

Fall 12-18-2015

# Phosphorus Release Potential of Agricultural Soils of the United States

Rebecca A. Young

University of Nebraska - Lincoln, [rputa@huskers.unl.edu](mailto:rputa@huskers.unl.edu)

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PHOSPHORUS RELEASE POTENTIAL OF AGRICULTURAL  
SOILS OF THE UNITED STATES

by

Rebecca Ann Puta Young

A DISSERTATION

Presented to the Faculty of  
The Graduate College at the University of Nebraska  
In Partial Fulfillment of Requirements  
For the Degree of Doctor of Philosophy

Major: Natural Resource Sciences  
(Soil Science)

Under the Supervision of Professor Mark S. Kuzila

Lincoln, Nebraska

December, 2015

# PHOSPHORUS RELEASE POTENTIAL OF AGRICULTURAL SOILS OF THE UNITED STATES

Rebecca Ann Puta Young, Ph.D.

University of Nebraska - Lincoln, 2015

Advisor: Mark S. Kuzila

Phosphorus (P) is one of the leading causes of surface water quality decline in the United States, leading to algal blooms and hypoxia in lakes and streams. Decreasing conservation funds dictate that agencies such as the Natural Resources Conservation Service, maximizes its effectiveness and efficiency in implementing practices to address P management and runoff on agricultural lands. Additional information on P behavior in soil is needed to improve P management plans to reduce pollution risk at the watershed, farm, and field scales. This research focuses on the development of total soil P release models, to be included into assessment and management tools to better identify agricultural soils that pose the greatest threat to surface water if eroded, and to improve existing nutrient loss models.

Soil P sorption behaviors and relationships with other soil properties were investigated on 313 agricultural surface soils from across the U.S. Different soil grouping schemes were investigated when analyzing and modeling soil P sorption behaviors at the national-level. Three large watershed areas with known P issues were also investigated to compare watershed-specific models to overall national-level models.

Overall results showed that, (a) oxalate extractable and Mehlich-3 extractable P tests are the most appropriate soil P tests for estimating total P release and P adsorption in

most soils, (b) total P release prediction models improve when soils are grouped based on their calcium carbonate content and degree of weathering or modeled at a large watershed level, than at a general national-scale, (c) the majority of statistically significant and reliable total P release prediction models include clay and either oxalate or Mehlich-3 extractable Al, (d) potential risk models can differ greatly within a given area or watershed, depending on the employed modeling scheme (i.e. area-specific vs. national-level), and that (d) with further research and refinement, the relationships and models developed in these studies have the potential of improving current P Indices and assessment tools, and subsequent management recommendations and practices.

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## **Dedication**

This work is dedicated to my parents, Ed and Rhonda Puta. Lovers of all things in the natural world, who have always held unwavering pride and confidence in their daughter.

## **Acknowledgements**

I am indebted in many ways to a number of individuals. First, I received strong support and encouragement from my academic advisor, Dr. Mark Kuzila, and my project advisor, Dr. Michael Robotham of the United States Department of Agriculture Natural Resources Conservation Service, during some very difficult times. I also received indispensable guidance and advice from the other members of my Supervisory Committee, Drs. Steven Comfort, Dennis McCallister, and Terrance Loecke.

Candiss Williams made critical contributions in assisting with the data analysis of this project, and from whom I am know I learned more from than what she can imagine. Patty Jones, Caitlin Miller, Daniel Robotham, and Joshua Gates greatly assisted in helping me complete laboratory work, for which I will be forever grateful.

Finally, I would like to thank my family and friends for all of their love, support, and motivation to keep working hard to get to this point. I would especially like to thank my husband, Aaron, and mother, Rhonda, for their unconditional love and patience during some of my more stressful moments.

Thank you all.

### **Grant Information**

This project was funded through a USDA-NRCS Contract (#68-7482-12-503), as part of their Phosphorus Loading Potential Project. This project was also funded in part by a single-year scholarship grant from the Midwest Federation of Mineralogical & Geological Societies as part of the American Federation of Mineralogical Societies Scholarship Foundation.



## Table of Contents

<b>List of Figures</b> .....	ix
<b>List of Tables</b> .....	xiv
 <b>General Introduction</b> .....	 1
<b>Chapter 1</b> Literature Review .....	7
<b>Chapter 2</b> Phosphorus Desorption Characteristics and Relationships of U.S. Agricultural Soils .....	24
Appendix A Classification Information for Chapter 2 Data .....	89
Appendix B Descriptive Statistics of Soil Properties and Quartiles for P Sorption Variables for Chapter 2 Data .....	97
Appendix C Desorption Regression Equation Components Table and Log-Transformed Desorption Plots for Chapter 2 Data .....	107
Appendix D Regression Modeling Steps Table for Chapter 2 Data .....	109
Appendix E Additional Validation Results Table for Chapter 2 Data .....	112
Appendix F Quartiles/Potential Risk Tables for Great Groups for Chapter 2 Data .....	113
<b>Chapter 3</b> Phosphorus Desorption Characteristics and Relationships of Agricultural Soils in the Chesapeake Bay Watershed .....	114
Appendix G Desorption Regression Equation Components Table, Log- Transformed Desorption Plots, and Regression Modeling Steps Table for the Chesapeake Bay Watershed .....	159
<b>Chapter 4</b> Phosphorus Desorption Characteristics and Relationships of Agricultural Soils in the Upper Mississippi Sub-basin .....	163
Appendix H Desorption Regression Equation Components Table, Log- Transformed Desorption Plots, and Regression Modeling Steps Table for the Upper Mississippi River Sub-basin .....	207
<b>Chapter 5</b> Phosphorus Desorption Characteristics and Relationships of	

Agricultural Soils in the California Bay-Delta/Central Valley Watershed .....	212
Appendix I Desorption Regression Equation Components Table, Log- Transformed Desorption Plots, and Regression Modeling Steps Table for the California Bay-Delta/Central Valley Watershed .....	253
<b>Chapter 6</b> Synthesis .....	256

## List of Figures

### Chapter 1

Figure 1.1: The adsorption process of P in soil over time .....	9
---	---

### Chapter 2

Figure 2.1: Locations of all modeling and validation samples investigated .....	31
Figure 2.2: Boxplots of AER variables for the All Soils modeling and validation datasets .....	42
Figure 2.3: Boxplot of PSI variable for the All Soils modeling and validation datasets .....	43
Figure 2.4: Boxplot of SMAX variable for the All Soils modeling and validation datasets .....	44
Figure 2.5: Predicted amounts of P released (mg P/kg soil) for soils in the All Soils datasets .....	55
Figure 2.6: Plots of measured versus predicted values, as determined by the All Soils prediction models listed in Table 2.7, for AER1, AER23, and AER24, when applied to the All Soils validation dataset .....	66
Figure 2.7: Plots of measured versus predicted values, as determined by the All Soils prediction models listed in Table 2.7, for PSI and $S_{MAX}$ , when applied to the All Soils validation dataset .....	67
Figure 2.8: Plots of measured versus predicted AER24 values, as determined by the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils prediction models listed in Table 2.7 .....	70
Figure 2.9: Plots of measured versus predicted AER24 values, as determined by the Argiustolls, Hapludalfs, and Hapludults prediction models listed in Table 2.7 .....	71
Figure 2.10: Potential risk agricultural soils pose to contributing to P loading, with total P release estimated averaged by taxonomic Great Groups from the	

All Soils modeling dataset .....	76
Figure 2.10: Potential risk agricultural soils pose to contributing to P loading, overlain by the measured AER24 values of samples from the all soils modeling dataset .....	77
Figure B.1: Boxplots displaying the quartile statistics AER variable, for samples in the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils datasets .....	98
Figure B.2: Boxplots displaying the quartile statistics AER variable, for samples in the Argiustolls, Hapludalfs, and Hapludults datasets .....	98
Figure B.3: Boxplots displaying the quartile statistics of PSI, for samples in the Calcareous soils, Highly Weathered soils, Slightly Weathered soils datasets .....	99
Figure B.4: Boxplots displaying the quartile statistics of PSI, for samples in the Argiustolls, Hapludalfs, and Hapludults datasets .....	99
Figure B.5: Boxplots displaying the quartile statistics of $S_{MAX}$ , for samples in the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils datasets .....	100
Figure B.6: Boxplots displaying the quartile statistics of $S_{MAX}$ , for samples in the Argiustolls, Hapludalfs, and Hapludults datasets .....	100
Figure C.1: Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for all agricultural modeling soils .....	108

### Chapter 3

Figure 3.1: Locations of all modeling and validation samples investigated from the Chesapeake Bay watershed study area .....	120
Figure 3.2: USDA NRCS Major Land Resource Areas of the Chesapeake Bay watershed study area .....	122
Figure 3.3: General physiographic areas of the Chesapeake Bay watershed study area .....	124

Figure 3.4: Boxplots displaying the quartile statistics of each measured AER variable for the Chesapeake Bay watershed datasets .....	133
Figure 3.5: Boxplots displaying the quartile statistics for the PSI variable for the Chesapeake Bay watershed datasets .....	134
Figure 3.6: Boxplots displaying the quartile statistics for the SMAX variable for the Chesapeake Bay watershed modeling dataset .....	135
Figure 3.7: Predicted amounts of P released (mg P/kg soil) for samples from the Chesapeake Bay datasets .....	140
Figure 3.8: Plots of measured versus predicted values, as determined by the models listed in Table 3.6, for AER1, AER23, AER24, and PSI .....	146
Figure 3.9: Measured versus predicted AER24 values as determined by the models listed in Table 3.6 .....	148
Figure 3.10: Potential risk agricultural soils of the Chesapeake Bay watershed pose to contributing to P loading .....	150
Figure G.1: Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for samples in the Chesapeake Bay watershed modeling dataset .....	161

## Chapter 4

Figure 4.1: Locations of all modeling and validation samples investigated from the Upper Mississippi River Sub-basin study area .....	168
Figure 4.2: USDA NRCS Land Resource Regions of the Upper Mississippi River Sub-basin study area .....	170
Figure 4.3: Boxplots displaying the quartile statistics of each measured AER variable for the Upper Mississippi River Sub-basin datasets .....	182
Figure 4.4: Boxplots displaying the quartile statistics for the PSI variable for the Upper Mississippi River Sub-basin datasets .....	183
Figure 4.5: Boxplots displaying the quartile statistics for the $S_{MAX}$ variable for	

the Upper Mississippi River Sub-basin datasets .....	184
Figure 4.6: Predicted amounts of P released (mg P/kg soil) for samples from the Upper Mississippi River Sub-basin datasets .....	188
Figure 4.7: Plots of measured versus predicted values, as determined by the models listed in Table 4.6, for AER1, AER23, AER24, and PSI .....	195
Figure 4.8: Measured versus predicted AER24 values as determined by the models listed in Table 4.6 .....	197
Figure 4.9: Potential risk agricultural soils of the Upper Mississippi River Sub-basin pose to contributing to P loading .....	200
Figure H.1: Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for samples in the Upper Mississippi River Sub-basin modeling dataset .....	210

## Chapter 5

Figure 5.1: Locations of all modeling and validation samples investigated from the California Bay-Delta/Central Valley study area .....	218
Figure 5.2: USDA NRCS Major Land Resource Areas of the California Bay-Delta/Central Valley study area .....	219
Figure 5.3: Boxplots displaying the quartile statistics of each AER variable for the California Bay-Delta/Central Valley datasets .....	230
Figure 5.4: Boxplots displaying the quartile statistics for the PSI variable for the California Bay-Delta/Central Valley datasets .....	231
Figure 5.5: Boxplots displaying the quartile statistics for the $S_{MAX}$ variable for the California Bay-Delta/Central Valley modeling dataset .....	232
Figure 5.6: Predicted amounts of P released (mg P/kg soil) for samples from the California Bay-Delta/Central Valley datasets .....	236
Figure 5.5: Potential risk agricultural soils of the California Bay-Delta/ Central Valley region pose to contributing to P loading .....	245

Figure I.1: Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for samples in the California Bay-Delta/ Central Valley modeling dataset .....	254
--	-----

## List of Tables

### Chapter 2

Table 2.1: Descriptive statistics of the P sorption variables analyzed for CONUS study .....	39
Table 2.2: Descriptive statistics of the P sorption variables analyzed for CONUS study Great Groups .....	41
Table 2.3: Correlation coefficients between the P sorption variables and soil properties know to affect P sorption, for samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets .....	47
Table 2.4: Correlation coefficients between the P sorption variables and soil properties know to affect P sorption, for samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets .....	49
Table 2.5: Correlation coefficients between the P sorption variables and soil P tests, for samples in the all soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets .....	52
Table 2.6: Correlation coefficients between the P sorption variables and soil P tests, for samples in the Argiustolls, Hapludalfs, and Hapludults datasets .....	54
Table 2.7: The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets .....	59
Table 2.8: The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets .....	63
Table 2.9: The number of All Soils validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for each of the all soils prediction models listed in Table 2.7 for each P sorption variable .....	68
Table 2.10: The number of validation sample values accurately predicted	



within 10 %, 15 %, and 20 % of the measured value for the AER24 prediction models listed in Tables 2.7 and 2.8 .....	72
Table 2.11: P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the All Soils modeling dataset .....	75
Table A.1: Classification information for samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils datasets .....	89
Table A.2: Classification information for samples in the Argiustolls, Hapludalfs, and Hapludults modeling and validation datasets .....	95
Table B.1: Descriptive statistics of the soil properties for samples in the All Soils, Calcareous Soils, Highly Weathered Soils, and Slightly Weathered Soils modeling datasets .....	101
Table B.2: Descriptive statistics of the soil properties for samples in the All Soils, Calcareous Soils, Highly Weathered Soils, and Slightly Weathered Soils validation datasets .....	103
Table B.3: Descriptive statistics of the soil properties for samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets .....	105
Table B.4: Descriptive statistics of the soil properties for samples in the Argiustolls, Hapludalfs, and Hapludults validation datasets .....	106
Table C.1: Linear regression equation <sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for soils in the All Soils modeling and validation datasets .....	107
Table D.1: Regression modeling example from the All Soils modeling datasets, for AER23 and AER24 .....	110
Table E.1: The number of validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for the AER1, AER23, PSI, and S <sub>MAX</sub> prediction models listed in Tables 2.7 and 2.8 for each grouping scheme .....	112
Table F.1: P Index Risk Potential classifications by AER24 quartile statistics	

from samples in the Argiustolls, Hapludalfs, and Hapludults datasets .....	113
--	-----

### Chapter 3

Table 3.1: Classification information for the 46 Chesapeake Bay watershed agricultural surface soils investigated .....	121
Table 3.2: Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the modeling dataset .....	131
Table 3.3: Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the validation dataset .....	132
Table 3.4: Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption .....	137
Table 3.5: Correlations coefficients between the P sorption variables and soil P tests, for samples in the modeling dataset .....	138
Table 3.6: The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the modeling dataset .....	144
Table 3.7: The number of validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for each of the prediction models listed in Table 3.6 .....	147
Table 3.8: P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the modeling dataset .....	151
Table G.1: Linear regression equation <sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for all Chesapeake Bay watershed soils investigated .....	160
Table G.2: Regression modeling example from the Chesapeake Bay modeling datasets, for AER1 and AER23 .....	162

### Chapter 4

Table 4.1: Classification information for the 57 Upper Mississippi River
--

Sub-basin agricultural surface soils investigated .....	169
Table 4.2: Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the modeling dataset .....	179
Table 4.3: Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the validation dataset .....	180
Table 4.4: Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption .....	185
Table 4.5: Correlations coefficients between the P sorption variables and soil P tests, for samples in the modeling dataset .....	187
Table 4.6: The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable .....	194
Table 4.7: The number of validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for each of the prediction models listed in Table 4.6 .....	196
Table 4.8: P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the modeling dataset .....	199
Table H.1: Linear regression equation <sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for all Upper Mississippi River Sub-basin soils investigated .....	208
Table H.2: Regression modeling example from the Upper Mississippi River Sub-basin modeling datasets, for AER1 .....	211

## Chapter 5

Table 5.1: Classification information for the 14 California Bay-Delta/Central Valley agricultural surface soils investigated .....	220
Table 5.2: Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the modeling dataset .....	227
Table 5.3: Descriptive statistics of the soil properties and P sorption variables	

analyzed for samples in the validation dataset .....	228
Table 5.4: Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption .....	233
Table 5.5: Correlations coefficients between the P sorption variables and soil P tests, for samples in the modeling dataset .....	235
Table 5.6: The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable .....	241
Table 5.7: The reliability of the prediction models listed in Table 5.6, when applied to the two samples in the validation dataset .....	242
Table 5.8: P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the modeling dataset .....	246
Table I.1: Linear regression equation <sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for all California Bay-Delta/Central Valley region soils investigated .....	253
Table I.2: Regression modeling example from the California Bay-Delta/ Central Valley modeling datasets, for AER23 .....	255

## GENERAL INTRODUCTION

“Essentially, all life depends upon the soil ... There can be no life without soil and no soil without life; they have evolved together.” Charles E. Kellogg, 1938

The above quotation from the 1938 USDA Yearbook of Agriculture is relevant to the topic of soil phosphorus as phosphorus is an essential element for plant growth in agriculture, and plays an important role maintaining all forms of life: respiration in mammals, photosynthesis in green leaves and algae, microbial turnover, and litter decomposition, all of which require phosphorus (Cole et al., 1977). Technological advances and dramatic population growth in the last 150 years, however, have brought soil phosphorus behaviors to the forefront of nutrient studies first as an agricultural need, and later as an environmental concern.

The production and use of inorganic, commercial fertilizers for agricultural crop production dramatically increased following the conclusion of World War II, of which phosphorus, and nitrogen, fertilizers were of the most commonly used (Roberts and Dibb, 2011; Trautmann et al., 2012). The mining of phosphorus and transporting it in fertilizers, animal feeds, and agricultural crops is causing phosphorus to accumulate in some of the world's soil, altering the global phosphorus cycle. The accumulation of phosphorus in upland soils may affect freshwater ecosystems, and production in most freshwater lakes depends on phosphorus inputs (Schindler, 1977). Eutrophication, the process of nutrient enrichment of surface waters, from excess inputs of phosphorus can

negatively impact aquatic ecosystems, resulting in the loss of their aesthetic, ecological, and economic value.

Eutrophication problems due to excessive phosphorus inputs have grown, and continue to grow, worldwide. As a result, there has been a notable shift in the focus of soil phosphorus sorption studies, or, how soils retain and release phosphorus. Since the 1970s, the focus has shifted from agricultural purposes towards the realm of environmental improvement, particularly in attempting to develop reliable soil-to-water transfer predictions and models. More information about the physio-chemical property relationships with soil P sorption behavior, as well as understanding the role of local hydrology, however, is required in order to make more accurate and reliable predictions of the soil-to-water transfer of phosphorus (Vadas et al., 2006).

The purpose of this research was to develop predictive relationships between P desorption behaviors and other soil properties using simple and multiple linear regression models, providing researchers and land managers with a useful tool to target high-risk soils more efficiently and more effectively.

### *RESEARCH APPROACH*

The quantity and behavior of P in soil varies considerably depending primarily on the parent material and degree of weathering, and, to a lesser degree, the extent of P loss via leaching. Predicting or modeling how a particular soil will desorb P is an important environmental concern and relates to the physical and chemical properties of the soil. For this study, P desorption behaviors and release were investigated and prediction

models were developed at the conterminous United States (CONUS) scale and also at the large watershed/sub-basin scale for three specific regions of the United States.

The comprehensive hypothesis is that P desorption behavior-soil property relationships will become more precise and that P release prediction models will improve when soils are investigated at a large watershed/sub-basin scale vs. a CONUS scale, or when soils are investigated in groups based on their calcium carbonate contents and degree of weathering.

Agricultural surface soils of four areas were identified to test the above hypothesis: 1) the contiguous United States; 2) the Chesapeake Bay watershed; 3) the Upper Mississippi River Sub-basin; and 4) the California Bay-Delta/Central Valley watershed. Specific hypotheses for these areas constitute the basis of the present research, and are addressed as chapters in this dissertation. Briefly, the topics and their respective significance are:

**Chapter 2:** *Phosphorus Desorption Characteristics and Relationships of United States Agricultural Soils.* Surface waters across the U.S. are negatively impacted by agricultural P so potential soil P desorption prediction models are generated for all agricultural soils of the U.S. However, is it applicable or reasonable to use prediction models generated at such a large scale? The hypothesis is that these prediction models will improve when these soils are grouped and analyzed based on the calcium carbonate contents and degree of weathering.

**Chapter 3:** *Phosphorus Desorption Characteristics and Relationships of*

*Agricultural Soils in the Chesapeake Bay Watershed.* Agricultural soil P

movement into the Chesapeake Bay has been and remains a great environmental concern. The hypothesis is that potential soil P desorption prediction models will improve for the Chesapeake Bay watershed when only soils from this region are investigated. However, will the great variability in the degree of weathering and the properties of these soils have an effect on these prediction models?

**Chapter 4:** *Phosphorus Desorption Characteristics and Relationships of*

*Agricultural Soils in the Upper Mississippi Sub-basin.* Phosphorus from

agricultural practices in the upper reaches of the Mississippi River basin is a significant driver in the development of the hypoxic Dead Zone of the Gulf of Mexico. However, little research on the relationships between P desorption and soil properties has been conducted for this region. The hypothesis is that potential soil P desorption prediction models will improve for the Upper Mississippi River Sub-basin watershed when only soils from this region are investigated.

**Chapter 5:** *Phosphorus Desorption Characteristics and Relationships of*

*Agricultural Soils in the California Bay-Delta/Central Valley Watershed.*

Agricultural runoff from the highly intensive agricultural California Central Valley makes its way into and has detrimental effects on the Bay-Delta, the unique and highly publicized estuary near San Francisco, CA. The hypothesis is that potential soil P desorption prediction models will improve for the California



Bay-Delta/Central Valley watershed region when only soils from this region are investigated. However, will a relatively few number of samples bias the results of these relationships and models?

Finally, in the synthesis of this dissertation, the results and observations from these chapters are put into perspective.

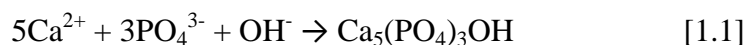
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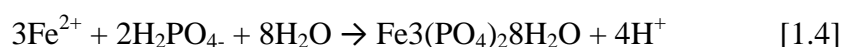
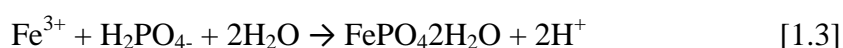
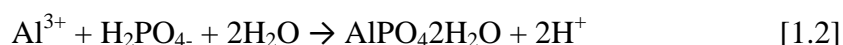
## CHAPTER 1

### LITERATURE REVIEW

Phosphorus (P) has long been recognized as an essential element for plant growth and to maintain profitable crop production. Plants deficient in P will have stunted growth, delayed maturity, and often red or purple leaf pigmentation. The quantity of P in soil varies considerably depending primarily on the parent material and the degree of weathering, and, to a lesser degree, the extent of P loss via leaching. Total P concentrations, native and amended, are generally higher in the near-surface horizons of soils due to the recycling of P by plants, and the tendency of P to be adsorbed on colloidal surfaces to form insoluble complexes with divalent and trivalent cations. These complexes cause P compounds to be relatively immobile in soil, a behavior that was first noted by Way (1850). The amount of P that is plant available is usually less than 20% of the total P in the soil (Schachtman et al., 1998). Native P in soils is derived from the apatite minerals of soil-forming rocks. Weathering and soil genesis liberate the P of apatite which is then either (a) adsorbed and recycled by plants, (b) incorporated into the soil organic matter, or (c) converted to insoluble or slowly soluble mineral forms (iron (Fe), aluminum (Al), and calcium (Ca) phosphates) (Stevenson, 1986). In alkaline soils, the stable minerals that control the P concentration in the soil solution are forms of Ca phosphates (Sanyal and De Datta, 1991). As noted in the following equation, a precipitation reaction occurs between the Ca ions and phosphate, in this case forming hydroxyapatite:



In acid soils, however, the stable minerals that typically control the P concentration in soil solution are forms of Al and Fe hydrous oxides (Sanyal and De Datta, 1991). As noted in the following equations, some secondary minerals of phosphate that are formed in acid soils include variscite, strengite, and vivianite, respectively:



Widespread deficiency of P in agricultural soils, due to removal by crops, led to phosphorus adsorption and desorption by soils becoming a widely researched areas of study. The rendering of soluble phosphate in soils to less soluble forms that are unavailable to plants is due, in large part, to phosphorus adsorption (Figure 1.1). Sanyal and De Datta (1991) describe the general P adsorption process as, "...the surface accumulation on soil components which can be accompanied by the penetration of the adsorbed P by diffusion into the absorbent component, leading to further absorption of the adsorbed species." P desorption is described as the release of P from or through a soil component. The term *sorption* is generally used to denote both the adsorption and desorption processes taking place simultaneously. Being able to predict and model how a particular soil will sorb and desorb P is an important environmental concern and relates to the physical and chemical properties of the soil. A major subject of study is understanding how different soil properties affect or control these P-related processes.

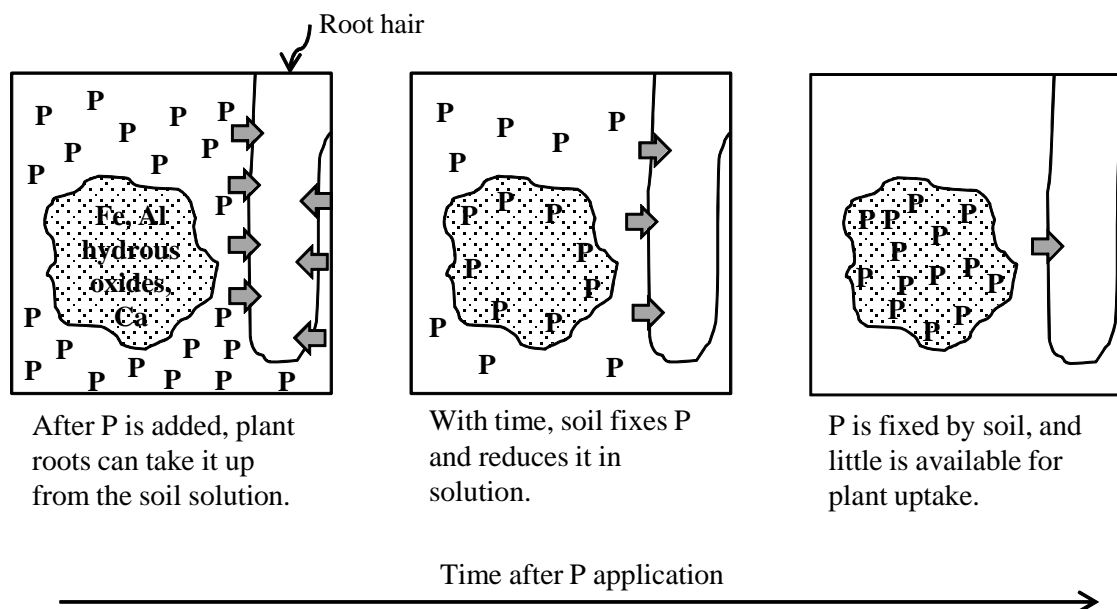


Figure 1.1. The adsorption process of P in soil over time.

P adsorption in soils generally occurs in two phases; a rapid initial adsorption via rapid ligand exchange and strong covalent bonding, and a slower, longer adsorption phase that can occur over days or weeks, continuing to lower plant P availability and extractability (Sanyal and De Datta, 1991; Sparks, 2003). Wild (1950) noted in a literature review of P retention by soil constituents, that P retention was generally the result of the calcium carbonate and hydrous oxides of Al and Fe in alkaline and acidic soils, as well as clay minerals and soil organic matter (Jones et al., 1979). The researchers cited by Wild (1950) suggested that P was either chemically bonded to cations along the surfaces of soil minerals, or that P was precipitated as Ca-, Fe-, or Al-phosphates, which lead to early assumptions that P retention in soil involved adsorption or precipitation. Because aluminum and iron oxides have high reactivity and specific surface areas, they have a significant effect on soil chemical processes (i.e. phosphorus sorption), even if they are not found in high quantities within the soil (Sparks, 2003.)

The amount of P sorbed in a soil will ultimately depend on the pH, P concentration of the soil solution, temperature, and time of the reaction (Kurtz, 1953; Sample et al., 1980).

Wild (1950) noted that researchers were finding that phosphorus added to calcareous soils was often being adsorbed and converted to an insoluble calcium phosphate (dicalcium or tricalcium phosphate) or apatite, or was simply retained by exchangeable calcium. Numerous studies conducted on the sorption of P by clay minerals in soil indicate a significant correlation between P sorption and clay content (Sanyal and De Datta, 1991). Several researchers have concluded that due to the similarities of P adsorption by clay minerals and hydrous oxides, the sorption mechanisms for the two mineral groups are the same, or nearly so (Sample et al., 1980). Similarly, many researchers have found a significant positive correlation between P sorption and soil organic matter content (Sample et al., 1980; Sanyal and De Datta, 1991). This positive relationship has often been found to be the result of soil organic matter associations with Fe, Al, and Ca cations, all of which are capable of adsorbing P (Sample et al., 1980).

Early analytical methods used to determine the amount of soil available P (extractable) were originally developed to estimate fertilizer requirements by determining the amount of P available for crop uptake and the probability of crop response to added P (SERA-IEG 17, 2009). Some of these traditional soil P tests, such as Bray P-1, Olsen P, Mehlich-1 and -3 P, water soluble, and acid oxalate extractable P, have been widely used in P-related environmental studies, including P sorption/desorption and predictive modeling of P runoff and leaching (Burt et al., 2002; Gartley and Sims, 1994; Heckrath et al., 1995; Pote et al., 1996; Sharpley, 1996; Sims et al., 1998). The Bray P-1 procedure uses a weak, acidified ammonium fluoride solution that will selectively remove a portion

of the adsorbed form of P in the soil (Bray and Kurtz, 1945). However, due to the neutralization of the dilute acid by carbonates in calcareous soils, this method for estimating available P in the soil has been most successful on acid soils (Olsen and Sommers, 1982). The Olsen P procedure is most applicable to neutral to calcareous soils (Buurman et al., 1996) as a 0.5 M sodium bicarbonate solution at pH 8.5 is used to extract available P from soil. The Mehlich-1 P procedure uses a double acid method for extracting available P from soil, with 0.05 N hydrochloric acid and 0.025 N sulfuric acid (Mehlich, 1954), and was shown to not work well on neutral to alkaline soils (Mehlich, 1984). The Mehlich-3 P method was designed as a multi-element soil extraction and to be applicable for extracting available P from across a wide range of soil properties (Mehlich, 1984). In the Mehlich-3 P method P is extracted by reaction with acetic acid and fluorine compounds, which is less aggressive towards apatite and other Ca-phosphate and neutralized less by carbonate compounds than the Mehlich-1 P extractant (Burt, 2004). It has been shown that Mehlich-3 P correlates well with Mehlich-1 P, with Bray P-1 on acid to neutral soils ( $R^2 = 0.966$ ), and with Olsen P on calcareous soils ( $R^2 = 0.918$ ), but not with Bray P-1 on calcareous soils (Soil and Plant Analysis Council, 1999). Water soluble P is measured in a water extract, or, often in dilute salt extracts such as 0.01 M  $\text{CaCl}_2$  (Olsen and Sommers, 1982). Water soluble P primarily consists of inorganic orthophosphate ions in the water soluble fraction, but some organic P has also been evident (Rigler, 1968). The acid oxalate, or ammonium oxalate, P procedure uses a selective dissolution extractant for noncrystalline Fe and Al oxides (Burt, 2004; Guo and Yost, 1999), which P is often highly associated with in soils due to their large surface areas (Hodges and Zelazny, 1980) and high reactivity with phosphates (Saunders, 1965).

Several soil test P techniques, which are often correlated with P sorption and desorption behaviors in soils, rely on the use of various chemicals and solutions that do not accurately mimic a natural in-field process, and in some cases, the effectiveness of some extractants is reduced in some soils (e.g. acid oxalate in calcareous soils), which could limit the interpretation of the P data for that method or soil type (Burt et al., 2002). Fox and Kamprath (1970) were among the first to use adsorption isotherms, the process of adding varying amounts of P to a soil solution and measuring the amount adsorbed by the soil to generate a quantity vs. intensity curve for the soil to estimate the amount of P a soil could adsorb. A standard adsorption isotherm method was later proposed by Nair et al. (1984), which was later reviewed, updated, and proposed by the SERA-IEG 17 (2009) as a standard P adsorption method. This method continues to be widely used in P sorption studies. Methods using anion exchange resins and iron oxide impregnated strips have also been developed and applied to soils to assess P desorption in runoff and surface waters as they act as P-sinks in a soil solution, although the iron oxide strip method tends to be more problematic in practice and has more errors associated with its estimations of P (Uusitalo and Yli-Halla, 1999). The development and increasing use of computer models over the last few decades has also been incorporated into the estimation of P sorption in a landscape, the results of which could be quite informative about how P is moving on and in a particle area or watershed. More information about how various soils sorb P and how that behavior relates to the soil's physical and chemical characteristics, as well as understanding the role of local hydrology, is required in order to make more accurate and reliable predictions of the soil-to-water transfer of P (Vadas et al., 2006).



### *An Agricultural Need, An Environmental Problem ...*

The production and use of inorganic, commercial fertilizers for agricultural crop production dramatically increased in the U.S. following the conclusion of World War II, of which P fertilizers were of the most commonly used to increase crop growth and yield (Roberts and Dibb, 2011; Trautmann et al., 2012). High concentrations of P in animal manures and the increased availability of inorganic fertilizers for agricultural production has led to abundant application, and often over application of P to soils and landscapes. There is no gaseous component to the P cycle, so any P removed from the landscape will do so via erosion, runoff or leaching processes and will eventually find its way to a surface water system, thereby increasing nutrient loading and eutrophication in freshwater systems (Sharpley and Rekolainen, 1997; Stevenson, 1986). Eutrophication is the process of nutrient enrichment of surface waters such as lakes, streams and ponds, which gives rise to an increase in the growth of aquatic plants such as algae (Stevenson, 1986). Eutrophication has been, and remains a notable environmental issue in the U.S. and around the world since the latter half of the twentieth century. Eutrophication came to the forefront of environmental issues within the U.S. in the 1960s in the Great Lakes region, and similar issues began to arise soon after in the British Isles and Western Europe as well (Tunney et al., 1997). The Clean Water Act of 1972 and the development of conservation programs and task forces, such as the Hypoxia Task Force of the Gulf of Mexico and the Chesapeake Bay Program, were initiated to combat water pollution, with the latter programs focusing specifically on nutrient loading and contamination issues in their respective areas. Eutrophication was initially thought to arise from point-source inputs such as sewage effluent, for example, the case of Lake Washington near Seattle,

WA (Edmondson et al., 1956). However, as the point-source inputs were remediated, hypoxic regions were not significantly decreasing in size and were increasing in rural or agriculturally dominated catchments and drainages, such as the case of Grand Lake St. Marys in western Ohio (Hoorman et al., 2008). It soon became apparent that non-point source agricultural phosphorus was the significant input influencing eutrophication in water bodies (Tunney et al., 1997). The management of phosphorus inputs is of great importance for reducing eutrophication of fresh waters in the U.S.

According to the United States Environmental Protection Agency (U.S. EPA, 2013), each of the 50 states is impacted by nutrient pollution, and excess P is one of the most serious water pollution issues in the U.S. The EPA also notes that one of the largest contributors of excess nutrients to surface waters is agriculture, particularly from animal manure, excess fertilizer, and soil erosion (U.S. EPA, 2013). Phosphorus is lost from a cropping system primarily through overland runoff, soil erosion, and, in some cases, leaching. Many studies have shown that P from fertilizers, animal wastes, and other soil amendments accumulates in agricultural topsoils, where it is bound to the most erodible soil components (clays, organic matter, and Fe and Al oxides), thus justifying erosion and runoff as important transport processes of P. Three major watersheds that have known and significant P loading issues include the Upper Mississippi sub-basin, the Chesapeake Bay watershed, and the Bay Delta-Central Valley watershed of California (Figure 1.1).

The Mississippi River basin spans 31 states and is the third largest river basin in the world. The basin drains into the Gulf of Mexico, where a large hypoxic zone is fueled by excess nutrient loads, which consumes dissolved oxygen and triggers massive algae growths every summer (Mississippi River/Gulf of Mexico Watershed Nutrient Task

Force, 2013). The Upper Mississippi Sub-basin watershed is one of the basin's six major sub-basins, which are organized geographically, and includes portions of South Dakota, Minnesota, Wisconsin, Iowa, Illinois, Indiana, and Missouri. Over 60% of the land use in this area is dominated by cropland or pasture agriculture (Jordahl, 2013). Alexander et al. (2008) found that 80% of P entering the Gulf of Mexico comes from agricultural uses (i.e. crops, pasture, and range), and that the percentage of total phosphorus nutrient load in streams of the Upper Mississippi Sub-basin that are delivered to the Gulf of Mexico can contribute as much as 90% of the P to the hypoxic Dead Zone. Having better control over the amount of P leaving the Upper Mississippi region is necessary to further combat this environmental issue downstream to the Gulf of Mexico.

The Chesapeake Bay watershed, along the mid-Atlantic coastal region of the U.S., covers roughly 64,000 square miles and portions of six states, including New York, Pennsylvania, West Virginia, Virginia, Maryland, and Delaware. Almost one-quarter of the watershed is devoted to agriculture, which has been noted as the single largest source of nutrient and sediment pollution entering the Chesapeake Bay (Chesapeake Bay Program, 2012). In 1987, the Chesapeake Bay Agreement was established, with the aim to lower the amounts of P entering into the Bay which was promoting large algae blooms and hypoxic zones (Chesapeake Bay Program, 2012). The Chesapeake Bay Agreement, however, has not resulted in rapid dramatic improvements to the region (Chesapeake Bay Program, 2012). The Chesapeake Bay Program reported that the Maryland Department of Natural Resources and Virginia Department of Environmental Quality measured and found the hypoxic volume of the Chesapeake Bay for the summer of 2013 to be slightly above average, compared to the last 30 years of summer measurements, and about 5.6%

larger than the summer of 2012 (Chesapeake Bay Program, 2012). The Chesapeake Bay area continues to be a region of high interest in terms of P loading studies aiming to reduce eutrophication in that area.

The third large watershed of interest is the California Central Valley-Bay Delta watershed and is comprised of three large watersheds, the San Francisco River watershed, the San Joaquin River watershed, and the Tulare Lake Basin watershed, that drain the Central Valley region of California into the San Francisco Bay Delta. A vitally important ecosystem and ecological area, the Bay Delta creates a habitat for hundreds of aquatic and terrestrial species that are threatened by nutrient and sediment loading which alters and degrades the ecosystem (Bay Delta Conservation Plan, 2013). As one of the most important agricultural centers of the world (Schneider et al., 1998), the Central Valley watersheds support large areas of row crop, pasture, and irrigated agricultural lands (Hart et al., 1998). According to the California Regional Water Quality Control Board for the Central Valley Region, P is considered a biostimulatory substance in that it promotes the growth of aquatic species in concentration that cause nuisance or adversely affect water for beneficial uses (Hart et al., 1998; Schneider et al., 1998). Over the last 20 years, the state of California has listed several of the rivers draining catchments in the basins as impaired water bodies due to excess nutrient loading (Kratzer and Shelton, 1998; Sobota et al., 2011). Sobota et al. (2011) further highlight the necessity to understand the spatial patterns and relative magnitudes of the various land-based P sources, predominately from agricultural areas, in order to reduce inputs to surface waters that drain to the Bay Delta.

Phosphorus plays an essential role in agriculture, and for the continued growth of life on earth. Excess land applications of P to agricultural fields and mismanagement of

nutrient sources has led to P becoming an environmental issue due to the negative impacts on water quality, and it will continue to be an issue until land, water, and nutrient management practices improve. The continued development of our understanding about the P sorption, particularly desorption, behaviors of soils is a major component to improving predictive models and developing better management practices at various scales.

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## CHAPTER 2

### PHOSPHORUS DESORPTION CHARACTERISTICS AND RELATIONSHIPS OF UNITED STATES AGRICULTURAL SOILS

#### ABSTRACT

Phosphorus (P) loss from agricultural soils has clearly been shown to be a major environmental issue, however concerns about the effectiveness of current approaches to attaining water quality and environmental goals continue. The P Index assessment tool relies on soil test P values as an Index source component, which do not accurately predict soil P release behaviors. A collection of 313 agricultural surface soils from across the United States (U.S.) were analyzed for P sorption and desorption, using double-point anion exchange resin (DP-AER), P sorption index (PSI), and adsorption isotherm methods. Objectives of this study were to determine relationships between P desorption behaviors and other soil properties, to develop predictive models to provide better estimates of pollution risk at the watershed, farm, and field levels, and possibly improve existing models that predict nutrient losses to target management practices. Linear regression models were developed and validated for each P sorption variable, and were compared to models developed when soils are grouped by calcium carbonate content and degree of weathering, and by taxonomic Great Group. Models for the indicated grouping schemes were notably better at accurately predicting total P release from soils. Overall, the significant ( $p < 0.05$ ) P sorption prediction model components all included clay, total carbon, or pH, with oxalate Al and/or Fe or Mehlich-3 extractable Al, Ca, Fe, Mg, and/or

Mn. The models developed in this study have to the potential of improving current assessment and management planning tools, and also indicate the need for soil testing facilities to include oxalate and Mehlich-3 extraction analyses as standard analyses for all soil samples in order to develop more accurate prediction models to combat this major environmental issue.

## ABBREVIATIONS

**AER1** - phosphorus released from soil during the 1 hour extraction period (mg P/kg soil); **AER23** - phosphorus released from soil during the 23 hour extraction period (mg P/kg soil); **AER24** - total phosphorus released from soil in 24 hours (mg P/kg soil); **Al<sub>M</sub>** - Mehlich No. 3 extractable aluminum (mg Al/kg); **Al<sub>ox</sub>** - acid oxalate extractable aluminum content (%); **CaCO<sub>3</sub>** - calcium carbonate equivalent (%); **Ca<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Ca<sub>M</sub>** - Mehlich No. 3 extractable calcium (mg Ca/kg); **CONUS** - conterminous United States; **DP-AER** - double-point anion exchange resin; **Fe<sub>M</sub>** - Mehlich No. 3 extractable iron (mg Fe/kg); **Fe<sub>ox</sub>** - acid oxalate extractable iron content (%); **ICP-AES** - inductively coupled plasma atomic emission spectrometry; **KSSL** - Kellogg Soil Survey Laboratory; **Mg<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Mg<sub>M</sub>** - Mehlich No. 3 extractable magnesium (mg Mg/kg); **Mn<sub>M</sub>** - Mehlich No. 3 extractable manganese (mg Mn/kg); **NLCD** - National Land Cover Dataset; **NRCS** - Natural Resources Conservation Service; **NSSC** - National Soil Survey Center; **P<sub>Bray1</sub>** - Bray-1 extractable phosphorus (mg P/kg soil); **P<sub>CaCl2</sub>** - 0.01 M calcium chloride extractable phosphorus (mg P/kg soil); **P<sub>M</sub>** - Mehlich No. 3 extractable phosphorus (mg P/kg soil), measured using ICP-AES; **P<sub>M3</sub>** - Mehlich No. 3 extractable phosphorus (mg

P/kg soil), measured using a spectrophotometer at 882 nm; **P<sub>ox</sub>** - acid oxalate extractable phosphorus content (mg P/kg soil); **PSI** - phosphorus sorption index (L/kg); **P<sub>ws</sub>** - water soluble phosphorus content (mg P/kg soil); **SERA-IEG 17** - Southern Extension and Research Activity - Information Exchange Group 17; **S<sub>max</sub>** - phosphorus sorption maximum (mg/kg); **TC** - total carbon content (%); **USDA** - United States Department of Agriculture.

## INTRODUCTION

Eutrophication and the contaminating of surface waters with phosphorus (P) is a major environmental issue throughout the United States. Accelerated algae and aquatic plant growth in lakes and streams (eutrophication) indicate water quality degradation by P contamination (Sharpley et al., 1999). In many cases, sediment attributed to runoff and erosion from agricultural lands has been noted as a source of the P degrading waters. Phosphorus has long been recognized as an essential element for plant growth and a fertilization component to maintain profitable crop production. The widespread deficiency of P in agricultural soils initiated the study of phosphorus sorption and desorption by soils. The characteristics and behaviors of P movement, retention, and release in soil continues to be a highly studied area due to the abundance of P-loading issues in freshwater systems that are primarily driven by erosion and leaching from agricultural areas. Early analytical methods used to determine the amount of soil available P (Bray P-1, Olsen P, Mehlich-1 and -3 P, water soluble, and acid oxalate extractable P) were originally developed to estimate fertilizer requirements by determining the amount of P available for crop uptake and the probability of crop

response to added P (SERA-IEG, 2009). These methods have also often been used in environmental comparative studies where they have been shown to have good correlations with other soil properties (Kleinman and Sharpley, 2002) and with other soil P tests (Kleinman et al., 2001). These traditional soil P tests have also been used in P sorption/desorption and predictive modeling of P runoff and leaching (Burt et al., 2002; Gartley and Sims, 1994; Heckrath et al., 1995; Pote et al., 1996; Sharpley, 1996; Sims et al., 1998).

P sorption isotherms are often used to determine the P sorption capacity of soils by plotting the amount of P adsorbed from several solutions of known initial concentration versus the P concentration at equilibrium for each solution. Fox and Kamprath (1970) noted that P sorption isotherms account for both intensity and capacity factors of P sorption in soils and was a method studying P reactions that was more closely related to plant needs than other soil test P methods. Nair et al. (1984) proposed a standard P adsorption isotherm procedure that would produce consistent results over a wide range of soils. This procedure was later evaluated and revised, and proposed as a standardized P adsorption procedure by the SERA-IEG 17 group (2009). This method, however, is very labor and time intensive, and has thus led to the development and use of other P sorption procedures, including a single-point isotherm method known as the P sorption index (PSI) (Bache and Williams, 1971; SERA-IEG, 2009), P extraction with iron oxide impregnated filter paper (Chardon et al., 1996; SERA-IEG, 2009), and P extraction with anion exchange resin beads (Amer et al., 1955; Burt et al., 2004; Elrashidi et al. 2003). The latter two methods have been applied to soils to assess P desorption in runoff and surface waters as they act as P-sinks in a soil solution, though the iron oxide

strip method tends to be more problematic in practice, and has more errors associated with its estimations of P (Uusitalo and Yli-Halla, 1999). Over a century of studies on soil P retention or P sorption from around the world have noted that these processes are greatly influenced soil properties. At least nine studies (Burt et al., 2002; Juo and Fox, 1977; Leytem and Westermann, 2003; McCallister and Logan, 1978; Owa and Kato, 1989; Syers et al., 1981; Tunesi et al., 1999; Wild, 1950; Zhou and Li, 2000) found that clay content influences P retention or sorption. Six studies (Harter, 1969; Lopez-Hernandez and Burnham, 1974; Saunders, 1965; Simard et al., 1994; Wild, 1950; Zhou et al., 1997) found that organic carbon influences P retention or sorption. Twenty studies (Bolland et al., 1996; Cross and Schlesinger, 1995; Efimov et al., 2001; Fox and Searle, 1978; Freese et al., 1992; Giesler et al., 2005; Harter, 1969; Leytem and Westermann, 2003; Loveland et al., 1983; Mozaffari and Sims, 1996; Reddy et al., 1998; Russell et al., 1988; Saunders, 1965; Sharpley et al., 1989; Simard et al., 1994; Syers and Curtin, 1988; Tunesi et al., 1999; Wild, 1950; Williams et al., 1971; Yuan and Lavkulich, 1994; Zhou et al., 1997;) found that Al and Fe oxides and hydroxides influence P retention or sorption. Lastly, eleven studies (Al-Sewailam, 1999; Burt et al., 2002; Carey et al., 2001; Kleinman and Sharpley, 2002; Kuo and Lotse, 1972; Larsen and Widdowson, 1970; Lindsay, 1979; Schierer et al., 2006; Sharpley et al., 1989; Wild, 1950) found that calcium carbonates and Ca ions influence P retention or sorption in soils.

Fox and Kamprath (1970) noted several years ago that when evaluating P buffering properties, observing the desorption of soil P would probably be more pertinent than P sorption. Several studies have focused on using soil test P to determine the relationships between P in surface soils and runoff water (Eghball and Gilley, 1999; Pote



et al., 1996; Westerman et al., 2001), but Elrashidi et al. (2003) note that since P losses by runoff is a function of P source and transport parameters, using only the soil tests to estimate these losses from agricultural watersheds is questionable. P desorption methods that utilize anion exchange resins (AER), which use water matrices and mimic natural conditions better than analyses that use chemical extractants, have been used to measure soil P concentration, capacity, and rate of release (Amer et al., 1955; Elrashidi et al., 2003; Sibbesen, 1978; Uusitalo and Yli-Halla, 1999; Vaidyanathan and Talibudeen, 1970). However, more information about how various soils sorb P and how that behavior relates to the soil's physical and chemical characteristics, as well as understanding the role of local hydrology, is required in order to make more accurate and reliable predictions of the soil-to-water transfer of P (Vadas et al., 2006).

The objective of this study was to develop predictive relationships between P desorption behaviors and other soil properties using simple and multiple linear regression models. The outcomes of these objectives are; (1) the identification of agricultural soils that contain high amounts of P, relative to their sorptive potential, that would have the most negative effect on surface water if eroded, (2) the classification of soils as to their potential to contribute P to surface waters, and (3) the evaluation of how soils retain (adsorption) and release P (desorption), to provide better estimates of pollution risk at the watershed, farm, and field levels, and possibly improve existing models that predict nutrient losses.

## **MATERIALS AND METHODS**

### **Laboratory Sample Selection**

A total of 313 archived agricultural surface soil samples collected from across the conterminous U.S. (CONUS) by the NRCS were analyzed for this study. Samples were selected based on the availability of following data; (1) spatial location of the pedon and date of collection, more recently collected samples were given a higher preference, (2) pedon location is designated as agricultural land on the 2011 National Land Cover Data (NLCD) geospatial layers, and (3) availability of data in the NSSC-KSSL database on the general properties known to effect P retention (e.g. clay, pH, calcium carbonate, iron and aluminum oxalate, total carbon). Samples were also chosen in an attempt to ensure adequate representation of agricultural soil series and spatial randomness. A subset of 78 samples was randomly selected to be used to validate the prediction equations developed to model P desorption and adsorption. The subset of validation samples is comprised of three smaller subsets of randomly selected samples that represent 25% of the samples that fall into a group determined by the sample's  $\text{CaCO}_3$  content and degree of weathering (discussed in the Results and Discussion section), as follows: calcareous soils, 11 validation samples; highly weathered soils, 16 validation samples; slightly weathered soils, 51 validation samples. Sample locations for both modeling and validation samples are shown in Figure 2.1 and pedon taxonomic information for each sample is listed in Appendix A.

Study samples were also stratified into groups based on the Great Group category, defined by the U.S. Soil Taxonomy classification system. The study samples comprised a total of 81 taxonomic Great Groups. The Great Groups Argiustolls, Hapludalfs, and

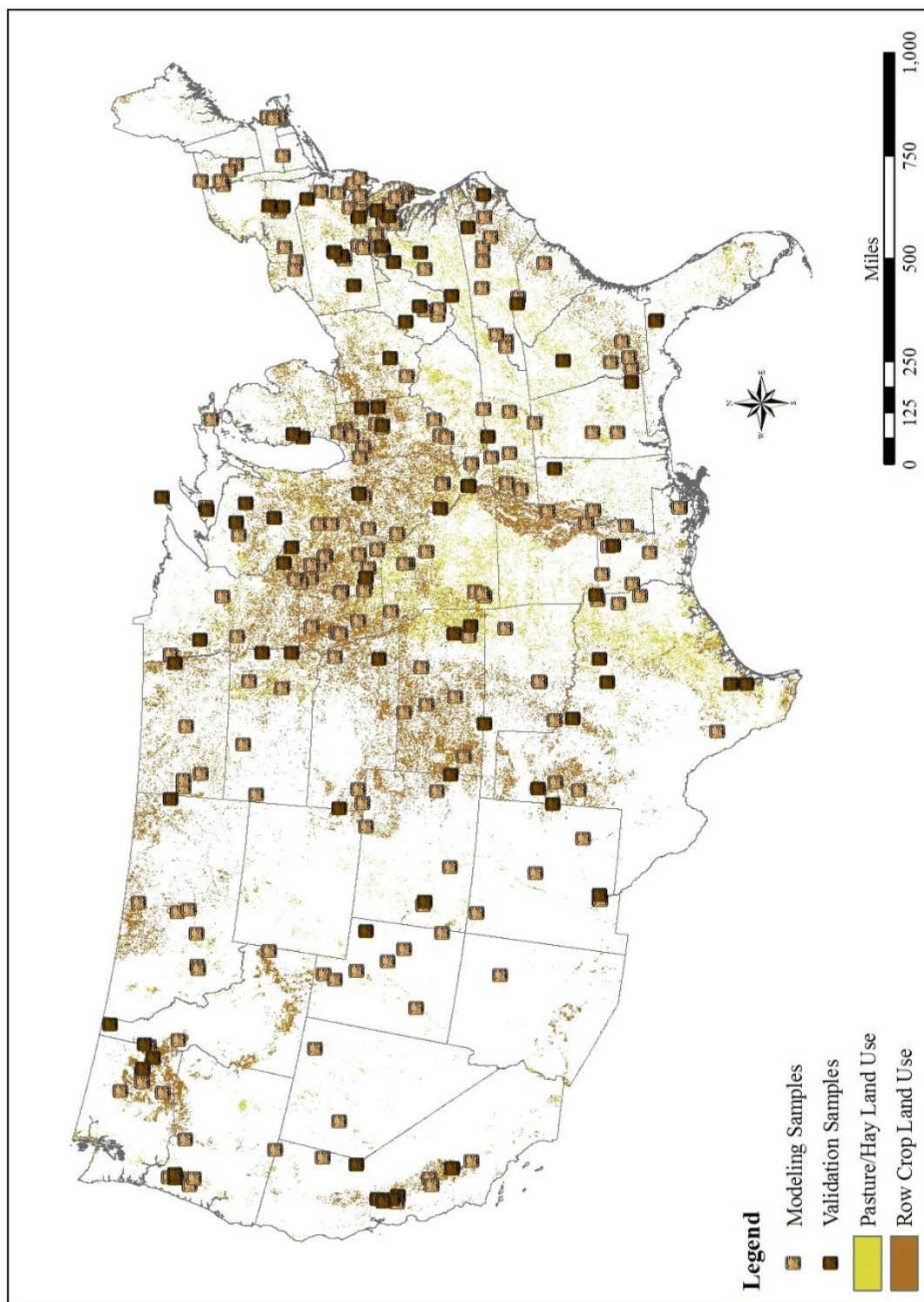


Figure 2.1. Locations of all modeling and validation samples investigated.

Hapludults had the most number of samples per Great Group, with 16, 39, and 19 samples, respectively. From each of these Great Groups, a subset of 25% of the samples from each group was randomly selected to be used to validate the prediction equations developed to model P desorption and adsorption. Taxonomic information for the Argiustolls, Hapludalfs, and Hapludults is listed in Appendix A.

### **Standard Sample Characterization Analyses**

All samples in this study received laboratory characterization by analytical procedures described in the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004) with representative alphanumeric codes for standard operating procedures in parentheses. All standard analyses were performed on air-dried <2-mm soil, with resulting data reported on an oven-dry basis. Analyzed characterization properties included particle-size analysis, total carbon, acid oxalate extractable Al, Fe, and P, Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P), cation exchange capacity, pH, calcium carbonate equivalent, and water extractable P.

Particle-size analysis was determined by sieve and pipette (3A1a), following pre-treatments for removal of organic matter and soluble salts, and chemical dispersion with sodium hexametaphosphate. Total carbon (TC) content was determined by dry combustion (4H2a) on air-dried <180- $\mu$ m (80 mesh) soil. Acid oxalate (4G2a) extracts were analyzed for Fe<sub>OX</sub>, Al<sub>OX</sub>, and P<sub>OX</sub> by inductively coupled plasma atomic emission spectrometry (ICP-AES). Mehlich-3 (4D6b) extracts were analyzed for Al<sub>M</sub>, Ca<sub>M</sub>, Fe<sub>M</sub>, Mg<sub>M</sub>, Mn<sub>M</sub>, and P<sub>M</sub> by ICP-AES, and Mehlich-3 (4D6a) extractable phosphorus (P<sub>M3</sub>) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm. Soil pH

(4C1a2a) was measured using a 1:1 soil-water solution. Calcium carbonate ( $\text{CaCO}_3$ ) equivalent (4E1a1a1a1) was determined by treating the soil with hydrochloric acid, manometrically measuring the evolved carbon dioxide, and then calculating the percent  $\text{CaCO}_3$ . Ammonium acetate extractable calcium ( $\text{Ca}_{\text{NH}_4}$ ) and magnesium ( $\text{Mg}_{\text{NH}_4}$ ) were measured with  $\text{NH}_4\text{OAc}$  buffered at pH 7.0 (4B1a) and measured by ICP-AES. Water extractable phosphorus (4D2a) ( $\text{P}_{\text{ws}}$ ) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm.

### **Sample Phosphorus Sorption Analyses**

The primary objective in selecting methods was to choose methods that could simulate natural field conditions, meet the objectives of determining the maximum capacity of agricultural soils to hold phosphorus (P capacity), and determine how much P would desorb from eroded sediment. To determine P capacity, the standard “P sorption index” (PSI) method outlined by Sims in SERA-IEG 17 (2009) was utilized. The method used to determine phosphorous desorption was the standard double-point anion exchange resin (DP-AER) method, as outlined in Elrashidi et al (2003) and the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004). The standard method of P adsorption isotherm determination, as proposed originally proposed in Nair et al. (1984), and again by Graetz and Nair in SERA-IEG 17 (2009), was used to further understand the P retention and sorption capacity of the soils.

### *P Sorption Index (PSI)*

This single-point isotherm method was developed to overcome the limitations of the more time-consuming and complicated standard P adsorption isotherm methods. PSI has been found by several researchers to be well correlated with soil P adsorption maxima and a wide variety of chemical and physiological properties (Bache and Williams, 1971; Mozaffari and Sims, 1994; Sharpley et al., 1984; Simard et al., 1994). As outlined by Sims in SERA-IEG 17 (2009) following the Bache and Williams (1971) method, 2.25-g, <2-mm, air-dried soil sample was shaken at room temperature with 45 mL of a 75 mg P/L as  $\text{KH}_2\text{PO}_4$  solution and two drops of chloroform to inhibit microbial activity for 18 hours at 100 oscillations/min. The sample was then centrifuged at 2000 rpm for 30 minutes, after which the sample extract was filtered using a Whatman 45 filter. The P-saturated soil samples were allowed to air-dry and used to analyze soil P desorption with the double-point anion exchange resin procedure (following). P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962). PSI (L/kg) of the soil sample was then determined with the following equations:

$$\text{PSI (L/kg)} = X / \log C \quad [2.1]$$

where X is the amount of P adsorbed (mg P/kg) and C is the concentration of P after 18 hour equilibration (mg/L).

### *Double-Point Anion Exchange Resin*

An anion exchange resin technique using a soil and water suspension and a dilute sodium chloride extracting solution, was found to be a sufficient method for estimating the quantity of P released and the rate of P-release from soil. This method is analogous to

a more natural process for P removal from soil solution than attempting to estimate P release with the various chemical extracts utilized in other P methods (Amer et al., 1955). Following Elrashidi et al (2003) and Burt (2004), a 2-gram, <2-mm, air-dried soil sample, was shaken with a 4-gram perforated bag of spherical anion exchange resin beads and 100 mL of deionized water for 1 hour at 100 oscillations/min at room temperature. The resin bag was removed from the soil suspension and shaken with 50 mL of 1.0 *M* sodium chloride (NaCl) for 1 hour to remove P retained by the resin. Another 4-gram resin bag was added to the soil suspension and shaken for an additional 23 hours at 100 oscillations/min at room temperature. The second resin bag was removed and rinsed with 1.0 *M* NaCl and shaken for 1 hour. The NaCl extracting solutions were filtered to 150 mm using Whatman 42 filter paper. A 2- mL concentration of 12 *N* hydrochloric acid (HCl) was added to each filtered extract. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) using a spectrophotometer at 880 nm, within 72 hours of extraction. Extract P (mg/L) was then converted to mass of soil P (mg/kg) using the following equation:

$$\text{AER (mg/kg)} = [(A*B*C*R*1000)/E] \quad [2.2]$$

where A is the sample extract concentration (mg/L), B is the extract volume (L), C is the dilution (if performed), R is the air-dry/oven-dry weight ratio, and E is the sample weight (g), for P released after one hour (AER1), P released after an additional 23 hours (AER23), and total P released after a total of 24 hours (AER24).

### *Phosphorus Adsorption Isotherm Determination*

Phosphorus adsorption isotherms were performed following the method of Graetz and Nair (2009). A 0.75-g, <2-mm, air-dried soil sample was shaken for 24 hours at 100 oscillations/min at room temperature with 20 mL of a 0.01 M calcium chloride ( $\text{CaCl}_2$ ) solution containing 0, 0.1, 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 mg P/L as  $\text{KH}_2\text{PO}_4$  and two drops of chloroform to inhibit microbial activity. The sample was then centrifuged at 3000 rpm for 10 minutes, after which the sample extract was filtered using a Whatman 45 filter. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) at 880 nm using a spectrophotometer, within 72 hours of extraction. 0.01 M calcium chloride extractable phosphorus ( $\text{P}_{\text{CaCl}_2}$ ) was then determined from the extracts from the soil mixed with the  $\text{CaCl}_2$  solution containing 0 mg P/L. Results were analyzed and sorption parameters were determined using the linearized Langmuir equation:

*Linearized Langmuir equation:*

$$C / S = (1 / kS_{\text{MAX}}) + (C / S_{\text{MAX}}) \quad [2.3]$$

where S is the total amount of P retained (mg/kg), C is the concentration of P after 24 hour equilibration (mg/L),  $S_{\text{MAX}}$  is the P sorption maximum (mg/kg), and k is a constant related to the bonding energy (L/mg P).

### *Statistical Analysis*

Study samples were analyzed using routine statistical analyses, including descriptive statistics, correlation, and multiple linear regression using the statistical software program, SAS<sub>TM</sub> v. 9.4. The assumptions of the Person correlation include (a) each variable is continuous in measurement, (b) each observation has a pair of values, (c)



the absence of outliers in either variable, (d) the normality of each variable, (e) a linear relationship between variables, and (f) homoscedasticity, a tube-like shape between values on a scatterplot and the linear trend line between the variables. The assumptions of multiple linear regression include (a) a linear relationship between the independent and dependent variables, (b) multivariate normality, (c) no or little multicollinearity, (d) no auto-correlation, and (e) homoscedasticity. The SAS CORR procedure with the PEARSON option was used for correlation analyses, while the REG procedure was used for regression analyses and to develop the final prediction equations. Not all assumptions were met when study data was applied to the correlation and regression analyses.

## **RESULTS AND DISCUSSION**

Several studies have shown that various soil P predictions are strongly influenced by and dependent on soil chemical, mineralogical, and physical properties and related to soil Taxonomy (Burt et al., 2002; Sharpley et al., 1984; Sharpley et al., 1985; Tiessen et al., 1984). Similar to the findings of Sharpley et al (1984), preliminary analysis of data in this study indicated relationships between the soil properties and the P sorption properties improved when soils were divided into groups based on the presence of  $\text{CaCO}_3$  and their degree of weathering. These groups were defined as follows in Sharpley et al (1984): calcareous soils - soils with free  $\text{CaCO}_3$ ; highly weathered soils - Ultisols, Oxisols, Quartzipsamments, Ultic subgroups of Alfisols, and acidic Ochrepts; slightly weathered soils - all other soils.

## Phosphorus Sorption Relationships with Soil Properties

Descriptive statistics were determined for the measured P sorption variables (AER1, AER23, AER24, PSI,  $S_{MAX}$ ) for both the modeling and validation datasets for All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils (Table 2.1). Descriptive statistics were also determined for the measured P sorption variables for both the modeling and validation datasets for Argiustolls, Hapludalfs, and Hapludults (Table 2.2). Overall, AER1 ranged from 18.90 to 437.41 mg P/kg soil, AER23 ranged from 10.27 to 377.89 mg P/kg soil, and AER24 ranged from 45.44 to 754.77 mg P/kg soil (Table 2.1). Average AER1 was 111.35 mg P/kg soil, average AER23 was 90.07 mg P/kg soil, and average AER24 201.59 mg P/kg soil, for the All Soils modeling dataset (Table 2.1). PSI ranged from 0 to 682.79 L/kg, while  $S_{MAX}$  ranged from 0 to 3333.33 mg/kg, overall (Table 2.1). Average PSI was 115.16 L/kg and average  $S_{MAX}$  was 240.36 mg/kg, for the All Soils modeling dataset (Table 2.1). With the exception of  $S_{MAX}$ , ranges for each P sorption variable in the validation datasets were within the overall ranges noted in the respective modeling datasets (Tables 2.1 and 2.2). The influence of high-end outliers is often noted by mean values greater than median values for each P sorption variable (Tables 2.1 and 2.2), resulting in non-normal distributions. Boxplots were developed for the AER variables for the All Soils modeling and validation datasets (Figure 2.2). Boxplots were also developed for the PSI (Figure 2.3) and  $S_{MAX}$  (Figure 2.4) variables for the All Soils modeling and validation datasets. Boxplots were developed for the P adsorption variables and boxplots of distributions for all P sorption variables for Calcareous soils, Highly Weathered soils, and Slightly Weathered soils datasets, and the Argiustolls, Hapludalfs, and Hapludults datasets (Appendix B).

Table 2.1. Descriptive statistics of the P sorption variables analyzed for samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling and validation datasets.

	AER1	AER23	AER24	PSI	S <sub>MAX</sub>		AER1	AER23	AER24	PSI	S <sub>MAX</sub>
	---- mg P/kg soil ----			L/kg	mg/kg		---- mg P/kg soil ----			L/kg	mg/kg
All Soils - Modeling Dataset						All Soils - Validation Dataset					
Mean	111.35	90.07	201.59	115.16	240.36	Mean	124.53	98.56	223.09	141.06	278.24
Standard Error	3.84	4.07	6.82	6.17	27.09	Standard Error	7.50	7.30	12.37	11.67	85.09
95% Confidence Level for Mean	7.57	8.01	13.43	12.16	53.64	95% Confidence Level for Mean	14.93	14.53	24.64	23.24	171.38
Median	103.99	75.18	181.61	100.42	162.61	Median	107.75	80.60	215.49	121.59	113.70
Minimum	18.90	10.27	45.44	0.00	0.00	Minimum	36.45	21.50	58.74	7.74	0.00
Maximum	437.41	377.89	754.77	682.79	1666.67	Maximum	380.56	371.82	602.96	557.95	3333.33
N	235	235	235	235	120	N	78	78	78	78	46

	AER1	AER23	AER24	PSI	S <sub>MAX</sub>		AER1	AER23	AER24	PSI	S <sub>MAX</sub>
	---- mg P/kg soil ----			L/kg	mg/kg		---- mg P/kg soil ----			L/kg	mg/kg
Calcareous Soils - Modeling Dataset						Calcareous Soils - Validation Dataset					
Mean	141.73	68.58	210.31	105.75	159.86	Mean	193.29	68.97	262.26	167.23	160.99
Standard Error	13.31	10.55	22.71	13.16	54.91	Standard Error	24.45	7.75	29.64	17.02	74.38
95% Confidence Level for Mean	27.08	21.47	46.21	26.78	114.93	95% Confidence Level for Mean	54.48	17.28	66.04	37.93	182.00
Median	131.31	60.64	179.40	95.36	44.86	Median	188.11	70.18	235.47	171.93	111.11
Minimum	48.62	10.27	61.21	5.55	0.00	Minimum	105.67	32.14	139.15	91.17	30.21
Maximum	437.41	317.37	754.77	374.22	1000.00	Maximum	380.56	114.48	495.03	306.67	588.24
N	34	34	34	34	20	N	11	11	11	11	7

Table 2.1. Continued.

AER1    AER23    AER24    PSI    S <sub>MAX</sub>						AER1    AER23    AER24    PSI    S <sub>MAX</sub>					
---- mg P/kg soil ----				L/kg	mg/kg	---- mg P/kg soil ----				L/kg	mg/kg
Highly Weathered Soils - Modeling Dataset						Highly Weathered Soils - Validation Dataset					
Mean	105.68	96.05	202.55	98.36	206.98	Mean	193.29	68.97	262.26	181.25	776.39
Standard Error	10.69	8.33	15.28	10.87	58.22	Standard Error	24.45	7.75	29.64	35.47	377.44
95% Confidence Level for Mean	21.52	16.77	30.76	21.87	120.75	95% Confidence Level for Mean	54.48	17.28	66.04	75.59	870.39
Median	98.21	87.74	194.22	101.51	88.50	Median	188.11	70.18	235.47	122.08	217.39
Minimum	19.54	17.72	49.20	0.00	0.00	Minimum	105.67	32.14	139.15	20.66	35.21
Maximum	419.04	252.43	467.50	318.64	1250.00	Maximum	380.56	114.48	495.03	557.95	3333.33
N	47	47	47	47	23	N	16	16	16	16	9

AER1    AER23    AER24    PSI    S <sub>MAX</sub>						AER1    AER23    AER24    PSI    S <sub>MAX</sub>					
---- mg P/kg soil ----				L/kg	mg/kg	---- mg P/kg soil ----				L/kg	mg/kg
Slightly Weathered Soils - Modeling Dataset						Slightly Weathered Soils - Validation Dataset					
Mean	106.37	92.99	199.37	122.36	271.25	Mean	117.36	96.73	214.08	122.81	156.15
Standard Error	3.74	5.11	7.90	8.29	35.54	Standard Error	8.10	9.26	15.27	13.04	44.48
95% Confidence Level for Mean	7.38	10.10	15.60	16.38	70.78	95% Confidence Level for Mean	16.28	18.60	30.67	26.20	90.97
Median	99.78	77.32	178.90	100.67	200.00	Median	104.99	82.21	203.34	104.94	79.78
Minimum	18.90	13.23	45.44	0.00	0.00	Minimum	36.45	21.50	58.74	7.74	0.00
Maximum	289.91	377.89	564.87	682.79	1666.67	Maximum	286.49	371.82	602.96	461.78	1250.00
N	154	154	154	154	77	N	51	51	51	51	30

Table 2.2. Descriptive statistics of the P sorption variables analyzed for samples in the Argiustolls, Hapludalfs, and Hapludults modeling and validation datasets.

