods were ranked as follows: resin > Bray P_1 > water > Olsen methods. The similarity in the r-value of resin-P and Bray-P to Al-P may also suggest the suitability of Bray-P_1, in these acid soils as shown by Udo and Ogunwale, (1978).

Table 4.2.9. Correlation matrix of phosphate forms and phosphorus extractable by chemical soil tests.

Property	Total P	Org. P	Al-P	Fe-P	Ca-P	Red Sol-P	Active-P	Bray-P	Wat-P	Olsen-P	Resin-P
Total	1.00	0.59**	0.40*	0.79**	0.57**	0.81**	0.84**	0.13	-0.06	0.32	0.15
Org-P		1.00	0.39	0.26	0.24	0.32	0.36	0.35	0.21	0.25	0.34
Al-P			1.00	0.57**	0.12	0.21	0.62**	0.91**	0.58**	0.86**	0.90**
Fe-P				1.00	0.34**	0.77	0.98**	0.35	-0.00	0.56**	0.32
Ca-P					1.00	0.61**	0.56**	0.04	0.00	0.11	0.02
Red. Sol-P						1.00	0.84**	-0.02	0.05	0.18	0.06
Active-P							1.00	0.39	0.14	0.58**	0.41*
Bray-P								1.00	0.70**	0.83*	0.96**
Wat-P									1.00	0.46*	0.84**
Olsen-P										1.00	0.78**
Resin-P											1.00

*, ** - Significant at 5 and 1 % probability levels

4.3. Adsorption of Added Phosphorus

4.3.1 Phosphorus vs time interaction

The P vs time isotherms for selected test soils are presented in Figure 4.3.1. Results revealed two phases of phosphate reactions. An initial rapid phase which lasted for between 2 to 4 days, followed by a slow phase with gentle slope of the isotherm, with no reasonably true equilibrium attained before 12 days in any of the soils considered. This finding corroborates some earlier works on some Nigerian soils (Adepetu, 1981; Anyaduba and Adepetu, 1983), and supports the findings of Willett et al., (1988) who established, in well crystallized goethite, that the first rapid phase could last for as long as 3 days. P reactions in this phase has been attributed to the existence of unoccupied high energy sorption sites on the surfaces (Munns and Fox, 1976; Parfitt et al., 1989). The slow reaction thereafter is attributed to the formation of iron phosphate as coating on the oxides (van der Zee and van Riemsdijk, 1986), or equally valid, to the migration of phosphate into aggregate iron oxides, particularly ferrihydrite (Willett et al., 1988; and Parfitt, 1988). The less buffered soils in this study (surface soils and soils high in coarse quartzite) attained equilibrium much slower because of the influence of OM and lower contents soils oxides and clay. They were consequently less reactive. Deriving from this results, 12 day equilibration was also used to generate sorption data for more detailed studies on phosphate sorption using the special soils.

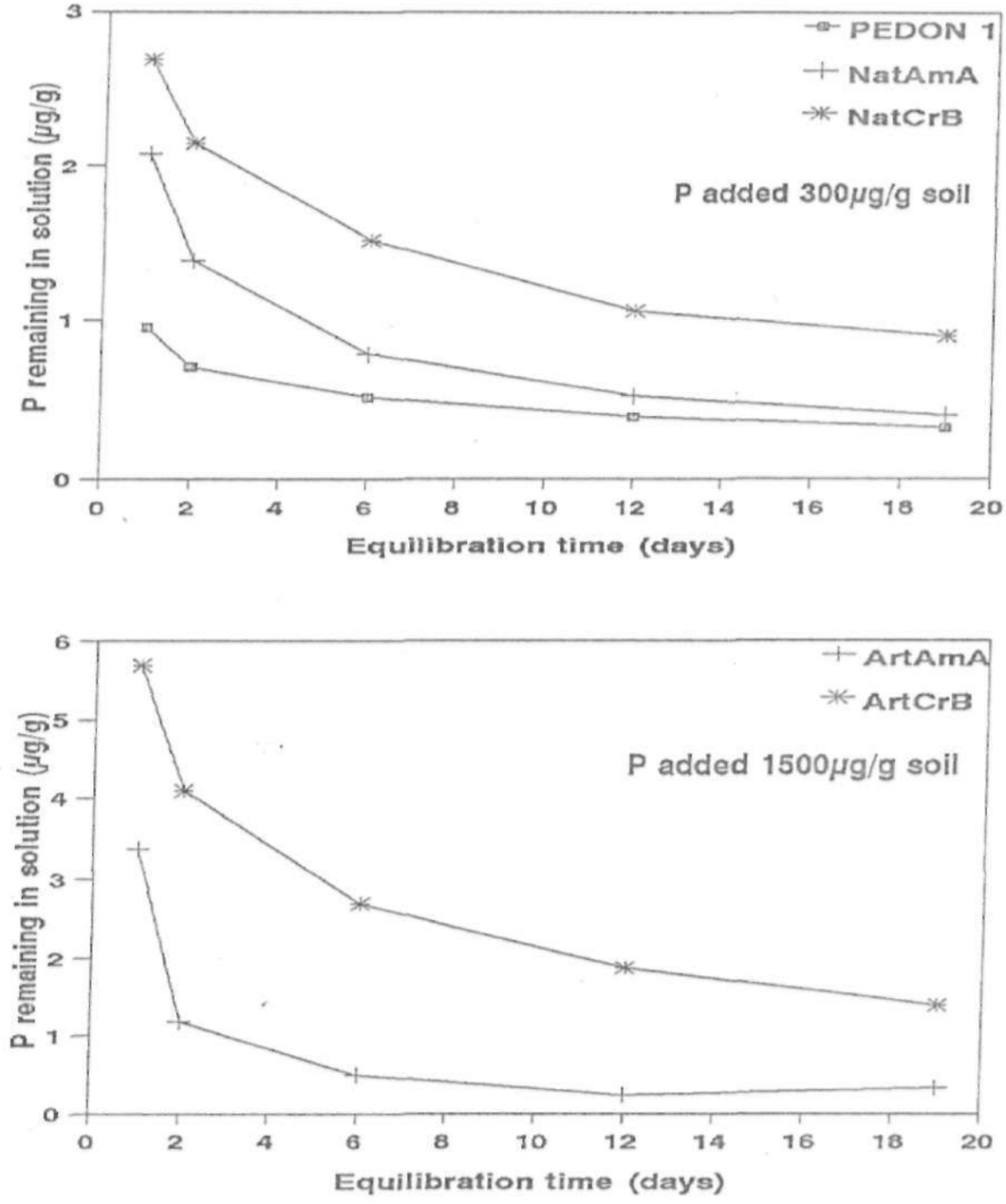


Figure 4.3.1: Equilibrium solution concentration with time of reaction in days of some natural and artificial soils and pedon 1 (0-15cm).

4.3.2. Description of adsorption isotherms for the profiles

Phosphorus sorption curves relating P adsorbed to equilibrium solution P concentration for the profiles are shown in Figures 4.3.2. a,b,c. The sorption curves for all soils, except the surface soil of Pedon 2 were similar indicating similarity in the nature of adsorption reaction, but differed in the intrinsic characteristics such as the slope of the isotherms and adsorption capacity. These characteristics tended to reflect the nature of the parent material, amount and nature of surface oxides and inherent phosphate fertility of the soils. The profile soils of pedon 3 formed on amphibolite rich metasediments with higher content of micro-crystalline oxides, adsorbed more P than the hydromorphic soils of pedon 1 and the well drained profile from the savanna. The later soil had crystalline oxides as dominant. The slopes of the sorption isotherms increased with depth reflecting increase in P sorption with decrease in organic matter. Generally the steeper sorption slopes were the more highly buffered (Peaslee and Fox, 1978), lower in solution P concentration, and more prone to be P deficient. Soil solution phosphate decreased with depth, consistent with decrease in OM. Evidence that organic matter depresses P sorption by soils have been presented (Juo and Fox, 1977; Fox, 1974; Fox, Plucket and Whitney, 1968). The sorption characteristics of the hydromorphic soils differed from that of the surface soils of the well drained profiles, possibly due to effects of crystallinity of the soil oxides. The results also show that the surface soil of pedon 1, much

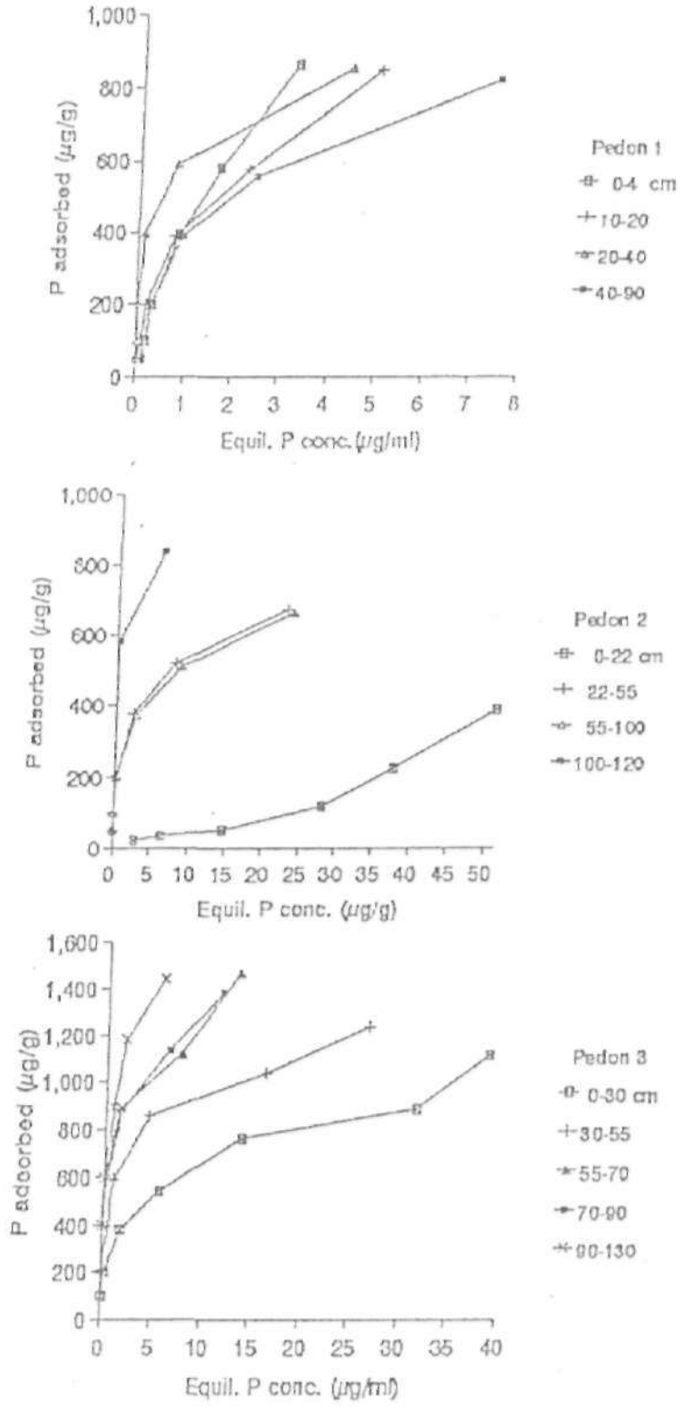


Figure 4.3.2: Phosphorus adsorption isotherms for the soils of the profiles.

higher in organic matter, was in this case more buffered than the subsurface soils of the same pedon, indicating enhanced adsorption by OM in these sols with amorphous oxides dominant. Similar findings have been reported on some poorly drained soils of Nigeria (Juo and Fox, 1977).

Evaluating the P sorption characteristics of the surface soils should provide information on the phosphate fertility of the respective profiles. The slope of the P sorption isotherm of the savanna hydromorphic soil was steeper, and so was more buffered at comparable levels of solution P than the savanna Alfisol and the forest Oxisol. The texture of the savanna Alfisol was coarse which indicates easy diffusion of P in soil. Despite the high oxide content of the forest Oxisol, it was intermediate in slope characteristic. From the results, we could infer that the capacity of the soils to replenish soil solution P was in the following order: pedon 2 > pedon 3 > pedon 1, considering their P buffer characteristics.

The nature of soil organic matter is a fundamental factor influencing phosphate reactions in soils, in particular, the low molecular weight organic ligand which are considered more reactive, and therefore more effective in desorbing P (Rovira, 1969; Huang and Violante, 1986; Violante and Giafreda, 1993). The humic acid fraction was dominant in pedon 1 (Table 4.1.11). Considering the sorption property of this profile, we could also infer that this humic fraction was less effective in influencing phosphate desorption reactions. Deriving therefore from the characteristics of the sorption isotherms, we could deduce a triple interaction of surface

inorganic oxides, clay and organic colloids in influencing phosphate adsorption in the soils.

4.3.3. Description of P adsorption isotherms for the special soils

Phosphate sorption isotherm drawn for the special soils are presented in Figure 4.3.3 a,b. Sorption curves for the natural soils revealed that soils with the crystalline oxides (NatCrA and NatCrB) adsorbed less P and were less buffered that the amorphous soils (NatAmA and NatAmB). More so, the surface soils retained less P than the subsoils in each soil pair. These findings are consistent with the conventional concepts that crystalline oxides adsorbs less P than the amorphous oxides (Schwertmam, 1986; Jones and Wild, 1975; Udo and Uzu, 1972; Greenland, 1972), and that OM depresses P retention by soils (Sibanda and Young, 1986; Ryden et al., 1977). Though the artificial soils differed from the natural soils in slope characteristics, adsorption trend in both systems were comparably identical (Figure 4.3.3 a & b). The crystallized Fe dominant soils (ArtCrA and ArtCrB) adsorbed less P than the amorphous soils (ArtAmA and ArtAmB). The 'surface' soil also retained less P than the 'subsurface' soil.

Estimates of some sorption parameters were derived by graphic plots of the sorption data, relating P sorbed (quantity factor) to the equilibrium solution P (intensity factor), at solution P concentration range of 0.4 - 0.8 µg P/ml. P sorbed at 0.6 µg/ml solution was extrapolated. The

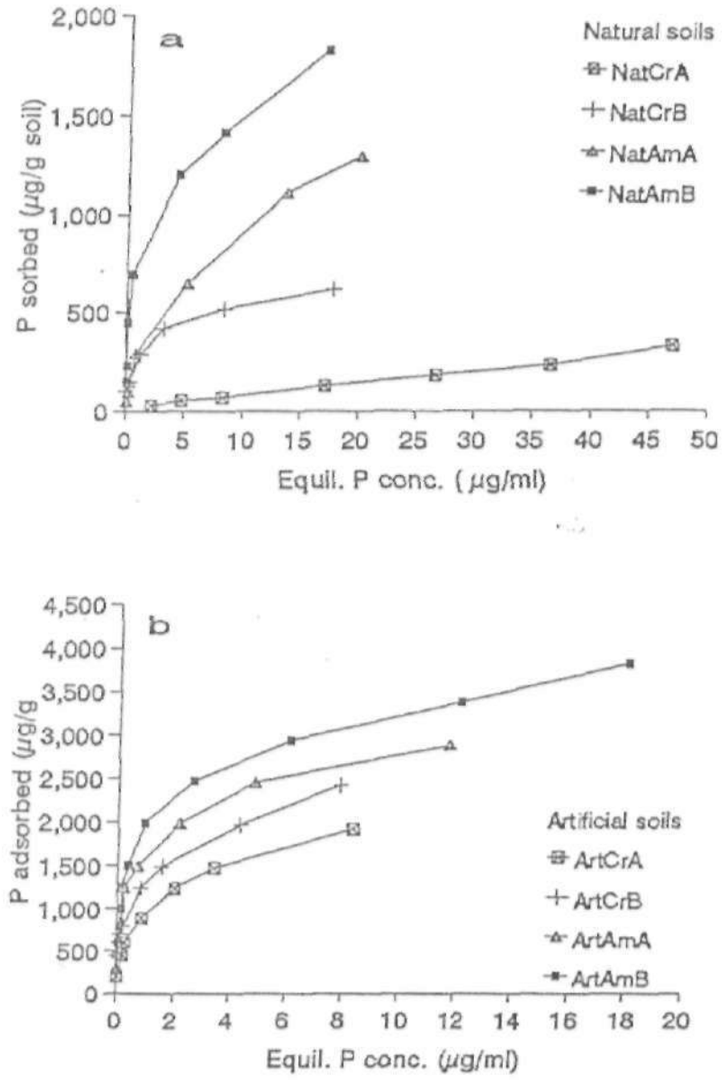


Figure 4.3.3: Phosphorus adsorption isotherms for the special soils; a - natural soils, b - prepared soils.

affinity value, K, at this condition was calculated from the relationship:

$$BC = K * X \qquad (4.1)$$

where BC = buffer capacity at 0.6 µg P/ml solution concentration, K = bonding energy and X = P sorbed at this P solution concentration. Values are presented in Table 4.3.1. Previous findings by Udo, (1972), had shown that 0.6 - 0.8 µg/ml solution P was a more realistic range for P nutrition of crops in tropical soils under laboratory conditions. Results showed that the crystalline Fe soils were less buffered, and this was more so in the soils with OM fraction for both natural and artificial systems. Deriving from the homogenous (artificial) system, it was apparent that the buffer capacity

Table 4.3.1. Buffer capacity and affinity constants of the respective special soils obtained from graphic plots at the dilute range of solution P (0 - 10 µg/g P), and P sorbed at 0.6 µg/g equilibrium phosphate concentration.

Soil	Buffer capacity	P Sorbed at 0.6 µg ml $^{-1}$ solution P	Estimated Affinity Constant (K)
		µg g^{-1}	ml µg^{-1}
NatCrA	15	5.0	0.33
ArtCrA	625	725.0	1.16
NatCrB	140	213.0	1.52
ArtCrB	643	1080.0	1.68
NatAmA	225	247.0	1.10
ArtAmA	625	1430.0	2.28
NatAmB	425	740.0	1.74
ArtAmB	993	1700.0	1.71

did not adequately describe the P release pattern in the soils, but that this property was related to the affinity constant, K. In both soil systems, OM seemed to have enhanced the tenacity with which P was held in the amorphous Fe oxide soils. Where OM was low or absent, K did not vary with oxide crystallinity, but P_{max} varied appreciably with surface area, a parameter that was higher in the soils with the amorphous oxides dominant (Table 4.1.5, Juo and Fox, 1977). The difference in P sorbed at 0.60 µg P/ml for ArtCrB and ArtAmB (1080 and 1700 µg/g) was attributable to the effects of crystallinity and specific surface area.

The study has shown clearly that amorphous oxides were more responsible for P sorption in the soils. Approximations derived from Table 4.3.1. attributes 72 % of P sorbed at 0.6 µg P/ml solution P exclusively to the amorphous oxide content of soils. Also at the 2.5 % OC content of soils as used in this study, 30 % of P sorbed by the amorphous soils was as a result of the enhancing effects of OM on P sorption. Though the derivations reflect a true ranking of the factors that govern phosphate reaction in tropical soil systems, they are suggestive, and can only be verified by more detailed kinetic studies. Soil texture, P fertility, amount and form of soil oxides and soil mineralogy could impose tremendous influence the adsorption - desorption characteristic of soils, deriving from the reactions and relationships in the natural soils.

4.3.3. Comparison of adsorption equations.

4.3.3.1 Profile soils

To describe the sorption isotherms, sorption data were fitted to the Langmuir, Freundlich and Temkin equations. Goodness of fit was evaluated by the coefficient of determination, R^2, and the root mean square error (RMSE). These were derived from the non-linear (NLIN) regression analysis using the SAS statistical package. Over the whole range of equilibrium solution P considered, the Langmuir and Freundlich models produced good fits (Table 4.3.2) under described conditions. Soils with OM were better described by the Langmuir equation.

Comparative assessment of the LIN and NLIN models (Table 4.3.3) revealed that the NLIN equations were superior for all three equations except with the Langmuir equation at low OM content. This is clearly shown by the values in pedon I and surface soils of pedons 2 and 3. An advantage of the NLIN regression method rests in the satisfaction that true parameter estimates can be obtained rather than the improved R^2 (Kinniburgh, 1986). The NLIN Langmuir equation was therefore used to generate parameter estimate for the description of data and comparison of soils.

Visual conformity to the various sorption models were tested by linearized equations adjudged by the linearity of the curves. Figure 4.3.4 a, b, c shows the linearized Langmuir plots. A plot of C/x vs C gave gentle curves indicating that the assumption on which the equation was based was not completely satisfied, possibly due to the existence of

Table 4.3.2: The R^2 and root mean square error (RMSE) for the comparison of the adsorption models for the description of P adsorption by the soils fitted by non-linear regression models.

Profile	Depth (cm)	Langmuir Model		Freundlich Model		Temkin Model	
		R^2	RMSE	R^2	RMSE	R^2	RMSE
Pedon 1	0 - 4	0.998	22.89	0.995	40.15	0.988	62.41
	10 - 20	0.991	51.87	0.995	38.47	0.988	60.79
	20 - 40	0.988	62.11	0.970	97.42	0.996	34.68
	40 - 90	0.993	43.85	0.996	32.46	0.972	93.04
Pedon 2	0 - 22	0.986	11.27	0.978	17.91	0.851	89.7
	22 - 55	0.984	60.05	0.994	34.24	0.993	38.57
	55 - 100	0.966	86.05	0.995	31.89	0.992	40.28
	100 - 120	0.973	98.14	0.928	161.39	0.960	120.55
Pedon 3	0 - 30	0.980	106.28	0.992	52.52	0.978	111.14
	30 - 55	0.980	109.53	0.995	66.45	0.990	95.57
	55 - 70	0.970	201.64	0.995	82.99	0.992	106.12
	70 - 90	0.955	255.00	0.996	64.99	0.986	122.5
	90 - 130	0.969	219.94	0.995	92.17	0.990	126.42

Table 4.3.3: Comparative effectiveness of the linear and non-linear models of the sorption equations in describing the P sorption data for the soils as shown by the R^2 values.

Profile	Depth (cm)	Langmuir Model		Freundlich Model		Temkin Model	
		LIN	NLIN	LIN	NLIN	LIN	NLIN
Pedon 1	0 - 4	0.739	0.998	0.959	0.995	0.968	0.988
	10 - 20	0.975	0.991	0.951	0.995	0.969	0.988
	20 - 40	0.996	0.988	0.822	0.970	0.990	0.996
	40 - 90	0.978	0.993	0.990	0.996	0.925	0.976
Pedon 2	0 - 22	0.049	0.986	0.924	0.998	0.679	0.851
	22 - 55	0.990	0.984	0.953	0.994	0.974	0.993
	55 - 100	0.985	0.966	0.933	0.995	0.977	0.992
	100 - 120	0.996	0.973	0.864	0.928	0.906	0.960
Pedon 3	0 - 30	0.964	0.980	0.993	0.992	0.920	0.978
	30 - 55	0.989	0.980	0.978	0.995	0.953	0.990
	55 - 70	0.974	0.970	0.980	0.995	0.952	0.992
	70 - 90	0.985	0.955	0.940	0.996	0.941	0.986
	90 - 130	0.990	0.969	0.926	0.995	0.933	0.990

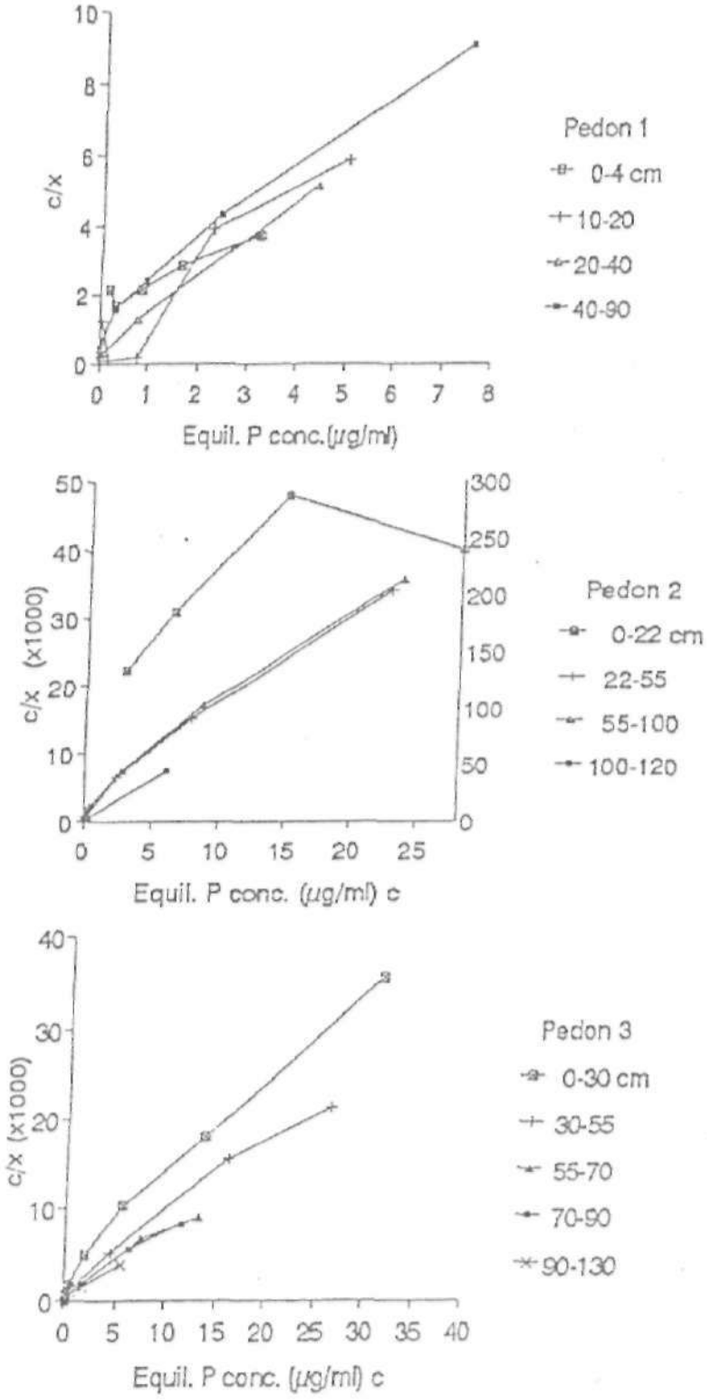


Figure 4.3.4: Langmuir plots of the sorption data for the soil profiles.

two or more energetically different sites on which P was adsorbed. In systems as heterogenous as those of soil colloids, it may be natural to consider sorption energies as forming a continuum in soil systems contrary to the provisions of the Langmuir model (Sposito, 1982; Holford et al., 1974; Polyzopoulos, et al., 1985).

The Freundlich equation that proposed decreasing energy with adsorption, also produced gentle curves (Fig 4.3.5 a,b, c). Similar curves of the linearized plots have also been observed (Bache and Williams, 1971). This may imply that the character of the exponent needs some adjusting, possibly by the introduction of a functional constant to fit the data adequately.

The Temkin equation, described by the plot of x vs log C also produced gentle curves over the whole range of solution P considered (Figure 4.3.6 a,b,c). Such development indicates a non linear decrease in bonding energy with sorption.

Non of the equations examined represented successfully P sorption by all the soils. As was observed by Polyzopoulos et al., (1985), only complex mechanistic models like that used by Bowden et al., (1977) can successfully account for all factors involved in, and all changes taking place during P sorption. Due to lack of satisfactory conformity to the basic classical equations (Olsen and Wanatabe, 1957; Gunary, 1970; Bache and Williams, 1971; Holford, et al.,1974), extended equation or modifications of the equations have been used to describe orption data more adequately (Shapiro and Fried, 1959; Syers et al., 1973; Holford et al., 1974, Sibbesen, 1979). Sibbesen,

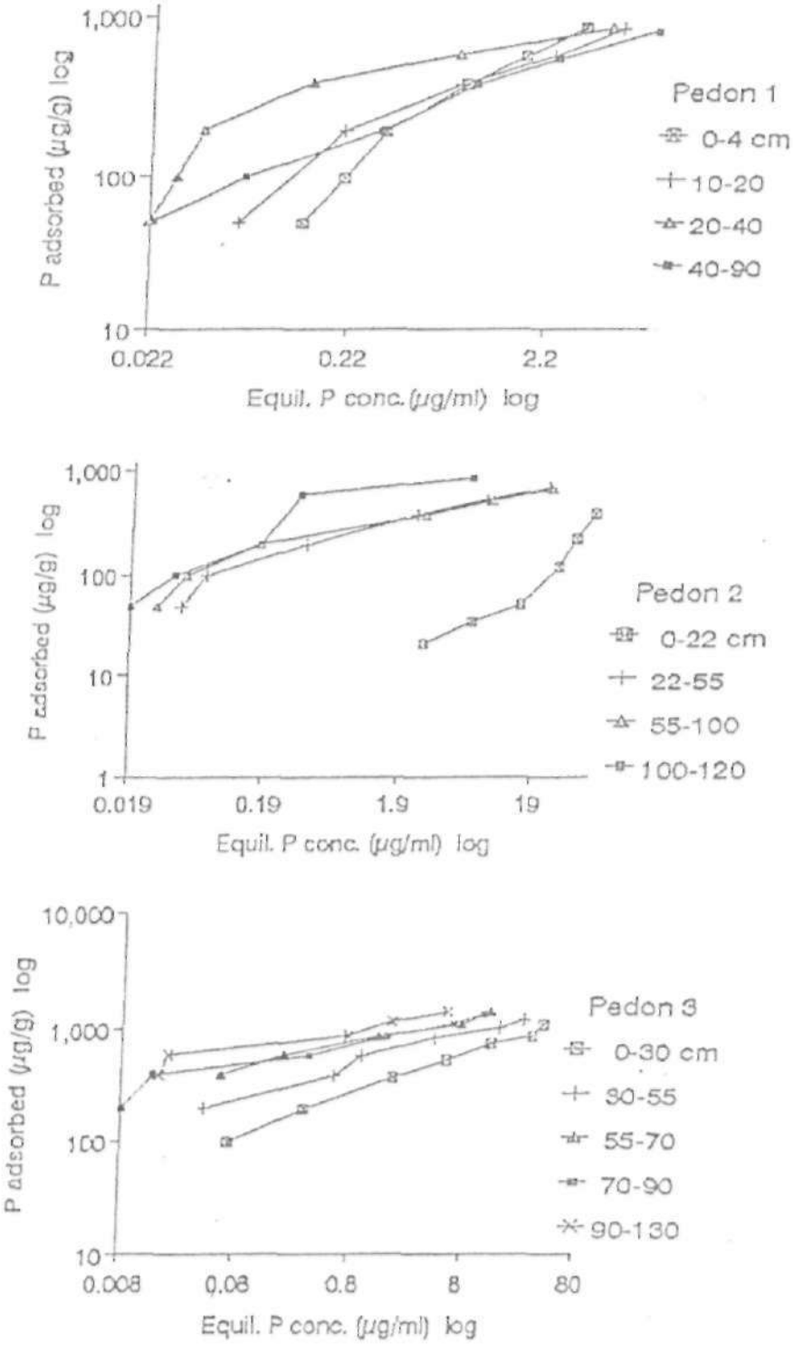


Figure 4.3.5: Freundlich isotherms for the soils - log x vs log c.

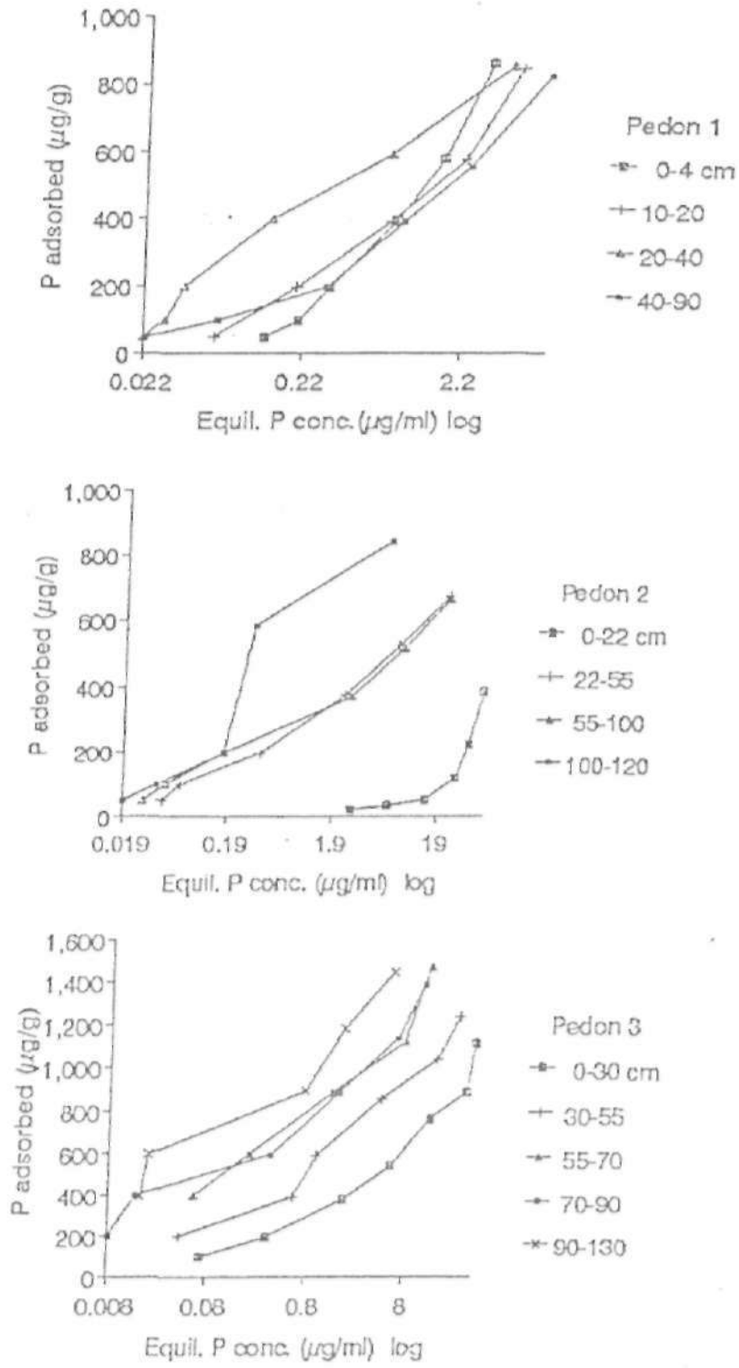


Figure 4.3.6: Temkin adsorption isotherms (x vs log C).

(1979), observed that a mechanistic model was preferable to an empirical equation, but this can only be developed from an intimate physical and chemical knowledge of the behaviour of the phosphate ions in the soil solution system. Some of these determinations are non-routine and cumbersome to predict.

This study showed that the Langmuir plots were more linear in comparison to the Freundlich and Temkin plots, and was used to generate correlative parameters (adsorption maximum and bonding energy) for comparing soils. The Freundlich and Temkin equations were found to be of value where the soil oxide content was high. They have also been shown to be appropriate where large concentration range, such as could be found around fertilizer granules, is considered. Because of the log function component of these equations, the wide concentration range of interest in soils can be conveniently accommodated. Also, the intensity factor that is of fundamental importance in soil phosphate studies is considered a chemical potential, therefore a log function of concentration (Bache, 1965; Bache and Williams, 1971). For the estimation of sorption parameters for correlative purposes in dilute solutions (< 10 µg P/ml), the LIN Langmuir equation was used.

4.3.3.2. Special soils

The sorption data for the special soils were fitted to the LIN and NLIN models of the Langmuir, Freundlich and Temkin equations as was done for the profile soils. The R^2 and RMSE values derived from the NLIN regression analysis are shown in

Table 4.3.4. For all the levels of P considered, the Freundlich equation was superior to all other equations tested. The Langmuir equation was least efficient as a predictive equation in the natural soils. Exponential decrease in energy with P adsorption as expressed by the Freundlich equation seem more logical in nature (Barrow, 1978; Polyzopoulos et al., 1985). The linearized and non-linear models were compared (Table 4.3.5), and it was observed that the NLIN Freundlich model produced a better fit when the homogenous group of soils were considered.

Conformity of the sorption data to the various adsorption equation were also evaluated by graphic plots. These are shown in Figures 4.3.7 - 4.3.9. Deviation from linearity was more obvious in the heterogenous natural soils than in the

Table 4.3.4: The R^2 and root mean square error (RMSE) for the comparison of the adsorption models for the description of P adsorption by the natural and artificial soils fitted by non-linear regression models.

	Langmuir Model		Freundlich Model		Temkin Model	
Soil	R^2	RMSE	R2	RMSE	R^2	RMSE
NatCrA	0.995	14.60	0.996	12.50	0.951	46.24
ArtCrA	0.989	137.30	0.998	58.74	0.982	176.86
NatCrB	0.986	56.56	0.996	29.55	0.975	76.74
ArtCrB	0.966	292.66	0.999	30.74	0.986	187.63
NatAmA	0.990	82.52	0.998	27.54	0.954	176.91
ArtAmA	0.986	268.99	0.995	164.86	0.997	127.50
NatAmB	0.964	231.84	0.997	64.19	0.985	149.40
ArtAmB	0.982	314.08	0.994	172.54	0.997	112.44

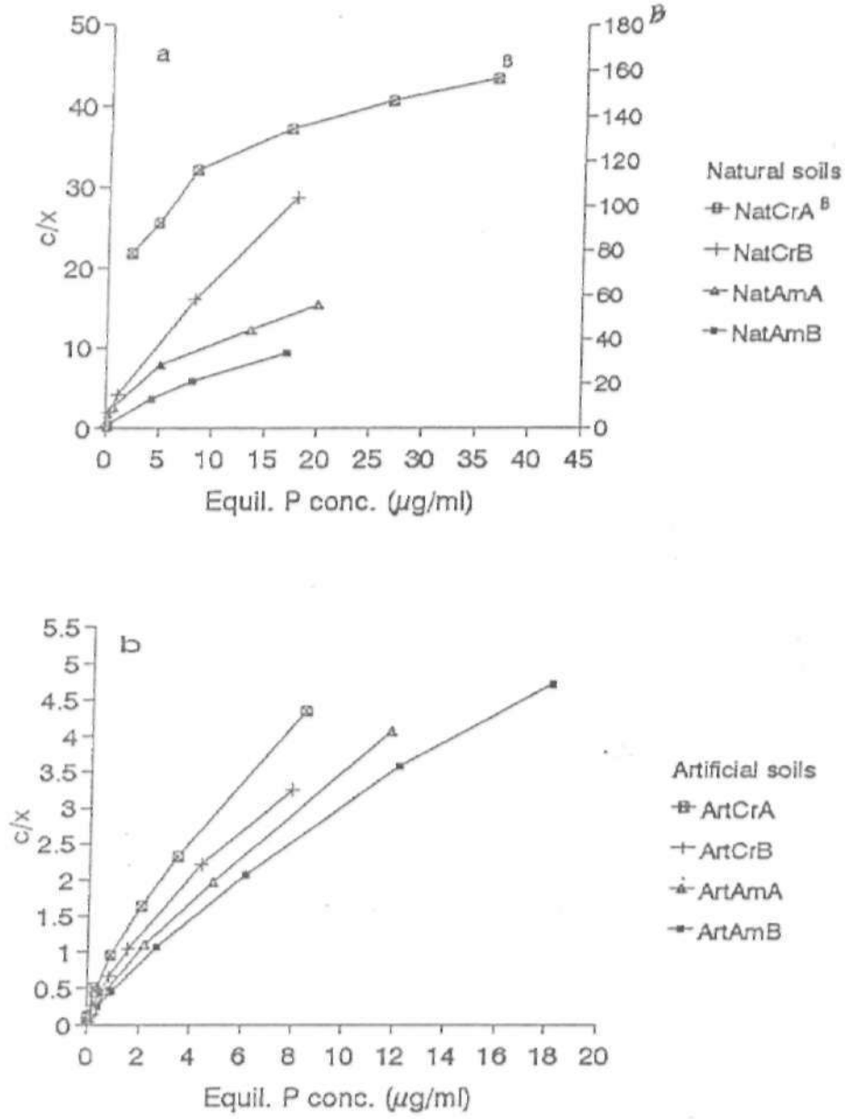


Figure 4.3.7: Langmuir adsorption isotherms for the special soils.

