

2002

Modeling of soil phosphorus sorption and control of phosphorus pollution with acid mine drainage floc

Bharpoor Singh Sekhon
West Virginia University

Follow this and additional works at: <https://researchrepository.wvu.edu/etd>

Recommended Citation

Sekhon, Bharpoor Singh, "Modeling of soil phosphorus sorption and control of phosphorus pollution with acid mine drainage floc" (2002). *Graduate Theses, Dissertations, and Problem Reports*. 1713.
<https://researchrepository.wvu.edu/etd/1713>

This Dissertation is protected by copyright and/or related rights. It has been brought to you by the The Research Repository @ WVU with permission from the rights-holder(s). You are free to use this Dissertation in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you must obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/ or on the work itself. This Dissertation has been accepted for inclusion in WVU Graduate Theses, Dissertations, and Problem Reports collection by an authorized administrator of The Research Repository @ WVU. For more information, please contact researchrepository@mail.wvu.edu.

**MODELING OF SOIL PHOSPHORUS SORPTION AND CONTROL OF
PHOSPHORUS POLLUTION WITH ACID MINE DRAINAGE FLOC**

Bharpoor Singh Sekhon

**Dissertation submitted to the
Davis College of Agriculture, Forestry, and Consumer Sciences
at West Virginia University
in partial fulfillment of the requirements for the
degree of**

**Doctor of Philosophy
in
Plant and Soil Sciences**

**Devinder K. Bhumbla, Ph.D., Chair
John C. Sencindiver, Ph.D.
Louis M. McDonald, Jr., Ph.D.
Henry W. Rauch, Ph.D.
Sanjay B. Shah, Ph.D.**

Division of Plant and Soil Sciences

**Morgantown, West Virginia
2002**

**Keywords: Phosphorus Sorption, Soil, Modeling, Non-point Source, Acid Mine
Drainage, Acid Mine Drainage Floc, Iron and Aluminum Oxides,
Inositol Hexaphosphate, Soil-Test Phosphorus, and West Virginia**

ABSTRACT

Modeling of Soil Phosphorus Sorption and Control of Phosphorus Pollution with Acid Mine Drainage Floc

Bharpoor S. Sekhon

The study was conducted to investigate and model phosphorus sorption in soils and to study the effectiveness of acid mine drainage (AMD) floc in controlling phosphorus (P) loss to surface runoff from soils. Phosphorus sorption capacity of surface and subsurface horizons of four benchmark soil series - Berks, Huntington, Lindside, and Monongahela - of West Virginia was measured. The soils of these four series were loaded with increasing amounts of P up to 60% of their P retention capacity. Though amount of P released to the solution increased with increase in degree of P saturation, most of the soils did not release considerable amounts of P. Phosphorus sorption capacity of surface and subsurface horizons of these soil series was predicted by using the standard characterization data on the amounts of Fe and Al oxides, pH, organic carbon, clay content, exchangeable Al and Mn, extractable acidity, and basic cations. Various statistical modeling techniques involving variable selection through stepwise ordinary least-squares regression (OLSR), and the principal components regression (PCR) were used for individual soils and for all soils in common. Models developed using the PCR technique performed the best. Use of AMD floc, an Fe and Al rich waste product generated after neutralization of AMD with chemicals like ammonium hydroxide, calcium hydroxide, and sodium hydroxide, in attenuating P in runoff or in soils was examined. AMD floc attenuated more inositol hexaphosphate (IHP)-P, which is a major organic-P form in poultry and swine manure, than it attenuated inorganic-P. Higher retention of IHP-P suggested that soils could receive more organic P than inorganic P. AMD floc did not catalyze the hydrolysis of IHP-P appreciably. Citrate and oxalate, companion anions of inorganic and IHP-P in manures, competed with both inorganic- and IHP-P for sorption sites onto AMD flocs only at low pH. Sorption of inorganic P was more affected by citrate and oxalate than the IHP-P sorption. Citrate impaired P sorption more than did oxalate, but with increase in pH (range 4-9) citrate competed less with P than did oxalate. Incorporation of AMD floc into soils lowered soil-test P, and degree of P saturation levels significantly in four different soils, and increased their P retention capacity. Results of the present study indicate that P retention capacity of the soils can be predicted from the data collected routinely as a part of soil survey or classification program, and AMD floc can be effectively used in controlling loss of P from soil to the water bodies.

Dedicated

To

The Eternal Memory of My Dear Brother-in-Law

S. RAJINDER SINGH BADESHA

And To

The Everlasting Memory of My Dear Father

S. BHAG SINGH SEKHON

Acknowledgements

First and foremost, I thank my major advisor **Dr. Devinder Kumar Bhumbla** for his expert guidance and huge moral support. A few words cannot recount the merits of my marvelous advisor. His remarkable ability to integrate his outstanding knowledge of soil chemistry into research has had an enduring impression on me. He created a highly congruous environment for my work and was always unsparing in all kinds of help. He stood with me through thick and thin and readily lent his shoulder to lean upon during bad times. This endeavor could not have been possible at all without his magnanimous help. This life is too short for me to repay his generosity. Association with him was a turning point in my life. I feel like having obtained a degree in philanthropy in tandem under his superb guidance.

I am highly thankful to my other committee members for their immense cooperation and valuable inputs to my research work and for whetting my skills through their wonderful teaching. These individuals are **Dr. John C. Sencindiver**, **Dr. Louis M. McDonald, Jr.**, **Dr. Henry W. Rauch**, and **Dr. Sanjay B. Shah**.

I thank again **Dr. John C. Sencindiver** for the field characterization of the soil data. I am grateful to Mr. **Brian Cooley** for helping with the basic soil characterization. Additionally, I thank my co-workers in the laboratory for their help and joyful company. These individuals are **Matt Stroud**, **Wendy Igo**, **Jennifer Lewis**, **Rosa Lee Miller**, **Jacqueline Davis**, and **Kendall Fridley**. Besides, I thank my **fellow graduate students** for their moral support and pleasant company.

I am extremely grateful to my friend **Dr. Ramkumar Bendapudi** for his moral support and enjoyable company. I feel indebted to **Dr. R.N. Singh** and **Dr. Joginder Nath** for their moral support.

I would be remiss if I do not acknowledge my lovely wife **Amrit** who underwent untold difficulties on my behalf and stayed oceans apart from me for a long time with my adorable daughters **Arshdeep** and **Jasmine**. Thanks to the telephony, which made this jovial trio liven me up every other day.

I owe a debt of gratitude to **my dear mother** for letting me do whatever I wanted to do. My studies deprived her of any help from me during her old age. I feel inexpressibly indebted to **my dear sisters** who sacrificed their future for me and provided me immense love and unlimited support. I am thankful to my nephews, nieces, and brother-in-laws for their love and moral support.

I will be ingrate if I do not thank **my in-laws** for their looking after my family in my absence. I could not have completed my studies without their comprehensive support. I am extremely fortunate for having such caring in-laws.

Finally, I gratefully acknowledge West Virginia University for providing graduate research assistantship through Hatch funds. I also acknowledge the Punjab State Department of Agriculture, India for granting me leave for pursuing this study.

TABLE OF CONTENTS

Dedication.....	iii
Acknowledgements.....	iv
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	ix
LIST OF FIGURES.....	xii
Chapter 1. Introduction.....	1
1.1. Objectives.....	4
Chapter 2. Review of Literature.....	5
2.1. Environmental Importance of Phosphorus.....	5
2.2. Build-up of Phosphorus in the Soil.....	7
2.3. Environmental Indices of Phosphorus.....	8
2.4. Loss of Phosphorus through Runoff and Leaching.....	10
2.5. Factors Affecting P Sorption in Soils.....	11
2.6. Organic Phosphorus and its Sorption on Soil Components.....	15
2.7. Hydrolysis of Inositol Phosphates.....	18
2.8. Use of Chemical Amendments in Controlling P Loss.....	18
References.....	20
Chapter 3. Phosphorus Retention Characteristics of Some Benchmark Soils of West Virginia.....	33
3.1. Introduction.....	33
3.2. Materials and Methods.....	34
3.2.1. Study Area and the Soils.....	34
3.2.2. Laboratory Techniques.....	34
3.3. Results and Discussion.....	36
3.3.1. Phosphorus Sorption Capacity.....	36
3.3.2. Effect of Phosphorus Saturation on P Leaching through Soils.....	42
3.3.3. Effect of Soil-Test (Mehlich-1 P) on Leachability of Phosphorus.....	43
3.4. Conclusions.....	53
References.....	53
Chapter 4. Modeling Phosphorus Sorption in Soils.....	55
4.1 Introduction.....	55
4.2. Materials and Methods.....	58
4.2.1. Laboratory Analyses.....	58
4.2.2. Statistical Analyses.....	59
4.3. Results and Discussion.....	59
4.4. Conclusions.....	102
References.....	102
Chapter 5. Sorption of Phosphorus onto Acid Mine Drainage Floc.....	105
5.1. Introduction.....	105
5.2. Materials and Methods.....	106
5.2.1. Preparation of Acid Mine Drainage Floc Suspensions.....	106
5.2.2. Sorption Experiments.....	107

5.2.3. Laboratory Analyses.....	108
5.2.4. Laboratory Measurements and Statistical Analyses.....	108
5.3. Results and Discussion.....	110
5.3.1. Sorption Isotherms.....	110
5.3.2. Implications of Sorption Isotherms for Degree of P Saturation Index.....	118
5.4. Conclusions.....	123
References.....	123
Chapter 6. Hydrolysis of Inositol Hexaphosphate by Acid Mine Drainage Floc..	126
6.1. Introduction.....	126
6.2. Materials and Methods.....	127
6.3. Results and Discussion.....	130
6.4. Conclusions.....	135
References.....	135
Chapter 7. Competitive Sorption of Organic Anions and Phosphorus onto Acid Mine Drainage Floc.....	137
7.1. Introduction.....	137
7.2. Materials and Methods.....	138
7.2.1. Preparation of Acid Mine Drainage Floes.....	138
7.2.2. Sorption Experiments.....	138
7.3. Results and Discussion.....	141
7.3.1. Effect of Citrate Loadings on P sorption.....	141
7.3.2. Effect of pH on P Sorption at Various Levels of Citrate Loadings.....	142
7.3.3. Effect of Oxalate Loadings on P Sorption.....	151
7.3.4. Effect of pH on P Sorption at Various Levels of Oxalate Loadings.....	152
7.3.5. Comparison between Citrate and Oxalate Effects.....	153
7.3.6. Effect of Citrate and Oxalate on the Fe, Al, and Ca Concentrations.....	162
7.4. Conclusions.....	162
References.....	163
Chapter 8. Controlling Soil-test Phosphorus and Degree of P Saturation with Acid Mine Drainage Floc.....	165
8.1. Introduction.....	165
8.2. Materials and Methods.....	166
8.3. Results and Discussion.....	170
8.3.1. Acid Mine Drainage Floc Additions and Degree of P Saturation.....	170
8.3.2. Relationship between Degree of P Saturation and Soil-Test Phosphorus.....	171
8.3.2.1 Mehlich-1 P.....	171
8.3.2.2. Mehlich-3 P.....	189
8.3.2.3. Degree of P Saturation and CaCl ₂ -extractable P..	190
8.3.2.4. Degree of P Saturation and P Sorption Capacity..	191
8.3.3. Relationships between Soil-test P and CaCl ₂ -extractable P...	192

8.4. Conclusions.....	194
References.....	194
Chapter 9. Summary and Conclusions.....	197
Appendix.....	204

LIST OF TABLES

3.1. Phosphorus sorption capacity of Berks soils.....	38
3.2. P sorption capacity of Huntington soils.....	39
3.3. P sorption capacity of Lindside soils.....	40
3.4. P sorption capacity of Monongahela soils.....	41
4.1. Data (Part-I) used for modeling P sorption capacity (PSC) in Berks soil.....	62
4.2. Data (Part-II) used for modeling P sorption capacity in Berks soil.....	63
4.3. Data (Part-I) used for modeling P sorption capacity in Huntington soils...	64
4.4. Data (Part-II) used for modeling P sorption capacity in Huntington soil.....	65
4.5. Data (Part-I) used for modeling P sorption capacity in Lindside soil.....	66
4.6. Data (Part-II) used for modeling P sorption capacity in Lindside soil.....	67
4.7. Data (Part-I) used for modeling P sorption capacity in Monongahela soil.....	68
4.8. Data (Part-II) used for modeling P sorption capacity in Monongahela soil.....	69
4.9. Estimated coefficients for regression model based on ordinary least squares regression (OLSR) model using all variables (OLSR full model).....	79
4.10. Summary of various diagnostic statistics of models developed by using ordinary least square regression (OLSR) on all variables (OLSR full model), OLSR on variables selected through stepwise OLSR (OLSR reduced model) and principal components regression (PCR).....	80
4.11. Variance Inflation factors (VIF; indicators of multicollinearity) for various variables.....	83
4.12. Regression estimates for the models developed using variable selection with stepwise ordinary least squares regression (OLSR: OLSR reduced model).....	87
4.13. Variation (%) explained by different principal components extracted from the data for individual soils and from the combined data from all the soils.....	88
4.14. Regression coefficients for principal components (PCs) selected for using as independent variables for modeling P sorption capacity in various soils.....	90
4.15. Composition of the selected principal components (PCs) used in the model developed by using the combined data from all the four soils.....	91
4.16. Composition of the principal components (PCs) selected for regression in Berks soil.....	92
4.17. Composition of principal components (PCs) selected for regression	

in Huntington soil.....	93
4.18. Composition of principal components (PCs) selected for regression in Linside soil.....	94
4.19. Composition of the principal components (PCs) selected for regression in Monongahela soil.....	95
4.20. Coefficients for the simplified models using principal components regression (PCR) for various soils.....	96
5.1. Elemental composition, pH, and P sorption capacity of three different acid mine drainage (AMD) flocs prepared by neutralizing AMD with ammonium hydroxide, calcium hydroxide, and sodium hydroxide.....	109
5.2. Ratio of inositol hexaphosphate-P (IHP-P) and inorganic P sorbed onto ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage floc at various initial P loadings.....	116
5.3. Coefficients of linearized Langmuir sorption isotherms for the sorption of inorganic-P and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs...	117
6.1. Elemental composition, pH, and P sorption capacity of ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs used for the study.....	128
6.2. Carbon: phosphorus (C:P) ratio of solutions of ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage floc suspensions equilibrated with 5.16 mM inositol hexaphosphate (IHP)-P solution.....	131
6.3. Orthophosphate concentrations in 200 mg L ⁻¹ inositol hexaphosphate-P solution at various pH values.....	133
7.1 Combinations of organic anions (citrate and oxalate) and P (inorganic and inositol hexaphosphate) solutions used for studying the competitive sorption of citrate and oxalate with inorganic-P and inositol hexaphosphate (IHP)-P.....	140
7.2. Amounts of inorganic-P and inositol hexaphosphate (IHP)-P sorbed by ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs in the presence of varying levels of citrate at different pH levels.....	147
7.3. Amounts of inorganic-P and inositol hexaphosphate (IHP)-P sorbed by ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs in the presence of various concentrations of oxalate.....	150
8.1. Some relevant properties of the soils (0-5 cm) used for the study.....	169
8.2. Soil-test (Mehlich-1 and Mehlich-3) P, CaCl ₂ -extractable P, measured degree of P saturation (DPS), and P sorption capacity of the soils at different target DPS (calculated based upon the ammonium oxalate extractable Fe and Al added through acid mine drainage floc)...	172
8.3. F values (from analysis of variance) for the effect of acid mine drainage floc additions on soil-test P (Mehlich-1 and Mehlich-3 P), CaCl ₂ -extractable P, P sorption capacity and measured degree of P saturation (DPS).....	173

8.4. Degrees of P saturation (DPS) based upon the ammonium oxalate extractable Fe, Al, and P in the soils after acid mine drainage (AMD) floc additions as compared to the DPS (target DPS) calculated from the amount of ammonium oxalate extractable Fe and Al added through AMD floc.....	174
8.5. Decrease in Mehlich-1 P, Mehlich-3 P, CaCl ₂ -extractable P, and increase in P sorption capacity with per unit decrease in target degree of P saturation (DPS).....	175
8.6. Regression equations for the relations of Mehlich-1 P, Mehlich-3 P, CaCl ₂ -extractable P, and P sorption capacity with degree of P saturation (DPS) for various soils.....	193
A1. Dissolution of Fe in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by citrate additions at various pH levels and in the presence of inorganic-P and inositol hexaphosphate (IHP)-P.....	205
A2. Dissolution of Fe in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by oxalate additions at various pH levels in the presence of inorganic-P and inositol hexaphosphate(IHP)-P.....	206
A3. Dissolution of Al in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by citrate additions at various pH levels in the presence of inorganic-P and inositol hexaphosphate (IHP)-P.....	207
A4. Dissolution of Al in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by oxalate additions at various pH levels and in the presence of inorganic-P and inositol hexaphosphate(IHP)-P.....	208
A5. Effect of citrate additions on dissolution of Ca in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs at various pH levels.....	209
A6. Effect of oxalate additions on dissolution of Ca in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs at various pH levels in the presence of inorganic-P and inositol hexaphosphate (IHP)-P.....	210

LIST OF FIGURES

3.1. Dissolved P at various degrees of P saturation in A, B, and C horizons of Berks soil.....	45
3.2. Dissolved P at various degrees of P saturation in A, B, and C horizons of Huntington soils.....	46
3.3. Dissolved P at various degrees of P saturation in A, B, and C horizons of Lindside soils.....	47
3.4. Dissolved P at various degrees of P saturation in A, B, and C horizons of Monongahela soils.....	48
3.5. Relationship between soil-test (Mehlich-1) P and dissolved P in various horizons of Berks soils.....	49
3.6. Relationship between soil-test (Mehlich-1) P and dissolved P in A, B, and C horizons of Huntington soils.....	50
3.7. Relationship between soil-test (Mehlich-1) P and dissolved P in A, B, and C horizons of Lindside soil.....	51
3.8. Relationship between soil-test (Mehlich-1) P and dissolved P in A, B, and C horizons of Monongahela soil.....	52
4.1. Relationship between P sorption capacity and ammonium oxalate extractable Al (A) and ammonium oxalate extractable Fe (B) in Berks, Huntington, Lindside, and Monongahela soils.....	70
4.2. Relationship between P sorption capacity (PSC) and dithionite-citrate-bicarbonate (DCB) extractable Al (A) and Fe (B) in Berks, Huntington, Lindside, and Monongahela soils.....	71
4.3. Relationship between P sorption capacity (PSC) and clay content in Berks, Huntington, Lindside, and Monongahela soils.....	72
4.4. Relationship between P sorption capacity (PSC) and ammonium acetate extractable Ca in Berks, Huntington, Lindside, and Monongahela soils.....	73
4.5. Relationship of P sorption capacity (PSC) with extractable acidity (A) and KCl-extractable Al (B) in Berks, Huntington, Lindside, and Monongahela soils.....	74
4.6. Relationship between P sorption capacity (PSC) and sum of cations in Berks, Huntington, Lindside, and Monongahela soils.....	75
4.7. Relationship between total carbon and P sorption capacity in Berks, Huntington, Lindside, and Monongahela soils.....	76
4.8. Relationship between KCl-extractable Mn and P sorption capacity (PSC) in Berks, Huntington, Lindside, and Monongahela soils.....	77
4.9. Relationship between P sorption capacity and pH (CaCl ₂ ;(A)) and pH (in water;(B)) in Berks, Huntington, Lindside, and Monongahela soils.....	78
4.10. Relationship between measured P sorption capacity (PSC) and the PSC predicted by the PCR model developed for all soils.....	97
4.11. Relationship between measured P sorption capacity in Berks and Monongahela soils and the PSC predicted by using the principal components regression (PCR) model developed for all soils.....	98

4.12. Relationship between the measured P sorption capacity (PSC) in Huntington and Lindside soils and the PSC predicted by using principal components regression (PCR) model developed for all soils.....	99
4.13. Relationship between the measured P sorption capacity in Berks and Monongahela soil and the PSC predicted by using respective principal components regression (PCR) models developed for individual soils.....	100
4.14. Relationship between the measured P sorption capacity (PSC) in Huntington and Lindside soils and the PSC predicted by using respective principal components regression (PCR) models developed for individual soils.....	101
5.1. Sorption of inorganic P onto ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.....	112
5.2. Sorption of organic P (inositol hexaphosphate (IHP)-P) onto ammonia-treated, lime-treated and sodium hydroxide-treated flocs.....	113
5.3. Ratio of inositol hexaphosphate (IHP)-P and inorganic P sorbed onto ammonia-treated, lime-treated, and sodium hydroxide-treated flocs.....	115
5.4. Moles of inorganic P sorbed per mole of Fe+Al in relation to moles of inorganic P added per mole of Fe+Al in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.....	120
5.5. Moles of inositol hexaphosphate (IHP)-P sorbed per mole of Fe+Al in ammonia-treated, lime-treated, and sodium hydroxide-treated flocs.....	121
5.6. Moles of inorganic-P and inositol hexaphosphate (IHP)-P sorbed per mole of Fe+Al in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs to the moles of P added per mole of Fe+Al.....	122
6.1. Carbon: Phosphorus ratio of solutions of inositol hexaphosphate equilibrated with or without (control) ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.....	132
6.2. Orthophosphate-P concentrations in 200 mg L ⁻¹ inositol hexaphosphate-P solution (in 0.01M NaCl) at various pH levels.....	134
7.1. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium-hydroxide treated floc as affected by increasing citrate loadings at pH 4 and 5.....	144
7.2. Sorption of inorganic and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated and sodium hydroxide-treated acid mine drainage flocs, as affected by increasing citrate additions at pH 6 and 7.....	145
7.3. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on various acid mine drainage flocs as affected by increasing citrate concentrations at pH 8 and 9.....	146
7.4. Effect of pH on the sorption of inorganic and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs in the absence of	

any citrate addition and in the presence of 1.72mM citrate.....	148
7.5. Effect of pH on the sorption of inorganic and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide treated AMD flocs in the presence of 3.44mM and 5.16mM citrate.....	149
7.6. Sorption of inorganic- and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by oxalate additions at pH 4 and 5.....	157
7.7. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by oxalate additions at pH 6 and 7.....	158
7.8. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by oxalate additions at pH 8 and 9.....	159
7.9. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by pH in the absence and in the presence of 1.72mM oxalate.....	160
7.10. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by pH in the presence of 3.44mM and 5.16mM oxalate.....	161
8.1. Relationship between degree of P saturation (DPS) and Mehlich-1 P in Berks-I and Berks-II soils.....	176
8.2. Relationship between degree of P saturation (DPS) and Mehlich-1 P in Lindsida and Monongahela soils.....	177
8.3. Relationship between degree of P saturation (DPS) and Mehlich-3 P in Berks-I and Berks-II soils.....	178
8.4. Relationship between degree of P saturation and Mehlich-3 P in Lindsida and Monongahela soils.....	179
8.5. Relationship between CaCl ₂ -extractable P and degree of P saturation in Berks-I and Berks-II soils.....	180
8.6. Relationship between degree of P saturation (DPS) and CaCl ₂ -extractable-P in Lindsida and Monongahela soils.....	181
8.7. Relationship between degree of P saturation and P sorption capacity in Berks-I and Berks-II soils.....	182
8.8. Relationship between degree of P saturation (DPS) and P sorption capacity in Lindsida and Monongahela soils.....	183
8.9. Relationship between Mehlich-1 P and CaCl ₂ -extractable P in Berks-I and Berks-II soils.....	184
8.10. Relationship between Mehlich-1 P and CaCl ₂ -extractable P in Lindsida and Monongahela soils.....	185
8.11. Relationship between Mehlich-3 P and CaCl ₂ -extractable P in Berks-I and Berks-II soils.....	186
8.12. Relationship between Mehlich-3 P and CaCl ₂ -extractable P in Lindsida and Monongahela soils.....	187

Chapter 1

Introduction

Excess phosphorus (P) causes eutrophication of surface waters. Eutrophication is the increase in biological productivity of surface waters brought on by nutrient enrichment. This process can be greatly accelerated by human activities that increase nutrient loadings to water. Eutrophication has been recognized as the main cause of impaired water quality. Eutrophication limits water use for fisheries, recreation, industry, and drinking due to the increased growth of undesirable algae and aquatic weeds and due to the dissolved oxygen shortages caused by their death and decomposition. Drinking water supplies may be affected by periodic surface blooms of cyanobacteria (blue-green algae) and may affect human and animal health adversely. Recent outbreaks of the dinoflagellate *Pfiesteria piscicida* in the eastern United States, especially in Chesapeake Bay tributaries, have been connected to the excessive nutrient build-up in waters.

Eutrophication of most of the fresh waters around the world is accelerated by P inputs. Thus, P is often the limiting nutrient in most fresh waters, and its control is of great importance in reducing the eutrophication of fresh waters. Inputs of P to surface waters from point sources, the sources with a clearly identifiable point of discharge (for example, outflow from a wastewater treatment plant), have largely been controlled through technological developments and environmental regulations. However, inputs of P from non-point sources, the sources with no obvious point of discharge, still need to be controlled satisfactorily. Agricultural runoff is the largest non-point source of P to natural waters.

Phosphorus in agricultural runoff arises from the excessive build-up of soil-test P. Several studies report increased P loss to runoff with increasing levels of soil-test P. The rise in soil-test P generally results from the improper land-application of animal wastes and relatively meager crop-uptake of P.

Animal agriculture is a major source of agricultural income in several USA states, particularly eastern states. Animal manure is produced in large amounts. Animal manure can improve soil structure and enhance vegetative cover. However, when manure is applied in excess of crop needs, it leads to the build-up of nutrients, particularly P, in the soils. Poultry manures are the most important source of excessive P in soils. Grains constitute a considerable part of poultry feed. Most of the P in grains is in phytate or inositol phosphate form. Poultry are monogastric animals or non-ruminants. Monogastric animals do not have the requisite enzyme phytase for the digestion of inositol phosphates. Thus, poultry and other monogastric animals such as swine simply provide a transit to the phytate or inositol phosphate-P from feed to manures. Most animal operations do not have enough land for the proper disposal of manures. Therefore, increased accumulation of P in soils leads to the increased loss of P through leaching and runoff.

Runoff from soils is the predominant pathway of P loss from soils; but losses through leaching or subsurface runoff also are substantial in many soils. In well-drained soils, losses through subsurface flow could be substantial. Losses through subsurface flow are governed both by hydrological factors and chemical factors. Physical properties of the soils control hydrological features of the soils. Physical properties are in turn affected by some mineralogical properties of the soils. Formation of wide cracks within the soil profile, hence the formation of preferential pathways, is controlled by the amount

and type of swelling and shrinking clays. Chemical interaction of P with soil components also depends upon the type and amount of minerals present in soils. Factors such as presence of Fe and Al oxides and low pH imply increased P retention. Thus, P retention and release characteristics could be specific to each soil series. However, P retention and release characteristics are not routinely measured. Site-specific data on these characteristics are not available. These can be potentially predicted based upon the characterization data routinely collected from different soils for soil classification purposes.

Phosphorus in surface runoff is in both soluble and particulate forms with particulate P constituting a major part of total P. However, the predominant form of P loss through leaching or subsurface flow is dissolved P. Dissolved P is more readily available for biological uptake than particulate P. Most of the current best management practices, such as buffer strips, riparian zones, and conservation tillage, aim at containing particulate P loss only. These practices do not reduce dissolved P concentrations adequately. Therefore, in order to address the problem comprehensively, some best management practices aimed at curbing dissolved P loss need be designed.

Various chemical amendments, consisting chiefly of salts of iron and aluminum, have been used to control dissolved P loss. Certain industrial and mining wastes that are rich in iron and aluminum oxides have the potential to attenuate dissolved P loss or lower soil-test P levels, because hydroxylated surfaces of these metal oxides have great affinity for P. Acid mine drainage (AMD) floc consists mainly of amorphous iron and aluminum hydrous oxides. Large amounts of AMD floc are generated during the treatment of AMD before its discharge into receiving water bodies. This floc is considered as a waste

product with no productive use. Furthermore, the increased thermodynamic stability of these flocs reduces the likelihood of secondary leaching of the floc back into the environment and hence allows their use for remediation purposes.

In a watershed where streams are impaired by non-point sources of P, especially by phosphorus in agricultural runoff, loss of P from land to water bodies cannot be curtailed without lowering the soil-test P levels. Lowering soil-test P levels through crop removal is a long-term process. The large P retention capacity of AMD floc may help reduce high soil-test P levels to safer levels in a short period of time.

1.1. Objectives

Specific objectives of the present study were to:

1. Investigate and predict P sorption characteristics of some benchmark soils of West Virginia.
2. Examine the effect of various AMD flocs, resulting from the use of various chemicals used to neutralize AMD, on the sorption of organic (inositol phosphates) and inorganic P.
3. Explore the possibility of using AMD floc for effecting rapid decline in soil-test P levels.

Chapter 2

Review of Literature

2.1. Environmental Importance of Phosphorus

Phosphorus is an essential element for plant and animal growth, and its input has long been recognized as necessary to maintain profitable crop and animal production (Sharpley et al., 1999). However, P inputs can also increase the biological productivity of natural waters by accelerating eutrophication. Eutrophication is the natural aging of lakes or streams by nutrient enrichment. Lakes and reservoirs can be broadly classified as ultra-oligotrophic, oligotrophic, mesotrophic, eutrophic or hypereutrophic depending on the concentration of nutrients in the body of water and/or based on ecological manifestations of the nutrient loading (UNEP, 2000). In general, oligotrophic lakes and reservoirs are characterized by low nutrient inputs, high transparency, and a diverse biota. Eutrophic waters, on the other hand, have high nutrient inputs, low transparency, and a high biomass of fewer species with a greater proportion of cyanobacteria than in oligotrophic waters.

A subtle result of enrichment of lakes with nutrients is increased growth of algae. Cyanobacteria are an especially troublesome group that are known to form unsightly surface scums, to cause severe oxygen depletion and fish mortalities, and to lead to death of cattle and other animals from ingestion of algal toxins (UNEP, 2000). Filamentous species of cyanobacteria or green algae (chlorophytes) can clog filters in water treatment or industrial facilities. Dinoflagellates are another group of phytoplankton that can cause

toxic conditions. One by-product of algal blooms can be high concentrations of dissolved organic carbon (DOC). When water with high DOC is disinfected by chlorination, potentially carcinogenic and mutagenic trihalomethanes are formed (UNEP, 2000). Another consequence of eutrophication is the excessive growth of aquatic plants. Dense mats of floating aquatic plants, such as water hyacinth (*Eichhornia crassipes*), an aquatic fern (*Salvinia molesta*) and Nile cabbage (*Pistia stratiotes*), can cover large areas near-shore and can float into open water. These mats block light from reaching submerged vascular plants and phytoplankton, and often produce large quantities of organic detritus that can lead to anoxia and emission of gases, such as methane and hydrogen sulfide. The material derived from these plants is usually of low nutritional quality and is not often an important component of the food for zooplankton or fish. Accumulations of aquatic macrophytes can restrict access for fishing or recreational uses of lakes and reservoirs and can block irrigation and navigation channels and intakes of hydroelectric power plants.

A by-product of increases in the abundance of algae and aquatic macrophytes is generation of more organic matter. As this organic matter decomposes in the water column or in the sediments, the concentration of dissolved oxygen decreases. In shallow lakes and where plant production is large, complete deoxygenation of the sediments and water can occur. Such conditions are adverse to the survival of fishes and invertebrates. In addition, phosphate may be released into the water from anoxic sediments, further enriching the lake (UNEP, 2000). Another result of eutrophication is the shifts in the abundance and species composition of aquatic organisms. Decline in underwater light levels because of dense algal blooms or floating macrophytes can reduce or eliminate

submerged macrophytes. Changes in food quality associated with shifts in algal or aquatic macrophyte composition, and declines in oxygen concentration could alter the species composition of fishes.

The eutrophication process can be greatly accelerated by human activities that increase nutrient loading rates to water. Nutrient enrichment is the leading cause of pollution of lakes and estuaries and the second leading cause of pollution of rivers, behind sediment (USEPA, 1998). By early 1970s, P was generally accepted as the limiting nutrient for eutrophication of most of the waters in United States (Schindler, 1975; Likens, 1972). Phosphorus is generally the limiting nutrient (Sharpley et al., 1994) because plant P content is much larger than P content of natural waters (Wetzel, 1983). Historically, indiscriminate use of detergents and inputs of P fertilizers were considered to be the main source of P in natural waters (Litke, 1999). However, due to a ban imposed by many states on manufacturing of P-based detergents and with the passage of the Clean Water Act, 1972, contribution of P from point sources was greatly reduced. Thus, P remediation efforts in 1990s were mainly focused at non-point sources like agricultural runoff (Litke, 1999).

2.2. Build-up of Phosphorus in the Soil

Intensive livestock and agricultural production has led to the build-up of excessive soil-test P levels in many soils (Alley, 1991; Sims, 1992). According to a USDA-ERS study (Gollehon et al., 2001), in 1997 confined animal operations produced 462,000 tons of excess P, over that which can be applied to soil in an agronomically proper way, in the form of manures. Of this, 52% was contributed by poultry, 22% by beef, 18% by swine, and 8% by dairy operations. Thus, increase in soil-test phosphorus levels can be ascribed

to the limited land availability for disposal of these nutrients, exclusive use of animal wastes for agricultural production, and land-application of animal wastes based solely upon crop nitrogen requirements (Sims, 1995; Whalen and Chang, 2001). Scant and sluggish removal of P by crops (McCollum, 1991; Whalen and Chang, 2001) is also implicated in build-up of P in soils. Nitrogen-phosphorus ratio of most of the manures and composts is significantly less than that of crop uptake (Gilbertsen et al., 1979; Eghball et al., 1997). Varying requirements of P levels by the same crop on different soils (Abekoe and Sahrawat, 2001) also aid in the build-up.

2.3. Environmental Indices of Phosphorus

Environmental thresholds of P are those critical levels of P in soil above which the amount of P released by the soil to the runoff or leachate is detrimental to the environment. There are three general approaches by which environmental thresholds can be determined. The first is the agronomic approach (Kleinman et al., 2000). The agronomic approach establishes agronomic soil P standards as environmental thresholds. This approach has been commonly used by many state agencies (Sharpley et al., 1996; Sibbesen and Sharpley, 1997; Sims, 1999). The rationale for this approach is that soil P in excess of crop needs is vulnerable to removal by surface runoff or leaching. Since agronomic guidelines, that is, nutrient recommendations for different crops, already exist for soils, this approach needs little investment in research and can be easily implemented. However, a major problem with equating agronomic P levels with environmental thresholds is that the controlling processes by which plants access soil P are different from those that determine soil P availability for runoff.

The second approach for assessing soil P thresholds requires correlation of P in the runoff or leachate with P in the soil (Pote et al., 1996, 1999; Sharpley et al., 1996). This approach has been used in the Netherlands, where soil P saturation degree is used as a guide for agricultural P management.

The third approach has been suggested by Kleinman et al. (2000). They called it a soil chemical approach. This approach recommends determining those levels of various indices of extent of sorption of P in soils above which a significant part of soil P is not sorbed but remains soluble or labile for release to runoff or leaching. In other words, this approach suggests finding the 'change-point'. Change-point is a point (or the level of index of P saturation in soil) in the relation between an index of P saturation (such as soil-test P or degree of P saturation) and P lost through runoff or leaching above which soil has more tendency to release P to the solution than it had below that level. This change-point has been reported widely in literature (Hesketh and Brookes, 2000; Heckrath et al., 1995).

The concept of degree of P saturation (DPS) can be used both in the second and the third approach. Degree of P saturation concept considers the amorphous phases of Fe and Al as the principal controllers of P release in the soils. It is usually defined as the ratio of moles of P associated with one mole of amorphous Fe+Al. It is given by the following equation (Beauchemin and Simard, 1999):

$$DPS = \frac{P_{ox}}{\alpha(Fe + Al)_{ox}} \quad [2.1]$$

where P_{ox} stands for the moles of ammonium oxalate extractable P, and $(Fe+Al)_{ox}$ represents the moles of ammonium oxalate extractable Fe+Al. Ammonium oxalate is often used to extract amorphous phases of Fe and Al. The α factor represents the

maximum moles of P that can be sorbed by one mole of amorphous Fe+Al. Different values of α have been used in different studies (Beauchemin and Simard, 1999; Kleinman et al., 2000).

2.4. Loss of Phosphorus through Runoff and Leaching

Several workers have reported an increased loss of P in runoff with increasing application rates of P fertilizers (Romkens and Nelson, 1974), dairy manure (Mueller et al., 1984; Withers et al., 2001), poultry litter (Westerman et al., 1983; Edwards and Daniel, 1992; Edwards and Daniel, 1993), and swine manure (Edwards and Daniel, 1994). The loss may either be incidental or may be due to the build-up of P in the soil.

Several studies report that release of P to solution (apt to leaching and runoff loss) is directly related to the soil-test P by two linear relationships of significantly different slopes on either side (above or below) of the change-point: a point above which amount of dissolved P abruptly increases with increase in soil-test P (Heckrath et al., 1995; Hesketh and Brookes, 2000; McDowell et al., 2001). Thus, the change-point can serve as an environmental threshold for soil-test P.

Phosphorus lost through runoff is either in dissolved form or in suspended (sediment P or particulate P) form (Sharpley et al., 1992). Particulate P may be bioavailable (Sharpley et al., 1992) and may form the major part of total P concentration in the runoff (Westermann et al., 2001), but several studies have reported little decrease in eutrophic levels of receiving water bodies following reduced influx of particulate P (Young and De Pinto, 1982; Gray and Kirkland, 1986; Peterjohn and Correll, 1984; Gilliam, 1994). The conventional conservation practices involving the use of increased vegetative cover, no-tillage, reduced tillage, contour tillage, buffer strips, riparian zones, terracing, and

impoundments, help in controlling particulate P, but these practices are not effective in controlling loss of dissolved P.

2.5. Factors Affecting P Sorption in Soils

The foremost factor affecting P retention capacity of soils is the presence of Fe and Al oxides. These oxides are also known variously as hydrous oxides or oxyhydroxides. In the presence of water, surfaces of Fe and Al oxides are usually covered with hydroxyl groups or aquo (water) groups (Stumm and Morgan, 1996). These hydroxyl groups can be exchanged for phosphate groups (Goldberg and Sposito, 1984; White, 1981; Parfitt, 1978). The crystalline forms of these oxides, the most common being goethite (FeOOH) and gibbsite ($\text{Al}(\text{OH})_3$) (Hsu, 1977; Schwertmann and Taylor, 1977), exhibit variable-charge surfaces. Variable-charge surfaces are those surfaces which have unsatisfied bonds on their surface (Barrow, 1985) and in order to gain stability (Schindler, 1981), these surfaces coordinate with water molecules. These coordinated water molecules or aquo-groups can then become protonated (H^+ attached) or deprotonated, or can become positively charged or negatively charged, depending upon the pH of the solution. Thus, protonated surfaces or positively charged surfaces can enhance phosphate sorption through increasing electrostatic affinity for the negatively charged phosphate groups (Arai and Sparks, 2001). Thus, oxide surfaces have positive charge, negative charge, or no net charge depending upon the pH of the solution. A point in pH where positively charged sites equal negatively charged sites, or where net surface charge is zero, is called point of zero charge (PZC; Stumm and Morgan, 1996). When the oxide surfaces are below PZC, they will have positive charge and hence will help in the sorption of anions like phosphates (Hingston, 1981).

There is a large body of scientific literature on various aspects of metal oxides – P interactions. The mechanism of sorption has been widely studied. Spectroscopic studies (Tejedor – Tejedor and Anderson, 1990) indicate that P predominantly forms bidentate complexes that get protonated at low pH. At high pH, monodentate complexes are formed. Binuclear surface complexes connote strong sorption, because simultaneous removal of P from two center atoms is harder than the removal from one center atom (Bondietti et al., 1993). Concentration of phosphorus in the solution also has a bearing on the mechanism of sorption. Phosphorus chemisorbs initially, but with time excessive P gets sequestered in the form of large polymeric phosphate structures (Murrell et al., 1997) or sorbs physically (Celi et al., 2000). At high P concentration singly coordinated surface groups are formed and sorption is strongly affected by ionic strength as well (Celi et al., 2000).

Amorphous fractions (variously known as poorly-crystalline phases and active phases) are usually extracted with ammonium oxalate-oxalic acid solution (Loeppert and Inskeep, 1996; Bertsch and Bloom, 1996; Jackson et al., 1986; McKeague and Day, 1966; Schwertmann, 1964). Crystalline phases are usually determined by dithionite-citrate-bicarbonate (DCB) solution (Loeppert and Inskeep, 1996; Holmgren, 1967; Mehra and Jackson, 1960). Thus, it can be concluded that ammonium oxalate extractable Fe and Al, DCB-extractable Fe and Al, and pH have a great influence on P retention capacity of the soils. Pierzynski et al. (1994) observed similarly. Phosphorus retention capacity of the soils can also be affected by organically-bound Al (Zhou et al, 1997), which is usually extracted by Cupric chloride (Zhou et al, 1997; Bertsch and Bloom, 1996).

Clay particles have a large surface area. Moreover, many clays, besides Fe and Al oxides, may have a pH-dependent charge or variable charge (Barrow, 1985) and so they can sorb anions like phosphates. McKercher and Anderson (1989) observed a positive effect of clay content on P retention.

Retention of P in soils is also reported to be affected by organic carbon (Holford et al., 1997; Reddy et al., 1980; Kingery et al., 1994; Boudot et al., 1986). Most of these studies reported a negative correlation between P retention and organic carbon content. Holford et al. (1997) ascribed this to competitive effect of organic anions on the sorption of P by soils. However, Brennan et al. (1994) reported a positive effect of organic carbon on P sorption.

Competition between P species and other anions, especially organic, also has been investigated. This aspect becomes especially important for understanding P chemistry in soils, because manures are rich in low-molecular weight organic acids (Baziramakenga and Simard, 1998). Most of the studies report unfavorable effect of organic anions on P sorption (Dubus and Becquer, 2001; Liu and Huang, 1999; Geelhoed et al., 1998; Violante et al., 1991; Nagarajah et al., 1970). On the contrary, some studies suggest virtually no or little effect of anions like carbonate (Wijnja and Schulthess, 2000) and tartarate (De Cristofaro et al., 2000) on P sorption.

Effect of cations, especially calcium, on the sorption of P onto hydroxylated surfaces also has been reported. Interactions between Ca and P merit notice due to the following reasons: first, many soils and animal wastes are rich in calcium; second, natural waters contain appreciable amounts of Ca (concentration varies from 0.1 mMol L⁻¹ (fresh surface waters) to 10 mMol L⁻¹ (sea water); and last, these interactions are especially

important at high pH, and hence in eutrophic waters where increased photosynthesis expends bicarbonates and subsequently generates hydroxyls (Rietra et al., 2001). Addition of Ca^{2+} and Mg^{2+} enhances P sorption possibly through the effects on surface charge and solution speciation (Barrow et al., 1980; Yao and Millero, 1996). Overall, alkaline earth cations are effective in increasing the P sorption onto oxide surfaces in the order: $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ (Kawashima et al., 1986).

Sorption of P onto oxide surfaces is also affected by drying - wetting. Drying increases the surface area of aluminum oxides (Goldberg et al., 2001). Increased P sorption following the dry season can be ascribed to the increased surface area of amorphous oxides (Pote et al., 1999).

Comparisons between affinities of Fe and Al oxides for P also have been made. Iron oxides sorb P more strongly than do Al oxides, but Al oxides have a larger P sorption capacity (Bolan and Barrow, 1984; Adams et al., 1987; Parfitt et al., 1989). Phosphorus associated with Al oxides is more desorbable or exchangeable than that associated with iron oxides (He et al., 1992; Maguire et al., 2000).

Redox status of the soil also affects P sorption onto oxide surfaces. Reduced conditions facilitate dissolution of P associated with iron oxides (Moore and Reddy, 1994; Miller et al., 2001; Young and Ross, 2001). Less P is sorbed under reduced conditions.

Phosphate sorbed onto the surface of amorphous oxides imparts stability to the structure. This is suggested by its counter effect on the dissolution of these oxides (Bondietti et al., 1993; Hiradate and Inoue, 1998).

2.6. Organic Phosphorus and Its Sorption on Soil Components

Dominant forms of the soil organic P are inositol phosphates (Anderson, 1980). Inositol phosphates are an abundant plant constituent. They typically make up 60-90 percent of the total P in seeds (Lolas et al., 1976). Grains make a significant part of animal or poultry diets. However, non-ruminants like poultry and swine lack the requisite enzyme phytase (myo-inositol hexaphosphate hydrolase) to digest inositol phosphates or phytates in the grains. Thus, these animals transmit a large part of phytate P in manures. Most of the current feeding strategies for non-ruminants involve the addition of commercially available microbial phytase (mostly EC 3.1.3.8, 3-phytase) to enhance availability of phytate P present in the feeds. However, notwithstanding phytase addition, a substantial portion of phytate remains indigestible (Zyla et al, 2000). Thus, inositol phosphates predominate in manure from these animals. Barnett (1994a and 1994b) analyzed various manures for different forms of organic P. His work indicated that acid-soluble (mostly inositol phosphate) phosphorus makes 29.7, 53.4, and 33.2 percent of total organic P in hog, broiler, and layer manures, respectively. Peperzak et al. (1959) analyzed different manures for inorganic P, and different forms of organic P. Their results showed that inositol hexaphosphate was prominent only in poultry manure. McAuliffe and Peech (1949) reported the presence of inositol phosphates in sheep manure.

Though, according to Anderson (1980) inositol phosphates are the largest component of soil organic P. However, the multitude of extraction methods and spatial variability has effected different claims about the relative abundance of inositol phosphates in soils. Caldwell and Black (1958a) reported that inositol phosphates made up an average 16

percent (range 3-52 percent) of total organic P. Williams and Anderson (1968) reported that inositol penta- and hexaphosphates constituted an average 16 percent (range 0.4 to 38 percent) of soil organic P. Studies by Oniani et al. (1973) suggested that inositol phosphates share 17-45 percent of total organic P. Borie et al. (1989) stated that in volcanic soils of Chile, inositol phosphates comprise 42-67 percent of organic P.

Myo- inositol is the most common stereoisomer of inositol in soils (Cosgrove, 1980). However, certain other stereoisomers also have been detected in soils (Caldwell and Black, 1958b; Cosgrove, 1963; and Irving and Cosgrove, 1982).

Soil inositol phosphate content has also been related to certain factors. Caldwell and Black (1958 a) reported that forest soils had a higher content than grasslands. Studies of McKercher and Anderson (1968) on Canadian soils corroborated these findings. Williams and Anderson (1968) reported the accumulation of inositol phosphates in leguminous pastures. Caldwell and Black (1958a) also stated that the content decreased with increasing pH and decreasing organic matter. However, Williams and Anderson (1968) found no significant correlation between any other soil property and inositol phosphate content. Their profile studies indicated that inositol phosphates tended to accumulate in the surface horizon. Also, they found inositol phosphates to be decomposing at a lower rate than organic matter upon cultivation. Warman and Munroe (2000) found that amount of inositol phosphates associated with low molecular weight fractions of organic matter increased with increasing rate of compost addition.

Adsorption of inositol phosphates on soil surfaces has been studied from various aspects, namely adsorption mechanism, kinetics, comparison with inorganic phosphates and other organic phosphates, and pH effects. Ognalaga et al. (1994) studied glucose –1-

phosphate and myo-inositol hexaphosphate adsorption on goethite, in comparison to inorganic P adsorption. From electrophoretic and pH measurements, they concluded that adsorption mechanism involves phosphate groups only; organic moiety does not play any role. Work of Celi et al. (1999) justified the proposed mechanism, excepting for their view that organic moiety can create conformational hindrance during adsorption. Shang et al. (1990) studied kinetics of adsorption of inositol hexaphosphate, inositol monophosphate, and glucose-6-phosphate by short - range ordered precipitates of aluminum. Adsorption of inositol hexaphosphate was much greater than that of inositol monophosphate and glucose -6- phosphate. According to them, the adsorption during study went through two stages: fast adsorption before one hour and slow adsorption between one hour and 24 hours. The adsorption was first- order throughout. Another study by Shang et al. (1992) examined pH effects on kinetics of adsorption of organic and inorganic phosphates and validated the aforementioned nature of kinetics. They found that increasing pH decreased the adsorption rate; and adsorption of inositol hexaphosphate and glucose-6 phosphate involved higher exchange of hydroxyls for phosphorus adsorption.

McKercher and Anderson (1989) reported that adsorption of inositol phosphates in acidic soils reached a maximum and then declined but in alkaline soils it did not decrease after attaining maxima. Anderson et al. (1974) reported that higher additions of organic P suppressed the adsorption of inorganic phosphorus, but higher additions of inorganic phosphorus failed to counter the preferential adsorption of inositol phosphates.

2.7. Hydrolysis of Inositol Phosphates

Some studies report that metal oxides can hydrolyze phosphate esters (Baldwin et al., 2001; Baldwin et al., 1996; Baldwin et al., 1995; Torrents and Stone, 1993a; Torrents and Stone, 1993b). It is believed that coordination of phosphate ester to a metal ion increases the electrophilicity at the P center, which facilitates hydroxyl attack (Baldwin et al., 1995). However, hydrolytic ability of metal oxides can be affected by co-adsorbed ions (Torrents and Stone, 1993a) and by dissolved organic matter (Torrents and Stone, 1993b). However, most studies consider inositol phosphates refractory in nature and consider enzyme-mediated hydrolysis of inositol phosphates more likely (Suzumura and Kamatani, 1993; 1994, 1995a; Suzumura et al., 1998; Wild and Oke, 1966). Submerged conditions are reported to enhance mineralization of inositol phosphates, probably due to consequent pH rise and enhanced solubility (Furukawa and Kawaguchi, 1969). Suzumura and Kamatani (1995b) also reported higher mineralization of inositol phosphates under anaerobic conditions.

2.8. Use of Chemical Amendments in Controlling P Loss

Various chemical amendments – mainly consisting of iron and/or aluminum salts – have the potential to control dissolved P (Hsu, 1973, 1975, and 1976; Moore and Miller, 1994; Shreve et al., 1995; Baker et al., 1998; Huang and Chiswell, 2000; Lu and O’Connor, 2001; Maguire et al., 2000, 2001; Smith et al., 2001). Hydroxylated mineral surfaces like iron and aluminum oxides and 1:1 clays have strong affinity for some oxyanions like phosphate, arsenate, selenate, and molybdate. Hydroxylated mineral surfaces can sorb phosphate specifically (Hingston et al., 1967; and Goldberg and Sposito, 1985). There are a number of industrial and mining wastes that are rich in iron

and/or aluminum oxides (Goyette, 1992; Salinger et al., 1994; Baker et al., 1998; Huang and Chiswell, 2000; Peacock and Rimmer, 2000; Skousen et al., 2000; Codling et al., 2000) and thus have the potential for mitigating dissolved P loss.

Attenuation of dissolved contaminants through sorption onto the surface of adsorbents increases with an increase in the surface area of the adsorbents. Amorphous phases of minerals generally possess more surface area than their crystalline counterparts. Acid mine drainage precipitates consist largely of amorphous iron oxides (Singh et al., 1999), but they also have varying amounts of crystalline phases of goethite, jarosite, lepidocrocite, ferrihydrite, and schwertmannite (Brady et al., 1986; Filipek et al., 1987; Milnes et al., 1992; Crosby et al., 1983; Schwertmann et al., 1995).

The literature review hints that prediction of combined influence of all the factors that affect P retention capacity of soils can provide significant input to P management practices. Since soil survey personnel routinely collect the data relevant to some of these factors, these may be helpful in developing statistical models for P retention capacity. The review of literature also suggests that wastes consisting of oxides and hydroxides of Fe and Al need be evaluated for their use in controlling loss of soil P. These wastes can help lower the degree of P saturation (DPS). Degree of P saturation is the ratio of moles of P associated with amorphous Fe and Al phases to moles of amorphous Fe and Al. However, the review also implies that before embarking on a plan to use these wastes for this purpose, there is a need to evaluate the relation between the soil-test P and DPS; because, routine analysis for soil-test phosphorus levels is more common and easier than determination of DPS. This relationship will facilitate the application of AMD floc on the basis of soil-test P levels. Furthermore, a considerable part of total dissolved P in runoff

may be organic P. Besides P; the dissolved organic carbon may have certain other organic anions. These anions can impair P attenuation capacity of AMD through competitive sorption. Effects of such incidental anions need be examined. It needs be evaluated whether organic P compounds are sorbed as such onto Fe and Al oxide materials or these materials facilitate hydrolysis of organic P compounds and then sorb inorganic P produced by hydrolysis. Also, the variation in chemical composition of the wastes may have a bearing on their P attenuation capacity. Presence of calcium and other ions may affect P attenuation capacity. The present study was planned to address all these issues.

References

- Abekoe, M.K., and K.L. Sahrawat. 2001. Phosphate retention and extractability in soils of the humid zone in West Africa. *Geoderma* 102: 175-187.
- Adams, W.A., S.N. Gafoor, and M.I. Karim. 1987. Composition and properties of poorly - ordered minerals in Welsh soils. II. Phosphate adsorption and reactivity towards NaF solution. *J. Soil Sci.* 38: 95-103.
- Alley, M.M. 1991. Environmental implication for phosphorus management in mid – Atlantic United States. p. 63 –71. *In Proc. Western Phosphate and Sulfur Workshop.* Ft. Collins, CO. 22-23 March 1991. Colorado State University, Ft. Collins.
- Anderson, G. 1980. Assessing organic phosphorus in soils. *In* F.E. Khasawneh et al. (ed.) *The role of phosphorus in agriculture.* ASA, Madison, WI.
- Anderson, G., E.G. William, and J.O. Moir. 1974. A comparison of the sorption of inorganic orthophosphate and inositol hexaphosphate by six acid soils. *J. Soil Sci.* 25: 51-62.
- Arai, Y., and D.L. Sparks. 2001. ATR-FTIR spectroscopic investigation on phosphate adsorption mechanisms at the ferrihydrite-water interface. *J. Colloid Interface Sci.* 241: 317-326.

- Baker, M. J., D.W. Blowes, and C.J. Ptacek. 1998. Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite waste water disposal systems. *Environ. Sci. Technol.* 32: 2308 – 2316.
- Baldwin, D.S., J. K. Beattie, L.M. Coleman, and D.R. Jones. 1995. Phosphate ester hydrolysis mediated by mineral phases. *Environ. Sci. Technol.* 29: 1706 – 1709.
- Baldwin, D.S., J.K. Beattie, and D.R. Jones. 1996. Hydrolysis of organic phosphorus compound by iron oxide impregnated filter strips. *Water Res.* 30: 1123-1126.
- Baldwin, D.S., J.K. Beattie, L.M. Coleman, and D.R. Jones. 2001. Hydrolysis of an organophosphate ester by manganese dioxide. *Environ. Sci. Technol.* 35: 713-716.
- Barnett, G.M. 1994a. Phosphorus forms in animal manures. *Bioresource Technol.* 49: 139-147.
- Barnett, G.M. 1994b. Manure P fractionation. *Bioresource Technol.* 49: 149-155.
- Barrow, N.J. 1985. Reaction of anions and cations with variable-charge soils. *Adv. Agron.* 38: 183-230.
- Barrow, N.J., J.W. Bowden, A.M. Posner, and J.P. Quirk. 1980. Describing the effects of electrolyte on adsorption of phosphate by variable charge surface. *Aust. J. Soil Res.* 18: 395-404.
- Baziramakenga, R., and R.R. Simard. 1998. Low molecular weight organic acid contents of composted manure. *J. Environ. Qual.* 27: 557-561.
- Beauchemin, S., and R.R. Simard. 1999. Soil phosphorus saturation degree: Review of some indices and their suitability for P management in Quebec, Canada. *Can. J. Soil Sci.* 79: 615-625.
- Bertsch, P.M., and P.R. Bloom. 1996. Aluminum. Ch. 18, p. 517-550. *In* J.M. Bigham et al. (ed.) *Methods of soil analysis. Part 3 – Chemical methods.* SSSA-ASA, Madison, WI.
- Bolan, N.S., and N.J. Barrow. 1984. Modelling the effect of adsorption of phosphate and other ions on the surface charge of variable charge oxides. *J. Soil Sci.* 35: 273-281.
- Bondietti, G., J. Sinniger, and W. Stumm. 1993. The reactivity of Fe (III) (hydr) oxides: effect of ligands in inhibiting the dissolution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 79: 157-167.
- Borie, F., H.Zunino, and L. Martinez. 1989. Macromolecule-P associations and inositol phosphates in some Chilean volcanic soils of temperate regions. *Commun. Soil Sci. Plant Anal.* 20: 1881-1894.

- Boudot, J.P., B.A. BelHadj, and T. Chone. 1986. Carbon mineralization in Andosols and aluminium rich highland soils. *Soil Biol. Biochem.* 18: 457-461.
- Brady, K.S., J.M. Bigham, W.F. Jaynes, and T.J. Logan. 1986. Influence of sulfate on Fe-oxide formation: Comparisons with a stream receiving acid mine drainage. *Clay Clay Miner.* 34: 266-274.
- Brennan, R. F., M.D.A. Bolland, R.C. Jeffery, and D.G. Allen. 1994. Phosphorus adsorption by a range of western Australian soils related to soil properties. *Commun. Soil Sci. Plant Anal.* 25: 275-2795.
- Caldwell, A.G., and C.A. Black. 1958a. Inositol hexaphosphate III. Content in soils. *Soil Sci. Soc. Amer. Proc.* 22: 296-298.
- Caldwell, A.G., and C.A. Black. 1958b. Inositol hexaphosphate: II. Synthesis by soil microorganisms. *Soil Sci. Soc. Amer. Proc.* 22: 293-296.
- Celi, L., S. Lamachia, F.A. Marson, and E. Barberis. 1999. Interaction of inositol hexaphosphate on clays: adsorption and charging phenomena. *Soil Sci.* 164: 574-585.
- Celi, L., E. Barberis, and F. Ajmone – Marsan. 2000. Sorption of phosphate on goethite at high concentrations. *Soil Sci.* 165: 657-664.
- Celi, L., M. Presta, F. Ajmore – Marsan, and E. Barberis. 2001. Effect of pH and electrolytes on inositol hexaphosphate interaction with goethite. *Soil Sci. Soc. Am. J.* 65: 753-760.
- Codling, E.E., R.L. Chaney, and C.L. Mulchi. 2000. Use of aluminum- and iron-rich residues to immobilize phosphorus in poultry litter and litter-amended soils. *J. Environ. Qual.* 29: 1924-1931.
- Cosgrove, D.J. 1980. *Inositol phosphates: Their chemistry, biochemistry and physiology.* Elsevier Scientific Publishing Co., New York.
- Cosgrove, D.J. 1963. The chemical nature of soil organic phosphorus. I. Inositol phosphates. *Aust. J. Soil Res.* 1: 203-214.
- Crosby, S.A., D.R. Glasson, A.H. Cutter, I. Buttler, D.R. Turner, M. Whitfield, and G.E. Millward. 1983. Surface areas and porosities of Fe (III) and Fe (II) - derived oxyhydroxides. *Environ. Sci. Technol.* 17: 709-713.
- Daniel, T.C., D.R. Edwards, and A.N. Sharpley. 1993. Effect of extractable soil surface phosphorus on runoff water quality. *Trans. ASAE* 36: 1079-1085.