Argiustolls - Modeling Dataset						Argiustolls - Validation Dataset					
Mean	95.14	45.03	140.17	71.31	113.07	Mean	99.88	66.30	166.18	68.22	312.50
Standard Error	9.90	4.22	12.24	11.50	39.67	Standard Error	25.72	17.71	42.14	24.27	0.00
95% Confidence Level for Mean	21.79	9.29	26.94	25.31	126.24	95% Confidence Level for Mean	81.85	56.36	134.11	77.25	-
Median	92.36	44.30	142.55	56.79	133.55	Median	86.13	67.78	153.90	58.50	312.50
Minimum	43.77	26.02	69.79	17.72	0.00	Minimum	56.76	21.50	78.26	24.91	312.50
Maximum	169.65	73.01	214.47	135.56	185.19	Maximum	170.51	108.13	278.64	130.96	312.50
N	12	12	12	12	4	N	4	4	4	4	1
Hapludalfs - Modeling Dataset						Hapludalfs - Validation Dataset					
Mean	88.63	102.13	190.76	97.87	233.76	Mean	77.67	72.70	150.37	120.80	107.76
Standard Error	5.94	11.67	16.80	10.53	34.57	Standard Error	9.64	7.37	14.71	31.62	43.65
95% Confidence Level for Mean	12.16	23.90	34.41	21.56	74.14	95% Confidence Level for Mean	21.80	16.66	33.27	71.53	121.19
Median	84.43	90.87	175.67	93.32	217.39	Median	72.05	73.02	170.87	112.59	82.64
Minimum	28.26	27.32	55.57	3.18	0.00	Minimum	26.53	34.30	60.83	17.96	20.28
Maximum	157.54	336.58	494.12	281.68	555.56	Maximum	126.57	111.47	206.97	307.66	263.16
N	29	29	29	29	15	N	10	10	10	10	5
Hapludults - Modeling Dataset						Hapludults - Validation Dataset					
Mean	117.80	98.62	219.16	89.95	310.34	Mean	106.91	126.48	233.39	174.05	274.25
Standard Error	18.69	11.92	22.14	24.81	173.05	Standard Error	17.47	19.03	32.56	40.49	71.69
95% Confidence Level for Mean	40.39	25.76	47.83	53.60	423.45	95% Confidence Level for Mean	48.52	52.83	90.39	112.41	308.46
Median	105.84	91.61	233.45	76.99	50.51	Median	97.28	124.51	219.65	117.33	217.39
Minimum	19.54	29.65	49.20	0.00	0.00	Minimum	68.99	77.99	152.28	107.41	188.68
Maximum	275.48	167.55	364.00	318.64	1250.00	Maximum	159.19	184.10	343.29	305.44	416.67
N	14	14	14	14	7	N	5	5	5	5	3

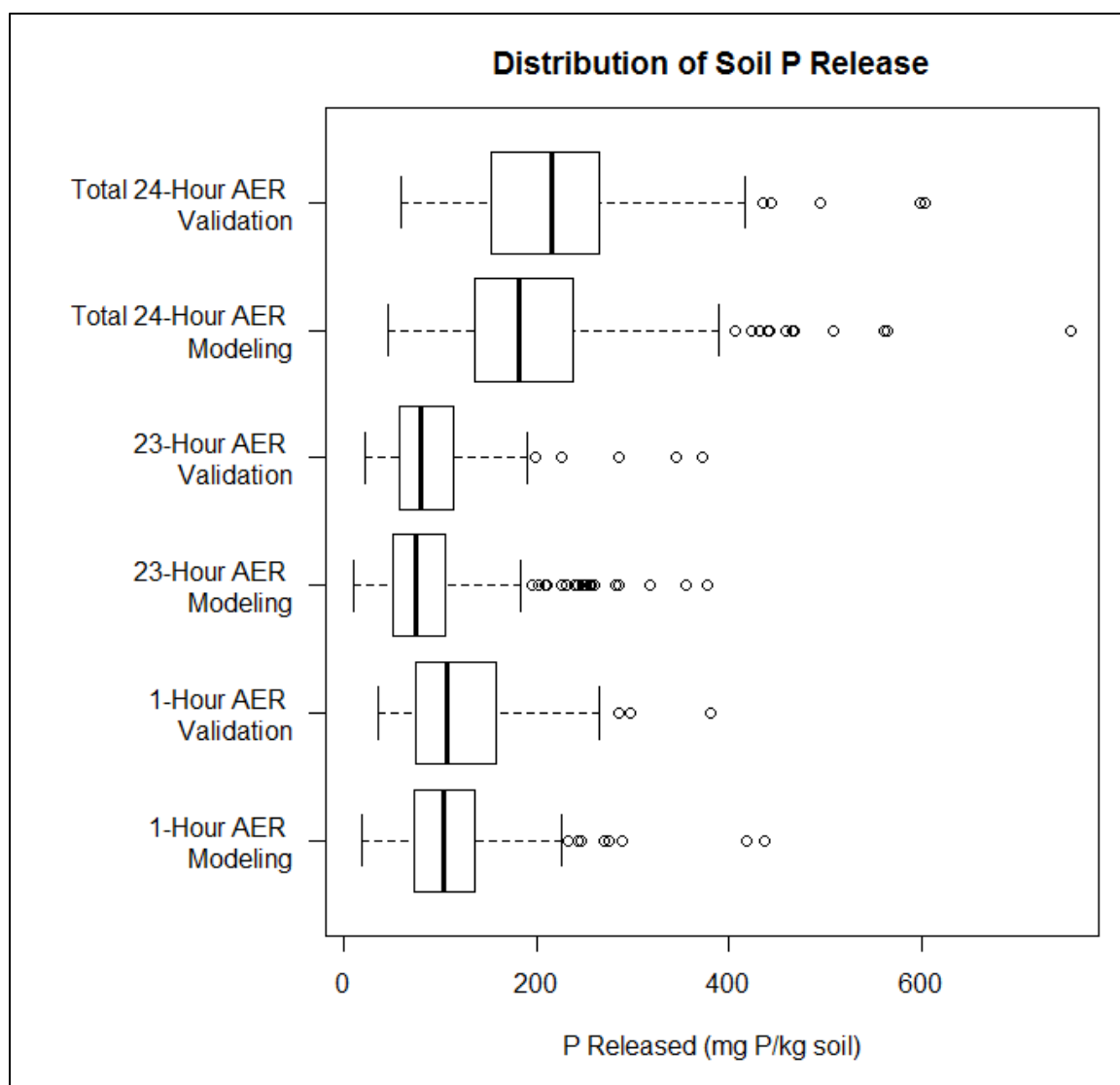


Figure 2.2. Boxplots displaying the quartile statistics of each measured P desorption variable (AER1, AER23, and AER24), for the All Soils modeling and validation datasets. The left and right ends of the box represent the first and third quartiles, respectively, and the bold band inside the box represents the median. The ends of the lines, or whiskers, represent the lowest datum still within 1.5 interquartile range of the lower quartile and the highest datum still within 1.5 interquartile range of the upper quartile. Outliers are plotted as individual points.

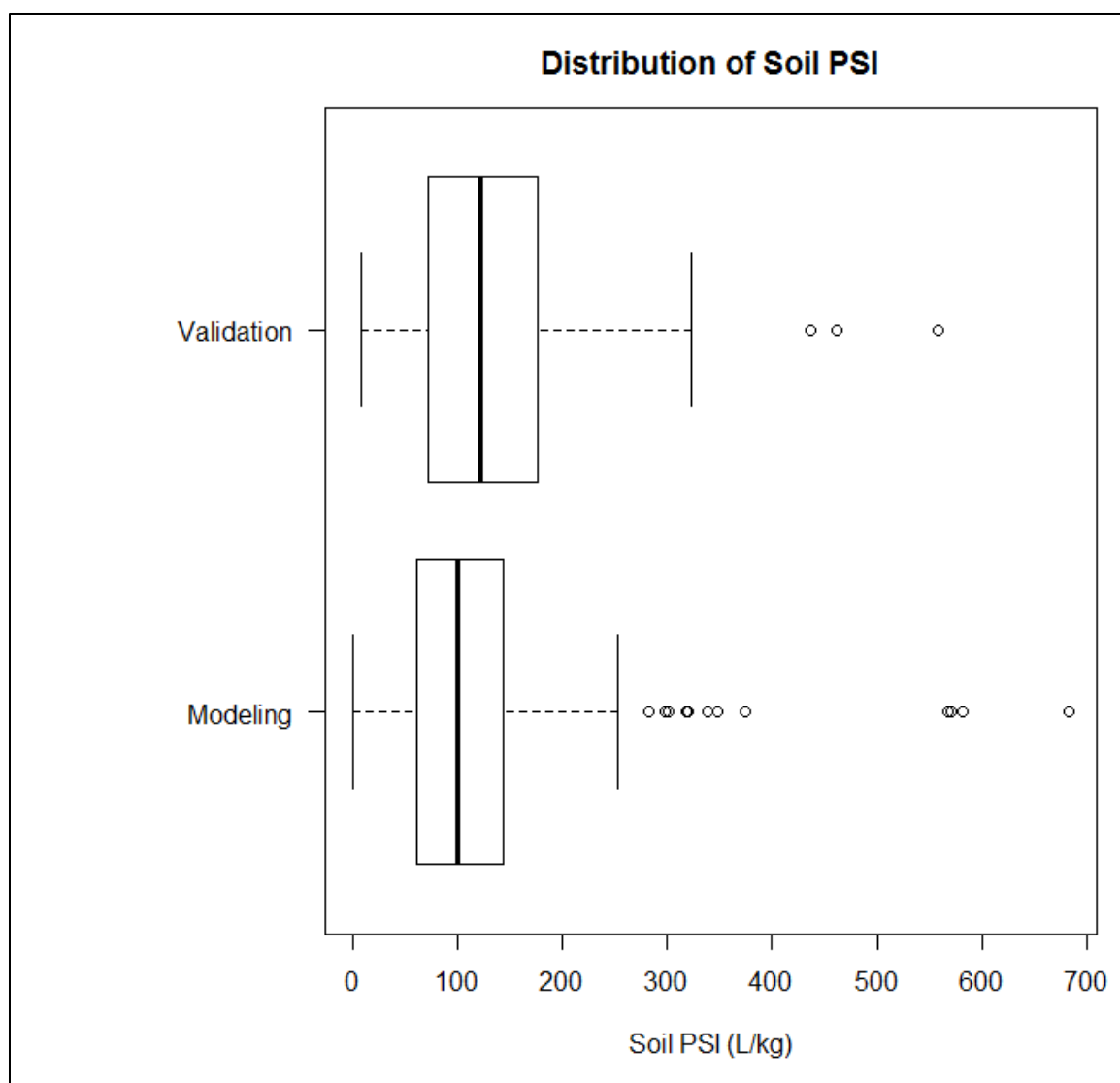


Figure 2.3. Boxplots displaying the quartile statistics of the PSI adsorption variable for the All Soils modeling and validation datasets.

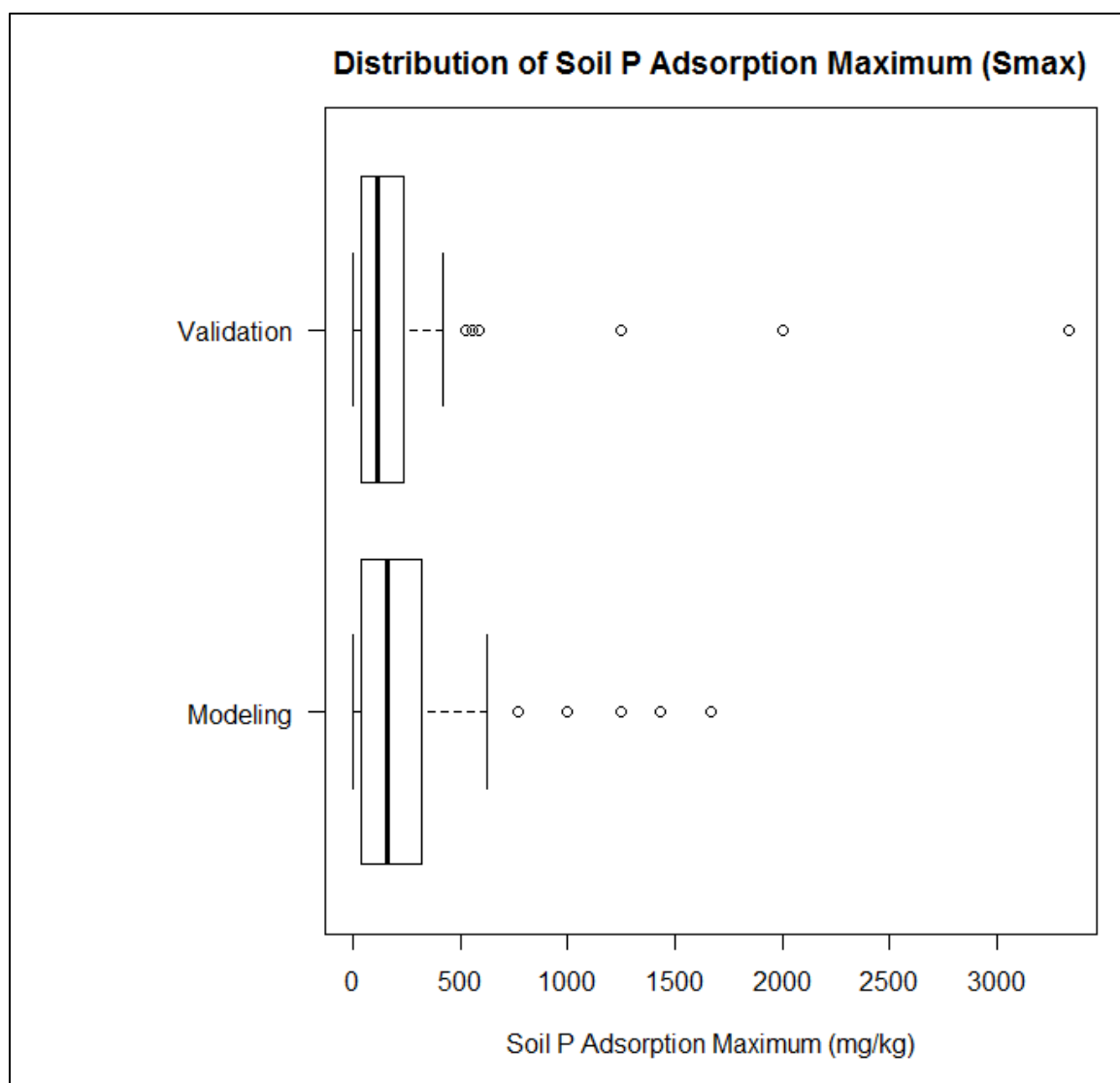


Figure 2.4. Boxplots displaying the quartile statistics of the  $S_{MAX}$  adsorption variable for the All Soils modeling and validation datasets.



Descriptive statistics were also determined for the analyzed soil properties known to affect soil P sorption for all modeling datasets and all validation datasets (Appendix B). Most properties encompassed a wide range of values in each grouping, and the influence of high-end outliers was often noted by mean values greater than median values for a particular property. Soil property ranges were 1.40 to 85.60 % for clay, 0.18 to 49.63 % for TC, and 0 to 75 % for  $\text{CaCO}_3$  content. Average clay was 20.31%, average TC was 3.12%, and average  $\text{CaCO}_3$  contents 0.91%, for samples in the All Soils modeling dataset. Average pH for samples in the all soils modeling dataset was 6.25, and the overall range for all samples was 3.6 to 8.5. Soil property ranges were 200 to 6900 mg Al/kg soil for  $\text{Al}_{\text{OX}}$  and 0 to 18700 mg Fe/kg soil for  $\text{Fe}_{\text{OX}}$ . Average  $\text{Al}_{\text{OX}}$  and  $\text{Fe}_{\text{OX}}$  for samples in the All Soils modeling dataset were 1223.40 mg Al/kg soil and 2741.70 mg Fe/kg soil, respectively. Soil property ranges were 1.10 to 1503.10 mg Al/kg soil for  $\text{Al}_{\text{M}}$ , 11.40 to 615.60 mg Fe/kg soil for  $\text{Fe}_{\text{M}}$ , and 0.50 to 1352.20 mg Mn/kg soil for  $\text{Mn}_{\text{M}}$ . Average  $\text{Al}_{\text{M}}$  was 584.95 mg Al/kg soil, average  $\text{Fe}_{\text{M}}$  was 147.93 mg Fe/kg soil, and average  $\text{Mn}_{\text{M}}$  was 133.05 mg Mn/kg soil, for samples in the All Soils modeling dataset. Soil property ranges were 14.00 to 37129.60 mg Ca/kg soil for  $\text{Ca}_{\text{M}}$  and 0.70 to 3827.20 mg Mg/kg soil for  $\text{Mg}_{\text{M}}$ . Average  $\text{Ca}_{\text{M}}$  and  $\text{Mg}_{\text{M}}$  for samples in the All Soils modeling dataset were 2384.69 mg Ca/kg soil and 356.41 mg Mg/kg soil, respectively. Property ranges were 0 to 91.00 cmol/kg for  $\text{Ca}_{\text{NH}_4}$  and 0 to 39.10 cmol/kg for  $\text{Mg}_{\text{NH}_4}$ . Average  $\text{Ca}_{\text{NH}_4}$  was 15.00 cmol/kg and average  $\text{Mg}_{\text{NH}_4}$  was 3.41 cmol/kg, for samples in the All Soils modeling dataset.

Average clay,  $\text{CaCO}_3$ , and pH were higher in the Calcareous soils modeling dataset, while average TC was higher in the Highly Weathered soils modeling dataset and

average clay was higher in the Slightly Weathered soils modeling dataset. Average  $Al_{ox}$  and  $Fe_{ox}$  were higher in the Slightly Weathered modeling dataset, while average  $Al_{ox}$  was also higher in the Hapludults modeling dataset and  $Fe_{ox}$  was higher in the Hapludalfs modeling dataset. Average  $Al_M$ ,  $Fe_M$ , and  $Mn_M$  were higher for samples in the Highly Weathered soils modeling dataset, and  $Al_M$  and  $Fe_M$  were higher for samples in the Slightly Weathered soils modeling dataset. Average  $Al_M$  was higher in the Hapludults modeling dataset and average  $Fe_M$  was higher in the Hapludalfs modeling dataset. Average  $Ca_M$  and  $Mg_M$  were higher in the Calcareous soils modeling dataset, and average  $Mg_M$  was higher in the Slightly Weathered soils modeling dataset. Average  $Ca_{NH4}$  and  $Mg_{NH4}$  were higher for samples in the Calcareous soils modeling dataset, and average  $Mg_{NH4}$  was higher in the Slightly Weathered soils modeling dataset.

Pearson correlation coefficients were calculated between the P sorption variables and soil properties known to affect P sorption in soils for each modeling dataset. Correlations were determined for the All Soils modeling dataset and the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets (Table 2.3). With the exception of  $S_{MAX}$  in the Slightly Weathered soils dataset, all P sorption variables in each dataset were significantly ( $p < 0.05$ ) correlated with clay. All P sorption variables in each dataset were also significantly correlated with  $Al_{ox}$ , with the exception of AER1 in the Highly Weathered soils dataset and AER23 in the Calcareous soils dataset. AER1 and AER24 were significantly correlated with TC,  $Ca_M$ ,  $Mg_M$ ,  $Ca_{NH4}$ , and  $Mg_{NH4}$  in each dataset. In the All Soils dataset, each soil property was significantly correlated with at least two of the measured P sorption variables. This also occurred in the Slightly Weathered soils dataset. In the Calcareous soils dataset, P sorption variables

Table 2.3. Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption, for samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets.

All Samples											
Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Mg <sub>NH4</sub>
AER1	0.6204 <sup>***</sup>	0.199 <sup>***</sup>	0.1513 <sup>*</sup>	0.3229 <sup>***</sup>	0.1634 <sup>*</sup>	0.0495	0.4956 <sup>***</sup>	0.0226	0.4690 <sup>***</sup>	0.260 <sup>***</sup>	0.4024 <sup>***</sup>
AER23	0.3130 <sup>***</sup>	0.1024	-0.2590 <sup>***</sup>	<b>0.6977</b> <sup>***</sup>	0.5270 <sup>***</sup>	0.5424 <sup>***</sup>	0.1162	0.4121 <sup>***</sup>	0.0518	0.1852 <sup>***</sup>	0.0513
AER24	0.5364 <sup>***</sup>	0.2920 <sup>***</sup>	-0.0682	0.5992 <sup>***</sup>	0.4058 <sup>***</sup>	0.3525 <sup>***</sup>	0.3478 <sup>***</sup>	0.2574 <sup>***</sup>	0.2940 <sup>***</sup>	0.2568 <sup>***</sup>	0.2564 <sup>***</sup>
P SI	0.3168 <sup>***</sup>	0.0693	-0.1855 <sup>**</sup>	<b>0.6714</b> <sup>***</sup>	0.5614 <sup>***</sup>	0.5220 <sup>***</sup>	0.1758 <sup>**</sup>	0.3207 <sup>***</sup>	0.0933	0.2876 <sup>***</sup>	0.0961
Smax	0.2265 <sup>*</sup>	0.0409	-0.3229 <sup>**</sup>	0.6115 <sup>***</sup>	0.4591 <sup>***</sup>	0.5357 <sup>***</sup>	-0.0728	0.3849 <sup>***</sup>	-0.0191	0.0217	0.0072
Calcareous Soils											
Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Mg <sub>NH4</sub>
AER1	<b>0.7420</b> <sup>***</sup>	0.5844 <sup>***</sup>	-0.1388	0.5889 <sup>**</sup>	-0.1484	0.2824	0.4900 <sup>***</sup>	-0.0401	0.4952 <sup>***</sup>	0.0656	0.6325 <sup>***</sup>
AER23	0.4407 <sup>***</sup>	0.6477 <sup>***</sup>	-0.2538	0.3261	0.0205	0.1761	0.6192 <sup>***</sup>	0.0814	0.2824	0.2056	0.3651 <sup>*</sup>
AER24	0.6403 <sup>***</sup>	0.3791 <sup>*</sup>	-0.1989	0.4973 <sup>**</sup>	-0.0776	0.2473	0.5753 <sup>**</sup>	0.0140	0.4217 <sup>*</sup>	0.1344	0.5401 <sup>***</sup>
P SI	0.5852 <sup>**</sup>	0.7603 <sup>***</sup>	0.0040	0.3803 <sup>*</sup>	-0.1036	0.1241	<b>0.7648</b> <sup>***</sup>	-0.0340	0.3500 <sup>*</sup>	0.1820	0.5783 <sup>**</sup>
Smax	0.4949 <sup>*</sup>	0.1603	-0.3628	0.5029 <sup>*</sup>	0.2519	0.3924	0.0917	0.1685	0.2345	0.0470	0.2836
Highly Weathered Soils											
Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Mg <sub>NH4</sub>
AER1	0.3749 <sup>*</sup>	0.6246 <sup>***</sup>	-0.1748	0.1980	0.1641	-0.1223	<b>0.8121</b> <sup>***</sup>	0.0087	0.6316 <sup>***</sup>	0.8340 <sup>***</sup>	<b>0.6791</b> <sup>***</sup>
AER23	0.5152 <sup>***</sup>	-0.2464	0.0547	<b>0.7606</b> <sup>***</sup>	<b>0.6549</b> <sup>***</sup>	0.6145 <sup>***</sup>	0.0543	0.1661	-0.0036	0.0450	0.0902
AER24	0.5494 <sup>***</sup>	0.2995 <sup>*</sup>	-0.0778	0.5589 <sup>***</sup>	0.4726 <sup>***</sup>	0.2662	0.5841 <sup>***</sup>	0.0949	0.4226 <sup>***</sup>	0.5875 <sup>***</sup>	0.3824 <sup>**</sup>
P SI	0.4753 <sup>***</sup>	-0.3746 <sup>**</sup>	-0.0792	0.6085 <sup>***</sup>	0.5870 <sup>***</sup>	<b>0.6085</b> <sup>***</sup>	-0.3471 <sup>*</sup>	0.0418	-0.2642	-0.0898	-0.1402
Smax	0.4605 <sup>*</sup>	-0.3393	-0.1428	<b>0.6875</b> <sup>**</sup>	0.3011	0.4857 <sup>*</sup>	-0.3050	-0.0790	-0.2076	-0.0076	-0.0969
Slightly Weathered Soils											
Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Mg <sub>NH4</sub>
AER1	<b>0.7047</b> <sup>***</sup>	0.3041 <sup>***</sup>	0.1689 <sup>*</sup>	0.4487 <sup>***</sup>	0.3288 <sup>***</sup>	0.2683 <sup>**</sup>	0.5469 <sup>***</sup>	0.1569	0.4331 <sup>***</sup>	-0.0166	0.5455 <sup>***</sup>
AER23	0.3101 <sup>***</sup>	0.5746 <sup>***</sup>	-0.3006 <sup>**</sup>	<b>0.7321</b> <sup>***</sup>	0.6031 <sup>***</sup>	0.5921 <sup>***</sup>	0.0363	0.5051 <sup>***</sup>	0.0534	0.2435 <sup>**</sup>	0.0477
AER24	0.5343 <sup>***</sup>	0.5160 <sup>***</sup>	-0.1148	<b>0.6865</b> <sup>***</sup>	0.5462 <sup>***</sup>	0.5102 <sup>***</sup>	0.2860 <sup>**</sup>	0.4007 <sup>***</sup>	0.2424 <sup>***</sup>	0.1489	0.3191 <sup>***</sup>
P SI	0.2439 <sup>***</sup>	0.6479 <sup>***</sup>	-0.3062 <sup>**</sup>	<b>0.7116</b> <sup>***</sup>	0.6136 <sup>***</sup>	0.6429 <sup>***</sup>	0.0731	0.4145 <sup>***</sup>	0.0667	0.4497 <sup>***</sup>	0.0938
Smax	0.1664	0.6164 <sup>***</sup>	-0.4536 <sup>***</sup>	0.6099 <sup>***</sup>	0.4933 <sup>***</sup>	0.6043 <sup>***</sup>	-0.1465	0.5173 <sup>***</sup>	-0.0404	0.0159	-0.1081

\*p ≤ 0.05; \*\*p ≤ 0.01; \*\*\*p ≤ 0.001; significant correlation coefficients ≥ 0.65 in bold.

were only significantly correlated with clay, TC, CaCO<sub>3</sub>, Al<sub>OX</sub>, Ca<sub>M</sub>, Mg<sub>M</sub>, Ca<sub>NH4</sub>, and Mg<sub>NH4</sub>. P sorption variables in the Highly Weathered soils dataset were only significantly correlated with clay, TC, Al<sub>OX</sub>, Fe<sub>OX</sub>, and Al<sub>M</sub>, as well as Ca<sub>M</sub>, Mg<sub>M</sub>, Ca<sub>NH4</sub>, and Mg<sub>NH4</sub>. In the Slightly Weathered soils dataset, all five of the measured P sorption variables were significantly correlated with TC, Al<sub>OX</sub>, Fe<sub>OX</sub>, and Al<sub>M</sub>. Four of the five P sorption variables were also significantly correlated with clay, pH and Fe<sub>M</sub>.

Correlations were also determined for the Argiustolls, Hapludalfs, and Hapludults modeling datasets (Table 2.4). In the Argiustolls dataset, AER1 was significantly ( $p < 0.05$ ) correlated with clay, CaCO<sub>3</sub>, Al<sub>OX</sub>, and Al<sub>M</sub>, AER23 was significantly correlated with Al<sub>M</sub>, Mg<sub>M</sub>, and Mg<sub>NH4</sub>, and AER24 was significantly correlated with clay, Al<sub>OX</sub>, Ca<sub>M</sub>, Ca<sub>NH4</sub>, and Mg<sub>NH4</sub>. PSI was significantly correlated with Ca<sub>NH4</sub>, and S<sub>MAX</sub> was significantly correlated with clay in the Argiustolls dataset. In the Hapludalfs dataset, all measured P sorption variables were significantly correlated with clay, TC, Al<sub>OX</sub>, Fe<sub>OX</sub>, Ca<sub>M</sub>, Mg<sub>M</sub>, Mn<sub>M</sub>, Ca<sub>NH4</sub>, and Mg<sub>NH4</sub>. All P sorption variables were also significantly correlated with Fe<sub>M</sub>, with the exception of AER1. PSI was also significantly correlated with Al<sub>M</sub>. In the Hapludults dataset, AER1 was significantly correlated with Ca<sub>M</sub>, Mg<sub>M</sub>, and Mn<sub>M</sub>, AER23 was significantly correlated with Al<sub>OX</sub>, Fe<sub>OX</sub>, and Al<sub>M</sub>, and AER24 was not significantly correlated with any soil property. PSI was significantly correlated with clay and Al<sub>OX</sub>, while S<sub>MAX</sub> was significantly correlated with Al<sub>OX</sub>, in the Hapludults dataset. Overall, more P was lost from soil during the first hour of P desorption than during the following 23 hours (Table 2.1), so the total P lost from soil (AER24) has relationships to other soil properties similar to those of AER1, in most datasets.

Table 2.4. Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption, for samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets.

Argiustolls												
Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>
AER1	<b>0.7313**</b>	-0.0478	<b>0.6842*</b>	0.3440	<b>0.6539*</b>	-0.0645	<b>0.7513**</b>	<b>0.8271</b>	-0.2227	0.4217	-0.3932	<b>0.8408</b>
AER23	0.4880	0.1572	-0.0044	-0.3501	0.5190	0.5034	<b>0.7863**</b>	0.0719	0.3985	0.6476*	0.3667	<b>0.7704**</b>
AER24	<b>0.7597**</b>	0.0166	0.5518	0.1575	<b>0.7078**</b>	0.1214	<b>0.8787</b>	<b>0.6937*</b>	-0.0427	0.5644	-0.1915	<b>0.7267**</b>
PSI	0.4785	-0.2083	0.4436	0.5122	0.4847	-0.2429	0.3691	0.5638	-0.4888	0.1783	-0.3053	0.5923*
Smax	<b>0.9593*</b>	<b>-0.7352</b>	.	0.1330	0.2929	<b>-0.7076</b>	0.5498	0.5026	-0.1776	<b>0.8434</b>	0.5464	<b>0.8201</b>
Hapludalfs												
Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>
AER1	<b>0.7187***</b>	0.3715*	-0.0749	0.1853	0.5930**	0.3782*	0.2600	0.4912**	0.2598	0.3711*	0.4224*	0.4881**
AER23	0.5771**	0.5624**	-0.1069	0.1892	0.5553**	0.4644*	0.1557	0.4546*	0.4381*	0.4724**	0.3796*	0.6053**
AER24	<b>0.6549**</b>	0.5220**	-0.1007	0.1970	0.5954**	0.4564*	0.2001	0.4894**	0.3962*	0.4593*	0.4130*	0.5931**
PSI	<b>0.7743***</b>	0.5357**	-0.0473	0.0204	0.5735**	0.5906**	0.4557*	0.5164**	0.4670*	<b>0.6722***</b>	0.4268*	0.6095**
Smax	<b>0.8998***</b>	<b>0.6512**</b>	-0.0134	0.1166	<b>0.8097**</b>	<b>0.7428**</b>	0.5126	0.5257*	0.6432**	<b>0.8560***</b>	0.5694*	<b>0.8583***</b>
Hapludults												
Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>
AER1	-0.2918	0.5459	.	-0.3312	-0.1264	-0.1736	-0.5346	<b>0.8465**</b>	0.1072	<b>0.8559**</b>	<b>0.7879**</b>	-0.1818
AER23	0.5257	-0.5299	.	0.2562	<b>0.8431**</b>	0.6268*	0.6429*	-0.4274	0.1108	-0.4114	-0.2464	0.2029
AER24	0.0920	0.1851	.	-0.0835	0.3964	0.2112	0.0189	0.4523	0.1450	0.4213	0.4852	-0.0478
PSI	<b>0.7873**</b>	-0.4389	.	0.0806	0.6427*	0.4623	0.5569	-0.4162	-0.3586	-0.3790	-0.0220	0.0036
Smax	0.6334	-0.4526	.	-0.3182	<b>0.7919*</b>	0.2335	0.6299	<b>-0.6622</b>	-0.3305	-0.5035	-0.1056	-0.4769
*p ≤0.05; **p ≤0.01; ***p ≤0.001; significant correlation coefficients ≥ 0.65 in bold.												

\*p ≤ 0.05; \*\*p ≤ 0.01; \*\*\*p ≤ 0.001; significant correlation coefficients ≥ 0.65 in bold.

These correlations indicate that when all soils are considered together at the CONUS level, P sorption appears to be influenced by several soil physical and chemical properties, including clay, Al and Fe oxides, and Ca, Mg, and Mn ions. When the soils are grouped, however, more distinct and specific relationships are revealed. In the Calcareous soils, P sorption is primarily influenced by clay, TC, and the Ca and Mg ions in the soil, as well as amorphous Al oxides. Similar relationships were noted by Tunesi et al. (1999), Burt et al., (2002), Kleinman and Sharpley (2002), and Carey et al. (2007). In the Highly Weathered soils, readily desorbable P is predominantly controlled by TC and the Ca and Mg ions in the soil. Total P desorption and P adsorption in the Highly Weathered soils, however, is primarily controlled by clay, amorphous Al and Fe oxides, and crystalline Al oxides, similar to the findings of Paulter and Sims (2000). This is to be expected as P solubility is controlled by Fe and Al in acid soils (Lindsay, 1979). The Slightly Weathered soils reveal significant correlations between P sorption and clay, TC, and amorphous and crystalline forms of Al and Fe, as well as Ca and Mg ions with readily desorbable P. Overall, the relationships among the Slightly Weathered soils mirror those of the All Soils modeling dataset correlations, which is to be expected as the majority of soils investigated classify as Slightly Weathered. Clay and Al oxides, both amorphous and crystalline forms, control most of the P desorption in Argiustolls, as well as Ca and Mg ions. Clay also appears to influence P adsorption in Argiustolls. P sorption in Hapludalfs is controlled by a combination of clay, TC, amorphous Al and Fe oxides, crystalline Fe oxides, and Ca, Mg, and Mn ions in the soil. In Hapludults, readily desorbable P is controlled by Ca, Mg, and Mn ions, while total desorbable P is influenced

by amorphous Al and Fe oxides and crystalline Al oxides. P adsorption in these soils is influenced by clay and amorphous Al oxides.

### **Phosphorus Sorption Relationships with Soil P Tests**

Extracted P also varied greatly in study soils and with each grouping (Appendix B). Overall,  $P_{OX}$  ranged from 0 to 2699.10 mg P/kg soil, with an average of 371.17 mg P/kg soil in the All Soils modeling dataset.  $P_M$  ranged from 0 to 782.20 mg P/kg soil and  $P_{M3}$  ranged from 1.20 to 742.00 mg P/kg soil, overall. Average  $P_M$  and  $P_{M3}$  were 90.76 mg P/kg soil and 77.99 mg P/kg soil, respectively, in the All Soils modeling dataset. Overall,  $P_{Bray1}$  ranged from 0 to 472.00 mg P/kg soil, with an average of 62.33 mg P/kg soil in the All Soils modeling dataset.  $P_{WS}$  ranged from 0 to 25.64 mg P/kg soil and  $P_{CaCl2}$  ranged from 0 to 385.53 mg P/kg soil, overall. Average  $P_{WS}$  and  $P_{CaCl2}$  were 0.75 mg P/kg soil and 12.08 mg P/kg soil, respectively, in the All Soils modeling dataset. With the exception of the Hapludults validation dataset, average soil test P values decreased in the following pattern in each modeling and validation dataset:  $P_{OX} > P_M > P_{M3} > P_{Bray1} > P_{CaCl2} > P_{WS}$ . The highest  $P_{OX}$ ,  $P_M$ ,  $P_{M3}$ , and  $P_{Bray1}$  values occurred in soils in the Slightly Weathered soils modeling dataset, while the highest  $P_{WS}$  and  $P_{CaCl2}$  values occurred in samples from the Highly Weathered soils modeling dataset.

Pearson correlation coefficients were also calculated between the P sorption variables and soil P tests for each modeling dataset. Correlations were determined for the All Soils modeling dataset and the Calcareous, Highly Weathered, and Slightly Weathered soils modeling datasets (Table 2.5). All P sorption variables were significantly ( $p < 0.05$ ) correlated with  $P_{OX}$  in each dataset, with the exception of PSI and

Table 2.5. Correlations coefficients between the P sorption variables and soil P tests, for samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets.

All Samples						
	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Brayl</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.3978***	0.3155***	0.2590***	0.1845*	0.3459***	0.2312*
AER23	0.5623***	0.3765***	0.3563***	0.3384**	-0.0257	-0.0671
AER24	0.5595***	0.4022***	0.3585***	0.3062**	0.1769**	0.0749
PSI	0.2314**	-0.1908**	-0.1905**	-0.2873**	-0.1960**	-0.2034*
Smax	0.3262**	0.0094	0.0071	-0.0924	-0.1224	-0.1228
Calcareous Soils						
	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Brayl</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	<b>0.7017***</b>	0.6151**	0.5981**	0.1596	0.0452	0.1783
AER23	<b>0.7270***</b>	0.6357***	0.6313***	-0.0354	-0.0300	0.0623
AER24	<b>0.7488***</b>	<b>0.6553***</b>	0.6435***	0.0586	0.0129	0.1303
PSI	0.3550*	0.1275	0.1154	-0.4061	-0.2583	-0.1556
Smax	<b>0.7477**</b>	<b>0.7276**</b>	<b>0.7294**</b>	0.2080	-0.1407	0.1078
Highly Weathered Soils						
	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Brayl</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.4379**	0.5632***	0.4611**	0.3174	<b>0.6948***</b>	<b>0.7567***</b>
AER23	<b>0.6943***</b>	0.3505*	0.4870**	0.5220*	-0.2039	-0.2768
AER24	<b>0.6865***</b>	0.5752**	0.5847***	0.4539*	0.3516*	0.2833
PSI	-0.1242	-0.5192**	-0.4205**	-0.3258	-0.4489**	-0.5063*
Smax	-0.0486	-0.1851	-0.0956	-0.0139	-0.3063	-0.3156
Slightly Weathered Soils						
	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Brayl</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.3105***	0.1478	0.1037	0.1794	0.1832*	0.1806
AER23	0.5279***	0.3590***	0.2710**	0.3562**	0.3448***	0.3397**
AER24	0.4888***	0.3023**	0.2246**	0.3180**	0.3100***	0.3063**
PSI	0.2681**	-0.1196	-0.1621*	-0.2864**	-0.1717*	-0.1179
Smax	0.3170**	-0.0175	-0.0762	-0.1099	0.1488	0.2145

\*p ≤ 0.05; \*\*p ≤ 0.01; \*\*\*p ≤ 0.001; significant correlation coefficients ≥ 0.65 in bold.

S<sub>MAX</sub> in the highly weathered soils dataset. In the All Soils dataset, each soil P test was significantly correlated with at least two P sorption variables, though S<sub>MAX</sub> was only significantly correlated with P<sub>OX</sub>. In the Calcareous soils dataset, the P sorption variables, except PSI, were also significantly correlated with P<sub>M</sub> and P<sub>M3</sub>. In the Highly Weathered soils dataset, the P sorption variables, with the exception of S<sub>MAX</sub>, were also significantly



correlated with  $P_M$  and  $P_{M3}$ . AER1 was also significantly correlated with  $P_{WS}$  and  $P_{CaCl2}$ , while AER23 was also significantly correlated with  $P_{Bray1}$ , and AER24 was also significantly correlated with  $P_{Bray1}$  and  $P_{WS}$ . PSI was also significantly correlated with  $P_{WS}$  and  $P_{CaCl2}$ , and  $S_{MAX}$  was not significantly correlated with any soil P test in the Highly Weathered soils dataset. With the exception of  $S_{MAX}$ , all P sorption variables in the Slightly Weathered soils dataset were significantly correlated with  $P_{WS}$ . AER23 and AER24 were also significantly correlated with  $P_M$ ,  $P_{M3}$ ,  $P_{Bray1}$ , and  $P_{CaCl2}$ . PSI was also significantly correlated with  $P_{M3}$  and  $P_{Bray1}$ , and  $S_{MAX}$  was only significantly correlated with  $P_{OX}$  in the Slightly Weathered soils dataset.

Correlations were also determined for the Argiustolls, Hapludalfs, and Hapludults modeling datasets (Table 2.6). In the Argiustoll dataset, only AER23 was significantly ( $p < 0.05$ ) correlated with any soil P tests, which included  $P_{OX}$ ,  $P_M$ ,  $P_{M3}$ , and  $P_{WS}$ . In the Hapludalf dataset, AER1, AER23, and AER24 were all significantly correlated with  $P_{OX}$ ,  $P_M$ , and  $P_{M3}$ . AER23 and AER24 were also significantly correlated with  $P_{Bray1}$  and  $P_{WS}$ .  $S_{MAX}$  was significantly correlated with  $P_{OX}$  and PSI was not significantly correlated with any soil P test. AER24 and  $S_{MAX}$  were not significantly correlated with any soil P test in the Hapludult dataset. AER1 was significantly correlated with  $P_{WS}$  and  $P_{CaCl2}$ , and AER23 was also significantly correlated with  $P_{CaCl2}$ . PSI was significantly correlated with  $P_M$ . From these correlations, it is apparent that, overall, readily desorbable P is related to water soluble and more readily available forms of soil P in the Highly Weathered soils, and to available forms and total soil P in the Calcareous and Slightly Weathered soils. Total desorbable P, overall, is most strongly related to total soil P, and available forms of soil P to a lesser extent. The significant correlations of AER24 reflect the influence of

the readily desorbable soil P on total P desorption. P adsorption appears to be negatively related to water soluble and readily available forms of soil P, overall.

Table 2.6. Correlations coefficients between the P sorption variables and soil P tests, for samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets.

Argiustolls						
	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bray1</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.0381	-0.1118	0.1363	<b>0.9337</b>	-0.1572	-0.7724
AER23	<b>0.7662**</b>	<b>0.7820**</b>	<b>0.7737**</b>	<b>0.9897</b>	<b>0.6890*</b>	-0.1988
AER24	0.2951	0.1793	0.3771	<b>0.9574</b>	0.1105	-0.6113
PSI	-0.0592	-0.0662	-0.1985	0.9110	-0.0369	-0.5206
Smax	0.6601	0.6914	0.7088	.	0.3634	-0.0918
Hapludalfs						
	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bray1</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.5214**	0.4324*	0.4310*	0.3478	0.3178	0.0154
AER23	<b>0.8480***</b>	<b>0.6946***</b>	<b>0.6929***</b>	<b>0.6716**</b>	0.5548**	0.1324
AER24	<b>0.7734***</b>	0.6354**	0.6337**	0.6038*	0.4978**	0.0937
PSI	0.0521	-0.2387	-0.2420	-0.3393	-0.2579	-0.4067
Smax	0.5369*	0.0430	0.0425	-0.0636	-0.0434	-0.3236
Hapludults						
	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bray1</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.0034	0.5585	0.2031	0.0003	<b>0.7955**</b>	<b>0.8675*</b>
AER23	0.4345	0.1328	0.4197	0.5651	-0.5403	<b>-0.7785*</b>
AER24	0.2613	0.5520	0.4696	0.2299	0.2643	0.2383
PSI	-0.4276	<b>-0.7159**</b>	-0.5356	-0.4409	-0.5391	-0.6076
Smax	-0.3749	-0.4496	-0.1544	-0.8925	-0.4737	-0.4668

\* $p \leq 0.05$ ; \*\* $p \leq 0.01$ ; \*\*\* $p \leq 0.001$ ; significant correlation coefficients  $\geq 0.65$  in bold.

## Phosphorus Release Characteristics

Predicted amounts of P released (mg P/kg soil) were plotted for soils that represent the distribution of P desorption during both the 1-hour and 24-hour extraction periods for samples in the All Soils modeling and validation datasets (Figure 2.5). It is apparent that while there was a large range of soil P release during both extraction periods, the majority of soils released less than 150 mg P/kg soil during the first hour of AER extraction, and less than 250 mg P/kg soil during the following 23 hours of AER

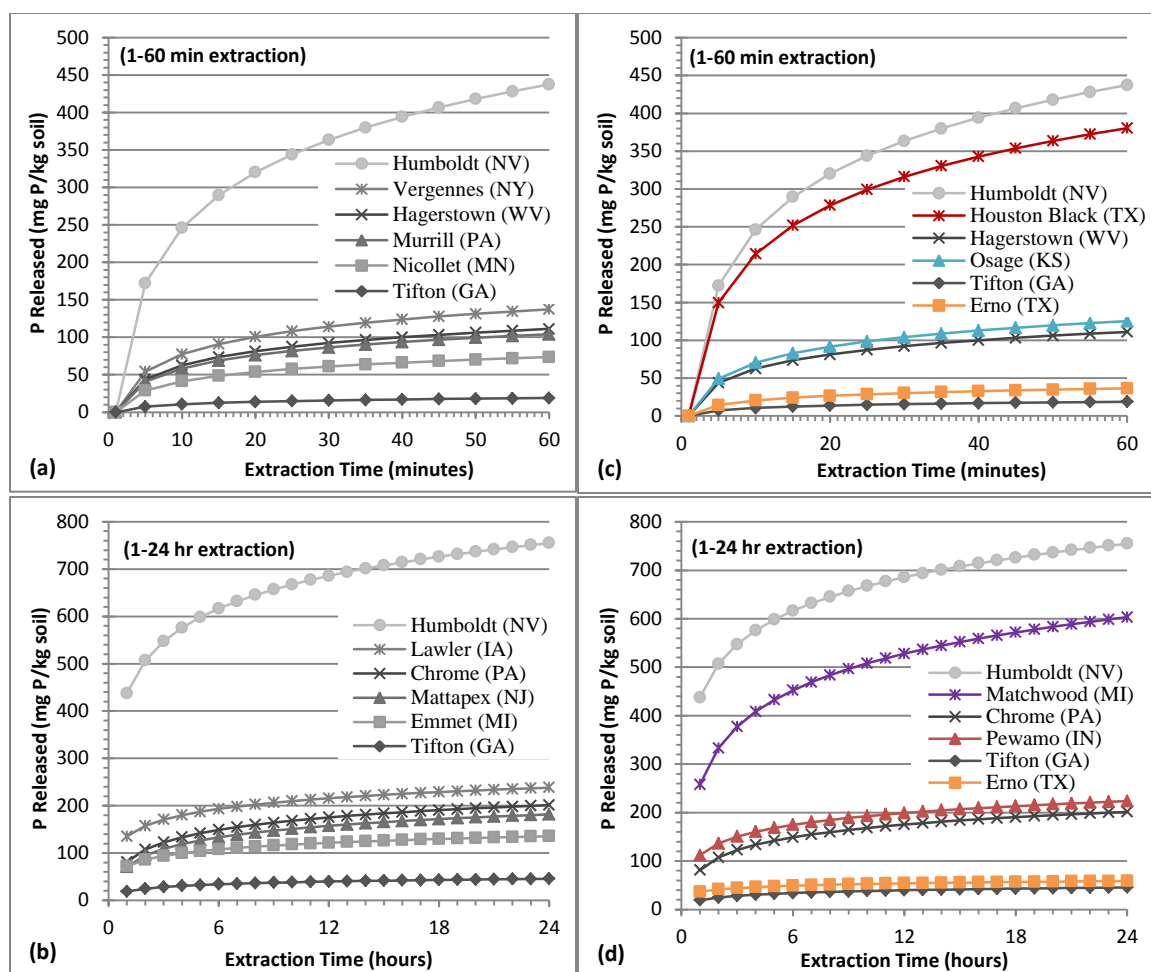


Figure 2.5. Predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, first quartile, median, mean, third quartile, and maximum for samples in the All Soils modeling dataset during the (a) 1-60 minute and (b) 1-24 hour extraction periods, and soils that represent the minimum, mean, and maximum for samples in the All Soils modeling and validation (colored curves) datasets during the (c) 1-60 minute and (d) 1-24 hour extraction periods.

extraction. These plots also reveal the similar desorption behaviors between the soils that released the least, average, and maximum in the All Soils modeling and validation datasets, during both extraction periods. The linear regression equations to predict P released by AER extraction for the soils in Figure 2.5 are listed in Appendix C. Linear relationships are always produced when the amount of P released is plotted against the log of the AER extraction period (Elrashidi et al., 2012; Elrashidi et al., 2003). The

linear relationships for the soils plotted in Figure 2.5 are also plotted in a figure in Appendix C.

During both the 1-hour and 24-hour extraction periods the Humboldt soil released the most P overall. The Humboldt soil is a Calcareous soil with high clay, TC,  $\text{Ca}_M$ ,  $\text{Mg}_M$ ,  $\text{Ca}_{\text{NH}_4}$ ,  $\text{Mg}_{\text{NH}_4}$ , and PSI, and the highest  $\text{P}_{\text{OX}}$ ,  $\text{P}_M$ ,  $\text{P}_{\text{M}_3}$ , and  $\text{S}_{\text{MAX}}$  of the samples in the Calcareous soils modeling dataset (data not shown). The Houston Black soil released the most P of soils in the All Soils validation dataset during the 1-hour extraction period. The Houston Black soil is also a Calcareous soil, with high clay,  $\text{Fe}_{\text{OX}}$ ,  $\text{Ca}_M$ ,  $\text{Ca}_{\text{NH}_4}$ , and  $\text{P}_{\text{OX}}$ , and the highest  $\text{Al}_{\text{OX}}$  and PSI of the samples in the Calcareous soils validation dataset (data not shown). The Matchwood soil released the most P during of soils in the All Soils validation dataset during the 24-hour extraction period. The Matchwood soil is a Slightly Weathered soil with high TC,  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Ca}_{\text{NH}_4}$ ,  $\text{P}_{\text{OX}}$ ,  $\text{P}_{\text{M}_3}$ , and PSI, and the highest clay overall (data not shown). The Matchwood soil was not analyzed for Mehlich-3 elements due to lack of adequate sample. The Tifton and Erno soils released the least P of samples in the All Soils modeling and validation datasets, respectively. Both the Tifton soil and Erno soil are Slightly Weathered soils, and both soils have low clay, TC,  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Al}_M$ ,  $\text{Ca}_M$ ,  $\text{Fe}_M$ ,  $\text{Mg}_M$ ,  $\text{Ca}_{\text{NH}_4}$ ,  $\text{Mg}_{\text{NH}_4}$ ,  $\text{P}_{\text{OX}}$ , PSI, and  $\text{S}_{\text{MAX}}$  (data not shown). Overall, the soils that released the most P during the AER desorption process had high amounts of the components known to retain P and high amounts of P already in the soil, and thus easily released large amounts of P in solution. The soils that released the least P during the desorption process had low amounts of the components known to retain P, and released less amounts of P due to not having the physio-chemical ability to readily retain P.

## Predicting Soil Phosphorus Behavior

Most agronomic soil testing facilities in the United States only routinely analyze all soil samples for particle-size (sand, silt, and clay), carbon content, and pH, and do not have the means or capability to perform more detailed analyses such as oxalate or Mehlich-3 extractions. Of all soil parameters investigated, only clay, TC, and pH are routinely analyzed on all soil samples processed at the KSSL as well. At the KSSL, analyses such as acid oxalate extractable Al, Fe, and P, and Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P) are additional analyses for select samples requested by the project researcher or investigator, limiting the data available for these properties. As mentioned previously, P sorption behaviors in soil have been found to be related to soil clay, TC, and/or pH (Burt et al., 2002; Harter, 1969; Juo and Fox, 1977; Lopez-Hernandez and Burnham, 1974; McCallister and Logan, 1978, Sharpley et al., 1989, Syers et al., 1971). For each of the five P sorption variables of interest (AER1, AER23, AER24, PSI, and  $S_{MAX}$ ), linear regression equations were developed. Clay, TC, and pH were modeled independently and additional variables ( $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ ,  $Ca_M$ ,  $Fe_M$ ,  $Mg_M$ ,  $Mn_M$ ,  $Ca_{NH4}$ ,  $Mg_{NH4}$ ) were progressively added to the regression models. Models contained one to three variables, with clay, TC, or pH in each equation. The use of clay, TC, or pH in additional models was dependent on the significance of the respective independent models. Clay, TC, and/or pH were used in additional modeling if, (a) the  $p$  value of the independent model was significant ( $p \leq 0.05$ ), or (b) if no independent model was significant, the independent model with the lowest  $p$  value was used. An example of the progressive linear regression modeling method for the AER23 and AER24 sorption

variables from the All Soils modeling dataset is listed in Appendix D. This example shows that for AER23 in the All Soils modeling dataset, the independent models with clay and pH were both significant and were used in the additional modeling steps. For AER24 in this dataset, the independent models with clay and TC were both significant and were used in the additional modeling steps.

The three most significant ( $p < 0.05$ ) P sorption prediction equations for AER1, AER23, AER24, PSI, and  $S_{MAX}$  for the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets, those with the lowest  $p$  values and highest  $R^2$  values, were examined (Table 2.7). The prediction models for the All Soils dataset indicate that readily desorbable P can be estimated with only clay, TC, and pH, but also with  $Ca_M$  and  $Mn_M$  variables, overall. The prediction models also indicate that overall, total P desorption and P adsorption can be estimated more accurately with the inclusion of amorphous Al and Fe oxide variables in the models. However, when soils are grouped based on their calcium carbonate content and degree of weathering, the variables included in the best models for predicting P sorption change.

The P sorption prediction models for the Calcareous soils include  $Ca_M$ ,  $Al_M$ , and/or  $Mg_M$  components in each set of models, indicating the influence of these properties on P sorption behaviors in Calcareous soils when clay or TC is also considered. The prediction model components for the Highly Weathered soils are less consistent with each P sorption variable. The AER1, AER24, and PSI prediction models include  $Ca_M$ ,  $Mn_M$ , and/or crystalline Al components whereas the AER23 and  $S_{MAX}$  models include amorphous Al and Fe oxide variables. These models indicate the influence of Ca, Mn, and crystalline Al oxides on readily desorbable P, total desorbable

Table 2.7. The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling datasets.

All Samples						Calcareous Soils					
AER1						AER1					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
-1.89 + 3.05Clay + 5.33TC + 5.71pH	0.5842	0.0001	38.31	234		10.09 + 3.32Clay + 0.05AlM + 0.01CaM	0.7030	0.0001	44.66	34	
31.45 + 3.21Clay + 5.03TC	0.5743	0.0001	38.67	234		120.94 + 3.46Clay + 11.50TC - 12.31pH	0.7016	0.0001	44.77	34	
32.16 + 2.63Clay + 0.01CaM + 0.08MnM	0.5295	0.0001	40.22	230		24.03 + 3.52Clay + 11.30TC	0.6967	0.0001	44.40	34	
AER23						AER23					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
24.70 + 0.52Clay + 0.04AlOX + 0.004FeOX	0.4908	0.0001	46.31	234		-5.79 + 6.57TC + 0.09AlM + 0.01CaM	0.5494	0.0001	43.37	34	
57.81 - 3.76pH + 0.04AlOX + 0.004FeOX	0.4877	0.0001	46.37	235		13.59 + 0.67Clay + 0.08AlM + 0.01CaM	0.5419	0.0001	43.73	34	
25.71 + 0.59Clay + 0.04AlOX	0.4679	0.0001	47.23	234		290.43 + 0.97Clay + 13.47TC - 35.98pH	0.5418	0.0001	43.73	34	
AER24						AER24					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
64.15 + 3.55Clay + 0.05AlOX + 0.003FeOX	0.4832	0.0001	77.02	234		-3.64 + 4.00Clay + 0.13AlM + 0.01CaM	0.6634	0.0001	80.64	34	
64.73 + 3.59Clay + 0.05AlOX	0.4804	0.0001	77.06	234		410.10 + 4.44Clay + 24.93TC - 48.14pH	0.6577	0.0001	81.32	34	
14.04 + 3.43Clay + 0.15AlM + 0.01CaM	0.4548	0.0001	78.25	230		12.24 + 6.23Clay + 0.01CaM - 0.04MgM	0.6394	0.0001	83.47	34	
PSI						PSI					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
5.46 + 1.20Clay + 0.06AlOX + 0.01FeOX	0.5016	0.0001	67.16	234		-12.91 + 3.53Clay + 0.01CaM - 0.04MgM	0.8185	0.0001	34.30	34	
-19.33 + 6.35pH + 0.06AlOX + 0.01 FeOX	0.4917	0.0001	67.89	235		-17.64 + 1.80Clay + 0.07AlM + 0.01CaM	0.8023	0.0001	35.80	34	
7.37 + 1.23Clay + 0.07AlOX	0.4644	0.0001	69.47	234		-18.59 + 2.32Clay + 0.01CaM + 0.14MnM	0.7853	0.0001	37.30	34	
Smax						Smax					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
303.43 - 43.42pH + 0.13AlOX + 0.01FeOX	0.4055	0.0001	231.75	120		1300.38 + 7.47Clay - 172.73pH	0.3518	0.0251	209.02	20	
309.75 - 43.84pH + 0.15AlOX	0.4018	0.0001	231.48	120		-51.27 + 7.85Clay	0.2449	0.0265	219.23	20	
20.16 + 0.07Clay + 0.14AlOX + 0.01FeOX	0.3765	0.0001	237.70	119		-78.27 + 12.34Clay - 0.12MgM	0.2990	0.0488	217.36	20	

Table 2.7. Continued.

Highly Weathered Soils						Slightly Weathered Soils					
AERI						AERI					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
30.14 + 1.34Clay + 0.03CaM + 0.17MnM	0.8036	0.0001	32.06	45		17.35 + 2.17Clay + 0.04AlM + 0.01FeM	0.5700	0.0001	30.76	151	
46.61 + 0.43TC + 0.03CaM + 0.17MnM	0.7867	0.0001	33.24	46		33.72 + 2.67Clay + 0.01AlOX + 0.0003FeOX	0.5619	0.0001	31.11	154	
13.42 + 1.96Clay + 0.12FeM + 0.28MnM	0.7772	0.0001	34.15	45		33.88 + 2.68Clay + 0.01AlOX	0.5616	0.0001	31.02	154	
AER23						AER23					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
25.21 + 0.83Clay + 0.04AlOX + 0.01FeOX	0.5966	0.0001	37.79	46		26.98 + 7.18TC + 0.03AlOX + 0.004FeOX	0.5744	0.0001	43.74	154	
34.83 - 0.35TC + 0.04AlOX + 0.01FeOX	0.5956	0.0001	37.56	47		29.85 + 8.36TC + 0.03AlOX	0.5448	0.0001	45.08	154	
22.95 + 1.01Clay + 0.05AlOX	0.5901	0.0001	37.65	46		23.17 + 0.54Clay + 0.03AlOX + 0.01FeOX	0.5424	0.0001	45.35	154	
AER24						AER24					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
-16.78 + 3.11Clay + 0.15AlM + 0.07CaM	0.6300	0.0001	65.68	45		56.89 + 3.21Clay + 0.04AlOX + 0.01FeOX	0.5857	0.0001	65.52	154	
13.48 + 4.12Clay + 0.12AlM + 0.29MnM	0.6124	0.0001	67.22	45		59.45 + 3.34Clay + 0.05AlOX	0.5652	0.0001	66.90	154	
32.57 + 6.20Clay + 0.26FeM + 0.26MnM	0.6066	0.0001	67.73	45		105.35 + 8.97TC + 0.04AlOX + 0.01FeOX	0.5024	0.0001	71.81	154	
PSI						PSI					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
-3.33 + 4.24Clay + 0.10AlM - 0.03CaM	0.5875	0.0001	48.64	45		11.83 + 15.76TC + 0.04AlOX + 0.01FeOX	0.6356	0.0001	62.74	154	
-21.13 + 3.26Clay + 0.13AlM - 0.07MgM	0.5265	0.0001	52.11	45		-48.22 + 18.07TC + 0.17AlM + 0.18MnM	0.6330	0.0001	63.39	151	
57.43 + 5.78Clay - 0.06CaM + 0.10MnM	0.5199	0.0001	52.47	45		16.21 + 17.56TC + 0.05AlOX	0.6069	0.0001	64.95	154	
Smax						Smax					
Variable(s)	R <sup>2</sup>	p	MSE	N		Variable(s)	R <sup>2</sup>	p	MSE	N	
-31.09 - 3.89TC + 0.23AlOX	0.5076	0.0008	205.50	23		-134.67 + 57.94TC + 0.47AlM - 0.55MnM	0.5750	0.0001	210.28	75	
-5.96 - 4.92TC + 0.29AlOX - 0.05FeOX	0.5481	0.0015	201.97	23		181.88 + 95.48TC - 0.22MgM - 0.63MnM	0.5394	0.0001	218.90	75	
-114.91 + 5.30Clay + 0.22AlOX	0.4792	0.0020	213.99	22		-97.20 + 55.92TC + 0.38AlM - 0.11MgM	0.5238	0.0001	222.58	75	



P, and P adsorption when clay or TC is also considered. The models also indicate that amorphous Al and Fe oxides influence the release of more tightly bound P and P adsorption as well in Highly Weathered soils, when clay or TC is also considered. The similarity of model components in the AER1 and AER24 models also further demonstrates the influence of readily desorbable P on total P release in highly weathered soils. The prediction model components for the Slightly Weathered soils are similar to those of the All Soils dataset, though there are a few differences. The P desorption and PSI prediction models include an Al oxide component in each significant model, and a Fe oxide or Mn component as well, in some cases. The Al oxide component, and Fe oxide component, included most often in these models is the amorphous form. The  $S_{MAX}$  prediction models, however, include crystalline Al oxide components as well as  $Mg_M$  and  $Mn_M$  variables. These models indicate that, in Slightly Weathered soils, P desorption is controlled by amorphous Al and Fe oxides, and that P adsorption is controlled by both amorphous and crystalline Al and Fe oxides, when clay or TC is also considered.

Overall, prediction model accuracy improved when soils were grouped by their calcium carbonate content and degree of weathering, as noted by higher  $R^2$  values and lower mean square errors. This is to be somewhat expected as the soils are generally grouped based on the soil components most likely to influence P sorption in each group (i.e. Ca in Calcareous soils, Al and Fe in Highly Weathered soils), generating a more nuanced view of soil P sorption behaviors within these soils. The exceptions to this are the  $S_{MAX}$  prediction models for the Calcareous Soils dataset and the AER1 prediction models for Slightly Weathered soils dataset, which had  $R^2$  values similar to or lower than those of the All Soils prediction models. Differences in significant prediction model

components also occur when soils are grouped by their taxonomic Great Group classification.

The three most significant ( $p < 0.05$ ) P sorption prediction equations for AER1, AER23, AER24, PSI, and  $S_{MAX}$  for the Argiustolls, Hapludalfs, and Hapludults modeling datasets were also examined (Table 2.8). The prediction model components for the Argiustolls primarily include calcium components with readily desorbable P, and  $Al_M$  with  $Ca_M$  or  $Mn_M$  for total desorbable P. This would indicate that AER1 is highly influenced by Ca ions in the soil while AER23 and AER24 are influenced by crystalline Al, when clay or TC is also considered. The significant P adsorption models for the Argiustolls only include clay and TC variables. The AER1 prediction models for the Hapludalfs include  $Ca_{NH4}$  and  $Mg_{NH4}$  components, while the AER23 and AER24 prediction models also include  $Al_{OX}$  and  $Fe_{OX}$  components. The PSI prediction models also include  $Al_{OX}$  and  $Fe_{OX}$  components, as well as  $Al_M$  and  $Mg_M$  variables. The  $S_{MAX}$  prediction models also include  $Al_M$  and  $Mg_M$  variables, as well as  $Ca_{NH4}$  and  $Mg_{NH4}$  components. These models indicate that when clay or TC is considered, Ca, Mg, and crystalline Al oxides influence readily desorbable P and P adsorption in Hapludalfs, while amorphous Al and Fe oxides also influence P adsorption and total P release. In addition to clay, TC, or pH, the prediction models for the Hapludults include the various Mehlich 3 extracted elements for each P sorption variable, with the exception of AER23. The models indicate that when clay or TC is considered, Ca, Mn, Mg, and crystalline Al oxides predominately influence P sorption behaviors in Hapludults, though amorphous Al and Fe also influence the release of more tightly bound soil P. When the soils were grouped by their Great Group classification, the P sorption prediction model accuracy

Table 2.8. The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets.

Argiustolls					Hapludalfs				
AER1					AER1				
Variable(s)	R <sup>2</sup>	p	MSE	N	Variable(s)	R <sup>2</sup>	p	MSE	N
-36.05 + 2.79Clay + 0.30FeM + 0.02CaM	0.9324	0.0001	10.46	12	38.66 + 2.06Clay + 2.40CaNH <sub>4</sub> - 0.28MgNH <sub>4</sub>	0.5700	0.0001	22.18	29
28.57 + 4.00Clay + 0.01CaM - 0.35MnM	0.9003	0.0002	12.70	12	38.79 + 2.04Clay + 2.35CaNH <sub>4</sub>	0.5699	0.0001	21.76	29
-2.67 + 3.03Clay + 2.86CaNH <sub>4</sub>	0.8548	0.0002	14.45	12	-13.56 + 3.03Clay - 1.81TC + 9.98pH	0.5656	0.0001	28.94	29
AER23					AER23				
Variable(s)	R <sup>2</sup>	p	MSE	N	Variable(s)	R <sup>2</sup>	p	MSE	N
-43.06 + 2.01TC + 0.10AIM + 0.23MnM	0.8038	0.0033	7.60	12	8.18 + 14.35TC + 0.04AlOX + 0.004FeOX	0.5587	0.0001	44.18	29
-40.14 - 0.20Clay + 0.11AIM + 0.23MnM	0.8009	0.0035	7.65	12	11.05 + 15.27TC + 0.05AlOX	0.5417	0.0001	44.15	29
-22.60 + 0.48Clay + 0.12AIM - 0.01CaM	0.7859	0.0047	7.93	12	32.96 + 2.56Clay + 15.33MgNH <sub>4</sub>	0.4417	0.0005	48.73	29
AER24					AER24				
Variable(s)	R <sup>2</sup>	p	MSE	N	Variable(s)	R <sup>2</sup>	p	MSE	N
-53.21 + 2.78Clay + 0.21AIM + 0.01CaM	0.9183	0.0001	14.21	12	52.29 + 18.72TC + 0.07AlOX + 0.005FeOX	0.5567	0.0001	63.74	29
-29.76 + 3.81Clay + 0.23AIM - 0.33MnM	0.9128	0.0001	14.68	12	55.77 + 19.84TC + 0.08AlOX	0.5446	0.0001	63.35	29
-67.18 + 3.28Clay + 0.25AIM	0.8697	0.0001	16.92	12	56.53 + 4.53Clay + 8.42CaNH <sub>4</sub>	0.5149	0.0001	65.38	29
PSI					PSI				
Variable(s)	R <sup>2</sup>	p	MSE	N	Variable(s)	R <sup>2</sup>	p	MSE	N
13.82 + 3.95Clay - 16.08TC	0.2814	0.0226	37.34	12	-6.32 + 3.18Clay + 0.06AIM + 0.11MgM	0.7058	0.0001	32.54	29
					-0.03 + 4.09Clay + 0.01AlOX + 0.01FeOX	0.6913	0.0001	33.34	29
					3.07 + 4.35Clay + 0.01FeOX	0.6874	0.0001	32.89	29
Smax					Smax				
Variable(s)	R <sup>2</sup>	p	MSE	N	Variable(s)	R <sup>2</sup>	p	MSE	N
-360.07 + 23.08Clay	0.9203	0.0407	27.44	4	24.86 + 13.71Clay 0.09AIM - 0.33MnM	0.9042	0.0001	46.76	15
					79.31 + 9.83Clay - 7.55CaNH <sub>4</sub> + 29.32MgNH <sub>4</sub>	0.8882	0.0001	50.51	15
					-59.71 - 2.53TC + 0.30AIM + 0.47MgM	0.8882	0.0001	50.51	15

Table 2.8. Continued.

<b>Hapludults</b>				
<b>AER1</b>				
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>
110.95 - 10.07pH + 0.05CaM	0.7343	0.0013	31.29	13
61.66 + 0.81TC + 0.04CaM	0.7238	0.0016	31.89	13
68.48 + 1.41TC + 0.15MnM	0.7192	0.0017	32.16	13
<b>AER23</b>				
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>
36.33 - 0.13TC + 0.04AlOX	0.7279	0.0008	25.30	14
32.49 + 0.59Clay + 0.04AlOX	0.7154	0.0019	26.28	13
36.18 - 0.10TC + 0.04AlOX + 0.004FeOX	0.7324	0.0033	26.31	14
<b>AER24</b>				
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>
81.67 + 7.04Clay + 0.18MgM	0.5875	0.0186	55.22	12
87.81 + 5.93Clay + 0.04CaM	0.5382	0.0309	58.42	12
36.26 + 4.96Clay + 0.58FeM + 0.23MnM	0.6406	0.0346	54.67	12
<b>PSI</b>				
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>
-8.30 + 6.78Clay + 0.18AlM - 1.08FeM	0.8934	0.0003	35.23	12
-50.03 + 14.23Clay - 12.38CaNH <sub>4</sub>	0.7143	0.0019	54.33	13
-14.84 + 2.33TC + 0.33AlM - 1.33FeM	0.7907	0.0021	49.02	13
<b>Smax</b>				
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>
728.74 + 8.69TC - 0.80CaM + 1.99MnM	0.9094	0.0450	194.89	7
-370.09 + 13.76TC + 1.56AlM - 5.42FeM	0.9071	0.0467	197.39	7

tended to improve compared the All Soils prediction models, as noted by the higher R<sup>2</sup> values and lower mean square errors, with the exception of the Hapludalfs AER1 and AER23 prediction models. With the Argiustolls and Hapludults datasets, however, this is likely due to the low number of samples used to develop these models.

Overall, the significant P sorption behavior prediction models ( Tables 2.7 and 2.8) indicate that if analytical soil testing laboratories like the KSSL are interested, or become interested, in improving models and overall understanding of soil P sorption behaviors, additional analyses will be required. Specifically, Mehlich-3 element extraction and acid oxalate extractable Al and Fe, in addition to the standard PSDA, total carbon, and pH analyses. These models also reveal that these additional analyses could be tailored to Calcareous, Highly Weathered, and Slightly Weathered soils, specifically,

only requiring Mehlich-3 element extraction on the Calcareous soils. Tailoring additional analyses based on a soil's calcium carbonate content and degree of weathering is more realistic than doing so based on the soil's Great Group classification as the former can usually be determined more accurately than the latter without laboratory analyses. These analyses could also be specifically required if soil samples originate from regions with known P loading issues, such as the Chesapeake Bay watershed or the Upper Mississippi River Sub-basin.

