

The Pennsylvania State University  
The Graduate School  
Department of Ecosystem Science and Management

**SOIL-PLANT SYSTEM RESPONSE TO LIME AND PHOSPHORUS  
AMENDMENTS OF AN ANDISOL OF THE ANDEAN HIGHLANDS OF ECUADOR**

A Thesis in

Soil Science

by

Kathleen Ann Webber

© 2013 Kathleen Ann Webber

Submitted in Partial Fulfillment  
of the Requirements  
for the Degree of

Master of Science

December 2013

The thesis of Kathleen Webber was reviewed and approved\* by the following:

Richard Stehouwer  
Professor of Environmental Soil Science  
Thesis Advisor

Carmen Enid Martínez  
Associate Professor of Environmental Soil Chemistry

Jonathan Lynch  
Professor of Plant Nutrition

Michael Messina  
Professor of Forest Resources  
Head of the Department of Ecosystem Science and Management

\*Signatures are on file in the Graduate School

## ABSTRACT

Strong phosphorus sorption limits the agronomic productivity of volcanic soils (Andisols). It is understood that in acidic Andisols, P sorption occurs due to reaction with variable charge mineralogy developed from weathering of volcanic ejecta, soil organic matter content, and aluminum and iron (hydr)oxides. It has been demonstrated that because of the extremely high P sorption rates in these soils there is little residual effect of phosphorus fertilizer carrying over from an initial application into a second crop. As a result, managers of these soils, which are frequently found in semi-subsistent farming systems, find themselves obligated to apply high rates of P with every cycle: a situation much the opposite of those who are currently trying to reduce excess phosphorus runoff and leaching from their nutrient-laden fields in other parts of our world.

There have been numerous studies conducted on the P sorption mechanism of Andisols, and there have also been studies conducted on how to reduce phosphorus sorption in these soils with the obvious potential to benefit agronomic production, however, these studies remain inconclusive in their evidence on how to treat Andisols with high P-sorption which is attributed to the methods of study used, interpretation of results, and also because of the variable nature of the soils themselves. Andisols have variable OM content and mineralogy depending on stage of weathering and parent material, and phosphorus sorption response is highly dependent on these factors. Therefore, it is important to conduct further studies on the nature of soil and plant response to P-sorption in order to develop a technique for managing Andisols for better agronomic production.

The main goal of this study was to examine the interactive effects of lime and P fertilizer amendments on P sorption and plant P availability in a moderate pH, moderately low soil test-P Andisol from the central Andean highlands of Ecuador. A two-way factorial consisting of three

rates (0, 90, or 180 kg ha<sup>-1</sup>) of P<sub>2</sub>O<sub>5</sub> and three rates (0, 3, or 6 tons ha<sup>-1</sup>) of calcium carbonate (CaCO<sub>3</sub>) were mixed with equal volumes of soil and seeded with barley (*Hordeum vulgare*, L.) in a greenhouse experiment. Soils were sampled two times during an initial incubation with lime and two times after fertilizers were added and barley seeded. Aboveground plant tissues were harvested at 53 days of growth.

To determine the treatment effect on phosphorus sorption in the soil, Mehlich-3 and Olsen extractable P, Al, and Ca and soil pH were determined on soil samples taken before liming and at 21, 32, 46, and 85 days after liming. The 46 and 85 day marks coincide with the 14th and 53rd days after planting (dap). Additional laboratory work was done in University Park, PA, to build sorption and desorption isotherms, study P fractionation, and identify soil mineralogy.

To quantify the impact of the treatments on plant P uptake and growth, biomass and physical response, as well as tissue P and other nutrient content were determined on whole barley plants harvested at 53 dap.

Observations show that barley grown in this Andisol responded strongly to P fertilizer additions, and had smaller responses to lime, however there were no notable lime and P interactive effects. Lime did not cause any change in P uptake or P concentration with liming, however it did improve plant nutrition and increase biomass production. These findings suggest lime could be a beneficial addition to management practices for subsistence farmers in the Andean Highlands, however additional research should be done to further develop this information and to evaluate the cost-benefit ratio of a liming effect on production.

## TABLE OF CONTENTS

LIST OF FIGURES .....	vi
LIST OF TABLES .....	ix
ACKNOWLEDGEMENTS .....	x
Chapter 1 Introductions and Objectives, and Characterization of an Andic soil from the Andean Highlands .....	1
Abstract .....	1
Introduction and Objectives .....	1
Materials and Methods .....	8
Results .....	9
References .....	14
Chapter 2 Soil-Plant System Response to Lime and Phosphorus Amendments in a Greenhouse Study .....	18
Abstract .....	18
Introduction .....	18
Materials and Methods .....	21
Results .....	24
Discussion .....	43
Conclusion .....	46
References .....	48
Chapter 3 Phosphorus Sorption, Desorption, and Fractionation of an Andisol after receiving Different Fertility Treatments in a Greenhouse Experiment.....	50
Abstract .....	50
Introduction .....	50
Materials and Methods .....	52
Results .....	55
Discussion .....	60
Conclusion .....	62
References .....	63
Chapter 5 Summary and Future Needs .....	65
Appendix A Greenhouse Study .....	67
Appendix B Laboratory Analysis .....	73

## LIST OF FIGURES

Figure 1-1: Location of Chimborazo volcano in relation to Quito, Baños, and Riobamba, three large cities in the Ecuadorean Highlands. Figure modified from the original published by Barba et al., 2008.....	5
Figure 1-2: The Illangama Watershed located in the Bolívar Province of Ecuador in the Andean Highlands near project site. Photo taken in June 2012 by K. Webber.....	12
Figure 1-3: Powder-XRD peaks of the La Copa Soil fitted with modified Reitveld analysis.....	13
Figure 1-4: Mineralogy of the La Copa soil sample from the Illangama Watershed.....	13
Figure 2-1: Mehlich-3 extractable P is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance on the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3. ....	26
Figure 2-2: Olsen extractable P is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3. ....	27
Figure 2-3: Soil pH is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3 .....	30
Figure 2-4: Exchangeable aluminum is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3. ....	31
Figure 2-5: Mehlich-3 Extractable Fe is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3. ....	32
Figure 2-6: Olsen Extractable Fe is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects	

of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3. ....	33
Figure 2-7: Mehlich-3 extractable Ca is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3. ....	34
Figure 2-8: Olsen extractable Ca is shown at four sampling points in an Andisol treated with lime (L) and P fertilizer (P). Repeated measures analysis show that only lime has an effect on Ca concentration in the soil.....	35
Figure 2-9: Dry plant biomass production of barley in an Andisol treated with lime and P fertilizer increased due to P fertilization and due to lime additions. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on the graph. ....	36
Figure 2-10: Tiller production of barley in an Andisol treated with lime and P fertilizer increased due to P fertilization additions. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on the graph.....	37
Figure 2-11: Plant height of barley in an Andisol treated with lime and P fertilizer increased due to P fertilization and due to lime additions. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on the graph.....	37
Figure 2-12: The response of barley grown in an Andisol that received no lime with P treatments increasing from left to right: 0, 90, and 180 kg P <sub>2</sub> O <sub>5</sub> ha <sup>-1</sup> .....	38
Figure 2-13: The response of barley grown in an Andisol that received 3 tons ha <sup>-1</sup> lime with P treatments increasing from left to right: 0, 90, and 180 kg P <sub>2</sub> O <sub>5</sub> ha <sup>-1</sup> . ....	38
Figure 2-14: The response of barley grown in an Andisol that received 6 tons ha <sup>-1</sup> lime with P treatments increasing from left to right: 0, 90, and 180 kg P <sub>2</sub> O <sub>5</sub> ha <sup>-1</sup> . ....	39
Figure 2-15: Plant P concentration and plant P uptake per pot grown in an Andisol treated with lime (L) and P fertilizer (P) are shown. There was no effect of lime or P on plant uptake; there was a P fertilizer effect on P uptake. Lowercase letters shown with groups indicate significant results of LSD mean separation of significant ANOVA parameters.....	41
Figure 2-16: Plant Fe concentration and Fe uptake per pot grown in an Andisol treated with lime (L) and P fertilizer (P) are shown. There was a significant effect of lime on Fe concentration, while uptake was dependent on P fertilizer and a lime and P interaction.....	41
Figure 2-17: Ca concentration and uptake were both increased by lime applications in an Andisol treated with lime (L) and P fertilizer (P) are shown. Ca uptake was also increased by P fertilizer.....	42

Figure 2-18: Mn concentration and uptake in an Andisol treated with lime (L) and P fertilizer (P) were both decreased by liming, adding P fertilizer, and also by an interaction effect between these two effects (LxP). .....	42
Figure 3-1: Image from Nair et al. (1995) showing fractionation sequence. ....	53
Figure 3-2: Average adsorbed P is shown on the Y-axis versus equilibrium P on the X-axis across four treatments after equilibration with eight solution P concentrations. Adsorbed P increased with increasing applied concentration, while the rate of P sorption is decreasing with increasing concentrations of P in solution. ....	55
Figure 3-3: Linearized Langmuir isotherm with $K_d$ ( $q/C_{eq}$ =equilibrium/adsorbed P) on the Y-axis and with $q$ (equilibrium P) on the X-axis is shown for data obtained through sorption isotherms on four different soil treatments. There was no significant difference of treatment on P sorption. ....	55
Figure 3-4: Cumulative P desorption of a soil previously treated with rates of lime (L) and/or P fertilizer (P) is shown over five sequential extractions. Analysis of Variance is shown in the inset. ....	56
Figure 3-5: Effect of previous soil treatment is shown as the difference in cumulative P desorbed from the control soil. LSD mean separation is shown by a letter above those fractions with a significant treatment effect. ....	57
Figure 3-6: Chemical fractionation of an Andisol previously treated with rates of lime (L) and/or P fertilizer (P) is shown in five user-defined fractions. Analysis of Variance is shown in the inset box, while LSD mean separation is shown by a letter above those fractions with a significant treatment effect. Letters are only comparable within each graph. ....	58

## LIST OF TABLES

Table <b>1-1</b> : pH and Modified Olsen extractable P of fourteen soils sampled in the Illangama Watershed in Ecuador. ....	10
Table <b>1-2</b> : Soil test results from Santa Catalina.....	11
Table <b>1-3</b> : Soil fertility testing results in Modified Olsen extracts at Santa Catalina. ....	11
Table <b>1-4</b> : Soil fertility testing results in Mehlich-3 extracts from AASL at Penn State. ....	11
Table <b>2-1</b> : Equivalent field application rates of lime and fertilizer used in each treatment in the greenhouse pot study testing the effect of lime and P fertilizer amendments on plant growth in an Andisol.....	23
Table <b>2-2</b> : Rates of lime and fertilizer applied to each treatment in the greenhouse pot study testing the effect of lime and P fertilizer amendments on plant growth in an Andisol.....	24
Table <b>2-3</b> : F values of Repeated Measures ANOVA analysis on effect of lime, P fertilizer and sampling time as well as their interactions on extractable P, pH, and extractable Al, Fe and Ca using both Mehlich-3 and Olsen tests. Degrees of Freedom in numerator (DF); Degrees of Freedom in denominator (DFd); Lime Effect (L); P Fertilizer Effect (P); Time Effect (T); interactions shown with astericks. ....	28

## ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Richard Stehouwer for his guidance throughout my Master's work and the writing of this thesis. His grasp of concepts and the structured process he works by helped me develop these skills and understand how much really goes into the creation of a well-developed and well-written scientific document. His kindness during times of difficulty in my academic career and in my personal life, and his respect for me as an individual are deeply appreciated. I also want to thank Dr. Soraya Patricia Alvarado Ochoa, my mentor and advisor at the Santa Catalina Experimental Research Station in Quito, Ecuador, for her guidance and for being a powerful role model. Soraya's courage in standing up against daily adversity, machismo, corruption, and the aggravating unfairness of her world, matched with her tender love for her children and family, formed a matrix of personal strength unmatched in my experiences, and she is an example after which women professionals everywhere should model themselves.

In addition to these two advisors, I would like to thank my committee members Dr. Carmen Enid Martínez and Dr. Jonathan Lynch for their contributions and thoughtful commentary on this document. I am also grateful to Dr. Jack Watson, to my fellows in Writing Group, and to others who lent me their ears and their time in the development of my thesis.

Thank you to USAID SANREM-CRSP for financial support of this work. For technical assistance I thank Danny Farías and other research scientists who ran the greenhouse project and did analysis at Santa Catalina on my behalf, Dr. Ephraim Govere for his technical expertise and for my use of the Soil Cluster Lab, and to my undergraduate assistant Karlie Hoy. Thank you to Nichole Wonderling and the Materials Characterization Lab, and Paulyanna Stecko and Dr. John Spargo at the Agricultural Analytical Services Lab for assistance and analyses of my soil.

Finally, thank you to my family, my friends, and my sweet Quincy Cat. All of you have an immense presence in my life and you make my heart burst with love both given and received.

## **Chapter 1**

### **Introductions and Objectives, and Characterization of an Andic soil from the Andean Highlands**

#### **Abstract**

Soil pH and Olsen extractable P content were determined in fourteen soil samples from sites located within the SANREM-CRSP project study area in the watershed of the Illangama River in Bolívar Province, Ecuador, near the inactive stratovolcano Chimborazo. Of the fourteen initially tested, a soil with a pH of 5.88 and extractable phosphorus of 6.32 ppm was selected to be used in greenhouse and laboratory experiments testing the effects of lime and P fertilizer amendments on P sorption. 250 kilograms of the chosen soil was collected from the site and subsamples were taken and analyzed again for pH and P as well as for organic matter content, plant available water content, mineralogy, and base fertility. The soil was found to be a representative Andisol of those we studied in this region with moderate acidity of 1.32 meq  $100\text{ g}^{-1}$ , low plant available water content of 33.2 g  $\text{H}_2\text{O}$   $100\text{ g}^{-1}$  soil and a high organic matter content of 13%. Powder-XRD analysis revealed andic mineralogy including plagioclase feldspar minerals, pyroxenes, amphiboles, and amorphous clays originating from volcanic glass and parent material.

#### **Introductions and Objectives**

Population increases and the resulting increased demand for food production have driven Ecuadorean farmers in the Andean Highlands to produce more food faster than before. This is causing the abandonment of historically sustainable farm practices and the introduction and use of chemical fertilizers. As demand increases and fields become less inherently productive, the physical extent of farm fields has crept further and further up steep mountain slopes and into more unstable ecosystems. Farmers are faced with loss of productivity and sustainability of the volcanic soils they farm as the erosion of topsoil, disintegration of soil structure, and loss of native soil fertility, increase.

Phosphorus is essential to the growth of all plants (FAO, 2006) and is a limiting nutrient for crop production in volcanic soils (Andisols) (Guadalix and Pardo, 1994; Johnson and Loeppert, 2006; Redel et al., 2008). The pH of the soil system influences how strongly these variables affect soil P sorption, with low pH systems experiencing more sorption than neutral or basic systems (Haynes and Mokolobate, 2001). Acid Andisols have high P sorption rates due to irreversible chemisorption of P to amorphous minerals such as allophane, imogolite, and iron and aluminum hydroxides, precipitation as Al and Fe phosphates, and complexation with organometallic complexes (Shoji et al., 1993; Wada and Gunjigake, 1979).

Lime applications increase soil pH and cause the precipitation of soluble and exchangeable Al and Fe, dissociation of organometallic complexes, and a decrease in chemisorption with amorphous minerals. This reduction of sorptive species in the soil is expected to reduce overall P sorption, however lime treatments have been shown to increase (Curtin and Syers, 2001; Mora et al., 1999), decrease (Murrman and Peech, 1969), or not change (Fox et al., 1991) phosphorus sorption in the soil. This diversity of P sorption responses to liming has been attributed to different analytical methods, to wetting and drying cycles (Haynes, 1982), and to differences in organic matter content, solution Al, or mineralogy (Barrow, 1984). It has also been shown that liming increases P uptake by plants (Fox et al., 1991), however Haynes (1984) suggests that plant P uptake is as variable as P sorption, and can either increase, decrease, or not change with liming. The variable and unclear effects of lime on P sorption and desorption, solubility, and plant P uptake indicate a need for additional phosphorus sorption and uptake studies to be conducted on specific soils related to a location of interest (Guadalix and Pardo, 1994). Given the potential that soil liming and pH changes could alter P sorption characteristics of Andisols I conducted greenhouse and laboratory experiments to investigate lime and P fertilizer interactions in an Andisol from the Andean Highlands of Ecuador. The hypotheses investigated in this research are:

1. The use of lime and P fertilizer together will increase plant P uptake and plant biomass production compared to application of P fertilizer alone.

2. The co-application of lime and P fertilizer will increase soil test P compared to the application of P fertilizer alone.

If a lime amendment increases P availability and uptake efficiency, it could extend the sustainability and enhance the productivity of farmers' lands and ultimately improve the livelihoods of people who rely on them. The research objectives of this study were to:

1. Characterize a soil from the project region of the USAID SANREM-CRSP in the Andean Highlands of Ecuador to predict and evaluate the effect of lime and fertilizer amendments in reducing phosphorus sorption and increasing P availability.
2. Conduct a greenhouse study to evaluate the effect of lime and phosphorus amendments in reducing P sorption and increasing P availability.
3. Construct sorption and desorption isotherms and perform a P fractionation procedure on four of the treatments used in the greenhouse study to evaluate the effect of amendments on soil chemistry and P behavior on the first and subsequent crops grown in the soil.

Characterization of the Andisol used in this study is presented in this chapter. Soil samples collected in Ecuador were transported to The Pennsylvania State University in University Park, PA and several physical and chemical properties were measured including soil pH, fertility tests, and mineralogy. Additionally, information on the study site were collected and are detailed in this chapter.

In Chapter 2 a greenhouse project is detailed that was conducted to evaluate soil and plant response to lime and P fertilizer in a factorial design with three rates of lime and three rates of P using barley (*Hordeum vulgare* L.) as the test crop. Soil was analyzed to determine treatment effects on pH, Melich-3 and Olsen extractable P, Ca, Al, and Fe. Foliar material was analyzed for differences in plant growth and tissue P, Ca, Fe, and Mn after the termination of the experiment.

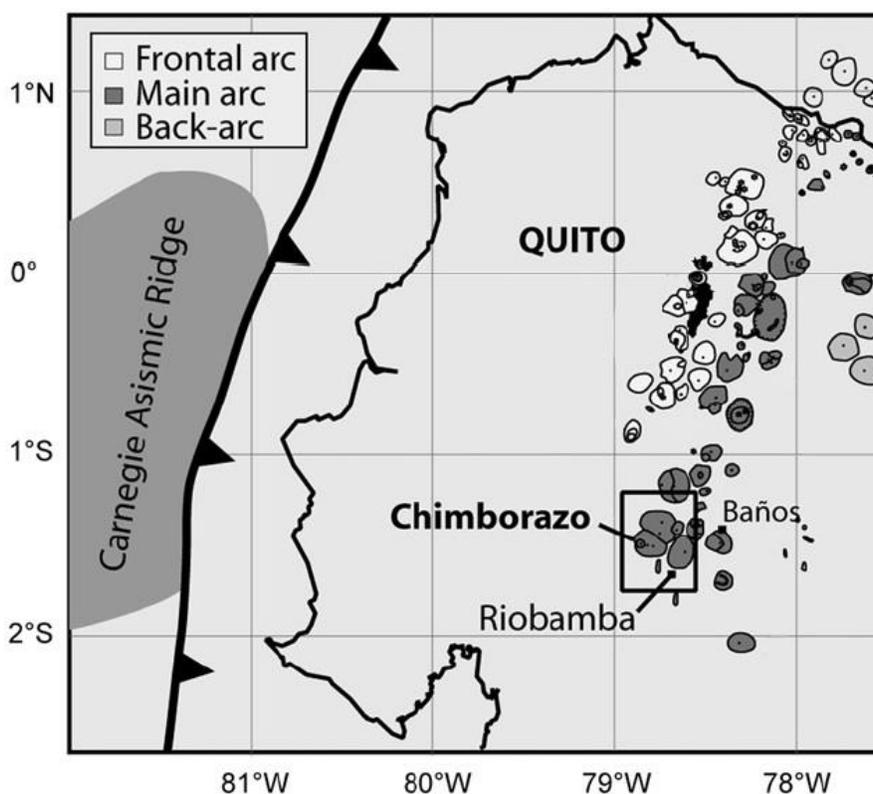
The objectives of Chapter 3 were to construct a sorption and desorption isotherm and perform P fractionation work on soils collected at the end of the 55-day-long greenhouse experiment described in Chapter 2 in order to explore the mechanisms responsible for P sorption and subsequent P availability.

Chapter 4 describes overall conclusions drawn from this work and explains follow-up work that might be conducted in the future.

Andisols were first recognized as a soil order with the publishing of the 4<sup>th</sup> edition USDA-NRCS Keys to Soil Taxonomy in 1990 (Parfitt and Claydon, 1991; Smith, 1978; Soil Survey Staff, 1990), but volcanic soils were already being recognized as having different traits from other orders due overwhelmingly to their distinct parent material and resulting characteristics. According to the Keys to Soil Taxonomy (Soil Survey Staff, 2010) Andisols are classified as soils having volcanic parent material and Andic properties in sixty percent or more of the soil profile either within 60 cm of the soil surface or an organic layer with andic properties, or above an impenetrable limiting feature like a densic, lithic, or paralithic contact or duripan or petrocalcic horizon. In addition to these requirements, potential Andisols must have less than 25% percent organic matter. Organic matter accumulates readily in these soils due to fixation with soluble aluminum and iron. 2-8% organic matter in Ecuadorean Andisols is considered a 'low' range, 10% is common, and 25% is the upper cutoff, at which point a soil classifies as an organic soil (Histosol) (Breemen and Buurman, 2003; Buytaert et al., 2005). The formation of organometallic compounds is what creates the dark color of the surface horizon of Andisols. The volcanic parent material is also responsible for the low bulk density, high exchangeable aluminum and iron content, high nutrient and water retention, and high erosion potential of Andisols. There are a variety of suborders of Andisols ranging from frozen (gelands and cryands) to bi-seasonal xerands, to tropical (udands and ustands) soils, from very wet (aquands) to dry (torrands), and even vitrands which refers to the glassy nature of the parent material. In order to classify as an Andisol, the bulk density must be less than  $0.9 \text{ g cm}^{-3}$ , and contain 2.0% or more acid-oxalate-extractable Al (Parfitt and Childs, 1988; Parfitt and Claydon, 1991; Soil Survey Staff, 2010). The high rate of P sorption in Andisols is due primarily to chemisorption with variable charge

amorphous clays such as allophane and imogolite and aluminum and iron hydroxides, as well as precipitation with aluminum and iron ions from the soil solution and complexation with Al- and Fe- humic complexes.