- De Cristofaro, A., J.Z. He, D.H. Zhou, and A. Violante. 2000. Adsorption of phosphate and tartarate on hydroxy-aluminum-oxalate precipitates. *Soil Sci. Soc. Am. J.* 64: 1347-1355.
- Dubus, I.G., and T. Becquer. 2001. Phosphorus sorption and desorption in oxide-rich Ferralsols of New Caledonia. *Aust. J. Soil Res.* 39: 403-414.
- Edwards, D.R., and T.C. Daniel. 1992. Potential runoff quality effects of poultry manure slurry applied to fescue plots. *Trans.ASAE* 35: 1827-1832.
- Edwards, D.R., and T.C. Daniel. 1993. Effects of poultry litter application rate and rainfall intensity on quality of runoff from fescue grass plots. *J. Environ. Qual.* 22: 361-365.
- Edwards, D.R., and T.C. Daniel. 1994. Runoff quality impacts of swine manure applied to fescue plots. *Trans. Am. Soc. Agric. Eng.* 36: 81-86.
- Eghball, B., J.F. Power, J.E. Gilley, and J.W. Doran. 1997. Nutrient, carbon and mass loss of beef cattle feedlot during composting. *J. Environ. Qual.* 26: 189-193.
- Filipek, L.H., D.K. Nordstrom, and W.H. Ficklin. 1987. Interaction of acid mine drainage with waters and sediments of West Squaw Creek in West Shasta Mining District, California. *Environ. Sci. Technol.* 21: 388-396.
- Furukawa, H., and K. Kawaguchi. 1969. Contribution of organic phosphorus to the increase of easily soluble P in waterlogged soil, especially related to phytic phosphorus (Inositol hexaphosphate). *Nippon Dojohiryogaku Zasshi (Journal of the Science of Soil and Manure, Japan)* 40: 141-148.
- Geelhoed, J.S., T. Hiemstra, and W.H. Van Riemsdijk. 1998. Competitive interaction of phosphate and citrate on goethite. *Environ. Sci. Technol.* 32: 2119-2123.
- Gilbertsen, C.B., F.A. Norstadt, A.C. Mathers, R.F. Holt, L.R. Shuyler, A.P. Barnett, T.M. McCalla, C.A. Onstad, R.A. Young, L.A. Christensen, and D.L. VanDyne. 1979. Animal waste utilization on cropland and pastureland: A manual for evaluating agronomic and environmental effects. USDA Utilization Research Report No. 6, Washington, DC.
- Gilliam, J.W. 1994. Riparian wetlands and water quality. *J. Environ. Qual.* 23: 896-900.
- Goldberg, S., I. Lebron, D.L. Suarez, and Z.R. Hinedi. 2001. Surface characterization of amorphous aluminum oxides. *Soil Sci. Soc. Am. J.* 65: 78-86.
- Goldberg, S., and G. Sposito. 1985. On the mechanism of specific phosphate sorption by hydroxylated mineral surfaces: A review. *Commun. Soil Sci. Plant Anal.* 16: 801-821.

- Goldberg, S., and G. Sposito. 1984. A chemical model of phosphate adsorption by soils. I. Reference oxide minerals. *Soil Sci. Soc. Am. J.* 48: 772-778.
- Gollehon, N., M. Casbell, M. Ribaud, R. Kellog, C. Lander, D. Letson. 2001. Confined animal production and nutrients. ERS Agricultural Information Bulletin No. 771, June 2001.
- Goyette, G. 1992. Mineral ore coproduct (iron-oxide) as a growth medium component. M.S. thesis. Univ. of Delaware, Newark.
- Gray, C.B.J., and R.A. Kirkland. 1986. Suspended sediment phosphorus composition in tributaries of Okanagan Lakes, BC. *Water Res.* 20: 1193-1196.
- Haustein, G.K., T.C. Daniel, and D.M. Miller. 2000. Aluminum-containing residuals influence high-phosphorus soils and runoff water quality. *J. Environ. Qual.* 29: 1954-1959.
- He, Z. L., K.N. Yuan, Z.X. Zhu, and Q.Z. Zhang. 1992. Assessing the fixation and availability of sorbed phosphate in soil using an isotopic exchange method. *J. Soil Sci.* 42: 661-669.
- He, Z. and C.W. Honeycutt. 2001. Enzymatic characterization of organic phosphorus in animal manure. *J. Environ. Qual.* 30: 1685-1692.
- Heckrath, G., P.C. Brookes, P.R. Poulton, and K.W.T. Goulding. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadwalk experiment. *J. Environ. Qual.* 24: 904-910.
- Hesketh, N., and P.C. Brookes. 2000. Development of an indicator for risk of phosphorus leaching. *J. Environ. Qual.* 29: 105-110.
- Hingston, F.J., R.J. Atkinson, A.M. Posner, and J.P. Quirk. 1967. Specific adsorption of anions. *Nature (London)* 215: 459-461.
- Hingston, F.J. 1981. A review of anion adsorption. p.51-90. *In* M.A. Anderson and A.J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science, Ann Arbor, MI.
- Hiradate, S., and K. Inoue. 1998. Interaction of mugineic acid with iron (hydr) oxides: sulfate and phosphate influences. *Soil Sci. Soc. Am. J.* 62: 159-165.
- Hofer, R., M. Textor, and N.D. Spencer. 2001. Alkyl phosphate monolayers self assembled from aqueous solution onto metal oxide surfaces. *Langmuir* 17: 4014-4020.

- Holford, I.C.R., C. Hird, and R. Lawrie. 1997. Effects of animal effluents on the phosphorus sorption characteristics of soils. *Aust. J. Soil Res.* 35: 365-373.
- Holmgren, G.G.S. 1967. A rapid citrate-dithionite extractable iron procedure. *Soil Sci. Soc. Am. Proc.* 31: 210-211.
- Hsu, P. H. 1973. Complementary role of iron (III), sulfate and calcium in precipitation of phosphate from solution. *Environ. Lett.* 5: 115-136.
- Hsu, P.H. 1975. Precipitation of phosphate from solution using aluminum salt. *Water Res.* 9: 1155-1161.
- Hsu, P.H. 1976. Comparison of iron (III) and aluminum in precipitation of phosphate from solutions. *Water Res.* 10: 903-907.
- Hsu, P.H. 1977. Aluminum hydroxides and oxyhydroxides. p.99-144. *In* J.B. Dixon and S.B. Weed (ed.) *Minerals in soil environment*. Soil Sci. Soc. Am. Madison, WI.
- Huang, S. -H., and B. Chiswell. 2000. Phosphate removal from wastewater using spent aluminum sludge. *Water Sci. Technol.* 42: 295-300.
- Hyde, J.E., and T.F. Morris. 2000. Phosphorus availability in soils amended with dewatered water treatment residual and metal concentrations with time in residual. *J. Environ. Qual.* 29: 1896-1904.
- Irving, G.C.J., and D.J. Cosgrove. 1982. The use of gas-liquid chromatography to determine the proportions of inositol isomers present as pentakis- and hexakisphosphates in alkaline extracts. *Commun. Soil Sci. Plant Anal.* 13: 957-967.
- Jackson, M.L., C.H. Lim, and L.W. Zelazny. 1986. Oxides, hydroxides, and aluminosilicates. p. 101-150. *In* A. Klute (ed.) *Methods of soil analysis*. Part 1. 2nd edition, Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Kawashima, M., Y. Tainaka, T. Hori, M. Koyama, and T. Takamatsu. 1986. Phosphate adsorption onto hydroxy manganese (IV) oxide in the presence of divalent cations. *Water Res.* 20: 471-475.
- Kingerly, W.L., C.W. Wood, D.P. D.P. Delaney, J.C. Williams, and G. L. Mullins. 1994. Impact of long-term application of broiler litter on environmentally related soil properties. *J. Environ. Qual.* 23: 139-147.
- Kleinman, P.J.A., R.B. Bryant, W.S. Reid, A.N. Sharpley, and D. Pimentel. 2000. Using soil phosphorus behavior to identify environmental thresholds. *Soil Sci.* 165: 943-950.

- Koski- Vahala, J., H. Hartikainen, and P. Tallberg. 2001. Phosphorus mobilization from various sediment pools in response to increased pH and silicate concentration. *J. Environ. Qual.* 30: 546-552.
- Likens, G. E. 1972. Nutrients and eutrophication – The limiting nutrient controversy: *Limnology and Oceanography Special Symposium 1*, 328p.
- Litke, D.W., 1999. Review of phosphorus control measures in the United States and their effects on water quality. USGS Water-resources investigation report 99-4007. National Water –Quality Assessment Program. United States Geological Survey, Denver, CO.
- Liu, C., and P. M. Huang. 1999. Atomic force microscopy and surface characteristics of iron oxides formed in citrate solutions. *Soil Sci. Soc. Am. J.* 63: 65-72.
- Loeppert, R.H., and W.I. Inskeep. 1996. Iron. Ch. 23. In Bigham et al. (ed.) *Methods of soil analysis. Part 3 – Chemical methods*. SSSA-ASA, Madison, WI.
- Lolas, G.M., N. Palamidis, and P. Markakis. 1976. The phytic acid – total phosphorus relation in barley, oats, soybeans and wheat. *Cereal Chem.* 53: 867-871.
- Lu, P., and G.A. O'Connor. 2001. Biosolids effects on phosphorus retention and release in some sandy Florida soils. *J. Environ. Qual.* 30: 1059-1063.
- Maguire, R.O., J.T. Sims, and F.J. Coale. 2000. Phosphorus fractionation in biosolids - amended soils: Relationship to soluble and desorbable phosphorus. *Soil Sci. Soc. Am. J.* 64: 2018-2024.
- Maguire, R.O., J.T.Sims, S.K. Dentel, F.J. Coale, and J.T. Mah. 2001. Relationships between biosolids treatment process and soil phosphorus availability. *J. Environ. Qual.* 30: 1023-1033.
- McAuliffe, C., and M. Peech. 1949. Utilization by plants of phosphorus in farm manure: I. Labeling of phosphorus in sheep manure with ³²P. *Soil Sci.* 68: 179-184.
- McCollum, R.E. 1991. Build up and decline in soil phosphorus: 30- year trends in a Typic Umprabuult. *Agron. J.* 83: 77-85.
- McDowell, R., A.N. Sharpley, P.C. Brookes, and P.R. Poulton. 2001. Relationship between soil test phosphorus and phosphorus release to solution. *Soil Sci.* 166: 137-149.
- McKeague, J.A., and J.H. Day. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* 46: 13-22.

- McKercher, R.B., and G. Anderson. 1968. Content of inositol penta- and hexaphosphates in some Canadian soils. *J. Soil Sci.* 19: 47-55.
- McKercher, R.B., and G. Anderson. 1989. Organic phosphate sorption by neutral and basic soils. *Commun. Soil Sci. Plant Anal.* 20: 723-732.
- Mehra, O. P. and M. L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* 7:317-327.
- Miller, R.J., E.A.G. Schuur, and O.A. Chadwick. 2001. Redox control of phosphorus pools in Hawaiian montane forest soils. *Geoderma* 102: 219-237.
- Milnes, A.R., R.W. Fitzpatrick, P.G. Shelf, A.W. Fordhan, and S.G. McClure. 1992. Natural iron precipitates in a mine retention pond near Jaibru, Northern Territory, Australia. p. 233-261. *In* H.C.W. Skinner and R.W. Fitzpatrick (ed.) *Biom mineralization processes of iron and manganese: Modern and ancient environments.* Catena Supplement, 21, Cremlingen - Destedt.
- Moore, P.A. Jr., and D. M. Miller. 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. *J. Environ. Qual.* 23: 325-330.
- Moore, P.A. Jr., and K.R. Reddy. 1994. Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. *J. Environ. Qual.* 23: 955-964.
- Mueller, D.H., R.C. Wendt, and T.C. Daniel. 1984. Phosphorus losses as affected by tillage and manure application. *Soil Sci. Soc. Am. J.* 48: 901-905.
- Murrell, T.S., M.G. Nooney, L.R. Ilossner, and D.W. Goodman. 1997. Growth kinetics of phosphate films on metal oxide surfaces. p. 71-86. *In* ACS series 656. *Solid – Liquid electrochemical interfaces.* American Chemical Society, Washington, DC.
- Nagarajah, S., A.M. Posner, and J.P. Quirk. 1970. Competitive adsorption of phosphate with polygalactouronate and other organic anions on kaolinite and oxide surfaces. *Nature (London)* 228: 83-85.
- Nayini, N.R., and P. Markakis. 1986. Phytases. Chapter 6, p.101-118. *In* E. Graf ed. *Phytic Acid: Chemistry and Applications.* Pilatus Press, Minneapolis, Minnesota.
- Ognalaga, M., E. Frossard, and F. Thomas. 1994. Glucose-1-phosphate and myo-inositol hexaphosphate adsorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* 58: 332-337.
- Olah, J., and E.O. Toth. 1978. The function of alkaline phosphatase enzyme in the phosphorus cycle of fertilized fish ponds. *Aquacult. Hong.* 1: 15-23.

- Oniani, O.G., M.Chater, and G. E. G. Mattingly. 1973. Some effects of fertilizers and farmyard manure on the organic phosphorus in soils. *J. Soil Sci.* 24: 1-9.
- Parfitt, R.L. 1978. Anion adsorption by soils and soil materials. *Adv. Agron.* 30: 1-50.
- Parfitt, R.L. 1989. Phosphate reactions with natural allophane, ferrihydrite and goethite. *J. Soil Sci.* 40: 359-369.
- Peacock, S., and D.L. Rimmer. 2000. The suitability of an iron oxide-rich gypsum byproduct as a soil amendment. *J. Environ. Qual.* 29: 1969-1975.
- Peperzak, P., A.G. Caldwell, R.R. Hunziker, and C.A. Black. 1959. Phosphorus fractions in manures. *Soil Sci.* 87: 293-302.
- Peterjohn, W.T., and D.T. Correll. 1984. Nutrient dynamics in an agricultural watershed: Observations on the role of a riparian forest. *Ecology* 65: 1466-1475.
- Pierzynski, G.M., J.T. Sims, and G.F. Vance. 1994. *Soils and environmental quality.* Lewis Publishers, Boca Raton, FL.
- Pote, D.H., T.C. Daniel, A.N. Sharpley, P.A. Moore, Jr., D.R. Edwards, and D.J. Nichols. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 60: 855-859.
- Pote, D.H., T.C. Daniel, D.J. Nichols, P.A. Moore Jr., D.M. Miller, and D.R. Edwards. 1999. Seasonal and soil drying effects on runoff phosphorus relationships to soil phosphorus. *Soil Sci. Soc. Am. J.* 63: 1006-1012.
- Reddy, K. R., M.R. Overcash, R. Khaleel, and P.W. Westerman. 1980. P adsorption – desorption characteristics of 2 soils utilized for disposal of animal wastes. *J. Environ. Qual.* 9: 86-92.
- Rietra, Rene P.J.J., T. Hiemsta, and W.H. van Riemsdijk. 2001. Interaction between calcium and phosphate adsorption on goethite. *Environ. Sci. Technol.* 35: 3369-3374.
- Romkens, M.J.M., and D.W. Nelson. 1974. Phosphorus relationships in runoff from fertilized soil. *J. Environ. Qual.* 3: 10-13.
- Salinger, Y., D.L. Sparks, M. Ghodrati, and G.J. Henricks. 1994. Kinetics of ion removal from an iron-rich industrial coproduct: Chloride. *J. Environ. Qual.* 23: 1194-1200.
- Schindler, P.W. 1981. Surface complexes at oxide-water interface. p. 1-49. *In* M.A. Anderson and A.J. Rubin (ed.) *Adsorption of organics at solid-liquid interfaces.* Ann Arbor Science, Ann Arbor, MI.

- Schindler, D.W. 1975. Whole-lake eutrophication experiments with phosphorus, nitrogen, and carbon. *Verhandlungen Internationale Vereinigung Limnologie* 19: 3221-3231.
- Schwertmann, U., J.M. Bigham, and E.Murad. 1995. The first occurrence of schwertmannite in a natural stream environment. *Eur. J. Miner.* 7: 547-552.
- Schwertmann, U. 1964. The differentiation of iron oxides in soils by a photochemical extraction with acid ammonium oxalate. *Z. Pflanzeneraehr. Dueng. Bodenkund.* 105: 194-221.
- Schwertmann, U., and R.M. Taylor. 1977. Iron oxides. p. 145-176. *In* J.B. Dixon and S.B. Weed (ed.) *Minerals in soil environment*. Soil Sci. Soc. Am., Madison, WI.
- Shang, C., J.W.B. Stewart, and P.M. Huang. 1992. pH effects on kinetics of adsorption of organic and inorganic phosphates by short-range ordered aluminum and iron precipitates. *Geoderma* 53: 1-14.
- Shang, C., P.M. Huang, and J.W.B. Stewart. 1990. Kinetics of adsorption of organic and inorganic phosphates by short-range ordered precipitate of aluminum. *Can. J. Soil Sci.* 70: 461-470.
- Sharpley, A.N., S.C. Chapra, R. Wedepohl, J.T. Sims, K.C. Daniel, and K.R. Reddy. 1994. Managing agricultural phosphorus for protection of surface waters: issues and options. *J. Environ. Qual.* 23: 437-451.
- Sharpley, A.N., T.C. Daniel, J.T. Sims, and D.H. Pote. 1996. Determining environmentally sound soil phosphorus levels. *J. Soil Water Conserv.* 51: 160-166.
- Sharpley A.N., T.C. Daniel, J.T. Sims, J. Lemunyon, R. Steven, and R. Parry.1999. Agricultural phosphorus and eutrophication. United States Department of Agriculture. Agricultural Research Service. ARS-149.
- Sharpley, A.N., S.J. Smith, D.R. Jones, W.A. Berg, and G.A. Coleman. 1992. The transport of bioavailable phosphorus in agricultural runoff. *J. Environ. Qual.* 21: 30-35.
- Sharpley, A.N., R.W. McDowell, L.W. Jennifer, and P.J.A. Kleinmann. 2001. Assessing site vulnerability to phosphorus loss in an agricultural watershed. *J. Environ. Qual.* 30: 2026-2036.
- Shreve, B.R., P.A. Moore Jr., T.C. Daniel, D.R. Edwards, and D.M. Miller. 1995. Reduction of phosphorus in runoff from field-applied poultry litter using chemical amendments. *J. Environ. Qual.* 24: 106-111.

- Sibbeson, E., and A.N. Sharpley. 1997. Setting and justifying upper critical limits for phosphorus in soils. *In* H.Tuney, O.T. Carton, and P.C. Brookes, and A.E. Johnston (eds.). Phosphorus loss from soil to water. CAB International, Wallingford, CT, pp. 151-176.
- Sims, J.T. 1999. The role of soil testing in environmental risk assessment for phosphorus. *In* Agriculture and Phosphorus Management: The Chesapeake Bay. A.N. Sharpley (ed.). Lewis Publishers, Boca Raton, FL.
- Sims, J.T. 1992. Environmental management of phosphorus in agriculture and municipal wastes. p. 59-64. *In* F.J. Sikora (ed.). Future directions for agricultural phosphorus research. Natl. Fert. Environ. Res. Center, TVA, Muscle Shoals, AL.
- Sims, J.T. 1995. Characteristics of animal wastes and waste - amended soils: An overview of the agricultural and environmental issues. p.1-33. *In* K. Steele (ed.) Animal waste and the land-water interface, Lewis Publishers, Boca Raton, FL.
- Sims, J.T. 1998. Phosphorus soil testing: Innovations for water quality protection. *Commun. Soil Sci. Plant Anal.* 29: 1471-1489.
- Singh, B., M.J. Wilson, W.J. McHardy, A.R. Fraser, and G. Merrington. 1999. Mineralogy and chemistry of ochre sediments from an acid mine drainage near a disused mine in Cornwall, UK. *Clay Miner.* 34: 301-317.
- Skousen, J.G., A.Sexstone, and P.F. Ziemkiewicz. 2000. Acid mine drainage control treatment. p. 131-168. *In* R.I. Barnhisel, W.L. Daniels, and R.G. Darmody (ed.) Reclamation of drastically disturbed lands. ASA-CSSA-SSSA, Madison, WI.
- Smith, D.R., P.A. Moore, Jr., C.L. Griffis, T.C. Daniel, D.R. Edwards, and D.L. Boothe. 2001. Effects of alum and aluminum chloride on phosphorus runoff from swine manure. *J. Environ. Qual.* 30: 992-998.
- Stumm, W., and J.J. Morgan. 1996. Aquatic chemistry. Chemical equilibria and rates in natural waters. 3rd edition. John-Wiley & Sons, Inc. New York.
- Suzumura, M., and A. Kamatani. 1995a. Origin and distribution of inositol hexaphosphate in estuarine and coastal sediments. *Limnol. Oceanogr.*40: 1254-1261.
- Suzumura, M., and A. Kamatani. 1995b. Mineralization of inositol hexaphosphate in aerobic and anaerobic marine sediments: Implications for the phosphorus cycle. *Geochimica et Cosmochimica Acta* 59: 1021-1026.
- Suzumura, M., and A. Kamatani. 1994. Origin and fate of inositol hexaphosphates in coastal sediments. *Eos* 75: 111.

- Suzumura, M., and A. Kamatani. 1993. Isolation and determination of inositol hexaphosphate in sediments from Tokyo Bay. *Geochimica et Cosmochimica Acta* 57: 2197-2202.
- Suzumura, M., K. Ishikawa, and H. Ogawa. 1998. Characterization of dissolved organic phosphorus in coastal seawater using ultrafiltration and phosphohydrolytic enzymes. *Limnol. Oceanogr.* 43: 1553-1564.
- Takamatsu, T., M. Kawashima, and M. Koyama. 1985. The role of Mn²⁺-rich hydrous manganese oxide in the accumulation of arsenic in the lake sediments. *Water Res.* 19: 1029-1032.
- Tejedor- Tejedor, M.I., and M.A. Anderson. 1990. The protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility. *Langmuir* 6: 602-611.
- Torrents, A., and A.T. Stone. 1993a. Catalysis of picolinate ester hydrolysis at oxide/water interface: inhibition by co-adsorbed species. *Environ. Sci. Technol.* 27: 1060-1067.
- Torrents, A., and A.T. Stone. 1993b. Catalysis of picolinate ester hydrolysis at oxide/water interface: inhibition by adsorbed natural organic matter. *Environ. Sci. Technol.* 27: 2381-2386.
- UNEP. 2000. Planning and management of lakes and reservoirs: An integrated approach to eutrophication. United Nations Environment Programme. Division of technology, industry, and economics. International environment technology centre.
- USEPA, 1998. National strategy for the development of regional nutrient criteria: Washington, D.C. United States Environmental Protection Agency report EPA-822-R-98-002.
- Violante, A., C. Colombo, and A. Buondonno. 1991. Competitive adsorption of phosphate and oxalate by aluminum oxides. *Soil Sci. Soc. Am. J.* 55: 65-70.
- Warman, P.R., and M.D. Munroe. 2000. Analysis of total inositol phosphates in municipal solid waste compost-treated soils by two extraction methods. *Biol. Fertil. Soils* 32: 89-93.
- Westerman, P. W., T.L. Donnelly, and M.R. Overcash. 1983. Erosion of soil and poultry manure – a laboratory study. *Trans.ASAE.* 26: 1070-1078,1084.
- Westermann, D.T., D.L. Bjornberg, J.K. Aase, and C.W. Robbins. 2001. Phosphorus losses in furrow irrigation runoff. *J. Environ. Qual.* 30: 1009-1015.

- Wetzel, R.G., 1983. Limnology. Harcourt Brace.
- Whalen, J.K., and C. Chang. 2001. Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. *J. Environ. Qual.* 30: 229-237.
- White, R.E. 1981. Retention and release of phosphate by soil and soil constituents. p. 71-114. *In* P.B. Tinker (ed.) *Soils and agriculture*. John Wiley, New York.
- Wijnja, H., and C.P. Schulthess. 2000. Interaction of carbonate and organic anions with sulfate and selenate adsorption on aluminum oxide. *Soil Sci. Soc. Am. J.* 64: 898-908.
- Wild, A., and O.L. Oke. 1966. Organic phosphate compounds in calcium chloride extracts of soils. *J. Soil Sci.* 17: 356-371.
- Williams, C.H., and G. Anderson. 1968. Inositol phosphates in some Australian soils. *Aust. J. Soil Res.* 6: 121-130.
- Withers, P.J.A., S.D. Clay, and V.G. Breeze. 2001. Phosphorus transfer in runoff following application of fertilizer, manure, and sewage sludge. *J. Environ. Qual.* 30: 180-188.
- Yao, W., and F.J. Millero. 1996. Adsorption of phosphate on manganese dioxide in seawater. *Environ. Sci. Technol.* 30: 536-541.
- Young, E.O., and D.S. Ross. 2001. Phosphate release from seasonally flooded soils: a laboratory microcosm study. *J. Environ. Qual.* 30: 91-101.
- Young, T.C., and J.V. De Pinto. 1982. Algal availability of particulate phosphorus from diffuse and point sources in the lower Great Lakes basin. *Hydrobiologia* 91: 111-119.
- Zhou, M., R.D. Rhue, and W.G. Harris. 1997. Phosphorus sorption characteristics of Bh and Bt horizons from sandy coastal plain soils. *Soil Sci. Soc. Am. J.* 61: 1364-1349.
- Zyla, K., A. Wikiera, J. Koreleski, S. Swiatkiewicz, J. Piironen, and D.R. Ledoux. 2000. Comparison of the efficacies of a novel *Aspergillus niger* mycelium with separate and combined effectiveness of phytase, acid phosphatase, and pectinase in dephosphorylation of wheat-based feeds fed to growing broilers. *Poultry Sci.* 79: 1434-1443.

Chapter 3

Phosphorus Retention Characteristics of Some Benchmark Soils of West Virginia

3.1. Introduction

Most of the work on P transfer from soil to water bodies has been on P reactions in surface soil horizons. This is because P is predominantly lost through surface runoff. However, significant losses of P through subsurface drainage are not uncommon (Hesketh and Brookes, 2000; Smith et al., 1998). Both hydrological and pedological properties of soils can affect P transfer from soil to the water sources. Pedological factors can also influence hydrology of the soil. For instance, type and amount of clays, degree of aggregation, and pore size distribution all affect permeability of the soils. Shrinking and swelling clays can create preferential pathways or bypass flows (Haygarth et al., 2000). Thus, each soil series may have different mechanisms for P transfer (Haygarth et al., 2000) and hence different potential for P loss. Potential of soils to lose P through surface or subsurface flow can be assessed by studying P retention and release characteristics of various horizons in a soil profile. The choice of soil series scale for studying P behavior in soils can offer useful insight into the ability of the soil to retain excessive P applied through improper land-application of manures and fertilizers. The literature does not report any series-specific P retention and release data.

A number of reports in the recent years (Sims et al., 1998, Pote et al., 1996) have shown that amount of dissolved P, desorbable P and the P loss in runoff are related to degree of P saturation (DPS). When P loss through subsurface leaching is a concern, DPS above 25-40 percent is considered to be a potential source of P (Breeuwsma et al., 1995, van der Zee et al., 1990). Many soils in the Eastern Panhandle of West Virginia are well-

drained soils. In such soils, a considerable part of runoff may be due to subsurface runoff. It needs be evaluated whether these soils will release considerable amount of dissolved P the above-mentioned critical DPS levels.

The objectives of the present study were to assess P retention and release characteristics of four benchmark soil series of West Virginia by evaluating P sorption capacity and effect of different P loadings on the dissolved P concentrations.

3.2. Materials and Methods

3.2.1. Study Area and the Soils

The study area lies in the Eastern Panhandle, primarily from Hardy County of, West Virginia. This area has witnessed a rapid growth in poultry industry during recent years. As a result, a large amount of poultry manure is produced. However, the soils at the sites sampled for this study have not received manure applications during the recent past. Four benchmark soil series – Berks, Huntington, Lindside, and Monongahela were selected for this study. Four pedons were sampled for each soil series (total 16 profiles and 98 horizons).

3.2.2 Laboratory Techniques

Phosphorus sorption capacity or P sorption maxima was determined by generating Langmuir sorption isotherms by equilibrating with a series of inorganic P (from dihydrogen potassium phosphate, Primary Standard) concentrations in 0.005M CaCl₂ for 18 hours on an end-over-end shaker. The equilibrated suspensions were filtered through Whatman # 42 filter paper. The amount of P adsorbed was calculated from the amount of P added and amount of P left after equilibration.

Phosphorus has been shown to undergo slow reactions in the soil. Barrow and Shaw (1975) showed that slow reactions in the soil could be simulated by incubating the soils at high temperature. Therefore, in this study long-term and repeated P additions to the soil were simulated by incubating the soils at 335 ± 1 K. Six replicates (10 g each) of the soil from each horizon were weighed into 50 mL-plastic centrifuge tubes and loaded with calculated amounts of 1000 mg L^{-1} P solution (from dihydrogen potassium phosphate, Primary Standard) so as to add P equal to the 0,5,10, 20, 40, and 60 percent of their maximum P sorption capacity. All soils in these investigations were collected from sites that had not received P applications in recent past, so the initial P saturation of these soils was assigned 0% P saturation based on determined P sorption capacity. 5 mL of deionized distilled water was added to each sample in the centrifuge tube. These samples were dried at 335 ± 1 K for 48 hours and then enough deionized distilled water was added so as to bring the moisture content to 25 percent. These drying-wetting cycles were continued for 12 weeks. At the end, incubated samples were taken out and analyzed for desorbable or leachable P and soil-test P. Desorbable or leachable P was determined by extracting 0.5g (duplicate) of the sample with 12.5 mL of 0.01M CaCl_2 by shaking for 16 hours on an end-over-end shaker. Soil-test P was determined by using Mehlich-1 extractant (0.0125M H_2SO_4 + 0.05M HCl; soil-solution ratio 1:5) by shaking the suspensions for five minutes on a rotary shaker. Phosphorus concentration in the solutions was measured on Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer (ICP-AES; Perkin-Elmer; P400).

3.3. Results and Discussion

3.3.1. Phosphorus Sorption Capacity

In Berks soils the highest P sorption capacity was observed in surface horizons (Table 3.1). The high P sorption capacity of the organic horizons of this soil has little significance for P retention in these soils due to the following two reasons: firstly, organic horizons (Oe and Oe/Oa) are very thin horizons, less than 3 cm thick in all soils of this study; and secondly, these soil horizons have very low bulk density and results for P sorption are expressed on mass bases ($\mu\text{g g}^{-1}$). Similarly the thickness of A horizons of Berks soils was 5 cm or less. Berks soils are well-drained soils and most pasture lands in the poultry producing area of West Virginia are located on these soils. It is postulated that P in these soils will be lost via subsurface flow; however, the subsurface horizons in these soils have considerable P fixation capacity. As expected, P fixation capacity of most C and Cr horizons in these soils was lower than the P fixation capacity of A and B horizons.

The two flood plain soils, Huntington and Lindside, had lower P sorption capacity than upland Berks and Monongahela soils (Tables 3.1 through 3.4). The P fixation capacity per unit mass of Huntington soil series was lower than that of Berks soil series. However, A horizons in Huntington soil series were much thicker (Table 3.2). Thus, total capacity to retain P will be higher in these soils. P sorption capacities for B horizons were higher than those for A horizons in three Huntington soil profiles.

There was a wide range in P sorption capacity (248 to 595 $\mu\text{g g}^{-1}$) in A horizons of Lindside soils. Most B horizons had higher P sorption capacity than the overlying A horizons. P sorption capacities for this soil were very similar to those of Huntington soil. Both Huntington and Lindside are floodplain soils.

P sorption maxima for the A horizons of Monongahela soils ranged between 461 to 713 $\mu\text{g g}^{-1}$ (Table 3.4). Among all the soil horizons, P sorption capacities were the highest for Btx horizons of Monongahela soils. The highest P sorption capacity was observed in the Btx3 horizon of Monongahela-3. These horizons are called fragipans. Fragipans have high bulk density and slow permeability (Soil Survey Staff, 1998). Thus, though these fragipans have very high P sorption capacity, this capacity is not available for attenuation of phosphorus in the excessively manured fields. In soils with fragipans, P containing leachate tends to by-pass such horizons and it flows through certain preferential paths. Thus, higher P sorption capacity is not the sole indicator of decreased loss of P through leaching. Moreover, the results also show that since low pH favors P sorption, Berks and Monongahela soils, which had lower pH values than the pH values of Huntington and Lindside soil, sorbed generally more P than the Huntington and Lindside soils.

Table 3.1. Phosphorus sorption capacity of Berks soils.

Soil #	Horizon	Depth (cm)	P sorption capacity ($\mu\text{g g}^{-1}$)
Berks 1	Oe	0-2	567
	A/E	2-5	1088
	Bw1	5-20	613
	Bw2	20-54	630
	C	54-72	639
Berks 2	A	0-4	1235
	B/E	4-19	933
	Bw1	19-39	771
	Bw2	39-54	608
	C	54-66	735
Berks 3	Oe/Oa	0-3	1273
	A	3-5	1332
	Bw	5-22	755
	C	22-57	616
	R	57-86	633
Berks 4	Oe	0-2	932
	A	2-5	940
	BA	5-10	678
	Bw1	10-20	636
	Bw2	20-41	503
	C	41-52	516
	Cr	52-56	510

Table 3.2. P sorption capacity of Huntington soils.

Soil #	Horizon	Depth (cm)	P sorption capacity ($\mu\text{g g}^{-1}$)
Huntington 1	Ap1	0-18	345
	Ap2	18-31	378
	Bw1	31-53	600
	Bw2	53-98	557
	Bw3	98-131	499
	BC	131-170	405
Huntington 2	Ap1	0-9	269
	Ap2	9-28	528
	BA	28-41	419
	Bw	41-113	507
	BC	113-150	414
Huntington 3	Ap	0-15	364
	BA	15-37	494
	Bw1	37-64	501
	Bw2	64-120	601
	BC	120-139	411
	C	139-154	464
Huntington 4	Ap1	0-9	458
	Ap2	9-27	511
	Bw2	87-126	655
	Bw3	126-151	720
	Bc	151-175	717

Table 3.3. P sorption capacity of Lindside soils.

Soil #	Horizon	Depth (cm)	P sorption capacity ($\mu\text{g g}^{-1}$)
Lindside 1	Ap	0-25	595
	AB	25-37	584
	Ab	37-54	757
	Bwb	54-95	566
	BCb	95-146	590
Lindside 2	Ap	0-15	248
	AB	15-37	292
	Bw	37-53	486
	Bgb1	53-80	708
	Bgb2	80-117	535
	BC	117-155	677
Lindside 3	Ap1	0-10	549
	Ap2	10-28	563
	Bw1	28-49	690
	Bw2	49-102	469
	BC	102-128	511
Lindside 4	Ap	0-12	539
	AB	12-33	583
	Bw1	33-54	535
	Bw2	54-94	626
	Bc	94-118	653
	C	118-147	544

Table 3.4. P sorption capacity of Monongahela soils.

Soil #	Horizon	Depth (cm)	P sorption capacity ($\mu\text{g g}^{-1}$)
Monongahela 1	Ap	0-17	462
	Bt1	17-48	338
	Bt2	48-73	571
	Btx1	73-95	831
	Btx2	95-128	1141
	2C	128-170	1099
Monongahela 2	Ap	0-10	492
	BA	10-26	577
	Bw	26-43	649
	Bt1	43-56	635
	Bt2	56-79	669
	Btx1	79-109	1017
	Btx2	109-117	1034
	Btx3	117-139	993
Monongahela 3	Btx4	139-166	691
	Oi/Oe	3-5	799
	A/E	5-9	639
	BE1	9-17	536
	BE2	17-37	426
	Bt	37-57	807
	Btx1	57-83	1267
	Btx2	83-116	1723
Monongahela 4	Btx3	116-150	1768
	Ap	0-11	713
	Bt1	11-14	760
	Bt2	14-22	746
	Btx1	22-34	933
	Btx2	34-43	1494
	2C	43-65	1093

3.3.2. Effect of Phosphorus Saturation on P Leaching through Soils

Effect of degree of P saturation (DPS) on concentration of dissolved (leachable) P shows that in Berks A horizon a DPS of 40% produced most leachate with dissolved concentration of less than 1 mg L^{-1} (Fig. 3.1). For A horizons, DPS was not the best indicator of P leachability in Berks soils. There was a wide range in the concentrations of dissolved P for a given DPS. At a DPS of 60% Berks 2 had a dissolved P concentration of less than 0.5 mg L^{-1} , while P concentration in Berks 3 was higher than 1.5 mg L^{-1} . In the B-horizon of Berks soil, even when DPS was 60%, dissolved P concentrations in any of the four profiles did not exceed 0.5 mg L^{-1} . Not only dissolved concentrations in B-horizons of Berks were low, but also these concentrations had a very narrow spread. These results indicate that although B horizons of Berks had a lower P fixation capacity than A horizons, yet at the same DPS B horizons of this soil released very small amounts of dissolved P. Practical implications of these results are that even when these soil horizons have a DPS of 60% they still act as a potential sink for phosphorus. Thus the P saturation value of 25% that is considered critical for sandy soils may not be relevant for this soil. The C horizon of this soil also had very low concentrations of dissolved P even when DPS was 60 percent.

In horizons of the Huntington series, in all soils (Huntington 1, 2, 3, and 4) at the DPS of 40%, dissolved P concentration was less than 1 mg L^{-1} (Fig. 3.2). However, at 60 % DPS the soil had a wide range of dissolved P concentrations. When the DPS was 40%, dissolved P concentrations in B horizons of Huntington series were less than 0.5 mg L^{-1} . Similar results were obtained for C horizon of these soils. The A horizons of Lindside soil series had higher P sorption capacity than the A horizons of Huntington soils, but at

the same DPS this soil produced less dissolved P (Fig. 3.3). Even when DPS was 60%, most horizons had a dissolved P concentration of less than 1.0 mg L^{-1} . In B horizons of this soil when DPS was 60%, dissolved P concentration rarely exceeded 0.5 mg L^{-1} . The dissolved P concentration in the C-horizon at 60% DPS was extremely small. These results again suggest that a DPS of 25% that is commonly used in the sandy coastal soils will be extremely conservative for these soils.

Dissolved P in the Monongahela A horizons never exceeded 1 mg L^{-1} , even when DPS was 60% (Fig. 3.4). B horizons of the Monongahela soils had very high P fixation capacities, and they held P very tightly as is evident from low dissolved P concentrations at a DPS of 60%. These results show that horizons underlain by the fragipan have a very high affinity for P. Dissolved P concentration in Monongahela fragipans was less than 0.5 mg L^{-1} , when DPS was 40%.

The general less release of P in Berks and Monongahela soils than the release of P in Huntington and Lindside soils indicated that P was more tightly held in soils with lower pH. Berks and Monongahela soils were generally lower in pH than Huntington and Lindside soils.

These results show that soils of the Eastern Panhandle of West Virginia will release very little P for leaching even when DPS exceeds 40%. If hydrological factors are not considered, subsurface horizons are likely to retain P released by surface horizons upon increased P loadings.

3.3.3. Effect of Soil-Test (Mehlich-1) P on Leachability of Phosphorus

Soil test P data are routinely available for most agricultural soils. Therefore, dissolved P concentrations were determined for various P saturation and corresponding

soil test P values. For A horizons of Berks soils there was a wide range in the dissolved P concentrations for a given soil-test P value (Fig. 3.5). In the A horizon of Berks 2 soil, the dissolved P concentration approached 1 mg L^{-1} at the soil-test value of 50 mg kg^{-1} . On the other hand, in the Berks 3 soil a soil-test value exceeding 150 mg kg^{-1} was required to achieve the same dissolved P concentration. However, in the B horizons of the same soil, dissolved P concentrations never exceeded 0.5 mg L^{-1} . Similar results were observed for C horizons of Berks soils.

In A horizons of Huntington soil series dissolved P concentrations rarely exceeded 1.0 mg L^{-1} when soil-test values were less than 150 mg kg^{-1} (Fig. 3.6). In B horizons of this soil, there was a linear increase in dissolved P concentration with soil-test P. In Huntington B horizons, dissolved P increased with increase in soil-test P and similar results were observed for Huntington C horizon. These results were very similar to those for Lindsie soil (Fig. 3.7).

Dissolved P concentrations in A horizons of all soils of Monongahela soil series other than Monongahela 3, never exceeded 1.0 mg L^{-1} (Fig. 3.8). Phosphorus in the B horizon of this soil series was very tightly held as is evident from low dissolved P concentrations even when soil-test values were rather high. For Bx horizons of this soil series at soil test values nearing 250 mg kg^{-1} , dissolved P concentration was lower than 1.0 mg L^{-1} . Similar results were obtained for the C horizon.

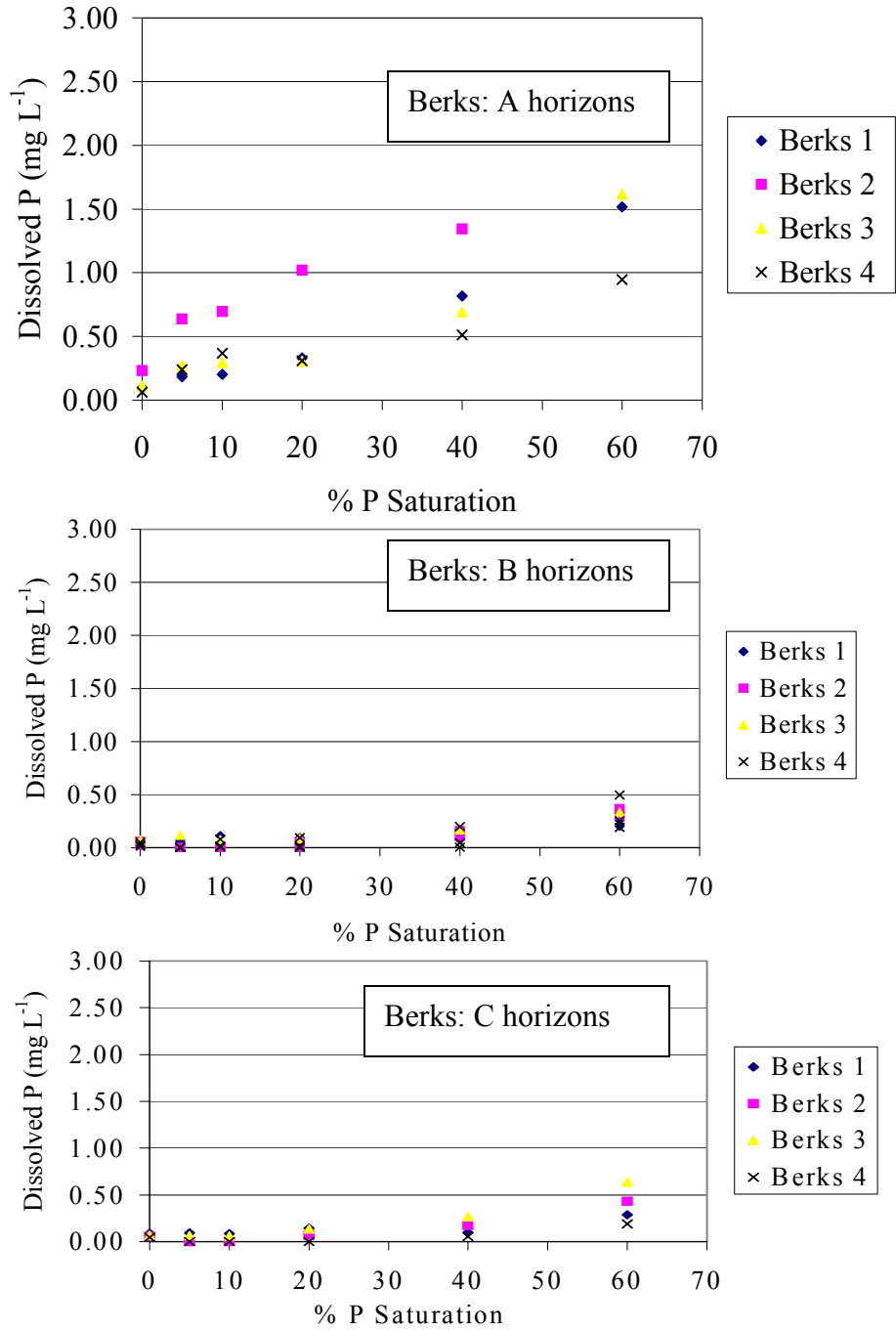


Figure 3.1. Dissolved P at various degrees of P saturation in A, B, and C horizons of Berks soils.

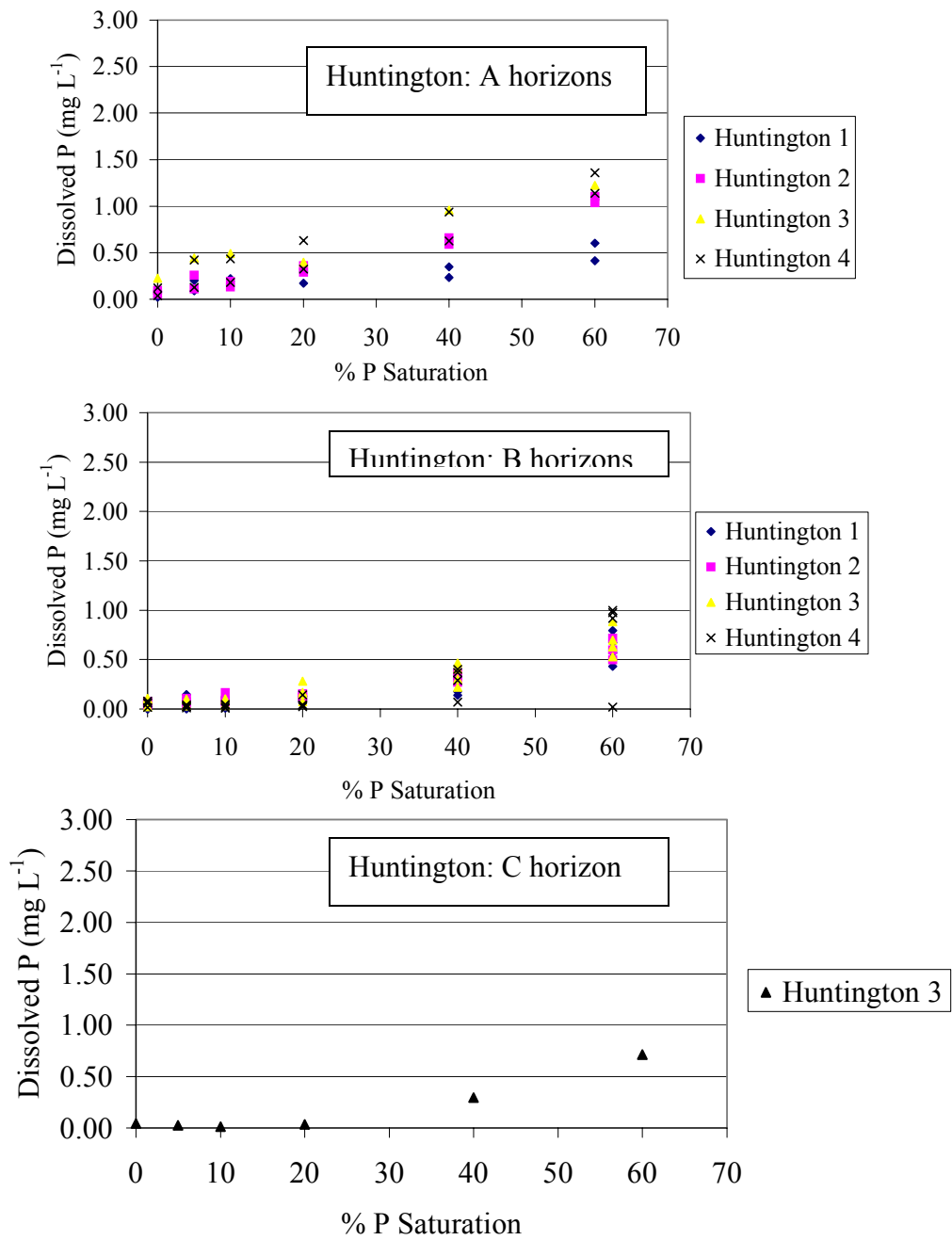


Figure 3.2. Dissolved P at various degrees of P saturation in A, B, and C horizons of Huntington soils.

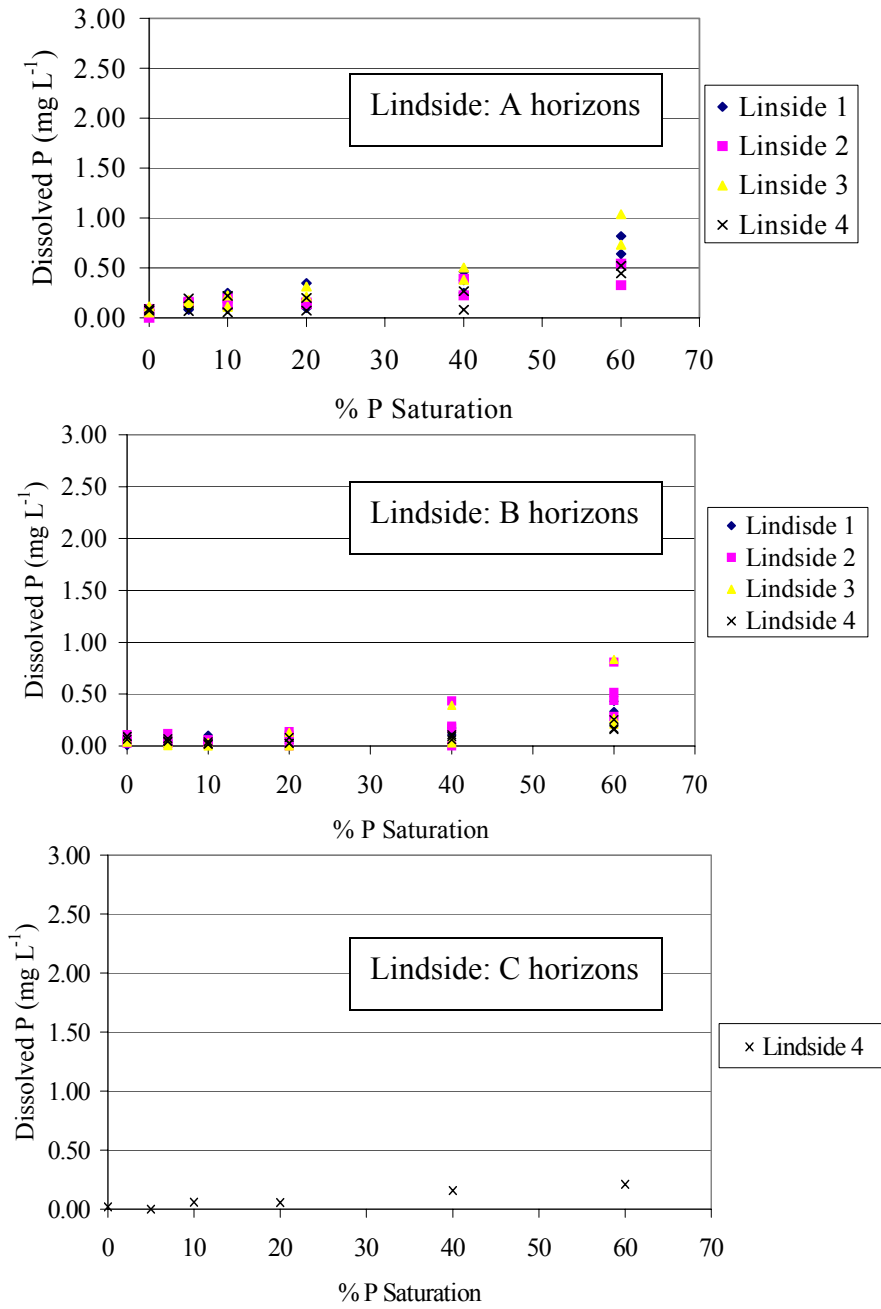


Figure 3.3. Dissolved P at various degrees of P saturation in A, B, and C horizons Linside soils.

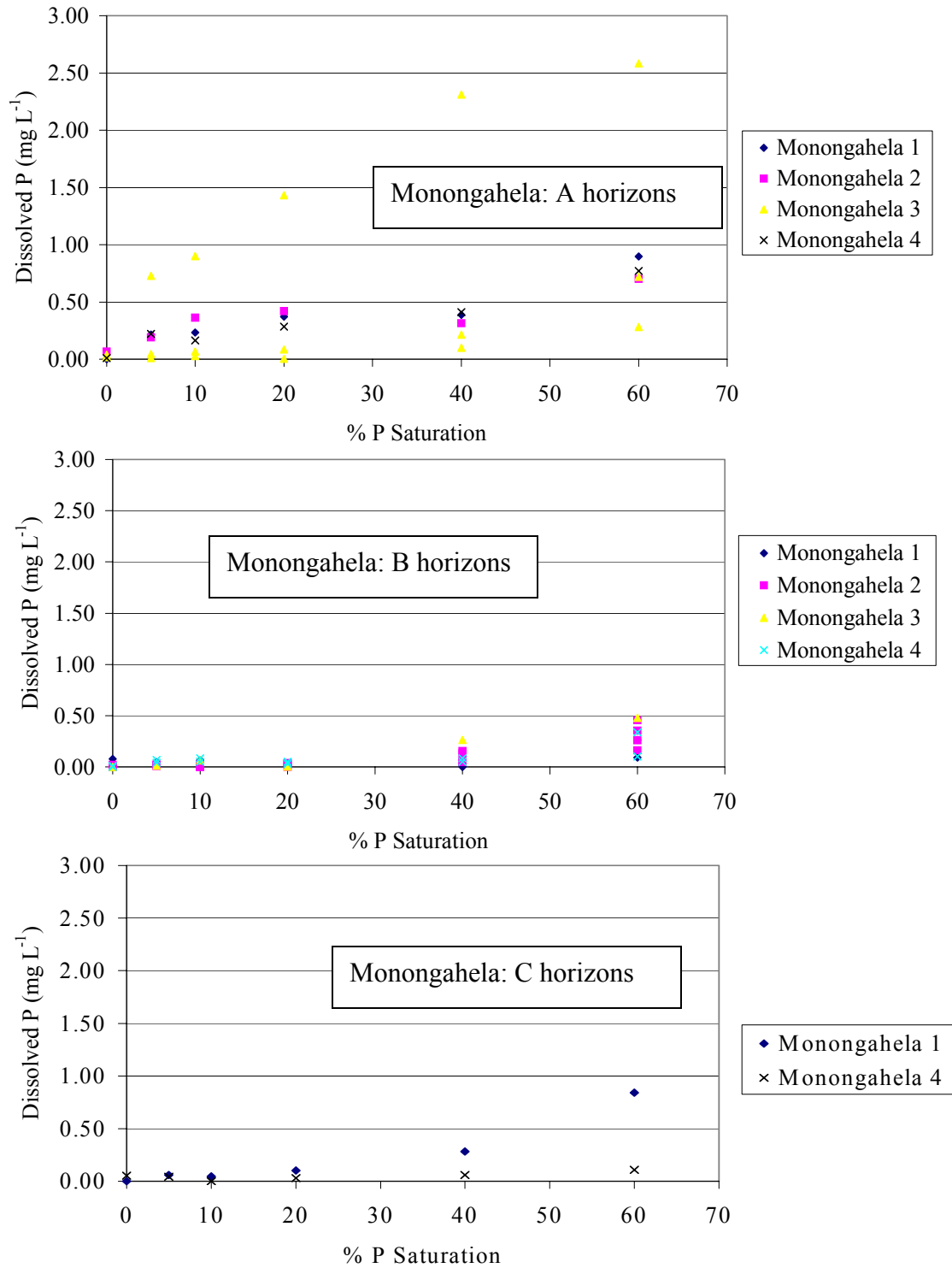


Figure 3.4. Dissolved P at various degrees of P saturation in A, B, and C horizons of Monongahela soils.

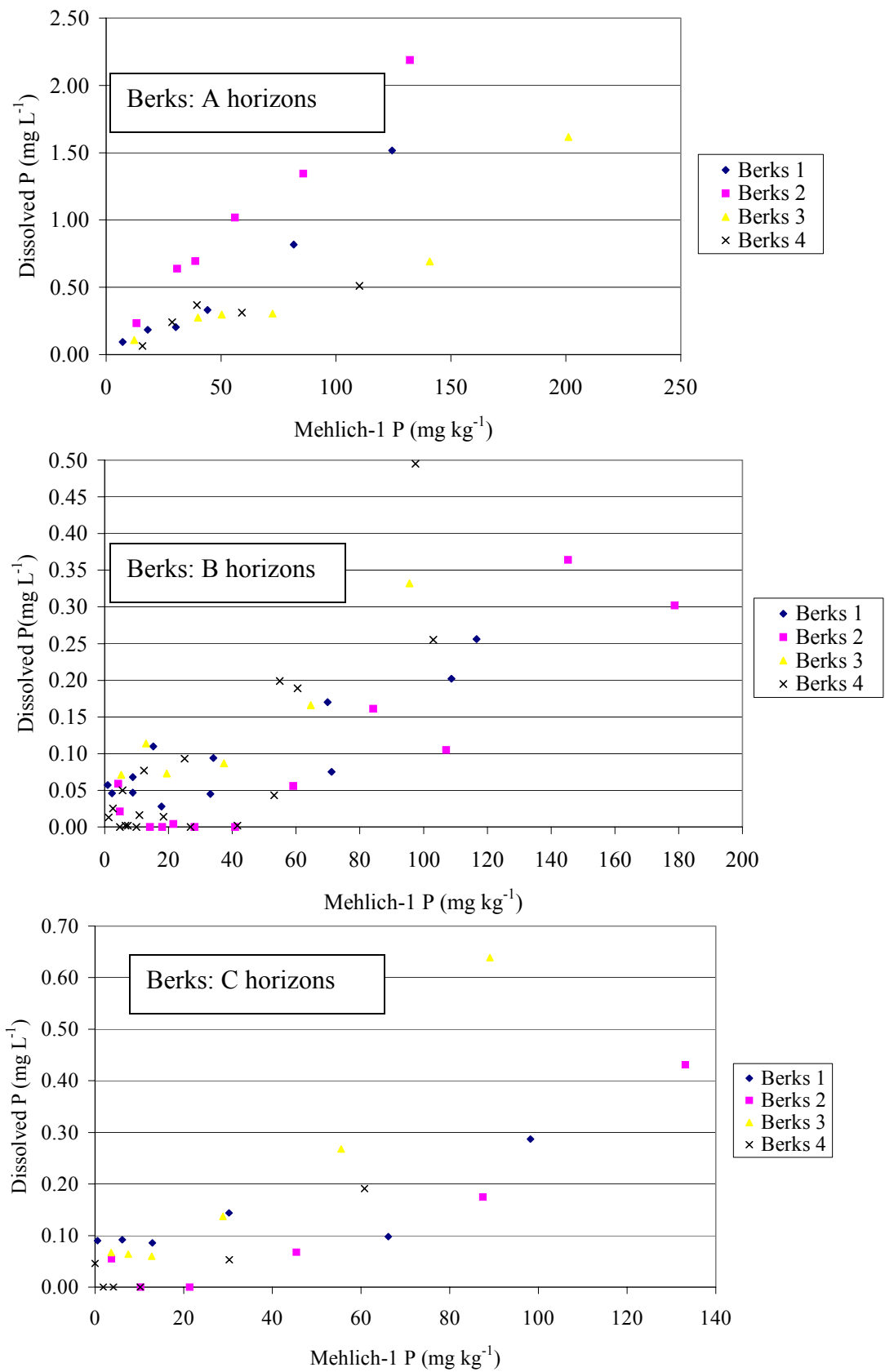


Figure 3.5. Relationship between soil-test (Mehlich-1) P and dissolved P in various horizons of Berks soils.