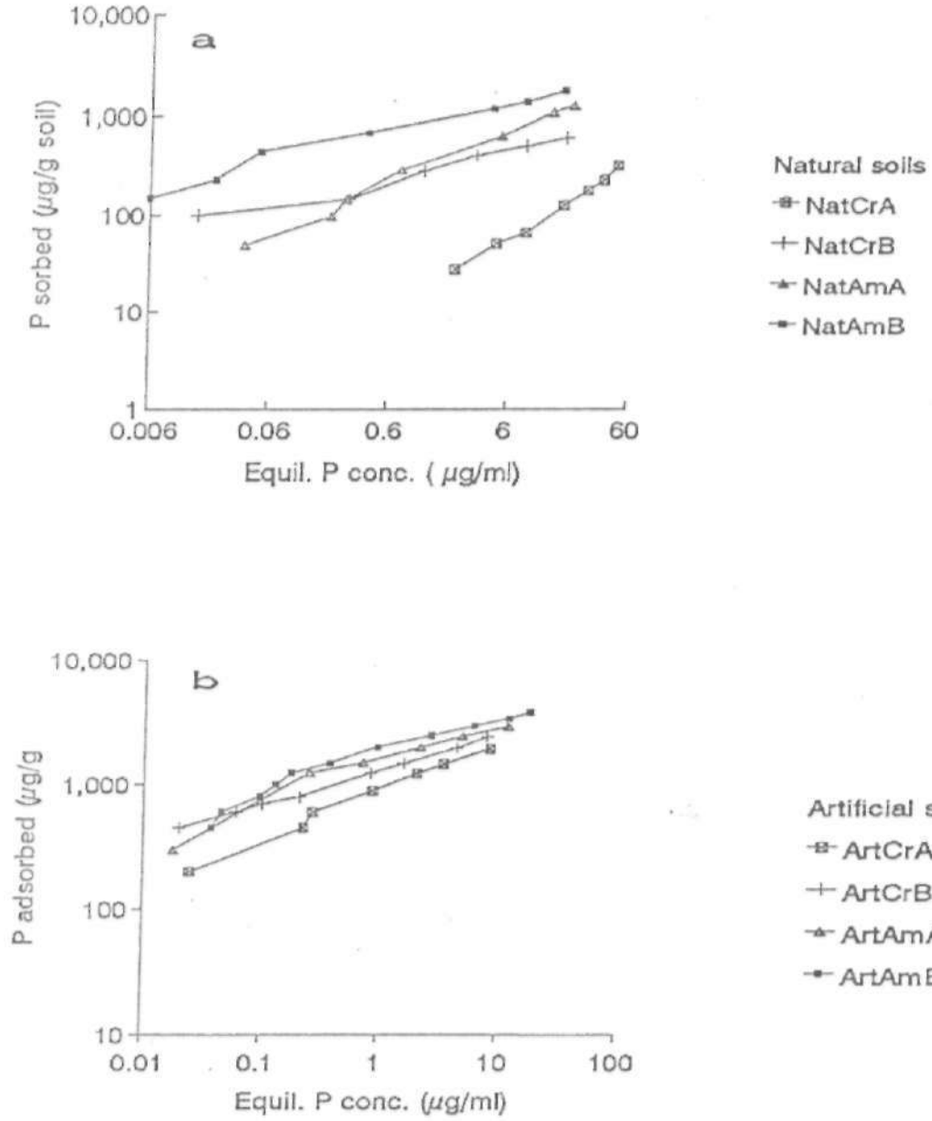


Figure 4.3.8: Freundlich adsorption isotherms for the special soils.

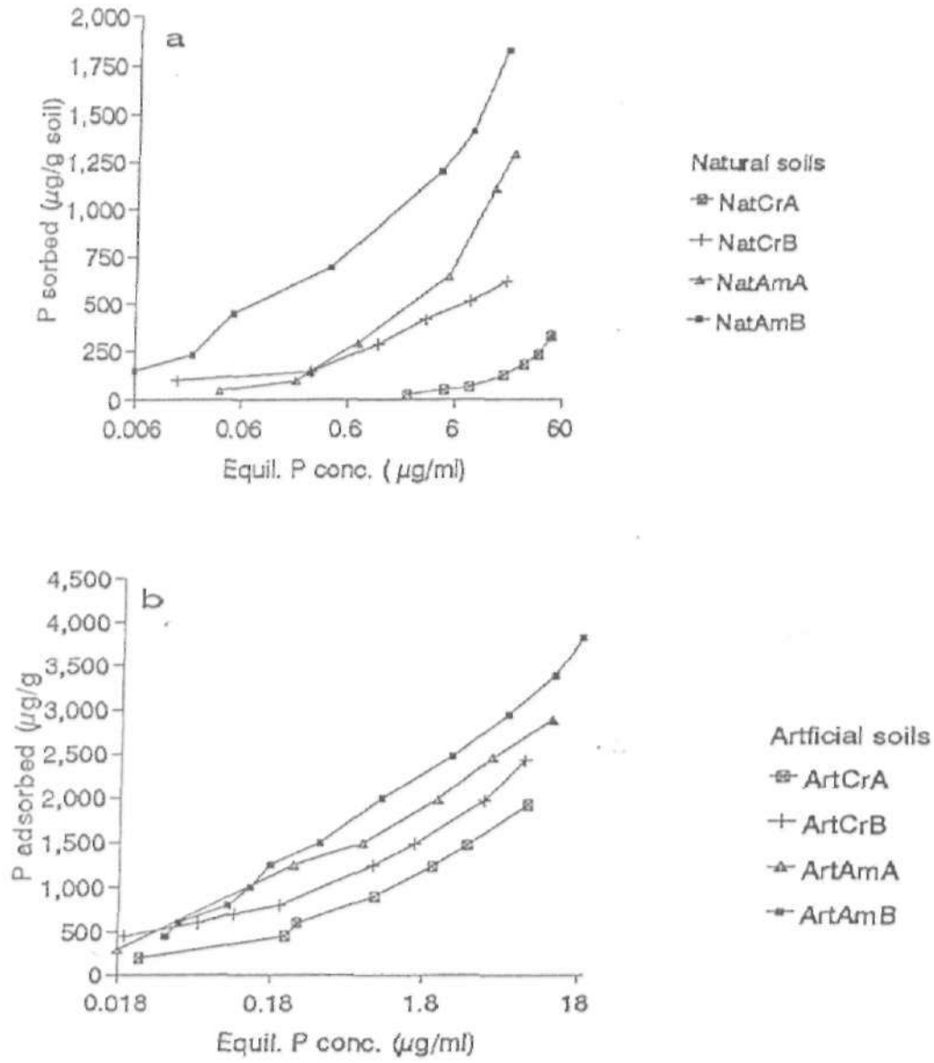


Figure 4.3.9: Temkin adsorption isotherm for the special soils.

Table 4.3.5: The R^2 linear and non-linear regressions for the adsorption models fitted to the P sorption data for the natural and artificial soils.

Soil	Langmuir Model		Freundlich Model		Temkin Model	
	LIN	NLIN	LIN	NLIN	LIN	NLIN
NatCrA	0.976	0.995	0.991	0.996	0.882	0.951
ArtCrA	0.980	0.989	0.990	0.998	0.929	0.982
NatCrB	0.989	0.986	0.997	0.996	0.889	0.975
ArtCrB	0.979	0.966	0.998	0.999	0.939	0.986
NatAmA	0.962	0.990	0.991	0.998	0.900	0.954
ArtAmA	0.992	0.986	0.943	0.995	0.984	0.977
NatAmB	0.975	0.964	0.971	0.997	0.954	0.985
ArtAmB	0.990	0.982	0.952	0.994	0.991	0.997

artificial soils. Over the whole range of P considered, the Langmuir, Temkin and Freundlich plots produced gentle curves in the artificial system. The parameters were estimated by the least square iterative process to produce the best fit. Predicted values from the Langmuir iteration process was plotted and compared with the observed values for ArtCrB (Figure 4.3.10). The deviation observed, suggests a lack of fit which indicate that a multi-surface Langmuir model, which also reverts in the limiting case, to the Freundlich equation, or the Freundlich equation *per se*, will describe the adsorption reaction in the these soils better.

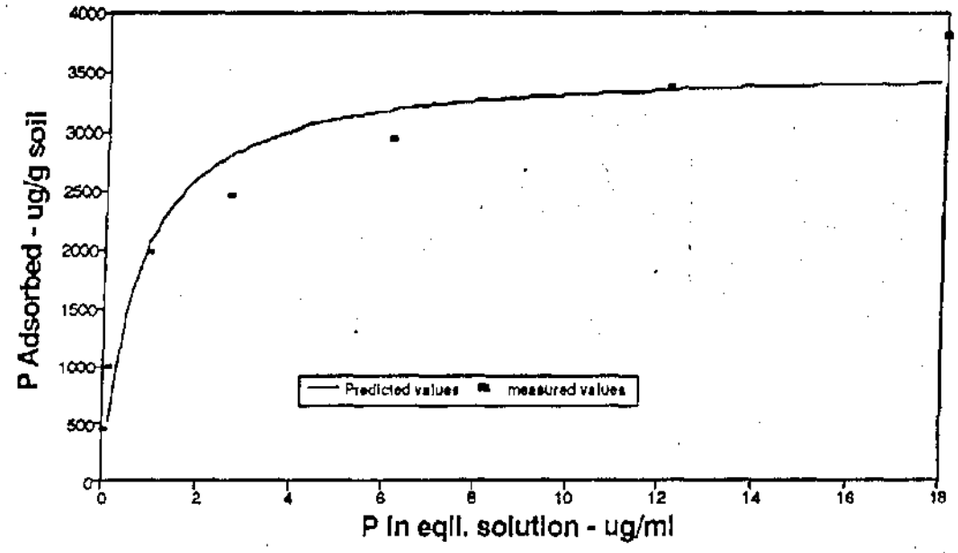


Figure 4.3.10. Curve fit to the Langmuir prediction model for ArtAmB

4.3.4 Phosphorus sorption parameters and buffer indices.

4.3.4.1. Profile soils

Phosphorus adsorption maximum and affinity constant estimated from the LIN and NLIN Langmuir equations for the whole range of P concentration used are presented in Table 4.3.6. The adsorption maximum (P_{max}) estimated from the LIN model decreased with depth in the poorly drained pedon 1, but increased with depth in the well drained profiles (Pedons 2 and 3). The affinity constant (K) varied more with the F_{ed} content of the soil (r=0.83**). Results obtained in this study showed that P_{max} did not always vary with K. While physical attributes like surface area determined the magnitude of P_{max}, K was more a chemical process related to the oxide content and reactions in soils as shown in the Bsg and Btvm horizons of pedons 1 and 3 respectively (Appendix 3.1).

Parameters used for correlation were estimated from the linearized Langmuir model at 0 - 10 µg P/ml range of equilibrium solution concentration (Table 4.3.7). In pedons 2 and 3, P_{max} increased with depth along with a decrease in OM and increase in surface oxides. The forest Oxisol adsorbed more P than the savanna Alfisol at similar levels of

Table 4.3.6. Phosphorus adsorption indices estimated from the Langmuir adsorption models for the soils at the whole range of P concentrations used.

Profile	Depth	Adsorption max P_{max} NLIN	Adsorption max P_{max} LIN	P Affinity index K NLIN	P Affinity index K LIN	MBC NLIN
	cm	-- µg g^{-1} --		-- ml g^{-1} --		
Pedon 1	0 - 4	1564.4	1934.2	0.374	0.260	585
	10 - 20	1009.9	999.0	0.792	0.891	800
	20 - 40	839.6	903.3	5.367	3.791	4506
	40 - 90	946.8	898.4	0.728	1.112	689
Pedon 2	0 - 22	-	11394.7	<0.001	0.003	-16
	22 - 55	659.4	698.1	0.742	0.836	489
	55 - 100	562.9	671.6	2.326	0.944	1309
	100 - 120	898.4	886.5	3.255	2.856	2924
Pedon 3	0 - 30	1105.1	1084.6	0.211	0.302	233
	30 - 55	1175.4	1237.6	0.892	0.778	1048
	55 - 70	1251.5	1445.0	4.431	1.514	5545
	70 - 90	1285.9	1373.6	2.282	2.247	2934
	90 - 130	1079.6	1474.0	4.692	4.402	9427

equilibrium P concentration. The K values varied from 0.13 to 4.94 ml/µg in both profiles and also decreased consistently with depth. Observed decrease in P_{max} with depth in the hydromorphic soil is consistent with similar studies in Nigeria (Juo and Fox, 1977). The K values varied consistently with the special phosphate requirement (SPR), that is P sorbed at 0.2 µg P/ml solution P concentration. At this solution concentration, most plants are expected to be well nourished (Beckwith, 1965; Fox and Kamprath, 1970). The SPR varied from 95 to 388 µg P/g soil in pedon 1, 1.95 - 274 µg P/g soil in

Table 4.3.7: Estimates of phosphate sorption indices for the soils calculated from the linearized model at 0 - 10 µg/ml equilibrium solution P concentration.

Pedon	Depth	P Max (M)	P Affinity (K)	SPR at 0.2 µg/ml	MBC
	cm	µg/g	ml/µg	µg/g	ml/g
Pedon 1	0 - 4	1931	0.26	95	502
	10 - 20	1000	0.89	151	895
	20 - 40	903	3.77	388	3407
	40 - 90	896	1.12	163	1002
Pedon 2	0 - 22	79	0.13	1.95	10
	22 - 55	550	1.67	137	919
	55 - 100	523	2.37	168	1241
	100 - 120	882	2.36	274	1996
Pedon 3	0 - 30	592	1.58	142	936
	30 - 55	942	1.99	269	1880
	55 - 70	1148	4.38	536	5039
	70 - 95	1149	4.94	571	5683
	95 - 130	1476	4.38	689	6465

pedon 2, and 142 - 689 µg P/g soil in pedon 3. The variation was consistent with the maximum buffer capacity (MBC), a product of P_{max} and K (Holford and Mattingly, 1976b), and the soils were classified as medium for pedon 1, very low - medium for pedon 2 and medium - high for pedon 3, based on the scale of Juo and Fox, (1977). The forest Oxisol required more P to attain the same level of equilibrium P concentration due to the much higher oxide content of this profile. Generally, the parameters (P_{max}, K, SPR, MBC) increased with decrease in OM, and increased along with increase in soil oxide and clay content. From the result, the two factors that influence adsorption the most were OM and the free oxide content. Much of the P sorbed in pedon 1 may be readily available considering the low K values observed for soils of the profile.

4.3.4.2. Special soils

Despite the poor predictive ability of the Langmuir one-surface equation to describe sorption reactions in soils, it is has been found useful for reducing sorption data to manageable proportions (Harter and Smith, 1981; Harter, 1984).

The adsorption maximum (P_{max}), bonding energy (K) and the maximum buffering capacity (MBC) for the special soils, derived from the LIN and NLIN regression equations for the whole range of P used are presented in Table 4.3.8. The P_{max} values of both models (NLIN and LIN) were comparable except in the crystalline Fe dominant surface soil which showed a

Table 4.3.8: Phosphorus adsorption indices estimated from the Langmuir models for the prepared and natural soils for the entire range of P added.

Soil	Adsorption Max		P Affinity index		
	M	M	K	K	MBC
	NLIN	LIN	NLIN	LIN	NLIN
	µg g^{-1}		ml g^{-1}		
NatCrA	3674.0	129.2	0.002	0.131	7.3
ArtCrA	1979.4	2036.6	1.065	1.177	2108.0
NatCrB	631.3	642.3	0.733	0.886	462.7
ArtCrB	2147.1	2467.3	2.950	2.107	6333.9
NatAmA	1690.9	1402.5	0.147	0.353	248.5
ArtAmA	2723.4	2967.3	2.190	1.636	5964.2
NatAmB	1571.0	1792.1	2.460	1.431	3864.6
ArtAmB	3346.7	3759.4	2.480	1.556	8299.8

spurious trend. In both natural and artificial soils, P_{max} was found to decrease with increase in OM, consistent with the trend in the profile soils. Generally, soil with the OM faction were less buffered, had lower K and P_{max} values.

Parameter estimates from solution concentrations less than 10 µg P/ml are presented in Tables 4.3.9 and 4.3.10. Deductively, we could infer form the results of the artificial system (the homogenous soils) that the crystallinity of the free oxides influence P sorption appreciably, even with OM present. The amorphous soils adsorb more P, and K values are higher, making P management in soils like the forest Oxisol (pedon 3) where OM turnover is appreciable, still a critical issue.

4.3.5 Soil properties affecting phosphate sorption

4.3.5.1. Profile soils

Sorption parameters estimated from the Langmuir one-surface equation at 0 - 10 µg P/ml solution concentration

Table 4.3.9: Phosphate adsorption indices for the special soils at equilibrium solution P less than 10 µg P/ml (Calculated from the Langmuir equation).

Soil	Depth simulation	P_{max}	P Affinity (K)	MBC	SPR	SPR-OBS*
		µg/g	ml/µg		µg/g	µ/g
NatCrA	Top	129	0.13	17	3.3	5.0
ArtCrA	Top	2025	1.18	2397	387.0	425.0
NatCrB	Sub	548	1.45	796	123.0	145.0
ArtCrB	Sub	2432	2.10	5123	722.0	800.0
NatAmA	Top	776	0.93	721	121.7	100.0
ArtAmA	Top	2451	2.45	6013	806.0	1065.0
NatAmB	Sub	1406	4.26	5994	647.3	615.0
ArtAmB	Sub	3011	3.27	9846	1190.0	1320.0

* From graphic plot of sorption data.

Table 4.3.10: Phosphate adsorption indices for equilibrium solution P less than 10 µg P calculated from the Langmuir equation: Mean values with respect to treatments.

Treatment	P max (M)	P Affinity (K)	MBC	SPR
	µg/g	ml/µg		µg/g
Top-soil	2322	2.32	5996	802
Sub-soil	2462	2.81	9061	1067
Artificial	2480	2.25	5847	776
Natural	715	1.59	1882	223

range were correlated with selected soil properties. The correlation coefficients are presented in Table 4.3.11. Correlation coefficient with additional soil factors are contained in Appendix 4.1.2. Simple correlation analysis showed that clay (soil texture) had a strong influence on the P sorption indices. P_{max} was significantly correlated with OC (r=0.42*), Al_{ox} (r=0.44*) and strongly correlated with Fe_{ox} (r =0.61**), Fe_{py} (r = 0.51**) and specific surface area (SAREA, r = 0.80**). P_{max} was poorly correlated with ECEC (r = 0.23), but strongly correlated with CEC at pH 8.4 (r = 0.71**) (Appendix 4.1.2). This implies an increase in the negative charge density as pH is increased with most of the increase coming from the dissociation of the functional groups on OM. The positive correlation of P_{max} and OC means enhanced P adsorption by OM either directly in which phosphate replaces organic hydroxyl ($-OH^-$) (Lopez-Hernandez and Burnham, 1974; Harter, 1969), or by associating with metal ions (such as Al^{3+} and Fe^{3+}) by chelation on which P is subsequently sorbed (Reddy et al, 1980; Parfitt, 1979).

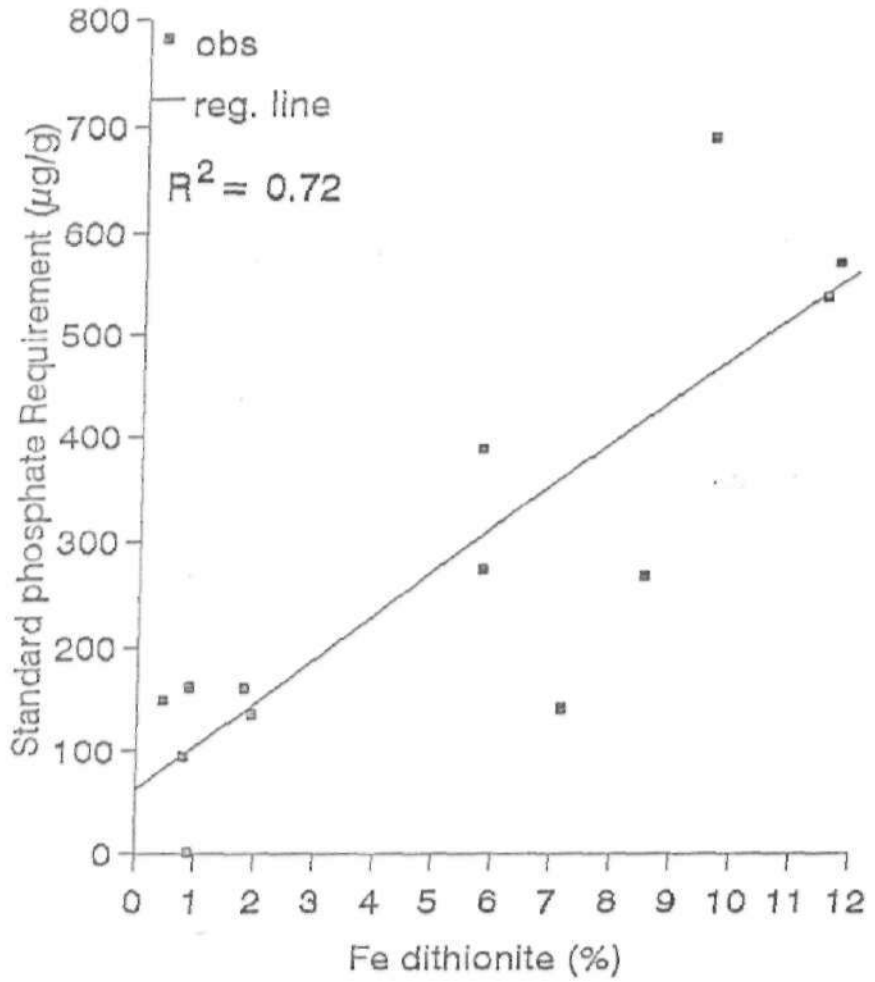
The K, SPR and MBC parameter were influenced by the same set of soil properties. All parameter were positively correlated with ZPC and negatively correlated with ECEC indicating the importance of charge density on P sorption reactions. The K, SPR and MBC were also strongly correlated with Fe_d (Table 4.3.11), which explained about 72% of the variation in the sorption parameters. The relationship between SPR and Fe_d is presented in Figure 4.3.11. The linear equations for the estimation of P_{max}, K and MBC are presented

Table 4.3.11: Correlation coefficients of selected soil properties and P sorption indices for the profile soils.

Parameter	P_{max}	Affinity (K) ml/µg	SPR P at 0.20 (µg P/ml)	MBC
Clay	0.72**	0.54**	0.61**	0.61**
Silt	0.57**	-0.15	-0.08	-0.09
Sand	-0.75**	-0.45*	0.53**	0.52**
Org C	0.42*	-0.58**	-0.47*	0.46*
pH (H_2O)	-0.58**	0.11	0.03	0.05
pH ($CaCl_2$)	-0.47*	0.24	0.20	0.23
Acidity	0.42*	-0.45*	-0.39	-0.37
ECEC	0.23	-0.72**	-0.66**	-0.64**
Fe_d	0.22	0.83**	0.85**	0.85**
Fe_{ox}	0.61**	0.36	0.42*	0.42*
Fe_{PY}	0.51**	-0.48*	-0.40*	-0.39
Al_d	0.02	-0.19	-0.22	-0.20
Al_{ox}	0.44*	0.26	0.28	0.32
Al_{PY}	0.14	-0.33	-0.35	-0.38
SAREA	0.80**	-0.07	0.02	-0.01
ZPC	0.36	0.53**	0.61**	0.56**

as footnote to Figure 4.3.11.

The best combination of soil properties for the estimation of P sorption parameter and buffer index fromroutine and non-routine parameters were determined by multiple regression analysis (Table 4.3.12). Clay in combination with ECEC offered a reasonable estimate of K, MBC and SPR. Exchangeable Fe influenced P_{max} appreciably, and in combination with sand, gave an improved estimate from the routine parameters. Improved estimate of K and SPR from non-



K = 0.65 + 0.32 Fe-d (r2 = 0.72)
MBC = 136 + 422 Fe-d (r2 = 0.71)
Pmax = -29.3 + 14.9 SREA (r2 = 0.60)

Figure 4.3.11: Relationship between standard phosphate requirement (SPR) and Fe_d. Estimation equations for some phosphate parameters are given as foot notes.

routine parameter were obtained with a combination of properties shown in Table 4.3.12. About 90 % estimation of the parameters were obtained with the equations which emphasized the significance of surface area and the amorphous fractions of the Fe and Al oxides contents of the soils. The simple correlation coefficients of the P forms with P sorption parameters are given in Table 4.3.13. P_{max} was not significantly related with soil test P indicating that adsorption maximum is not a reliable index for the prediction of available P in highly weathered soils of the tropics. K, SPR and MBC were negatively correlated with soil test P and so extractable P should decrease correspondingly as these parameters increase. The SPR was positively correlated with Fe-P ($r = 0.85^{**}$), and the relationship with OC ($r = -0.47^{*}$), though not strongly significant. The implication of this is that OM enhanced P desorption in these soils. Organic matter has been shown to increase the availability of P by the principle of chelation (Nagarajah, 1968), and blocking of P sorption sites by low molecular weight organic acids in compitition with P (Parfitt, 1978; Sibanda and Young, 1986).

Table 4.3.12: Multiple regression equations for estimating the P adsorption indices from soil properties.

Routine parameters			
P_{max}	=	4242 - 30.9 sand + 1.47 Fe - 636 cond - 27.5 clay + 355 OC - 134 ECEC	R^2= 0.94
,,	=	1246 - 12 sand + 1.1 Fe	R^2= 0.71
P Affinity (K)	=	2.56 - 0.36 ECEC + 0.04 clay	R^2= 0.80
MBC	=	1784 - 418 ECEC + 63.8 clay	R^2= 0.76
SPR	=	1539 - 514 pH($H_2$0) - 67.1 OC - 126 Acidity - 129 cond + 1.03 Fe + 366 pH($CaCl_2$)	R^2= 0.94
,,	=	223 - 41 ECEC + 63 clay	R^2= 0.80
Non-routine parameters			
P_{max}	=	362 + 7.6 SAREA + 10.6 clay + 555 Al_{py} - 110 pH($CaCl_2$)	R^2= 0.78
,,	=	-220 + 9.8 clay + 9.9 SAREA	R^2= 0.70
P Affinity (K)	=	2.08 + 0.21 Fe_d - 1.73 PC - 10.4 Fe_{py} + 0.05 SAREA + 2.2 Fe_{ox} + 54.9 Al_{ox}	R^2= 0.96
,,	=	3 + 0.42 Fe_d - 0.96 PC	R^2= 0.76
SPR	=	242 + 203 Al_{py} - 1117 Fe_{py} + 9468 Al_{ox} + 476 Fe_{ox} 3.09 SAREA	R^2= 0.88
,,	=	8.4 + 40.9 Fe_d + 3.3 Fe_{py}	R^2= 0.71

Table 4.3.13: Correlation coefficients of phosphate forms, extractable P and P sorption indices for the profile soils.

Property	P_{max}	P Aff.	MBC	SPR
Bray-P	0.35	-0.61**	-0.46*	-0.50*
Wat-P	-0.25	-0.58**	-0.44*	-0.51**
Olsen-P	0.323	-0.30	-0.15	-0.18
Resin-P	0.21	-0.60**	-0.43*	-0.48*
Active-P	0.62**	0.35	0.52	0.49*
Al-P	0.52**	-0.41*	-0.23	0.26
Fe-P	0.73**	0.43	0.58	0.56**
Ca-P	0.22	0.32	0.39	0.32
Red Sol-P	-0.26	0.53**	0.67**	0.63**
Org-P	-0.36	-0.30	-0.32	-0.31
Total-P	0.42	0.38	0.45*	0.45*
P_{max}	1.00	0.20	0.36	0.39
P Affinity (K)		1.00	0.95**	0.94**
MBC			1.00	0.99**
SPR				1.00

4.3.5.2 Special soils

The correlation matrixes of selected soil properties and phosphate sorption indices for the special soils, and separately for the natural soils and artificial soils are presented in Tables 4.3.14 to 4.3.16. Effects on P_{max}, P affinity constant (K), maximum buffer capacity (MBC), SPR at 0.2 µg P/ml solution concentration calculated from the regression estimate, and SPR-obs from graphic estimates were evaluated. For all soils, factors responsible for much of the variation in P_{max} were ECEC, ZPC and specific surface area. Of

these, ZPC correlated strongly in the natural soils, whereas P_{max} was not particularly related to any single factor in the more homogenous artificial system (Table 4.3.15). The affinity constant (K) correlated at the 5 and 1 % levels with OC (r = -0.59*) and ZPC (r = 0.76**) respectively for all soils. These factors were also equally important in both systems (natural and artificial systems). The high correlation of ZPC in the artificial soils emphasize the huge role of charge density in the binding of P to the sorbing surfaces.

ZPC and OC were the most influencing factors for MBC, SPR and SPR-obs when all soils were considered, and ZPC and SAREA for the natural soil system. In the artificial system, surface area and OC were less important as shown by the correlation coefficients.

Relative effects of the Fe and Al oxide fractions on P

Table 4.3.14: Correlation matrix of selected soil properties and phosphate sorption indices for the special soils combined.

	P_{max}	P Affinity	MBC	SPR	SPR-obs
pH H_2O	0.49	0.41	0.62*	0.61*	0.58*
pH $CaCl_2$	0.19	0.31	0.53*	0.47	-0.40
ECEC	0.69**	-0.14	0.27	0.38	0.45
Org C	0.18	-0.59*	-0.24	-0.16	-0.06
ZPC	0.84**	0.76**	0.81**	0.85**	0.85**
SAREA	0.91**	0.48	0.70**	0.77**	0.79**
P_{max}	1.00	0.53*	0.70**	0.88**	0.94**
P Affinity (K)		1.00	0.83**	0.80**	0.73**
MBC			1.00	0.98**	0.93**
SPR				1.00	0.98**

**, *: Significant at 1 and 5% levels of probability.

Table 4.3.15: Correlation matrix of selected soil properties and phosphate sorption indices for the artificial soils.

	P_{max}	P Affinity	MBC	SPR	SPR-obs
pH H_2O	0.35	0.78*	0.73*	0.72*	0.64
pH $CaCl_2$	0.39	0.86**	0.81*	0.78*	0.69*
ECEC	-0.21	-0.80*	-0.75*	-0.65	-0.45
Org C	-0.07	-0.64	-0.56	-0.52	-0.39
ZPC	0.58	0.98	0.96**	0.93**	0.83**
SAREA	0.44	0.60	0.61	0.58	0.52
P_{max}	1.00	0.66	0.73*	0.82*	0.93**
P Affinity		1.00	0.99**	0.97**	0.88**
MBC			1.00	0.98**	0.91**
SPR				1.00	0.97**
SPR-OBS					1.00

Table 4.3.16: Correlation matrix of selected soil properties and phosphate sorption indices for the natural soils.

	P_{max}	P Affinity	MBC	SPR	SPR-obs
pH H_2O	-0.63	0.14	-0.29	-0.33	-0.33
pH $CaCl_2$	-0.29	0.39	-0.07	-0.11	-0.05
ECEC	-0.51	-0.74*	-0.81**	-0.77*	-0.78*
Org C	-0.54	-0.94**	0.75*	-0.74*	-0.71*
ZPC	0.96**	0.75*	0.81*	0.84**	0.82*
SAREA	0.63	0.50	0.36	0.41	0.36
P_{max}	1.00	0.77*	0.91**	0.94**	0.93**
P Affinity (K)		1.00	0.88**	0.88**	0.84**
MBC			1.00	0.99**	0.99**
SPR				1.00	0.99**

**, *: Significant at 1 and 5% levels of probability.

sorption indices, organic C, surface area and ZPC are presented in Table 4.3.17. When all soils were considered, P adsorption maximum was strongly correlated with Fe_{ox}. Fe_{ox} was strongly correlated with adsorption maximum (r = 0.93**), MBC (r = 0.64**) and SPR (0.73**). The amorphous iron oxide

Table 4.3.17: Relationship between Fe and Al oxide fractions and phosphorus adsorption indices and selected soil properties for the soils as influenced by treatments.

	P max	P Affinity	MBC	SPR	Org C	SAREA	ZPC
All-soils							
Fe_d	0.43	0.41	0.31	0.36	-0.06	0.35	0.68**
Fe_{ox}	0.93**	0.27	0.64**	0.73**	0.33	0.88**	0.65**
Fe_{py}	0.39	-0.34	0.00	0.08	0.87**	0.45	0.15
Al_d	-0.48	-0.29	-0.42	0.46	-0.37	-0.38	-0.19
Al_{ox}	-0.01	-0.15	-0.04	-0.07	0.27	0.21	0.19
Al_{py}	-0.39	-0.66**	-0.46	-0.48	0.61*	-0.32	-0.45
Artificial							
Fe_d	0.25	-0.42	-0.34	-0.24	0.66	-0.02	-0.50
Fe_{ox}	0.71*	0.02	0.10	0.25	0.25	-0.10	-0.04
Fe_{py}	0.22	-0.45	-0.35	0.28	0.95**	-0.09	0.55
Al_d	-0.75	-0.22	-0.33	-0.40	-0.50	-0.31	-0.07
Al_{ox}	-0.03	0.15	0.16	-0.10	0.14	0.56	0.13
Al_{py}	0.14	-0.37	-0.27	-0.24	0.91**	0.08	-0.46
Natural							
Fe_d	0.98**	0.63	0.86**	0.88**	-0.38	0.56	0.93**
Fe_{ox}	0.81*	0.27	0.62	0.64	0.01	0.45	0.75*
Fe_{py}	-0.12	-0.57	-0.49	-0.45	0.77*	0.40	0.04
Al_d	0.26	-0.23	0.08	0.09	0.41	0.09	0.23
Al_{ox}	0.21	-0.28	-0.17	-0.12	0.55	0.59	0.35
Al_{py}	-0.33	-0.81*	0.61	-0.59	-0.45	-0.18	0.10

Table 4.3.17: continues.

	P max	P Affinity	MBC	SPR	Org C	SAREA	ZPC
Top-soils							
Fe_d	0.75*	0.81*	0.63	0.66	0.69	0.89**	0.98**
Fe_{ox}	0.96**	0.83**	0.85**	0.87**	0.98**	0.86**	0.75*
Fe_{py}	0.78*	0.90**	0.74*	0.75*	0.70*	0.85**	0.94**
Al_d	-0.78*	-0.79*	-0.90**	-0.88**	-0.74*	-0.48	-0.44
Al_{ox}	-0.14	0.03	-0.22	-0.20	-0.19	0.22	0.35
Al_{py}	-0.62	-0.38	-0.51	-0.54	-0.70	-0.45	-0.27
Sub-Soils							
Fe_d	0.15	0.20	0.10	0.13	-0.41	-0.18	0.45
Fe_{ox}	0.94**	0.19	0.75	0.78*	0.93**	0.94**	0.72*
Fe_{py}	0.86**	0.34	0.34	0.80	0.93**	0.94**	0.63
Al_d	0.00	-0.59	-0.59	-0.28	-0.10	-0.25	0.01
Al_{ox}	0.74*	0.91**	0.91**	0.91**	0.29	0.65	0.88**
Al_{py}	-0.16	0.47	0.47	0.07	-0.45	-0.18	0.10

fractions (Fe_{ox} and Fe_{py}) were significantly correlated with organic C, surface area and ZPC, the three soil properties that were earlier shown to influence phosphate sorption parameters appreciably in the soils. The results have shown that the amorphous oxides are largely responsible for P sorption in tropical soils high in ferric properties. The migration of retained P to the inner sorption sites of the amorphous gel on soil particle surfaces provide additional sites for P sorption, which explains the high amount of P sorbed by the soils. The effects of the amorphous oxides on the parameters varied with the presence or absence of OM.

Fe oxide was important in the top soils, but Al_{ox} was equally important in the subsoil. Between 40 - 86 % of the

adsorption indices were explained by the amorphous iron oxide (Fe_{ox}). The relationship between P sorption maximum and Fe_{ox} is given in Figure 4.3.12.

The best combination of factors useful for estimating the P sorption indices were determined by multiple regression analysis (Table 4.3.18). The effect of ZPC, consequently charge density was apparent. However, as shown by the equation for the estimation of P_{max}, Fe_{ox} was threefold more important than OM based on the regression coefficients. Interestingly, ZPC, Fe_{ox} and surface area were the three parameters which accounted appreciably for the variation in P_{max}, K and SPR in a more homogenous setting (the artificial soils). The importance of OM becomes obvious in the heterogenous system brought about by differences in mineralogy, fertility and soil texture.

In conclusion, deriving from the reaction of P in all systems (profile and special soils), we can infer that most Nigerian soils of basement complex origin are low to medium sorbing, therefore, crops should respond to moderate levels of P application in the soils. Organic matter depresses P sorption. OM conservation measures are therefore imperative for efficient management of the P resource in tropical soils.

Since amounts of P sorbed increases with increase in solution concentration, defining a true P_{max} according to the Langmuir one surface equation is unrealistic at high P concentrations. The Freundlich equation best described P reactions in the soils.

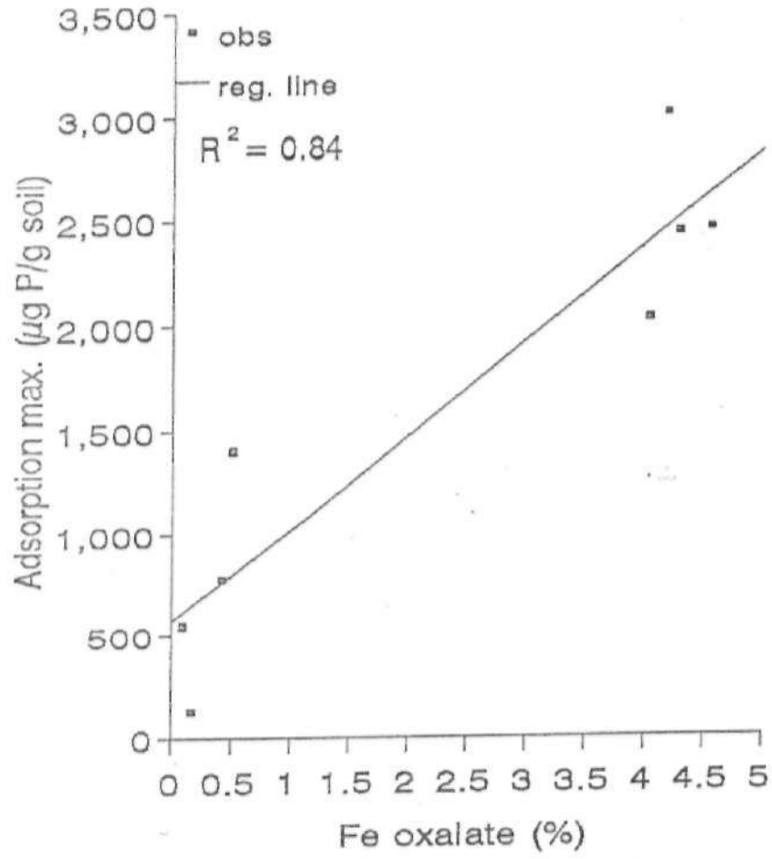


Figure 4.3.12: The relationship between P adsorption maximum and Fe_{ox} in all soils.