The reliability of the prediction models developed for AER1, AER23, AER24, PSI, and  $S_{MAX}$  was observed when the equations were applied to the samples from the All Soils validation dataset. The results of the measured values versus the predicted values for the prediction models for each AER variable were plotted, as applied to the All Soils validation dataset (Figure 2.6). The results of the measured values versus predicted values for the prediction models for the PSI and  $S_{MAX}$  variables were also plotted, as applied to the All Soil validation dataset (Figure 2.7). By fitting a linear trendline to the results of each prediction model and calculating the  $R^2$  of the trendline, one can note that in each case the most significant prediction model always has the highest  $R^2$  associated with its trendline, indicating that it is the best of the three models. The exception to this is AER23, though the  $R^2$  values for the three models are all very similar. These plots reflect how trends in the measured values compare to trends in the predicted values, but do not easily provide an indication of the overall accuracy of the prediction models, i.e. how close the predicted values are to the measured values. The number of predictions within 10 %, 15 %, and 20 % of the measured P sorption value for each of the significant

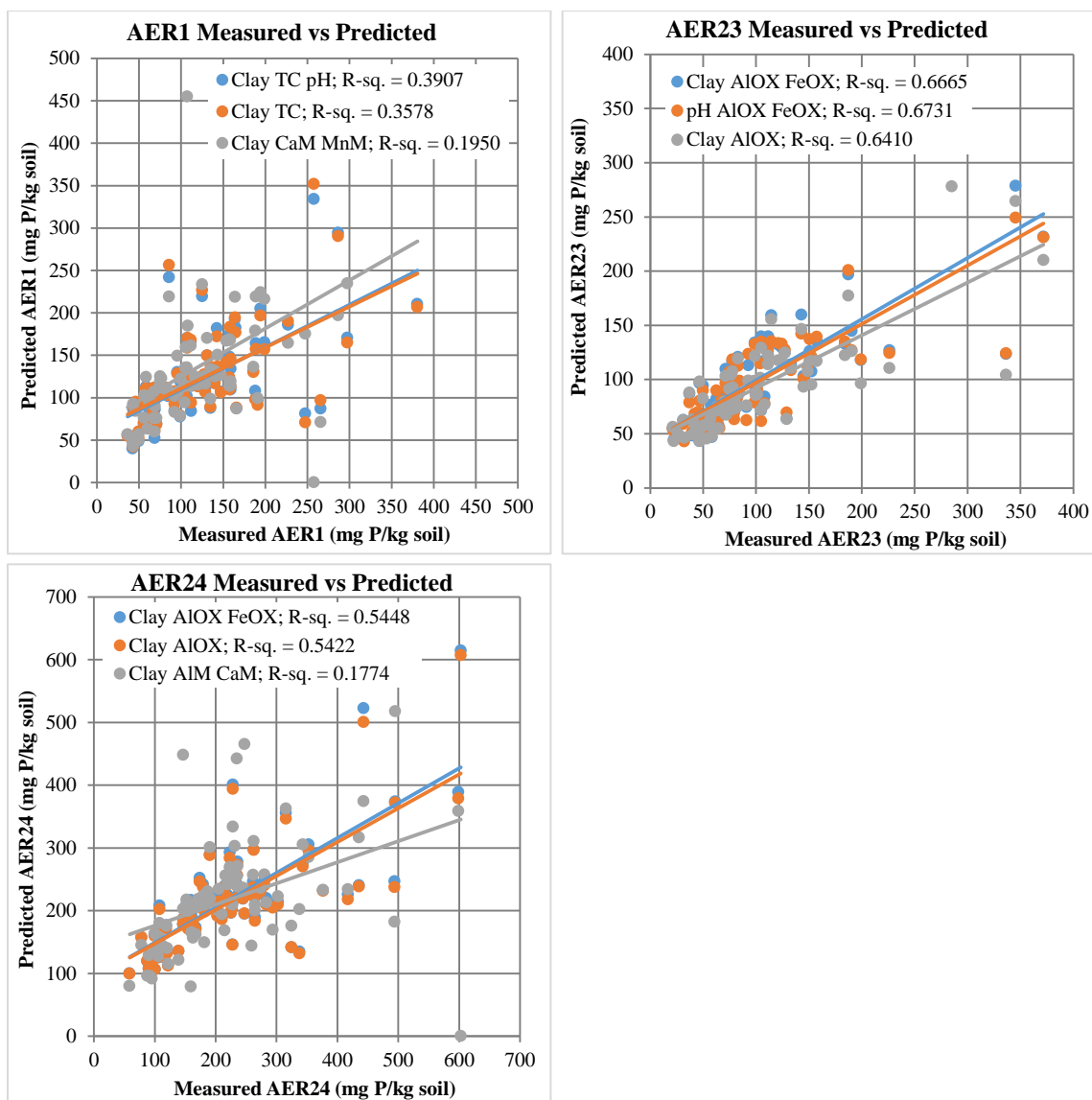


Figure 2.6. Plots of measured versus predicted values, as determined by the All Soils prediction models listed in Table 2.7, for AER1, AER23, and AER24, when applied to the All Soils validation dataset.

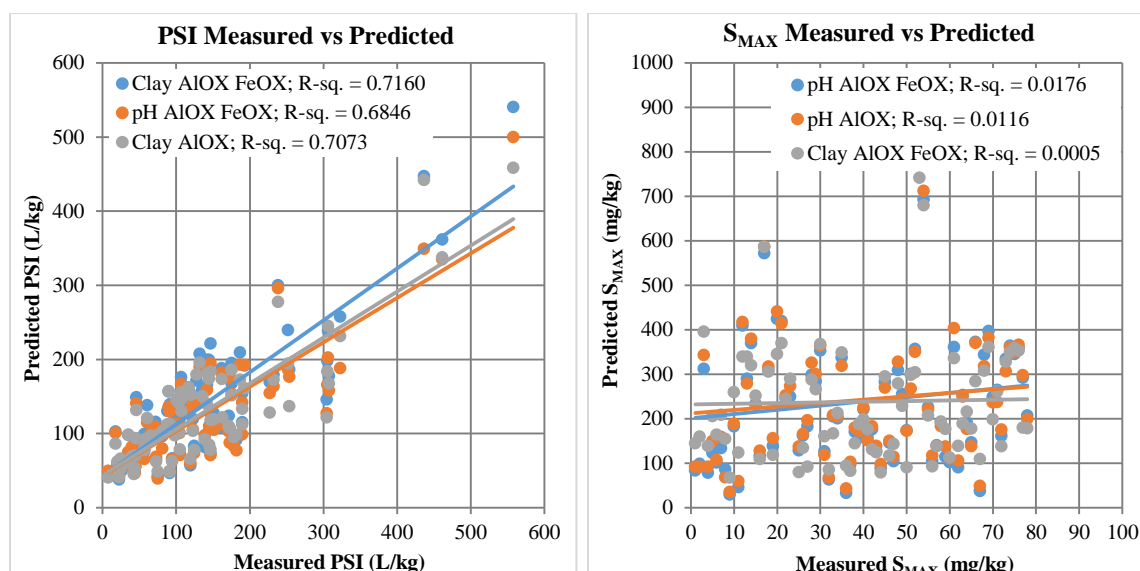


Figure 2.7. Plots of measured versus predicted values, as determined by the All Soils prediction models listed in Table 2.7, for PSI and  $S_{MAX}$ , when applied to the All Soils validation dataset.

All Soils prediction models for each P sorption variable for samples in the All Soils validation dataset were also examined (Table 2.9).

Overall, the prediction models for the P desorption variables predicted more accurate values than the PSI and  $S_{MAX}$  models. The  $S_{MAX}$  prediction models predicted the least number of accurate values of all models, likely due to the lower number of samples analyzed for  $S_{MAX}$ . The P desorption prediction models accurately predicted 22 - 31 % of the validation sample values within 10 % of the measured AER values, 33-42 % of the validation sample values within 15 % of the measured AER values, and 42 - 54 % of the validation sample values within 20 % of the measured AER values. The PSI prediction models accurately predicted 8 - 13 % of the validation sample values within 10 % of the measured value, 13 - 23 % of the validation sample values within 15 % of the measured value, and 19 - 24 % of the validation sample values within 20 % of the measured value. The  $S_{MAX}$  prediction models only accurately predicted about 3 - 12 % of the validation

Table 2.9. The number of All Soils validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for each of the all soils prediction models listed in Table 2.7 for each P sorption variable.

All Samples				
<b>AER1</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay TC pH	22	30	36	78
Clay TC	18	27	38	78
Clay Ca <sub>M</sub> Mn <sub>M</sub>	20	29	33	78
<b>AER23</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	17	31	39	78
pH Al <sub>OX</sub> Fe <sub>OX</sub>	18	26	37	78
Clay Al <sub>OX</sub>	24	36	42	78
<b>AER24</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	18	32	39	78
Clay Al <sub>OX</sub>	22	33	42	78
Clay Al <sub>M</sub> Ca <sub>M</sub>	18	28	33	78
<b>PSI</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	6	11	16	78
pH Al <sub>OX</sub> Fe <sub>OX</sub>	10	18	19	78
Clay Al <sub>OX</sub>	8	10	15	78
<b>Smax</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
pH Al <sub>OX</sub> Fe <sub>OX</sub>	4	7	9	46
pH Al <sub>OX</sub>	3	5	8	46
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	2	4	7	46

sample values within 20 % of the measured value, though fewer samples were used to develop and validate the prediction models, and the most significant models had lower  $R^2$  values and relatively high mean square errors compared to the prediction models for the other P sorption variables (Table 2.7). The difference between the number of accurately predicted values within the defined ranges between the significant models for each P sorption variable ranged from two to nine, with an overall average of 4.3. For the AER variables, the average difference between the number of accurately predicted values within the defined ranges was about five, while the average differences for the PSI and S<sub>MAX</sub> models were about five and two, respectively. The most significant model did not



always accurately predict the most P sorption values for each P sorption variable, with the exception of  $S_{MAX}$ .

The AER24 behavior models and relationships are the most likely to be used by researchers and management planners to estimate potential P release or P loading risk if P saturated soils become eroded and incorporated into surface runoff as they model total P release. The results of the measured values versus the predicted values for the prediction models for total P released (AER24) were plotted, as applied to the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils validation datasets (Figure 2.8). The results of the measured values versus the predicted values for the prediction models for total P released (AER24) were plotted, as applied to the Argiustolls, Hapludalfs, and Hapludults validation datasets (Figure 2.9). The most significant prediction model developed from the All Soils modeling dataset was also applied to these validation datasets and is included in these plots (Figures 2.8 and 2.9), indicated by the ‘CONUS’ term following the prediction model variables in the plot legends. Linear trendlines were again fitted to the results of each prediction model and an  $R^2$  was calculated for each trendline. The Calcareous, Highly Weathered, and Slightly Weathered validation plots (Figure 2.8) indicate that the ‘CONUS’ model is the best model for predicting total P release in Calcareous soils, while the most significant prediction models developed for the Highly Weathered and Slightly Weathered soils are the best models for predicting total P release in those soil groups. The Argiustolls, Hapludalfs, and Hapludults validation plots (Figure 2.8) also indicate that the ‘CONUS’ model is the best model for predicting soil P release in Argiustolls, Hapludalfs, and Hapludults. Again, these plots reflect how trends in the measured values compare to trends in the predicted values, not

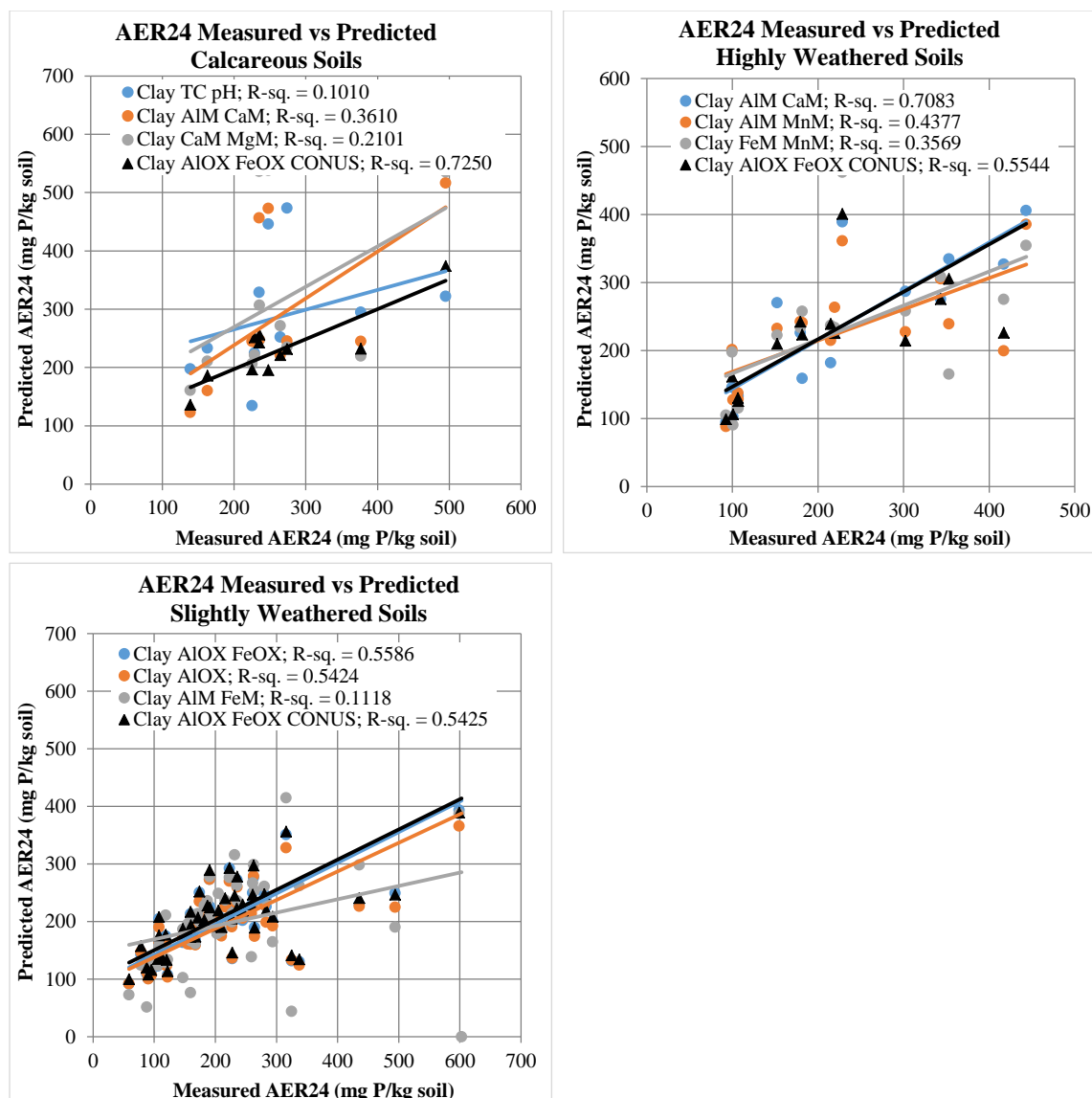


Figure 2.8. Plots of measured versus predicted AER24 values, as determined by the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils prediction models listed in Table 2.7, when applied to the corresponding validation datasets with the most significant All Soils AER24 prediction model.

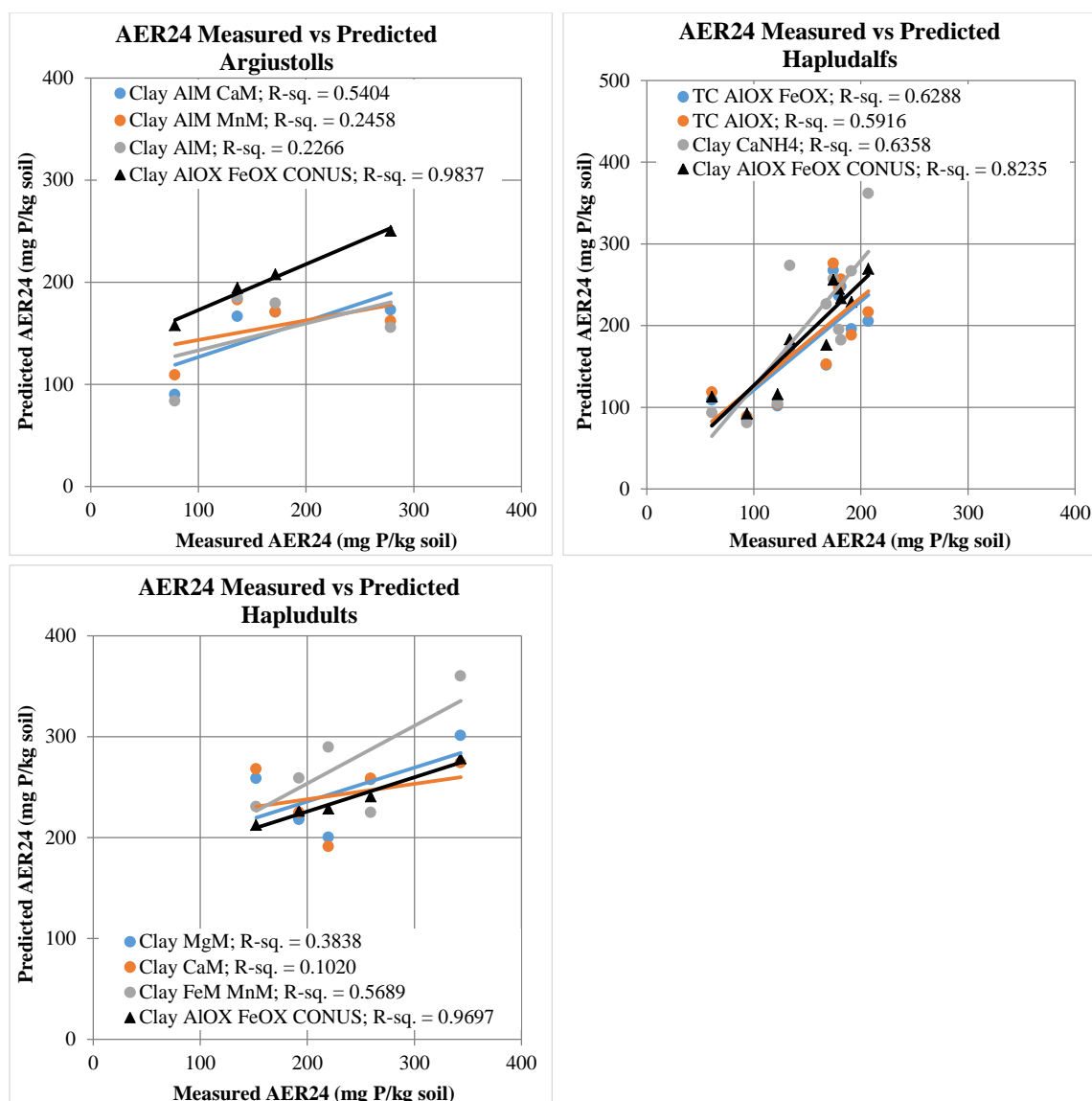


Figure 2.9. Plots of measured versus predicted AER24 values, as determined by the Argiustolls, Hapludalfs, and Hapludults prediction models listed in Table 2.7, when applied to the corresponding validation datasets with the most significant All Soils AER24 prediction model.

necessarily the overall accuracy of the prediction models. The number of predictions within 10 %, 15 %, and 20 % of the measured P sorption value for each of the significant prediction models for total P released (AER24) for the Calcareous soils, Highly Weathered soils, Slightly Weathered soils, Argiustolls, Hapludalfs, and Hapludults validation datasets were examined also (Table 2.10). Appendix E lists the number of

Table 2.10. The number of validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for the AER24 prediction models listed in Tables 2.7 and 2.8 for each grouping scheme, when applied to their corresponding validation datasets. The results of the most significant All Soils prediction model applied to each grouping are also listed for comparison.

Calcareous Soils					Argiustolls				
AER24	10%	15%	20%	N	AER24	10%	15%	20%	N
Clay TC pH	3	3	3	11	Clay Al <sub>M</sub> Ca <sub>M</sub>	1	2	2	4
Clay Al <sub>M</sub> Ca <sub>M</sub>	5	7	8	11	Clay Al <sub>M</sub> Mn <sub>M</sub>	1	1	1	4
Clay Ca <sub>M</sub> Mg <sub>M</sub>	4	5	6	11	Clay Al <sub>M</sub>	2	2	2	4
Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	4	6	8	11	Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	0	1	1	4
Highly Weathered Soils					Hapludalfs				
AER24	10%	15%	20%	N	AER24	10%	15%	20%	N
Clay Al <sub>M</sub> Ca <sub>M</sub>	6	7	9	16	TC Al <sub>OX</sub> Fe <sub>OX</sub>	4	4	5	10
Clay Al <sub>M</sub> Mn <sub>M</sub>	2	4	4	16	TC Al <sub>OX</sub>	4	4	5	10
Clay Fe <sub>M</sub> Mn <sub>M</sub>	4	7	8	16	Clay Ca <sub>NH4</sub>	2	4	4	10
Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	0	0	0	16	Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	3	3	4	10
Slightly Weathered Soils					Hapludults				
AER24	10%	15%	20%	N	AER24	10%	15%	20%	N
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	13	22	30	51	Clay Mg <sub>M</sub>	2	3	3	5
Clay Al <sub>OX</sub>	12	24	32	51	Clay Ca <sub>M</sub>	1	2	2	5
Clay Al <sub>M</sub> Fe <sub>M</sub>	12	19	21	51	Clay Fe <sub>M</sub> Mn <sub>M</sub>	1	2	2	5
Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	12	21	25	51	Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	2	2	3	5

predictions within 10 %, 15 %, and 20 % of the measured P sorption value for each of the significant prediction models for AER1, AER23, PSI, and S<sub>MAX</sub> for these same validation datasets. Table 2.10, and the table listed in Appendix E, also include the number of predictions within 10 %, 15 %, and 20 % of the measured P sorption value using the most significant model developed from the All Soils modeling dataset for each P sorption variable on these specific validation datasets, which are indicted by ‘CONUS’ following the prediction model variables in the tables.

With the exception of the Highly Weathered soils, the most significant CONUS prediction model accurately predicted a similar amount of values within the defined ranges as the grouping-specific prediction models. Overall, the prediction models

accurately predicted similar percentages, or more, for AER24 values when grouped by calcium carbonate content and degree of weathering or by Great Group. The prediction models accurately predicted up to about 72 % of the validation sample values within 20 % of the measured value for Calcareous soils, about 56 % for Highly Weathered soils, about 63 % for Slightly Weathered soils, about 50 % for both Argiustolls and Hapludalfs, and about 60 % for Hapludults. In sum, the prediction models for total soil P release developed for soils grouped by their calcium carbonate content and degree of weathering or their taxonomic Great Group are statistically better models (higher  $R^2$  and similar or lower mean square error), and can accurately predict total P release values within 20 % of a measured value as reliably, or more so, than an over-arching model for all soils. The Calcareous, Highly Weathered, and Slightly Weathered models group soils at a more general level than the Great Group models, but require less analytical data to accurately group soils, are better models than a set of “all soils” models, and are a good starting point for continuing research for improving P sorption models.

### **Potential Risk of Phosphorus Loading**

With the rise of P loading and eutrophication issues, forty-eight states have each developed a P Index, an assessment tool used to identify critical source areas and to develop targeted management practices to reduce P loss, to combat eutrophication issues. Each P Index is part of a state-specific nutrient management plan, and typically includes a soil test P value as a contributing P Index factor. The soil test P method and the associated break-point values also vary with each specific P Index. As noted previously in Chapter 1, most soil test P techniques rely on the use of various chemicals and

solutions that do not accurately mimic a natural in-field process. Sharpley et al. (2006) note that to mimic the interaction between surface soil and release of P to runoff water, water extractions are the ideal methods. Therefore, the data and predictive models developed in this study in relation to total P release have the potential to be used as an additional component for a P Index or other assessment tool, and resulting management and planning strategies, that are more reflective of actual P release into runoff. An example of how this study data could be used as part of a P Index system follows, using AER24 values from the All Soils modeling dataset and the U.S. Soil Taxonomy classification system.

The U.S. Soil Taxonomy classification system was developed and first published in 1960, and, compared to previous historic classification systems, was new in design and nomenclature, and is continually evolving. Though originally developed to serve the U.S. National Cooperative Soil Survey, the U.S. Soil Taxonomy classification system is used throughout the U.S. and around the world. One of the desired attributes of the Taxonomy classification system is that, "...differentiae should be soil properties that can be observed in the field or quantitatively measured by reliable techniques," (Buol et al., 2011). The structure of the Taxonomy system is one that progresses from high to low levels of generalization through size categories. The taxonomic Great Group category is the third level of the generalization system, which was used to apply total P desorption values to soil map units in the USDA-NRCS CONUS 2015 Gridded Soil Survey (gSSURGO) Database. AER24 values were averaged by the Great Groups listed in the All Soils modeling dataset (Appendix A). A field was added to the 'component' attribute table of the gSSURGO MuRas\_90m raster layer and using the Field Calculator Tool and

Python code, the averaged AER24 values were applied to the map units based on their Great Group classification. Map units that did not coincide with agricultural land uses in the 2011 National Land Cover Database (NLCD) were removed from the spatial layer. Map units with Great Group classifications not analyzed in this study had AER24 values set to null. Quartiles were determined for AER24 values of samples in the All Soils modeling dataset, which were used to determine break-points for a potential P loading risk index (Table 2.11). The results of this process are shown in Figure 2.10.

Table 2.11. P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the All Soils modeling dataset.

All Soils		
P Index (Potential)	Quartile	AER24 (mg P/kg soil)
Low	< 25%	≤ 135.43
Moderate	25 - 50%	135.44 - 181.61
High	50 - 75%	181.62 - 238.09
Very High	> 75%	> 238.10

From this figure it would appear that most agricultural soils would classify as posing a “Moderate” or “High” risk to contributing to P loading, using the Great Group averaging method. Areas that classified as being “Very High” risk also occur, specifically in eastern Washington, sporadically in the California Central Valley region and the Chesapeake Bay watershed, throughout the Midwest in Minnesota, Iowa, Illinois, and Indiana, and along the lower Mississippi River in Arkansas, Tennessee, and Alabama. These “Very High” risk areas are regions with known P loading issues (Alexander et al., 2008; HeideI et al., 2006; Phillips, 2007), which indicates that even this simple example of how total P desorption data and models could be used with other land and nutrient management planning tools can identify high-risk areas of P loading. Figure

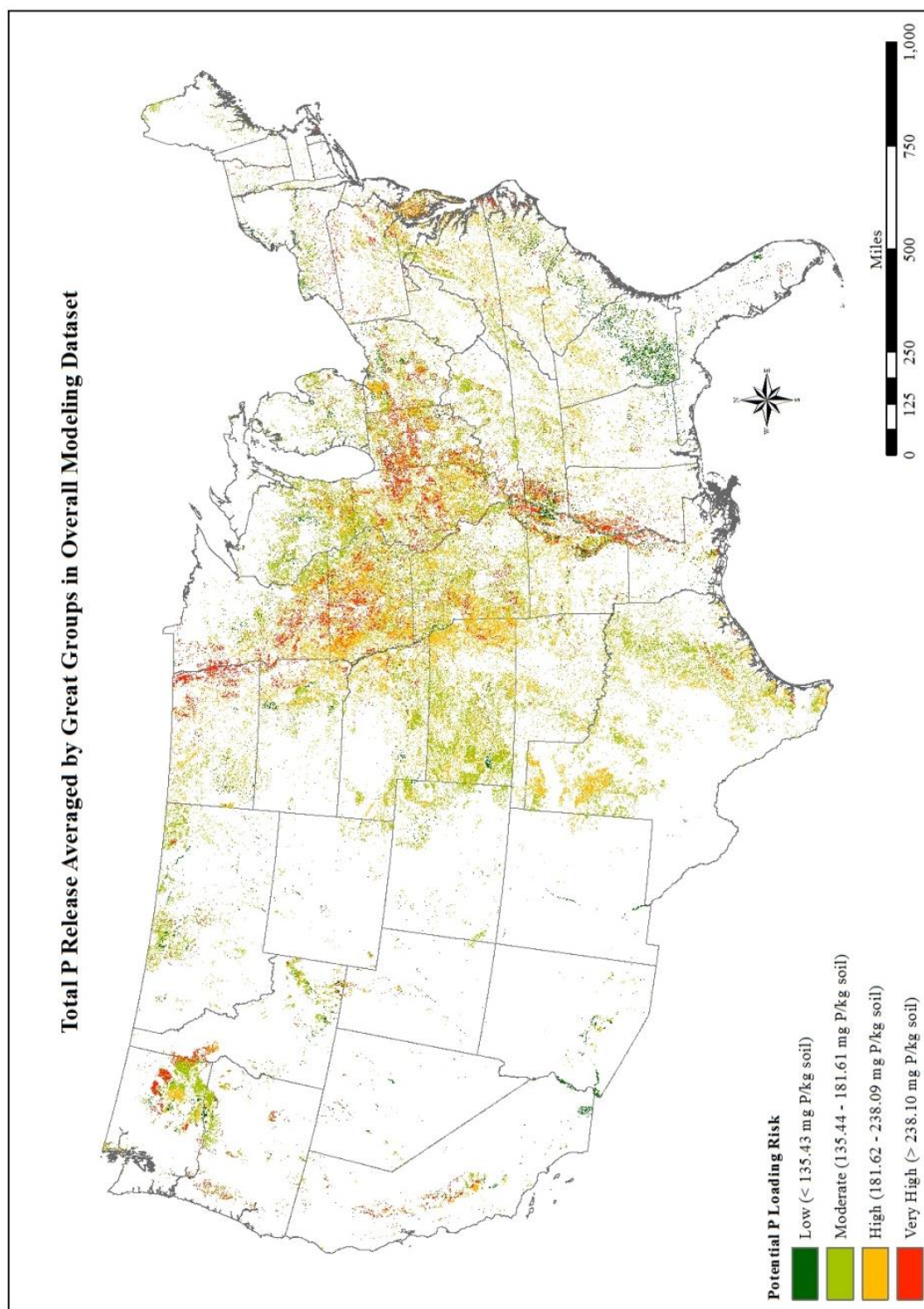


Figure 2.10. Potential risk agricultural soils pose to contributing to P loading, with total P release estimated averaged by taxonomic Great Groups from the All Soils modeling dataset.



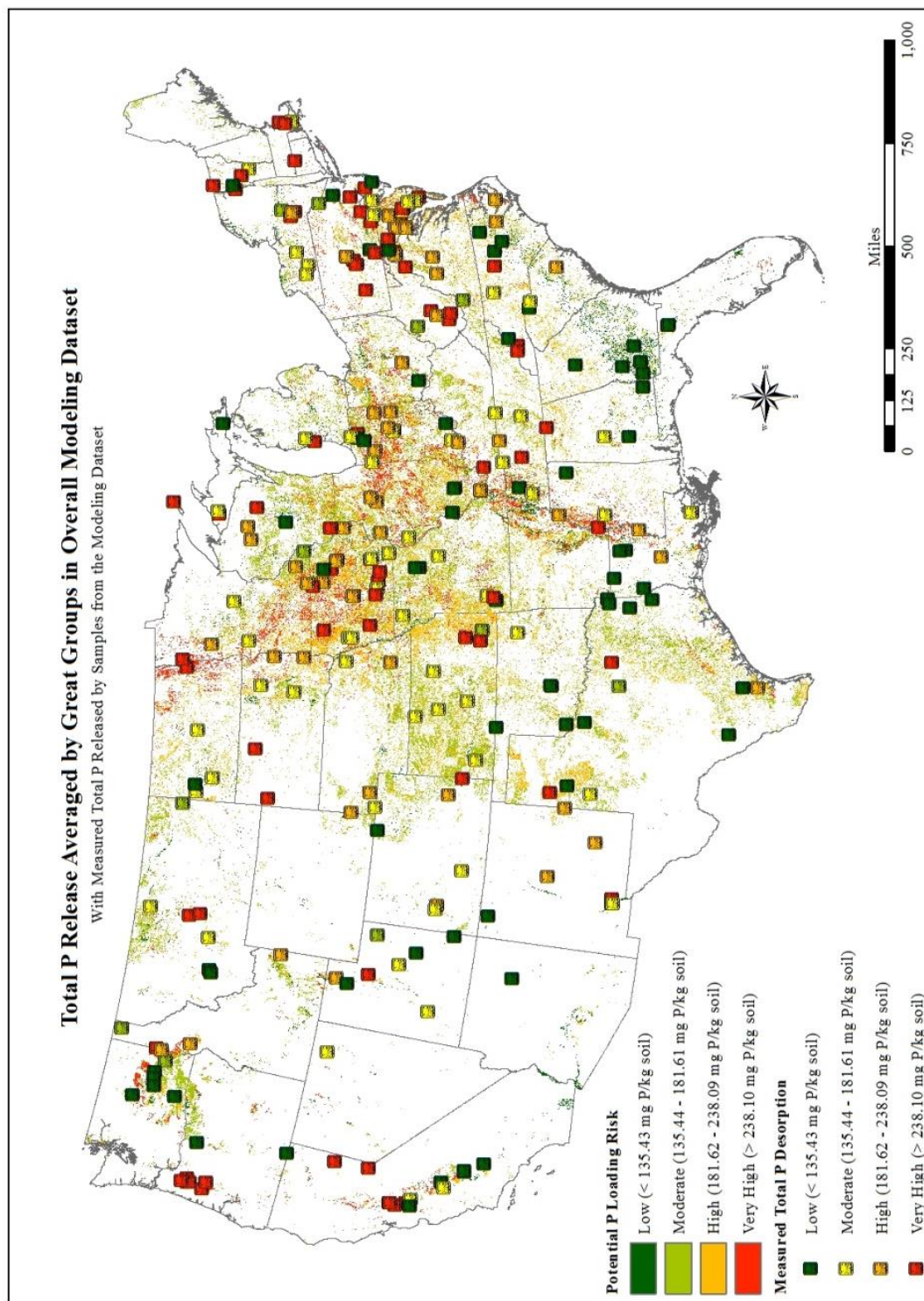


Figure 2.11. Potential risk agricultural soils pose to contributing to P loading, with total P release estimated averaged by taxonomic Great Groups from the All Soils modeling dataset, overlain by the measured AER24 values of samples from the all soils modeling dataset.

2.11 shows the measured total P desorption values for the study samples, with the same P loading risk index applied to those values, overlain on the same potential risk map from Figure 2.10. By including the measured sample values, it is clear that some precision is lost when soil behaviors are modeled based on averaged or grouped values or properties, as there are several instances of “Very High” risk sample points in “Moderate” risk areas, and vice versa. In sum, the data and models derived in this study have the potential of proving to be a useful addition in P modeling tools and thus nutrient management plans, though additional research and refinement of the models is needed.

## CONCLUSIONS

The results of this study indicate that, overall, P sorption behaviors are primarily influenced and controlled by the clay and amorphous Al and Fe oxides in the soil, but that better relationships and models occur when soils are grouped by their calcium carbonate content and degree of weathering. Relationships and models also improved when soils were grouped by taxonomic Great Group, though statistical bias could be present due to the few number of samples available in each Great Group. Additional research is needed for the latter grouping scheme. Overall, results indicate that P sorption in calcareous soils is controlled by the clay, Ca and Mg ions, and crystalline Al in the soil, while P sorption in slightly weathered soils is controlled by the clay, total carbon, and crystalline and amorphous Al and Fe oxides in the soil. P sorption in highly weathered soils is controlled by a variety of factors. Readily desorbable P is controlled by the clay, total carbon, and Ca and Mn ions in the soil; the release of more tightly bound P is controlled by the clay, total carbon, and amorphous Al and Fe oxides of the

soil; and P adsorption is controlled by the clay, total carbon, crystalline and amorphous Al and Fe oxides, and Ca and Mg ions in the soil. Oxalate and Mehlich-3 extractable P were most significantly ( $p < 0.05$ ) and highly correlated with total P release and P sorption in all soils, with the exception of total P release in slightly weathered soils. Thus, if estimating total P release or P adsorption, either extraction would be the most appropriate in most cases. The statistically significant ( $p < 0.0001$ ) and most reliable total soil P release prediction models for all soils together and slightly weathered soils included clay and amorphous Al, while the models for calcareous soils and highly weathered soils included clay, crystalline Al, and Ca. These results show that oxalate and Mehlich-3 extraction methods are necessary for modeling soil P release, and that it is more appropriate to model this behavior by grouping soils by their calcium carbonate content and degree of weathering than all together.

The results from this study also show that the inclusion of a P desorption variable or prediction model has the potential of proving to be a useful addition in P modeling and assessment tools, such as a state P Index, and thus nutrient management plans. P Indices and other assessment tools are typically used and applied at a regional or state level. Chapters 3, 4, and 5 detail the results of soil P sorption behaviors and relationships in areas with known soil P-eutrophication issues, specifically, in the Chesapeake Bay watershed, the Upper Mississippi River Sub-basin, and the California Central Valley-Bay Delta region, respectively. Eutrophication and the contaminating of surface waters with phosphorus remains a major environmental issue throughout the United States, particularly in relation to agricultural runoff and non-point source pollution. The relationships and models developed in this study have great potential for improving soil P

assessment tools, and to better inform P management related decision-making at the watershed, farm, and field scales. Failing to meet all assumptions for the statistical analyses used will require additional research and refinement of these models, and research into appropriate potential-risk break-point values is also suggested, before implementation into assessment tools. Implementing oxalate and Mehlich-3 extraction methods as standard analyses for all soils, at soil testing labs like the KSSL, will be necessary to further refine the P desorption models and improve our understanding of soil P sorption behaviors.

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## APPENDIX A

## CLASSIFICATION INFORMATION TABLES FOR CHAPTER 2 DATA

Table A.1. Classification information for samples in the All Soils, Calcareous soils, Highly Weathered soils, and Slightly Weathered soils modeling and validation datasets.

State	Pedon	Soil Series	User	Pedon ID	Great Group	Calcareous/ Weathering Group	State	Pedon	Soil Series	User	Pedon ID	Great Group	Calcareous/ Weathering Group
AZ	Sheppard		82AZ01	7008	Torrripsamment	Calcareous	NY	Howard		S08NY003002		Hapludalf	Calcareous
CA	Humboldt		00CA03	5002	Endoaquoll	Calcareous	OH	Warsaw		S02OH-129-009		Argiudoll <sup>a</sup>	Calcareous
CA	Aresh		92CA10	7002	Torrarent	Calcareous	PA	Hagerstown		S04PA061-008		Hapludalf	Calcareous
CA	Aresh		92CA10	7003	Torrarent	Calcareous	SD	Buse		93SD115037		Calciboroll	Calcareous
CA	Hesperia		94CA01	19001	Xerochrept	Calcareous	SD	Moody*		S03SD-099-001		Haplustoll <sup>a</sup>	Calcareous
CA	Cervo		94CA01	19002	Haplocambid	Calcareous	TX	Grayrock		00TX365001		Udorthent	Calcareous
CO	Norte		79CO10	09003	Ustorthent	Calcareous	TX	Houston Black*		92TX085001		Calcistert	Calcareous
CO	Persayo*		S03CO-085-001		Torrorthent	Calcareous	TX	Victoria*		S01TX-355-001		Haplustert	Calcareous
CO	Fruitland		S03CO-085-008		Haplocambid	Calcareous	UT	Turzo*		91UT047001		Torrorthent	Calcareous
IA	Reedscreek		92IA17	7003	Udfluvient	Calcareous	UT	Greenson		99UT005001		Calcixeroll	Calcareous
IA	Ida		95IA04	7005	Udorthent	Calcareous	UT	Cudhy		99UT051001		Calciquoll <sup>a</sup>	Calcareous
IA	Marshall		S06IA02	9-003	Hapludoll	Calcareous	UT	Layton		99UT057001		Haploxeroll	Calcareous
ID	Schnoorson*		97ID02	1009	Fluvaquent	Calcareous	UT	Ravola		S07UT007001		Haplocambid	Calcareous
ID	Ririe		S06ID08	1-005	Haploxeroll	Calcareous	UT	Penoyer		S07UT015001		Torrifluent	Calcareous
IL	Buckhart		S02IL-	099-023	Argiudoll	Calcareous	WV	Huntington*		S05WV-037-007		Hapludoll <sup>a</sup>	Calcareous
IN	Crosier		93IN03	9008	Epiaqualf	Calcareous	AL	Malbis		81AL131001		Paleudult	Highly Weathered
KS	Bridgeport*		S03KS-07	5-004	Natrustalf	Calcareous	AL	Decatur		S03AL089-005		Paleudult <sup>a</sup>	Highly Weathered
MIN	Fargo		93MN11	19020	Epiaquert	Calcareous	AL	Savannah		S06AL007-002		Fragiudult	Highly Weathered
MN	Winger*		99MN00	5006	Endoaquoll	Calcareous	AL	Dothan*		S07AL067-001		Kandiudult	Highly Weathered
MN	Bearden		99MN00	5007	Calciquoll	Calcareous	CA	Tallac*		S04CA-061-008		Haploxeralf	Highly Weathered
MN	McIntosh		99MN00	5008	Calcudoll	Calcareous	FL	Susquehanna*		S02FL-121-004		Paleudult	Highly Weathered
MT	Judith		S06MT	045-001	Calcistoll <sup>a</sup>	Calcareous	FL	Albany		S02FL-121-005		Hapludult	Highly Weathered
MT	Promise		S06MT	107006	Haplustoll	Calcareous	GA	Faceville		83GA099015		Kandiudult	Highly Weathered
ND	Bearden*		S06ND	035-01	Calciquoll	Calcareous	GA	Pacolet*		83GA247001		Hapludult	Highly Weathered
NE	Rosebud		01NE03	3001	Argistoll <sup>a</sup>	Calcareous	GA	Red Bay		85GA261001		Kandiudult	Highly Weathered
NE	Canyon		S02NE-	105-002	Calcistoll	Calcareous	IL	Menfro		S05IL181005		Hapludalf	Highly Weathered
NE	Ulysses*		S05NE	157004	Haplocambid	Calcareous	LA	Kenefick		S06LA085018		Hapludalf	Highly Weathered
NM	Harkey		99NM01	3	Torrifluent <sup>a</sup>	Calcareous	LA	Ruston		88LA013013		Paleudult	Highly Weathered
NM	Anthony		99NM01	3	Torrifluent <sup>a</sup>	Calcareous	MD	Queponco		00MD039005		Hapludult	Highly Weathered
NV	Humboldt		S06NV02	7-001	Endoaquoll	Calcareous	MD	Lenni		00MD041022		Endoaquill	Highly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

Table A.1. Continued.

State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group	State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group
MD	Butlertown	94MD003013	Fragiudult <sup>a</sup>	Highly Weathered	PA	Glenelg	S03PA-071-003	Hapludult	Highly Weathered
MD	Beltsville	94MD033001	Fragiudult	Highly Weathered	PA	Murrill*	S04PA027-006	Hapludult	Highly Weathered
MD	Christiana	94MD033002	Hapludult <sup>a</sup>	Highly Weathered	PA	Murrill	S04PA027-007	Hapludult	Highly Weathered
MD	Deale*	99MD003010	Endoaquilt	Highly Weathered	PA	Hublersburg	S04PA061-009	Hapludult	Highly Weathered
MD	Annermessex	S01MD-039-007	Hapludult	Highly Weathered	SC	Rains	83SC089020	Paleaquilt	Highly Weathered
MD	Quindocqua	S02MD-039-008	Endoaquilt	Highly Weathered	SC	Dorian*	S08SC091-005	Paleudult	Highly Weathered
MD	Manokin	S02MD-039-010	Hapludult	Highly Weathered	TN	Dickson	98TN015001	Fragiudult	Highly Weathered
MD	Crosiadore*	S04MD-029-003	Hapludult	Highly Weathered	TN	Mountview	98TN027001	Paleudult	Highly Weathered
MD	Tent	S04MD-029-005	Endoaquilt	Highly Weathered	TN	Paden	99TN085002	Fragiudult	Highly Weathered
MD	Croom	S04MD-033-036	Hapludult	Highly Weathered	TX	Bowie	94TX067002	Paleudult	Highly Weathered
MO	Captina	71MO109001	Fragiudult <sup>a</sup>	Highly Weathered	VA	Rabun*	S04VA-003-001	Rhodudult	Highly Weathered
NC	Hiwassee	00NC067001	Kandiudult	Highly Weathered	VA	Wheeling*	S04VA-121-003	Hapludalf	Highly Weathered
NC	Goldsboro	00NC147001	Paleudult	Highly Weathered	VA	Frederick	S04VA-163-001	Paleudult	Highly Weathered
NC	Cecil	00NC183004	Kanhapludult	Highly Weathered	WV	Lily	S01WV-081-004	Hapludult <sup>a</sup>	Highly Weathered
NC	Norfolk	81NC101001	Paleudult	Highly Weathered	WV	Braddock	S05WV-037-006	Paleudult	Highly Weathered
NC	Statler	86NC087006	Hapludalf	Highly Weathered	WV	Gilpin*	S06WV067-001	Hapludult	Highly Weathered
NC	Hayesville	88NC115001	Kanhapludult	Highly Weathered	WV	Cookport	S06WV081-001	Fragiudult	Highly Weathered
NC	Emporia*	89NC083001	Paleudult	Highly Weathered	WV	Buchanan	S07WV031005	Fragiudult	Highly Weathered
NC	Tirzah	S04NC001001	Kanhapludult	Highly Weathered	CA	Rindge*	91CA077001	Medisaprist	Slightly Weathered
NJ	Mattapex	91NJ033002	Hapludult	Highly Weathered	CA	Zacharias*	92CA099001	Xerochrept	Slightly Weathered
NJ	Sassafras	93NJ005002	Hapludult <sup>a</sup>	Highly Weathered	CA	Vernalis	92CA099002	Xerochrept	Slightly Weathered
NJ	Evesboro	94NJ001002	Quartzipsammen	Highly Weathered	CA	Capay*	92CA099005	Haploxerert	Slightly Weathered
OR	Jory*	S06OR071-011	Haploxerult	Highly Weathered	CA	Henneke	92CA099007	Argixeroll	Slightly Weathered
PA	Ernest*	05PA063780	Fragiudult	Highly Weathered	CA	Jerryslu*	92CA107001	Natridurid	Slightly Weathered
PA	Murrill*	99PA027095	Hapludult <sup>a</sup>	Highly Weathered	CA	Calicreek	93CA029001	Torrifluent	Slightly Weathered
PA	Chrome	S01PA-029-007	Hapludalf	Highly Weathered	CA	Itano*	S2012CA077004	Fluvaquent	Slightly Weathered
PA	Elioak	S03PA-071-001	Hapludalf	Highly Weathered	CA	Ryde	S2014CA077001	Endoaquoll	Slightly Weathered
PA	Elioak	S03PA-071-001	Hapludalf	Highly Weathered	CO	Wiley	91CO061001	Haplostalf	Slightly Weathered
PA	Chester	S03PA-071-002	Hapludult	Highly Weathered	CO	Olney	91CO123003	Camborthid	Slightly Weathered
PA	Chester*	S03PA-071-002	Hapludult	Highly Weathered	CT	Broadbrook	99CT003010	Dystrodept	Slightly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

Table A.1. Continued.

State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group	State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group
GA	Orangeburg	82GA007010	Hapludalf	Slightly Weathered	IL	Rozetta	94IL001007	Hapludalf	Slightly Weathered
GA	Tifton	99GA277001	Kandiudalf	Slightly Weathered	IL	Arrowsmith	94IL123037	Argiudoll	Slightly Weathered
IA	Tama*	86IA005040	Argiudoll	Slightly Weathered	IL	Alford*	96IL181003	Hapludalf	Slightly Weathered
IA	Clarion	87IA169001A	Hapludoll	Slightly Weathered	IL	Flanagan	S02IL-099-016	Argiudoll	Slightly Weathered
IA	Zwingle	92IA105002	Albaqualf	Slightly Weathered	IL	Sable*	S02IL-099-018	Endoaquoll	Slightly Weathered
IA	Clarion	93IA015001	Argiudoll	Slightly Weathered	IL	Muscatine	S02IL-099-019	Argiudoll	Slightly Weathered
IA	Pershing	94IA117007	Epiaqualf <sup>a</sup>	Slightly Weathered	IL	Catlin	S02IL-099-020	Argiudoll	Slightly Weathered
IA	Belinda	94IA117011	Albaqualf <sup>a</sup>	Slightly Weathered	IL	Menfro	S05IL181002	Fragiudalf	Slightly Weathered
IA	Sharpsburg	94IA181001	Argiudoll	Slightly Weathered	IL	Menfro	S05IL181003	Hapludalf	Slightly Weathered
IA	Sharpsburg	94IA181002	Argiustoll	Slightly Weathered	IL	Bunkum	S05IL181004	Hapludalf	Slightly Weathered
IA	Sac	95IA041005	Hapludoll	Slightly Weathered	IL	Winfield	S05IL181007	Eutrudept	Slightly Weathered
IA	Napier	95IA047003	Hapludoll	Slightly Weathered	IL	Winfield	S05IL181008	Eutrudept	Slightly Weathered
IA	Bucknell*	95IA107011	Epiaqualf	Slightly Weathered	IL	Hosmer*	S05IL181009	Fragiudalf	Slightly Weathered
IA	Armstrong	95IA107012	Hapludalf	Slightly Weathered	IL	Muscatine	S07IL187002	Argiudoll	Slightly Weathered
IA	Rinda	95IA111001	Epiaqualf	Slightly Weathered	IN	Brookston	93IN039007	Argiaquoll	Slightly Weathered
IA	Bucknell	95IA135002	Epiaqualf	Slightly Weathered	IN	Bonnie	94IN123003	Fluvaquent	Slightly Weathered
IA	Gosport	95IA179001	Dystrochrept	Slightly Weathered	IN	Crider	97IN043002	Paleudalf	Slightly Weathered
IA	Webster	S01IA-015-001	Endoaquoll <sup>a</sup>	Slightly Weathered	IN	Brookston	98IN131003	Argiaquoll	Slightly Weathered
IA	Lawler	S08IA017001	Hapludoll	Slightly Weathered	IN	Crumstown	S01IN-141-002	Hapludalf	Slightly Weathered
IA	Hayfield	S08IA019001	Hapludalf	Slightly Weathered	IN	Gilford	S01IN-141-004	Endoaqualf	Slightly Weathered
IA	Marshall	S08IA019002	Endoaquoll	Slightly Weathered	IN	Crosby*	S04IN-057-003	Epiaqualf	Slightly Weathered
IA	Hayfield	S08IA037001	Hapludalf	Slightly Weathered	IN	Metea	S04IN-099-001	Hapludalf	Slightly Weathered
IA	Marshall	S08IA067001	Endoaquoll	Slightly Weathered	IN	Kentland	S04IN-111-001	Argiaquoll	Slightly Weathered
IA	Lawler	S08IA195001	Hapludoll	Slightly Weathered	IN	Blount*	S04IN-179-006	Epiaqualf	Slightly Weathered
ID	Nez Perce	86ID061001	Argialboll	Slightly Weathered	IN	Patton	S05IN-159-001A	Endoaquoll	Slightly Weathered
ID	Palouse	S03ID-009-002	Haploxeroll	Slightly Weathered	IN	Xenia	S05IN-159-004	Hapludalf	Slightly Weathered
ID	Southwick*	S04ID-009-003	Argixeroll	Slightly Weathered	IN	Pewamo*	S07IN135002	Argiaquoll	Slightly Weathered
IL	Belknap	90IL081004	Endoaquept	Slightly Weathered	IN	Zanesville	S09IN147001	Fragiudalf	Slightly Weathered
IL	Bluford	90IL081014	Epiaqualf	Slightly Weathered	KD	Harney	88KS167001	Argiustoll	Slightly Weathered
IL	Coulterville*	93IL163014	Endoaqualf	Slightly Weathered	KS	Crete	01KS027002	Argiustoll <sup>a</sup>	Slightly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

Table A.1. Continued.

State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group	State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group
KS	Osage*	97KS031001	Epiaquept	Slightly Weathered	MO	Hayfield	S08MN090001	Hapludalf	Slightly Weathered
KS	Richfield	99KS067002	Argistoll	Slightly Weathered	MO	Marshall*	S08MN109001	Endoaquoll	Slightly Weathered
KS	Holdrege	S04KS-147-001	Argistoll	Slightly Weathered	MO	Grundy	77MO147001	Argistoll <sup>a</sup>	Slightly Weathered
KS	Funmar	S05KS185001	Argistoll	Slightly Weathered	MO	Adco	87MO121024	Hapludalf	Slightly Weathered
KS	Zaar	S05KS205002	Endoaquept	Slightly Weathered	MO	Mexico	87MO121026	Albaqualf	Slightly Weathered
KS	Parsons*	S06KS133-001	Albaqualf	Slightly Weathered	MO	Pembroke	91MO057074	Paleudalf	Slightly Weathered
KY	Nicholson	82KY055004	Fragiudalf	Slightly Weathered	MO	Mexico	95MO027001	Epiaqualf	Slightly Weathered
LA	Moreland	88LA079001	Haplaquoll	Slightly Weathered	MO	Creldon	S01MO-109-001	Fragiudalf	Slightly Weathered
LA	Commerce	96LA107004	Fluvaquept	Slightly Weathered	MS	Tunica	99MSI43001	Epiaquept <sup>a</sup>	Slightly Weathered
LA	Gramercy	S00LA-095-001	Endoaquept	Slightly Weathered	MS	Sharkey	99MSI51001	Epiaquept <sup>a</sup>	Slightly Weathered
LA	Cancienne	S02LA-095-001	Epiaquept	Slightly Weathered	MS	Dundee	S04MS-053-001	Endoaquall <sup>a</sup>	Slightly Weathered
LA	Sterlington	S07LA073-001	Hapludalf	Slightly Weathered	MS	Mantachie*	S07MS081-001	Endoaquept	Slightly Weathered
LA	Rilla*	S07LA073-003	Hapludalf	Slightly Weathered	MT	Varney	91MT093002	Argistoll*	Slightly Weathered
MA	Ipswich	S08MA023001	Sulfaquept	Slightly Weathered	MT	Telstad	92MT041004	Argiboroll	Slightly Weathered
MA	Merrimac	S08MA023002	Dyst rudept	Slightly Weathered	MT	Reedwest	S04MT-059-010	Argistoll	Slightly Weathered
MA	Winooski	S08MA023004	Dyst rudept	Slightly Weathered	MT	Williams*	S06MT083-001	Argistoll <sup>a</sup>	Slightly Weathered
MD	Crosiadore	00MD041021	Hapludalf	Slightly Weathered	NC	Guyot	00NC087001	Dyst rudept	Slightly Weathered
MD	Nassawango	00MD041023	Hapludalf	Slightly Weathered	NC	Hydeland*	89NC095008	Umbraquept	Slightly Weathered
MD	Cedartown	97MD045018	Hapludalf	Slightly Weathered	ND	Williams	87ND083439	Argiboroll	Slightly Weathered
MD	Glenelg	98MD021133	Fragiudept	Slightly Weathered	ND	Lonna	93ND053398	Halpustept <sup>a</sup>	Slightly Weathered
MI	Emmet	82MI097005	Eutroboralf	Slightly Weathered	ND	Amor	98ND053494	Argistoll	Slightly Weathered
MI	Amnicon	S01MI-131-016	Hapludalf	Slightly Weathered	ND	Belfield	S02ND-089-007	Argistoll	Slightly Weathered
MI	Matchwood*	S03MI-131-011	Endoaqualf	Slightly Weathered	NE	Judson	93NE173002	Haplustoll	Slightly Weathered
MI	Minong	S06MI083-012	Udofolist	Slightly Weathered	NE	Pawnee*	S06NE109-100	Argistoll	Slightly Weathered
MI	-*	S07MI139011	Haplofibrist	Slightly Weathered	NJ	Chatfield	95NJ037002	Dyst rudept	Slightly Weathered
MI	Granby	S08MI123001	Endoaquoll	Slightly Weathered	NM	Reakor	91NM005002	Haplocalcid	Slightly Weathered
MI	Kingsville*	S08MI123002	Pammaquept	Slightly Weathered	NM	Manzano	91NM057002	Haplustoll	Slightly Weathered
MN	Barnes	91MN149001	Hapludoll	Slightly Weathered	NM	Onite*	92NM013001	Haplocambid	Slightly Weathered
MN	Duluth	94MN095045	Hapludalf	Slightly Weathered	NM	Turley	92NM045002	Haplocambid	Slightly Weathered
MN	Nicollet	96MN085003	Hapludoll <sup>a</sup>	Slightly Weathered	NV	Welch	81NV007490	Endoaquoll	Slightly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.



Table A.1. Continued.

State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group	State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group
NY	Tioga	00NY003013	Eurudept	Slightly Weathered	SC	Brewback	S08SC091-003	Hapludalf	Slightly Weathered
NY	Barbour*	86NY025004	Dystrochrept	Slightly Weathered	SD	Vebar	94SD041001	Haploboroll	Slightly Weathered
NY	-*	86NY025006	Fragiaquept	Slightly Weathered	SD	Barnes*	S07SD039002	Hapludoll	Slightly Weathered
NY	Chippewa	91NY077006	Fragiaquept	Slightly Weathered	SD	Clarno	S07SD073001	Haplustoll	Slightly Weathered
NY	Chenango Fan	91NY077008	Dystrochrept	Slightly Weathered	SD	Kyle, terrace	S08SD019001	Haplustert	Slightly Weathered
NY	Honeoye*	99NY043001	Hapludalf	Slightly Weathered	TN	Routon	85TN053002	Ochraqualf	Slightly Weathered
NY	Vergennes	S02NY-031-002	Hapludalf	Slightly Weathered	TN	Memphis	85TN075001	Hapludalf	Slightly Weathered
NY	Lansing	S09NY123030	Hapludalf	Slightly Weathered	TN	Crider*	98TN147001	Paleudalf	Slightly Weathered
OH	Miamian*	S02OH-129-015	Hapludalf <sup>a</sup>	Slightly Weathered	TN	Nolin	S07TN161-006	Eurudept	Slightly Weathered
OH	Clermont	S08OH015002	Glossaqualf	Slightly Weathered	TX	Tillman*	00TX487001	Natrustoll	Slightly Weathered
OK	Port	00OK051001	Haplustoll	Slightly Weathered	TX	Acuft*	06TX369001	Paleustoll	Slightly Weathered
OK	Grant	87OK051001	Argiustoll	Slightly Weathered	TX	Duval	79TX507001	Haplustalf	Slightly Weathered
OK	Dennis	92OK131001	Paleudoll	Slightly Weathered	TX	Olton	93TX069001	Paleustoll	Slightly Weathered
OK	St. Paul*	94OK059001	Argiustoll <sup>a</sup>	Slightly Weathered	TX	Pullman*	99TX117001	Paleustoll	Slightly Weathered
OK	Hollister	96OK065006	Haplustert	Slightly Weathered	TX	Erno*	S00TX-067-001	Glossudalf	Slightly Weathered
OK	Tipton	98OK065002	Argiustoll	Slightly Weathered	TX	Amarillo	S04TX-219-001	Paleustalf	Slightly Weathered
OR	Salsbury	79OR037003	Durixeroll	Slightly Weathered	TX	Tuscosso	S06TX405001	Eurudept	Slightly Weathered
OR	Bakeoven	89OR065001	Haploxeroll	Slightly Weathered	TX	Bolar*	S07TX367-002	Calcistoll	Slightly Weathered
OR	Jory	S01OR-053-004	Argixeroll	Slightly Weathered	TX	Orelia*	S09TX0252801	Natrustoll	Slightly Weathered
OR	Dayton*	S02OR-047-002	Albaqualf	Slightly Weathered	UT	Manderfield	99UT001001	Xerocrept	Slightly Weathered
OR	Sawtell	S03OR-005-003	Argixeroll	Slightly Weathered	UT	Monticello	S07UT037001	Argiustoll	Slightly Weathered
OR	Bashaw	S03OR-043-002	Endoaquert	Slightly Weathered	VI	Dodgeville	S04WI-065-002	Argudoll	Slightly Weathered
OR	Woodburn	S04OR-071-011	Argixeroll	Slightly Weathered	VT	Tunbridge	87VT027003	Haplorhod	Slightly Weathered
PA	Allegheny	93PA055038	Haplocalcid	Slightly Weathered	VT	Cabot	92VT027002	Fluvaquent	Slightly Weathered
PA	Weikert	93PA055039	Dystrodept <sup>a</sup>	Slightly Weathered	VT	Hadley	S07VT007001	Udifluent	Slightly Weathered
PA	Weikert	93PA055040	Dystrodept <sup>a</sup>	Slightly Weathered	VT	Lordstown	S08VT011007	Dystrodept	Slightly Weathered
PA	Unadilla*	93PA103000	Dystrodept <sup>a</sup>	Slightly Weathered	WA	Athens*	85WA075002	Haploxeroll	Slightly Weathered
PA	Chrome	S01PA-029-008	Hapludalf	Slightly Weathered	WA	Touhey	90WA017103	Durixeroll	Slightly Weathered
PA	Hagerstown	S04PA027-003	Hapludalf	Slightly Weathered	WA	Quincy	90WA021004	Torrissamment	Slightly Weathered
PA	Hagerstown*	S04PA027-004	Hapludalf	Slightly Weathered	WA	Walla Walla*	91WA001001	Haploxeroll	Slightly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

Table A.1. Continued.

State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group
WA	Ritzville	91WA001005	Haploxeroll	Slightly Weathered
WA	Shano	91WA001007	Camborthid	Slightly Weathered
WI	Menahga	94WI057004B	Udipsamment	Slightly Weathered
WI	Menahga*	94WI057004C	Udipsamment	Slightly Weathered
WI	Antigo*	98WI067001	Glossudalf	Slightly Weathered
WI	Magnor*	S00WI-099-001	Fragiudept	Slightly Weathered
WI	Sconsin	S03WI-107-006	Fraglossudalf	Slightly Weathered
WV	Berks	S02WV-019-012	Dystrudept <sup>a</sup>	Slightly Weathered
WV	Moshannon*	S03WV-087-001	Eutrudept <sup>a</sup>	Slightly Weathered
WV	Chilhowie	S05WV-037-001	Paleudalf	Slightly Weathered
WV	Hagerstown	S05WV-037-002	Paleudalf	Slightly Weathered
WV	Hagerstown	S05WV-037-008	Hapludalf	Slightly Weathered
WV	Clarksburg*	S07WV031001	Fragiudalf	Slightly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

Table A.2. Classification information for samples in the Argiustolls, Hapludalfs, and Hapludults modeling and validation datasets.

Calcareous/ Weathering Group				Calcareous/ Weathering Group			
State	Pedon Soil Series	User Pedon ID	Great Group	State	Pedon Soil Series	User Pedon ID	Great Group
NE	Rosebud	01NE033001	Argiustoll <sup>a</sup>	IL	Alford*	96IL181003	Hapludalf
IA	Sharpsburg*	94IA181002	Argiustoll	IL	Menfro	S05IL181003	Hapludalf
KD	Harney	88KS167001	Argiustoll	IL	Bunkum	S05IL181004	Hapludalf
KS	Crete	01KS027002	Argiustoll <sup>a</sup>	IN	Crumstown	S01IN-141-002	Hapludalf
KS	Richfield	99KS067002	Argiustoll	IN	Metea	S04IN-099-001	Hapludalf
KS	Holdrege	S04KS-147-001	Argiustoll	IN	Xenia	S05IN-159-004	Hapludalf
KS	Funmar	S05KS185501	Argiustoll	LA	Sterlington*	S07LA073-001	Hapludalf
MT	Varney	91MT093002	Argiustoll <sup>a</sup>	LA	Rilla*	S07LA073-003	Hapludalf
MT	Reedwest	S04MT-059-010	Argiustoll	MD	Crosiadore	00MD041021	Hapludalf
MT	Williams*	S06MT083-001	Argiustoll	MD	Nassawango	00MD041023	Hapludalf
ND	Amor	98ND053494	Argiustoll	MD	Cedartown	97MD045018	Hapludalf
ND	Belfield*	S02ND-089-007	Argiustoll	MI	Amnicon	S01MI-131-016	Hapludalf
OK	Grant	87OK051001	Argiustoll	MN	Duluth	94MNO95045	Hapludalf
OK	St. Paul*	94OK059001	Argiustoll <sup>a</sup>	MN	Hayfield	S08MN099001	Hapludalf
OK	Tipton	98OK065002	Argiustoll	MO	Adco*	87MO121024	Hapludalf
UT	Monticello	S07UT037001	Argiustoll	NY	Honeoye*	99NY043001	Hapludalf
NY	Howard	S08NY003002	Hapludalf	NY	Vergennes	S02NY-031-002	Hapludalf
PA	Hagerstown*	S04PA061-008	Hapludalf	NY	Lansing	S09NY123030	Hapludalf
IL	Menfro	S05IL181005	Hapludalf	OH	Miamian*	S02OH-129-015	Hapludalf <sup>a</sup>
LA	Kenefick	86LA085018	Hapludalf	PA	Chrome	S01PA-029-008	Hapludalf
NC	Statler	86NC087006	Hapludalf	PA	Hagerstown	S04PA027-003	Hapludalf
PA	Chrome	S01PA-029-007	Hapludalf	PA	Hagerstown*	S04PA027-004	Hapludalf
PA	Elioak	S03PA-071-001	Hapludalf	SC	Brewback	S08SC091-003	Hapludalf
PA	Elioak	S03PA-071-001	Hapludalf	TN	Memphis	85TN075001	Hapludalf
VA	Wheeling*	S04VA-121-003	Hapludalf	WV	Hagerstown	S05WV-037-008	Hapludalf
GA	Orangeburg*	82GA007010	Hapludalf	FL	Albany	S02FL-121-005	Hapludult
IA	Armstrong	95IA107012	Hapludalf	GA	Pacolet	83GA247001	Hapludult
IA	Hayfield	S08IA019001	Hapludalf	MD	Queponco	00MD039005	Hapludult
IA	Hayfield	S08IA037001	Hapludalf	MD	Christiana	94MD033002	Hapludult <sup>a</sup>
IL	Rozetta	94IL001007	Hapludalf	MD	Annesmessex	S01MD-039-007	Hapludult

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

Table A.2. Continued.

State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group
MD	Manokin	S02MD-039-010	Hapludult	Highly Weathered
MD	Crosiadore*	S04MD-029-003	Hapludult	Highly Weathered
MD	Croom	S04MD-033-036	Hapludult	Highly Weathered
NJ	Mattapex	91NJ033002	Hapludult	Highly Weathered
NJ	Sassafras	93NJ005002	Hapludult <sup>a</sup>	Highly Weathered
PA	Murrill*	99PA027095	Hapludult <sup>a</sup>	Highly Weathered
PA	Chester*	S03PA-071-002	Hapludult	Highly Weathered
PA	Chester	S03PA-071-002	Hapludult	Highly Weathered
PA	Glenelg	S03PA-071-003	Hapludult	Highly Weathered
PA	Murrill*	S04PA027-006	Hapludult	Highly Weathered
PA	Murrill	S04PA027-007	Hapludult	Highly Weathered
PA	Hublersburg	S04PA061-009	Hapludult	Highly Weathered
WV	Lily	S01WV-081-004	Hapludult <sup>a</sup>	Highly Weathered
WV	Gilpin*	S06WV067-001	Hapludult	Highly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

## APPENDIX B

### DESCRIPTIVE STATISTICS OF SOIL PROPERTIES AND QUANTILES FOR P SORPTION VARIABLES FOR CHAPTER 2 DATA

Figure B.1. Boxplots displaying the quartile statistics of each measured P desorption variable (AER1, AER23, and AER24), for samples in the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils datasets.

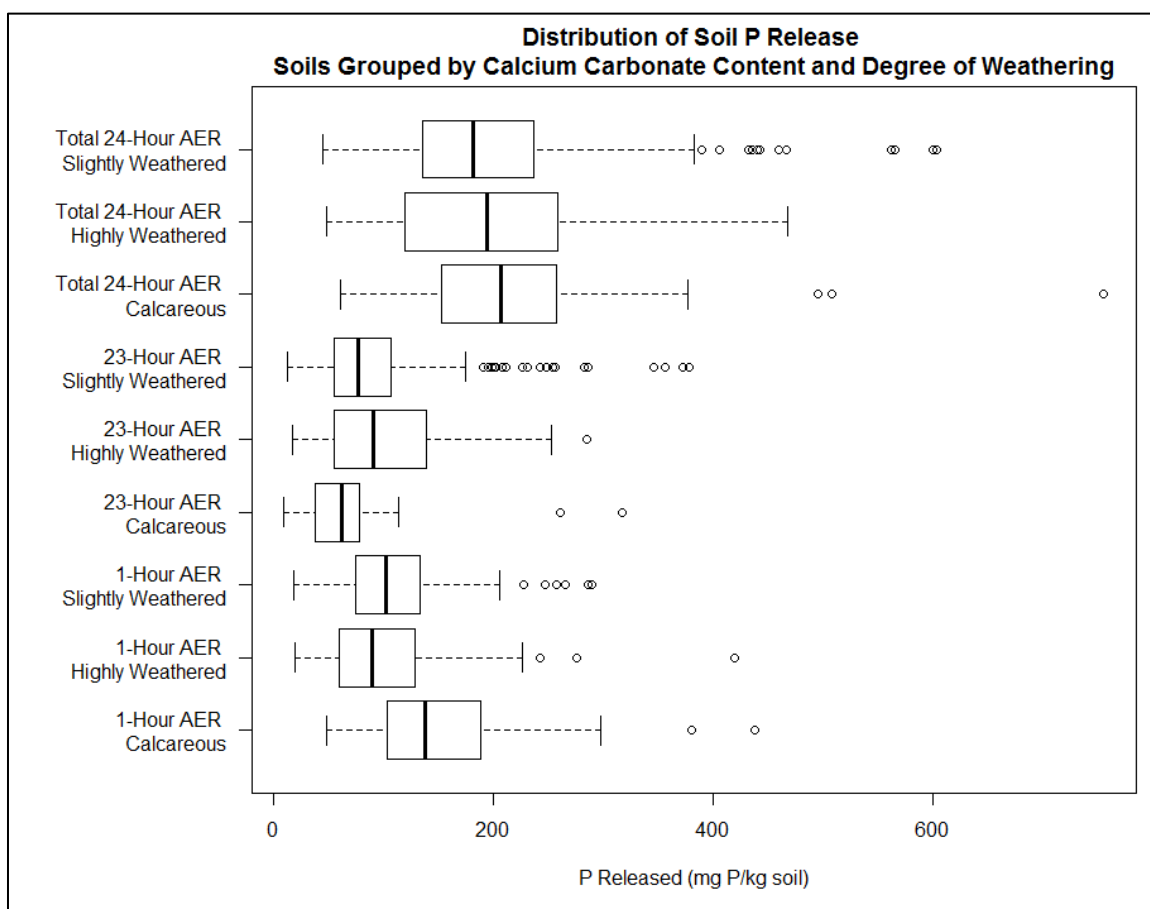


Figure B.2. Boxplots displaying the quartile statistics of each measured P desorption variable (AER1, AER23, and AER24), for samples in the Argiustolls, Hapludalfs, and Hapludults datasets.