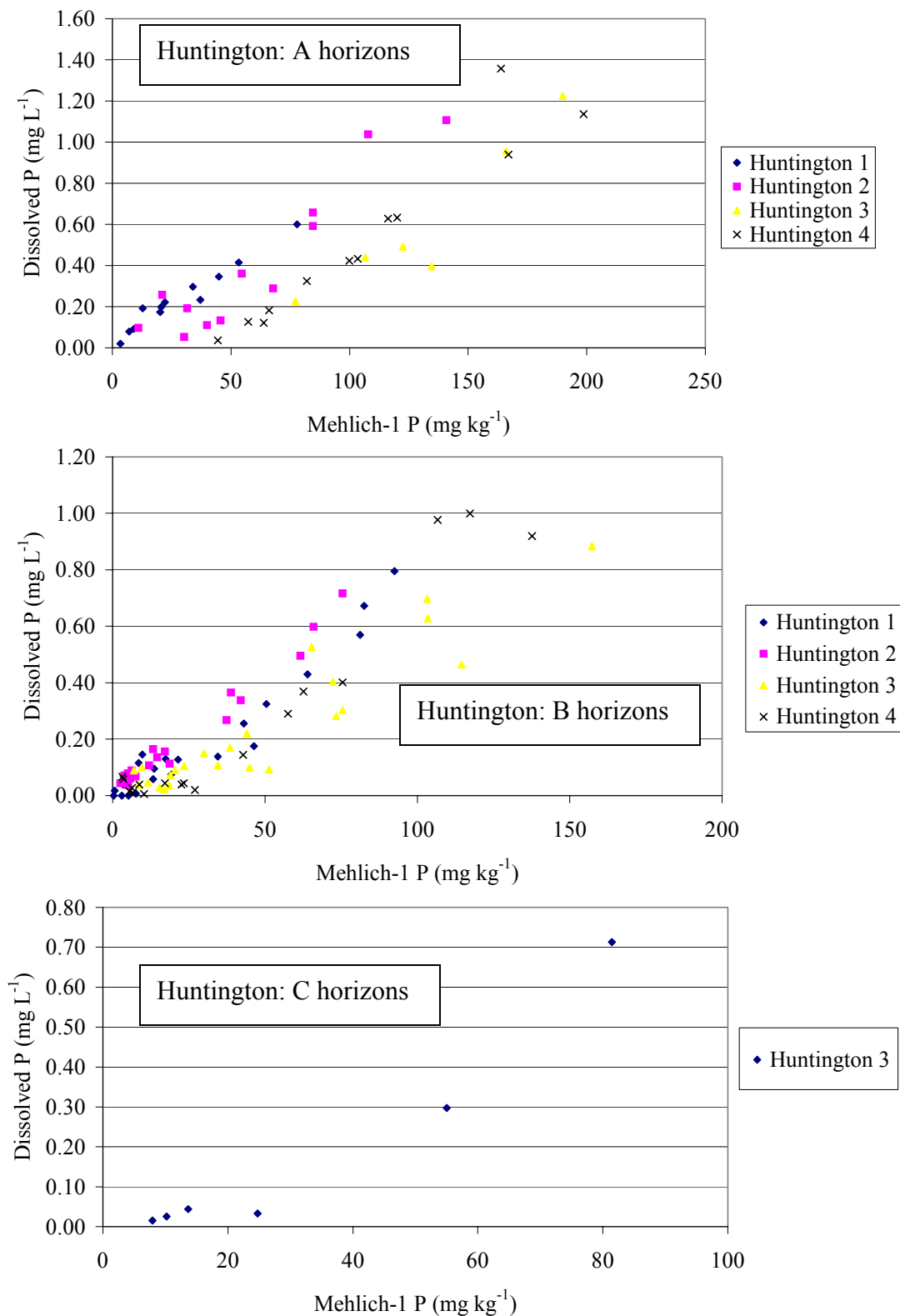


Figure 3.6. Relationship between soil-test (Mehlich-1) P and dissolved P in A, B, and C horizons of Huntington soils.

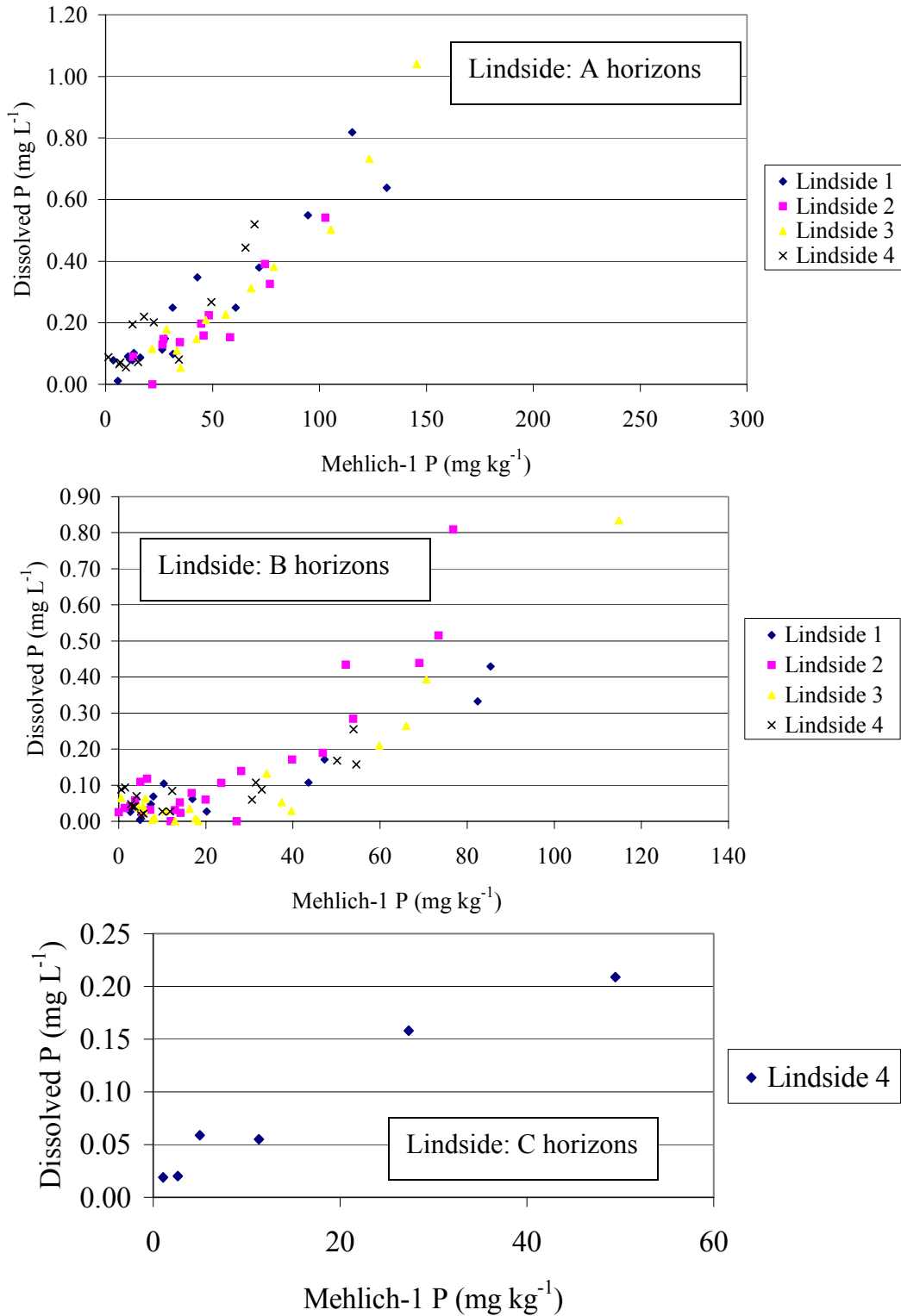


Figure 3.7. Relationship between soil-test (Mehlich-1) P and dissolved P in A, B, and C horizons of Lindside soils.

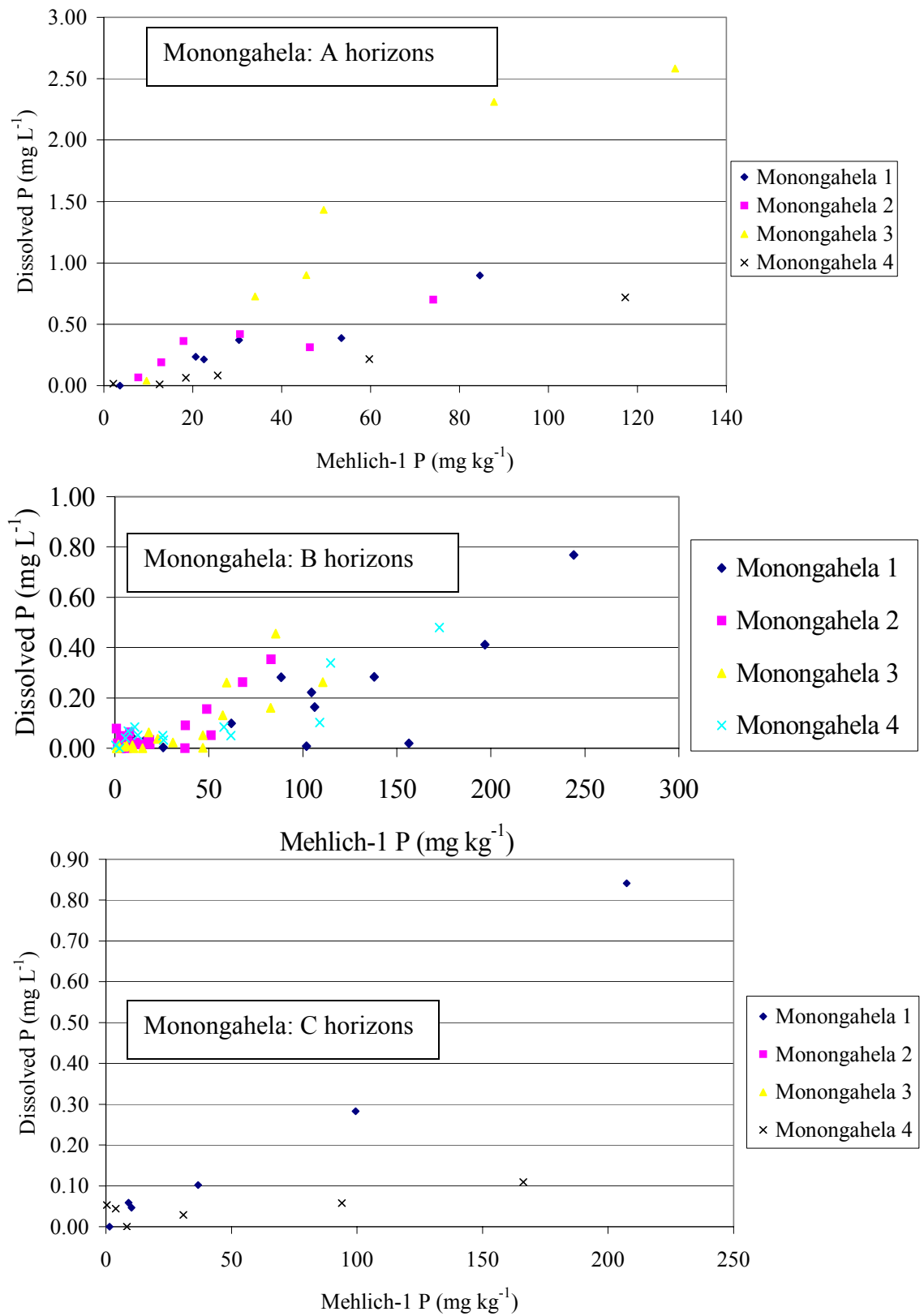


Figure 3.8. Relationship of soil-test (Mehlich-1) P and dissolved P in A, B, and C horizons of Monongahela soils.

3.4. Conclusions

Soils of the Eastern Panhandle of West Virginia are generally expected not to release considerable amounts of P to the environment through leaching, even when they are loaded with high P amounts. Subsurface horizons of these soils have a considerable P attenuation capacity. Even though some horizons may have large P attenuation capacity, but their effect on dissolved P concentrations depends also upon their thickness and permeability.

References

- Barrow, N.J., and T.C. Shaw. 1975. The slow reactions between soil and anions. 2. Effect of time and temperature on the decrease in phosphate concentration in the soil solution. *Soil Sci.* 119: 167-177.
- Breeuwsma, A., J.G.A. Reijerink, and O.F. Schoumans. 1995. Impact of manure on accumulation and leaching of phosphate in areas of intensive livestock farming. *In* K. Steele (ed.) *Animal Waste and the Land-Water Interface*. Lewis Publishers-CRC Press, New York.
- Haygarth, P.M., A.L. Heathwaite, S.C. Jarvis, and T.R. Harrod. 2000. Hydrological factors for phosphorus transfer from agricultural soils. *Adv. Agron.* 69: 153-178.
- Hesketh, N., and P.C. Brookes. 2000. Development of an indicator for risk of phosphorus leaching. *J. Environ. Qual.* 105-110.
- Pote, D.H., T.C. Daniel, A.N. Sharpley, P.A. Moore, Jr., D.R. Edwards, and D.J. Nichols. 1996. Relating extractable phosphorus to phosphorus losses in runoff. *J. Environ. Qual.* 60: 855-859.
- Sims, J.T., A.C. Edwards, O.F. Schoumans, and R.R. Simard. 2000. Integrating soil phosphorus testing into environmentally based agricultural management practices. *J. Environ. Qual.* 29: 60-71.
- Sims, J.T., A.S. Andres, J.M. Denver, W.J. Gangloff, P.A. Vadas, and D.R. Ware. 1998. Assessing the impact of agricultural drainage on ground and surface water quality in Delaware: development of best management practices for water quality protection. Final project report. Delaware Department of Natural Resources and Environmental Control, Dover, DE.

Smith, K.A., A.G. Chalmers, B.J. Chalmers, and P. Christie.1998. Organic manure phosphorus accumulation, mobility, and management. *Soil Use Manage.* 14: 154-159.

Soil Survey Staff. 1998. *Keys to soil taxonomy*. Eighth edition. USDA-NRCS.

van der Zee, S.E.A.T.M., W.H. van Riemsdijk, and F.A. M. de Haan. 1990. *Het protocol fosfaatverzadigde gronden. Deel I: Toelichting Vakgroep bodemkunde en plantenvoeding*. Landbouwniversiteit, Wageningen (in Dutch).

Chapter 4

Modeling Phosphorus Sorption in Soils

4.1. Introduction

Soils act simultaneously as a sink and source for phosphorus. However, soils become a source of P only when their P-attenuation capacity declines either due to P additions or by adsorption of competing ions. Phosphorus that cannot be sorbed by soil is lost through leaching and runoff. P sorption capacity (PSC) or ability of the soils to sequester P from the solution depends upon a number of factors. The most important factor in determining PSC of soils is the presence of Fe and Al oxides. Hydroxylated surfaces of Fe and Al oxides have great affinity for phosphorus. Retention of both dissolved organic and inorganic species of P in soils increases with increased content of Fe and Al oxides, especially amorphous oxides (Bridgham et al, 2001; Villapando and Greatz, 2001; Khiari et al, 1999; Sundareshwar and Morris, 1999; Anderson et al., 1974). Phosphorus retention capacity of the soils depends considerably on pH as well. With decrease in pH, mineral surfaces develop a positive charge, which helps increase the sorption of anions like phosphate (Stumm and Morgan, 1996). Sorption of both inorganic and organic P decreases with an increase in pH (Celi et al, 2001; Ortas and Rowell, 2000; Barrow, 1993; Shang et al., 1992; Bolan et al, 1986; Barrow et al, 1980). Organic matter influences P retention capacity, but the contribution of organic matter to P attenuation capacity of soils depends upon the nature of organic matter. Some studies report a decrease in phosphorus attenuation capacity with increase in organic matter content (Vadas and Sims, 1999; Holford et al., 1997). On the other hand, other studies report the positive effect of organic matter on P sorption capacity of soils (Zhou et al., 1997; Ohno and Crannel, 1996). In spodosols, an increase in organic matter is also

accompanied by an increase in amorphous oxides of Fe and Al. Thus, it is not the organic functional groups as such, but associated Fe and Al that increase PSC. Further, since organic matter is a variable charge substance, its effect may depend upon soil pH also (Barrow, 1999). Phosphorus sorption capacity of soils depends upon the clay content (Cox, 1994; Moughli et al., 1993), as clays provide more surface area for coatings of Fe and Al oxyhydroxides that bind P. However, sorption of P onto clays depends greatly upon the nature of clay (Celi et al., 1999; Anderson et al., 1974). Calcium is also reported to affect P sorption (Celi et al., 2001). The relative contribution of these factors towards P sorption capacity varies among soils due to the likely interaction among soil properties.

Historically, P sorption on soils and soil components has been modeled based on the interactions of P anions with a single adsorbent system or by borrowing models that were originally developed for physical adsorption of gas molecules on smooth uncharged surfaces. Sometimes, these models were based on surface complexation reactions (Goldberg and Sposito, 1984). However, in all these modeling attempts the system is assumed to consist of a well-characterized single phase. In a multiphase system, assumptions of uniform distribution of surface reactive groups and the absence of any interaction between surface reactive groups of different adsorbents are made either explicitly or implicitly. Mechanisms implied in these modeling approaches are hard to prove or disprove when adsorption is observed in a multiphase system such as soils. Statistical modeling provides a tool for developing predictive models for P sorption and helps to understand the relationship between various components and their properties without the need for invoking any specific P sorption mechanism.

Data on physico-chemical properties of soils are routinely collected as part of soil survey programs. Therefore, these data can possibly be used to predict PSC of the soils by developing models that best explain the relation between PSC and the soil characteristics. However, the most striking limitation of such an effort could be the presence of multicollinearity in the data. Multicollinearity is a condition when variables move along each other due to near-linear dependencies between them. Two possible solutions for multicollinearity are: (i) the deletion of variables that are prone to multicollinearity, and (ii) the use of some alternative methods of regression (Myers, 1986). Use of the first method often leads to deletion of important variables under the pretext of multicollinearity (Morzuch and Ruark, 1991). Principal components regression (PCR) method handles multicollinearity in the data set by transforming independent variables into a set of new variables that are linear combinations of all original variables and are called principal components (PCs). These new variables or PCs are orthogonal or uncorrelated to each other (Jolliffe, 1986; Morzuch and Ruark, 1991). These PCs are then used as independent variables in developing a model with ordinary least squares regression (OLSR).

The objective of this study was to predict P sorption capacity with various statistical modeling approaches by using the data collected on the following variables: ammonium oxalate-extractable Fe and Al, which generally represent amorphous phases of Fe and Al; dithionite-citrate-bicarbonate Fe and Al, which indicate both amorphous and crystalline phases; KCl-extractable Al and Mn, which are used to determine exchangeable Al and Mn; total carbon, extractable acidity; sum of cations like Na, Ca,

Mg, and K along with H^+ ; ammonium acetate extractable Ca, which estimates exchangeable Ca; clay content; soil pH in water; and soil pH in 0.01M $CaCl_2$.

4.2. Materials and Methods

Four pedons each (98 horizons: 16 surface and 82 subsurface horizons) of the Berks (loamy-skeletal, mixed, active, mesic, Typic Dystrudepts), Huntington (fine-silty, mixed, active, mesic, Fluventic Hapludolls), Lindside (fine-silty, mixed, active, mesic, Fluvaquentic Eutrudepts), and Monongahela (fine-loamy, mixed, semiactive, mesic, Typic Fragiudults) soils were sampled from the Eastern Panhandle of West Virginia. Characterization data, including P sorption capacity (PSC), used for modeling are given in Tables 4.1-4.8.

4.2.1. Laboratory Analyses

Ammonium oxalate extractable Fe and Al were determined by the method described by Guo and Yost (1999). Dithionite-citrate-bicarbonate (DCB) extractable Fe and Al were determined by the method described by Mehra and Jackson (1960). Exchangeable Al and Mn were extracted with 1.0N KCl (Method 6G and 6G9, Soil Survey Staff, 1996). Extractable acidity was determined by extraction with barium chloride-triethanolamine (Method 6H, 6H5, Soil Survey Staff, 1996). Exchangeable Ca, Mg, Na, and K were determined by using 1.0N ammonium acetate buffered at pH 7.0 (Method 6N, 6O, 6P, and 6Q, Soil Survey Staff, 1996). Total carbon was determined by using LECO CNS-2000 (LECO Corp., St. Joseph, MI). Particle-size distribution was determined by the pipet method (Method 3A, Soil Survey Staff, 1996). Measurements for pH (soil-water ratio 1:1 and soil-0.01M calcium chloride ratio 1:2) were made on Accumet 15 pH meter (Method 8C1, 8C1f; Soil Survey Staff, 1996). Phosphorus sorption

capacity was determined by an 18-hour equilibration of 0.5g of soil with 30 mL of 0.01M CaCl₂ solutions containing a series of P concentrations. Phosphorus concentrations in the equilibrium solution were measured on Perkin Elmer P400 Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer. Phosphorus sorption maxima or PSC was calculated from Langmuir sorption isotherms.

4.2.2. Statistical Analyses

All statistical analyses were carried out by using JMP version 4.0.4 (SAS Institute Inc.; Sall et al., 2001). P sorption capacity was predicted by using the linear modeling techniques.

4.3. Results and Discussion

Data relevant to various soil properties are given in Tables 4.1 through 4.8. In a first assessment of relating P sorption capacity to soil properties, PSC was compared to each individual soil property (Figs. 4.1-4.9). The following results were encountered:

- PSC increased with increase in ammonium oxalate extractable Al (Fig. 4.1(A)). The effect was more pronounced in Berks and Monongahela soils.
- The relationship between PSC and ammonium oxalate extractable Fe was not clear (Fig. 4.1(B)). Maguire et al. (2001) also found that PSC was comparatively less dependent on ammonium oxalate extractable Fe than on ammonium oxalate extractable Al.
- PSC increased with an increase in DCB-extractable Al (Fig.4.2 (A)). The effect was clear in Berks and Monongahela soils.

- The positive relationship between PSC and DCB- extractable Fe was not as clear. A clear positive effect of DCB-extractable Fe was, however, observed for Monongahela (Fig. 4.2(B)).
- PSC increased with an increase in clay content in all the soils (Fig. 4.3).
- Effect of exchangeable Ca on PSC was not discernible (Fig.4.4). However, PSC decreased with increase in exchangeable Ca in Monongahela soil (Fig. 4.4).
- Phosphorus sorption capacity generally increased with increase in extractable acidity (Fig. 4.5(A)) in every soil.
- PSC increased with increase in KCl-extractable Al (Fig. 4.5(B)).
- The relationship between sum of cations and PSC was not too clear (Fig. 4.6).
- Effect of total carbon on P sorption capacity was not obvious (Fig. 4.7).
- The relationship between PSC and KCl-extractable Mn was not much interpretable (Fig. 4.8).
- PSC appeared to decrease with increase in pH in 0.01M CaCl₂ (Fig. 4.9(A)) and with increase in pH in water (Fig. 4.9(B)).

Although these figures reveal some relationships between soil properties and PSC, many soil variables did not have obvious effects on P sorption capacity. Therefore, composite effects of these variables rather than their individual impact on PSC may be of significance. To predict these effects, a series of regression analyses on the data set for an individual soil series and on the combined data set for all the four soil series were performed. First, PSC was predicted by using ordinary least squares regression (OLSR) on the original independent variables. Summary of various diagnostic statistics obtained

by OLSR on all the original variables (referred to as OLSR full model), by OLSR on some of the original variables selected through stepwise OLSR (referred to as OLSR reduced model), and by stepwise OLSR on principal components (referred to as PCR model) for the individual soils and for all soils is given in Table 4.10. OLSR full model results show that very high coefficients of determination (R^2) values were obtained in OLSR full model (Table 4.10).

Excepting the models common to all soils, OLSR full model R^2 was higher than the R^2 in OLSR reduced model and in the PCR model. However, R^2 is not always a good criterion for comparing the candidate models. High R^2 values could result from the spread in the data set and from the over-fitting of the model. Another statistic, adjusted- R^2 can be used to compare candidate models. Adjusted- R^2 in OLSR full model in Berks soil was higher (0.9090) than adj- R^2 in the reduced OLSR model (0.8790), but it was lower than the adj- R^2 obtained in PCR model. In Huntington soil, adj- R^2 comparisons indicate that OLSR full model (adj- R^2 0.5937) was not better than OLSR reduced model (adj- R^2 0.7177) and the PCR model (0.6982). In Lindside and Monongahela soils, the full OLSR model was not better, in terms of adj- R^2 than the OLSR reduced model and the PCR model.

Another useful statistic for comparing candidate models is PRESS, which stands for prediction error sum of squares (Allen, 1974). PRESS is the sum of those residuals which are generated by first deleting one by one each value of response variable, then fitting the model to the rest of the data set, and then predicting the deleted value of response variable based upon the model developed by using the remaining values. This statistic ensures that a given measurement is not used simultaneously for developing a model and

Table 4.1. Data (part-I) used for modeling P sorption capacity (PSC) in Berks soils.

Soil	Horizon	Depth (cm)	P sorption capacity	Ammonium	Ammonium	DCB [†]	DCB	KCl
				oxalate extractable Al	oxalate extractable Fe	extractable Al	extractable Fe	extractable Mn
.....(mg kg ⁻¹).....								
Berks1	Oe	0-2	567	1,192	1,933	1,194	3,706	127.5
	A/E	2-5	1,088	1,640	3,028	1,618	6,822	22.7
	Bw1	5-20	613	1,086	1,294	1,762	7,221	5.6
	Bw2	20-54	630	872	667	1,761	8,593	0.7
	C	54-72	639	879	637	1,838	10,406	8.1
Berks2	A	0-4	1,235	1,996	3,736	2,131	6,363	84.9
	B/E	4-19	933	1,573	1,473	2,001	8,841	4.9
	Bw1	19-39	770	1,185	812	1,918	10,468	0.7
	Bw2	39-54	608	929	632	1,614	9,928	0.6
	C	54-66	735	889	575	1,699	11,812	1.0
Berks3	Oe/Oa	0-3	1,274	3,557	1,980	3,085	4,082	129.1
	A	3-5	1,333	2,202	3,208	2,575	8,140	502.8
	Bw	5-22	755	1,187	1,997	1,831	9,354	46.5
	C	22-57	616	678	802	1,413	9,675	8.0
Berks4	Oe	0-2	932	3,115	1,859	1,986	6,552	32.6
	A	2-5	940	2,690	2,626	2,642	4,978	56.7
	BA	5-10	678	1,435	3,073	2,279	7,098	67.9
	Bw1	10-20	636	769	1,050	1,731	8,878	34.4
	Bw2	20-41	503	681	789	1,740	11,152	29.1
	C	41-52	516	544	675	1,763	13,957	6.4

[†] DCB: dithionite-citrate-bicarbonate

Table 4.2. Data (Part-II) used for modeling P sorption capacity in Berks soils.

Soil	Horizon	Depth (cm)	Clay	Total carbon	Ammonium acetate extractable-Ca	Extractable acidity	KCl extractable Al	Sum of cations	pH (soil: water) (1:1)	pH (soil:0.01M CaCl ₂) (1:1)
		 (percent)....(cmol _c kg ⁻¹).....						
Berks 1	Oe	0-2		27.7	6.0	46.4	1.0	50.0	4.0	3.3
	A/E	2-5	13.2	8.0	0.8	20.9	7.1	21.6	3.9	3.3
	Bw1	5-20	12.4	1.1	0.1	8.8	3.2	9.1	4.4	4.0
	Bw2	20-54	15.9	0.5	0.1	9.4	3.3	9.9	4.6	4.0
	C	54-72	21.0	0.3	0.1	11.6	2.9	12.9	5.0	4.1
Berks 2	A	0-4	19.7	8.9	2.1	29.0	7.9	31.9	3.6	3.3
	B/E	4-19	19.3	1.7	0.5	15.9	5.9	16.6	4.3	3.7
	Bw1	19-39	21.3	0.7	0.3	11.8	5.0	12.3	4.5	3.8
	Bw2	39-54	19.6	0.6	0.3	9.7	4.0	10.4	4.6	3.9
	C	54-66	24.5	0.6	0.8	9.6	3.5	11.4	4.9	3.9
Berks 3	Oe/Oa	0-3		24.2	27.7	31.7	0.2	64.1	5.5	5.0
	A	3-5	20.3	8.2	1.7	33.2	3.5	36.1	4.4	3.8
	Bw	5-22	18.2	1.7	0.6	12.5	3.4	13.3	4.5	3.9
	C	22-57	20.3	0.9	4.0	7.6	1.6	12.5	5.0	4.1
Berks 4	Oe	0-2		14.8	36.2	11.7	0.3	52.7	6.3	6.1
	A	2-5	19.2	7.7	20.5	16.1	0.2	39.2	5.8	5.7
	BA	5-10	17.3	3.0	6.8	10.4	0.0	18.3	5.7	5.1
	Bw1	10-20	18.7	0.5	0.4	3.8	2.2	4.5	4.7	3.9
	Bw2	20-41	21.8	0.4	1.3	6.1	1.9	8.1	4.9	4.0
	C	41-52	28.6	0.3	3.4	5.5	0.9	10.3	5.3	4.3

Table 4.3. Data (Part-I) used for modeling P sorption capacity in Huntington soils.

Soil	Horizon	Depth (cm)	P sorption capacity	Ammonium oxalate extractable	Ammonium oxalate extractable	DCB [†] extractable	DCB extractable	KCl extractable
				Al	Fe	Al	Fe	Mn
.....(mg kg ⁻¹).....								
Huntington 1	Ap1	0-18	345	696	2,238	1,385	11,303	23.6
	Ap2	18-31	378	724	2,175	1,403	11,385	27.8
	Bw1	31-53	600	1,105	2,449	1,800	14,232	22.7
	Bw2	53-98	557	951	2,251	1,763	15,133	14.3
	Bw3	98-131	499	848	2,455	1,678	14,539	10.6
	BC	131-170	405	803	2,270	1,625	13,845	9.7
Huntington 2	Ap1	0-9	269	386	1,690	688	8,122	2.8
	Ap2	9-28	528	704	2,389	1,014	10,062	4.1
	BA	28-41	419	864	2,537	1,340	11,950	4.7
	Bw	41-113	507	1,095	2,542	1,355	11,566	9.6
	BC	113-150	414	964	2,291	1,370	11,381	5.9
Huntington 3	Ap	0-15	364	846	3,080	1,111	9,462	3.2
	BA	15-37	494	1,127	3,335	1,494	11,531	3.5
	Bw1	37-64	501	1,165	3,054	1,530	10,618	6.6
	Bw2	64-120	601	1,140	3,178	1,680	12,429	15.0
	BC	120-139	411	821	2,509	1,243	10,398	13.4
Huntington 4	C	139-154	464	703	2,073	1,351	11,040	17.7
	Ap1	0-9	458	859	3,310	1,164	10,233	23.3
	Ap2	9-27	511	963	3,485	1,207	10,737	12.6
	Bw2	87-126	655	1,270	3,115	1,620	12,662	7.3
	Bw3	126-151	720	873	2,447	1,471	12,534	14.2
BC	151-175	717	813	2,814	1,390	12,594	19.0	

[†] DCB: dithionite-citrate-bicarbonate.

Table 4.4. Data (part-II) used for modeling P sorption capacity in Huntington soils.

Soil	Horizon	Depth (cm)	Clay	Total Carbon	Ammonium acetate extractable Ca	Extractable acidity	KCl extractable Al	Sum of cations	pH soil: water (1:1)	pH soil 0.01M CaCl ₂ (1:2)
			...(percent)...		(cmol _c kg ⁻¹).....				
Huntington 1	Ap1	0-18	19.8	2.0	8.3	9.3	0.03	19.0	6.2	5.6
	Ap2	18-31	18.8	1.3	7.1	9.1	0.02	17.2	6.1	5.3
	Bw1	31-53	27.6	1.5	10.4	6.9	0.02	18.8	6.2	5.5
	Bw2	53-98	28.7	1.0	10.3	4.4	0.03	16.2	6.5	5.7
	Bw3	98-131	29.5	0.9	10.0	4.5	0.04	16.0	6.7	5.7
	BC	131-170	28.5	0.7	9.0	6.9	0.08	17.7	6.7	5.7
Huntington 2	Ap1	0-9	11.0	1.3	9.1	1.9	0.07	12.1	7.3	6.7
	Ap2	9-28	20.6	1.9	12.1	3.6	0.05	16.9	7.3	6.6
	BA	28-41	22.6	1.3	10.7	4.8	0.08	17.6	7.1	6.3
	Bw	41-113	29.0	1.3	11.7	6.1	0.02	16.7	6.8	5.9
	BC	113-150	25.1	0.7	9.3	5.1	0.07	22.2	6.7	5.7
Huntington 3	Ap	0-15	24.1	2.4	16.1	3.3	0.02	15.4	7.3	6.5
	BA	15-37	31.1	0.8	10.7	4.6	0.04	12.9	7.2	6.3
	Bw1	37-64	30.2	0.6	7.3	7.3	0.20	15.9	5.9	4.9
	Bw2	64-120	32.5	0.5	7.7	8.6	0.85	16.7	5.4	4.5
	BC	120-139	24.7	0.3	6.7	6.3	0.61	14.8	5.5	4.5
	C	139-154	24.8	0.3	7.1	5.7	0.46	19.5	5.5	4.6
Huntington 4	Ap1	0-9	24.9	2.5	12.4	5.7	0.08	19.4	6.5	6.0
	Ap2	9-27	27.2	1.3	11.6	4.7	0.07	17.0	6.9	6.0
	Bw1	27-87	35.2	0.7	11.0	7.0	0.11	19.7	6.1	5.1
	Bw2	87-126	34.9	0.9	10.8	7.5	0.09	19.8	6.5	5.5
	Bw3	126-151	32.5	0.5	10.9	5.2	0.13	17.4	6.1	5.1
	BC	151-175	33.3	0.4	10.1	5.1	0.24	16.0	6.0	5.0

Table 4.5. Data (part-I) used for modeling P sorption capacity in Lindside soils.

Soil	Horizon	Depth (cm)	P sorption capacity	Ammonium oxalate extractable Al	Ammonium oxalate extractable Fe	DCB [†] extractable Al	DCB extractable Fe	KCl extractable Mn
		(mg kg ⁻¹).....					
Lindside 1	Ap	0-25	595	887	4,526	1,655	13,712	7.2
	AB	25-37	584	820	3,984	1,512	12,726	3.6
	Ab	37-54	757	1,260	3,837	2,100	13,846	2.3
	Bwb	54-95	566	905	3,083	1,824	15,926	1.6
	BCb	95-146	590	920	3,761	1,920	16,024	1.2
Lindside 2	Ap	0-15	248	415	2,118	717	8,650	1.5
	AB	15-37	292	616	3,813	811	9,155	2.8
	Bw	37-53	486	807	5,541	811	9,787	2.2
	Bgb1	53-80	708	112	7,671	762	9,424	3.6
	Bgb2	80-117	535	901	4,371	1,060	16,721	4.8
	BCgb	117-155	677	855	2,532	1,244	14,801	7.3
Lindside 3	Ap1	0-10	549	847	3,225	1,213	10,832	30.3
	Ap2	10-28	563	919	3,454	1,293	10,590	24.1
	Bw1	28-49	690	1,084	2,873	1,460	11,129	16.8
	Bw2	49-102	469	991	3,218	1,621	12,146	20.4
	BC	102-128	511	554	2,086	1,355	10,790	15.8
Lindside 4	Ap	0-12	539	831	4,404	1,355	9,843	36.2
	AB	12-33	583	1,246	4,874	1,684	11,677	48.6
	Bw1	33-54	535	1,208	3,978	1,833	13,479	24.3
	Bw2	54-94	626	1,125	3,327	2,098	14,905	21.4
	BC	94-118	653	858	2,134	2,079	14,889	25.9
	C	118-147	544	585	1,572	1,452	12,333	13.6

[†] DCB: dithionite-citrate-bicarbonate.

Table 4.6. Data (part-II) used for modeling P sorption capacity in Lindside soils.

Soil	Horizon	Depth (cm)	Variable							
			Clay	Total Carbon	Ammonium acetate extractable Ca	Extractable acidity	KCl extractable Al	Sum of cations	pH	
			----- percent-----	-----cmol _c kg ⁻¹ -----					soil: water (1:1)	soil:0.01M CaCl ₂ (1:2)
Lindside 1	Ap	0-25	27.5	2.8	13.7	5.8	0.1	21.5	6.7	6.2
	AB	25-37	22.0	1.6	10.0	4.1	0.1	15.7	6.9	6.2
	Ab	37-54	30.8	1.8	12.4	5.3	0.1	19.4	6.9	6.2
	Bwb	54-95	30.8	0.8	10.1	4.5	0.1	16.2	7.0	6.2
	BCb	95-146	32.4	0.5	9.2	4.4	0.1	15.2	7.2	6.4
Lindside 2	Ap	0-15	12.7	1.8	17.3	2.8	0.0	21.1	7.2	6.7
	AB	15-37	22.0	1.7	14.2	3.5	0.0	19.0	7.2	6.6
	Bw	37-53	26.3	1.2	12.2	5.1	0.0	18.8	7.1	6.4
	Bgb1	53-80	37.5	1.5	13.1	8.7	0.1	24.0	6.3	5.6
	Bgb2	80-117	43.2	0.9	11.7	7.3	0.0	21.8	6.1	5.2
BCgb	117-155	47.3	0.8	13.4	6.7	0.0	23.9	6.2	5.4	
Lindside 3	Ap1	0-10	25.9	2.3	8.7	7.6	0.1	22.8	6.0	5.8
	Ap2	10-28	27.9	2.3	14.0	5.9	0.1	22.7	6.2	5.9
	Bw1	28-49	32.3	1.3	14.0	5.9	0.2	21.6	5.8	5.6
	Bw2	49-102	27.6	0.5	9.9	5.2	0.1	14.6	5.7	5.4
	BC	102-128	21.2	0.4	6.2	3.6	0.1	16.6	6.1	5.8
Lindside 4	Ap	0-12	23.8	2.4	10.4	8.9	0.0	18.3	6.2	5.6
	AB	12-33	29.1	1.2	7.7	10.9	0.1	20.7	5.8	4.8
	Bw1	33-54	32.6	0.7	8.4	8.7	0.1	18.6	6.1	5.0
	Bw2	54-94	33.8	0.6	7.9	9.4	0.1	18.6	6.0	4.9
	BC	94-118	31.6	0.4	7.1	8.7	0.6	16.7	5.7	4.6
	C	118-147	24.2	0.3	5.4	5.1	0.3	13.2	5.8	4.6

Table 4.7. Data (part 1) used for modeling P sorption capacity in Monongahela soils.

Soil	Horizon	Depth (cm)	P sorption capacity	Ammonium	Ammonium	DCB [†]	DCB	KCl
				oxalate extractable Al	oxalate extractable Fe	extractable Al	extractable Fe	extractable Mn
(mg kg ⁻¹)								
Monongahela 1	Ap	0-17cm	462	734	1,604	1,460	7,882	62.0
	Bt1	17-48	338	424	818	1,637	10,456	12.6
	Bt2	47-73	571	523	1,034	1,761	10,826	5.7
	Btx1	73-95	831	934	949	1,992	11,602	1.7
	Btx2	95-128	1141	941	1,093	2,418	13,523	0.2
	2C	128-170	1099	19	12	2,178	15,624	0.2
Monongahela 2	Ap	0-10	492	1,021	1,445	1,942	8,680	167.6
	BA	10-26	577	1,097	1,518	2,090	9,072	90.6
	Bw	26-43	649	672	1,112	1,640	9,792	55.5
	Bt1	43-56	635	559	976	2,028	13,549	16.8
	Bt2	56-79	669	675	1,068	2,150	13,862	5.8
	Btx1	79-109	1017	982	1,259	2,501	17,875	1.2
	Btx2	109-117	1034	802	1,758	2,688	22,923	2.6
	Btx3	117-139	993	761	965	2,115	16,327	2.3
Btx4	139-166	691	711	840	1,803	13,859	3.8	
Monongahela 3	Oi/Oe	3-5	799	2,664	1,015	2,613	1,197	201.2
	A/E	5-9	639	1,091	1,317	1,407	3,215	87.1
	BE1	9-17	536	747	1,376	1,373	5,171	7.7
	BE2	17-37	426	607	595	1,426	5,514	5.1
	Bt	37-57	807	865	646	1,693	7,528	0.9
	Btx1	57-83	1267	1,681	847	3,592	17,169	0.9
	Btx2	83-116	1723	2,079	902	3,968	21,843	62.0
Btx3	116-150	1768	2,269	944	3,888	25,239	12.6	
Monongahela 4	Ap	0-11	714	1,914	1,445	3,487	8,675	5.7
	Bt1	11-14	760	1,024	720	3,153	11,388	1.7
	Bt2	14-22	746	796	515	2,852	10,140	0.2
	Btx1	22-34	933	938	562.2	3,104	11,243	0.2
	Btx2	34-43	1494	1,346	531	4,604	18,259	167.6
	2C	43-65	1093	1,132	517	3,547	18,162	90.6

[†] DCB: dithionite-citrate-bicarbonate.

Table 4.8 Data (part-II) used for modeling P sorption capacity in Monongahela soils.

Soil	Horizon	Depth (cm)	Variable							
			Clay	Total Carbon	Ammonium acetate extractable Ca	Extractable acidity	KCl-extractable Al	Sum of cations	pH	
			-----percent----	-----cmol _c kg ⁻¹ -----						
Monongahela 1	Ap	0-17	14.6	2.2	4.4	9.6	0.0	15.1	5.7	5.1
	Bt1	17-48	17.4	0.3	3.7	7.9	0.1	12.7	5.9	5.1
	Bt2	47-73	23.3	0.2	3.8	7.8	0.1	14.1	5.8	5.0
	Btx1	73-95	26.8	0.2	2.6	10.5	1.6	15.9	5.4	4.4
	Btx2	95-128	34.7	0.1	1.5	15.4	5.5	19.9	5.3	4.0
	2C	128-170	34.1	0.1	0.9	15.9	6.2	19.4	5.1	3.9
Monongahela 2	Ap	0-10	15.8	2.0	2.5	10.9	0.6	14.3	4.9	4.4
	BA	10-26	15.0	0.8	1.6	8.5	0.6	10.7	5.1	4.4
	Bw	26-43	17.6	0.4	2.1	5.5	0.5	8.5	5.1	4.4
	Bt1	43-56	23.2	0.2	3.5	4.3	0.4	9.5	5.3	4.6
	Bt2	56-79	23.6	0.2	4.0	6.1	1.1	12.2	5.2	4.4
	Btx1	79-109	21.7	0.1	2.0	9.0	4.4	12.7	4.8	4.0
	Btx2	109-117	16.1	0.2	0.9	8.9	3.6	11.0	4.6	3.9
	Btx3	117-139	17.7	0.1	0.9	7.8	3.8	10.1	4.7	3.9
Btx4	139-166	17.8	0.1	1.1	7.6	3.8	10.7	4.7	3.9	
Monongahela 3	Oi/Oe	3-5		28.5	3.1	13.4	0.7	18.1	4.5	3.8
	A/E	5-9	8.8	9.4	1.0	24.2	3.6	25.7	3.9	3.5
	BE1	9-17	9.6	1.5	0.1	8.8	2.0	9.0	4.3	3.8
	BE2	17-37	11.8	0.5	0.0	5.5	1.5	5.6	4.5	4.1
	Bt	37-57	21.7	0.3	0.0	9.3	4.3	9.8	4.3	3.8
	Btx1	57-83	41.0	0.2	0.1	15.8	8.1	18.2	4.6	3.8
	Btx2	83-116	52.8	0.2	0.0	21.1	11.6	23.9	5.0	3.8
Btx3	116-150	57.3	0.2	0.0	24.6	13.8	27.7	5.1	3.8	
Monongahela 4	Ap	0-11	18.1	1.5	6.1	8.6	0.0	15.1	6.4	5.6
	Bt1	11-14	22.6	0.4	4.5	6.3	0.3	11.1	6.0	4.9
	Bt2	14-22	20.9	0.2	4.0	5.3	0.3	9.6	5.8	4.9
	Btx1	22-34	24.7	0.1	2.3	7.6	1.6	10.2	5.1	4.2
	Btx2	34-43	32.7	0.2	2.5	10.7	2.9	13.6	4.9	4.1
	2C	43-65	27.9	0.1	1.5	10.1	4.2	12.0	4.7	4.0

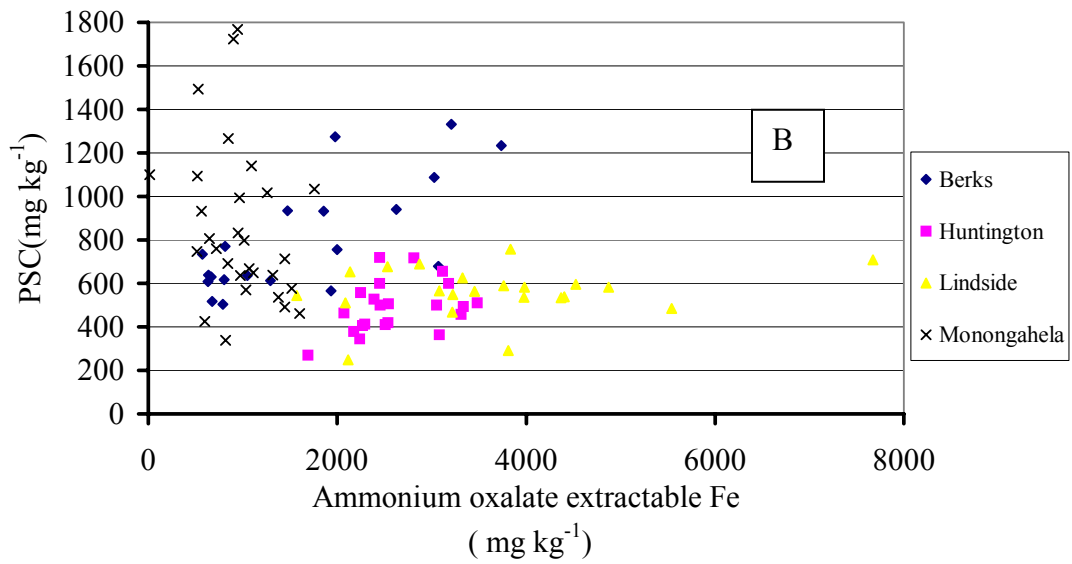
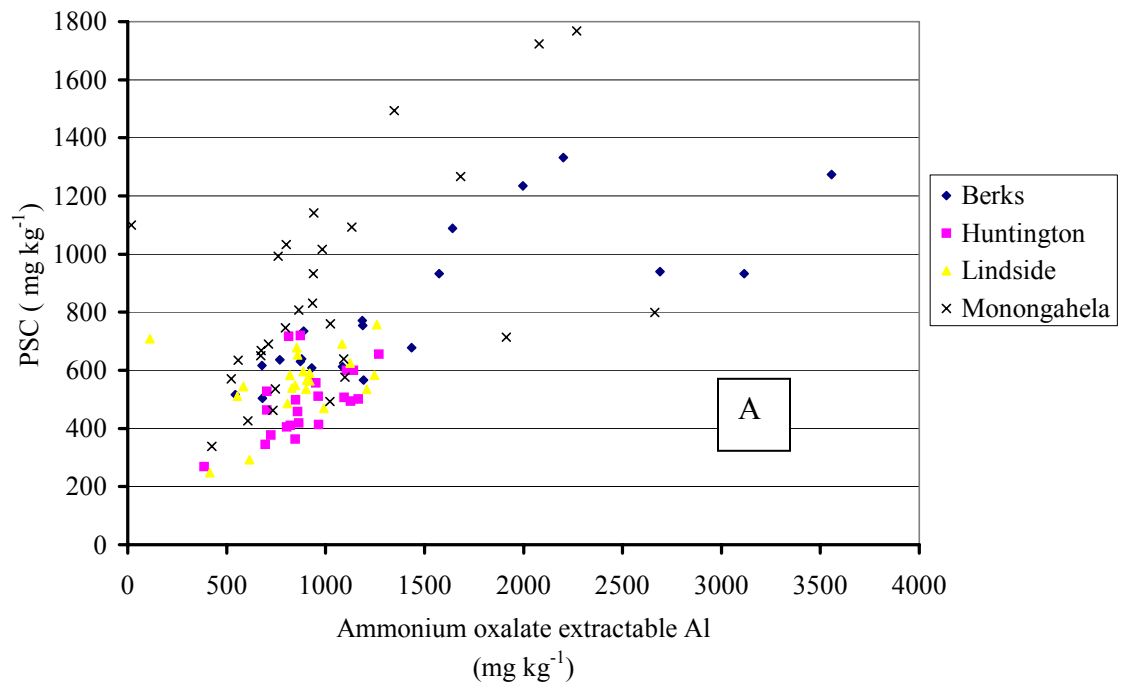


Figure 4.1. Relationship between P sorption capacity and ammonium oxalate extractable Al (A) and ammonium oxalate extractable Fe (B) in Berks, Huntington, Lindside, and Monongahela soils.

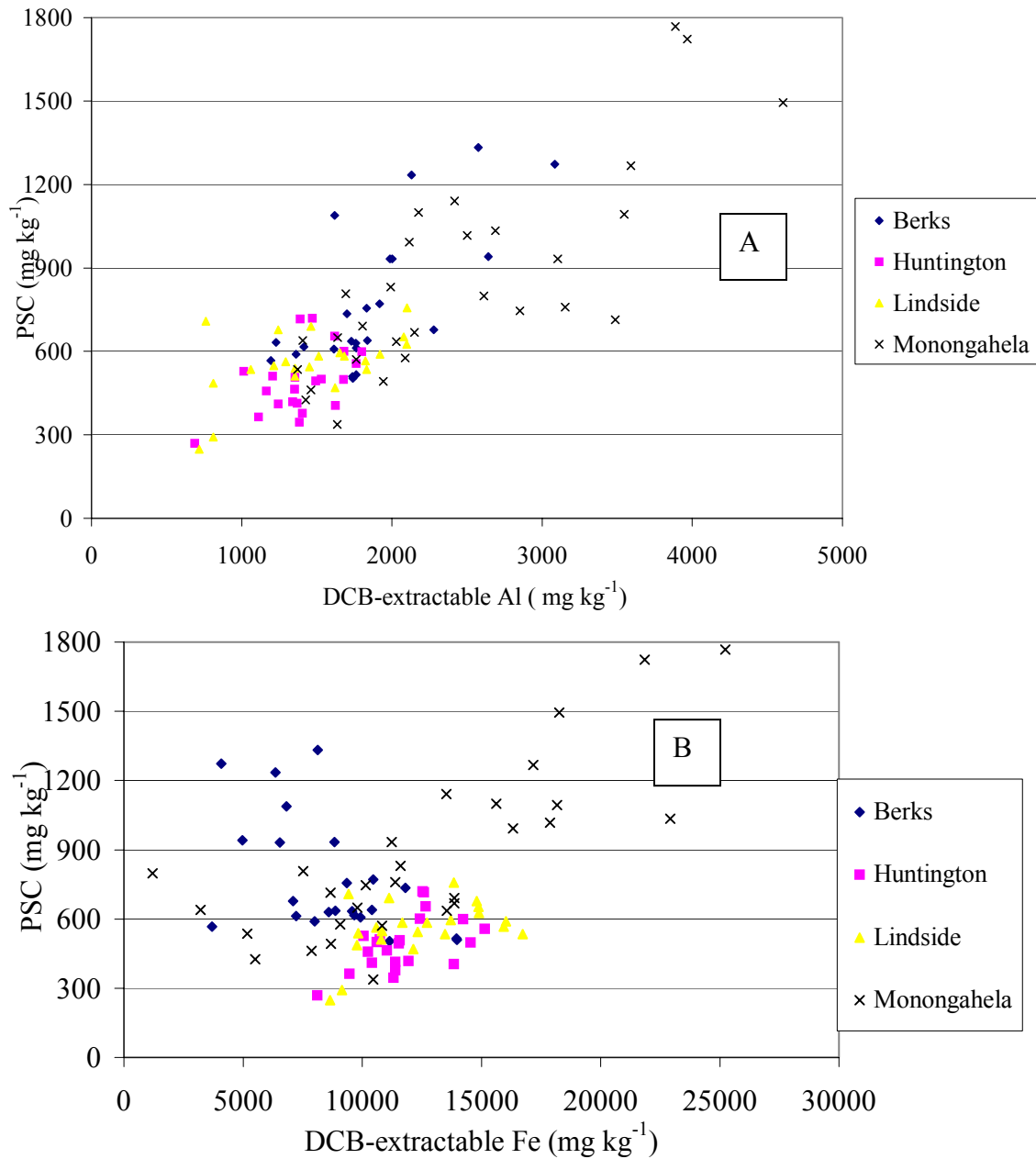


Figure 4.2. Relationship between P sorption capacity (PSC) and dithionite-citrate-bicarbonate (DCB) extractable Al (A) and Fe (B) in Berks, Huntington, Lindside, and Monongahela soils.

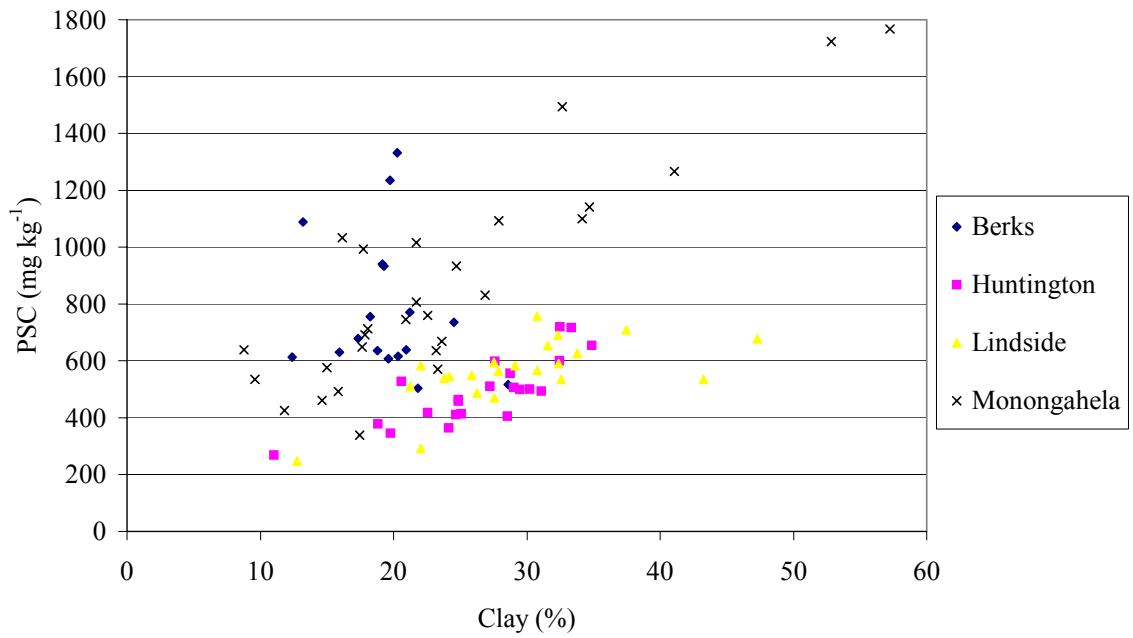


Figure 4.3. Relationship between P sorption capacity (PSC) and clay content in Berks, Huntington, Lindside, and Monongahela soils.

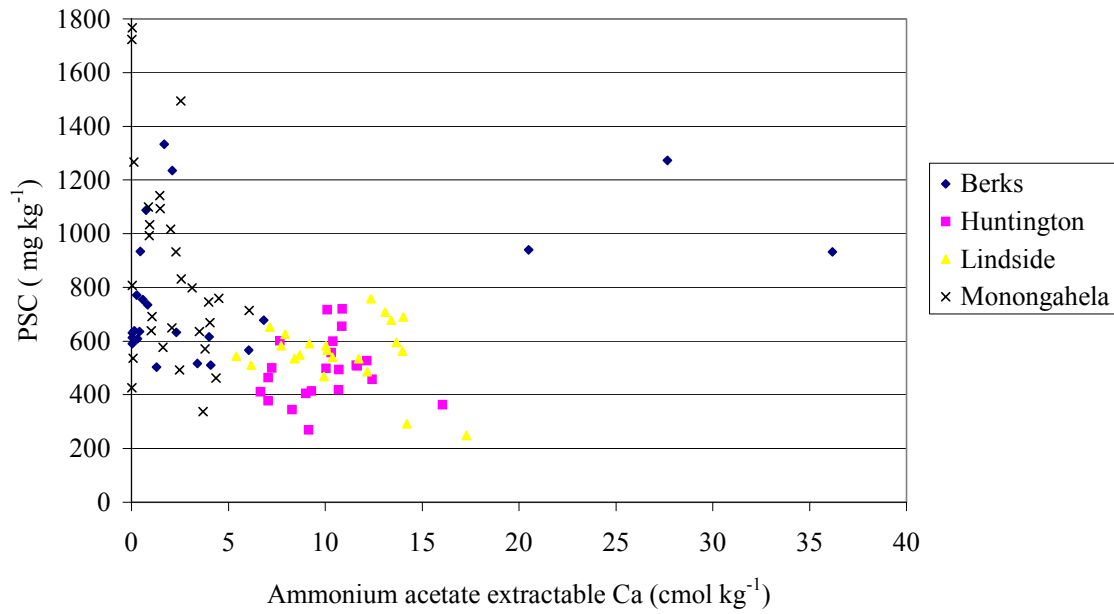


Figure 4.4. Relationship between P sorption capacity (PSC) and ammonium acetate extractable Ca in Berks, Huntington, Lindside, and Monongahela soils.