In Ecuador the Western and Central Andean ranges, or *Cordilleras*, run through the middle of the country on a North-South transect. The volcanoes in Ecuador are found along the Cordilleras, and are distinguished by their location on arcs in the Northern Volcanic Zone (Figure 2-1) (Barba et al., 2008). There are active volcanoes in Ecuador including Chimborazo's neighbors to the East on the Central Cordillera, Tungurahua and Sangay volcanoes, which erupted 2013 and 2012, respectively. At night, Tungurahua can be observed emitting smoke and spewing fire, a menacing reminder of the potential for change in the landscape.



**Figure 1-1. Location of Chimborazo volcano in relation to Quito, Baños, and Riobamba, three large cities in the Ecuadorean Highlands. Figure modified from the original published by Barba et al., 2008.**

The volcanic parent material of Andisols gives them physical, mineralogical and chemical properties distinct from the other soil orders. However, within the Andic regime there are differences in mineralogy, pH, fertility, and physical appearance of Andisols generating large variability within the order. Although Ecuador is only about the size of Colorado, it is one of the world's most ecologically diverse countries, containing varied climate, topography, biomes, and vegetative and animal communities. Of the five soil forming factors first described by Jenny (1941), Andisols across the Ecuadorean Andes are influenced most strongly by climate and parent material (Buytaert, 2007). Soils in the SANREM-CRSP study area of the Illangama River Watershed present characteristics of Andisols like high P sorption and amorphous mineralogy and are located near the base of the Chimborazo volcano.

Common constituents of Andisol mineralogy include volcanic glass, olivine, plagioclase feldspars, pyroxenes, and amphiboles, and ferromagnesian minerals, and as a result of weathering of these minerals, Andisols tend to have high Fe, Al, and Si concentrations (Breemen and Buurman, 2003). X-ray diffraction patterns of other soil samples taken in Ecuador showed primary minerals are cristobalite, feldspars, hornblende, and quartz, mixed with amorphous minerals like allophane, imogolite, and Fe and Al hydroxides (Buytaert et al., 2005; Wada and Kakuto, 1985). Phosphorus sorption in Andisols has been attributed in part to their amorphous clay mineralogy which is dominated by the presence of non-crystalline hydrous aluminosilicates like allophane, imogolite, halloysite and iron and aluminum hydroxides (Shoji et al., 1993; Wada and Gunjigake, 1979). These amorphous species form naturally in Andisols during rapid weathering of volcanic glass and have high aluminum contents (Shoji et al. 1993).

Along the Cordilleras in the northern part of the country near Quito where the climate is wet and cool, Andisols are younger and are dominated by allophanic mineralogy (Zehetner, 2003). Allophanic Andisols are not greatly weathered, receive more than 1000 mm of precipitation a year, have a pH greater than 4.9, and mineralogy dominated by allophane, imogolite, and other amorphous minerals. In allophanic Andisols, phosphate is chemisorbed to soil minerals in inner-sphere exchange reactions which are driven by the exchange and release of aluminum for silica in the soil solution. In Southern Ecuador, ash

contributions are older, and increased precipitation and temperature result in more weathered soils with stable, non-allophanic mineralogy (Buytaert et. al, 2005, 2007; Zehetner, 2003). Non-allophanic Andisols receive 500-1000 mm of precipitation annually, have a pH of less than 4.9, and can still contain traces of allophane, although they tend to contain other variable-charge surfaces such as halloysite and accumulate Al-humic complexes (Buytaert et. al, 2005). The formation of Al-humic complexes in non-allophanic Andisols can prevent the formation of other short-range order minerals (Qafoku, 2004). As distance from volcanic activity increases, i.e. the altitude of sites decreases and temperature and precipitation increases, soils with Andic properties can classify out as Mollisols, Entisols, Inceptisols, or Histosols (Zehetner, 2003).

Reference material on soils of Ecuador includes a country-wide soils map produced in 1986 by the Ecuadorian Soil Science Society under NRCS Keys to Soil Taxonomy guidelines, as well as monographs focused on smaller, selectively mapped areas. Because these maps predate the official NRCS delineation of the Andisol order in 1990, Andisols in Ecuador are mapped mostly as Andic Inceptisols (Andepts), along with other orders (Vallejo and Moldanado, 1986).

It was determined that a study would be conducted on the ability of lime to increase phosphorus fertilizer efficiency and reduce phosphorus sorption in Andisols found at the base of the volcano Chimborazo. This land falls within the Illangama River watershed. This area is part of a large-scale socio-economic study funded by USAID and directed by Virginia Tech in Blacksburg, Virginia as a Sustainable Agriculture and Natural Resource Management – Collaborative Research Support Program (SANREM-CRSP) project. The host country collaborator of the SANREM project is the National Institute of Agricultural Investigations (INIAP) at the Santa Catalina Experimental Research Station in Quito, Ecuador.

Soils were sampled from farms across the watershed and evaluated for pH and extractable P in order to identify a soil with typical andic traits to be used for subsequent greenhouse and laboratory studies in which we would evaluate the management and mechanisms of Andisol P sorption. The soil selected for use in the testing of our hypotheses was a moderate pH, moderately low P Andisol from a farm located only

11 miles from the Chimborazo volcano. Further characterization of the Andic properties of this soil were carried out at INIAP in Quito and at Penn State in University Park, PA.

### **Materials and Methods**

Fourteen soils were sampled at farms within the Río Illangama sub-watershed of the Chimbo River. At each location, several samples of the top 20 cm of the soil profile were taken and combined to create an aggregate sample and delivered in plastic bags to the INIAP Santa Catalina Experimental Research Station (Santa Catalina). Upon arrival to Santa Catalina, the soils were air-dried, passed through a 2mm sieve, and then stored in sealed plastic containers until analysis. On all fourteen samples, pH was measured in a 1:2.5 soil to water ratio and Modified Olsen extractable phosphorus was measured in a 1:10 soil to solution ratio by photolorimetry. The methods used are protocol of the Department of Soil and Water Management (Departamento de Manejo de Suelos y Aguas –Estación Experimental Santa Catalina-INIAP).

Once a soil was chosen for the experiments, researchers returned to the sampling site and 250 kilograms of soil were manually collected from the top 20 cm of the soil profile with a hoe and shovel and brought to Santa Catalina in 55 kilogram-capacity sacks. Subsamples of this soil were taken for fertility analysis and physical measurements. The soil for the greenhouse project was screened to 5mm remove rocks, roots, and debris before installation of the greenhouse project.

On the soil chosen for the greenhouse project, moisture content, field capacity, wilting point, pH, acidity, exchangeable aluminum, and macro and micronutrient content were measured. Moisture content was calculated as the ratio of the soil water to the entire soil. Field capacity and wilting point were determined with pressure plates after an overnight saturation of soil samples. Texture was determined by the Bouyoucos method. As stated above, pH was measured in a 1:2.5 soil to water ratio. Acidity and  $[H^+]$  were extracted in a 1N KCl solution and determined through titration, with exchangeable aluminum calculated as the difference between the two measurements. Macro and micronutrient contents were extracted in a 1:10 soil to solution ratio of Modified Olsen solution and then P, N, S, and B were measured

photocolorimetrically, while K, Ca, Mg, Zn, Cu, Fe and Mn were measured with atomic adsorption (AA) spectrophotometry.

Samples of the La Copa soil used in the greenhouse project were shipped to University Park, PA, USA, for further analysis. A sample of the soil was taken to the Agricultural Analytical Services Laboratory (AASL) at Penn State for additional fertility analysis, where Mehlich-3 extractable P, K, Mg, Ca, and exchangeable Al were measured by ICP spectroscopy (Wolf and Beegle, 1995). pH was measured in a 1:1 soil to water ratio (Eckert and Sims, 1995). Acidity was measured by the Mehlich Buffer pH method (Mehlich, 1976), and CEC was established through the summation method (Ross, 1995). Another sample was prepared for clay mineralogy analysis by grinding until the sample could pass in entirety through a 52  $\mu\text{m}$  sieve. Mineralogy was determined using semi-quantitative powder-XRD analysis at the Materials Characterization Lab of the Materials Research Institute at the Millennium Science Complex at Penn State. The whole-pattern results of this analysis were fitted to the ICSD database using modified Reitveld technology which assumed that the amorphous phase had the density of silica,  $2.5 \text{ g cm}^{-3}$ .

## **Results**

Screening of fourteen farms soils indicated a rather narrow moderate pH range, and a somewhat wider but also relatively moderate-low range of Olsen extractable P (Table 2-1). After evaluating results, the La Copa soil from Salinas was chosen to use in the greenhouse and laboratory experiments because it had the lowest Modified Olsen extractable P content and had one of the lowest pHs.

The La Copa soil is an Andic soil located 11 miles west of the base of Chimborazo in Bolívar Province, near the SANREM project sites. A photograph of the landscape in Bolívar Province can be seen in Figure 2-2. The coordinates of the location where the soil was harvested are  $1^{\circ}30'26.50''\text{S}$ ,  $79^{\circ}3'5.69''\text{W}$ .

Annual precipitation is 500 - 1300 mm and the site is located approximately 3000 meters above sea level. Seasonality, like in most of the tropics, is separated into wet and dry seasons. The wet season goes from December to May, and then the dry season spans June to November. Temperature stays fairly constant

from about 7°-13 °C. The native vegetation or biome would be subalpine or boreal, and is similar to that of the *páramo*, a dry, cold region with scrubby grassland found above 3,500 meters above sea level in the Andean range.

**Table 1-1. pH and Modified Olsen extractable P of fourteen soils sampled in the Illangama Watershed in Ecuador.**

Site ID	pH (1:2.5 H <sub>2</sub> O)	Olsen P ppm
La Copa (Salinas)	5.88	6.32
Tres Mercedes de Punin	5.85	7.66
Quinuacorral	5.66	16.40
Quindigua Alto	5.73	12.77
Larcaloma	5.67	11.83
Quilitagua	5.84	11.83
Cuatro Esquinas	6.36	11.42
Marcopamba	5.83	16.80
Mutanga	5.82	11.83
Pucarapamba	6.03	10.08
Quindigua Central	6.09	18.15
Mulanga 1	6.51	13.04
Mulanga 2	6.29	11.69
Mulanga 3	6.09	14.38

More comprehensive fertility analysis of the soil collected for the greenhouse experiment, revealed a slightly lower pH and slightly higher P content than in the initial sample, but the soil still within the desired low ranges for the greenhouse study (Tables 2-2, 2-3, and 2-4). The Mehlich-3 extractable soil P measured is significantly higher than the published results of Henry et al. (2012), which was on average 1.07 mg P kg<sup>-1</sup> soil and was sampled within the region as well, however my test results were consistent at Santa Catalina and AASL given slight differences due to analytical technique. Although these values were much lower than those found in our work, the soil is still relatively low in P compared to other orders. In addition to those characteristics, the high iron (Table 2-3) and aluminum (Table 2-4) contents of the soil are consistent with the dissolution of the minerals found in Andisols (Breemen and Buurman, 2003). The large organic matter content and small plant available water holding capacity of this soil are also typical of these Andisols. The discrepancy in acidity and aluminum content (Table 2-2 and Table 2-4) is due to the

extracts used to determine them. At Santa Catalina, an unbuffered salt solution was used, while at AASL an acid, buffered Mehlich-3 solution is used to measure acidity. Texture was determined to be a silt loam with 37% sand, 56% silt, and 7% clay.

**Table 1-2. Soil test results from Santa Catalina.**

pH	Organic Matter	Acidity (Al <sup>3+</sup> + H <sup>+</sup> )	Exchangeable Al	Field Capacity	Wilting Point	Plant Available Water Content	Moisture Content
	%	— meq 100g <sup>-1</sup> soil—					%
				g water	100 g <sup>-1</sup> soil		
5.6	13.2	1.32	0.58	77.2	40	33.2	50.45

**Table 1-3. Soil fertility testing results in Modified Olsen extracts at Santa Catalina.**

N	P	Zn	Cu	Fe	Mn	B	K	Ca	Mg
			ppm						
							— meq 100 g <sup>-1</sup> soil —		
37.63	9.95	8.06	12.90	927.42	17.61	0.43	0.54	4.70	1.59

**Table 1-4. Soil fertility testing results in Mehlich-3 extracts from AASL at Penn State.**

pH	P	K	Mg	Ca	Zn	Cu	S	Al	Acidity (Al <sup>3+</sup> + H <sup>+</sup> )	CEC
					ppm				— meq 100g <sup>-1</sup> soil—	
5.00	8.00	217.00	164.00	613.00	7.60	3.80	21.80	1707.90	9.30	14.30

The semi-quantitative mineralogy analysis showed that the soil is dominated by aluminosilicates including the primary plagioclase feldspar mineral andesine along with amorphous minerals, with lesser contents of clinopyroxene, a pyroxene mineral which is a product of volcanic glass weathering, quartz, and an amphibole mineral identified tentatively as holmquistite (Figures 2-2 and 2-3).

Although this analysis does not qualify the specific amorphous phases found in this soil, Kaufhold et al. (2007) showed that Reitveld analysis of powder-XRD gives an accurate measurement of the quantity of amorphous materials present. It should be noted that the hydroxide phase holmquistite is an amphibole

that was the best-fit of the Rietveld analysis performed on the samples, however, the database structure is slightly different than that of the experimental result. It is possible that this form of holmquistite simply has more aluminum or iron substitution in its structure than other occurrences of holmquistite but regardless, its hydroxide nature is of more interest to us than the specific mineral present as it will influence P sorption in the soil.

The La Copa soil is characteristic of young allophanic Andisols that we sampled from this region. It contains typical mineralogy of slightly weathered Andisols like feldspars, pyroxenes, and amphibole hydroxides of volcanic origin in addition to having high allophane content. Analysis of soil fertility shows high organic matter content, moderate acidity, moderate pH, low plant available water content, moderately low test phosphorus, and high soluble aluminum and iron.



**Figure 1-2. The Illangama Watershed located in the Bolívar Province of Ecuador in the Andean Highlands near project site. Photo taken in June 2012 by K. Webber.**

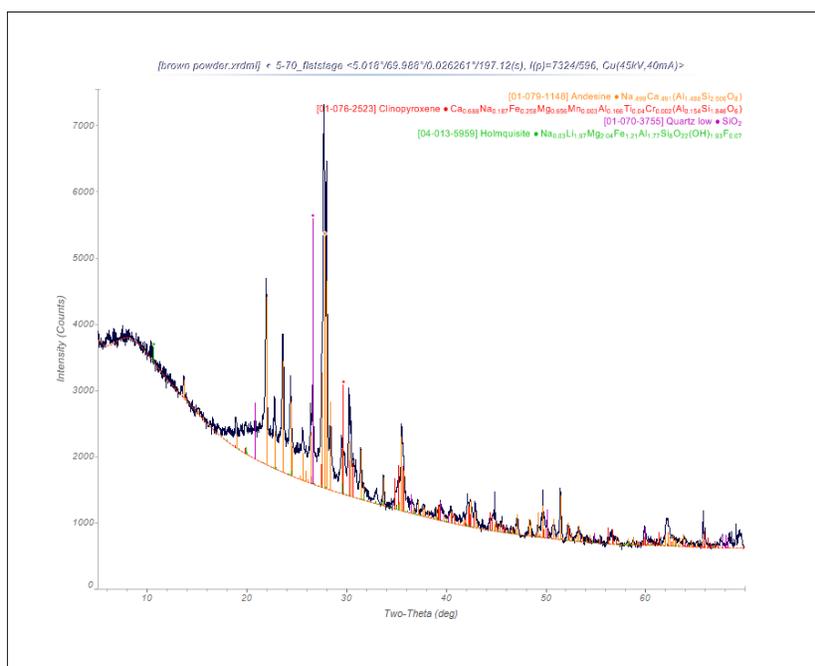


Figure 1-3. Powder-XRD peaks of the La Copa Soil fitted with modified Reitveld analysis.

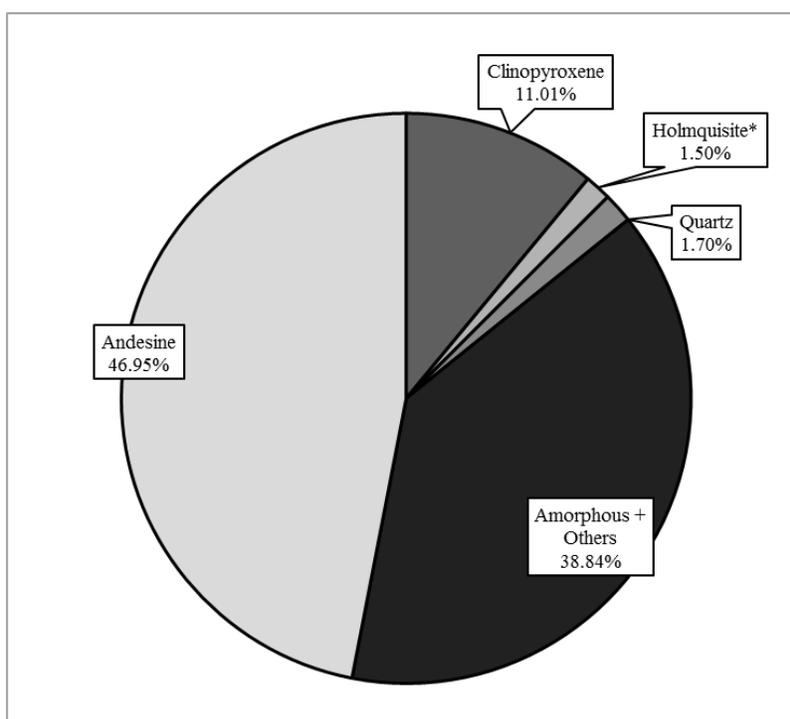


Figure 1-4. Mineralogy of the La Copa soil sample from the Illangama Watershed.

## References

- Barba, D., C. Robin, P. Samaniego, J.P. Eissen. Holocene recurrent explosive activity at Chimborazo volcano (Ecuador). *Journal of Volcanology and Geothermal Research*. 176:27-35.
- Barba, D., P. Samaniego, J.P. Eissen, C. Robin, M. Fornari, J. Cotton, B. Beate. 2008. Geology and structure of the late Pleistocene to Holocene Chimborazo stratovolcano (Ecuador). 6<sup>th</sup> International Symposium on Andean Geodynamics. Extended Abstracts: 90-93.
- Barrow, N.J. 1984. Modeling the effects of pH on phosphate sorption by soils. *Journal of soil science*. 35(2): 283.
- Brady, N.C. and R.R. Weil. 2010. *Elements of the Nature and Properties of Soils*, 3rd Edition. Pearson Prentice Hall. Upper Saddle River, NJ
- Breemen, N. van, and P. Buurman. 2003. Formation of Andisol. 285-306. *In* (2nd ed.) *Soil Formation*. Kluwer Academic Publishers. Dordrecht, Netherlands.
- Buytaert, W., J. Sevink, B. De Leeuw, J. Deckers. 2005. Clay mineralogy of the soils in the south Ecuadorian páramo region. *Geoderma*. 127:114-129.
- Buytaert, W., J. Deckers, and G. Wyseure. 2007. Regional variability of volcanic ash soils in south Ecuador: the relation with parent material, climate and land use. *Catena*. 70:143–154.
- Curtin, D., and J.K. Syers. 2001. Lime-induced changes in indices of soil phosphate availability. *Soil Sci. Soc. Am. J.* 65:147–152.
- Delhaize, E., and P.R. Ryan. 1995. Update: aluminium toxicity and tolerance in plants. *Plant Physiol.* 107:315–321.
- Food and Agriculture Organization. 2006. *Plant nutrition for food security: a guide for integrated nutrient management*. FAO Fertilizer and Plant Nutrient Bulletin 16. FAO.
- Fox, R.L., N.V. Hue, R.C. Jones, and R.S. Yost. 1991. Plant-soil interactions associated with acid, weathered soils. *Plant and Soil* 134: 65-72.

- Guadalix, M.E., and M.T. Pardo. 1994. Effects of liming on soil properties and P solubility in some Spanish Andosols. *Geoderma*. 63:53-6.
- Haynes, R.J. 1982. Effects of liming on phosphate availability. *Plant Soil*. 68:289–308.
- Haynes, R.J. 1984. Lime and phosphate in the soil–plant system. *Adv. Agron*. 37:249–315.
- Haynes, R.J., and M.S. Mokolobate. 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. *Nutrient Cycling in Agroecosystems*. 59:47–63.
- Henry A., L. Mabit, R.E. Jaramillo, Y. Cartagena, J.P. Lynch. 2012. Land use effects on erosion and carbon storage in the Río Chimbo watershed, Ecuador. *Plant Soil* 367(1-2): 477-491.
- Eckert, D. and J. Thomas Sims. 1995. Recommended Soil pH and Lime Requirement Tests. p. 11-16. *In* J. Thomas Sims and A. Wolf (eds.) Recommended Soil Testing Procedures for the Northeastern United States. Northeast Regional Bulletin #493. Agricultural Experiment Station, University of Delaware, Newark, DE.
- Evans, C.E. and E.T. Kamprath. 1970. Lime responses as related to percent Al saturation, solution Al and organic matter content. *Soil Sci. Soc. Am. Proc.* 34:893–896.
- Haynes, R.J., and M.S. Mokolobate. 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. *Nutrient Cycling in Agroecosystems*. 59:47–63.
- Jenny, H. 1941. Factors of soil formation. A system of quantitative pedology. 1st ed. McGraw-Hill Book Co. New York.
- Johnson, S.E., and R.H. Loeppert. 2006. Role of organic acids in phosphate mobilization from iron oxide. *Soil Sci. Soc. Am. J.* 70:222–234.
- Mehlich, A. 1976. New buffer pH method for rapid estimation of exchangeable acidity and lime requirement of soils. *Commun. Soil Sci. Plant Analysis*. 7, 637-652.

- Mokolobate, M.S., and R.J. Haynes. 2002a. Increases in pH and soluble salts influence the effect that additions of organic residues have on concentrations of exchangeable and soil solution aluminum. *European Journal of Soil Science*. 53:481-489.
- Mora, M.L., B. Schnettler and R. Demanet. 1999. Effect of liming and gypsum on soil chemistry, yield, and mineral composition of ryegrass grown in an acidic Andisol. *Commun. Soil Sci. Plant Anal.* 30(9&10):1251-1266.
- Murrman, R.P. and M. Peech. 1969. Effect of pH on labile and soluble phosphate in soils. *Soil Sci. Soc. Am. Proc.* 33:205-210.
- Nanzyo, M. 2003. Unique properties of volcanic ash soils. *Global Environmental Research*, 6(2):83-97.
- Parfitt, R.L., and C.W. Childs. 1988. Estimation of forms of Fe and Al: a review, and analysis of contrasting soils by dissolution and Mossbauer methods. *Aus. J. Soil Res.* 26:121-144.
- Parfitt, R.L., and B. Claydon. 1991. Andisols - the development of a new order in Soil Taxonomy. *Geoderma*. 49:181-198.
- Qafoku, N.P., E. Van Ranst, A. Noble, and G. Baert. 2004. Variable charge soils: Their mineralogy, chemistry, and management. *Advances in Agronomy*. 84:159-203.
- Redel, Y., R. Rubio, R. Godoy, and F. Borie. 2008. Phosphorus fractions and phosphatase activity in an Andisol under different forest ecosystems. *Geoderma*. 145:216-221.
- Ross, D. 1995. Recommended soil tests for determining soil cation exchange capacity. p. 62-69. *In* J. Thomas Sims and A. Wolf (eds.) *Recommended Soil Testing Procedures for the Northeastern United States*. Northeast Regional Bulletin #493. Agricultural Experiment Station, University of Delaware, Newark, DE.
- Shoji, S., M. Nanzyo, and R. Dahlgren. 1993. Productivity and utilization of volcanic ash soils. *Volcanic ash soils: genesis, properties and utilization*. Elsevier Science Publishers, The Netherlands.
- Soil Survey Staff. 2010. *Keys to Soil Taxonomy*, 11th ed. USDA-Natural Resources Conservation Service, Washington, DC.