Table 4.3.18: Multiple regression equations for estimating the P adsorption indices from properties of the special soils.

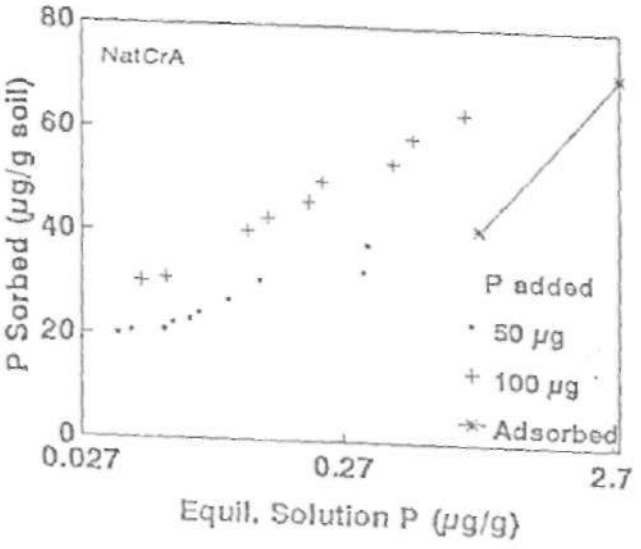
Adsorption indices		Regression model	R^2
All soils			
P_{max}	=	-5039 + 458 pH(H_2O) - 30 ECEC + 1036 ZPC + 91 Org C + 268 Fe_{ox}	R^2 = 0.99
SPR	=	-9105 + 1115 pH H_2O + 636 ZPC + 168 Org C - 1115 Fe_{ox} + 72 Fe_d	R^2 = 0.96
MBC	=	-42947 + 5371 pH H_2O + 2789 PC + 629 Fe_d	R^2 = 0.89
P Affinity	=	0.507 - 0.28 ECEC + 1.22 PC + 0.42 Fe_{ox} + 0.15 Fe_d	R^2 = 0.94
For the Artificial Soils			
P_{max}	=	-4219 + 1283 ZPC + 411 Fe_{ox} + 185 SAREA	R^2 = 0.99
SPR	=	-5187 + 994 ZPC + 497 Fe_{ox} + 2.38 SAREA	R^2 = 0.99
MBC	=	-65512 + 5745 pH $CaCl_2$ + 7020 ZPC + 1448 Org C + 2263 Fe_{ox}	R^2 = 0.99
P Affinity	=	-14.5 + 2.46 ZPC + 1.64 Fe_{ox} + 0.008 SAREA	R^2 = 0.99
For the Natural soils			
P_{max}	=	-196 + 58 Fe_d + 39 Org C + 508 PC - 39.8 ECEC - 73 pH $CaCl_2$ + 58 Fe_{ox}	R^2 = 1.00
SPR	=	528 - 20 pH $CaCl_2$ - 39 ECEC - 120 Fe_{ox} + 68 Fe_d	R^2 = 1.00
MBC	=	4308 - 425 ECEC + 568 Fe_d	R^2 = 0.99
P Affinity	=	1.68 = 0.18 ECEC + 0.47 ZPC - 0.42 Org C + 0.27 Fe_d	R^2 = 0.99

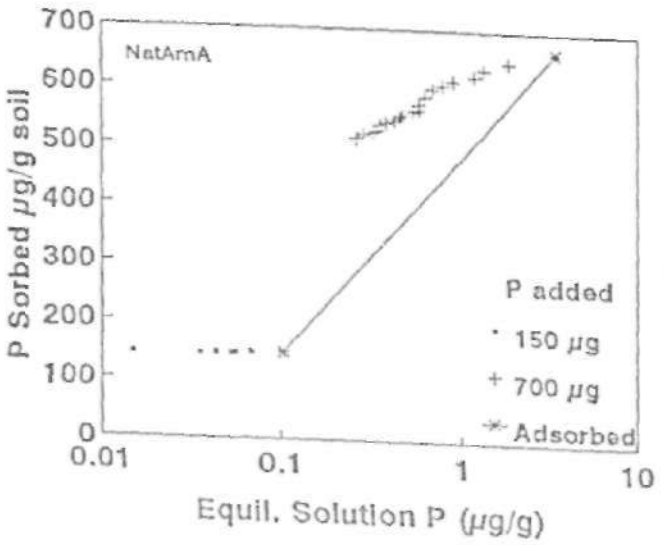
4.4. Phosphorus Desorption

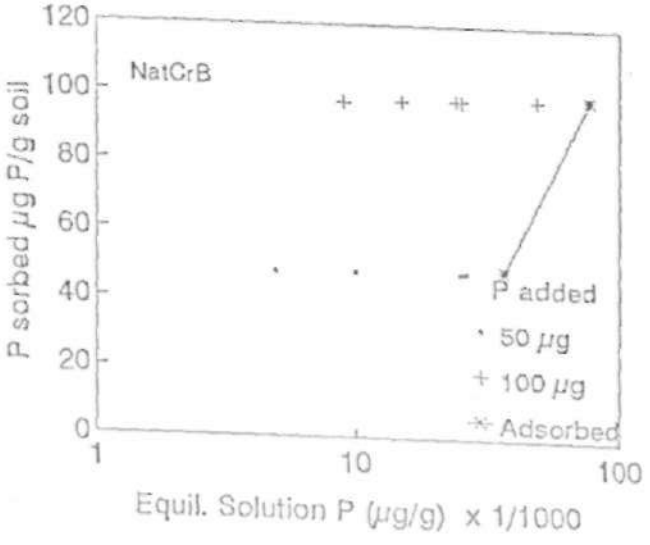
Plants take up nutrients from soil solution. The rate at which nutrients in soil solution is replenished, defines the availability coefficient for that nutrient, and this is highly dependent on the adsorption-desorption reactions (Q/I relationships). This is a unique property for all soils. This section examines the desorption characteristics of the special soils as influenced by the treatments.

4.4.1. Phosphorus desorption isotherms and hysteresis

The phosphate desorption isotherms constructed for the special soils are presented in Figures 4.4.1 and 4.4.2. Regardless of the P levels and soils, P was desorbed progressively with each sequential extraction, resulting in a desorption curve which was clearly different from the adsorption curve. This observation is consistent with the findings on diverse soils (Bowman and Olsen, 1985c; Fox and Kamprath, 1970, Kafkafi et al., 1967; Okajima et al., 1983). Several reasons for hysteretic phenomenon has been advanced. Hingston et al., (1974), in support of Kafkafi et al., (1967) postulated that with desorption, P - metal oxide bonding changes from a monodentate to a binuclear complex which makes reversibility less likely. Muljadi et al., (1966) and Ryden and Syers, (1977) advocated a phase change of P during desorption. Also the possibility of the formation of relatively insoluble P precipitates (Okajima el al., 1983) could provide some explanation for observed hysteresis. However, soils with a low P sorption coefficient have been







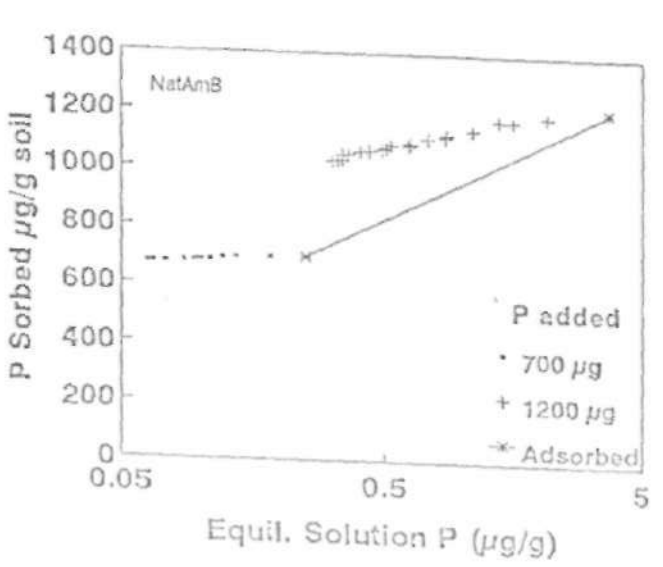


Figure 4.4.1: Phosphorus desorption isotherms for the natural soils.

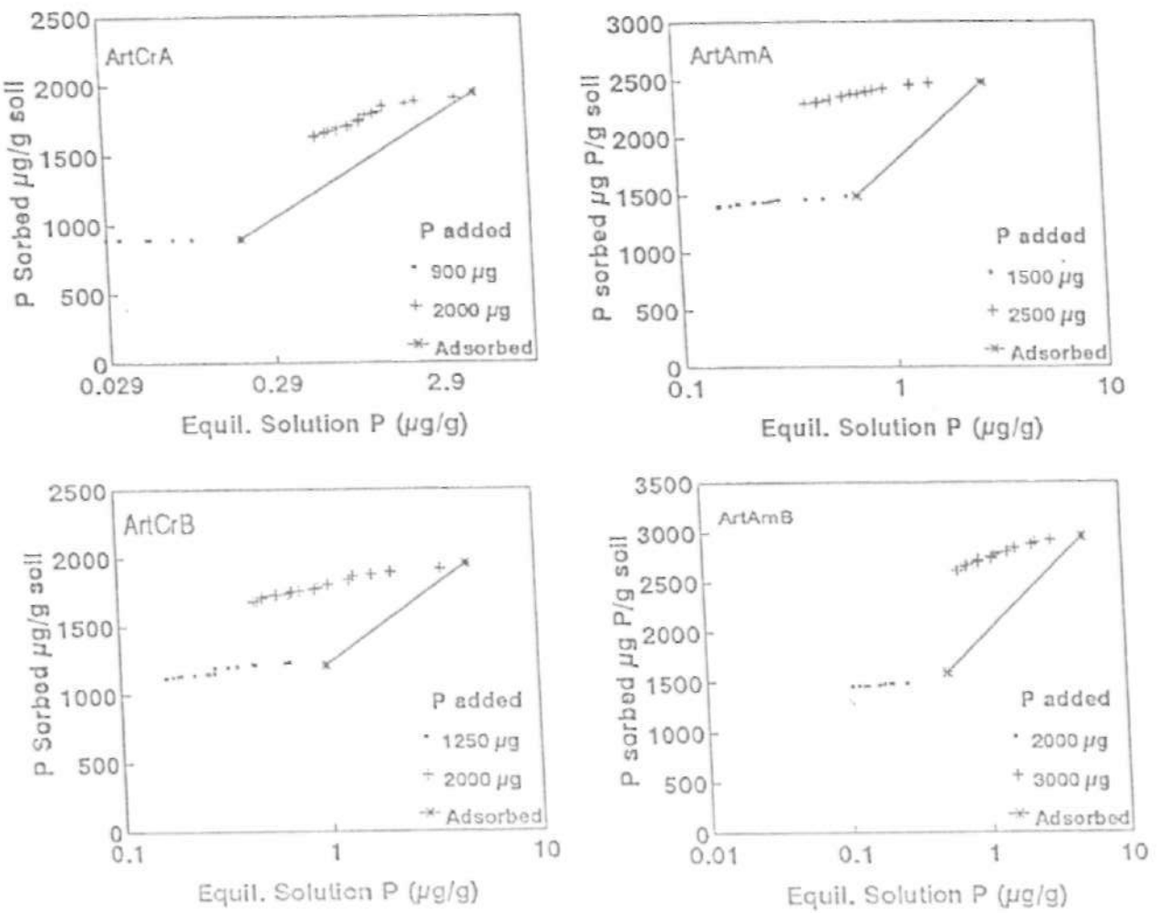


Figure 4.4.2: Phosphorus desorption isotherms for the artificial soils.

shown to exhibited a reversible type of the reaction process(Okajima et al., 1983). In this study, soils with low adsorption capacity were soils high in OM and with crystalline Fe oxide forms dominating the clay fraction, as is characteristic of the well drained savanna Alfisol, and all soils containing the OM fraction.

Ryden et al., (1977 a,b,c) have demonstrated that P sorption involves a concurrent chemisorption of P and a more physical potential-determining (p.d.) sorption. It was shown that P is essentially desorbed in the physical adsorption range at solution P concentration in excess of 0.2 µg P/ml, equivalent to 6 µM solution P L^{-1} determined by Ryden and Syers, (1977). P sorbed below this value is assumed to be chemically sorbed and somewhat irreversible. The significance of P sorbed at 0.2 µg/ml or SPR as advocated by Beckwith, (1965) and Fox and Kamprath,(1970), could therefore be said to be based on a valid concept. It is argued however that the longer the adsorption period relative to desorption, the smaller the proportion of phosphate that can be desorbed (Barrow and Shaw, 1975).

Evaluating the desorptive capacity of the soils in relation to OM and soil oxides, data for the natural soils (Figure 4.4.1) indicate that the desorptive potentials as described by he slope of the desorption curve for soils with similar P treatment, increased with increase in OM (Figures 4.4.1 a and b; c and d) and decreased with increase in the active content of soil oxides (a and c). The results obtained with the artificial soils, revealed a striking conformity to

the underlying concept (Figure 4.4.2). When the slope characteristics at 2000 µg/g P added was considered in isolation, hysteresis was less with ArtCrA representing an organic soil with crystalline oxide forms dominant, than it was in the amorphous Fe dominant soils with no organic matter. This has far reaching implications in the management of applied phosphate and economic viability of fertilization programmes. Documented factors that are shown to influence hysteresis include pH of ambient solution, changes in ionic species and other interactions in soil systems (Bowman and Olsen, 1985; Bache and Ireland, 1980; Barrow and Shaw, 1977). These changes become more evident with continuous cultivation and fertilization. Desorption isotherm may prove more logical for the estimation of P requirements in soils in comparison to adsorption isotherms, but desorption methodologies are generally believed to be more prone to analytical errors and lack reproducibility (Bowman and Olsen, 1985; Fox and Kamprath, 1970).

4.4.2. Adsorption - desorption relationships and critical P

A practical approach to quantify the adsorption - desorption hysteresis was proposed (Agbenin, 1992), by defining a critical P (P_{crit}) as P adsorbed on soil surface below which desorption was practically negligible. P_{crit} may very well be the upper limit of the amount of P sorbed chemically on soil surfaces, defined by P sorbed in regions I and II of the multi-surface Langmuir isotherm (Ryden and Syers, 1977). P_{crit} was determined by fitting a linear

regression on the adsorption - desorption relationship and extrapolating the line to zero desorption. Table 4.4.1 shows the calculated P_{crit} values for the special soils along with the regression equation and R^2 values for the relationships for each soil. P_{crit} was highly correlated with graphic SPR (r = 0.95). Assuming the validity of P_{crit} as an estimate of chemisorbed P, then the contributory role of OM in efficient management of P stems from its ability to induce availability of the chemisorbed P as shown by comparing P_{crit} and SPR in this study. P chemisorbed on crystalline oxides could be more readily released than P sorbed on amorphous surfaces. In the homogenous system, 55 % of P sorbed was ascribed to physical adsorption (and therefore readily desorbed) when surfaces are

Table 4.4.1: Relationship between P dosorbed (y) and P adsorbed (x) expressed in simple linear regression. Estimates of critical P (P_{crit}) and % of P assumed to be physically sorbed (P_{max}-P_{crit}) were calculated from the expression.

Soil	Depth Simulation	Regression equation	R_2	P_{crit}	Physically Sorbed P
				µg/g	%
NatCrA	Top	y = -2.96 + 0.160x	0.87	18.5	85.6
ArtCrA	Top	y = -142.40 + 0.160x	0.81	890.0	56.2
NatCrB	Sub	y = -28.3 + 0.29x	0.80	97.4	84.8
ArtCrB	Sub	y = -34.40 + 0.032x	0.78	1075.5	56.3
NatAmA	Top	y = -17.50 + 0.123x	0.96	142.3	89.8
ArtAmA	Top	y = -69.50 + 0.048x	0.85	1379.3	53.5
NatAmB	Sub	y = -29.70 + 0.045x	0.89	661.4	63.0
ArtAmB	Sub	y = -55.30 + 0.038x	0.91	1425.9	62.0

P saturated (at maximum adsorption). Due to economic constraints in tropical Africa, P requirements of soils are often not fully met by fertilization. The soils are therefore perpetually P deficient even at best efforts. Soils with high P_{crit} have relatively high P adsorption capacity. Organic matter was observed to lower P_{crit} in the crystalline Fe oxide dominant soils, P_{crit} values were also low.

The coefficients of the adsorption - desorption relationships gives an estimate of the magnitude of hysteresis. The reciprocal of the regression coefficient quantifies the amount of P that should be sorbed to release one unit of P beyond P_{crit} during a desorption process. This factor (inverse coefficient) could be referred to as productivity coefficient, and was correlated with K (bonding energy, r = 0.92) and SPR (r = 0.82), and P_{max} (r = -0.31). Figure 4.4.3 illustrates the magnitude of this coefficient for the various soils.

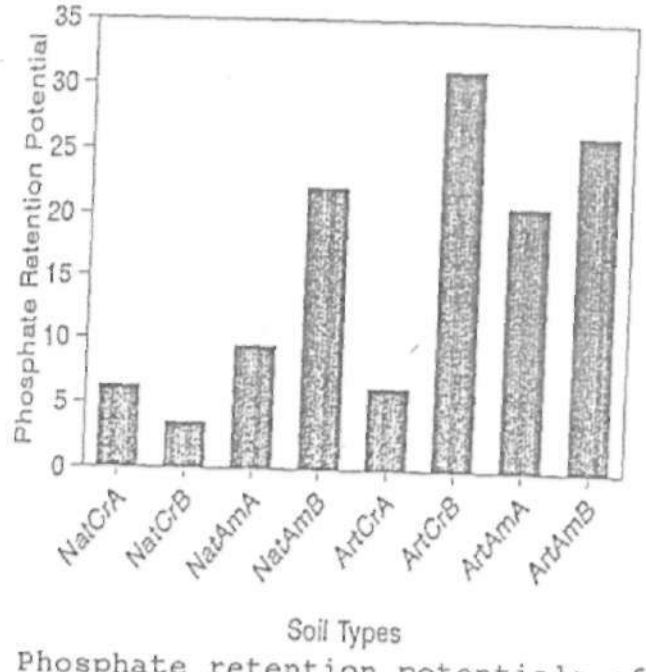


Figure 4.4.3: Phosphate retention potentials of the soils as affected by treatments.

4.5. Greenhouse Evaluation of Maize in P Adjusted Soils

4.5.1. Soils and fertilization

The amount of applied phosphate required to adjust the solution P levels in the soils varied accordingly with the slope characteristics of the sorption isotherms (Table 3.4), and the variation was significantly for each level of P adjustment. The capacity of the natural soils to adsorb P were less than the artificial soils. For soils with comparable properties, the pattern of variation in P requirements were similar. As was shown in the last section, this observation further confirms that the characteristics of the natural soils were successfully simulated in the artificial soils. The selected profile soils that constituted the natural soils, and the artificial soils, prepared from a bulk soil provided a homogenous setting in texture and mineralogy for the assessment of the treatments.

4.5.2. Response to phosphate application.

The sources of variation and mean square (MS) values for the response of maize to P rates, as influenced by treatments and the interactions are presented in Table 4.5.1. Variation in maize response in the soils was statistically significant, and just as well, the response of some plant parameters to adjusted P levels were highly significant. This implies that the soils were phosphate deficient. Maize response to the main treatments (type - natural and artificial soils; cryst. - crystalline and amorphous; and depth - top and subsurface) were statistically significant at 1 or 5 % probability levels,

Table 4.5.1 Analysis of variance table for the response of some agronomic parameters as function of treatment effects in the greenhouse.

Source of variation	df	Mean square values			
		DMYLD	PLT HT-3	LeafL-3	LeafW-3
Rep	2	0.25	24.84	28.08	0.060
Rep - Soil Stratum					
Soil	7	2.57**	102.35**	46.79**	0.656**
rate	5	6.71**	300.67**	143.64**	1.140**
Soil x rate	35	0.40**	33.23**	19.50**	0.105**
Error	80	0.06	11.32	4.74	0.038
Total	143	-	-	-	-
Rep - Type stratum					
Type	1	11.12*	107.28^{ns}	33.54*	3.071**
Cryst	1	2.41**	139.81**	46.74**	0.461**
Depth	1	1.07**	87.19**	31.30*	0.406**
Type x Cryst	1	0.13^{ns}	73.23*	12.35^{ns}	0.137^{ns}
Type x depth	1	0.50*	52.33*	31.37*	0.007^{ns}
Cryst x depth	1	0.24^{ns}	145.95**	79.18**	0.003^{ns}
Depth x rate	5	0.84**	85.34**	39.35**	0.191**
Cryst x rate	5	0.41**	10.70^{ns}	10.70^{ns}	0.107**
Type x Cryst x depth	1	2.49**	110.65**	93.09**	0.507**
Type x Cryst x rate	5	0.10^{ns}	11.11^{ns}	11.39*	0.111*
Type x depth x rate	5	0.33**	17.92^{ns}	20.97**	0.068^{ns}
Cryst x depth x rate	5	0.15^{ns}	60.19**	27.08**	0.052^{ns}
Error	97	0.07	12.16	4.67	0.037
Total	143				
SE ±		0.064	0.84	0.53	0.039
Mean		2.03	35.35	27.60	2.56
CV		13.34	10.08	8.20	7.59
R^2		0.905	0.73	0.77	0.79
RMSE		0.27	3.56	2.28	0.19

*,** - Significant at 5 and 1% levels of probability,
^{ns} - not significant,
Type - Natural and artificial.
Cryst - Crystalline and amorphous.
Depth - Top and sub (organic and dehumified soils).
rate - Adjusted equilibrium solution P levels.

except for plant height in the natural and artificial systems which was nonsignificant. The effects of the interactions of 'Type x cryst x rate' and 'cryst x depth and rate' on dry matter yield were not significant. The mean response to the treatments were similar in each case, therefore, the natural and artificial soils were comparable in reaction.

The absolute yield and response of plant component to adjusted P levels are given in Table 4.5.2. Dry matter yield increased consistently with increase in adjusted solution P levels. Yield values were higher in the more buffered soils but declined at the highest rate of adjusted P level, especially in the soils with the OM fraction removed. The ameliorating effects of OM even at toxic levels of applied nutrients, like phophorus, were therefore shown by the results. Yield levels were consistently higher in soils with the OM fraction. The response patterns of all other agronomic parameters considered (plant height, leaf length, leaf width) were similar to the dry matter yield. The relative response as influenced by treatments were quantified using regression models.

4.5.2.1 *Response models for the soils.*

Response surface analysis was used to estimate response to phosphate treatment as influenced by variation in OM content and crystallinity of the oxides. The simplicity of the quadratic function in evaluating yield responses, despite critisisms, has made the procedure common and endearing to most scientists (Cox, 1992; Melsted and Peck, 1977). The

Table 4.5.2: Agronomic response to varying rates of phosphate amendments in relation to soil type, oxide form and OM interaction: Dry matter yield and plant height at 3 weeks.

	Crystalline				Amorphous			
Soil	Top (NatCrA)	Top (ArtCrA)	Sub (NatCrB)	Sub (ArtCrB)	Top (NatAmA)	Top (ArtAmA)	Sub (NatAmB)	Sub (ArtAmB)
Adjusted P rate								
DM Yield (g)								
0.00	1.45	1.06	0.87	1.20	1.11	1.10	1.04	1.16
0.02	1.19	1.67	1.29	2.45	1.12	1.01	2.00	2.60
0.06	1.25	1.79	1.65	2.48	1.25	2.57	2.42	2.29
0.20	1.32	2.13	1.66	2.89	1.72	2.51	2.53	2.98
0.60	1.94	2.37	1.95	2.90	2.30	2.91	2.51	2.68
1.50	2.11	3.07	2.51	2.58	2.61	3.32	2.43	1.90
Mean	1.54	2.01	1.65	2.41	1.68	2.56	2.15	2.27
Se ±				0.157**				
PLT HT-3 (cm)								
0.00	31.6	26.3	29.2	30.0	30.2	30.0	31.9	28.3
0.02	32.8	30.8	33.4	36.8	28.4	29.1	40.1	37.4
0.06	29.2	32.4	34.5	36.1	33.7	38.8	37.9	33.7
0.20	23.8	34.3	35.6	43.9	35.6	40.9	37.8	36.7
0.60	35.3	37.0	35.5	41.6	40.2	45.3	38.4	37.8
1.5	31.8	42.3	37.6	39.3	41.3	44.8	38.3	34.4
Mean	31.2	38.0	34.3	38.2	34.9	38.2	37.4	34.7
SE ±				2.05**				

quadratic response surface was estimated by least square regression (SAS Institute 1987) and the model used to predictthe optimum yield values had the form:

$$y = \beta o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_1^2 + \beta_4 X_2^2 + \beta_5 X_1 X_2 + \varepsilon \qquad (4.2)$$

where:

y = maize yield in grams or response for the respective soil or treatment effect,

βo = average yield response of the soil without P application (intercept),

X_1 = adjusted P level,

X_2 = effect due to soil depth,

X_3 = effect due to state of crystallinity,

ε = residual error.

β1 - β5 = regression coefficients.

Yield prediction equations, statistical parameters, point of maximum response and yield at 0.2 µg/ml solution P for the respective soils are given in Table 4.5.3. Yield values were higher in the subsoils than in the top soils at higher solution P concentrations (0.4 - 0.9 µg/ml), but was the reverse at 0.2 µg/ml when P concentrations were lower. This indicates that P retained by the more buffered soils at high levels of added P, provide a sizable sink of P for plants. At low to medium P levels, the diffusive supply in these highly buffered soils was low as P is held more tenaciously on soil particles. Yields levels were correspondingly low in these soils as a result. The magnititude of the regression coefficients were a reflection of the estimated maximum yield

Table 4.5.3. Response surface analysis of maize dry matter to adjusted solution P levels. Yield prediction equation, R^2, RMSE, point of maximum response, and yield estimate at 0.20 ug P/ml equilibrium solution concentration for the special soils.

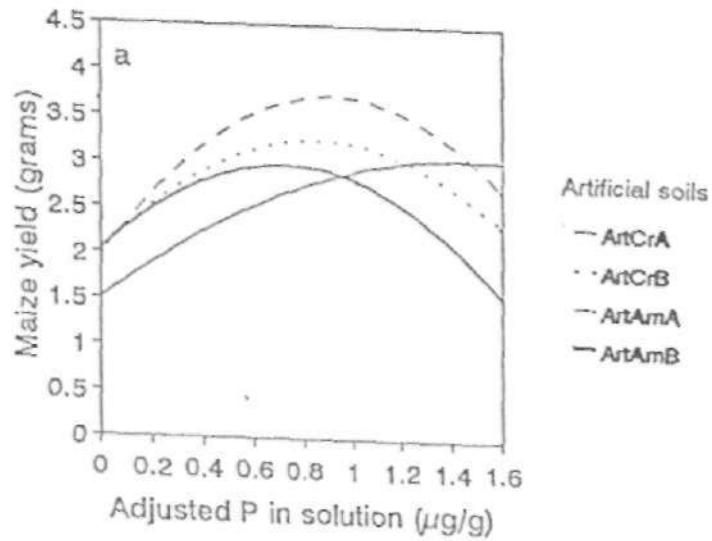
Soil	Regression Model*	R^2	RMSE	Maximum Point		0.2 µg P/ml	
				Yield	Equil. P	Yield	% of yld max
				g/pot	µg/ml	g/pot	%
NatCrA	$y = 1.24 + 1.29x - 0.46x^2$	0.75	0.209	2.13	1.38	1.48	69
ArtCrA	$y = 1.49 + 2.19x - 0.76x^2$	0.76	0.356	3.05	1.43	1.89	62
NatCrB	$y = 1.23 + 1.72x - 0.58x^2$	0.57	0.447	2.50	1.47	1.55	62
ArtCrB	$y = 2.02 + 2.88x - 1.68x^2$	0.39	0.522	2.25	0.83	2.52	78
NatAmA	$y = 1.11 + 2.27x - 1.18x^2$	0.90	0.251	2.74	1.17	1.62	59
ArtAmA	$y = 1.96 + 3.90x - 2.10x^2$	0.52	0.589	3.74	0.91	2.65	71
NatAmB	$y = 1.79 + 2.38x - 1.31x^2$	0.39	0.467	2.87	0.90	2.21	77
ArtAmB	$y = 2.03 + 2.65x - 1.84x^2$	0.33	0.565	2.98	0.72	2.46	83

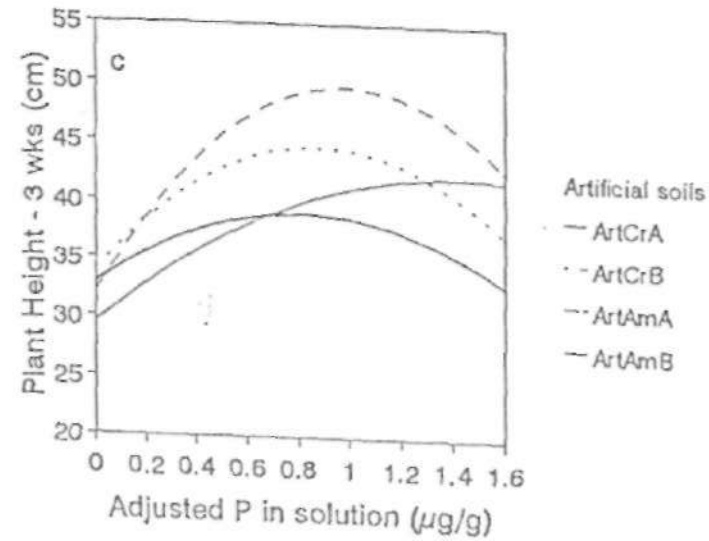
* y = yield (g/pot)

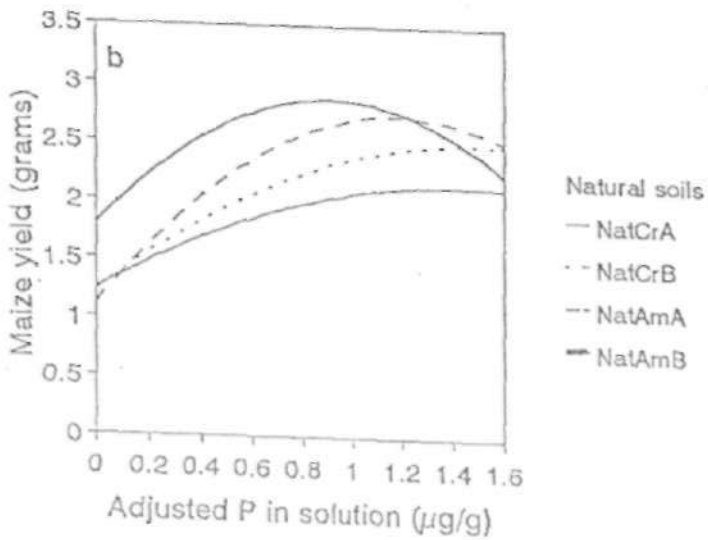
x = equilibrium solution P.

for each soil. However, the capacity to utilize applied P was higher in the top soils as shown by the R^2 and RMSE values. The significance of this is that the productive capacity of soils should vary along with the buffer index and OM once P is not limiting. Maximum yield was higher in the artificial soils with higher buffering index. The predicted yield and plant height response curves in relation to adjusted P levels in soil solution are presented in Figure 4.5.1. The solution phosphate concentration at point of maximum response ranged between 0.90 and 1.47 µg/ml in the natural soils, and 0.72 and 1.43 µg/ml in the artificial soils. At 0.2 µg/ml equilibrium solution P, the percent of maximum yield varied between 59 and 83 %. This is considered low and was inconsistent with the response trend for maximum yield. Though it is argued that accepted yield levels should be a percentage of the maximum yield, based on the economics of the situation (Cox, 1992), 95 % yield maximum as indicated by Fox and Kamprath, (1970) and Fox et al., (1981) represented a statistically valid point below which yield levels were reduced significantly. This was regarded as the critical point and the equilibrium solution P required for the attainment of this yield level should be rightly described as the critical phosphate level.

Figure 4.5.2. shows the yield advantage over control expressed as relative yield in relation to adjusted P levels. In the soils dominated by crystalline oxides, the natural and artificial systems were highly comparable and P in the soils behaved similarly. This was not the case for the amorphous Fe dominant soils with comparable treatments. This extent of







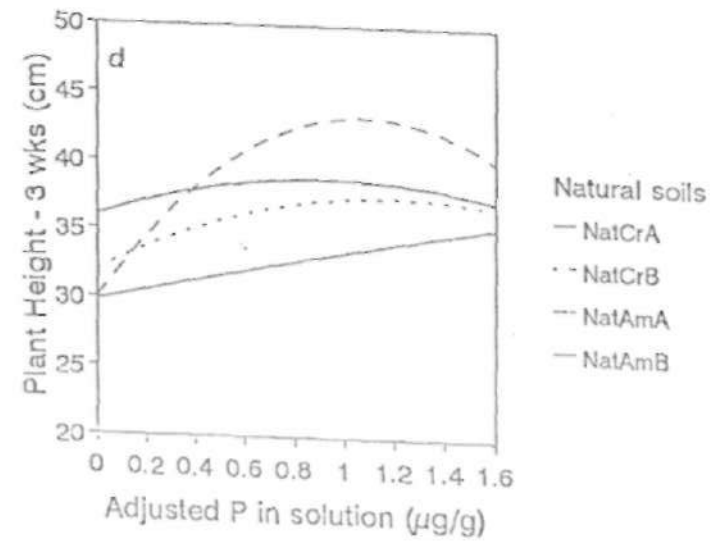


Figure 4.5.1: Response curves for yield and plant height at 3- weeks in relation to adjusted solution P levels.

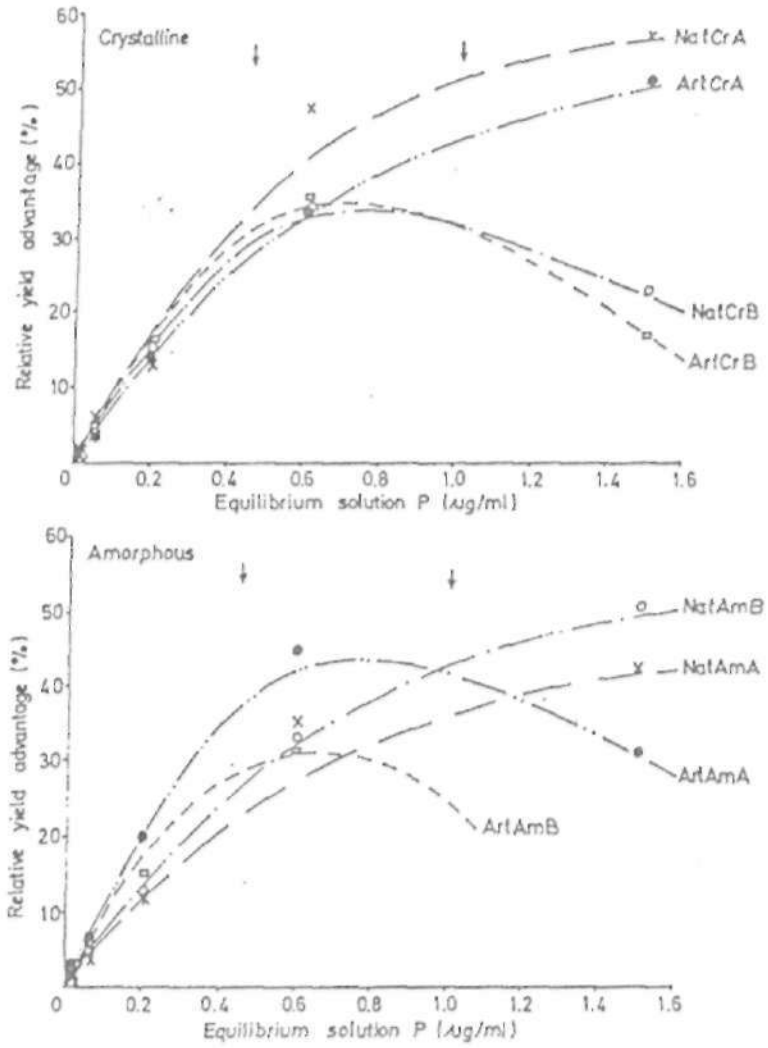


Figure 4.5.2: Relative yield advantage in relation to equilibrium solution P for the soils.

deviation in properties relevant to P reactions in soils may be expected in soils in which effects of hysteresis are excessive (Fox and Kamprath, 1970) as was the case with the amorphous Fe dominant soils. Equilibrium P for 95% of maximum yield as deduced from the graph (Figure 4.5.2) fell between 0.45 to 1.0 µg/ml solution P, depending on the soil buffer index. Response to applied P was better predicted in the

crystalline Fe dominant soils relative to the amorphous Fe soils due to ease of P diffusion in the soils. The inconsistency in P reactions in soils with the amorphous oxides dominant, may be linked to the occurrence of the various intergrade of non- to micro-crystalline oxides that influence surface area, and which imposes a huge control on the magnitude of P sorption in soils.

4.5.2.2 Response model for treatment effects.

The relative response of maize dry matter yield to the various treatments considered were evaluated by response surface regression models (Table 4.5.4). It is expected that the regression coefficients would provide the relevant quantitative factors which could be used as bases for comparison. 'Organic matter x soil type' interaction revealed similar coefficients for the top and sub-soils in the natural soils (2.03 and 2.05 respectively), but had only 10 % yield advantage due to OM in the artificial system (3.04 and 2.76 for top and sub respectively). On the average, 6% yield advantage due to OM was obtained. However, the artificial soils represent a more homogenous system, therefore 10% yield enhancement could be rightly attributed to the effect of OM in these soils.

The effect of crystallinity on P release potential of soils was assessed by regression coefficients derived from 'crystallinity x OM interaction'. Generally, the amorphous soils were more highly buffered. About 40 % yield potential was attributable to the highly buffered amorphous system, and

Table 4.5.4: Response surface analysis for maize response to adjusted solution P levels. Yield prediction equations, R^2, RMSE, point of maximum response and yield estimate at 0.20 g P/ml: mean interaction effect of OM and state of soil oxides forms.