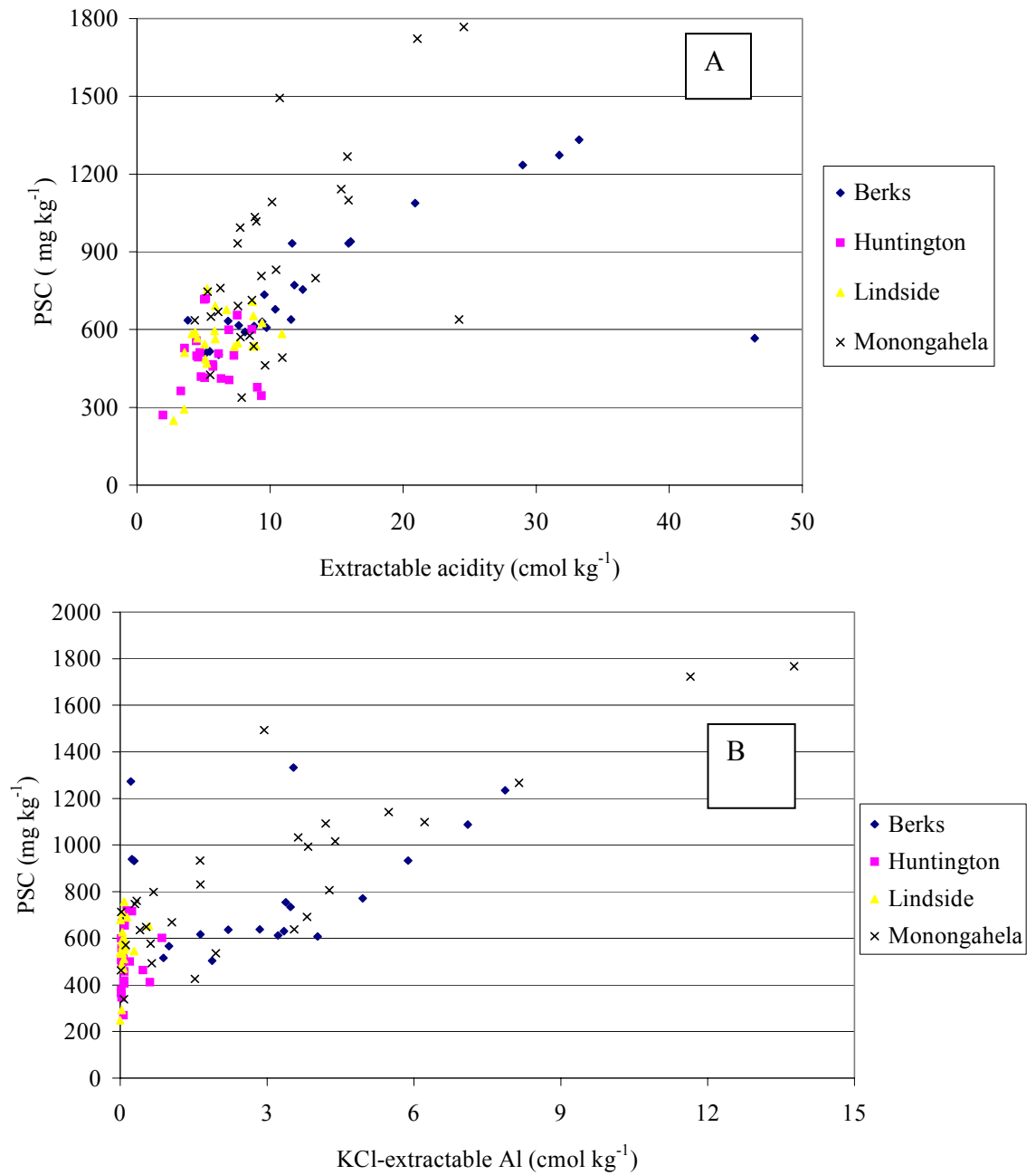


Figure 4.5. Relationship of P sorption capacity with extractable acidity (A) and KCl-extractable Al (B) in Berks, Huntington, Lindside, and Monongahela soils.

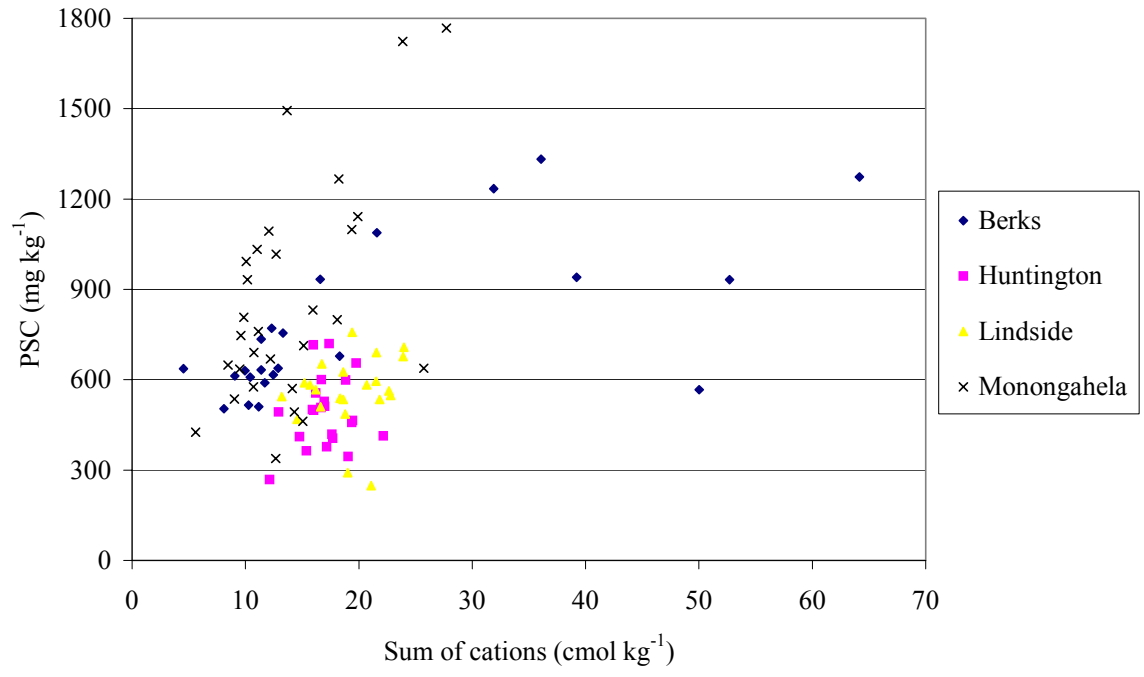


Figure 4.6. Relationship between P sorption capacity (PSC) and sum of cations in Berks, Huntington, Lindside, and Monongahela soils.

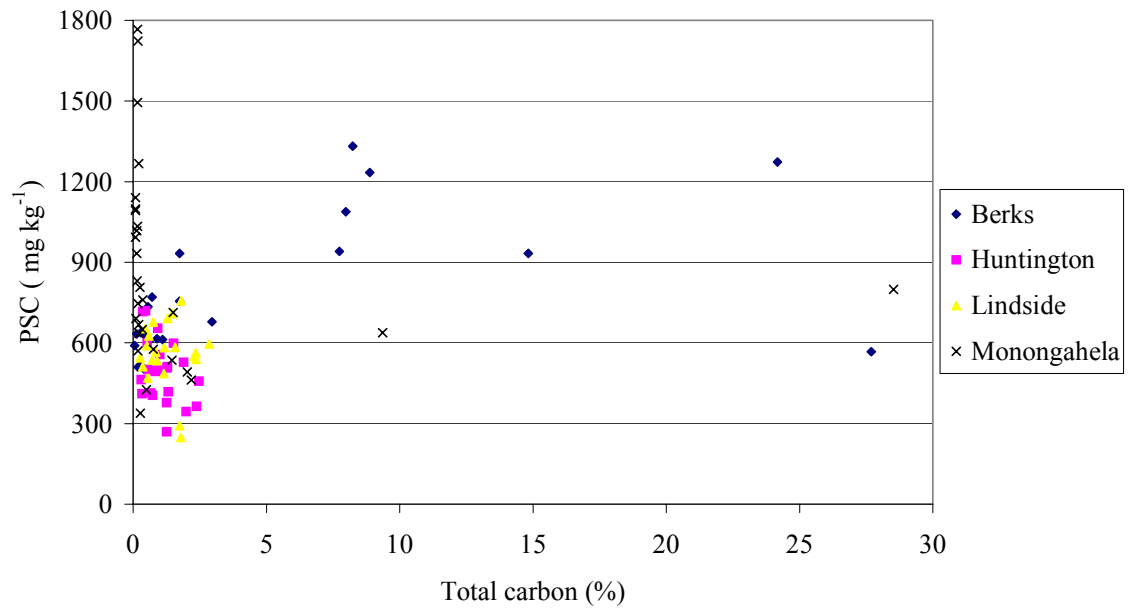


Figure 4.7. Relationship between total carbon and P sorption capacity (PSC) in Berks, Huntington, Lindside, and Monongahela soils.

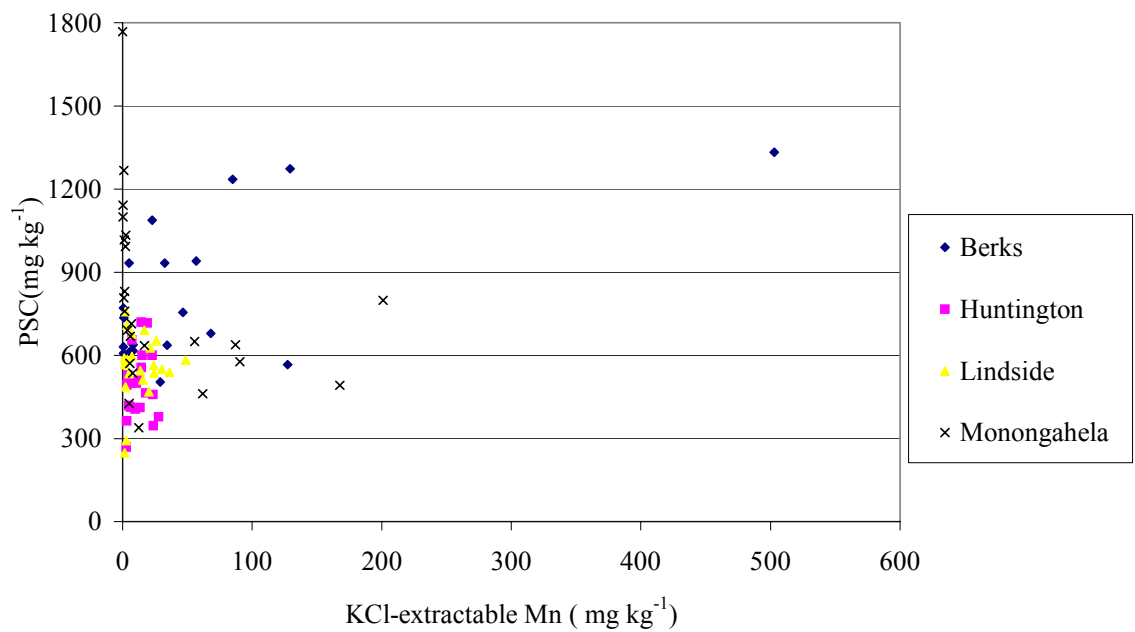


Figure 4.8. Relationship between KCl-extractable Mn and P sorption capacity (PSC) in Berks, Huntington, Lindside, and Monongahela soils.

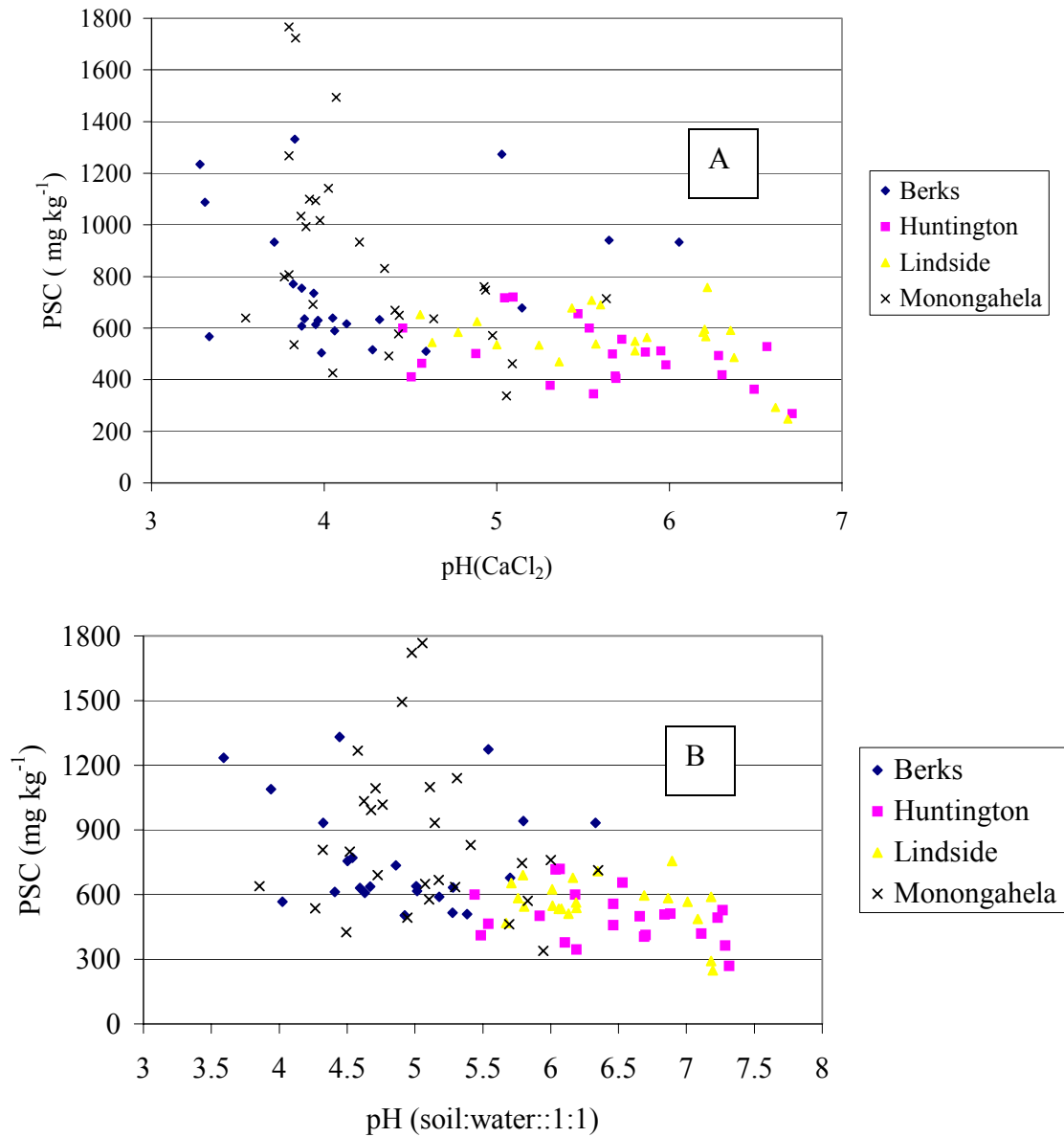


Figure 4.9. Relationship between P sorption capacity (PSC) and pH (CaCl₂;(A)) and pH (in water;(B)) in Berks, Huntington, Lindside, and Monongahela soils.

Table 4.9. Estimated coefficients for regression model based on ordinary least squares regression (OLSR) model using all variables (OLSR full model).

Variable	Berks	Huntington	Lindside	Monongahela	All Soils
Intercept	259	674	493	690	354
Ammonium oxalate extractable Al	0.15 (0.017)	0.20 (0.664)	-0.03 (0.051)	-0.04 (0.057)	-0.08 (3.13)
Ammonium oxalate extractable Fe	0.146 (0.050)	-0.027 (0.062)	0.013 (0.229)	0.1323 (0.969)	0.030 (6.53 [†])
Clay	-9.41 (0.004)	17.39 (1.151)	14.35 (4.703)	7.71 (0.662)	3.70 (2.20)
Ammonium Acetate Extractable Ca	-155.0 (0.052)	28.8 (0.615)	-19.4 (2.720)	30.6 (0.086)	5.01 (0.34)
Extractable Acidity	-198.7 (0.041)	19.7 (0.402)	-11.2 (0.082)	9.2 (0.013)	-14.6 (2.07)
KCl-extractable Al	147.4 (0.050)	-69.4 (0.127)	139.9 (0.571)	44.8 (0.690)	71.2 (47.02 ^{**})
Sum of cations	181.6 (0.042)	0.26 (0.001)	10.4 (0.551)	-16.3 (0.067)	9.3 (2.25)
Total Carbon	-45.0 (0.027)	-152.3 (1.026)	56.2 (1.476)	17.8 (0.060)	16.9 (1.31)
KCl-extractable Mn	1.81 (0.068)	-0.18 (0.001)	-4.18 (0.733)	-0.60 (0.519)	0.76 (7.95 ^{**})
DCB-extractable Fe	0.004 (0.0003)	0.042 (0.635)	-0.035 (3.652)	0.003 (0.041)	0.001 (0.01)
DCB-extractable Al	-0.160 (0.132)	-0.475 (1.589)	0.263 (8.84 [*])	0.126 (1.182)	0.221 (37.48 ^{**})
pH (soil: water:: 1:1)	250.6 (0.164)	-517.4 (2.134)	-49.5 (0.185)	262.5 (0.975)	-14.9 (0.07)
pH (soil: CaCl ₂ :: 1:2)	-266.7 (0.120)	453.3 (2.09)	8.31 (0.004)	-439.4 (2.69)	-60.3 (0.98)

[†] Figures in the parentheses are F-values. F-values with * are significant at 5% level, and with ** are significant at 1% level. All other F-values are non-significant at either level.

Table 4.10. Summary of various diagnostic statistics of models developed by using ordinary least square regression (OLSR) on all variables (OLSR full model), OLSR on variables selected through stepwise OLSR (OLSR reduced model) and principal components regression (PCR).

Soil	Statistic								
	R ²			Adj-R ^{2†}			PRESS ^{††}		
	OLSR (Full)	OLSR (Reduced)	PCR	OLSR (Full)	OLSR (Reduced)	PCR	OLSR (Full)	OLSR (Reduced)	PCR
Berks	0.9829	0.9093	0.9697	0.9090	0.8790	0.9596	3383829	921726	70123
Huntington	0.8452	0.7849	0.7988	0.5937	0.7177	0.6982	484437	158869	140140
Lindside	0.8605	0.8395	0.8501	0.6337	0.7592	0.7752	362593	106224	95280
Monongahela	0.9608	0.9533	0.9347	0.9041	0.9432	0.9244	729532	284428	254773
All soils	0.9014	0.9093	0.8888	0.8830	0.8790	0.8817	1100134	921726	690188

† Adjusted R²;

†† PRESS: Prediction error sum of squares.

predicting the response. Thus, it can be used to validate a model. Comparison of PRESS values (Table 4.10) suggests that the OLSR full model predicted poorer than the OLSR reduced model and the PCR model. Furthermore, most of the parameters in OLSR full models showed non-significant effects (Table 4.9). In models developed individually for each soil, no effect was significant in Barks and Huntington soils. Only DCB-extractable Al was significant at the 5% level. However, in the model common to all soils, four variables had significant effect: ammonium oxalate extractable Al (at 5% level), KCl-extractable Al (1% level), KCl-extractable Mn (1% level), and DCB-extractable Al (1% level). Poor performance of the OLSR full models can be ascribed to the over-fitting, that is some unimportant variables have been included in the model, and to the presence of multicollinearity. Multicollinearity makes the regression coefficients highly unstable, so the regression coefficients depend heavily on the data used to generate them. If another set of data would be used, regression estimates would vary considerably, thus prediction becomes highly inaccurate. This is especially true when values of the variables lie in a region where extrapolation is involved. Multicollinearity can be diagnosed by using a simple correlation matrix of regressor variables, but a more productive measure of multicollinearity is the variance inflation factor (VIF). Variance inflation factors are the diagonals of the inverse of the correlation matrix of the regressors. High VIF values suggest the problem of multicollinearity. VIF values greater than 10 usually indicate a severe problem of multicollinearity (Myers, 1986). VIF values for different variables (Table 4.11) indicate that there are many variables that are collinear and hence can lead to poor estimation of regression coefficients in ordinary least-squares regression. Berks soil is extremely infested with multicollinearity. One strategy for combating multicollinearity

is to delete variables that are seriously affected by multicollinearity, and if Myers' (1986) criterion of VIF is used, then virtually all the variables need be deleted for Berks soil. Therefore, for deleting redundant original variables (or to make OLSR reduced models), stepwise regression (probability to enter 0.25, probability to leave 0.10, forward direction) was used. During the selection of variables with stepwise regression, other two criteria – Mallow's Conceptual Predictive (C_p) criterion (Mallow, 1973) and Akaike's information criterion (AIC; Akaike, 1974) were also used. Regression estimates for the OLSR reduced models are given in Table 4.12.

In Berks soil, five variables were selected. Of these, extractable acidity, KCl-extractable Al, sum of cations, and KCl-extractable Mn were significant at the 1% level, whereas ammonium oxalate extractable Fe did not give a significant effect. Similarly, five variables were selected for Huntington soil. Of these, clay content was significant at the 1% level, and total carbon, pH (soil: water:: 1:1), and pH (soil:0.01M CaCl₂) were significant at the 5% level, whereas ammonium acetate extractable Ca was not significant at either level. In Lindsie soil, seven variables were selected. Four of these, ammonium acetate extractable Ca, clay content, DCB-extractable Fe, and DCB extractable Al were significant at 1% level, whereas total carbon and KCl-extractable Mn were significant at 5% level. KCl-extractable Al did not show any statistically significant effect. In Monongahela soil, five variables were selected. Of these, KCl-extractable Al, DCB extractable Al, and pH (soil: water:: 1:1) were statistically significant (at 1% level). However, the effect of ammonium oxalate extractable Fe was not statistically significant. The model common to all soils extracted seven variables: ammonium oxalate extractable

Table 4.11. Variance Inflation factors (VIF; indicators of multicollinearity) for various soil variables.

Variable	Berks	Huntington	Lindsay	Monongahela	All soils
	VIF				
Ammonium oxalate extractable Al	1,456	9.8	4.1	13.6	4.3
Ammonium oxalate extractable Fe	1,526	9.5	5.6	5.8	2.8
Clay	988	32.6	10.0	23.2	4.9
Ammonium Acetate extractable Ca	33415	24.7	5.3	70.3	21.3
Extractable Acidity	178,987	12.6	30.4	409.8	34.8
KCl-extractable Al	6,095.9	6.6	2.2	68.0	7.2
Sum of cations	236,666	1.8	7.7	251.2	14.9
Total Carbon	2,336	34.7	4.9	42.9	8.9
KCl-extractable Mn	1,993	12.3	17.0	2.6	2.8
DCB-extractable Fe	525	29.9	8.1	15.0	3.8
DCB-extractable Al	62.4	37.3	6.1	15.3	4.9
pH (soil: water:: 1:1)	107.3	155.6	15.7	57.5	29.9
pH (soil: CaCl ₂ :: 1:2)	572	148.8	30.7	45.2	36.6

Fe, extractable acidity, KCl-extractable Al, sum of cations, KCl-extractable Mn, DCB-Al, and pH (soil:0.01M CaCl₂: 1:2). All of these had statistically significant effects (at 1% level). Comparison of different statistics given in Table 4.10 reveals that the OLSR reduced model for Berks soil yielded better R² than the OLSR full model and PCR model. However, adj-R² was not better than adj-R² in any other model. However, PRESS was lower than the OLSR full model, but it was still higher than that in PCR model. In Huntington soil, R² was the least among all the models, but adj-R² was better even than that obtained in PCR model. PRESS value in the reduced model was much less than the PRESS in OLSR full model; however, it was greater than the PRESS values in PCR model. In Lindside soil, R² was not better than that obtained with any of the other two models. However, adj-R² was better than that in full model. PRESS was quite lower than that in OLSR full model, but it was greater than the PRESS in PCR model. In Monongahela soil model, R² was better than that obtained with PCR model. Adjusted-R² was the greatest among the three models. PRESS was less than that in the OLSR full model, but it was not lower than that in PCR model. In the model based on the data from all the four soils, the OLSR reduced model gave the highest R², but it gave the lowest adj-R². PRESS was lower than that in the OLSR full model, but it was higher than the PRESS in PCR model. To counter the effect of multicollinearity and to avoid sacrificing original variables that have an effect on PSC of soils, another approach, principal components regression (PCR) was also used. Principal components (PCs) were generated for each data set. Variation explained by these PCs is given in Table 4.13. Results show that PC analysis was very effective in decreasing the dimensionality of data. In Berks soil, first three PCs explained about 90% of the total variation in the regressor variables.

However, in Huntington soil the first three PCs could explain about 75% of the variation only, and in Lindside and Monongahela soils first three PCs explained respectively 72 and 80% of the variation. Likewise, in the analysis based upon the combined data more than 80% variation was explained by the first three PCs. Then PSC was regressed against these PCs with OLSR. Important PCs were selected through stepwise regression using the method followed for selecting original variables with OLSR. Regression estimates for the PCs selected for making a model common to all four soils and for individual soils are given in Table 4.14. For Berks soil, PC1, 2, 3, and 9 were selected. The selection of the last few PCs, like PC9, is not altogether unusual in PCR. This observation has also been made by Mardia et al. (1979) and Jolliffe (1986). However, the effects of PCs were much stronger than effects of original variables. This is suggested by very high F-values of effect tests. In the PCR model for Berks soil, F-value for the effect of PC1 was 307, whereas the highest F-value in OLSR reduced model was one associated with the effect of KCl-extractable Al in the model common to all soils. This observation further indicates that PCR provides more stable regression estimates; that is, coefficients worked out by using one data set will not change appreciably when another data set is used. This property of PCR imparts reliability to the use of these models for prediction in a wide range of conditions. In Huntington soil, seven PCs were selected. Of these, PC1, 2, and PC6 were significant at 1% level, whereas PC7, 10, 11, 13 were not statistically significant. More of the last few PCs made their way into regression equation in Huntington soil. This can be ascribed to the large spread of variation explained by different PCs in this soil (Table 4.14). In Lindside soil model, seven PCs were selected. Of these, PC1, 2, 3, 6, and PC10 were statistically significant, whereas PC8 and PC12

were not statistically significant. In Monongahela soil, only three PCs: PC1, 2, and PC4 were selected. PC1 and PC2 gave significant effects, however, PC4 did not give a statistically significant effect. In the model common to all soils, PC1, 2, 3, 7, and PC11 were selected and each PC had a significant effect. In Berks soil, the PCR model gave higher R^2 than OLSR reduced model. However, $\text{adj-}R^2$ and PRESS were higher than the other two models. In Huntington soil, R^2 was higher than R^2 in OLSR reduced model, $\text{adj-}R^2$ was higher than the OLSR full model, and the PRESS was the lowest among all the three models. In Lindside soil, R^2 was higher than that in OLSR reduced model; and $\text{adj-}R^2$ was the highest and PRESS was the lowest among all the three models. In the model common to all soils, R^2 was lower than that in other two models, $\text{adj-}R^2$ was higher than the OLSR reduced model, and PRESS was lower than that in other two models.

As stated earlier, principal components are linear combinations of original variables. Principal components in this work were calculated using correlation matrix. Though, principal components based on correlation matrix are more complex to interpret than the PCs based on the covariance matrix, but the use of different measurement units for different variables makes the use of covariance matrix inappropriate (Jolliffe, 1986). However, the algorithm used by the statistical package facilitated computation of the composition of these PCs. Composition of PCs selected for modeling is given in Tables 4.15 through 4.19. Each variable goes into the linear combination after multiplication with its respective coefficient. These coefficients resulted from the multiplication of eigenvalues of the PCs with standardized variables. A simplified model was (Table 4.20) developed by compositing the effect of variables across different PCs.

Table 4.12. Regression coefficients for the models developed using variable selection with stepwise ordinary least squares regression (OLSR: OLSR reduced model).

Parameter	Soil				
	Berks	Huntington	Lindside	Monongahela	All soils
Intercept	324	576	378	623	338
Ammonium oxalate extractable Al	--	--	--	--	--
Ammonium oxalate extractable Fe	0.046 (2.57 [†])	--	--	0.04 (0.70)	0.04 (15.1 ^{**})
Clay	--	16.1 (13.1 ^{**})	18.0 (44.4 ^{**})	--	--
Ammonium Acetate Extractable Ca	--	24.8 (3.12)	-18.2 (5.75 [*])	--	--
Extractable Acidity	-18.2 (35.0 ^{**})	--	--	--	-15.1 (16.6 ^{**})
KCl-extractable Al	84.8 (51.2 ^{**})	--	158 (1.91)	40.0 (22.1 ^{**})	69.0 (118 ^{**})
Sum of cations	16.5 (49.1 ^{**})	--	--	--	14.3 (43.3 ^{**})
Total Carbon	--	-120.2 (5.7 [*])	74.0 (8.5 [*])	--	--
KCl-extractable Mn	1.17 (22.3 ^{**})	--	-4.24 (8.2 [*])	--	0.56 (7.7 ^{**})
DCB-extractable Fe	--	--	-0.04 (12.4 ^{**})	--	--
DCB-extractable Al	--	--	0.23 (18.3 ^{**})	0.21 (80.6 ^{**})	0.19 (99.0 ^{**})
pH (soil: water:: 1:1)	--	-441.4 (7.8 [*])	--	295.6 (9.3 ^{**})	--
pH (soil: CaCl ₂ :: 1:2)	--	398.4 (5.9 [*])	--	-454.2 (13.0 ^{**})	-67.1 (11.1 ^{**})

[†] Values in the parentheses are F-values for testing whether variables have significant effect or not.

The values with ** are significant at 1% level and those with * are significant at 5% level. All other F-values are non-significant at either level.

Table 4.13. Variation (%) explained by different principal components extracted from the data for individual soils and from the combined data from all the soils.

Principal Component Number	Berks	Huntington	Lindside	Monongahela	All soils
1	49.87 (49.87) [†]	40.29 (40.29)	36.83 (36.83)	37.52 (37.52)	37.6 (37.6)
2	28.93 (78.80)	21.26 (61.55)	20.07 (56.90)	24.00 (61.52)	25.0 (62.6)
3	11.53 (90.33)	13.47 (75.02)	14.66 (71.56)	18.75 (80.27)	17.5 (80.1)
4	5.16 (95.49)	10.31 (85.33)	10.19 (81.75)	8.75 (89.02)	5.8 (85.9)
5	2.05 (97.54)	5.45 (90.78)	7.02 (88.77)	4.26 (93.28)	5.0 (90.9)
6	1.35 (98.89)	4.12 (94.90)	5.10 (93.87)	3.58 (96.86)	2.9 (93.8)
7	0.53 (99.42)	2.20 (97.10)	2.01 (95.88)	1.72 (98.58)	2.2 (96.0)
8	0.27 (99.69)	1.35 (98.45)	1.32 (97.20)	0.60 (99.18)	1.5 (97.5)
9	0.14 (99.83)	0.85 (99.30)	0.99 (98.19)	0.44 (99.62)	1.1 (98.6)
10	0.12 (99.95)	0.44 (99.74)	0.86 (99.05)	0.18 (99.80)	0.6 (99.2)
11	0.03 (99.98)	0.16 (99.90)	0.50 (99.55)	0.14 (99.94)	0.5 (99.7)
12	0.01 (99.99)	0.09 (99.99)	0.35 (99.90)	0.05 (99.99)	0.2 (99.9)
13	0.01 (100.0)	0.01 (100.0)	0.10 (100.0)	0.01 (100.0)	0.1 (100.0)

[†]Values in parentheses are cumulative explained variation.

Relationship between predicted PSC and actual PSC is shown in Figures 4.10 through 4.14. The relationship between actual PSC and the PSC predicted by using the PCR model developed for all soils is shown in Figures 4.10 through 4.12. These figures reveal that the common PCR model is a good predictor of PSC in Berks and Monongahela soils, but it did not seem to predict much accurately in Huntington and Lindside soil. However, the PCR model in Huntington and Lindside soil was generally better than the OLSR-full model and the OLSR-reduced model.

Table 4.14. Regression coefficients for principal components (PCs) selected for using as independent variables for modeling P sorption capacity in various soils.

Parameter	Estimate				
	Berks	Huntington	Lindside	Monongahela	All soils
PC#1	84.9 (307 ^{**}) [†]	27.9 (21.1 ^{**})	26.0 (21.5 ^{**})	138 (254 ^{**})	84.3 (383 ^{**})
PC#2	-47.2 (55.1 ^{**})	35.6 (18.1 ^{**})	19.8 (6.8 [*])	40.9 (14.3 ^{**})	30.0 (32.3 ^{**})
PC#3	41.8 (17.2 ^{**})		36.1 (16.5 ^{**})		84.2 (177 ^{**})
PC#4				33.8 (3.6)	
PC#5					
PC#6		62.0 (11.0 ^{**})	47.4 (9.9 ^{**})		
PC#7		-48.0 (3.4)			45.7 (6.4 [*])
PC#8			-50.6 (2.9)		
PC#9	188 (4.3)				
PC#10		97.4 (2.9)	-157 (18.6 ^{**})		
PC#11		158 (2.6)			182.2 (4.8 ^{**})
PC#12			-103.2 (3.2)		
PC#13		-379.9 (2.2)			

[†] F-values, to test whether effects are significant or not, are given in parentheses; the values with ** are significant at 1% level and those with * are significant at 5% level; and all other values are non-significant at either level.

Table 4.15. Composition of the selected principal components (PCs) used in the model developed by using the combined data from all the four soils.

Variable	PC#1	PC#2	PC#3	PC#7	PC#11
Ammonium oxalate extractable Al	5.26E-04 [†]	8.17E-04	3.93E-04	-2.80E-04	-7.12E-04
Ammonium oxalate extractable Fe	-1.80E-04	2.60E-04	3.64E-05	3.81E-04	4.90E-05
Clay content	-1.17E-02	1.10E-02	6.79E-02	-6.20E-02	1.30E-02
Ammonium Acetate extractable Ca	-7.27E-02	5.48E-02	1.24E-02	-3.28E-02	9.88E-02
Extractable Acidity	6.76E-02	5.03E-02	7.41E-03	3.36E-03	-6.49E-02
KCl-extractable Al	1.51E-01	-1.11E-02	8.71E-02	9.25E-02	1.75E-01
Sum of Cations	3.29E-03	8.62E-02	2.37E-02	-3.69E-02	-2.43E-02
Total Carbon	8.00E-02	2.28E-01	-1.35E-01	1.21E-01	5.14E-02
KCl-extractable Mn	3.05E-03	5.15E-03	-3.02E-03	-7.20E-04	3.89E-03
DCB-extractable Fe	-9.90E-06	-3.60E-05	1.66E-04	1.31E-04	-6.10E-05
DCB-extractable Al	4.98E-04	7.13E-06	6.05E-04	2.63E-04	5.81E-04
pH (water)	-4.31E-01	1.21E-01	1.18E-01	9.79E-02	-3.04E-01
pH (CaCl ₂)	-4.29E-01	1.70E-01	2.09E-02	1.74E-01	5.76E-02
Constant	3.46	-5.44	-6.27	-1.93	1.29

[†]Coefficient for the corresponding variable. Each variable is multiplied by the corresponding coefficient and all terms are added to form a principal component.

Table 4.16. Composition of the principal components (PCs) selected for regression in Berks soil.

Variable	PC#1	PC#2	PC#3	PC#9
Ammonium oxalate extractable Al	6.33E-04 [†]	7.65E-05	-5.19E-05	7.79E-04
Ammonium oxalate extractable Fe	3.24E-04	-4.90E-05	-4.80E-05	2.18E-04
Clay	-3.36E-02	4.18E-02	1.75E-01	5.95E-02
Ammonium Acetate Extractable Ca	3.96E-02	8.12E-02	-2.54E-02	1.31E-02
Extractable Acidity	4.25E-02	-2.48E-02	2.88E-02	-1.78E-02
KCl-extractable Al	4.38E-02	-2.12E-01	-1.12E-02	1.28E-01
Sum of cations	3.71E-02	6.60E-03	1.33E-02	-1.73E-02
Total Carbon	1.14E-01	-2.12E-02	7.21E-03	1.30E-01
KCl-extractable Mn	2.09E-03	-2.40E-04	3.66E-03	2.62E-03
DCB-extractable Fe	-1.40E-04	2.66E-06	2.18E-04	-9.50E-05
DCB-extractable Al	9.61E-04	6.06E-04	5.12E-04	-1.29E-03
pH (soil: water:: 1:1)	-1.15E-01	8.96E-01	3.37E-02	3.14E-01
pH (soil: CaCl ₂ :: 1:2)	1.12E-01	8.68E-01	-2.19E-01	8.35E-02
Constant	-2.94	-8.97	-6.19	-7.28

[†] Coefficient for the corresponding variable. Each variable is multiplied by the corresponding coefficient and all terms are added to form a principal component.

Table 4.17. Composition of principal components (PCs) selected for regression in Huntington soil.

Variable	PC#1	PC#2	PC#6	PC#7	PC#10	PC#11	PC#13
Ammonium oxalate extractable Al	1.13E-03 [†]	2.20E-03	-1.6E-03	9.49E-05	2.01E-03	3.10E-04	2.05E-04
Ammonium oxalate extractable Fe	1.22E-04	8.36E-04	-7.6E-05	-2.5E-04	-5.9E-04	-2.8E-04	-2.2E-04
Clay	4.88E-02	6.94E-02	4.07E-02	-4.7E-02	6.91E-03	9.4E-02	2.47E-02
Ammonium Acetate Extractable Ca	-1.2E-01	1.87E-01	2.19E-01	2.96E-02	6.41E-02	-2.2E-01	-8.1E-02
Extractable Acidity	1.75E-01	-2.8E-02	-3.0E-01	2.54E-02	6.80E-02	-5.9E-02	-7.6E-02
KCl-extractable Al	1.18	-1.11	1.06	3.27	1.51	3.58E-02	2.82E-01
Sum of cations	7.21E-02	4.15E-02	9.38E-02	3.76E-02	-1.1E-02	-3.4E-03	-5.0E-03
Total Carbon	-4.4E-01	1.70E-01	-2.9E-02	6.48E-01	-5.0E-01	6.6E-01	4.13E-01
KCl-extractable Mn	2.9E-02	-2.6E-02	3.9E-02	-4.0E-02	6.10E-02	-7.9E-03	1.62E-02
DCB-extractable Fe	1.5E-04	1.45E-04	1.06E-04	1.73E-04	2.28E-05	9.9E-05	-4.4E-05
DCB-extractable Al	1.3E-03	1.03E-03	-4.6E-04	9.60E-04	-1.3E-03	-1.5E-03	1.38E-04
pH (soil: water:: 1:1)	-6.6E-01	3.92E-01	-3.8E-01	1.06E-01	5.64E-01	-3.1E-01	1.14
pH (soil: CaCl ₂ :: 1:2)	-6.2E-01	2.61E-01	-2.6E-01	2.34E-01	4.98E-01	3.7E-01	-9.6E-01
Constant	3.5E-01	-1.53	1.24	-5.32	-6.67	7.59	-1.32

[†] Coefficient for the corresponding variable. Each variable is multiplied by the corresponding coefficient and all terms are added to form a principal component.

Table 4.18. Composition of principal components (PCs) selected for regression in Lindsie soil.

Variable	PC#1	PC#2	PC#3	PC#6	PC#8	PC#10	PC#12
Ammonium oxalate extractable Al	8.91E-04 [†]	1.28E-04	1.05E-03	-7.9E-04	3.17E-05	6.4E-04	-3.30E-04
Ammonium oxalate extractable Fe	-9.90E-05	2.85E-04	1.26E-04	3.12E-04	-1.60E-04	-5.00E-05	2.36E-04
Clay	2.41E-02	3.30E-02	6.73E-02	-8.24E-03	-1.70E-02	-1.88E-02	-6.24E-02
Ammonium Acetate Extractable Ca	-1.16E-01	5.80E-02	5.35E-02	-9.58E-03	-6.33E-03	6.75E-02	5.68E-02
Extractable Acidity	1.29E-01	2.01E-01	-3.8E-04	7.90E-02	1.75E-01	9.86E-02	-8.59E-02
KCl-extractable Al	1.96	-1.22	-1.82	5.50	9.55E-01	3.60E-01	4.42E-01
Sum of cations	-4.71E-02	1.62E-01	3.86E-02	-2.48E-02	1.13E-01	-1.18E-01	8.12E-02
Total Carbon	-3.42E-01	3.79E-01	-1.2E-01	4.49E-01	-6.06E-01	2.29E-01	-4.14E-01
KCl-extractable Mn	2.11E-02	2.09E-02	-2.7E-02	-1.19E-02	1.44E-02	6.20E-03	2.01E-02
DCB-extractable Fe	1.02E-04	-6.60E-05	2.19E-04	3.69E-05	-3.50E-05	1.73E-04	2.06E-04
DCB-extractable Al	7.49E-04	-4.10E-04	5.22E-04	5.80E-04	1.22E-05	-1.42E-03	-1.50E-05
pH (soil: water:: 1:1)	-6.53E-01	-4.06E-01	4.42E-01	4.37E-01	1.17E+00	3.91E-01	-5.14E-01
pH (soil: CaCl ₂ :: 1:2)	-6.33E-01	-2.38E-01	2.04E-01	5.33E-02	1.23E-01	-4.32E-01	3.34E-01
Constant	5.59	-2.42	-1.14	-5.42	-9.35	5.68	-1.36

[†] Coefficient for the corresponding variable. Each variable is multiplied by the corresponding coefficient and all terms are added to form a principal component.

Table 4.19. Composition of the principal components (PCs) selected for regression in Monongahela soil.

Soil Property	PC#1	PC#2	PC#4
Ammonium oxalate extractable Al	5.23E-04 [†]	2.64E-04	6.91E-04
Ammonium oxalate extractable Fe	-2.90E-04	-1.70E-04	1.64E-03
Clay	3.41E-02	2.31E-02	-1.47E-02
Ammonium Acetate Extractable Ca	-1.48E-01	2.03E-01	-8.40E-02
Extractable Acidity	6.61E-02	-3.23E-02	-4.79E-02
KCl-extractable Al	1.35E-01	-8.97E-03	2.52E-03
Sum of cations	5.97E-02	-4.69E-03	-6.45E-02
Total Carbon	-9.33E-03	-1.91E-01	-1.02E-01
KCl-extractable Mn	-3.14E-03	-5.98E-03	2.46E-03
DCB-extractable Fe	5.59E-05	4.62E-05	5.23E-05
DCB-extractable Al	3.97E-04	4.75E-04	3.09E-04
pH (soil: water:: 1:1)	-2.39E-01	7.85E-01	-3.71E-01
pH (soil: CaCl ₂ :: 1:2)	-5.08E-01	7.01E-01	-2.42E-01
Constant	-5.98E-01	-8.85	1.16

[†] Coefficient for the corresponding variable. Each variable is multiplied by the corresponding coefficient and all terms are added to form a principal component.

Table 4.20. Coefficients for the simplified models using principal components regression (PCR) for various soils.

Parameter	Coefficients				
	Berks	Huntington	Lindside	Monongahela	All soils
Intercept	556	280	512	382	395
Ammonium oxalate extractable Al	0.19	0.15	-0.04	0.11	-0.04
Ammonium oxalate extractable Fe	0.069	0.011	0.014	0.008	0.022
Clay	13.7	16.1	13.6	5.16	4.61
Ammonium Acetate Extractable Ca	0.93	15.1	-16.6	-15.0	13.1
Extractable Acidity	2.63	3.51	-4.47	6.19	-3.84
KCl-extractable Al	37.4	-83.3	70.7	18.4	55.9
Sum of cations	0.138	5.62	6.65	5.87	-1.25
Total Carbon	-13.5	-109.8	53.0	-12.6	17.1
KCl-extractable Mn	0.835	1.74	-4.35	-0.600	0.833
DCB-extractable Fe	-0.021	0.041	-0.036	0.011	0.007
DCB-extractable Al	-0.168	-0.495	0.283	0.085	0.211
pH (soil: water:: 1:1)	8.313	-451	-55.9	-13.5	-73.7
pH (soil: CaCl ₂ :: 1:2)	-24.9	464	16.2	-49.8	-10.9

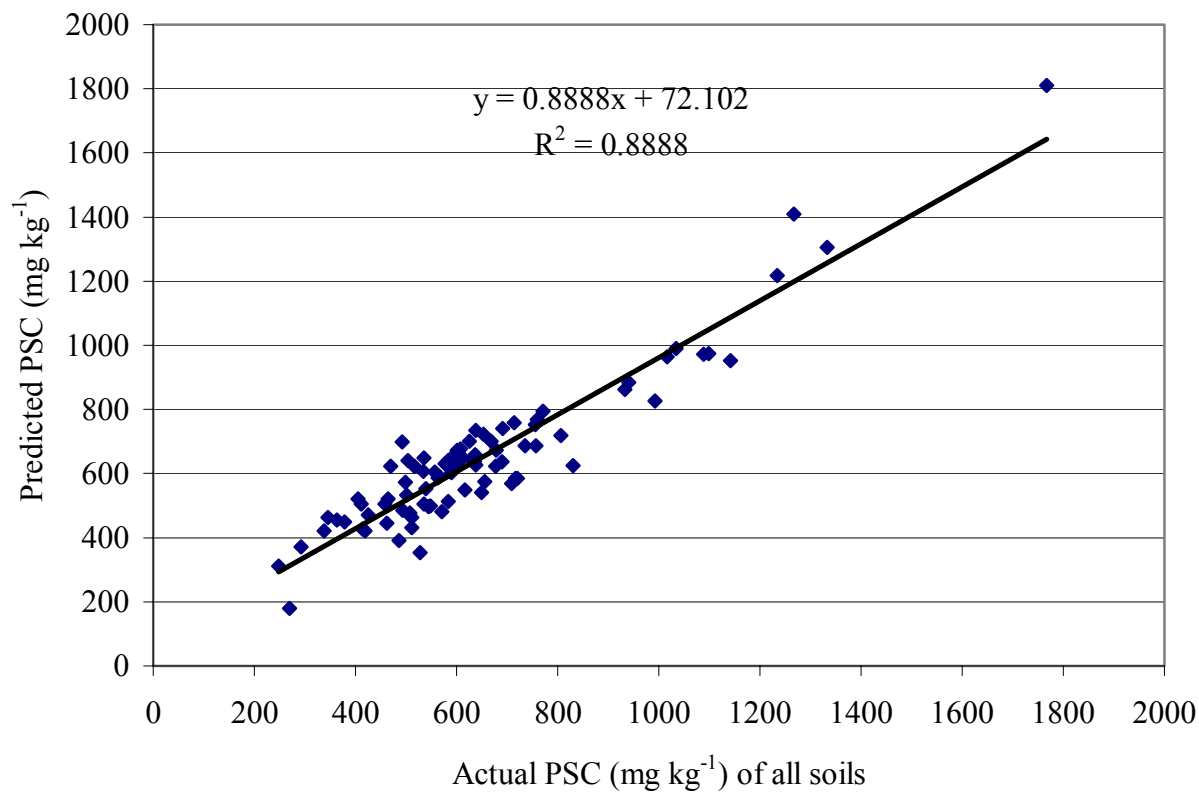


Figure 4.10. Relationship between measured P sorption capacity (PSC) and the PSC predicted by the PCR model developed for all soils.

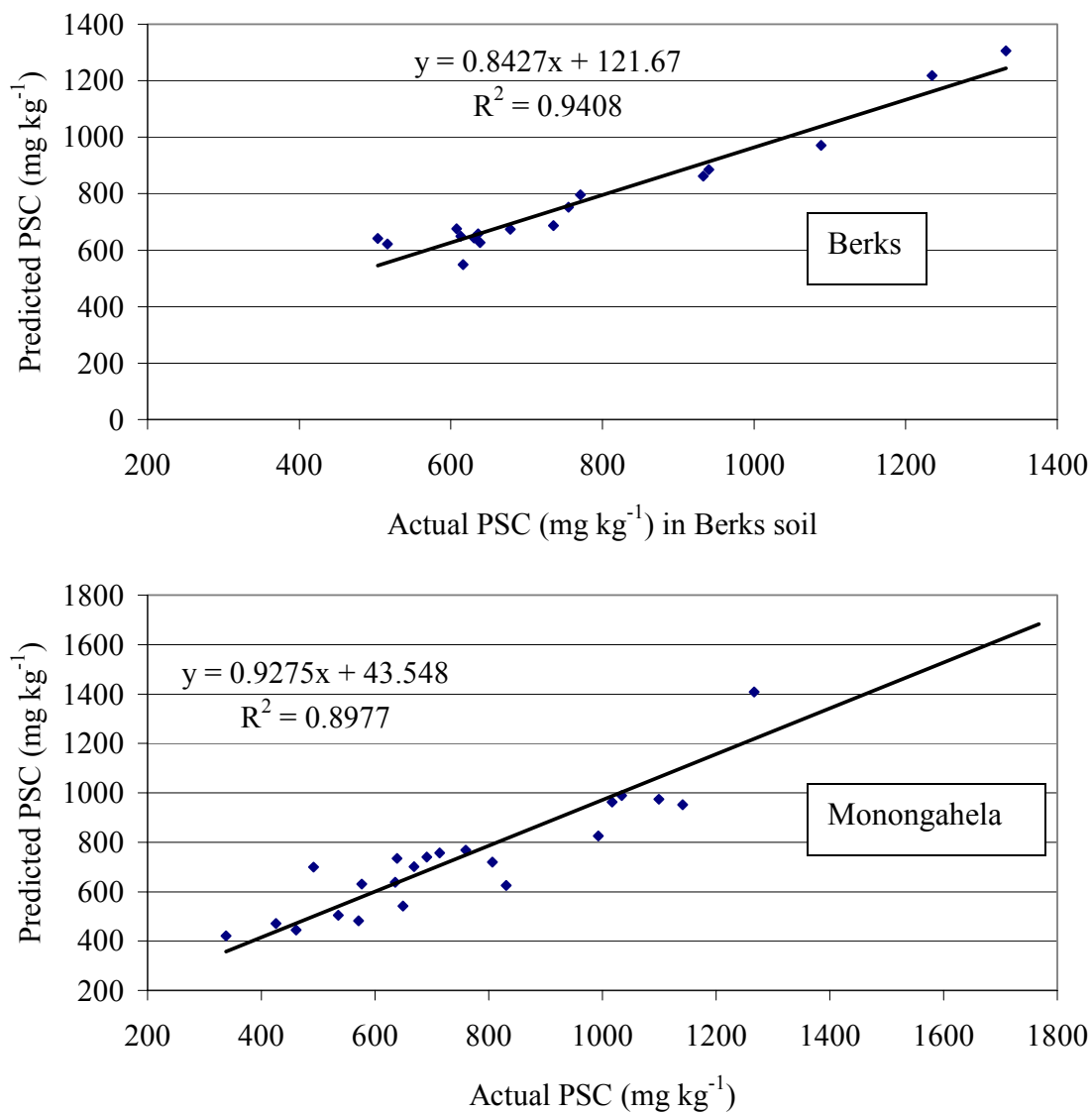


Figure 4.11. Relationship between measured P sorption capacity (PSC) in Berks and Monongahela soils and the PSC predicted by using the principal components regression (PCR) model developed for all soils.

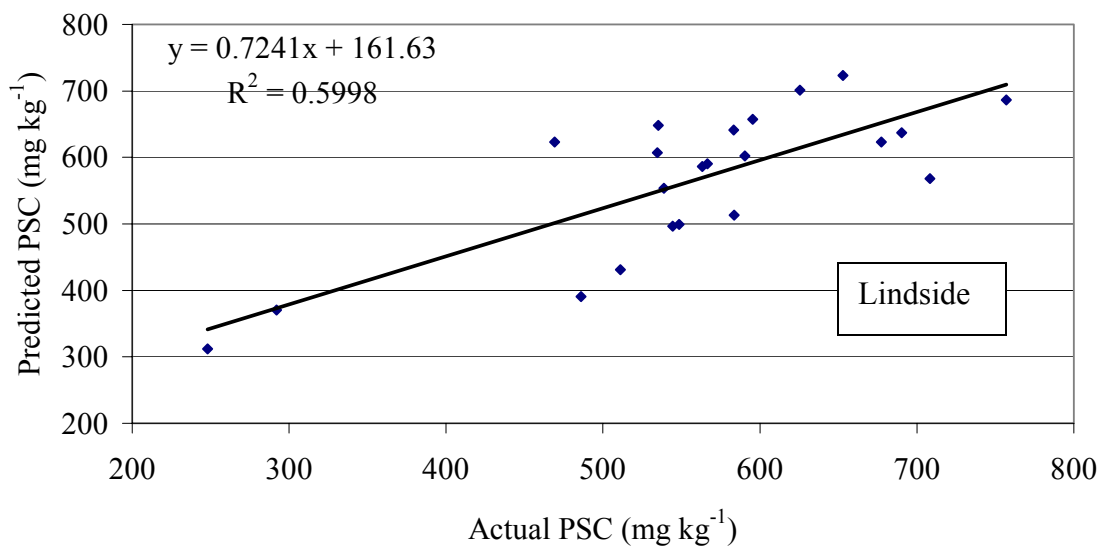
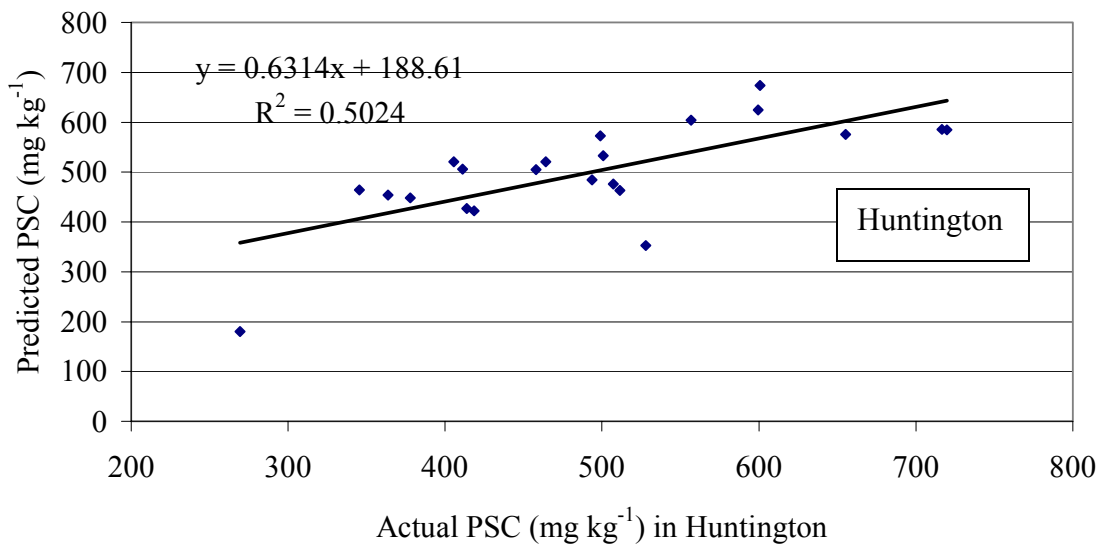


Figure 4.12. Relationship between the measured P sorption capacity (PSC) in Huntington and Lindside soil and the PSC predicted by using the principal components regression (PCR) model developed for all soils.

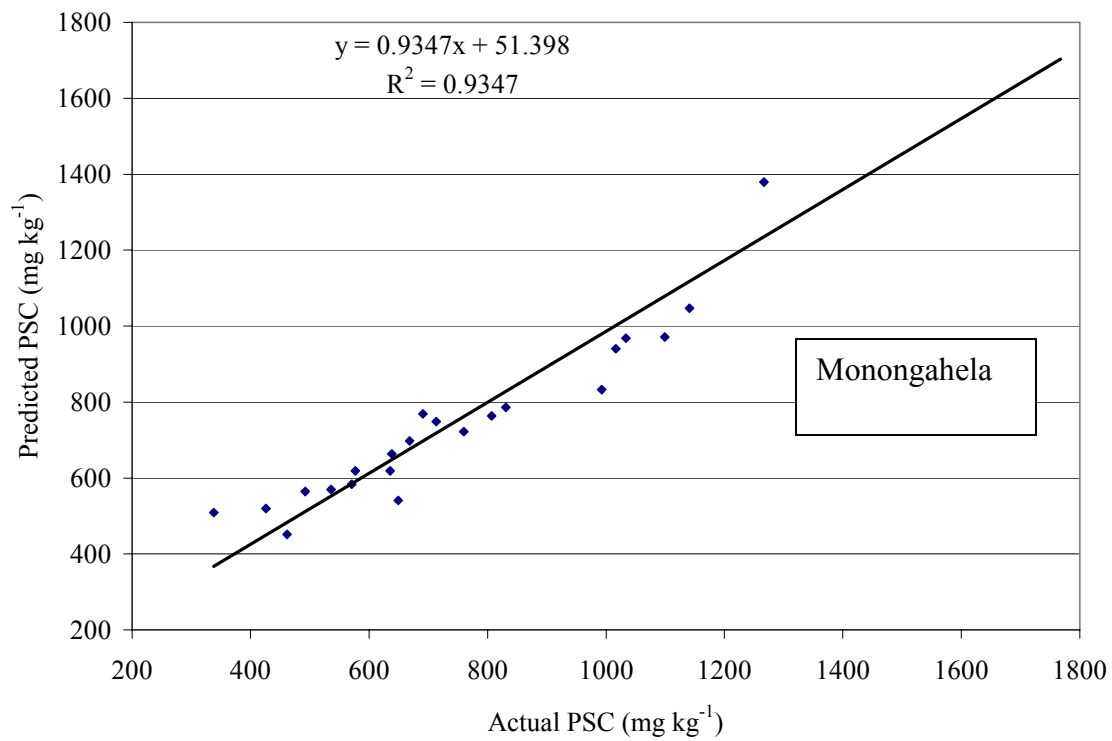
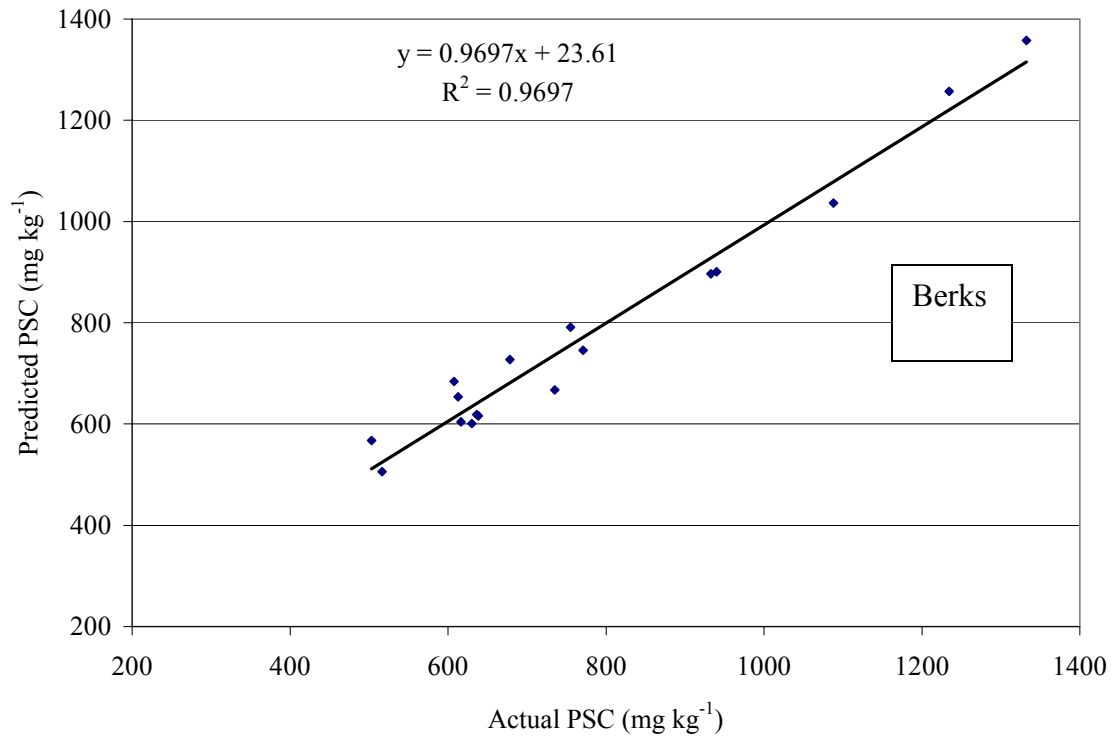


Figure 4.13. Relationship between the measured P sorption capacity (PSC) in Berks and Monongahela soil and the PSC predicted by the respective principal components regression (PCR) models developed for individual soils.