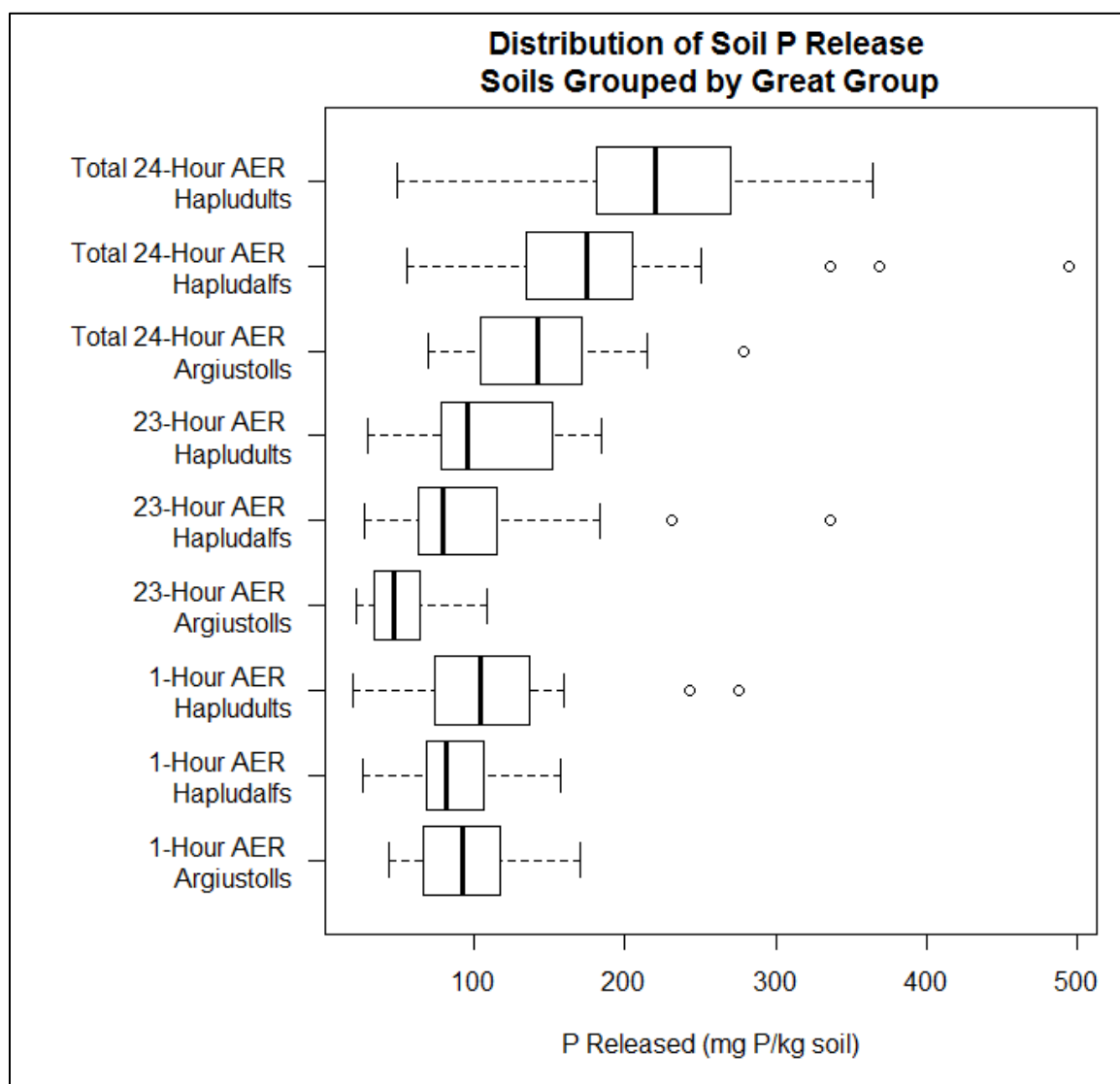


Figure B.3. Boxplots displaying the quartile statistics of PSI, for samples in the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils datasets.

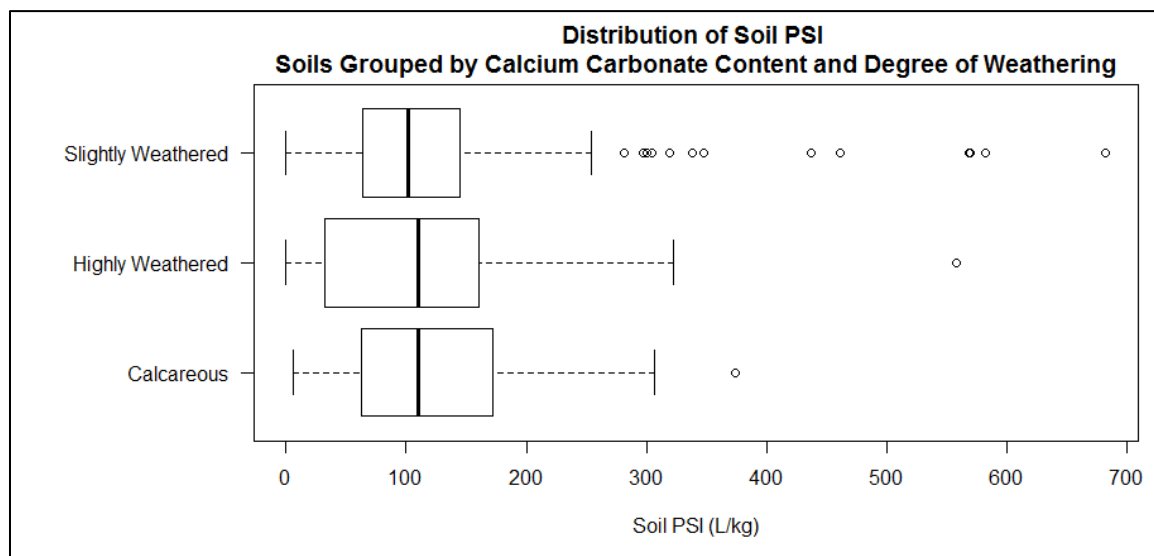


Figure B.4. Boxplots displaying the quartile statistics of PSI, for samples in the Argiustolls, Hapludalfs, and Hapludults datasets.

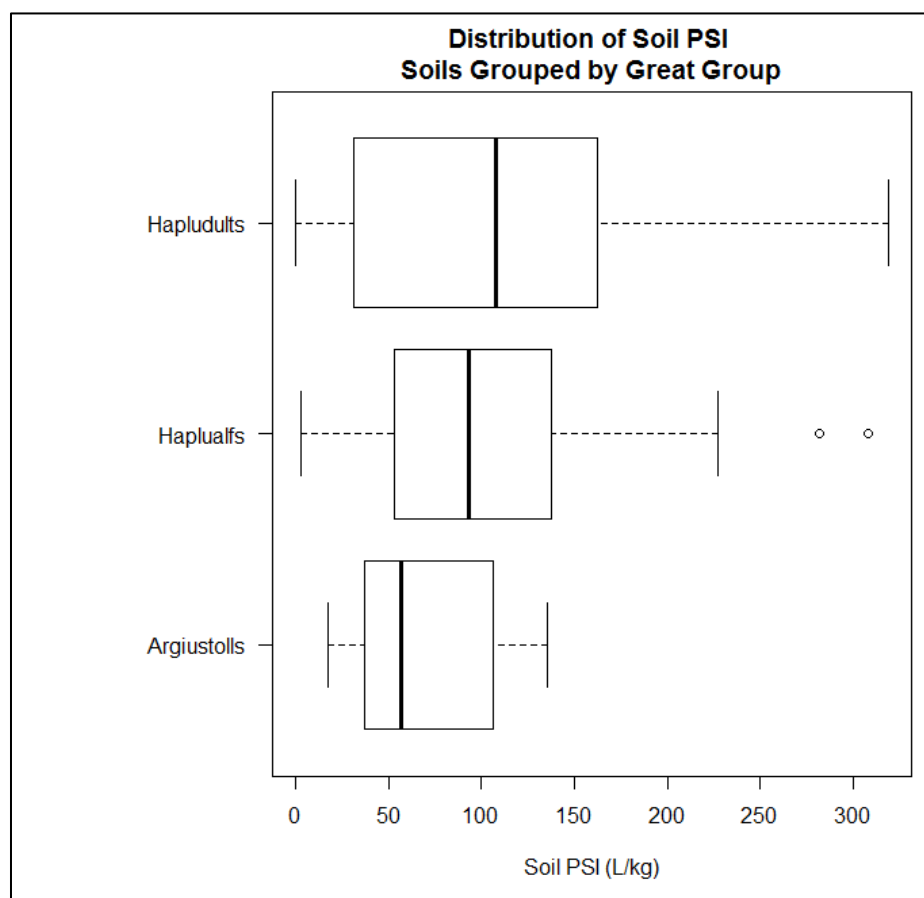


Figure B.5. Boxplots displaying the quartile statistics of  $S_{MAX}$ , for samples in the Calcareous soils, Highly Weathered soils, and Slightly Weathered soils datasets.

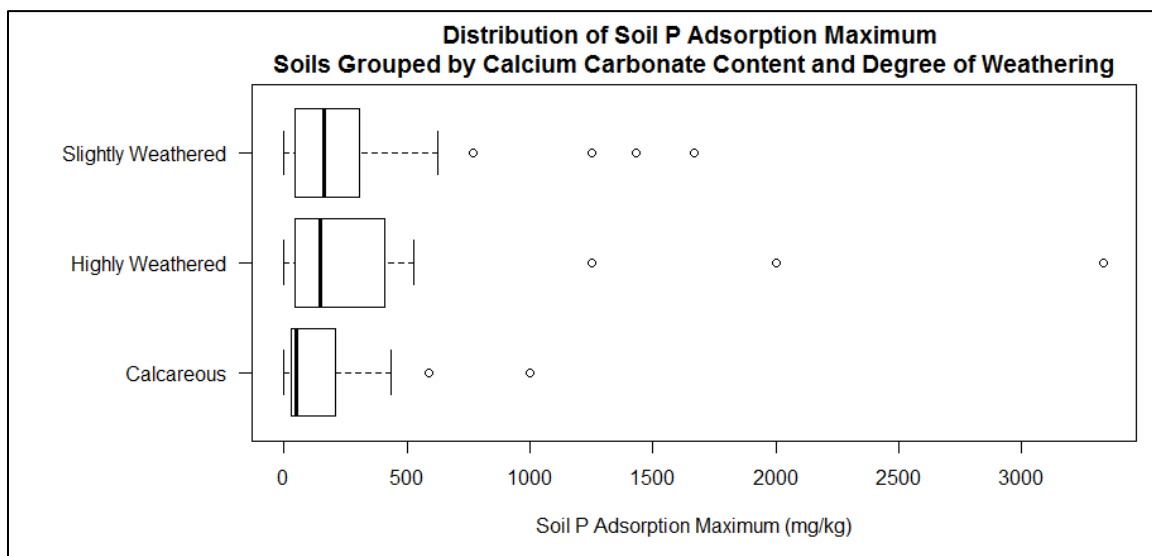


Figure B.6. Boxplots displaying the quartile statistics of  $S_{MAX}$ , for samples in the Argiustolls, Hapludalfs, and Hapludults datasets.

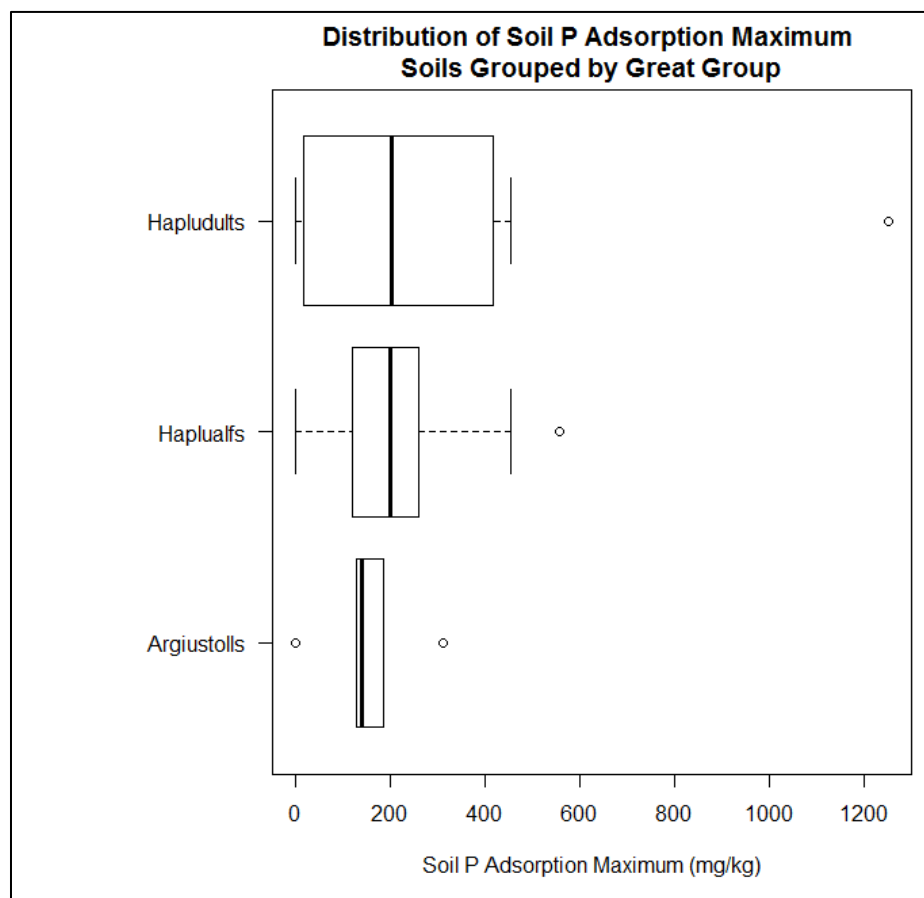




Table B.1. Descriptive statistics of the soil properties for samples in the All Soils, Calcareous Soils, Highly Weathered Soils, and Slightly Weathered Soils modeling datasets.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>m</sub>	Ca <sub>m</sub>	Fe <sub>m</sub>	Mg <sub>m</sub>	Mn <sub>m</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>ox</sub>	P <sub>M</sub>	P <sub>MB</sub>	P <sub>Bay1</sub>	P <sub>WS</sub>	P <sub>CuCl2</sub>	
	----- % -----				----- mg Element/kg soil -----										----- mg P/kg soil -----					
	All Soils																			
Mean	20.31	3.12	0.91	6.25	1223.40	2741.70	584.95	2384.69	147.93	356.41	133.05	15.00	3.41	371.17	90.76	77.99	62.33	0.75	12.08	
Standard Error	0.74	0.39	0.35	0.07	61.77	192.29	19.04	196.95	7.26	27.20	9.44	0.95	0.27	21.48	7.64	7.54	8.06	0.18	4.99	
95% Confidence Level for Mean	1.45	0.76	0.68	0.14	121.70	378.83	37.52	388.05	14.31	53.60	18.60	1.88	0.54	42.32	15.06	14.85	15.96	0.36	9.88	
Median	19.25	1.83	0.00	6.20	1000.00	1900.00	577.20	1679.40	117.70	261.40	106.50	10.70	2.40	290.30	52.50	37.80	30.00	0.21	0.72	
Minimum	1.40	0.18	0.00	3.60	200.00	0.00	1.10	30.10	12.10	7.80	0.50	0.00	0.00	0.00	0.00	1.20	0.00	0.00	0.00	
Maximum	67.30	49.63	75.00	8.50	6900.00	18700.00	1503.10	35928.90	615.60	3827.20	1352.20	91.00	39.10	2699.10	782.20	742.00	472.00	25.64	385.53	
N	234	235	235	235	235	235	231	231	231	231	231	235	235	235	231	234	119	234	120	
	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>m</sub>	Ca <sub>m</sub>	Fe <sub>m</sub>	Mg <sub>m</sub>	Mn <sub>m</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>ox</sub>	P <sub>M</sub>	P <sub>MB</sub>	P <sub>Bay1</sub>	P <sub>WS</sub>	P <sub>CuCl2</sub>	
	----- % -----				----- mg Element/kg soil -----										----- mg P/kg soil -----					
	Calcareous Soils																			
Mean	24.43	2.64	6.26	7.80	894.12	1588.24	299.72	5955.25	78.25	593.49	111.11	37.40	5.91	413.15	72.44	65.38	40.45	0.38	3.75	
Standard Error	2.38	0.46	2.21	0.08	84.22	241.39	42.99	1014.85	11.34	101.85	11.63	3.59	1.03	57.11	14.50	14.54	10.41	0.10	1.80	
95% Confidence Level for Mean	4.84	0.94	4.51	0.16	171.35	491.10	87.45	2064.73	23.08	207.22	23.67	7.31	2.09	116.19	29.49	29.59	22.33	0.20	3.77	
Median	21.25	1.97	2.50	7.80	900.00	1200.00	276.30	5242.85	54.20	407.60	101.80	34.10	4.50	356.20	48.40	39.05	25.00	0.22	0.73	
Minimum	5.20	0.22	1.00	7.00	200.00	0.00	1.10	1454.90	19.00	109.20	23.20	8.60	0.70	60.90	8.30	7.00	0.00	0.00	0.00	
Maximum	58.90	13.01	75.00	8.50	2100.00	6600.00	878.60	35928.90	297.80	2846.80	347.30	91.00	29.60	1983.40	486.50	486.50	132.00	3.18	32.98	
N	34	34	34	34	34	34	34	34	34	34	34	34	34	34	34	34	15	34	20	

Table B.1. Continued.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>OX</sub>	Fe <sub>OX</sub>	Al <sub>M</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	Cd <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bray1</sub>	P <sub>WS</sub>	P <sub>Cd12</sub>	
	----- % -----				----- mg P/kg soil -----															
	----- mg Element/kg soil -----																			
	Highly Weathered Soils																			
Mean	14.34	6.09	0.00	5.38	1212.77	1431.91	699.07	893.77	150.67	154.24	149.32	5.55	1.34	308.89	143.04	107.66	101.07	2.33	51.67	
Standard Error	1.19	1.76	0.00	0.13	116.52	202.76	41.22	133.43	16.52	26.14	30.08	1.02	0.21	39.02	23.85	21.96	25.79	0.90	24.66	
95% Confidence Level for Mean	2.40	3.54	0.00	0.26	234.54	408.13	83.03	268.74	33.28	52.65	60.59	2.06	0.41	78.55	48.04	44.23	53.49	1.81	51.13	
Median	13.25	1.88	0.00	5.30	1000.00	1100.00	678.35	576.25	115.80	113.00	96.25	3.30	1.00	212.00	88.10	42.80	46.10	0.32	2.69	
Minimum	1.40	0.53	0.00	3.90	200.00	0.00	30.60	30.10	21.20	7.80	0.50	0.10	0.00	0.00	0.00	1.20	7.00	0.00	0.00	
Maximum	32.90	49.63	0.00	7.00	3600.00	5900.00	1317.50	3817.50	600.60	882.20	1113.20	38.50	5.80	1004.30	651.60	592.10	466.70	25.64	385.53	
N	46	47	47	47	47	47	46	46	46	46	46	47	47	47	46	46	23	46	23	
	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>OX</sub>	Fe <sub>OX</sub>	Al <sub>M</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	Cd <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bray1</sub>	P <sub>WS</sub>	P <sub>Cd12</sub>	
	----- % -----				----- mg P/kg soil -----															
	----- mg Element/kg soil -----																			
	Slightly Weathered Soils																			
Mean	21.19	2.33	0.00	6.17	1299.35	3396.10	614.40	2034.91	162.79	364.61	133.04	12.94	3.50	380.91	78.96	71.90	55.38	0.37	2.42	
Standard Error	0.87	0.18	0.00	0.07	84.43	267.59	21.20	117.79	9.14	31.49	10.88	0.69	0.32	27.77	8.23	8.77	8.84	0.04	0.63	
95% Confidence Level for Mean	1.73	0.35	0.00	0.15	166.79	528.64	41.90	232.73	18.07	62.22	21.50	1.37	0.64	54.86	16.25	17.33	17.60	0.08	1.25	
Median	20.55	1.66	0.00	6.10	1000.00	2600.00	580.30	1688.90	126.20	276.60	108.70	11.40	2.50	276.95	52.40	36.20	30.00	0.19	0.57	
Minimum	1.70	0.18	0.00	3.60	300.00	0.00	23.40	81.40	12.10	11.10	2.80	0.00	0.10	16.40	4.50	1.30	0.00	0.00	0.00	
Maximum	67.30	13.68	0.00	8.40	6900.00	18700.00	1503.10	9253.30	615.60	3827.20	1352.20	55.30	39.10	2699.10	782.00	742.00	472.00	3.06	29.37	
N	154	154	154	154	154	154	151	151	151	151	151	154	154	154	151	151	81	154	77	



Table B.2. Continued.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>OX</sub>	Fe <sub>OX</sub>	Al <sub>M</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bny1</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
	----- % -----																		
	----- mg Element/kg soil -----																		
	Highly Weathered Soils - Validation Dataset																		
	----- cmol/kg -----																		
Mean	20.61	2.01	0.00	5.63	1787.50	3356.25	806.06	894.59	155.12	131.65	101.64	5.91	1.28	332.98	90.87	87.09	59.55	0.31	1.24
Standard Error	3.65	0.32	0.00	0.23	332.40	863.04	75.16	165.69	29.24	24.97	22.06	1.05	0.21	55.08	23.79	23.93	17.49	0.10	0.67
95% Confidence Level for Mean	7.79	0.69	0.00	0.49	708.49	1839.52	160.19	353.17	62.32	53.22	47.03	2.23	0.44	117.40	50.70	51.01	38.97	0.20	1.55
Median	17.65	1.92	0.00	5.80	1800.00	3100.00	736.75	705.20	113.85	98.20	94.95	6.45	1.05	317.70	59.10	46.45	45.90	0.09	0.42
Minimum	4.40	0.33	0.00	4.20	400.00	0.00	425.20	14.00	57.70	0.70	10.30	0.30	0.10	30.80	1.30	1.60	1.80	0.00	0.00
Maximum	62.60	4.82	0.00	7.20	5700.00	14200.00	1332.40	2189.10	514.70	347.80	336.80	12.40	3.00	782.30	321.80	290.20	153.00	1.20	6.11
N	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	11	16	9
	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>OX</sub>	Fe <sub>OX</sub>	Al <sub>M</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>OX</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bny1</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
	----- % -----																		
	----- mg Element/kg soil -----																		
	Slightly Weathered Soils - Validation Dataset																		
	----- cmol/kg -----																		
Mean	22.49	3.45	0.00	5.98	1284.31	2723.53	630.71	2883.96	174.57	349.03	119.07	14.62	3.55	323.46	72.48	63.20	36.18	0.70	11.76
Standard Error	1.93	0.74	0.00	0.13	116.93	284.23	38.96	731.81	17.47	41.19	14.37	1.73	0.44	29.67	8.23	8.97	6.35	0.26	6.86
95% Confidence Level for Mean	3.88	1.49	0.00	0.25	234.87	570.90	78.30	1470.62	35.11	82.77	28.88	3.47	0.88	59.60	16.54	18.01	13.05	0.51	14.03
Median	21.60	1.95	0.00	5.90	1100.00	2300.00	624.75	1753.15	133.80	274.80	90.75	10.20	2.70	279.70	60.90	43.90	26.00	0.22	0.74
Minimum	2.60	0.46	0.00	3.70	400.00	100.00	8.00	224.70	11.40	16.10	1.90	1.10	0.10	63.10	4.50	0.60	2.00	0.00	0.00
Maximum	85.60	35.61	0.00	8.00	4700.00	6900.00	1365.30	35917.20	563.10	1184.70	529.20	55.40	12.10	1069.90	287.80	339.90	136.40	10.57	152.89
N	51	51	51	51	51	51	50	50	50	50	50	51	51	51	50	51	27	51	30

Table B.3. Descriptive statistics of the soil properties for samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>OX</sub>	Fe <sub>OX</sub>	Al <sub>M</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	mg Element/kg soil		cmol/kg		mg P/kg soil					P <sub>CaCl2</sub>
												P <sub>OX</sub>	P <sub>M</sub>	P <sub>M5</sub>	P <sub>Bay1</sub>	P <sub>WS</sub>					
Argustolls																					
Mean	20.34	1.43	0.08	6.47	858.33	825.00	562.46	2041.51	87.11	309.36	113.98	12.65	2.77	185.33	46.45	30.40	30.67	0.38	0.33		
Standard Error	1.42	0.16	0.08	0.23	120.26	140.95	32.34	366.21	12.05	22.22	7.98	2.21	0.27	40.27	8.99	8.58	21.79	0.12	0.20		
95% Confidence Level for Mean	3.13	0.36	0.18	0.50	264.70	310.23	71.19	806.02	26.51	48.91	17.56	4.86	0.60	88.63	19.78	18.89	93.75	0.26	0.62		
Median	21.75	1.15	0.00	6.30	700.00	800.00	549.65	1878.25	87.80	302.40	112.55	11.40	2.55	138.95	34.25	16.45	13.00	0.24	0.28		
Minimum	14.00	0.81	0.00	5.10	500.00	300.00	379.80	831.20	27.10	219.90	59.40	4.70	1.80	76.60	16.50	6.80	5.00	0.07	0.00		
Maximum	28.60	2.32	1.00	7.90	1700.00	2000.00	748.60	5704.60	160.90	456.40	169.10	34.40	4.60	589.00	111.40	104.60	74.00	1.38	0.76		
N	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	3	12	4		
Hapludalfs																					
Mean	16.02	2.09	0.03	5.75	1213.79	3465.52	588.13	1058.33	181.58	180.93	153.30	7.32	1.84	491.18	127.49	117.77	89.53	0.44	3.18		
Standard Error	1.55	0.37	0.03	0.13	115.19	473.91	39.60	108.00	20.04	34.45	12.71	0.75	0.31	92.40	30.20	29.59	26.28	0.09	1.40		
95% Confidence Level for Mean	3.17	0.77	0.07	0.26	235.96	970.75	81.12	221.22	41.04	70.56	26.04	1.54	0.63	189.28	61.86	60.60	56.36	0.19	3.00		
Median	15.90	1.54	0.00	5.60	1000.00	3300.00	589.30	950.90	156.30	122.70	145.70	6.50	1.40	357.20	66.90	60.40	43.00	0.30	0.57		
Minimum	1.40	0.42	0.00	4.60	300.00	0.00	197.70	98.60	70.80	19.80	33.60	1.00	0.40	48.10	22.50	7.80	13.00	0.00	0.00		
Maximum	37.50	11.09	1.00	7.10	3300.00	12200.00	1063.00	2348.30	615.60	899.80	293.80	16.60	7.80	2699.10	782.20	742.00	392.90	1.80	17.68		
N	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	15	29	15		
Hapludults																					
Mean	13.49	8.45	0.00	5.21	1478.57	1421.43	772.45	931.47	125.78	170.52	168.51	4.26	0.95	363.12	197.85	144.67	118.96	4.18	109.72		
Standard Error	1.88	4.40	0.00	0.27	231.38	318.16	90.77	246.67	19.57	64.93	51.65	1.08	0.23	80.53	56.59	54.20	54.96	2.55	68.66		
95% Confidence Level for Mean	4.10	9.49	0.00	0.59	499.86	687.35	197.78	537.44	42.64	141.47	112.55	2.33	0.50	173.98	123.30	118.09	129.97	5.55	168.00		
Median	12.80	1.58	0.00	5.20	1550.00	1500.00	836.30	706.60	96.40	97.00	132.00	3.15	0.90	357.05	126.90	41.80	52.05	0.23	2.69		
Minimum	1.50	0.33	0.00	4.00	200.00	0.00	30.60	14.00	63.50	0.70	9.80	0.20	0.00	30.80	1.30	2.20	9.20	0.00	0.00		
Maximum	23.30	48.16	0.00	7.00	3600.00	4300.00	1317.50	3158.30	301.50	882.20	698.10	12.30	2.80	987.00	563.10	592.10	466.70	25.64	385.53		
N	13	14	14	14	14	14	13	13	13	13	13	14	14	14	13	13	8	13	7		



## APPENDIX C

### DESORPTION REGRESSION EQUATION COMPONENTS TABLE AND LOG- TRANSFORMED DESORPTION PLOTS FOR CHAPTER 2 DATA

Table C.1. Linear regression equation<sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for samples that represent the minimum, first quartile, median, mean, third quartile, and maximum for soils in the All Soils modeling and validation datasets, during the 1-60 minute and 1-24 hour extraction periods.

User Pedon ID	Soil Series	Grouping	Intercept (I)	Slope (S1) (1-60 min)	Slope (S2) (1-24 hr)
			----- mg P/kg soil -----		
99GA277001	Tifton	S	18.90	10.62	19.23
S00TX-067-001	Erno*	S	36.45	20.48	16.15
91NJ033002	Mattapex	H	70.53	39.62	80.49
82MI097005	Emmet	S	71.93	40.41	46.02
96MN085003	Nicollet	S	73.49	41.28	32.53
S01PA-029-007	Chrome	H	81.01	45.51	87.24
S04PA027-007	Murrill	H	103.99	58.42	56.19
S05WV-037-002	Hagerstown	S	111.14	62.44	88.21
S07IN135002	Pewamo*	S	111.76	62.78	80.91
97KS031001	Osage*	S	125.28	70.38	138.08
S08IA195001	Lawler	S	134.95	75.81	74.74
S02NY-031-002	Vergennes	S	137.45	77.22	167.58
S03MI-131-011	Matchwood*	S	257.60	144.72	250.26
92TX085001	Houston Black*	C	380.56	213.80	82.95
S06NV027-001	Humboldt	C	437.41	245.73	229.98

<sup>a</sup>  $P = I + S1 \times (\log h)$  for 1-60 min;  $P = I + S2 \times (\log h)$  for 1-24 hr extraction period; where P = P released (mg P/kg soil), I = intercept, S1 = slope of the 1-60 min extraction period, S2 = slope of the 1-24 hr extraction period, and h = extraction period.

\* Indicates sample in the validation dataset.

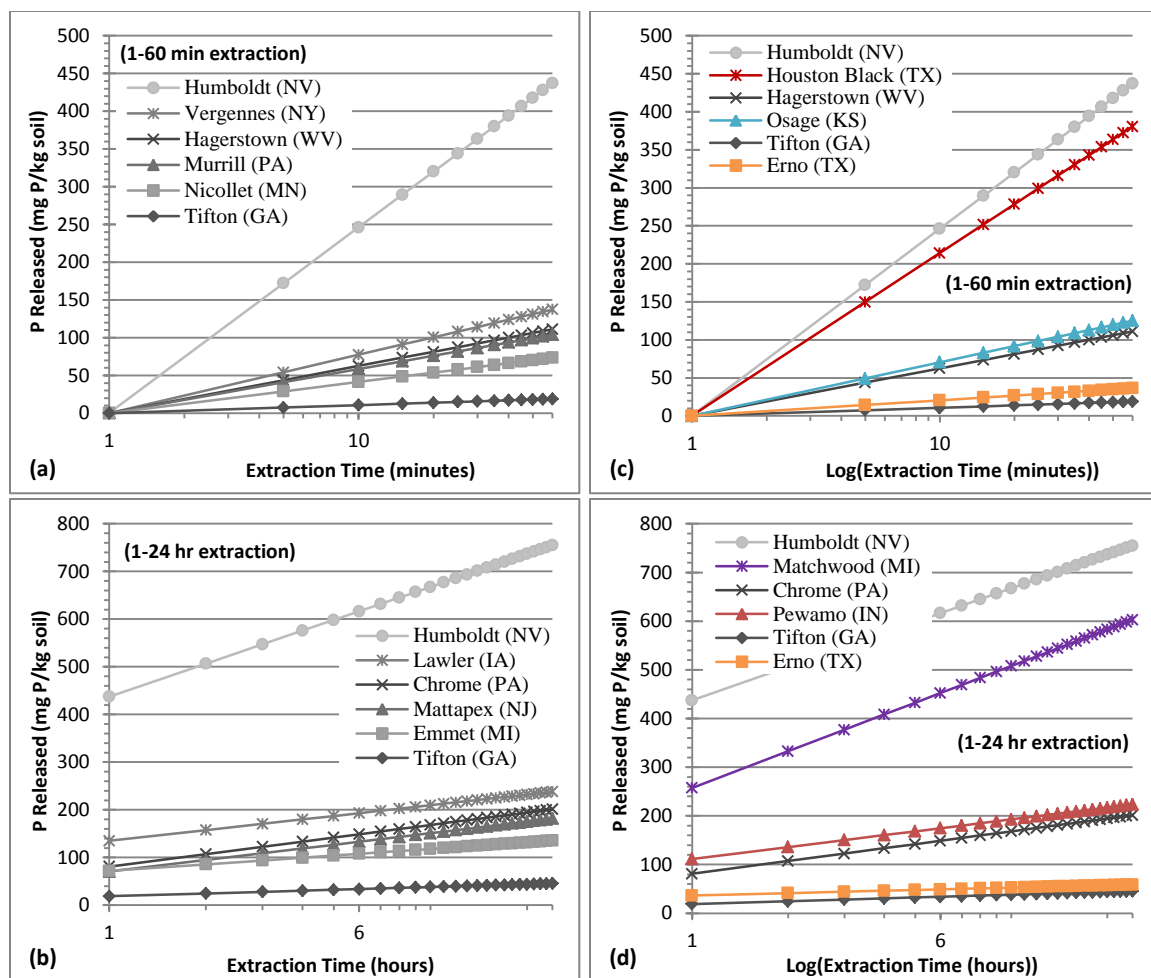


Figure C.1. Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, first quartile, median, mean, third quartile, and maximum for all agricultural modeling soils during the (a) 1-60 minute and (b) 1-24 hour extraction periods, and soils that represent the minimum, mean, and maximum for all agricultural modeling soils and validation soils (colored curves) during the (c) 1-60 minute and (d) 1-24 hour extraction periods.



**APPENDIX D****REGRESSION MODELING STEPS TABLE FOR CHAPTER 2 DATA**

Table D.1. An example of the progressive regression modeling method used on samples from the All Soils modeling datasets, for AER23 and AER24.

AER23						AER24					
Model	Variable(s)	R <sup>2</sup>	p	MSE	N	Model	Variable(s)	R <sup>2</sup>	p	MSE	N
1	Clay	0.0980	0.0001	59.45	234	1	Clay	0.2877	0.0001	88.58	234
2	TC	0.0105	0.1173	62.16	235	2	TC	0.0853	0.0001	100.17	235
3	pH	0.0671	0.0001	60.35	235	3	pH	0.0047	0.2979	104.49	235
4	Clay TC	0.1154	0.0001	59.00	234	4	Clay TC	0.3926	0.0001	81.97	234
5	Clay pH	0.2335	0.0001	54.92	234	5	Clay pH	0.3398	0.0001	85.47	234
6	TC pH	0.0683	0.0003	60.45	235	6	TC pH	0.0854	0.0001	100.38	235
7	Clay TC pH	0.2350	0.0001	54.98	234	7	Clay TC pH	0.4152	0.0001	80.61	234
8	<b>Clay AIOX</b>	0.4972	0.0001	44.48	234	8	<b>Clay AIOX</b>	0.4967	0.0001	74.62	234
9	Clay FeOX	0.3147	0.0001	51.93	234	9	Clay FeOX	0.3708	0.0001	83.44	234
10	<b>Clay AIOX FeOX</b>	0.5149	0.0001	43.78	234	10	<b>Clay AIOX FeOX</b>	0.4981	0.0001	74.68	234
11	Clay AIM	0.3687	0.0001	49.17	230	11	Clay AIM	0.3939	0.0001	80.92	230
12	Clay CaM	0.1018	0.0001	58.65	230	12	Clay CaM	0.3287	0.0001	85.16	230
13	Clay FeM	0.2755	0.0001	52.68	230	13	Clay FeM	0.3713	0.0001	82.42	230
14	Clay MgM	0.1238	0.0001	57.93	230	14	Clay MgM	0.3054	0.0001	86.63	230
15	Clay MnM	0.1261	0.0001	57.85	230	15	Clay MnM	0.3471	0.0001	83.99	230
16	Clay AIM CaM	0.4266	0.0001	46.97	230	16	<b>Clay AIM CaM</b>	0.4901	0.0001	74.39	230
17	Clay AIM FeM	0.4345	0.0001	46.64	230	17	Clay AIM FeM	0.4214	0.0001	79.24	230
18	Clay AIM MgM	0.3696	0.0001	49.25	230	18	Clay AIM MgM	0.3974	0.0001	80.87	230
19	Clay AIM MnM	0.3831	0.0001	48.71	230	19	Clay AIM MnM	0.4278	0.0001	78.80	230
20	Clay FeM CaM	0.2818	0.0001	52.56	230	20	Clay FeM CaM	0.4144	0.0001	79.72	230
21	Clay FeM MgM	0.3067	0.0001	51.64	230	21	Clay FeM MgM	0.3722	0.0001	82.54	230
22	Clay FeM MnM	0.2976	0.0001	51.98	230	22	Clay FeM MnM	0.4113	0.0001	79.93	230
23	Clay CaM MgM	0.1252	0.0001	58.01	230	23	Clay CaM MgM	0.3318	0.0001	85.16	230
24	Clay CaM MnM	0.1261	0.0001	57.98	230	24	Clay CaM MnM	0.3709	0.0001	82.63	230
25	Clay MgM MnM	0.1471	0.0001	57.28	230	25	Clay MgM MnM	0.3471	0.0001	84.17	230
26	Clay CaNH <sub>4</sub>	0.1258	0.0001	58.65	234	26	Clay CaNH <sub>4</sub>	0.2903	0.0001	88.61	234
27	Clay MgNH <sub>4</sub>	0.1176	0.0001	58.92	234	27	Clay MgNH <sub>4</sub>	0.2892	0.0001	88.68	234
28	Clay CaNH <sub>4</sub> MgNH <sub>4</sub>	0.1374	0.0001	58.38	234	28	Clay CaNH <sub>4</sub> MgNH <sub>4</sub>	0.2929	0.0001	88.64	234
29	pH AIOX	0.4931	0.0001	44.58	235	29	TC AIOX	0.4222	0.0001	79.79	235
30	pH FeOX	0.3033	0.0001	52.27	235	30	TC FeOX	0.2459	0.0001	91.15	235
31	<b>pH AIOX FeOX</b>	0.5117	0.0001	43.85	235	31	TC AIOX FeOX	0.4270	0.0001	79.62	235
32	pH AIM	0.2953	0.0001	51.86	231	32	TC AIM	0.2064	0.0001	92.40	231
33	pH CaM	0.1640	0.0001	56.49	231	33	TC CaM	0.1823	0.0001	93.79	231
34	pH FeM	0.1837	0.0001	55.82	231	34	TC FeM	0.1305	0.0001	96.72	231
35	pH MgM	0.0922	0.0001	58.86	231	35	TC MgM	0.1472	0.0001	95.78	231
36	pH MnM	0.0982	0.0001	58.67	231	36	TC MnM	0.1055	0.0001	98.10	231
37	pH AIM CaM	0.4155	0.0001	47.34	231	37	TC AIM CaM	0.4222	0.0001	79.01	231
38	pH AIM FeM	0.3629	0.0001	49.42	231	38	TC AIM FeM	0.2152	0.0001	92.09	231
39	pH AIM MgM	0.3105	0.0001	51.41	231	39	TC AIM MgM	0.2944	0.0001	87.32	231
40	pH AIM MnM	0.3166	0.0001	51.19	231	40	TC AIM MnM	0.2177	0.0001	91.94	231
41	pH FeM CaM	0.2664	0.0001	53.03	231	41	TC FeM CaM	0.2599	0.0001	89.42	231
42	pH FeM MgM	0.1886	0.0001	55.77	231	42	TC FeM MgM	0.1876	0.0001	93.70	231
43	pH FeM MnM	0.2104	0.0001	55.02	231	43	TC FeM MnM	0.1527	0.0001	95.69	231
44	pH CaM MgM	0.1651	0.0001	56.58	231	44	TC CaM MgM	0.1998	0.0001	92.99	231
45	pH CaM MnM	0.1783	0.0001	56.13	231	45	TC CaM MnM	0.2038	0.0001	92.76	231

AER23						AER24					
Model	Variable(s)	R <sup>2</sup>	p	MSE	N	Model	Variable(s)	R <sup>2</sup>	p	MSE	N
46	pH MgM MnM	0.1127	0.0001	58.32	231	46	TC MgM MnM	0.1690	0.0001	94.76	231
47	pH CaNH <sub>4</sub>	0.1177	0.0001	58.82	235	47	TC CaNH <sub>4</sub>	0.1701	0.0001	95.62	235
48	pH MgNH <sub>4</sub>	0.0839	0.0001	59.94	235	48	TC MgNH <sub>4</sub>	0.1361	0.0001	97.56	235
49	pH CaNH <sub>4</sub> MgNH <sub>4</sub>	0.1210	0.0001	58.84	235	49	TC CaNH <sub>4</sub> MgNH <sub>4</sub>	0.1828	0.0001	95.09	235

\* $p \leq 0.0001$  highlighted in green;  $0.0001 > p \leq 0.01$  highlighted in yellow; three models with lowest  $p$  and highest R<sup>2</sup> in bold

## APPENDIX E

### ADDITIONAL VALIDATION RESULTS TABLES FOR CHAPTER 2 DATA

Table E.1. The number of validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for the AER1, AER23, PSI, and  $S_{MAX}$  prediction models listed in Tables 2.7 and 2.8 for each grouping scheme, when applied to their corresponding validation datasets. The results of the most significant All Soils prediction model applied to each grouping are also listed for comparison.

Calcareous Soils					Highly Weathered Soils					Slightly Weathered Soils				
AER1	10%	15%	20%	N	AER1	10%	15%	20%	N	AER1	10%	15%	20%	N
Clay TC pH	2	4	4	11	Clay CaM MnM	5	6	7	16	Clay AIM CaM	9	16	23	51
Clay TC	4	4	4	11	TC CaM MnM	1	1	2	16	Clay AIOX FeOX	13	20	22	51
Clay AIM CaM	1	3	7	11	Clay FeM MnM	5	5	5	16	Clay AIOX	14	20	24	51
Clay TC pH CONUS	3	5	6	11	Clay TC pH CONUS	0	0	0	16	Clay TC pH CONUS	15	19	22	51
AER23	10%	15%	20%	N	AER23	10%	15%	20%	N	AER23	10%	15%	20%	N
TC AIM CaM	0	0	0	11	Clay AIOX FeOX	6	7	7	16	TC AIOX FeOX	15	18	24	51
Clay TC pH	1	3	4	11	TC AIOX FeOX	4	6	8	16	Clay AIOX FeOX	17	22	26	51
Clay FeM CaM	0	0	1	11	Clay AIOX	4	5	7	16	TC AIOX	14	19	21	51
Clay AIOX FeOX CONUS	3	3	3	11	Clay AIOX FeOX CONUS	0	0	0	16	Clay AIOX FeOX CONUS	12	21	24	51
PSI	10%	15%	20%	N	PSI	10%	15%	20%	N	PSI	10%	15%	20%	N
Clay CaM MgM	1	1	3	11	Clay AIM CaM	4	5	6	16	TC AIOX FeOX	12	16	19	51
Clay AIM CaM	2	3	4	11	Clay AIM MgM	1	4	4	16	TC AIM MnM	6	11	12	51
Clay CaM MnM	2	6	6	11	Clay CaM MnM	2	2	3	16	TC AIOX	12	17	22	51
Clay AIOX FeOX CONUS	0	0	1	11	Clay AIOX FeOX CONUS	2	2	2	16	Clay AIOX FeOX CONUS	4	10	15	51
Smax	10%	15%	20%	N	Smax	10%	15%	20%	N	Smax	10%	15%	20%	N
Clay pH	0	0	0	7	TC AIOX	1	1	1	9	TC AIM MnM	2	4	5	30
Clay	0	1	1	7	TC AIOX FeOX	1	1	2	9	TC MgM MnM	2	3	3	30
Clay MgM	1	1	1	7	Clay AIOX	1	1	1	9	TC AIM MgM	2	2	3	30
pH AIOX FeOX CONUS	0	1	1	7	pH AIOX FeOX CONUS	1	2	2	9	Clay AIOX FeOX CONUS	2	4	6	30
Argacolls					Hapludalfs					Hapludults				
AER1	10%	15%	20%	N	AER1	10%	15%	20%	N	AER1	10%	15%	20%	N
Clay FeM CaM	3	3	3	4	Clay CaNH4 MgNH4	2	3	5	10	pH CaM	0	1	1	5
Clay CaM MnM	1	2	2	4	Clay CaNH4	2	3	5	10	TC CaM	1	1	1	5
Clay CaNH4	2	2	2	4	Clay TC pH	2	4	4	10	TC MnM	0	0	0	5
Clay TC pH CONUS	0	1	2	4	Clay TC pH CONUS	2	2	4	10	Clay TC pH CONUS	1	2	3	5
AER23	10%	15%	20%	N	AER23	10%	15%	20%	N	AER23	10%	15%	20%	N
TC AIM MnM	0	0	2	4	TC AIOX FeOX	1	2	2	10	TC AIOX	0	1	2	5
Clay AIM MnM	0	0	2	4	TC AIOX	1	1	2	10	Clay AIOX	0	1	2	5
Clay AIM CaM	1	1	1	4	Clay MgNH4	3	4	4	10	TC AIOX FeOX	0	2	2	5
Clay AIOX FeOX CONUS	2	3	3	4	Clay AIOX FeOX CONUS	2	3	3	10	Clay AIOX FeOX CONUS	0	2	2	5
PSI	10%	15%	20%	N	PSI	10%	15%	20%	N	PSI	10%	15%	20%	N
Clay TC	1	1	1	4	Clay AIM MgM	0	0	0	10	Clay AIM FeM	0	1	1	5
					Clay AIOX FeOX	3	3	3	10	Clay CaNH4	1	1	3	5
					Clay FeOX	3	3	3	10	TC AIM FeM	1	1	1	5
					Clay AIOX FeOX CONUS	0	0	2	10	Clay AIOX FeOX CONUS	0	0	0	5
Smax	10%	15%	20%	N	Smax	10%	15%	20%	N	Smax	10%	15%	20%	N
Clay	0	1	1	1	Clay AIM MnM	0	0	0	5	TC CaM MnM	0	0	0	3
					Clay CaNH4 MgNH4	0	1	1	5	TC AIM FeM	0	0	0	3
					TC AIM MgM	1	1	1	5					
pH AIOX FeOX CONUS	0	0	0	1	pH AIOX FeOX CONUS	1	1	1	5	pH AIOX FeOX CONUS	1	1	1	3

## APPENDIX F

### QUARTILES/POTENTIAL RISK TABLES FOR GREAT GROUPS FOR

#### CHAPTER 2 DATA

Table F.1. P Index Risk Potential classifications by AER24 quartile statistics from samples in the Argiustolls, Hapludalfs, and Hapludults modeling datasets.

Argiustolls			Hapludalfs		
P Index (Potential)	Quartile	AER24 (mg P/kg soil)	P Index (Potential)	Quartile	AER24 (mg P/kg soil)
Low	< 25%	$\leq 100.78$	Low	< 25%	$\leq 138.94$
Moderate	25 - 50%	100.79 - 142.55	Moderate	25 - 50%	138.95 - 175.67
High	50 - 75%	142.56 - 170.97	High	50 - 75%	175.68 - 232.30
Very High	> 75%	> 170.98	Very High	> 75%	> 232.31

Hapludults		
P Index (Potential)	Quartile	AER24 (mg P/kg soil)
Low	< 25%	$\leq 174.69$
Moderate	25 - 50%	174.70 - 233.45
High	50 - 75%	233.46 - 278.18
Very High	> 75%	> 278.19

### CHAPTER 3

#### PHOSPHORUS DESORPTION CHARACTERISTICS AND RELATIONSHIPS OF AGRICULTURAL SOILS IN THE CHESAPEAKE BAY WATERSHED

##### ABSTRACT

Phosphorus (P) loss from agricultural soils and subsequent water quality issues remain a significant problem in the Chesapeake Bay watershed, though concerns about the effectiveness of current approaches to attaining water quality and environmental goals continue. The P Index assessment tool relies on soil test P values as an Index source component, but these do not accurately predict soil P release behaviors. A collection of 46 agricultural surface soils from across the Chesapeake Bay watershed were analyzed for P sorption and desorption, using double-point anion exchange resin (DP-AER), P sorption index (PSI), and adsorption isotherm methods. Objectives of this study were to determine relationships between P desorption behaviors and other soil properties, to develop predictive models to provide better estimates of pollution risk at the watershed, farm, and field levels, to compare the effectiveness of watershed-specific models to general national-level models, and potentially improve existing models that predict nutrient losses to target management practices. Linear regression models were developed and validated for each P sorption variable. Results indicate that the soil P sorption behaviors in this region are predominately related to the amorphous and crystalline Al oxides in the soil, in addition to the clay and total carbon contents. Watershed-specific prediction models for total P release did not perform as well as the overall CONUS-level

models developed in Chapter 2. Comparisons of the CONUS-level and watershed-specific potential risk models also resulted in differences in areas classified as “High” or “Very High” risk to contributing to P loading if the surface soil were eroded into runoff.

## ABBREVIATIONS

**AER1** - phosphorus released from soil during the 1 hour extraction period (mg P/kg soil); **AER23** - phosphorus released from soil during the 23 hour extraction period (mg P/kg soil); **AER24** - total phosphorus released from soil in 24 hours (mg P/kg soil); **Al<sub>M</sub>** - Mehlich No. 3 extractable aluminum (mg Al/kg); **Al<sub>ox</sub>** - acid oxalate extractable aluminum content (%); **CaCO<sub>3</sub>** - calcium carbonate equivalent (%); **Ca<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Ca<sub>M</sub>** - Mehlich No. 3 extractable calcium (mg Ca/kg); **CONUS** - conterminous United States; **DP-AER** - double-point anion exchange resin; **Fe<sub>M</sub>** - Mehlich No. 3 extractable iron (mg Fe/kg); **Fe<sub>ox</sub>** - acid oxalate extractable iron content (%); **ICP-AES** - inductively coupled plasma atomic emission spectrometry; **KSSL** - Kellogg Soil Survey Laboratory; **Mg<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Mg<sub>M</sub>** - Mehlich No. 3 extractable magnesium (mg Mg/kg); **Mn<sub>M</sub>** - Mehlich No. 3 extractable manganese (mg Mn/kg); **NLCD** - National Land Cover Dataset; **NRCS** - Natural Resources Conservation Service; **NSSC** - National Soil Survey Center; **P<sub>Bray1</sub>** - Bray-1 extractable phosphorus (mg P/kg soil); **P<sub>CaCl2</sub>** - 0.01 M calcium chloride extractable phosphorus (mg P/kg soil); **P<sub>M</sub>** - Mehlich No. 3 extractable phosphorus (mg P/kg soil), measured using ICP-AES; **P<sub>M3</sub>** - Mehlich No. 3 extractable phosphorus (mg P/kg soil), measured using a spectrophotometer at 882 nm; **P<sub>ox</sub>** - acid oxalate extractable phosphorus content (mg P/kg soil); **PSI** - phosphorus sorption index (L/kg); **P<sub>ws</sub>** - water

soluble phosphorus content (mg P/kg soil); **SERA-IEG 17** - Southern Extension and Research Activity - Information Exchange Group 17;  $S_{MAX}$  - phosphorus sorption maximum (mg/kg); **TC** - total carbon content (%); **USDA** - United States Department of Agriculture.

## INTRODUCTION

The Chesapeake Bay watershed is one of the largest and most diverse ecosystems in the Eastern U.S., covering about 64,000 mi<sup>2</sup> over six states (Chesapeake Bay Program, 2012). According to the Chesapeake Bay Program (CBP) (2012), the area contains over 11,500 mi of shoreline, 150 major rivers and streams, and over 17 million people. Almost one-quarter of the watershed is devoted to animal-based agriculture that has produced and applied vast amounts of animal manure, and thus phosphorus (P), to the landscape, which has had detrimental effects on the health of the Chesapeake Bay. For several decades the Chesapeake Bay has been the focus of water-quality and ecological restoration (Phillips, 2007; U.S. Environmental Protection Agency, 2008), due to serious and continual incidents of eutrophication. Agriculture has been found to be the single largest sources of nutrient and sediment pollution entering the Bay (CBP, 2012), largely as agricultural runoff. Since 1993 laws have been enacted in several states requiring the development and implementation of P nutrient management plans by certain farmers. The requirement of implementing P nutrient management plans are typically dictated by an area's classification under the state-specific P Index, whose soil test P components and resulting recommendations varying from state-to-state. In 2005 an animal-manure



management strategy was adopted throughout the Chesapeake Bay watershed, in hopes of further reducing P and nutrient loading in the Bay.

The Chesapeake Bay watershed has been a hub for soil P sorption and transport studies, particularly with a goal of identifying the soil physiochemical properties that influence P sorption in the region (Penn et al., 2005; McDowell and Sharpley, 2002; Sims et al., 2002; Vadas and Sims, 2002; Maguire et al., 2001; Maguire et al., 2000; Paulter and Sims, 2000; Mozaffari and Sims, 1996; Mozaffari and Sims, 1994). Discharges of P have been shown to be influenced more by transport of suspended soil particles than by the land use (Jordan et al., 1997). Transport of soil P is largely dependent on soil type, slope, and rainfall intensity as P tends to be particle-bound (Boesch et al., 2001).

Mozaffari and Sims (1994) investigated 12 soil series over 48 sites in Delaware using a standard P adsorption isotherm method proposed by Nair et al. (1984). They observed that P sorption was highly correlated to the clay content of the soil, that the PSI method proposed by Bache and Williams (1971) was a viable option for determining a ranking of soils by P sorption capacity, and that application of manures and fertilizers greatly increased soil P test levels in excess of crop requirements. Maguire et al. (2000) studied eight sites across Delaware, Virginia, and Maryland with soils amended by biosolids and found that desorbable P was greater in the amended soils, P retention was correlated with Al and Fe oxides, and oxalate extractable P ( $P_{ox}$ ) was a good predictor of desorbable P release. Paulter and Sims (2000) also observed that P sorption was significantly correlated to soil Al and Fe oxides in 41 Delaware soils. Penn et al. (2005) found that P sorption was better explained, or correlated, with mineralogy, which accounts for both clay and Al and Fe oxides, from 36 Virginia soils. Even with decades of attention to soil

P behaviors and Bay restoration, agricultural nutrient loading of Chesapeake Bay waters continues to be a major environmental concern.

Multiple-linear regression prediction models were developed for agricultural surface soils across the conterminous United States (CONUS) in Chapter 2 to better identify agricultural areas that have a high potential for contributing to P export and loading. The objectives of this study were to develop predictive relationships between P desorption behaviors and other soil properties using simple and multiple linear regression models specifically for the soils of Chesapeake Bay watershed. The outcomes of these objectives would then be to (1) identify agricultural soils that contain high amounts of P, relative to their sorptive potential, (2) classify the soils as to their potential to contribute P to surface waters, (3) evaluate how soils retain (adsorb) and release P (desorb), and (4) determine the reliability of a set of watershed-specific models compared to CONUS-level predictive models.

## **MATERIALS AND METHODS**

### **Laboratory Sample Selection**

Forty-six archived agricultural surface soil samples collected from the Chesapeake Bay watershed area by the Natural Resource Conservation Service (NRCS) were analyzed for this study. Samples were selected based on the availability of following data; (1) spatial location of the pedon and date of collection, more recently collected samples were given a higher preference, (2) pedon location is designated as agricultural land on the 2011 National Land Cover Data (NLCD) geospatial layers, and (3) availability of data in the NSSC-KSSL database on the general properties known to

effect P retention (e.g. clay, pH, calcium carbonate, iron and aluminum oxalate, total carbon). Samples were also chosen in an attempt to ensure adequate representation of agricultural soil series of the Chesapeake Bay watershed area and spatial randomness. A subset of 10 samples was randomly selected to be used to validate the prediction equations developed to model P desorption and adsorption. Sample locations for both modeling and validation samples from the study area are shown in Figure 3.1 and pedon taxonomic information for each sample is listed in Table 3.1. Table 3.1 reveals that the majority of samples investigated were a mixture of highly weathered and slightly weathered soils, with a few calcareous soils, as defined by Sharpley et al. (1984). Most of the soils originated from Maryland (N = 16) and Pennsylvania (N = 15), with the remainder from West Virginia (N = 7), New York (N = 6), and Virginia (N = 2). The study samples also represent five of the twelve orders of soil taxonomy; Ultisols (N = 22), Alfisols (N = 15), Inceptisols (N = 7), Mollisols (N = 1), and Aridisols (N = 1).

### **Study Area Physiography**

The Chesapeake Bay watershed encompasses portions of six NRCS Land Resource Regions, which are comprised of 15 smaller Major Land Resource Areas (MLRA), geographically associated land resource units (Figure 3.2). The Atlantic Coast Flatwoods, Tidewater Area, Northern Tidewater Area, and Mid-Atlantic Coastal Plain MLRAs comprise the portion of the Atlantic and Gulf Coast Lowland Forest and Crop Region in the watershed. The Southern Coastal Plain and Southern Piedmont MLRAs comprise the portion of the South Atlantic and Gulf Slope Cash Crops, Forest, and Livestock Region in the watershed. The Northern Coastal Plain, Northern Piedmont, and

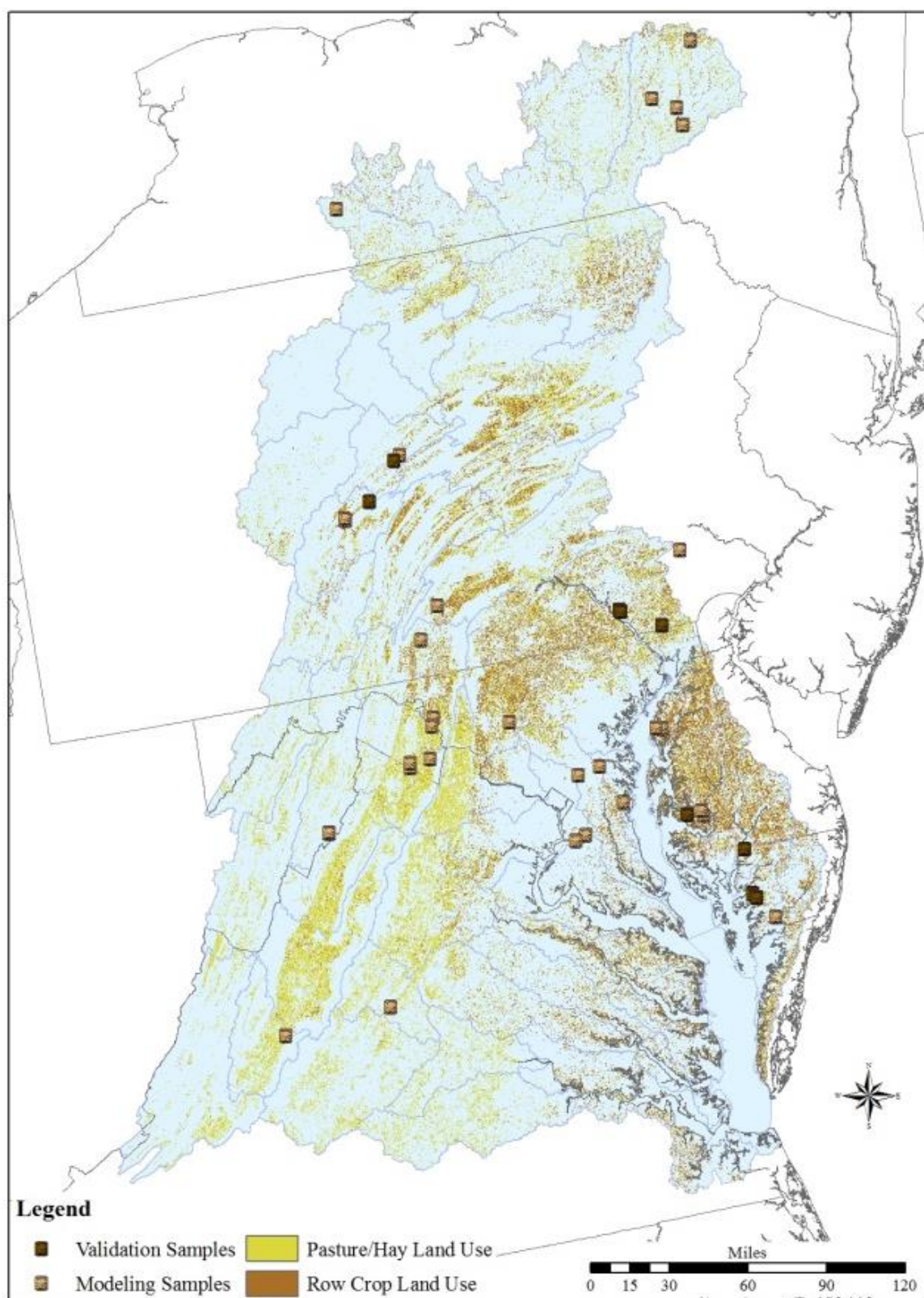


Figure 3.1. Locations of all modeling and validation samples investigated from the Chesapeake Bay watershed study area.

Table 3.1. Classification information for the 46 Chesapeake Bay watershed agricultural surface soils investigated.

State	Pedon	Soil Series	User	Pedon ID	Great Group	Calcareous/ Weathering Group	State	Pedon	Soil Series	User	Pedon ID	Great Group	Calcareous/ Weathering Group
MD	Queponco		00MD039005		Hapludult	Highly Weathered	PA	Murrill*		99PA027095		Hapludult <sup>a</sup>	Highly Weathered
MD	Lenni		00MD041022		Endoaquilt	Highly Weathered	PA	Chrome		S01PA-029-007		Hapludalf	Highly Weathered
MD	Butlertown		94MD003013		Fragiudult <sup>a</sup>	Highly Weathered	PA	Elioak*		S03PA-071-001		Hapludalf	Highly Weathered
MD	Beltsville		94MD033001		Fragiudult	Highly Weathered	PA	Chester*		S03PA-071-002		Hapludult	Highly Weathered
MD	Christiana		94MD033002		Hapludult <sup>a</sup>	Highly Weathered	PA	Glenelg		S03PA-071-003		Hapludult	Highly Weathered
MD	Deale		99MD003010		Endoaquilt	Highly Weathered	PA	Murrill		S04PA027-006		Hapludult	Highly Weathered
MD	Annesessex		S01MD-039-007		Hapludult	Highly Weathered	PA	Murrill*		S04PA027-007		Hapludult	Highly Weathered
MD	Quindocqua*		S02MD-039-008		Endoaquilt	Highly Weathered	PA	Hublersburg		S04PA061-009		Hapludult	Highly Weathered
MD	Manokin*		S02MD-039-010		Hapludult	Highly Weathered	PA	Allegheny		93PA055038		Haplocalcid	Slightly Weathered
MD	Crosiadore		S04MD-029-003		Hapludult	Highly Weathered	PA	Weikert		93PA055039		Dystrodept <sup>a</sup>	Slightly Weathered
MD	Tent		S04MD-029-005		Endoaquilt	Highly Weathered	PA	Weikert		93PA055040		Dystrodept <sup>a</sup>	Slightly Weathered
MD	Groom		S04MD-033-036		Hapludult	Highly Weathered	PA	Chrome*		S01PA-029-008		Hapludalf	Slightly Weathered
MD	Crosiadore*		00MD041021		Hapludult	Slightly Weathered	PA	Hagerstown		S04PA027-003		Hapludalf	Slightly Weathered
MD	Nassawango		00MD041023		Hapludalf	Slightly Weathered	PA	Hagerstown*		S04PA027-004		Hapludalf	Slightly Weathered
MD	Cedartown*		97MD045018		Hapludalf	Slightly Weathered	VA	Rabun		S04VA-003-001		Rhodudult	Highly Weathered
MD	Glenelg		98MD021133		Fragiudept	Slightly Weathered	VA	Frederick		S04VA-163-001		Paleudult	Highly Weathered
NY	Howard		S08NY003002		Hapludalf	Calcareous	WV	Huntington		S05WV-037-007		Hapludoll <sup>a</sup>	Calcareous
NY	Barbour		86NY025004		Dystrochrept	Slightly Weathered	WV	Braddock		S05WV-037-006		Paleudult	Highly Weathered
NY	-		86NY025006		Fragiaquept	Slightly Weathered	WV	Buchanan		S07WV031005		Fragiudult	Highly Weathered
NY	Chippewa		91NY077006		Fragiaquept	Slightly Weathered	WV	Chilhowie		S05WV-037-001		Paleudalf	Slightly Weathered
NY	Chenango Fan		91NY077008		Dystrochrept	Slightly Weathered	WV	Hagerstown		S05WV-037-002		Paleudalf	Slightly Weathered
NY	Honeoye		99NY043001		Hapludalf	Slightly Weathered	WV	Hagerstown		S05WV-037-008		Hapludalf	Slightly Weathered
PA	Hagerstown		S04PA061-008		Hapludalf	Calcareous	WV	Clarksburg		S07WV031001		Fragiudalf	Slightly Weathered

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

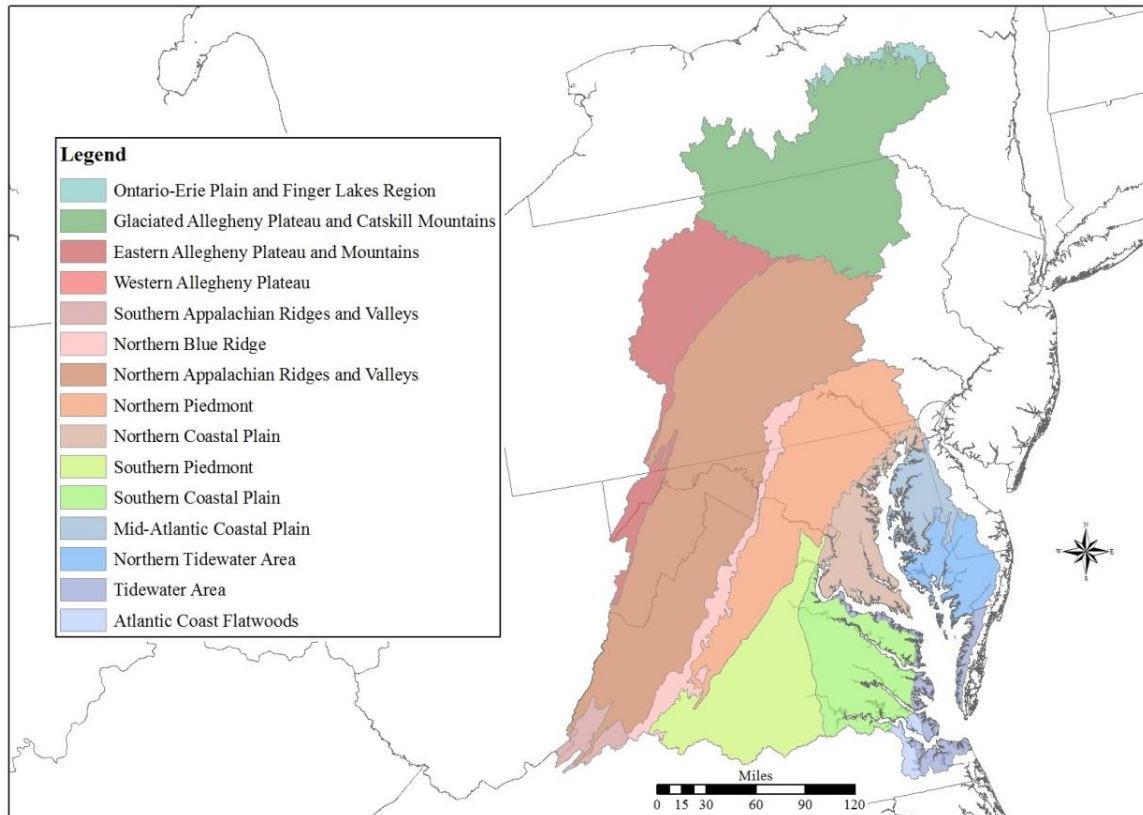


Figure 3.2. USDA NRCS Major Land Resource Areas of the Chesapeake Bay watershed study area.

Northern Appalachian Ridges and Valleys MLRAs comprise the portion of the Northern Atlantic Slope Diversified Farming Region in the watershed. The Eastern Allegheny Plateau and Mountains, Western Allegheny Plateau, Southern Appalachian Ridges and Valleys, and Northern Blue Ridge MLRAs comprise the portion of the East and Central Farming and Forest Region in the watershed. Lastly, the Glaciated Allegheny Plateau and Catskill Mountains MLRA comprises the portion of the Northeastern Forage and Forest Region, while the Ontario-Erie Plain and Finger Lakes Region MLRA comprises the portion of the Lake States Fruit, Truck Crop, and Dairy Region in the watershed. Due to the physiological variability of the area, this region is often generalized into three large

physiographic areas - the Atlantic Coastal Plain, Piedmont Plateau, and Appalachian Province (Figure 3.3).

The Atlantic Coastal Plain is primarily underlain by loosely compacted, unconsolidated ancient alluvial materials which are often mixed with marine sediments (Chesapeake Bay Program, 2012; United States Department of Agriculture, Natural Resources Conservation Service (USDA-NRCS), 2006). Some areas in this region are covered with loess, though usually  $< 1\text{m}$  (USDA-NRCS, 2006). Regional agriculture consists predominately of grain, fruits and vegetables, tobacco, and cranberry and blueberry cropland (USDA-NRCS, 2006). The agricultural soils are primarily Ultisols, with Entisols, Inceptisols, and Alfisols to a lesser extent (USDA-NRCS, 2006).

The Piedmont Plateau area is underlain by dense crystalline rocks in the east, and by sandstones, shales, and siltstones mantling limestone bedrock in the west (Chesapeake Bay Program, 2012). Cash-grain crops, forage crops, soybeans, and grains dominate the cropland agriculture in this area, and dairy and poultry production is locally important (USDA-NRCS, 2006). The agricultural soils are predominately Ultisols, Alfisols, and Inceptisols (USDA-NRCS, 2006).