Soil & Water Science Department, University of Florida. eSoil Science: Andisols.

<http://soils.ifas.ufl.edu/faculty/grunwald/teaching/eSoilScience/andisols.shtml> (October 27, 2013). Sabine Grunwald, Gainesville, FL.

Smith, G.D. 1978. A preliminary proposal for the reclassification of Andepts and some Andic subgroups (Reprinted as: The Andisol proposal 1978. NZ Soil Bureau Record, 96, 1984).

Vallejo, L.M., and E.C. Moldanado. 1986. Mapa general de suelos del Ecuador. ISRIC – World Soil Information Database. Available at:  
<http://library.wur.nl/isric/index2.html?url=http://library.wur.nl/WebQuery/isric/17544> (verified April 29, 2012). Sociedad Ecuatoriana de la Ciencia del Suelo. Ecuador. Scale 1:1000000.

Wada, K., and N. Gunjigake. 1979. Active aluminum and iron and phosphate adsorption in Ando soils. *Soil Sci.* 128(6):331-336.

Wada, K., Kakuto, Y., 1985. Embryonic halloysites in Ecuadorian soils derived from volcanic ash. *Soil Sci. Soc. Am. J.* 49, 1309– 1317.

Wolf, A.M., and D.B. Beegle. 1995. Recommended soil tests for macronutrients: phosphorus, potassium, calcium, and magnesium. Recommended Soil Testing Procedures for the Northeastern United States. Northeast Regional Bulletin #493. p. 25-34. Agricultural Experiment Station, University of Delaware, Newark, DE.

Zehetner, F., W.P. Miller, and L.T. West. 2003. Pedogenesis of volcanic ash soils in Andean Ecuador. *Soil Sci. Soc. Am. J.* 67:1797-1809.

## Chapter 2

### Soil-plant system response to lime and phosphorus amendments in a greenhouse study

#### Abstract

A greenhouse experiment was conducted to test the effect of lime and P fertilizer on P uptake and biomass production in an Andisol with pH 5.8 and initial 6.32 ppm Olsen extractable P. The experiment was designed to be a two way factorial of three rates of lime (0, 3, and 6 tons  $\text{CaCO}_3 \text{ ha}^{-1}$ ) and three rates of phosphorus (0, 60, and 180 kg  $\text{P}_2\text{O}_5 \text{ ha}^{-1}$ ) and was seeded with barley (*Hordeum vulgare* L.). The experiment had an initial 32 day lime incubation before adding fertilizer and sowing barley. Soils were sampled four times during the experiment, and aboveground barley biomass was harvested at 53 days. Results of soil analysis show that lime decreases soil test P, increases pH, decreases soil Fe and Al, and increases soil Ca. Despite the decrease in soil test P with lime, results of plant analysis show that there is no effect of lime on P uptake or concentration, and a small increase caused by lime in biomass production. Lime causes a large decrease in uptake and concentration of Fe and Al and an increase in uptake and concentration of Ca in the plant. Results also show that Mehlich-3 and Olsen extracts used to measure soil P are not sensitive to changes in plant available P content when the results of these data are compared to the results of plant P uptake, and that development of a more calibrated test for soil P is needed for Andisols.

#### Introduction

In volcanic ash soils (Andisols), phosphorus is readily chemisorbed with amorphous, variable-charge minerals, precipitated with free iron and aluminum, and complexed with organometallic species with large surface areas, limiting agricultural production. In Ecuadoran Andisols it has been observed that deviation for even one crop cycle from the high rates of 150 and 300 kg  $\text{P}_2\text{O}_5 \text{ ha}^{-1}$  of phosphorus fertilizer reduces average potato yields of 32.65 and 35.54 metric tons  $\text{ha}^{-1}$  to 11.32 and 12.44 metric tons  $\text{ha}^{-1}$ ,

respectively (Espinosa, 2006). There are many factors influencing the efficiency of phosphorus fertilizer in the soil, such as the type of mineralogy and composition of the soil (Chapter 1 of this thesis), the sorption capacity of the soil (discussed in Chapter 3), and the pH of the soil system.

Soil acidity is generated naturally through weathering and biological activity, and can also be increased by humans through the use of ammoniacal fertilizers and leaching of acid rain through the profile (Brady and Weil, 2010). Andic minerals contain large amounts of aluminum and iron, which exchanges with basic plant nutrient cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) on the exchange complex when released through weathering. The cations are then lost through leaching of the soil profile, lowering pH. In systems below pH 5.5, aluminosilicates like allophane and aluminum and iron oxides are more soluble, and as such, there is more dissolution and release of additional Al and Fe from minerals. The soluble aluminum and iron lowers pH and acts as a positive feedback into the generation of more acidity into solution. As pH increases, it is thought that Fe and Al are precipitated (less active) from the soil solution.

Phosphorus sorption in Andisols is dependent on the pH of the soil system because of the variable-charge surfaces present (Fox et al., 1991). The Point of Zero Charge (PZC) is a pH value at which variable charge minerals are neither net positively or net negatively charged; at pH values lower than the PZC, minerals are positively charged and sorb anions, while at pH values higher than the PZC, they are negatively charged and sorb cations (Appel et al., 2003). Variable-charge minerals allophane and imogolite have charged surface areas that have been shown to become more net positive or negative in acidic or basic conditions, respectively (Nanzyo, 2003). Increasing the pH of the soil system increases the negative surface charge of these colloids and reduces the potential for adsorption by the phosphate anion (Haynes 1984).

Organic matter has large surface area and is negatively charged, however at low pH it forms Al-humic complexes which are capable of complexing P. As pH increases, organic matter cation exchange capacity (CEC) increases through dissolution of organic acid groups (Breeman and Buurman, 2002) and the positive charge of aluminum is neutralized, eliminating positive exchange sites and reducing phosphorus sorption. At low pH around 4.5-5.5, free aluminum and iron precipitate with phosphorus as

non- or weakly-crystalline hydroxide minerals. Aluminum and iron species precipitate independently of phosphorus above a pH of 6.5, however within this range it is also possible that calcium and magnesium in solution will form insoluble precipitates with phosphate (Haynes, 1984; Haynes and Mokolobate, 2001; Naidu et al., 1990).

Andisols have a large buffering capacity due to the enormous surface area of the soils and so large changes in the anion or cation exchange capacities of the soil (AEC and CEC) may not be marked by changes in pH as is expected in other soil orders, so an attempt to adjust soil pH to a determined PZC may be a futile one. The important functions of pH adjustment like increasing negative charge on mineral surfaces or precipitation of aluminum can still be managed with small units of pH change (Qafoku et al., 2004). By altering the pH of the soil, it is possible to make the net charge of the soil surface more negative, reducing phosphorus sorption (Haynes, 1982; 1984).

It is thought that lime amendments may reduce high rates of P sorption in Andisols by raising pH and precipitating or crystalizing free aluminum and iron in the soil and increasing the negative surface charge of soil colloids (Haynes, 1984; Haynes and Mokolobate 2001) thereby reducing active sorption sites (Evans and Kamprath, 1970; Guadalix and Pardo, 1994; Haynes and Mokolobate, 2001). However, lime treatments have been shown to increase (Curtin and Syers, 2001; Mora et al., 1999), decrease (Murrman and Peech, 1969), or not change (Fox et al., 1991) phosphorus sorption in the soil (Haynes 1982; 1984). This variability in soil P sorption response to liming has been attributed to different analysis methods (Haynes, 1982), wetting and drying cycles during incubation in experimental testing (Haynes, 1982), and different inherent soil traits including soil pH, mineralogy, and soil organic matter content (Barrow, 1984). Curtin and Syers (2001), and Sorn-Srivichai et al. (1984) found that the popular Olsen extract reported a decrease in extractable soil P with liming, which Sorn-Srivichai et al. believed to be caused by precipitation of calcium phosphates caused by the high pH (8.5) of the Olsen extract. Sorn-Srivichai et al., (1984) found that the decrease in Olsen extractable P had no adverse effects on plant P uptake.

Lime applications increase soil pH and cause the precipitation of free Al and Fe, dissociation of organometallic complexes, and a decrease in chemisorption with amorphous minerals. The reduction of sorptive species in the soil is expected to reduce overall P sorption, however lime treatments have been shown to increase (Curtin and Syers, 2001; Mora et al., 1999), decrease (Murrman and Peech, 1969), or not change (Fox et al., 1991) phosphorus sorption in the soil. The effect of lime application of P uptake seems to be dependent on lime and fertilizer rates, individual soil properties like pH, mineralogy, or organic matter content, and crop tolerances to soil acidity and aluminum toxicity (Haynes, 1984). It has also been shown that liming increases P uptake by plants (Fox et al., 1991), however Haynes (1984) suggests that P uptake is as variable as P sorption, and can either increase, decrease, or not change with liming. The variable and unclear effects of lime on P sorption and desorption, solubility, and plant P uptake indicate a need for additional phosphorus sorption and uptake studies to be conducted on specific soils related to a location of interest (Guadalix and Pardo, 1994).

Ultimately, the variability and uncertainty in the effect of lime on P sorption, solubility, and plant P uptake in Andisols, as well as a lack of a test or model for lime \* P interactions in high P sorbing soils, has led to the need for additional phosphorus sorption and uptake studies on soils of interest (Curtin and Syers, 2001; Guadalix and Pardo, 1994). Therefore I conducted a greenhouse experiment to investigate the effects of lime on the uptake of phosphorus fertilizer in a moderate pH, moderately low P Andisol. The objective of this experiment was to investigate the effect of lime on plant phosphorus availability in an andic soil, and to compare the effects of Olsen and Mehlich-3 extracts in measuring plant available phosphorus in soil samples.

### **Methods**

Phosphorus and lime interactions were tested in a short-term greenhouse pot experiment using barley (*Hordeum vulgare*, cult. INIAP Cañipapa 2003) as a test crop. The soil used in this experiment was collected from a farm (La Copa) in the Bolívar Province in South Central Ecuador and had a pH of 5.57

and an initial Olsen extractable P measurement of 6.32 ppm. About 250 kilograms of soil were collected from the site by first scraping foliage and thatch off the surface of the soil, then loosening 20 cm depth soil with a hoe and shoveling the soil into canvas bags. The soil was transported by truck to the Santa Catalina Experimental Research Station (Santa Catalina) in southern Quito, Ecuador. Upon arrival at the station, the soil was passed through a 5 mm sieve to remove roots, debris, rocks, macroscopic insects, and break up large aggregates. The screened soil was repacked without drying into the same canvas sacks before the start of the greenhouse experiment.

Ecuador consistently receives about 12 hours of sunlight per day, and the Santa Catalina Research Station is located at 3000 meters above sea level in Southern Quito, the capital city of Ecuador. The coordinates of the research station are 0°22'7.15"S, 78°33'17.25"W.

This experiment utilized a 3 x 3 factorial design with lime and P fertilizer rate as the factors. The treatments were arranged in randomized complete blocks with three replications for a total of 27 pots. The lime rates used were 0 tons ha<sup>-1</sup>, 3 tons ha<sup>-1</sup>, and 6 tons ha<sup>-1</sup>, or 0 and approximately 1 and 2 times the liming rates recommended for acidic Andisols being cultivated in Ecuador (D.M.S.A., INIAP). To achieve these rates 0, 11.74, or 23.48 grams of calcium carbonate (CaCO<sub>3</sub>) were thoroughly mixed with 7.75 kg of soil and incubated for 32 days in plastic bags at 50% moisture content. After incubation P fertilizer was applied at rates of 0, 90, and 180 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup>, corresponding to 0, 1, and 2 times the recommended fertilizer rates for barley. After 32 days of incubation, 0, 0.606, or 1.202 grams of 11-52-0 fertilizer, as well as 0.424, 0.222, or 0.0202 grams of ammonium nitrate to supplement N in the NPK fertilizer were added to the soils. Additionally, 0.202 grams K<sub>2</sub>SO<sub>4</sub> and 0.0438 g Micronized S were added to provide these nutrients to plants as well. These fertilizers were added to the lime treatment levels and mixed with the entire volume of soil. The soils were then packed into round plastic pots with a (27 cm diameter by 14 cm height) to an approximate bulk density of 0.9 grams cm<sup>-3</sup>. The amendment rates, fertilizer sources, and description of the resulting nine treatments are given in Table 2-1 and 2-2. The pots were planted with 15 barley seeds using a grid to space seeds evenly. After establishment barley plants were thinned to 10 plants per pot. Watering

was done by hand and soil was kept moist to prevent water stress in the plants. The greenhouse temperature was controlled by the opening and closing of roof panels, which prevented extreme highs during the day and extreme lows at night. At tillering, an additional 0.424 grams (40 kg ha<sup>-1</sup>) N as NH<sub>4</sub>NO<sub>3</sub> was top-dressed in each pot. The height of the barley and number of tillers in each pot were recorded at 53 days after planting (which coincides with the last soil sampling event), after which plants were harvested by cutting at the soil surface, dried in a plant-drying oven, and weighed. Foliar analysis was performed through wet digestion with nitric perchloric acid and quantified for P, K, Ca, Mg, Zn, Cu, Fe, and Mn using Inductively Coupled Plasma (ICP) spectrometry.

**Table 2-1. Equivalent field application rates of lime and fertilizer used in each treatment in the greenhouse pot study testing the effect of lime and P fertilizer amendments on plant growth in an Andisol.**

Treatment Code	Amendment Application Rate				
	Lime —ton ha <sup>-1</sup> —	P <sub>2</sub> O <sub>5</sub>	N	K <sub>2</sub> O	S
T1: 0L, 0P	0	0	80	30	20
T2: 0L, 1P	0	90	80	30	20
T3: 0L, 2P	0	180	80	30	20
T4: 1L, 0P	3	0	80	30	20
T5: 1L, 1P	3	90	80	30	20
T6: 1L, 2P	3	180	80	30	20
T7: 2L, 0P	6	0	80	30	20
T8: 2L, 1P	6	90	80	30	20
T9: 2L, 2P	6	180	80	30	20

Soil samples were collected at 21, 32, 46, and 85 days after lime application. The samples were dried on trays in the greenhouse, passed through a 2mm sieve, and then stored in plastic containers until laboratory analysis could be performed. pH was measured in a 1:2.5 soil to water solution, and a 1N KCl solution was used to extract [H<sup>+</sup>] and acidity [Al+H], which was measured volumetrically. Exchangeable Al was calculated as the difference between those two. Modified Olsen and Mehlich-3 solutions were both used to measure plant available nutrients. The Modified Olsen solution (pH 8.5) was used in a 1:10 soil to water solution. The Mehlich-3 procedure was done according to Wolf and Beegle (1995) to extract soils.

All extracts were analyzed for K, Ca, Mg, Zn, Cu, Fe, and Mn by atomic adsorption. P, N, S, and B were analyzed by photolorimetry.

**Table 2-2. Rates of lime and fertilizer applied to each treatment in the greenhouse pot study testing the effect of lime and P fertilizer amendments on plant growth in an Andisol.**

Treatment Code	Sources and Quantities of Added Amendments					
	At planting					At tillering stage
	CaCO <sub>3</sub>	11-52-0	NH <sub>4</sub> NO <sub>3</sub> (33% N)	K <sub>2</sub> SO <sub>4</sub> (52% K <sub>2</sub> O and 45 %SO <sub>3</sub> )	S micronized (80%)	NH <sub>4</sub> NO <sub>3</sub> (33% N)
	g pot <sup>-1</sup>					
T1: 0L, 0P	0	0	0.424	0.202	0.0438	0.424
T2: 0L, 1P	0	0.606	0.222	0.202	0.0438	0.424
T3: 0L, 2P	0	1.212	0.0202	0.202	0.0438	0.424
T4: 1L, 0P	11.74	0	0.424	0.202	0.0438	0.424
T5: 1L, 1P	11.74	0.606	0.222	0.202	0.0438	0.424
T6: 1L, 2P	11.74	1.212	0.0202	0.202	0.0438	0.424
T7: 2L, 0P	23.48	0	0.424	0.202	0.0438	0.424
T8: 2L, 1P	23.48	0.606	0.222	0.202	0.0438	0.424
T9: 2L, 2P	23.48	1.212	0.0202	0.202	0.0438	0.424

Statistical analysis was performed using R 3.0 software. Repeated Measures ANOVA was performed on the soil data across Times 3 and 4, as these points were sampled during plant growth and after fertilizer had been applied. Analysis of Variance (ANOVA) was used to compare the means of soil data at each time period in order to cross-check the interaction effects of time with our amendments.

ANOVA was also used to analyze the means of plant data. Treatment effects were significant if

$Pr > F \leq 0.05$ .

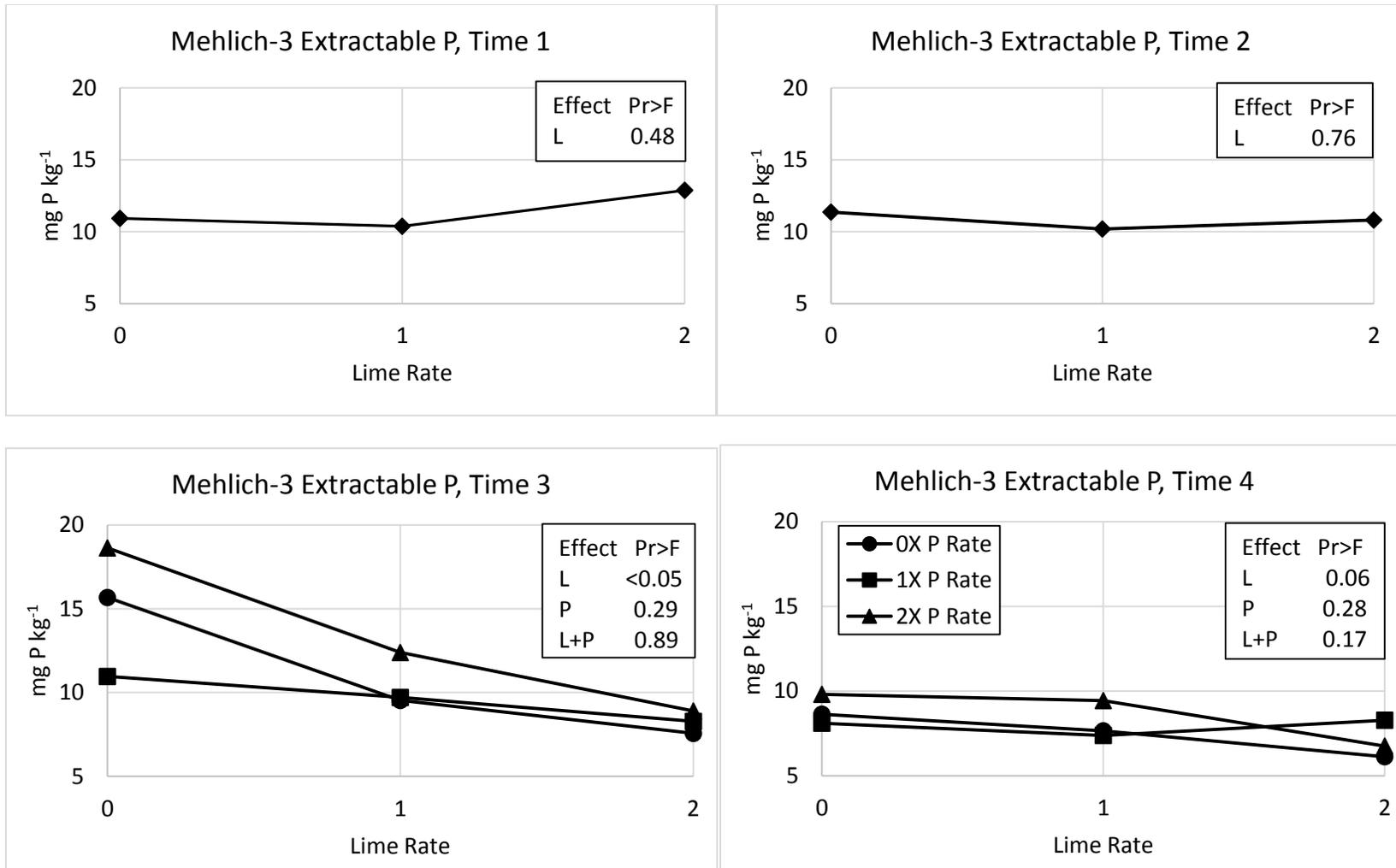
## Results

### Soil Chemistry

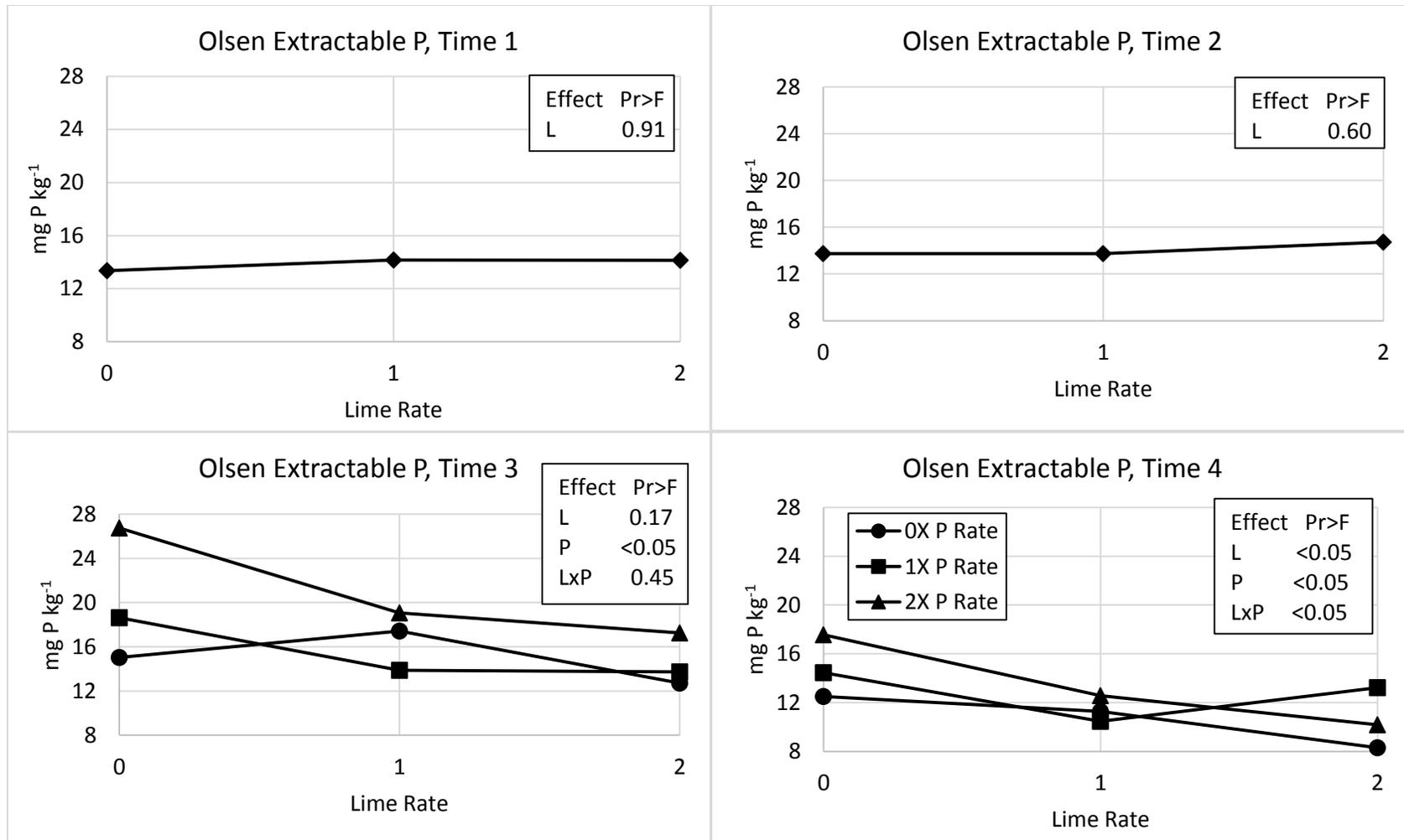
#### *Soil P*

Repeated measures ANOVA analysis (RMA) of Times 3 and 4 showed that Mehlich-3 P was decreased by liming, and that it decreased from Time 3 to Time 4 (Table 3-2). However, there was no effect of P fertilizer on Mehlich-3 P. There were no interactive effects observed in the repeated measures analysis. At Times 1 and 2, only native soil P was being measured as fertilizer had not been added yet. Native soil P was not affected by lime at either time. Lime additions to the soil decreased Mehlich-3 extractable P at Time 3. At Time 4 there is a trend in decreased P content with increased lime applications that is close to significant and should be considered, however it does not meet the criteria for our cutoff of  $P > F \leq 0.05$  (Figure 3-1). Likewise at Times 3 and 4 P fertilizer did not change Mehlich-3 P. There were no interactive lime and P fertilizer effects on Mehlich-3 P, showing that a combination of lime and P amendments did not change Mehlich-3 extractable P in the soil.