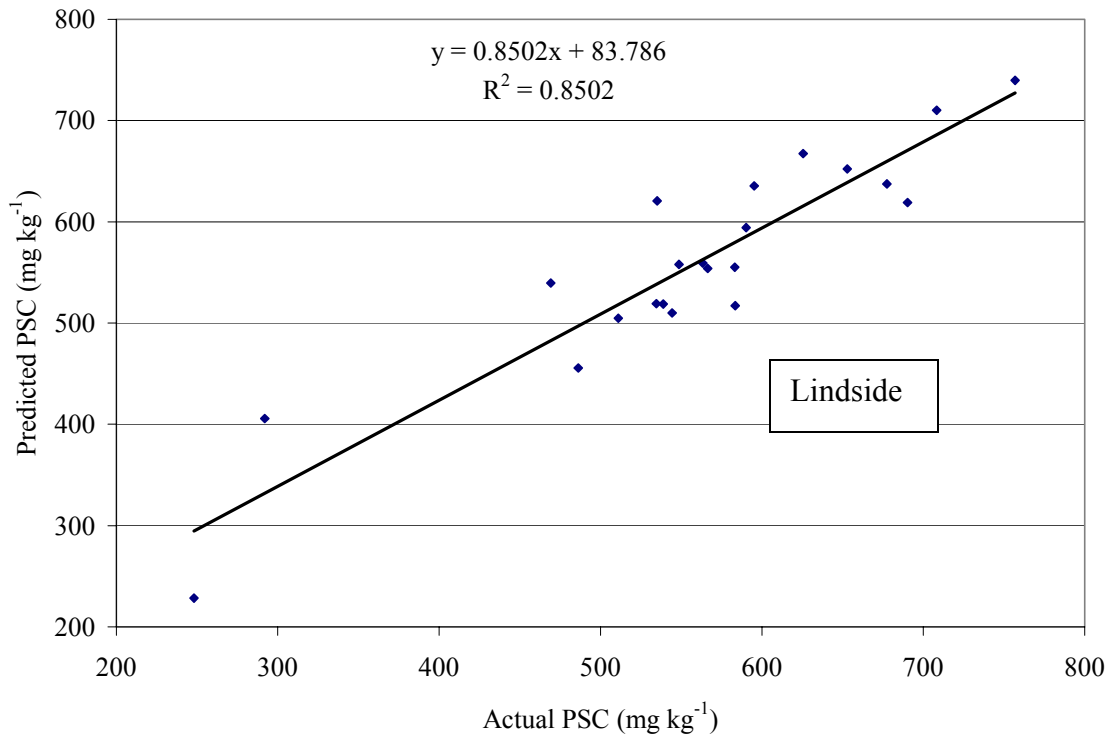
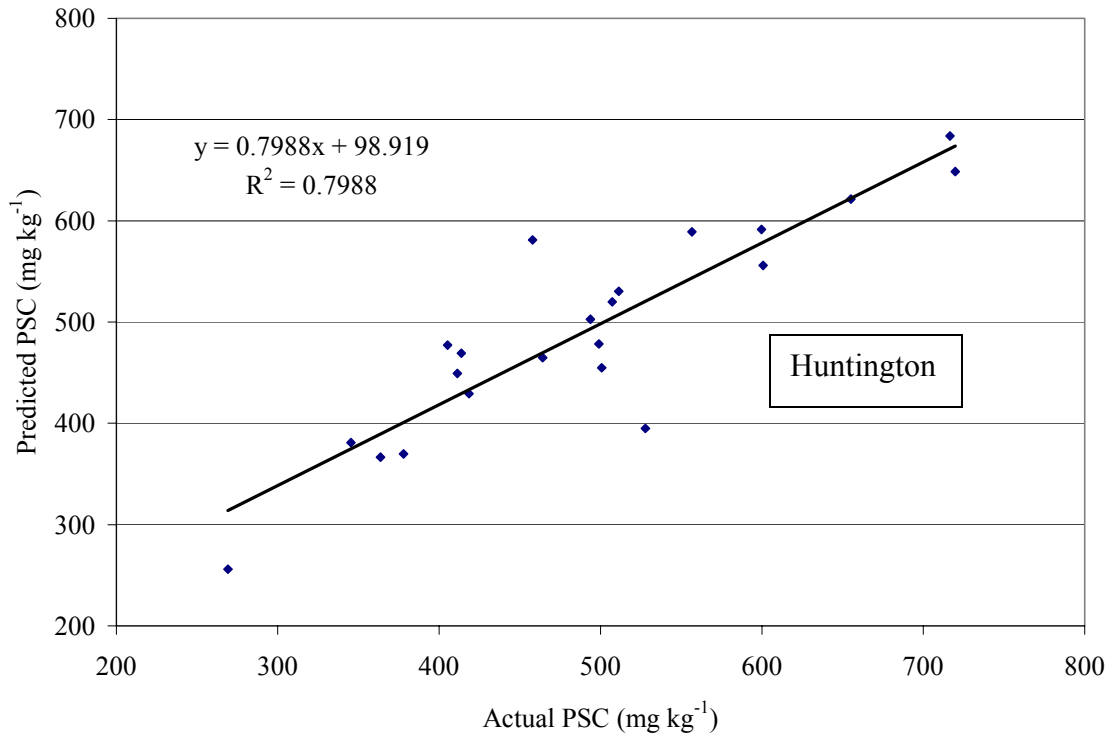


Figure 4.14. Relationship between the measured P sorption capacity (PSC) in Huntington and Lindside soils and the PSC predicted by their principal components regression (PCR) models developed for individual soils.

4.4 Conclusions

Principal components regression approach is definitely a better approach than the ordinary least squares regression approach in modeling P sorption capacity in soils. PCR reduces multicollinearity effects. It predicts more accurately than ordinary least square regression on the original variables; PRESS values were the lowest with models developed by using PCR approach. It obviates the need for variable deletion. Overall, PCR approach can be useful in evolving P management strategies by predicting PSC from the basic soil characterization data.

References

- Akaike, H. 1974. Factor analysis and AIC. *Psychometrika* 52: 317-332.
- Allen, D.M., 1974. The relationship between variable selection and data augmentation and a method of prediction. *Technometrics* 16: 125-127.
- Anderson, G., E.G. Williams, and J.O. Moir. 1974. A comparison of the sorption of inorganic phosphate and inositol hexaphosphate by six acid soils. *J. Soil Sci.* 25: 51-62.
- Barrow, N.J. 1999. The four laws of soil chemistry: the Leeper lecture 1998. *Aust. J. Soil Res.* 37: 787-829.
- Barrow, N.J. 1993. Effects of surface heterogeneity on ion adsorption by metal oxides and by soils. *Langmuir* 9: 2606-2611.
- Barrow, N.J., J.W. Bowden, A.M. Posner, and J.P. Quirk. 1980. Describing the effects of electrolyte on adsorption of phosphate by variable charge surface. *Aust. J. Soil Res.* 18: 395-404.
- Bolan, N.S., J.K. Syers, and R.W. Tillman. 1986. Ionic strength effects on surface charge and adsorption of phosphate and sulphate by soils. *J. Soil Sci.* 37: 379-388.
- Bridgham, S.D., C.A. Johnson, B. Schubauer, and P. Joseph. 2001. Phosphorus sorption dynamics in soils and coupling with surface and pore water in riverine lands. *Soil Sci. Soc. Am. J.* 65: 577-588.

- Celi, L., S. Lamacchia, F. Ajmore-Marsan, and E. Barberis. 1999. Interaction of inositol phosphate on clays: adsorption and charging phenomena. *Soil Sci.* 164: 574-585.
- Celi, L., M. Presta, F. Ajmore-Marsan, and E. Barberis. 2001. Effects of pH and electrolytes on inositol hexaphosphate interaction with goethite. *Soil Sci. Soc. Am. J.* 65: 753-760.
- Cox, F.R. 1994. Predicting increase in extractable phosphorus from fertilizing soils of varying content. *Soil Sci. Soc. Am. J.* 58: 1249-1253.
- Goldberg, S., and G. Sposito. 1984. A chemical model of phosphate adsorption by soils. II. Noncalcareous soils. *Soil Sci. Soc. Am. J.* 48: 779-783.
- Guo, F., and R.S. Yost. 1999. Quantifying the available soil phosphorus pool with the acid ammonium oxalate method. *Soil Sci. Soc. Am. J.* 63: 651-656.
- Holford, I.C.R., C. Hird, and R. Lawrie. 1997. Effects of animal effluents on the phosphorus sorption characteristics of soils. *Aust J. Soil Res.* 35: 365-373.
- Jolliffe, I. T. 1986. *Principal components analysis*. Springer-Verlag, New York.
- Khiari, L., A. Pellerin, J. Fortin, and L.E. Parent. 1999. A soil phosphorus saturation index decreasing scooped weight effect in Mehlich-3 procedure. *Commun. Soil Sci. Plant Anal.* 30: 2157-2168.
- Maguire, O.P., R.H. Foy, J.S. Bailey, and J.T. Sims. 2001. Estimation of the phosphorus sorption capacity of acidic soils in Ireland. *Europ. J. Soil Sci.* 52: 479-487.
- Mallow, C.L. 1973. Some comments on C_p . *Technometrics* 15: 661-675.
- Mardia, K.V., J.T. Kent, and J.M. Bibby. 1979. *Multivariate analysis*. Academic Press, London.
- Mehra, O.P. and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite citrate system buffered with sodium bicarbonate. *In Clays and Clay Minerals. Proc. Seventh National Congress*, Pergamon, London.
- Morzuch, B.J., and G.A. Ruark, 1991. Principal components regression to mitigate the effects of multicollinearity. *Forest Sci.* 37: 191-199.
- Moughli, L., D.G. Westfall, and A. Boukhial. 1993. Use of adsorption and buffer capacity in soil testing for phosphorus. *Commun. Soil Sci. Plant Anal.* 24: 1959-1974.
- Myers, R.H. 1986. *Classical and modern regression with applications*. Duxbury Press, Boston, Massachusetts.

- Ohno, T. and B.S. Crannell. 1996. Green and animal manure-derived dissolved organic matter effects on phosphorus sorption. *J. Environ. Qual.* 25: 1137-1143.
- Ortas, I., and D.L. Rowell. 2000. Effect of pH on amount of phosphorus extracted by 10mM calcium chloride from three Rothamsted soils. *Commun. Soil Sci. Plant Anal.* 31: 2917-2923.
- Sall, J., A. Lehman, and L. Creighton. 2001. JMP® Start Statistics. A guide to statistics and data analysis using JMP® and JMP IN® software. SAS Institute Inc. Duxbury, Pacific Grove, CA.
- Shang, C., J.W.B. Stewart, and P.M. Huang. 1992. pH effect on kinetics of adsorption of organic and inorganic phosphates by short-range ordered aluminum and iron precipitates. *Geoderma* 53: 1-14.
- Soil Survey Staff. 1996. USDA-NRCS-National Soil Survey Center. Soil survey laboratory methods manual. Soil survey investigation report no. 42, version 3.0.
- Stumm, W., and J.J. Morgan. 1996. Aquatic chemistry. Chemical equilibria and its rates in natural waters. Third edition. John-Wiley and Sons, Inc. New York.
- Sundareshwar, P.V., and J.T. Morris. 1999. Phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient. *Limnol. Oceanogr.* 1693-1701.
- Vadas, P.A., and J.T. Sims. 1999. Phosphorus sorption in manured Atlantic Coastal Plain soils under flooded and drained conditions. *J. Environ. Qual.* 28: 1870-1877.
- Villapando, R.R., and D.A. Greetz. 2001. Phosphorus sorption and desorption properties of the spodic horizon from selected Florida spodosols. *Soil Sci. Soc. Am. J.* 65: 331-339.
- Zhou, M., R.D. Rhue, and W.G. Harris. 1997. Phosphorus sorption characteristics of Bh and Bt horizons from sandy coastal plain soils. *Soil Sci. Soc. Am. J.* 61: 1364-1349.

Chapter 5

Sorption of Phosphorus onto Acid Mine Drainage Floc

5.1. Introduction

Sorption of phosphorus onto iron and aluminum oxyhydroxides controls the mobility and bioavailability of P in soils and aquatic systems. Study of sorption of P onto acid mine drainage (AMD) floc provides a direct measure of P attenuation capacity of the floc. Soils receive both inorganic and organic P loadings. Inositol phosphates or phytates are the most abundant form of organic P in soils (Anderson, 1980). Sorption of inositol hexaphosphate (IHP)-P is reported to be similar to that of free orthophosphate ion (Celi et al., 1999; Goldberg and Sposito, 1985; Parfitt et al., 1976), and is affected by a similar set of factors like pH, porosity of the mineral structure, and electrolyte concentration (Celi et al., 2001; Ognalaga et al., 1994; Shang et al., 1992). Various AMD flocs may vary from each other in terms of these factors and mineralogical composition of the flocs. Therefore, sorption of both inorganic and organic P onto AMD flocs needs to be studied to assess their P attenuation potential accurately.

Degree of P saturation (DPS) is a commonly used index for assessing environmental risks of P (Beauchemin and Simard, 1999). Degree of P saturation represents the number of moles of P associated with one mole of amorphous Fe+Al (Eq. 2.1). DPS index uses a factor α . Factor α stands for the maximum number of moles of P that can be adsorbed by one mole of amorphous Fe+Al. Review of literature reveals that $\alpha = 0.5$ is the most commonly used value (Kleinman et al., 2000; Beauchemin and Simard, 1999; Breeuwsma and Silva, 1992). However, when soils have been historically receiving IHP-P through excessive land application of poultry or swine manure, for the

given content of amorphous Fe+Al soils may have much higher IHP-P than inorganic P associated with amorphous Fe+Al phases (or ammonium oxalate extractable-P). Since α is used in the denominator of the equation (2.1) used for calculating DPS, using a lower α -value may overestimate DPS. On the other hand, if a higher α -value is used for the soils that have accumulated inorganic P, and where amorphous Fe and Al control the P mobility, DPS may be underestimated.

Viewing this, this investigation was undertaken in order to assess P remediation potential of various AMD flocs and to help determine environmental thresholds of P for those soils in which amorphous Fe and Al oxides are the main controllers of release of P to the solution. Environmental thresholds can be based upon those levels of P loadings above which flocs do not sorb much of the added P.

5.2. Materials and Methods

5.2.1. Preparation of Acid Mine Drainage Floc Suspensions

Acid mine drainage was collected from Omega underground mine located in Monongalia County of West Virginia, approximately 8 km. south of city of Morgantown. This mine was operated during the early to mid- 1980s and has since been abandoned (Anonymous, 2000). Depending upon the season and amount of precipitation in the area, four to ten discrete acid mine discharges emanate from the down-dip outcrop of the mined coal seam. One part of AMD collected in plastic tubs (75 liters capacity) was titrated at the site of discharge with 1.0 M ammonium hydroxide (NH₄OH, ACS certified grade, assay 28.9%) to pH 7.0. Suspensions were stirred with wooden sticks during titration. This process was continued for many days. Each day fresh AMD was collected and then titrated to pH 7.0 until an adequate amount of floc was produced. Similarly, the

other part of AMD was titrated to pH 7.0 with 1.0 M sodium hydroxide (NaOH; ACS certified pellets, 99-100%). Lime-treated floc was collected from the treatment facility at the site. These three different kinds of flocs were given a series of washings with reagent grade water, centrifuged, and then supernatant discarded. Solid matter content of these flocs was determined by drying at 378K in an oven for 30 hours. Based upon solid matter content, 5 g L⁻¹ suspensions of flocs were made in reagent grade water. These flocs were allowed to hydrate for three days.

5.2.2. Sorption Experiments

Nine mL of each floc suspension (5g L⁻¹), so as to obtain 45 mg of solid dried floc, was transferred to a series of 50 mL plastic centrifuge tubes. To one set of tubes, 36 mL of each of 0, 2, 5, 8, 12, 15, 20, 25, 30, 60, 100, 160, 200, 320, 400, and 600 mg L⁻¹ of inorganic P solution (from potassium dihydrogen phosphate, primary standard) in 0.01 M NaCl was added so as to obtain an initial solution concentration of 0, 1.6, 4.0, 6.4, 9.6, 12.0, 16.0, 20.0, 24.0, 48.0, 80.0, 128.0, 160.0, 256.0, 320.0, and 480.0 mg L⁻¹ (total volume 45 mL (9 mL floc suspension +36 mL of P solution, therefore P solution diluted by a factor of 0.8 (45/36)). To the other set of tubes, a series of concentration of IHP-P (Dipotassium phytic acid salt, K₂C₆H₁₆O₂₄P₆, water content one mole per mole, Sigma Chemical) were added. Phosphorus concentrations used for IHP-P were the same as those for inorganic P. However, for calculating sorbed amounts actual initial concentrations, based upon the analysis of blank solutions (P solutions without floc suspension) for P, were used. Phosphorus solutions were added dropwise so as to avoid local supersaturation with respect to various P minerals. Each set was prepared in triplicate. The samples were shaken at an end-over-end shaker for 24 hours. Equilibrated solutions

were centrifuged and then filtered. The sorbed amounts were calculated by the difference in initial and equilibrium concentrations.

5.2.3 Laboratory Analyses

Floc samples were digested for total elemental analysis with a hydrofluoric acid-nitric acid- hydrochloric acid mixture on Microwave Accelerated Reaction System (CEM, Mars5). Ammonium oxalate extractable Fe and Al were determined by using the method described by Guo and Yost (1999). However, ratio of floc to oxalate solution was so chosen that there was at least one mL of oxalate solution for one mg of total Fe+Al (Schwertmann and Cornell, 1991). Single point P sorption capacity of the three kinds of flocs was determined by equilibrating 4 mL of 5 g L⁻¹ floc suspension with 45 mL of inorganic P solution (from potassium dihydrogen phosphate (KH₂PO₄); Primary standard) of 60 mg P L⁻¹ concentration in 0.01 M sodium chloride (NaCl). The samples were equilibrated by shaking on an end-over-end shaker for 24 hours, filtered, and then P in equilibrating solution was determined. Amount of P sorbed was calculated by using the initial amount added and the amount left in the equilibrated solution.

5.2.4. Laboratory Measurements and Statistical Analyses

Both inorganic P and IHP-P and all metals were measured on Perkin-Elmer PE 400 Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer (ICP-AES). Results of a preliminary study (data not reported here) showed that ICP- AES could detect IHP-P in the solution completely at a wavelength of 213.618nm. Measurements for pH were made on Accumet15 pH meter. All statistical analyses were performed by using JMP (version 4.0.4; SAS Institute Inc.; Sall et al., 2001).

Table 5.1. Elemental composition, pH, and P sorption capacity of three different acid mine drainage (AMD) flocs prepared by neutralizing AMD with ammonium hydroxide, calcium hydroxide, and sodium hydroxide.

Property	Floc		
	Ammonia-treated	Lime-treated	NaOH-treated
Iron (g kg ⁻¹)	322 [†]	317	314
Aluminum (g kg ⁻¹)	105	81	86
Ammonium oxalate extractable iron (g kg ⁻¹)	322	315	313
Ammonium oxalate-extractable aluminum (g kg ⁻¹)	105	79	85
Amorphous Al (% of total Al)	100	97.5	98.8
Amorphous Fe (% of total Fe)	100	99.4	99.7
Calcium (g kg ⁻¹)	3.8	5.2	6.5
Magnesium (g kg ⁻¹)	1.9	2.1	5.4
Cadmium (mg kg ⁻¹)	bdl ^{††}	bdl	bdl
Cobalt (mg kg ⁻¹)	155	205	185
Copper (mg kg ⁻¹)	213	219	185
Chromium (mg kg ⁻¹)	41	43	21
Lead (mg kg ⁻¹)	bdl	bdl	bdl
Manganese (mg kg ⁻¹)	252	1086	595
Nickel (mg kg ⁻¹)	754	560	727
Phosphorus (mg kg ⁻¹)	bdl	bdl	bdl
pH (5g L ⁻¹ slurry)	6.9	5.5	7.3
Phosphorus sorption capacity (μMol g ⁻¹)	2503	2253	2400

[†] Each value is mean of three replicates.

^{††} bdl stands for 'below detection limit' of ICP-AES.

5.3. Results and Discussion

5.3.1. Sorption isotherms

Acid mine drainage flocs, which were generated by neutralizing the same AMD with three different neutralizing agents, were predominantly composed of amorphous oxides of Fe and Al (Table 5.1). Ammonium oxalate extractable Fe constituted more than 99% of the total Fe in the floc, whereas ammonium oxalate extractable Al was more than 97% of the total Al. Webster et al. (1998), however, reported that only about 10 percent of the Fe in the AMD floc was soluble in acidified oxalate solution. Amorphous phases of Fe and Al have larger surface area than their crystalline counterparts. Thus, amorphous phases may have higher P attenuation capacity than that of crystalline phases.

The shape of the adsorption isotherms for P adsorption on each of the three types of the floc was H-type (Fig. 5.1). These types of isotherms can be further classified as 2-H type of isotherms according to Giles et al. (1974). Based on the shape of the curve, we can infer that P sorption in these flocs at the concentration investigated never exceeded the monolayer coverage. At the initial low P loading rates, P was being sorbed on high-energy sites and at low loading rates no differences were observed among various AMD flocs. However, at high P loading rates the highest amounts of P were sorbed by AMD floc that was generated by neutralizing AMD with ammonium hydroxide, and the least amounts were sorbed by the AMD floc prepared by neutralizing AMD with calcium hydroxide. These differences in P sorption may not be related to the nature of P sorbing sites in these flocs, but may be related to surface areas available for P sorption. High dissolved and sorbed Ca^{2+} concentrations in the floc prepared by neutralizing AMD with

calcium hydroxide resulted in a denser floc that could cause a decline in surface area available for P sorption.

Sorption of IHP-P was similar to the sorption of inorganic P (Fig. 5.2). When P loading rates were lower or when more sorption sites were available, there was no difference between the sorbed amounts of inorganic P and organic P (Fig. 5.3). However, when due to increased P loadings sorption sites became scarce, sorption of IHP-P was about 2.5-3 times the inorganic-P (Fig. 5.3; Table 5. 2.). This can be attributed to the mechanism of sorption of IHP-P. Phytic acid (IHP) contains six phosphate groups attached at each end of a hexagonal carbon ring. It is postulated that each IHP molecule having six P molecules gets sorbed on the Fe and Al surfaces by attachment of two contiguous phosphate groups. Therefore, compared to the sorption of two inorganic-P molecules, six IHP-P molecules can be sorbed. This mechanism of sorption of IHP-P makes the sorption of IHP-P about three times more than the inorganic P. This mechanism of sorption of IHP-P did not depend on the type of floc. However, Celi et al. (1999) observed that in case of goethite, IHP molecule occupied the sites equivalent to those sorbed by four inorganic P molecules. However, for illite and kaolinite, they observed that area occupied by IHP molecule was equivalent to about two sites for inorganic P.

Ratios of IHP-P to inorganic P sorbed at different P loadings (Table 5.2) were not significantly different (at 5% level). Higher sorption of IHP-P can be related to generally lower pH of the equilibrium solution in case of sorption of IHP-P. Phytic acid salt solution or IHP solution is quite acidic. Cosgrove (1966) demonstrated that phytic acid has 12 replaceable protons. Six are strongly dissociated at a pK_a of 1.84, two are weak

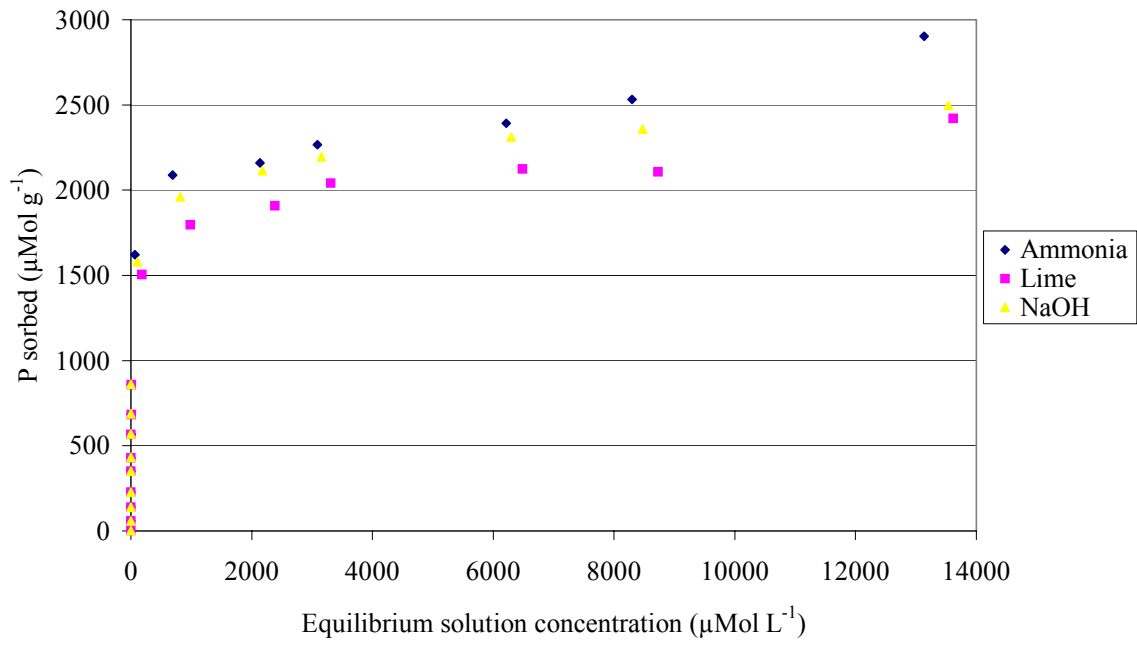


Figure 5.1. Sorption of inorganic P onto ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.

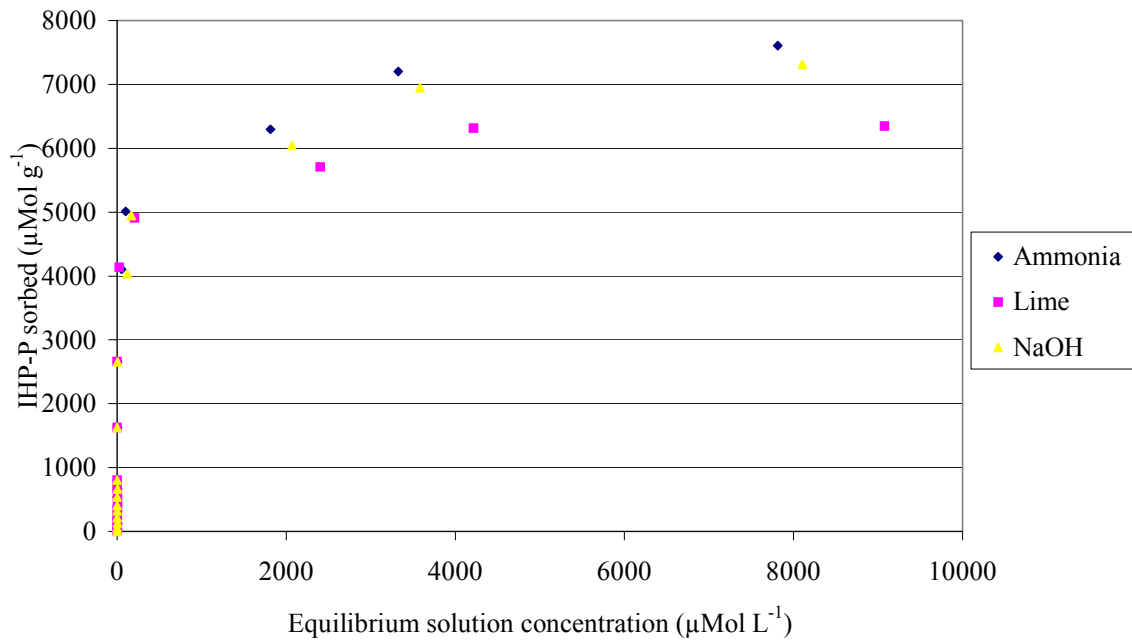


Figure 5.2. Sorption of organic P (inositol hexaphosphate (IHP) – P) onto ammonia-treated, lime-treated and sodium hydroxide-treated flocs.

acids with pK_a of 6.3, and others are weakly dissociated at pK_a of 9.7. Therefore, phytic acid exists as a negatively charged molecule over a wider pH range (Tsao et al., 1997). However, the sorption of protons on mineral surfaces helps increase electrostatic attraction for negatively charged molecules (Stumm and Morgan, 1996) and subsequently aids in the specific sorption of P onto mineral surfaces. Moreover, lower pH might have effected deflocculation (Lahann, 1976) of the AMD flocs and thus might have caused an increase in surface area. Thus, higher IHP-P sorption can be related to the structure of the IHP molecule and the lower pH.

Sorption of both inorganic P and IHP-P was adequately described by Langmuir equation. Parameters of Langmuir equation for both forms of P are given in Table 5.3. K-values are usually considered a measure of affinity of the mineral surface for the adsorbate. K-values suggest that floc surfaces usually had more affinity for IHP-P than inorganic P. Lime-treated floc had higher affinity ($K=0.0171 \text{ L } \mu\text{Mol}^{-1}$) as compared to ammonia-treated floc ($K=0.0107 \text{ L } \mu\text{Mol}^{-1}$) and NaOH-treated floc ($0.0154 \text{ L } \mu\text{Mol}^{-1}$). However, a comparison of K-values for inorganic P sorption hints that ammonia-treated floc led in affinity for inorganic P ($K=0.0061 \text{ L } \mu\text{Mol}^{-1}$), and was followed by NaOH-treated floc ($0.0057 \text{ L } \mu\text{Mol}^{-1}$) and lime-treated floc ($0.0051 \text{ L } \mu\text{Mol}^{-1}$).

As suggested by sorption isotherms (Figs. 5.1 and 5.2), P sorption maxima for both inorganic-P and IHP-P were the highest for ammonia-treated floc, and the lowest for lime-treated floc. These Langmuir P sorption maxima are in close agreement with the single-point P sorption maxima (Table 5.1; measured by using a single high P loading

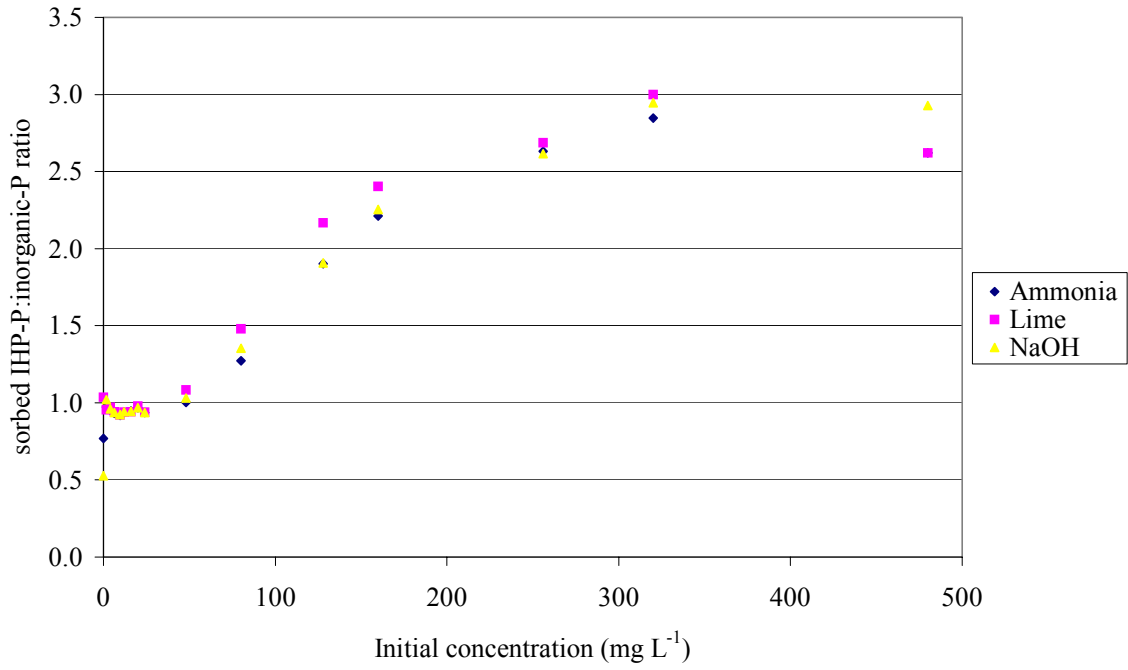


Figure 5.3. Ratio of inositol hexaphosphate (IHP) - P and inorganic-P sorbed onto ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage floccs.

Table 5.2. Ratio of inositol hexaphosphate-P (IHP-P) and inorganic P sorbed onto ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs at various initial P loadings.

Initial P concentration (mg L ⁻¹)	Floc		
	Ammonia-treated	Lime-treated	NaOH-treated
(IHP-P to inorganic-P ratio) [†]		
1.6	0.97	0.96	1.02
4.0	0.95	0.97	0.96
6.4	0.93	0.94	0.94
9.6	0.91	0.92	0.92
12.0	0.94	0.94	0.94
16.0	0.95	0.94	0.94
20.0	0.97	0.98	0.97
24.0	0.94	0.94	0.94
48.0	1.00	1.08	1.03
80.0	1.27	1.48	1.35
128.0	1.90	2.17	1.91
160.0	2.21	2.40	2.25
256.0	2.63	2.69	2.61
320.0	2.85	3.00	2.95
480.0	2.62	2.62	2.93

[†] Differences among means for the various flocs were not significant at 5% level (with Tukey-Kramer's HSD).

Table 5.3. Coefficients of linearized Langmuir sorption isotherms for the sorption of inorganic-P and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.

Floc	X_{\max}		K		Adjusted-R ²	
	(μMol g ⁻¹)		(L μMol ⁻¹)			
	Inorganic-P	IHP-P	Inorganic P	IHP-P	Inorganic P	IHP-P
Ammonia-treated	2744	7599	6.0E-03	1.1E-02	0.989	0.997
Lime-treated	2321	6357	5.0E-03	1.7E-02	0.992	0.999
NaOH-treated	2468	7257	6.0E-03	1.5E-02	0.995	0.997

instead of deriving empirically from Langmuir sorption isotherm generated by using a series of P loadings).

5.3.2. Implications of Sorption Isotherms for Degree of P Saturation Index

As mentioned in section 5.1, degree of phosphorus saturation (DPS) index employs a factor α ; α is a factor that represents the moles of phosphorus that can be sorbed by a unit molar amount of amorphous Fe+Al. To investigate connections of P sorption data with α -value, P loading rates and the amounts of P sorbed were normalized with amount of amorphous Fe+Al. That is, P loading rates were converted as moles of P added per unit mole of amorphous Fe+Al, and similarly amounts of P sorbed were expressed as moles of P sorbed on unit mole of amorphous Fe+Al. If it is decided that α -value should stand for a molar ratio of maximum sorbed P and amorphous Fe+Al after which the affinity of the surface for P declines sharply, then it follows from these sorption isotherms that in case of inorganic P sorption, an acceptable α -value is around 0.25 (Figs. 5.4 and 5.6). However, in case of IHP-P (Figs. 5.5 and 5.6) an acceptable α -value is about 0.80.

This suggests that if soils are rich in IHP-P following excessive application of manures from non-ruminants like poultry and swine, using a single α -value of around 0.25, may make the DPS index highly conservative. This is because α -value is used in the denominator for calculating DPS (Eq. 2.1): lower α -value will thus overestimate DPS. On the other hand, using an α -value of 0.50, which is quite common (Kleinman et al., 2000; Beauchemin and Simard, 1999; Breeuwsma and Silva, 1992), can lead to underestimation of DPS, especially if soils are rich in inorganic P.

Plots of normalized values also bring forth real differences among flocs with respect to sorption of inorganic and IHP-P. For instance, the sorption isotherms drawn on the basis of moles of P sorbed per gram of floc suggest the higher affinity of ammonia-treated floc for inorganic and IHP-P than lime-treated and NaOH-treated flocs. Evidently, this can be ascribed to the correspondingly higher amorphous Fe+Al content in ammonia-treated floc. However, plots in Figs. 5.4 and 5.5 suggest that in general NaOH-treated floc had more affinity for inorganic or phytate-P than any other floc. This may be ascribed to the likely differences in porosity of amorphous Fe and Al phases in various flocs.

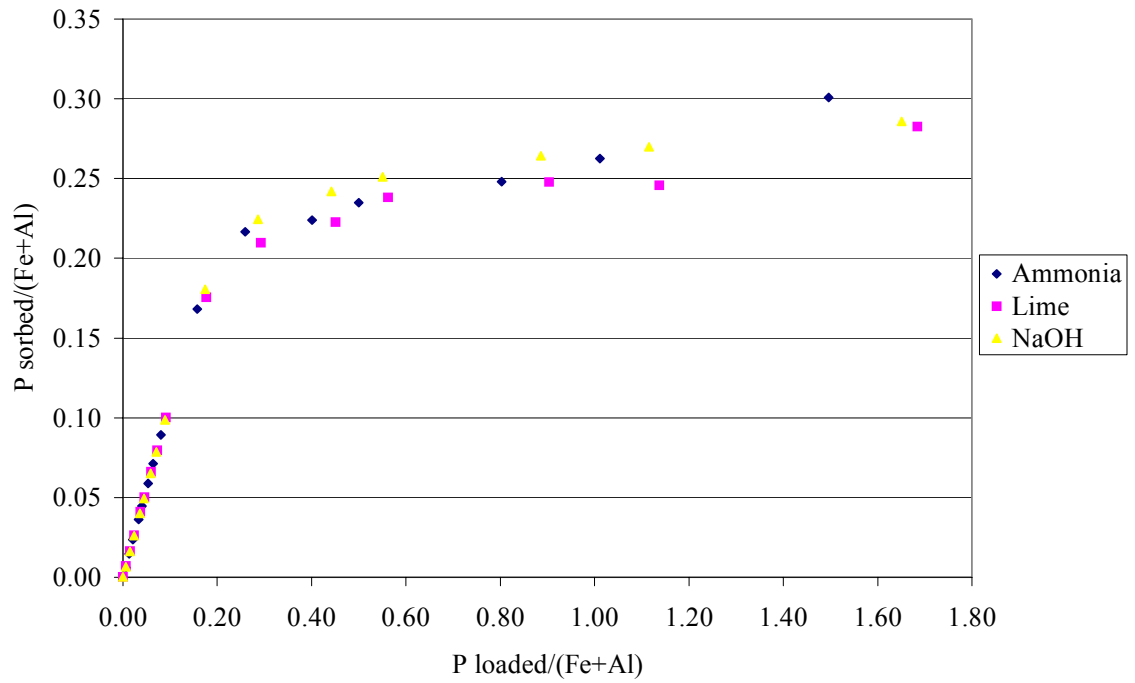


Figure 5.4. Moles of inorganic P sorbed per mole of Fe+Al in relation to moles of inorganic P added per mole of Fe+Al in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.

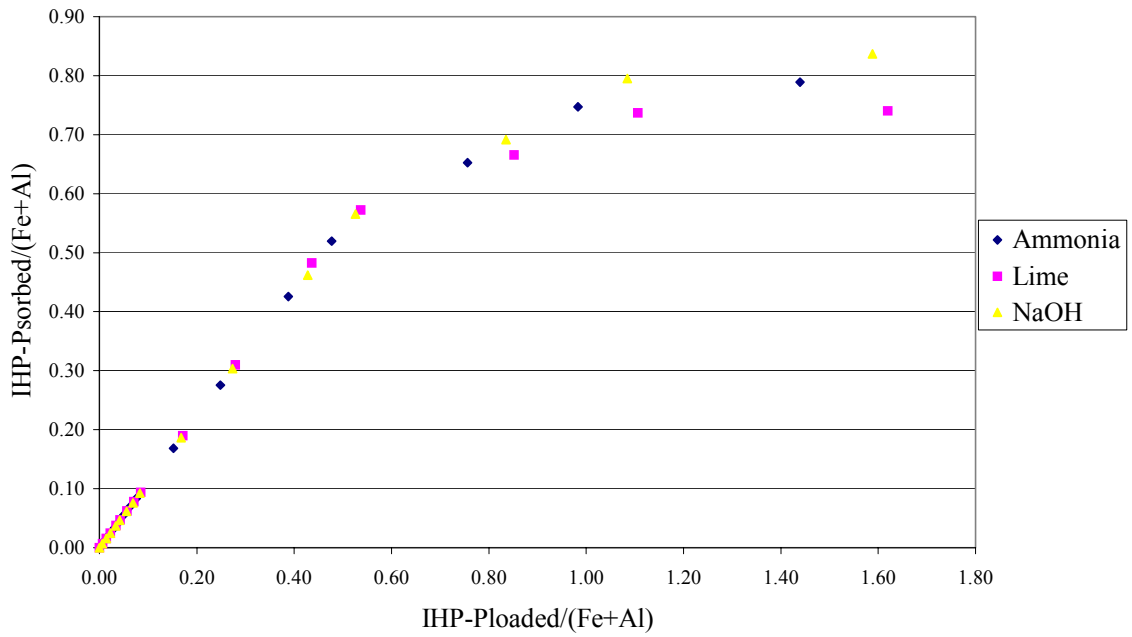


Figure 5.5. Moles of inositol hexaphosphate (IHP)-P sorbed per mole of Fe+Al in relation to moles of IHP-P added per mole of Fe+Al in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.

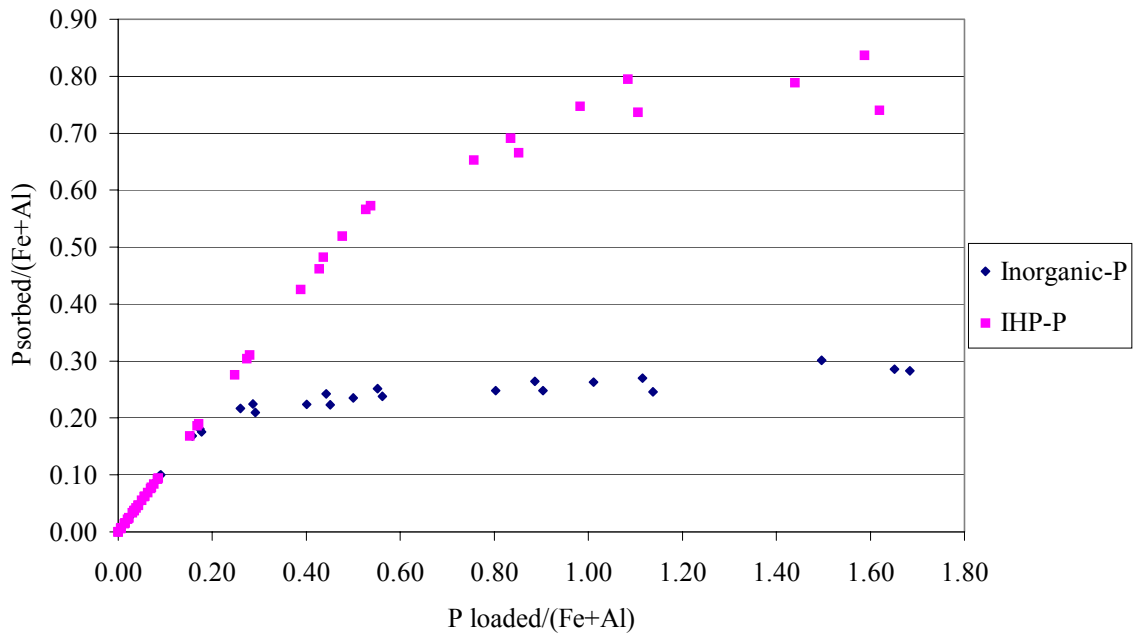


Figure 5.6. Moles of inorganic-P and inositol hexaphosphate (IHP)-P sorbed per mole of Fe+Al in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs to the moles of P added per mole of Fe+Al.

5.4. Conclusions

Various kinds of AMD flocs can sorb significant amounts of P. However, for a given P loading rate of inorganic P or IHP-P, the flocs sorbed far greater amounts of IHP-P than inorganic P. This observation suggests that if P sorption capacity of the soils is to be used for determining an environmental threshold, type of phosphorus loaded onto the soil needs be duly considered. However, flocs may vary in their P attenuation capacity due to the likely difference in the surface area or porosity of reactive components. When P loading rates and amounts of P sorbed by various flocs normalized with their respective amorphous Fe+Al content, or amounts of P sorbed by a unit amount of Fe+Al in the floc (instead of unit amount of floc) are used for plotting sorption isotherms, a useful insight into the dependence of α -value, which is used for calculating degree of phosphorus saturation (DPS) index, on the type of P being added to the soils can be obtained. A soil that has been heavily loaded with P through manures from monogastric animals like poultry and swine may exhibit a higher DPS due to greater amounts of P associated with amorphous Fe and Al phases and due to the use of a blanket value of α valid for the sorption of inorganic P. Therefore, in order to make DPS index reliable α -value should not be used arbitrarily; type of P added should be considered.

References

- 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, Madison, WI.
- Anonymous. 2000. Injection of coal combustion byproducts (CCBs) into the Omega mine for the reduction of acid mine drainage. Project Facts. June 2000. U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA.
- Beauchemin, S., and R.R. Simard. 1999. Soil phosphorus saturation degree: review of some indices and their suitability for P management in Quebec, Canada. *Can. J. Soil Sci.* 79: 615-625.

- Breeuwsma, A., and S. Silva. 1992. Phosphorus fertilisation and environmental effects in Netherlands and the Po region (Italy). Report 57. DLO, The Winand Staring Centre, Wageningen, Netherlands.
- Celi, L., M. Presta, F. Ajmore-Marsan, and E. Barberis. 2001. Effect of pH and electrolytes on inositol hexaphosphate interaction with goethite. *Soil Sci. Soc. Am. J.* 65: 753-760.
- Celi, L., S. Lamacchia, F. Ajmore-Marsan, and E. Barberis. 1999. Interaction of inositol hexaphosphate on clays: adsorption and charging phenomena. *Soil Sci.* 164: 574-585.
- Cosgrove, D.J. 1966. The chemistry and biochemistry of inositol polyphosphates. *Rev. Pure Appl. Chem.* 16: 209-252.
- Giles, C.H., D. Smith, and A. Huitson. 1974. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *J. Colloid Interface Sci.* 47: 755-765.
- Goldberg, S., and G. Sposito. 1984. A chemical model of phosphate adsorption by soils: I. Reference oxide minerals. *Soil Sci. Soc. Am. J.* 772-778.
- Guo, F., and R.S. Yost. 1999. Quantifying the available soil phosphorus pool with the acid ammonium oxalate method. *Soil Sci. Soc. Am. J.* 63: 651-656.
- Kleinman, P.J.A., R.B. Bryant, W.S. Reid, A.N. Sharpley, and D. Pimentel. 2000. Using soil phosphorus behavior to identify environmental thresholds. *Soil Sci.* 165: 943-950.
- Ognalaga, M., E. Frossard, and F. Thomas. 1994. Glucose-1-phosphate and myoinositol hexaphosphate adsorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* 58: 332-337.
- Parfitt, R.L., J.D. Russell, and V.C. Farmer. 1976. Confirmation of the surface structure of goethite and phosphated goethite. *J. Chem. Soc. Faraday Trans. I.* 72: 1082-1087.
- Sall, J., A. Lehman, and L. Creighton. 2001. JMP® Start Statistics. A guide to statistics and data analysis using JMP® and JMP IN® software. SAS Institute Inc. Duxbury, Pacific Grove, CA.
- Shang, C., J.W.B. Stewart, and P.M. Huang. 1992. pH effects on the kinetics of adsorption of organic and inorganic phosphates by short-range ordered aluminum and iron precipitates. *Geoderma* 53: 1-14.
- Schwertmann, U., and R.M. Cornell. 1991. Iron oxides in the laboratory. Preparation and characterization. VCH, New York.

- Stumm, W., and J.J. Morgan. 1996. *Aquatic Chemistry. Chemical equilibria and rates in natural waters*. Third edition. John Wiley & Sons Inc., New York.
- Tejedor-Tejedor, M.I., and M. Anderson. 1990. Protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility. *Langmuir* 6: 602-611.
- Tsao, G.T., Y. Zheng, J. Lu, and C.S. Gong. 1997. Adsorption of heavy metal ions by immobilized phytic acid. *Appl. Biochem. Biotechnol.* 63-65.
- Webster, J.G., P.J. Swedlund, and K.S. Webster. 1998. Trace metal adsorption onto an acid mine drainage iron(III) oxyhydroxysulfate. *Environ. Sci. Technol.* 32:1361-1368.

Chapter 6

Hydrolysis of Inositol Hexaphosphate by Acid Mine Drainage Floc

6.1. Introduction

Inositol hexaphosphate (IHP) or phytate sorbs strongly onto iron and aluminum oxides. Strong sorption of IHP-P on mineral surfaces can reduce their bioavailability (McKelvie et al., 1997; Suzumura and Kamatani, 1995). However, many studies report that metal oxides facilitate hydrolysis of organic compounds (Baldwin et al., 1995; Torrents and Stone, 1993a; Torrents and Stone, 1993b). Metal oxides, especially Fe and Al oxides, have a great affinity for phosphate groups also. Thus, if P is retained after hydrolysis of IHP by oxide surfaces and inositol ring is released to the solution, then it can impair organic P sorption capacity of the oxide surfaces; because, a fewer number of P molecules per unit surface area will be sorbed. If two contiguous P groups bond an IHP molecule to the mineral surfaces, they can take four more P groups along with. On the other hand, if six P groups are sorbed individually after hydrolysis, they occupy three-times more sites. Furthermore, this supposed hydrolytic effect of Fe and Al oxides may help enhance bioavailability or mobility of organic P in soils and sediments.

A useful diagnostic of the mechanism of IHP-P sorption can be the carbon: phosphorus (C: P) ratio of the equilibrium solution. If IHP-P is sorbed after hydrolysis, C: P ratio of the equilibrium solution should increase; because, only phosphate groups are sorbed, whereas inositol is released to the solution. On the other hand, if mineral surfaces do not cleave phosphate groups from the carbon ring, C: P ratio should equal that of the IHP solution that has not been equilibrated with mineral surfaces.

Both IHP-P sorption (Celi et al., 2001; Shang et al., 1992) and hydrolysis of organic compounds (Baldwin et al., 1995) depend on pH considerably. Hydrolysis of organic compounds aided by mineral surfaces depends on co-adsorbed ions (Torrents and Stone, 1993a) and dissolved organic matter (Torrents and Stone, 1993b) as well.

The present study was designed to ascertain whether IHP-P sorbs onto floc surface *per se* or only P groups are retained and inositol ring is released to the solution via hydrolytic action of reactive surfaces. Another objective of the study was to examine the effect of pH on the hydrolysis of inositol hexaphosphate solution in the absence of mineral phases.

6.2. Materials and Methods

Three different kind of flocs – ammonia-treated, lime-treated, and NaOH-treated were used for this experiment. Ammonia-treated floc and NaOH-treated floc were prepared as described in section 5.2.1. However, lime-treated floc was collected from the AMD treatment facility at Omega underground mine located in Monongalia County of West Virginia, approximately 8 km. south of city of Morgantown. Lime-treated floc was not washed and was used as such so as to retain the influence of minerals like gypsum and calcite, which it may have (Rose and Ghazi, 1997). Major chemical properties of the various flocs are described in Table 6.1.

Each floc suspension (5 g L^{-1} ; as described in section 5.2.1) was divided into six portions so as to obtain floc suspensions with six different pH levels of 4, 5, 6, 7, 8, and 9. Different pH levels were obtained by adding 0.1M hydrochloric acid (HCl; trace-metal grade) or 0.1M sodium hydroxide (NaOH; ACS certified) with 100 μL Eppendorf pipets. All pH adjustments were made under argon atmosphere so as to obviate the effect of

Table 6.1. Elemental composition, pH, and P sorption capacity of the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs used for the study.

Property	Floc		
	Ammonia-treated	Lime-treated [†]	NaOH-treated
Iron (g kg ⁻¹)	322 ^{††}	245	314
Aluminum (g kg ⁻¹)	105	70	86
Ammonium oxalate extractable iron (g kg ⁻¹)	322	240	313
Ammonium oxalate-extractable aluminum (g kg ⁻¹)	105	68	85
Calcium (g kg ⁻¹)	3.8	15.2	6.5
Magnesium (g kg ⁻¹)	1.9	6.3	5.4
Cadmium (mg kg ⁻¹)	bdl ^{†††}	bdl	bdl
Cobalt (mg kg ⁻¹)	155	115	185
Copper (mg kg ⁻¹)	213	193	185
Chromium (mg kg ⁻¹)	41	15	21
Lead (mg kg ⁻¹)	bdl	bdl	bdl
Manganese (mg kg ⁻¹)	252	1,144	595
Nickel (mg kg ⁻¹)	754	472	727
Phosphorus (mg kg ⁻¹)	bdl	bdl	Bdl
pH (5g L ⁻¹ slurry)	6.9	6.3	7.3
Phosphorus sorption capacity (μMol g ⁻¹)	2,503	1,950	2,400

[†] Lime-treated floc was not washed with deionized distilled water for removing excess of salts.

^{††} Each value is mean of three replicates.

^{†††} bdl stands for 'below detection limit' of ICP-AES.

atmospheric carbon dioxide. These pH-adjusted floc suspensions were stored in argon-filled plastic bottles.

After transferring the suspension to these bottles, their headspace was again filled with argon and the bottles were tightly capped. Then, 6.45mM IHP-P (dipotassium inositol hexaphosphate salt; $K_2C_6H_{16}O_{24}P_6$; water content one mole per mole, Sigma Chemical) was prepared in 0.01M sodium chloride (NaCl; Certified ACS grade) and the solution was divided into six portions for adjusting pH to six different levels – 4, 5, 6, 7, 8, and 9. Levels of pH were adjusted under argon atmosphere with 0.1M HCl and 0.1M NaOH and the solutions were stored in plastic bottles pre-filled with argon. Headspace of the bottles was again filled with argon.

Nine mL of the floc suspension (pH pre-adjusted, 5 g L^{-1}), so as to get 45 mg of solid dried floc, was transferred to argon-filled 50mL plastic centrifuge tubes. To each tube, 36 mL of 6.45mM IHP-P solution of the corresponding pH was added dropwise to the suspension, under argon atmosphere, so as to avoid local supersaturation with respect to various P minerals. This solution gave an initial concentration of 5.16mM IHP-P (36 mL of 6.45mM diluted to 45 mL (36mL P-solution plus 9mL floc suspension)). Thereafter, headspace of these tubes was again filled with argon and the samples were allowed to equilibrate on an end-over-end shaker for 20 hours. After equilibration, the samples were centrifuged and filtered. Measurements for inositol hexaphosphate-P were made on Inductively Coupled Plasma Atomic Emission Spectrophotometer (Perkin-Elmer, P400). Orthophosphate-P was measured in 6.45mM IHP-P solutions on Lachat QuickChem 8000 flow injection analyzer (Zellweger Analytics) by the method described

by Murphy and Riley (1962). Total organic carbon was measured on Total Organic Carbon analyzer (Dohrmann Rosemount, DC-190).

The experimental design was a completely randomized. There were three floc types and six different pH levels. Each observation had three replicates. The data were analyzed statistically by using PROC GLM SAS (version 8.0).

6.3. Results and Discussion

Ratios of carbon to phosphorus in various equilibrium solutions are given in Table 6.2. These data and Fig.6.1 show that C:P ratios in solutions having no acid mine drainage floc (named control) were not generally much different from the solutions containing various flocs (control versus others(that is, all other treatments) contrast was not statistically significant). However, in ammonia-treated floc at pH 6-8, C:P ratios were lower than that in 'control' or in other flocs. In general, the results suggest that AMD flocs did not facilitate significant hydrolysis by way of cleaving phosphate groups on the inositol hexaphosphate molecule. If the phosphate groups could have been cleaved before they were sorbed onto the surfaces of floc materials, C:P ratio of the equilibrium solution must have been higher than that in 'control' solutions. Celi et al. (1999) also observed no hydrolysis of inositol hexaphosphate.

Orthophosphate-P concentrations in 200 mg P L⁻¹ inositol hexaphosphate-P solutions, at various pH levels, indicate that hydrolysis was negligible (about 2% at pH 4) in general (Table 6.3; Fig. 6.2). The pH effect on orthophosphate concentrations was significant statistically. More inositol hexaphosphate-P was hydrolyzed at lower pH than at higher pH. However, amounts hydrolyzed are so small and the pH conditions are so unlikely that they will not have much impact on the IHP-P in the field. Ognalaga et al.

Table 6.2. Carbon:phosphorus (C:P) ratio of solutions of ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage floc suspensions equilibrated with 5.16 mM inositol hexaphosphate (IHP)-P solution.

pH	Treatment			
	Control	Ammonia-treated floc	Lime-treated floc	NaOH-treated floc
C:P ratio.....			
4.0	0.91 [†]	0.98	0.84	1.08
5.0	0.87	0.88	0.98	0.93
6.0	0.87	0.67	0.82	0.73
7.0	0.90	0.71	0.83	0.81
8.0	0.89	0.76	0.83	0.97
9.0	0.96	0.94	0.95	1.08

[†] Each value is mean of three replicates.

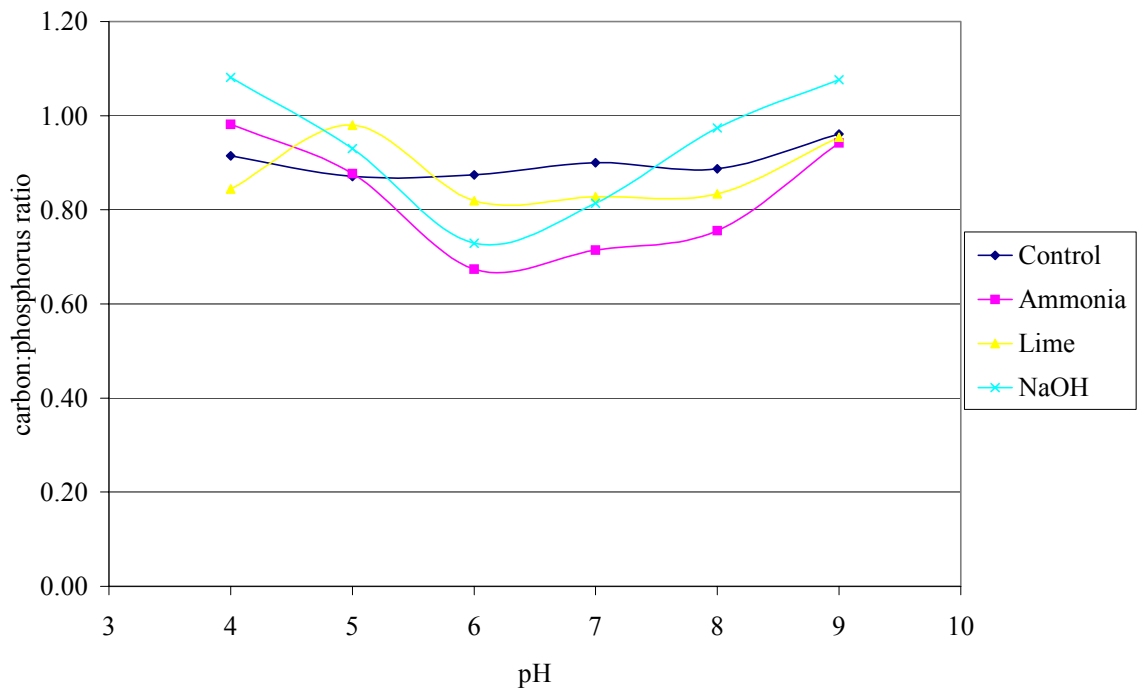


Figure 6.1. Carbon:Phosphorus ratio of solutions of inositol hexaphosphate equilibrated with or without(control) ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs.