The Appalachian Province comprises the northern and western half of the watershed, and is underlain by sedimentary bedrock of sandstone, siltstone, shale, and limestone (Chesapeake Bay Program, 2012). Areas in the northern part of this province are often overlain by a glacial drift mantle (USDA-NRCS, 2006). Cropland is primarily dedicated to corn, small grain, and forage grains, and fruits and vegetables to a lesser extent (USDA-NRCS, 2006). Poultry, dairy, and beef comprise major agricultural products in the region, while forest land uses become more predominant in the north

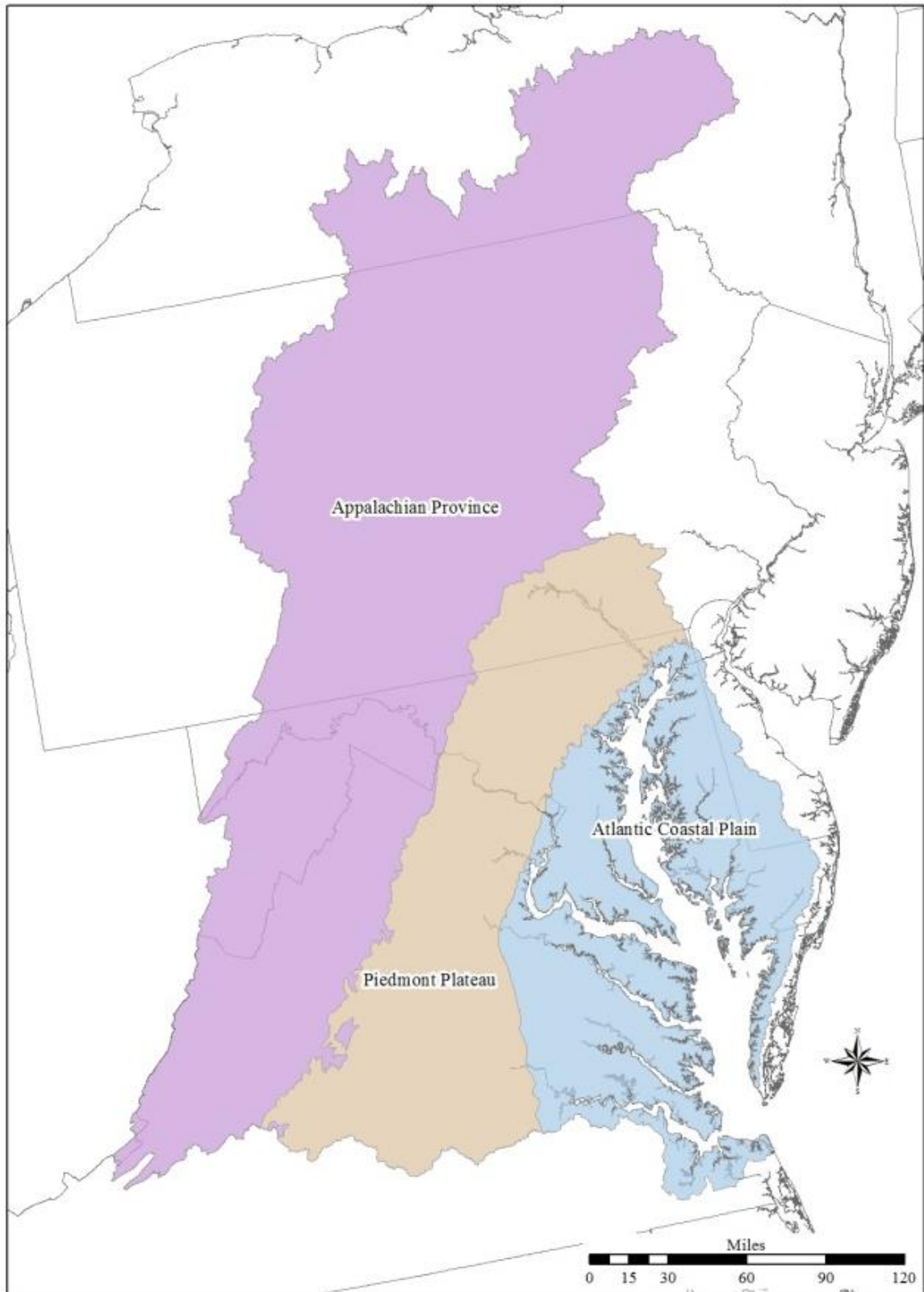


Figure 3.3. General physiographic areas of the Chesapeake Bay watershed study area.



(USDA-NRCS, 2006). The agricultural soils are primarily Inceptisols, Ultisols, and Alfisols (USDA-NRCS, 2006).

### **Standard Sample Characterization Analyses**

All samples in this study received laboratory characterization by analytical procedures described in the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004) with representative alphanumeric codes for standard operating procedures in parentheses. All standard analyses were performed on air-dried <2-mm soil, with resulting data reported on an oven-dry basis. Analyzed characterization properties included particle-size analysis, total carbon, acid oxalate extractable Al, Fe, and P, Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P), cation exchange capacity, pH, calcium carbonate equivalent, and water extractable P.

Particle-size analysis was determined by sieve and pipette (3A1a), following pre-treatments for removal of organic matter and soluble salts, and chemical dispersion with sodium hexametaphosphate. Total carbon (TC) content was determined by dry combustion (4H2a) on air-dried <180- $\mu$ m (80 mesh) soil. Acid oxalate (4G2a) extracts were analyzed for Fe<sub>ox</sub>, Al<sub>ox</sub>, and P<sub>ox</sub> by inductively coupled plasma atomic emission spectrometry (ICP-AES). Mehlich-3 (4D6b) extracts were analyzed for Al<sub>M</sub>, Ca<sub>M</sub>, Fe<sub>M</sub>, Mg<sub>M</sub>, Mn<sub>M</sub>, and P<sub>M</sub> by ICP-AES, and Mehlich-3 (4D6a) extractable phosphorus (P<sub>M3</sub>) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm. Soil pH (4C1a2a) was measured using a 1:1 soil-water solution. Calcium carbonate (CaCO<sub>3</sub>) equivalent (4E1a1a1a1) was determined by treating the soil with hydrochloric acid, manometrically measuring the evolved carbon dioxide, and then calculating the percent

CaCO<sub>3</sub>. Ammonium acetate extractable calcium (Ca<sub>NH4</sub>) and magnesium (Mg<sub>NH4</sub>) were measured with NH<sub>4</sub>OAc buffered at pH 7.0 (4B1a) and measured by ICP-AES. Water extractable phosphorus (4D2a) (P<sub>ws</sub>) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm.

### **Sample Phosphorus Sorption Analyses**

The primary objective in selecting methods was to choose methods that could simulate natural field conditions, meet the objectives of determining the maximum capacity of agricultural soils to hold phosphorus (P capacity), and determine how much P would desorb from eroded sediment. To determine P capacity, the standard “P sorption index” (PSI) method outlined by Sims in SERA-IEG 17 (2009) was utilized. The method used to determine phosphorous desorption was the standard double-point anion exchange resin (DP-AER) method, as outlined in Elrashidi et al (2003) and the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004). The standard method of P adsorption isotherm determination, as proposed originally proposed in Nair et al. (1984), and again by Graetz and Nair in SERA-IEG 17 (2009), was used to further understand the P retention and sorption capacity of the soils.

#### *P Sorption Index (PSI)*

This single-point isotherm method was developed to overcome the limitations of the more time-consuming and complicated standard P adsorption isotherm methods. PSI has been found by several researchers to be well correlated with soil P adsorption maxima and a wide variety of chemical and physiological properties (Bache and

Williams, 1971; Mozaffari and Sims, 1994; Sharpley et al., 1984; Simard et al., 1994). As outlined by Sims in SERA-IEG 17 (2009) following the Bache and Williams (1971) method, 2.25-g, <2-mm, air-dried soil sample was shaken at room temperature with 45 mL of a 75 mg P/L as  $\text{KH}_2\text{PO}_4$  solution and two drops of chloroform to inhibit microbial activity for 18 hours at 100 oscillations/min. The sample was then centrifuged at 2000 rpm for 30 minutes, after which the sample extract was filtered using a Whatman 45 filter. The P-saturated soil samples were allowed to air-dry and used to analyze soil P desorption with the double-point anion exchange resin procedure (following). P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962). PSI (L/kg) of the soil sample was then determined with the following equations:

$$\text{PSI (L/kg)} = X / \log C \quad [3.1]$$

where X is the amount of P adsorbed (mg P/kg) and C is the concentration of P after 18 hour equilibration (mg/L).

#### *Double-Point Anion Exchange Resin*

An anion exchange resin technique using a soil and water suspension and a dilute sodium chloride extracting solution, was found to be a sufficient method for estimating the quantity of P released and the rate of P-release from soil. This method is analogous to a more natural process for P removal from soil solution than attempting to estimate P release with the various chemical extracts utilized in other P methods (Amer et al., 1955). Following Elrashidi et al (2003) and Burt (2004), a 2-gram, <2-mm, air-dried soil sample, was shaken with a 4-gram perforated bag of spherical anion exchange resin beads and 100 mL of deionized water for 1 hour at 100 oscillations/min at room temperature. The

resin bag was removed from the soil suspension and shaken with 50 mL of 1.0 M sodium chloride (NaCl) for 1 hour to remove P retained by the resin. Another 4-gram resin bag was added to the soil suspension and shaken for an additional 23 hours at 100 oscillations/min at room temperature. The second resin bag was removed and rinsed with 1.0 M NaCl and shaken for 1 hour. The NaCl extracting solutions were filtered to 150 mm using Whatman 42 filter paper. A 2- mL concentration of 12 N hydrochloric acid (HCl) was added to each filtered extract. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) using a spectrophotometer at 880 nm, within 72 hours of extraction. Extract P (mg/L) was then converted to mass of soil P (mg/kg) using the following equation:

$$\text{AER (mg/kg)} = [(A*B*C*R*1000)/E] \quad [3.2]$$

where A is the sample extract concentration (mg/L), B is the extract volume (L), C is the dilution (if performed), R is the air-dry/oven-dry weight ratio, and E is the sample weight (g), for P released after one hour (AER1), P released after an additional 23 hours (AER23), and total P released after a total of 24 hours (AER24).

#### *Phosphorus Adsorption Isotherm Determination*

Phosphorus adsorption isotherms were performed following the method of Graetz and Nair (2009). A 0.75-g, <2-mm, air-dried soil sample was shaken for 24 hours at 100 oscillations/min at room temperature with 20 mL of a 0.01 M calcium chloride (CaCl<sub>2</sub>) solution containing 0, 0.1, 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 mg P/L as KH<sub>2</sub>PO<sub>4</sub> and two drops of chloroform to inhibit microbial activity. The sample was then centrifuged at 3000 rpm for 10 minutes, after which the sample extract was filtered using a Whatman 45

filter. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) at 880 nm using a spectrophotometer, within 72 hours of extraction. 0.01 M calcium chloride extractable phosphorus ( $P_{CaCl_2}$ ) was then determined from the extracts from the soil mixed with the  $CaCl_2$  solution containing 0 mg P/L. Results were analyzed and sorption parameters were determined using the linearized Langmuir equation:

*Linearized Langmuir equation:*

$$C / S = (1 / kS_{MAX}) + (C / S_{MAX}) \quad [3.3]$$

where S is the total amount of P retained (mg/kg), C is the concentration of P after 24 hour equilibration (mg/L),  $S_{MAX}$  is the P sorption maximum (mg/kg), and k is a constant related to the bonding energy (L/mg P).

### *Statistical Analysis*

Study samples were analyzed using routine statistical analyses, including descriptive statistics, correlation, and multiple linear regression using the statistical software program, SAS<sub>TM</sub> v. 9.4. The assumptions of the Person correlation include (a) each variable is continuous in measurement, (b) each observation has a pair of values, (c) the absence of outliers in either variable, (d) the normality of each variable, (e) a linear relationship between variables, and (f) homoscedasticity, a tube-like shape between values on a scatterplot and the linear trend line between the variables. The assumptions of multiple linear regression include (a) a linear relationship between the independent and dependent variables, (b) multivariate normality, (c) no or little multicollinearity, (d) no auto-correlation, and (e) homoscedasticity. The SAS CORR procedure with the PEARSON option was used for correlation analyses, while the REG procedure was used

for regression analyses and to develop the final prediction equations. Not all assumptions were met when study data was applied to the correlation and regression analyses.

## RESULTS AND DISCUSSION

### Phosphorus Sorption Relationships with Soil Properties

Descriptive statistics were determined for both the modeling (Table 3.2) and validation datasets (Table 3.3). From this data it is apparent that the soils examined in this study varied widely in physical and chemical properties known to influence P sorption in soils. Property ranges and averages for the samples in the validation dataset were smaller and lower than those of the modeling dataset, except for the averages for pH and  $Mn_M$ , which were higher for the validation dataset than the modeling dataset. Average clay was 20.77 %, average TC was 4.86 %, and average  $CaCO_3$  contents was 2.28 % for the samples in the modeling dataset. Average pH for the samples in the modeling dataset was 5.69, with an overall range of 4.2 to 7.8 for all. Average  $Al_{OX}$  and  $Fe_{OX}$  for the samples in the modeling dataset were 1802.78 mg Al/kg soil and 2988.89 mg Fe/kg soil, respectively. Average  $Al_M$  was 809.27 mg Al/kg soil,  $Fe_M$  was 198.47 mg Fe/kg soil, and  $Mn_M$  was 153.51 mg Mn/kg soil for samples in the modeling dataset. Average  $Ca_M$  and  $Mg_M$  for samples in the modeling dataset were 2277.63 mg Ca/kg soil and 184.47 mg Mg/kg soil, respectively. Average  $Ca_{NH_4}$  was 9.57 cmol/kg and average  $Mg_{NH_4}$  was 1.79 cmol/kg for samples in the modeling dataset.

The P sorption variables investigated in this study also varied widely. Boxplots were developed for the AER variables for both the modeling and validation datasets (Figure 3.4). Boxplots were also developed for the PSI (Figure 3.5) and  $S_{MAX}$  (Figure 3.6)

Table 3.2. Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the modeling dataset.

	Clay	Silt	Sand	TC	CuCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Cu <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	Cu <sub>sh</sub>	Mg <sub>sh</sub>	P <sub>ox</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>hoy1</sub>	P <sub>ws</sub>	P <sub>Cd12</sub>	AER1	AER23	AER24	PSI	S <sub>MAX</sub>			
	----- % -----							mg Element/kg soil -----								----- cmol/kg -----				----- mg P/kg soil -----								L/kg	mg/kg
Mean	20.77	55.65	23.58	4.86	2.28	5.69	1802.78	2988.89	809.27	2277.63	198.23	184.47	153.51	9.57	1.79	448.91	148.26	118.36	74.81	1.51	23.29	107.31	129.06	236.37	150.58	313.18			
Standard Error	1.71	2.13	2.20	1.42	1.98	0.17	220.80	318.87	47.68	1003.71	20.38	23.04	23.20	1.42	0.25	48.99	27.99	26.54	22.80	0.77	13.46	6.69	11.18	16.06	22.02	55.47			
95% Confidence Level for Mean	3.48	4.33	4.48	2.89	4.03	0.35	448.25	647.34	96.80	2037.63	41.38	46.76	47.09	2.88	0.50	99.46	56.82	53.87	48.33	1.55	27.35	13.58	22.70	32.60	44.71	112.72			
Median	20.20	56.20	19.40	2.46	0.00	5.80	1350.00	2650.00	778.25	1262.55	163.40	140.25	112.50	8.55	1.30	358.60	82.10	55.05	30.00	0.23	0.73	101.93	108.31	219.11	112.98	263.16			
Minimum	7.90	24.50	4.80	0.18	0.00	4.20	800.00	400.00	2.30	138.30	35.70	39.70	4.10	0.60	0.40	62.00	15.20	0.20	2.00	0.00	0.00	46.15	48.98	117.09	0.00	0.00			
Maximum	62.60	82.90	64.10	48.16	71.00	7.80	6400.00	7000.00	1503.10	37129.60	600.60	593.20	637.90	45.20	6.30	1219.00	651.60	592.10	353.00	25.64	385.53	205.95	356.14	562.09	582.03	1666.67			
N	35	35	35	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	17	36	35	36	36	36	35			

Table 3.3. Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the validation dataset.

	Clay	TC	CuCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>m</sub>	C <sub>h</sub> <sub>m</sub>	Fe <sub>m</sub>	Mg <sub>m</sub>	Mn <sub>m</sub>	C <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>ox</sub>	P <sub>M</sub>	P <sub>Me</sub>	P <sub>Bmp1</sub>	P <sub>ws</sub>	P <sub>CdCl2</sub>	AER1	AER23	AER24	PSI	S <sub>MAX</sub>
	----- %	-----	-----	-----	----- mg Element/kg soil	-----	-----	-----	-----	-----	-----	----- cmol/kg	-----	-----	-----	-----	-----	----- mg P/kg soil	-----	-----	-----	-----	----- L/kg	----- mg/kg
Mean	15.89	1.81	0.00	6.02	1470.00	2230.00	423.23	653.46	103.94	77.75	162.28	7.04	1.42	649.73	237.17	203.28	169.79	0.62	-	108.47	118.23	226.70	77.27	-
Standard Error	2.01	0.30	0.00	0.20	157.09	517.91	36.23	135.35	14.61	23.97	34.91	1.28	0.39	237.43	76.31	72.33	46.52	0.21	-	9.98	26.46	34.86	15.03	-
95% Confidence Level for Mean	4.54	0.67	0.00	0.46	355.37	1171.60	81.96	306.18	33.06	54.21	78.97	2.90	0.88	537.11	172.63	163.62	105.23	0.48	-	22.58	59.86	78.86	34.00	-
Median	16.30	1.61	0.00	5.95	1600.00	1500.00	458.25	588.90	92.25	56.40	182.65	6.55	1.00	397.10	157.65	123.80	130.15	0.40	-	106.26	90.99	186.97	76.98	-
Minimum	2.30	0.58	0.00	5.10	600.00	400.00	197.70	98.60	57.70	19.80	3.70	1.80	0.40	186.40	55.10	41.80	46.10	0.10	-	44.24	39.44	83.68	3.18	-
Maximum	24.90	4.14	0.00	7.00	2100.00	5800.00	563.10	1701.10	206.80	262.80	336.80	16.60	4.40	2699.10	782.20	742.00	466.70	1.90	-	157.54	336.58	494.12	162.19	-
N	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	0	10	10	10	10	0



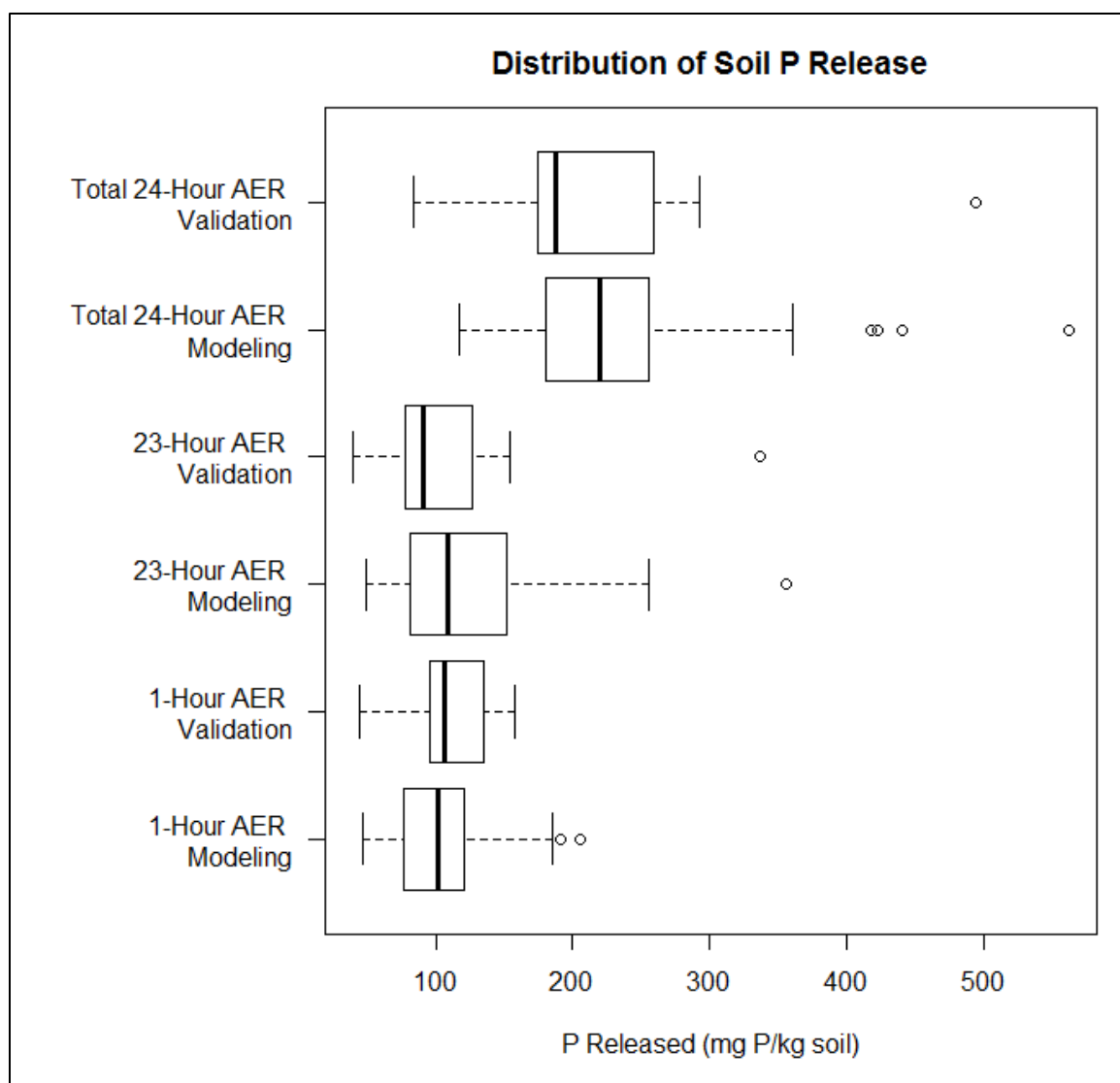


Figure 3.4. Boxplots displaying the quartile statistics of each measured AER variable for the Chesapeake Bay watershed modeling dataset and validation dataset.

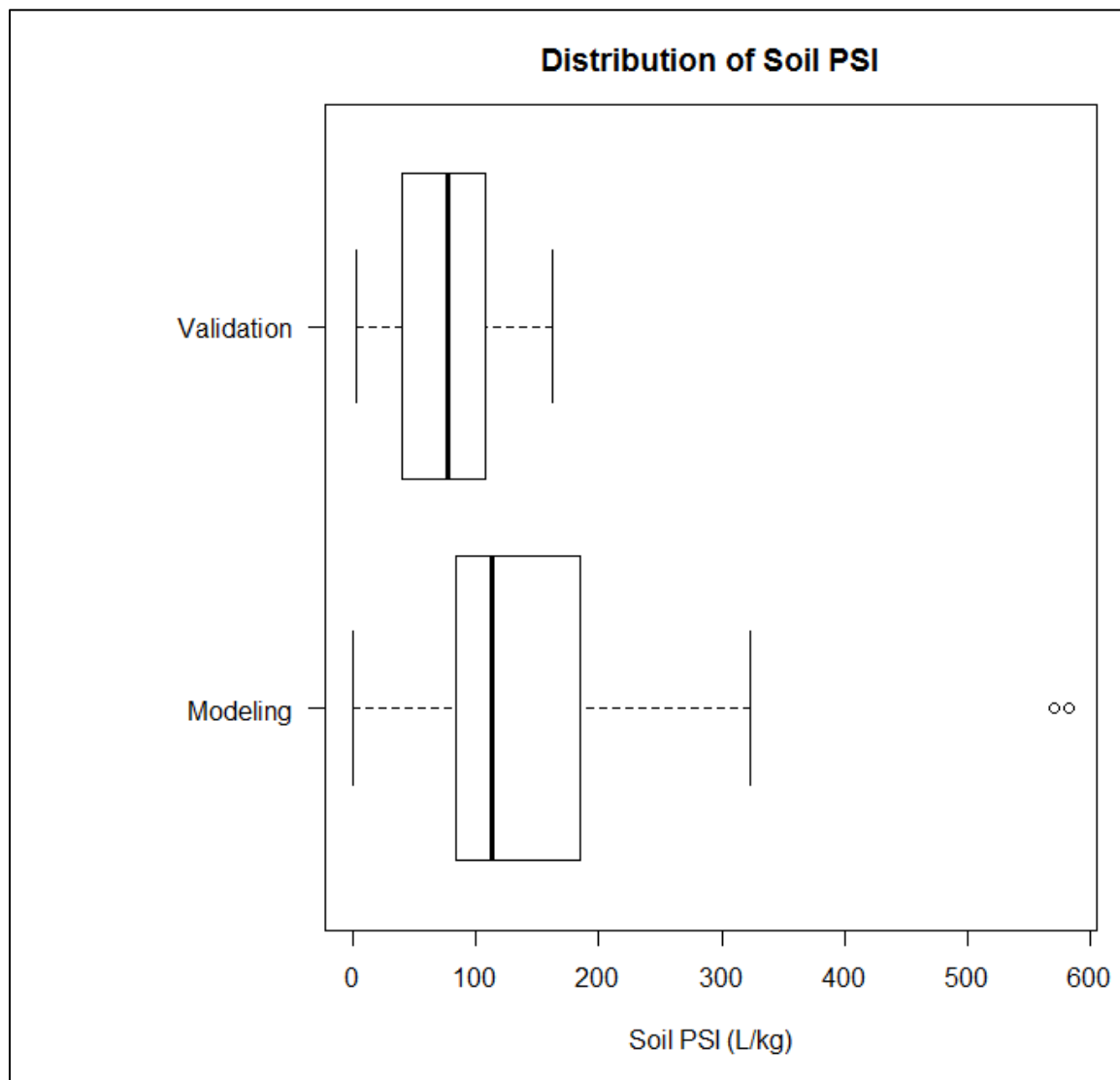


Figure 3.5. Boxplots displaying the quartile statistics for the PSI variable for the Chesapeake Bay watershed modeling dataset and validation dataset.

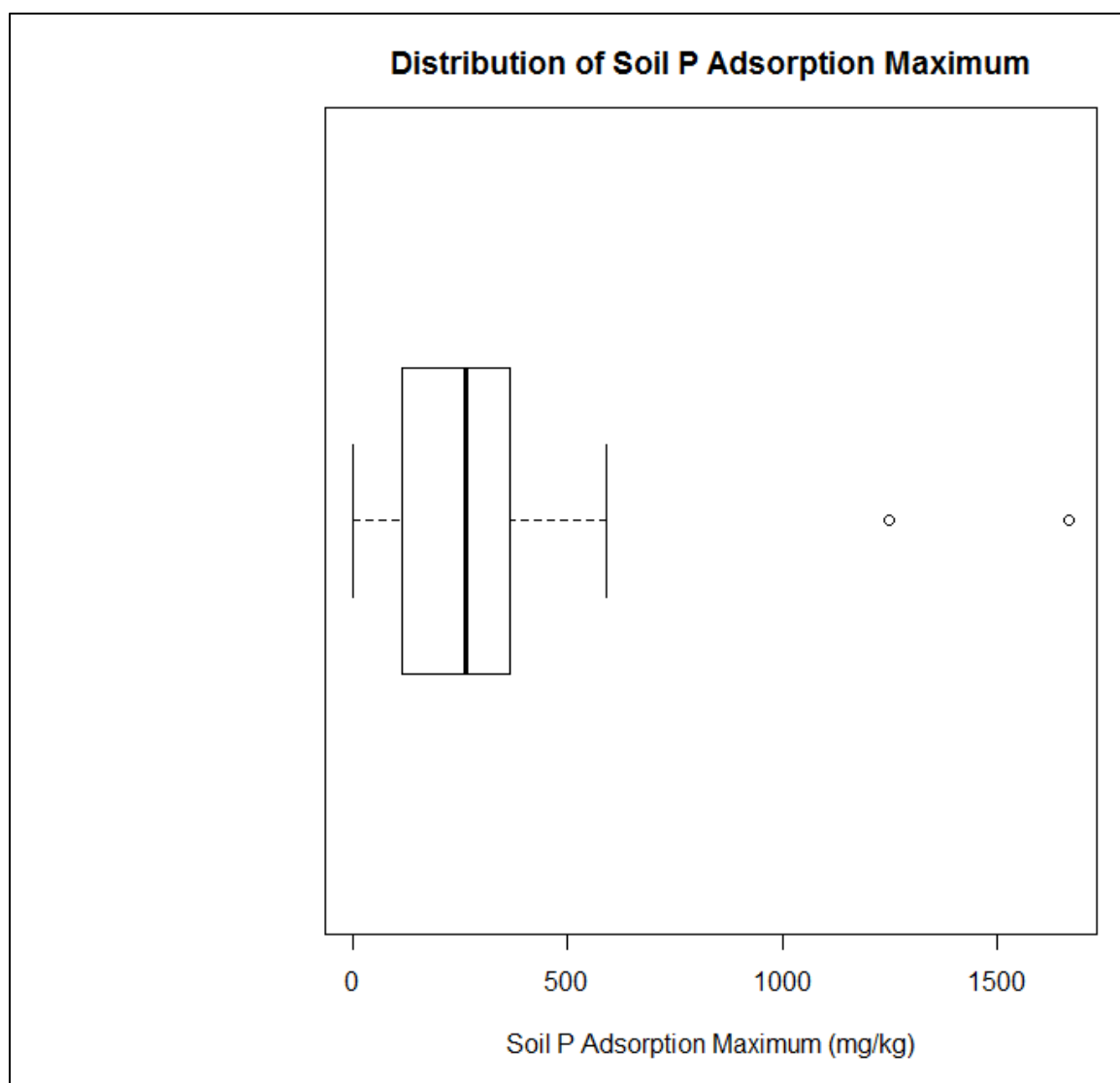


Figure 3.6. Boxplots displaying the quartile statistics for the  $S_{\text{MAX}}$  variable for the Chesapeake Bay watershed modeling dataset.

variables in the modeling and validation datasets. The ranges and averages for the P sorption variables were smaller and lower for the samples in the validation dataset than those in the modeling dataset, except for average AER1. Average AER1 was 107.31 mg P/kg soil, AER23 was 129.06 mg P/kg soil, and AER24 was 236.37 mg P/kg soil for samples in the modeling dataset. The average PSI for the samples in the modeling dataset was 150.58 L/kg.  $S_{MAX}$  was only determined on the samples in the modeling dataset, which had an average of 313.18 mg/kg.

Pearson correlation coefficients were calculated for the samples in the modeling dataset, between the P sorption variables and soil properties known to affect P sorption in soils (Table 3.4). AER1 was significantly ( $p < 0.05$ ) correlated with  $Ca_{NH_4}$ , TC,  $Al_{OX}$ , and  $Fe_M$ . AER23 and AER24 were both significantly correlated with  $Al_{OX}$ ,  $Al_M$ , and  $Fe_{OX}$ . PSI was significantly correlated with  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ , clay, and  $Mn_M$ , while  $S_{MAX}$  was significantly correlated with  $Al_{OX}$  and  $Al_M$ .

These correlations indicate that P sorption is primarily controlled by Al and Fe oxides in soils of the Chesapeake Bay watershed. Readily desorbable P, however, would appear to be influenced more by the total carbon and calcium ions of the soil, while total desorbable P is influenced by Al and Fe oxides in the soil. All soil P sorption variables are significantly correlated with a crystalline form of Al or Fe, but are more strongly and more significantly correlated with amorphous forms of Al. These findings are similar to those noted by Penn et al. (2005), Maguire et al. (2000), Paulter and Sims (2000), and Mozaffari and Sims (1996).

Table 3.4. Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption, for samples in the modeling dataset.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>h</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	C <sub>NH4</sub>	Mg <sub>NH4</sub>
AER1	0.0684	0.4076*	0.1602	0.0669	0.3823*	0.1121	0.2110	0.2079	0.3376*	0.3057	0.1979	0.4606**	0.3082
AER23	0.1654	-0.1228	-0.0806	-0.1181	<b>0.7882</b> ***	0.5160**	0.6302***	-0.0710	0.2160	-0.1637	0.2502	-0.0477	-0.1227
AER24	0.1413	0.0843	0.0106	-0.0543	<b>0.7079</b> ***	0.4058*	0.5266**	0.0372	0.2910	0.0133	0.2566	0.1586	0.0429
PSI	0.3812*	-0.0682	0.0406	-0.2203	<b>0.7620</b> ***	0.6025**	0.5512**	0.0018	0.0225	-0.2872	0.3631*	-0.0947	-0.2111
Smax	0.0032	-0.0775	0.1273	-0.2282	0.4425**	0.1533	0.4183*	0.0984	0.1197	-0.2537	-0.1162	-0.1192	-0.2390

\*p ≤ 0.05; \*\*p ≤ 0.01; \*\*\*p ≤ 0.001; significant correlation coefficients ≥ 0.65 in bold.

### Phosphorus Sorption Relationships with Soil P Tests

Extracted soil P also varied greatly in the study soils (Tables 3.2 and 3.3).

Average soil test P values decreased in the following pattern in both the modeling and validation datasets:  $P_{OX} > P_M > P_{M3} > P_{Brayl} > (P_{CaCl2}) > P_{WS}$ . Average soil test P values were lower for samples in the modeling dataset, except for  $P_{WS}$ . Like  $S_{MAX}$ ,  $P_{CaCl2}$  was not determined for samples in the validation dataset.

Pearson correlation coefficients were calculated between the P sorption variables and soil P tests for the samples in the modeling dataset (Table 3.5). All desorption variables are highly ( $R > 0.50$ ) and significantly ( $p < 0.01$ ) correlated with  $P_{OX}$ . AER1, AER24, and PSI were also significantly correlated with  $P_M$  and  $P_{M3}$ . AER1 was significantly correlated with  $P_{WS}$  and  $P_{CaCl2}$ , and PSI was also significantly correlated with  $P_{WS}$ .  $S_{MAX}$ , however, was not significantly correlated with any soil P test. From these correlations, it is apparent that readily desorbable P is related to water soluble and more readily available forms of soil P, while equilibrium desorbable P is related to total soil P. The significant correlations of AER24 reflect the influence of the readily desorbable soil P on total P desorption. P adsorption appears to be negatively related to the water soluble and readily available forms of soil P.

Table 3.5. Correlations coefficients between the P sorption variables and soil P tests, for samples in the modeling dataset.

	$P_{OX}$	$P_M$	$P_{M3}$	$P_{Brayl}$	$P_{WS}$	$P_{CaCl2}$
AER1	0.5189**	0.4342**	0.3853*	0.2189	0.3722*	0.4043*
AER23	<b>0.6617***</b>	0.2266	0.2659	-0.1799	-0.1949	-0.2369
AER24	<b>0.6767***</b>	0.3386*	0.3456*	-0.0354	0.0194	-0.0007
PSI	0.1329	-0.4187*	-0.3996*	-0.4423	-0.3300*	-0.3265
Smax	0.1500	-0.1720	-0.1405	-0.1523	-0.2447	-0.2524

\* $p \leq 0.05$ ; \*\* $p \leq 0.01$ ; \*\*\* $p \leq 0.001$ ; significant correlation coefficients  $\geq 0.65$  in bold.

### Phosphorus Release Characteristics

Figure 3.7 shows the relationship between the predicted P released (mg P/kg soil) and the AER extraction periods (minutes (a, c) and hours (b, d)) that represent the minimum, first quartile, median, mean, third quartile, and maximum P released for the soils from the modeling dataset (a, b) and soils from the validation dataset (c, d). For soils from the modeling dataset investigated in this study ( $N = 36$ ), an average of 45 % of P was released during the first hour of AER extraction, while the remaining 55 % of P was released during the following 23 hours of AER extraction. For soils in the validation dataset, an average of 48 % of P was released during the first hour of AER extraction. When soils in the modeling dataset were grouped based on the presence of  $\text{CaCO}_3$  and their degree of weathering, during the first hour of AER extraction there was an increase from 45 % of P released to 58 % for calcareous soils ( $N = 3$ ), a slight increase to 47 % of P released for highly weathered soils ( $N = 18$ ), and slight decrease to 42% of P released for slightly weathered soils ( $N = 15$ ) (data not shown).

The linear regression equations to predict P released (mg P/kg soil) by AER extraction for both 1 and 24-hr extraction periods are listed in Appendix G. Linear relationships are always produced when the amount of P released (mg P/kg soil) is plotted against the log of the AER extraction period (Elrashidi et al., 2012; Elrashidi et al., 2003). These linear relationships are also shown for the soils from the modeling dataset that represent the minimum, first quartile, median, mean, third quartile, and maximum P released for the Chesapeake Bay soils (Appendix G). The amount of P released after the first hour of AER extraction mainly represents the readily available P in the soil. This 1-hour extraction P released value varied greatly within the Chesapeake

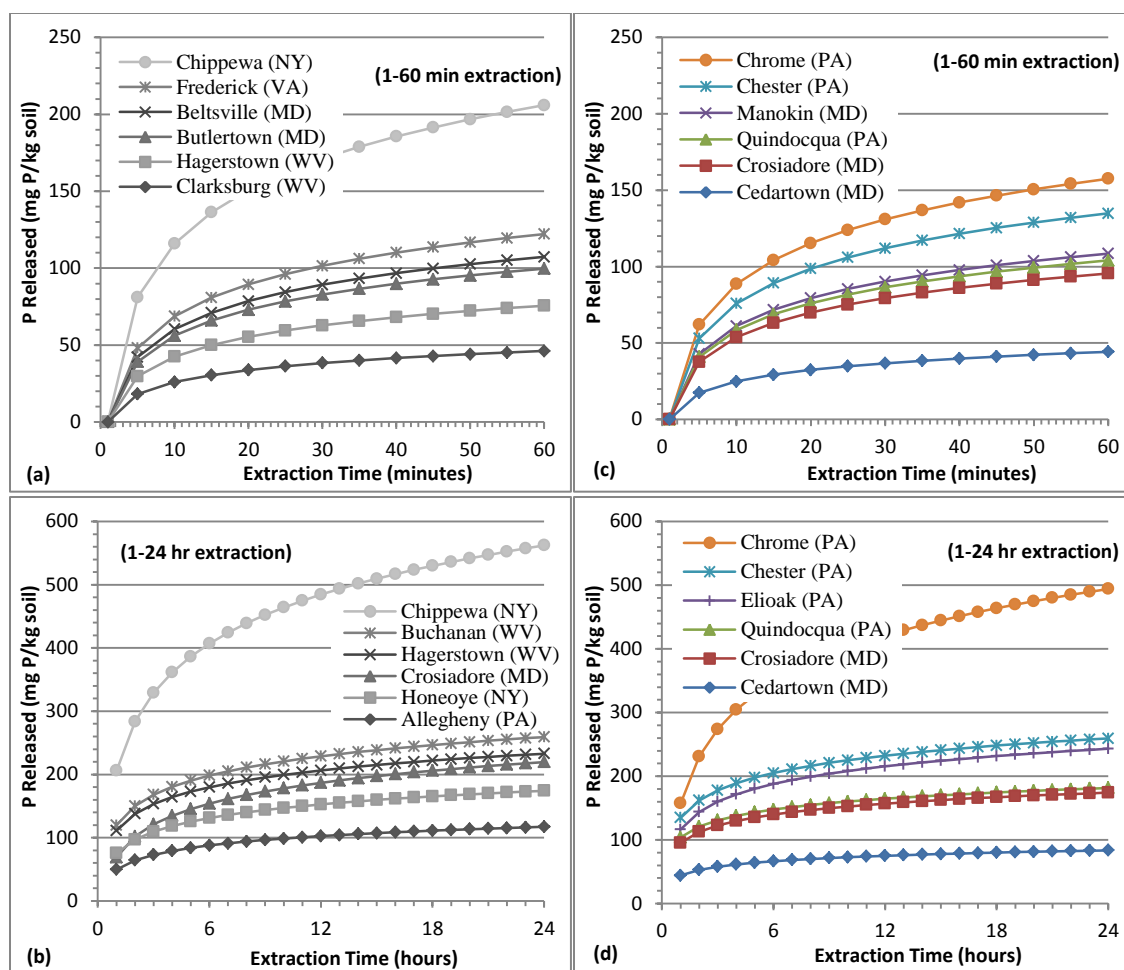


Figure 3.7. Predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, first quartile, median, mean, third quartile, and maximum for samples from the modeling dataset during the (a) 1-60 minute and (b) 1-24 hour extraction periods, and for samples from the validation dataset (colored curves) during the (c) 1-60 minute and (d) 1-24 hour extraction periods.

Bay soils, with a range of 46.15 mg P/kg soil to 205.95 mg P/kg soil (Table 3.2). This is likely due to the high variability in soils when classified by calcium carbonate content and degree of weathering (Table 3.1), as detailed by Sharpley et al (1984). The AER1 range for the calcareous soils in this region, however, is notably narrower, 76.19 mg P/kg soil to 142.76 mg P/kg soil (data not shown). The total P released value (AER24) also varied greatly for soil within the Chesapeake Bay, with a range of 117.09 mg P/kg soil to



562.09 mg P/kg soil (Table 3.2). Again, the AER24 range for the calcareous soils in this region is notably narrower, with a range of 143.41 mg P/kg soil to 247.84 mg P/kg soil (data not shown). Overall, the three calcareous soils investigated had low  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ , and  $Fe_M$  concentrations, high  $Ca_M$  and  $Ca_{NH4}$  concentrations, and moderate to high PSI values (data not shown). AER1 varied greatly for highly weathered and slightly weathered soils, with ranges of 68.99 mg P/kg soil to 191.07 mg P/kg soil and 44.24 mg P/kg soil to 205.95 mg P/kg soil, respectively (data not shown). Total P released also varied greatly for the highly weathered and slightly weathered soils, with ranges of 152.29 mg P/kg soil to 422.99 mg P/kg soil and 83.69 mg P/kg soil to 562.14 mg P/kg soil, respectively (data not shown).

From Figure 3.7 it is clear that of all soils investigated from the Chesapeake Bay watershed, the Chippewa soil from the modeling dataset released the most P during the 1-hour extraction period and overall after 24 hours of extraction, followed by the Chrome soil from the validation dataset. Figure 3.7 also shows that the Clarksburg soil and Allegheny soil from the modeling dataset released the least P during the 1 hour extraction period and overall after 24 hours of extraction, respectively. The Cedartown soil from the validation dataset, however, released the least amount of P of all investigated Chesapeake Bay soils, during both extraction periods (Figures 3.7). The Chippewa soil had high TC,  $Al_{OX}$ ,  $Fe_{OX}$ , and  $P_{OX}$ , and the highest  $Al_M$  and PSI values for soils in the modeling dataset (data not shown). The Chrome soil had high  $Fe_{OX}$ , and the highest  $P_{OX}$  value of all soils investigated, as well as more than double the amount of  $P_M$ ,  $P_{M3}$ ,  $P_{Bray1}$ , and  $P_{WS}$  than the Chippewa soil. It was noted previously that increasing soil desorption in these soils is related to increasing TC, Al and Fe oxides,  $P_{OX}$ ,  $P_M$ ,  $P_{M3}$ , and  $P_{WS}$ . The

Clarksburg soil had low  $\text{Al}_{\text{OX}}$ ,  $\text{Al}_{\text{M}}$ , and  $\text{P}_{\text{OX}}$ , moderate  $\text{Fe}_{\text{OX}}$  and PSI, and  $\text{P}_{\text{M}}$  and  $\text{P}_{\text{M3}}$  comparable to that of the Chippewa soil (data not shown). The Allegheny soils also had low  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Al}_{\text{M}}$ ,  $\text{Fe}_{\text{M}}$ ,  $\text{P}_{\text{OX}}$ ,  $\text{P}_{\text{M}}$ , and  $\text{P}_{\text{M3}}$ , and a moderate PSI value (data not shown). The Cedartown soil, however, had the lowest clay content of all soils, low TC, the lowest  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Ca}_{\text{M}}$ ,  $\text{Mg}_{\text{M}}$ ,  $\text{Ca}_{\text{NH4}}$ , and  $\text{Mg}_{\text{NH4}}$  of the validation soils, higher  $\text{P}_{\text{OX}}$ ,  $\text{P}_{\text{M}}$ ,  $\text{P}_{\text{M3}}$ ,  $\text{P}_{\text{Bray1}}$ , and  $\text{P}_{\text{WS}}$  than the Clarksburg and Allegheny soils, and the lowest PSI value of the validation soils (data not shown). The soils that released the most P during the AER desorption process had high amounts of the components known to retain P and high amounts of P already in the soil, and thus easily released large amounts of P in solution. The soils that released the least P during the desorption process had low amounts of the components known to retain P, and released less amounts of P due to not having the ability to readily retain P.

### **Predicting Soil Phosphorus Behavior**

Most soil testing facilities only routinely analyze soils for particle-size (sand, silt, and clay), carbon content, and pH, and do not have the means or capability to perform more detailed analyses such as oxalate or Mehlich-3 extractions. Of all soil parameters investigated, only clay, TC, and pH are routinely analyzed on all soil samples processed at the KSSL. At the KSSL, analyses such as acid oxalate extractable Al, Fe, and P, and Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P) are additional analyses for select samples requested by the project researcher or investigator, limiting the data available for these properties. As mentioned previously, P sorption behaviors in soil have been found to be related to soil clay, TC, and/or pH (Burt et al., 2002; Harter, 1969; Juo and Fox,

1977; Lopez-Hernandez and Burnham, 1974; McCallister and Logan, 1978, Sharpley et al., 1989, Syers et al., 1971). For each of the five P sorption variables of interest (AER1, AER23, AER24, PSI, and  $S_{MAX}$ ), linear regression equations were developed. Clay, TC, and pH were modeled independently and additional variables ( $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ ,  $Ca_M$ ,  $Fe_M$ ,  $Mg_M$ ,  $Mn_M$ ,  $Ca_{NH4}$ ,  $Mg_{NH4}$ ) were progressively added to the models. Models contained one to three variables, with clay, TC, or pH in each equation. The use of clay, TC, or pH in additional models was dependent on the significance of the respective independent models. Clay, TC, and/or pH were used in additional modeling if, (a) the  $p$  value of the independent model was significant ( $p \leq 0.05$ ), or (b) if no independent model was significant, the independent model with the lowest  $p$  value was used. An example of the progressive linear regression modeling method for the AER1 and AER23 variables is listed in Appendix G. For AER1, only the independent model with TC was significant, so it was used in the additional modeling steps. For AER23 and AER24, none of the independent models with clay, TC, and pH were significant. The model with clay as a single predictor variable had the lowest  $p$  value, and was used in the additional modeling steps for each P sorption variable. For PSI, only the independent model with clay was significant, so it was used in the additional modeling steps. For  $S_{MAX}$ , none of the independent models with clay, TC, and pH were significant. The model with pH as a single predictor variable had the lowest  $p$  value, and was used in the additional modeling steps for each P sorption variable.

The three most significant P sorption prediction equations for AER1, AER23, AER24, PSI, and  $S_{MAX}$ , developed with the samples in the modeling dataset, those with the lowest  $p$  values and highest  $R^2$  values, are listed in Table 3.6. The inclusion of  $Al_{OX}$

Table 3.6. The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the modeling dataset.

<b>AER1</b>					
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>	
74.41 + 2.07TC + 0.01Al <sub>OX</sub>	0.3397	0.0011	33.59	36	
77.62 + 1.99TC + 0.01Al <sub>OX</sub> - 0.002Fe <sub>OX</sub>	0.3451	0.0033	33.97	36	
83.92 + 1.38TC + 1.74Ca <sub>NH4</sub>	0.2902	0.0035	34.82	36	
<b>AER23</b>					
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>	
70.07 - 0.76Clay + 0.04Al <sub>OX</sub> + 0.0007Fe <sub>OX</sub>	0.6262	0.0001	42.89	35	
70.78 - 0.74Clay + 0.04Al <sub>OX</sub>	0.6260	0.0001	42.23	35	
-68.35 + 1.41Clay + 0.20Al <sub>M</sub> + 0.004Ca <sub>M</sub>	0.5725	0.0001	45.87	35	
<b>AER24</b>					
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>	
161.27 - 1.00Clay + 0.06Al <sub>OX</sub> - 0.003Fe <sub>OX</sub>	0.5160	0.0001	71.19	35	
158.87 - 1.07Clay + 0.05Al <sub>OX</sub>	0.5147	0.0001	70.16	35	
-23.25 + 1.66Clay + 0.26Al <sub>M</sub> + 0.01Ca <sub>M</sub>	0.4496	0.0003	75.92	35	
<b>PSI</b>					
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>	
-155.94 - 2.59Clay + 0.37Al <sub>M</sub> + 0.01Ca <sub>M</sub>	0.6341	0.0001	83.30	35	
-21.17 + 1.56Clay + 0.06Al <sub>OX</sub> + 0.01Fe <sub>OX</sub>	0.6035	0.0001	86.70	35	
-11.55 + 1.84Clay + 0.07Al <sub>OX</sub>	0.5916	0.0001	86.61	35	
<b>S<sub>MAX</sub></b>					
<b>Variable(s)</b>	<b>R<sup>2</sup></b>	<b>p</b>	<b>MSE</b>	<b>N</b>	
-214.93 - 19.38pH + 0.71Al <sub>M</sub> + 0.02Ca <sub>M</sub>	0.3228	0.0065	282.80	35	
424.43 - 52.29pH + 0.10Al <sub>OX</sub>	0.2223	0.0179	298.23	35	
-28.04 - 4.00pH + 0.58Al <sub>M</sub> - 0.68Mn <sub>M</sub>	0.2506	0.0282	297.50	35	

or Al<sub>M</sub> in each prediction equation indicates the significant influence of both crystalline and amorphous Al oxides on soil P sorption behaviors in soils of this region. The prediction models also indicate that, overall, soil P desorption is influenced by the total and amorphous Al and Fe oxide soil components while P adsorption is influenced by the available and crystalline forms of Al and Fe oxides. Ca<sub>M</sub> is also an important P sorption predictor variable in these soils, as noted by its inclusion in the AER23, AER24, PSI, and S<sub>MAX</sub> models with Al<sub>M</sub>. The AER23, AER24, and PSI prediction equations also have stronger, or higher, R<sup>2</sup> values than the AER1 and S<sub>MAX</sub> equations, due to the stronger

relationships between AER23, AER24, and PSI and these soil properties (Table 3.4).

These findings are in line with those in previous studies, where the authors note that for soils from this region, P sorption is often related to clay content (Mozaffari and Sims, 1994; Mozaffari and Sims, 1996; Atalay, 2001), organic carbon (Atalay, 2001; Vadas and Sims, 2002), Al and Fe oxides (Maguire et al., 2000; Mozaffari and Sims, 1996; Paulter and Sims, 2000; Vadas and Sims, 2002), and mineralogy that accounts for both clay and Al and Fe (Penn et al., 2005).

The reliability of the prediction models developed for AER1, AER23, AER24, and PSI was analyzed when the equations developed from samples in the modeling dataset were applied to the samples in the validation dataset. Plots of the measured P sorption values against the predicted values for AER1, AER23, AER24, and PSI, respectively, with an overlaid linear trendline for each model are shown in Figure 3.8. These plots reveal that the AER1 model that with TC and  $\text{Ca}_{\text{NH}_4}$  variables was the best of the three models for predicting one-hour P release, with an  $R^2$  of 0.4807. The AER23 and AER24 performed models performed quite poorly overall, as noted by the low  $R^2$  values. The AER23 model with clay,  $\text{Al}_{\text{OX}}$ , and  $\text{Fe}_{\text{OX}}$  variables was a slightly better model for predicting P release after an additional 23 hours in solution, and the AER24 model with clay and  $\text{Al}_{\text{OX}}$  was the slightly better model for predicting total P release. The PSI model, also with clay,  $\text{Al}_{\text{OX}}$ , and  $\text{Fe}_{\text{OX}}$  variables, was the best model for predicting P sorption, with an  $R^2$  of 0.6671 (Figure 3.8). Overall, the AER23 and AER24 validation comparisons reveal that these models performed quite poorly, as noted by the low  $R^2$  values.

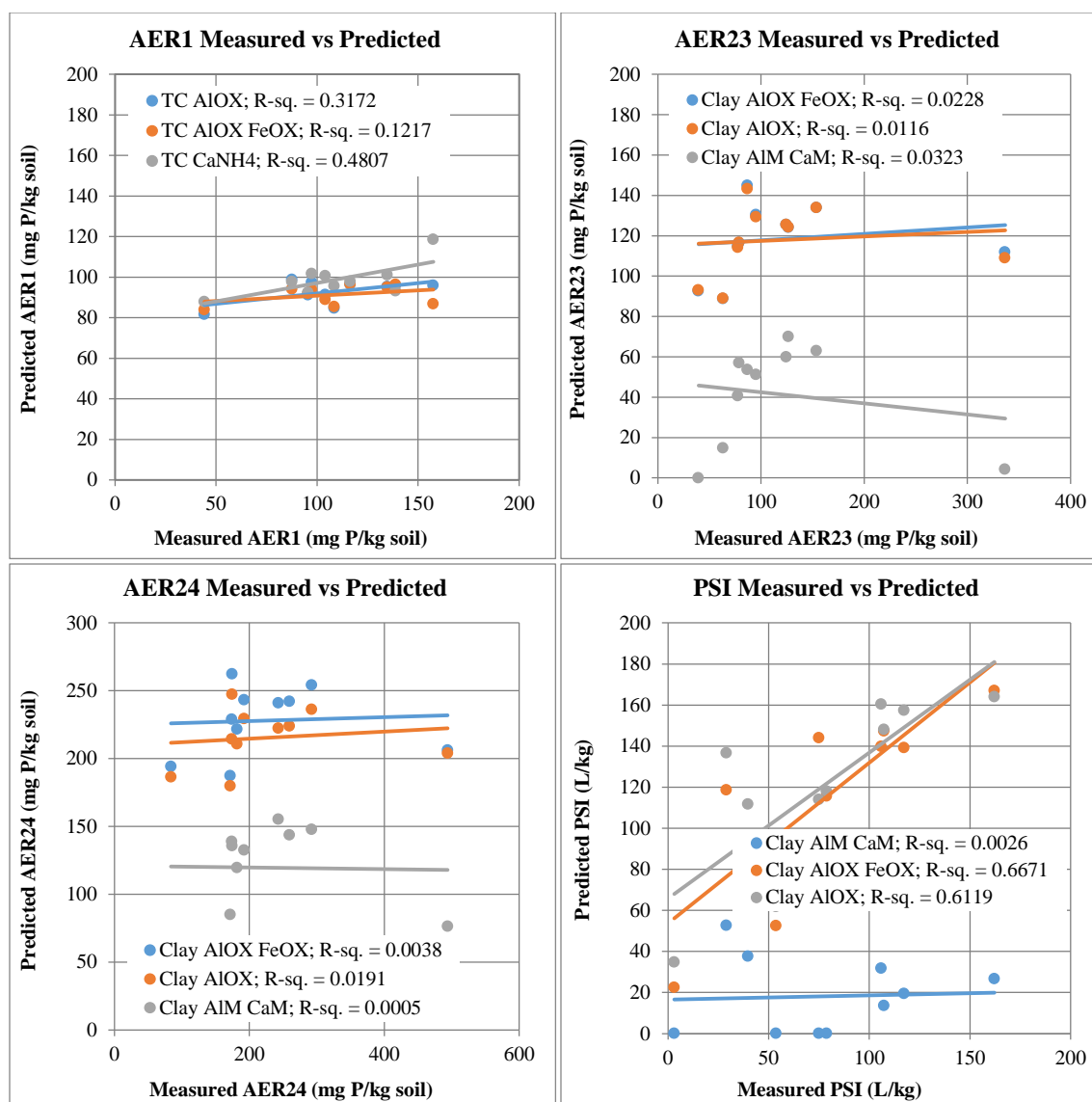


Figure 3.8. Plots of measured versus predicted values, as determined by the models listed in Table 3.6, for AER1, AER23, AER24, and PSI.

The number of predictions within 10 %, 15 %, and 20 % of the measured P sorption value for each of the significant prediction models for each P sorption variable, except  $S_{\text{MAX}}$ , for samples in the validation dataset were also examined (Table 3.7). The prediction equations for AER1 worked moderately well at predicting P release values within 20 % of the measured AER1 value. The AER23, AER24, and the PSI models

Table 3.7. The number of validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for each of the prediction models listed in Table 3.6 for AER1, AER23, AER24, and PSI, and for the most significant AER24 model from Chapter 2 for all CONUS agricultural soils.

<b>AER1</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
TC Al <sub>OX</sub>	2	4	5	10
TC Al <sub>OX</sub> Fe <sub>OX</sub>	3	4	5	10
TC Ca <sub>NH4</sub>	3	5	6	10
<b>AER23</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	2	3	3	10
Clay Al <sub>OX</sub>	2	3	3	10
Clay Al <sub>M</sub> Ca <sub>M</sub>	0	0	0	10
<b>AER24</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	3	4	4	10
Clay Al <sub>OX</sub>	2	3	6	10
Clay Al <sub>M</sub> Ca <sub>M</sub>	0	0	0	10
Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	3	5	6	10
<b>PSI</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>M</sub> Ca <sub>M</sub>	1	1	1	10
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	2	2	3	10
Clay Al <sub>OX</sub>	1	1	2	10

performed slightly worse, only predicting few P sorption values within 20% of the measured values, despite the higher  $R^2$  values of the models. One sample from the validation dataset had AER1, AER23, and AER24 values outside of the ranges measured for the samples in the modeling dataset, which were slightly lower than the minimum measured values.

As mentioned in Chapter 2, the AER 24 behavior models and relationships are the most likely to be used by researchers and management planners to estimate potential P release or P loading risk if P saturated soils become eroded and incorporated into surface runoff as they model total P release. The Chesapeake Bay watershed-specific prediction models were also compared to the most significant AER24 prediction model developed from the All Soils modeling dataset in Chapter 2. The results are shown in Figure 3.9,

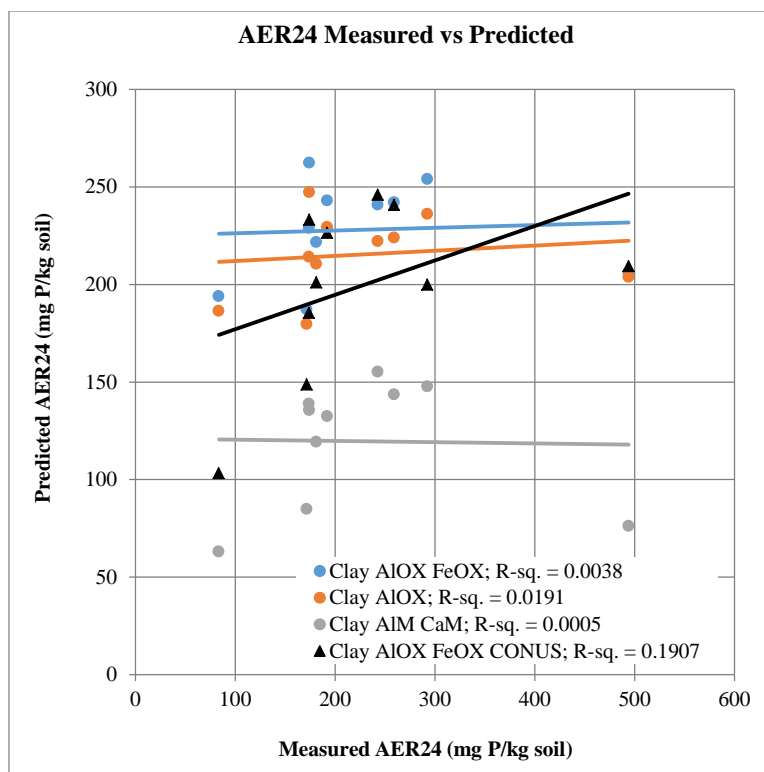


Figure 3.9. Measured versus predicted AER24 values as determined by the models listed in Table 3.6 and the most significant AER24 prediction model from Chapter 2 for all CONUS agricultural soils.

and also included in Table 3.7, with the Chapter 2 model noted by the ‘CONUS’ term in each case. Both Figure 3.9 and Table 3.7 show that the Chapter 2 CONUS is the better model for predicting total P release in the Chesapeake Bay watershed, with a higher  $R^2$  value and accurately predicting more AER24 values within 20% of the actual measured values. Both the CONUS model and the most significant watershed-specific model contain clay,  $Al_{OX}$ , and  $Fe_{OX}$  as model components and accurately predicted a similar number of AER24 values within 20% of the measured value. These results would indicate additional research and refinement is needed to create reliable watershed-specific models for total P release.



## Potential Risk of Phosphorus Loading

As mentioned earlier, P management programs and P Indices have been in use in the Chesapeake Bay watershed for two decades, though water quality issues and P loading in agricultural runoff continues. Each P Index is state-specific and typically includes a soil test P value as a contributing P Index factor. The soil test P method and the associated break-point values also vary with each specific P Index. As noted previously in Chapter 1, most soil test P techniques rely on the use of various chemicals and solutions that do not accurately mimic a natural in-field process. Sharpley et al. (2006) note that to mimic the interaction between surface soil and release of P to runoff water, water extractions are the ideal methods. Therefore, the data and predictive models developed in this study in relation to total P release have the potential to be used as an additional component for a P Index, or other assessment tool, and resulting management and planning strategies, that are more reflective of actual P release into runoff in the Chesapeake Bay watershed.

In Chapter 2, a model was developed by averaging AER24 values by taxonomic Great Groups in the overall modeling dataset, then applying those averaged values to the soil map units in the gSSURGO MuRas\_90m raster layer, based on the map unit's Great Group classification. This process was repeated with the AER24 values and Great Groups from the Chesapeake Bay watershed modeling dataset, and compared to the results from the Chapter 2 model (Figure 3.10). Quartiles for the watershed-specific model (Figure 3.10 (b)) were determined for AER24 values of samples in the Chesapeake Bay watershed modeling dataset, which were used to determine break-points for a potential P loading risk index, as listed in Table 3.8.

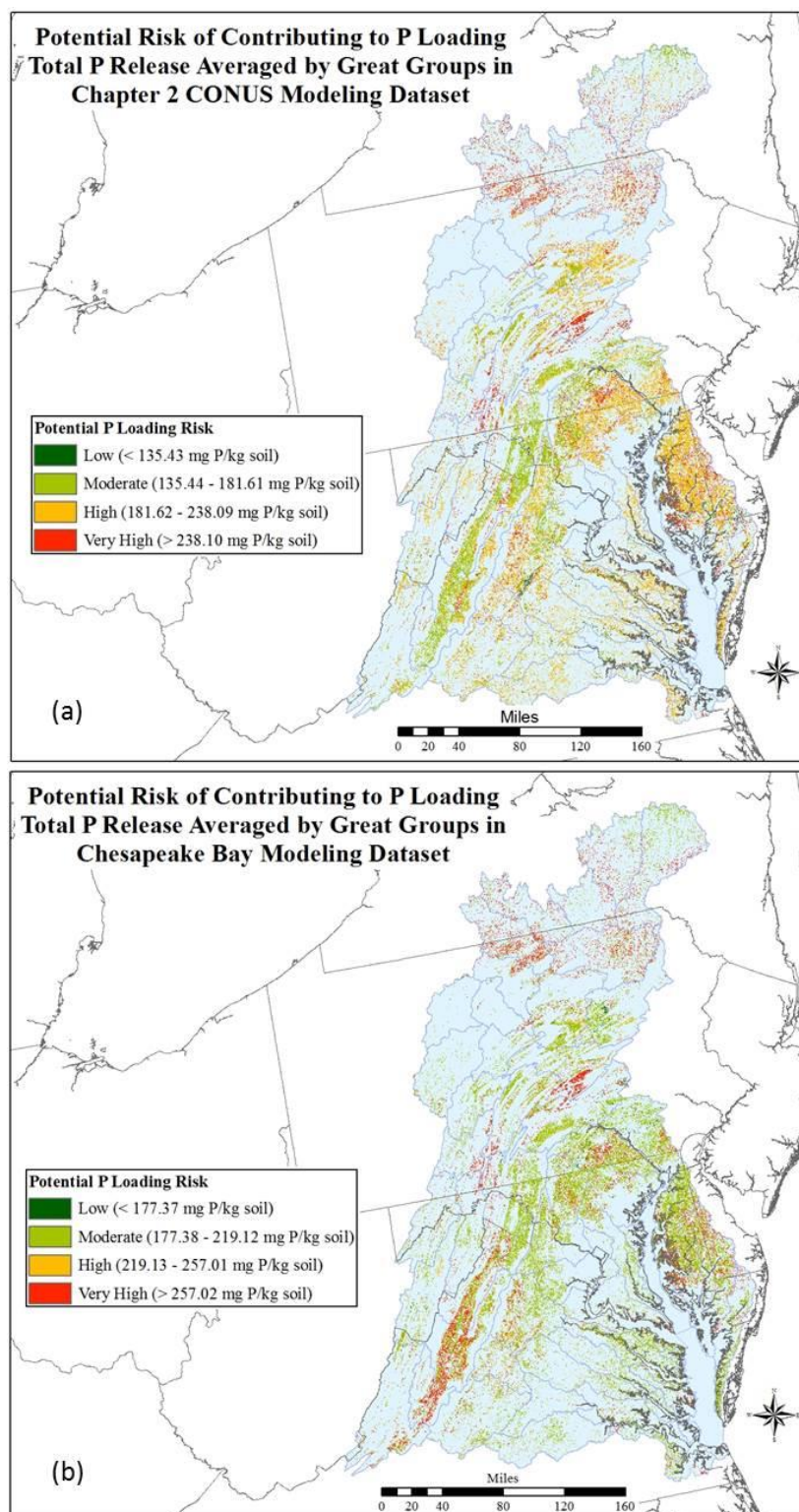


Figure 3.10. Potential risk agricultural soils of the Chesapeake Bay watershed pose to contributing to P loading, with total P release estimated averaged by taxonomic Great Groups from the Chapter 2 CONUS modeling dataset (a) and by taxonomic Great Groups from the Chesapeake Bay watershed modeling dataset (b).

Table 3.8. P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the modeling dataset.

<b>P Index (Potential)</b>	<b>Quartile</b>	<b>AER24</b>
Low	< 25%	$\leq 177.37$
Moderate	25 - 50%	177.38 - 219.12
High	50 - 75%	219.13 - 257.01
Very High	> 75%	> 257.02

Several observations can be made from the comparison of the potential P loading risk maps displayed in Figure 3.10. First, there is slight decrease in the map units that were given averaged total P release values in the model developed using samples from the Chesapeake Bay modeling dataset due to a difference in the number of taxonomic Great Groups used in each model. Table 3.1 lists the taxonomic Great Groups for the samples analyzed in this study, of which there are 14 different Great Groups. The CONUS modeling data in Chapter 2 used to develop the corresponding model included samples that encompassed 81 different taxonomic Great Groups. However, both models indicate that soils in the northern portion of the watershed, specifically in the Glaciated Allegheny Plateau and Catskill Mountains MLRA (Figure 3.2), potentially pose a very high risk, overall, to contributing to P loading in the watershed (Figure 3.8). Both models also indicate very high risk areas in the Northern Appalachian Ridges and Valleys MLRA, in central Pennsylvania. The numerical breaks between the potential risk categories are higher for the model developed using samples from the Chesapeake Bay modeling dataset, which led differences in potential risk designations between the models. Specifically, in the Northern Piedmont, Mid-Atlantic Coastal Plain, and Northern Tidewater Area MLRAs (Figure 3.2), map units designated with high risk potential in the CONUS model are designated with a moderate risk potential in the model

developed using only Chesapeake Bay watershed soils (Figure 3.10). Alternately, in the Southern Appalachian Ridges and Valleys MLRA and the southern portion of the Northern Appalachian Ridges and Valleys MLRA (Figure 3.2), map units designated with a moderate risk potential in the CONUS model are designated with a very high risk potential in the model developed using only Chesapeake Bay watershed soils (Figure 3.10). While both visual models were developed using similar processes, the samples used to develop each model are the drivers behind the differences between the models. If used in combination with additional data and tools for nutrient management planning strategies, these models and the differences between them could potentially have significant effects on not only the allocation of materials, practices, and financial support, but on the overall success of reducing P loading in the watershed system.

## CONCLUSIONS

The Chesapeake Bay watershed is a unique region with a highly variable landscape and soils. Results from this study indicate that the soil P sorption behaviors in this region are predominately related to the amorphous and crystalline Al oxides in the soil, in addition to the clay and total carbon contents. Oxalate or Mehlich-3 extractable soil P tests would be most appropriate for estimating total P desorption or P adsorption in soils of the Chesapeake Bay watershed, as they the most significantly ( $p < 0.05$ ) and highly correlated soil P tests to those P sorption behaviors. The CONUS-level prediction model developed in Chapter 2 for predicting total P release from soil performed similarly to the watershed-specific prediction models developed in this study, and with similar model components, though the watershed-specific models were statistically stronger

models. The modeling dataset from this study and the overall modeling dataset from Chapter 2 also generated very different potential P-loading risk models for agricultural soils within the watershed, with “High” and “Very High” risk areas being located in different areas in each model. The low sample size and high variability of the soils in this region are the likely drivers behind these results. To account for the variability of the landscape and soils within this area, additional research and refinement could focus on developing specific P desorption models for each physiographic region within the area, or by grouping soils by their calcium carbonate content and degree of weathering as relationships and models have been shown to improve by doing so (Chapter 2).

The relationships and models developed in this study have great potential for improving soil P assessment tools in the Chesapeake Bay watershed, and to better inform P management related decision-making at the watershed, farm, and field scales. Additional research and refinement of these models and appropriate potential-risk break-point values is suggested before implementation into assessment tools. Implementing oxalate and Mehlich-3 extraction methods as standard analyses for all soils at soil testing labs like the KSSL, will be necessary to further refine the P desorption models and improve our understanding of soil P sorption behaviors in this region, and elsewhere.

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**APPENDIX G**

DESORPTION REGRESSION EQUATION COMPONENTS TABLE, LOG-  
TRANSFORMED DESORPTION PLOTS, AND REGRESSION MODELING STEPS  
TABLE FOR THE CHESAPEAKE BAY WATERSHED

Table G.1. Linear regression equation<sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for all Chesapeake Bay watershed soils investigated, during the 1-60 minute and 1-24 hour extraction periods.