Repeated Measures ANOVA analysis (RMA) of Time 3 and 4 Olsen P data showed that Olsen P was decreased by liming, increased by P fertilizer, and decreased from Time 3 to Time 4 (Figure 3-2, Table 3-2). There were no lime \* P fertilizer interactive effects in the RMA. Again at Time 1 and 2, only native P was being measured as fertilizer had not been added yet. Analysis of sampling times 3 and 4 individually showed that P fertilizer increased Olsen P at both times. It can be seen that there was little change in Olsen P from the 0X P to the 1X P rate, while there is a much larger increase from the 1X P rate to the 2X P rate. This effect was most pronounced at the time 3 sampling, however the magnitude of the change was less than that of Time 3. The lime \* P fertilizer interactive effect at Time 4 was due to the 1X P rate giving the largest Olsen extractable soil P at the 3X lime rate.



**Figure 2-1.** Mehlich-3 extractable P is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance on the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.



**Figure 2-2.** Olsen extractable P is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.

### *Soil pH, Al, Fe, and Ca*

Soil pH was increased after liming (Figures 2-3; Table 2-3). There was a decrease in pH with time and a small P fertilization effect, however both were much smaller than the lime effect. The most notable effect of P fertilization on soil pH was the decrease in pH from Time 3 to Time 4 with the 0X P addition.

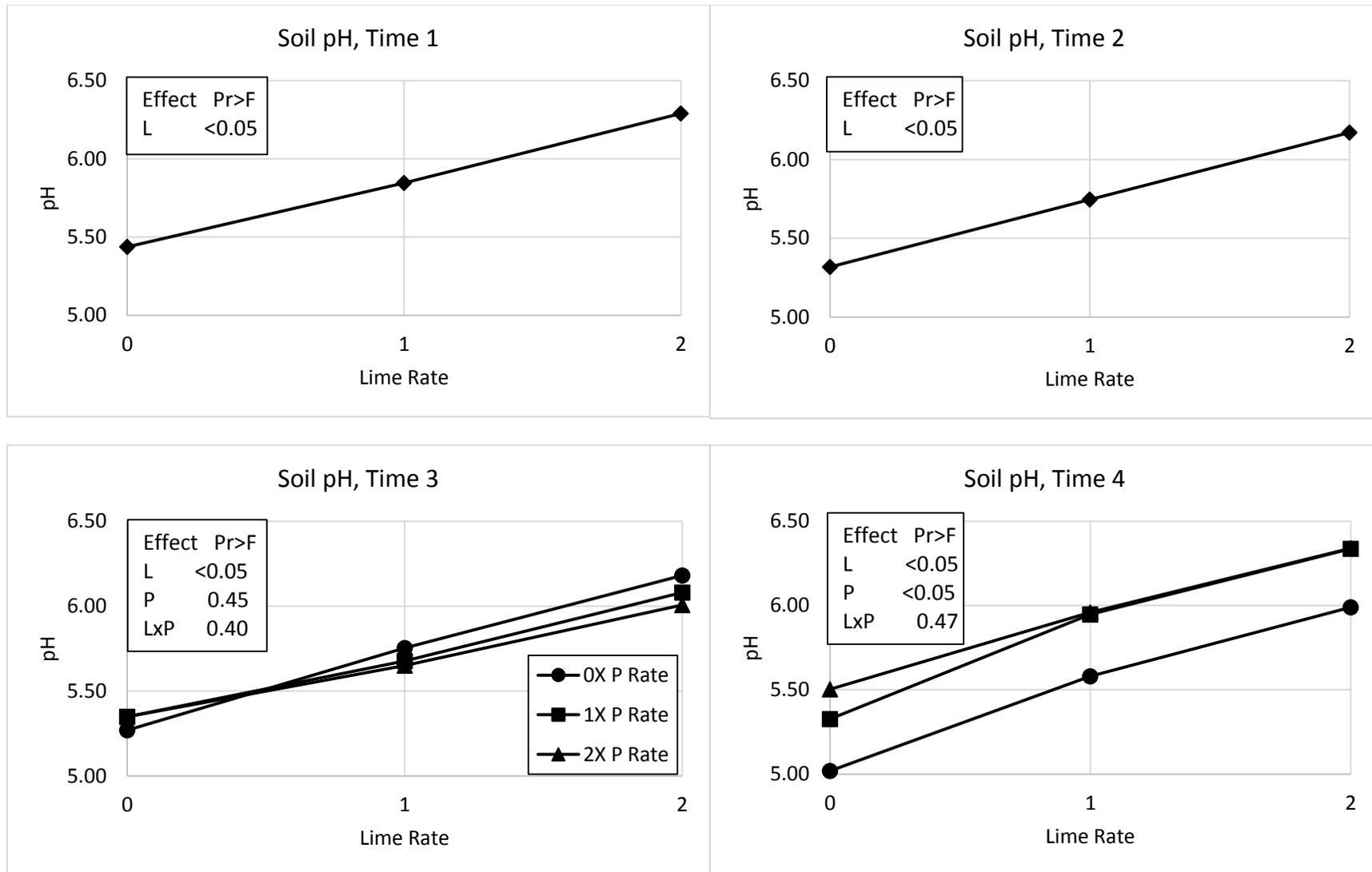
Similar responses were observed with exchangeable Al and Mehlich-3 and Olsen extractable Fe and Ca in that each of these showed a clear response to liming with much smaller or no effects of P fertilization and changes with time of sampling. Exchangeable aluminum fluctuated slightly across all sampling times (Figure 2-4; Table 2-3) but was clearly decreased by lime at all sampling times.

**Table 2-3. F values of Repeated Measures ANOVA analysis on effect of lime, P fertilizer and sampling time as well as their interactions on extractable P, pH, and extractable Al, Fe and Ca using both Mehlich-3 and Olsen tests. Degrees of Freedom in numerator (DF); Degrees of Freedom in denominator (DFd); Lime Effect (L); P Fertilizer Effect (P); Time Effect (T); interactions shown with asterisks.**

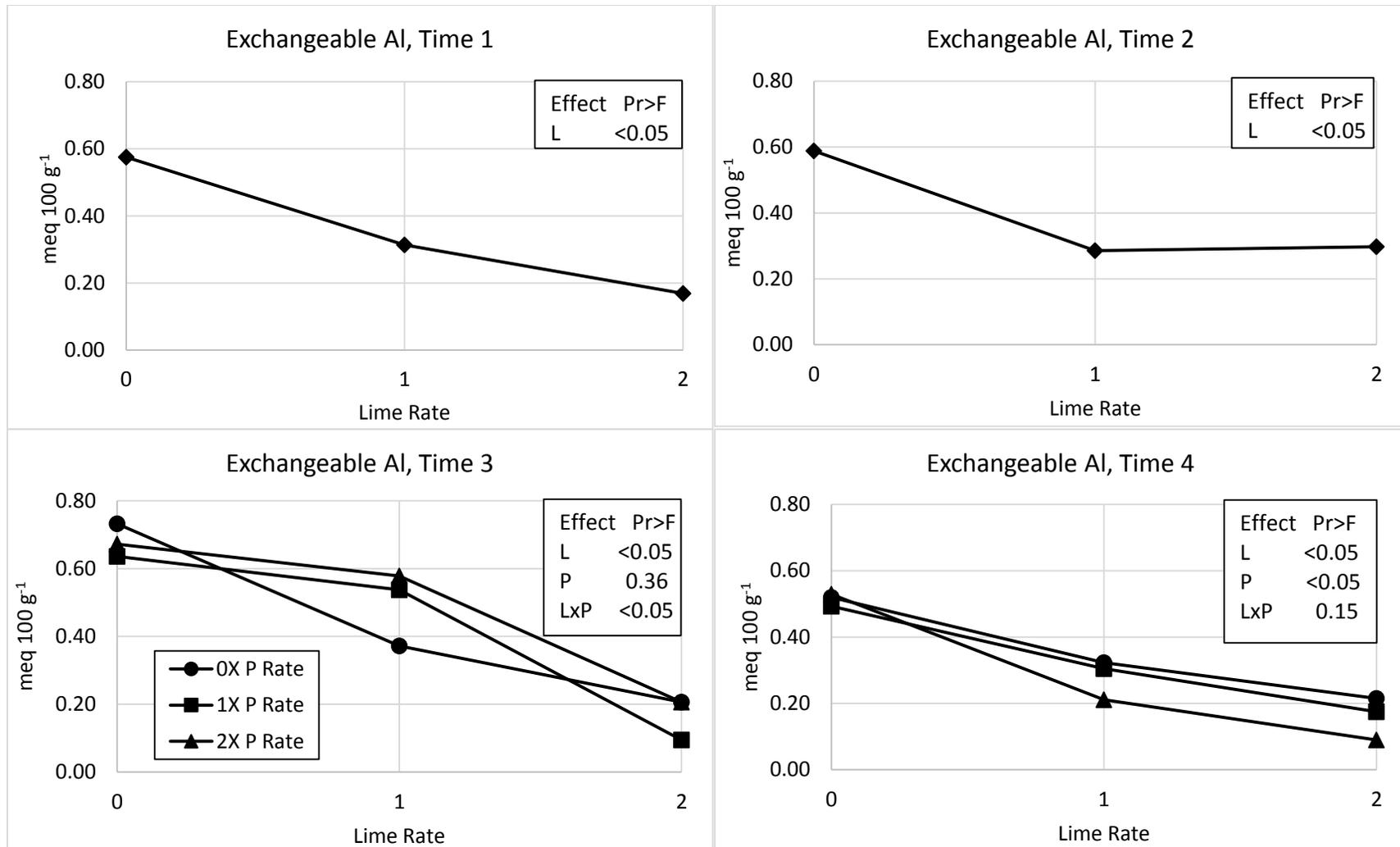
Effect	DF	DFd	Mehlich-3 P	Olsen P	pH	Al	Mehlich-3 Fe	Olsen Fe	Mehlich-3 Ca	Olsen Ca
----- F value-----										
<i>Significant values of P&lt;0.05 are indicated with an asterisk*</i>										
Lime (L)	2	18	5.58*	5.86*	238.67*	279.62*	88.26*	285.39*	163.87*	86.01*
P Fertilizer (P)	2	18	1.87	5.63*	11.67*	0.74	3.25	0.34	0.80	0.22
Time (T)	1	18	13.18*	28.15*	11.58*	43.05*	2.24	45.28*	8.85*	2.72
L * P	4	18	0.69	1.75	1.06	2.93*	4.18*	4.57*	1.44	0.09
L* T	2	18	2.11	0.34	6.80*	8.54*	9.56*	3.76*	1.06	0.88
P * T	2	18	0.67	1.93	43.01*	2.94	1.29	0.11	1.72	0.22
L * P * T	4	18	0.11	0.67	0.96	3.96*	4.32*	0.47	2.27	0.57

Mehlich-3 and Olsen extractable Fe were clearly decreased by lime application at all sampling times, with small decreases from P fertilizer and small overall decrease with time (Figure 2-5; Table 2-3). There is a lime and P fertilizer interaction in the Time 3 Mehlich-3 Fe, however it appears there is some unexplained noise in this data set. It should also be noted that Olsen extractable Fe was approximately two

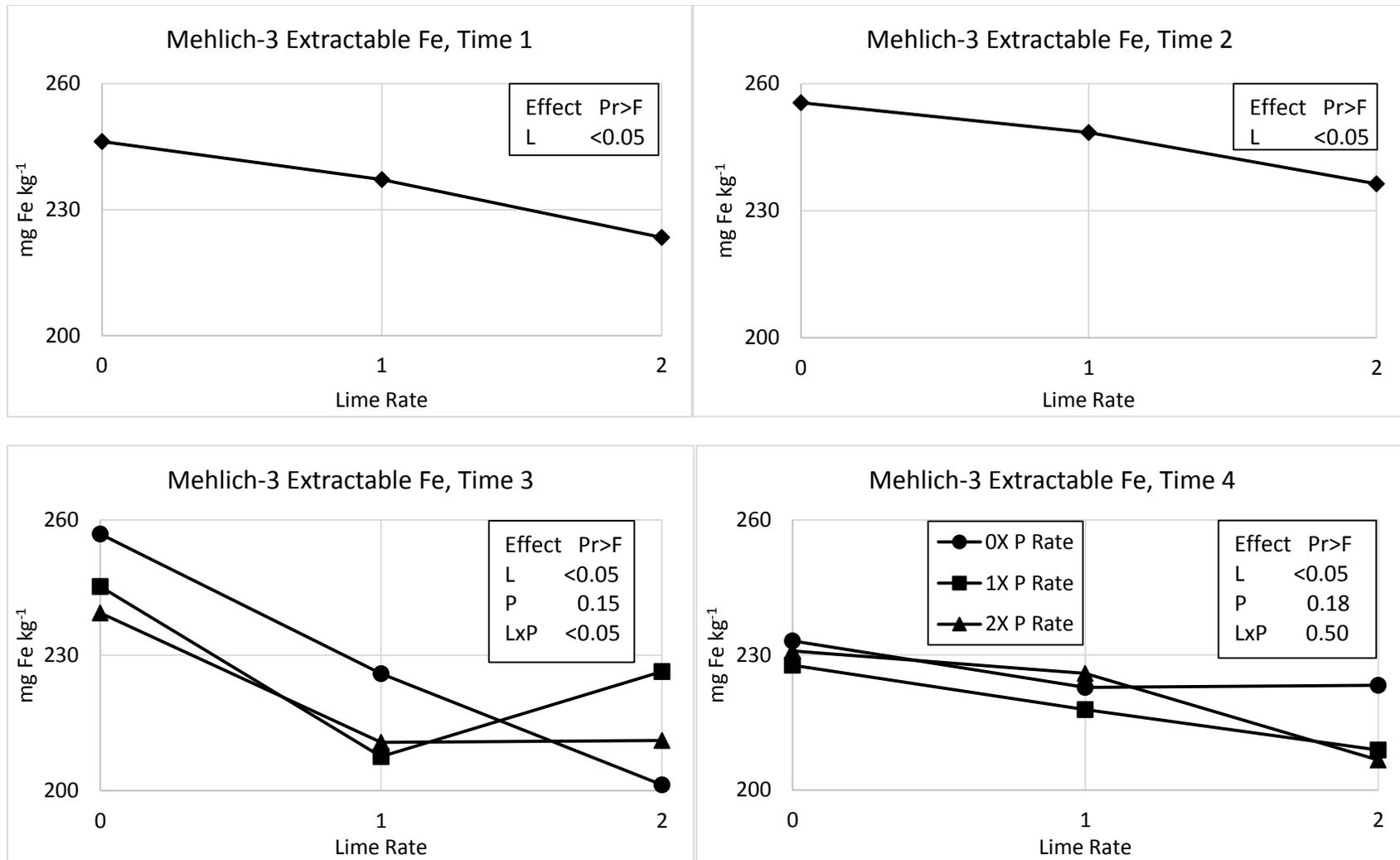
times greater than Mehlich-3 extractable Fe, and Olsen Ca was two times or greater than Mehlich-3 Ca. Both Mehlich-3 and Olsen extractable Ca were increased by lime application and exhibited relatively small fluctuations with time, but were not affected by P fertilizer (Figures 2-7 and 2-8; Table 2-3). Similar to extractable Fe, the Olsen extract solubilized approximately two times more Ca than the Mehlich-3 extract.



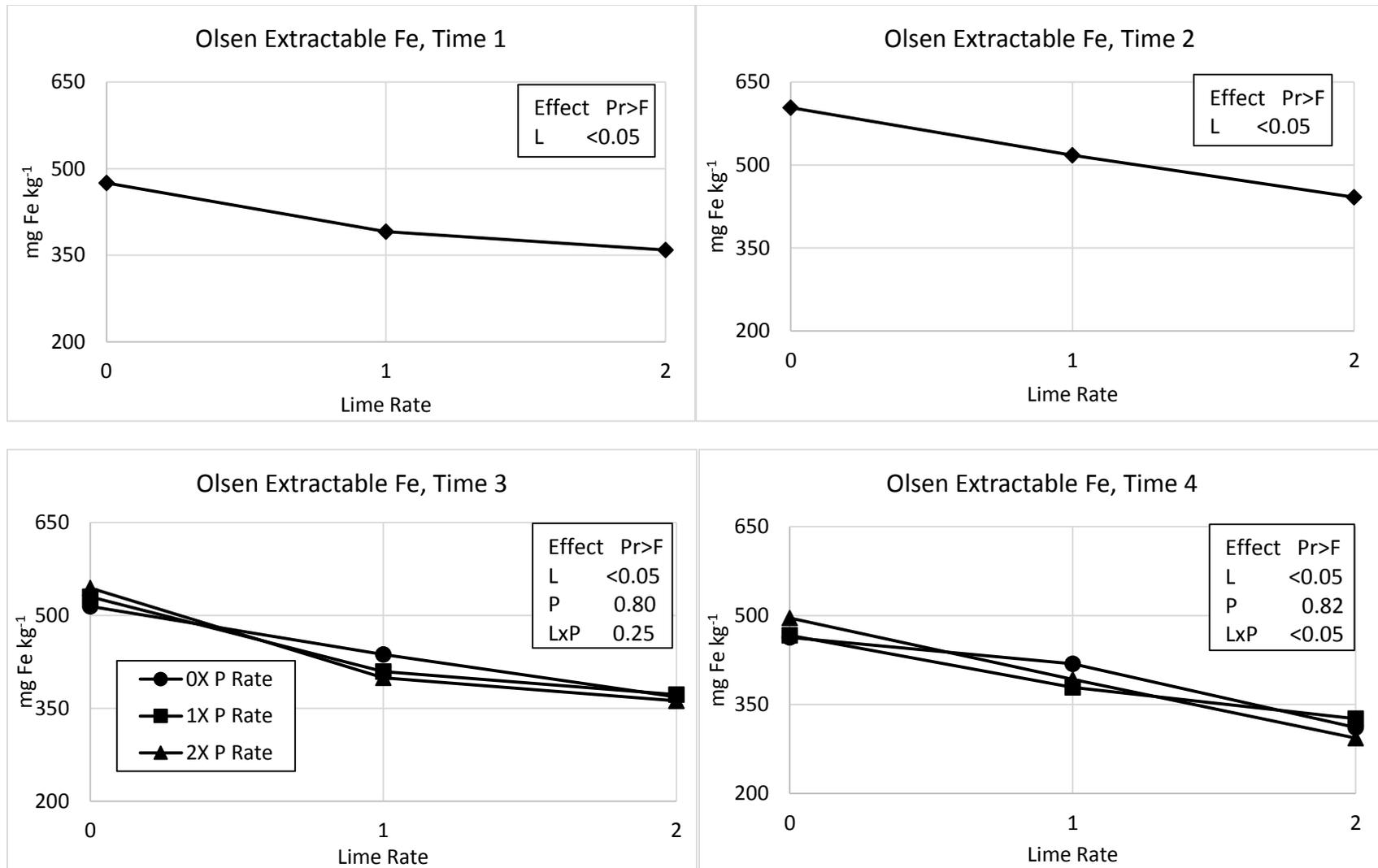
**Figure 2-3.** Soil pH is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.