Table 6.3. Orthophosphate concentrations in 200 mg L⁻¹ inositol hexaphosphate-P solution at various pH values.

pH	Orthophosphate-P concentration (mg L ⁻¹)
4.0	4.1 ^{a†}
5.0	3.9 ^b
6.0	3.7 ^{cd}
7.0	3.7 ^{cd}
8.0	3.7 ^{cd}
9.0	3.6 ^d

[†] Each value is mean of three replicates; figures with the same letter are not significantly different.

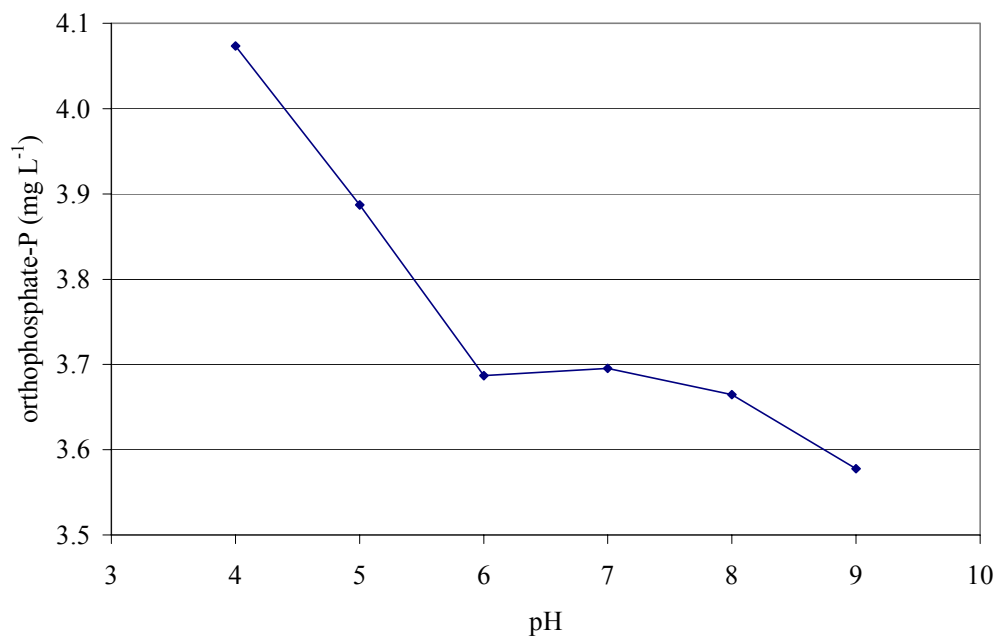


Figure 6.2. Orthophosphate-P concentrations in 200 mg L⁻¹ inositol hexaphosphate-P solution (in 0.01M NaCl) at various pH levels.

(1994) also observed no significant hydrolysis of IHP-P (from dodecasodium salt of myo-inositol hexaphosphate) in the solution.

6.4. Conclusions

Results indicate that generally inositol hexaphosphate is adsorbed onto the surface of acid mine drainage floc, or Fe and Al oxides (of which acid mine drainage floc is largely composed), as an intact inositol hexaphosphate ion and remains adsorbed *per se*. Changes in pH levels did not effect appreciable hydrolysis of inositol hexaphosphate P. These observations hint that AMD flocs can attenuate much more inositol phosphate-P than inorganic P, and it is unlikely that AMD floc will help enhance the bioavailability of organic P.

References

- Baldwin, D.S., J.K. Beattie, L.M. Coleman, and D.R. Jones. 1995. Phosphate ester hydrolysis facilitated by mineral phases. *Environ. Sci. Technol.* 29: 1706-1709.
- Celi, L., M. Presta, F. Ajmore-Marsan, and E. Barberis. 2001. Effect of pH and electrolytes on inositol hexaphosphate interaction with goethite. *Soil Sci. Soc. Am. J.* 65: 753-760.
- Celi, L., S. Lamacchia, F. Ajmore-Marsan, and E. Barberis. 1999. Interaction of inositol hexaphosphate on clays: adsorption and charging phenomena. *Soil Sci.* 164: 574-585.
- McKelvie, I.D., B.T. Hart, T.J. Cardwell, R.W. Cattrall. 1997. Use of immobilized 3-phytase and flow injection for the determination of phosphorus species in natural waters. *Talanta* 45: 47-55.
- Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27: 31-36.
- Ognalaga, M., E. Frossard, and F. Thomas. 1994. Glucose-1-phosphate and myo-inositol hexaphosphate adsorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* 58: 332-337.

- Rose, S., and A.M. Ghazi.1997. Release of sorbed sulfate from iron oxyhydroxides precipitated from acid mine drainage associated with coal mining. *Environ. Sci. Technol.* 31: 2136-2140.
- Shang, C., J.W.B. Stewart, and P.M. Huang. 1992. pH effect on kinetics of adsorption of organic and inorganic phosphates by short-range ordered aluminum and iron precipitates. *Geoderma* 53: 1-14.
- Suzumura, M., and A. Kamatani. 1995. Mineralization of inositol hexaphosphate in aerobic and anaerobic marine sediments: implications for the phosphorus cycle. *Geochim. et. Cosmochim. Acta.* 59: 1021-1026.
- Torrents, A., and A.T. Stone.1993a. Catalysis of picolinate ester hydrolysis at the oxide/water interface: inhibition by co-adsorbed species. *Environ. Sci. Technol.* 27: 1060-1067.
- Torrents, A., and A.T. Stone. 1993b. Catalysis of picolinate ester hydrolysis at oxide/water interface: inhibition by adsorbed natural organic matter. *Environ. Sci. Technol.* 27: 2381-2386.

Chapter 7

Competitive Sorption of Organic Anions and Phosphorus onto Acid Mine Drainage Floc

7.1. Introduction

The sorption of phosphorus on metal oxyhydroxides in soils and sediments influences the mobility and bioavailability of phosphorus. Besides P, certain small organic anions like oxalate and citrate also have great affinity for surfaces of Fe and Al oxides. These anions have been shown to compete with P for sorption onto the surfaces of the minerals (Geelhoed et al., 1998; Cajuste et al., 1996; Violante et al., 1991; Lopez-Hernandez et al., 1986; Sibanda and Young, 1986).

Simple organic acids in soils may be released by root exudates (Huang and Violante, 1986; Rovira, 1969). However, a more important source in the context of the problem of release of P from soils can be the application of manures. Manures contain considerable amounts of low-molecular weight acids (Bazirakenga and Simard, 1998; Hirai et al, 1983). Manures from non-ruminants like poultry and swine contain considerable amounts of total P as phytate-P or inositol phosphate-P. Thus, competitive sorption of organic acids onto acid mine drainage (AMD) floc can affect their P attenuation capacity.

Competitive sorption of organic acids with inorganic phosphates has been widely studied (Geelhoed et al., 1998; Lopez-Hernandez et al., 1986). However, the competitive sorption of organic acids and inositol hexaphosphate (IHP)-P, an important form of organic P in soils and manures has not been reported in the literature. The objective of this study was to examine the effect of varying loadings of citrate and oxalate on the sorption of inorganic and IHP-P onto various AMD flocs at different pH levels.

7.2. Materials and Methods

7.2.1. Preparation of Acid Mine Drainage Floes

Three different kind of floes – ammonia-treated, lime-treated, and NaOH-treated were used for this experiment. Ammonia-treated floe and NaOH-treated floe were prepared as described in section 5.2.1. However, lime-treated floe was collected from the AMD treatment facility at Omega underground mine located in Monongalia County of West Virginia, approximately 8 km south of city of Morgantown. Lime-treated floe was not washed and was used as such so as to retain the influence of minerals like gypsum and calcite, which it may have (Rose and Ghazi, 1997). Major chemical properties of the various floes are described in Table 6.1.

7.2.2. Sorption Experiments

Each floe suspension (5 g L^{-1} ; as described in section 5.2.1) was divided into six portions so as to obtain floes with six different pH levels of 4, 5, 6, 7, 8, and 9. Different pH levels were obtained by adding 0.1M hydrochloric acid (HCl; trace-metal grade) or 0.1 M sodium hydroxide (NaOH; ACS certified) with 100 μL Eppendorf pipets. All pH adjustments were made under argon atmosphere so as to remove the effect of atmospheric carbon dioxide. These pH-adjusted floe suspensions were stored under argon atmosphere.

Solutions of citrate, oxalate, inorganic P, and IHP-P in 0.01M sodium chloride (NaCl; Certified ACS grade) were prepared from sodium citrate ($\text{Na}_2\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$; Certified ACS grade), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$; Certified ACS grade), potassium dihydrogen phosphate (KH_2PO_4 ; Primary Standard), and dipotassium phytic acid salt, ($\text{K}_2\text{C}_6\text{H}_{16}\text{O}_{24}\text{P}_6$; water content one mole per mole, Sigma Chemical), respectively.

Initially, stock solutions of citrate (2000 mg L^{-1}), oxalate (2000 mg L^{-1}), inorganic P (1000 mg L^{-1}) and IHP-P (1000 mg P L^{-1}) were prepared in 0.01M NaCl . Calculated quantities of these solutions were mixed to get the various combinations (listed in Table 7.1) of concentrations of oxalate or citrate and P in the suspension. These combinations were chosen so as to examine the competitive effect of linear increase in concentration of organic anions on the sorption of P from a solution having constant P concentration. Each combination was further divided into six portions for adjusting pH, so as to obtain six different levels of 4, 5, 6, 7, 8, and 9. Adjustments for pH were made with 0.1M HCl or 0.1M NaOH under argon atmosphere.

The experiment had a completely randomized design. There were six pH levels, two organic anion types (citrate and oxalate), four organic anion levels (0.00 , 1.72 , 3.44 , and 5.16 mM citrate or oxalate), two P types (inorganic P and IHP-P), one P level (5.16 mM), and three different flocs. The experiment was run in triplicate.

Nine mL of the floc suspension (pH pre-adjusted, 5 g L^{-1}), so as to get 45 mg of solid dried floc, was transferred to argon-filled 50mL plastic centrifuge tubes. To each tube, 36 mL solution of a given organic anion type, P-type, and anion level combination (Table 7.1) with the corresponding pH was added in dropwise quantities, under argon atmosphere, so as to avoid local supersaturation with respect to various P minerals.

Thereafter, headspace of these tubes was filled with argon and the samples were allowed to equilibrate on an end-over-end shaker for 20 hours. After equilibration, the samples were centrifuged and filtered. Measurements for P, Fe, Al, and Ca were made on Inductively Coupled Plasma Atomic Emission Spectrophotometer (Perkin-Elmer, P400).

Table 7.1 Combinations of organic anions (citrate and oxalate) and P (inorganic and inositol hexaphosphate) solutions used for studying the competitive sorption of citrate and oxalate with inorganic-P and inositol hexaphosphate (IHP)-P.

Combination #	Citrate	Inorganic-P	IHP-P	Oxalate	Inorganic-P	IHP-P
.....(mM).....						
1	0.00	5.16				
2	1.72	5.16				
3	3.44	5.16				
4	5.16	5.16				
5	0.00		5.16			
6	1.72		5.16			
7	3.44		5.16			
8	5.16		5.16			
9				0.00	5.16	
10				1.72	5.16	
11				3.44	5.16	
12				5.16	5.16	
13				0.00		5.16
14				1.72		5.16
15				3.44		5.16
16				5.16		5.16

Amounts of P sorbed were calculated using initial and final equilibrium solution concentrations.

7.3. Results and Discussion

7.3.1. Effect of Citrate Loadings on P Sorption

Sorption of P decreased with increase in citrate loading at pH 4.0 (Fig. 7.1). Citrate loading of 1.72 mM caused 23-24 percent decline in the sorption of inorganic P in lime-treated and NaOH-treated flocs. Doubling the citrate loading to 3.44 mM, reduced the P sorption further by 35, 28, and 16 percent, respectively in ammonia-treated, lime-treated and NaOH-treated floc. A further 1.5 times increase in citrate loading (5.16mM) caused just 16, 13, and 15 percent reduction in the ammonia-treated, lime-treated, and sodium hydroxide-treated floc. Thus, effect of citrate addition was not linear, but it tended to level off at higher loadings.

Sorption of IHP-P was affected in the same way in every floc type. However, the citrate did not compete so strongly with IHP-P for sorption. Citrate loading of 1.72mM cut down the sorption by about 19, 13, and 15 percent, respectively, in ammonia-treated, lime-treated, and NaOH-treated floc. However, subsequent loadings did not cause appreciable decline in IHP-P sorption. Doubling the citrate concentration to 3.44mM reduced the P sorption just by 4, 6, and 7 percent in the same order. Further increase in the citrate-loading cut down the IHP-P sorption by 4, 6, and 3 percent only, in the same order. This may have resulted from the more intense competition from IHP-P due to its larger molecular structure than inorganic P. It is likely that increased citrate loadings increased ionic strength of the solution. Increase in ionic strength favors the sorption of P (Arai and Sparks, 2001).

At pH 5 (Fig. 7.1), trends similar to that of P sorption at pH 4 were observed. However, at this pH the effect of citrate leveled off with citrate additions higher than 3.44 mM. At pH 6, every successive citrate loading decreased the inorganic P sorption almost linearly, that is, the effects of citrate loadings at concentrations greater than 1.72 mM did not level off (Fig.7.2). It is likely that at pH 6 most carboxylic groups of citrate might be dissociated. Citric acid has three acid dissociation constants or $pK_{a,s}$ of 3.14, 4.77, and 6.39 at 293K (Lide, 1997). Thus, at pH 6, it will have a negative charge higher than it had at pH 4 or 5, and this charge might have been high enough to compete inorganic P. Citrate has been reported to sorb as a trivalent anion, that is as a completely dissociated citric acid (Bowden et al., 1980) and maximum sorption of citrate is reported to occur around its pK_a . Thus, effect of citrate was felt only until pH 7. However, sorption of inorganic P was still affected by increasing citrate amounts. At pH 8 and 9, there was virtually no effect of citrate loadings on the sorption of both IHP-P and inorganic P (Fig. 7.3).

7.3.2. Effect of pH on P sorption at Various Levels of Citrate Loadings

Effect of pH on P sorption for a given citrate loading is shown in Figures 7.4 and 7.5. Effect of pH on the P sorption was more drastic at lower citrate loadings. At a citrate loading of 1.72 mM, the sorption of inorganic P on ammonia-treated floc decreased from pH 4 to pH 9 by about 62 per cent. However, the corresponding decreases at citrate loadings of 3.44 and 5.16mM were about 43 percent only. Effect of higher concentrations of citrate in competing with P for sorption might have been offset by the favorable effect of increased ionic strength on P sorption. In lime-treated floc, decline in P sorption due to increase in pH was less at high loadings of citrate. At a citrate concentration of 1.72 mM,

rise in pH from 4 to 9 caused 34 percent reduction in inorganic P sorption. However, at 3.44 mM and 5.16 mM citrate levels, for the same decrease in pH, decline in P sorption was just 13 and 15 percent, respectively. It is likely that in lime-treated soils competitive sorption of citrate was being diminished by citrate complexation with Ca. Lime-treated floc evidently had higher amounts of Ca than other flocs. Also, there is a likelihood of competition from high sulfate concentration (Rose and Ghazi, 1997) in the unwashed lime-treated floc. P sorption might have also been favored by increased Ca^{2+} sorption with increase in pH (Rietra et al., 2001; Celi et al., 2001).

Sorption of IHP-P was comparably less affected by increase in pH in the presence of citrate. For instance, in the absence of citrate addition, change in pH from 4 to 9 effected a 56 percent reduction in sorption of IHP-P on ammonia-treated floc, 45 percent in lime-treated floc, and 42 percent in NaOH-treated floc. When 1.72mM citrate was loaded, respective declines in sorption of IHP-P were 35, 31, and 33 percent only. At 3.44 mM citrate level, these were 49, 21, and 29 percent, respectively; and at 5.16mM citrate level, change in pH from 4 to 9 caused 29, 9, and 27 percent decline in IHP-P sorption, respectively, in ammonia-treated, lime-treated, and NaOH-treated floc. This suggests that citrate sorption was more strongly affected by changes in pH than was P sorption. Similar

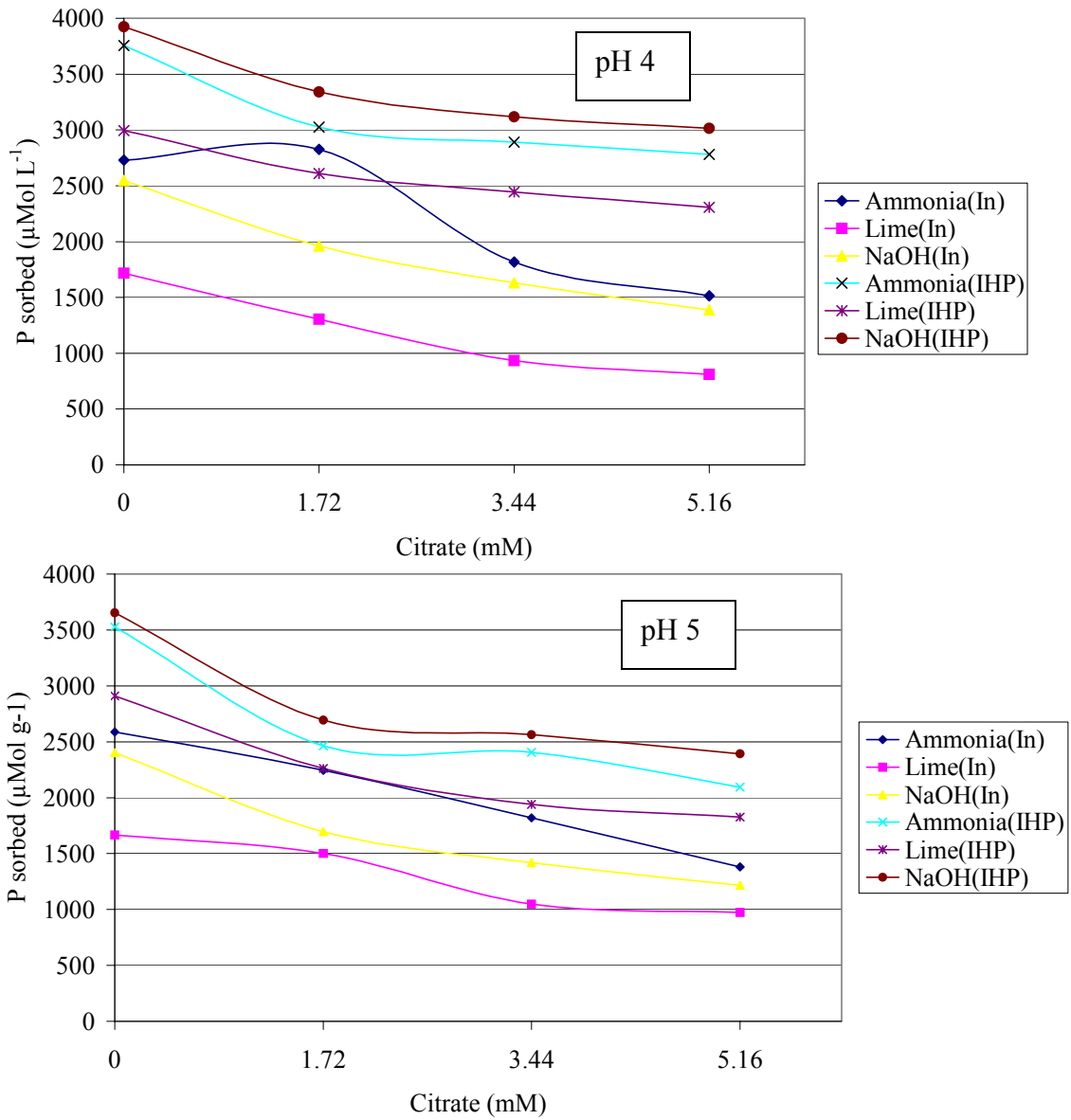


Figure 7.1. Sorption of inorganic- and inositol hexaphosphate(IHP)-P on ammonia-treated, lime-treated, and sodium-hydroxide treated flocculant as affected by increasing citrate loadings at pH 4 and 5.

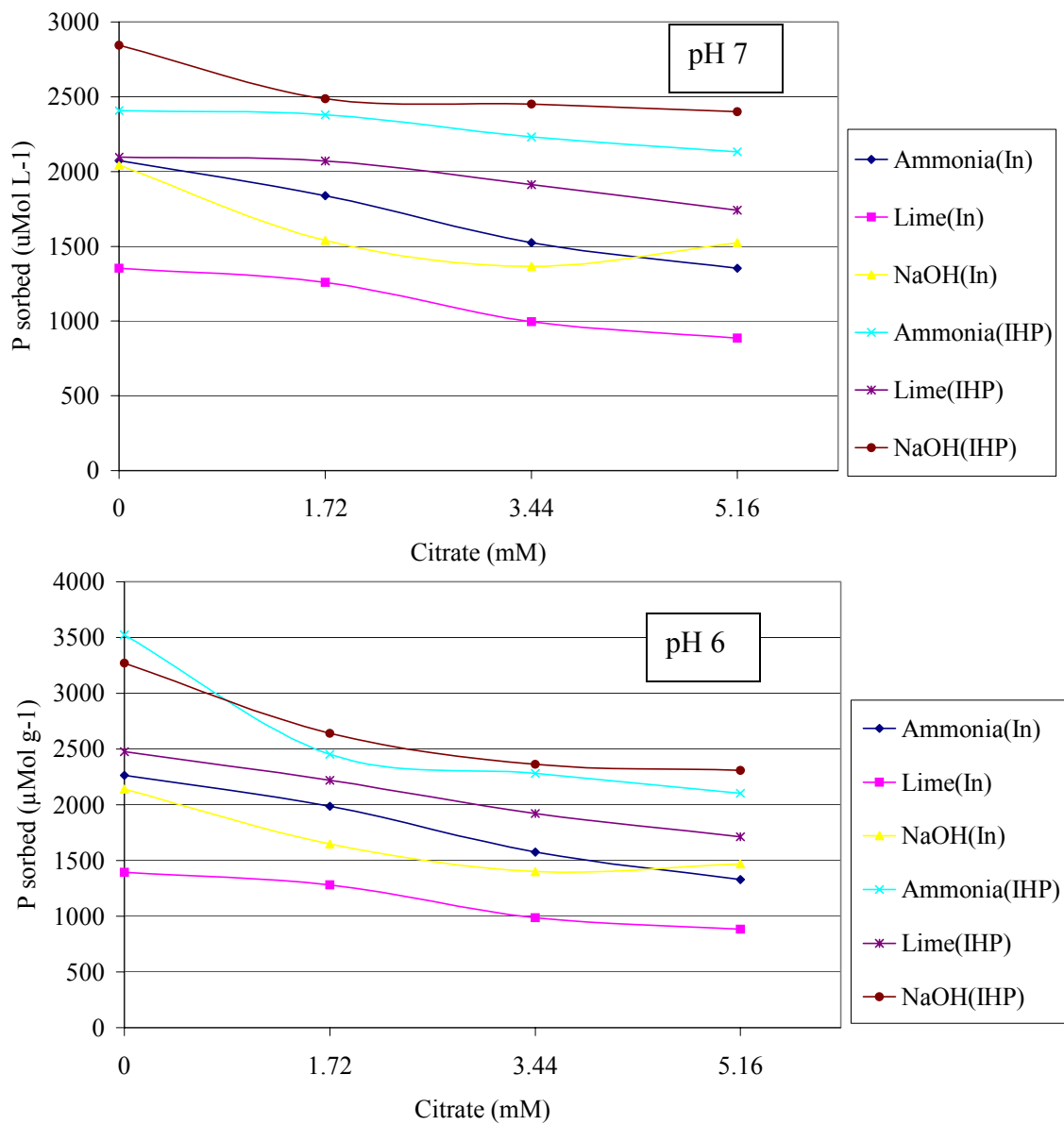


Figure 7.2. Sorption of inorganic and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated and sodium hydroxide-treated acid mine drainage flocs, as affected by increasing citrate additions at pH 6 and 7.

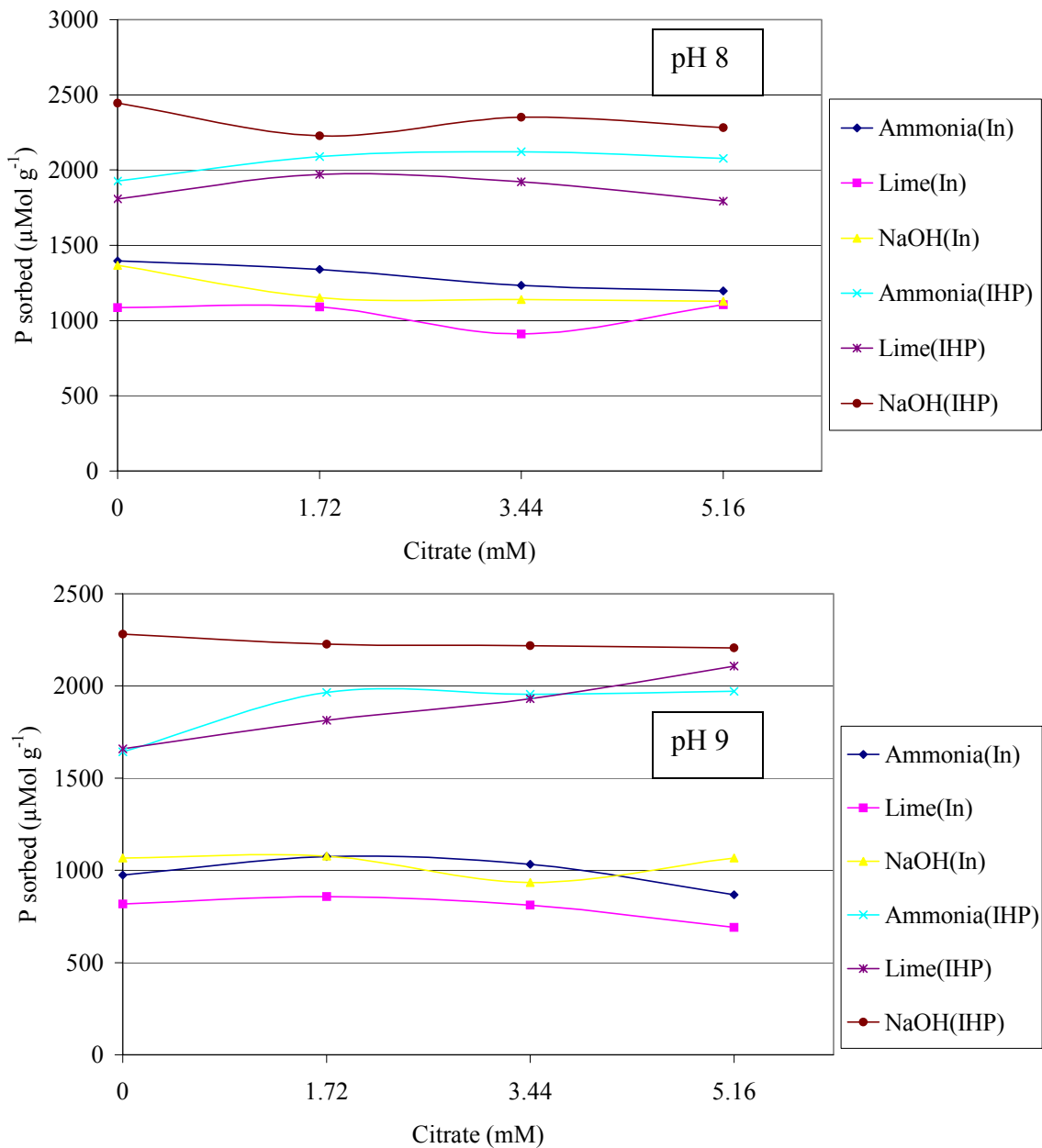


Fig. 7.3. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by increasing citrate concentrations at pH 8 and 9.

Table 7.2. Amounts of inorganic-P and inositol hexaphosphate (IHP)-P sorbed by ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs in the presence of varying levels of citrate at different pH levels.

Citrate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic-P	IHP-P	Inorganic-P	IHP-P	Inorganic-P	IHP-P
P sorbed ($\mu\text{Mol g}^{-1}$)							
0.00	4	2,731 [†]	3,756	1,715	2,995	2,548	3,924
0.00	5	2,586	3,525	1,666	2,910	2,404	3,654
0.00	6	2,265	2,919	1,395	2,475	2,142	3,272
0.00	7	2,074	2,407	1,354	2,096	2,043	2,843
0.00	8	1,397	1,926	1,086	1,809	1,368	2,444
0.00	9	975	1,643	817	1,658	1,066	2,281
1.72	4	2,827	3,026	1,303	2,609	1,960	3,341
1.72	5	2,246	2,464	1,502	2,262	1,695	2,694
1.72	6	1,987	2,451	1,281	2,218	1,647	2,640
1.72	7	1,839	2,379	1,259	2,070	1,540	2,487
1.72	8	1,341	2,089	1,091	1,971	1,152	2,229
1.72	9	1,074	1,965	857	1,813	1,077	2,226
3.44	4	1,815	2,890	935	2,443	1,631	3,119
3.44	5	1,819	2,407	1,048	1,938	1,418	2,564
3.44	6	1,575	2,282	987	1,922	1,399	2,362
3.44	7	1,524	2,231	996	1,911	1,366	2,451
3.44	8	1,235	2,121	911	1,922	1,139	2,352
3.44	9	1,032	1,954	810	1,931	934	2,219
5.16	4	1,514	2,781	810	2,306	1,386	3,016
5.16	5	1,381	2,095	974	1,825	1,216	2,394
5.16	6	1,328	2,102	883	1,711	1,469	2,309
5.16	7	1,352	2,131	885	1,742	1,524	2,400
5.16	8	1,196	2,077	1,104	1,794	1,127	2,281
5.16	9	868	1,971	689	2,108	1,067	2,207

[†] Each value is mean of three replicates.

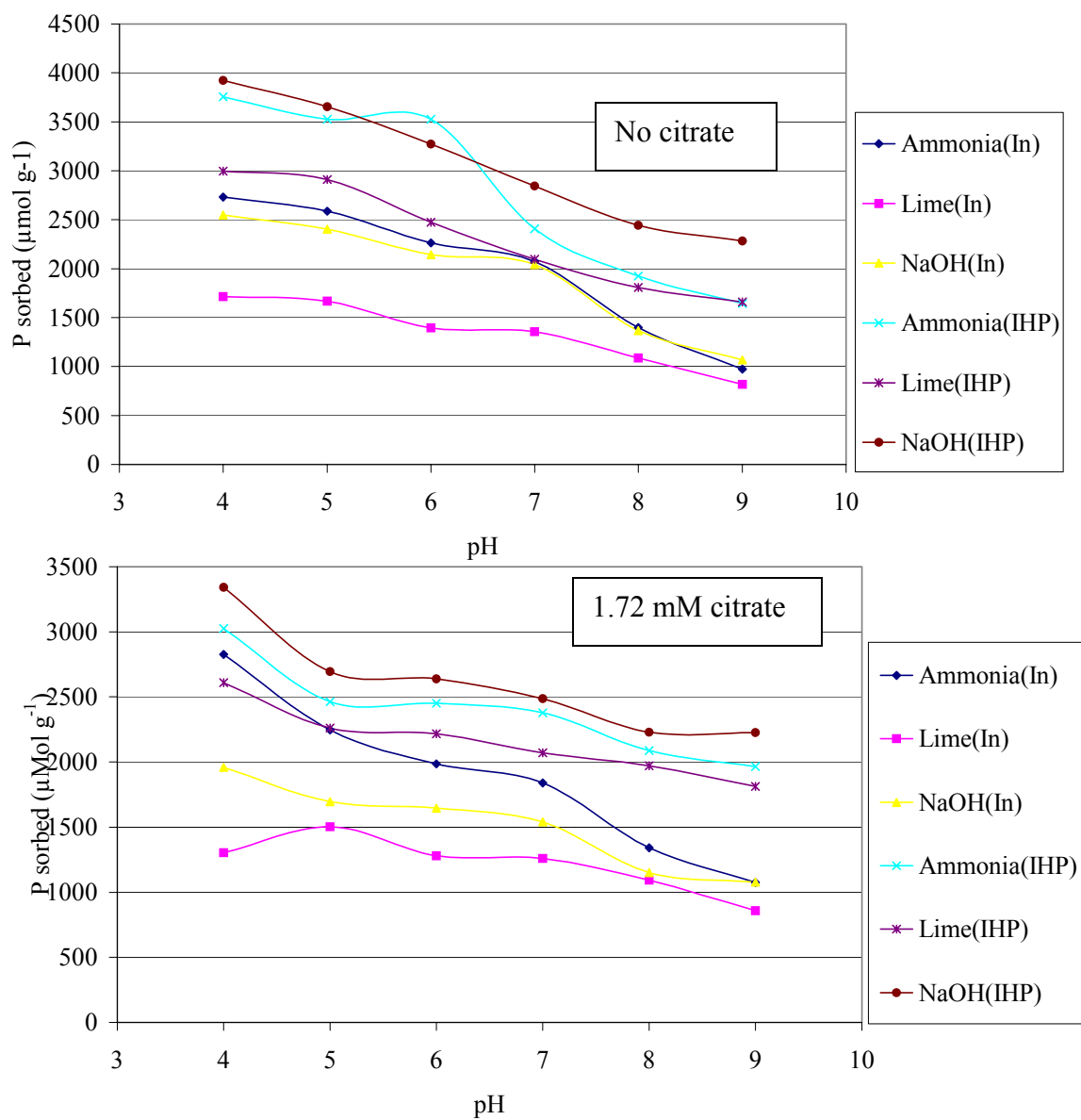


Figure 7.4. Effect of pH on the sorption of inorganic and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide-treated AMD floes in the absence of any citrate addition and in the presence of 1.72mM citrate.

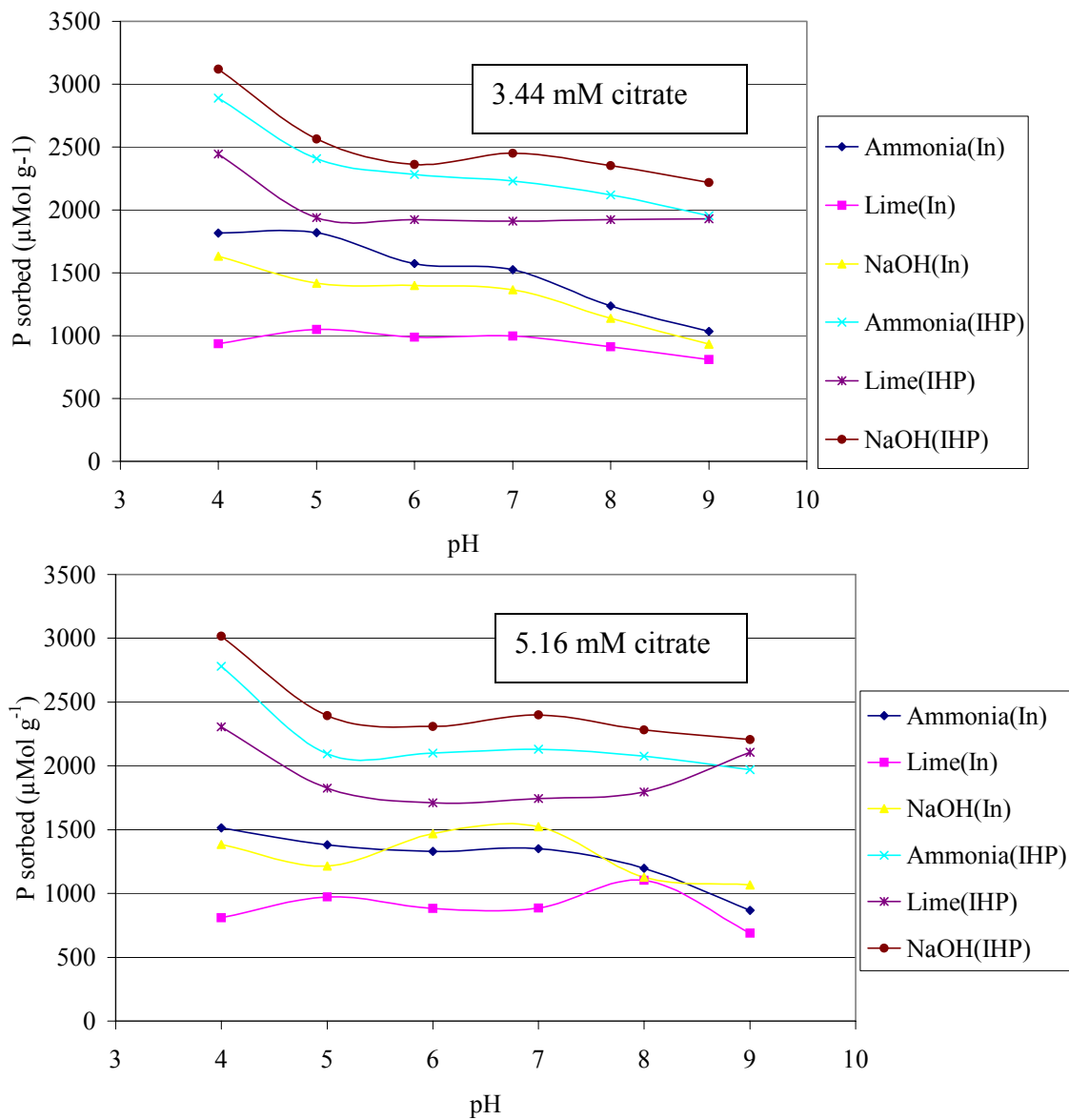


Figure 7.5. Effect of pH on the sorption of inorganic and inositol hexaphosphate(IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs in the presence of 3.44mM and 5.16mM citrate.

Table 7.3. Amounts of inorganic-P and inositol hexaphosphate(IHP)-P sorbed by ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs in the presence of various concentrations of oxalate.

Oxalate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic-P	IHP-P	Inorganic P	IHP-P	Inorganic P	IHP-P
P sorbed ($\mu\text{Mol g}^{-1}$)							
0.00	4	2,731 [†]	3,756	1,715	2,995	2,548	3,924
0.00	5	2,586	3,525	1,666	2,910	2,404	3,654
0.00	6	2,265	2,919	1,395	2,475	2,142	3,272
0.00	7	2,074	2,407	1,354	2,096	2,043	2,843
0.00	8	1,397	1,926	1,086	1,809	1,368	2,444
0.00	9	975	1,643	817	1,658	1,066	2,281
1.72	4	2,410	3,909	1,547	2,836	2,322	4,185
1.72	5	2,214	3,431	1,390	2,661	2,095	3,578
1.72	6	2,215	2,616	1,260	2,019	2,092	2,734
1.72	7	1,760	2,036	1,243	1,797	1,790	2,351
1.72	8	1,337	2,160	1,113	1,926	1,407	2,521
1.72	9	1,070	1,782	917	1,447	1,078	2,148
3.44	4	2,282	3,908	1,538	2,560	2,230	3,993
3.44	5	2,229	3,290	1,492	2,261	2,187	3,434
3.44	6	1,954	2,601	1,265	1,979	1,949	2,857
3.44	7	1,974	2,256	1,451	2,087	1,938	2,794
3.44	8	1,214	1,955	962	1,534	1,374	2,276
3.44	9	1,067	1,736	889	1,397	1,217	2,188
5.16	4	2,034	3,286	1,419	1,916	2,161	3,428
5.16	5	1,920	2,945	1,211	1,778	1,918	3,134
5.16	6	1,800	2,183	1,190	1,786	1,822	2,821
5.16	7	1,768	2,124	1,186	1,734	1,794	2,557
5.16	8	1,191	1,885	773	1,692	1,199	2,312
5.16	9	1,022	1,668	829	1,416	1,296	2,020

[†] Each value is mean of three replicates.

observations were made by Geelhoed et al. (1998).

In soils that have received excessive applications of P through manure additions, concerns are that as manure contains low molecular weight organic acids such as citric acid, competitive sorption of these acids will result in higher concentrations of inorganic and organic P in soil solution. Our data show that competition between inorganic and organic-P species and citrate ions is more intense at low pH (4.0). Most soils testing excessive in P have near-neutral pH, as P neutralizes exchangeable Al^{3+} in the soil. Thus, at near neutral or higher pH values, competitive adsorption between citrate and P is unlikely to drastically increase P concentration in the soil solution. Similarly, increasing citrate concentrations can at best affect marginally the sorption of P.

7.3.3. Effect of Oxalate Loadings on P Sorption

When 1.72 mM oxalate was added and pH was maintained at 4, the sorption of inorganic P decreased by 12 percent in ammonia-treated floc, and by 9 percent each in lime-treated floc and sodium hydroxide-treated floc (Fig. 7.6, Table 7.3). When oxalate concentration was doubled to 3.44 mM, it did not cause appreciable decline in inorganic P sorption in ammonia-treated floc (5 percent less P sorption than the P sorption in the presence of 1.72 mM in lime-treated floc (1 percent) and in NaOH-treated floc (4 percent decline). However, when oxalate loading was further increased to 5.16 mM, inorganic P sorption in ammonia-treated floc was lower than the P sorption at 3.44 mM oxalate level by about 11 percent in ammonia-treated floc, and by 8 percent in lime-treated floc, and by 3 percent in NaOH-treated floc. The effects of oxalate at higher pH levels were not as large as the effects at pH 4.

For IHP-P sorption, initial 1.72 mM loading of oxalate at pH 4 reduced the P sorption by 5.6 percent in lime-treated floc (Fig. 7.6, Table 7.3). However, for other flocs the trends were anomalous. When oxalate loading was doubled to 3.44 mM, the sorption of IHP-P in comparison to the sorption at 1.72 mM level, largely remained unaffected. However, in lime-treated floc and NaOH-treated floc, the sorption of IHP-P decreased by 10 and 5 percent, respectively with respect to the IHP-P sorption at 1.72 mM oxalate level. A further increase in oxalate loading (5.16mM) effected 16, 25, and 14 percent reduction in the IHP-P sorption over the sorption at 3.44 mM oxalate level, respectively, in ammonia-treated, lime-treated, and NaOH-treated floc. Effect of oxalate loadings on IHP-P sorption at higher pH levels was not as strong as the effects at pH 4(Figs. 7.6-7.8). Again, as was observed for citrate, oxalate was a very weak competition to P for sorption.

7.3.4. Effect of pH on P Sorption at Various Levels of Oxalate Loadings

Although, P sorption decreased with an increase in both pH and oxalate level, but the two factors did not have an additive effect. For instance, in the absence of any oxalate addition, sorption of inorganic P in ammonia decreased with increase in pH from 4 to 9 by 64, 52, and 58 percent in ammonia-treated, lime-treated, and NaOH-treated floc, respectively. When 1.72 mM oxalate was added, same increase in pH decreased inorganic P sorption by 55, 40, and 54 percent in the same order. Similarly, when oxalate addition was doubled to 3.44 mM , for the same change in pH, the decline in inorganic P sorption was 53, 42, and 45 percent, respectively, in ammonia-treated, lime-treated, and NaOH-treated floc. At 5.16mM oxalate level, the inorganic P sorption decreased with an increase in pH from 4 to 9 by 50, 42, and 40 percent in ammonia-treated, lime-treated, and NaOH-treated floc, respectively. Therefore, the effect of pH was stronger than the

effect of oxalate additions alone. It appears that efficiency of P in reducing oxalate adsorption increased with increase in pH. Therefore, effect of oxalate additions failed to support the effect of increasing pH. Violante et al. (1991) made similar observations during the study of competitive adsorption of oxalate and phosphate on Al oxides.

Inositol hexaphosphate-P sorption also did not show the additive effect of both pH and oxalate additions. In the absence of any oxalate addition, with increase in pH from 4 to 9, sorption of IHP-P decreased by 56, 45, and 42 percent, respectively, in ammonia-treated, lime-treated, and NaOH-treated floc. However, when 1.72 mM oxalate was added, the same increase in pH reduced the IHP-P sorption by 54 percent in ammonia-treated floc, and by 49 percent in both lime-treated floc and NaOH-treated floc. A two-fold increase in oxalate loading (3.44 mM) reduced the IHP-P sorption by 56 percent in ammonia-treated floc and by 45 percent in both lime-treated and NaOH-treated floc. A three-fold increase in oxalate loading (5.16 mM) cut down the IHP-P sorption by 49, 26, and 41 percent, respectively, in ammonia-treated, lime-treated, and NaOH-treated floc. These data again show that at high pH, P sorption is relatively less affected by the presence of oxalate ions.

7.3.5. Comparison between Citrate and Oxalate Effects

Analysis of variance results showed that oxalate and citrate had significantly different effects ($\text{Prob}>F < 0.0001$). At pH 4 and citrate or oxalate loading of 1.72 mM, oxalate reduced the inorganic P sorption by 10 percent in the lime-treated floc, whereas citrate decreased it by 24 percent. When oxalate or citrate loading was further increased to 3.44 mM, oxalate loading effected 5 percent reduction in ammonia-treated floc over the sorption at 1.72 mM level, whereas citrate caused 36 percent reduction in inorganic P

sorption at the same pH level. In lime-treated floc, oxalate reduced inorganic P sorption just by one percent, whereas citrate cut it down by 28 percent. Similarly in NaOH-treated floc, the respective reductions by oxalate and citrate were 4 percent and 17 percent. When organic anion concentration was further raised to 5.16 mM, in ammonia-treated floc oxalate caused 11 percent reduction in inorganic P sorption over the P sorption at 3.72 mM level, and citrate decreased it by 16 percent. In lime-treated floc, the corresponding declines were 8 and 13 percent; whereas in NaOH-treated floc, these were 3 and 15 percent at the same pH level of 4.0. Larger effect of citrate can be ascribed to the larger size of the citrate ion as compared to the oxalate ion size. Also, it is likely that citrate complexed more Ca^{2+} than did oxalate. Decreased sorption of Ca^{2+} in citrate systems did not allow much P sorption.

In case of IHP-P sorption, effect of citrate was not always greater than oxalate in decreasing P sorption. At pH 4 and citrate or oxalate loading of 1.72 mM, oxalate reduced the IHP-P sorption by 5 percent, and citrate by 13 percent in ammonia-treated floc. However, at citrate or oxalate loading of 3.44mM pH 4, oxalate reduced the P sorption by 10 percent over that at 1.72 mM in lime-treated floc, whereas citrate effected a 6 percent reduction in IHP-P sorption. In NaOH-treated floc, the respective reductions were 5 per cent and 7 percent. When citrate or oxalate loadings were further increased to 5.16mM, oxalate was more effective than citrate in causing decline in IHP-P sorption at pH 4. At this level, in ammonia-treated floc oxalate reduced P sorption by 16 percent, whereas citrate could effect 4 percent reduction only. Similarly, in lime-treated floc oxalate reduced the IHP-P sorption by 25 percent, and citrate could decrease it by 6 percent only. In NaOH-treated floc, oxalate caused a 14 percent reduction over the P

sorption at 3.44 mM level, whereas citrate reduced IHP-P sorption by 3 percent only. Thus, effect of citrate and oxalate on P sorption depended upon the type of P, whether inorganic or inorganic (P-type and organic anion type interaction effect significant at less than 1% level). The effect of citrate and oxalate varied depending upon the floc also. Scheffe's groupings for significant differences indicated that flocs differed significantly from each other in P sorption in the presence of oxalate and citrate.

It was observed that with an increase in pH, citrate was less efficient in competing with phosphate for sorption than was oxalate. At 1.72 mM citrate or oxalate loading, with change in pH from 4 to 9 inorganic P sorption was reduced by 56 and 62 percent, respectively, by oxalate and citrate in ammonia-treated floc; in lime-treated floc the respective declines were 41 and 34 percent; and in NaOH-treated floc, these were 54 and 55 percent. At citrate or oxalate loading of 3.44mM, oxalate and citrate effected 53 and 43 percent reductions in inorganic P sorption in ammonia-treated floc with a pH increase from 4 to 9. In lime-treated floc, the respective effects were 42 and 13 percent; and in NaOH-treated floc, they were 45 and 43 percent, respectively. When citrate or oxalate concentration was 5.16 mM, oxalate produced 50 percent decline in inorganic P sorption and citrate caused 43 percent decrease. In lime-treated floc, their respective effects were 42 and 15 percent, and in NaOH-treated floc these were 40 and 23 percent.

The differences between the competitive abilities of citrate and oxalate as affected by pH were quite obvious in case of sorption of IHP-P. At citrate or oxalate loading of 1.72mM, with change in pH from 4 to 9, the sorption of IHP-P was reduced by 54 percent by oxalate and 35 percent by citrate in ammonia-treated floc. In lime-treated floc, the respective effects were 49 and 31 percent, and in NaOH-treated floc these were

49 and 33 percent. At a citrate or oxalate loading of 3.44 mM, the declines in IHP-P sorption caused by oxalate and citrate were 56 and 50 percent, respectively, in ammonia-treated floc. In lime-treated floc, the respective effects were 45 and 21 percent, and in NaOH-treated floc these were 45 and 29 percent. At 5.16 mM loading, sorption of IHP-P was sized down by 49 and 29 percent, respectively, by oxalate and citrate in case of ammonia-treated floc; by 26 and 9 percent in lime-treated floc; and by 41 and 27 percent in NaOH-treated floc.

These comparisons reveal that citrate sorption was more affected by pH than the oxalate sorption. Competitive effect of citrate was particularly marginalized in lime-treated floc. This can be ascribed to the Ca-citrate complexes in the lime-treated floc. It may be noted that these differences among citrate and oxalate are relative. In terms of absolute effects, it can be observed that citrate inhibited P sorption more effectively until pH increases to 7. After that, oxalate inhibited P sorption more effectively. Several studies report that the maximum sorption of an anion is around the pK_a of its weak acid (Nagarajah et al., 1970; Hingston et al., 1972). Citric acid is a triprotic acid with pK_a 's of 3.14, 4.77, and 6.39. Bowden et al. (1980) reported that citrate is preferably adsorbed as trivalent anion. Therefore, it is likely that citrate sorption can decrease drastically with increase in pH past 7. On the other hand, oxalate is a diprotic acid with pK_a 's of 1.23 and 4.19 (Lide, 1997). Thus, it should not have inhibited P sorption beyond pH 5, which it did not. However, relatively less impact of pH on oxalate sorption as compared to the effect on citrate sorption cannot be explained by the relationship between pK_a and the maximum sorption of an anion of a weak acid around its pK_a values.

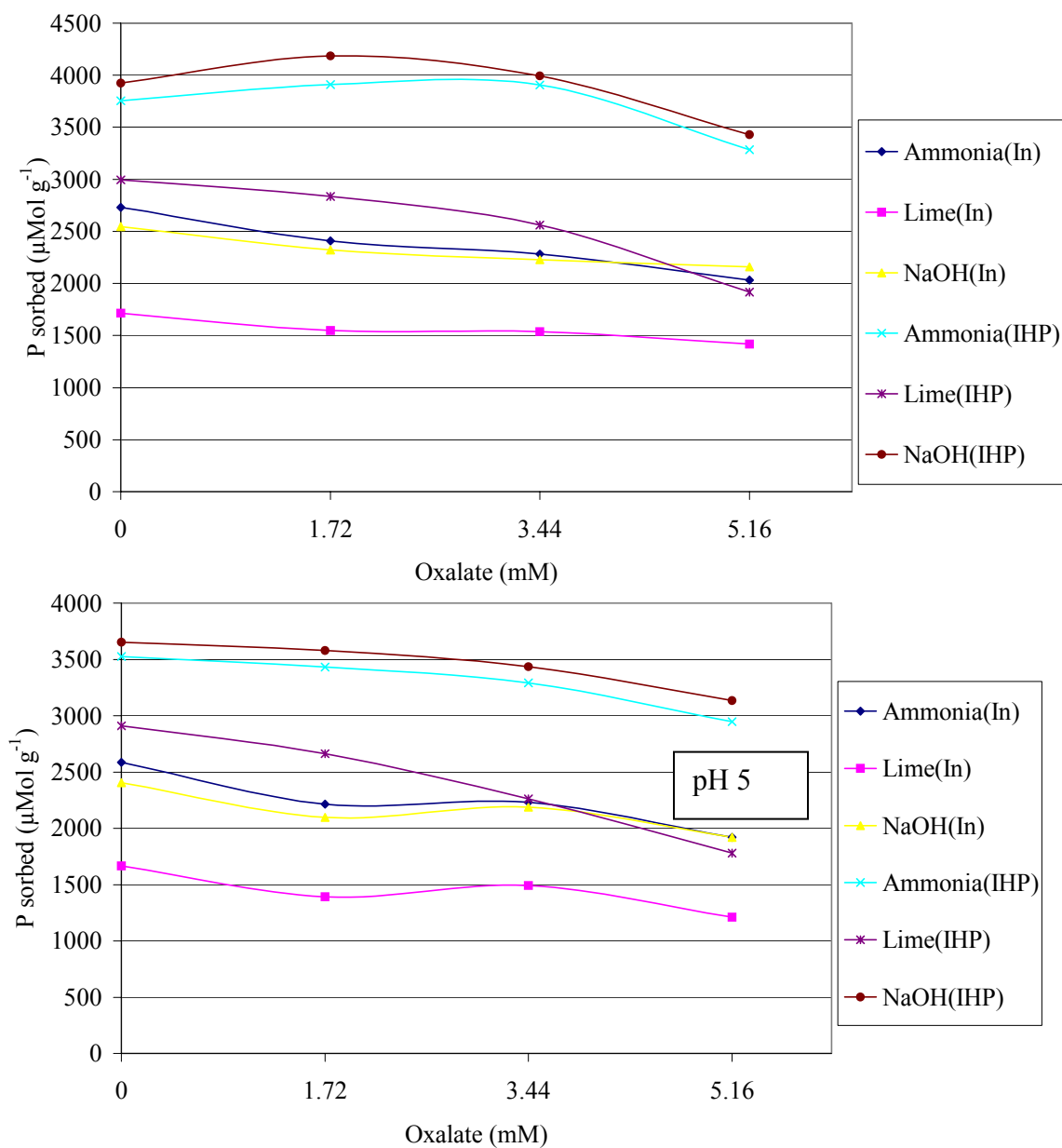


Figure 7.6. Sorption of inorganic- and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated and sodium hydroxide-treated AMD flocs as affected by increasing oxalate concentrations at pH 4 and 5.

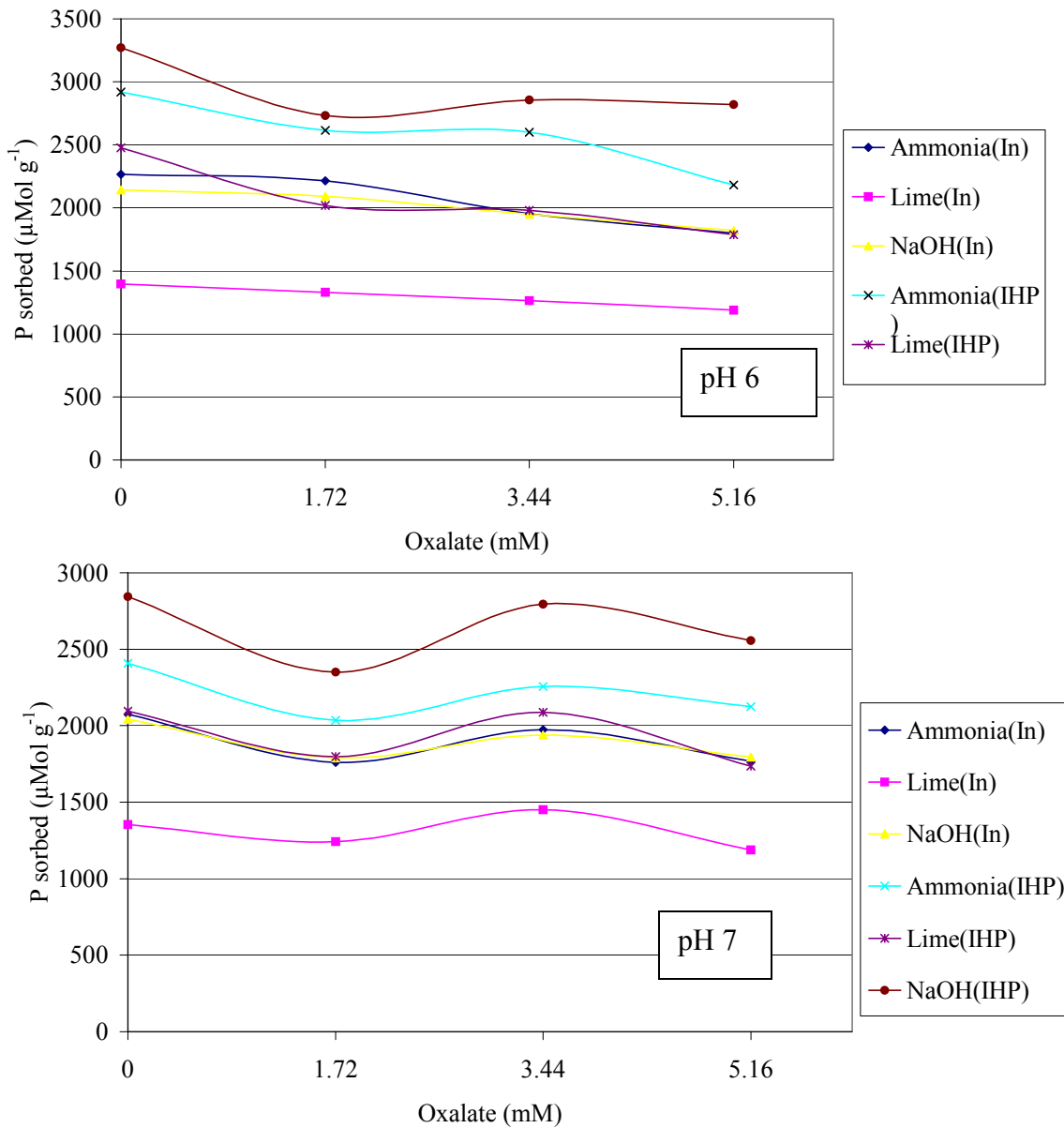


Figure 7.7. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD floccs as affected by oxalate additions at pH 6 and 7.