User Pedon ID	Soil Series	Grouping	Intercept (I)	Slope (S1) (1-60 min)	Slope (S2) (1-24 hr)
			----- mg P/kg soil -----		
00MD039005	Queponco	H	73.02	41.02	58.80
00MD041022	Lenni	H	98.21	55.17	66.22
94MD003013	Butlertown	H	99.73	56.03	92.58
94MD033001	Beltsville	H	107.38	60.32	76.92
94MD033002	Christiana	H	156.70	88.03	43.46
99MD003010	Deale	H	191.07	107.34	163.94
S01MD-039-007	Annemessex	H	108.31	60.85	113.49
S02MD-039-008*	Quindocqua	H	108.53	60.97	45.79
S02MD-039-010*	Manokin	H	138.91	78.04	111.39
S04MD-029-003	Crosiadore	H	68.99	38.76	109.17
S04MD-029-005	Tent	H	182.48	102.52	35.49
S04MD-033-036	Croom	H	88.10	49.50	76.60
00MD041021*	Crosiadore	S	95.51	53.66	57.00
00MD041023	Nassawango	S	107.95	60.64	103.57
97MD045018*	Cedartown	S	44.24	24.86	28.58
98MD021133	Glenelg	S	185.36	104.14	184.56
S08NY003002	Howard	C	76.19	42.80	48.70
86NY025004	Barbour	S	82.74	46.48	75.52
86NY025006	-	S	104.15	58.51	114.05
91NY077006	Chippewa	S	205.95	115.70	258.07
91NY077008	Chenango Fan	S	108.11	60.74	80.05
99NY043001	Honeoye	S	75.29	42.30	71.66
S04PA061-008	Hagerstown	C	126.57	71.10	58.27
99PA027095*	Murrill	H	97.28	54.65	68.94
S01PA-029-007	Chrome	H	81.01	45.51	87.24
S03PA-071-001*	Elioak	H	116.38	65.38	91.77
S03PA-071-002*	Chester	H	134.82	75.74	90.23
S03PA-071-003	Glenelg	H	107.70	60.51	121.42
S04PA027-006	Murrill	H	74.29	41.73	56.51
S04PA027-007*	Murrill	H	103.99	58.42	56.19
S04PA061-009	Hublersburg	H	98.39	55.27	110.03
93PA055038	Allegheny	S	49.64	27.89	48.88
93PA055039	Weikert	S	63.88	35.89	66.79
93PA055040	Weikert	S	104.12	58.50	185.53
S01PA-029-008*	Chrome	S	157.54	88.51	243.90
S04PA027-003	Hagerstown	S	88.73	49.85	85.64
S04PA027-004*	Hagerstown	S	87.53	49.18	62.92

User Pedon ID	Soil Series	Grouping	Intercept (I)	Slope (S1) (1-60 min)	Slope (S2) (1-24 hr)
			----- mg P/kg soil -----		
S04VA-003-001	Rabun	H	85.86	48.24	103.51
S04VA-163-001	Frederick	H	122.23	68.67	74.64
S05WV-037-007	Huntington	C	142.76	80.20	76.13
S05WV-037-006	Braddock	H	170.52	95.80	182.92
S07WV031005	Buchanan	H	119.76	67.28	100.95
S05WV-037-001	Chilhowie	S	75.20	42.25	54.61
S05WV-037-002	Hagerstown	S	111.14	62.44	88.21
S05WV-037-008	Hagerstown	S	75.61	42.48	39.85
S07WV031001	Clarksburg	S	46.15	25.93	52.82

<sup>a</sup>  $P = I + S1 \times (\log h)$  for 1-60 min;  $P = I + S2 \times (\log h)$  for 1-24 hr extraction period; where  $P$  = P released (mg P/kg soil),  $I$  = intercept,  $S1$  = slope of the 1-60 min extraction period,  $S2$  = slope of the 1-24 hr extraction period, and  $h$  = extraction period.

\* Indicates sample in the validation dataset.

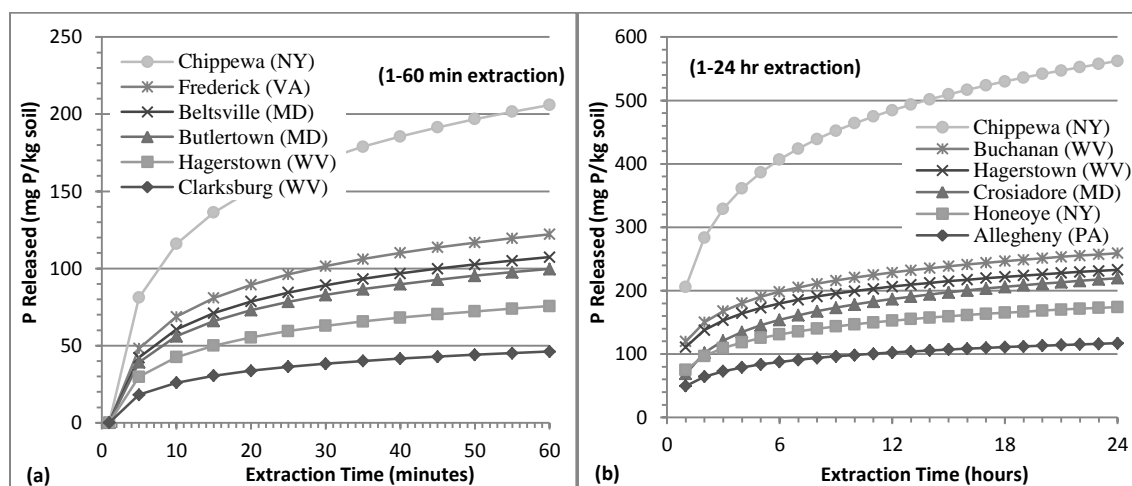


Figure G.1. Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, first quartile, median, mean, third quartile, and maximum for samples in the Chesapeake Bay watershed modeling dataset, during the (a) 1-60 minute and (b) 1-24 hour extraction periods.

Table G.2. An example of the progressive regression modeling method used on samples from the Chesapeake Bay modeling datasets, for AER1 and AER23.

AER1						AER23					
Model	Variable(s)	R <sup>2</sup>	p	MSE	N	Model	Variable(s)	R <sup>2</sup>	p	MSE	N
1	Clay	0.0047	0.6964	40.31	35	1	Clay	0.0274	0.3423	67.06	35
2	TC	0.1661	0.0136	37.18	36	2	TC	0.0151	0.4754	67.54	36
3	pH	0.0450	0.6981	40.63	36	3	pH	0.0139	0.4928	67.58	36
4	Clay TC	0.2202	0.0187	36.23	35	4	Clay TC	0.0315	0.5994	67.95	35
5	Clay pH	0.0191	0.7346	40.63	35	5	Clay pH	0.0624	0.3567	66.86	35
6	TC pH	0.2108	0.0201	36.72	36	6	TC pH	0.0431	0.4836	67.58	36
7	Clay TC pH	0.2744	0.0177	35.51	35	7	Clay TC pH	0.0629	0.5631	67.91	35
8	<b>TC AlOX</b>	0.3397	0.0011	33.59	36	8	<b>Clay AlOX</b>	0.6260	0.0001	42.23	35
9	TC FeOX	0.2112	0.0200	36.71	36	9	Clay FeOX	0.2462	0.0109	59.95	35
10	<b>TC AlOX FeOX</b>	0.3451	0.0033	33.97	36	10	<b>Clay AlOX FeOX</b>	0.6262	0.0001	42.89	35
11	TC AlM	0.0260	0.0222	36.83	36	11	Clay AlM	0.4810	0.0001	49.75	35
12	TC CaM	0.1856	0.0338	37.30	36	12	Clay CaM	0.0363	0.5538	67.79	35
13	TC FeM	0.2453	0.0096	35.91	36	13	Clay FeM	0.1424	0.0856	63.94	35
14	TC MgM	0.1986	0.0259	37.00	36	14	Clay MgM	0.0557	0.3996	67.10	35
15	TC MnM	0.1808	0.0373	37.41	36	15	Clay MnM	0.0807	0.2601	66.20	35
16	TC AlM CaM	0.2930	0.0104	35.29	36	16	<b>Clay AlM CaM</b>	0.5725	0.0001	45.87	35
17	TC AlM FeM	0.2675	0.0176	35.92	36	17	Clay AlM FeM	0.5366	0.0001	47.76	35
18	TC AlM MgM	0.2833	0.0127	35.53	36	18	Clay AlM MgM	0.4870	0.0001	50.25	35
19	TC AlM MnM	0.2091	0.0546	37.33	36	19	Clay AlM MnM	0.4815	0.0001	50.51	35
20	TC FeM CaM	0.2949	0.0100	35.25	36	20	Clay FeM CaM	0.1430	0.1823	64.94	35
21	TC FeM MgM	0.2915	0.0107	35.33	36	21	Clay FeM MgM	0.1680	0.1222	63.99	35
22	TC FeM MnM	0.2924	0.0105	35.31	36	22	Clay FeM MnM	0.2400	0.0345	61.16	35
23	TC CaM MgM	0.2159	0.0481	37.17	36	23	Clay CaM MgM	0.0621	0.5685	67.94	35
24	TC CaM MnM	0.2068	0.0569	37.38	36	24	Clay CaM MnM	0.0844	0.4275	67.13	35
25	TC MgM MnM	0.2079	0.0558	37.36	36	25	Clay MgM MnM	0.1250	0.2400	65.62	35
26	<b>TC CaNH4</b>	0.2902	0.0035	34.82	36	26	Clay CaNH4	0.0365	0.5512	67.78	35
27	TC MgNH4	0.2092	0.0208	36.76	36	27	Clay MgNH4	0.0484	0.4523	67.36	35
28	TC CaNH4 MgNH4	0.3010	0.0088	35.09	36	28	Clay CaNH4 MgNH4	0.0512	0.6472	68.34	35

\*  $p \leq 0.0001$  highlighted in green;  $0.0001 > p \leq 0.01$  highlighted in yellow;  $0.01 > p \leq 0.05$  highlighted in orange; three models with lowest  $p$  and highest  $R^2$  in bold

## CHAPTER 4

### PHOSPHORUS DESORPTION CHARACTERISTICS AND RELATIONSHIPS OF AGRICULTURAL SOILS IN THE UPPER MISSISSIPPI RIVER SUB-BASIN

#### ABSTRACT

The Upper Mississippi River Sub-basin is dominated by agricultural practices, from which phosphorus (P)-loaded runoff is delivered downstream, further contributing to eutrophication problems. Fifty-seven agricultural surface soils from the Upper Mississippi River Sub-basin were analyzed for phosphorus (P) sorption and desorption, using double-point anion exchange resin (DP-AER), P sorption index (PSI), and adsorption isotherm methods. Objectives of this study were to determine relationships between P desorption behaviors and other soil properties, to develop predictive models to provide better estimates of pollution risk at the watershed, farm, and field levels, to compare the effectiveness of watershed-specific models to general national-level models, and possibly improve existing models that predict nutrient losses to target management practices. Linear regression models were developed and validated for each P sorption variable. Results indicate that the soil P sorption behaviors in this region are predominately related to the amorphous and crystalline Al oxides in the soil, in addition to the clay content. Sub-basin-specific prediction models for total P release performed similarly to the overall CONUS-level model developed in Chapter 2. Comparisons of the CONUS-level and Sub-basin-specific potential risk models, however, resulted in distinct differences in areas classified as “High” or “Very High” risk to contributing to P loading

if the surface soil were eroded into runoff, which would have a great effect on management plans developed from the results.

## ABBREVIATIONS

**AER1** - phosphorus released from soil during the 1 hour extraction period (mg P/kg soil); **AER23** - phosphorus released from soil during the 23 hour extraction period (mg P/kg soil); **AER24** - total phosphorus released from soil in 24 hours (mg P/kg soil); **Al<sub>M</sub>** - Mehlich No. 3 extractable aluminum (mg Al/kg); **Al<sub>ox</sub>** - acid oxalate extractable aluminum content (%); **CaCO<sub>3</sub>** - calcium carbonate equivalent (%); **Ca<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Ca<sub>M</sub>** - Mehlich No. 3 extractable calcium (mg Ca/kg); **CONUS** - conterminous United States; **DP-AER** - double-point anion exchange resin; **Fe<sub>M</sub>** - Mehlich No. 3 extractable iron (mg Fe/kg); **Fe<sub>ox</sub>** - acid oxalate extractable iron content (%); **ICP-AES** - inductively coupled plasma atomic emission spectrometry; **KSSL** - Kellogg Soil Survey Laboratory; **Mg<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Mg<sub>M</sub>** - Mehlich No. 3 extractable magnesium (mg Mg/kg); **Mn<sub>M</sub>** - Mehlich No. 3 extractable manganese (mg Mn/kg); **NLCD** - National Land Cover Dataset; **NRCS** - Natural Resources Conservation Service; **NSSC** - National Soil Survey Center; **P<sub>Bray1</sub>** - Bray-1 extractable phosphorus (mg P/kg soil); **P<sub>CaCl2</sub>** - 0.01 M calcium chloride extractable phosphorus (mg P/kg soil); **P<sub>M</sub>** - Mehlich No. 3 extractable phosphorus (mg P/kg soil), measured using ICP-AES; **P<sub>M3</sub>** - Mehlich No. 3 extractable phosphorus (mg P/kg soil), measured using a spectrophotometer at 882 nm; **P<sub>ox</sub>** - acid oxalate extractable phosphorus content (mg P/kg soil); **PSI** - phosphorus sorption index (L/kg); **P<sub>ws</sub>** - water soluble phosphorus content (mg P/kg soil); **SERA-IEG 17** - Southern Extension and



Research Activity - Information Exchange Group 17;  $S_{MAX}$  - phosphorus sorption maximum (mg/kg); **TC** - total carbon content (%); **USDA** - United States Department of Agriculture.

## INTRODUCTION

The Upper Mississippi River Sub-basin watershed is one of six major sub-basins of the Mississippi River basin, the third largest river basin in the world, which drains into the Gulf of Mexico. The Upper Mississippi River Sub-basin includes portions of seven Mid-West states, including South Dakota, Minnesota, Wisconsin, Iowa, Illinois, Indiana, and Missouri. Every summer a large hypoxic zone forms in the Gulf of Mexico, fueled by excess nutrient loads that consume dissolved oxygen and trigger massive algae growths (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2013). Over 60% of the land use in this area is dominated by cropland or pasture agriculture (Jordahl, 2013). Alexander et al. (2008) found that 80% of P entering the Gulf of Mexico comes from agricultural uses (i.e. crops, pasture, and range). Alexander et al. (2008) also noted that the percentage of total phosphorus nutrient load in streams of the Upper Mississippi River Sub-basin that are delivered to the Gulf of Mexico can range from 10 to 90%, further adding to any additional P loading downstream. Several studies from the region have investigated the relationships between various soil test P analyses (Mallarino, 1997), between soil test P and agronomic practices such as manure applications (Atia and Mallarino, 2002), and determining anthropogenic inputs of P to riverine systems (David and Gentry, 2000; Bundy and Sturgul, 2001; Klatt et al., 2003; James and Larson, 2008), but none have examined the relationships between soil P sorption and other soil

properties within this region. Having a better understanding of the soil factors influencing P desorption and better control over the amount of P leaving the Upper Mississippi region is necessary to further combat this environmental issue downstream to the Gulf of Mexico.

Multiple-linear regression prediction models were developed for agricultural surface soils across the conterminous United States (CONUS) in Chapter 2 to better identify agricultural areas that have a high potential for contributing to P export and loading. The objectives of this study were to develop predictive relationships between P desorption behaviors and other soil properties using simple and multiple linear regression models for the Upper Mississippi River Sub-basin. The outcomes of these objectives would then be to (1) identify agricultural soils that contain high amounts of P, relative to their sorptive potential, that would have the most negative effect on surface water if eroded, (2) classify the soils as to their potential to contribute P to surface waters, (3) evaluate how soils retain (adsorption) and release P (desorption), to provide better estimates of pollution risk at the watershed, farm, and field levels, and possibly improve existing models that predict nutrient losses, and (4) determine the effectiveness of a set of region-specific models compared to CONUS-level predictive models.

## **MATERIALS AND METHODS**

### **Laboratory Sample Selection**

Fifty-seven archived agricultural surface soil samples collected from the Upper Mississippi River Sub Basin region by the Natural Resource Conservation Service (NRCS) were analyzed for this study. Samples were selected based on the availability of

following data; (1) spatial location of the pedon and date of collection, more recently collected samples were given a higher preference, (2) pedon location is designated as agricultural land on the 2011 National Land Cover Data (NLCD) geospatial layers, and (3) availability of data in the NSSC-KSSL database on the general properties known to effect P retention (e.g. clay, pH, calcium carbonate, iron and aluminum oxalate, total carbon). Samples were also chosen in an attempt to ensure adequate representation of agricultural soil series of the Upper Mississippi River Sub-basin and spatial randomness. A subset of 11 samples was selected to be used to validate the prediction equations developed to model P desorption and adsorption. Sample locations for both modeling and validation samples from the study area are shown in Figure 4.1 and pedon taxonomic information for each sample is listed in Table 4.1. Table 4.1 reveals that the majority of samples investigated were slightly weathered ( $N = 53$ ), with a few calcareous ( $N = 3$ ) and highly weathered ( $N = 1$ ) soils, as defined by Sharpley et al. (1984). Most of the soils originated from Iowa ( $N = 21$ ) and Illinois ( $N = 17$ ), with the remainder from Wisconsin ( $N = 6$ ), Indiana ( $N = 5$ ), Minnesota ( $N = 5$ ), Missouri ( $N = 2$ ), and South Dakota ( $N = 1$ ). The study samples also represent four of the twelve orders of soil taxonomy; Alfisols ( $N = 26$ ), Mollisols ( $N = 24$ ), Inceptisols ( $N = 4$ ), and Entisols ( $N = 3$ ).

### **Study Area Physiography**

The Upper Mississippi River Sub-basin encompasses portions of five NRCS Land Resource Regions, which are comprised of 35 smaller Major Land Resource Areas (MLRA), geographically associated with land resource units (Figure 4.2). The Northern Minnesota Gray Drift, Northern Minnesota Glacial Lake Basins, Wisconsin central

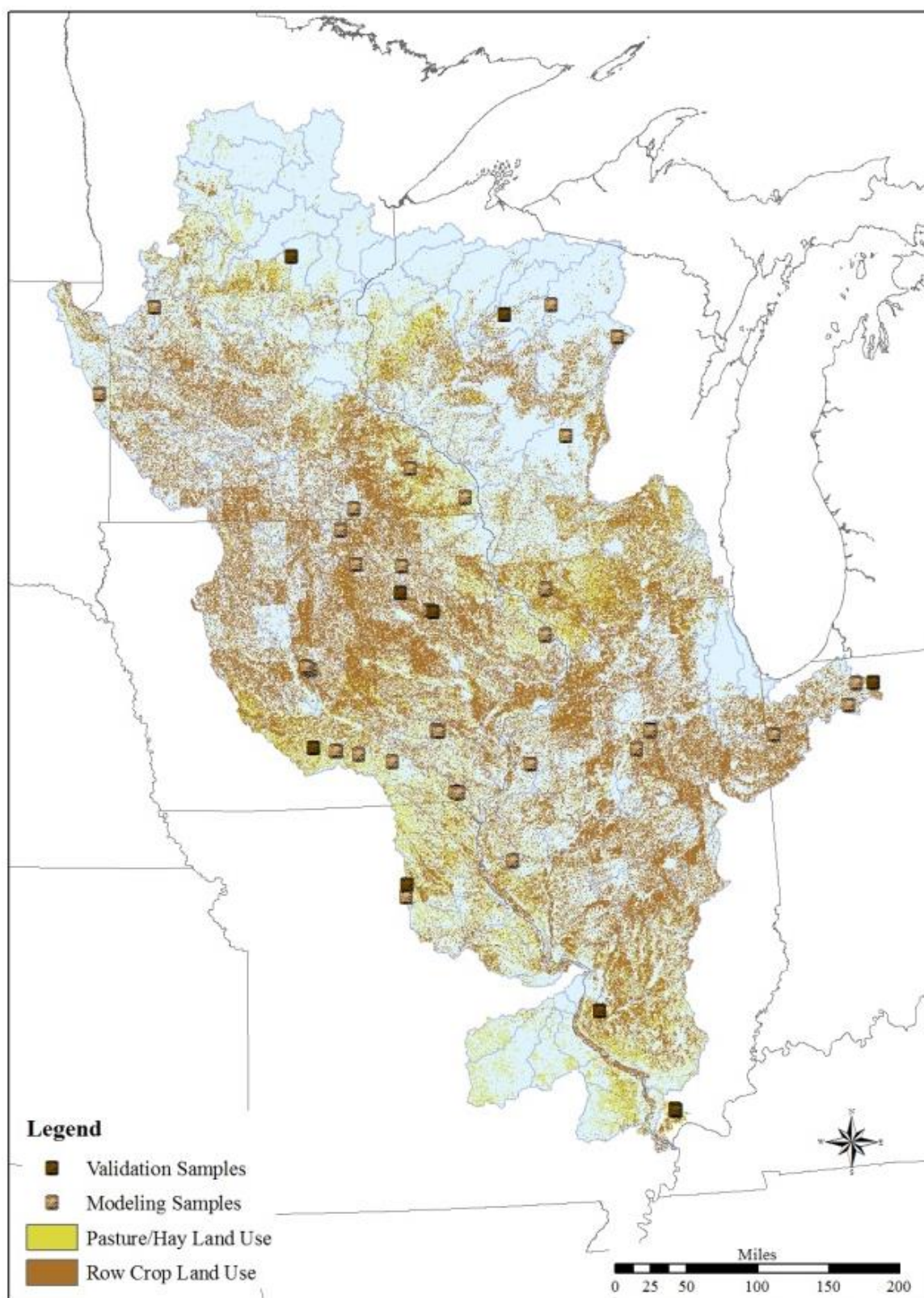


Figure 4.1. Locations of all modeling and validation samples investigated from the Upper Mississippi River Sub-basin study area.

Table 4.1. Classification information for the 57 Upper Mississippi River Sub-basin agricultural surface soils investigated.

State	Pedon	Soil Series	User	Pedon ID	Great Group	Calcareous/ Weathering Group	State	Pedon	Soil Series	User	Pedon ID	Great Group	Calcareous/ Weathering Group
IA	Reedcreek	92IA177003			Udifluvent	Calcareous	IL	Catin	S02IL-099-020			Argiudoll	Slightly Weathered
IA	Tama	86IA005040			Argiudoll	Slightly Weathered	IL	Menfro	S05IL181002			Fragiudalf	Slightly Weathered
IA	Clarion	87IA169001A			Hapludoll	Slightly Weathered	IL	Menfro*	S05IL181003			Hapludalf	Slightly Weathered
IA	Zwingle	92IA105002			Albaqualf	Slightly Weathered	IL	Bunkum	S05IL181004			Hapludalf	Slightly Weathered
IA	Clarion	93IA015001			Argiudoll	Slightly Weathered	IL	Winfield	S05IL181007			Eutrudept	Slightly Weathered
IA	Pershing	94IA117007			Epiaqualf <sup>a</sup>	Slightly Weathered	IL	Winfield*	S05IL181008			Eutrudept	Slightly Weathered
IA	Belinda	94IA117011			Albaqualf <sup>a</sup>	Slightly Weathered	IL	Hosmer*	S05IL181009			Fragiudalf	Slightly Weathered
IA	Sharpsburg*	94IA181001			Argiudoll	Slightly Weathered	IL	Muscatine	S07IL187002			Argiudoll	Slightly Weathered
IA	Sharpsburg	94IA181002			Argistoll	Slightly Weathered	IN	Crosier*	93IN039008			Epiaqualf	Calcareous
IA	Bucknell	95IA107011			Epiaqualf	Slightly Weathered	IN	Brookston	93IN039007			Argiaquoll	Slightly Weathered
IA	Armstrong	95IA107012			Hapludalf	Slightly Weathered	IN	Crumstown	S01IN-141-002			Hapludalf	Slightly Weathered
IA	Rinda	95IA111001			Epiaqualf	Slightly Weathered	IN	Metea	S04IN-099-001			Hapludalf	Slightly Weathered
IA	Bucknell	95IA135002			Epiaqualf	Slightly Weathered	IN	Kentland	S04IN-111-001			Argiaquoll	Slightly Weathered
IA	Gosport	95IA179001			Dystrochrept	Slightly Weathered	MN	Barnes	91MN149001			Hapludoll	Slightly Weathered
IA	Webster	S01IA-015-001			Endoaquoll <sup>a</sup>	Slightly Weathered	MN	Duluth*	94MN095045			Hapludalf	Slightly Weathered
IA	Lawler*	S08IA017001			Hapludoll	Slightly Weathered	MN	Nicollet	96MN085003			Hapludoll <sup>a</sup>	Slightly Weathered
IA	Hayfield*	S08IA019001			Hapludalf	Slightly Weathered	MN	Hayfield	S08MN099001			Hapludalf	Slightly Weathered
IA	Marshall	S08IA019002			Endoaquoll	Slightly Weathered	MN	Marshall	S08MN109001			Endoaquoll	Slightly Weathered
IA	Hayfield	S08IA037001			Hapludalf	Slightly Weathered	MO	Adco	87MO121024			Hapludalf	Slightly Weathered
IA	Marshall	S08IA067001			Endoaquoll	Slightly Weathered	MO	Mexico*	87MO121026			Albaqualf	Slightly Weathered
IA	Lawler	S08IA195001			Hapludoll	Slightly Weathered	SD	Barnes	S07SD039002			Hapludoll	Slightly Weathered
IL	Buckhart	S02IL-099-023			Argiudoll	Calcareous	VI	Dodgeville	S04WI-065-002			Argiudoll	Slightly Weathered
IL	Menfro	S05IL181005			Hapludalf	Highly Weathered	WI	Menahga	94WI057004B			Udipsammen	Slightly Weathered
IL	Coulterville*	93IL163014			Endoaqualf	Slightly Weathered	WI	Menahga	94WI057004C			Udipsammen	Slightly Weathered
IL	Rozetta	94IL001007			Hapludalf	Slightly Weathered	WI	Antigo	98WI067001			Glossudalf	Slightly Weathered
IL	Arrowsmith	94IL123037			Argiudoll	Slightly Weathered	WI	Magnor*	S00WI-099-001			Fragiudept	Slightly Weathered
IL	Alford	96IL181003			Hapludalf	Slightly Weathered	WI	Sconsin	S03WI-107-006			Fraglossudalf	Slightly Weathered
IL	Flanagan	S02IL-099-016			Argiudoll	Slightly Weathered							
IL	Sable	S02IL-099-018			Endoaquoll	Slightly Weathered							
IL	Muscatine	S02IL-099-019			Argiudoll	Slightly Weathered							

\* Indicates sample in the validation dataset.

<sup>a</sup> Indicates Great Group determined from Official Series Description information.

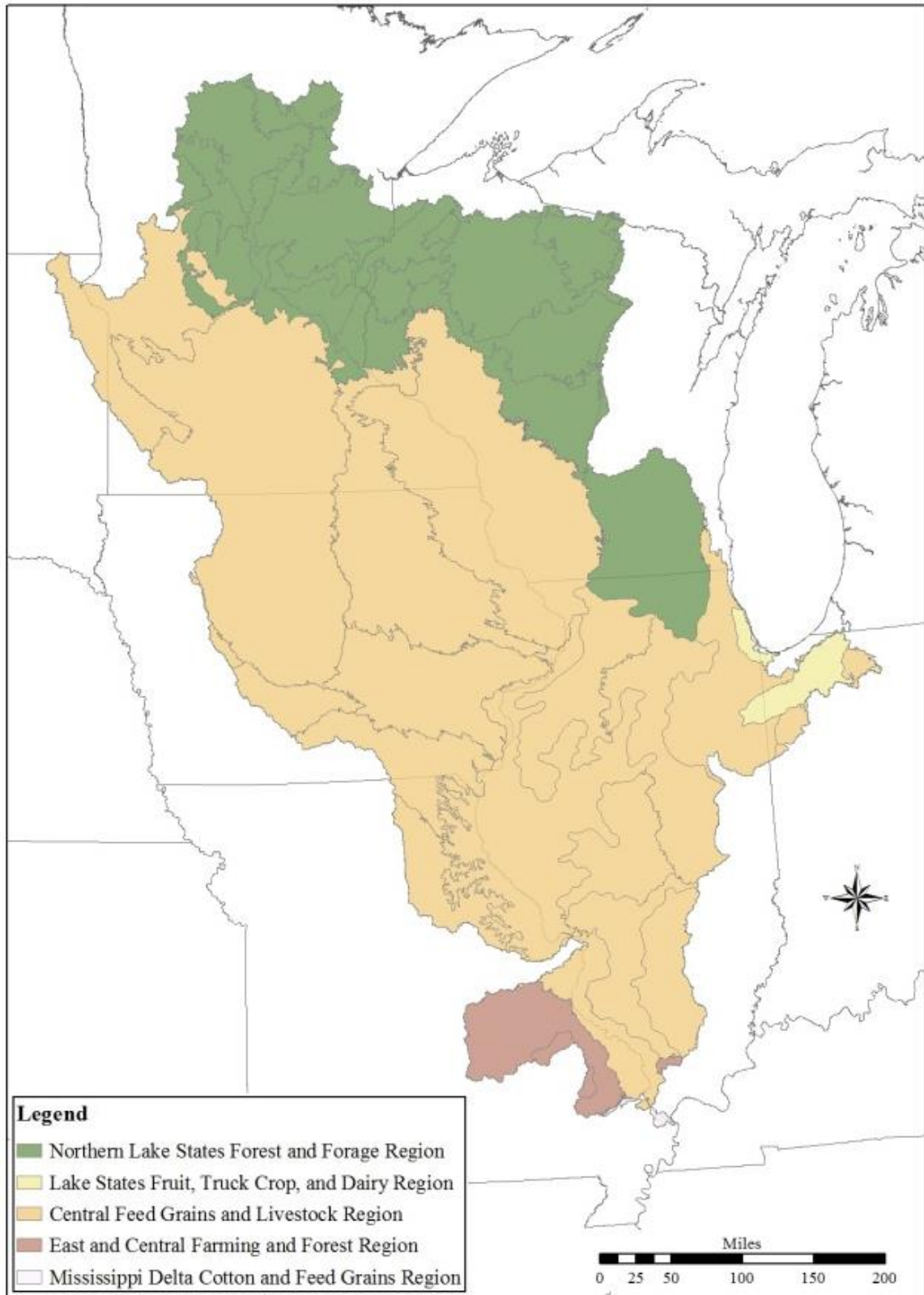


Figure 4.2. USDA NRCS Land Resource Regions of the Upper Mississippi River Sub-basin study area.

Sands, Wisconsin and Minnesota Thin Loess and Till (Northern Part), Wisconsin and Minnesota Thin Loess and Till (Southern Part), Central Minnesota Sandy Outwash, Wisconsin and Minnesota Sandy Outwash, Superior Stony and Rocky Loamy Plains and Hills (Western Part), Superior Stony and Rocky Loamy Plains and Hills (Eastern Part), Northern Highland Sandy Drift, and Southern Wisconsin and Northern Illinois Drift Plain MLRAs comprise the portion of the Northern Lake States Forest and Forage Region in the Sub-basin. The Southwestern Michigan Fruit and Truck Crop Belt and Southern Michigan and Northern Indiana Drift Plain MLRAs comprise the portion of the Lake States Fruit, Truck Crop, and Dairy Region in the Sub-basin. The Rolling Till Prairie, Central Iowa and Minnesota Till Prairies, Eastern Iowa and Minnesota Till Prairies, Northern Mississippi Valley Loess Hills, Iowa and Minnesota Loess Hills, Iowa and Missouri Deep Loess Hills, Illinois and Iowa Deep Loess and Drift (Eastern Part), Illinois and Iowa Deep Loess and Drift (East-Central Part), Illinois and Iowa Deep Loess and Drift (West-Central Part), Illinois and Iowa Deep Loess and Drift (Western Part), Iowa and Missouri Heavy Till Plain, Northern Illinois and Indiana Heavy Till Plain, Indiana and Ohio Till Plain (Northwestern Part), Indiana and Ohio Till Plain (Western Part), Central Claypan Areas, Southern Illinois and Indiana Thin Loess and Till Plain (Western Part), Central Mississippi Valley Wooded Slopes (Western Part), and Central Mississippi Valley Wooded Slopes (Northern Part) MLRAs comprise the portion of the Central Feed Grains and Livestock Region in the Sub-basin. The Ozark Highland, St. Francois Knobs and Basins, and Kentucky and Indiana Sandstone and Shale Hills and Valleys (Southern Part) MLRAs comprise the portion of the East and Central Farming and Forest Region in

the Sub-basin. The Southern Mississippi River Alluvium MLRA comprises the portion of the Mississippi Delta Cotton and Feed Grains Region in the Sub-basin.

The Northern Lake States Forest and Forage Region in the northern portion of the Upper Mississippi River Sub-basin (Figure 4.2), is a glaciated region with numerous lakes and wetlands (USDA-NRCS, 2006). The agricultural soils are primarily Histosols, Alfisols, Spodosols, and Entisols, with Mollisols and Inceptisols to a lesser extent (USDA-NRCS, 2006). Corn, wheat, alfalfa, oats, barley, and soybeans dominate cropland agriculture in this area, and sunflowers, potatoes, beans, sweet corn, peas, berries, and fruit are produce to a lesser extent (USDA-NRCS, 2006). Dairy and beef cattle enterprises are also agriculturally important in this area (USDA-NRCS, 2006).

The Lake States Fruit, Truck Crop, and Dairy Region in the eastern portion of the Upper Mississippi River Sub-basin (Figure 4.2), is characterized as a gently sloping glaciated plain whose soils and climate favor agriculture (USDA-NRCS, 2006). Regional agriculture is dominated by dairy productions, and some beef cattle enterprises (USDA-NRCS, 2006). Canning crops, corn, winter wheat, beans, sugar beets, and fruit are also produced in this region (USDA-NRCS, 2006). The agricultural soils in this region are predominately Alfisols, Entisols, and Spodosols, with some Histosols to a less extent (USDA-NRCS, 2006).

The Central Feed Grains and Livestock Region, which covers the majority of the Upper Mississippi River Sub-basin (Figure 4.2), is a gently sloping dissected glaciated plain, whose soils and climate also favor agriculture (USDA-NRCS, 2006). This area is famous for its production of corn, soybeans, and feed grains, as well as beef cattle production (USDA-NRCS, 2006). Agricultural soils in this region are primarily Alfisols,



Entisols, Inceptisols, and Mollisols, with some Histosols to a lesser extent (USDA-NRCS, 2006).

The East and Central Farming and Forest Region, which covers a small area of the southern portion of the Upper Mississippi River Sub-basin (Figure 4.2), is characterized by nearly level to gently rolling uplands, floodplains, and stream terraces, areas of Precambrian knobs and hills, and deeply dissected sedimentary hills (USDA-NRCS, 2006). Agricultural soils in this region are primarily Alfisols (USDA-NRCS, 2006). Regional agriculture is dominated by forage and grain production for regional beef and dairy cattle enterprises (USDA-NRCS, 2006).

The small portion of the Mississippi Delta Cotton and Feed Grains Region at the southern-most point of the Upper Mississippi River Sub-basin (Figure 4.2), is an alluvial plain landscape (USDA-NRCS, 2006). Cropland agricultural in this area is dominated by soybeans and corn, and rice to a lesser extent (USDA-NRCS, 2006). Agricultural soils in this region are predominately Alfisols, Vertisols, Inceptisols, and Entisols (USDA-NRCS, 2006).

### **Standard Sample Characterization Analyses**

All samples in this study received laboratory characterization by analytical procedures described in the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004) with representative alphanumeric codes for standard operating procedures in parentheses. All standard analyses were performed on air-dried <2-mm soil, with resulting data reported on an oven-dry basis. Analyzed characterization properties included particle-size analysis, total carbon, acid oxalate extractable Al, Fe,

and P, Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P), cation exchange capacity, pH, calcium carbonate equivalent, and water extractable P.

Particle-size analysis was determined by sieve and pipette (3A1a), following pre-treatments for removal of organic matter and soluble salts, and chemical dispersion with sodium hexametaphosphate. Total carbon (TC) content was determined by dry combustion (4H2a) on air-dried <180- $\mu\text{m}$  (80 mesh) soil. Acid oxalate (4G2a) extracts were analyzed for  $\text{Fe}_{\text{OX}}$ ,  $\text{Al}_{\text{OX}}$ , and  $\text{P}_{\text{OX}}$  by inductively coupled plasma atomic emission spectrometry (ICP-AES). Mehlich-3 (4D6b) extracts were analyzed for  $\text{Al}_{\text{M}}$ ,  $\text{Ca}_{\text{M}}$ ,  $\text{Fe}_{\text{M}}$ ,  $\text{Mg}_{\text{M}}$ ,  $\text{Mn}_{\text{M}}$ , and  $\text{P}_{\text{M}}$  by ICP-AES, and Mehlich-3 (4D6a) extractable phosphorus ( $\text{P}_{\text{M3}}$ ) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm. Soil pH (4C1a2a) was measured using a 1:1 soil-water solution. Calcium carbonate ( $\text{CaCO}_3$ ) equivalent (4E1a1a1a1) was determined by treating the soil with hydrochloric acid, manometrically measuring the evolved carbon dioxide, and then calculating the percent  $\text{CaCO}_3$ . Ammonium acetate extractable calcium ( $\text{Ca}_{\text{NH}_4}$ ) and magnesium ( $\text{Mg}_{\text{NH}_4}$ ) were measured with  $\text{NH}_4\text{OAc}$  buffered at pH 7.0 (4B1a) and measured by ICP-AES. Water extractable phosphorus (4D2a) ( $\text{P}_{\text{ws}}$ ) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm.

### **Sample Phosphorus Sorption Analyses**

The primary objective in selecting methods was to choose methods that could simulate natural field conditions, meet the objectives of determining the maximum capacity of agricultural soils to hold phosphorus (P capacity), and determine how much P would desorb from eroded sediment. To determine P capacity, the standard “P sorption

index” (PSI) method outlined by Sims in SERA-IEG 17 (2009) was utilized. The method used to determine phosphorous desorption was the standard double-point anion exchange resin (DP-AER) method, as outlined in Elrashidi et al (2003) and the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004). The standard method of P adsorption isotherm determination, as proposed originally proposed in Nair et al. (1984), and again by Graetz and Nair in SERA-IEG 17 (2009), was used to further understand the P retention and sorption capacity of the soils.

#### *P Sorption Index (PSI)*

This single-point isotherm method was developed to overcome the limitations of the more time-consuming and complicated standard P adsorption isotherm methods. PSI has been found by several researchers to be well correlated with soil P adsorption maxima and a wide variety of chemical and physiological properties (Bache and Williams, 1971; Mozaffari and Sims, 1994; Sharpley et al., 1984; Simard et al., 1994). As outlined by Sims in SERA-IEG 17 (2009) following the Bache and Williams (1971) method, 2.25-g, <2-mm, air-dried soil sample was shaken at room temperature with 45 mL of a 75 mg P/L as  $\text{KH}_2\text{PO}_4$  solution and two drops of chloroform to inhibit microbial activity for 18 hours at 100 oscillations/min. The sample was then centrifuged at 2000 rpm for 30 minutes, after which the sample extract was filtered using a Whatman 45 filter. The P-saturated soil samples were allowed to air-dry and used to analyze soil P desorption with the double-point anion exchange resin procedure (following). P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962). PSI (L/kg) of the soil sample was then determined with the following equations:

$$\text{PSI (L/kg)} = X / \log C \quad [4.1]$$

where X is the amount of P adsorbed (mg P/kg) and C is the concentration of P after 18 hour equilibration (mg/L).

#### *Double-Point Anion Exchange Resin*

An anion exchange resin technique using a soil and water suspension and a dilute sodium chloride extracting solution, was found to be a sufficient method for estimating the quantity of P released and the rate of P-release from soil. This method is analogous to a more natural process for P removal from soil solution than attempting to estimate P release with the various chemical extracts utilized in other P methods (Amer et al., 1955). Following Elrashidi et al (2003) and Burt (2004), a 2-gram, <2-mm, air-dried soil sample, was shaken with a 4-gram perforated bag of spherical anion exchange resin beads and 100 mL of deionized water for 1 hour at 100 oscillations/min at room temperature. The resin bag was removed from the soil suspension and shaken with 50 mL of 1.0 M sodium chloride (NaCl) for 1 hour to remove P retained by the resin. Another 4-gram resin bag was added to the soil suspension and shaken for an additional 23 hours at 100 oscillations/min at room temperature. The second resin bag was removed and rinsed with 1.0 M NaCl and shaken for 1 hour. The NaCl extracting solutions were filtered to 150 mm using Whatman 42 filter paper. A 2- mL concentration of 12 N hydrochloric acid (HCl) was added to each filtered extract. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) using a spectrophotometer at 880 nm, within 72 hours of extraction. Extract P (mg/L) was then converted to mass of soil P (mg/kg) using the following equation:

$$\text{AER (mg/kg)} = [(A*B*C*R*1000)/E] \quad [4.2]$$

where A is the sample extract concentration (mg/L), B is the extract volume (L), C is the dilution (if performed), R is the air-dry/oven-dry weight ratio, and E is the sample weight (g), for P released after one hour (AER1), P released after an additional 23 hours (AER23), and total P released after a total of 24 hours (AER24).

#### *Phosphorus Adsorption Isotherm Determination*

Phosphorus adsorption isotherms were performed following the method of Graetz and Nair (2009). A 0.75-g, <2-mm, air-dried soil sample was shaken for 24 hours at 100 oscillations/min at room temperature with 20 mL of a 0.01 M calcium chloride ( $\text{CaCl}_2$ ) solution containing 0, 0.1, 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 mg P/L as  $\text{KH}_2\text{PO}_4$  and two drops of chloroform to inhibit microbial activity. The sample was then centrifuged at 3000 rpm for 10 minutes, after which the sample extract was filtered using a Whatman 45 filter. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) at 880 nm using a spectrophotometer, within 72 hours of extraction. 0.01 M calcium chloride extractable phosphorus ( $\text{P}_{\text{CaCl}_2}$ ) was then determined from the extracts from the soil mixed with the  $\text{CaCl}_2$  solution containing 0 mg P/L. Results were analyzed and sorption parameters were determined using the linearized Langmuir equation:

*Linearized Langmuir equation:*

$$C / S = (1 / kS_{\text{MAX}}) + (C / S_{\text{MAX}}) \quad [4.3]$$

where S is the total amount of P retained (mg/kg), C is the concentration of P after 24 hour equilibration (mg/L),  $S_{\text{MAX}}$  is the P sorption maximum (mg/kg), and k is a constant related to the bonding energy (L/mg P).

### *Statistical Analysis*

Study samples were analyzed using routine statistical analyses, including descriptive statistics, correlation, and multiple linear regression using the statistical software program, SAS<sub>TM</sub> v. 9.4. The assumptions of the Person correlation include (a) each variable is continuous in measurement, (b) each observation has a pair of values, (c) the absence of outliers in either variable, (d) the normality of each variable, (e) a linear relationship between variables, and (f) homoscedasticity, a tube-like shape between values on a scatterplot and the linear trend line between the variables. The assumptions of multiple linear regression include (a) a linear relationship between the independent and dependent variables, (b) multivariate normality, (c) no or little multicollinearity, (d) no auto-correlation, and (e) homoscedasticity. The SAS CORR procedure with the PEARSON option was used for correlation analyses, while the REG procedure was used for regression analyses and to develop the final prediction equations. Not all assumptions were met when study data was applied to the correlation and regression analyses.

## **RESULTS AND DISCUSSION**

### **Phosphorus Sorption Relationships with Soil Properties**

Descriptive statistics were determined for both the modeling (Table 4.2) and validation datasets (Table 4.3). From this data, it is apparent that the soils examined in this study varied widely in physical and chemical properties known to influence P sorption in soils. Property ranges and averages for the samples in the validation dataset were narrower than those of the modeling dataset. Average clay was 22.48 %, average

Table 4.2. Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the modeling dataset.

	Clay	Silt	Sand	TC	CuCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>M</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	Ca <sub>SH</sub>	Mg <sub>SH</sub>	P <sub>ox</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>bio1</sub>	P <sub>WS</sub>	P <sub>Cd12</sub>	AER1	AER23	AER24	PSI	S <sub>MAX</sub>	
	----- % -----			-----			-----			-----			-----			-----			-----			-----			L/kg		mg/kg
Mean	22.48	52.55	24.97	2.42	0.04	6.14	1178.26	3256.52	629.21	2422.84	183.98	417.44	112.88	15.40	3.93	359.48	64.49	65.61	46.00	0.36	2.23	112.29	93.03	205.32	119.81	225.17	
Standard Error	1.46	3.20	4.05	0.19	0.03	0.12	64.97	246.63	30.60	222.60	16.33	41.88	12.51	1.38	0.40	42.31	6.67	11.82	15.49	0.08	0.65	5.50	6.50	10.74	8.45	23.98	
95% Confidence Level for Mean	2.94	6.44	8.15	0.37	0.06	0.25	130.86	496.74	61.72	448.92	32.93	84.46	25.23	2.78	0.81	85.21	13.46	23.81	31.68	0.16	1.30	11.08	13.10	21.62	17.02	48.30	
Median	25.45	59.55	13.10	2.09	0.00	6.30	1100.00	3100.00	622.45	2402.70	146.25	400.20	98.00	15.00	3.55	294.05	52.60	39.70	24.60	0.19	0.72	111.96	80.07	198.39	111.57	227.74	
Minimum	1.70	1.30	1.10	0.42	0.00	4.10	400.00	500.00	62.90	81.40	20.10	12.90	15.10	0.00	0.10	81.70	10.50	1.30	3.00	0.00	0.00	28.26	27.32	55.57	35.47	13.64	
Maximum	41.90	83.10	97.00	5.93	1.00	7.70	2200.00	7000.00	1079.90	6518.80	558.00	1164.00	529.20	41.90	11.50	1790.40	229.80	351.70	472.00	3.06	26.72	204.46	285.83	466.65	319.17	769.23	
N	46	46	46	46	46	46	46	46	44	44	44	44	44	46	46	46	44	46	30	46	46	46	46	46	46	46	46

Table 4.3. Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the validation dataset.

	Clay ----- % -----	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>cl</sub>	C <sub>cl</sub>	Fe <sub>cl</sub>	Mg <sub>cl</sub>	Mn <sub>cl</sub>	Cd <sub>cl</sub>	Mg <sub>cl</sub>	P <sub>ox</sub>	P <sub>cl</sub>	P <sub>mt</sub>	P <sub>bt</sub>	P <sub>vs</sub>	P <sub>cacl2</sub>	AER1	AER23	AER24	PSI	S <sub>max</sub> mg/kg
Mean	20.04	1.99	0.09	6.04	1209.09	4354.55	371.27	1104.81	125.23	175.07	151.95	12.75	2.99	370.52	78.48	59.92	47.47	0.28	-	126.61	90.08	216.69	102.60	-
Standard Error	2.05	0.28	0.09	0.30	137.81	449.11	23.39	115.43	9.88	24.27	21.45	1.53	0.43	45.43	17.37	16.35	13.19	0.09	-	10.61	7.47	17.00	14.16	-
95% Confidence Level for Mean	4.56	0.62	0.20	0.67	307.06	1000.69	52.11	257.20	22.01	54.08	47.79	3.42	0.97	101.22	38.71	36.43	29.39	0.21	-	23.64	16.65	37.88	31.55	-
Median	19.30	1.68	0.00	5.90	1100.00	4400.00	368.30	1090.20	112.60	173.60	143.30	11.30	2.90	365.80	63.80	29.90	33.60	0.10	-	120.10	94.69	215.58	91.72	-
Minimum	9.10	0.96	0.00	4.60	700.00	1900.00	271.80	390.20	94.70	55.60	41.10	3.60	0.90	111.00	27.40	18.00	13.00	0.10	-	58.32	49.84	108.16	43.49	-
Maximum	30.40	3.68	1.00	7.50	1900.00	6200.00	493.20	1663.90	192.60	320.30	234.70	20.00	5.20	608.70	206.30	172.80	161.00	1.00	-	180.98	131.76	312.74	175.86	-
N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	0	11	11	11	11	0



TC was 2.42 %, and average  $\text{CaCO}_3$  contents was 0.04 %, for the samples in the modeling dataset. Average pH for the samples in the modeling dataset was 6.14, and 6.04 for the samples in the validation dataset. The overall range of pH for all samples was 4.1 to 7.7. Average  $\text{Al}_{\text{OX}}$  and  $\text{Fe}_{\text{OX}}$  for the samples in the modeling dataset were 1178.26 mg Al/kg soil and 3256.52 mg Fe/kg soil, respectively. Average  $\text{Al}_{\text{M}}$  was 629.21 mg Al/kg soil, average  $\text{Fe}_{\text{M}}$  was 183.98 mg Fe/kg soil, and average  $\text{Mn}_{\text{M}}$  was 112.88 mg Mn/kg soil for samples in the modeling dataset. Average  $\text{Ca}_{\text{M}}$  and  $\text{Mg}_{\text{M}}$  for samples in the modeling dataset were 2422.84 mg Ca/kg soil and 417.44 mg Mg/kg soil, respectively. Average  $\text{Ca}_{\text{NH}_4}$  was 15.40 cmol/kg and average  $\text{Mg}_{\text{NH}_4}$  was 3.93 cmol/kg for samples in the modeling dataset.

The P sorption variables investigated in this study also varied widely. Boxplots were developed for the AER variables for both the modeling and validation datasets (Figure 4.3). Boxplots were also developed for the PSI (Figure 4.4) and  $S_{\text{MAX}}$  (Figure 4.5) variables in the modeling and validation datasets. The ranges and averages for the P sorption variables were also narrower than those of the modeling dataset. Average AER1 was 112.29 mg P/kg soil, average AER23 was 93.03 mg P/kg soil, and average AER24 was 205.32 mg P/kg soil for samples in the modeling dataset. The average PSI for the samples in the modeling dataset was 119.81 L/kg.  $S_{\text{MAX}}$  was only determined on the samples in the modeling dataset, which had an average of 225.17 mg/kg.

Pearson correlation coefficients were calculated for the samples in the modeling dataset, between the P sorption variables and soil properties known to affect P sorption in soils (Table 4.4). AER1 was significantly ( $p < 0.05$ ) correlated with clay,  $\text{Mg}_{\text{M}}$ ,  $\text{Al}_{\text{OX}}$ ,  $\text{Ca}_{\text{M}}$ ,  $\text{Ca}_{\text{NH}_4}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Mg}_{\text{NH}_4}$ , and pH, respectively. AER23 was significantly correlated with

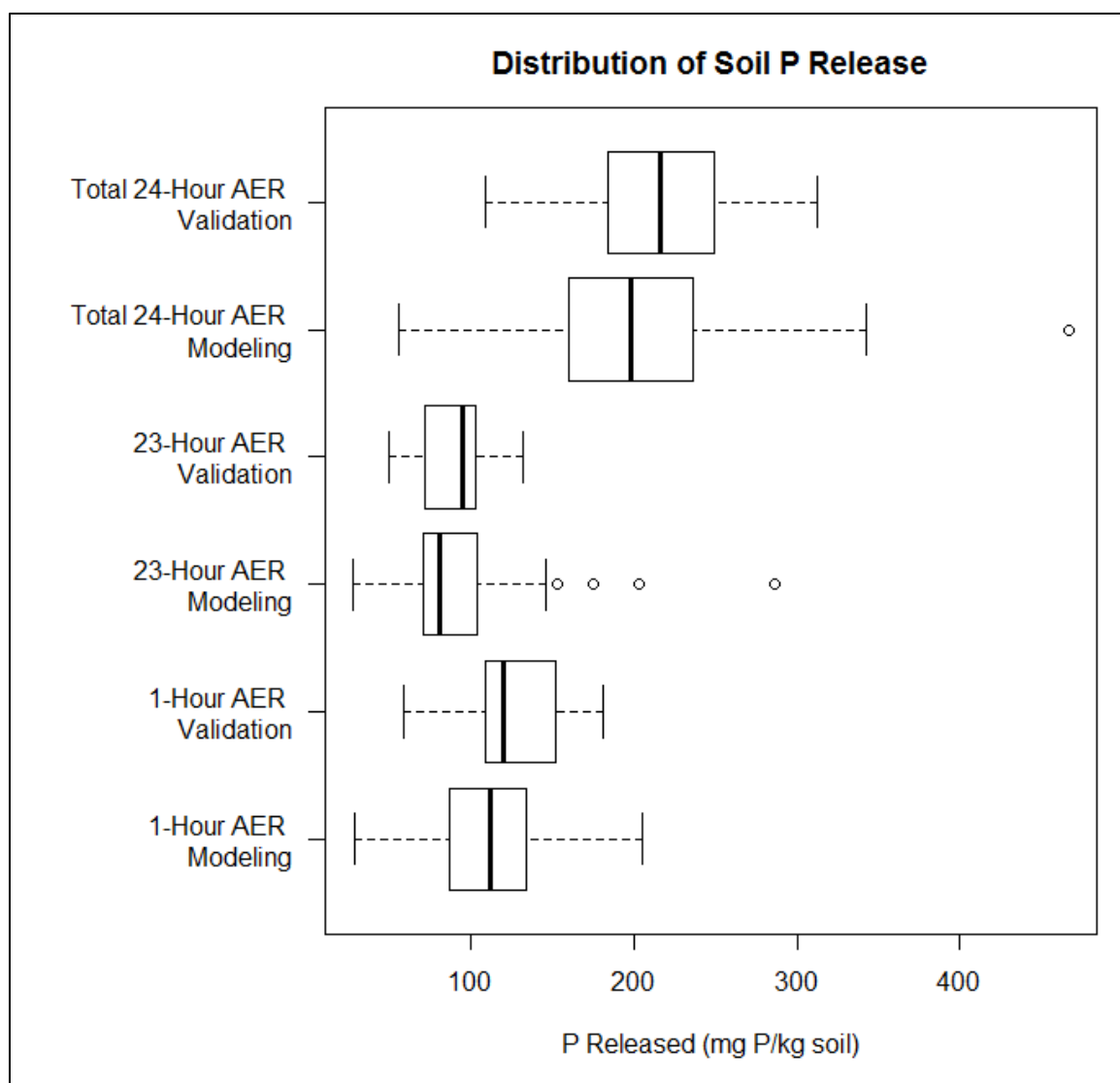


Figure 4.3. Boxplots displaying the quartile statistics of each measured AER variable for the Upper Mississippi River Sub-basin modeling and validation datasets.

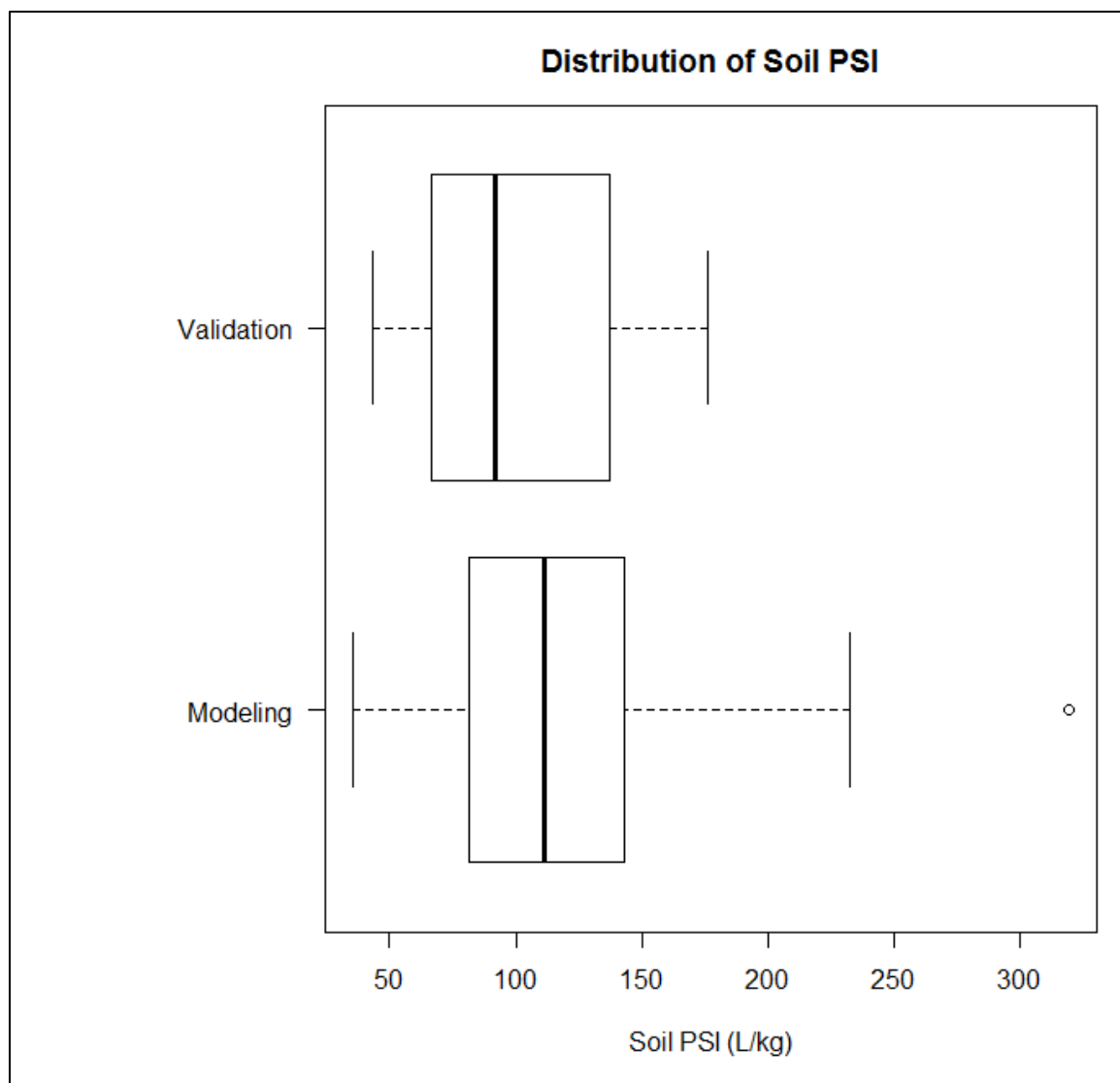


Figure 4.4. Boxplots displaying the quartile statistics for the PSI variable for the Upper Mississippi River Sub-basin modeling and validation datasets.

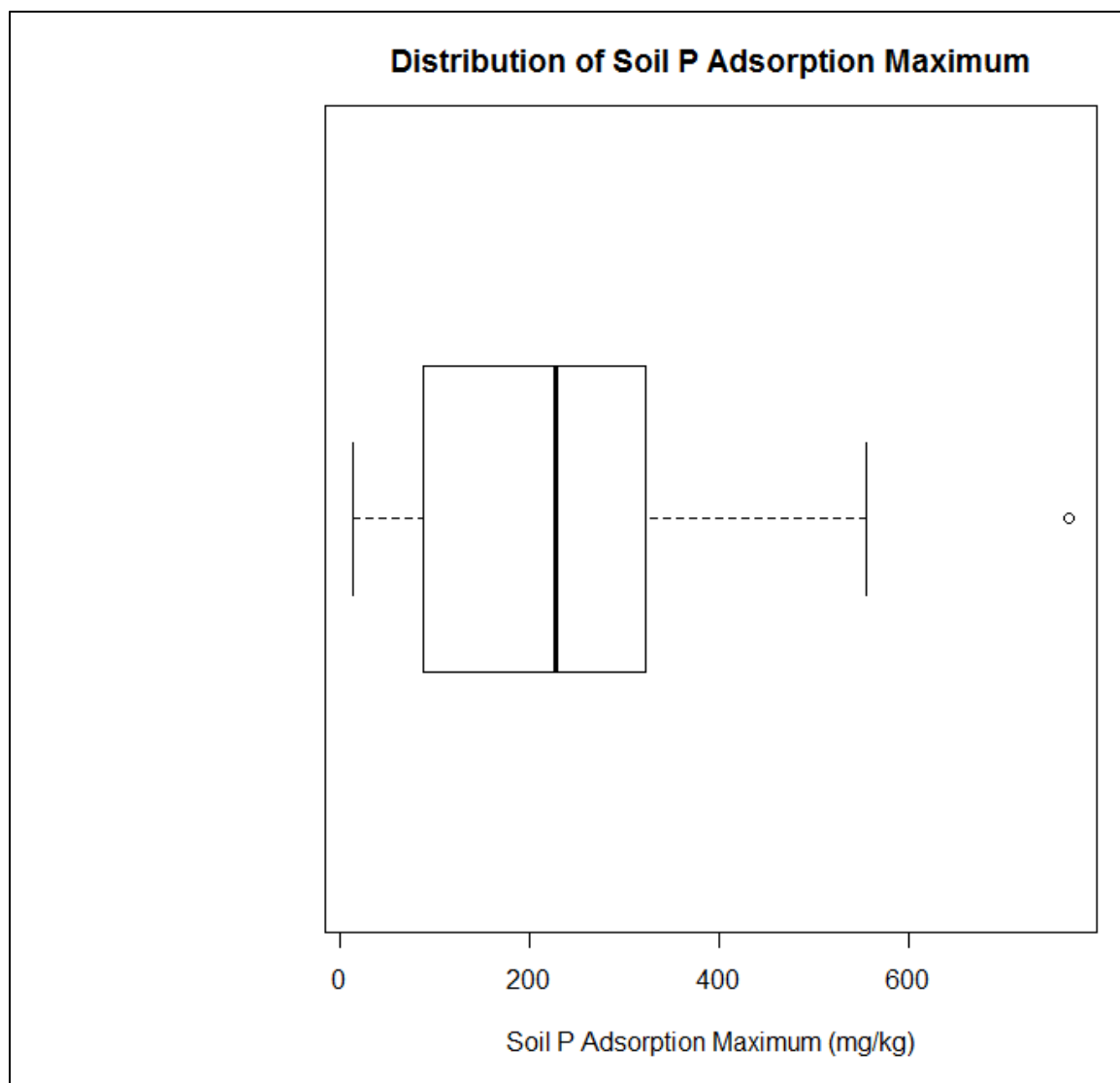


Figure 4.5. Boxplot displaying the quartile statistics for the  $S_{MAX}$  for the Upper Mississippi River Sub-basin modeling dataset.

Table 4.4. Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption, for samples in the modeling dataset.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>h</sub>	Ca <sub>M</sub>	Fe <sub>M</sub>	Mg <sub>M</sub>	Mn <sub>M</sub>	C <sub>ANH4</sub>	M <sub>GNH4</sub>
AER1	<b>0.7051***</b>	0.2661	0.0635	0.3916**	0.6468***	0.4676**	0.1463	0.5152**	-0.0085	<b>0.6521***</b>	0.0418	0.4793**	0.4263**
AER23	0.2234	0.1699	-0.1096	-0.0156	0.4377**	0.5044**	0.3339*	0.1391	0.4296**	0.1710	0.1990	0.0916	0.0745
AER24	0.4968**	0.2393	-0.0339	0.1913	0.5967***	0.5452***	0.2648	0.3760*	0.2272	0.4732**	0.1320	0.3012*	0.2636
PSI	0.3505*	0.1240	-0.1301	-0.1738	0.5397**	0.4865**	0.3828*	0.1883	0.0938	0.2005	0.1273	0.0666	0.0229
S <sub>max</sub>	0.1713	0.0567	-0.0164	-0.1607	0.2532	0.3387*	0.3645*	-0.0153	0.3867**	-0.0794	0.2524	-0.0385	0.0300

\* $p \leq 0.05$ ; \*\* $p \leq 0.01$ ; \*\*\* $p \leq 0.001$ ; significant correlation coefficients  $\geq 0.65$  in bold.

$\text{Fe}_{\text{OX}}$ ,  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{M}}$ , and  $\text{Al}_{\text{M}}$ , respectively. AER24 was significantly correlated with  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ , clay,  $\text{Mg}_{\text{M}}$ ,  $\text{Ca}_{\text{M}}$ , and  $\text{Ca}_{\text{NH}_4}$ , respectively. PSI was significantly correlated with  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Al}_{\text{M}}$ , and clay, respectively, while  $\text{S}_{\text{MAX}}$  was significantly correlated with  $\text{Fe}_{\text{M}}$ ,  $\text{Al}_{\text{M}}$ , and  $\text{Fe}_{\text{OX}}$ , respectively.

These correlations indicate that P sorption is primarily influenced by clay, Al and Fe oxides, and calcium and magnesium ions in the soils of the Upper Mississippi River Sub-basin. The influence of calcium and magnesium ions of the soils is apparent in readily desorbable P (AER1) and total desorbable (AER24). More tightly bound and slowly desorbable P (AER23) is only influenced by the Al and Fe oxides in these soils. All soil P sorption variables, except  $\text{S}_{\text{MAX}}$ , are significantly correlated with the amorphous forms of Al and Fe, while AER23, PSI, and  $\text{S}_{\text{MAX}}$  are also significantly correlated with the crystalline forms of Al and/or Fe. These findings are similar to those noted by Burt et al. (2002), Sharpley et al. (1989), and McCallister and Logan (1978).

### **Phosphorus Sorption Relationships with Soil P Tests**

Extracted P also varied greatly in the study soils (Tables 4.2 and 4.3). Average soil test P values decreased in the following pattern in the modeling dataset:  $\text{P}_{\text{OX}} > \text{P}_{\text{M}_3} > \text{P}_{\text{M}} > \text{P}_{\text{Bray1}} > \text{P}_{\text{CaCl}_2} > \text{P}_{\text{WS}}$ . Average  $\text{P}_{\text{M}}$  was greater than average  $\text{P}_{\text{M}_3}$  in the validation dataset. Average  $\text{P}_{\text{OX}}$ ,  $\text{P}_{\text{M}}$ , and  $\text{P}_{\text{Bray1}}$  values were greater for samples in the validation dataset while average  $\text{P}_{\text{M}_3}$  and  $\text{P}_{\text{WS}}$  values were lower for samples in the validation dataset. Like  $\text{S}_{\text{MAX}}$ ,  $\text{P}_{\text{CaCl}_2}$  was not determined for samples in the validation dataset.

Pearson correlation coefficients were calculated between the P sorption variables and soil P tests for the samples in the modeling dataset (Table 4.5). AER1 and PSI were

Table 4.5. Correlations coefficients between the P sorption variables and soil P tests, for samples in the modeling dataset.

	P <sub>ox</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bray1</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.1868	0.1048	0.2725	0.3086	0.3079*	0.3091*
AER23	0.2755	0.4901**	0.3759**	<b>0.7484***</b>	<b>0.6637***</b>	<b>0.7003***</b>
AER24	0.2626	0.3261*	0.3674*	0.6280**	0.5598***	0.5826***
PSI	0.1563	-0.1677	-0.1410	-0.3383	-0.3567*	-0.3091*
S <sub>max</sub>	0.2505	0.2943	0.1189	0.0678	0.1284	0.1092

\* $p \leq 0.05$ ; \*\* $p \leq 0.01$ ; \*\*\* $p \leq 0.001$ ; significant correlation coefficients  $\geq 0.65$  in bold.

significantly ( $p < 0.05$ ) correlated with P<sub>WS</sub> and P<sub>CaCl2</sub>. AER23 and AER24 were significantly correlated with P<sub>Bray1</sub>, P<sub>CaCl2</sub>, P<sub>WS</sub>, P<sub>M</sub>, and P<sub>M3</sub>. S<sub>MAX</sub> was not significantly correlated with any soil P test. From these correlations, it is apparent that readily desorbable P is related to water soluble forms of soil P, while total desorbable P is related to more plant-available forms soil P. The significant correlations of AER24 reflect the influence of the more tightly bound and slowly desorbable soil P on total P desorption. P adsorption appears to be negatively related to the water soluble and readily available forms of soil P.

### Phosphorus Release Characteristics

Figure 4.6 shows the relationship between the predicted P released (mg P/kg soil) and the AER extraction periods (minutes (a, c) and hours (b, d)) that represent the minimum, first quartile, median, mean, third quartile, and maximum P released for the soils from the modeling dataset (a, b) and soils from the validation dataset (c, d). For soils from the modeling dataset investigated in this study ( $N = 46$ ), an average of 55 % of P was released during the first hour of AER extraction, while the remaining 45 % of P was released during the following 23 hours of AER extraction. For soils in the validation

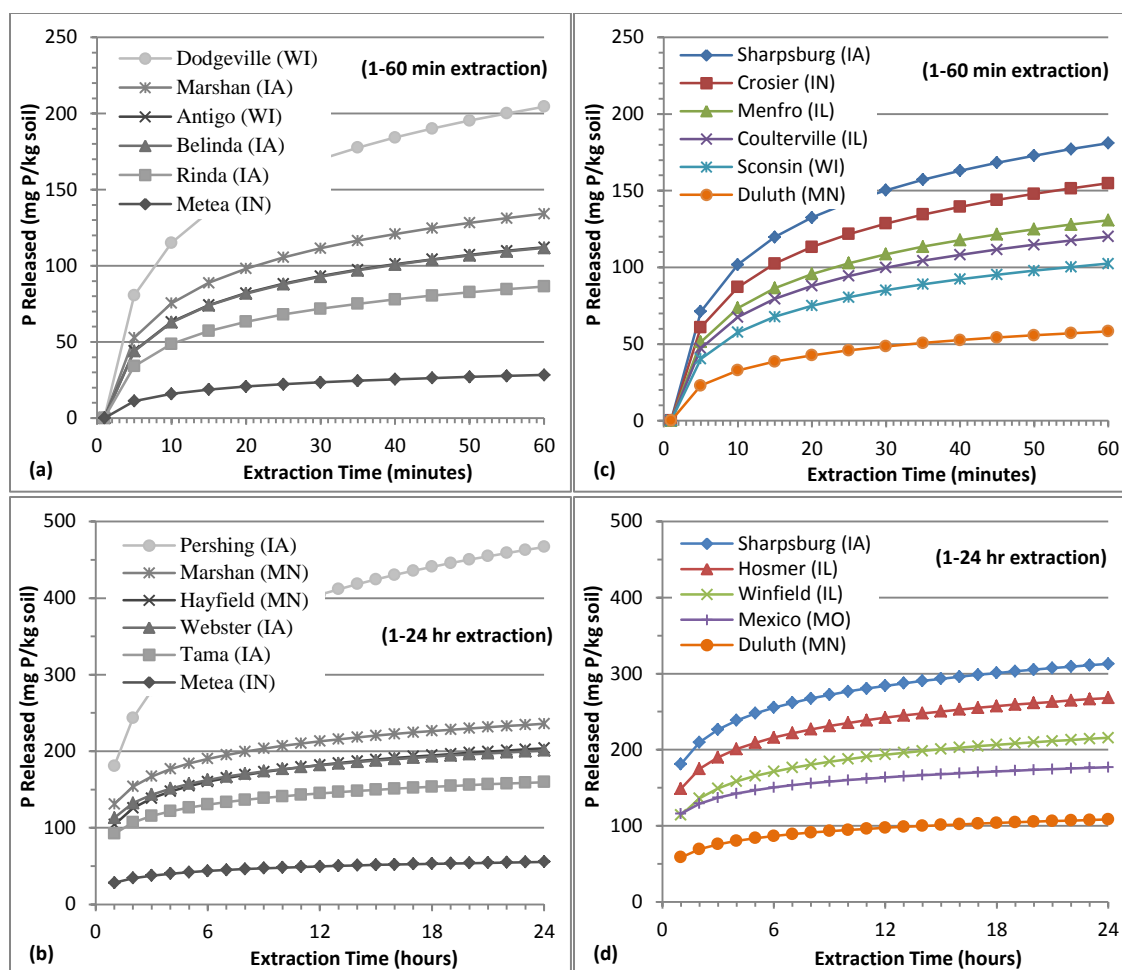


Figure 4.6. Predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, first quartile, median, mean, third quartile, and maximum for samples from the modeling dataset during the (a) 1-60 minute and (b) 1-24 hour extraction periods, and for samples from the validation dataset (colored curves) during the (c) 1-60 minute and (d) 1-24 hour extraction periods.

dataset, an average of 58 % of P was released during the first hour of AER extraction.