**Figure 2-4.** Exchangeable aluminum is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.



**Figure 2-5.** Mehlich-3 Extractable Fe is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.



**Figure 2-6.** Olsen Extractable Fe is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.

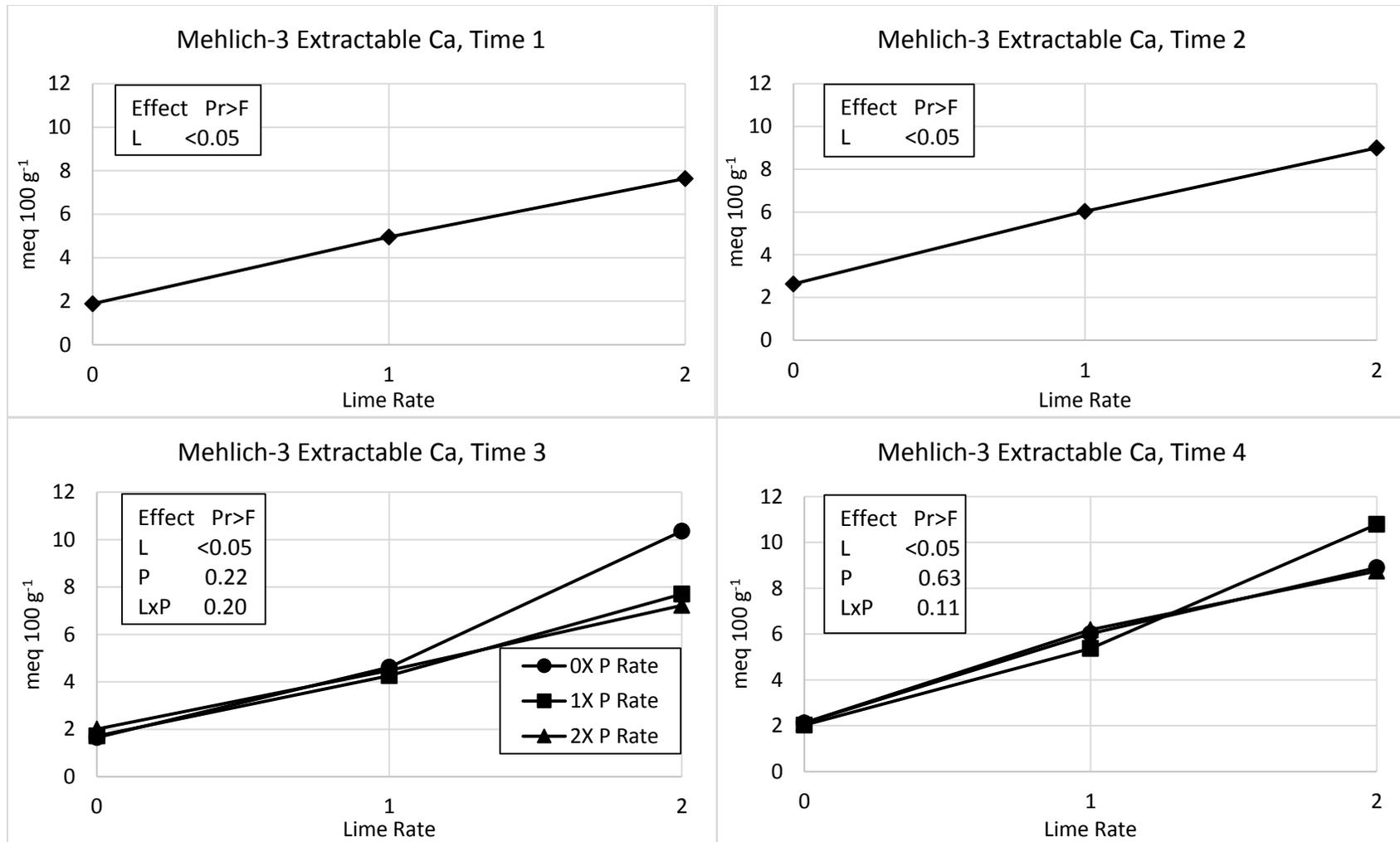
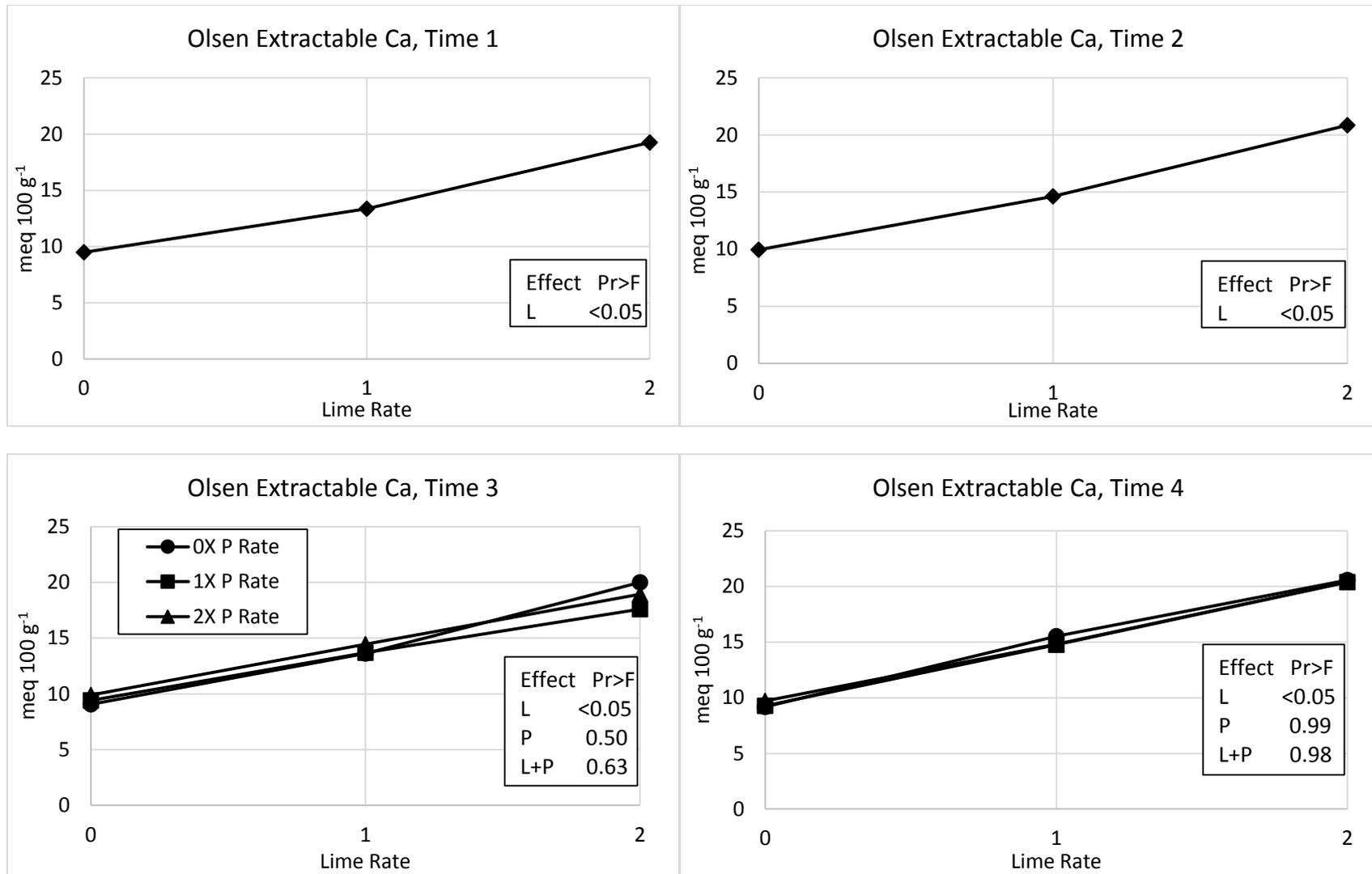


Figure 3-7. Mehlich-3 extractable Ca is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.

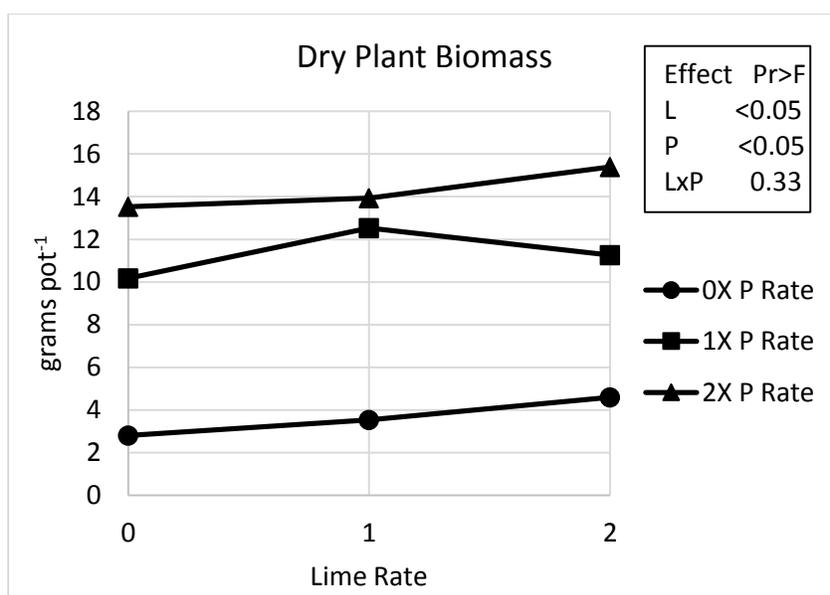


**Figure 2-8.** Olsen extractable Ca is shown at four sampling times during an experiment testing barley growth in an Andisol treated with lime and P fertilizer. Fertilizer was added to the soil between Time 2 and 3. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on each graph. Repeated measures ANOVA results are shown in Table 2-3.

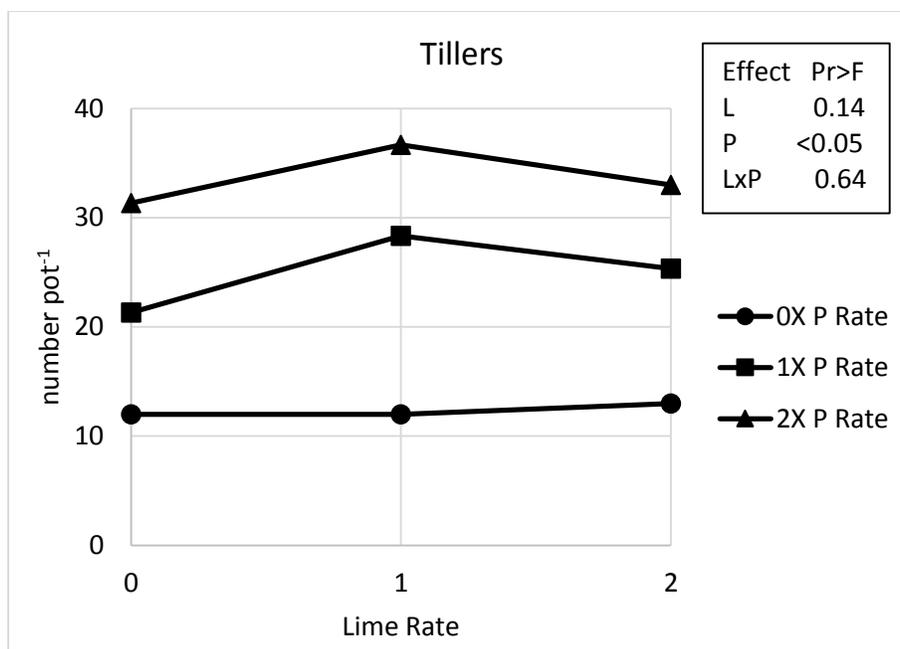
## Plant Growth

### *Biomass, Tiller production, and Height*

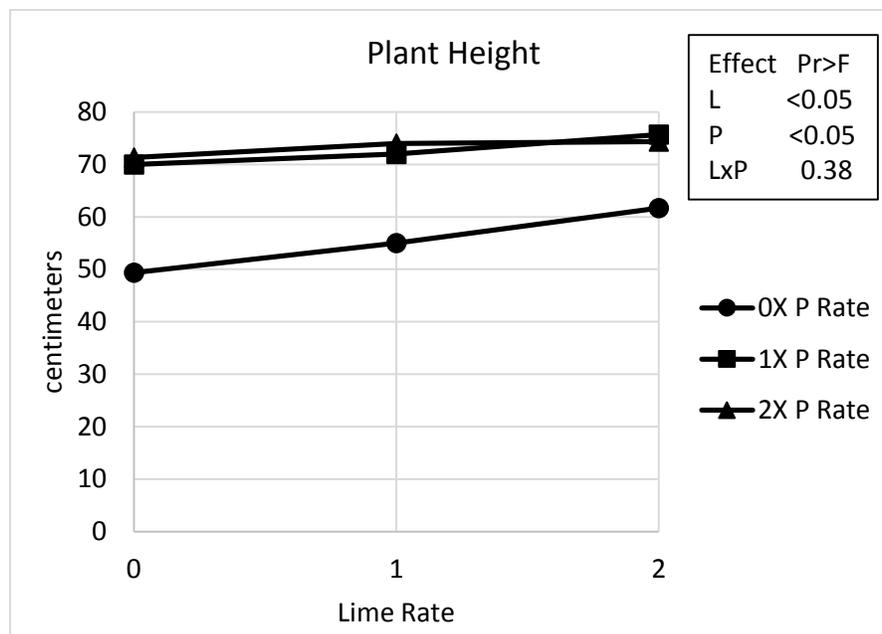
Phosphorus fertilization produced large increases in plant biomass and tiller production, as well as plant height (Figures 2-9, 2-10, and 2-11). Plant biomass and tiller production increased 2 to 3 fold from the 0X to the 1X rate. Likewise, for all three of the parameters the greatest increase occurred from the 0X to the 1X rate of P with a smaller increase from the second increment of P fertilizer. Liming increased biomass production and plant height, although the effect was smaller than the P fertilizer effect. The effect of liming on biomass production and on height was most pronounced in the treatments with no fertilizer P addition. Images of plant growth towards the end of the experiment can be seen in Figures 2-12, 2-13, and 2-14, and are separated by lime rate, with the P rate increasing from left to right.



**Figure 2-9.** Dry plant biomass production of barley in an Andisol treated with lime and P fertilizer increased due to P fertilization and due to lime additions. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on the graph.



**Figure 2-10.** Tiller production of barley in an Andisol treated with lime and P fertilizer increased due to P fertilization additions. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on the graph.



**Figure 2-11.** Plant height of barley in an Andisol treated with lime and P fertilizer increased due to P fertilization and due to lime additions. Analysis of Variance p values of the effects of lime (L), P fertilizer (P), and an interaction (LxP) are shown on the graph.



**Figure 2-12.** The response of barley grown in an Andisol that received no lime with P treatments increasing from left to right: 0, 90, and 180 kg  $P_2O_5$  ha<sup>-1</sup>.



**Figure 2-13.** The response of barley grown in an Andisol that received 3 tons ha<sup>-1</sup> lime with P treatments increasing from left to right: 0, 90, and 180 kg  $P_2O_5$  ha<sup>-1</sup>.



**Figure 2-14.** The response of barley grown in an Andisol that received 6 tons  $\text{ha}^{-1}$  lime with P treatments increasing from left to right: 0, 90, and 180  $\text{kg P}_2\text{O}_5 \text{ ha}^{-1}$ .

### **Plant Nutrient Content**

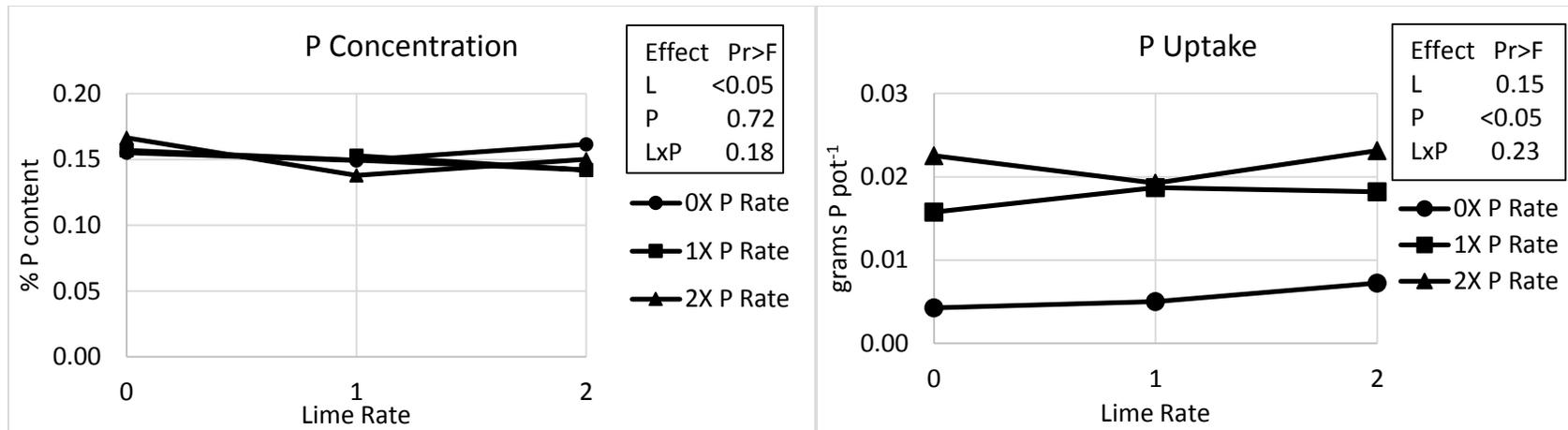
Plant P concentrations were not significantly influenced by P fertilizer (Figure 2-15). The significant lime effect was due to the small decrease in tissue P concentration at the 2X P lime rate, and there was no overall increasing or decreasing trend. Plant P uptake was increased by P fertilizer and not affected by lime (Figure 2-16). Barley P uptake was approximately 10% of the amount of P fertilizer applied in the 1X and 2X treatments, which is consistent with fertilizer P uptake values observed by Haynes (1984). There were no lime effects or lime by P fertilizer interactive effects on P concentration or uptake.

The increased biomass production caused by P fertilization increased plant nutrient uptake of Fe, Ca, and Mn, however, Fe and Ca nutrient concentrations did not change due to P fertilizer, showing that the increase in uptake was due to increased production of biomass only. Although Fe and Ca concentrations were not changed by P fertilizer applications, they were greatly affected by liming.

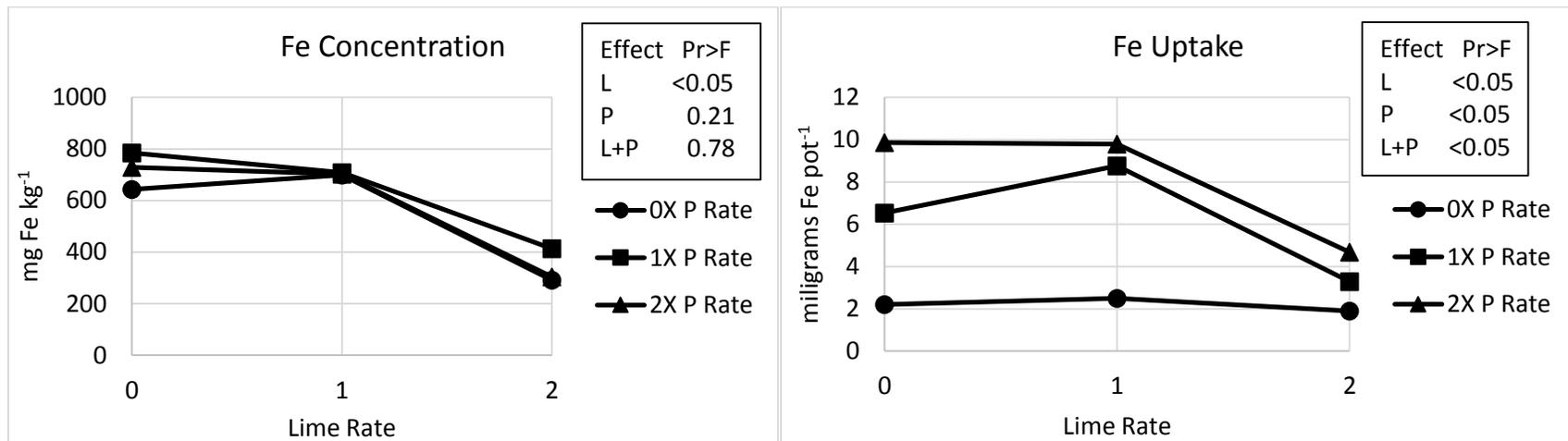
Plant Fe concentration and uptake were decreased by liming (Figure 2-16). There was no interaction effect on Fe concentration, however there was a significant interaction effect on Fe uptake by the plants in the 1X and 2X P rates (Figure 2-16). The Fe concentration in these plants (Table 2-4) are more than 2 to almost 8 times the recommended values (50-100 mg kg dry matter<sup>-1</sup>) (Fageria et al., 1997), and the Fe content is never reduced to a level with the range of recommended nutrition at the rates of lime we used.

Liming increased Ca concentration in the plants (Figure 2-17). There were no P fertilizer or interaction effects on Ca concentration. The plants grown in non-limed soils with 0X and 1X P were Ca deficient (<3 g Ca kg<sup>-1</sup> dry matter), while all limed treatments, as well as the non-limed, 2X P treatment, all had adequate Ca content, showing that lime amendments do help improve plant nutrition.

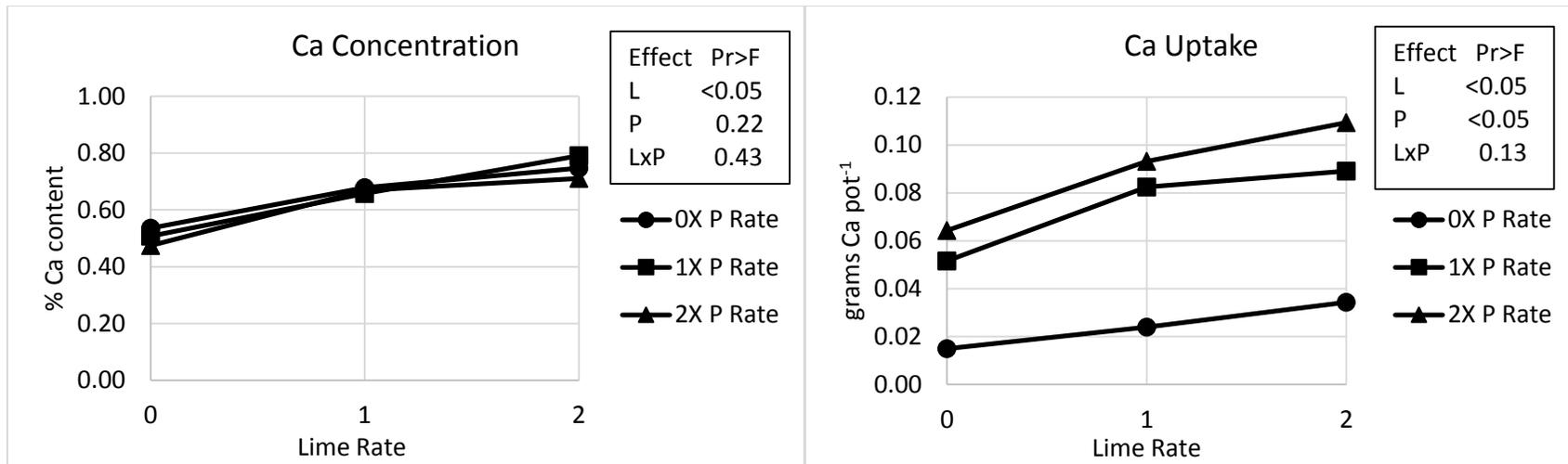
Manganese concentrations can be very high in Andisols and cause toxicity in plants grown in these soils. With no lime or P fertilizer, tissue Mn concentration was just above the recommended range (25-100 mg Mn kg<sup>-1</sup> dry matter) of nutrition. With all other treatments, tissue Mn concentrations decreased, indicating that lime and P fertilizer could reduce potential Mn toxicity in Andisols.