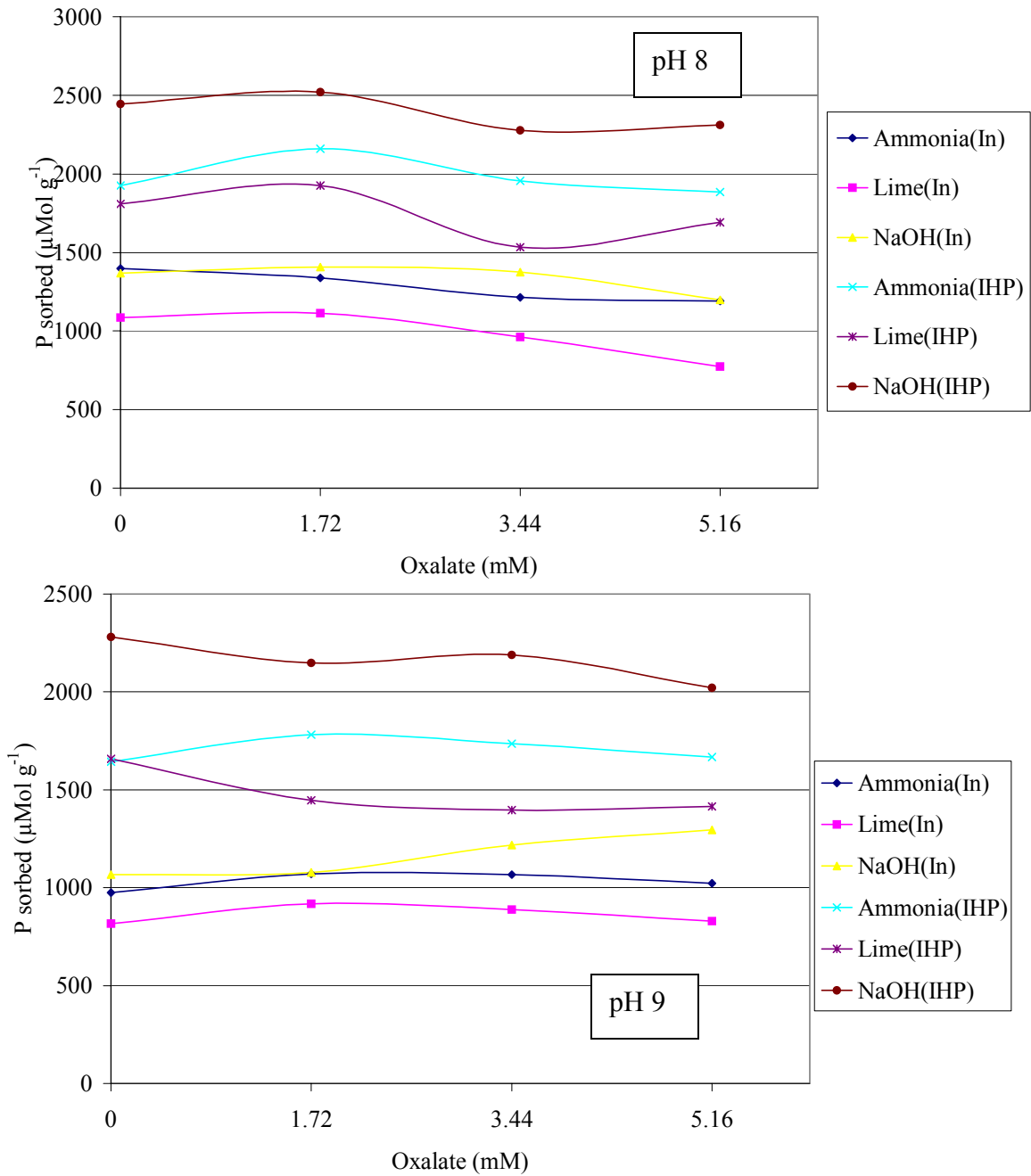


Figure 7.8. Sorption of inorganic- and inositol hexaphosphate(IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by oxalate additions at pH 8 and 9.

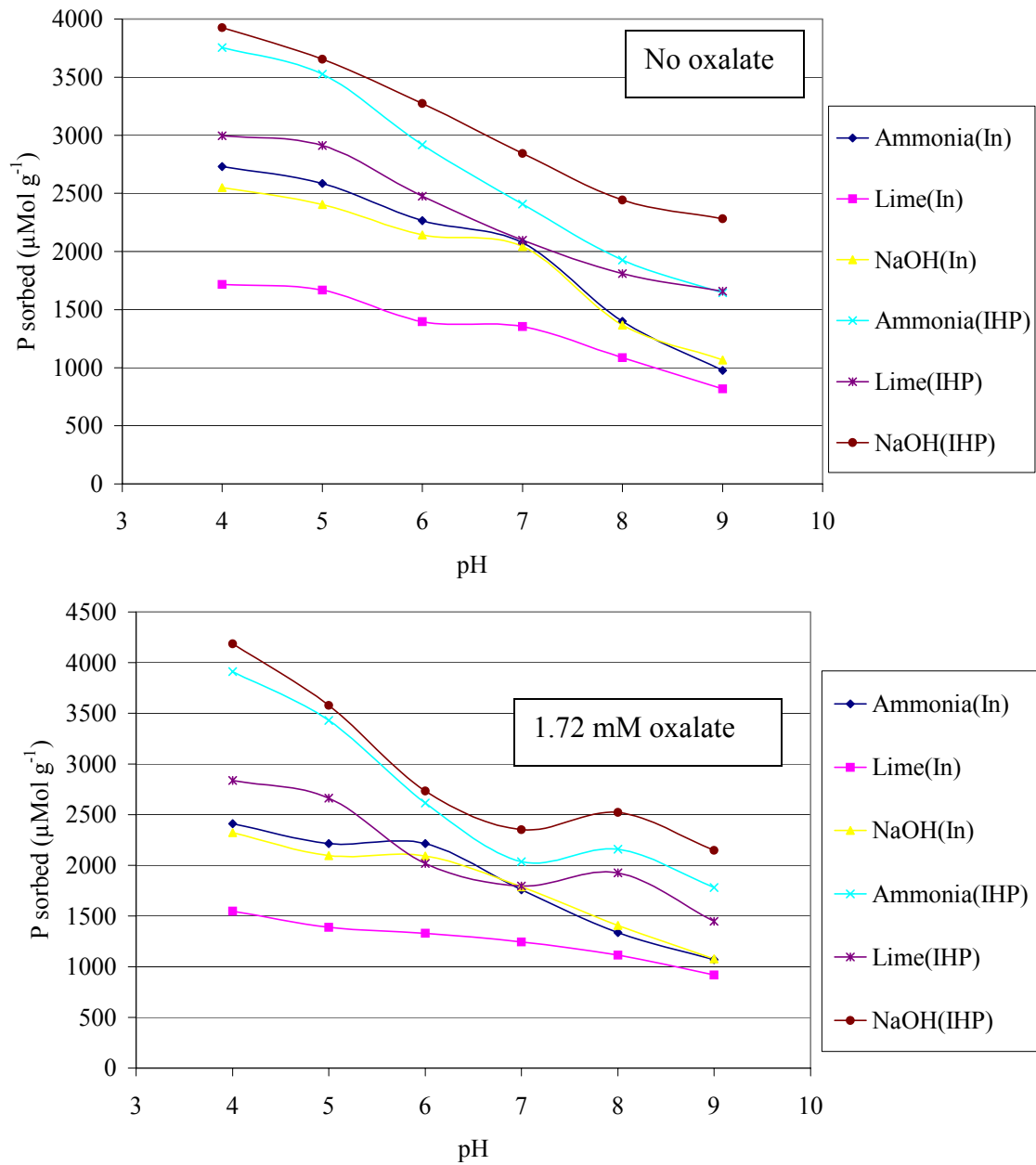


Figure 7.9. Sorption of inorganic- and inositol hexaphosphate (IHP)-P on ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by pH in the absence and in the presence of 1.72mM oxalate.

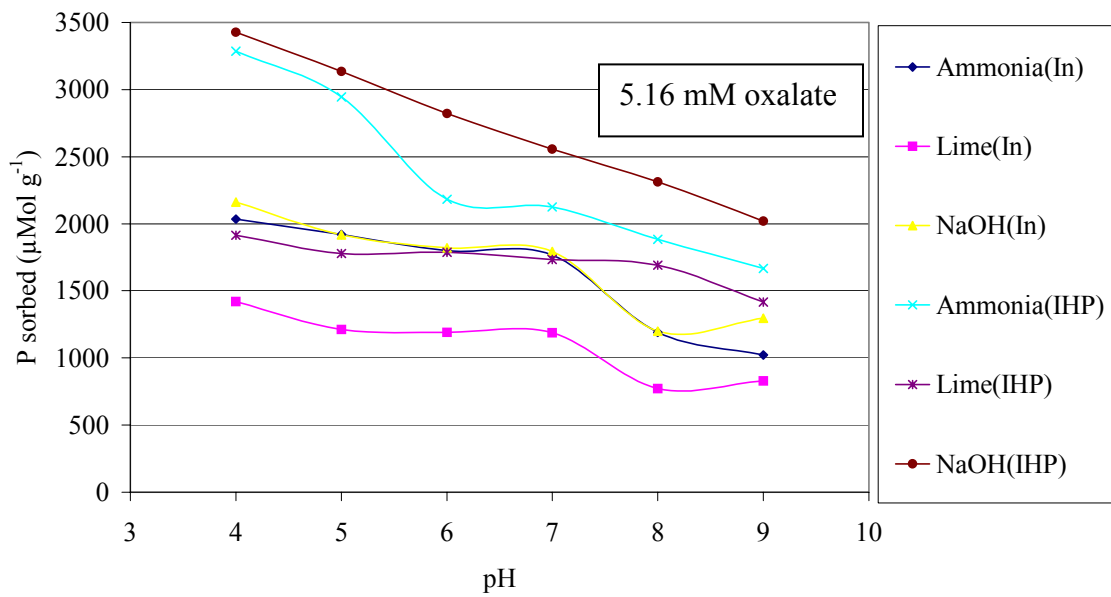
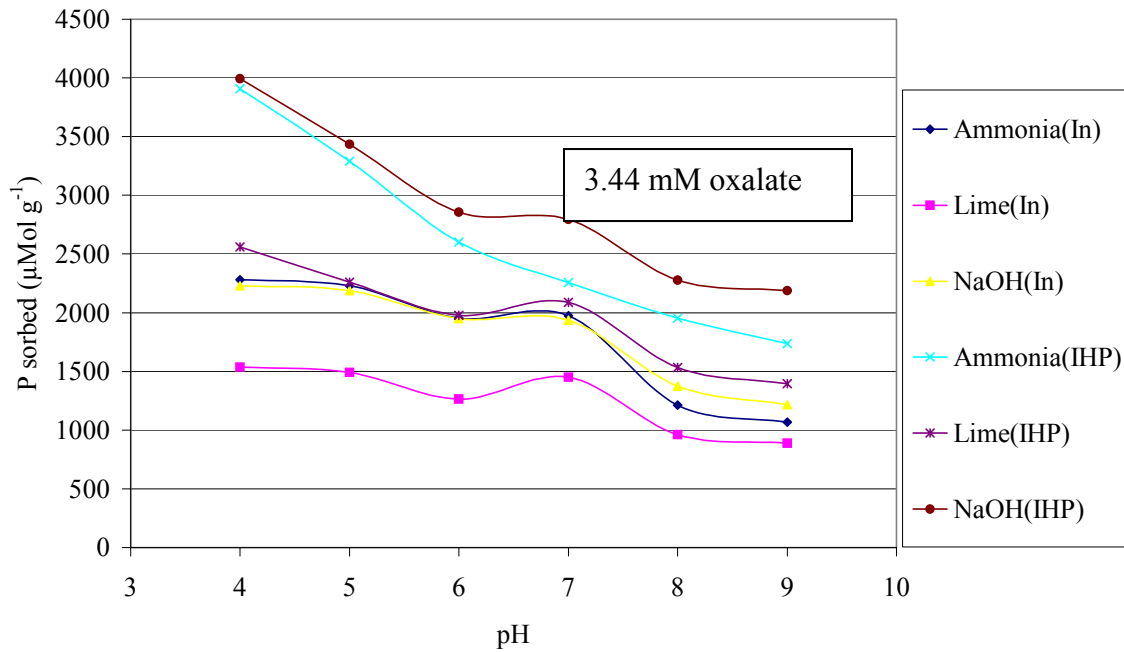


Figure 7.10. Sorption of inorganic- and inositol hexaphosphate (IHP)-P onto ammonia-treated, lime-treated, and sodium hydroxide-treated AMD flocs as affected by pH in the presence of 3.44mM and 5.16mM oxalate.

7.3.6. Effect of Citrate and Oxalate on the Fe, Al, and Ca Concentrations

To assess the likelihood of decrease in surface area of the flocs due to the dissolution caused by citrate and oxalate, concentrations of Fe, Al, and Ca in the equilibrium solutions were measured (Tables A1 through A6, Appendix 3). Higher dissolution rates were observed at low pH levels only.

Some studies report that sorption of Ca^{2+} increases the sorption of P even at higher pH, because sorption of Ca^{2+} helps increase positive charge on the surface (Rietra et al., 2001; Celi et al., 2001) and sorption of Ca^{2+} increases with increase in pH. Effect of increase sorption of Ca^{2+} (Table A5 and A6) in increasing the P sorption was observed in lime-treated floc. However, this effect was observed only for pH change from 4 to 5. Moreover, only inorganic P sorption was favorably affected. Sorption of IHP-P did not increase with increase in sorption of Ca^{2+} (Table 7.2). This happened due to the sorption of Ca^{2+} on highly negatively charged IHP molecule (Tsao et al., 1997). Further, the favorable effect of Ca^{2+} was observed only when citrate was added; oxalate did not affect P sorption in any way that can be linked to the effect of increased sorption of Ca^{2+} in lime-treated floc.

7.4. Conclusions

Citrate and oxalate were effective in blocking P sorption sites on all the three types of flocs. However, the effects were considerable only at low pH levels. Sorption of inorganic P was more adversely affected than the IHP-P sorption. Therefore, competitive adsorption of citrate or oxalate cannot be implicated in increasing dissolved P concentrations in the soils having near-neutral or higher pH. The soils that receive large applications of manures usually do not have low pH, because organic ligands complex

Al³⁺. If acid mine drainage floc is used for lowering high P levels in soils, competitive sorption of organic anions is unlikely to impair its ability to sequester P.

References

- Arai, Y., and D.L. Sparks. 2001. ATR-FTIR spectroscopic investigation on phosphate adsorption mechanism at the ferrihydrite-water interface. *J. Colloid Interface Sci.* 241: 317-326.
- Baziramakenga, R., and R.R. Simard. 1998. Low molecular weight organic acid contents of composted manure. *J. Environ. Qual.* 27: 557-561.
- Bowden, J.W., S. Nagarajah, N.J. Barrow, and A.M. Posner. 1980. Describing the adsorption of phosphate, citrate, and selenite on a variable-charge mineral surface. *Aust. J. Soil Res.* 18: 49-60.
- Cajuste, L.J., R.J. Laird, L. Cajuste-B. Jr., and B.G. Cuevas. 1996. Citrate and oxalate influence on phosphate, aluminum, and iron in tropical soils. *Commun. Soil Sci. Plant Anal.* 27:1377-1386.
- Chang, H., -C., and E. Matizevic. 1983. Interactions of metal hydrous oxides with chelating agents. IV. Dissolution of hematite. *J. Colloid Interface Sci.* 92: 479-488.
- Geelhoed, J.S., T. Hiemstra, and W.H. Van Riemsdijk. 1998. Competitive interaction of phosphate and citrate on goethite. *Environ. Sci. Technol.* 32: 2119-2123.
- Hingston, F.J., A.M. Posner, and J.P. Quirk. 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. *Discuss. Faraday Soc.* 52: 334-342.
- Hirai, M.F., V. Chanyasak, and H. Kubota. 1983. A standard measurement for compost maturity. *BioCycle* 24: 54-56.
- Huang, P.M., and A. Violante. 1986. Influence of organic acids on crystallization 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. SSSA, Madison, WI.
- Lide, D.R. 1997. *CRC handbook of chemistry and physics.* CRC Press, LLC, Boca Raton, FL.
- Lopez-Hernandez, D., G. Siegert, and J.V. Rodriguez. 1986. Competitive sorption of phosphate with malate and oxalate by tropical soils. *Soil Sci. Soc. Am. J.* 50: 1460-1462.

- Nagarajah, S., A.M. Posner, and J.P. Quirk. 1970. Competitive adsorption of phosphate with polygalacturonate and other organic anions on kaolinite and oxide surfaces. *Nature (London)* 228: 83-85.
- Rietra, R.P.J.J., T. Hiemstra, and W.H. van Riemsdijk. 2001. Interaction between calcium and phosphate adsorption on goethite. *Environ. Sci. Technol.* 35: 3369-3374.
- Rose, S., and A.M. Ghazi. 1997. Release of sorbed sulfate from iron oxyhydroxides precipitated from acid mine drainage associated with coal mining. *Environ. Sci. Technol.* 31: 2136-2140.
- Rovira, A.D. 1969. Plant root exudates. *Bot. Rev.* 35: 35-57.
- Sibanda, H.M., and S.D. Young. 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite, and two tropical soils. *J. Soil Sci.* 37: 197-204.
- Tsao, G.T., Y. Zheng, J. Lu, and C.S. Gong. 1997. Adsorption of heavy metal ions by immobilized phytic acid. *Appl. Biochem. Biotech.* 63-65: 731-741.
- Violante, A., C. Colombo, and A. Buondonno. 1991. Competitive adsorption of phosphate and oxalate by aluminum oxides. *Soil Sci. Soc. Am. J.* 55: 65-70.

Chapter 8

Controlling Soil-Test Phosphorus and Degree of P Saturation with Acid Mine Drainage Floc

8.1. Introduction

Runoff from fields and manure-disposal sites of animal-feeding operations (Litke, 1999) is a major agricultural non-point source of P. Phosphorus in the agricultural runoff arises from the excessive build-up of soil-test P (STP) in the soil. Several studies report increased loss of soil P through runoff or leaching with increasing levels of STP (Daniel et al., 1993; Pote et al., 1996; Cox and Hendricks, 2000; McDowell et al., 2001). High STP levels cannot be lowered by crop removal over a short period of time (McCollum, 1991). Thus, fields that have accumulated excessive P, have the potential to lose P to the runoff or drainage water for a long time, even though they do not receive further application of manures or fertilizers. Therefore, those control measures that have a prompt response and help restore P sorption capacity of the soil are needed.

To estimate the risk of P pollution of surface waters, a number of approaches are employed (Beauchemin and Simard, 1999; Kleinman et al., 2000). One commonly used approach is the agronomic approach (Sharpley et al., 1996; Sims et al., 1999). It considers agronomically sufficient P level as an environmental threshold. Another promising approach, which has been used in the Netherlands, (Breeuwsma and Silva, 1992) relies on soil P sorption saturation or degree of phosphorus saturation (DPS). The DPS concept is based on the assumption that amorphous phases or oxalate-extractable fractions of Fe and Al are the reactive phases for P sorption. Thus, these phases control the release of P to the solution. DPS is expressed as the molar ratio of ammonium oxalate

extractable P to ammonium oxalate extractable Fe and Al (Eq. 2.1; Beauchemin and Simard, 1999; Kleinman et al., 2000).

Another approach for developing environmental thresholds for P is based on the actual behavior of soil P. This approach establishes threshold as a soil-test P level above which a soil has more tendency to lose P to the solution than it had if it were below that point (Kleinman et al., 2000). This point is commonly called 'change-point' (Heckrath et al, 1995).

This study was conducted to investigate the effect of using acid mine drainage (AMD) floc in reducing STP levels to environmentally safe levels in a short period of time. Acid mine drainage floc is rich in amorphous Fe and Al oxyhydroxides. Oxides of Fe and Al, especially amorphous materials, have great affinity for P. The second objective of this study was to examine the effect of AMD floc additions on degree of P saturation.

8.2. Materials and Methods

Four soils were used in this study. Top soils (0-5 cm) were collected. Two soils were Berks (loamy-skeletal, mixed, active, mesic, Typic Dystrudepts), one was Lindside (fine-silty, mixed, active, mesic, Fluvaquentic Eutrudepts), and one was Monongahela (fine-loamy, mixed, semiactive, mesic, Typic Fragiudults). These soils were collected from sites different from those collected for modeling and investigating P retention and release characteristics of some benchmark soils of West Virginia (Chapter 3 and 4). Some properties of these soils are listed in Table 8.1. Degree of P saturation of these soils was calculated by using α -value of 0.21. This α -value was decided based upon the sorption characteristics of inorganic P onto AMD floc (Chapter 5). Acid mine drainage

floc was collected from an AMD treatment facility at Omega Mine Project in Monongalia County of West Virginia. This AMD floc was generated by neutralization of AMD with lime. Total elemental composition and some other properties of the AMD floc are listed in Table 6.1.

The experiment had a completely randomized design. Amounts of AMD floc required to reduce the original DPS of the soils to 150, 80, 60, 40, 20, and 10 percent were weighed in triplicate. The weighed floc samples were mixed with distilled deionized water and were shaken for 24 hours on an end-over-end shaker to form slurries. Each soil was weighed in triplicate; 20 g of each soil was taken in each tube. The AMD floc slurries were then mixed with the soil samples. A total of 45 mL distilled de-ionized water was used for each sample for making slurry and mixing the slurry with the soil. The mixed samples were then incubated for 120 hours at 318K. Thereafter, the samples were taken out of incubation and 14 mL water was added to each sample. The samples were incubated again for 96 hours at 318K. The samples were air-dried, crushed and sieved through a 2mm sieve. The samples were then analyzed for CaCl_2 - extractable P, soil-test P (Mehlich-1 and Mehlich-3 P), ammonium oxalate extractable Fe, Al, and P, and P sorption capacity (PSC). CaCl_2 -extractable P was determined by shaking the soil with 0.01 M CaCl_2 solution (soil: solution ratio 1: 5) for 30 minutes. Mehlich-1 P was determined by shaking the soil with a solution (soil: solution ratio 1:5) 0.05 M in HCl and 0.0125M in H_2SO_4 for five minutes on a reciprocal shaker. Mehlich-3 P was determined by following the method proposed by Mehlich (1984). Ammonium oxalate extractable Fe, Al, and P were determined by the method described by Guo and Yost (1999). Elemental composition of the AMD floc was determined by digesting the floc with

hydrochloric-hydrofluoric-nitric acid mixture. All measurements were made on a Perkin-Elmer P400 Inductively Coupled Plasma Atomic Emission spectrophotometer. Statistical analyses were done by using JMP software (version 4.0.4) and PROC GLM (version 8.0) of SAS Institute Inc.

Table 8.1. Some relevant properties of the soils (0-5 cm) used for the study.

Property	Soil			
	Berks-I	Berks-II	Lindside	Monongahela
Sand (%)	62.2	48.2	6.9	19.0
Silt (%)	26.3	37.5	48.2	57.3
Clay(%)	11.5	23.7	44.9	23.7
pH	6.2	6.0	5.8	6.5
CaCl ₂ -P (mg L ⁻¹)	2.95	3.28	17.87	1.69
Mehlich-1 P (mg kg ⁻¹)	784	801	828	800
Mehlich-3 P (mg kg ⁻¹)	864	817	1287	735
Ammonium oxalate extractable Fe (mg kg ⁻¹)	1,343	2,809	5,083	2,079
Ammonium oxalate extractable Al (mg kg ⁻¹)	616	915	1,523	1,302
Ammonium oxalate extractable P (mg kg ⁻¹)	997	1,535	2,673	1,362
P sorption capacity (mg kg ⁻¹)	26	132	103	312
DPS (%) ($\alpha = 0.21$)	327	280	279	245

8.3. Results and discussion

8.3.1. Acid Mine Drainage Floc Additions and Degree of P Saturation

Though calculated (based upon ammonium oxalate extractable Fe+Al content of AMD floc) quantities of AMD floc were added to achieve various degrees of P saturation (DPS), actual DPS values did not always equal targeted DPS values (Table 8.2). Targeted DPS values were computed by using the sum of the ammonium oxalate extractable Fe and Al in the AMD floc added and the original content of ammonium oxalate extractable Fe and Al in the soil. Actual DPS values represent the values that were determined by extracting the soils after AMD floc addition for ammonium oxalate extractable Fe and Al. Actual DPS values were compared with targeted DPS values by using Dunnett's test (Table 8.4). At 150 percent target DPS value, except for Berks-I soil actual DPS values were significantly greater than the corresponding target DPS value of 150 per cent. At 80 per cent DPS level, the same trend was observed. At 60 percent DPS level, excepting Linside soil all soils had higher actual DPS values. However, at 40 percent or lower levels actual DPS values were comparable to the corresponding targeted DPS values. Analysis of variance (ANOVA) results (Table 8.3) suggested that a decrease in DPS was mainly brought by AMD floc additions. However, soil type modified the effect of AMD floc. Seemingly higher than targeted values of DPS at low levels of AMD floc addition suggested that upon addition to soil, amorphous phases of Fe and Al in the AMD floc reacted with soil components. Because of that their P retention capacity was lower than that observed for pure AMD floc. However, this may be an experimental artifact. High P content of the soils may have reduced the oxalate extractable Fe and Al (Bondietti et al., 1993).

Dissolution of amorphous phases by oxalate is a surface-controlled process (Chang and Matijevic, 1983). Certain anions capable of adsorbing specifically may inhibit dissolution of oxalate-extractable Fe and Al amorphous phases (Borggaard, 1991). Formation of calcium-oxalate complexes may also affect Fe and Al extraction by acidified ammonium oxalate (Beauchemin and Simard, 1999). Monongahela soil had a high amount of organic carbon and Lindside soil had the highest amount of soil-test P (Table 8.1). Lindside soil showed smaller decline in DPS with AMD additions than other soils at low levels of AMD floc addition. Higher P content of this soil (Table 8.1) interfered with the oxalate extraction of amorphous Fe and Al in this soil and thus caused a less decline in DPS. Therefore, comparative lower recovery of amorphous phases of Fe and Al at lower levels of AMD floc addition may have resulted in higher DPS. Anions capable of adsorbing specifically onto Fe and Al oxides inhibit transformation of amorphous Fe and Al oxides (Baltpurvins et al., 1996; Cornell et al., 1987). Thus, relatively lower recovery of Fe and Al oxides with oxalate cannot be due to the transformation of amorphous phases to crystalline phases.

8.3.2. Relationship between Degree of P Saturation and Soil-Test Phosphorus

8.3.2.1 Mehlich-1 P

With decrease in target DPS following AMD floc additions, Mehlich-1 P decreased significantly (Tables 8.2 and 8.5). When DPS was brought down to 150 percent, for each one percent decrease in DPS, Mehlich-1 P decreased at a rate of 1.3, 1.8, 2.9, and 2.4 mg kg⁻¹ in Berks-I, Berks-II, Lindside, and Monongahela soil, respectively (Table 8.5).

Table 8.2. Soil-test (Mehlich-1 and Mehlich-3) P, CaCl₂-extractable P, measured degree of P saturation (DPS), and P sorption capacity of the soils at different target DPS (calculated based upon the ammonium oxalate extractable Fe and Al added through acid mine drainage floc) levels.

Target DPS (%)	Wet floc added (g kg ⁻¹)	Measured DPS (%)	Mehlich-1 P (mg kg ⁻¹)	Mehlich-3 P (mg kg ⁻¹)	CaCl ₂ -extractable P (mg kg ⁻¹)	P sorption capacity (mg kg ⁻¹)
Berks-I soil						
327	0	327 [†]	783	864	2.95	26
150	41	154	546	606	0.46	265
80	105	88	344	274	0.12	756
60	150	64	252	164	0.10	1,026
40	240	42	128	45	0.08	1,581
20	511	21	30	10	0.03	2,934
10	1,053	10	7	5	0.03	3,853
Berks-II soil						
280	0	280	801	817	3.28	132
150	47	165	561	594	0.87	504
80	139	86	296	290	0.31	976
60	205	68	186	175	0.20	1,275
40	336	42	60	61	0.12	2,097
20	730	21	5	10	0.11	3,494
10	1,517	9	0.6	6	0.07	3,905
Lindside soil						
279	0	279	828	1,287	17.87	136
150	99	170	450	878	3.62	522
80	277	99	166	424	0.88	1,281
60	404	62	60	204	0.59	1,936
40	658	41	16	69	0.38	2,934
20	1,419	20	1.7	8	0.18	3,848
Monongahela soil						
245	0	245	800	735	1.69	312
150	44	171	576	522	0.52	563
80	128	98	322	256	0.15	1,017
60	188	72	185	128	0.10	1,499
40	308	41	35	29	0.07	2,369
20	667	22	5	6	0.06	3,512
10	1,386	10	0.5	3	0.05	3,923

[†] Each value is a mean of three replicates

Table 8.3. F values (from analysis of variance) for the effect of acid mine drainage floc additions on soil-test P (Mehlich-1 and Mehlich-3 P), CaCl₂-extractable P, P sorption capacity and measured degree of P saturation (DPS).

Source	Degrees of Freedom	F value [†]				
		Mehlich-1 P	Mehlich-3 P	CaCl ₂ -extractable P	P sorption capacity	DPS
Treatment	6	19463	24828	7539	7350	11183
Soil	3	514	2314	5931	437	18
Treatment-soil interaction	17	92	433	2835	38	65

[†] Probability > F was less than 0.0001 in all cases.

Table 8.4. Degrees of P saturation (DPS) based upon the ammonium oxalate extractable Fe, Al, and P in the soils after acid mine drainage (AMD) floc additions as compared to the DPS (target DPS) calculated from the amount of ammonium oxalate extractable Fe and Al added through AMD floc.

Target DPS (%)	Soil			
	Berks-I	Berks-II	Lindside	Monongahela
	Measured DPS (%)			
150	154	165 ^{*†}	170 [*]	171 [*]
80	88	86 [*]	99 [*]	98 [*]
60	64 [*]	68 [*]	62	72 [*]
40	42	42	41	41
20	21	21	20	22 [*]
10	10	9 [*]		10

† Values with * are significantly different at 5% level from the corresponding target DPS value.

Table 8.5. Decrease in Mehlich-1 P, Mehlich-3 P, CaCl₂-extractable P, and increase in P sorption capacity with per unit decrease in target degree of P saturation (DPS).

Range in target DPS	Soil			
	Berks-I	Berks-II	Lindsay	Monongahela
Decrease in Mehlich-1 P (mg kg ⁻¹) with one per cent decrease in DPS				
Control [†] -150	1.3	1.8	2.9	2.4
150-80	2.9	3.8	4.1	3.6
80-60	4.6	5.5	5.3	6.9
60-40	6.2	6.3	2.2	7.5
40-20	4.9	2.8	0.7	1.5
20-10	2.3	0.4		0.5
Decrease in Mehlich-3 P (mg kg ⁻¹) with one per cent decrease in DPS				
Control-150	1.5	1.7	3.2	2.2
150-80	4.7	4.3	6.5	3.8
80-60	5.5	5.8	11.0	6.4
60-40	6.0	5.7	6.8	5.0
40-20	1.8	2.6	3.1	1.2
20-10	0.5	0.4		0.3
Decrease in CaCl ₂ -extractable P (mg L ⁻¹) with one per cent decrease in DPS				
Control-150	0.014	0.019	0.110	0.012
150-80	0.005	0.008	0.039	0.005
80-60	0.001	0.006	0.015	0.003
60-40	0.001	0.004	0.011	0.002
40-20	0.003	0.001	0.010	0.001
20-10	0.000	0.004		0.001
Increase in P sorption capacity (mg kg ⁻¹) with one per cent decrease in DPS				
Control-150	1.4	2.9	3.0	2.6
150-80	7.0	6.7	10.8	6.5
80-60	13.5	15.0	32.8	24.1
60-40	27.8	41.1	49.9	43.5
40-20	67.7	69.9	45.7	57.2
20-10	91.9	41.1		41.1

[†] Degrees of P saturation (DPS) for control treatments of Berks-I, Berks-II, Lindsay, and Monongahela were 327, 280, 279, and 245 percent, respectively.

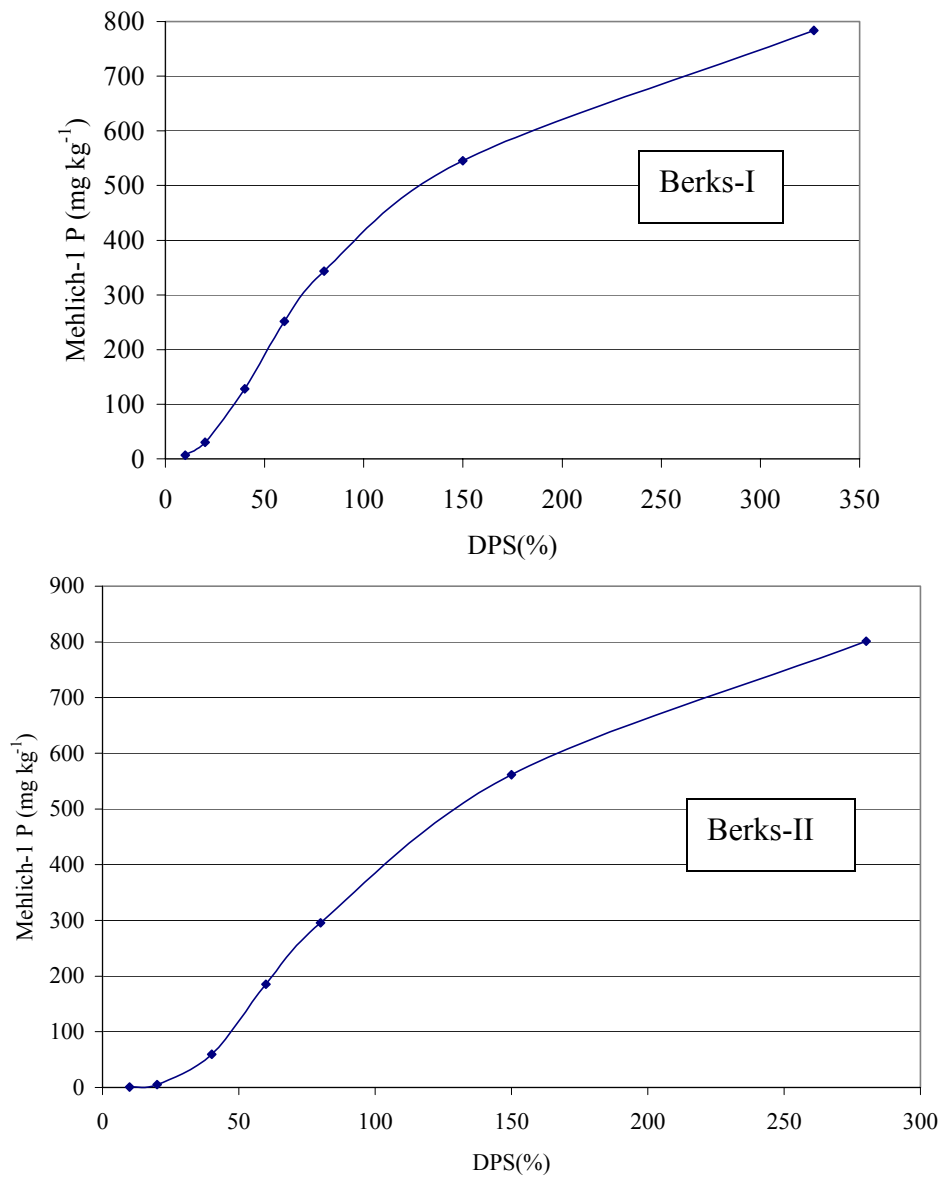


Figure 8.1. Relationship between degree of P saturation (DPS) and Mehlich-1 P in Berks-I and Berks-II soils.

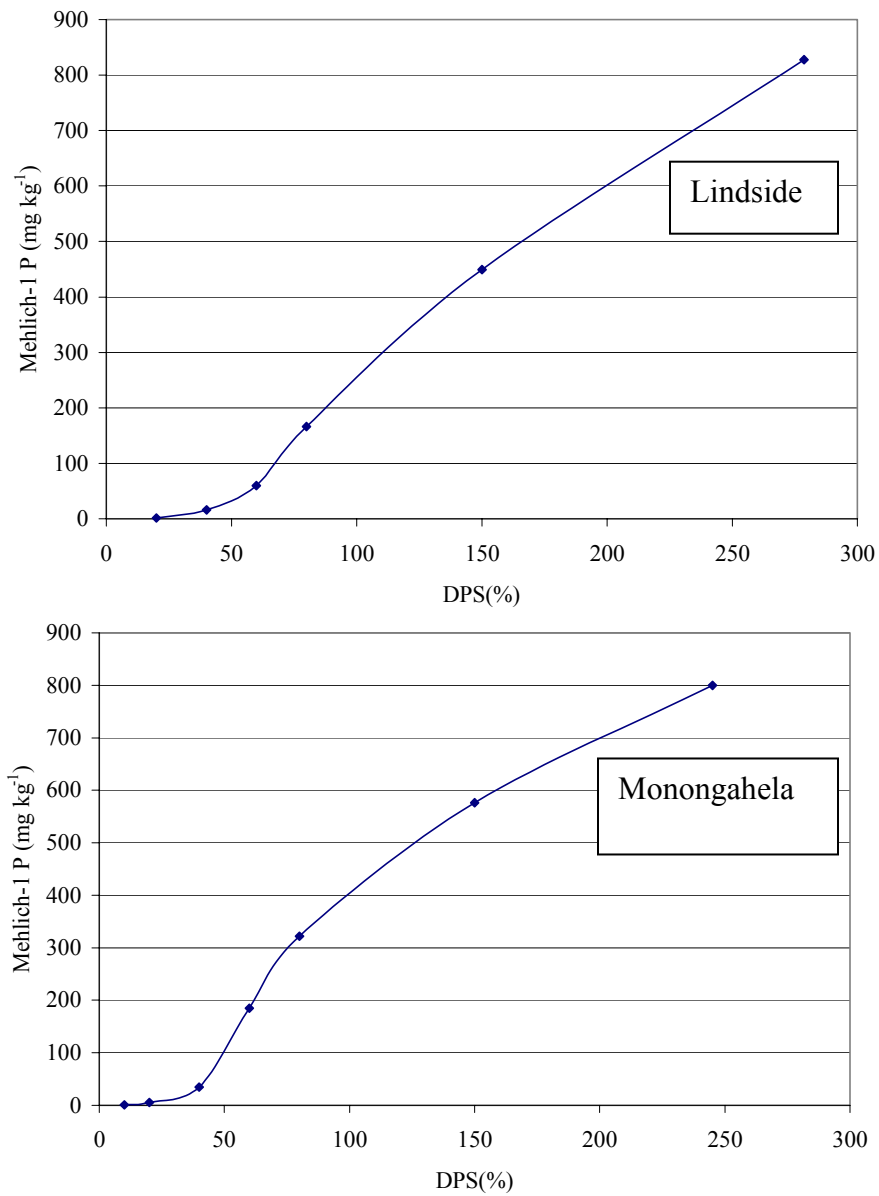


Figure 8.2. Relationship between degree of P saturation (DPS) and Mehlich-1 P in Lindside and Monongahela soils.

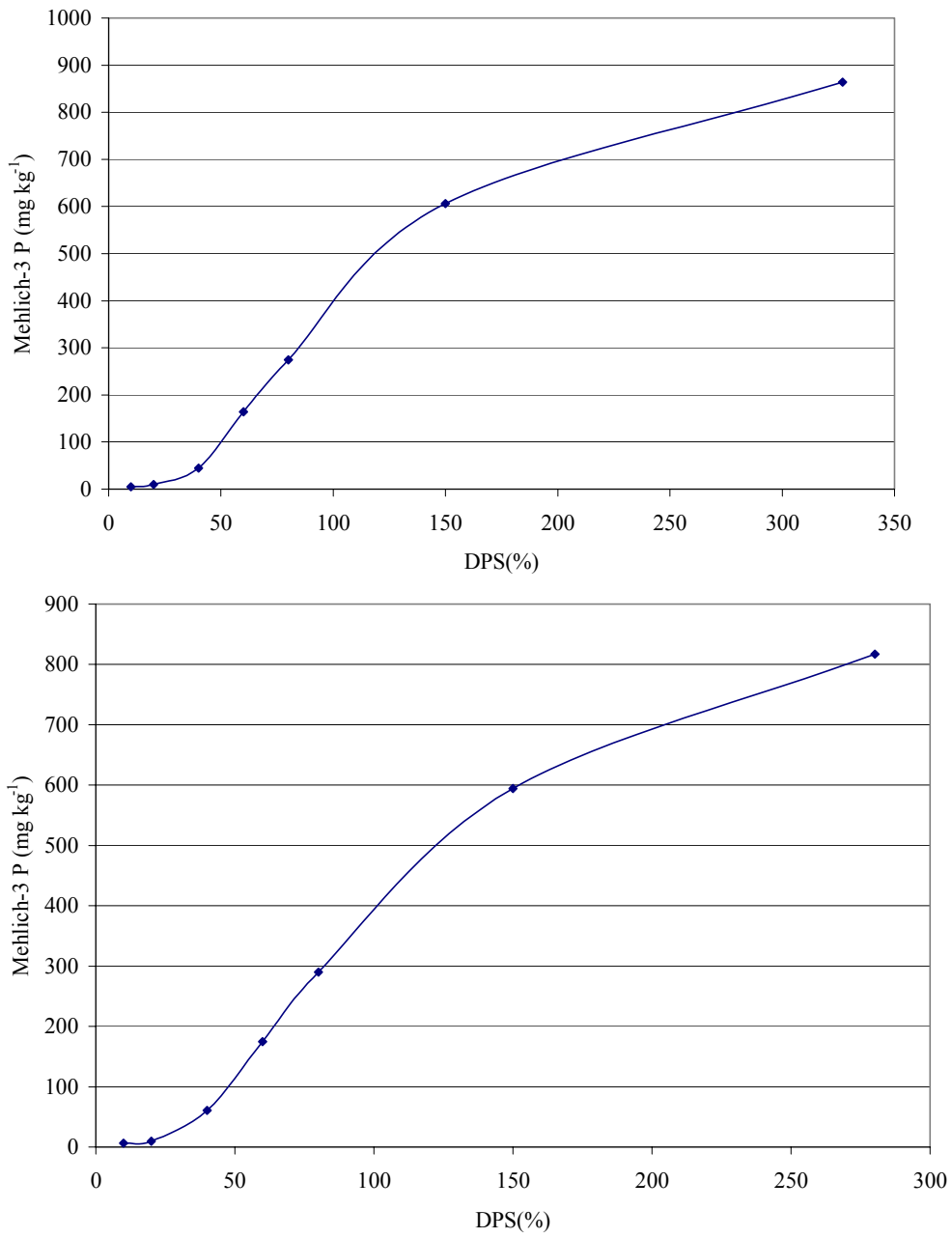


Figure 8.3. Relationship between degree of P saturation (DPS) and Mehlich-3 P in Berks-I and Berks-II soils.

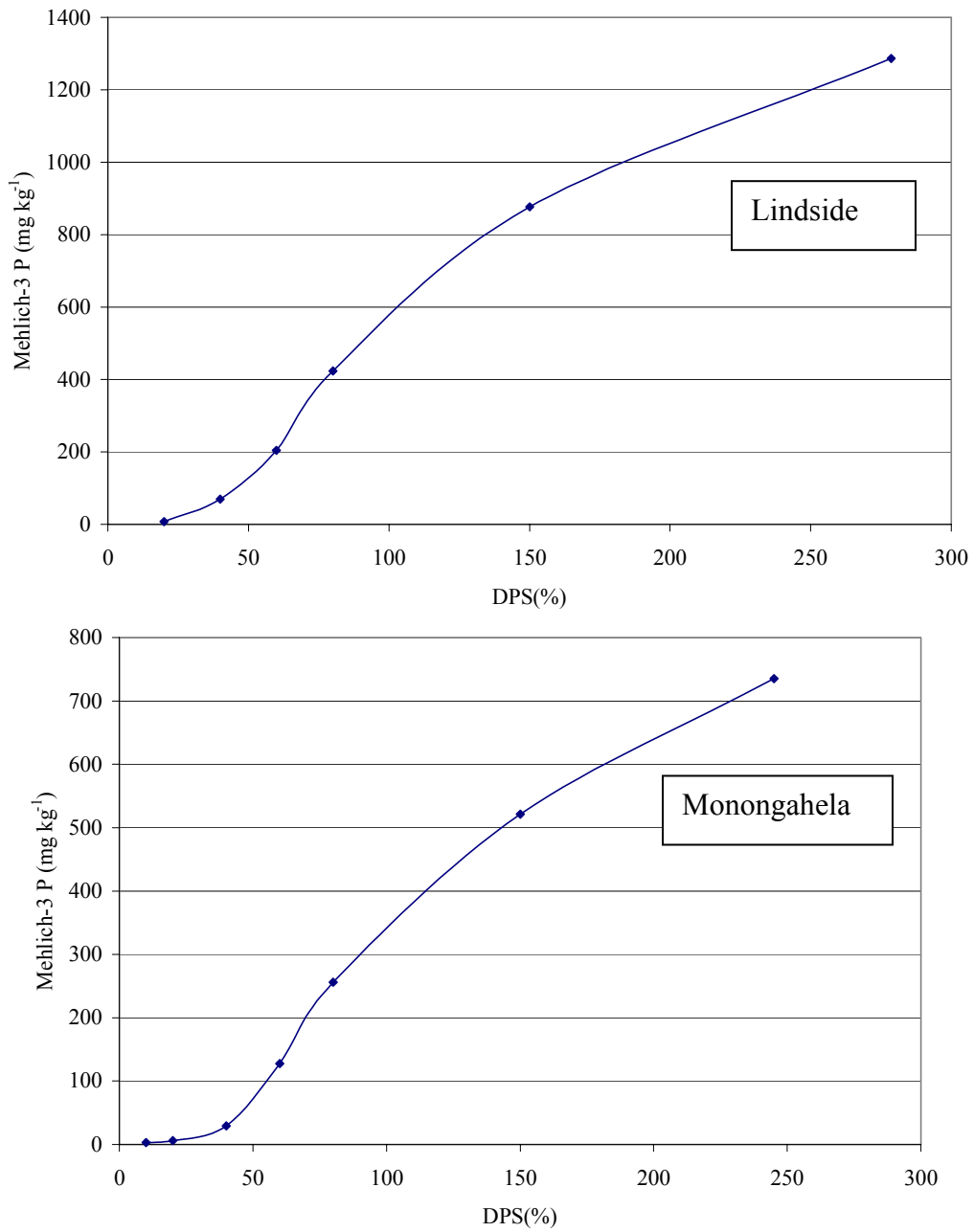


Figure 8.4. Relationship between degree of P saturation and Mehlich-3 P in Lindside and Monongahela soils.

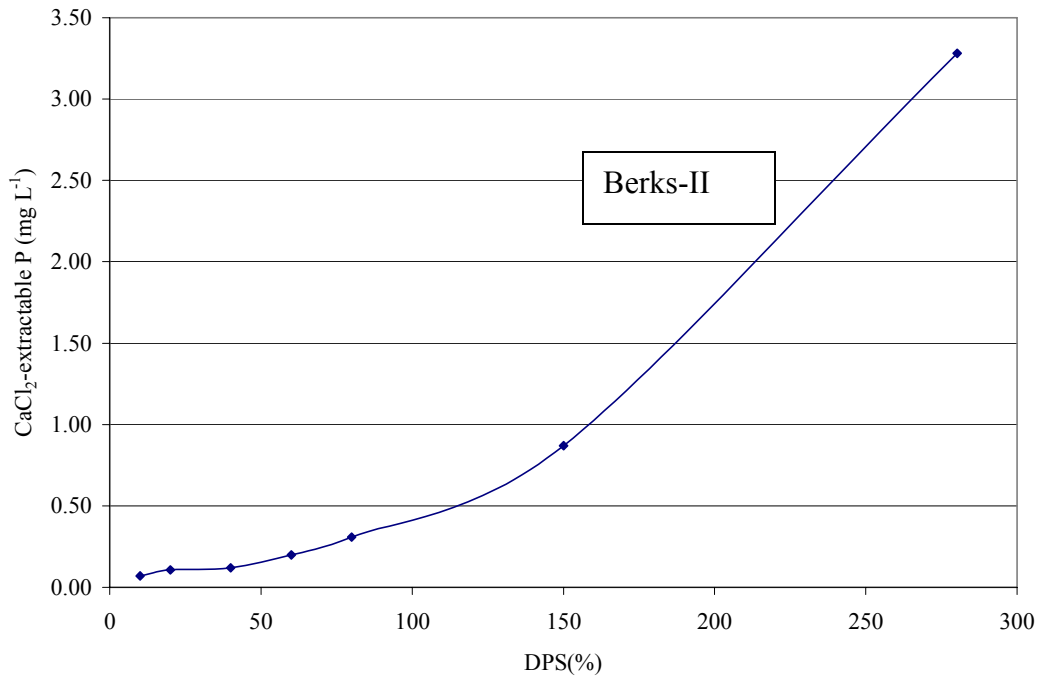
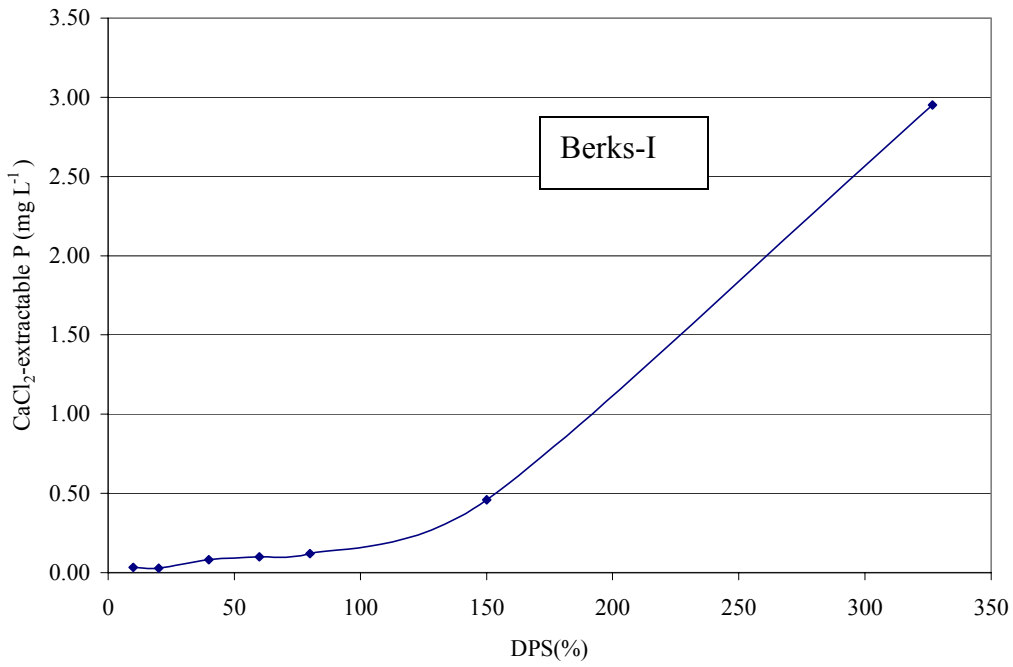


Figure 8.5. Relationship between CaCl₂-extractable P and degree of P saturation in Berks-I and Berks-II soils.

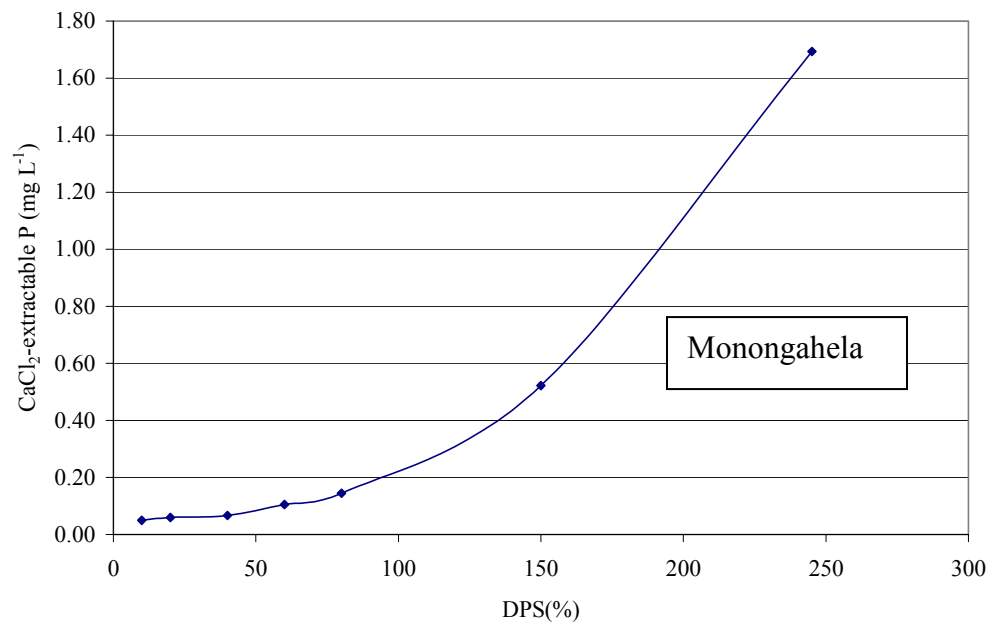
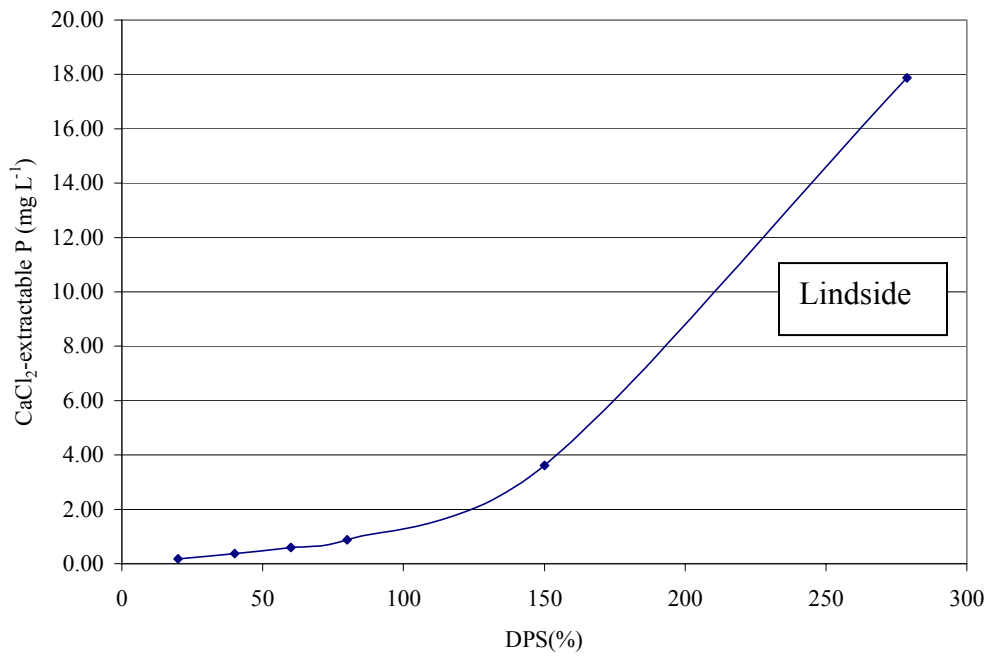


Fig. 8.6. Relationship between degree of P saturation (DPS) and CaCl₂-extractable-P in Lindside and Monongahela soils.

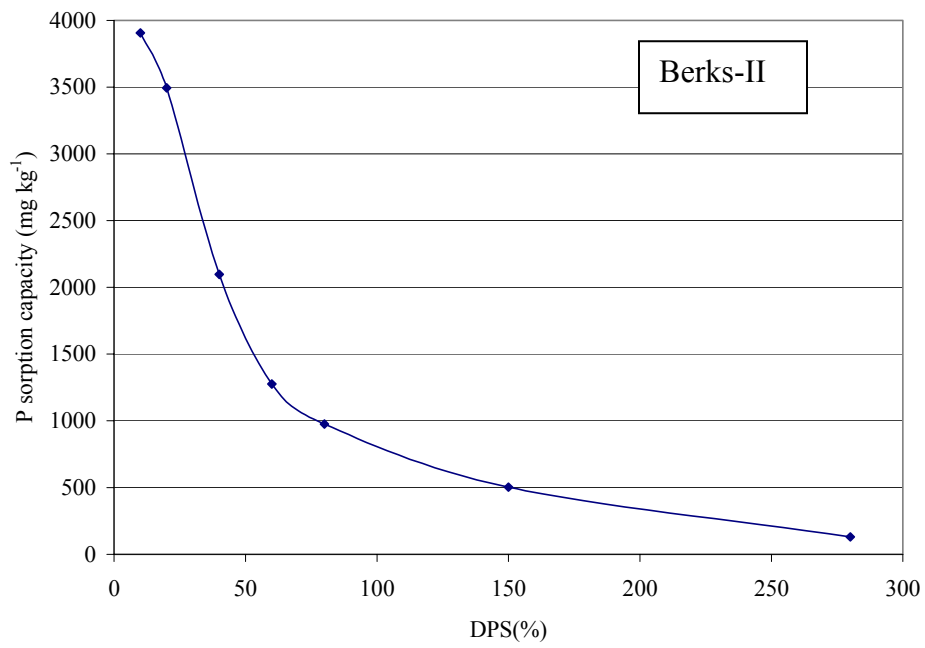
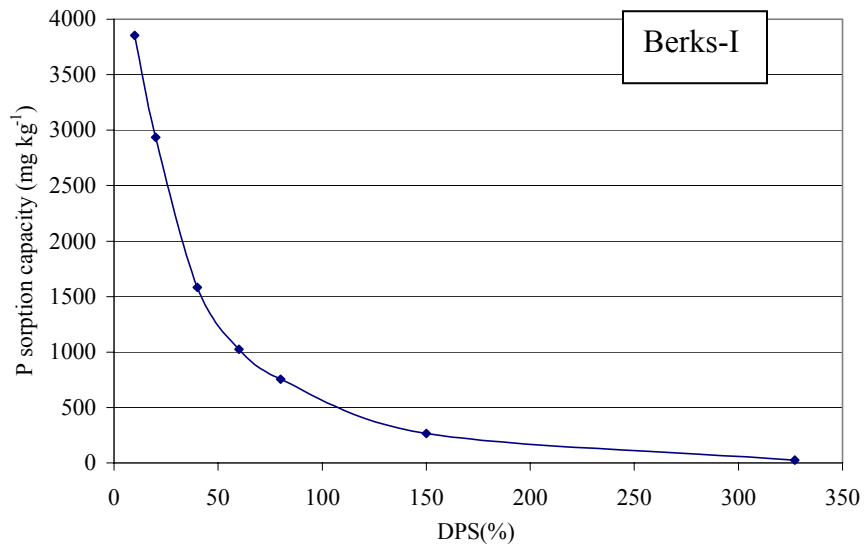


Fig. 8.7. Relationship between degree of P saturation and P sorption capacity in Berks-I and Berks-II soils.