When soils in the modeling dataset were grouped based on the presence of  $\text{CaCO}_3$  and their degree of weathering, during the first hour of AER extraction there was an increase from 55 % of P released to 64 % for calcareous soils ( $N = 2$ ), a slight decrease to 53 % of P released for highly weathered soils ( $N = 1$ ), and slight decrease to 54 % of P released for slightly weathered soils ( $N = 43$ ) (data not shown).



The linear regression equations to predict P released (mg P/kg soil) by AER extraction for both 1 and 24-hr extraction periods are listed in Appendix H. Linear relationships are always produced when the amount of P released (mg P/kg soil) is plotted against the log of the AER extraction period (Elrashidi et al., 2012; Elrashidi et al., 2003). These linear relationships are also shown for the soils from the modeling dataset that represent the minimum, first quartile, median, mean, third quartile, and maximum P released for the Upper Mississippi River Sub-basin soils in Appendix H. The amount of P released after the first hour of AER extraction mainly represents the readily available P in the soil. This 1-hour extraction P released value varied greatly within the Upper Mississippi River Sub-basin soils, with a range of 28.26 mg P/kg soil to 204.46 mg P/kg soil (Table 4.2). The AER1 range for the calcareous soils in this region, however, is notably narrower, 104.25 mg P/kg soil to 142.31 mg P/kg soil (data not shown), primarily due to the low number of samples analyzed for this group. The total P released value (AER24) also varied greatly for soils within the Upper Mississippi River Sub-basin, with a range of 55.57 mg P/kg soil to 466.65 mg P/kg soil (Table 4.2). Again, the AER24 range for the calcareous soils in this region is notably narrower, with a range of 166.90 mg P/kg soil to 220.87 mg P/kg soil (data not shown). The two calcareous soils investigated had low  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ , and  $Fe_M$  concentrations, high  $Ca_M$  and  $Ca_{NH4}$  concentrations, and moderate to high PSI values (data not shown), which, based on the P desorption relationships noted in Table 4.3, would lead to slightly higher than average levels of 1-hour P release and slightly lower than average levels of total P release. AER1 and total P released values were lower than their respective means and medians (Table 4.2) for the one highly weathered sample analyzed from this region. AER1 for the highly

weathered soil was 84.43 mg P/kg soil, while total P released was 159.94 mg P/kg soil. This highly weathered soil had lower than average clay, TC,  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Ca_M$ ,  $Mg_M$ ,  $Ca_{NH4}$ ,  $Mg_{NH4}$ , and soil test P values, and higher than average  $Mn_M$  and  $S_{MAX}$  (data not shown). These values would suggest lower levels of 1-hour and total P release, based on the relationships noted previously (Table 4.3). AER1 and total P released varied the most for slightly weathered soils, with values encompassing the total ranges for both AER1 and AER24 of soils in the modeling dataset.

Of all the soils investigated from the Upper Mississippi River Sub-basin, the Dodgeville soil from the modeling dataset released the most P during the 1-hour extraction period while the Pershing soil from the modeling dataset released the most P overall after 24 hours of extraction (Figure 4.6). The Sharpsburg and Lawler soils from the validation dataset released second and third most P, respectively, during both the 1-hour extraction period and overall after 24 hours of extraction (Figure 4.6). Figure 4.6 also shows that the Metea soil from the modeling dataset released the least P during the 1 hour extraction period and overall after 24 hours of extraction. The Duluth soil from the validation dataset released slightly more P than the Metea soil, but the least P during the 1 hour extraction period and overall after 24 hours of extraction for soils in the validation dataset (Figure 4.6). The Dodgeville soil had low TC,  $Mg_{NH4}$ , and  $S_{MAX}$ , and high  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ ,  $Fe_M$ ,  $Mg_M$ ,  $Mn_M$ ,  $P_{OX}$ ,  $P_M$ ,  $P_{M3}$ ,  $P_{CaCl2}$ , and PSI (data not shown). The Pershing soil had low clay, TC,  $Mg_{NH4}$ ,  $P_{OX}$  and PSI, and high  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Ca_{NH4}$ ,  $P_{M3}$ ,  $P_{Bray1}$ ,  $P_{WS}$ ,  $P_{CaCl2}$ , and  $S_{MAX}$  (data not shown). There was limited sample available for the Pershing soil so Mehlich-3 element extraction data is not known. The Sharpsburg soil had low  $Ca_M$ ,  $Mg_M$ , and PSI, and high  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Mn_M$ ,  $Ca_{NH4}$ ,  $P_{OX}$ ,  $P_M$ , and  $P_{M3}$  (data not shown).

The Lawler soil had low  $\text{Ca}_M$ ,  $\text{Mn}_M$ , and  $\text{P}_{M3}$ , and high  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Ca}_{\text{NH}_4}$ ,  $\text{P}_{\text{OX}}$ , and PSI (data not shown). The Duluth soil had low clay,  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Al}_M$ ,  $\text{Ca}_M$ ,  $\text{Fe}_M$ ,  $\text{Mg}_M$ ,  $\text{Ca}_{\text{NH}_4}$ ,  $\text{Mg}_{\text{NH}_4}$ ,  $\text{P}_{\text{OX}}$ ,  $\text{P}_M$ ,  $\text{P}_{M3}$ , and PSI (data not shown). The Metea soil also had low clay,  $\text{Al}_M$ ,  $\text{Ca}_M$ ,  $\text{Fe}_M$ ,  $\text{Mg}_M$ ,  $\text{Ca}_{\text{NH}_4}$ ,  $\text{P}_{\text{OX}}$ , and PSI, as well as low  $\text{Mg}_{\text{NH}_4}$ ,  $\text{P}_{\text{WS}}$ ,  $\text{P}_{\text{CaCl}_2}$ , and  $\text{S}_{\text{MAX}}$  (data not shown). The Metea soil also had the lowest TC,  $\text{Al}_{\text{OX}}$ , and  $\text{Fe}_{\text{OX}}$  values overall, and moderate PM and  $\text{P}_{M3}$  (data not shown). It was noted previously that soil P desorption is primarily controlled by clay, Al and Fe oxides, and calcium and magnesium ions in these soils. The Upper Mississippi River Sub-basin soils that released the most P during the AER desorption process had high amounts of these components and high amounts of P already in the soil, and thus easily released large amounts of P in solution. The soils that released the least P during the desorption process had low amounts of these components known to retain P and low to moderate amount of P already in the soil, and thus released less amounts of P due to not having the ability to readily retain P.

### **Predicting Soil Phosphorus Behavior**

Most soil testing facilities only routinely analyze soils for particle-size (sand, silt, and clay), carbon content, and pH, and do not have the means or capability to perform more detailed analyses such as oxalate or Mehlich-3 extractions. Of all soil parameters investigated, only clay, TC, and pH are routinely analyzed on all soil samples processed at the KSSL. At the KSSL, analyses such as acid oxalate extractable Al, Fe, and P, and Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P) are additional analyses for select samples requested by the project researcher or investigator, limiting the data available for these properties. As mentioned previously, P sorption behaviors in soil have been found

to be related to soil clay, TC, and/or pH (Burt et al., 2002; Harter, 1969; Juo and Fox, 1977; Lopez-Hernandez and Burnham, 1974; McCallister and Logan, 1978, Sharpley et al., 1989, Syers et al., 1971). For each of the five P sorption variables of interest (AER1, AER23, AER24, PSI, and  $S_{MAX}$ ), linear regression equations were developed. Clay, TC, and pH were modeled independently and additional variables ( $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ ,  $Ca_M$ ,  $Fe_M$ ,  $Mg_M$ ,  $Mn_M$ ,  $Ca_{NH4}$ ,  $Mg_{NH4}$ ) were progressively added to the models. Models contained one to three variables, with clay, TC, or pH in each equation. The use of clay, TC, or pH in additional models was dependent on the significance of the respective independent models. Clay, TC, and/or pH were used in additional modeling if, (a) the  $p$  value of the independent model was significant ( $p \leq 0.05$ ), or (b) if no independent model was significant, the independent model with the lowest  $p$  value was used. An example of the progressive linear regression modeling method for the AER1 variable is listed in Appendix H. For AER1, the independent models with clay and pH were both significant, so they were used in the additional modeling steps. For AER23, none of the independent models with clay, TC, and pH were significant. The model with clay as a single predictor variable had the lowest  $p$  value, and was used in the additional modeling steps. For AER24, only the independent model with clay was significant but the model with TC was close to significant, so both were used in the additional modeling steps. For PSI, only the independent model with clay was significant but the model with pH was close to significant, so both were used in the additional modeling steps. For  $S_{MAX}$ , none of the independent models with clay, TC, and pH were significant. The models with clay and pH as a single predictor variable had the lowest, but similar,  $p$  values, and were used in the additional modeling steps.

The three most significant P sorption prediction equations for AER1, AER23, AER24, PSI, and  $S_{MAX}$ , developed with the samples in the modeling dataset, those with the lowest  $p$  values and highest  $R^2$  values, were examined (Table 4.6). The inclusion of  $Al_{OX}$  and  $Fe_{OX}$  in the most significant prediction equations for each variable, except  $S_{MAX}$ , indicates the significant influence of amorphous Al and Fe oxides on soil P sorption behaviors in soils of this region (Table 4.6). The prediction equations also indicate a significant influence of crystalline Al and Fe oxides on soil P sorption behaviors in soils of this region, specifically with AER23, AER24, and  $S_{MAX}$  (Table 4.6). Soil P sorption behaviors are also influenced, to a lesser extent, by the calcium, magnesium, and manganese components of these soils, as noted by the inclusion of  $Ca_M$ ,  $Mg_M$ , and  $Mn_M$  in some the  $S_{MAX}$  and AER1 prediction equations (Table 4.6). These findings are similar to those noted by Burt et al. (2002), that soil P was highly related to clay and Al and Fe oxides in non-calcareous soils.

The reliability of the prediction equations developed for AER1, AER23, AER24, and PSI was observed when the equations were applied to the samples from the validation dataset. Plots of the measured P sorption values against the predicted values for AER1, AER23, AER24, and PSI, respectively, with an overlaid linear trend line for data from each model are shown in Figure 4.7. These plots reveal that the AER1 model that with clay,  $Mg_M$ , and  $Mn_M$  variables is the best model for predicting one-hour P release, with an  $R^2$  of 0.6998. The AER23 model with clay and  $Fe_M$  variables is a slightly better model for predicting P release after an additional 23 hours in solution, with an  $R^2$  of 0.5998. The AER24 model with clay,  $Al_M$ , and  $Fe_M$  variables is the best model for predicting total P release, with an  $R^2$  of 0.9103. The PSI predictive model with pH,  $Al_{OX}$ ,

Table 4.6. The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the modeling dataset.

AER1					
Variable(s)	R <sup>2</sup>	p	MSE	N	
26.12 + 1.61Clay + 0.03Al <sub>OX</sub> + 0.005Fe <sub>OX</sub>	0.6237	0.0001	23.70	46	
33.22 + 1.89Clay + 0.03Al <sub>OX</sub>	0.5898	0.0001	24.46	46	
45.92 + 2.25Clay + 0.02Mg <sub>M</sub> + 0.05Mn <sub>M</sub>	0.5603	0.0001	25.15	44	
AER23					
Variable(s)	R <sup>2</sup>	p	MSE	N	
22.75 - 0.92Clay + 0.04Al <sub>OX</sub> + 0.01Fe <sub>OX</sub>	0.3796	0.0001	35.96	46	
15.23 + 1.14Clay + 0.04Al <sub>M</sub> + 0.13Fe <sub>M</sub>	0.3663	0.0004	27.94	44	
34.62 + 1.23Clay + 0.15Fe <sub>M</sub>	0.3171	0.0004	28.65	44	
AER24					
Variable(s)	R <sup>2</sup>	p	MSE	N	
48.86 + 0.69Clay + 0.07Al <sub>OX</sub> + 0.02Fe <sub>OX</sub>	0.5217	0.0001	52.13	46	
54.67 - 3.58TC + 0.09Al <sub>OX</sub> + 0.02Fe <sub>OX</sub>	0.5192	0.0001	52.26	46	
55.16 + 3.81Clay + 0.05Al <sub>M</sub> + 0.15Fe <sub>M</sub>	0.4701	0.0001	47.28	44	
PSI					
Variable(s)	R <sup>2</sup>	p	MSE	N	
105.87 - 16.04pH + 0.06Al <sub>OX</sub> + 0.01Fe <sub>OX</sub>	0.4702	0.0001	43.19	46	
12.88 - 0.42Clay + 0.06Al <sub>OX</sub> + 0.01Fe <sub>OX</sub>	0.4208	0.0001	45.16	46	
135.30 - 16.69pH + 0.07Al <sub>OX</sub>	0.3483	0.0001	47.34	46	
S <sub>MAX</sub>					
Variable(s)	R <sup>2</sup>	p	MSE	N	
-4.12 + 12.35Clay + 0.62Fe <sub>M</sub> - 0.39Mg <sub>M</sub>	0.3324	0.0010	140.05	44	
-89.51 + 2.83Clay + 0.23Al <sub>M</sub> + 0.55Fe <sub>M</sub>	0.2712	0.0051	146.32	44	
23.71 + 7.59Clay + 0.67Fe <sub>M</sub> - 0.04Ca <sub>M</sub>	0.2510	0.0085	148.34	44	

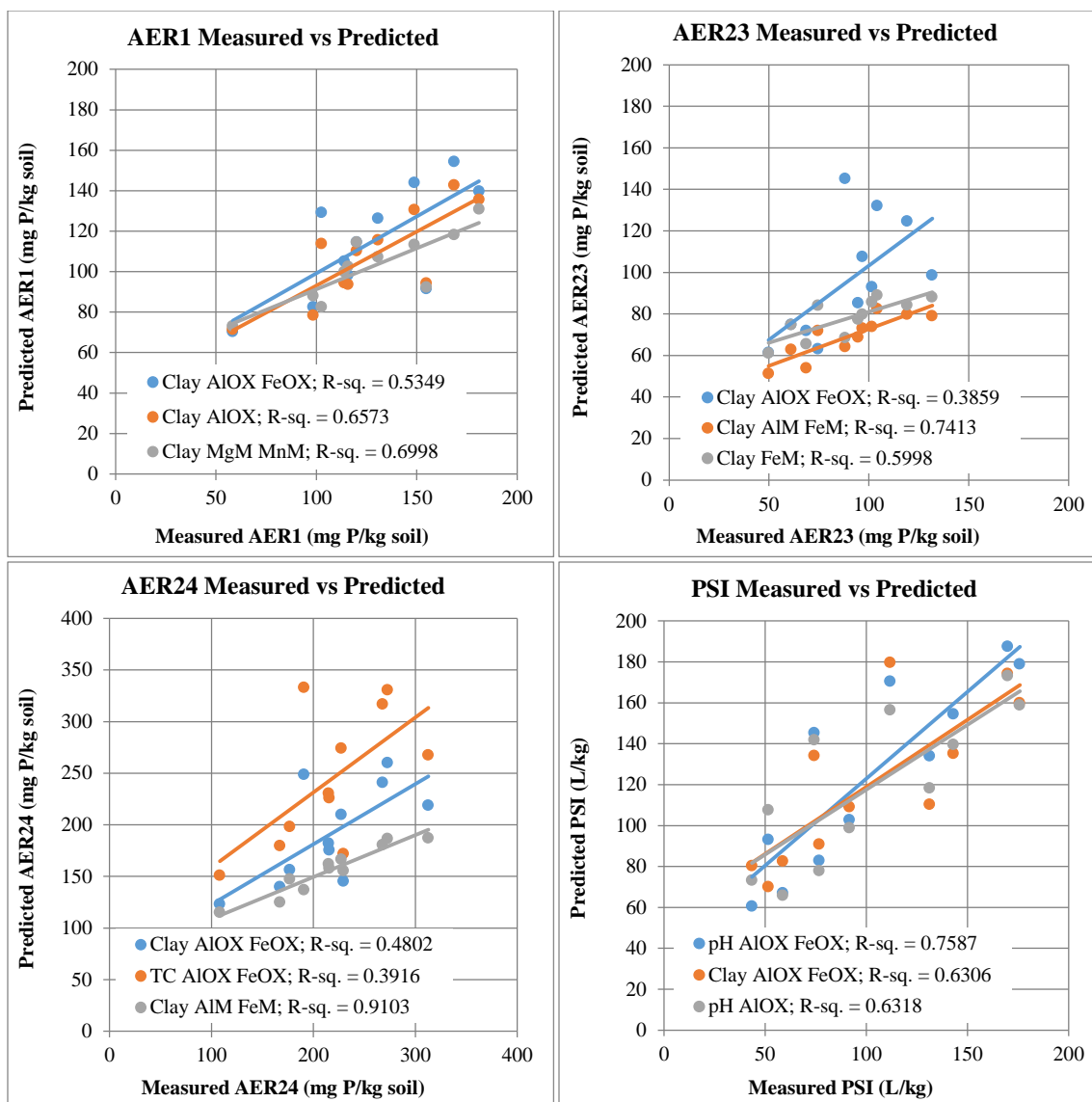


Figure 4.7. Plots of measured versus predicted values, as determined by the models listed in Table 4.6, for AER1, AER23, AER24, and PSI.

and  $\text{Fe}_{\text{OX}}$  variables is the best model for predicting P sorption, with an  $R^2$  of 0.7587 (Figure 4.7).

The number of predictions within 10 %, 15 %, and 20 % of the measured P sorption value for each of the significant prediction models for each P sorption variable, except  $S_{\text{MAX}}$ , for samples in the validation dataset were also examined (Table 4.7). The

prediction equations for AER1 worked moderately well at predicting P release values within 20 % of the measured AER1 value. The AER23, AER24, and the PSI models performed slightly worse, predicting fewer P sorption values within 20 % of the measured values, likely due to the lower  $R^2$  values of the models (Table 4.6).

Table 4.7. The number of validation sample values accurately predicted within 10 %, 15 %, and 20 % of the measured value for each of the prediction models listed in Table 4.6 for AER1, AER23, AER24, and PSI, and for the most significant AER24 model from Chapter 2 for all CONUS agricultural soils.

<b>AER1</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	5	6	8	11
Clay Al <sub>OX</sub>	1	4	7	11
Clay Mg <sub>M</sub> Mn <sub>M</sub>	1	4	6	11
<b>AER23</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	4	5	6	11
Clay Al <sub>M</sub> Fe <sub>M</sub>	3	3	3	11
Clay Fe <sub>M</sub>	1	2	6	11
<b>AER24</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	2	5	8	11
TC Al <sub>OX</sub> Fe <sub>OX</sub>	3	4	6	11
Clay Al <sub>M</sub> Fe <sub>M</sub>	1	1	2	11
Clay Al <sub>OX</sub> Fe <sub>OX</sub> CONUS	6	8	9	11
<b>PSI</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>	<b>N</b>
pH Al <sub>OX</sub> Fe <sub>OX</sub>	4	7	7	11
Clay Al <sub>OX</sub> Fe <sub>OX</sub>	3	3	6	11
pH Al <sub>OX</sub>	4	7	7	11

As mentioned in Chapter 2, the AER 24 behavior models and relationships are the most likely to be used by researchers and management planners to estimate potential P release or P loading risk if P saturated soils become eroded and incorporated into surface runoff as they model total P release. The Upper Mississippi River Sub-basin-specific prediction models were also compared to the most significant AER24 prediction model developed from the All Soils modeling dataset in Chapter 2. The results are shown in Figure 4.8, and also included in Table 4.7, with the Chapter 2 model noted by the



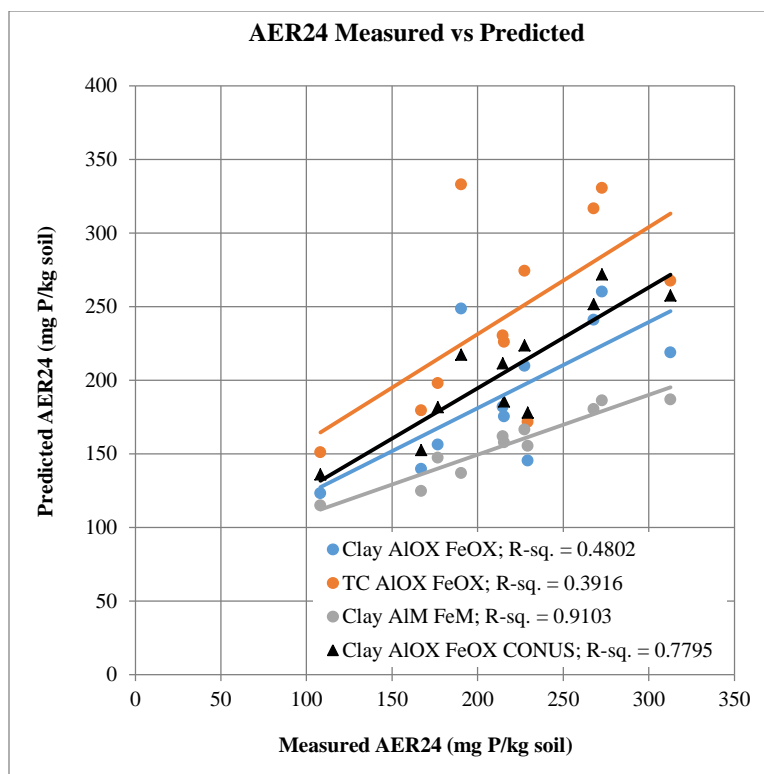


Figure 4.8. Measured versus predicted AER24 values as determined by the models listed in Table 4.6 and the most significant AER24 prediction model from Chapter 2 for all CONUS agricultural soils.

‘CONUS’ term in each case. Figure 4.8 indicates that the Sub-basin-specific model with clay,  $Al_M$  and  $Fe_M$  components is the best of the four prediction models, with the CONUS model as the second best model. Table 4.7, however, shows that the Chapter 2 CONUS is the best model for accurately predicting more AER24 values within 10 % and 15 %, but only accurately predicts one more AER24 value within 20 % of the actual measured values than the most significant Sub-basin-specific model. Both the CONUS model and the most significant Sub-basin-specific model contain clay,  $Al_{OX}$ , and  $Fe_{OX}$  as model components and accurately predicted a similar number of AER24 values within 20% of the measured value. These results would indicate additional research and refinement is needed to create reliable watershed-specific models for total P release.

### **Potential Risk of Phosphorus Loading**

As mentioned earlier, the Upper Mississippi River Sub-basin is currently receiving much attention due to contributing large amounts of P via agricultural runoff to downstream eutrophication problems. Forty-eight states have each developed a P Index, an assessment tool used to identify critical source areas and to target management practices to reduce P loss, to combat these issues, including the six states within the Upper Mississippi River Sub-basin. Each P Index is state-specific and typically includes a soil test P value as a contributing P Index factor. The soil test P method and the associated break-point values also vary with each specific P Index. As noted previously in Chapter 1, most soil test P techniques rely on the use of various chemicals and solutions that do not accurately mimic a natural in-field process. Sharpley et al. (2006) note that to mimic the interaction between surface soil and release of P to runoff water, water extractions are the ideal methods. Therefore, the data and predictive models developed in this study in relation to total P release have the potential to be used as an additional component for a P Index, or other assessment tool, and resulting management and planning strategies, that would be more reflective of actual P release into runoff in the Upper Mississippi River Sub-basin.

In Chapter 2, a model was developed by averaging AER24 values by taxonomic Great Groups in the overall modeling dataset, then applying those averaged values to the soil map units in the gSSURGO MuRas\_90m raster layer, based on the map unit's Great Group classification. This process was repeated with the AER24 values and Great Groups from the Upper Mississippi River Sub-basin modeling dataset, and compared to

the results from the Chapter 2 model, shown in Figure 4.9. Quartiles for the Sub-basin-specific model (Figure 4.9 (b)) were determined for AER24 values of samples in the Upper Mississippi River Sub-basin modeling dataset, which were used to determine break-points for a potential P loading risk index, as listed in Table 4.8.

Table 4.8. P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the modeling dataset.

<b>P Index (Potential)</b>	<b>Quartile</b>	<b>AER24</b>
Low	< 25%	$\leq 159.47$
Moderate	25 - 50%	159.48 - 198.39
High	50 - 75%	198.40 - 236.46
Very High	> 75%	> 236.47

Several observations can be made from the comparison of the potential P loading risk maps displayed in Figure 4.9. First, there is slight decrease in the map units that were given averaged total P release values in the model developed using samples from the Upper Mississippi River Sub-basin modeling dataset due to a difference in the number of taxonomic Great Groups used in each model. Table 4.1 lists the taxonomic Great Groups for the samples analyzed in this study, of which there are 15 different Great Groups. The CONUS modeling data in Chapter 2 used to develop the corresponding model included samples that encompassed 81 different taxonomic Great Groups. However, both models indicate that soils in the Central Feed Grains and Livestock Region MLRA (Figure 4.2), potentially pose a high to very high risk, overall, to contributing to P loading in the watershed (Figure 4.9). The numerical breaks between the potential risk categories are similar between the two models, with slightly higher breaks for the Low-Medium and Medium-High classification for the model developed using samples from the Upper Mississippi River Sub-basin modeling dataset. As a result,

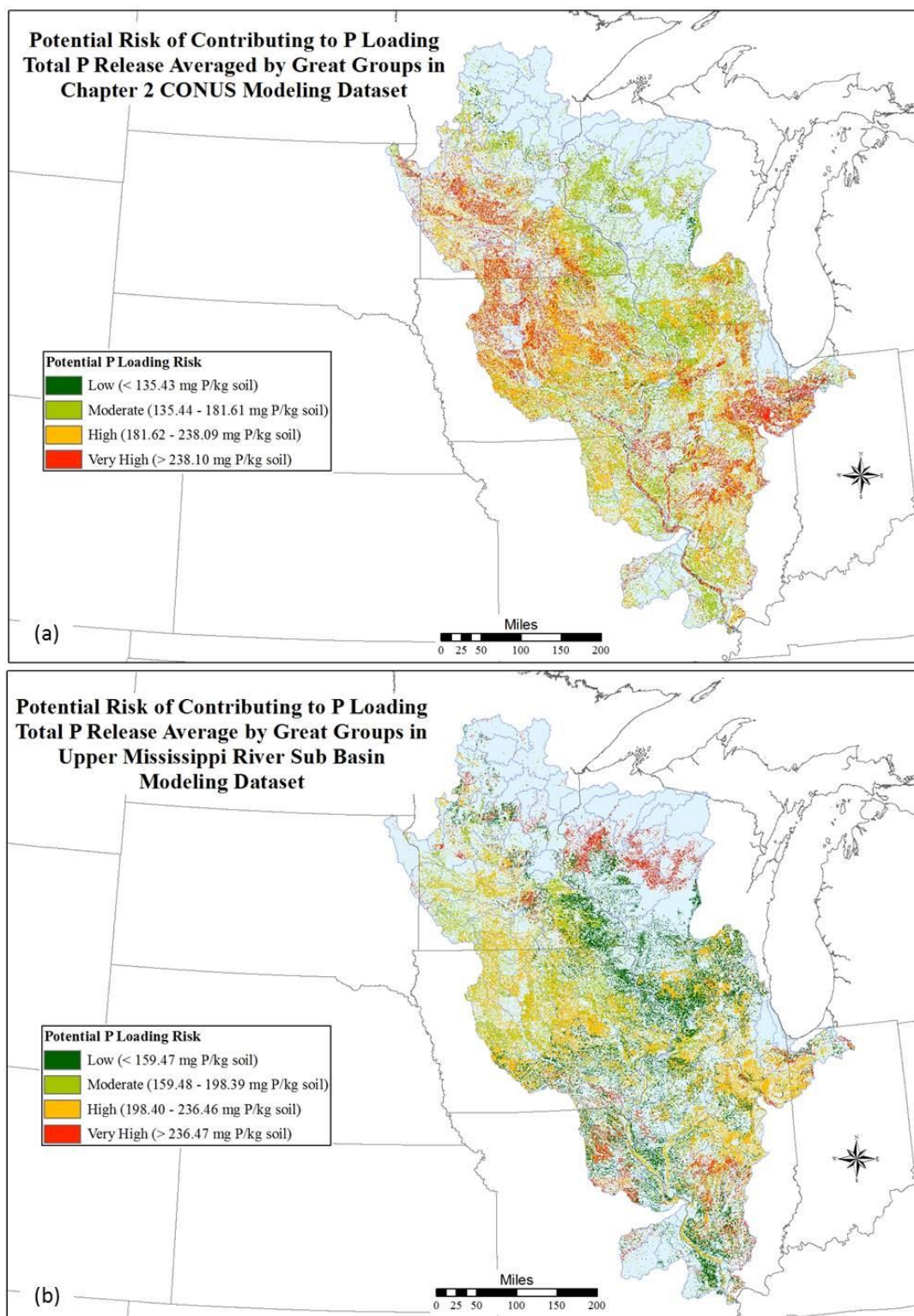


Figure 4.9. Potential risk agricultural soils of the Upper Mississippi River Sub-basin pose to contributing to P loading, with total P release estimated averaged by taxonomic Great Groups from the Chapter 2 CONUS modeling dataset (a) and by taxonomic Great Groups from the Upper Mississippi River Sub-basin modeling dataset (b).

it would appear that more “Very High” risk map units from the CONUS model classify into “Low” or “Moderate” risk potentials with the region-specific model (Figure 4.9). Another notable difference between the two models is in the Northern Lake States Forest and Forage Region MLRA (Figure 4.2), specifically in northern WI. In this area, map units classify as “Moderate” or “High” with the CONUS model, and predominately classify as “Very High” with the region-specific model (Figure 4.9). This also occurs with soil map units in northeastern MO. Overall, the region-specific model results in soil map units being classified in lower risk categories, with more concentrated areas of “Very High” risk potential map units, compared to the CONUS-level model (Figure 4.9). While both visual models were developed using similar processes, the samples used to develop each model are the drivers behind the differences between the models. If used in combination with additional data and tools for nutrient management planning strategies, these models and the differences between them could potentially have significant effects on not only the allocation of materials, practices, and financial support, but on the overall success of reducing P loading in the watershed system.

## CONCLUSIONS

The Upper Mississippi River Sub-basin is an area dominated by intense agricultural and known nationally for contributing to downstream eutrophication problems due to agricultural runoff loaded with phosphorus. Results from this study indicate that P sorption behaviors in this region are related to the clay content and Al and Fe oxides (amorphous and crystalline) in soil. Water or calcium chloride extractable soil P tests would be most appropriate for estimating total P desorption, while oxalate

extractable or Mehlich-3 extractable P tests would be most appropriate for estimating P adsorption in soils of the Upper Mississippi River Sub-basin, as they the most significantly ( $p < 0.05$ ) and highly correlated soil P tests to those P sorption behaviors. The CONUS-level prediction model developed in Chapter 2 for predicting total P release from soil performed similarly to the Sub-basin-specific models in accurately predicting total P release from soils, and with similar model components, though the Sub-basin-specific models were statistically stronger models. The modeling datasets from the two studies generated distinctly different potential P-loading risk models for agricultural soils within the Sub-basin, with “High” and “Very High” risk areas being located in different areas in each model. To account for the variability of the soils and their forming factors over such a large area, additional research and refinement could focus on developing specific P desorption models for each Land Resource Region, soil temperature zones, or smaller sub-regions based on other soil forming characteristics, or by grouping soils by their calcium carbonate content and degree of weathering.

The relationships and models developed in this study have great potential for improving soil P assessment tools in the Upper Mississippi River Sub-basin, and to better inform P management related decision-making at the watershed, farm, and field scales. Additional research and refinement of these models and appropriate potential-risk break-point values is suggested before implementation into assessment tools. Implementing oxalate and Mehlich-3 extraction methods as standard analyses for all soils at soil testing labs like the KSSL, will be necessary to further refine the P desorption models and improve our understanding of soil P sorption behaviors in this region, and elsewhere.

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**APPENDIX H**

DESORPTION REGRESSION EQUATION COMPONENTS TABLE, LOG-  
TRANSFORMED DESORPTION PLOTS, AND REGRESSION MODELING STEPS  
TABLE FOR THE UPPER MISSISSIPPI RIVER SUB-BASIN

Table H.1. Linear regression equation<sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for all Upper Mississippi River Sub-basin soils investigated, during the 1-60 minute and 1-24 hour extraction periods.

User Pedon ID	Soil Series	Grouping	Intercept (I)	Slope (S1) (1-60 min)	Slope (S2) (1-24 hr)
			----- mg P/kg soil -----		
92IA177003	Reeds Creek	C	104.25	58.57	45.40
86IA005040	Tama	S	92.35	51.88	48.77
87IA169001A	Clarion	S	98.05	55.09	43.88
92IA105002	Zwingle	S	132.18	74.26	61.75
93IA015001	Clarion	S	108.01	60.68	46.23
94IA117007	Pershing	S	180.82	101.58	207.13
94IA117011	Belinda	S	111.75	62.78	57.74
94IA181001*	Sharpsburg	S	180.98	101.67	95.48
94IA181002	Sharpsburg	S	170.51	95.79	78.36
95IA107011	Bucknell	S	160.89	90.39	60.33
95IA107012	Armstrong	S	72.67	40.83	56.29
95IA111001	Rinda	S	86.43	48.55	52.54
95IA135002	Bucknell	S	143.43	80.58	73.37
95IA179001	Gosport	S	127.97	71.90	105.91
S01IA-015-001	Webster	S	113.01	63.49	63.71
S08IA017001*	Lawler	S	168.55	94.69	75.57
S08IA019001*	Hayfield	S	98.37	55.27	49.80
S08IA019002	Marshan	S	107.33	60.30	64.15
S08IA037001	Hayfield	S	74.74	41.99	43.29
S08IA067001	Marshan	S	134.16	75.37	66.26
S08IA195001	Lawler	S	134.95	75.81	74.74
S02IL-099-023	Buckhart	C	142.31	79.95	56.93
S05IL181005	Menfro	H	84.43	47.43	54.72
93IL163014*	Coulterville	S	120.10	67.47	68.62
94IL001007	Rozetta	S	74.46	41.83	51.61
94IL123037	Arrowsmith	S	118.66	66.66	53.93
96IL181003	Alford	S	116.36	65.37	54.10
S02IL-099-016	Flanagan	S	160.20	90.00	77.69
S02IL-099-018	Sable	S	108.04	60.70	60.05
S02IL-099-019	Muscatine	S	129.61	72.81	53.33
S02IL-099-020	Catlin	S	134.15	75.36	58.30
S05IL181002	Menfro	S	167.20	93.93	126.86
S05IL181003*	Menfro	S	130.70	73.43	70.14
S05IL181004	Bunkum	S	93.90	52.75	68.22
S05IL181007	Winfield	S	107.50	60.39	86.47
S05IL181008*	Winfield	S	113.93	64.00	73.66
S05IL181009*	Hosmer	S	148.71	83.54	86.41

User Pedon ID	Soil Series	Grouping	Intercept (I)	Slope (S1) (1-60 min)	Slope (S2) (1-24 hr)
			----- mg P/kg soil -----		
S07IL187002	Muscatune	S	134.11	75.34	53.87
93IN039008*	Crosier	C	154.82	86.98	54.07
93IN039007	Brookston	S	139.40	78.32	147.12
S01IN-141-002	Crumstown	S	57.02	32.03	40.96
S04IN-099-001	Metea	S	28.26	15.88	19.79
S04IN-111-001	Kentland	S	81.40	45.73	70.91
91MN149001	Barnes	S	120.14	67.49	46.08
94MN095045*	Duluth	S	58.32	32.77	36.12
96MN085003	Nicollet	S	73.49	41.28	32.53
S08MN099001	Hayfield	S	104.02	58.44	72.32
S08MN109001	Marshan	S	130.92	73.55	76.09
87MO121024	Adco	S	67.46	37.90	47.97
87MO121026*	Mexico	S	115.72	65.01	44.35
S07SD039002	Barnes	S	139.78	78.53	55.37
94WI057004B	Menahga	S	40.37	22.68	51.06
94WI057004C	Menahga	S	43.16	24.25	34.30
98WI067001	Antigo	S	112.17	63.01	110.45
S00WI-099-001	Magnor	S	98.88	55.55	93.49
S03WI-107-006*	Sconsin	S	102.46	57.56	63.85
S04WI-065-002	Dodgeville	S	204.46	114.87	96.64

<sup>a</sup>  $P = I + S1 \times (\log h)$  for 1-60 min;  $P = I + S2 \times (\log h)$  for 1-24 hr extraction period; where P = P released (mg P/kg soil), I = intercept, S1 = slope of the 1-60 min extraction period, S2 = slope of the 1-24 hr extraction period, and h = extraction period.

\* Indicates sample in the validation dataset.

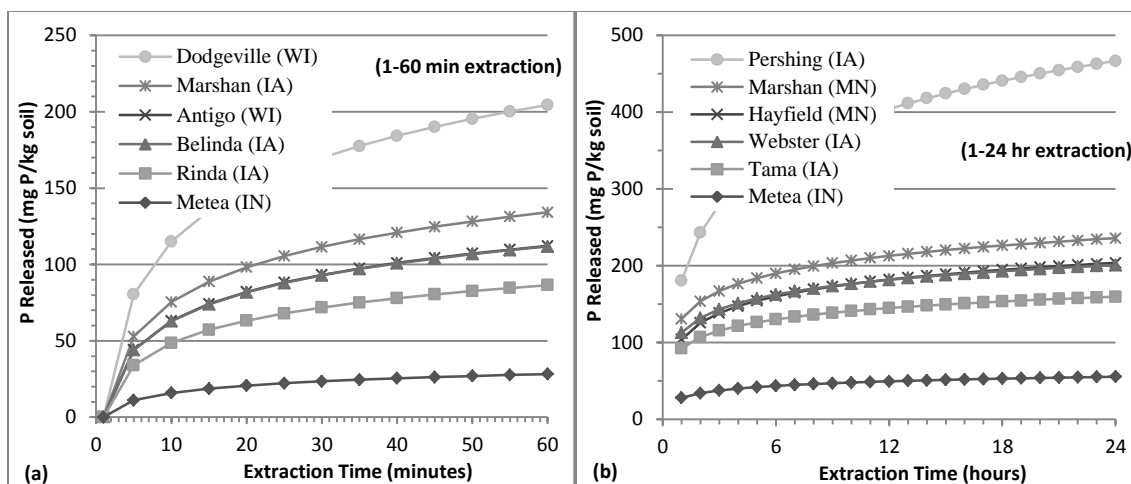


Figure H.1. Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, first quartile, median, mean, third quartile, and maximum for samples in the Upper Mississippi River Sub-basin modeling dataset, during the (a) 1-60 minute and (b) 1-24 hour extraction periods.

Table H.2. An example of the progressive regression modeling method used on samples from the Upper Mississippi River Sub-basin modeling datasets, for AER1.

AER1									
Variable(s)	R <sup>2</sup>	p	MSE	N	Variable(s)	R <sup>2</sup>	p	MSE	N
1 Clay	0.4972	0.0001	26.77	46	26 Clay CaNH <sub>4</sub>	0.4972	0.0001	27.08	46
2 TC	0.0708	0.0739	36.39	46	27 Clay MgNH <sub>4</sub>	0.5200	0.0001	26.45	46
3 pH	0.1533	0.0071	34.73	46	28 Clay CaNH <sub>4</sub> MgNH <sub>4</sub>	0.5201	0.0001	26.77	46
4 Clay TC	0.4975	0.0001	27.07	46	29 TC AlOX	0.4227	0.0001	29.01	46
5 Clay pH	0.5179	0.0001	26.51	46	30 TC FeOX	0.2663	0.0013	32.71	46
6 TC pH	0.2211	0.0046	33.70	46	31 TC AlOX FeOX	0.5150	0.0001	26.91	46
7 Clay TC pH	0.5193	0.0001	26.79	46	32 TC AlM	0.1175	0.0711	35.19	44
8 <b>Clay AlOX</b>	0.5898	0.0001	24.46	46	33 TC CaM	0.2663	0.0017	32.09	44
9 Clay FeOX	0.5373	0.0001	25.97	46	34 TC FeM	0.1028	0.1081	35.48	44
10 <b>Clay AlOX FeOX</b>	0.6237	0.0001	23.70	46	35 TC MgM	0.4588	0.0001	27.56	44
11 Clay AlM	0.5459	0.0001	25.24	44	36 TC MnM	0.0929	0.1356	35.68	44
12 Clay CaM	0.5410	0.0001	25.38	44	37 TC AlM CaM	0.2913	0.0030	31.93	44
13 Clay FeM	0.5456	0.0001	25.25	44	38 TC AlM FeM	0.1350	0.1180	35.27	44
14 Clay MgM	0.5474	0.0001	25.20	44	39 TC AlM MgM	0.4977	0.0001	26.88	44
15 Clay MnM	0.5526	0.0001	25.06	44	40 TC AlM MnM	0.1200	0.1594	35.58	44
16 Clay AlM CaM	0.5459	0.0001	25.56	44	41 TC FeM CaM	0.2663	0.0058	32.48	44
17 Clay AlM FeM	0.5492	0.0001	25.46	44	42 TC FeM MgM	0.4588	0.0001	27.90	44
18 Clay AlM MgM	0.5570	0.0001	25.24	44	43 TC FeM MnM	0.1030	0.2213	35.92	44
19 Clay AlM MnM	0.5551	0.0001	25.30	44	44 TC CaM MgM	0.4610	0.0001	27.85	44
20 Clay FeM CaM	0.5462	0.0001	25.55	44	45 TC CaM MnM	0.2783	0.0042	32.22	44
21 Clay FeM MgM	0.5523	0.0001	25.38	44	46 TC MgM MnM	0.4642	0.0001	27.76	44
22 Clay FeM MnM	0.5540	0.0001	25.33	44	47 TC CaNH <sub>4</sub>	0.2368	0.0030	33.36	46
23 Clay CaM MgM	0.5477	0.0001	25.51	44	48 TC MgNH <sub>4</sub>	0.2095	0.0064	33.95	46
24 Clay CaM MnM	0.5527	0.0001	25.37	44	49 TC CaNH <sub>4</sub> MgNH <sub>4</sub>	0.2800	0.0030	32.78	46
25 <b>Clay MgM MnM</b>	0.5603	0.0001	25.15	44					

\* $p \leq 0.0001$  highlighted in green;  $0.0001 > p \leq 0.01$  highlighted in yellow; three models with lowest  $p$  and highest  $R^2$  in bold

## CHAPTER 5

### PHOSPHORUS DESORPTION CHARACTERISTICS AND RELATIONSHIPS OF AGRICULTURAL SOILS IN THE CALIFORNIA BAY-DELTA/CENTRAL VALLEY WATERSHED

#### ABSTRACT

Eutrophication and phosphorus loading issues from agricultural runoff are not recent problems in the intense agricultural Central Valley and uniquely sensitive aquatic areas of the Bay-Delta in California, but have only recently been receiving national-level attention compared to other nutrient-impacted area in the U.S. A collection of 14 agricultural surface soils from the California Bay-Delta/Central Valley watershed were analyzed for phosphorus (P) sorption and desorption, using double-point anion exchange resin (DP-AER), P sorption index (PSI), and adsorption isotherm methods. Objectives of this study were to determine relationships between P desorption behaviors and other soil properties, to develop predictive models to provide better estimates of pollution risk at the watershed, farm, and field levels, and improve existing models that predict nutrient losses. Linear regression models were developed and validated for each P sorption variable. Results indicate that the soil P sorption behaviors in this region are predominately related to the amorphous and crystalline Al and Fe oxides in the soil, in addition to the soil pH and total carbon content. The reliability and performance of the watershed-specific prediction models and CONUS-level models developed in Chapter 2 could not be adequately assessed due to having only two samples in the validation



dataset. Comparisons of the CONUS-level and watershed-specific potential risk models resulted in differences overall model coverage and in areas classified as “High” or “Very High” risk to contributing to P loading if the surface soil were eroded into runoff.

## ABBREVIATIONS

**AER1** - phosphorus released from soil during the 1 hour extraction period (mg P/kg soil); **AER23** - phosphorus released from soil during the 23 hour extraction period (mg P/kg soil); **AER24** - total phosphorus released from soil in 24 hours (mg P/kg soil); **Al<sub>M</sub>** - Mehlich No. 3 extractable aluminum (mg Al/kg); **Al<sub>ox</sub>** - acid oxalate extractable aluminum content (%); **CaCO<sub>3</sub>** - calcium carbonate equivalent (%); **Ca<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Ca<sub>M</sub>** - Mehlich No. 3 extractable calcium (mg Ca/kg); **CONUS** - conterminous United States; **DP-AER** - double-point anion exchange resin; **Fe<sub>M</sub>** - Mehlich No. 3 extractable iron (mg Fe/kg); **Fe<sub>ox</sub>** - acid oxalate extractable iron content (%); **ICP-AES** - inductively coupled plasma atomic emission spectrometry; **KSSL** - Kellogg Soil Survey Laboratory; **Mg<sub>NH4</sub>** - ammonium acetate extractable calcium (cmol/kg); **Mg<sub>M</sub>** - Mehlich No. 3 extractable magnesium (mg Mg/kg); **Mn<sub>M</sub>** - Mehlich No. 3 extractable manganese (mg Mn/kg); **NLCD** - National Land Cover Dataset; **NRCS** - Natural Resources Conservation Service; **NSSC** - National Soil Survey Center; **P<sub>Bray1</sub>** - Bray-1 extractable phosphorus (mg P/kg soil); **P<sub>CaCl2</sub>** - 0.01 M calcium chloride extractable phosphorus (mg P/kg soil); **P<sub>M</sub>** - Mehlich No. 3 extractable phosphorus (mg P/kg soil), measured using ICP-AES; **P<sub>M3</sub>** - Mehlich No. 3 extractable phosphorus (mg P/kg soil), measured using a spectrophotometer at 882 nm; **P<sub>ox</sub>** - acid oxalate extractable phosphorus content (mg P/kg soil); **PSI** - phosphorus sorption index (L/kg); **P<sub>ws</sub>** - water

soluble phosphorus content (mg P/kg soil); **SERA-IEG 17** - Southern Extension and Research Activity - Information Exchange Group 17;  $S_{MAX}$  - phosphorus sorption maximum (mg/kg); **TC** - total carbon content (%); **USDA** - United States Department of Agriculture.

## INTRODUCTION

The California Bay-Delta/Central Valley watershed and is comprised of three large watersheds, the San Francisco River watershed, the San Joaquin River watershed, and the Tulare Lake Basin watershed, that drain the Central Valley region of California into the San Francisco Bay-Delta. A vitally important ecosystem and ecological area, the Bay-Delta creates a habitat for hundreds of aquatic and terrestrial specie that is threatened by nutrient and sediment loading which alters and degrades the ecosystem (Bay-Delta Conservation Plan, 2013). As one of the most important agricultural centers of the world (Schneider et al., 1998), the Central Valley watersheds support large areas of row crop, pasture, and irrigated agricultural lands, which accounts for most of the water use in the basin (Hart et al., 1998). According to the California Regional Water Quality Control Board for the Central Valley Region, phosphorus (P) is considered a biostimulatory substance in that it promotes the growth of aquatic species in concentration that cause nuisance or adversely affect water for beneficial uses (Hart et al., 1998; Schneider et al., 1998). Over the last 20 years, the state of California has listed several of the rivers draining catchments in the basins as impaired water bodies due to excess nutrient loading (Kratzer and Shelton, 1998; Sobota et al., 2011). Sobota et al. (2011) further highlight the necessity to understand the spatial patterns and relative magnitudes of the various

land-based P sources, predominately from agricultural areas, in order to reduce inputs to surface waters that drain to the Bay-Delta.

Some of the world's largest ecosystem restoration efforts are under way to mitigate anthropogenic alterations to the San Francisco Bay, as it is one of the most anthropogenically altered estuaries in the United States (Nichols et al., 1986). Plant-available P has increased in the Central Valley region by as much 15 to 17 % over the last 50+ years (Sobota et al., 2011), due to the intense amount of agriculture in the region (Clerck et al., 2003). Clerk et al. (2003) noted that between 1945 and 2001, average plant-available P increased from 71.82 ppm to 84.61 ppm statewide, and that there was a significant increase ( $p < 0.1$ ) in row crop systems (87.61 ppm to 105.21 ppm, respectively). Overall, P loading to estuarine systems has increased 2- to 6-fold between 1900 and 2000 (Conley, 2000), and over the last 50+ years, anthropogenic P inputs have doubled, and in some cases tripled, in the smaller catchments of the Bay-Delta/Central Valley watershed, primarily from agricultural fertilizer and manure applications (Sobota et al., 2011). As a result, annual P loading rates (dissolved inorganic P concentrations) to the San Francisco Bay were 10x higher than in the Chesapeake Bay in 1997 (Cloern, 2001), which is related to the differences in regional hydrology and distribution of P inputs in each region (Sobota et al., 2011). The Bay-Delta estuary has not yet faced severe eutrophication issues like the Chesapeake, however, due to attributes that dampen direct enrichment responses (i.e. bottom waters that never reach hypoxia and primary production 20x lower than the Chesapeake Bay) (Cloern, 2001), but the relative sensitivity to P limitation in the Bay-Delta system appears to be increasing (Jassby, 2005). Having a better understanding of the P desorption behaviors and the relationships

of those behaviors to other soil properties in the California Bay-Delta/Central Valley region could improve watershed, estuary, and ecosystem restoration and agricultural land management in this area.

Multiple-linear regression prediction models were developed for agricultural surface soils across the conterminous United States (CONUS) in Chapter 2 to better identify agricultural areas that have a high potential for contributing to P export and loading. The objectives of this study were to develop predictive relationships between P desorption behaviors and other soil properties using simple and multiple linear regression models for the California Bay-Delta/Central Valley watershed. The outcomes of these objectives would then be to (1) identify agricultural soils that contain high amounts of P, relative to their sorptive potential, that would have the most negative effect on surface water if eroded, (2) classify the soils as to their potential to contribute P to surface waters, (3) evaluate how soils retain (adsorption) and release P (desorption), to provide better estimates of pollution risk at the watershed, farm, and field levels, and possibly improve existing models that predict nutrient losses, and (4) to determine the effectiveness of a set of watershed-specific models compared to CONUS-level predictive models.

## **MATERIALS AND METHODS**

### **Laboratory Sample Selection**

Fourteen archived agricultural surface soil samples collected from the California Bay-Delta/Central Valley region by the Natural Resource Conservation Service (NRCS) were analyzed for this study. Samples were selected based on the availability of following data; (1) spatial location of the pedon and date of collection, more recently

collected samples were given a higher preference, (2) pedon location is designated as agricultural land on the 2011 National Land Cover Data (NLCD) geospatial layers, and (3) availability of data in the NSSC-KSSL database on the general properties known to effect P retention (e.g. clay, pH, calcium carbonate, iron and aluminum oxalate, total carbon). Samples were also chosen in an attempt to ensure adequate representation of agricultural soil series of the California Bay-Delta/Central Valley watershed area and spatial randomness. A subset of two samples was selected to be used to validate the prediction equations developed to model P desorption and adsorption. Sample locations for both modeling and validation samples from the study area are shown in Figure 5.1 and pedon taxonomic information for each sample is listed in Table 5.1.

### **Study Area Physiography**

The California Bay-Delta/Central Valley watershed encompasses portions of three NRCS Land Resource Regions, which are comprised of 13 smaller Major Land Resource Areas (MLRA), geographically associated with land resource units (Figure 5.2). The watershed is located almost entirely in the state of California, with a small portion extending north into south-central Oregon. The Coastal Redwood Belt and Siskiyou-Trinity Area MLRAs comprise the portion of the Northwestern Forest, Forage, and Specialty Crop Region in the watershed. The Central California Coastal Valleys, Central California Coast Range, California Delta, Sacramento and San Joaquin Valleys, Sierra Nevada Foothills, and Southern California Mountains MLRAs comprise the California Subtropical Fruit, Truck, and Specialty Crop Region in the watershed. The Klamath and Shasta Valleys and Basins, Sierra Nevada Mountains, Southern Cascade Mountains,

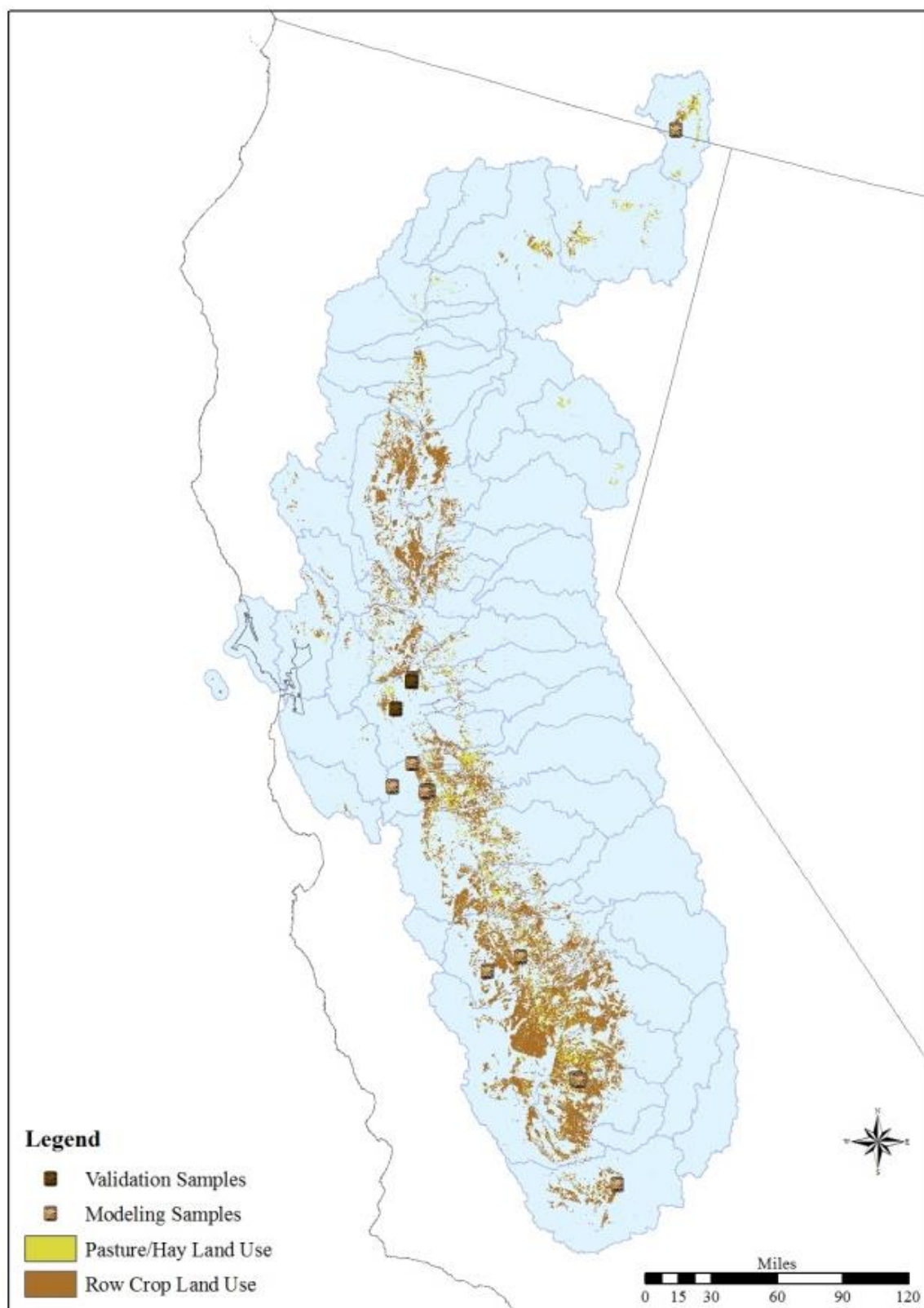


Figure 5.1. Locations of all modeling and validation samples investigated from the California Bay-Delta/Central Valley study area.

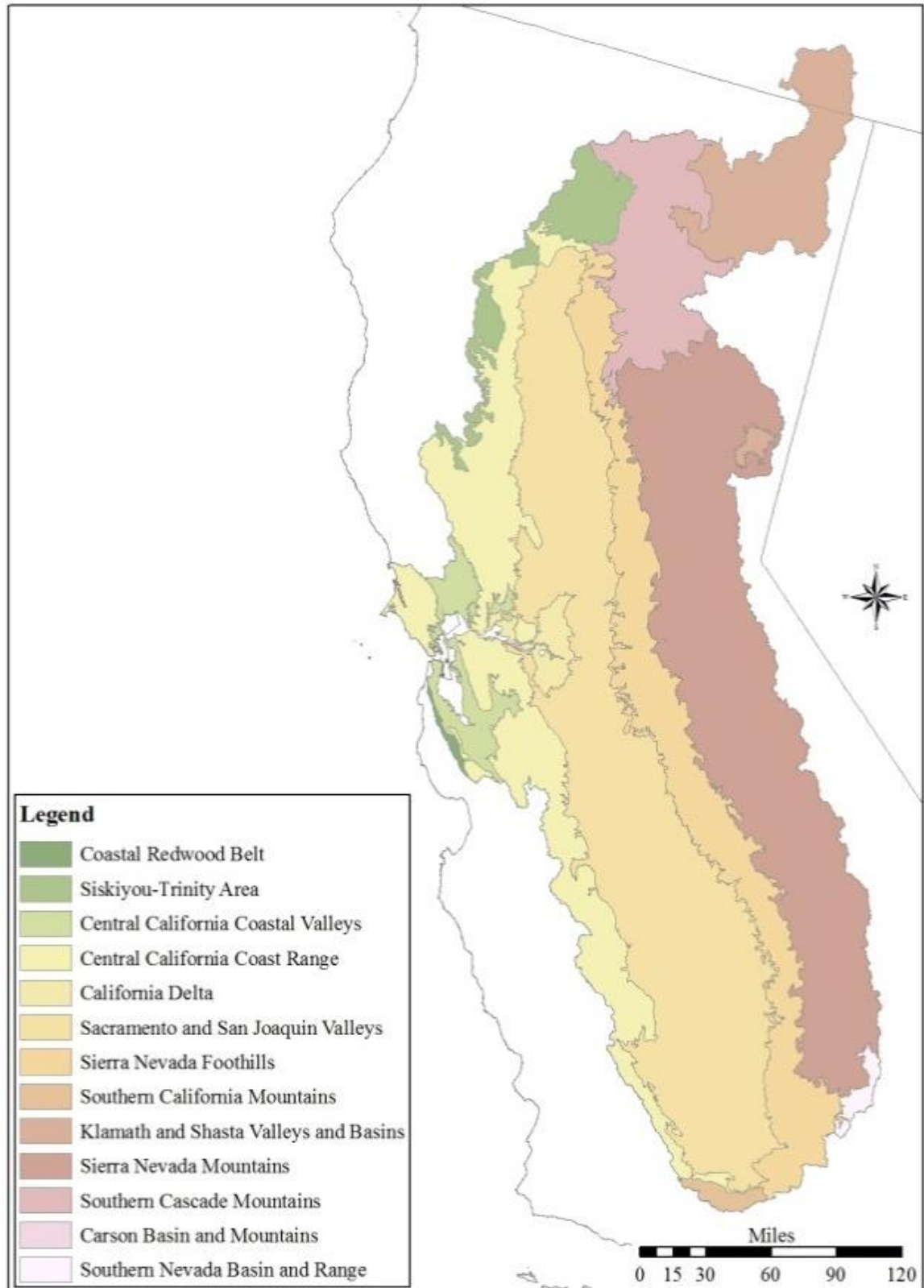


Figure 5.2. USDA NRCS Major Land Resource Areas of the California Bay-Delta/Central Valley study area.

Table 5.1. Classification information for the 14 California Bay-Delta/Central Valley agricultural surface soils investigated.

State	Pedon Soil Series	User Pedon ID	Great Group	Calcareous/ Weathering Group
CA	Atesh	92CA107002	Torriarent	Calcareous
CA	Atesh	92CA107003	Torriarent	Calcareous
CA	Hesperia	94CA019001	Xerochrept	Calcareous
CA	Ciervo	94CA019002	Haplocambid	Calcareous
CA	Rindge	91CA077001	Medisaprist	Slightly Weathered
CA	Zacharias	92CA099001	Xerochrept	Slightly Weathered
CA	Vernalis	92CA099002	Xerochrept	Slightly Weathered
CA	Capay	92CA099005	Haploxerert	Slightly Weathered
CA	Henneke	92CA099007	Argixeroll	Slightly Weathered
CA	Jerryflu	92CA107001	Natridurid	Slightly Weathered
CA	Calicreek	93CA029001	Torrifluent	Slightly Weathered
CA	Itano*	S2012CA077004	Fluvaquent	Slightly Weathered
CA	Ryde*	S2014CA077001	Endoaquoll	Slightly Weathered
OR	Salisbury	79OR037003	Durixeroll	Slightly Weathered

\* Indicates sample in validation dataset.

Carson Basin and Mountains, and Southern Nevada Basin and Range comprise the portion of the Western Range and Irrigated Region in the watershed.

The Northwestern Forest, Forage, and Specialty Crop Region, along the western edge of the California Bay-Delta/Central Valley watershed (Figure 5.2), is dominated by the Klamath Mountains. The tilted, folded, and faulted sedimentary and metamorphic rocks of the Klamath Mountains lend to a landscape of steep mountains and narrow to broad, gently sloping valleys and plains (USDA-NRCS, 2006). Agricultural soils in this region are primarily Alfisols, Entisols, Inceptisols, and Ultisols. Cultivated land in this region is primarily used for forage and grain production for regional livestock, with small acreages for fruit and vegetable production to a lesser extent (USDA-NRCS, 2006). Agricultural lands are also used for hay crop and pasture or grazing in this area (USDA-NRCS, 2006).

The California Subtropical Fruit, Truck, and Specialty Crop Region encompasses about half of the California Bay-Delta/Central Valley watershed (Figure 5.2), and is



dominated by low mountains and broad valleys (USDA-NRCS, 2006). This region is used intensively for agriculture, with a wide variety of crop production and agricultural enterprises (USDA-NRCS, 2006). Regional crops include vegetables, rice, sugar beets, cotton, grain, hay, and fruit, and dairy and beef cattle are the primary livestock managed in the area (USDA-NRCS, 2006). Agricultural soils in this region are predominately Alfisols, Entisols, Mollisols, and Vertisols (USDA-NRCS, 2006).

The Western Range and Irrigated Region, along the eastern edge of the California Bay-Delta/Central Valley watershed (Figure 5.2), separates the watershed from the semidesert and desert regions of Nevada and Arizona to the east. This area is dominated by lava plateaus, rolling volcanic mountains, and many valleys and basins to the north, and hilly to steep mountain relief with occasional mountain valleys in the central and southern portions (USDA-NRCS, 2006). Agricultural soils in the region are primarily Alfisols, Entisols, Inceptisols, Mollisols, and Ultisols, with Andisols, Aridisols, and Histosols to a much lesser extent (USDA-NRCS, 2006). There is very little cropland for agriculture in this region. Agriculture is predominately focused on potatoes, grain, seed crops, hay, and pasture in the north, and deciduous fruits, grain, hay, and livestock grazing in the central and southern portions (USDA-NRCS, 2006).

### **Standard Sample Characterization Analyses**

All samples in this study received laboratory characterization by analytical procedures described in the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004) with representative alphanumeric codes for standard operating procedures in parentheses. All standard analyses were performed on air-dried <2-mm

soil, with resulting data reported on an oven-dry basis. Analyzed characterization properties included particle-size analysis, total carbon, acid oxalate extractable Al, Fe, and P, Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P), cation exchange capacity, pH, calcium carbonate equivalent, and water extractable P.

Particle-size analysis was determined by sieve and pipette (3A1a), following pre-treatments for removal of organic matter and soluble salts, and chemical dispersion with sodium hexametaphosphate. Total carbon (TC) content was determined by dry combustion (4H2a) on air-dried <180- $\mu$ m (80 mesh) soil. Acid oxalate (4G2a) extracts were analyzed for Fe<sub>OX</sub>, Al<sub>OX</sub>, and P<sub>OX</sub> by inductively coupled plasma atomic emission spectrometry (ICP-AES). Mehlich-3 (4D6b) extracts were analyzed for Al<sub>M</sub>, Ca<sub>M</sub>, Fe<sub>M</sub>, Mg<sub>M</sub>, Mn<sub>M</sub>, and P<sub>M</sub> by ICP-AES, and Mehlich-3 (4D6a) extractable phosphorus (P<sub>M3</sub>) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm. Soil pH (4C1a2a) was measured using a 1:1 soil-water solution. Calcium carbonate (CaCO<sub>3</sub>) equivalent (4E1a1a1a1) was determined by treating the soil with hydrochloric acid, manometrically measuring the evolved carbon dioxide, and then calculating the percent CaCO<sub>3</sub>. Ammonium acetate extractable calcium (Ca<sub>NH4</sub>) and magnesium (Mg<sub>NH4</sub>) were measured with NH<sub>4</sub>OAc buffered at pH 7.0 (4B1a) and measured by ICP-AES. Water extractable phosphorus (4D2a) (P<sub>WS</sub>) was analyzed by measuring extract absorbance using a spectrophotometer at 882 nm.

### **Sample Phosphorus Sorption Analyses**

The primary objective in selecting methods was to choose methods that could simulate natural field conditions, meet the objectives of determining the maximum

capacity of agricultural soils to hold phosphorus (P capacity), and determine how much P would desorb from eroded sediment. To determine P capacity, the standard “P sorption index” (PSI) method outlined by Sims in SERA-IEG 17 (2009) was utilized. The method used to determine phosphorous desorption was the standard double-point anion exchange resin (DP-AER) method, as outlined in Elrashidi et al (2003) and the *USDA NRCS Soil Survey Laboratory Methods Manual, Version 4.0* (Burt, 2004). The standard method of P adsorption isotherm determination, as proposed originally proposed in Nair et al. (1984), and again by Graetz and Nair in SERA-IEG 17 (2009), was used to further understand the P retention and sorption capacity of the soils.

#### *P Sorption Index (PSI)*

This single-point isotherm method was developed to overcome the limitations of the more time-consuming and complicated standard P adsorption isotherm methods. PSI has been found by several researchers to be well correlated with soil P adsorption maxima and a wide variety of chemical and physiological properties (Bache and Williams, 1971; Mozaffari and Sims, 1994; Sharpley et al., 1984; Simard et al., 1994). As outlined by Sims in SERA-IEG 17 (2009) following the Bache and Williams (1971) method, 2.25-g, <2-mm, air-dried soil sample was shaken at room temperature with 45 mL of a 75 mg P/L as  $\text{KH}_2\text{PO}_4$  solution and two drops of chloroform to inhibit microbial activity for 18 hours at 100 oscillations/min. The sample was then centrifuged at 2000 rpm for 30 minutes, after which the sample extract was filtered using a Whatman 45 filter. The P-saturated soil samples were allowed to air-dry and used to analyze soil P desorption with the double-point anion exchange resin procedure (following). P

concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962). PSI (L/kg) of the soil sample was then determined with the following equations:

$$\text{PSI (L/kg)} = X / \log C \quad [5.1]$$

where X is the amount of P adsorbed (mg P/kg) and C is the concentration of P after 18 hour equilibration (mg/L).

#### *Double-Point Anion Exchange Resin*

An anion exchange resin technique using a soil and water suspension and a dilute sodium chloride extracting solution, was found to be a sufficient method for estimating the quantity of P released and the rate of P-release from soil. This method is analogous to a more natural process for P removal from soil solution than attempting to estimate P release with the various chemical extracts utilized in other P methods (Amer et al., 1955). Following Elrashidi et al (2003) and Burt (2004), a 2-gram, <2-mm, air-dried soil sample, was shaken with a 4-gram perforated bag of spherical anion exchange resin beads and 100 mL of deionized water for 1 hour at 100 oscillations/min at room temperature. The resin bag was removed from the soil suspension and shaken with 50 mL of 1.0 M sodium chloride (NaCl) for 1 hour to remove P retained by the resin. Another 4-gram resin bag was added to the soil suspension and shaken for an additional 23 hours at 100 oscillations/min at room temperature. The second resin bag was removed and rinsed with 1.0 M NaCl and shaken for 1 hour. The NaCl extracting solutions were filtered to 150 mm using Whatman 42 filter paper. A 2- mL concentration of 12 N hydrochloric acid (HCl) was added to each filtered extract. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) using a spectrophotometer at 880

nm, within 72 hours of extraction. Extract P (mg/L) was then converted to mass of soil P (mg/kg) using the following equation:

$$\text{AER (mg/kg)} = [(A*B*C*R*1000)/E] \quad [5.2]$$

where A is the sample extract concentration (mg/L), B is the extract volume (L), C is the dilution (if performed), R is the air-dry/oven-dry weight ratio, and E is the sample weight (g), for P released after one hour (AER1), P released after an additional 23 hours (AER23), and total P released after a total of 24 hours (AER24).

#### *Phosphorus Adsorption Isotherm Determination*

Phosphorus adsorption isotherms were performed following the method of Graetz and Nair (2009). A 0.75-g, <2-mm, air-dried soil sample was shaken for 24 hours at 100 oscillations/min at room temperature with 20 mL of a 0.01 M calcium chloride (CaCl<sub>2</sub>) solution containing 0, 0.1, 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 mg P/L as KH<sub>2</sub>PO<sub>4</sub> and two drops of chloroform to inhibit microbial activity. The sample was then centrifuged at 3000 rpm for 10 minutes, after which the sample extract was filtered using a Whatman 45 filter. P concentrations of the extracts were determined colorimetrically (Murphy and Riley, 1962) at 880 nm using a spectrophotometer, within 72 hours of extraction. 0.01 M calcium chloride extractable phosphorus (P<sub>CaCl2</sub>) was then determined from the extracts from the soil mixed with the CaCl<sub>2</sub> solution containing 0 mg P/L. Results were analyzed and sorption parameters were determined using the linearized Langmuir equation:

*Linearized Langmuir equation:*

$$C / S = (1 / kS_{\text{MAX}}) + (C / S_{\text{MAX}}) \quad [5.3]$$

where  $S$  is the total amount of P retained (mg/kg),  $C$  is the concentration of P after 24 hour equilibration (mg/L),  $S_{\text{MAX}}$  is the P sorption maximum (mg/kg), and  $k$  is a constant related to the bonding energy (L/mg P).