Treatment	Regression model	R^2	RMSE	Max. point		Yield at 0.20 g/ml	
				yield	Equil. P	Yield	% of yld max
				g/pot	g/ml	g/pot	%
Organic matter (OM) x Soil type							
Nat-Top*	$y = 1.71 + 2.03x - 0.83x^2$	0.78	0.254	2.43	1.23	1.54	63
Nat-Sub	$y = 1.51 + 2.05x - 0.95x^2$	0.37	0.527	2.62	1.08	1.88	72
Natural soils	$y = 1.34 + 2.04x - 0.88x^2$	0.50	0.434	2.50	1.15	1.71	68
Art-Top	$y = 1.72 + 3.04x - 1.45x^2$	0.50	0.569	3.32	1.05	2.27	68
Art-Sub	$y = 2.02 + 2.76x - 1.76x^2$	0.32	0.540	3.11	0.78	2.50	80
Artificial Soils	$y = 1.87 + 2.90x - 1.61x^2$	0.35	0.581	3.18	0.90	2.38	75
Top-soils	$y = 1.44 + 2.54x - 1.14x^2$	0.46	0.556	2.86	1.11	1.90	66
Sub-Soils	$y = 1.77 + 2.40x - 1.35x^2$	0.25	0.589	2.83	0.89	2.20	77
Crystallinity of oxides X OM							
Nat-Amorph	$y = 1.45 + 2.57x - 2.25x^2$	0.52	0.456	2.78	1.031	1.19	69
Nat-Crystalline	$y = 1.23 + 1.50x - 0.52x^2$	0.59	0.345	2.31	1.420	1.51	65
Art-Amorph	$y = 2.00 + 3.04x - 1.60x^2$	0.40	0.596	3.45	0.948	2.54	73
Art-Crystalline	$y = 1.75 + 2.53x - 1.22x^2$	0.45	0.520	3.06	1.034	2.21	72
Amorph-Top	$y = 1.53 + 3.34x - 1.66x^2$	0.41	0.636	3.21	1.004	2.13	66
Amorph-Sub	$y = 1.92 + 2.14x - 1.41x^2$	0.30	0.532	2.95	0.855	2.36	80
Cryst.-Top	$y = 1.36 + 1.73x - 0.61x^2$	0.59	0.394	2.59	1.414	1.68	65
Cryst.-Sub	$y = 1.62 + 2.30x - 1.13x^2$	0.29	0.635	2.29	1.010	2.03	72
Amorphous	$y = 1.73 + 2.84x - 1.48x^2$	0.37	0.597	3.09	0.959	2.24	72
Crystalline	$y = 1.49 + 2.02x - 0.87x^2$	0.38	0.539	2.66	1.150	1.86	70

* Nat and Art represent natural and artificial systems.

because the crystalline systems adsorbed less P, the equilibrium solution P was consequently higher for similar yield levels. In the natural system, 71 % improvement in yield was due attributed to the amorphous colloids, (Table 4.5.4), whereas the effect in the artificial soils was only 20 %. When the top and subsoils were isolated, 93 % advantage in yield potential was attributed to the amorphous system in soils with organic fraction, while the effect in soils without organic fraction was only 5 %. We could infer from the results presented that OM enhances productivity of soils with large enough reactive surface to maintain acceptable level of sorbed P that may contribute eventually to the P labile pool (McLaughlin et al., 1981; Borggaard, 1983). Similarly, deriving from the natural soils, about 88 % of yield enhancement in well managed tropical soils can be due to the effects of OM. OM reduces buffer capacity and enhances the P desorption property of soils. In effect, OM significantly reduced the amount of phosphate required to maintain a solution concentration necessary for crop growth, by direct competition with P for sorption sites (Apelt et al., 1975; Sibanda and Young, 1986; Borggaard, et al., 1990), or by the generation of unfavourable electrostatic field around OM molecule, thereby preventing P sorption (Sibanda and Young, 1986). The practical significance of the management of soil OM lies in the conservation measures necessary to prevent the depletion of organic carbon which can result from intensive cropping.

Maize yield and plant height response as influenced by the various interactions, based on the prediction equations in relation to adjusted solution P levels are presented in Figures 4.5.3 to 4.5.7. Yield at maximum point of response ranged from 2.31 g pot^{-1} in the natural crystallized soil system to 3.45 g pot^{-1} in the artificial amorphous soils. Corresponding equilibrium solution P for these yield levels were 1.42 and 0.948 µg/ml respectively. Yield levels at 0.2 g P/ml ranged between 63 and 80 % of maximum yield which in all cases were regarded as low, and solution P at this level was therefore insufficient for the attainment of near maximum yield in these soils under greenhouse conditions.

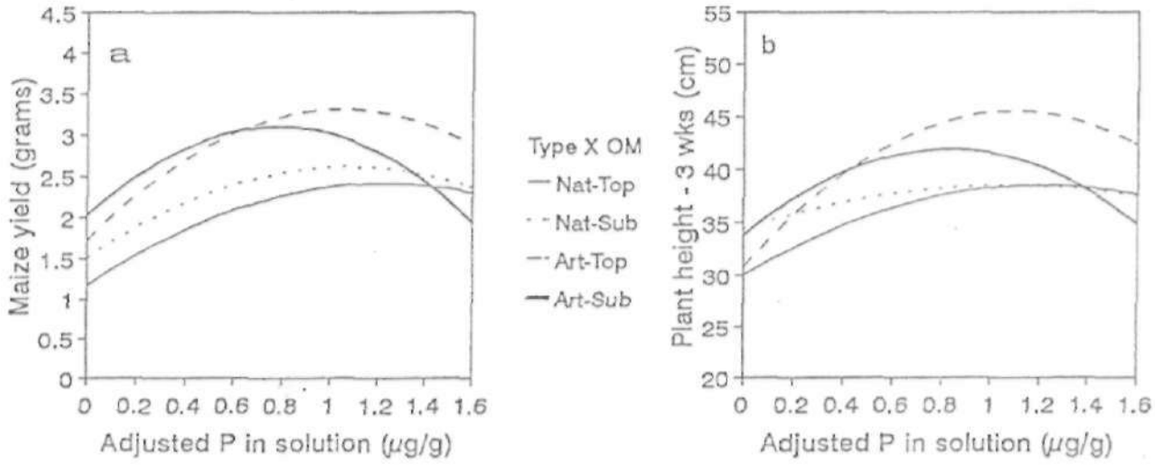


Figure 4.5.3: Effects of 'soil type X OM interaction' on the response of maize to adjusted solution P levels.

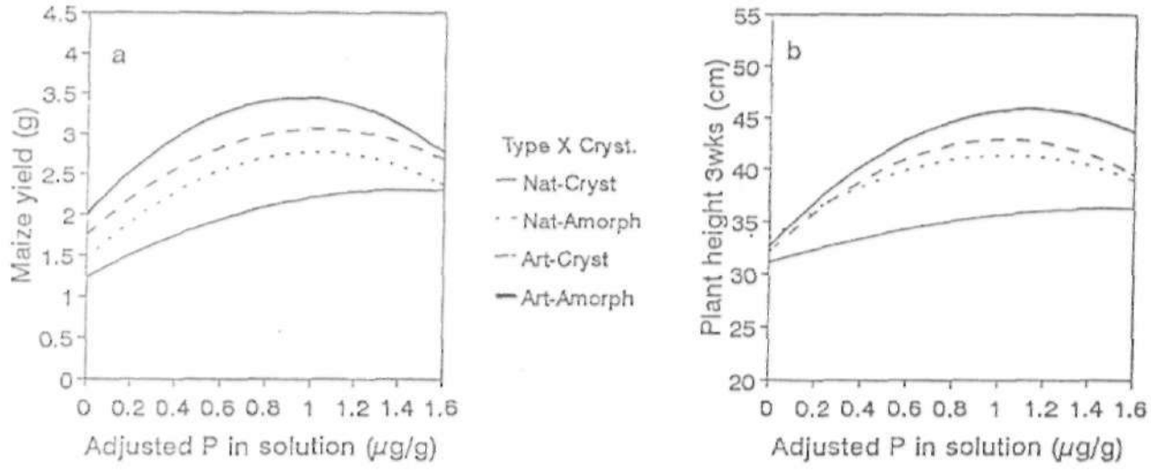


Figure 4.5.4: Yield response in relation to 'soil type X crystallinity'; a - DM yield, b - plant height.

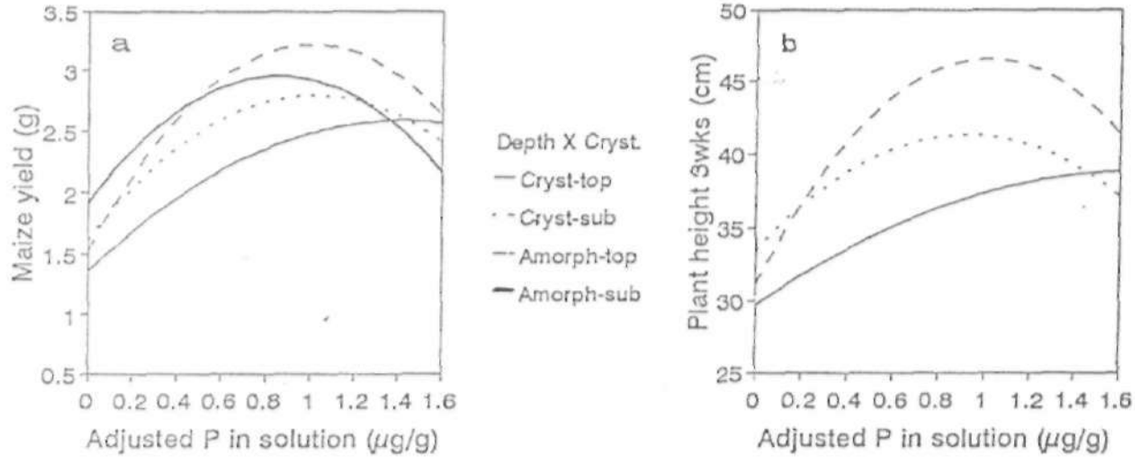


Figure 4.5.5: Yield response in relation to 'depth X crystallinity' for DM yield and plant height.

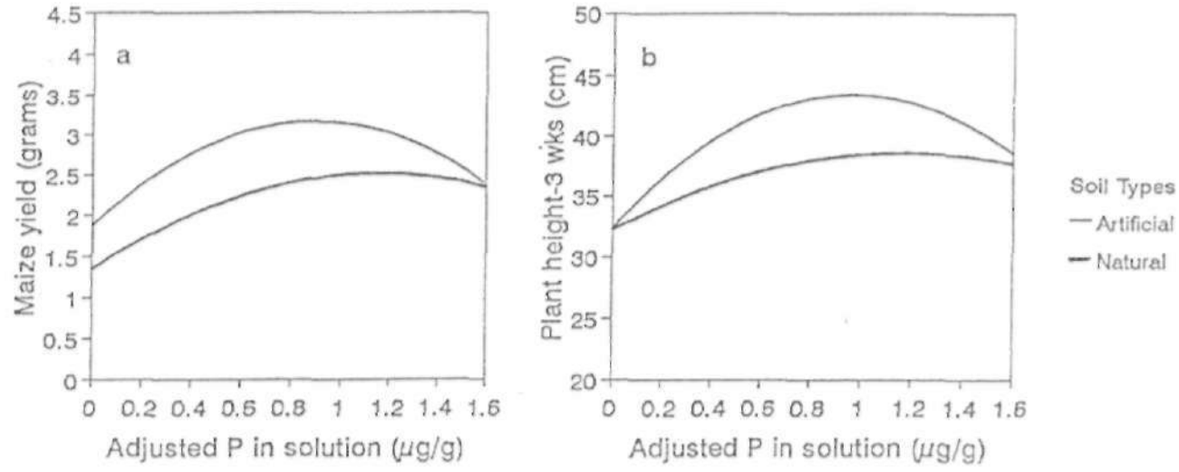


Figure 4.5.6: Mean response of maize to adjusted solution P levels in the natural and artificial soils .

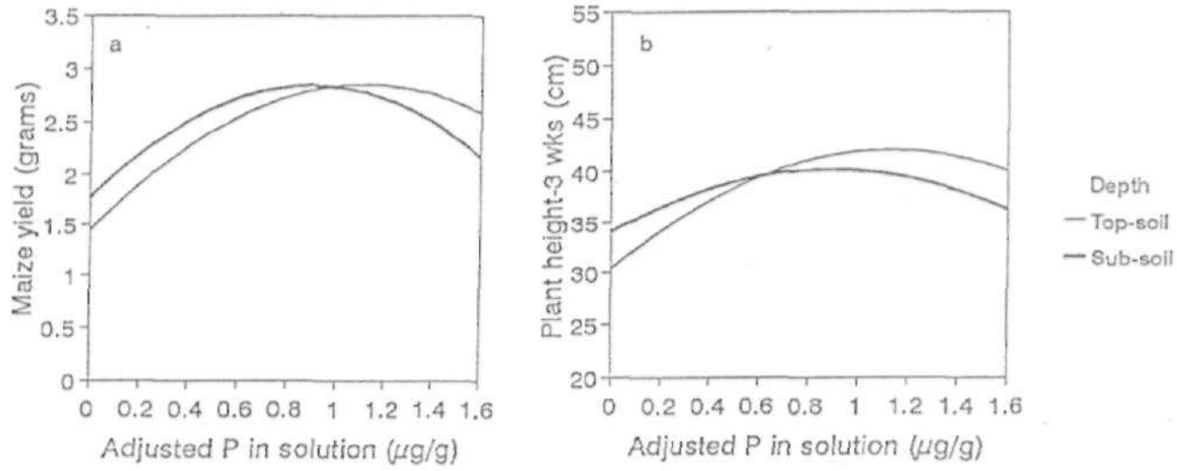


Figure 4.5.7: Mean response of maize to adjusted solution P levels as influenced by organic matter.

4.5.3. Effects of selected soil properties on yield and uptake.

The relative effects of treatment being evaluated on maize performance in response to applied phosphate were further considered by looking at the relationship of some soil parameters and the coefficients of relationship between P uptake and yield. Table 4.5.5 shows the simple regression relationships between uptake and yield. Though this relationship has no predictive substance, it could suffice as a factor with which to quantify the relative performance of maize in the soils. The regression coefficients were consistently higher for the top soils with the organic matter fraction. The coefficient of determination (R^2) indicates also that the relationship was better in soils with organic matter.

Table 4.5.5: The relationship between dry matter yield (y) and P uptake (x) in maize expressed in simple linear regression.

Soil	Regression model	R^2
NatCrA	y = -0.432 + 1.236x	0.75
ArtCrA	y = 1.073 + 0.378x	0.91
NatCrB	y = 0.877 + 0.394x	0.92
ArtCrB	y = 2.080 + 0.063x	0.41
NatAmA	y = 0.581 + 0.527x	0.89
ArtAmB	y = 1.927 + 0.138x	0.49
NatAmB	y = 1.775 + 0.108x	0.50
ArtAmB	y = 1.820 + 0.095x	0.32

The ability of the test plant to utilize soil applied phosphate efficiently should also be in consonance with the magnitude of the regression coefficients. Quantifying these relationship for both natural and artificial systems, the efficiency of utilizing applied P was 2.5 folds greater under crystallized top soils relative to the amorphous top soils. This shows that in agricultural soils with crystallized oxides dominant, phosphate supply potential could be 2.5 times greater than in soils dominant in micro-crystalline or amorphous oxides. In effect therefore, the efficiency of utilization of applied phosphate should be better in the savanna soils than in the humid rain forest Oxisol from south.

Of the sorption indices, the single factor that was not related to uptake and yield was the affinity constant (P=0.05, Table 4.5.6). SPR and P_{max} were highly correlated with yield.

Table 4.5.6. Correlation relationships between dry matter yield, P uptake and phosphate sorption parameters and soil oxide fractions for all soils.

Parameter	Dry matter yield	P uptake
SPR	0.89**	0.82*
Affinity (K)	0.66	0.55
P_{max}	0.90**	0.81*
MBC	0.82*	0.76
Fe_d	0.58	0.36
Fe_{ox}	0.83*	0.75*
Fe_{py}	0.26	0.03
Al_d	-0.15	-0.03
Al_{ox}	-0.15	-0.24
Al_{py}	-0.47	-0.52

*,** - Significant at 5 and 1 % levels of probability.

The Fe_o fraction was also significantly correlated with yield and P uptake. The factors which influence adsorption maximum and SPR should also influence growth parameters likewise.

4.5.4.1. Effects of treatments on extractable P values

The variation in soil test-P concentrations of pre-cropped incubated soils in relation to treatment effects are summarized in Table 4.5.7, showing the sources of variation and the mean square values. The CV were higher, and also the coefficient of determination (R^2) values were lower for the Bray-P soil test. The resin method was more sensitive to all treatments shown by the highly significant differences in mean values due to effects of treatments. It might appear apparent from Table 4.5.7. that the chemical nature of the extractants influenced the amount and nature of the labile P extracted, and consequently, the predictive capacity of the soil test methods. Considering the 'type x cryst.', as well as the 'type x cryst x rate' interactions, we may infer that the water-base extractants (resin and water) extracted P from the same phosphate pool, and differed from the chemical methods of Bray and Olsen.

Table 4.5.8 shows the interaction of soil type, crystallinity and OM for the P adjusted and incubated pre-cropped soils for the respective soils. Resin, in the HCO_3^- form, extracted more P from the soils than other extractant. The chelating ability of resin was more effective in desorbing P than other extractant. The Olsen method desorbed more P than Bray and Water. This capacity could be related to the

Table 4.5.7: Analysis of variance table for extractable P values as affected by treatment effects: P extracted from P amended soils prior to cropping.

Source of variation	df	Mean square values			
		Resin	Water	Bray	Olsen
		x 100		x 10	x 100
Rep	2	3.07	0.32	0.999	0.08
Rep - Soil Stratum					
Soil	7	1454**	3.0**	7.0**	216**
rate	5	1520**	1453**	1642**	284**
Soil x rate	35	122**	157**	59**	20**
Error	80	0.79**	1.9	3	0.6
Total	143				
Rep - Type stratum					
Type	1	5432**	4687**	21	613**
Cryst	1	1224***	315**	742**	183**
Depth	1	2622**	2009**	1059**	608**
Type x Cryst	1	135**	316**	2.4^{ns}	3.2^{ns}
Type x depth	1	610**	1155**	65**	72**
Cryst x depth	1	69**	24**	54**	25**
Depth x rate	5	185**	295**	209**	48**
Cryst x rate	5	115**	42**	163**	20**
Type x Cryst x depth	1	84**	0.14^{ns}	24**	12**
Type x Cryst x rate	5	7**	24**	2.0^{ns}	1.1^{ns}
Type x depth x rate	5	31**	111**	10.1*	4.4**
Cryst x depth x rate	5	8**	4.5^{ns}	4.6^{ns}	3.02
Error	97	1.06	2.1	4.2	0.7
Total	143				
SE ±		2.37	0.33	1.45	1.84
Mean		111.3	7.77	25.4	43.30
CV		9.04	18.4	24.2	18.0
R^2		0.99	0.99	0.97	0.98
RMSE		10.06	1.43	6.17	7.80

*,** - Significant at 5 and 1% levels of probability,
^{ns} - not significant,
Type - Natural and artificial.
Cryst - Crystalline and amorphous.
Depth - Top and sub (organic and dehumified soils).
rate - Adjusted equilibrium solution P levels.

Table 4.5.8: Effect of type*, crystallinity and depth interaction on P extractable by the various soil tests methods for P adjusted and incubated soils before cropping.

	Resin		Water		Bray		Olsen	
	Cryst	Amorph	Cryst	Amorph	Cryst	Amorph	Cryst	Amorph
	-------- µg/g --------							
Natural								
Top	22.8	32.7	1.5	0.8	12.5	19.5	6.5	11.9
sub	37.9	106.0	2.6	3.4	27.4	47.4	19.4	53.6
Artificial								
Top	69.9	149.0	4.4	9.4	10.9	24.8	24.9	47.8
Sub	197.9	274.1	16.6	23.5	22.5	38.9	77.5	105.6
Mean	111.3		7.7		25.5		43.3	
SE ±	2.94**		0.32^{ns}		1.37**		1.70**	

Type = natural and artificial

high pH of the extractant at which the Fe and Al oxides, largely responsible for P fixation, are expected to be inactive. The Bray-P soil test tended to overestimate available P in weekly buffered soils (natural soils), and to underestimate the index in highly buffered soils as shown by the Bray P/water P ratios. This implies that the Bray method was less sensitive to buffering. This corroborates the concept of unsatisfied equivalence of the extractant and soil Al and Fe oxides largely responsible for P fixation which was presented earlier in this thesis. Though the F^- component of the reagent essentially keeps the desorbed P in solution and reduces resorption, it may seem necessary to increase the F

concentration of the reagent for tropical soils with high oxide contents.

Soils with similar characteristics should extract the same amount of bio-available P if solution concentrations are adjusted to the same standard P level (Fox and Kamprath, 1970). Generally the relationship between easily extractable P and sorption parameters (P bonding energy or buffer capacity) had earlier been shown to be inverse, consistent with the findings of Holford and Mathingly, (1976) and Olsen and Khasawneh, (1980). Figure 4.5.8. shows the relationship between total dry matter yield and total plant P uptake with P sorption capacity across all soils. The relationship was positive when soils were P amended, but in the unamended soils, the relationship with yield was negative (not shown), though nonsignificant.

4.5.4.2 Total P uptake and efficiency of soil tests methods.

The variation in the decrease in soil test-P (pre- minus post-cropped extractable P) due to cropping and uptake as influenced by treatments are shown in Table 4.5.9. Results were consistent as observed with pre-cropped soil analysis data. The resin and water methods reacted similarly when 'soil type x cryst' interaction was considered, and different from the chemical methods of Bray and Olsen, as shown in the results earlier presented. The 'soil type x crystallinity x depth' interaction incorporates factors that were uppermost in influencing P reactions. The only single soil test that produced significant variation as was observed for uptake was

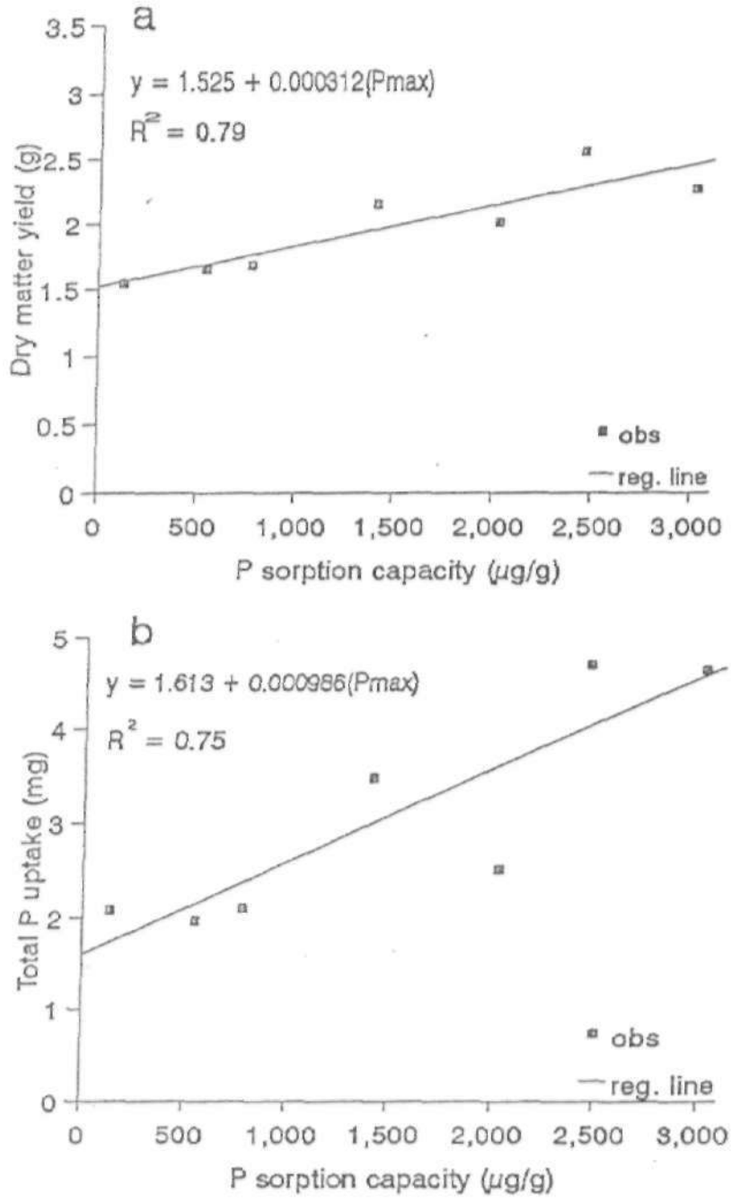


Figure 4.5.8: The relationship between P sorption capacity with yield (a) and P uptake (b).

Table 4.5.9: Analysis of variance table for difference in extractable P levels by the various soil tests due to cropping (Test-P pre minus Test-P post), and for P uptake by the maize plant.

Source of variation	df	Mean square values				
		Resin	Water	Bray	Olsen	Plant P Uptake
		x 100		x 10	x 100	
Rep	2	1.8	0.6	1.7	0.83	1.3
Rep - Soil Stratum						
Soil	7	57.8**	603**	23**	17.7**	54.9**
rate	5	87.6**	580**	190**	22.2**	83.6**
Soil x rate	35	6.1**	68**	4.9**	1.8*	5.9**
Error	80	1.1	1.8	1.08	1.02	1.60
Total	143					
Rep - Type stratum						
Type	1	224*	2024**	37.8*	28^{ns}	185*
Cryst	1	43**	99**	33.9**	17**	4.9^{ns}
Depth	1	98**	1299**	84.0**	61**	69.5**
Type x Cryst	1	6*	69**	1.3^{ns}	0.9^{ns}	5.3^{ns}
Type x depth	1	25**	545**	0.6^{ns}	11.8**	20.9**
Cryst x depth	1	1.8^{ns}	1.2^{ns}	2.8^{ns}	4.3*	19.0**
Depth x rate	5	7.9**	145**	65**	4.9**	3.4^{ns}
Cryst x rate	5					
Type x Cryst x depth	1	7.1*	3.5^{ns}	1.8^{ns}	0.1^{ns}	78**
Type x Cryst x rate	5	2.3^{ns}	12.9**	1.7^{ns}	0.5^{ns}	1.4^{ns}
Type x depth x rate	5	3.8**	24.7**	1.2^{ns}	0.8^{ns}	8.1**
Cryst x depth x rate	5	3.1*	6.2*	0.2^{ns}	0.7^{ns}	2.9^{ns}
Error	97	1.2	2.6	1.23	1.00	2.1
Total	143					
SE ±		3.57	0.32	0.83	2.40	0.32
Mean		28.40	5.30	8.06	11.17	3.54
CV		53.30	25.40	43.90	91.20	38.50
R^2		0.81	0.98	0.91	0.75	0.84
RMSE		15.18	1.34	3.50	10.2	1.36

*,** - Significant at 5 and 1% levels of probability,
^{ns} - not significant,
Type - Natural and artificial.
Cryst - Crystalline and amorphous.
Depth - Top and sub (organic and dehumified soils).
rate - Adjusted equilibrium solution P levels.

Table 4.5.10. Effects of type, crystallinity and depth interaction on P loss estimated by the various soil tests due to cropping, and total P uptake by the maize plant.

	Resin		Water		Bray		Olsen		Total P uptake	
Treatment	Cryst	Amorph	Cryst	Amorph	Cryst	Amorph	Cryst	Amorph	Cryst	Amorph
	mg pot^{-1}								mg pot^{-1}	
Natural										
Top	1.55	2.23	0.07	0.03	1.00	1.13	0.39	0.59	2.10	2.10
sub	2.43	3.78	0.31	0.43	1.55	2.15	0.88	2.28	2.00	3.50
Artificial										
Top	2.76	5.98	0.40	0.86	0.37	1.01	0.54	1.37	2.50	4.70
sub	7.50	8.70	1.90	2.33	0.90	1.60	2.89	4.61	6.90	4.60
Mean	4.36		0.80		1.21		1.69		3.54	
SE ±	0.42*		0.05^{ns}		0.12^{ns}		0.38^{ns}		0.39**	

*,** - Significant at 5 and 1% levels of probability.
ns - Not significant.

the resin method. Table 4.5.10 clearly supports this derivation. The estimated difference in resin P expressed in mg pot^{-1} was closer to plant uptake in absolute values. Water, Bray and Olsen methods were non-significant and they fell short of total P uptake in absolute amounts, and so does not present a holistic approach to evaluating plant uptake. The Olsen method provided a better estimate in the highly buffered soils whereas the Bray method was the next closest to resin in soils with low buffer capacity, represented by the natural soils.

Correlation relationship was used to rank the efficiencies of the extractant at the level of 0.60 µg/ml equilibrium solution P amendment. The results are shown in

Table 4.5.11. The order of ranking was resin > Water > Olsen > Bray. This finding corroborates the postulate of Sibbesen, (1978), and other workers like Beckett and White, (1964) and Dalal and Hallsworth, (1976). In these tropical soils high in Fe and Al oxides, the acid extractant may be highly

Table 4.5.11. Relationship between P uptake and P extractable at 0.6 µg P/ml equilibrium solution P adjusted and the difference in extractable P due to cropping.

	Correlation coefficient at 0.6 µg P/g	
Soil test	Pre-cropped	Difference
Resin	0.94**	0.95**
Water	0.92**	0.93**
Bray	0.53ns	0.35ns
Olsen	0.91**	0.84**

inefficient due to the concomitant activation of the oxide ions which eventually fix the desorbed P, thereby resulting in the underestimation of the availability index. It is therefore not surprising that correlation of Bray-P soil test with yield has always been spurious and low (Adepetu 1975).

4.5.4.3. Relationship between soil tests P and yield.

Total dry matter yield was significantly correlated with total P uptake ($P < 0.01$). This implies therefore that both

parameters may also be influenced by the same set of factors. The relationships between DM yield and the decrease in soil test-P (difference estimate) are presented in Table 4.5.12. When the natural and artificial soils were taken separately, all estimates (pre-cropped, post-cropped and the difference) were significantly correlated with yield. Combining the natural and artificial soils and evaluating the extractant as a factor of depth (OM), the level of relationship was also highly significant for all soil test parameters. The correlation relationship of the artificial system lends support to the fact that the Bray soil test was the least efficient (Table 4.5.12). No particular relationship between yield and any of the estimates of Bray-P in the subsoil was obtained.

It was therefore possible to derive from this study, that the resin method was universally superior to all other extractants used. The Olsen method was next in efficiency. The Bray method could be equally as efficient as the Olsen method but only in lowly buffered soils. The inefficiency of the Bray P_1 method in highly buffered soils suggests caution on its use as a general reagent. The water-P may prove suitable, ranking third after Olsen, but in these highly weathered tropical soils, P release could be largely induced by exchange of ions at the root surface. Though a chemical method could be more appropriate to simulate the plant uptake mechanism, the order of ranking of the methods in this study was: resin > Olsen > Water > Bray. The Bray reagent was reasonably efficient in soils with crystalline oxides dominant, like the

Table 4.5.12: Correlation relationships between dry matter yield and the various estimates of extractable P as influenced by organic matter and soil type.

	Resin			Water			Bray			Olsen		
Treatment	Pre	Post	Diff	pre	post	Diff	Pre	Post	Diff	Pre	Post	Diff
OM Effects												
Top	0.82**	0.81**	0.76**	0.72**	0.71**	0.70**	0.69**	0.75**	0.49**	0.88**	0.82**	0.65**
Sub	0.55**	0.49**	0.64**	0.43**	0.17	0.55**	0.34**	0.34**	0.33**	0.55**	0.55**	0.39**
Depth simulation												
ARTIFICIAL												
Top	0.82**	0.83**	0.73**	0.71**	0.71**	0.71**	0.71**	0.75**	0.59**	0.80**	0.88**	0.61**
Sub	0.42*	0.34*	0.56**	0.34*	0.02ns	0.53**	0.11	0.11	0.12	0.37*	0.41*	0.17*
All	0.51**	0.45**	0.59**	0.40**	0.20	0.48**	0.33**	0.34**	0.30**	0.45**	0.50**	0.24*
Natural												
Top	0.83**	0.83**	0.80**	0.73**	0.67**	0.60**	0.85**	0.81**	0.83**	0.84**	0.80**	0.72**
Sub	0.75**	0.72**	0.72**	0.57**	0.47**	0.50**	0.70**	0.68**	0.70**	0.74**	0.72**	0.71**
All	0.73**	0.68**	0.75**	0.53**	0.45**	0.49**	0.74**	0.69**	0.75**	0.71**	0.68**	0.71**

savanna soils. In the more P retentive soils where soil oxides are largely in the non- to micro-crystalline state, the Olsen method was more efficient. Though the resin method was found to be superior on all counts, the demands resources and skill are greater and can best be managed as a 'routine' procedure in large functional laboratories.

4.5.5. Soil test calibration for yield level estimation.

Regression models for yield level estimations in response to adjusted solution phosphorus were determined by the response surface regression analysis. Regression equations are presented in Table 4.5.3. and 4.5.4. for the respective soils and treatment interactions. Fox and Kamprath, (1970), and Juo and Fox, (1977), have used 95 % of maximum yield as a statistically acceptable limit for the definition of the optimum yield level. The amount of P required to obtain this yield level is referred to as the 'external phosphate requirement' (EPR). This yield level represents a critical value, below which deficiency would normally limit yield. Based on the regression models and the knowledge of the critical yield, yield levels can be scaled with due consideration to available resources over a range of production limits at the deficiency range. The lower limit of the deficiency range was considered as the threshold value.

Table 4.5.13 contains yield data for soil test calibration and the corresponding soil test-P for efficient prediction of fertilizer requirement. The 95 % yield estimate and corresponding solution P for its attainment were estimated

Table 4.5.13: Soil test calibration for yield level estimation based on regression models. Predicted critical and threshold yield response points and corresponding 'sufficient' and deficient levels for the soil test methods for the test soils.

	Critical yield level[a]			Threshold yield level[b]								
	95% Yield max.			Deficiency limit		Critical P levels				Threshold P levels		
Soil	Yield	Soln P	Uptake	Yield	Soln P	Resin	Water	Bray	Olsen	Resin	Water	Bray	Olsen
	g/pot	µg/ml	mg	g/pot	µg/ml	µg/g							
Natural Soils													
NatCrA	2.02	0.90	1.98	1.27	0.024	27.6	2.4	17.0	9.20	19.3	0.91	9.07	4.60
NatCrB	3.36	1.00	3.76	1.27	0.024	64.5	6.4	53.3	36.7	21.4	0.21	11.7	8.63
NatAmA	2.59	0.82	3.80	1.27	0.073	54.0	1.9	38.3	23.9	16.4	0.05	6.98	3.86
NatAmB	2.72	0.68	8.72	1.27	0.000	138.0	5.9	67.0	71.0	61.0	-0.31	19.91	28.20
Artificial Soil													
ArtCrA	2.90	0.98	4.83	1.62	0.06	133.9	10.2	25.9	38.2	40.0	1.50	2.27	9.00
ArtCrB	3.08	0.58	16.31	2.04	0.007	235.2	21.3	30.7	93.2	84.3	6.71	4.98	44.11
ArtAmA	3.55	0.65	11.71	2.04	0.021	192.8	13.4	35.2	63.0	69.6	3.46	9.25	25.40
ArtAmB	2.83	0.45	10.58	2.04	0.004	289.8	25.1	43.2	112.3	151.6	10.81	7.90	56.30

a - Optimum yield

b - Lower limit of allowable yield reduction

by least square regression. The threshold yield values used ranged from half the mean for the natural soils, to the grand mean for the artificial soils. Regression estimates of the threshold solution P levels were determined. An average of 0.85 and 0.66 µg/ml solution P was require to obtain 95 % yield maximum in the natural and artificial soil systems respectively. As earlier observed, the more highly buffered soils had relatively lower solution P requirement. On the whole, solution P values required for 95% yield maximum ranged from 0.45 to 0.98 µg/ml in the artificial soils and 0.68 to 1.00 µg/ml in the natural soils. The threshold value was about 0.025 µg P/ml and the pattern of variation was not particularly consistent as observed with the critical value.

The critical and threshold soil test-P concentrations for the soils were determined by simple regression analysis. Corresponding soil test-P for the critical and threshold yield levels are presented (Table 4.5.13). Critical or sufficient P estimates for the lowly buffered crystalline acid soil, like the savanna soils (natural soils) were 27.6, 17.0, 9.2 and 2.4 µg/g for resin, Bray, Olsen and water methods respectively whereas 54.0, 38.3, 23.9 and 1.9 µg/g were the respective critical values for the more buffered amorphous Fe dominant forest oxisol of the humid south. Results indicate that twice as much P is required in amorphous surface soils relative to the crystalline soils, and in each system, poor management of OM can only be compensated for by using more than three times the amount of P needed for soils where the OM has been properly managed.

The significance of the threshold soil test-P levels is that it represents the lower limit where visual deficiency symptoms start to emerge. In the natural soils, these values varied with texture and mineralogy, and the capacity of the soil to sorb P. The lower the index, the higher the threshold soil test-P.

In the artificial soils, critical and threshold soil test-P concentration increased consistently with sorption capacity and was inverse to the solution P concentration. Results in this study did not show much similarity in critical or threshold soil test-P in relation to adjusted solution P. This observation may be due to the strong influence of soil properties, and the chemical nature of the various extractant (Kuo, 1990; Olsen and Khasawneh, 1980; Pratt and Garber, 1964).

4.6. Phosphorus Depletion and Turnover in the Rhizosphere

Indices of available P are typically based on a single chemically extractable P pool, a practice that ignores the potential contribution of organic P (P_o) mineralization. This, in all considerations, has been found inadequate and has often resulted in the underestimation of plant available P (Hedley, *et al*., 1982; *Helal and Dressler, 1989; Thien and Myers, 1992;* Bowman and Cole, 1978). The quantity of P mobilized by plants has also been shown to depend on the nature of phosphate compounds present in the soil (extractable with different reagents), and changes in the pH of the root environment (Gahoonia and Nielsen, 1992). The various reaction processes that control the availability of P take place in the rhizosphere. This section deals with P_i and P_o depletion in the rhizozphere of maize and rape plants.

4.6.1. Relative fertility of the selected soils

An estimate of solution P concentration at soil particle surface was computed by a linear regression relationship between solution:soil ratio and P concentration in soil solution. P concentration at zero solution:soil ratio should gave an estimate of P concentration in soil solution at soil particle surface. This parameter indicates the ability to replenish the soil solution as P at the root surface is depleted in the respective soils, and therefore should have an inverse relationship to the soil buffer capacity. The reciprocal of the regression coefficients provided an index of

fertility which were weighted against the index for NatAmB, the least value, to give a weighted fertility index (FI) for the soils. The relative fertility of the soils were quantified and ranked by the FI coefficients.

Results are presented in Table 4.6.1. The Danish soils were comparatively more fertile relative to the tropical soils used. The Danish II had a weighted index value of 25.89, compared to 2.20 for the surface soil of the tropical savanna Alfisol (NatCrA). The tropical sub-soils, soils 2 and 3 (NatCrB and NatAmB) were least fertile. Phosphate acquisition from soil are influenced appreciably by the phosphate fertility of soil, which is described by the amount avialable, the differences in plant species (Clarkson, 1985; Jungk, 1989), and the forms of phosphate in soil (Hedley et al., 1982; Chang and Jackson, 1957). Phosphate depletion in soil is therefore governed by these factors.

Table 4.6.1: Regression relationship between soil solution P concentration and solution:soil ratio, solution P concentration at particle surface, and relative fertility indices for the soils.

Soil	Regression equation	R^2	SP	FI
			µg/g	
NatCrA	y = -0.92 + 37.28x	0.99	0.025	2.20
NatCrB	y = -1.30 + 78.00x	0.99	0.017	1.04
NatAmA	y = -1.51 + 80.86x	1.00	0.019	1.00
Pedon 1	y = -11.69 + 66.50x	0.97	0.178	1.22
Danish I	y = -5.69 + 18.70x	0.99	0.304	4.34
Danish II	y = -3.47 + 3.14x	0.98	1.105	25.89

y = solution:soil ratio,
x = solution P concentration,
FI = Fertility index,
SP = solution P concentration at particle surface.