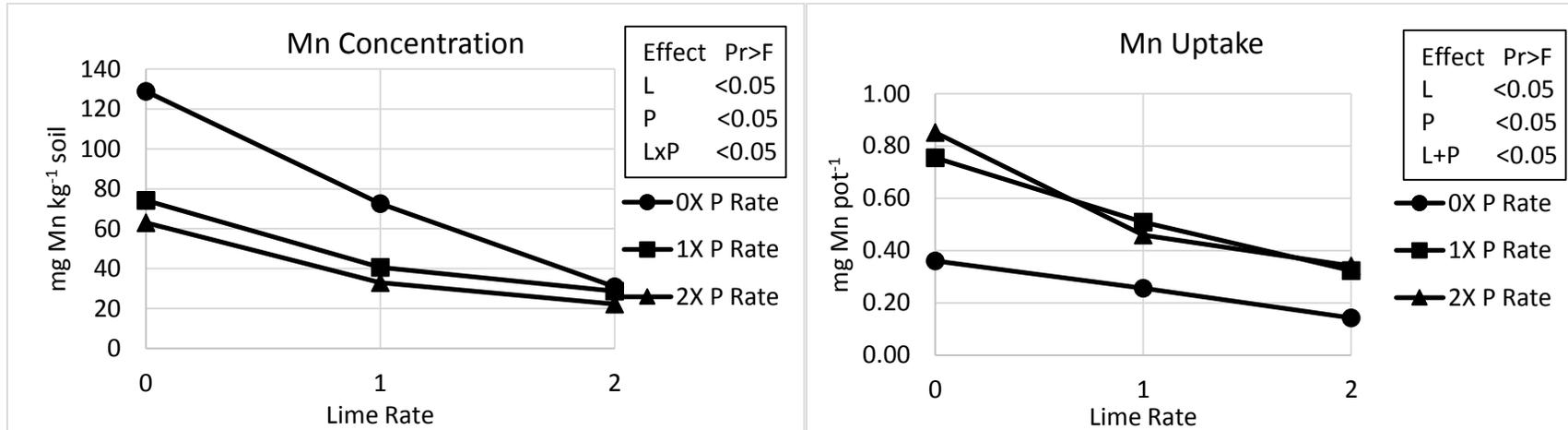
**Figure 2-15.** Plant P concentration and plant P uptake per pot grown in an Andisol treated with lime (L) and P fertilizer (P) are shown. There was no effect of lime or P on plant uptake; there was a P fertilizer effect on P uptake. Lowercase letters shown with groups indicate significant results of LSD mean separation of significant ANOVA parameters.



**Figure 2-16.** Plant Fe concentration and Fe uptake per pot grown in an Andisol treated with lime (L) and P fertilizer (P) are shown. There was a significant effect of lime on Fe concentration, while uptake was dependent on P fertilizer and a lime and P interaction.



**Figure 2-17** Ca concentration and uptake were both increased by lime applications in an Andisol treated with lime (L) and P fertilizer (P) are shown. Ca uptake was also increased by P fertilizer.



**Figure 2-18.** Mn concentration and uptake in an Andisol treated with lime (L) and P fertilizer (P) were both decreased by liming, adding P fertilizer, and also by an interaction effect between these two effects (LxP).

## Discussion

Due to the lack of any lime \* P fertilizer interactive effects on barley biomass, height, tiller number, tissue P concentration or P uptake this greenhouse experiment provided no evidence that application of lime together with P fertilizer will increase P fertilizer use efficiency in this moderate pH, moderately low test P Andisol.

Lime application had a very clear impact on soil chemistry in this Andisol, increasing pH and Ca, and decreasing extractable P. The increase in pH caused by lime was expected to reduce positively charged sorption sites on allophane and imogolite, cause precipitation of Fe and Al, (Evans and Kamprath, 1970; Haynes and Mokolobate, 2001) and increase dissolution of organic matter complexes (Guadalix and Pardo, 1994). Lime caused a significant decrease in Al and Fe through precipitation, however this did not cause increased soil test P as expected. According to the Mehlich-3 and Olsen extracts used in analysis, lime decreased soil test P. Sorn-Srivichai (1984) and Curtin and Syers (2001) also saw decreases in Olsen extractable P with liming. Sorn-Srivichai attributed this to potential precipitation of new calcium phosphates upon extraction due to the high pH and Ca content of the Olsen solution, while Curtin and Syers attributed it to P sorption to newly formed reactive faces after liming. Haynes (1982), in his observations on liming acid soils, also drew the latter conclusion based on the many pH dependent, P-sorbing phases of aluminum present in the soil. I conclude that because the pattern of decreased P with liming is observed in both the Mehlich-3 and Olsen extracts, the pH or constitution of the extract (Mehlich-3 pH 3.5; Olsen, pH 8.5) does not cause a change in the extractable P as much as the intrinsic formation of new sorptive phases in the soil could cause an initial decrease in P after liming. This experimental work provides no evidence that lime will increase soil test P response to P fertilizer compared to just P fertilizer alone in this soil.

Despite the negative effects of lime on soil P availability as indicated by Mehlich-3 and Olsen tests, lime increased barley biomass and height and did not cause a decrease in tissue P concentration or P uptake. Thus the decreased soil test P results were not reflected in the plant response which provided no evidence

that P fertilizer use efficiency was decreased by lime. Research should be conducted on an Andisol with lower pH (<5.0) and lower P content, like those values below 1.5 mg P kg<sup>-1</sup> observed in the region by Henry et al. (2012) may have responded differently to lime and P amendments, as these soils are less hospitable to plant growth. The impact of lime may have also caused an interaction effect in improving plant uptake or concentration when paired in a low pH soil, however this research should be conducted as well.

Barley response to added P fertilizer provides further evidence that Mehlich-3 and Olsen extractable P are not indicative of plant available P in this Andisol. In addition to barley plants taking up less P than was measured by the extracts, the distribution of patterns in the data do not correlate well between the extract data and the plant response data. The plants responded very strongly to the 1X P rate, tripling their P uptake and biomass production, and had an additional, smaller response to the 2X P rate. By contrast, the soil P data showed that there were hardly any differences in extractable P between the original unfertilized (0X) and the 1X P rate, with a larger (noticeable) increase from the 0X and 1X rate to the 2X rate of P. The change in Mehlich-3 extractable P was not even significant, suggesting this test may not be sensitive enough for use with this soil. The Mehlich-3 and Olsen tests measure test P in the bulk soil. Phosphorus solution chemistry occurring in the rhizosphere different from the bulk soil would be lost when samples were taken from the entire volume of soil. It is possible that the larger rhizospheres of the fertilized treatments would have caused the samples taken in these pots to have more rhizospheric soil than the unfertilized treatments, and it would be interesting to investigate differences in pH and nutrient availability in the rhizospheric and bulk soil. The root systems of future studies should be examined in order to evaluate if the reduced test P is related to the rhizosphere.

The major change in plant biomass and P uptake was observed in the increase from the 0X to the 1 and 2X P rates; not across lime treatments. It appears that the plants allocated additional P to increased production over increased P concentration, as the P concentration of all treatments was very similar and despite fertilization, P concentration did not meet recommendations for adequate barley nutrition (4.2-4.8 g P kg dry plant matter<sup>-1</sup>) (Fageria, 1997). This indicates that to absolutely maximize plant production or nutrition, much higher rates of P fertilizer may need to be applied which is impractical due to high cost and

the need for repeated yearly application due to the very low residual P effect of these soils (Espinosa, 1995). The lack of increase in P concentration at the rates of P added has been observed by Delhaize et al. as well (2013). At higher rates of P application, full P nutrition could be supplied to plants, however the cost implications of this could be prohibitive to farmers. There was a potentially confounding factor in the N fertilizer  $\text{NH}_4\text{NO}_3$  which was used to supplement N nutrition applied in the monoammonium phosphate (11-52-0) fertilizer used in this experiment. The addition of nitrate ( $\text{NO}_3$ ) increases rhizosphere pH while  $\text{NH}_4$  decreases it. The amount of  $\text{NH}_4\text{-N}$  was fairly consistent across treatments, however the initial  $\text{NH}_4\text{NO}_3$  application resulted in the unfertilized treatments receiving a larger amount of nitrate than the fertilized treatments, which may have had an effect on rhizosphere pH, which would affect nutrient availability in the soil. No measurements were made of rhizosphere pH or rhizosphere nutrient availability.

Although liming did not improve plant P nutrition, liming had other important beneficial effects on barley nutrition. Lime increased tissue Ca concentration mitigated the Ca deficiency that existed with the soil. Lime also reduced potential for Fe and Mn toxicity. Tissue Mn was reduced to below a toxic levels and approaching normal levels with lime and also with P fertilizer amendments. Halday and Mandal (1981) showed that P applications decreased some micronutrient uptake including Mn in rice plants, and other workers have also shown decreased micronutrient uptake in various crops after P uptake. There are several hypotheses for why this occurs including that these micronutrients are diluted in concentration as plant biomass production increases, which has been observed in our experiment as well (Haynes, 1984). Although tissue Fe was still above normal in barley grown on limed soil, lime reduced tissue Fe from around 700 to around 200 mg Fe  $\text{kg}^{-1}$  dry biomass. An even larger lime application may be needed to further improve plant nutrition in this Andisol.

The discrepancy between Mehlich-3 and Olsen soil test P results and plant growth response indicates that these soil test P methods lack of sensitivity at the level of soil P to which the plant responds. The Olsen solution extracted twice the amount of P that Mehlich-3 measured, which is attributed to the 8.5 pH of the extract, which would increase hydrolysis of organic P and also dissolve some Al- and Fe- bonded P (Adesanwo, et al., 2013). Upon comparing extractable P from the Mehlich-3 and Olsen solutions with P

uptake by the barley plants, I found that the Olsen solution measured about seven times as much “plant-available” P as was actually removed by the plants, and the Mehlich-3 solution measured about four times as much. Both the Olsen and Mehlich-3 solutions indicate a higher amount of available P in the soil than is actually present. The 0X Lime, 2X P treatment Olsen P result measures that 61% of the value of added P is available, while Mehlich-3 measures that 35% of the added P is available. However, plants only took up 10% of the value of added P. The results of the soil data are in contrast to the plant responses. The soil data suggests that soil P is decreased by lime, while the plants show a slight biomass increase and no decrease in plant nutrition due to lime application. The soil data show levels of extractable P that were much higher than those accessed by the plants. Finally, although the two extracts used in this experiment produced similar trends in the data, both extracts measured much higher rates of P than the plants took up. Because the soil extract data suggests that lime decreases P availability and the plant data suggests the opposite, or at least that there is no negative effect of lime on biomass production of P uptake, the plant data is more fitting to use to evaluate the outcomes of the greenhouse project as an effective bioindicator. This Andisol is not as strongly acid as some others that we would expect to find to the south of Ecuador or along warmer climate zones (Zehetner, 2007), nor is it as low in soil test P as others that have been tested in nearby regions (Henry, 2012). It would be prudent to test the effect of lime \* P on a strongly acidic, lower test P Andisol. The results of this greenhouse project show that lime has a beneficial effect on barley growth in this Andisol, however lime does not increase P uptake or P concentration in the plant, and this effect should be further investigated with more Andisols and using a wider range of amendments.

### **Conclusions**

This experiment shows that although lime application may not directly increase P fertilizer use efficiency by barley in this allophanic, moderately low pH Andisol, lime does cause an increase in biomass production and is beneficial in increasing Ca concentration and uptake and in reducing potentially toxic Fe and Mn. This experiment tested only one soil and given the broad range of Andic soil properties that affect

P sorption, it should be repeated with Andisols across the Andean highlands. The results of the Mehlich-3 and Olsen tests indicate that there is the need for development of a more sensitive indicator of plant available soil P. Future research should focus on increasing knowledge of the effect of liming Andisols to increase plant production by conducting greenhouse and field trials on soils representing a broader range of Andisols including those which have more weathered mineralogy, more acidic pH, and lower P content more typical of P-starved Andisols, as well as using a wider range of lime and P amendments to identify benefits of lime in subsistence farming or to identify the true sorption mechanisms occurring in the soil with added lime and P. Also needed are studies that evaluate the impact of liming and P fertilizer amendments on crop production of a subsequent planting cycle.

## References

- Adesanwo, O.O., D. V. Ige, L. Thibault, D. Flaten, W. Akinremi. 2013. Comparison of colorimetric and ICP methods of phosphorus determination in soil extracts. *Communications in Soil Science and Plant Analysis*. 44:3061–3075.
- Curtin D., and J.K. Syers. 2001. Lime-induced changes in indices of soil phosphate availability. *Soil Sci. Soc. Am. J.* 65:147–152.
- Delhaize, E., and P.R. Ryan. 1995. Update: aluminium toxicity and tolerance in plants. *Plant Physiol.* 107:315–321.
- Delhaize, E., P. Taylor, P.J. Hocking, R.J. Simpson, P.R. Ryan and A.E. Richardson. 2009. Transgenic barley (*Hordeum vulgare* L.) expressing the wheat aluminium resistance gene (*TaALMT1*) shows enhanced phosphorus nutrition and grain production when grown on an acid soil. *Plant Biotechnology Journal* 7:391–400.
- Espinosa, José. 2007. Fijación de fosforo en suelos derivados de ceniza volcánica. Quito: INPOFOS.
- Guadalix, M.E., and M.T. Pardo. 1994. Effects of liming on soil properties and P solubility in some Spanish Andosols. *Geoderma*. 63:53-6.
- Haldar, H. M., and L. N. Mandal. 1981. Effect of P and Zn on the Growth and P, Zn, Cu, Fe, and Mn Nutrition of Rice. *Plant Soil* 59:415-420.
- Haynes, R.J. 1984. Lime and phosphate in the soil-plant system. *Advances in Agronomy* 37: 249-305
- Henry A., L. Mabit, R.E. Jaramillo, Y. Cartagena, J.P. Lynch. 2012. Land use effects on erosion and carbon storage in the Río Chimbo watershed, Ecuador. *Plant Soil* 367(1-2): 477-491.
- Nanzyo, M. 2003. Unique properties of volcanic ash soils. *Global Environmental Research*, 6(2):83-97.
- Breemen, N. van, and P. Buurman. 2003. Formation of Andisol. 285-306. *In* (2nd ed.) *Soil Formation*. Kluwer Academic Publishers. Dordrecht, Netherlands.
- Wolf, A.M., and D.B. Beegle. 1995. Recommended soil tests for macronutrients: phosphorus, potassium, calcium, and magnesium. *Recommended Soil Testing Procedures for the Northeastern United*

- States. Northeast Regional Bulletin #493. p. 25-34. Agricultural Experiment Station, University of Delaware, Newark, DE.
- R Core Team. 2013. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <http://www.R-project.org/>.
- Sorn-Srivichai, P., R.W. Tillman, J.K. Syers, and I.S. Cornforth. 1984. Effect of soil pH on Olsen bicarbonate phosphate values. *J. Sci. Food Agric.* 35:257-264.
- Haynes, R.J., and M.S. Mokolobate. 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. *Nutrient Cycling in Agroecosystems.* 59:47–63.
- Penn, C.J., G. L. Mullins, and L. W. Zelazny. 2005. Mineralogy in relation to phosphorus sorption and dissolved phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 69:1532–1540.

## Chapter 3

### **Phosphorus Sorption, Desorption, and Fractionation of an Andisol after receiving Different Fertility Treatments in a Greenhouse Experiment**

#### **Abstract**

Sorption and desorption isotherms were constructed and a P fractionation experiment was carried out on four treatments of a soil previously used in a greenhouse experiment that tested the effect of lime and P fertilizer on uptake and biomass production of barley in an acid, low P Andisol. Rates of 0, 20, 50, 80, 100, 150, 200, and 400 mg P L<sup>-1</sup> were equilibrated for 24 hours with 1 gram samples of four of the treatments soils from the greenhouse experiment. The samples were centrifuged and filtered and analyzed for orthophosphate. The soil samples that were shaken with the highest rate of P (400 mg P L<sup>-1</sup>) were then extracted five times with 0.03M KCl solution that contained no P to determine cumulative P desorption. Finally, 2 gram samples of the same four treatments from the greenhouse experiment were sequentially extracted in a modified Hieltsjes and Lijklema fractionation procedure to determine the user-defined fractions of labile P, Al- and Fe-P, Ca- and Mg- P, humic, organic bound P, and finally, residual bound P. Results of these experiments show that although previous fertility treatments do not significantly affect P sorption, the lime does affect P desorption at very high levels of subsequent P application. It was also observed that although lime has a large effect of soil Ca, Fe, and Al, there is not a large treatment effect on the partitioning of P in this soil.

#### **Introduction**

Understanding soil phosphorus chemistry in Andisols may lead to better management for increased phosphorus availability. Soil pH management through liming has been shown to increase, decrease, or not change phosphorus availability in Andisols (Haynes, 1982). Sorption and desorption isotherms are used to evaluate the strength of the soil to sorb phosphorus and how much can be released again from that soil. In Andisols, rates of phosphorus sorption are very high. It is suggested that high organic matter, high allophane

soils sorb large amounts of phosphorus easily at low P application rates, but that as P application rate increases, more P reactive surfaces are exposed and P sorption continues to increase (Iñiguez and Val, 1984). Phosphorus sorption has been shown to be pH dependent, and occurs at high rates in low pH systems up until a pH of about 5.0, after which it starts to decrease with increasing pH (Haynes, 1982). However, Guadalix and Pardo showed that there was little change in P sorption with liming in soils already low in soluble Al, and Penn et al. showed that P desorption is very dependent on clay content, suggesting the success of managing P sorption is more related to native soil properties than pH management (1994; 2005). Haynes (1984) suggests that P sorption isotherms may be a fast, convenient way of determining soil P requirements, but concedes that, as determined in Chapter 2 of this thesis, soil P requirements are not a measurement of plant P nutrition requirements. Isotherms therefore appear to be important in identifying factors causing or changing P sorption, although they may only be used as a general guide and are not directly related to the effect of soil treatments on P uptake by plants.

In addition to measuring the sorption and desorption behavior of labile P, we are also interested in the final fate of P added to the soil, and the role that lime may play in altering P fractions in the soil. If pH change increases labile P content, plants may have more access to the nutrient. In pH systems below 5.5-6, phosphorus is sorbed through ligand bond fixation with amorphous, variable charge minerals like allophane and imogolite, to Al-humic complexes, and to solution aluminum and iron. In pH systems above 6-6.5, Mg/Ca-phosphates precipitate out of solution instead of Al/Fe phosphates. In soils that have been treated with lime, soluble aluminum and iron precipitate as crystalline minerals and are not as reactive with phosphate. Dissolved labile P can be greatly influenced by pH, as well (Devau et al., 2011). However, Haynes and Mokolobate (2001) found that there is also a dissolution of organic matter, and an increase in new hydroxide faces formed under pH increases in the soil that may or may not increase P sorption. It was found that in acid Argentine Andisols, P fertilization resulted in a decrease of labile P and an increase in moderately resistant inorganic fractions (Zubillaga, 1998). Haynes (1984) showed that 40% of applied fertilizer became part of the organic phosphorus sink after 28 days in the field. Since P is so critical to plant

nutrition, an understanding of the fate of fertilizer in the soil after treatment with lime and P fertilizer amendments with lime may bring us a clearer understanding of the behavior of the chemistry of the soil.

Soil samples from the greenhouse project described in Chapter 3 that had been treated with several rates of lime and/or phosphorus were used in laboratory studies to examine the P sorption and desorption behavior as well as to quantify phosphorus fractionation in the soil.

### **Methods**

Adsorption and desorption isotherms were carried out on four of the nine original treatments from the greenhouse experiment. The four treatments chosen were the soils with 0X or 2X lime along with 0X or 2X P with the assumption being that these samples would represent the extremes of possibilities from within the treated soils. Aggregate samples were created for use in the laboratory by combining 10 grams of soil from each of the three reps of the treatments from the greenhouse project.

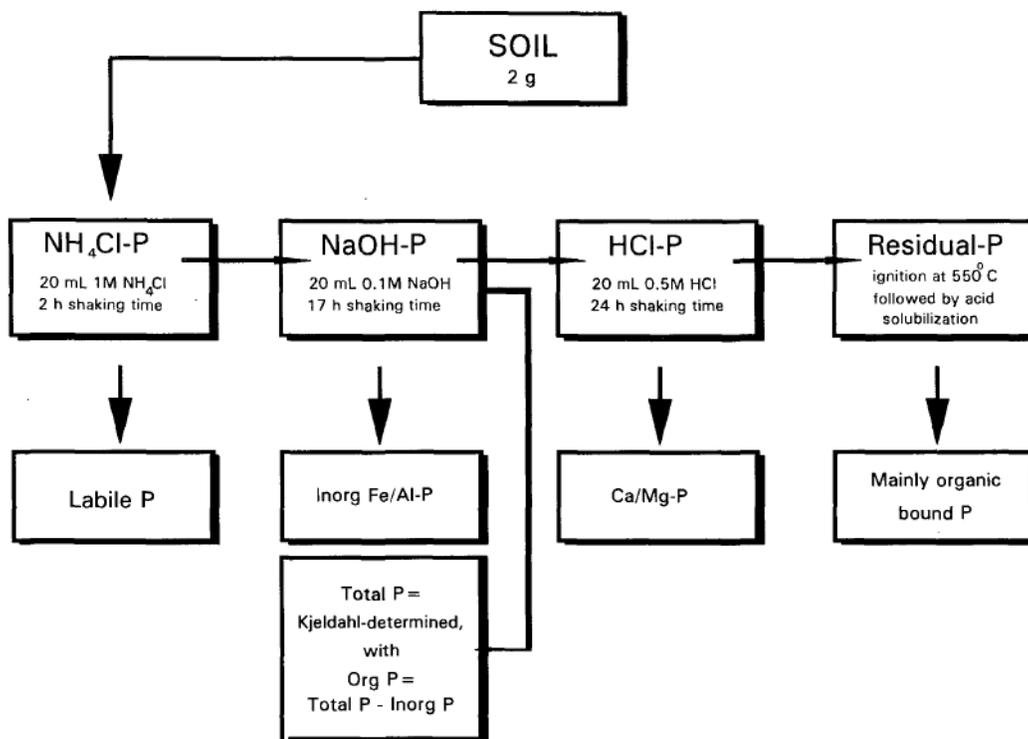
The adsorption isotherm protocol is that of Graetz and Nair (2009). Twenty four dried, sieved, one gram samples of each of the four treatments were measured into 50 mL conical bottomed centrifuge tubes, and the final weight of soil was recorded. Solutions of 0, 20, 50, 80, 100, 150, 200, and 400 mg P L<sup>-1</sup> were prepared in volumetric flasks using KH<sub>2</sub>PO<sub>4</sub> in a 0.03 M KCl matrix, designed to mimic the ionic concentration of the soil solution. 25 mL of a given solution were added to three samples of each treatment, producing 3 replications of each of the 4 treatments, and this was done for all eight P solutions. The additions were done by weight assuming an approximate density of 1 g mL<sup>-1</sup> for the solutions, and the final solution weight was also recorded. Samples were equilibrated for 24 hours in an end-over-end shaker at 25° C in the dark. After shaking samples were centrifuged at 1800 xg for 15 minutes at 25°C and then filtered through a 0.45 μm membrane. Extracts were then acidified with a drop of concentrated HCl (Elliott, 2013) and stored in the refrigerator for three days until they were analyzed by flow injection colorimetry on a Lachat QuickChem FIA+8000 Analyzer (Lachat Instruments, 2007).