### *Statistical Analysis*

Study samples were analyzed using routine statistical analyses, including descriptive statistics, correlation, and multiple linear regression using the statistical software program, SAS<sub>TM</sub> v. 9.4. The assumptions of the Person correlation include (a) each variable is continuous in measurement, (b) each observation has a pair of values, (c) the absence of outliers in either variable, (d) the normality of each variable, (e) a linear relationship between variables, and (f) homoscedasticity, a tube-like shape between values on a scatterplot and the linear trend line between the variables. The assumptions of multiple linear regression include (a) a linear relationship between the independent and dependent variables, (b) multivariate normality, (c) no or little multicollinearity, (d) no auto-correlation, and (e) homoscedasticity. The SAS CORR procedure with the PEARSON option was used for correlation analyses, while the REG procedure was used for regression analyses and to develop the final prediction equations. Not all assumptions were met when study data was applied to the correlation and regression analyses.

## **RESULTS AND DISCUSSION**

### **Phosphorus Sorption Relationships with Soil Properties**

Descriptive statistics were determined for both the modeling (Table 5.2) and validation datasets (Table 5.3). From the data listed in these tables, it is apparent that the

Table 5.2. Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the modeling dataset.

	Clay	Silt	Sand	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>d</sub>	Ca <sub>d</sub>	Fe <sub>d</sub>	Mg <sub>d</sub>	Mn <sub>d</sub>	C <sub>NH4</sub>	Mg <sub>NH4</sub>	P <sub>ox</sub>	P <sub>M</sub>	P <sub>AG</sub>	P <sub>biov</sub>	P <sub>WS</sub>	P <sub>CdCl2</sub>	AER1	AER2.3	AER2.4	PSI	S <sub>Max</sub>		
	----- % -----				----- mg Element/kg soil -----											----- cmol/kg -----		----- mg P/kg soil -----						----- L/kg -----		----- mg/kg -----		
Mean	22.38	31.38	46.24	1.90	0.75	7.35	966.67	1400.00	365.20	3621.94	93.00	533.44	121.07	23.81	6.08	369.16	66.21	93.99	37.38	0.44	2.73	99.06	68.55	167.62	84.16	141.39		
Standard Error	3.56	3.07	5.16	1.01	0.43	0.25	303.85	539.50	97.49	468.51	37.71	103.83	26.91	3.91	1.67	75.20	11.86	28.69	10.43	0.10	0.93	15.08	28.33	42.14	35.57	101.53		
95% Confidence Level for Mean	7.84	6.75	11.36	2.22	0.94	0.55	668.76	1187.43	214.57	1031.19	83.00	228.52	59.23	8.62	3.68	165.51	26.10	63.14	24.67	0.21	2.04	33.19	62.36	92.76	78.29	223.48		
Median	22.75	31.85	46.45	0.85	0.00	7.60	700.00	700.00	233.00	3809.75	57.10	389.25	76.85	24.55	3.40	302.85	53.45	59.35	27.00	0.32	1.40	78.62	41.10	121.19	55.19	39.26		
Minimum	5.40	11.30	15.20	0.39	0.00	5.20	300.00	300.00	34.60	1364.50	32.60	174.60	26.90	2.80	1.40	96.70	26.10	20.70	3.00	0.11	0.40	48.62	12.60	61.21	0.00	0.00		
Maximum	49.50	45.80	83.30	12.91	5.00	8.40	4200.00	6900.00	1254.40	5908.10	501.90	1184.70	286.90	43.00	20.30	1069.90	164.00	381.40	91.00	1.13	10.90	227.22	371.82	599.03	461.78	1250.00		
N	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	8	12	12	12	12	12	12	12		

Table 5.3. Descriptive statistics of the soil properties and P sorption variables analyzed for samples in the validation dataset.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>cl</sub>	Ca <sub>cl</sub>	Fe <sub>cl</sub>	Mg <sub>cl</sub>	Mn <sub>cl</sub>	Ch <sub>cl</sub>	Mg <sub>cl</sub>	P <sub>ox</sub>	P <sub>cl</sub>	P <sub>mt</sub>	P <sub>bt</sub>	P <sub>vs</sub>	P <sub>ccl</sub>	AER1	AER23	AER24	PSI	S <sub>max</sub>
	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Mean	29.95	2.84	0.00	6.10	1250.00	9500.00	336.30	2143.30	190.00	500.25	71.90	25.00	8.15	526.65	94.95	84.55	74.55	0.40	-	190.12	159.90	350.02	235.43	-
Standard Error	3.15	0.25	0.00	0.60	350.00	6700.00	68.00	682.30	69.20	29.95	5.60	7.80	0.55	155.65	72.05	65.25	61.85	0.30	-	4.25	51.68	55.93	112.15	-
95% Confidence Level for Mean	40.02	3.18	0.00	7.62	4447.17	85131.57	864.02	8669.44	879.27	380.55	71.15	99.11	6.99	1977.72	915.48	829.08	785.88	3.81	-	54.05	656.63	710.68	1425.06	-
Median	29.95	2.84	0.00	6.10	1250.00	9500.00	336.30	2143.30	190.00	500.25	71.90	25.00	8.15	526.65	94.95	84.55	74.55	0.40	-	190.12	159.90	350.02	235.43	-
Minimum	26.80	2.59	0.00	5.50	900.00	2800.00	268.30	1461.00	120.80	470.30	66.30	17.20	7.60	371.00	22.90	19.30	12.70	0.10	-	185.87	108.22	294.09	123.27	-
Maximum	33.10	3.09	0.00	6.70	1600.00	16200.00	404.30	2825.60	259.20	530.20	77.50	32.80	8.70	682.30	167.00	149.80	136.40	0.70	-	194.37	211.58	405.95	347.58	-
N	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	0	2	2	2	2	0



soils examined in this study varied widely in physical and chemical properties known to influence P sorption in soils. Average clay was 22.38 %, average TC was 1.90 %, and average  $\text{CaCO}_3$  contents was 0.75 % for the samples in the modeling. Average pH for the samples in the modeling dataset was 7.35, and the overall range of pH for all samples was 5.2 to 8.4. Average  $\text{Al}_{\text{OX}}$  and  $\text{Fe}_{\text{OX}}$  for the samples in the modeling dataset were 966.67 mg Al/kg soil and 1400 mg Fe/kg soil, respectively. Average  $\text{Al}_{\text{M}}$  was 365.20 mg Al/kg soil, average  $\text{Fe}_{\text{M}}$  was 93.00 mg Fe/kg soil, and average  $\text{Mn}_{\text{M}}$  121.07 mg Mn/kg soil was for samples in the modeling dataset. Average  $\text{Ca}_{\text{M}}$  and  $\text{Mg}_{\text{M}}$  for samples in the modeling dataset were 3621.94 mg Ca/kg soil and 533.44 mg Mg/kg soil, respectively. Average  $\text{Ca}_{\text{NH}_4}$  was 23.81 cmol/kg and average  $\text{Mg}_{\text{NH}_4}$  was 6.08 cmol/kg for samples in the modeling dataset.

The P sorption variables investigated in this study also varied widely. Boxplots were developed for the AER variables for both the modeling and validation datasets (Figure 5.3). Boxplots were also developed for the PSI (Figure 5.4) and  $S_{\text{MAX}}$  (Figure 5.5) variables in the modeling and validation datasets. Average AER1 was 99.06 mg P/kg soil, average AER23 was 68.55 mg P/kg soil, and average AER24 was 167.62 mg P/kg soil for samples in the modeling dataset. The average PSI for the samples in the modeling dataset was 84.16 L/kg.  $S_{\text{MAX}}$  was only determined on the samples in the modeling dataset, which had an average of 141.39 mg/kg.

Pearson correlation coefficients were calculated for the samples in the modeling dataset, between the P sorption variables and soil properties known to affect P sorption in soils (Table 5.4). All P sorption variables were significantly ( $p < 0.05$ ) correlated with

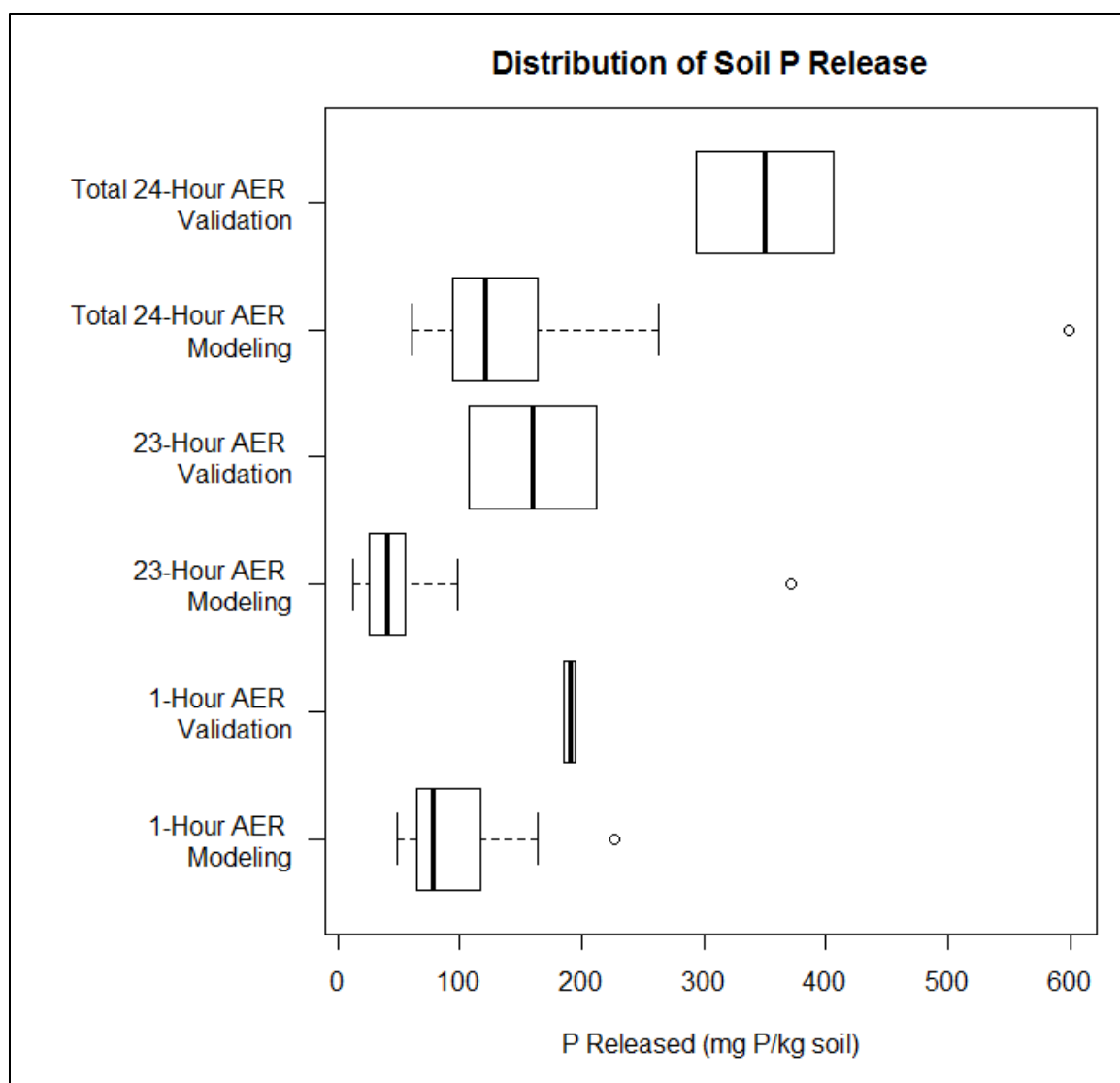


Figure 5.3. Boxplots displaying the quartile statistics of each measured AER variable for the California Bay-Delta/Central Valley modeling validation datasets.

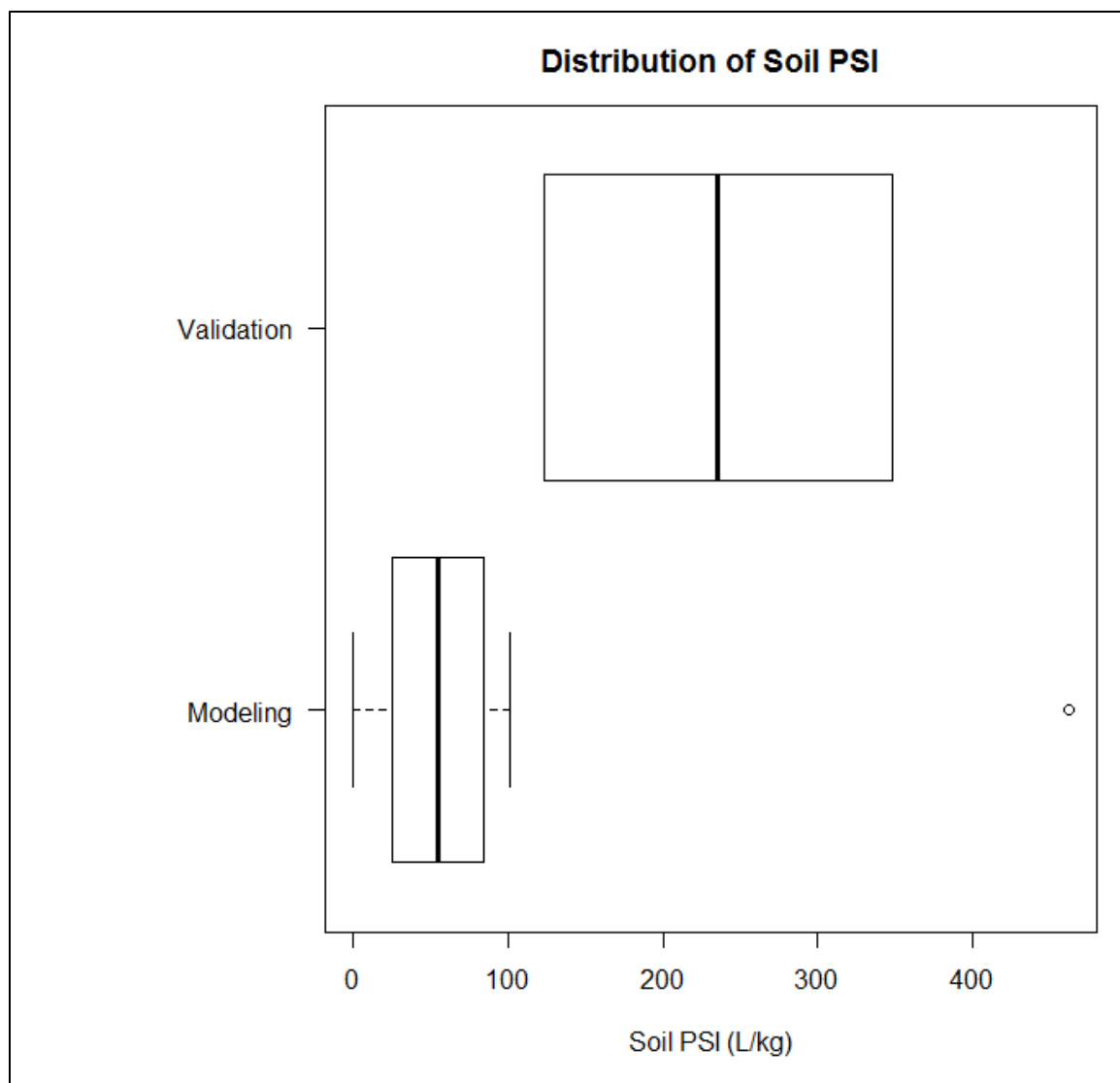


Figure 5.4. Boxplots displaying the quartile statistics for the PSI variable for the California Bay-Delta/Central Valley modeling validation datasets.

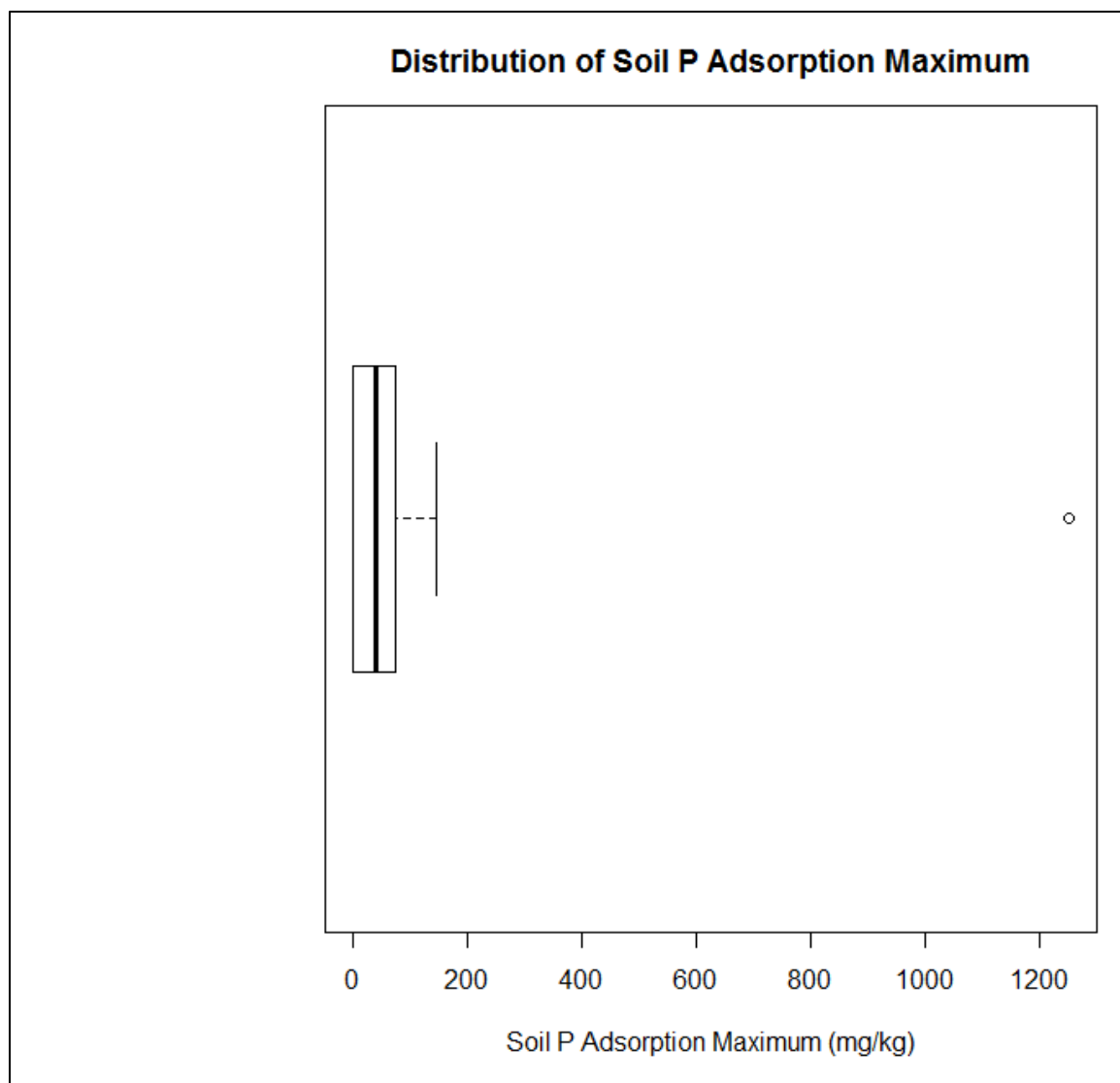


Figure 5.5. Boxplot displaying the quartile statistics for the  $S_{MAX}$  variable for the California Bay-Delta/Central Valley modeling dataset.

Table 5.4. Correlation coefficients between the P sorption variables and soil properties known to affect soil P sorption, for samples in the modeling dataset.

	Clay	TC	CaCO <sub>3</sub>	pH	Al <sub>ox</sub>	Fe <sub>ox</sub>	Al <sub>h</sub>	Ca <sub>m</sub>	Fe <sub>m</sub>	Mg <sub>m</sub>	Mn <sub>m</sub>	Ca <sub>NH4</sub>	Mg <sub>NH4</sub>
AER1	<b>0.6977*</b>	<b>0.7488**</b>	-0.2425	<b>-0.6778*</b>	<b>0.8200**</b>	<b>0.6690*</b>	<b>0.8299**</b>	0.3287	<b>0.8115**</b>	<b>0.7420**</b>	0.1218	0.2989	0.4027
AER23	0.3695	<b>0.9609***</b>	-0.2553	<b>-0.8390**</b>	<b>0.9597***</b>	<b>0.8898**</b>	<b>0.9162***</b>	0.2232	<b>0.9906***</b>	0.5735	-0.0695	0.2801	0.3505
AER24	0.4980	<b>0.9139***</b>	-0.2584	<b>-0.8066**</b>	<b>0.9385**</b>	<b>0.8375**</b>	<b>0.9129***</b>	0.2677	<b>0.9563***</b>	<b>0.6511*</b>	-0.0031	0.2952	0.3798
PSI	0.3565	<b>0.9583***</b>	-0.0939	<b>-0.7908**</b>	<b>0.9895***</b>	<b>0.8734**</b>	<b>0.8871**</b>	0.3439	<b>0.9653***</b>	0.5050	-0.0988	0.4101	0.2540
Smax	0.2836	<b>0.9819***</b>	-0.2087	<b>-0.8135**</b>	<b>0.9709***</b>	<b>0.9175***</b>	<b>0.8802**</b>	0.2748	<b>0.9932***</b>	0.4875	-0.1518	0.3428	0.2803

\* $p \leq 0.05$ ; \*\* $p \leq 0.01$ ; \*\*\* $p \leq 0.001$ ; significant correlation coefficients  $\geq 0.65$  in bold.

TC, pH,  $\text{Al}_{\text{OX}}$ ,  $\text{Fe}_{\text{OX}}$ ,  $\text{Al}_{\text{M}}$ , and  $\text{Fe}_{\text{M}}$ . AER1 was also significantly correlated with clay and  $\text{Mg}_{\text{M}}$ . AER24 was also significantly correlated with  $\text{Mg}_{\text{M}}$ .

These correlations indicate that P sorption is controlled by TC, pH, and Al and Fe oxides in the soils of the California Bay-Delta/Central Valley watershed. Readily desorbable P (AER1) is also influenced by clay and magnesium ions of the soils. Amorphous and crystalline Al have similar relationships to the P sorption variables, while crystalline Fe has a slightly stronger relationship to the P sorption variables than amorphous Fe (Table 5.4). These findings are similar to those noted by Burt et al. (2002), Sharpley et al. (1989), Lindsay (1979), and Harter (1969).

### **Phosphorus Sorption Relationships with Soil P Tests**

Extracted P also varied greatly in the study soils (Tables 5.2 and 5.3). Average soil test P values decreased in the following pattern in the modeling dataset:  $\text{P}_{\text{OX}} > \text{P}_{\text{M3}} > \text{P}_{\text{M}} > \text{P}_{\text{Bray1}} > \text{P}_{\text{CaCl2}} > \text{P}_{\text{WS}}$ . Average  $\text{P}_{\text{M}}$  was greater than average  $\text{P}_{\text{M3}}$  in the validation dataset. Average  $\text{P}_{\text{OX}}$ ,  $\text{P}_{\text{M}}$ , and  $\text{P}_{\text{Bray1}}$  values were greater for samples in the validation dataset while average  $\text{P}_{\text{M3}}$  and  $\text{P}_{\text{WS}}$  values were lower for samples in the validation dataset. Minimum  $\text{P}_{\text{M}}$ ,  $\text{P}_{\text{M3}}$ , and  $\text{P}_{\text{WS}}$  values were lower for samples in the validation dataset while maximum  $\text{P}_{\text{M}}$  and  $\text{P}_{\text{Bray1}}$  values were higher for samples in the validation dataset, compared to those in the modeling dataset. Like  $\text{S}_{\text{MAX}}$ ,  $\text{P}_{\text{CaCl2}}$  was not determined for samples in the validation dataset.

Pearson correlation coefficients were calculated between the P sorption variables and soil P tests for the samples in the modeling dataset (Table 5.5). All P sorption variables were significantly ( $p < 0.05$ ) correlated with  $\text{P}_{\text{OX}}$  and  $\text{P}_{\text{M}}$ . AER1 was also

Table 5.5. Correlations coefficients between the P sorption variables and soil P tests, for samples in the modeling dataset.

	P <sub>ox</sub>	P <sub>M</sub>	P <sub>M3</sub>	P <sub>Bray1</sub>	P <sub>WS</sub>	P <sub>CaCl2</sub>
AER1	0.6099*	<b>0.7659**</b>	0.1692	<b>0.7525*</b>	0.1162	0.2291
AER23	<b>0.7968**</b>	<b>0.8218**</b>	0.2141	0.5876	0.0439	0.2567
AER24	<b>0.7539**</b>	<b>0.8265**</b>	0.2045	<b>0.6622</b>	0.0711	0.2545
PSI	<b>0.8680**</b>	<b>0.7476**</b>	0.1132	0.5453	-0.0377	0.1900
Smax	<b>0.8327**</b>	<b>0.7798**</b>	0.1661	0.5016	-0.0210	0.2174

\* $p \leq 0.05$ ; \*\* $p \leq 0.01$ ; \*\*\* $p \leq 0.001$ ; significant correlation coefficients  $\geq 0.65$  in bold.

significantly correlated with P<sub>Bray1</sub>. These significant correlations indicate the influence of more tightly bound and slowly desorbable soil P on P desorption and adsorption, and the influence of water soluble form of soil P on readily desorbable P.

### Phosphorus Release Characteristics

Figure 5.6 shows the relationship between the predicted P released (mg P/kg soil) and the AER extraction periods (minutes (a, c) and hours (b, d)) for the soils from the modeling dataset that represent the minimum, median, mean, and maximum P released for the soils from the modeling dataset (a, b) and the two soils from the validation dataset (c, d). For soils from the modeling dataset investigated in this study (N = 12), an average of 59% of P was released during the first hour of AER extraction, while the remaining 41% of P was released during the following 23 hours of AER extraction. When soils in the modeling dataset were grouped based on the presence of CaCO<sub>3</sub> and their degree of weathering (Sharpley et al., 1984), during the first hour of AER extraction there was an increase from 59% of P released to 77% for calcareous soils (N = 4) and a slight decrease to 54% of P released for slightly weathered soils (N = 8) (data not shown). The soils in

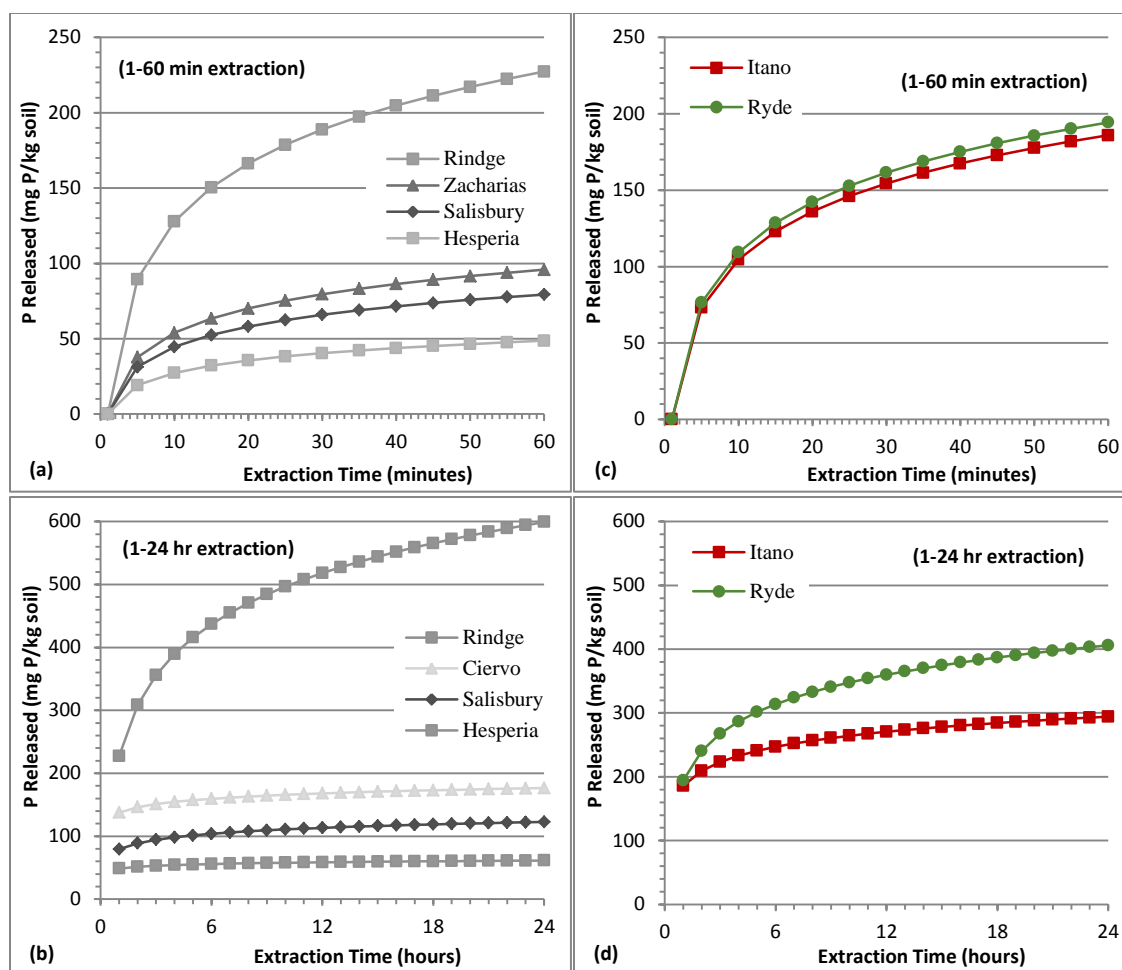


Figure 5.6. Predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, median, mean, and maximum for samples from the modeling dataset during the (a) 1-60 minute and (b) 1-24 hour extraction periods, and the two samples from the validation dataset (colored curves) during the (c) 1-60 minute and (d) 1-24 hour extraction periods.

the validation dataset ( $N = 2$ ) released 48% and 63% of P during the first hour of AER extraction, for an average of 56% 1-hour P release.

The linear regression equations to predict P released (mg P/kg soil) by AER extraction for both 1 and 24-hr extraction periods are listed in Appendix I. Linear relationships are always produced when the amount of P released (mg P/kg soil) is plotted against the log of the AER extraction period (Elrashidi et al., 2012; Elrashidi et



al., 2003). These linear relationships are also shown for the soils from the modeling dataset that represent the minimum, median, mean, and maximum P released for the California Bay-Delta/Central Valley watershed soils in Appendix I. The amount of P released after the first hour of AER extraction mainly represents the readily available P in the soil. This 1-hour extraction P released value varied greatly within the California Bay-Delta/Central Valley watershed soils, with a range of 48.62 mg P/kg soil to 227.22 mg P/kg soil (Table 5.2). The AER1 range for the calcareous soils in this region, however, is notably narrower, 48.62 mg P/kg soil to 137.56 mg P/kg soil (data not shown). The total P released value (AER24) also varied greatly for soils within the California Bay-Delta/Central Valley watershed, with a range of 61.21 mg P/kg soil to 599.03 mg P/kg soil (Table 5.2). Again, the AER24 range for the calcareous soils in this region is notably narrower, with a range of 61.21 mg P/kg soil to 176.47 mg P/kg soil (data not shown). Overall, the calcareous soils investigated had low TC, high pH, and low  $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ , and  $Fe_M$  concentrations (data not shown). Three of the four calcareous soils also had higher than average  $P_{OX}$  values, and all four had lower than average PM values (data not shown).

Of all the soils investigated from the California Bay-Delta/Central Valley watershed, the Rindge soil from the modeling dataset released the most P during the 1-hour extraction period and overall after 24 hours of extraction (Figure 5.6). The Hesperia soil from the modeling dataset released the least P during the 1-hour extraction period and overall after 24 hours of extraction (Figure 5.6). The Rindge soil had the highest TC,  $Al_{OX}$ ,  $Al_M$ ,  $Fe_M$ ,  $P_{OX}$ , PSI, and  $S_{MAX}$  overall, the highest  $Fe_{OX}$  of soils in the modeling dataset, high  $Mg_M$ ,  $P_{M3}$ , and  $P_{Bray1}$ , average  $P_{WS}$ , and the lowest pH overall (data not

shown). The Hesperia soil had the lowest  $Al_M$  and  $S_{MAX}$  overall, low clay, TC,  $Al_{OX}$ ,  $Fe_M$ ,  $Mg_M$ ,  $P_M$ ,  $P_{M3}$ , and PSI, average  $P_{WS}$ , and high pH,  $Fe_{OX}$ , and  $P_{OX}$  (data not shown).

The Ryde and Itano soils from the validation dataset released the second and third most P, respectively, during both the 1-hour extraction period and overall after 24 hours of extraction (Figure 5.6). Both soils exhibited similar behaviors of P release during the 1-hour extraction period (Figure 5.6), releasing similar amounts of P during that period (Table 5.3). The Ryde soil released even more P during the additional 23 hours of extraction, almost twice as much as the Itano soil (Table 5.3). Compared to the property averages of the soils in the modeling dataset (Table 5.2), the Itano soil had similar clay,  $Al_{OX}$ ,  $Fe_M$ , and  $P_{OX}$  values, slightly higher TC,  $Fe_{OX}$ ,  $Mg_M$ ,  $P_M$ ,  $P_{M3}$ ,  $P_{Bray1}$ ,  $P_{WS}$ , and PSI values, and slightly lower pH and  $Al_M$  values. Overall, the Ryde soil had the most  $Fe_{OX}$ , more TC,  $Mg_M$ , and PSI, low  $P_{Bray1}$ , and the lowest  $P_M$ ,  $P_{M3}$ , and  $P_{WS}$ . The Rindge soil also had  $Al_{OX}$ ,  $Al_M$ ,  $Fe_M$ , and  $P_{OX}$  concentrations about two-times greater than the Itano soil. It was noted previously that soil P desorption is primarily controlled by TC, pH, and Al and Fe oxides in these soils. The California Bay-Delta/Central Valley watershed soils that released the most P during the AER desorption process had high amounts of most of these components and high amounts of total P already in the soils, and thus easily released large amounts of P in solution. The soils that released the least P during the desorption process had low amounts of most of these components known to retain P and low to moderate amount of P already in the soil, and thus released less amounts of P due to not having a relatively strong ability to readily retain P.

## Predicting Soil Phosphorus Behavior

Most soil testing facilities only routinely analyze soils for particle-size (sand, silt, and clay), carbon content, and pH, and do not have the means or capability to perform more detailed analyses such as oxalate or Mehlich-3 extractions. Of all soil parameters investigated, only clay, TC, and pH are routinely analyzed on all soil samples processed at the KSSL. At the KSSL, analyses such as acid oxalate extractable Al, Fe, and P, and Mehlich-3 extractable elements (Al, Ca, Fe, Mg, Mn, P) are additional analyses for select samples requested by the project researcher or investigator, limiting the data available for these properties. As mentioned previously, P sorption behaviors in soil have been found to be related to soil clay, TC, and/or pH (Burt et al., 2002; Harter, 1969; Juo and Fox, 1977; Lopez-Hernandez and Burnham, 1974; McCallister and Logan, 1978, Sharpley et al., 1989, Syers et al., 1971). For each of the five P sorption variables of interest (AER1, AER23, AER24, PSI, and  $S_{MAX}$ ), linear regression equations were developed. Clay, TC, and pH were modeled independently and additional variables ( $Al_{OX}$ ,  $Fe_{OX}$ ,  $Al_M$ ,  $Ca_M$ ,  $Fe_M$ ,  $Mg_M$ ,  $Mn_M$ ,  $Ca_{NH_4}$ ,  $Mg_{NH_4}$ ) were progressively added to the models. Models contained one to three variables, with clay, TC, or pH in each equation. The use of clay, TC, or pH in additional models was dependent on the significance of the respective independent models. Clay, TC, and/or pH were used in additional modeling if, (a) the  $p$  value of the independent model was significant ( $p \leq 0.05$ ), or (b) if no independent model was significant, the independent model with the lowest  $p$  value was used. An example of the progressive linear regression modeling method for the AER23 variables is listed in Appendix I. For AER23, the independent models with TC and pH were both significant, so they were used in the additional modeling steps. For AER24, PSI, and  $S_{MAX}$ , the

independent models with TC and pH were also both significant for each case, so they were used in the additional modeling steps for each P sorption variable. For AER1, all three independent models were significant and were used in additional modeling steps.

The three most significant P sorption prediction equations for AER1, AER23, AER24, PSI, and  $S_{MAX}$  developed with the samples in the modeling dataset, those with the lowest  $p$  values and highest  $R^2$  values, were examined (Table 5.6). The inclusion of  $Fe_M$ , often also with  $Mg_M$ , in most of the significant prediction equations for each P desorption variable indicates the significant influence of crystalline Fe oxides on soil P release behaviors in soils of this region (Table 5.6). The soil P adsorption prediction equations also indicate a significant influence of crystalline Fe oxides on soil P adsorption behaviors in soils of this region, as well as the significant influence amorphous Al and Fe oxides (Table 5.6). Soil P sorption behaviors are also influenced, to a lesser extent, by the calcium and magnesium components of these soils, as noted by the inclusion of  $Ca_M$  and  $Mg_M$  in some the PSI and  $S_{MAX}$  prediction equations (Table 5.6). These findings are similar to the relationships noted by Burt et al. (2002), Sharpley et al. (1989), Lindsay (1979), and Harter (1969).

The reliability of the prediction equations developed for AER1, AER23, AER24 and PSI was examined when the models were applied to the samples from the validation dataset (Table 5.7). The most significant prediction equations for each P sorption variable developed from the overall modeling dataset in Chapter 2 are also included in Table 5.7, as noted by the 'CONUS' term, for comparison. For AER1, each significant model predicted AER1 values within 20 % of the measured AER1 value for one of the two samples. For AER23, the significant model with pH,  $Fe_M$ , and  $Mg_M$  predicted values

Table 5.6. The three most significant ( $p < 0.05$ ) prediction models developed for each P sorption variable, from samples in the modeling dataset.

AER1					
Variable(s)	R <sup>2</sup>	p	MSE	N	
19.78 + 4.03Clay + 0.33Fe <sub>M</sub> - 0.08Mg <sub>M</sub>	0.9304	0.0001	16.16	12	
13.18 + 2.10Clay + 0.26Fe <sub>M</sub> + 0.004Ca <sub>M</sub>	0.9146	0.0001	17.90	12	
28.42 + 2.52Clay + 0.25Fe <sub>M</sub> - 0.08Mn <sub>M</sub>	0.9111	0.0001	18.27	12	
AER23					
Variable(s)	R <sup>2</sup>	p	MSE	N	
-12.75 + 8.24TC + 0.47Fe <sub>M</sub> + 0.04Mg <sub>M</sub>	0.9914	0.0001	10.66	12	
-190.28 + 22.19pH + 0.10Al <sub>M</sub> + 0.64Fe <sub>M</sub>	0.9898	0.0001	11.63	12	
-28.31 + 2.06pH + 0.72Fe <sub>M</sub> + 0.03Mg <sub>M</sub>	0.9887	0.0001	12.25	12	
AER24					
Variable(s)	R <sup>2</sup>	p	MSE	N	
150.96 + 4.08Clay + 32.44TC - 18.55pH	0.9709	0.0001	29.22	12	
2.56 + 4.33Clay + 35.83TC	0.9661	0.0001	29.71	12	
28.98 + 15.06TC + 0.52Fe <sub>M</sub> + 0.12Mg <sub>M</sub>	0.9570	0.0001	35.49	12	
PSI					
Variable(s)	R <sup>2</sup>	p	MSE	N	
144.04 - 21.73pH + 0.11Al <sub>OX</sub> - 0.01Fe <sub>OX</sub>	0.9891	0.0001	15.09	12	
125.63 - 19.33pH + 0.10Al <sub>OX</sub>	0.9876	0.0001	15.16	12	
-76.51 + 16.55TC + 0.19Al <sub>M</sub> + 0.02Ca <sub>M</sub>	0.9831	0.0001	18.80	12	
S <sub>MAX</sub>					
Variable(s)	R <sup>2</sup>	p	MSE	N	
100.74 - 38.36pH + 2.39Fe <sub>M</sub> + 0.03Ca <sub>M</sub>	0.9957	0.0001	26.96	12	
-157.90 + 10.58TC + 2.36Fe <sub>M</sub> + 0.02Ca <sub>M</sub>	0.9947	0.0001	29.92	12	
-105.97 + 41.26TC + 1.53Fe <sub>M</sub> + 0.05Mg <sub>M</sub>	0.9922	0.0001	36.39	12	

Table 5.7. The reliability of the prediction models listed in Table 5.6, and the most significant ( $p < 0.05$ ) model for each P sorption variable developed in Chapter for all CONUS agricultural soils, when applied to the two samples in the validation dataset. Predicted values are highlighted when within 10 %, 15 %, or 20 % of the measured value.

AER1					AER23				
Measured	Clay FeM MgM	Clay FeM CaM	Clay FeM MnM	Clay TC pH CONUS	Measured	TC FeM MgM	pH AIM FeM	pH FeM MgM	Clay AIOX FeOX CONUS
185.87	130.02	112.37	120.85	131.27	108.22	84.18	62.54	86.68	72.81
194.37	196.29	156.03	170.43	146.39	211.58	155.74	138.08	185.65	149.50
AER24					PSI				
Measured	Clay TC pH	Clay TC	TC FeM MgM	Clay AIOX FeOX CONUS	Measured	pH AIOX FeOX	pH AIOX	TC AIM CaM	Clay AIOX FeOX CONUS
294.09	468.61	211.40	551.84	210.95	123.27	69.45	86.14	73.84	119.62
405.95	488.27	256.60	725.87	300.21	347.58	38.52	179.34	80.67	303.18
SMAX									
Measured	pH FeM CaM	TC FeM CaM	TC FeM MgM	pH AIOX FeOX CONUS					
.	217.21	211.10	209.23	157.52					
.	553.08	515.72	444.61	434.62					

Predicted value within 10% of measured value highlighted in yellow. Predicted value within 15% of measured value highlighted in peach. Predicted value within 20% of measured value highlighted in red-orange.

within 20 % of the measured AER23 values for both samples. For PSI, only the CONUS model accurately predicted values with 20 % of the measured PSI values, for both samples. Overall, the reliability of the prediction equations is difficult to assess due to low number of samples in the validation dataset ( $N = 2$ ). The significance of the prediction equations or models themselves also raises concerns as the low number of samples ( $N = 12$ ) used to develop these models could be creating a biased estimate, falsely inflating the  $R^2$  estimate and correspondingly the significance of these models. The low number of samples used in this study in the result of the availability of samples from the study area in KSSL archives and USDA Animal and Plant Health Inspection Service (APHIS) regulations on the collection and use of soil samples from the state of California. At the time of sample collection from the KSSL archive, the majority of archived samples from the state of California were on a quarantine list of samples not to be used or analyzed due to specific regulations regarding those soils. As a result, the prediction models provide an idea of the primary soil properties influencing P sorption behaviors in soils of the California Bay-Delta/Central Valley watershed. Research on additional surface soil samples from the area is needed to develop usable models generated from an appropriate sample size.

### **Potential Risk of Phosphorus Loading**

As mentioned earlier, the California Bay-Delta/Central Valley watershed is currently receiving more attention due to eutrophication problems and nutrient-laden runoff problems. Forty-eight states have each developed a P Index, an assessment tool used to identify critical source areas and to target management practices to reduce P loss,

to combat these issues, including the state of California. California's P Index is state-specific and typically includes a soil test P value as a contributing P Index factor. The soil test P method and the associated break-point values also vary with each specific P Index. As noted previously in Chapter 1, most soil test P techniques rely on the use of various chemicals and solutions that do not accurately mimic a natural in-field process. Sharpley et al. (2006) note that to mimic the interaction between surface soil and release of P to runoff water, water extractions are the ideal methods. Therefore, the data and predictive models developed in this study in relation to total P release have the potential to be used as an additional component for a P Index, or other assessment tool, and resulting management and planning strategies, that would be more reflective of actual P release into runoff in the California Bay-Delta/Central Valley watershed.

In Chapter 2, a model was developed by averaging AER24 values by taxonomic Great Groups in the overall modeling dataset, then applying those averaged values to the soil map units in the gSSURGO MuRas\_90m raster layer, based on the map unit's Great Group classification. This process was repeated with the AER24 values and Great Groups from the California Bay-Delta/Central Valley watershed modeling dataset, and compared to the results from the Chapter 2 model, shown in Figure 5.7. Quartiles for the Sub-basin-specific model (Figure 5.7 (b)) were determined for AER24 values of samples in the California Bay-Delta/Central Valley watershed modeling dataset, which were used to determine break-points for a potential P loading risk index, as listed in Table 5.8.

Several observations can be made from the comparison of the potential P loading risk maps displayed in Figure 5.7. First, there is distinct decrease in the map units that were given averaged total P release values in the model developed using samples from



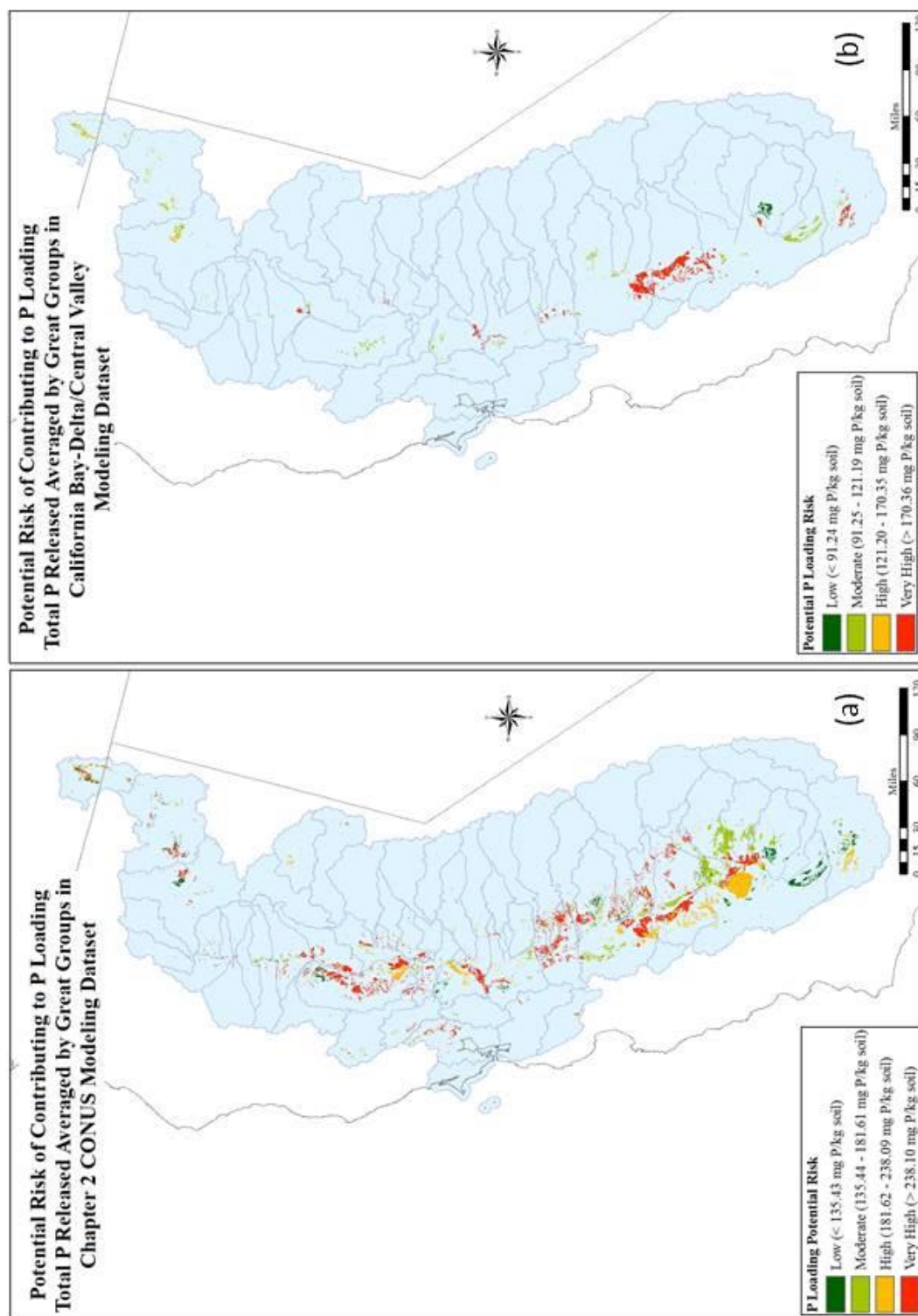


Figure 5.7. Potential risk agricultural soils of the California Bay-Delta/Central Valley region pose to contributing to P loading, with total P release estimated averaged by taxonomic Great Groups from the Chapter 2 CONUS modeling dataset (a) and by taxonomic Great Groups from the California Bay-Delta/Central Valley region modeling dataset (b).

Table 5.8. P Index Risk Potential classifications as determined by AER24 quartile statistics from the samples in the modeling dataset.

<b>P Index (Potential)</b>	<b>Quartile</b>	<b>AER24</b>
Low	< 25%	≤ 91.24
Moderate	25 - 50%	91.25 - 121.19
High	50 - 75%	121.20 - 170.35
Very High	> 75%	> 170.36

the California Bay-Delta/Central Valley modeling dataset due to a difference in the number of taxonomic Great Groups used in each model. Table 5.1 lists the taxonomic Great Groups for the samples analyzed in this study, of which there are 9 different Great Groups. The CONUS modeling data in Chapter 2 used to develop the corresponding model included samples that encompassed 81 different taxonomic Great Groups. For both models the majority of the modeled map units are scattered throughout the Sacramento and San Joaquin Valleys MLRA, the Southern Cascade Mountains MLRA, and the northern portion of the Sierra Nevada Mountains MLRA, with a few modeled map units in the Central California Coast Range MLRA as well (Figures 5.2 and 5.7). These MLRAs area also where the majority of agricultural is focused in the region (Figures 5.1 and 5.2). Both models generate concentrated areas of “High” and “Very High” risk potential map units, though these areas differ between the two models (Figure 5.7). The numerical breaks between the potential risk categories also differ between the two models, with notably lower break values for the region-specific model. While both visual models were developed using similar processes, the samples used to develop each model are the drivers behind the differences between the models. If used in combination with additional data and tools for nutrient management planning strategies, these models and the differences between them could potentially have significant effects on not only

the allocation of materials, practices, and financial support, but on the overall success of reducing P loading in the watershed system.

## CONCLUSIONS

The California Bay-Delta/Central Valley watershed is an area with highly concentrated, intense agricultural practices, and also unique and fragile aquatic systems. P loading and eutrophication issues are not new to this region, though attention to them is growing. Results from this study indicate that P sorption behaviors in this region are controlled by the total carbon content, pH, and crystalline and amorphous Al and Fe oxides in the soil. Oxalate or Mehlich-3 extractable soil P tests would be most appropriate for estimating total P desorption or P adsorption in soils of the California Bay-Delta/Central Valley watershed, as they the most significantly ( $p < 0.05$ ) and highly correlated soil P tests to those P sorption behaviors. Assessing the accuracy and reliability of the watershed-specific models, and CONUS-level model developed in Chapter 2, for predicting total P release from soils in this area is difficult due to the low number of validation samples. The watershed-specific models themselves may be biased due to the low number of samples in the modeling dataset used to develop them. The modeling datasets from the two studies, however, generated distinctly different potential P-loading risk models for agricultural soils within the watershed, with “High” and “Very High” risk areas being located in different areas in each model. The watershed-specific model was also only applicable to a small coverage area of the watershed, again, making the models difficult to compare.

The relationships and models developed in this study have great potential for improving soil P assessment tools in the California Bay-Delta/Central Valley watershed, and to better inform P management related decision-making at the watershed, farm, and field scales. Additional research and refinement of these models and appropriate potential-risk break-point values is required before implementation into assessment tools. Implementing oxalate and Mehlich-3 extraction methods as standard analyses for all soils at soil testing labs like the KSSL, will be necessary to further refine the P desorption models and improve our understanding of soil P sorption behaviors in this region, and elsewhere.

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## APPENDIX I

### DESORPTION REGRESSION EQUATION COMPONENTS TABLE, LOG- TRANSFORMED DESORPTION PLOTS, AND REGRESSION MODELING STEPS

#### TABLE FOR THE CALIFORNIA BAY-DELTA/CENTRAL VALLEY

Table I.1. Linear regression equation<sup>a</sup> components used to predict P released (mg P/kg soil) by anion exchange resin for all California Bay-Delta/Central Valley region soils investigated, during the 1-60 minute and 1-24 hour extraction periods.

User Pedon ID	Soil Series	Grouping	Intercept (I)	Slope (S1) (1-60 min)	Slope (S2) (1-24 hr)
			----- mg P/kg soil -----		
91CA077001	Rindge	S	227.22	127.65	269.43
92CA099001	Zacharias	S	95.82	53.83	37.12
92CA099002	Vernalis	S	93.06	52.28	42.69
92CA099005	Capay	S	164.20	92.25	71.39
92CA099007	Henneke	S	74.96	42.11	32.45
92CA107001	Jerryslu	S	61.68	34.65	19.04
92CA107002	Atesh	C	60.35	33.90	13.19
92CA107003	Atesh	C	77.90	43.76	18.18
93CA029001	Calicreek	S	68.05	38.23	23.92
94CA019001	Hesperia	C	48.62	27.31	9.13
94CA019002	Ciervo	C	137.56	77.28	28.20
S2012CA077004*	Itano	S	185.87	104.42	78.42
S2014CA077001*	Ryde	S	194.37	109.20	153.32
79OR037003	Salisbury	S	79.34	44.57	31.37

<sup>a</sup>  $P = I + S1 \times (\log h)$  for 1-60 min;  $P = I + S2 \times (\log h)$  for 1-24 hr extraction period; where P = P released (mg P/kg soil), I = intercept, S1 = slope of the 1-60 min extraction period, S2 = slope of the 1-24 hr extraction period, and h = extraction period.

\* Indicates sample in the validation dataset.

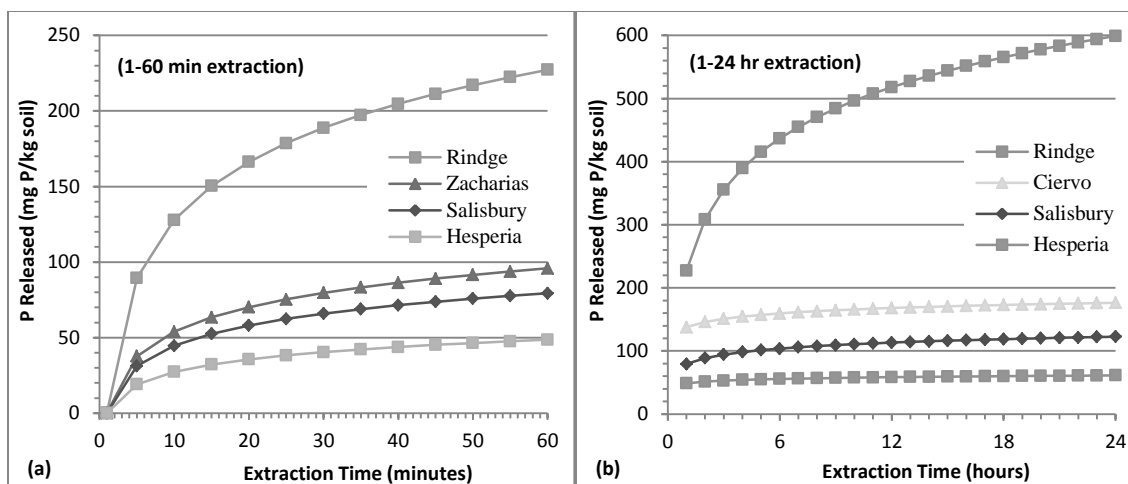


Figure I.1. Relationship between the log (extraction time) and the predicted amounts of P released (mg P/kg soil) for soils that represent the minimum, first quartile, median, mean, third quartile, and maximum for samples in the California Bay-Delta/Central Valley modeling dataset, during the (a) 1-60 minute and (b) 1-24 hour extraction periods.

Table I.2. An example of the progressive regression modeling method used on samples from the California Bay-Delta/Central Valley modeling datasets, for AER23.

AER23											
Model	Variable(s)	R <sup>2</sup>	p	MSE	N	Model	Variable(s)	R <sup>2</sup>	p	MSE	N
1	Clay	0.1365	0.2372	95.65	12	26	TC CaNH4	0.9367	0.0001	27.31	12
2	TC	0.9233	0.0001	28.50	12	27	TC MgNH4	0.9480	0.0001	24.74	12
3	pH	0.7039	0.0006	56.01	12	28	TC CaNH4 MgNH4	0.9492	0.0001	25.95	12
4	Clay TC	0.9737	0.0001	17.61	12	29	pH AlOX	0.9595	0.0001	21.85	12
5	Clay pH	0.7184	0.0033	57.58	12	30	pH FeOX	0.8623	0.0001	40.26	12
6	TC pH	0.9509	0.0001	24.04	12	31	pH AlOX FeOX	0.9602	0.0001	22.96	12
7	Clay TC pH	0.9848	0.0001	14.20	12	32	pH AlM	0.8466	0.0002	42.49	12
8	TC AlOX	0.9394	0.0001	26.71	12	33	pH CaM	0.8746	0.0001	38.42	12
9	TC FeOX	0.9256	0.0001	29.59	12	34	pH FeM	0.9815	0.0001	14.77	12
10	TC AlOX FeOX	0.9404	0.0001	28.10	12	35	pH MgM	0.7199	0.0033	57.43	12
11	TC AlM	0.9770	0.0001	16.45	12	36	pH MnM	0.8316	0.0003	44.53	12
12	TC CaM	0.9305	0.0001	28.61	12	37	pH AlM CaM	0.9148	0.0001	33.59	12
13	TC FeM	0.9814	0.0001	14.81	12	38	<b>pH AlM FeM</b>	0.9898	0.0001	11.63	12
14	TC MgM	0.9802	0.0001	15.28	12	39	pH AlM MgM	0.8863	0.0004	38.80	12
15	TC MnM	0.9638	0.0001	20.64	12	40	pH AlM MnM	0.9717	0.0001	19.35	12
16	TC AlM CaM	0.9797	0.0001	16.41	12	41	pH FeM CaM	0.9859	0.0001	13.67	12
17	TC AlM FeM	0.9866	0.0001	13.32	12	42	<b>pH FeM MgM</b>	0.9887	0.0001	12.25	12
18	TC AlM MgM	0.9856	0.0001	13.82	12	43	pH FeM MnM	0.9826	0.0001	15.18	12
19	TC AlM MnM	0.9788	0.0001	16.75	12	44	pH CaM MgM	0.8826	0.0004	39.43	12
20	TC FeM CaM	0.9842	0.0001	14.45	12	45	pH CaM MnM	0.8955	0.0003	37.20	12
21	<b>TC FeM MgM</b>	0.9914	0.0001	10.66	12	46	pH MgM MnM	0.9315	0.0001	30.11	12
22	TC FeM MnM	0.9828	0.0001	15.10	12	47	pH CaNH4	0.8393	0.0003	43.49	12
23	TC CaM MgM	0.9819	0.0001	15.49	12	48	pH MgNH4	0.7143	0.0036	58.00	12
24	TC CaM MnM	0.9651	0.0001	21.49	12	49	pH CaNH4 MgNH4	0.9142	0.0001	33.70	12
25	TC MgM MnM	0.9825	0.0001	15.22	12						

\*  $p \leq 0.0001$  highlighted in green;  $0.0001 > p \leq 0.01$  highlighted in yellow; three models with lowest  $p$  and highest  $R^2$  in bold.

## Chapter 6

### SYNTHESIS

Phosphorus (P) loss via agricultural runoff has been shown to be the primary source in controlling and influencing most freshwater eutrophication issues. Phosphorus transport models and assessment tools have been developed and refined over the last 20+ years, and currently forty-eight states in the U.S. have adopted a P Index as part of their NRCS 590 Nutrient Management Standard. However, even with widespread acceptance and use of these P management tools, the reductions in the extent of P-impaired surface waters have been minimal at best. In this dissertation, models utilizing soil physio-chemical properties to predict total P release from soils have been proposed as a potential source-component for improving current P Indices and assessment tools. The goals for the development and use of these models are; (1) identification of agricultural soils that contain high amounts of P, relative to their sorptive potential, that would have the most negative effect on surface water if eroded, (2) classification of soils as to their potential to contribute P to surface waters, and (3) evaluation of how soils retain (adsorption) and release P (desorption), to provide better estimates of pollution risk at the watershed, farm, and field levels, and possibly improve existing models that predict nutrient losses.

The first study in this dissertation (Chapter 2) focused on developing soil P sorption behavior relationships and prediction models at a large, national-scale for agricultural surface soils. Two grouping schemes were investigated and compared to the results of the general, national-level prediction models. Soils were analyzed all together,

grouped by their calcium carbonate content and degree of weathering, and also grouped by taxonomic Great Group classification for comparisons. Relationships were determined between soil P adsorption and desorption behaviors and soil physical and chemical properties known to affect P sorption, such as clay content, total carbon content, pH, oxalate extractable Al and Fe, and Mehlich-3 extractable Al, Ca, Fe, Mg, and Mn. Overall, results indicated that P sorption behaviors were primarily controlled by the clay and amorphous Al and Fe oxides in the soils. Total soil P desorption and soil P adsorption were also found to be significantly related to both oxalate and Mehlich-3 extractable forms of P. Results also indicated that the relationships and predictive models improved when soils were grouped by calcium carbonate content and degree of weathering. Relationships and predictive models also improved when soils were grouped by taxonomic Great Group, though the few number of samples available in each Great Group could have created statistical bias. The statistically significant and most reliable predictive models for total soil P release always contained a clay and Al oxide component in the model, when soils were considered all together, or grouped by calcium carbonate content and degree of weathering. The total P release predictive models for calcareous soils and highly weathered soils included the crystalline form of Al, and also contained a Ca component. It was concluded that, (a) the inclusion of a total P desorption variable or prediction model has the potential to be a useful addition in P modeling and assessment tools, such as a state P Index, and thus nutrient management plans, (b) oxalate and Mehlich-3 extraction methods should be included as standard soil sample analyses at soil testing laboratories, (c) oxalate extractable P could also be used to estimate total soil P desorption and/or adsorption in all soils, while Mehlich-3 extractable P could be used to

estimate total soil P desorption and/or adsorption in calcareous and highly weathered soils, and (d) additional research and refinement of models is needed before implementation into assessment tools.

The second study (Chapter 3) used the same methods, techniques, and statistical analyses applied in Chapter 2, but only focused on agricultural surface soils in the Chesapeake Bay watershed. The underlying hypothesis was that watershed-specific soil P sorption relationships would be more distinct and prediction models would be more reliable when applied within the watershed than the national-level models developed in Chapter 2. Investigated soils were primarily a combination of highly weathered and slightly weathered soils, with a few calcareous soils. Overall, soil P sorption behaviors were primarily controlled by the clay, total carbon, and amorphous and crystalline Al oxides in the soils. Oxalate and Mehlich-3 extractable P were also noted as the most appropriate soil P tests for estimating total P desorption or P adsorption of agricultural surface soils in the Chesapeake Bay watershed. The most significant and reliable watershed-specific total soil P release model included clay and amorphous Al, like the national-level model from Chapter 2, but was a statistically stronger model. Simple potential-risk models developed with the Chapter 2 data and the watershed-specific data resulted in very different models. Logically, the watershed-specific models would be more appropriate to consider for inclusion into P assessment tools, though further research into the soil P release behaviors in the Chesapeake Bay region is needed due to the poor performance and reliability of the models generated in this study. To further improve and refine the P sorption models for this region, relationships and prediction models could be developed by grouping soils within each distinct physiographic area to

account for the variability of the landscape and soils within the area, or by their calcium carbonate content and degree of weathering.

The third study (Chapter 4) was similar to that of the second study (Chapter 3), in that the sample methods, techniques, and statistical analyses applied in Chapter 2 were again used, but the focus was on agricultural surface soils in the Upper Mississippi River Sub-basin. Again, the underlying hypothesis was that Sub-basin-specific soil P sorption relationships would be more distinct and prediction models would be more reliable when applied within the Sub-basin than the national-level models developed in Chapter 2. Most of the soils investigated in this study were slightly weathered, with a few calcareous soils and one highly weathered soil. Soil P sorption in this region was shown to be controlled by the clay content and amorphous and crystalline Al and Fe oxides in the soil. Calcium chloride and water extractable P were also noted as the most appropriate soil P tests for estimating total P desorption of agricultural surface soils in the Upper Mississippi River Sub-basin, though oxalate and Mehlich-3 extractable P were noted as the most appropriate soil P tests for estimating soil P adsorption. The most significant and reliable Sub-basin-specific total soil P release prediction model included clay and amorphous Al and Fe, similar to the components of the national-level model from Chapter 2, and was also a statistically stronger model. Simple potential-risk models were developed with the Chapter 2 data and the Sub-basin-specific data again resulted in very different models. The Sub-basin-specific models would, logically, be more appropriate to consider for inclusion into P assessment tools within the region, though further research into the soil P release behaviors in the Upper Mississippi River Sub-basin is encouraged. To account for the variability of the soils and their forming factors over

such a large area, additional research and refinement could focus on developing specific P desorption models for each Land Resource Region, soil temperature zones, or smaller sub-regions based on other soil forming characteristics, or by grouping soils by their calcium carbonate content and degree of weathering.

Finally, the fourth study in this dissertation (Chapter 5) was also similar to that of the second study (Chapter 3), in that the sample methods, techniques, and statistical analyses applied in Chapter 2 were again used, but the focus was on agricultural surface soils in the California Bay-Delta/Central Valley watershed. The soils investigated from this region were a mix of slightly weathered and calcareous soils. Soil P sorption behaviors in soils of this region were shown to be controlled by clay content, total carbon content, pH, and crystalline and amorphous Al and Fe oxides in the soil. Oxalate and Mehlich-3 extractable P were also noted as the most appropriate soil P tests for estimating total P desorption or P adsorption of agricultural surface soils in the California Bay-Delta/Central Valley watershed. The most significant and reliable watershed-specific total soil P release prediction model included clay, total carbon, and pH, quite different from the components of the national-level model from Chapter 2, and was also a statistically stronger model. Assessing the accuracy and reliability of the models was difficult as there were very few samples with which to work. This has likely led to statistically biased watershed-specific models as well. Similar to the Chesapeake Bay and Upper Mississippi investigations, the potential-risk models developed with the Chapter 2 data and the watershed-specific data again resulted in very different models, specifically in the coverage of soils that could be predicted with the watershed-specific models. Additional research on soil P sorption behaviors is needed to develop a better



understanding of these behaviors in this unique region, and to further refine total P release models that have the potential for improving soil P assessment tools and nutrient management decisions.

Overall, the culmination of this dissertation has shown that, (a) oxalate extractable and Mehlich-3 extractable P tests are the most appropriate soil P tests for estimating total P release and P adsorption for most soils, (b) total P release prediction models improve when soils are grouped based on their calcium carbonate content and degree of weathering or modeled at a large watershed level, compared to prediction models at a general national-scale, (c) the majority of significant and reliable total P release prediction models include clay and either oxalate or Mehlich-3 extractable Al, (d) potential risk models can differ greatly within a given area or watershed, depending on the employed modeling scheme (i.e. area-specific vs. national-level), and (d) with further research and refinement, the relationships and models developed in these studies have the potential of improving current P Indices and assessment tools, and subsequent management recommendations and practices.

#### Future Research Needs

The relationships and models developed in this study indicate the potential for improvements in current P assessment tools and management plans, and help to identify the needs of future research.

- **Additional standard analyses.** Most soil testing laboratories, including the national NRCS KSSL facility, rarely include oxalate extractions or Mehlich-3 extractions as standard analyses on all samples. The relationships and

predictive models from these studies show that for soil P sorption research, modeling, and management to truly become a priority, these analyses will need to be incorporated as standard methods for at least all analyzed surface soil samples.

- **Setting total P release break-point values.** Forty-eight U.S. states currently use a P Index as part of their nutrient management plan, each with a specific soil P test and break-point values. Determining appropriate break-points for total P release via an anion exchange resin method was difficult due to a lack of research into its relationship with other soil P tests. Though the soil P tests used in the various P Indices are well known by researchers and producers alike, these methods are primarily used for agronomic and crop production purposes. The anion exchange resin method more accurately mimics the interaction between surface soil and P release into runoff, and understanding the relationships between this environmental soil P test and the more agronomic soil P tests could prove invaluable for modeling and assessing soil P issues.
- **Refinement of current P Indices.** As previously mentioned, the majority of U.S. states have adopted the practice of incorporating a P Index into their nutrient management plans. Though this assessment tool has been in use for several years in many states, eutrophication and P loading issues persist in many areas, with little or no noticeable improvements. In areas like the Chesapeake Bay watershed and Upper Mississippi River Sub-basin, several states are included within the area of interest, each with its own P Index and

subsequent management recommendations and plans. Like the rest of nature and natural processes, soil P sorption behaviors do not change with political borders. It would be prudent to consider refining current P Indices to, (a) incorporate an additional environmental model or set of models specific to different natural areas, like a large watershed, within the state and overlapping into other states, that are also (b) consistent between states assessing within the same natural area.

- **Inclusion into easy-access data sources.** With a large estimated soil property database and easy-access spatial data sources such as Web Soil Survey and gridded Soil Survey (gSSURGO), the NRCS has the opportunity and tools for increasing public understanding and awareness of soil P sorption behaviors. The relationships and models from this study could be further refined, applied, and incorporated as a standard soil characteristic within these highly accessible soil data resources. Increased public awareness and understanding of P loading as a serious environmental concern could generate the needed interest and funding at various levels to adequately combat and mitigate these issues.
- **Inclusion into soil-water-nutrient transport models.** Modeling tools such as the APEX (Agricultural Policy/Environmental eXtender) model (Williams and Izaurradle, 2006), are becoming increasingly important tools and resources to assess the effects of agricultural conservation practices on water quality and other environmental problems (Gassman et al., 2005; Williams et al., 2008). Francesconi et al (2014), note the necessity of further calibration

and validation of the APEX model to improve the mode's prediction capability and reliability. The P sorption relationships and models from this study could be further refined and used in such modeling programs to further improve their predictions and assessments.

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