4.6.2. Crop yield and plant parameters

The dry matter yield and some chemical parameters of plant tissue, and uptake values for rape and maize at 7 and 14 days growth periods are presented in Table 4.6.2. Results show that at the early stages of growth (7 day period), the complete nutrient supply solution adequately met the requirements of the crops irrespective of the soil, at least the differences were not apparent. However, at later stages of growth the differences in the soil properties became evident, especially with the rape plant. The response by the rape plant was consistent with the relative fertility coefficient (FI) earlier presented. This observation was absent in the maize crop. Both crops therefore differed in their acquisitive capacity for nutrients form available sources. In the tropical soils, yield values for rape at 14 days were about similar, but was much higher in the temperate Danish soils. Both groups of soils (tropical and temperate) differed in the predominant phosphate compounds (Table 4.2.3) which also varied in solubility and availability (Lindsay and Moreno, 1960). In tropical soils, P is mainly sorbed on Fe and Al surfaces by specific anion adsorption (Parfitt, 1978), and P mobilization (availability to plants) is essentially by ligand exchange (Earl, et al., 1979). The high Ca-P content of the temperate soils (to be presented later) indicates that P availability was mainly controlled by solubility (Welp, et al., 1983). Differences in P acquisition by the rape plant from the various soils was therefore a function of the predominant phosphate fractions. The acquisitive power of

Table 4.6.2: Dry matter yield, plant nutrient concentration and uptake for maize and rape at 7 and 14 day growth periods in the growth chamber.

		Concentration in plant			Total uptake		
Soil	DMYLD	P	N	Zn	P	N	Zn
	g pot^{-1}	%	%	µg/g	mg pot^{-1}		
			Rape 7 days				
NatCrA	2.26	0.27	5.58	247	6.08	131	0.56
NatCrB	2.07	0.18	5.46	220	3.64	113	0.46
NatAmA	2.13	0.21	5.68	194	4.52	121	0.41
Pedon 1	2.19	0.20	5.36	258	4.27	117	0.57
Danish I	2.50	0.31	5.77	227	7.78	144	0.57
Danish II	2.47	0.47	5.88	212	11.68	145	0.52
			Rape 14 days				
NatCrA	3.60	0.30	5.73	164	10.76	206	0.59
NatCrB	3.77	0.20	5.32	142	7.73	200	0.53
NatAmA	4.00	0.24	5.52	215	9.63	220	0.86
Pedon 1	3.86	0.20	5.50	285	7.63	212	1.10
Danish I	4.60	0.25	5.63	218	11.68	258	1.00
Danish II	6.58	0.30	5.32	164	20.07	350	1.08
			Maize 7 days				
NatCrA	6.11	0.35	4.13	103	21.38	253	0.63
NatCrB	7.22	0.31	3.72	116	22.67	268	0.84
NatAmA	7.00	0.33	4.12	126	22.82	288	0.88
Pedon 1	6.85	0.38	4.01	130	25.76	275	0.89
Danish I	7.55	0.25	4.00	105	18.87	302	0.79
Danish II	6.29	0.29	3.86	138	18.24	242	0.87
			Maize 14 days				
NatCrA	15.32	0.24	3.21	126	36.10	491	1.93
NatCrB	14.57	0.20	3.33	86	28.40	485	1.25
NatAmA	14.05	0.19	3.34	68	26.10	469	0.95
Pedon 1	13.55	0.19	3.18	60	25.34	430	0.81
Danish I	14.18	0.13	3.28	57	18.43	465	0.81
Danish II	12.80	0.15	3.11	53	19.58	398	0.67
			Control (Pre-experimental harvest)				
Rape	0.71	0.26	6.58	308	1.86	46	0.22
Maize	2.22	0.64	5.42	190	14.18	120	0.42

maize was weaker than rape which invariably reflects the differences in root induced rhizosphere conditions, especially in the secretion of organic acids and root phosphatase (Marschner et al., 1986), that influence the mobilization of soil P by plant roots (Grinsted et al., 1982; Gahoonia et al., 1991).

Table 4.6.2 also showed that the nitrogen content of rape at 7 and 14 days were about similar in all soils, and for maize separately at both time steps. This is an indication that the plants were well nourished by the supply solution, and the NH_4^+ to NO_3^- ratio of the supply solution maintained the pH at the rhizosphere fairly constant (Schjorring and Nielson), which implies that the perculiar cationic and anionic requirements of the respective plants were satisfied. The reaction processes at the rhizosphere were therefore representative of that of a single root of a healthy plant, equipped with root hairs, in a planer rather than a radial dimension.

4.6.3 Mobilization of P in the soils by the growing plants

There was appreciable depletion of P in the rhizosphere, and P depletion decreased with distance from the soil-root interface. Table 4.6.3 shows the total P_i and P_o depleted from the root zones of differing proximity to the root mat for two tropical soils (1 and 2) and the two Danish soils (I & II), for rape at 7 and 14 days, and for maize at 7 days. To produce a healthy growing plant, it was pertinent to include P in the supply solution. Though P balance study was not

Table 4.6.3: Total P_i and P_o depleted in each soil as a function of proximity to the root mat for rape and maize plants.

Distance (mm)	NatCrA		NatCrB		Danish I		Danish II	
	P_i	P_o	P_i	P_o	P_i	P_o	P_i	P_o
	total µg P							
				Rape 7 days				
0.0 - 0.4	39.6	-21.0	10.2	-2.2	79.8	-16.3	100.4	-8.9
0.4 - 1.0	40.2	-13.6	8.4	4.1	82.7	-1.8	104.1	1.3
1.0 - 2.5	26.3	3.1	1.0	14.2	113.8	19.3	136.6	12.0
2.5 - 5.0	5.1	98.3	6.9	34.4	38.5	29.4	69.8	8.4
Total	111.2	66.8	26.5	50.5	314.8	30.6	410.9	12.8
				Rape 14 days				
0.0 - 0.4	47.3	-42.4	10.7	-6.9	121.6	-27.0	332.2	-84.3
0.4 - 1.0	64.1	-49.6	2.0	-2.6	159.0	-11.8	383.2	-73.0
1.0 - 2.5	49.1	-83.0	14.2	-5.5	247.3	17.4	400.2	-30.1
2.5 - 5.0	25.6	-18.9	4.7	20.9	121.0	104.9	127.0	-20.0
Total	186.1	-193.9	31.6	5.9	649.0	83.5	1242.6	-200.4
				Maize 7 days				
0.0 - 0.4	28.5	-4.1	8.1	-2.0	-	-	-	-
0.4 - 1.0	9.0	-3.1	0.9	5.3	-	-	-	-
1.0 - 2.5	-1.5	15.8	-0.6	12.3	-	-	-	-
2.5 - 5.0	5.1	30.6	0.2	25.5	-	-	-	-
Total	41.1	47.7	8.6	41.1	-	-	-	-

conducted, Gahoonia et al., (1992) had shown that P depletion can be used as an indicator of P mobilization in a temperate luvisol. The magnitude of P depleted was a reflection of the interaction between the differential uptake potentials of the crops and the labile P status of the soils. The depletion zone of the inorganic P (P_i) extended beyond the 5 mm distance considered in this study. The amount of P_i depleted increased with time for both crops as should be expected. The organic P (P_o) was also depleted appreciably from distances away from the root surface at 7 days for both crops with resultant accumulation at the root surface. This invariably implies that P_o was mobilized from distances exceeding 5 mm, with concomitant transport to the soil-root interface to account for the P_o accumulation. Comparatively, phosphate depletion and/or accumulation at the rhizosphere was greater with rape than with maize, a reflection of their relative P acquisitive power.

The depletion and/or accumulation of the various P_i and P_o fractions by rape and maize as a function of proximity to root surface are illustrated in Figures 4.6.1 and 4.6.2. For a tropical soil of same mineralogy, differing in the OM content (NatCrA and NatCrB), it was clear that the rape plant was more efficient in mobilizing native P from the soils. Because of its low acquisitive power, the maize plant seemed to switch effectively to depend on the P_o fraction for its P requirements in P deficient soils, a mechanism that modifies the available phosphate pool to suit the competitive capacity of the plant in conditions of P stress.

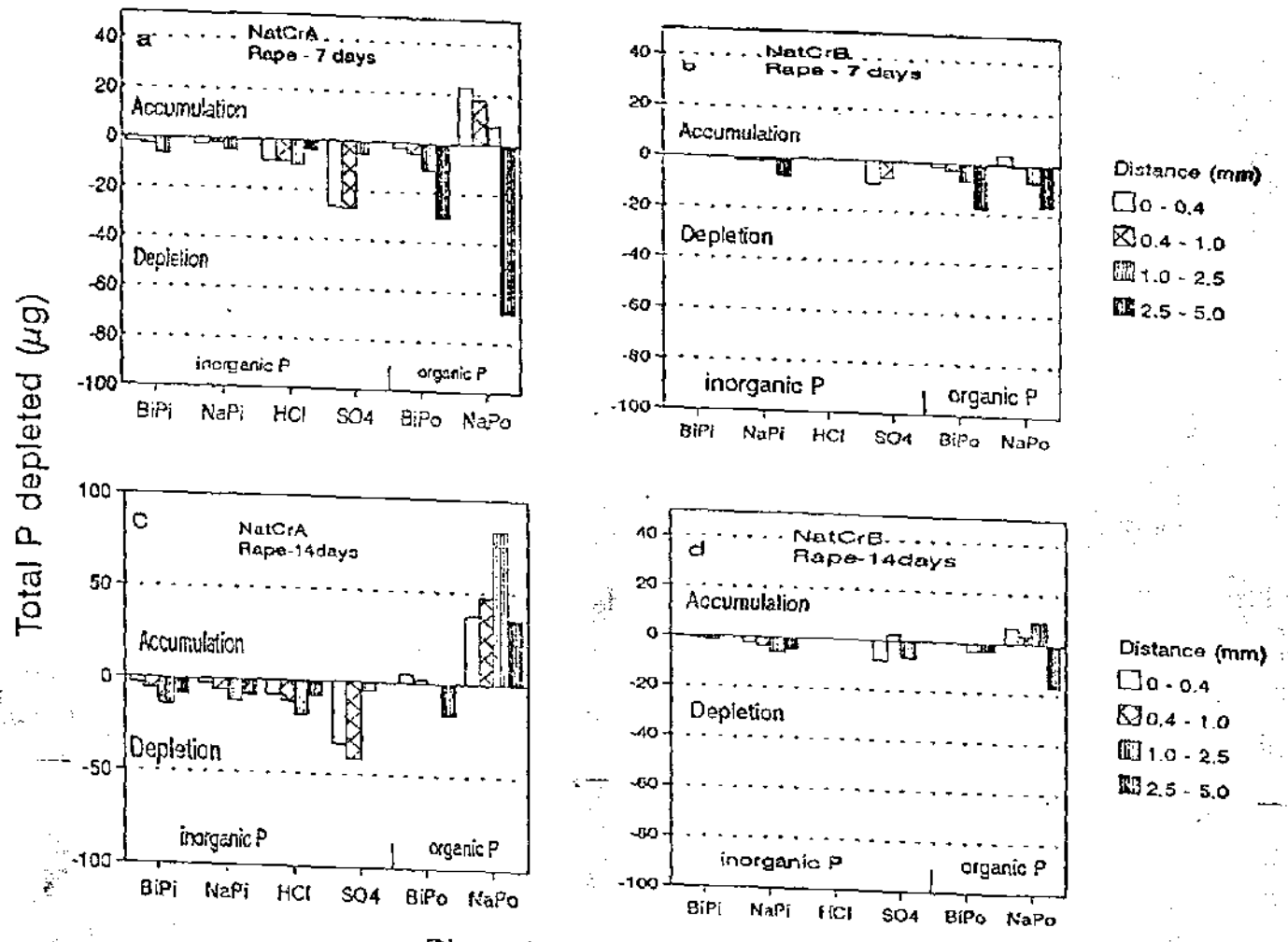


Figure **4.6.1:** Total depletion of phosphate fractions by rape as **function of proximity** to root surface at 7 and 14 days in selected soils.

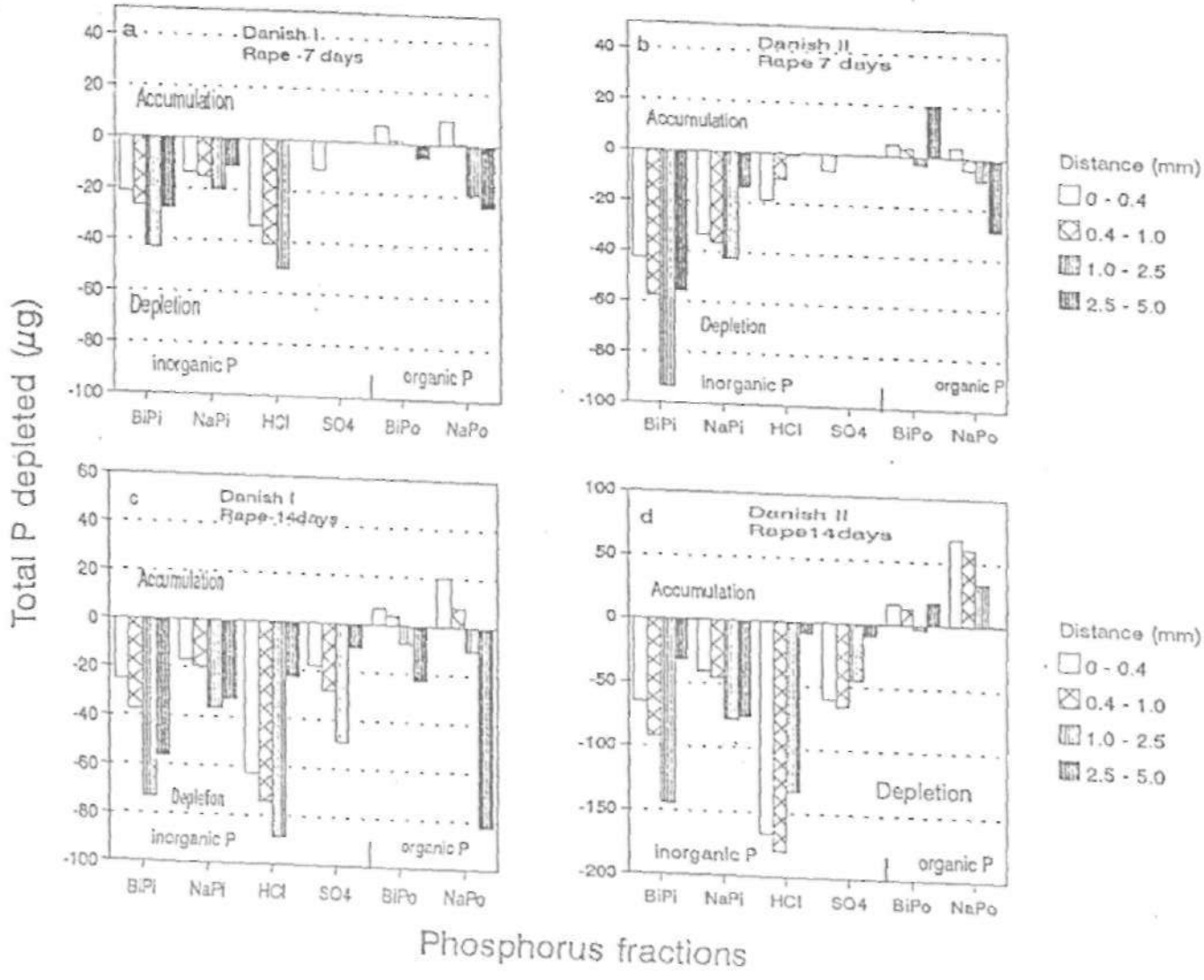


Figure 4.6.1 continues.

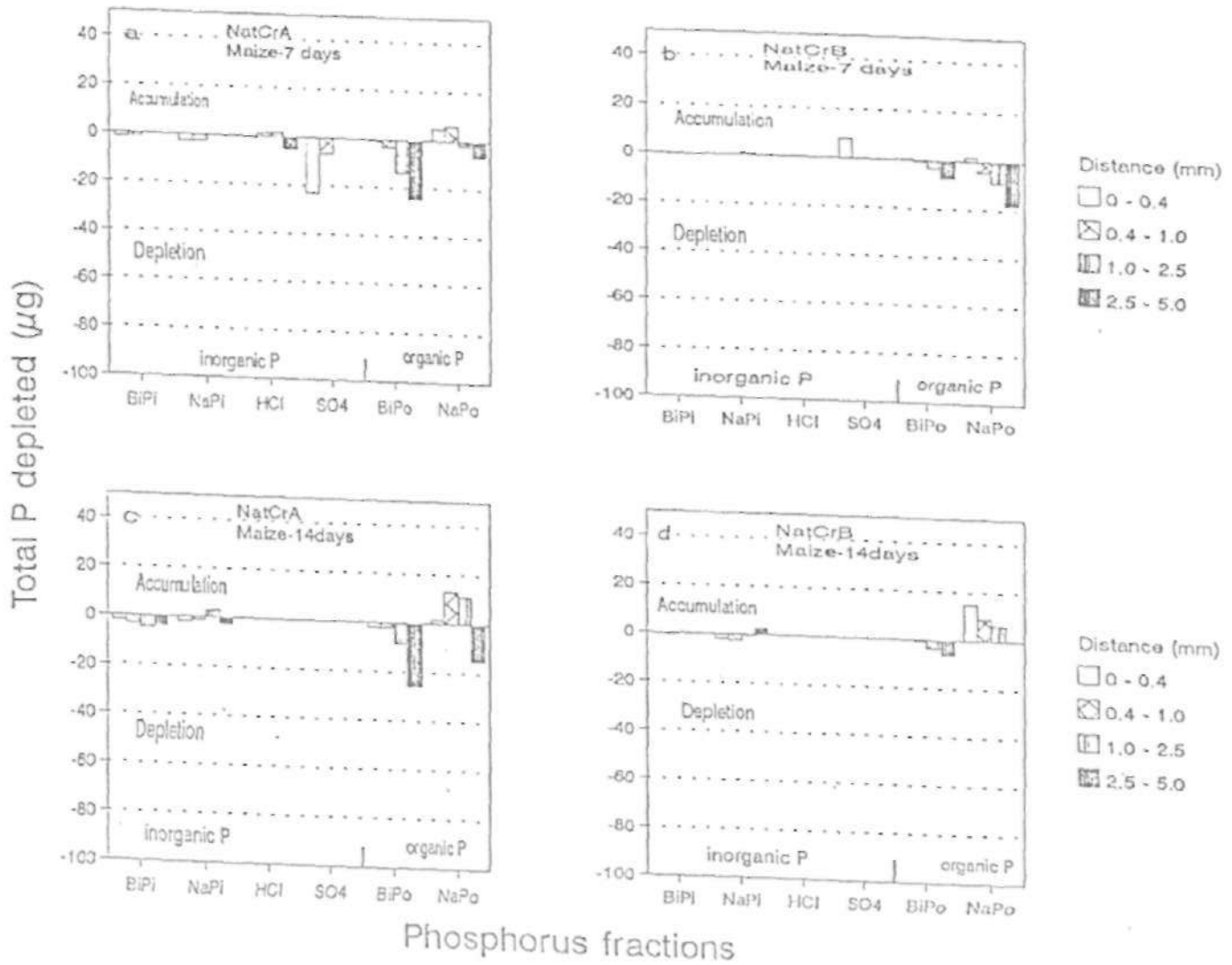


Figure 4.6.2: Total depletion of phosphate fractions by maize as function of proximity to root surface at 7 and 14 days in selected soils.

Rape depleted considerable amount of P from all P_i fractions and from the residual P (H_2SO_4-P) from all rhizosphere zones considered in soil I (NatCrA). Relative mobility of the $NaHCO_3$ and NaOH P_o fraction differed indicatingconsiderable transformation, transport and mineralization of the $NaHCO_3$ P_o fraction in this tropical topsoil. Due to the low labile P status of soil 2, uptake preferences seem to differ slightly. P mobilization from the P_o and residual fractions were significant in this soil low in OM. This results substantiates the classical opinion that limited P supply induces physiological changes related to P acquisition, such as the induction of microbial and root phosphatase (Helal and Sauerbeck, 1989; Helal and Dressler, 1989).

In the temperate soils, there were substantial depletion from the $NaHCO_3$-P and HCl-P fractions. The NaOH P_i and the residual fractions contributed less to P depleted by rape especially in the more fertile Danish soil II. The P_o fractions were less important in these apparently rich soils.

Organic phosphate (P_o) accumulation in the soil-root interface was generally observed in all soils. However, due to high phosphatase activity in the rhizosphere, an accumulation of P_o in a free state in this zone was considered unlikely. Helal and Dressler (1989) and Helal and Sauerbeck, (1984) suggested that these fraction might have been extracted partially from the microbial biomas.

Table 4.6.4 shows the relative importance of the P_i and P_o fractions. In the fertile Danish soils, rape preferentially

Table 4.6.4: Relative contributions of the inorganic and organic phosphate forms to the phosphate pool depleted by the plants.

	P_i	P_o	Total P depleted
	%		µg P
NatCrA			
Rape - 7	62.5	37.2	178.0
Rape - 14	100.0	0.0	-7.8
maize - 7	46.3	53.9	88.8
NatCrB			
Rape - 7	33.0	66.9	76.9
Rape - 14	83.8	16.1	37.6
Maize - 7	16.6	83.4	49.4
Danish I			
Rape - 7	91.5	8.5	344.2
Rape - 14	88.6	11.4	732.5
Danish II			
Rape - 7	97.2	2.8	422.9
Rape - 14	100.0	0.0	1095.3

Highlighted '0' values, and negative values were accumulations.

depleted the P_i fraction. About 90-95 % of P mobilized in these temperate soils was inorganic. The P_o fraction depleted was insignificant (<10 %), even at later growth stages (14 days). It must however be emphasized that there is a constant flux between fractions, even in the mineralization and turnover of P_o in the rhizosphere. The net effect seem to indicate P_i as the dominant contributor to the available phosphate pool in these fertile soils.

In the tropical soils, contrary to established concept, the contribution of the P_o fraction was tremendous. With rape,

the contribution of the P_i fraction to P mobilized increased with time in both soil that differed in OM content. At 7 days, the P_o fraction contributed substantially to the P nutrition of rape, especially in the subsoil (67%) relative to the top soil (37%). The net contribution of P_o decreased with time, all of which go to suggest the importance of organic phosphates at the rhizosphere in these P deficient tropical soils. With time, there was considerable mineralization of P_o to P_i forms which were readily available to the plants. The high active role of P_o in tropical acid soils has long been recognized (Adepetu and Corey, 1976; Anderson, 1980; Tiessen et al., 1984). Plant demand for P regulate the mineralization of P_o for increased P absorption (Barber, 1980), by increased production of phosphatase enzymes (Bieleski and Johnson, 1972; Cole et al., 1977). In P deficient soils, Olsen and Wanatabe (1963, 1966) showed that the P_i values along with the capacity and diffusive characteristic were far too low to account for plant responses without considering the mineralization of a labile P_o pool. This was evident in the tropical subsoil for rape. For maize, 83 % and 54 % of P mobilized at 7 days was organic in the tropical subsoil and top soil respectively.

Results in this study show that in P deficient soils, to satisfy the short-term P requirement of a crop like maize, considered a heavy feeder, requires considerable transport of P to the roots which can be effectively carried out in organic forms. The high concentration of 2 - ketogluconic acid in the rhizosphere of wheat, a cereal, has been associated with increased P uptake (Moghimi et al., 1978). The maize and the

rape plants, belonging to different plant species may rely on different native phosphate forms as the predominant P sink for their uptake. This will be discussed subsequently in the section for lability of P forms.

4.6.4. Phosphate depletion Profiles.

Due to the low mobility of P in soils, a depletion zone evolves in the rhizosphere of soil grown roots (Jungk and Claassen, 1989). A three point technique was used to characterize P the depletion profiles in this study. By the principle of regeneration of Nielsen (1984) and the plant growing and thin slicing technique of Gahoonia and Nielsen, (1991), rhizosphere samples of healthy growing rape and maize plants, differing in proximity to the root surface, were generated. The P fractions of the generated samples were subsequently characterized by a modified fractionation scheme of Hedley et al., 1982).

Previous evaluations of P depletion profiles have used P deficient plants (Kuchenbuch and Jungk, 1982, Gahoonia, 1987). The depletion profiles are bound to differ from that of a healthy growing plant root as used in this study. The P supply and uptake mechanisms can therefore be better understood, on which more realistic indices for fertilizer recommendations and yield maximization can be based. This section describes the depletion profiles of the different P fractions that differ in lability in the various soils of varied fertility and origin.

4.6.4.1. Depletion of $NaHCO_3$ P_i

In the tropical Fe-crystallized surface soil (NatCrA, Fig. 4.6.3 a) the rape and maize plants exhibited characteristic profile that intensified in size with time. The depletion zone of rape was considerably larger than maize in this soil which could be attributed to the difference in their acquisitive power.

In comparison, the pattern of depletion in the tropical crystalline Fe dorminant subsoils differed (Figure 4.6.3 b). P accumulation at the root surface reflects a highly induced mineralization of P_o to P_i to partially meet the plant needs in this P deficient soils. The pattern for both maize and rape were similar at 14 days, but the morphological characteristic of rape root-hairs shown by the zone of exploitation, reveals the superior acquisitive power of rape over maize.

Figure 4.6.3 d-f show the depletion in the more fertile soils (Soils 4-6). More P_i was depleted in these soils, and the size of the depletion profiles were larger. The depletion zone was in excess of 5 mm in the Danish soils, and was less than 1 mm for maize in all soils.

Results show that the P dynamics in the rhizosphere is tremendous, and the transformation and mineralization products were extractable by the $NaHCO_3$ reagent. This was highly emphasized in the P deficient tropical soils where the products of transformation/mineralization could be detected at the soil-root interface. The fact that such accumulation were not detected at the soil-root interface of the more fertile soils strongly implicates the P_o pool in the $NaHCO_3$ P_i activity

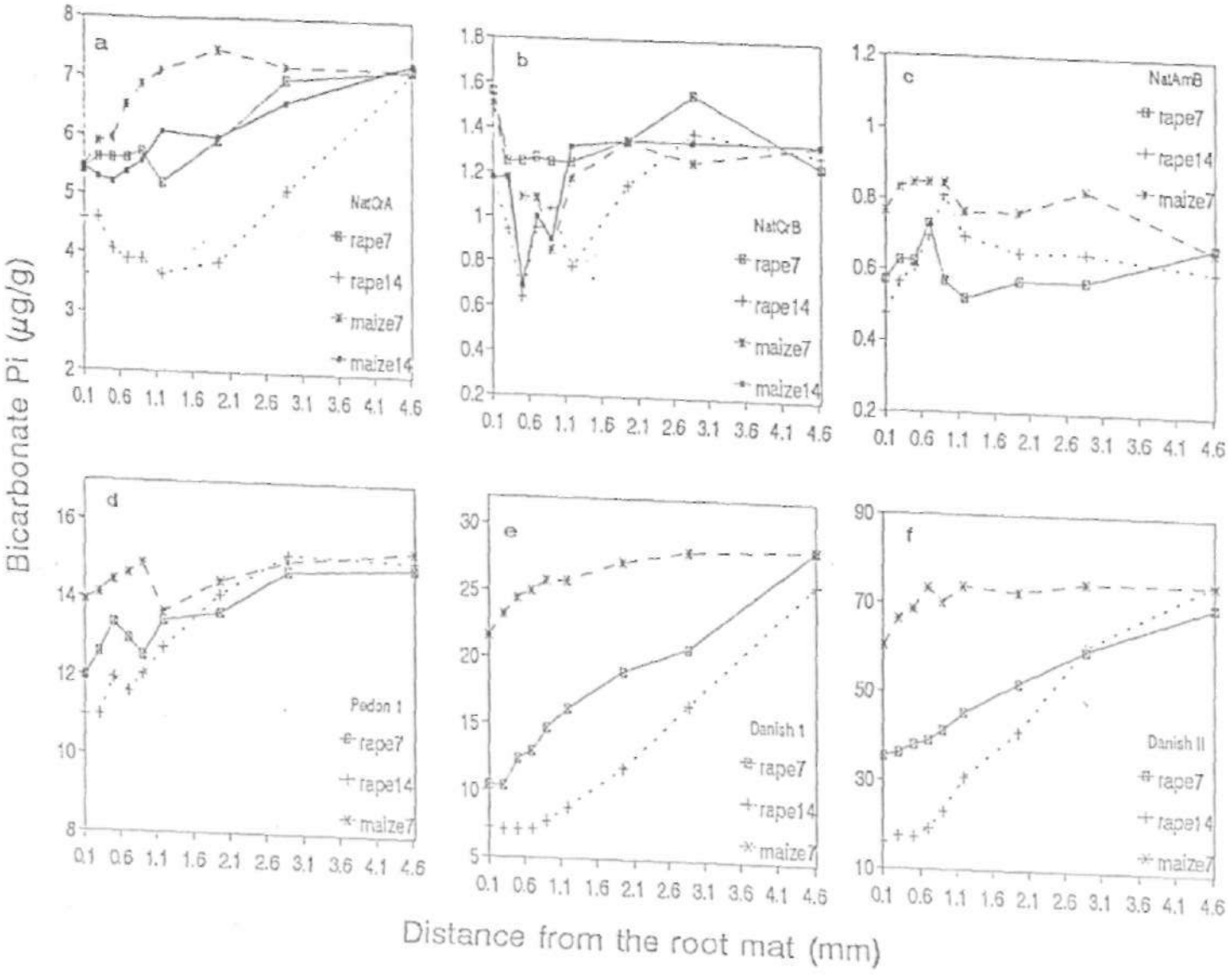


Figure 4.6.3: Bicarbonate P_i depletion profiles of the soils.

in the rhizosphere.

4.6.4.2 Depletion of $NaHCO_3$ P_o

The depletion and/or accumulation profiles for $NaHCO_3$ extractable P_o, the P_o fraction sorbed on soil surface, plus some microbial P (Bowman and Cole, 1978), for the soils are presented in Figure 4.6.4. a-f. In all soils, except soil 3 (the Fe amorphous tropical subsoil low in available P), the accumulation of P at the rhizosphere with concomitant depletion of this fraction at distances from the root mat was consistent. The composition of this P_o fraction has been shown to include nucleic acid - P, sugar - P, Lipid - P, phytins (inositol phosphates) and other high molecular weight P compounds (Thomas and Bowman, 1966; McKercher, 1968), which are quickly mineralized.

Figure 4.6.4. a-f reveals considerable transport of P_o to the root surface. Results show that there was some depletion of $NaHCO_3$ P_o in the tropical amorphous subsoil by rape. Net accumulation of P in the rhizosphere of maize was observed however.

4.6.4.3. Depletion of NaOH P_i and Po, HCl and Residual fractions.

The depletion profiles of NaOH P_i and P_o, and the residual fractions in a tropical top and subsoil are shown in Figure 4.6.5 for illustration.

The depletion of the NaOH P_i fraction in tropical savanna soils high in Fe and Al oxides were low, and the maize plant

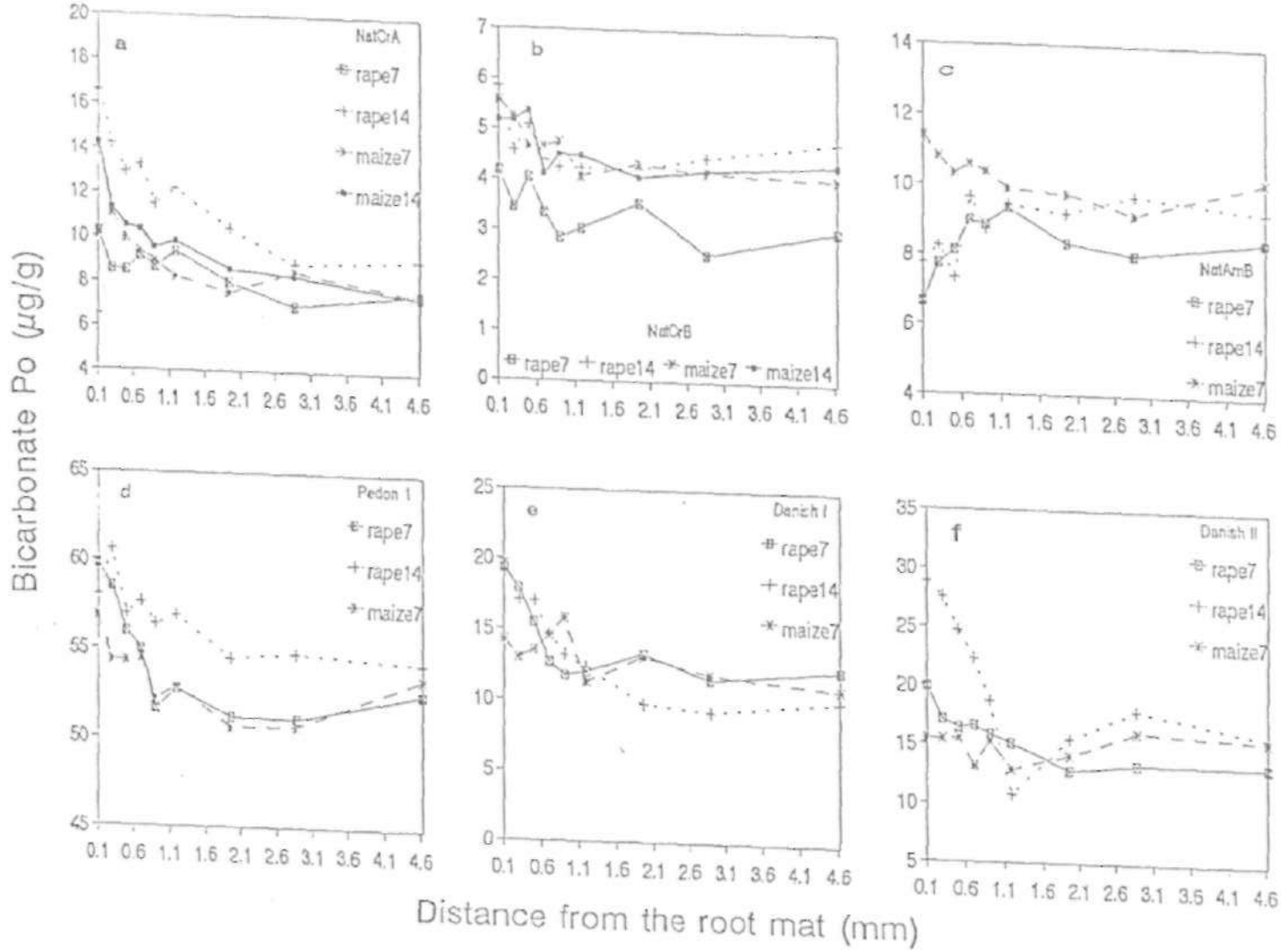


Figure 4.6.4: Bicarbonate P_0 depletion/accumulation profiles of the soils.

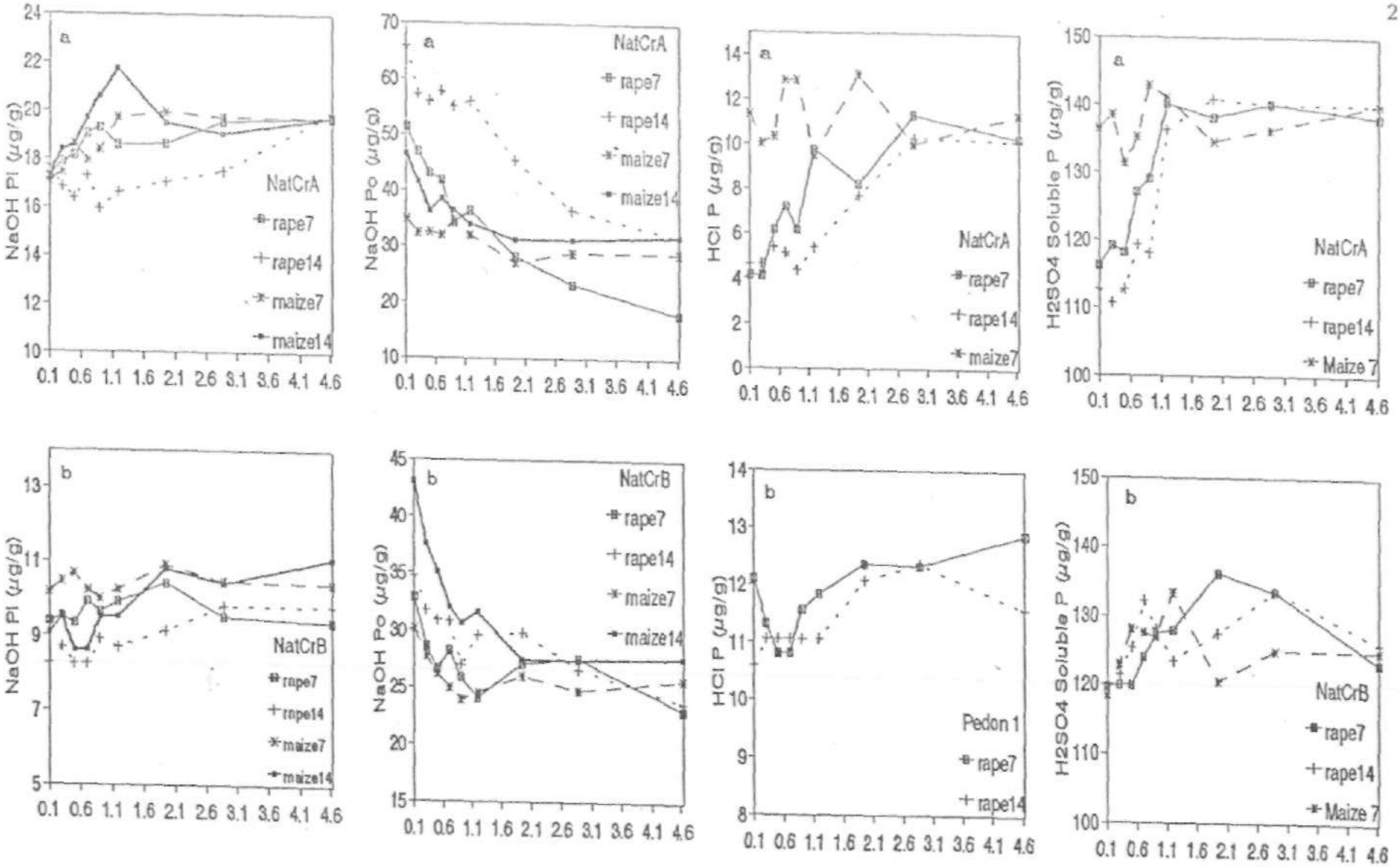


Figure 4.6.5: Phosphate depletion profiles for NaOH P_i and P_o, HCl and residual fractions in two tropical soils

preferentially depleted this fraction compared to rape. P sorbed on Fe and Al surfaces, are rendered available essentially by ligand exchange with organic acids, secreted in higher amounts in the rhizosphere of cereals than of legumes (Moghimi et al., 1978).

Consistent with the organic P fractions, there was net accumulation of the NaOH P_o fraction at the root surface. P_o accumulation across the 5 mm rhizosphere soil increased with time, indicating possible transportation from distances, orinduced transformation of other more stable fractions.

The HCl P which is largely Ca-bound P, was absent in the tropical sub soil, low in the tropical top soil but was high in the Danish soils This fraction was preferentially depleted by rape but was only slightly depleted by maize. HCl-soluble P accumulation in the high clay tropical soil was observed.

Substantial depletion of the fraction was found for rape in soil I and the Danish soils (Soils 5 and 6) and for maize in the soils low in organic matter (Soils 2 and 3). In P deficient soils, this fraction could become important as a reliable source to replenish the available phosphate pool.

4.6.5. Turnover and transport of P in the rhizosphere

The flux of P between the various fractions and the transport of P in the rhizosphere could be determined by considering the percentage depletion or accumulation of P as a function of proximity to the root surface. Activities in the rhizosphere of rape and maize will be described in this section.