Desorption isotherms were carried out using the three reps of all four treatments from the sorption isotherm that received 400 mg P L<sup>-1</sup>, the highest rate of applied P in that experiment. After the 400 mg P L<sup>-1</sup>

<sup>1</sup> samples were filtered in the last step of the sorption experiment, the soil plug was retained in the conical-bottomed centrifuge tube, and a 0.03 M KCl solution containing no phosphorus was used to wash any soil from the filter back into the tube. A total of 40 mL of 0.03 M KCl solution was added to the tubes, again measured by weight, assuming an approximate density ratio of 1 g mL<sup>-1</sup>. The samples were shaken in an end-over-end shaker for 1 hour, centrifuged for 15 minutes at 1800 xg and 25°C, and filtered through a 0.45 µm membrane. Any residual soil on the filter was washed back into the tube using KCl, and then the process was repeated four more times, for a total of five sequential desorption points. These samples were acidified with a drop of concentrated HCl (Elliot, 2013) and refrigerated for two days until they were analyzed by flow injection colorimetry on a Lachat QuickChem FIA+8000 Analyzer (Lachat Instruments, 2007).

Phosphorus fractionation was carried out on soil samples of the same four treatments listed above. Phosphorus fractionation is an operationally defined sequential extraction, meaning that the fractions of P measured in analysis are defined by the user and dependent on each other, and in this case we used a version of the Hieltjes and Lijklema fractionation procedure as modified by Nair et al. (1995). The procedure is given in the schematic Figure 3-1, adopted from Nair et al. In this case, three replicates of two grams of each treatment of dried, sieved soil were added to 50 mL conical-bottomed test tubes and the weight of soil was recorded. 20 mL of 1 M NH<sub>4</sub>Cl was added to the soils by weight, assuming an approximate density of 1g mL and shaken for two hours. The tubes were centrifuged at 3700 xg for 15 minutes at 25 and 25°C, and filtered through a 0.45 µm membrane. After filtering, the solution from the next step in the process, 0.1 M NaOH, was used to wash soil particles from the filter back into the centrifuge tube. Enough NaOH solution was then added to bring the solution to 20 mL. This procedure was repeated for the 0.5 M HCl solution extraction. After the 0.05 M HCl extraction, the soil plugs were dried at 130° C and then 1 gram of each was ashed in a muffle furnace at 550° C for 2 hours. 25 grams of 6 M HCl were added used to rinse the samples into a flask and they were left to digest 15 minutes, after which they were diluted to 100mL in a volumetric flask with DI water for a final acid concentration 1.5 M HCl. These samples were left to settle overnight and decanted and filtered through a 0.45 µm membrane. The 1 M NH<sub>4</sub>Cl (labile P) solution, the 0.1 M NaOH (Fe- and Al-P) solution, and the 0.5 M HCl (Ca- and Mg-P) solutions were all analyzed by

flow injection colorimetry on a Lachat QuickChem FIA+8000 Analyzer (Lachat Instruments, 2003, 2010, 2007). Instead of doing a Kjeldahl-determined Total P on a subsample of the 0.1 M NaOH extract, it was analyzed as produced on ICP, which is assumed to measure all P in solution, and the organic P was found as the difference in the two measured fractions. The 1.5 M HCl extracts were also analyzed by ICP to give residual bound P.



**Figure 3-1.** Image from Nair et al. (1995) showing fractionation sequence.

Results of adsorbed and desorbed isotherm and fractionation data were converted from  $\text{mg P L}^{-1}$  to  $\text{mg P g}^{-1}$  soil using the known weights of the soil and weight and concentration of solution added at each step.

Adsorption isotherms are graphical representations of sorption with equilibrium P (P remaining in solution after equilibration,  $C_{eq}$ ) on the X-axis and adsorbed P ( $q$ ) on the Y-axis, which is determined using Equation 3-1, where  $V_l$  is equal to the volume of liquid added,  $C_{in}$  is initial concentration of P in solution,  $C_{eq}$  is equilibrium concentration, and  $m_s$  is the mass of the sorbate.

$$q = \frac{V_l(C_{in} - C_{eq})}{m_s} \quad \text{Eq. 3-1}$$

The data can be linearized through graphing  $K_d$ , a distribution coefficient (Equation 3-2), against  $c_{eq}$ , which again is the equilibration concentration of P.

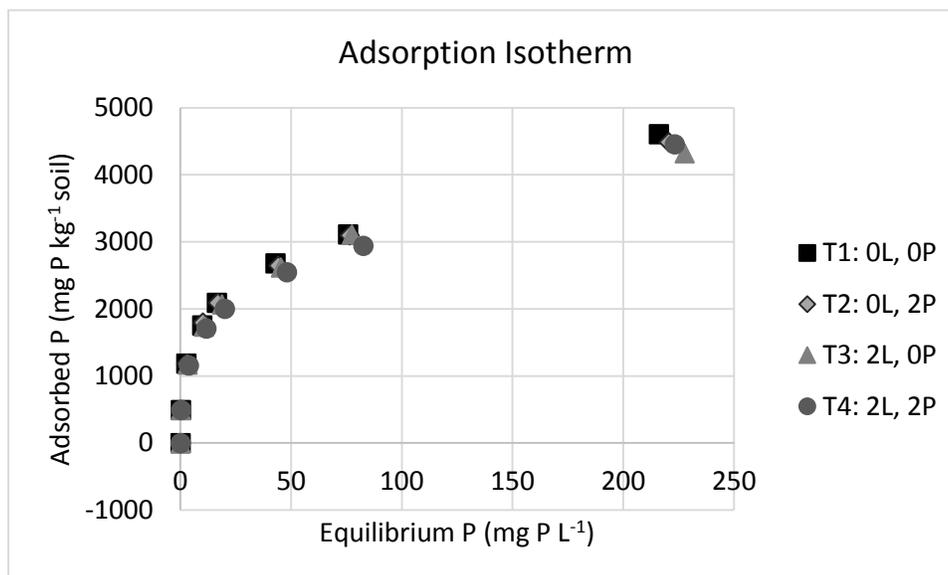
$$K_d = \frac{q}{c_{eq}} \quad \text{Eq. 3-2}$$

Statistical Analysis of Variance (ANOVA) was performed using R 3.0 software was used to analyze the slope of the linearized isotherms, the cumulative P desorption, and the differences within the distinct pools of P. Treatment effects were significant if  $\text{Pr} \leq F \leq 0.05$ . LSD mean separation tests were performed on results showing significant treatment effects.

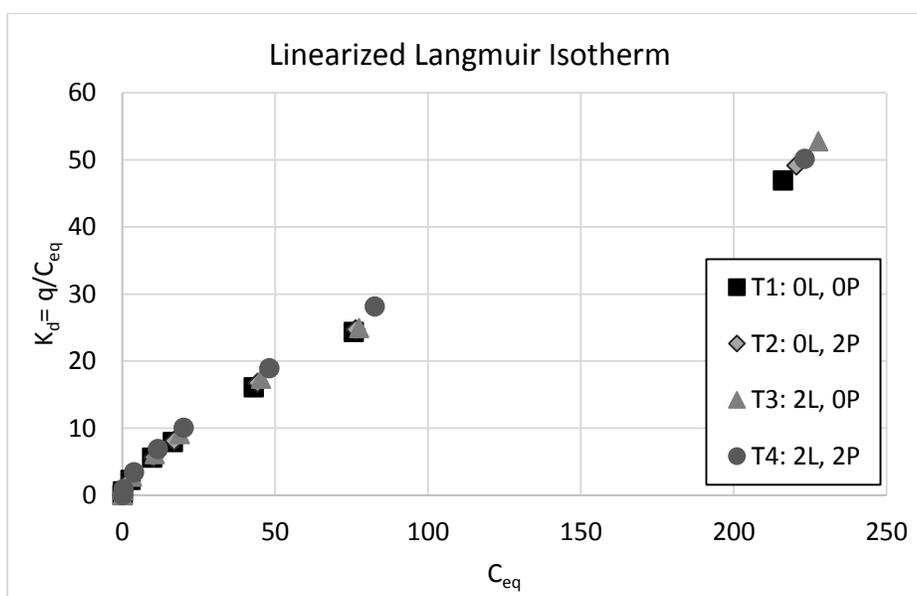
## **Results**

### ***Sorption Isotherms***

As applied solution P concentrations increased, soil P adsorption and soil equilibrium P also increased (Figure 3-2). Equilibration with solutions containing no P resulted in soil P release of 0.002-0.003 mg P g<sup>-1</sup> soil. The rate of equilibration slowed over time, signifying that maximum adsorption would eventually be reached. It cannot be confirmed if P sorption maxima was reached in this experiment because even at the very high rates used, there was no evidence that higher concentrations of added P would not cause additional sorption. The linearized isotherm model is shown in Figure 3-3. The previous lime and P fertilizer treatments applied to this soil in the greenhouse experiment had no significant effect on P sorption in this subsequent experiment.



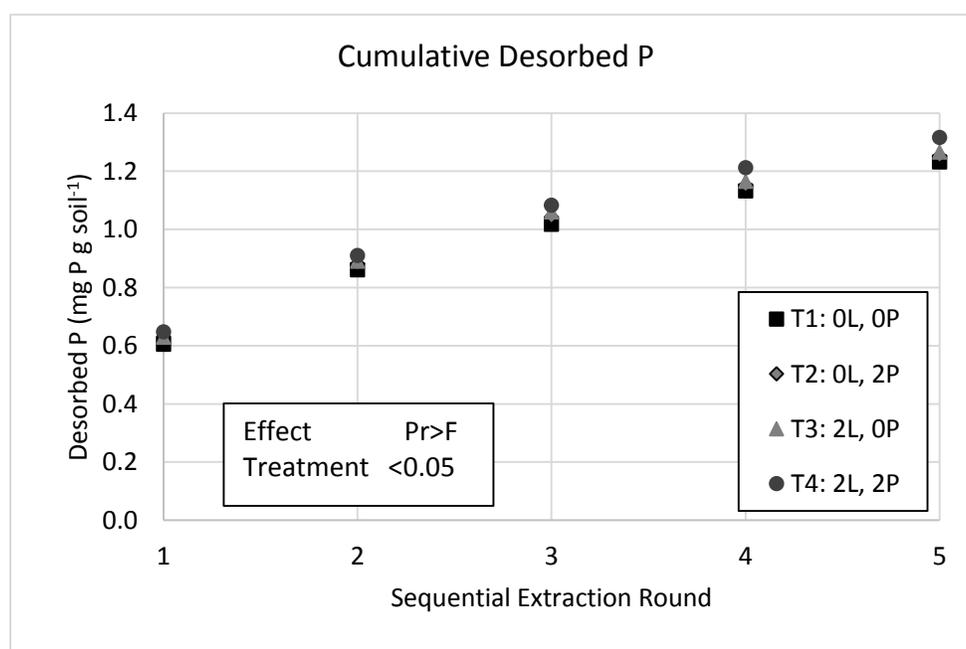
**Figure 3-2.** Average adsorbed P is shown on the Y-axis versus equilibrium P on the X-axis across four treatments after equilibration with eight solution P concentrations. Adsorbed P increased with increasing applied concentration, while the rate of P sorption is decreasing with increasing concentrations of P in solution.



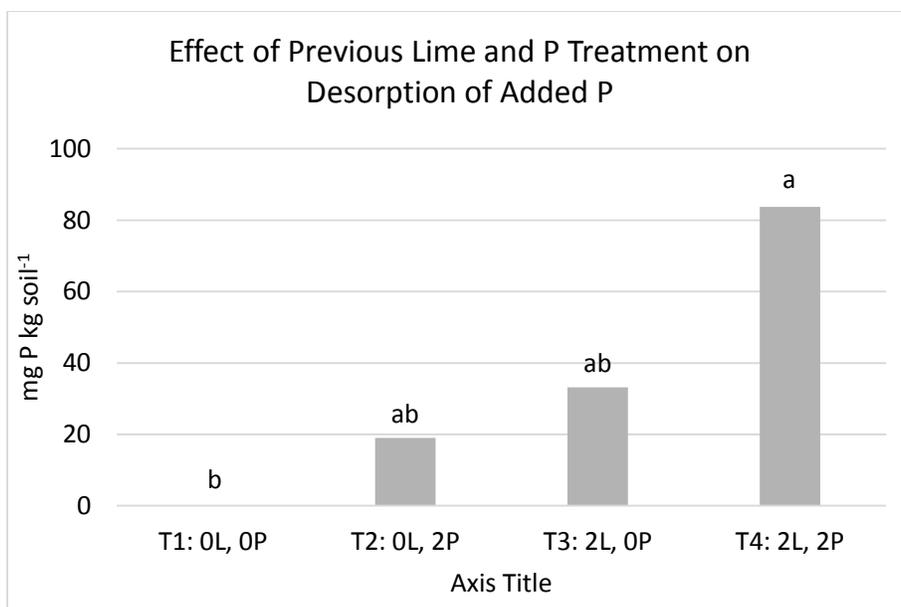
**Figure 3-3.** Linearized Langmuir isotherm with  $K_d$  ( $q/C_{eq}$ =equilibrium/adsorbed P) on the Y-axis and with  $q$  (equilibrium P) on the X-axis is shown for data obtained through sorption isotherms on four different soil treatments. There was no significant difference of treatment on P sorption.

### *Desorption Isotherms*

Prior treatment of this Andisol with lime and P fertilizer had a significant effect on P desorption at high rates of subsequently applied P ( $400 \text{ mg P L}^{-1}$ ) (Figures 3-4 and 3-5). LSD mean separation showed that cumulative P desorption was significantly larger in the treatment that received 2X lime and 2X P, however visual interpretation of the graph also shows that P desorption was increased by either amendment independently; 0X lime, 2X P desorbed some P while 2X lime, 0X P desorbed more than the fertilizer-only treatment. Because the limed, unfertilized treatment desorbed more P than the non-limed, fertilized treatment it appears that lime has an impact on P desorption in this soil.



**Figure 3-4. Cumulative P desorption of a soil previously treated with rates of lime (L) and/or P fertilizer (P) is shown over five sequential extractions. Analysis of Variance is shown in the inset.**

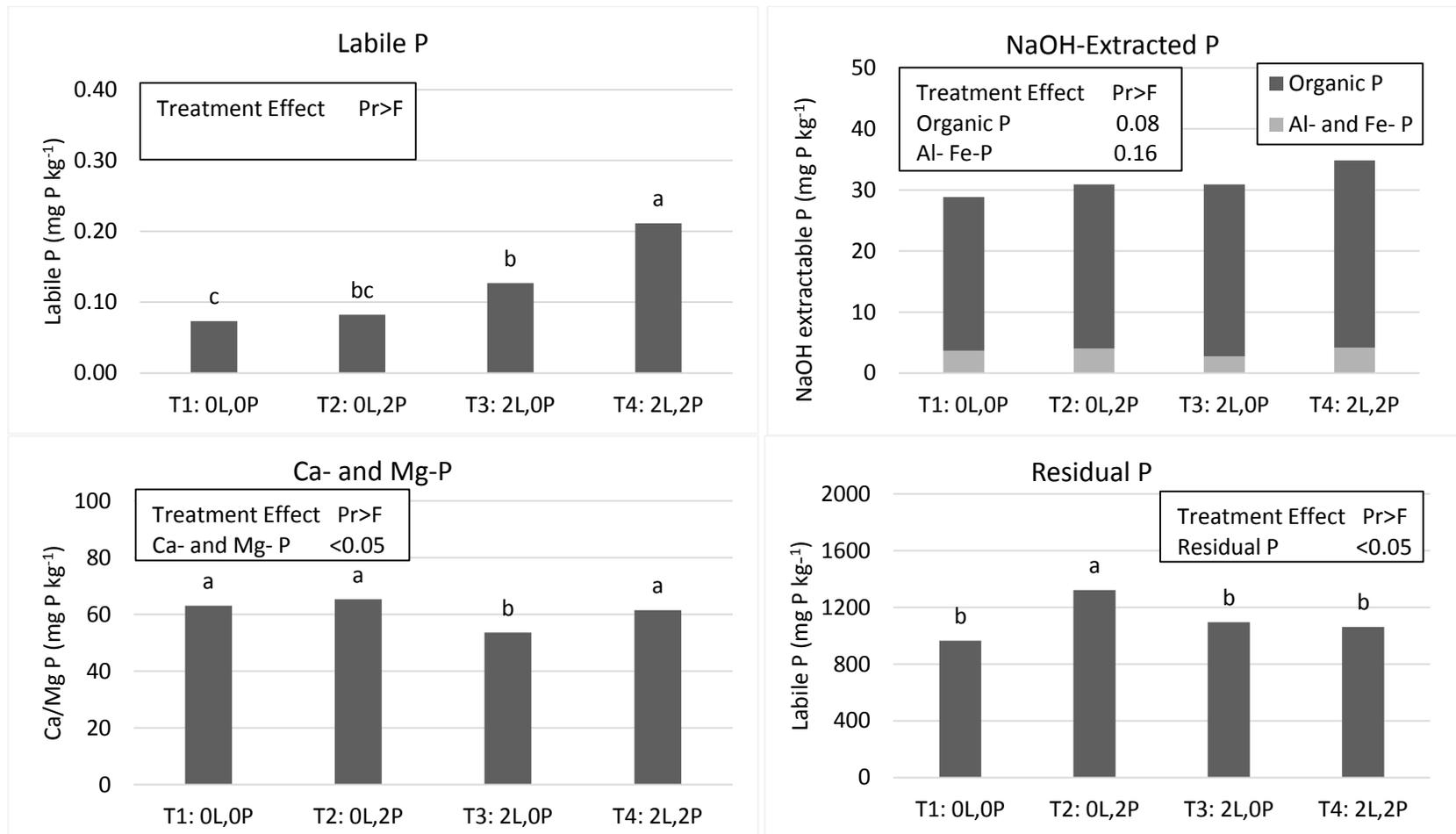


**Figure 3-5. Effect of previous soil treatment is shown as the difference in cumulative P desorbed from the control soil. LSD mean separation is shown by a letter above those fractions with a significant treatment effect.**

### *Phosphorus Fractionation*

Labile P was a very small fraction in this soil. Al- and Fe-P and organic bound P had second and third smallest fractions of P, and then Ca- and Mg-P, and finally residual bound P was the largest pool in this soil. There was no shift in the overall size of a fraction due to fertilizer or lime additions in the soil.

Labile P in this soil was increased by the lime and P fertilizer treatments with combined lime and P fertilizer giving the largest increase, however there was hardly any P in this fraction (Figure 3-5). There was no effect of treatment on Al- and Fe-P or organic P. We observed a significant effect of treatment on Ca- and Mg- bound P, which upon further analysis was shown through an LSD test to be a significantly smaller pool in the 2X lime, 0X P pool. Residual bound P, the “sink” for phosphorus, was found to be 89-91% of total P, which is slightly higher than the high end of reported values for acid soils (Haynes, 1984). Residual P was significantly affected by treatment, but again, LSD mean separation showed this to be an exception from the others in the 0X lime, 2X P treatment, and not a trend in the data.



**Figure 3-5.** Chemical fractionation of an Andisol previously treated with rates of lime (L) and/or P fertilizer (P) is shown in five user-defined fractions. Analysis of Variance is shown in the inset box, while LSD mean separation is shown by a letter above those fractions with a significant treatment effect. Letters are only comparable within each graph.

## Discussion

Sorption of P onto this Andisol was not influenced by prior treatment with lime and/or P fertilizer. The shape of the isotherm appears to have traits of an H-shape isotherm and some L-shape attributes at high P rates. L-shape isotherms show that a given sorbate has a low affinity for the soil surface, while H-shape isotherms have high affinity for sorption and indicate that a soil is forming inner sphere complexes forming, which we assumed due to the nature of the mineralogy and adsorption properties of the soil (Essington, 2004). At high rates of P application it is expected that most inner-sphere sites will be satisfied with P and the shape of the isotherm will mimic simple L-shape isotherms. Even in a controlled laboratory setting using rates of phosphorus application approaching the sorption maxima and far outside relevant agronomic rates, there is still no difference in P sorption on the soil due to the previously applied lime and P fertilizer treatments. This trend has been observed in soils with low solution Al and also in soils with amorphous mineralogy that do not have large Al-humic pH sensitive constituents (Guadalix and Pardo, 1994; Penn et al., 2005). These results are in agreement with the plant growth study in Chapter 3 in which lime had no effect on plant P concentration or uptake. Additionally, work at INIAP by Espinosa (1995), also showed that in Andisols fertilized with high rates of  $P_2O_5$  (150-300 kg ha<sup>-1</sup>) there was very little residual P effect from one crop to the next.

Although prior lime and P fertilizer treatment did not alter P sorption characteristics of this Andisol, these treatments significantly increased desorption of subsequently added P. Thus P sorbed by this treatment appears to be held less strongly if the soil was previously limed. This is interesting because it suggests that recent liming of this Andisol could impact plant availability of subsequently added P fertilizer. The mechanism for this lime effect on P desorption is not apparent but may be related to possible. Drying and re-wetting of limed treatments may cause precipitation of newly formed sorptive faces and more release of P compared to the non-limed treatments, or

caused by a mechanism of increased CEC due to dissolution of OM in the soil with pH increase (Haynes, 1982; Haynes and Mokolobate, 2001).

The results of the fractionation experiment are different from the isotherms described in this chapter because this experiment was carried out on soils from the greenhouse project that received no additional amendments of P, and focuses on how the treatments we applied to this soil changed the fate of P in the soil. The results give little indication of lime application altering P partitions in this Andisol. The clearest effect of lime was on the increase in the labile P fraction, which is consistent with desorption results. The lack or small presence of noticeable difference was observed in the greenhouse project as well.