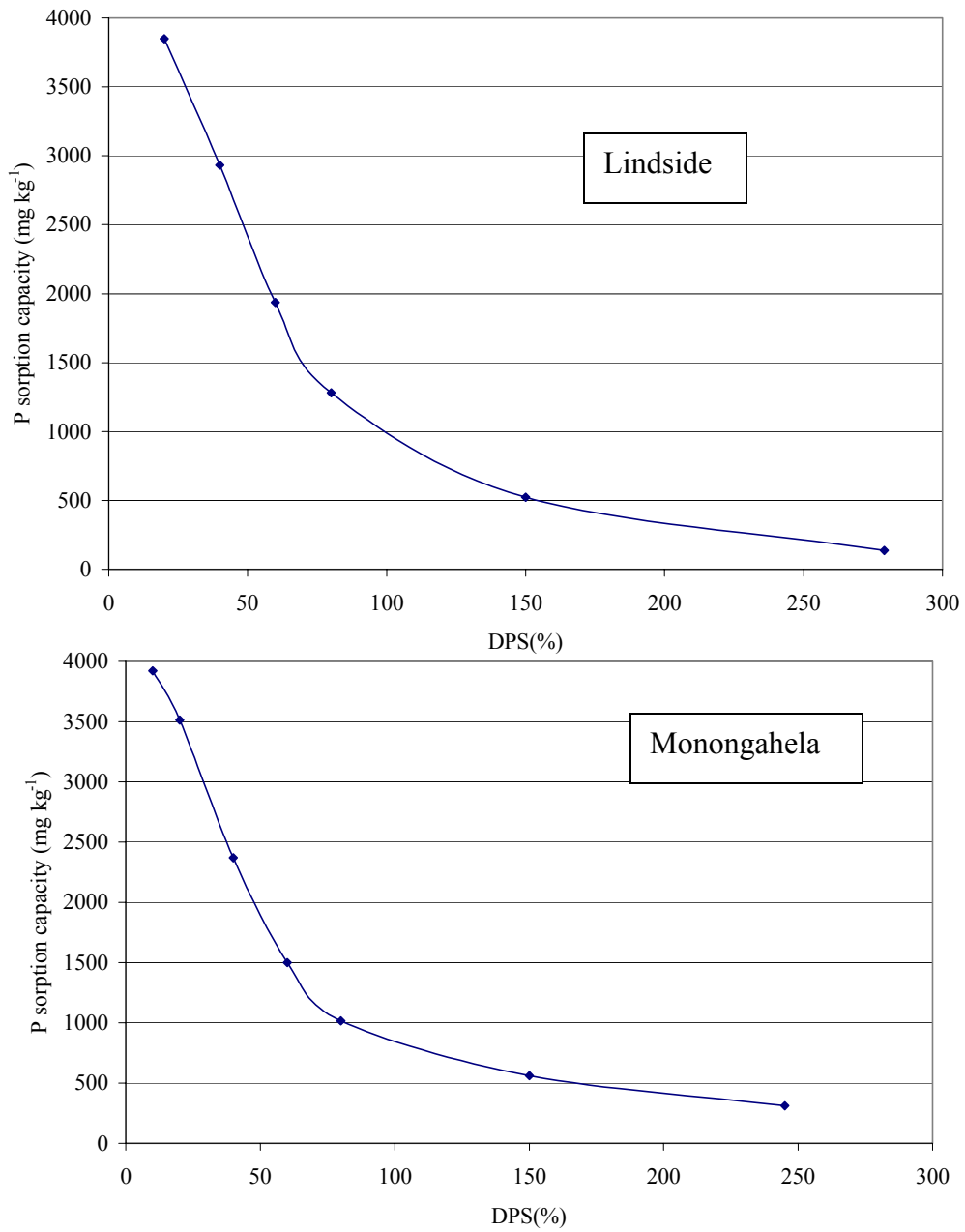


Figure 8.8. Relationship between degree of P saturation (DPS) and P sorption capacity in Lindside and Monongahela soils.

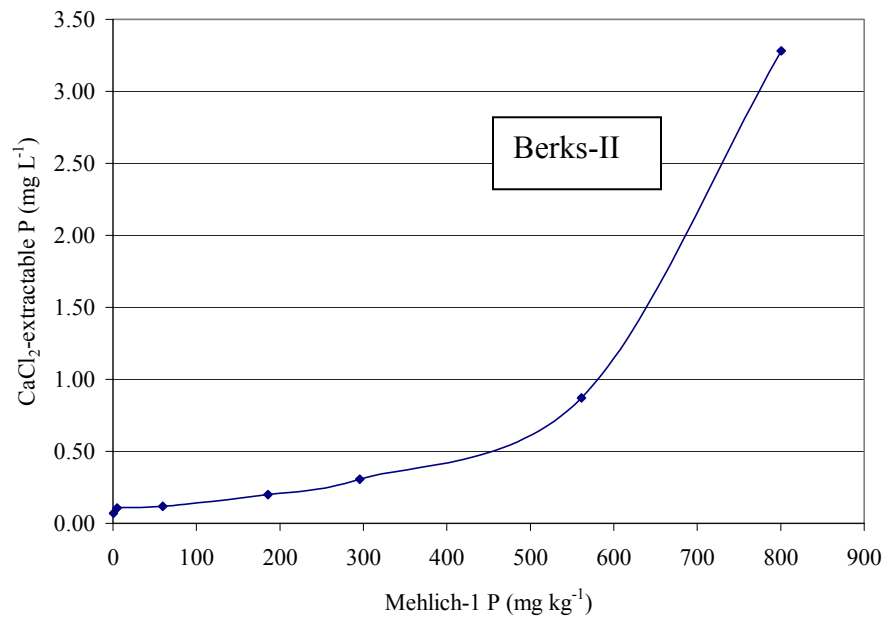
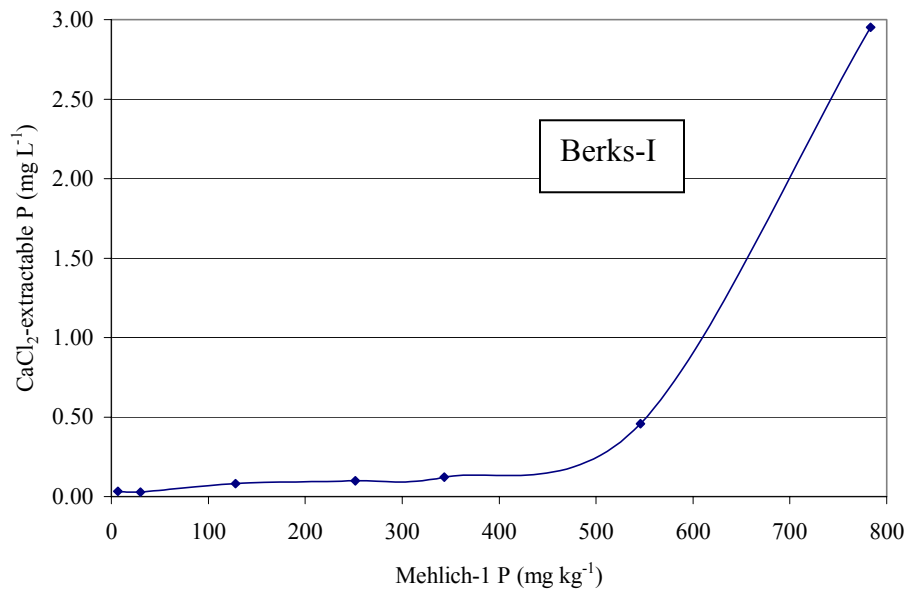


Figure 8.9. Relationship between Mehlich-1 P and CaCl₂-extractable P in Berks-I and Berks-II soils.

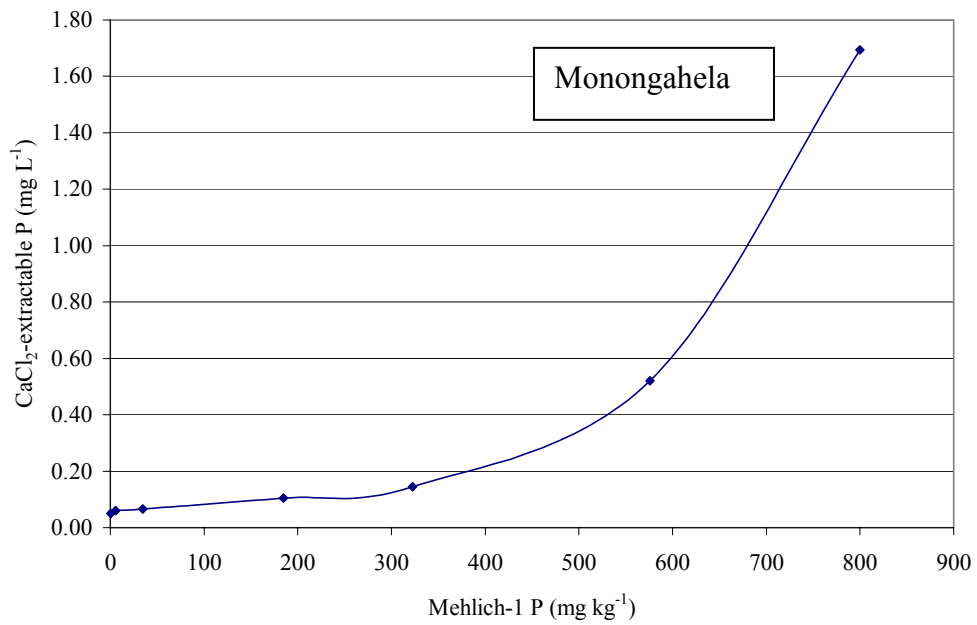
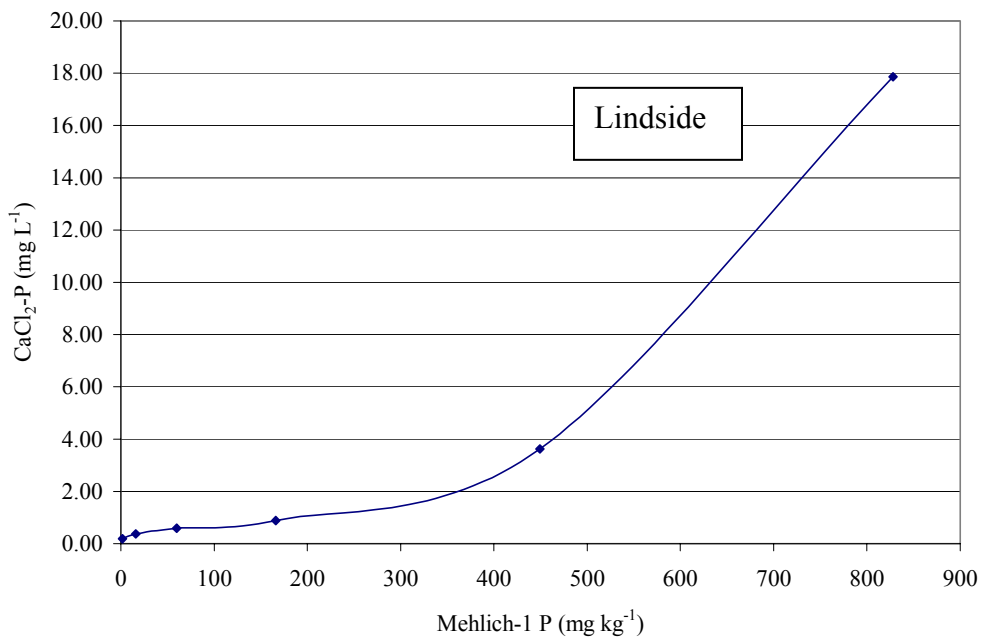


Figure 8.10. Relationship between Mehlich-1 P and CaCl₂-extractable P in Lindside and Monongahela soils.

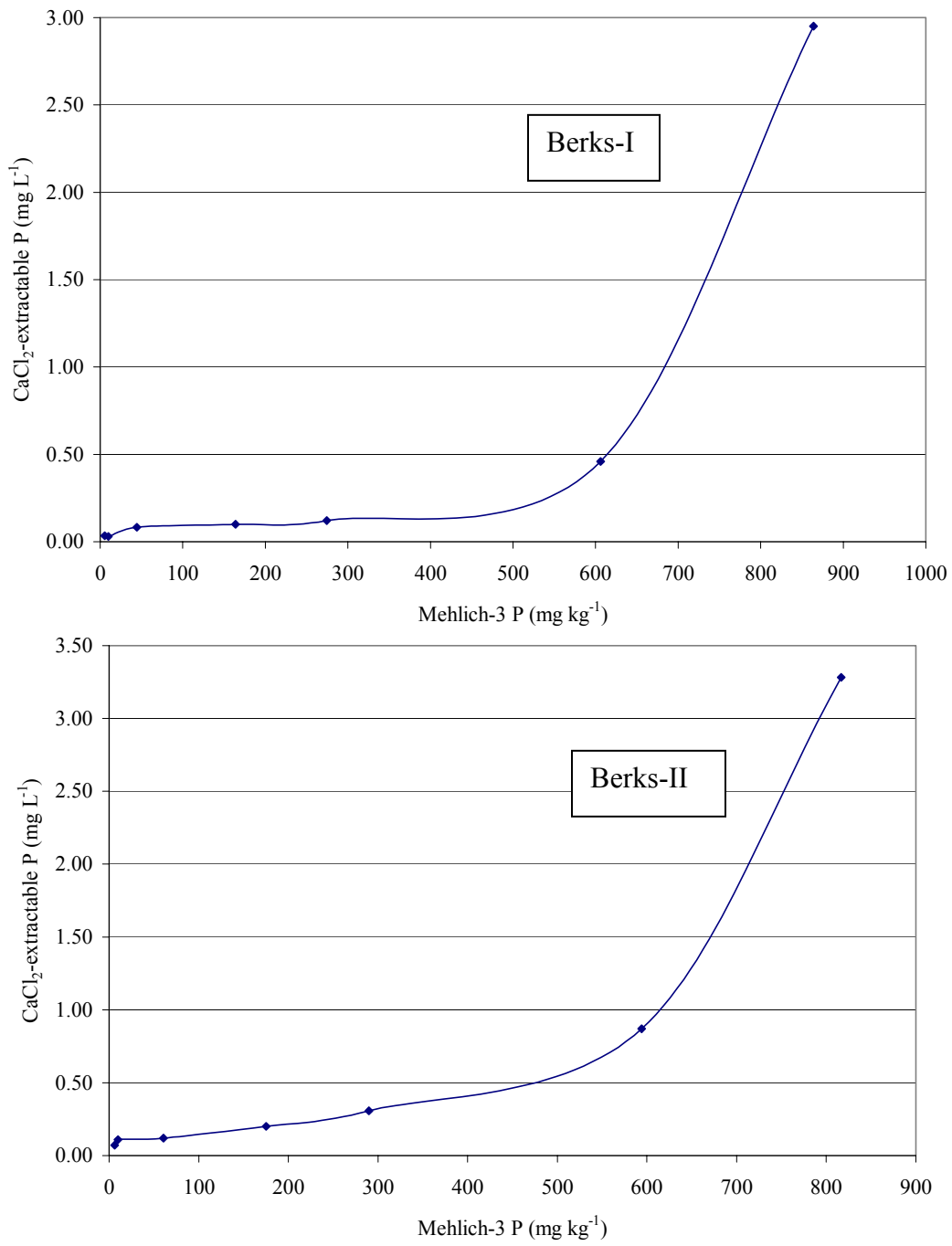


Figure 8.11. Relationship between Mehlich-3 P and CaCl₂-extractable P in Berks-I and Berks-II soils.

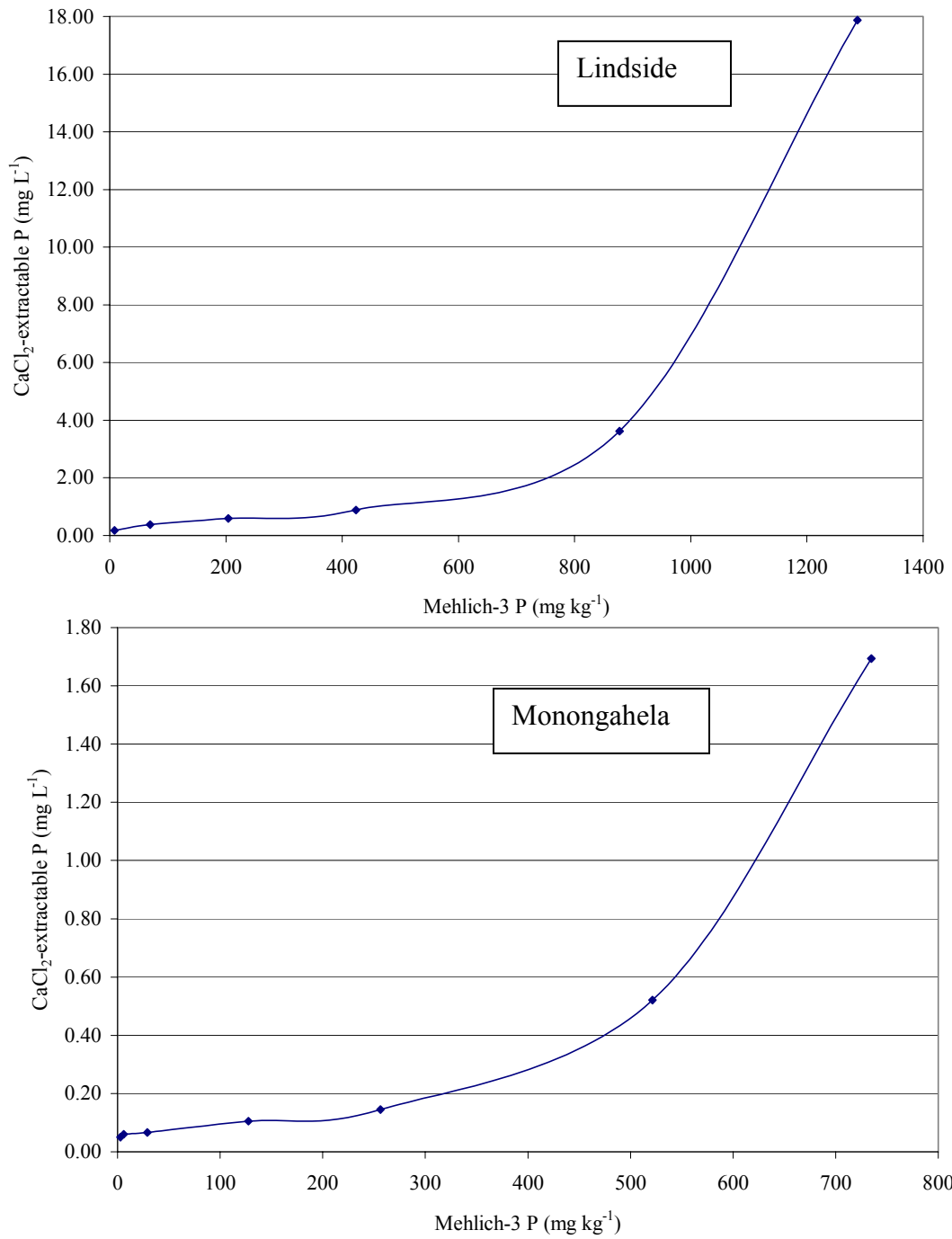


Figure 8.12. Relationship between Mehlich-3 P and CaCl₂-extractable P in Lindside and Monongahela soils.

However, when DPS was decreased down to 80 percent, the rates for the four soils were 2.9, 3.8, 4.1, and 3.6 mg kg⁻¹ in Berks-I, Berks-II, Lindside, and Monongahela soils. Therefore, in this range of DPS, the rate of decrease was higher. The rate of decline in Mehlich-1 P was the highest for most of the soils, when DPS was further lowered to 60 percent. These were 4.6, 5.5, 5.3, and 6.9 mg kg⁻¹ in Berks-I, Berks-II, Lindside, and Monongahela soils, respectively. However, when further additions of AMD floc were made to lower DPS from 60 to 40 percent, the respective rates of decrease in Mehlich-1 P with unit percent decrease in DPS went up to 6.2, 6.3, and 7.5 mg kg⁻¹ in Berks-I, Berks-II, and Monongahela soil, respectively. The rates were the lowest for the decline in DPS from 20 to 10 percent. These results signify the role of DPS in controlling Mehlich-1 P in soils. The results indicate that when soils are over-saturated with respect to P (DPS more than 100 per cent), P extractable with Mehlich-1 P solution is not intimately associated with amorphous phases of Fe and Al, but is associated with certain other phases, which are quite labile to dilute double acid solution. When amorphous materials of Fe and Al are added to the soil, only part of P associated with labile phases gets redistributed. This causes a decrease in Mehlich-1 P pool. Further additions of these materials continue decreasing Mehlich-1 P pool. However, when more of AMD floc is added, ratio of P to amorphous Fe+Al goes down sharply. At this stage, P forms strong complexes with surfaces of iron and aluminum oxides, which cannot be broken by the action of Mehlich-1 solution. The results also indicate that though the soils were brought to the same DPS values by adding calculated quantities of AMD floc, but the effects varied from soil to soil. Highly significant F-values ($P < 0.0001$, Table 8.3) for the soil factor and treatment-soil interaction effect hint that response of a particular soil depended upon the

level of addition of AMD floc also. For example, during decrease of DPS from 80 to 40 percent, through 60 percent, Lindside soil was not as responsive to AMD floc additions as were other soils. Plot of target DPS against Mehlich-1 P for all the soils (Figs. 8.1-8.2) reveal that in Berks-I and Berks-II soils the change-point (the point at which rate of increase in Mehlich-1 P with unit increase in DPS suddenly goes up) occurred at 20 percent DPS, whereas in Monongahela soil it was at 30 percent and in Lindside soil it was at 40 percent. These plots also suggest that excepting Lindside soil, all soils show the presence of three slopes in the relationship between DPS and Mehlich-1 P. Though the same model holds good for each soil, coefficients for the parameters differ greatly (Table 8.6). Different change-points associated with each soil show that amounts of AMD floc required to lower DPS and Mehlich-1 P will vary from soil to soil.

8.3.2.2. Mehlich-3 P

With decrease in DPS, Mehlich-3 P decreased with successive additions of AMD floc (Table 8.2). However, the decrease in Mehlich-3 P was not consistent throughout the entire range of DPS. When DPS was brought down to 150 percent, the rate of decrease of Mehlich-3 P with one percent decrease in DPS was, respectively, 1.5, 1.7, 3.2, and 2.2 mg kg⁻¹ in Berks-I, Berks-II, Lindside, and Monongahela soil (Table 8.5). When DPS was further lowered to 80 percent, the decline rates rose up to 4.7, 4.3, 6.5, and 3.8 mg kg⁻¹ in the same order. With further decrease in DPS from 80 percent to 60 percent, rates went up to 5.5, 5.8, 11.0, and 6.4 mg kg⁻¹ in the same order. However, upon subsequent additions of AMD floc decline rates of Mehlich-3 P went down. Plots of Mehlich-3 P versus DPS (Figs. 8.3-8.4) indicate that change-points occurred at 35, 20, 40, and 40 percent DPS, respectively, for Berks-I, Berks-II, Lindside, and Monongahela

soil. For Berks-II and Lindside soil the change-point for Mehlich-3 was the same as for Mehlich-1 P. However, in Berks-I and Monongahela soil, change-points for Mehlich-3 P were at a higher DPS than those for Mehlich-1 P. Like Mehlich-1 P, dependence of Mehlich-3 P on DPS is best predicted by an equation that is polynomial in fourth degree of DPS (Table 8.6). This relation explains more than 99 percent variation in Mehlich-3 P. Analysis of variance results for the different factors (Table 8.3) suggested that soil type modified the effect of AMD floc additions.

8.3.2.3. Degree of P saturation and CaCl₂-extractable P

CaCl₂-extractable P is often suggested for use as an index of P that can be lost through surface runoff or subsurface drainage (McDowell and Sharpley, 2001). When DPS decreased due to AMD floc additions, CaCl₂-extractable P also decreased (Table 8.2). When DPS was lowered to 150 per cent, with one per cent decline in DPS CaCl₂-extractable P declined by 14, 19, 110, and 12 µg L⁻¹ in Berks-I, Berks-II, Lindside, and Monongahela soil, respectively (Table 8.5). However, the rate of decrease in CaCl₂-extractable P was the highest in this range. Subsequent reductions in DPS did not reduce the rate of decrease of CaCl₂-extractable P. Very high levels of CaCl₂-extractable P were observed in Lindside soil as compared to other soils, though it had a comparable level of Mehlich-1 P. Sharpley et al. (2001) reported that in recently fertilized soil, dissolved P concentration in runoff may not be related to soil-test P. However, in their study this observation has been made for the relation between Mehlich-3 P and dissolved P in the runoff. But, Lindside soil had far higher levels of Mehlich-3 P. Therefore, our results showed a dependence between Mehlich-3 P and CaCl₂-extractable P, but not between Mehlich-1 P and CaCl₂-extractable P. Plots of DPS versus CaCl₂-extractable P indicate

that change-point for CaCl₂-extractable P occurred at higher DPS values as compared to the change-point for either Mehlich-1 P or Mehlich-3 P (Figs.8.5-8.6). It was present at 125, 120, 125, and 80 percent DPS, respectively in Berks-I, Berks-II, Lindside, and Monongahela soil. McDowell et al. (2001), however, reported a change-point range of about 65-85 percent (adjusted for differences in α -value; they used α -value of 0.5) in CaCl₂-extractable P and DPS relationship. In general, differences among soils indicate that any two soils may be similar in STP or DPS values, but they may have different amounts of P that can be released to solution. F-values in Table 9.3 also emphasize the importance of soil type in controlling DPS-CaCl₂-extractable P relationship. A comparison of these values with those for Mehlich-1 and Mehlich-3 P shows that soil type determines the CaCl₂-extractable P concentrations. Plots of DPS versus CaCl₂-extractable P also show that unlike in the case of Mehlich-1 P and Mehlich-3 P, CaCl₂-extractable P and DPS relationship has mainly two slopes (Figs.8.5-8.6). More than 99 percent variation in CaCl₂-extractable P can be explained by a quadratic equation (Table 8.6).

8.3.2.4. Degree of P Saturation and P Sorption Capacity

With decrease in DPS, P sorption capacity increased in all the soils (Table 8.2). When DPS was lowered to 150 percent, the rate of increase in PSC with one percent decrease in DPS was marginal (Table 8.5). It was 1.4, 2.9, 3.0, and 2.6 mg kg⁻¹ in Berks-I, Berks-II, Lindside, and Monongahela soil, respectively (Table 8.5). With subsequent decrease in DPS, rates of increase in P sorption capacity went up till 10 percent DPS in Berks-I soil, till 20 percent DPS in Monongahela and Berks-II soils, and till 40 percent DPS in Lindside soil. Plots of DPS versus P sorption capacity show that this relation, like

other relations such as between DPS and Mehlich-1 P, Mehlich-3 P, and CaCl₂-extractable P, is characterized by at least two different slopes (Figs. 8.7-8.8). These changes occurred at 50, 60, 70, and 65 percent DPS, respectively in Berks-I, Berks-II, Lindside, and Monongahela soil. F-values (Table 8.3) hint that P sorption capacity was mainly affected by AMD floc additions. Soil type did modify the effect or the effect of soil varied with the level of AMD floc, but these effects were not comparable to the main treatment effects. Regression results (Table 8.6) show that except for the direction of the relation, P sorption capacity is related to DPS in the same way as are Mehlich-1 P and Mehlich-3 P related to DPS. A polynomial that is fourth degree in DPS can explain more than 99% variation in the P sorption capacity.

8.3.3. Relationships between Soil-Test P and CaCl₂-extractable P

Plots of Mehlich-1 P versus CaCl₂-extractable P show that change-points for Berks-I, Berks-II, Lindside, and Monongahela soils were at Mehlich-1 P concentration of 490, 450, 400, and 400 mg kg⁻¹, respectively (Figs. 8.9-8.10).

Plots of relationships between Mehlich-3 P and CaCl₂-extractable P reveal that change-points occurred at Mehlich-3 P concentrations of 550, 540, 820, and 450 mg kg⁻¹ in Berks-I, Berks-II, Lindside, and Monongahela soil, respectively (Figs. 8.11-8.12).

Table 8.6. Regression coefficients for the relations of Mehlich-1 P, Mehlich-3 P, CaCl₂-extractable P, and P sorption capacity with degree of P saturation (DPS) for various soils.

	Soil				
	Berks-I	Berks-II	Lindside	Monongahela	All soils
Mehlich-1 P (mg kg ⁻¹)					
Intercept	-18.7 ^{NS}	25.6 [*]	89.8 ^{**}	67.5 ^{**}	-43.8 [*]
DPS	1.4 ^{NS}	-4.1 ^{**}	-7.2 ^{**}	-8.5 ^{**}	2.6 ^{**}
(DPS) ²	0.08 ^{**}	0.17 ^{**}	0.16 ^{**}	0.27 ^{**}	0.02 ^{NS}
(DPS) ³	-6.0E-04 ^{**}	-1.1E-03 ^{**}	-9.0E-04 ^{**}	-1.8E-03 ^{**}	-1.0E-04 ^{NS}
(DPS) ⁴	1.1E-06 ^{**}	2.0E-06 ^{**}	2.0E-06 ^{**}	4.0E-06 ^{**}	9.6E-8 ^{NS}
R ²	0.9988	0.9993	0.9993	0.9988	0.9699
Lack of fit	*	*	**	**	NS
Mehlich-3 P (mg kg ⁻¹)					
Intercept	37.1 ^{**}	31.8 ^{**}	149.6 ^{**}	58.3 ^{**}	-41.0 ^{NS}
DPS	-4.4 ^{**}	-4.0 ^{**}	-13.2 ^{**}	-6.8 ^{**}	1.9 ^{NS}
(DPS) ²	0.153 ^{**}	0.155 ^{**}	0.353 ^{**}	0.201 ^{**}	0.039 ^{NS}
(DPS) ³	-1.0E-03 ^{**}	-9.5E-04 ^{**}	-2.1E-03 ^{**}	-1.3E-03 ^{**}	-2.0E-04 ^{NS}
(DPS) ⁴	1.0E-05 ^{**}	2.0E-06 ^{**}	4.0E-06 ^{**}	3.0E-06 ^{**}	1.8E-7 ^{NS}
R ²	0.9995	0.9992	0.9996	0.9991	0.9142
Lack of fit	**	NS	**	**	**
CaCl ₂ -extractable P (mg L ⁻¹)					
Intercept	0.084 ^{**}	0.111 ^{**}	0.875 ^{**}	0.093 ^{**}	-0.202 ^{NS}
DPS	-2.4E-03 ^{**}	-1.6E-03 [*]	-2.7E-02 ^{**}	-2.4E-03 ^{**}	5.3E-03 ^{NS}
(DPS) ²	3.4E-05 ^{**}	4.6E-04 ^{**}	3.2E-04 ^{**}	3.6E-05 ^{**}	6.0E-05 ^{NS}
R ²	0.9974	0.9968	0.9986	0.9943	0.3823
Lack of fit	NS	NS	**	NS	**
P sorption capacity (mg kg ⁻¹)					
Intercept	5133 ^{**}	4861 ^{**}	4771 ^{**}	4572 ^{**}	4816 ^{**}
DPS	-142.1 ^{**}	-90.6 ^{**}	-41.7 ^{**}	-60.2 ^{**}	-86.6 ^{**}
(DPS) ²	1.66 ^{**}	0.64 [*]	-0.26 ^{NS}	0.08 ^{NS}	0.63 ^{**}
(DPS) ³	-0.008 ^{**}	-0.002 ^{NS}	0.004 [*]	0.002 ^{NS}	-0.002 ^{**}
(DPS) ⁴	1.0E-05 ^{**}	2.0E-06 ^{NS}	-8.0E-06 ^{**}	-1.0E-05 [*]	2.0E-06 ^{**}
R ²	0.9987	0.9930	0.9979	0.9970	0.9539
Lack of fit	NS	**	NS	**	NS

† Parameter coefficients and lack of fit with * are significant at 5% level, those with ** are significant at 1% level, and those with NS are not significant at either level.

However, McDowell et al. (2001) reported a range of 120-190 mg kg⁻¹ Mehlich-3 P in three different soils. These values clearly differ from those reported in this study. Our data show that soils of the Eastern Panhandle of West Virginia have a higher P retention capacity and thus have less potential to release P to the environment.

8.4. Conclusions

Acid mine drainage floc was highly effective in lowering DPS values of the four different soils. With decrease in DPS levels, Mehlich-1 P, Mehlich-3 P, and CaCl₂-extractable P levels also decreased, and P sorption capacity levels increased. When DPS levels were plotted against Mehlich-1 P levels, change-points were observed in the range of 20-40 percent DPS. For Mehlich-3 P, the same range was observed. However, for CaCl₂-extractable P, change-points were present at higher DPS values (80-125 percent). The relationship between CaCl₂-extractable P and STP showed some distinct change-points. The results showed that high STP levels in the soils could be reduced in a short period of time by addition of AMD floc to the soil. However, before embarking on this remediation strategy it is important to evaluate P sorption-desorption properties of the target soils and to form homogeneous groups of soils, because soil-type greatly modifies the effect of AMD floc additions on soil-test P and soluble P.

References

- Baltpurvins, K.A., R.C. Burns, and G. A. Lawrence. 1996. Effect of pH and anion type on the aging of freshly precipitated iron (III) hydroxide sludges. *Environ. Sci. Technol.* 30: 939-944.
- Beauchemin, S, and R.R. Simard. 1999. Soil phosphorus saturation degree: Review of some indices and their suitability for P management in Quebec, Canada. *Can. J. Soil Sci.* 79: 615-625.

- Bondietti, G., J. Sinniger, and W. Stumm. 1993. The reactivity of Fe (III) (hydr) oxides: effect of ligands in inhibiting the dissolution. *Colloids and Surfaces A* 79: 157-167.
- Borggaard, O.K. 1991. Effects of phosphate on iron oxide dissolution in ethylenediamine -N, N, N', N'- tetraacetic acid and oxalate. *Clay Clay Miner.* 39: 324-328.
- Breeuwsma, A., and S. Silva. 1992. Phosphorus fertilization and environmental effects in The Netherlands and Po region (Italy). Report 57. Agric. Res. Dept. The Winand Staring Centre for Integrated Land, Soil, and Water Research. Wageningen, The Netherlands.
- Chang, H. -C, and E. Matijevic. 1983. Interactions of metal hydrous oxides with chelating agents. IV. Dissolution of hematite. *J. Colloid Interface Sci.* 92: 469-478.
- Cornell, R.M., R. Giovanolli, and P.W. Schindler. 1987. *Clay Clay Miner.* 35: 21-28.
- Cox, F.R., and S.E. Hendricks. 2000. Soil test phosphorus and clay content effects on runoff water quality. *J. Environ. Qual.* 29: 1582-1586.
- Daniel, T.C., D. R. Edwards, and A.N. Sharpley. 1993. Effect of extractable soil surface phosphorus on runoff water quality. *Trans. ASAE* 36: 1079-1085.
- Galvez, N., V. Barron, and J. Torrent. 1999. Effect of phosphate on the crystallization of hematite, goethite, and lepidocrocite from ferrihydrite. *Clays Clay Miner.* 47: 304-311.
- Guo, F., and R.S. Yost. 1999. Quantifying the available soil phosphorus pool with the acid ammonium oxalate method. *Soil Sci. Soc. Am. J.* 63: 651-656.
- Heckrath, G., P.C. Brookes, P.R. Poulton, and K.W.T. Goulding. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadwalk experiment. *J. Environ. Qual.* 24: 904-910.
- Kleinman, P.J.A., R.B. Bryant, and W.S. Reid. 2000. Using soil phosphorus behavior to identify environmental thresholds. *Soil Sci.* 165: 943-950.
- Litke, D.W., 1999. Review of phosphorus control measures in the United States and their effects on water quality. Water-resources investigation report 99-4007. National Water-Quality Assessment Program. United States Geological Survey, Denver, Colorado.
- McCollum, R.E. 1991. Build up and decline in soil phosphorus: 30-year trends in a Typic Umprabuult. *Agron. J.* 83: 77-85.

- McDowell, R.W, and A.N. Sharpley. 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. *J. Environ. Qual.* 30: 508-520.
- McDowell, R., A.N. Sharpley, P.C. Brookes, and P.R. Poulton. 2001. Relationship between soil test phosphorus and phosphorus release to solution. *Soil Sci.* 166: 137-149.
- Mehlich, A. 1984. Mehlich-3 extractant: a modification of Mehlich-2 extractant. *Commun. Soil Sci. Plant Anal.* 15: 1409-1416.
- Pote, D.H., T.C. Daniel, A.N. Sharpley, P. A. Moore, Jr., D.R. Edwards, and D.J. Nichols. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 60: 855-859.
- Schindler, D.W. 1975. Whole-lake eutrophication experiments with nitrogen, phosphorus, and carbon: *Verhandlungen Internationale Vereinigung Limnologie* 19: 3221:3231.
- Sharpley, A.N., T.C. Daniel, J.T. Sims, and D.H. Pote. 1996. Determining environmentally sound phosphorus levels. *J. Soil Water Conserv.* 51: 160-166.
- Sharpley, A.N., R.W. McDowell, J.L. Weld, and P.J.A. Kleinman. 2001. Assessing site vulnerability to phosphorus loss in an agricultural watershed. *J. Environ. Qual.* 30: 2026-2036.
- Sims, J.T. 1999. The role of soil testing in environmental risk assessment for phosphorus. *In Agriculture and phosphorus management: The Chesapeake Bay.* A. N. Sharpley (ed.) Lewis Publishers, Boca Raton, Fl. pp. 57-81.

Chapter 9

Summary and Conclusions

Excess phosphorus (P) causes eutrophication of surface waters. Eutrophication of most of the fresh waters around the world is accelerated by P inputs. Agricultural runoff is the largest non-point source of P to natural waters. Phosphorus in agricultural runoff arises from the excessive build-up of soil-test P. The rise in soil-test P generally results from the improper land-application of animal wastes and relatively meager crop-uptake of P. Poultry manures are the most important source of excessive P in soils. Most of the organic P in poultry manures is inositol hexaphosphate (IHP)-P. Surface runoff from soils is the predominant pathway of P loss from soils; but losses through subsurface runoff also are considerable in many soils, especially in well-drained soils. Site-specific data on P retention and release characteristics are not routinely available. These can be potentially predicted based upon the characterization data routinely collected from different soils for soil classification purposes. The large P retention capacity of acid mine drainage (AMD) floc may help attenuate inorganic-P and IHP-P in the solution or in the soil and hence reduce high soil-test P levels to safe levels in a short period of time.

Specific objectives of the present study were to investigate and predict P sorption characteristics of some benchmark soils of West Virginia, examine the effect of various AMD flocs, resulting from the use of various chemicals used to neutralize AMD, on the sorption of organic (inositol phosphates) and inorganic P, and explore the possibility of using AMD floc for effecting rapid decline in soil-test P levels.

P retention and release characteristics of surface and subsurface horizons of four benchmark soil series of West Virginia, Berks, Huntington, Lindside, and Monongahela

were assessed by evaluating P sorption capacity (PSC) and effect of different P loadings on the dissolved P concentrations. Berks soils are well drained soils and most pasture lands in the poultry producing area of West Virginia are located on these soils. It is postulated that P in these soils will be lost via subsurface flow; however, the subsurface horizons in these soils had considerable P fixation capacity. P sorption capacities were the highest for Btx horizons of Monongahela soils. These horizons are called fragipans. Fragipans have high bulk density and slow permeability. Though these fragipans have very high PSC, this capacity is not available for attenuation of P in the excessively manured fields. In soils with fragipans, P containing leachate tends to by-pass such horizons and it flows through certain preferential paths.

Effect of degree of P saturation (DPS) on concentration of dissolved (leachable) P showed that in Berks A horizons a DPS of 40% produced most leachate with dissolved concentration of less than 1 mg L^{-1} . Dissolved P in the Monongahela A horizons never exceeded 1 mg L^{-1} , even when DPS was 60%. B horizons of the Monongahela soils had very high P fixation capacities, and released very little dissolved P concentrations at a DPS of 60%. Practical implications of these results are that even when these soil horizons have a DPS of 60% they still act as a potential sink for P.

For A horizons of Berks soils there was a wide range in the dissolved P concentrations for a given soil-test P value. However, in the B horizons of the same soil, dissolved P concentrations never exceeded 0.5 mg L^{-1} . In A horizons of Huntington soil series dissolved P concentrations rarely exceeded 1.0 mg L^{-1} when soil-test values were less than 150 mg kg^{-1} . In B horizons of this soil, there was a linear increase in dissolved P concentration with soil-test P. These results were very similar to those for Lindside soil.

Dissolved P concentrations in A horizons of all soils of Monongahela soil series other than Monongahela 3, never exceeded 1.0 mg L^{-1} . These results indicated that soils of the Eastern Panhandle of West Virginia are generally expected not to release considerable amounts of P to the environment through subsurface flow, even when they are loaded with high P amounts. Subsurface horizons of these soils have a considerable P attenuation capacity.

Phosphorus sorption capacity of the above-mentioned four benchmark soil series of West Virginia was predicted with various statistical modeling approaches by using the data collected on the following variables: ammonium oxalate-extractable Fe and Al; dithionite-citrate-bicarbonate Fe and Al phases; KCl-extractable Al and Mn; total carbon, extractable acidity; sum of cations like Na, Ca, Mg, and K along with H^+ ; ammonium acetate extractable Ca; clay content; and soil pH. A general comparison of relationships between PSC and various soil properties indicated that PSC increased with increase in ammonium oxalate extractable Al. The relationship between PSC and ammonium oxalate extractable Fe was not clear. PSC increased with an increase in DCB-extractable Al. The effect was clear in Berks and Monongahela soils. The positive relationship between PSC and DCB- extractable Fe was not as clear. PSC increased with an increase in clay content in all the soils. Effect of exchangeable Ca on PSC was not discernible. Phosphorus sorption capacity generally increased with increase in extractable acidity in every soil. P sorption capacity increased with increase in KCl-extractable Al. Effect of total carbon on P sorption capacity was not apparent. PSC appeared to decrease with increase in pH in 0.01M CaCl_2 and with increase in pH in water.

All the above-mentioned soil variables were badly prone to multicollinearity. Multicollinearity is a condition when variables are highly dependent on each other. Two methods were used to counter the effect of multicollinearity. In the first method, important variables were selected through stepwise ordinary least-squares regression (OLSR). To avoid sacrificing original variables that have an effect on PSC of soils, another approach, principal components regression (PCR) was also used. Principal components (PCs) are the linear combinations of original variables, and are orthogonal to each other. PCR models provided more stable regression estimates and gave best prediction performance. Overall, PCR approach can be useful in evolving P management strategies by predicting PSC from the basic soil characterization data.

Sorption of inorganic P and inositol hexaphosphate (IHP)-P onto AMD flocs, that were generated by neutralizing the same AMD with three different neutralizing agents ammonia, lime, and sodium hydroxide, was studied. The flocs were predominantly composed of amorphous oxides of Fe and Al. Ammonium oxalate extractable Fe constituted more than 99% of the total Fe in the floc, whereas ammonium oxalate extractable Al was more than 97% of the total Al. Amorphous phases of Fe and Al have larger surface area than their crystalline counterparts. Thus, amorphous phases may have higher P attenuation capacity than that of crystalline phases.

Sorption of IHP-P was similar to the sorption of inorganic P. When P loading rates were lower or when more sorption sites were available, there was no difference between the sorbed amounts of inorganic P and organic P. However, when due to increased P loadings sorption sites became scarce, sorption of IHP-P was about 2.5-3 times the inorganic-P. This can be attributed to the mechanism of sorption of IHP-P.

Phytic acid (IHP) contains six phosphate groups attached at each end of a hexagonal carbon ring. It is postulated that each IHP molecule having six P molecules got sorbed on the Fe and Al surfaces by attachment of two contiguous phosphate groups. Therefore, compared to the sorption of two inorganic-P molecules, six IHP-P molecules can be sorbed.

Some studies report that metal oxides can catalyze the hydrolysis of organic P compounds. The study was designed to ascertain whether IHP-P sorbs onto floc surface as such or only P groups are retained and inositol ring is released to the solution via hydrolytic action of reactive surfaces. Another objective of the study was to examine the effect of pH on the hydrolysis of IHP-P solution.

Ratios of carbon to phosphorus (C:P) in solutions having no AMD floc (named 'control') were not generally much different from the C:P ratios in solutions containing various flocs. If P in the IHP molecule could have sorbed as orthophosphate-P after the hydrolysis of IHP, C:P ratio of the equilibrium solution could have been higher than C:P ratio of the 'control'. However, in ammonia-treated floc at pH 6-8, C:P ratios were lower than that in 'control' or in other flocs. In general, the results suggested that AMD floc did not facilitate considerable hydrolysis by way of cleaving phosphate groups on the inositol hexaphosphate molecule during sorption.

The pH effect on orthophosphate concentrations was statistically significant. More IHP-P was hydrolyzed at lower pH than at higher pH. However, amounts hydrolyzed are so small and the pH conditions are so unlikely that they will not have much impact on the IHP-P in the field. These observations hint that AMD flocs can attenuate much more IHP-P than inorganic P.

In soils that have received excessive applications of P through manure additions, concerns are that as manure contains low molecular weight organic acids such as citric acid and oxalic acid, competitive sorption of these acids will result in higher concentrations of inorganic and organic P in soil solution. Three different kind of floes – ammonia-treated, lime-treated, and NaOH-treated were used for examining the effect of citrate and oxalate on the sorption of inorganic- and IHP-P at six different pH levels (4-9). Sorption of IHP-P was comparably less affected by increase in pH in the presence of citrate. Competition between P species and citrate ions was more intense at low pH (4.0). Similar observations were made for oxalate. Citrate offered stronger competition than did oxalate. However, with increase in pH effect of citrate was more weakened than the effect of oxalate. Most soils testing excessive in P have near-neutral pH, as P neutralizes exchangeable Al^{3+} in the soil. Thus, at near neutral or higher pH values, competitive adsorption of P with citrate or oxalate is unlikely to considerably increase P concentration in the soil solution.

The effect of AMD floc in reducing soil-test P and DPS of soils was examined. Four surface soils were used in this study. Two soils were Berks (loamy-skeletal, mixed, active, mesic, Typic Dystrudepts), one was Lindside (fine-silty, mixed, active, mesic, Fluvaquentic Eutrudepts), and one was Monongahela (fine-loamy, mixed, semiactive, mesic, Typic Fragiudults). Degree of P saturation of these soils was calculated. Amounts of AMD floc required to reduce the original DPS of the soils to 150, 80, 60, 40, 20, and 10 percent were mixed with the soils and then incubated. Though calculated (based upon ammonium oxalate extractable Fe+Al content of AMD floc) quantities of AMD floc were added to achieve various degrees of P saturation (DPS), measured DPS values did not

always equal targeted DPS values. With decrease in target DPS following AMD floc additions, soil-test (Mehlich-1 and Mehlich-3) P decreased significantly. Different change-points associated with each soil showed that amounts of AMD floc required to lower DPS and soil-test P would vary from soil to soil.

Plots of DPS versus CaCl_2 -extractable P indicated that change-point for CaCl_2 -extractable P occurred at higher DPS values as compared to the change-point for the relationship of either Mehlich-1 P or Mehlich-3 P with DPS. In general, differences among soils indicated that any two soils may be similar in STP or DPS values, but they may have different amounts of P that can be released to solution.

Thus, AMD floc was highly effective in lowering DPS values of the four different soils. With decrease in DPS levels, Mehlich-1 P, Mehlich-3 P, and CaCl_2 -extractable P levels also decreased, and P sorption capacity levels increased. The results showed that high STP levels in the soils could be reduced in a short period of time by addition of AMD floc to the soil.

Appendix

Table A1. Dissolution of Fe in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by citrate additions at various pH levels and in the presence of inorganic-P and inositol hexaphosphate (IHP)-P.

Citrate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic-P	IHP-P	Inorganic-P	IHP-P	Inorganic-P	IHP-P
Fe concentration (mg L ⁻¹)							
0.00	4	0.1 [†]	15.2	0.01	4.9	0.02	3.9
0.00	5	0.3	5.6	0.02	3.7	0.1	4.9
0.00	6	0.4	9.6	0.02	4.1	0.4	5.0
0.00	7	1.2	8.7	0.03	4.9	0.7	7.6
0.00	8	1.8	6.2	0.01	4.8	1.4	5.7
0.00	9	2.4	8.1	0.0	4.7	7.4	5.5
1.72	4	6.5	36.3	34.2	14.5	31.5	24.6
1.72	5	15.7	19.0	18.4	17.0	28.9	18.1
1.72	6	16.1	11.5	13.1	7.3	28.8	9.9
1.72	7	8.1	7.8	2.4	2.8	8.7	10.3
1.72	8	5.7	6.9	0.3	4.2	4.0	12.5
1.72	9	1.8	5.1	0.9	4.4	1.6	3.5
3.44	4	67.2	38.5	74.7	21.4	83.3	34.0
3.44	5	53.4	30.5	57.9	26.9	77.0	33.2
3.44	6	40.7	19.0	34.7	10.2	39.6	21.9
3.44	7	16.5	8.0	7.4	4.1	10.6	15.8
3.44	8	6.8	8.6	1.7	4.1	2.6	4.9
3.44	9	2.6	4.3	1.3	4.1	1.4	3.0
5.16	4	107.1	49.1	101.5	37.7	117.2	36.5
5.16	5	92.9	45.6	87.7	29.0	113.2	45.2
5.16	6	52.0	18.9	43.7	12.9	52.5	18.9
5.16	7	18.9	11.8	11.3	4.9	20.5	5.7
5.16	8	6.8	5.8	10.1	3.3	2.1	3.6
5.16	9	5.3	5.4	1.6	7.2	1.4	6.4

[†] Each value mean of three replicates

Table A2. Dissolution of Fe in the ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by oxalate additions at various pH levels in the presence of inorganic-P and inositol hexaphosphate (IHP)-P.

Oxalate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic-P	IHP-P	Inorganic-P	IHP-P	Inorganic-P	IHP-P
Fe concentration (mg L ⁻¹)							
0.00	4	0.1 [†]	15.2	0.01	4.9	0.02	3.9
0.00	5	0.3	5.6	0.02	3.7	0.1	4.9
0.00	6	0.4	9.6	0.02	4.1	0.4	5.0
0.00	7	1.2	8.7	0.03	4.9	0.7	7.6
0.00	8	1.8	6.2	0.01	4.8	1.4	5.7
0.00	9	2.4	8.1	0.04	4.7	7.4	5.5
1.72	4	10.4	18.5	2.9	6.5	3.5	8.4
1.72	5	5.5	9.4	2.2	5.3	7.4	7.8
1.72	6	4.6	7.1	1.5	4.8	10.1	8.1
1.72	7	1.2	10.2	0.3	5.7	1.1	13.8
1.72	8	0.7	6.2	0.1	3.8	6.2	9.3
1.72	9	2.3	7.0	0.1	3.6	4.6	3.9
3.44	4	7.0	18.5	11.9	16.4	15.1	15.3
3.44	5	11.5	8.1	5.7	6.0	13.1	8.2
3.44	6	6.2	8.1	4.3	4.4	9.8	11.9
3.44	7	0.8	38.5	1.3	7.9	9.1	6.9
3.44	8	1.2	6.7	0.2	5.1	5.1	4.9
3.44	9	1.2	6.8	0.1	4.8	0.8	5.7
5.16	4	18.6	28.0	20.8	28.3	26.6	24.5
5.16	5	9.5	8.7	8.2	9.4	12.8	6.0
5.16	6	6.5	37.3	4.8	3.4	13.0	8.1
5.16	7	1.7	9.1	0.9	4.5	12.9	10.5
5.16	8	0.6	7.0	0.3	4.9	0.5	4.0
5.16	9	0.5	6.0	0.2	2.8	2.8	6.2

[†] Each value mean of three replicates.

Table A3. Dissolution of Al in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by citrate additions at various pH levels in the presence of inorganic-P and inositol hexaphosphate(IHP)-P.

Citrate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic-P	IHP-P	Inorganic-P	IHP-P	Inorganic-P	IHP-P
Al concentration (mg L ⁻¹)							
0.00	4	0.1 [†]	5.6	0.1	1.6	0.1	1.2
0.00	5	0.2	2.5	0.1	1.2	0.1	1.4
0.00	6	0.2	5.0	0.1	1.3	0.2	1.8
0.00	7	0.4	7.6	0.1	1.8	0.2	3.9
0.00	8	0.7	8.7	0.1	3.0	0.5	4.9
0.00	9	2.1	9.0	0.3	3.8	3.3	4.7
1.72	4	5.2	16.3	12.7	4.1	13.6	6.7
1.72	5	12.5	13.6	9.2	6.1	14.6	7.2
1.72	6	12.9	9.1	7.0	3.7	14.8	5.2
1.72	7	6.7	7.0	2.6	1.8	6.5	4.8
1.72	8	3.1	9.0	1.6	3.8	2.3	6.8
1.72	9	2.2	7.9	1.7	3.0	2.0	4.4
3.44	4	36.4	17.5	24.2	6.1	28.6	9.3
3.44	5	32.9	19.1	20.9	9.1	29.3	11.6
3.44	6	29.3	13.6	14.7	5.0	20.0	9.3
3.44	7	14.6	7.6	7.0	2.7	9.3	6.7
3.44	8	4.7	9.7	4.5	3.0	2.9	5.2
3.44	9	3.0	7.9	2.8	3.9	2.3	4.5
5.16	4	49.2	21.7	31.0	11.0	37.2	9.8
5.16	5	47.2	24.3	27.9	9.4	37.8	14.6
5.16	6	34.7	15.0	17.2	6.0	22.7	9.0
5.16	7	17.7	9.4	8.5	3.5	12.7	4.4
5.16	8	5.3	9.0	5.6	3.2	4.6	4.7
5.16	9	4.6	8.0	3.3	3.6	2.7	5.2

[†] Each value mean of three replicates.

Table A4. Dissolution of Al in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs by oxalate additions at various pH levels and in the presence of inorganic-P and inositol hexaphosphate (IHP)-P.

Oxalate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic- P	IHP-P	Inorganic-P	IHP-P	Inorganic P	IHP-P
Al concentration (mg L ⁻¹)							
0.00	4	0.1 [†]	5.6	0.1	1.6	0.1	1.2
0.00	5	0.2	2.5	0.1	1.2	0.1	1.4
0.00	6	0.2	5.0	0.1	1.3	0.2	1.8
0.00	7	0.4	7.6	0.1	1.8	0.2	3.9
0.00	8	0.7	8.7	0.1	3.0	0.5	4.9
0.00	9	2.1	9.0	0.3	3.8	3.3	4.7
1.72	4	10.9	7.3	6.4	4.0	7.9	3.3
1.72	5	5.4	3.9	3.8	2.5	4.8	2.3
1.72	6	3.1	4.1	1.1	1.7	4.0	2.6
1.72	7	0.5	8.0	0.2	2.2	0.4	5.7
1.72	8	0.3	8.7	0.1	2.7	1.7	5.9
1.72	9	2.1	8.5	0.2	3.4	2.4	4.2
3.44	4	17.3	11.2	12.3	8.8	15.8	8.3
3.44	5	11.2	4.0	7.6	3.9	9.7	3.0
3.44	6	6.2	4.7	5.0	2.0	6.0	3.7
3.44	7	0.5	17.4	0.7	2.9	2.8	4.1
3.44	8	0.5	8.7	0.1	3.3	1.5	5.1
3.44	9	1.7	8.3	0.4	3.9	1.3	5.0
5.16	4	25.2	18.7	15.7	12.7	20.9	13.4
5.16	5	13.6	5.6	9.8	5.7	12.1	3.5
5.16	6	8.1	15.0	6.5	2.2	8.4	3.0
5.16	7	1.0	7.7	0.8	2.0	4.0	5.4
5.16	8	0.4	9.0	0.1	3.0	0.3	4.8
5.16	9	1.6	7.9	0.4	3.1	2.0	4.7

[†] Each value mean of three replicates.

Table A5. Effect of citrate additions on dissolution of Ca in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs at various pH levels.

Citrate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic-P	IHP-P	Inorganic-P	IHP-P	Inorganic-P	IHP-P
Ca concentration (mg L ⁻¹)							
0.00	4	4.3 [†]	1.0	16.2	5.4	7.0	1.0
0.00	5	3.1	0.8	15.9	5.2	5.3	1.1
0.00	6	1.8	1.1	13.0	4.7	3.5	1.2
0.00	7	0.7	1.1	7.3	4.4	1.3	1.3
0.00	8	0.2	0.9	3.0	4.1	0.3	1.2
0.00	9	0.2	1.0	1.1	4.8	0.3	1.5
1.72	4	2.5	0.8	13.3	8.2	6.8	1.8
1.72	5	0.9	0.6	11.6	7.1	3.5	1.3
1.72	6	0.3	0.6	10.5	6.7	3.8	1.3
1.72	7	0.7	0.5	8.9	5.6	4.2	1.1
1.72	8	0.8	0.0	6.9	4.2	1.6	0.8
1.72	9	0.0	0.1	4.9	4.2	0.0	0.9
3.44	4	4.6	1.3	19.1	10.0	7.3	2.8
3.44	5	1.4	1.0	12.9	9.3	4.6	2.3
3.44	6	2.4	1.2	14.8	9.0	5.6	2.6
3.44	7	3.3	0.9	14.5	7.7	5.5	1.9
3.44	8	2.2	0.1	12.4	4.9	3.1	0.8
3.44	9	0.4	1.8	7.3	4.6	0.7	1.0
5.16	4	4.9	1.6	18.8	11.3	7.7	3.3
5.16	5	1.7	1.8	15.5	10.2	5.7	3.2
5.16	6	3.5	1.4	16.2	10.6	6.2	3.1
5.16	7	3.9	0.3	15.8	9.1	6.2	2.2
5.16	8	2.7	0.1	3.9	5.7	12.2	0.8
5.16	9	0.6	8.2	7.8	2.7	0.9	0.9

[†] Each value mean of three replicates.

Table A6. Effect of oxalate additions on dissolution of Ca in ammonia-treated, lime-treated, and sodium hydroxide-treated acid mine drainage flocs at various pH levels in the presence of inorganic-P and inositol hexaphosphate (IHP)-P.

Oxalate conc. (mM)	pH	Floc type					
		Ammonia-treated		Lime-treated		NaOH-treated	
		Inorganic-P	IHP-P	Inorganic-P	IHP-P	Inorganic-P	IHP-P
Ca concentration (mg L ⁻¹)							
0.00	4	4.3 [†]	0.9	16.2	5.4	7.0	1.0
0.00	5	3.1	0.8	15.9	5.2	5.3	1.1
0.00	6	1.8	1.1	13.0	4.7	3.5	1.2
0.00	7	0.7	1.1	7.3	4.4	1.3	1.3
0.00	8	0.2	0.9	3.0	4.1	0.3	1.2
0.00	9	0.2	1.0	1.1	4.8	0.3	1.5
1.72	4	2.8	0.8	4.8	5.0	4.5	1.0
1.72	5	1.7	0.8	1.3	4.9	1.2	1.1
1.72	6	1.4	1.1	0.9	4.8	1.0	1.4
1.72	7	0.9	1.0	0.7	4.4	1.0	1.4
1.72	8	0.3	0.7	0.8	3.9	0.6	1.2
1.72	9	0.2	1.0	1.5	4.7	0.3	1.7
3.44	4	2.5	0.8	2.0	4.7	3.0	1.0
3.44	5	0.9	0.8	0.7	4.0	0.8	1.2
3.44	6	0.7	1.1	0.6	4.7	0.7	1.5
3.44	7	0.6	1.4	0.5	4.4	0.6	1.3
3.44	8	0.3	0.7	0.5	4.0	0.6	1.1
3.44	9	0.2	1.0	0.7	4.7	0.2	1.7
5.16	4	1.5	0.9	1.4	3.3	1.9	1.1
5.16	5	0.7	0.9	0.6	2.8	0.7	1.2
5.16	6	0.5	1.6	0.5	3.4	0.6	1.4
5.16	7	0.5	0.8	0.4	4.2	0.5	1.2
5.16	8	0.3	0.6	0.4	3.9	0.6	0.9
5.16	9	0.2	0.9	0.5	4.5	0.3	1.7

[†] Each value is mean of three replicates.