4.6.5.1 Turnover of P in the rhizosphere

Figure 4.6.6 shows the percentage distribution of P forms in the rhizosphere soil as function of proximity to root surface for rape at 7 and 14 days of growth. As shown, the percentage of the P_i fractions depleted in each rhizosphere zone increased with time from 7 to 14 days in each soil. The fact that non of the P_i fractions estimated even at 14 days was in excess of 100 % was a clear indication that mineralized P was continuously taken up by the active plant roots. Thesubstantial increase of the bicarbonate P_i fraction at 14 days in soil NatCrB (a low P status soil), despite increased root activities at this stage, indicate a tremendous turnover of P to this fraction, and could represent a transient sink of mineralized and solubilized P for plant uptake. The build-up of the NaOH P_i may have been the result of temporal contributions from solubilized sources which were resorbed on surfaces of Fe and Al oxides.

Most of the detectable changes in P fractions occurred in the organic fractions. Though the P_o fractions were of less importance in the fertile temperate Danish soils, the nature and positional depletion of P_o in the rhizosphere strongly suggest concomitant depletion, transport and accumulation of P at the root surface.

In the P deficient tropical top and subsoils (Figure 4.6.6 a,b,e and f), the bicarbonate P_o (BP_o) was substantially depleted at 7 days. At 14 days the concentration of this fraction was drastically reduced, with net accumulation at the

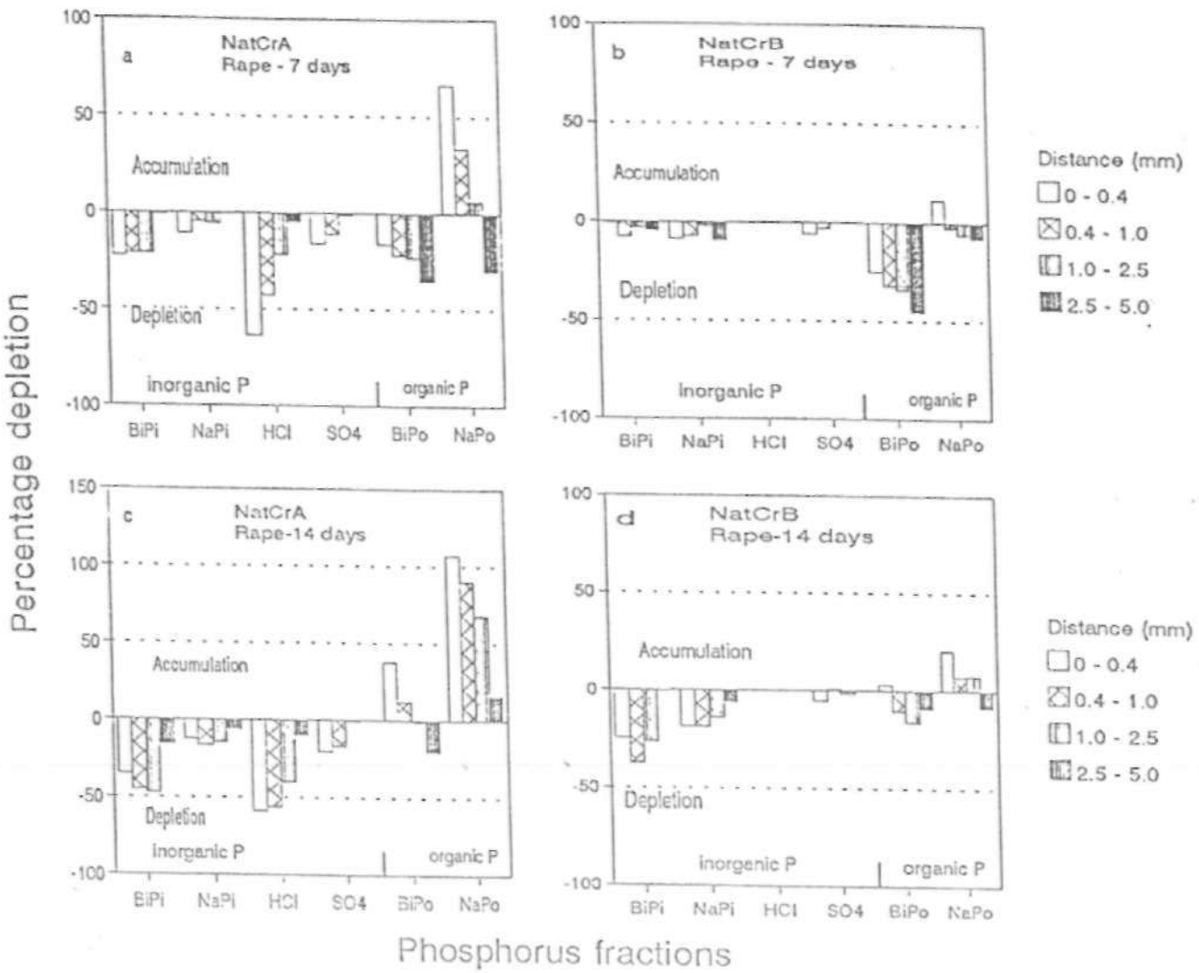


Figure 4.6.6: Percentage depletion of the various fractions as function of proximity to the root surface in 5 mm of rhizosphere soil: Rape.

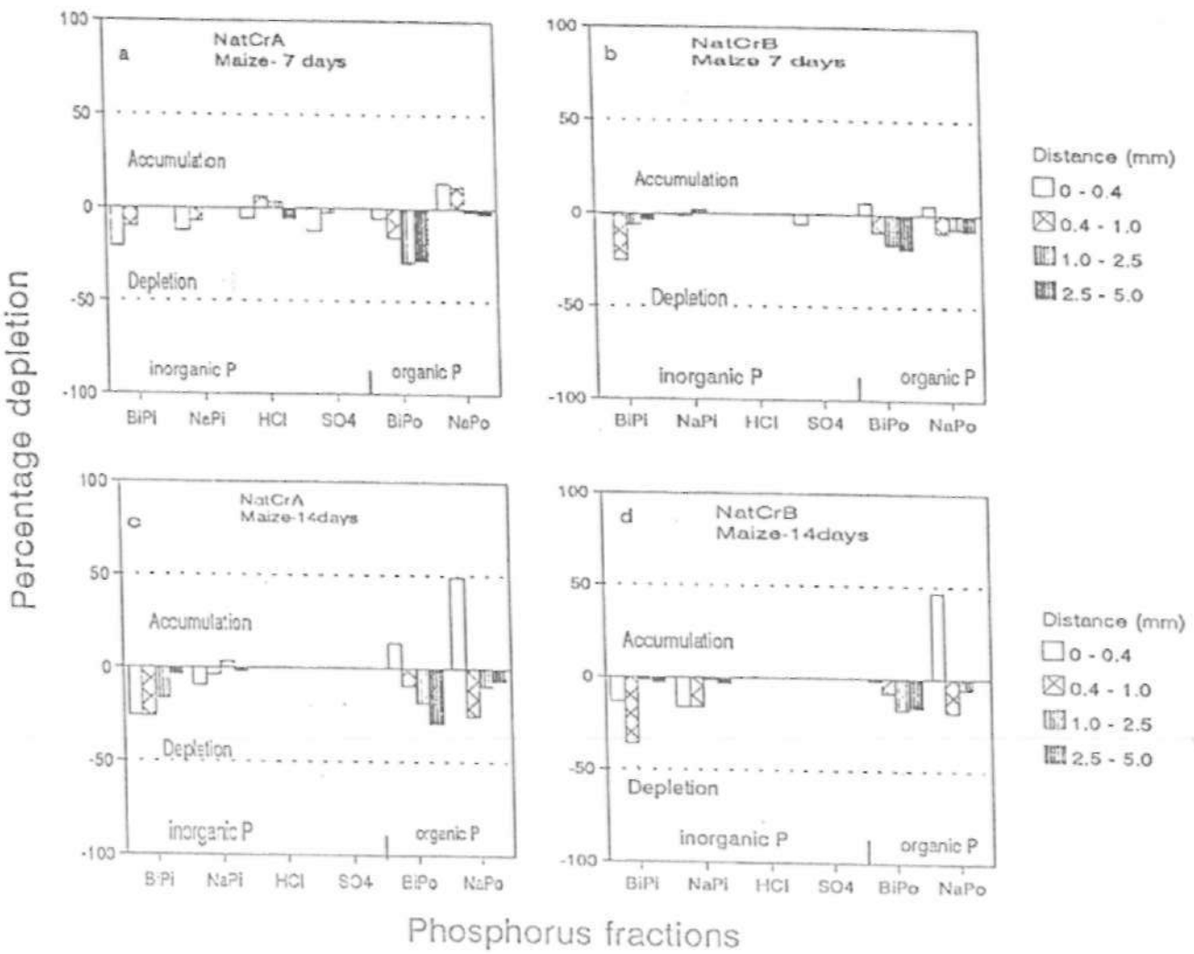


Figure 4.6.7: Percentage depletion of the various fractions as function of proximity to the root surface in 5 mm of rhizosphere soil: Maize.

surface. This is a clear indication of the transformation of this fraction, possibly to the readily utilizable P_i forms. The NaOH P_o fraction accumulated with time, indicating that this fraction was not transformed at the same rate as the $B_i P_o$ fraction to P_i, invariably indicating that it was the more stable fraction in comparison to the $B_i P_o$ fraction.

Results obtained with the maize crop in the tropical soils (Figure 4.6.7 a-d) were consistent with that of rape. The P_o fractions differed also in their relative importance since the $B_i P_o$ fraction seemed more readily mineralized. The products of P_o mineralization were essentially P_i extractable in 0.5 N $NaHCO_3$ and the 0.1 N NaOH reagents. These results corroborates earlier works (Hedley et al., 1982; Tiessen et al., 1984; Menon et al., 1991; Thien and Myers, 1992; Bowman and Cole, 1978). The results further revealed that the transformation, transport and availability of P forms was higher in the tropical topsoil than in the subsoil, low in OM. This is consistent with the reports of Thien and Myers (1992), Chauhan et al., (1979; 1981), Hedley et al., (1982).

4.6.5.2. Transport of P in the rhizosphere.

It is evident from the results of sections 4.6.2, 4.6.3 and 4.6.4, that the decrease in P_i at distances away from the root mat was rather limited in comparison to the P_o fractions that showed significant accumulation at the root surface. This reflects the low diffusive rate of P_i fractions (Nye and Tinker, 1977; Hendriks et al., 1981). Quite a sizeable amount of P depleted at distances in excess of 3 mm from the root mat

was in the organic form, indicating enhanced transport of P_o. In an explanation, Helal and Dressler (1989) advocated that the high microbial activity in the rhizosphere and the related turnover of P_o suggest a transient occurrence of soluble organic P in soil solution either as microbial metabolites, or as products of decomposition of OM.

As shown by Hannapel et al., (1964) and Helal and Dressler (1989), low molecular organic phosphates are readily translocated in soil. The intensity of accumulation (profile gradient) was higher in the organic matter soils (topsoils) than in the subsoils. The effects of the amorphous oxides clay further reduced P accumulation at the surface, as shown in soil NatAmB. Organic matter management is therefore crucial for efficient utilization of P in P deficient tropical soils.

4.6.6. Lability of P forms in soil.

The relative lability of the various phosphate fractions was determined by considering the relative contributions of the Hedley fractions depleted by the test plants. Evidence from the last four sections has shown considerable synthesis and transformation of P_o, and the preferential depletion of the P_i fraction for short-term uptake. Graphic illustrations in sections 4.6.3, 4.6.4 and 4.6.5 indicate clearly that the B_iP and HCl-P fractions were the most labile, while the NaOH P_i was only moderately labile. The contribution of the residual fraction was only significant in the P deficient tropical soils. It shows therefore that possible exhaustive depletion

of the labile fractions could induce the non-labile fractions to become labile. The lability of the residual fraction could be dependent, therefore, on the amount of readily available P fractions of soils.

Table 4.6.5 shows the relative contributions of the various P_i fractions (including the residual fraction) to total P_i depleted in the soils. With due recognition of the complexity of P reactions in tropical soils, true evaluation of the relative lability of the fractions can be deduced from the situation in the Danish soils. The lability ranking for

Table 4.6.5: Percentage contributions of the inorganic and residual factions to total P_i depleted in 5 mm of rhizosphere soil.

	Bicarb. P_i	NaOH P_i	HCl	H_2SO_4	Total P_i depleted
	% of total P_i				µg
NatCrA					
Rape - 7	10.4	8.6	28.1	52.9	111.1
Rape - 14	16.9	15.7	24.8	42.5	186.1
maize - 7	7.5	13.0	7.5	72.0	41.1
NatCrB					
Rape - 7	0.0	39.8	0.0	60.6	26.4
Rape - 14	8.9	51.9	0.0	39.1	31.5
Maize - 7	16.5	0.0	0.0	83.5	8.2
Danish I					
Rape - 7	37.8	18.8	39.9	3.5	314.8
Rape - 14	29.6	16.2	38.2	16.0	649.0
Danish II					
Rape - 7	60.8	30.4	7.1	1.6	410.9
Rape - 14	26.9	19.3	39.3	14.5	1242.6

Highlighted '0' values were accumulations.

rape in the Danish soils was HCl-P > $B_i P_i$ > NaOH P_i > H_2SO_4-P at 14 days. The HCl-P (Ca-P) and the bicarbonate P_i were the most labile fractions. As was the case in Danish II where the available P status was high, the $B_i P_i$ fraction was superior in lability at 7 days, but was quickly depleted. This goes further to support the fact that P transformation is a necessary mechanism for plants to meet their P requirements over time, especially in the more deficient soils.

In the tropical soil system where P deficiency may reach acute levels, the order of lability may be rather complex and inconsistent depending on P stress. This could induce physiological changes in the plant and in the P acquisition potential (Helal and Sauerbeck, 1989). In these soils the residual fraction contributed significantly to P_i depleted by both maize and rape plants. The composition of this fraction has not been fully known, but is considered stable. With due consideration to this fact, the order of lability in the tropical topsoil was $B_i P_i$ > HCl-P > NaOH P_i = $B_i P_o$. The accumulation of $B_i P_i$ (Al-P) in the subsoil at 7 days for rape suggest possible transformation of the less labile fractions to this fraction. The NaOH P_i fraction was superior for maize, possibly because of its high P requirement and larger turnover of the NaOH extractable P in comparison to the $NaHCO_3$ extractable P, indicating the significant role of soil micro-organisms in the nutrition of the maize plant.

Table 4.6.6 shows the comparative lability of the organic fractions. The fact that the $B_i P_o$ was of higher lability was

unquestionable. However in soils highly deficient in P, the NaOH P_o fraction was found to be superior for maize.

It is possible to infer from these results that $B_i P_o$ fraction contributes substantially to the available inorganic P pool under the influence of maize roots. The NaOH P_o was less important, except in P deficient soils, and for crops with high P requirement like maize. In some classical studies, Halm et al., (1972) and Cole et al., (1977) demonstrated that organic P interacted with all the inorganic

Table 4.6.6: Comparative net lability of the organic P forms (bicarbonate P_o and NaOH P_o) as shown by the relative amounts depleted or accumulated in 5 mm of rhizosphere soil, after 7 and 14 days of growth of maize and rape in the growth chamber.

	Bicarb. P_o	NaOH P_o	Total P_o
	%		total µg
NatCrA			
Rape-7	70.9	29.1	66.2
Rape-14	100.0	0.0	-193.9
Maize-7	94.3	5.7	47.7
NatCrB			
Rape-7	58.1	41.9	50.6
Rape-14	100.0	0.0	5.9
Maize-7	27.4	72.5	41.2
Danish I			
Rape-7	0.0	100.0	30.6
Rape-14	23.1	76.9	83.5
Danish II			
Rape-7	0.0	100.0	12.8
Rape-14	0.0	0.0	-207.4

Highlighted zero values and negative values indicate accumulations.

P fractions. In this study, all the P_i fractions were depleted, with the residual fraction assuming high importance in the P deficient tropical soils. The fact that a large fraction of soil P was in the residual fraction, accords prominence to the quantity factor in the scheme of P availability in soils. In general, the HCl-P, $B_i P_i$, NaOH P_i and $B_i P_o$ fractions contributed significantly to the depletion pool and so could be considered to constitute the conceptual pool of available P, with modifications induced by P status and plant species. In tropical soils, the available phosphate pool for rape varied slightly from that of maize, implying that both crops may not have competed for the same source of P. This therefore could be the underlying concept that explains the compatibility of crops in inter-crop that characterize the farming systems of tropical peasant agriculture. Cowpea and cereals in inter-crop have been shown to be perfectly compatible in tropical farming systems, and yield of both crops were always enhanced by the association (Steele, 1972; Phillip and Norman, 1961; Singh, 1974; Uyovbisere et. al., 1993). If crop species take up nutrient from different fractional sources, then yield reduction even at optimum sole crop population for each crop in association may be unlikely, so long as there is mutual compatibility. This hypothesis provides scope for future work.

CHAPTER 5

5. SUMMARY AND CONCLUSION

The widespread deficiency of phosphorus in the highly weathered soils of tropical Africa constitutes a serious limitation to food crop production in the region. Soil solution phosphorus is often low and insufficient to meet crop requirements because Al and Fe oxides sorb P strongly.

Good management practices can improve the availability of phosphate, but such management practices should be based on a sound knowledge of the soil reaction processes that control P availability. This study was initiated to test the application of phosphorus sorption isotherms for evaluating the phosphorus supplying capacity of soils, and to determine the lability of phosphate fractions. The objective is to generate P prediction indices, and determine the influence of OM on P sorption and release to plants.

Three typical soils on basement complex from Nigeria, that differed in OM content and forms of the oxides were used. These were: a Kanhaplic Haplustalf and an Acquic Kanhaplustalf from the savanna, and a Kandiustalfic Eustrustox, a rain forest Oxisol. Change in OM content down the profile provided variation in this property by which the influence was evaluated. For a better understanding of soil sorption reactions, 10% Al containing Fe oxide modified (artificial) soils, made to simulate selected natural soils in oxide crystallinity and OM content, were used to generate indices in the laboratory and in the greenhouse. To evaluate the

lability of P forms, two Danish (temperate) soils were introduced for comparison with the tropical soils.

The natural soils were acid to slightly acid in reaction, while the modified (artificial) soils were slightly acid to neutral in reaction. Mineralogical analysis revealed that the soils were kaolinitic, with haematite, goethite and ferrihydrite as common accessory minerals. Distribution of Fe oxides showed that Fe_d was dominant in the well drained profiles. The Fe_{ox} content of the soils was low in comparison, but amounts in the forest Oxisol was considerably greater than the savanna Alfisol of comparable drainage, implying that both soils should react differently.

The first section dealt with the native P status, phosphate sorption reactions and relationships. Total P (P_T) content of the surface soils ranged from 251 - 737 µg P/g for the pedons, with P_o constituting 25 - 40 % of P_T. The savanna soils were much lower in P. Generally, P_T correlated significantly with Fe_d (r=0.70**), Fe_{ox} (r=0.49*) and Al_{ox} (r= 0.65**). Results obtained in all systems showed that soil texture, OC and the amorphous oxide fractions greatly influenced specific surface area and ZPC, known to control P reactions in the soils. However, the effects due to Fe_{ox} on P adsorption was much greater than OM. Quantitatively, about 72 % of P sorbed was attributed to the amorphous oxide content, and 30 % of this was shown to be due to the enhancing effects of OM. There were indications from the results, that organic matter in association with amorphous oxides increased

adsorption, probably because of the inhibition of Fe oxide crystallization.

The adsorption isotherms for the soils differed in slope characteristics. Phosphorus buffering capacity was lower in soils dominated by crystalline oxides, and higher in soils with high amounts of amorphous oxides and low OM. At low P levels, P sorption was adequately described by the Langmuir equation, but not over the entire P concentration range tested, suggesting the existence of two or more energetically different sites on which P is adsorbed. The Freundlich equation modelled the P adsorption better over the range of P concentrations considered. The P_{max}, K, SPR and MBC derived from the Langmuir equation, increased with increase in the free oxide content and decreased with increasing OM. The SPR of the savanna soils ranged from 2 - 388 µg P/g, falling into the low and medium P requirement classifications of soils. The Oxisol sorbed more P (142 - 687 µg P/g) and classified as medium to high, apparently due to higher total oxide and amorphous oxide content.

Adsorption - desorption reactions showed distinct hysteresis especially in the amorphous oxide dominated and low OM soils. The use of adsorption isotherm could therefore underestimate the P requirements of soils.

The second section dealt with the greenhouse evaluation of the response of an index plant to adjusted solution P levels, and the efficiency of selected extractants for determining the P needs of soils. These were carried out using the selected natural and artificial soils. Results

indicate that the soils were P deficient, and when P was not limiting, the productive capacity of the soils increased with increase in buffer capacity. The study therefore demonstrated the usefulness of adsorption isotherm for determining the P needs of soils.

Critical P levels for 95 % of yield maximum ranged from 0.45 - 1.00 µg P/ml, consistent with Udo (1972). At 0.2 µg P/ml, yield levels were 59 - 83 % of yield maximum, which was considered low. In the amorphous oxide dominated soils, 93 % yield enhancement was attributed to OM as against a mere 5 % in low OM soils. The efficiency of P utilization was 2.5 times higher in crystalline oxide dominated topsoil relative to the amorphous oxide dominated topsoil.

Of the soil test methods evaluated, the resin method was more sensitive to buffering, most efficient and best approximated actual plant uptake in absolute values. The resin and water methods extracted P from about the same phosphate pool, and differed from the chemical methods of Bray and Olsen. With all factors considered, the efficiency of the methods were ranked as follows: Resin > Olsen > Water > Bray. The critical soil-test P levels for the natural soils were: 27.6, 9.2, 17.0 and 2.0 µg P/ml in the crystalline oxide dominated soil, and 54.0, 23.9, 38.3 and 1.9 µg P/ml in the amorphous oxide dominated soils in the order listed. The threshold values were not consistent. Regression estimates from the artificial system showed that three times as much P was required for same yield level in the soils high in amorphous oxides relative to the crystalline oxide dominant

soils. Generally, adsorption reactions and crop response of the artificial soils and their natural equivalents were strikingly similar, suggesting that the natural soils were fairly well simulated.

The third section considered the depletion profiles and lability of the Hedley P fractions. The P depletion zone extended beyond 5.00 mm distance, and much of the P depleted at distances in excess of 3.00 mm was organic. This indicates that transformation and transport of P in the rhizosphere was biologically mediated, consistent with P_o accumulation at the root surface. The P_i acquisitive power of rape was stronger than maize. To compensate in P deficient soils, the maize plant switched effectively to mobilize P from the P_o pool. About 90 % of P depleted in the fertile Danish soils was inorganic, whereas the P_o and residual fractions were important in the tropical soils. The bicarbonate P_i fraction was the most labile and constituted the possible transient sink for P transformation and uptake in soils. However, this fraction was quickly depleted by plant roots. This lends support to the mechanisms of P transformation and transport for short term P supply to plants in soils. With due consideration given to the amounts and solubilities of the various P_i fractions, and the importance of the P_o pool, the lability of the fractions were ranked as follows: $B_i P_i$ > HCl-P > NaOH P_i > H_2SO_4-P.

From these results and others presented, the following conclusions were derived:

1. Phosphorus adsorption reactions in tropical soils formed on basement complex are controlled largely by the amounts and crystallinity of soil oxides and OM. The forest Oxisol, with medium - high SPR, sorbed more P than the savanna Alfisol (low - medium SPR), due to the higher content of total and amorphous oxides in the Oxisol. OM reduced P sorption, which implies that P sorption and requirement in soils continuously cropped, were the OM fraction is seriously depleted, are expected to be high. Estimating P requirements of these soils is a complex process, and can only be based on Q/I relationships, derived from sorption isotherms, because of the changing properties of the soils.
2. The Langmuir equation was useful at low solution P levels, but over a larger P range, the Freundlich equation was superior. Since P sorption increases with increase in solution concentration, the Freundlich equation should be appropriate for describing the P sorption reactions of the soils.
3. The soils exhibited considerable hysteresis, indicating strong residual potentials which can be harnessed by proper management of OM.
4. The solution P levels for 95% yield maximum ranged from 0.45 - 1.00 µg P/g under greenhouse conditions, quite in excess of the standard concept of 0.2 µg P/g. Field conditions differ, and results suggest need for calibration for yield level estimation of field crops.

5. The efficiency of the soil test methods were dependent on the buffering capacity of the soils. The resin method was more sensitive to buffering and was superior to other methods tested. The study showed in addition that Bray P_1 may be appropriate for the savanna soils, and the Olsen method for the more buffered soils.
6. All phosphate fractions can contribute to the labile pool depending on the P stress. In P deficient soils, P availability is dictated by P_o. P transport in soils occur largely in the organic phase.
7. The bicarbonate P_i and P_o are the most labile. These fractions represent the transient sink of P transformation products for plant uptake.
8. The P acquisitive power of plants differ, as much as plants differ in P fractions preferentially depleted. Crops not competing for the same fractional P source are expected to be compatible in inter-crop systems.
9. Organic matter conservation and management is fundamental for improving the availability of P in tropical soils.
10. Most Nigerian soils on basement complex are low to medium phosphate sorbing, and would require moderate P fertilizer applications to satisfy crop needs in well managed cropping systems.

REFERENCES

Abbott, J.L. 1978. Importance of the organic phosphorus fraction in extracts of calcareous soil. Soil Sci. Soc. Am. J. 42:81-85.

Ackerson,K. T., Gallup, D. L., Rourke, J. D. and A. J. Vessel. 1968. Soils of the world (map), USDA. Government Printing Office, Washington, D.C.

Adams, J. A., D. T, Howarth, and A. S. Cambell. 1973. Plumbogummite minerals in strongly weathered New Zealand soil. J. Soil Sci. 24:225-231.

Adams, J. A., and T. W. Walker. 1975. Some properties ofchronotoposequence of soils from granite in New Zealand. 2. Forms and amount of phosphorus. Geoderma 13:41-51.

Adepetu, J.A. 1975. Evaluation of the kinetic process involved in phosphorus availability to plant roots in soil Ph.D. Thesis. Purdue University. 1975.

Adepetu, J.A. 1981. Characteristic phosphorus sorption and its implication in soils of Ondo state of Nigeria. Beitr. trop. Landwirtsefi Veterinarmed. 19:291-300.

Adepetu et al. 1979. A. preliminary survey of the fertility status of soils of Oudo State under traditional cultivation. Ife J. Agric. No. 2.

Adepetu, J.A. and R.B. Corey. 1975. Organic phosphorus as a predictor of plant available phosphorus in soils of southern Nigeria. Soil Sci. 122:159-164.

Agbenin, J.O. 1992. Phosphorus fractions, mineralogy and transformation in soils of two catenary sequences from northeast Brazil. Ph.D thesis, University of Saskachewan, Saskatoon, Canada. pp. 233.

Aleksandrova, L.N. 1960. The use of Na-pyrophosphate for isolating free humic substances and their organic mineral compounds from soil. Soviet Soil Sc. 2, 190-197.

Amer, F., Bouldin, D.R., Black, C.A. and Duke, F.E. 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P equilibration. Plant Soil, 6:391-408.

Anderson, G. 1980. Assessing organic phosphorus in soils. p. 411-431. In F.E. Khasawneh, et al. (ed.) The role of phosphorus in agriculture. ASA, CSSA, and SSSA, Madison, WI.

Anderson, G.,E.G. Williams and J.O. Muir. 1974. A comparison of the sorption of inorganic orthophosphate and inositol hexaphosphate by six acid soils. J. Soil Sci. 25:51-62.

Andreasen, A.H.M. 1939. The fineness of solids. Ingeniovidenska-belige Skrifter, No. 3. Copenhagen, 71 pp.

Anonymous. 1964. African soils. Commission for technical cooperation in Africa. Publ. Bureau, London, 156 pp.

Anyaduba, E. T., and J.A. Adepetu. 1983. Predicting the phosphorus fertilization needs of tropical soils: Significance of the relationship between critical soil solution P requirement of cowpea, P sorption potential and free iron content of the soil. Beitrage trop. Landwirtsch Veterinarmed. 21:1-30.

Appelt, H.N.T., Coleman and P.F. Pratt. 1975a. Interactions between organic compounds minerals and ions in volcanic-ash-derived soils: I. Adsorption of benzoate, p-OH benzoate, salicylate, and phthalate ions. Soil Sci. Soc. Am. proc. 39:623-627.

Appelt, H.N.T., Coleman and P.F. Pratt. 1975b. Interactions between organic compounds minerals and ions in volcanic-ash-derived soils: II. Effects of organic compounds on the adorption of phosphate. Soil Sci. Soc. Am. proc. 39:628-630.

Asher, C.J. and J.F. Loneragan. 1967. Response of plants to phosphate concentration in solution culture. I growth and phosphorus content. Soil Sci. 103:225-233.

Ayodele, O,J, and A.A. Agboola. 1983. Evaluation of phosphorus in savannah soils of western Nigeria under bush fallow systems. J. Agric. Sci. (Cambridge) 101:283-289.

Bache, B. W. 1965. The thermodynamics of soil phosphate. Soil Phosphorus, Min. Agric. Tech. Bull. 13,10-18.

Bache, B. W., and C. Ireland. 1980. Desorption of phosphate from soils using anion exchange resins. J. Soil Sci. 31:297-306.

Bache, B.W. and Williams, E.G. 1971. A. phosphate sorption index for soils. J. Soil Sci. 22:281-301.

Bahia Fillio, A.F.C., J.M. Braga, M. Resende and A.C. Ribeiro. 1983. Relation between phosphorus adsorption and clay mineralogical components of Latosols of the Central Plateau of Brazil. R. Bras. Ci. do solo 7:221-226.

Barber, S.A. 1980. Soil-plant interactions in phosphorus nutrition of plants. p. 591-615. In: F.E. Khasawneh et al. (ed.) The role of phosphorus in agriculture. ASA, CSSA, and SSSA, Madison, WI.

Barber, S. A. 1962. A diffusion and mass flow concept of soil nutrient availability. Soil Sci., 93. 39-49.

Barrow, N.J. 1961. Phosphorus in Soil organic matter. Soils Fertil.24:169-123.

Barrow, N.J. 1974. The slow reactions between soils and anions. I. Effects of time, temperature and water content of a soil on the decrease in effectiveness of phosphate for plant growth. Soil Sci. 118:380-386.

Barrow, N. J. 1978. The description of phosphate adsorption curves. Journal of soil Science 29,447-462.

Barrow, N.J. 1980. Differences amongst a wide ranging collection of soils in the rate of reaction with phosphate. Fert. Res. 4:51-61.

Barrow, N.J. 1985. Reactions of anions and cations with variable charge soils. Adv. Agron. 38:183-230.

Barrow, N. J., and T. C. Shaw. 1977. Factors affecting the amount of phosphate extracted from soil by anion exchanage resin. Geoderma 18:309-323.

Barrow, N. J. and Shaw, T. C. 1975. The slow reactions between soil and anions: 5. Effects of period of prior contact on the desorption of phosphate from soils.l Soil Sci. 119, 311-20.

Bar-Yosef, B.U. Kakkalfi, R. Rosenberg and G. Sposito. 1988. Phosphorus adsorption by kaolinites and montmorillonite. 1. Effect of time, ionic strength and pH. Soil Sci. Soc. Am. J. 52:1580-1585.

Bascomb, C.L. 1968. Distribution of pyrophosphate extractable Fe and organic C in soils. J. Soil Sc. 19, 251-268.

Bascomb, C.L. 1964. Rapid method for the determination of cation exchange capacity for calcarious and non-calcarious soils. J. Sci. Food Agric. 15:821-823.

Bates, J.A.R., and Baker, T.C.N. 1960. Studies on Nigerian forest soils. II. Distribution of P in soil profiles and in various soil fractions of a Nigerian soil. J Soil Sci. 2:257-260.

Batsula, A.A. and Krivonosova, G.M. 1973. Phosphorus in the humic and fulvic acids of some Ukrainian soils. Soviet Soil Sci. 5:347-350.

Beckett, P.H.T. and K.W. White. 1964. Studied on the phosphate potentials of soils. III. The pool of labile inorganic phosphate. Plant and Soil 21:253-282.

Beckwith, R.S. 1965. Sorbed phosphate at standard supernatant concentration as an estimate of the phosphate needs of soils. Aust. J. Exp. Agric. and An. Hus. 5:52-58.

Bekele, T., B.J. Cino, P.A.J. Ehlert, A.A. van der maas, A. van Diest. 1983. An evaluation of plant borne factors promoting the solubilization of alkaline rock phosphate.

Bhat, K.K.S. and Nye, P.H. 1973. Diffusion of phospahte to plant roots in soil. I. Quantitative autoradiography of depletion zone. Plant and Soil 38:161-175.

Bieleski, R.L. and P.N. Johnson. 1972. The external location of phosphatase activity in phosphorus-deficient Spirodela oligorrhiza. Aust. J. Biol. Sci. 25: 707-720.

Bingham, F.T. 1949. Soil test for phosphate. Calif. Agric. 3:(8) 11-14.

Blume, H.P. and Schwertmann, U. 1969. Genetic evaluation of profile distribution of Al, Fe and Mn oxides, Proc. Soil Sc. Soc. Am. 33, 438-444.

Bolt, G.H. and Bruggenwert, M.G.H. 1978. Soil Chemistry. B. Physico-chemical models. Elsevier Scientific Publishing Co., Amsterdam.

Borggaard, O. K. 1983. Influence of iron oxides on phosphate adsorption by soil. J. Soil Sci. 34, 333-341.

Borggaard, O. K. 1986. Iron oxides in relation to phosphate adsorption by soils. Acta. Agric. Scand., 36:107-118.

Borggaard, O. K., S. S. Jorgensen, J. P. Moberg and B. Raben-Lange. 1990. Influence of organic matter on phosphate adsorption by alumimium and iron oxides in sandy soils. Jour. of Soil Sci., 41:443-449.

Bowden, J.W., A.M. Posner, and J.P. Quirk. 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical-charge development and titration curves. Aust. J. Soil Res. 15:121-136

Bowman, R.A. and C.V. Cole. 1978. Transformation of organic phosphorus substrates in soils as evaluated by sodium bicarbonate extraction. Soil Sci. 125:49-54.

Bowman, R.A. and S.R. Olsen. 1985a. Assessment of phosphate buffering capacity. 1. Laboratory methods. Soil Sci. 140:287-292

Bowman, R.A. and S.R. Olsen. 1985b. Assessment of phosphate buffering capacity. 2. Greenhouse methods. Soil Sci. 140:387-392

Bowman and Olsen. 1985a,b. Relationship between P adsorption and desorption

Bowman, R.A., S.R. Olsen and F.S. Wanatabe. 1978. Greenhouse evaluation of residual phosphate by four phosphorus methods in

neutral and calcareous soils. Soil Sci. Soc. Am. I. 42:451-454.

Bowman, R.A. and C.V. Cole. 1978. Transformation of organic phosphorus substrates in soils evaluated by $NaHCO_3$ extraction. Soil Sci. 125:49-54.

Bray, R.H. and L.T. Kurtz. 1945. Determination of total organic and available forms of phosphorus in soils. Soil Sci. 59:39-45.

Breeuswsma, A. and J. Lyklemma. 1973. Physical and chemical adsorption of ions in the electric double layer of haematite (α Fe_2O).J. Colloid Int. Sci. 43:437-448.

Bremner, J.M. 1965. Inorganic forma of nitrogen. In C.A. Black, et. al., (ed.) Methods of Soil Analysis, Part 2. Agronomy 9:1179-1237. Am. Soc. of Agron. Inc. Madison, Wis.

Bretele, H. 1973. A comparison between ammonium and nitrate nutrition of young suger beet plants grown in nutrient solution at constant acidity. 1. Production of dry matter, ionic balance and chemical composition. Neth. J. Agric. Sci. 21, 227-244.

Bromfield, S.M. 1967. An examination of ammonium floride as a selective extractant for aluminium bound phosphate in partially phosphated system. Austr. J. Soil Res. 5:225-234.

Brown, G., Newmann, A. C. D., Rayner, J. H. and A. H. Weir 1978. The structures and chemistry of soil clay minerals. In: Greenland, D. J. and M. H. B. Hayes (Ed.) 1978. The Chemistry of Soil Constituents. John Wiley & Sons, Chichester. pp. 29-178.

Cabrera, F., P. De Arambari, L. Madrid and G.C. Toca. 1981. Desorption of phosphorus from iron oxide in relation to pH and *porosity*. *Geoderma* 26:203-216

Cady J.G. 1965. Petrographic Microscope Technique. In C.A. Black (Ed.). Methods of Soil Analysis, Part I. Agron. No. 9.

Chang, S.C., and A.S.R. Juo. 1962. Available phosphorus in relation to forms of phosphates in soils. Soil Sci. 95:91-96.

Chang, S. C. and Jackson, M. L. 1957. Fractionation of soil phosphorus. Soil. Sci., 84. 133-144.

Chang, S. C. and Jackson, M. L. 1958. Soil phosphorus in some representative soils. J. Soil Sci. 9:109-119.

Chapman, H.D. 1965. Cation exchange capacity. In C.A. Black (Ed). Methods of Soil Analysis, Part 2. !st Edn. of Agron. No. 9 pp 891-901.

Chater, M. and G.E. Mattingly. 1980. Changes in organic phosphorus content of soils from long-continued experiments at Rothamsted and Saxmundham. Rothamsted Exp. Stn. Harpenden. Herts, England.

Chauhan, B.S., Stewart, J.W.B. and Paul, E.A. 1979. Effects of carbon additions on soil labile inorganic, organic and micribially held phosphate. Can. J. Soil Sci. 59:387-396.

Chauhan, B.S., Stewart, J.W.B. and Paul, E.A. 1981. Effects of labile inorganic phosphate status and organic carbon additions on the microbial uptake of phosphorus in soils. Can. J. Soil Sci. 61:373-385.

Chien, R.Y., J.N. Butler and W. Stum. 1973. Kinetic study of phosphate reaction with aluminum oxide and kaolinite. Env. Sci. and Tech. 7:327-332.

Clarkson, D.T. 1985. Factors affecting mineral nutrient acquisition by plants. Annu. Rev. Plant Physiol. 36: 77-115.

Cole, C.V., G.S. Innins and J.W.R. Stewart. 1977. Simulations of phosphorus cycling in semiarid grassland. Ecology 58:1-15.

Cooke, I.J., Hislop, J. 1963. Use of anion-exchange resin for the assessment of available soil phosphate. Soil Sci. 96,308-312.

Cole, C.V., G.I. Innis and J.W.B. Stewart. 1977. Simulation of phosphorus cycling in semi arid grasslands. Ecology 58:1-15

Cosgrove, D.G. 1977. Microbial transformation in the phosphorus cycle p. 97-134. In M. Alexander (ed.) Advances in Microbial Ecology Plenum Press, New York.

Cox, F R. 1992. Range in Soil phosphorus critical level with time. Soil Sci. Soc. Am Jorun. 56:1504-1509.

Dabin, B. 1963. Appreciations des besoins en phosphore dans les sols tropicaux. Les formes du phosphore dans les sols e Côte d'Ivoire. Contr. ORSTOM, Ser. Pedol., I,3,27-42.

Dalal, R.C. and Hallsworth, E.G. 1976. Evaluation of the parameters of soil phosphorus availability factors in predicting yield response and phosphorus uptake. Soil Sci. Soc. Am I. 40:54-546.

Davidtz, J. C. and Sumner, M. E. 1965. Blocked charges on clay minerals in sub-tropical soils. J. Soil Sci., 16. 270-274.

Dean, L.A. 1938. An attempted fractionation of soil phosphorus. Soil Sci. 84:133-246.

de Villiers, J. M. and Jackson, M. L. 1967. Aluminous chlorite origin of pH-dependent cation exchange capacity variations. Soil Sci. Soc. Am. Proc., 31. 614-619.

Dolui, A.K., and S.K. Gangopadydyay. 1984. Fixation of P in relation properties of some red and lateritic soils of West Bengal. Indian J. Agric. Chem. 17:177-182.

Doormaar, J. 1972. Seasonal pattern of soil organic phosphorus. Can J. of Soil Sci. 52:107-122.

D'Hoore, J. L. 1968. The classification of tropical soils. In: Moss R. P. (Ed.). The Soil Resources of Tropical Africa,

Duback, P. and N.C. Mehta. 1963. The chemistry of humic substances. Soils Fertilizer 26:293-300.

Earl, K.D., J.K. Syers and J.R. Mclaughlin. 1979. Origin of the effects of citrate, tartrate and acetate on phosphate sorption by soil and synthetic gels. Soil Sci. Soc.Am. J. 43:674-678.

Environmental Protection Agency (EPA), 1971. Methods of chemical analysis of water and wastes. Environmental Protection Agency, Cincinnati Ohio.

Enwezor, W.O. 1977. Soil testing for phosphorus in some Nigerian soils. 1. Comparison of methods of determining available phosphorus in soils of S.E. Nigeria. Soil Dci. 123:48-53.

Enwezor, W.O. and Moore, A.W. 1966. Phosphorus status of some Nigerian soils. Soil Sci. 102:322-328.

Fageria, N.K. and M.P.B. Filho. 1987. Phosphorus fixation in Oxisols of Central Brazil. Fertilizers and Agriculture 94:33-37.

Fife, C.V. 1959., 1962, 1963. An evaluation of ammonium fluride as a selective extractant for aluminum-bound soil phospahte: I-IV. Soil Sci. 87:13-21, 83:88; 93:113--123; 96:112-120.

Filter, A.H. and Sutton, C.D. 1975. The use of the Freudlich isotherm for soil phosphate sorption data. J. Soil Sci. 26, 242-246.

Fixen, P.E. and A.E. Ludwick. 1982. Residual available phosphate in near-neutral and alkaline soils. 1. Solubility and capacity relationships. Soil Sci. Soc. Am. J. 46:332-334.

Flaig, W. Beutelspracher, H. and E. Rietz. 1975. Chemical composition and physical properties of humic substances. In. J.E. Gieseking (Ed) Soil Components. Vol. 1. Organic Components. Springer Verlag. N.Y. pp. 1-211.

Fordham, A.W., and Norrish, K. 1979. Arsenate-73uptake by components of several acidic soils and its implication for phosphate retention. Aust. J. Soil Res., 17:307-316.

Follet, E. A. C. 1965. The retention of amorphous, colloidal `ferric hydroxide' by kaolinite. J. Soil Sci., 16. 334-341.

Fox, R. L. and E. J. Kamprath 1970. Phosphate sorption isotherms for evaluating the phosphate requirements of soils. Soil Sci. Soc. Am. Proc., 34. 902-907.

Fox, R.L. 1974. Examples of anion and cation adsorption by soils of tropcial America. Trop. Agric. 51:200-210.

Fox, R.L., D.L. Plucknett and A.S. Whitney. 1968. Phosphate requirements of Hawaiian latosols and residual effects of fertilizer phosphorus. Trans. Inter. Congr. Soil Sci. 9th Congr.

Fox, R.L. Yost, R.S. and Memom, K.S. 1981. Estimation of phosphate fertilizer requirements in the tropics - Some tentative observations. Puspharnajah, E. & S.H.A. Hamid (1981). (ed.) Phosphorus & Potassium in the tropics. Malasia Proceedings.

Franklin, W.T., and H. M. Reisenauer. 1960. Chemical characteristics of soils related to phosphorus fixation and availability. Soil Sci. 90:192-200.

Fraps, G.S. 1096. Availability of phosphoric acid of the soil. J. Am. Soc. Agron. 28:823-834.

Fried, M. 1957. Measurement of plant nutirent supply of soils by radioactive isotopes. p. 1-18. In C.L. Comar (ed). Atomic energy and Agriculture, Am Assoc. Adv. Sci., Washinton, D.C.

Fuller, W.H. and W.T. McGeorge. 1951. Phosphates in calcareous Arizona soils: II. Organic phosphorus content. Soil Sci. 71:45-50.

Gahoonia, T.S., N. Classen and A. Jungk. 1992. Mobilization of phosphate in different soils by regress supplies with ammonium or nitrate. Plant and soil 140:241-248.

Gahoonia, T.S. and Nielsen, N.E. 1992. Control of pH at the soil-root interface. Plant and Soil, 140:49-54.

Gahoonia, T. S. 1987. Phosphate availability as induced by root induced changes of soil pH. Ph. D. Thesis. Göttingen.

Gahoonia, T.S. and Nielsen, N.E. 1991. A method to study rhizosphere processes in thin soil layers in the proximity to roots. Plant and Soil 135 (1):143-146.

Gallez, A., Juo, A. S. R., Herbillon, A. J. and F. R. Moormann 1975. Clay mineralogy of selected soils from southern Nigeria. Soil Sci. Soc. Am. Proc. 39. 577-585.

Ghani, M.O. 1943. Fractionation of soil phosphorus: I. Method of extraction. Indian J. Agric. Sci. 13:29-45.

Gillman, G.P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. Aust. J. Soil Res., 17:129-39.

Goh, K. M. 1980. Dynamics and stability of organic matter. In: Theng, B. K. G. (Ed.) 1980. Soils with variable charge. New Zealand Society of Soil Science. pp. 373-391

Goldsworthy, P.R. and Heathcote, R.G. 1963. Fertilizer trials with groundnuts in northern Nigeria. Emp. J. Expl. Agric. 31:351-366.

Greenland, D. J. 1972. Soil factors determining responses to phosphorus and nitrogen fertilizers used in tropical Africa. Afr. Soils, 17. 99-108

Greenland, D. J. 1971. Interactions between humic and fulvic acids and clays. Soil Sci., 111. 34-41.

Greenland, D. J. (Ed.) 1981. Characterization of soils (of the humid tropics). Clarendon Press. Oxford. pp. 446.

Greenland, D.J. and C.J.B. Mott 1978. Surfaces of soil particles. In. Greenland, D. J. and M. H. B. Hayes (Ed.) 1978. The Chemistry of Soil Constituents. John Wiley & Sons, Chichester. pp. 321 -353.

Greenland, D. J., and J. P. Quirk. 1964. Determination of the total specific surface areas of soils by adsorption of cetyl pyridinium bromide. J. Soil Sci. 15:178-191

Greenland, D. J., Oades, J. M. and Sherwin, T. W. 1968. Electronmicroscope observations of iron oxides in some red soils. J. Soil Sci., 19. 123-126.

Greenland, D.J. and Oades, J.M. 1968. Iron oxide and clay surfaces, Trans. 9th Int. Congr. Soil Sci. 1, 657-658.

Griffin, R.A. and J.J. Jurinak. 1973. Test of new model for the kinetics of adsorption-desorption processes. Soil Sci. Soc. Am. Proc. 37:869-872.

Grinsted, M.J., M.J. Hedley, R.E. White and P.H. Nye. 1982. Plant induced changes in the rhizosphere of rape seedlings. I. pH change and increase in concentration of soil solution.

Gunary, D. 1970. A new adsorption isotherm for phosphate in soil. J. Soil Sci. 21, 72-7.

Gunary, D. and C.D. Sutton. 1967. Soil factors affecting uptake of phosphate. J. Soil Sci. 18:167-173.

Gunnarison, O. and Frederiksson. 1951. A method for determining the amount of "Plant available phosphorus" in soil by means of P-32 Radioisotope Techniques. 1:427-431.

Habibullah, A.K.M., Greenland, D.J. and H. Bremmer. 1971. Clay mineralogy of some seasonally floded soils of Eastern Pakistan. Jour. Soil Sci. 22:179-190.

Halm, B,J., J.W. Stewart and R.L. Halstead. 1972. The phosphorus cycle in a native grassland ecosystem. p. 571-586. In Isotopes and radiation in soil plant relations including forestry. IAEA, Vienna.

Hannapel, J.R., W. Fuller, S. Bosma and J.S. Bullock. 1964. Phosphorus movement in a calcarious soil. I. Predominance of organic forms of phosphorus in phosphorus movement. Soil Sci. 97:350-357.

Harpstead, M. I.1974. The classification of some Nigerian soils. Soil Sci., 116. 437-443

Harter, R.D. 1969. Phosphorus adsorption sites in soil. Soil Sci. Soc. Am. Proc. 33:630-632.

Harter, R.D. 1984. Curve-fit errors in Langmuir adsorption maximum Soil Sci, Soc. Am J. 48:749-752.

Harter, R.D. and G. Smith. 1981. Langmuir equation and alternate methods of studying "adsorption" reactions in soils. P. 167-182. In. R.H. Dowdy et al. (ed.) Chemistry in the soil environment. Spc. publ. No. 40 Am Soc. of Agron. Madison, WI.

Haseman, J.F., Brown, E.H., and Whitt, C.D. 1950. Some reactions of phosphate with clays and hydrous oxides of iron and aluminium. Soil Sci. 70:257-271.

Hayes, M. H. B. and R. S. Swift. 1978. The chemistry of soil organic colloids. In: D. J. Greenland and M. H. B. Hayes (Editors), The Chemistry of Soil Constituents. John Wiley & Sons, Chichester. pp. 179-320.

Hayward, D.O. and Trapnell, B.M.W. 1964. Chemisorption.2nd ed., Butter-worth, London.

Heathcote R.G., and Stockinger, K.R. 1070. Soil fertility under continuous cultivation in northern Nigeria. II. Responses to fertilizers in the absence of organic manures. Expl. Agric., 6:345-350.

Hedley, M.J., J.W.B. Stewart and B.S. Chauban. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation and by laboratory incubations. Soil Sci. Soc. Am. J. 46:970-976

Helal, H.M. and Dressler, A. 1989. Mobilization and turn-over of soil phosphorus in the rhizosphere. Zeitschrift fur Pflanzen-ernahrung und Bodenkunde. 152(3): 175-180.

Helal, H.M. and D. Sauerbeck. 1984. Influence of plant roots in carbon and phosphorus metabolism in soil. Plant Soil 76:175-182.

Helal, H.M. and D. Sauerbeck. 1989. Soil and root phosphatase activity and the utilization of inositol phosphates as dependent on phosphorus supply. In: Plant root s and their environment. Ed. H. Persson, Elsevier Sci. Publ., Amsterdam.

Hendriks, L., N. Claassen, and A. Jungk. 1981. Phosphatverarmung des wurzelnahen Bodens und Phosphataufnafhme von Mais und Raps. Z. Pflanzenernaehr. Bodenkd. 144:486-499.

Herbillon, A. J. 1980. Mineralogy of Oxisols and oxic minerals. In: Theng, B. K. G. (Ed.) 1980. Soils with variable charge. New Zealand Society of Soil Science. pp. 109-123.

Heyler, K.R. and Spencer, K. 1977. Sodium bicarbonate soil test values and the phosphate bufferring capacity of soils. Aust. J. Soil Res. 15, 263-73.

Hingston, F.L., Atkinson, R.L. Posner, A.M. and J.P. Quirk. 1967. Specific adsorption of anions. Nature 215:1459-1461.

Hingston, F.J., A.M. Posner and J.P. Quirk. 1972. Anion adsorption by goethite and gibbsite: The role of the proton in determining adsorption envelopes. J. Soil Sci. 23:177-191.

Hingston, R.J., A.M. Posner and J.P. Quirk. 1974. Anion adsorption by goethite and gibbsite. 11. Desorption of anion from oxide surfaces. J. Soil Sci. 25:16-26.

Hingston, F.J., Atkinson, R.J. Posner, A.M. and Quirk, J.P. 1986. Specific adsorption of anions on goethite. 9th International Congress of Soil Sciences, Adelaide 1, 669-678.

Hislop, J. and I.J. Cooke. 1968. Anion exchange resin as a means of assessing soil phosphate status. A laboratory technique. Soil Sci. 105:8-11.

Holford, I.C.R. 1980. Greenhouse evaluation of four phosphorus soil tests in relation to buffering indices in soils. Soil Sci. Soc Am. J. 44:555-559.

Holford, I. C.R. 1979. Evaluation of soil phosphate buffering indices. Aust. J. Soil Res. 17:495-504.

Holford, I. C.R. and G.E.G. Mattingly. 1976. Phosphate adsorption and plant availability of phosphate. Plant Soil 44:377-389.

Holford, I.C.R. Wedderburn, R.W.M. and Mattingly, G.E.G. 1974. A Langmuir two-surface equataion as a model for phosphate adsorption by soils. J. Soil Sci. 25, 242-55.

Holford, I.C.R. 1979. Evaluation of soil phosphate buffering indices. Aust. J. Soil Res. 17:495-504.

Hoffland, E., Findenegg, G.R. and Nelemans, J. A. 1989. Solubilization of rock phosphate by rape. II. Local root exudation of organic acids as a response to P-starvation. Plant and Soil 113, 161-165.

Hoffland, E., G.R. Findenberg, J.A. Nelemans. 1989a. Solubilization of rock phosphate by rape. I. Evaluation of the role of uptake pattern. Plant and soil, 113, 155-160.

Holford, I.C.R. and Mattingly G.E.G. 1979. Effects of phosphate buffering on the extraction of labile phosphate by plants and soil tests. Aust. J. Soil Res. 17:511-514.

Holford, I.C.R. and G.T.C. Mattingly. 1976. A model for the behaviour of labile phosphate in soil. Plant Soil. 45:433-444.

Hooker, M.L.G., G. A. Sander and L.A. Daigger. 1980. Phosphate fraction in calcareous soils as affered by time and amount of added phosphate. Soil Sci. Soc. Am. J. 44:269-277

Hourigan, W.R., R.E. Franklin, E.O. Mclean and Bhumba. 1961. Growth and calcium uptake by plants as affected by rate and depth of liming. Soil Sci. Soc. Am. Proc. 25:491-494.

Hsu, P.H. and D.A. Rennie. 1962. Reactions of phosphate in aluminum systems. II Precipitation of phosphate by exchangeable Al as a cation exchange resin. Can I. Soil Sci. 42:210-221.

Hsu, P.H. 1964. Adsorption of phosphate by aluminum and iron in soils Soil Sci. Soc. Am. Proc. 28:474-478.

Huang, P.M. and A. Violante. 1986. Influence of organic acids on crystalization and surface properties of precipitation products of aluminum. p. 159-221. In P.M. Huang and M. Schnitzer (ed.) Interactions of soil minerals with natural organics and microbes. SSSA Spec Publ. 17. SSA, Madison, WI.

Hughes, J.C. 1978. Mineralogy of soil from southern Nigeria in relation to their classification and utilization. Ph.D. Thesis, University of Reading, UK.

Hughes, J.C. 1981. Mineralogy. In. Characterization of Soils.Greenland, D.J. Ed. Pp 31-50.

Ipimidum, W.R. 1973. Comparison of some methods for determining organic phosphorus in some Nigerian soils. Samaru research bulletin, 194:324-325.

John,k, M.K., Van Ryswsyk, Al. & Mason, J.L. 1967. Effect of soil order, pH, texture and organic matter on the correlation between phosphorus in alfalfa and soil test values. J. Can. Soil Sci., 47,157.

Jackson, M.L. 1956. Soil Chemical Analysis-Advanced Course. College Agric., Madison, Wis., 991 pp.

Jacquin, F., M. Carballas and T. Carballas. 1978. Interactions entre les ions aluminium et la mineralisation de la matiere organique dan les sols humiferes atlantiques. Comptes Rendus Acad. Sci Paris, Serie D, 286:511-514.

Jones, R.C. and Uehara, G. 1973. Amorphous coatings on mineral surfaces. Soil Sci. Soc. Am. J. 38:792-798

Jones, M. J.and A. Wild 1975. Soils of the West African Savaanna. Tech. Comm. No. 55. Commonwealth Bureau of Soils, Harpenden. pp. 246.

Jungerius, P. D. and T. W. Levelt 1964. The soils of eastern Nigeria. Publ. Serv. Geol. Luxemburg, 14. 185-198.

Jungk, A.O. 1991. Dynamics of nutrient movement at the soil-root interface. In: Plant roots: the hidden half. Eds. Yoav Utisel, Amram Eshel and Uzi Kafkafi. Marcel Dekker, Inc. NY.

Jungk, A., and Claassen, N. 1989. Availability in soil and acquisition by plants as the basis for phosphorus and potassium supply to plants. Z. Pflanzenerneahr. Bodenked. 152: 151-157.

Juo, A.S.R. 1981. Mineralogy of acid sands of southern Nigeria. Monograph No.1. Soil Sci. Soc. of Nigeria. pp 19-26.

Juo, A. S. R. and E. G. Boyd. 1967. Particle size distribuion of aluminum, iron, and calcium phosphates in soil profiles. Soil Sci. 106:374-380

Juo, A.S.R and B.G. Ellis. 1968. Particle size distribution of aluminum, iron and calcium phosphates in soil profiles. Soil Sci. 106:374-380.

Juo, A.S.R., F.R. Moormann and H. O. Maduakor. 1974. Forms and pedogenetic distribution of extractable iron and aluminum in selected soils of Nigeria. Geoderma 11:167-179.

Juo, A. S. R. and Fox, R. L. 1977. Phosphate sorption characteristics of some benchmark soils of West Africa. Soil Science, 124:370-376.

Juste, C., Delas, J.and M. Langon 1975. Comparison de la tabilité biologique de différents humates métalliques. Comptes Rendus Acad. Sci., Paris, Serie D, 281. 1685-1688

Kafkafi, U.A., M. Posner and J.P. Quirk. 1967. Desorption of phosphate from kaolinite. Soil Sci. Soc. Am. Proc. 31:348-353.

Kafkafi, U.A., Bar-Yosef, R. Rosenberg and G. Sposito. 1988. Phosphorus adsorption by kaolinite and montmorillonite. 11.

Organic anion competition. Soil Sci. Soc. Am. J. 52:1585-1589.

Kavanagh, B.V. and Quirk, J.P. 1978. The adsorption of polycationic Fe(III) species on Na-illite. Geoderma, 21:225 - 238.

Khin, A., and G.W. Leeper. 1960. Modifications in Chang and Jackson's procedure for fractionating soil phosphorus. Agrochimica 4:246-254.

Kibblewhite, M. G. and J. Tinsley 1979. Soil organic matter studies: extraction with formic acid/dimethyl sulphoxide mixtures and fractionation with Zr(IV). J. Soil Sci., 30. 303-314.

Kinniburgh D.A. 1986. General purpose adsorption isotherm. Environ. Sci. Technol. 20:895-904.

Kittrick, J.A. and M.L. Jackson. 1956. Electron microscope observations of the reaction of phosphate with minerals leading to a unified theory of phosphate fixation in soils. J. Soil Sci. 7:81-89.

Klinkenberg, K. and Higgins, G.M. 1968. An outline of northern Nigerian soils. Nigerian J. of Sci. 2:91-115.

Kodama, H., Schnitzer, M. 1977. Effect of fulvic acid on the crystallization of Fe (III) oxides. Geoderma. 19. 279-91.

Kononova, M. M. 1966. Soil Organic Matter, 2nd Edition. Pergamon Press, Oxford. 544 pp.

Kononova, M. M. 1975. Humus of virgin and cultivated soils. In: J. E. Gieseking (Ed.). Soil Components, Vol. 1. Organic Components. Springer Verlag, New York. pp. 475-525.

Kuchenbuch, R., and Jungk, A. 1982. A method for determining concentration profiles at the soil root interface by thin slicing rhizospheric soil. Plant and Soil 68:391-394.

Kuo, S. 1990. Phosphate sorption implications on phosphate soil tests and uptake by corn. Soil Sci. Soc. Am. Journ. 54:131-135.

Kuo, S. and E.G. Lotse. 1974. Kinetics of phosphate adsorption and desorption by haematite and gibbsite. Soil Sci. 116:400-406.

Kuo, S. and E.G. Lotse. 1972. Kinetics of phosphate sorption by calcium carbonate and Ca-kaolinite. Soil Sci. Soc. Amer. Proc. 36:725-729.

Kurtz, L. T. 1953. Inorganic phosphorus in acid and neutral soils. In: Soil and fertilizer phosphorus. (eds. W.H. Pierre and A.G. Norman). Agronomy 4:59-88.

Kwong, Ng Kee K.F. and P.M. Huang. 1981. Comparison of the influence of tannic acid and selected low-molecular-weight organic acids on precipitation products of aluminum. Geoderma 26:179-193.

Lan C.H. and Tan, K.S. Soong, N,K. 1981. Phosphorus associated with fulvic and humic acids in soil under different covers. In Puspharajah and Hamid, (Eds) Phosphorus and potassium in the tropics Malasia proceedings.

Landon, J.R. 1984. Booker Tropical Soil Manual, Longman.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and plantinum. J. Amer. Chem. Soc. 41:1361-1402.

Larsen, S. 1952. The use of 32-P in studies on the uptake of phosphorus by plants. Plant Soil 4:1-10.

Larsen, S. 1967. Soil phosphorus. Adv. Agron. 19:151-210.

Lathwell, D.J., Sanchez, M., Lisk, D.J. Peech, M. 1958. Availability of soil phosphorus as determined by several chemical methods. Agron. 50,366-369.

Lavesque, M. and M. Schnitzer. 1967. Organo-metalic interactions in soils. 6. Preparation and properties of fulvic acid-metal phosphate. Soil Science 103:183.

Lekwa, G. and E.P. Whiteside. 1986. Coastal plain soils of South eastern Nigeria II. Forms of extractable irons, aluminium and phosphorus. Soil Sci. Soc. Am. J. 50:160-166.

LeMare, P.H. 1982. Sorption of isotopically exchangeable and non-exchangeable phosphate by some soils of Columbia and Brazil, and comparison with soils of southern Nigeria. J. Soil. Sci. 33:691-707.

Lewis, D. G. and J. P. Quirk. 1967. Phosphate diffusion in soil and uptake by plants, III and IV. Plant and Soil, 26. 445-468.

Lindsay, W.L. and E.C. Moreno. 1960. Phosphate phase equilibria in soils. Soil Sci. Soc. Am. Proc. 24:177-182

Lindsay, W.L. and H.F. Stevenson. 1959. Nature of the reactions of monocalcium phosphate monohydrate in soils: IV. Repeated reactions with metastable triple-point solution. Soil Sci. Soc. Am. Proc. 23:440-445.

Lopez-Hernandez, D.G. Siegert and J.V. Rodriguez. 1986. Competitive adsorption of phosphate and oxalate by tropical soils. Soil Sci. Soc. Am. J. 50:1460-1462.

Lopez-Hernandez, D., D. Flore, G. Siegert and J.V. Rodrigues. 1979. The effects of some organic anions on phosphate removal from acid and calcareous soils. Soil Sci. 128:321-326.

Lopez-Hernandez, D. and Burnham, C.P. 1974. The covariance of phosphate sorption with other soil properties in some British and tropical soils. Journal of Soil Science 25.196-206.

Marschner. H. and V. Roemheld. 1983. In-vivo measurement of root induced pH changes at the root surface: Effects of plant species and nitrogen source. Z. Pflanzenphysiol. 111:241-251.

Marschner. H., V. Roemheld, W.J. Horst and P. Martin. 1986. Root induced changes in the rhizosphere: Importance for the mineral nutrient of plants. Z. Pflanzenernaehr. Bodenk. 149,441-456.

Martin, W.E. and Mikkelsen, D. S. 1960. Grain fertilization in Califonia. Calif. Agric. Exp. Stn. Bull. 775.

McAuliffe, C.D. Hall, N.S., Dean, L.A., Hendricks, A.B. 1947. Exchange reactions between phosphates and soils: Hydroxylic surfaces of soil minerals. Soil Sci. Am. Proc. 12. 119-123.

McKeague, J. A. 1971. Organic matter in particle-size and specific gravity fractions of some Ah horizons. Can. J. Soil Sci., 51. 499-505.

Mckeague, J.A. 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate dithionite in comparison to oxalate as extractant. Can. J. Soil Sc. 47, 95-99.

Mckeague, J.A., Brydou, J.E., and Miles, N.M. 1971. Differentiation of form of extractable Fe and Al in Soils. Proc. Soil Sc. Soc. Am. 35:33-38.

Mckeague, J.A., and Day, J.H. 1966. Dithionite and oxalate extractable Fe and Al as acids in differentiating different classes of soils. Can. J. Soil Sc. 46:13-22.

Mckercher, R.B. 1968. Studies on soil organic phosphorus. Trans. Inter. Congr. Soil Sci. 9th Congr., Adelaide 3:547-553.

McLaughlin, J.R., Ryden, J.C. and Syers, J.K. 1977. Development and evaluation of a Kinetic model to describe phosphorus sorption by hydro ferric oxide gels. Geoderma 18, 295-307.

McLaughlin, J.R., Ryden, J.C. and Syers, J.K. 1981. Sorption of inorganic phospahte by iron and aluminium-containing components. Journal of Soil Science 32, 365-377.

McLean, E.E. Reicoky, D.C. and Lakshnianan C. 1965 Interelations of organic matter, liming and extractable aluminium with permanent charge (KCl) and pH dependent CEC of surface soils. Soil Sci Soc. Am. Proc. 29:374-378.

Mead, J.A. 1981. A. comparison of the Langmuir Freundhich and Temkin equation to describe phosphate adsorption properties of Soils. Aust. J. Soil Res. 19:333-342.

Melsted, S. W., and T. R. Peck. 1977. The Mitscherlich-Bray growth function. p. 1-18. In T. R. Peck et al. (ed.) Soil testing: Correlating and interpreting the analytical results. ASA Spec. Publ. 29. ASA, CSSA, and SSA, Madison, WI.

Menon, R.G, S. H. Chien & Abd el Nabi Gadalla, 1991. Comparison of Olsen and P_i soil tests for evaluating phosphorus bioavailabilty in a calcareous soil treated with single superphosphate and partially acidulated phosphate rock. Fertilizer Research 29: 153-158.

Merha, O.P. and Jackson, M.K. 1960. Iron oxide removal from soils and clays by dithionite-citrate system buffered with bicarbonate. Clays and Clay Minerals. 7:317-327.

Mindaman, G. 1968. Addition, decomposition and accumulation of soil organic matter in forests. J. Ecology. 56: 355-367.

Moberg, J. P. and I. E. Esu. 1991. Characteristics and composition of some savanna soils in Nigeria. Geoderma, 48. 113-129.

Moghimi, A., Tate, M.E. and Oades, J.M. 1978. Characterization of rhizosphere products especially 2-ketogluconic acid. Soil Biol. Biochem. 10:283-287.

Mokwunye, A. U. 1977. Phosphorus fertilizers in Nigerian savanna soils: Use of phosphorus sorption isotherms to estimate the phosphorus requirement of maize at Samaru. Trop. Agric. (Trinidad) 54:265-271.

Mokwunye, U. 1975. The influence of pH on the adsorption of phosphate by soils from the Guinea and Sudan savanna zones of Nigeria. Soil Sci. Soc. Am. Proc. 39:1100-1103

Mokwunye, A. H, Chen, S. H. and E. Rhodes 1986. Phosphate reactions with tropical African soils. In: Mokwunye, A. H. and P. L. G. Vlek (Eds.), Management of nitrogen and phosphorus in sub-Saharan Africa, Nijhoff, Netherlands. pp. 263-281.

Molla, M.A.Z., A.A. Chowdhury, A. Islam and S. Hoque. 1984. Microbial mineralization of organic phosphate in soil. Plant Soil 78:393-399.

Morris, R.A., Sattel, R.R., and N.W. Christensen. 1992. Phosphorus sorption and uptake from Sri Lankan Alfisols. Soil Sci. Soc. Am. J. 56:1516-1520.

Mortland, M.M. and Kemper, W.D. 1965. Specific surface. In. Methods of Soil Analysis. C.A. Black (ED).

Moss, R. P. 1968. The soil resources of tropical Africa. Cambridge University Press, London.

Muljadi, W.A.M. Posner and J.P. Quirk. 1966. The mechanism of phosphate adsorption by kaolenite, gibbsite, and pseudobochmite: 1. The isotherms and the effects of pH on adsorption. J. Soil Sci. 17:212-229.

Munns, D.N. and R.L. Fox. 1976. The slow reaction which continues after phosphate adsorption. Kinetics and equilibrium in some troppical soils. Soil Sci. Soc. Am. J. 40:46-51.

Murphy, J. and J.P. Riley. 1962. A modified single solution for the determination of phosphorus in natural waters. Anal. Chim. Acta. 27:31-36.

Murrman, R.P. and M. Peech. 1969. Relative significance of labile and crystalline phosphate in soils. Soil Sci. 107:249-255.

Nagarajah, S., A.M. Posner and P.J. Quirk. 1968. Desorption of phospahte from kaolinite by citrate and bicarbonate. Soil Sci. Soc. Am. Proc. 32:507-510.

Nagarajah, S., A.M. Posner and J.P. Quirk. 1970. Competitive adsorption of phosphate with polygalacturonate and other organic anions on kaolinite and oxide surface. Nature (London). 228:83-84.

Nielsen, N.E. 1984. Proc. of 6th Congr. on Soil less Culture. Lunteren, The Netherlands. pp. 421-446.

Nye, P.H. and Bertheux, M.H. 1957. The distribution of phosphorus in forest and savannah soils of the Gold Coast and its agricutural significance. J. Agric. Sci. Camb, 49:141-159

Nye, P.H., and Tinker, P.B. 1977. Solute Movement in the Soil-Root System, Studies in Ecology, Vol. 4. Blackwell Scientific, Oxford.

Ojanuga, A. C. 1979. Clay mineralogy in the Nigerian tropical savanna regions. Soil Sci. Soc. Am. J., 43. 1237-1242.

Okajima, H., Kutota, H. and T. Sakumar. 1983. Hystersis in the phosphorus sortpion and desorption proceesses of soils. Soil Plant nutr, 29:271-283.

Olsen, S. R., and F. E. Khasawneh, 1980. Use and limitations of physical-chemical criteria for assessing the status of phosphorus in soils. p.361-410. In F. E. Khasawneh et al. (ed) The role of phosphorus in agriculture. ASA. CSSA. SSSA. Madison, WI.

Olsen, R. S. and F. S. Watanabe. 1963. Diffusion of phosphorus as related to soil texture and plant uptake. Soil Sci. Soc. Am. Proc., 27. 648-653.

Olsen, S.R. and **Watanabe, F.S.** 1975. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Am. Proc, 21,144-9

Olsen, R. S. and F. S. Watanabe 1966. Effective volume of soil around plant roots determined from phosphorus diffusion. Soil Sci. Soc. Am. Proc., 30. 598-602.

Olsen, S.R. and Sommers, L.E. 1982. Phosphorus. In. Methods of Soil Analysis: Part 2. Page, A.L., R.H. Miller and R.D. Keeney. Soil Sci. Soc. of Agron. pp. 404.

Olsen, S.R., C.V. Cole, F.S. Watanabe and L.A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate USDA Circ. 939. USDA, Washington, DC.

Olsen, S.R. and Wanatabe, F.S. 1970. Difference supply of phosphorus in relation to soil textural variations. Soil Sci. 110:318-327.

Omotosho, T.I. 1971. Organic phosphorus content of some cocoa growing soils of southern Nigeria. Soil Sci. 112:195-199.

Oteng, J.W. and Acquaye, D.K. 1971. Studies on the avaibility of phosphorus in representative soils of Ghana. I. Availability tests by conventional methods Ghana J. Agric. Sci. 4:171-183.

Ozanne, P.G. and T.C. Shaw. 1967. Phosphate sorption by soils as a measure of the phosphate requirement of soils. Aust. J. Agric. Res. 18:601-612.

Ozanne, P. G., and T. C. Shaw. 1968. Advantages of the recently developed phosphate sorption test over the older extractant methods for soil phosphate. Int. Congr. Soil Sci. Trans. 9th (Adelaide, Aust.) 11:273-280.

Parfitt, R. L. 1979. The availability of P from phosphate goettite bridging complexes. Plant Soil. 53:55-65.

Parfitt, R. L. 1978. Anion adsorption by soils and soil materials. Adv. Agron., 30. 1-50.

Parfitt, R. L. 1980. Chemical properties of variable charge soils. In: Theng, B. K. G. (Ed.) 1980. Soils with variable charge. New Zealand Society of Soil Science. pp. 167-194.

Parfitt, R.L., R.J. Atkinson and R. St. C. Smart. 1975. The mechanism of phosphate fixation by iron oxides. Soil Sci. Soc. Am. Proc. 39:837-841.

Peaslee, D. E. and R.L. Fox 1978. Phosphorus fertilizer requirements as estimated by phosphate sorption. Commun. Soil Sci. Plant Anal. 9:975-99.

Peterson, G.W. and R.B. Corey. 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphorus. Soil Sci. Soc. Am. Proc. 30:563-565.

Phillips, L. J. and M. J. T. Norman. 1961. Sorghum-peanut crop sequences at Katherine, N. T. Aust. J. Exp. Agric. Husb. 1:144-149.

Piper, C.S. 1942. Soil and Plant Analysis. (Univ.Adelaide).

Polyzopoulos, N.A., V.Z. Keramidas and H. Kiosse. 1985. Phosphate sorption by some Alfisols of Greece as described by the commonly used isotherms SSS An J. 49:81-84.

Posner, A.M. 1964. Titration curves of humic acids. Trans. 8th Int. Congr. Soil Sci., Bucharest, 2:161-173.

Posner, A.M. and Bowden, J.O. 1980. Adsorption isotherms. Should they be split? J.Soil Sci. 31:1010.

Pratt, P F. and M. J. Garber. 1964. Correlation of phosphorus availability by chemical tests with inorganic phosphorus fractionations. Soil Sci. Soc. Am Proc. 28:23-26.

Quirk, J.P. 1971. In surface chemistry of oxides. Disc. Fara. Soc. 52:348-351

Rajan, S.S.S., Perrott, K. W. and Sanders, W. M. H. 1974. Identification of phosphate reactive sites of hydrous alumina from proton consumption during phosphate adsorption at constant pH value. J. Soil Sci. 25:438-447.

Reddy, K.R., M.R. Overcash, R. Hkaleed and P.W. Westerman. 1980. phosphorus adsorption-desorption characteristics of two soils utilized for disposal of animal manure. J. Environ. Qual. 9(1):86-92.

Reeve, N.G. and M.E. Summers. 1970. Effect of aluminium and P fixation on crop growth in oxisols in Natal. Soil sci. Soc. Prec. 34:263-267.

Rengasamy, P. and J.M. Oades. 1979. The interactions of monomeric and polymeric species of metal ions with clay surfaces. IV. Mixed systems of aluminium (III) and iron (III). Aust. J. Soil Res. 17:141-154.

Roth, C. B., Jackson, M. L., Lotse, E. G. and Syers, J. K. 1968. Ferrous-ferric ratio and CEC changes on deferration of weathered micaceous vermiculite. Israel J. Chem., 6. 261-273.

Roth, C. B., Jackson, M. L., de Villiers, J.M., and Volk, V.V. 1967. Surface colloids on micaceous vermiculite: Soil Chemistry and Soil Fertility, (Edited by G.V. Jacks). Trans Comm.II and IV, Intern. Soc. Soil Sci., Aberdeen. Intl. Soc. Soil Sci pupl., pp. 217-221.

Roth, C. B.; M.L. Jackson and J. K. Syers. 1969. Defferation effect on structural ferrousterric iron ratio and CEC of vermiculites and soils. Clay and clay minerals, 17:253-264

Rovira, A.D. 1969. Plant root exudates. Bot. Rev. 35:35-57.

Roy, A.C. and S.K. DeDatta. 1985. P sorption isotherm for evaluating P requirement of wetland rice soils. Plant Soil 86:185-196.

Russel, J.D., E. Paterson, A.R. Fraser and V.C. Farmer. 1974. Surface structures of gibbsite, goethite and phosphated goethite. Nature 220:221

Russel, J.S., E.J. Kamprath and C.S. Andrew. 1988. Phosphorus sorption of subtropical acid soils as influenced by the nature of the cation suite. Soil Sci. Soc. Am. J. 52:1407-1410.

Ryden, J.C. and J.K. Syers. 1977. Desorption and isotopic exchange relationships of phosphate sorbed by soils and ferric oxide gel. J. Soil Sci. 28:596-609.

Ryden, J.C. and Syers, J.K. 1976. Origin of the labile phosphate pool in soils. Source

Ryden, J.C., McLaughlin, J.R, and Syers, J.K. 1977. Mechnisms of phospahte sorption by soils and hydrous ferric oxide gel. J. Soil Sci. 28, 72-9.

SAS Institute. 1987. SAS/STST quide to personal computers. Version 6 (ed.) SAS Inst. Cary NC.

Sanyal, S.K., S.K. de Datta and P.Y. Chan. 1993. Phosphate sorption-desorption behaviour of some aridic soils of South and southeast Asia. Soil Sci. Soc. Am. J. 57:937-945.

Sattel, R.R. and Morris, R.A. 1992. Phosphorus fractions and availability in Sri Lankan Alfisols. Soil Sci. Soc. Am. J. 56:1510-1515.

Saunders, W.M.H. 1965. Phosphate retention by New Zealand soils and its relationship to free sesquioxides, organic matter and other soil properties. New Zealand J. Agric. Res. 8:30-57

Saunders, W.M.H. and E.G. Williams. 1955. Observations on the determination of total organic phosphorus in soil. J. Soil Sci. 6:254-267.

Sayers, J.K., T.D. Evans, J.D.H. Williams and J. T. Murdock. 1971. Phosphate sorption parameters of representative soils from Rio Grande do Sul, Brazil. Soil Sci. 112:267-275.

Schnitzer, M. 1978. On permanganate oxidation of humic acids - a discussion. Geoderma, 21. 239-243.

Schnitzer, M. 1982. Organic matter characterization. In. Methods of Soil Analysis, Part 2. 2nd Edn. (Page et al. Eds.) Agron. No. 9, American Society of Agronomy.

Schnitzer, M. and S. U. Khan. 1972. Humic Substances in the Environment. Marcel Dekker, New York. pp.327.

Schnitzer, M. and S. U. Khan. 1978. Soil Organic Matter. Elsevier, Amstadam. pp. 319.

Schnitzer, M. and Hansen, E.H. 1970. Organo-metallic interactions in soils: 8. An evaluation of the methods for the determination of stability constants of metal-fulvic acid complexes. Soil Science 109:333-340.

Schofield, R.K. 1955. Can a precise meaning be given to "available" soil phosphorus? Soils Fert. 18,373-5.

Schjorring, J.K. and Nielsen, N.E. 1982. Planteegenskaber (parametre) der pavirker effektiviteten af planters udnyttelse af jord som naringsstofkilde. II. Bestemmelse af de transportki netiske parametre for phosphoroptaglse hos 9 bygsorter, havre rug og hvede. Rapport No. 1123, 167 p. Department of Soil Fertility and Plant Nutrition, The Royal Vet. and Agric. Univ. Copenhagen.

Schwertmann U, and W.R. Fischer. 1973. Natural "amorphous" ferric hydroxide. Geoderma, 10:237-247.

Schwertmann, U., W.R. Fischer and H. Papendorf. 1968. The influence of organic compounds for the formation of iron oxides. Int. Congr. Soil Sci., Trans. 9th (Adelaide, Austalia) 1:645-655.

Schwertmann, U., Schulze, D.G., and Murad, E. 1982. Identification of ferrihydride in soils by dissolution kinetics, differential X-ray diffraction and Mossbauer spectroscopy. Soil Sci. Soc. America Jour. 46:869-875.

Schwertmann, U. 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Z. Pflanzenernähr. Düng., Bodenk., 105. 194-202.

Schwertmann, U. 1966. Inhibitory effect of soil organic matter on the crystallization of amorphous ferric hydroxide. Nature, 212. 645-646.

Schwertmann, U. 1971. Transformations of hematite to goethite in soils. Nature, 232. 624-625.

Schwertmann, U., Kodama, H. and Fischer, W.R. 1986. Mutual interactions between organics and iron oxides. In Interactions of soil minerals with natural organics and microbes. (Eds, P.M. Huang and M. Schwitzer). pp 223-250. Soil Sci. Soc. Am. Spec. Publ. No. 17, Madison.

Sen, B. C. 1961. Studies on the bacterial decomposition of humic acid in the clay-humus mixtures. J. Indian Chem. Soc., 38. 737-740.

Shapiro, R. E., and M. Fried. 1959. Relative release and retentiveness of soil phosphates. Soil Ssci. Soc. Am. Proc. 23:195-198.

Sharpley, A.N., H. Tiessen and C.V. Cole. 1987. Soil phosphorus forms extracted by soil tests as a function of pedogenesis. Soil Sci. Soc. Am. J. 51:362-365.

Sherman, G.D., Matsusaka, Y., Ikawa, H. and Uehara, G. 1964. The role of amorphous fixation in the properties of tropical soils. Agrochimica. 8:146-163.

Shinha, M.K. 1971. Organo-metalic phosphates.I interactions of phosphorus compounds with humic substances. Pl. Soils. 35:471.

Sibanda, H.M. and Young, S.D. 1986. Competitive adsorption of humus acids and phospahte on goethite-gibbsite and two tropcial soils. Journal of Soil Science 37,197-204.

Sibbesen, E. 1978. An investigation of the anion-exchange resin method for soil phosphate extraction. Plant Soil, 50, 305-321.

Sibbesen, E. 1983. Phosphorus soil tests and their suitability to Assess the phosphate status of soil. J. Sci. Ford Agric. 34:1368-1374.

Singh, A. K. 1974. Effects of different crop rotations on the utilization of various forms of soil nitrogen, phosphorus and potassium. Indian J. of Agric. Sci. 44:329-338.

Singh, R., M.R.F. Moller and W.D.A. Ferreira. 1983a. Relation between phosphorus adsorption and clay mineralogical components of Latosols of the central Plateau of Brazil. R. bras. Ci. Solo 7:221-226.

Singh, R., M.R.F. Moller and W.D.A. Ferreira. 1983b. Kinetics of phosphorus adsorption in some soils of humid tropics of Amazon, Brazil. Brazil. R. bras. Ci. Solo 7:227-231.

Singh, R., M.R.F. Moller and W.D.A. Ferreira. 1983c. Characteristics of phosphorus adsorption in relation to selected soil properties of the humid tropics of Amazonia, Brazil. R. bras. Ci. Solo 7:233-241.

Smith, A.N. 1965. Distinction between iron and aluminum phosphate in Chang and Jackson's procedure for fractionating inorganic soil phosphorus. Agrochimica 9:162-168.

Soil Survey Staff, 1975. Soil Taxonomy. A basic system of soil classification for making and interpreting soil surveys. U.S. Dept. Agr., Handbook No. 436. 754 pp.

Sposito, G. 1979. Derivation of the Langmuir equation for ion exchange reaction in soils. Soil Sci. Soc. Am. J. 43:197-198.

Sposito, G. 1981. The thermodynamics of soil solutions. Clarendon Press, Oxford, U.K.

Sposito, G. 1982. On the use of Langmir equation in the interpretation of "adsorption" phenomena II The "two surface Langmir equation soil Sci, Soc. Am J. 46:1147-1152.

Sposito, G. 1989. The Chemistry of Soils. Oxford University Press.

Steele, W. N. 1972. Cowpea in Nigeria. Ph.D. Thesis, Reading University, U.K.

Stevenson, F. J. 1967. Organic acids in the soil. In: A. D. McLaren and G. H. Peterson (Eds), Soil Biochemisty, Vol. 1. Marcel Dekker, New York. pp. 119-146.

Stevenson, F. J. 1982. Humus Chemistry. Wiley, New York

Stevenson, F.J. and J.H.A. Butler. 1969. Chemistry of humic substances and related pigments. In. G. Eglinton and M.T.J. Murphy (Eds). Organic geochemistry. Longman. pp. 534-557.

Struthers, P.H. and D.V. Stieling. 1950. Effect of organic anion on phospahte precipitation by iron and aluminum as influenced by pH. Soil Sci. 69:205-213.

Syers, J.K., Browman, M.G., Smillie, G.W. and Corey, R.B. 1973. Phospahte sorption by soils evaluated by the Langmuir adorption equation. Soil Sci. Soc. Am. Proc. 37, 358-63.

Syers,J.K., Willams, J.D.H. Tyner, E.H. & Walker, T.W. (1969) Primary and secondary origin of "non-extractable" soil inorganic phosphorus. Soil Sci. Soc. Am. Proc. 33:635

Syers, J. K., J.D.H. Williams and T.W. Walker. 1968. The determination of total phosphorus in soils and parent material. New Zealand J. Agric. Res. 11:757-762.

Syers, J.K., Evans, T.D., Williams, J.D.H., and Murdoch, J.T. 1971. Phosphate sorption parameters of representative soils from Rio Grande do Sul, Brasil. Soil Sci., 112:267-275.

Tamm, O. 1922. Um bestämning qw de oorganiska komponenterna i markens gelkomplex. Medd. Statens Skogsforsokanst., 19. 384-404.

Tandon, H.L.S. 1987. Phosphorus Research and Agricultural Production in India. F.D.C.O. India. pp. 160.

Tate, K.R. and B.K.G. Theng. 1980. Organic matter and its interaction with inorganic soil constituents. In B.K.G. Theng

(Ed.) Soils with Variable Charge. New Zealand Soc. of Soil Sci. pp. 225-249.

Taylor, R.W. and B.G. Ellis. 1978. A mechanism to describe P adsorption on soil and anion resin surfaces. Soil Sci. Soc. Am. J. 42:432-436.

Thiband, M., Moreld, C and Fandean J. 1988. Contributions of phosphorus issued from crop residues to plant nutrient. Soil Sci. Plant nutr. 34:481-491.

Thien, S.J. and Myers R. 1992. Determination of Bio available phosphorus in soil. soil Sci. Soc. Am. J. 56:814-818.

Thomas, R.L., and B.T. Bowman. 1966. The occurrence of high molecular weight organic phosphorus compounds in soul. Soil Sci. Soc. Am. Proc. 30: 799-801.

Tiessen, H., J. W.B. Stewart and C.V. Cole. 1984. Pathways of phosphorus transformation in soils of differing pedogenesis. Soil Sci. Soc. Am. J. 48:853-858.

Tisdale, S.L. and W.L. Nelson. 1975. Soil fertility and fertilizers. Macmillan Co. New York.

Truog, E. 1930. The determination of readily available phosphorus of soils. J.Am Soc. Agron. 22,874-882.

Tweneboath, C. K., Greenland, D. J. and Oades, J. M. 1967. Changes in charge characteristics of soils after treatment with 0.5 M calcium chloride at pH 1.5. Aust. J. Soil Res., 5. 247-261.

Tyley, P. et al. 1972. The land resources of North-Eastern Nigeria. Land Resources Study, No. 9. Vol. 1.

Udo, E. J. 1976. Forms and distribution of phosphorus in three Nigerian soil profiles along a toposequence. Trop. Agric. 54:149-156.

Udo, E.J. & Ogunwale, J.A. 1978. Phosphorus determination. Laboratory Manual for the Analysis of soils, Plant and Water Samples. Department of Agronomy of Ibadan.

Udo, E.J. and J.A. Ogunwale. 1977. Phosphorus fractions in selected Nigerian soils. Soil Sci. Soc. Am. J. 41:1141-1146.

Udo, E. J. and Uzu, F. O. 1972. Characteristics of phosphorus adsorption by some Nigerian soils. Proc. Soil Sci. Soc. Am., 36. 879-883.

Udo, E.J., and Uzu, F.O. 1972. The determination of total phosphorus in some Nigerian Soils. Nigerian Journal of Sci. 5:127-131.

Uyovbisere, E.O. 1979. Influence of inorganic phosphate fractions on extractable phosphorus in the northern Guinea savanna ecological zone. M.Sc. Thesis, ABU, Zaria, Nigeria.

Uyovbisere, E. O., A. O. Ogungbile, V. O. Chude, J. Olukosi and A. Bationo. 1993. Long-term effects of different cropping systems on fertility and productivity of soils of the Nigerian savanna. Paper presented at the 10th Annual Workshop of WAFMEN, Cotonou, 5-9, April, 1993. Auspices of IFDC-Africa / CENAP. pp. 12.

Uzu, F.O.; A.S.R. Juo; and A.A. Fayemi. 1975. Forms of P in some important agricultural soils of Nigeria. Soil Sci. 120:212-219.

Vaidyanathan, L.V. and O. Talibudeen. 1970. Rate processes in the desorption of phosphate from soils by ion exchange resins. J. Soil Sci. 21:173-178.

Van Bladel, R. and Moreale, A. 1977. Adsorption of herbicide-derived p-chloroaniline residues in soils: a predictive equation. J. Soil Sci. 28, 93-102.

Van der Zee, S.E.A.T.M. and W. H. Van Riemsdijk. 1986. Sorption kinetics and transport of phosphate in sandy soils. Geoderma, 38. 293-309.

Van Raij, B. and Peech, M. 1972. Electrochemical properties of some oxisols and alfisols of the tropics. Proc. Soil Sci Soc. Am. 36:587-593.

Veith, J.A. and G. Sposito. 1977. Reactions of alumino-silicates, aluminium oxide with O-phosphate: The formation of X-ray amorphous analogs of variscite and montebrasite. Soil Sci. Soc. Am. J. 41:870-876.

Velayutham, K.S. Poudrilei, K.S. and Thiagalingam, K. 1981. Studies on the determination of available phosphorus in Papu a New guinea soils. In. Puspharajah and Hamid S.H.A. (Eds.) Phosphorus and Potassium in the tropcis. Malasia Proceedings.

Violante, A. and Gianfreda, L. 1993. Competition in adsorption between phosphate and oxalate on an aluminum hydroxide montmorillonite complex. Soil Sci Soc. Am. J. 57:1235-1241.

Wada, K. 1959. Reactions of phosphate with allophane and halloysite Soil Sci. 87:325-330.

Wada, K. and S. Aomine 1973. Soil development on volcanic materials during the Quaternary. Soil Sci., 116. 170-177.

Wada , K., and Gunjigake, N. 1979. Active aluminium and iron phosphate in Ando soils. Soil Sci. 128:331-336.

Walker, T.W. and **Adams, A.F.R.** 1958. Studies on soil organic matter: Influence of phosphorus content of parent materials on accumulation of carbon, nitrogen, sulphur and organic phosphorus in grassland soils. Soil Sci. 85:307-318.

Walker, W. and **J. K. Syes.** 1976. The fate of phosphorus during pedogeness. Geoderma 15:1-19.

Walkley, A., and **I.A. Black** 1934. An examination of Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-38.

Walmsley, D.,s & Cornforth, I.S. (1973) Methods of measuring available nutrients in West Indian Soils. II. Phosphorus. Pl.Soil, 39,93.

Welp, G., Herms, U. and **Brummer, G.** 1983. Einfluss von Bodenreaktion, Redombedingungen und organischer Substanz auf die Phosphagehalte der Bodenlosung. Z. Pflanzenernaehr. Bodenkd. 146, 38-52.

Westin, F.C and **De Britto, J. G.** 1969. Phosphorus fractions in some Venezuelan soils as related to their state of weathering. Soil Sci. 107:194-202.

White, R.E. 1981. Retention and release of phosphate by soil constituents. In. P.B. Tinker (ed) Soils and agriculture. Critical reports on Applied Chemistry. Vol.2 pp 71-114.

White, R.E and **P.H.T. Beckett.** 1964. Studies on the phosphate potential of soils. Plant Soil 20:1-16.

White, R.E and **A.W. Taylor.** 1977. Reactions of soluble phosphate with acid soils. The interpretation of adsorption isotherms. J. Soil Sci. 28:314-328.

Wild, A. 1958. The phosphorus content of Australian soils. Aust. J. of Agric. Res. 9:193-204.

Willett, I.R., Chartres, C.J. and **Nguyen, T.T.** 1988. Migration of phosphate with aggregated particles of ferrihydride. J. Soil Sci. 39:275-282

Williams, E. G. 1967. The intensity and quantity aspects of soil phosphate status and laboratory extraction values. Anales de Edafologia y Agrobiologia, 26. 525-546.

Williams, J.D.H. and **T.W. Walker.** 1969. Fractionation of soil phophorus in a maturity sequence of New Zeeland basaltic soils. soil Sci. 107:22-30.

White, R.E. and **Bockett, P.H.T.** 1964. Studies on the phosphate potentials of soils. plant I. The measurements of phosphate potential. Plant and soils XX(I):1-16

Williams, C.H. 1950. Studies on soil phosphorus: I. A method for the partial fractionation of soil phosphorus. J. Agric. Sci. 40:233-242.

Williams, E.G. 1960. Some aspects of phosphate retention and availability in soils. Trans. 7th in Cong. Soil Sci. 3, 604-11.

Williams, J.B., H.J. Mayer, T and Nriagu, J.O. 1980. Extractibility of phosphorus from phosphate minerals common in soils and sediments. Soil Sci. Soc. Am. J. 44:462-465.

Williams, J.D.H., J.K. Syers, R.F. Harris and D.E. Armstrong. 1971. Fractionation of inorganic phosphate in calcareous lake sediments. Soil Sci. Soc. Am. Proc. 35:250-255.

Williams, J.D.H., J.K. Syeres and T.W. Walker. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Sci. Am. Proc. 31:736-739.

Williams, E.G., Scott, N.M. and McDonal, M.J. 1958. soil properties and phosphate sorption. J.Sci. Food Agric. 9,551-9.

Williams E.G. and Knight, A.H. 1963. Evaluation of soil phosphate status by pot experiments, conventional extraction methods and labile phosphate values estimated with the aid of P-32. J. Sci. Food Agric. 8,555-63.

APPENDIX

APPENDIX 3.1: Profile description of study soils

Pedon 1

1. Classification:	clayey, kaolinitic, Aquic Kanhaplustalf
2. Location:	On the upper lacustrine, fluvial section of IAR's estate, Samaru, about 200 m north-northeast of the citrus orchard. Map coordinates: N 11°10'43" E 7°37'26"
3. Elevation:	675 m
4. Climate:	Tropical. Mean annual rainfall: 1090 mm rainy season: May-October soil moisture conditions: Aquic - after the dam nearby has been put up. annual temperature: mean monthly max. 30°, mean monthly min. 13°C soil temperature conditions: isohyperthermic
5. Vegetation:	General: Northern Guinea savanna (Grassland with shrubs.
6. Geology:	lacustrine to fluvial deposits from precambrian metasediments and metaigneous rocks of the Basement Complex.
7. Geomorphology and physiography:	Weakly undulating peneplain with inselbergs. The profile was situated on a northwest sloping footslope with 1-2% gradient.
8. Drainage:	poor, hydromorphic conditions.
9. Erosion:	accumulation area for eroded material.
10. Land use:	grazing.
11. Described:	E.O. Uyovbisere, T.T. Kparmwang, and J.P. Moberg
12. Remarks:	Iron-oxyhydroxide-rich mottles and root channel linings were present from the surface to at least 180 cm depth.

Horizonal description:

A 0 - 4/10	Very dark grey (10 YR 3/1, moist) humus-rich silt loam; very fine crumby to platy; slightly sticky and slightly plastic, very friable, loose; many very fine and fine medium continuous tubular pores; many very fine and

fine roots; termite and ant activity; abrupt, wavy boundary.

Ag 4/10 10-28 Dark grey (10YR 4/1, moist) matrix with common, fine distinct, clear dusky red (2.5YR 3/2, moist) mottles; silty loam; medium angular blocky; slightly sticky and slightly plastic, friable to firm, firm; common very fine and fine few medium vertical continuous tubular pores; common very fine and fine roots; common medium rounded voids due to termites and/or ants; gradual, wavy boundary.

Bsg 28-40 Dark grey (10YR 4/1, moist) matrix with many coarse distinct; clear brown (7.5YR 4/2, moist) mottles and porelinings; silty clay loam; coarse angular blocky; slightly sticky and plastic, friable to firm; no clay skins, common very fine and fine, and few medium vertically continuous tubular pores; common medium rounded voids due to termites and ants; gradual, waving boundary.

Cg 40 - 180 Grey (10YR 5.5/1, moist) matrix with few to common medium distinct clear strong brown (7.5YR 5/6, moist) mottles and porelinings; silty loam; coarse angular blocky to massive; non sticky and non plastic; few very fine and few medium vertically continuous tubular pores; few very fine and fine roots; no watertable was detected to the depth of 180 cm at the time of examination.

Pedon 2

1. Classification:	clayey, kaolinitic, Kandiustalfic Eutrustox
2. Location:	About 0.5 km north of the Isoya village, 10 km south of Ife. Map coordinates: N 7°22'40" E 4°32'55".
3. Elevation:	280 -285 m.
4. Climate:	Tropical climate. mean annual rainfall: 1375 mm rainy season: 9 - 10 months soil moisture conditions: Udic tropustic annual temperature: 26°C soil temperature conditions: isohyperthermic
5. Vegetation:	natural: moist forest
6. Geology:	formed from amphibolite of the Basement Complex metasediments.
7. Geomorphology and physiography:	undulating to rolling landscape with hills and V-formed valleys. The profile was situated on the lower concave south-facing footslope with 3-4% gradient.
8. Drainage:	well drained.
9. Erosion:	nil
10. Land use:	presently cropped to maize, yams, bananas, etc. With few scattered trees.
11. Described:	E.O. Uyovbisere, J.P. Moberg, and T.T. Kparmwang

Horizonal description:

Ap 0 - 30	Dark reddish brown (2.5YR 3/4, dry) humus containing loam; moderate to strong, medium to coarse crumby; non sticky and non plastic, friable, loose; common very fine and fine, few medium random continuous pores; many very fine and medium roots; earthworms were present, few medium rounded voids due to termites; very few stones (amphilbolites and quartzites); gradual, smooth boundary.
B 30-55	Red (2.5YR 4/6, dry) clay loam, moderate fine crumby; sticky and plastic, friable; patchy thin iron-oxyhydroxide-rich flow cutans; common very fine and fine random continuous pores; common fine, medium and coars roots; few medium to coarse rounded voids due to

termites; very few stones and gravel pieces (amphibolites and quartzite); many firm iron-oxyhydroxide-rich nodules, having the same colour as the matrix; diffuse, smooth boundary.

Btv 55-70 Dark red (10YR 3/6, dry) clay loam; weakly porous massive; sticky and plastic, firm; patchy thin iron-oxyhydroxide-rich cutans and clay skins; few to common micro and very few discontinuous voids; few very fine, fine, medium, and coarse roots; very few medium rounded voids due to termites; many small firm iron-oxyhydroxide-rich nodules, some of them with black Mn-oxyhydroxide-rich coatings, the colour of the matrix of the nodules was alike to soil matrix colour; the nodules and the soil matrix were weakly cemented together; diffuse, smooth boundary.

Bv1 70-95 Red (2.5YR 4/8, dry) matrix with common distinct yellowish coloured and few blackish coated nodules; clay loam; slightly porous massive; sticky and plastic, firm to hard; few to common micro and very few medium random voids due to termites; many small, very firm iron-oxyhydroxide-rich nodules, some of them coated black with Mn-oxyhydroxides; the nodules and matrix were weakly cemented together; arbitrary boundary.

Bv2 95-130 Dark red (2.5YR 3/6, dry) iron-oxyhydroxide-rich nodule matrix with some clay loam in between. The layer was sampled by auger.

Bulk samples were taken from: 0-25 cm, 35-50 cm, 60-70 cm, 75-90 cm, and 100-130 cm depth intervals.

Pedon 3

1. Classification:	Clayey, Kaolinitic, Kanhaplic Haplustalf
2. Location:	Harry Darling Rd. 23, Area C, Samaru) Map coordinates: N 11°10'33" E 7°37'34".
3. Elevation:	680 m.
4. Climate:	Tropical climate.
	mean annual rainfall: 1090 mm rainy season: May-October soil moisture conditions: typic tropustic
soil temperature.	mean temperature: max monthly 36°, mean monthly min. 13°C. Soil temperature conditions: isohyperthermic
5. Vegetation:	General:North Guinea savanna (wooded glassland).
6. Geology:	Precambrian complex, mainly metasediments and metaigneous rocks, plus some aeolean deposits.
7. Geomorphology and physiography:	inselberg landscape with lithoplinthite ridges, generally forming a weakly undulating lanscape.
8. Land form:	The profile was situated on the middle of a planar, about 1 km long north facing slope with 2-3% gradient.
9. Erosion:	nill, but sheet erosion when cultivated conventionally
10. Land use:	orchard - under an old mango tree.
11. Described:	E.O. Uyovbisere, T.T. Kparmwang, and J.P. Moberg
12. Remarks:	The soil was somewhat compacted from 22 to 55 cm depth. A petroplinthic layer was present from 105 to beyond 170 cm depth.

Horizonal description:

Ah 0 - 22	Dark brown (7.5YR 3/2, moist) humus containing sandy loam; weak, medium to fine crumby; non sticky and non plastic, friable, soft; many very fine and fine random continuous pores; many fine, medium and coarse roots; high activity of earthworms, termites and ants; few hard rounded iron-rich nodules; clear smooth boundary.

BE? 22-55 Red (2.5YR 3/9, moist) sandy clay loam to clay loam; slightly porous compact massive; sticky and plastic, very firm, hard; common very fine and fine, few medium random continuous pores; common fine, few medium roots; round, medium voids due to ants and termites; gradual, smooth boundary.

Bt 55-105 Red (3.75YR 4/4, moist) clay; porous massive; sticky and plastic, slightly hard; no clay skins observed; many very fine and fine, few medium, and very few coarse random continuous - some tubular - pores; a concentration of medium and coarse roots just above the horizon below; few medium to coarse, rounded voids due to termites and ants; clear, smooth boundary.

Btvm 105-160 cm Strong brown (7.5YR, moist) matrix with abundant medium, subangular to angular firm to hard iron-rich red (10YR 4/8, moist) nodules with reddish brown (2.5YR 4/4, moinst) coatings; very gravelly clay loam; compact porous massive; patchy, thick clay skins on nodule surfaces; common fine roots between the nodules; the petroplinthite layer continued beyond 170 cm depth.

Samples taken from the following depth intervals: 0-20 cm, 30-50 cm, 60-100 cm, and 110-160 cm.

Samples for bulk density determinations were taken from the following depth intervals: 2-7 cm, 35-40 cm and 75-80 cm depth.

Appendix 3.2: Nutrient rates and concentrations of elements in micro-nutrient mixture used for the greenhouse work.

Element	Source	Concentration
Macro-nutrients		Rate (ppm)
N	NH_4NO_3	130
K	K_2SO_4	80
Ca	$CaCl_2$	120
Micro-nutrient*		Weight in mixture (g)
Mg**	$MgSO_4.7H_2O$	1000
Mn	$MnSO_4.4H_2O$	100
Mo	$NH_4MO_4.2H_2O$	50
Cu	$CuSO_4.5H_2O$	100
B	$NaB_4O_7.IOH_2O$	100
Zn	$ZnSO_4.H_2O$	100

* 2.0 g of micronutrient mixture in 1 litre of solution, and 10 ml of solution was added to each pot.

** Mg was included in the micronutrient mixture.

Appendix 3.3: Nutrient content of the supply nutrient solution for the experimental stage of maize and rape in the growth chamber.

Nutrient	Maize	Rape
	---------- mM ----------	
Total N	72.26	113.2
NO_3^-	57.8	95.8
$H_2PO_4^{2-}$	1.35	1.3
SO_4^{2-}	3.05	6.1
K^+	37.60	35.8
Ca^{2+}	7.0	20.3
Mg^{2+}	1.7	8.1
NH_4^+	17.5	17.4
Cl^-	2.0	2.0
Na^+	1.20	1.2
	---------- µM ----------	
Mn^{2+}	61	61.0
Fe-EDTA	75	76.0
Zn^{2+}	26	26.0
Cu^{2+}	4.4	4.4
H_3Bo_3	52	52.0
MoO_4^{2-}	0.73	0.7
NH_4/NO_3	16.8/83.2	10.8/89.2

Appendix 4.1.1 Some macro- and micro-nutrient contents, pH $CaCl_2$ CEC (compulsive exchange and NH_4OAc saturation), and exchange acidity of the soil profiles.

Profile	Depth (cm)	Total N	pH $CaCl_2$	Exchangeable				CEC Gillman	CEC NH_4OAc	Exch. Acid	Micro-nutrients			
				Ca	Mg	K	Na				Fe	Cu	Mn	Zn
		%		$Cmol_c\ kg^{-1}$							ppm			
Pedon 1	0-4	0.500	4.22	6.1	2.9	0.78	0.150	11.0	26.8	3.36	545.0	4.40	144.5	13.9
	10-20	0.112	3.67	2.9	1.2	0.16	0.080	7.6	18.4	5.14	365.0	5.90	92.0	6.5
	20-40	0.060	4.10	3.4	1.4	0.14	0.160	7.6	16.9	1.00	155.0	3.10	132.0	4.5
	40-90	0.021	4.20	2.4	1.1	0.09	0.140	4.8	8.4	1.09	37.5	2.20	36.8	3.0
Pedon 2	0-22	0.131	6.41	6.4	1.4	0.39	0.078	7.7	10.7	0.58	35.0	0.70	98.0	16.5
	22-55	0.035	5.81	3.6	2.0	0.30	0.074	6.4	11.6	0.41	25.0	0.80	13.0	4.3
	55-100	0.025	5.61	3.1	1.6	0.23	0.039	6.1	10.0	0.42	11.0	0.70	6.2	3.0
	100-120	0.019	5.60	3.0	1.6	0.28	0.039	4.9	8.7	0.41	19.5	0.40	6.5	3.5
Pedon 3	0-30	0.208	5.46	6.2	1.8	0.15	0.078	9.1	17.2	0.36	35.0	5.00	659.0	12.0
	30-55	0.100	5.58	3.5	1.1	0.05	0.039	5.9	18.3	0.36	40.0	4.60	201.0	5.8
	55-70	0.102	5.58	2.8	0.9	0.02	0.020	5.0	14.2	0.36	65.0	2.70	80.0	3.3
	70-90	0.025	6.02	2.7	0.7	0.02	0.020	4.2	18.9	0.34	72.5	1.62	41.0	2.7
	90-130	0.023	5.72	2.4	1.1	0.02	0.020	4.4	18.0	0.40	64.0	0.80	39.8	2.4

Appendix 4.1.2. Physical and Chemical properties of the bulk soil from which the artificial soils were prepared.

General properties			P fractions	
Clay	%	= 57.1	Total P	= 275.0
silt	%	= 18.8	Saloid-P	= 4.5
Sand	%	= 24.1	Al-P	= 43.8
pH H_2O		= 4.5	Fe-P	= 107.5
pH $CaCl_2$		= 3.8	Ca-P	= 7.5
Org. C	%	= 2.8	Red Soil-P	= 6.3
ECEC $cmol_c\ kg^{-1}$		= 10.5	Water-P	= 1.5
ECEC*	,,	= 15.4	Resin-P	= 7.0
CEC*	,,	= 19.2	Bray-P	= 40.0
Exch. Ca	,,	= 3.8	Olsen-P	= 100.0
Mg	,,	= 1.7	Org-P	= 100.0
K	,,	= 0.3		
Na	,,	= 0.2		
Acidity H^+	,,	= 1.6	Fe & Al Oxide fractions	
Exch. Al^{3+}	,,	= 3.0	Fe_d %	= 1.21
Total N	%	= 0.2	Fe_{ox}	= 0.73
Zn	ppm	= 7.9	Fe_{py}	= 0.37
Fe	,,	= 4.8	Al_d	= 0.39
Cu	,,	= 5.1	Al_{ox}	= 0.05
Mn	,,	= 80.0	Al_{py}	= 0.77
SAREA M^2/g		= 92.6		
EC_e ($dS\ m^{-1}$)		= 0.8		

Appendix 4.1.3: Elemental composition of minerals identified in the soils.

Mineral	Chemical formular
Kaolinite	$Al_2Si_2O_5(OH)_4$
Illite	$K_{0.7}Al_2(Si,Al)_4O_{10}(OH)_2$
Quartz	SiO_2
Ilmenite	$FeTiO_3$
Plagioclase	$CaAl_2Si_2O_8$
Magnetite	Fe_3O_4
Goethite	-FeOOH
Haematite	$-Fe_2O_3$
Biotite	$K(MgFe)_3AlSi_3O_{10}(OH)_2$
Muscovite	$K_2Al_4(Si_6Al)O_{20}(OH)_4$
Opal	$SiO_2.nH_2O$
Microcline	$KAlSi_3O_8$
Hornblende	$(Ca,Na)_{2.26}(Mg,Fe,Al)_{5.15}$ $(Si,Al)_8O_{22}(OH)_2$

Appendix 4.3.1: Relations between P sorption indices at 6-day and 12-day equilibrium periods.

	P max- 6	P Affinity- 6	MBC- 6	SPR-6
P max-12	0.98**	0.59*	0.83**	0.90**
P Affinity-12	0.56*	0.85**	0.70**	0.71**
MBC-12	0.84**	0.83**	0.96**	0.97**
SPR-12	0.90**	0.78	0.95**	0.98**

Appendix 4.3.2: Parameter estimates from the Freundlich and Temkin equations as calculated by the Linear and Non-linear adsorption models for the prepared soils for the whole range of P added.

Soil	Freundlich Model				Temkin Model				
	A		N		b		A		Q
	LIN	LIN	NLIN	LIN	NLIN	LIN	NLIN	LIN	NLIN
6-day equilibrium									
NatCrA	8.9	11.3	0.89	0.96	-0.05	-197.7	0.298	163.6	-0.004
NatCrB	268.1	264.0	3.16	3.02	2549.9	346.1	86.8	77.5	79.74
NatAmA	234.2	254.1	1.91	2.02	1018.5	452.4	6.8	235.8	96.89
NatAmB	826.3	816.5	3.82	3.67	2999.9	1086.8	110.3	231.1	270.68
ArtCrA	837.5	749.2	2.49	2.02	5300.8	1121.1	15.7	406.9	870.31
ArtCrB	1236.9	1202.3	3.40	3.00	7948.4	1146.3	43.2	389.7	1249.92
ArtAmA	1561.8	1551.5	2.88	2.57	119.9	1771.9	51.2	450.1	21.79
ArtAmB	1868.7	1885.6	3.63	2.95	89.9	2070.5	175.6	400.2	14.53
12-day equilibrium									
NatCrA	9.7	14.3	1.11	1.27	19.7	-85.5	0.385	89.6	0.71
NatCrB	276.1	276.9	3.45	4.44	2309.8	338.6	88.1	75.5	70.36
NatAmA	295.3	279.5	2.00	1.89	1439.7	499.8	11.4	203.0	119.09
NatAmB	827.4	811.6	3.67	3.36	3349.8	1038.4	185.0	198.9	268.81
ArtCrA	912.3	895.2	2.78	2.25	-3139.8	1075.2	36.5	298.6	378.35
ArtCrB	1313.6	1314.2	3.41	3.57	3999.9	1481.2	100.2	321.4	518.75
ArtAmA	1590.5	1484.7	3.91	2.94	13071.2	1786.7	95.1	392.2	2068.45
ArtAmB	1790.8	1728.5	3.73	3.19	14248.6	2092.4	56.6	518.4	2980.37

Appendix 4.3.3: The R^2 and root mean square error (RMSE) for the comparison of the adsorption models for the description of P adsorption by the natural and artifical soils fitted by non-linear regression.

Soil	Langmuir Model		Freundlich Model		Temkin Model	
	R^2	RMSE	R^2	RMSE	R^2	RMSE
6-Day Equilibrium						
NatCrA	0.998	9.03	0.998	9.17	0.953	59.20
NatCrB	0.972	66.71	0.996	24.25	0.977	60.74
NatAmA	0.985	118.32	0.996	56.56	0.920	272.69
NatAmB	0.955	294.14	0.998	61.41	0.970	226.54
ArtCrA	0.982	118.84	0.996	85.28	0.970	232.05
ArtCrB	0.975	251.82	0.997	82.84	0.993	133.91
ArtAmA	0.989	170.66	0.995	116.58	0.981	225.86
ArtAmB	0.981	245.51	0.988	192.19	0.990	178.52

Appendix 4.2.8: The R^2 values for the linear and non-linear regressions for the adsorption models fitted to the P sorption data for the natural and artifical soils.

Soil	Langmuir Model		Freundlich Model		Temkin Model	
	LIN	NLIN	LIN	NLIN	LIN	NLIN
6-Day Equilibrium						
NatCrA	0.400	0.998	0.994	0.998	0.866	0.953
NatCrB	0.966	0.972	0.966	0.996	0.927	0.977
NatAmA	0.882	0.985	0.991	0.996	0.802	0.920
NatAmB	0.977	0.955	0.968	0.998	0.910	0.970
ArtCrA	0.969	0.982	0.951	0.996	0.931	0.970
ArtCrB	0.984	0.975	0.965	0.977	0.975	0.993
ArtAmA	0.987	0.989	0.988	0.995	0.935	0.981
ArtAmB	0.992	0.981	0.939	0.988	0.966	0.990

Appendix 4.5.1. Effects of phosphate ammendments on leaf length and plant height at 3 weeks as influenced by soil type, state of oxides crystallinity and OM interaction.

	Natural				Artificial			
	Crystalline		Amorphous		Crystalline		Amorphous	
Adjusted P rate	NatCrA (Top)	NatCrB (Sub)	NatAmA (Top)	NatAmB (Sub)	ArtCrA (Top)	ArtCrB (Sub)	ArtAmA (Top)	ArtAmB (Sub)
Leaf length - 3 wks								
0.00	25.0	23.1	23.6	25.3	20.8	23.4	23.4	21.7
0.02	25.5	26.1	21.4	31.3	24.1	28.8	29.1	32.2
0.06	23.2	26.8	26.4	29.0	25.1	27.8	30.1	26.1
0.20	23.2	27.1	27.6	28.5	26.4	33.7	31.5	29.2
0.60	27.4	27.1	31.1	29.8	28.4	32.1	30.9	29.2
1.50	27.9	32.3	31.8	29.7	32.6	30.1	34.3	22.2
mean	26.2	29.3	25.3	27.1	26.7	28.9	29.9	26.8
SE ±				1.317**				
Leaf width - 3 wks								
0.00	2.27	1.99	2.14	2.19	2.24	2.32	2.09	2.28
0.02	2.38	2.16	2.20	2.46	2.46	2.62	2.85	2.76
0.06	2.25	2.25	2.10	2.61	2.31	2.76	2.75	2.92
0.20	2.10	2.37	2.46	2.55	2.59	3.15	2.84	3.06
0.60	2.41	2.44	2.63	3.00	2.74	3.03	3.08	2.96
1.50	2.59	2.68	2.73	2.77	3.02	2.93	2.81	2.37
mean	2.33	2.31	2.40	2.60	2.55	2.80	2.73	2.72
SE ±				0.112**				

Appendix 4.5.2 Maize Plant height response at 3 weeks to adjusted solution P levels: Response surface model, R^2, RMSE and point of maximum response for the various soils.

Soil	Regression model	R^2	RMSE	Max. point	
				plt ht	equil. P
				cm	ug/ml
NatCrA	y = 29.8 + 3.9x - 0.23x2	0.12	5.49	46.8	8.58
NatCrB	y = 32.0 + 9.35x - 3.94x2	0.42	2.59	37.9	1.18
NatAmA	y = 30.0 + 24.8x - 11.50x2	0.72	2.79	43.4	1.07
NatAmB	y = 36.0 + 6.07x - 3.27x2	0.09	3.12	39.3	0.93
ArtCrA	y = 29.5 + 17.90x - 6.30x2	0.82	2.34	42.3	1.41
ArtCrB	y = 34.0 + 24.4x - 14.00x2	0.43	4.01	45.1	0.85
ArtAmA	y = 32.1 + 35.9x - 18.30x2	0.49	6.39	49.6	0.98
ArtAmB	y = 32.9 + 15.1x - 9.40x2	0.16	4.86	39.0	0.80

Appendix 4.5.3: Maize plant height response to adjusted solution P levels. Mean interactions of treatment effects (OM x oxide crystallinity) for the respective soils: Response surface model, R^2, RMSE, and point of maximum response.

Treament	Regression model	R^2	RMSE	Max. point yield	Max. point Equil. P
				g/pot	µg/ml
Organic matter (OM) x Soil type					
Nat-Top*	$y = 30.0 + 14.2x - 5.9x^2$	0.32	4.83	38.7	1.67
Nat-Sub	$y = 34.4 + 7.7x - 3.6x^2$	0.17	3.23	38.5	1.21
Natural soils	$y = 32.2 + 11.0x - 4.7x^2$	0.22	4.35	38.6	1.06
Art-Top	$y = 30.8 = 26.9x - 12.3x^2$	0.51	5.24	45.5	1.96
Art-Sub	$y = 33.8 + 19.7x - 11.9x^2$	0.25	4.63	42.0	1.84
Artific. Soils	$y = 32.3 + 23.3x - 12.3x^2$	0.34	5.15	43.5	1.42
Top-soils	$y = 30.4 + 20.6x - 9.1x^2$	0.39	5.25	42.0	1.29
Sub-Soils	$y = 34.1 + 13.7x - 7.7x^2$	0.19	4.00	40.2	1.13
Crystallinity of oxides X OM					
Nat-Amorph	$y = 32.6 + 23.3x - 10.2x^2$	0.37	6.00	45.8	1.13
Nat-Cryst.	$y = 32.1 + 21.1x - 10.3x^2$	0.46	4.16	42.9	1.02
Art-Amorph	$y = 33.4 + 15.3x - 7.4x^2$	0.37	3.66	41.3	1.03
Art-Cryst.	$y = 31.1 = 6.63x - 2.08x^2$	0.17	4.38	36.3	1.59
Amorph-Top	$y = 31.2 + 30.3x - 14.9x^2$	0.53	5.04	46.5	1.01
Amorph-Sub	$y = 34.7 + 9.8x - 5.1x^2$	0.12	4.27	39.5	0.97
Cryst.-Top	$y = 29.7 + 10.9x - 3.2x^2$	0.37	4.50	38.8	1.66
Cryst.-Sub	$y = 33 + 16.9x - 9.1x^2$	0.31	3.88	41.3	0.92
Amorphous	$y = 32.9 + 19.6x - 9.4x^2$	0.34	4.92	43.2	1.04
Crystalline	$y = 31.6 + 13.9x - 6.2x^2$	0.27	4.60	39.3	1.12

* Nat and Art represent natural and artificial systems.

Appendix 4.5.4. Mean relationship between P uptake and yield and the various forms of P extractable by the soil tests.

	Resin		Water		Bray		Olsen	
Parameter	pre	diff	pre	diff	pre	diff	pre	diff
Uptake	0.86**	0.91**	0.82*	0.85**	0.33	0.04	0.04	0.73*
Yield	0.80*	0.83**	0.68	0.70	0.38	-0.02	0.84**	0.12