We were anticipating that the treatments used in the soil would affect the Al- and Fe- P and Ca- and Mg-P pools, however there were not obvious trends indicating any change in P. This may mean that the increase in cumulative P desorbed in the previous experiment is due to a larger fraction of weakly held, labile P like the labile P fraction observed in our fractionation work, or it may have to do with the large amount of P that had been adsorbed to these treatments. Evaluating the Ca, Al, and Fe chemistry of the soil (Chapter 2) shows that lime does have a large effect on the amount of these elements in the soil, however the same effect is not seen in these pools of bound P. This suggests that more work should be done to analyze the fate of P in limed soils.

Unpublished ongoing research using radiotracers presented at the American Society of Agronomy -- Crop Science Society of America -- Soil Science Society of America (ASA-CSS-SSSA) International Annual Meeting this year (2013) in Tampa, FL, by Montalvo, et al., indicate that colloidal P (P in solutions filtered to  $< 0.45 \mu\text{m}$ ) is a very important source of P in Andisol plant nutrition, while Zubillaga (1998) showed that same moderately resistant inorganic P fraction (colloidal P) increased in fertilized Andisols. Future considerations of P fractionation tests in Andisols might be aimed at better quantifying Al- and Fe- and Ca- and Mg- phosphates in the moderately resistant organic fractions, how they change with lime and fertilizer treatments.

The results of these three tests show that there may be an increase in available soil P in a subsequent crop cycle after liming, however this information should be evaluated in a greenhouse or field trial, because as was observed in Chapter 2 or this thesis, the best way to measure the success of a soil treatment on crop response is to look directly at the crop response. A multi-cycle, split-plot trial to evaluate P available from one crop to the next with lime and P amendments may be a better option than continued laboratory trials in terms of knowing how these amendments affect crop growth.

### **Conclusions**

Neither liming nor prior applications of P fertilizer change the P sorption characteristics of this Andisol, although there were small changes in P desorption caused by these treatments. The P desorption experiment and the P fractionation results both indicate that prior liming and prior P application cause small increases in the most labile soil P fraction, however this increase in labile P is very small and does not seem to affect plant available P and P fertilizer use efficiency as was observed in the greenhouse study. The desorption experiments should be repeated on the points from the sorption study that had lower applied P in order to be more realistic to field conditions. Finally, field trials should be used to evaluate crop response to prior liming or fertilizing in this soil.

## References

- Devau, N. P. Hinisnger, E. Le Cadre, B. Colomb, F. Gérard. 2011. Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils. *Geochimica et Cosmochimica Acta* 75:2980-2996.
- Elliott, H. Personal communication. 2013.
- Espinosa, José. 2007. Fijación de fosforo en suelos derivados de ceniza volcánica. Quito: INPOFOS.
- Graetz, D. A., V.D. Nair. 2009. Phosphorus sorption isotherm determination. 33-37. *In* Kovar, J.L., G.M.
- Guadalix, M.E., and M.T. Pardo. 1994. Effects of liming on soil properties and P solubility in some Spanish Andosols. *Geoderma*. 63:53-6.
- Haynes, R.J. 1984. Lime and phosphate in the soil-plant system. *Advances in Agronomy* 37: 249-305
- Haynes, R.J., and M.S. Mokolobate. 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. *Nutrient Cycling in Agroecosystems*. 59:47–63.
- Iñiguez, J., and R. M. Val. 1984. Evaluation of phosphorus sorption by an allophanic soil. *Geoderma*, 33:119-134.
- Pierzynski (2<sup>nd</sup> ed.) Methods for phosphorus analysis for soils, sediments, residuals and waters. Virginia Tech University. Blacksburg, VA.
- Lachat Instruments. 2003. Determination of phosphorus in soil extracts by flow injection analysis colorimetry. QuikChem® Method 12-115-01-1-I. Lachat Instruments. Loveland, CO.
- Lachat Instruments. 2007. Determination of orthophosphate in waters by flow injection analysis colorimetry. QuickChem Method 10-115-01-1-T. Lachat Instruments. Loveland, CO.

- Lachat Instruments. 2010. Determination of orthophosphate in 0.1M HCl extracts by flow injection analysis colorimetry (Ultrahigh throughput). QuikChem® Method 12-115-01-1-O. Lachat Instruments. Loveland, CO.
- Montalvo, D., F. Degryse, M.J. McLaughlin. 2013. Potential availability of colloidal phosphorus from the soil solutions of Andisols and Oxisols. Oral presentation, ASA-CSSA-SSSA Annual Meetings, November 3-6. Tampa, Florida.
- Nair, V.D., D.A., Graetz, and K.M. Portier. 1995. Forms of phosphorus in soil profiles from dairies of South Florida. *Soil Sci. Soc. Am. J.* 59:1244-1249.
- Penn, C.J., G. L. Mullins, and L. W. Zelazny. 2005. Mineralogy in relation to phosphorus sorption and dissolved phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 69:1532–1540.
- R Core Team. 2013. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <http://www.R-project.org/>.
- Zubillaga, M.S., L. Giuffré de López Camelo. 1998. Pathways of native and fertilizer phosphorus in Argentine Soils. *Nutrient Cycling in Agroecosystems* 51:101-105.

## Chapter 4

### Summary and Future Needs

The objectives of this research were to evaluate the interactive effect of lime and P fertilizer on plant P availability and changes in soil P sorption. These results suggest that lime should not be applied to this moderately acidic Andisol in order to increase P uptake or concentration, however there are benefits of this amendment and more research should be conducted on the additional interactions, benefits, and outcomes that may result from the use of higher rates of lime. We found that lime amendments did not have a significant effect on P uptake of barley grown in these treatments, however they caused a small biomass increase. Lime ameliorated soil acidity, increased soil pH, reduced Al, Fe, and Mn, and increase Ca in the soil, and also reduced Fe and Mn and increased Ca uptake by plants. Overall, the benefits of liming this soil are welcomed, however in order to recommend this as a management strategy to farmers it would need to be shown that there was a positive correlation between liming and income.

Phosphorus applications increased plant biomass production and P uptake by the soil, however it did not increase plant P concentration or alleviate P deficiency in the barley plants, which indicates the rates applied were still low for this soil. Soil P tests used in this experiment were shown to not exhibit the changes observed in plant response. Plants were more sensitive to P changes in the soil solution than the Mehlich-3 or the Olsen extract. A more sensitive extract for soil P in Andisols should be developed, or alternatively, current tests should be calibrated for these soils. Considering that this soil has a higher test P than other soils in the region, there is still need for continued development of a means to achieve efficient P fertilizer use in this region.

Although liming is not recommended to improve P uptake and biomass production for this soil, there is wide variety of Andisols across Ecuador and so more research should be carried out

to identify characteristics of those Andisols which would benefit from applications of lime so that farmers can easily identify optimum management practices of their soils.

Supplemental laboratory work on the sorption mechanism of this soil supported the conclusion that liming this soil does not affect P sorption, and it was observed that changes in P desorption of a subsequent treatment occurred at extremely high levels of P application. P fractionation work concluded that there were treatment differences in accumulation of labile P due to treatment, however these differences were very small and not observed in the greenhouse study.

A major recommendation for additional research is to do more field and greenhouse trials of plant growth utilizing more acidic, lower P Andisols from Ecuador, given that in very low pH systems, liming may cause a stronger effect and be more useful to farmers of these lands. Additionally, use of a wider range of lime and P amendments may identify the lowest rates at which an additional benefit to crop production can be achieved. Finally, to further develop our knowledge of available P in the soil after liming, an experiment should be carried out over a multi crop cycle, in which way in a subsequent cultivation cycle any changes occurring in the soil due to the first year's amendments could be observed both in respect to additional amendments.

Although further investigation of the sorption mechanism may not fully explain the impact of that mechanism on plant growth, evaluating the fate of subsequent P after liming or after several cycles of fertility treatments may shed light on the chemistry causing sorption in the soil.

**Appendix A**  
**Supplemental Data for Chapter 2**

**Table A-1. Soil data averaged across three replicates produced in greenhouse experiment at Sampling Time\* 1 (21 days after liming).**

Treatment	Sampling time *	Olsen Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	meq 100 g <sup>-1</sup>			ppm			
T1: 0L, 0P	1	16.77	0.57	10.56	1.78	10.49	12.95	541.51	19.54
T2: 0L, 1P	1	11.13	0.47	8.92	1.38	7.62	11.07	437.51	14.97
T3: 0L, 2P	1	12.20	0.47	9.00	1.36	7.22	11.12	446.03	15.24
T4: 1L, 0P	1	15.47	0.53	13.07	1.45	7.93	11.70	471.58	15.42
T5: 1L, 1P	1	15.36	0.42	12.98	1.12	6.52	10.49	341.58	12.98
T6: 1L, 2P	1	11.63	0.48	14.05	1.33	6.50	10.49	359.06	11.66
T7: 2L, 0P	1	15.39	0.48	17.70	1.28	5.96	10.04	338.00	9.73
T8: 2L, 1P	1	13.15	0.56	20.73	1.55	9.32	11.25	375.20	12.06
T9: 2L, 2P	1	13.87	0.53	19.31	1.24	8.02	10.36	364.44	10.89

Treatment	Sampling time *	Mehlich-3 Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	-----meq 100 g <sup>-1</sup> --			-----ppm-----			
T1: 0L, 0P	1	15.54	0.52	1.99	1.15	7.44	4.71	250.13	30.89
T2: 0L, 1P	1	7.20	0.71	1.73	1.04	6.81	4.66	243.41	27.17
T3: 0L, 2P	1	10.07	0.46	1.92	1.16	6.86	4.44	245.20	29.99
T4: 1L, 0P	1	14.91	0.49	4.90	1.24	6.77	4.57	248.34	31.92
T5: 1L, 1P	1	9.22	0.46	4.77	1.24	6.32	4.57	227.95	28.51
T6: 1L, 2P	1	7.02	0.46	5.19	1.20	6.50	4.57	235.34	29.45
T7: 2L, 0P	1	15.54	0.47	5.80	1.24	6.28	4.57	225.48	27.79
T8: 2L, 1P	1	9.44	0.47	8.45	1.27	6.46	4.89	221.00	27.61
T9: 2L, 2P	1	13.66	0.43	8.66	1.19	5.74	4.71	223.69	28.20

Treatment	Sampling time *	pH	Al <sup>3+</sup> + H <sup>+</sup>	H <sup>+</sup>	Al <sub>exchangeable</sub>
		meq 100 g <sup>-1</sup>			
		T1: 0L, 0P	1	5.44	0.97
T2: 0L, 1P	1	5.43	0.96	0.41	0.56
T3: 0L, 2P	1	5.45	1.00	0.40	0.60
T4: 1L, 0P	1	5.79	0.63	0.26	0.37
T5: 1L, 1P	1	5.85	0.62	0.39	0.23
T6: 1L, 2P	1	5.90	0.69	0.35	0.34
T7: 2L, 0P	1	6.28	0.45	0.29	0.17
T8: 2L, 1P	1	6.27	0.45	0.29	0.17
T9: 2L, 2P	1	6.32	0.45	0.27	0.17

**Table A-2. Soil data averaged across three replicates produced in greenhouse experiment at Sampling Time\* 2 (32 days after liming).**

Treatment	Sampling time *	Olsen Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	meq 100 g <sup>-1</sup>			ppm			
T1: 0L, 0P	2	14.89	0.51	10.65	1.50	10.49	11.30	609.20	14.84
T2: 0L, 1P	2	13.08	0.53	9.84	1.37	10.27	10.94	592.16	14.30
T3: 0L, 2P	2	13.30	0.52	9.38	1.32	10.53	10.94	610.10	14.88
T4: 1L, 0P	2	15.03	0.52	13.13	1.32	9.91	11.07	580.96	12.82
T5: 1L, 1P	2	11.78	0.52	15.73	1.32	9.62	9.88	474.72	11.36
T6: 1L, 2P	2	14.45	0.50	15.03	1.17	9.32	10.18	497.58	11.12
T7: 2L, 0P	2	13.16	0.54	21.80	1.25	9.55	9.95	438.41	9.10
T8: 2L, 1P	2	15.76	0.50	20.94	1.46	8.56	9.32	443.34	9.68
T9: 2L, 2P	2	15.24	0.49	19.83	1.29	8.27	9.48	444.46	9.62

Treatment	Sampling time *	Mehlich-3 Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	meq 100 g <sup>-1</sup>			ppm			
T1: 0L, 0P	2	11.59	0.49	2.34	1.35	7.04	4.66	255.51	32.14
T2: 0L, 1P	2	11.59	0.68	2.50	1.42	7.22	4.66	257.76	32.23
T3: 0L, 2P	2	10.88	0.53	3.06	1.31	6.81	4.57	253.27	30.39
T4: 1L, 0P	2	13.75	0.52	4.95	1.40	7.08	4.62	257.76	34.02
T5: 1L, 1P	2	7.74	0.54	7.06	1.45	7.19	4.98	243.41	28.17
T6: 1L, 2P	2	9.08	0.52	6.11	1.47	6.99	4.66	244.31	30.62
T7: 2L, 0P	2	8.82	0.47	9.11	1.41	6.32	4.53	229.51	27.70
T8: 2L, 1P	2	11.33	0.49	9.44	1.40	6.72	4.30	241.62	30.62
T9: 2L, 2P	2	12.31	0.77	8.45	1.36	6.19	4.51	238.03	29.18

Treatment	Sampling time *	pH	Al <sup>3+</sup> + H <sup>+</sup>	H <sup>+</sup>	Al <sub>exchangeable</sub>
		meq 100 g <sup>-1</sup>			
T1: 0L, 0P	2	5.31	1.09	0.46	0.64
T2: 0L, 1P	2	5.31	1.06	0.46	0.60
T3: 0L, 2P	2	5.33	0.99	0.46	0.52
T4: 1L, 0P	2	5.62	0.61	0.34	0.27
T5: 1L, 1P	2	5.92	0.60	0.32	0.28
T6: 1L, 2P	2	5.69	0.65	0.35	0.30
T7: 2L, 0P	2	6.07	0.57	0.28	0.29
T8: 2L, 1P	2	6.27	0.57	0.30	0.28
T9: 2L, 2P	2	6.18	0.62	0.30	0.32

**Table A-3. Soil data averaged across three replicates produced in greenhouse experiment at Sampling Time\* 3 (46 days after liming and 14 days after planting barley).**

Treatment	Sampling time *	Olsen Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	meq 100 g <sup>-1</sup>			ppm			
T1: 0L, 0P	3	15.03	0.44	9.07	1.36	14.12	9.41	514.39	23.06
T2: 0L, 1P	3	18.64	0.43	9.41	1.41	12.42	9.73	529.85	24.65
T3: 0L, 2P	3	26.74	0.48	9.89	1.57	12.17	10.76	543.98	22.53
T4: 1L, 0P	3	17.42	0.44	13.62	1.45	11.16	9.37	436.61	18.15
T5: 1L, 1P	3	13.88	0.41	13.69	1.34	9.77	9.19	409.27	19.63
T6: 1L, 2P	3	19.08	0.40	14.45	1.37	9.46	9.06	399.41	18.02
T7: 2L, 0P	3	12.72	0.42	19.99	1.36	10.00	9.59	368.48	14.12
T8: 2L, 1P	3	13.73	0.39	17.60	1.39	8.70	9.06	372.06	13.63
T9: 2L, 2P	3	17.27	0.39	18.95	1.38	10.58	9.10	362.20	15.06

Treatment	Sampling time *	Mehlich-3 Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	meq 100 g <sup>-1</sup>			ppm			
T1: 0L, 0P	3	15.67	0.44	1.65	1.16	9.68	4.30	256.86	49.49
T2: 0L, 1P	3	10.97	0.43	1.72	1.13	8.61	3.90	245.20	47.38
T3: 0L, 2P	3	18.63	0.53	2.01	1.24	8.47	3.97	239.38	39.94
T4: 1L, 0P	3	9.53	0.46	4.61	1.20	8.47	4.26	225.93	35.46
T5: 1L, 1P	3	9.71	0.43	4.27	1.06	7.26	4.30	207.55	33.80
T6: 1L, 2P	3	12.40	0.44	4.48	1.10	7.80	4.35	210.69	32.99
T7: 2L, 0P	3	7.56	0.44	10.35	1.21	9.23	4.84	201.27	29.77
T8: 2L, 1P	3	8.28	0.43	7.70	1.21	8.11	4.17	226.38	27.52
T9: 2L, 2P	3	8.90	0.40	7.22	1.16	8.79	4.39	211.14	30.89

Treatment	Sampling time *	pH	Al <sup>+3</sup> + H <sup>+</sup>	H <sup>+</sup>	Al <sub>exchangeable</sub>
		meq 100 g <sup>-1</sup>			
T1: 0L, 0P	3	5.27	1.21	0.48	0.73
T2: 0L, 1P	3	5.35	1.10	0.47	0.64
T3: 0L, 2P	3	5.35	1.10	0.43	0.67
T4: 1L, 0P	3	5.75	0.70	0.33	0.37
T5: 1L, 1P	3	5.68	0.89	0.35	0.54
T6: 1L, 2P	3	5.65	0.83	0.25	0.58
T7: 2L, 0P	3	6.18	0.69	0.49	0.21
T8: 2L, 1P	3	6.08	0.54	0.44	0.09
T9: 2L, 2P	3	6.01	0.69	0.48	0.21

**Table A-4. Soil data averaged across three replicates produced in greenhouse experiment at Sampling Time\* 4 (85 days after liming and 53 days after planting barley).**

Treatment	Sampling time *	Olsen Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	meq 100 g <sup>-1</sup>				ppm		
T1: 0L, 0P	4	12.50	0.34	9.18	1.42	8.97	8.83	463.06	16.00
T2: 0L, 1P	4	14.46	0.14	9.28	1.45	8.56	9.28	466.65	14.93
T3: 0L, 2P	4	17.56	0.06	9.70	1.51	8.74	9.64	495.79	14.88
T4: 1L, 0P	4	11.27	0.33	15.53	1.53	8.20	8.83	418.68	14.84
T5: 1L, 1P	4	10.48	0.05	14.76	1.41	7.40	8.43	378.79	10.85
T6: 1L, 2P	4	12.57	0.04	14.81	1.43	7.80	8.83	392.68	12.42
T7: 2L, 0P	4	8.30	0.27	20.58	1.40	7.06	7.93	311.32	8.74
T8: 2L, 1P	4	13.22	0.05	20.40	1.32	6.90	7.89	326.34	7.17
T9: 2L, 2P	4	10.19	0.04	20.42	1.27	5.87	7.40	293.62	6.68

Treatment	Sampling time *	Mehlich-3 Extract							
		P	K	Ca	Mg	Zn	Cu	Fe	Mn
		ppm	meq 100 g <sup>-1</sup>				ppm		
T1: 0L, 0P	4	8.64	0.39	2.11	1.41	7.04	4.12	233.10	21.83
T2: 0L, 1P	4	8.10	0.69	2.02	1.26	6.72	4.17	227.72	20.13
T3: 0L, 2P	4	9.80	0.14	2.13	1.33	6.68	4.26	230.86	21.47
T4: 1L, 0P	4	7.65	0.37	6.01	1.41	6.54	4.30	222.79	22.46
T5: 1L, 1P	4	7.38	0.14	5.36	1.34	5.87	4.17	217.86	18.47
T6: 1L, 2P	4	9.44	0.20	6.19	1.41	7.04	4.39	225.93	19.77
T7: 2L, 0P	4	6.13	0.36	8.90	1.38	5.65	4.10	223.24	17.95
T8: 2L, 1P	4	8.28	0.18	10.78	1.26	5.83	4.39	208.89	15.55
T9: 2L, 2P	4	6.75	0.13	8.75	1.29	5.24	4.21	206.65	14.88

Treatment	Sampling time *	pH	Al <sup>3+</sup> + H <sup>+</sup>	H <sup>+</sup>	Al <sub>exchangeable</sub>
		meq 100 g <sup>-1</sup>			
		T1: 0L, 0P	4	5.02	0.96
T2: 0L, 1P	4	5.33	0.93	0.43	0.49
T3: 0L, 2P	4	5.50	0.88	0.35	0.53
T4: 1L, 0P	4	5.58	0.60	0.28	0.32
T5: 1L, 1P	4	5.95	0.66	0.35	0.30
T6: 1L, 2P	4	5.96	0.61	0.40	0.21
T7: 2L, 0P	4	5.99	0.49	0.28	0.22
T8: 2L, 1P	4	6.34	0.47	0.30	0.17
T9: 2L, 2P	4	6.34	0.43	0.34	0.09

**Table A-5. Plant data averaged across three replicates produced in greenhouse experiment after 53 days of plant growth.**

Treatment	Dry matter (g)	n° Plants	Plant height cm	P	K	Ca	Mg	Zn	Cu	Fe	Mn
					%				mg kg <sup>-1</sup>		
T1: 0L, 0P	2.80	12.00	49.33	0.15	5.35	0.54	0.28	158.20	12.00	784.80	128.90
T2: 0L, 1P	10.17	21.33	70.00	0.16	4.96	0.51	0.28	90.80	10.97	642.93	74.27
T3: 0L, 2P	13.53	31.33	71.33	0.17	4.39	0.47	0.27	69.37	11.17	728.97	62.97
T4: 1L, 0P	3.53	12.00	55.00	0.14	5.46	0.68	0.24	163.33	12.70	708.23	72.57
T5: 1L, 1P	12.53	28.33	72.00	0.15	4.25	0.66	0.25	76.93	10.90	698.53	40.60
T6: 1L, 2P	13.93	36.67	74.00	0.14	4.04	0.67	0.26	50.40	10.37	702.87	33.00
T7: 2L, 0P	4.60	13.00	59.50	0.15	6.70	0.75	0.19	142.85	12.75	249.60	31.10
T8: 2L, 1P	11.27	25.33	75.67	0.16	5.16	0.79	0.25	73.70	11.73	291.43	28.70
T9: 2L, 2P	15.40	33.00	74.33	0.15	3.89	0.71	0.23	51.33	10.90	303.83	22.17

**Appendix B****Supplementary Data for Chapter 3**

**Table B-1. Construction and soil response data produced in adsorption isotherms.**

Treatment	Weight		P Concentration in Solution		
	Soil	Solution	Initial	Equilibrium	Adsorbed
		g		mg P L <sup>-1</sup>	mg P kg <sup>-1</sup> soil
T1: 0L, 0P	1.00	25.00	0	0.10	-2.38
T1: 0L, 0P	1.00	25.01	20	0.27	493.07
T1: 0L, 0P	1.00	25.02	50	2.72	1182.23
T1: 0L, 0P	1.00	25.02	80	9.85	1753.62
T1: 0L, 0P	1.00	25.03	100	16.55	2087.73
T1: 0L, 0P	1.00	25.07	150	43.03	2677.74
T1: 0L, 0P	1.00	25.03	200	75.70	3109.54
T1: 0L, 0P	1.00	25.10	400	216.13	4606.00
T2: 0L, 2P	1.00	25.01	0	0.09	-2.28
T2: 0L, 2P	1.00	25.02	20	0.30	492.51
T2: 0L, 2P	1.00	25.03	50	2.76	1181.87
T2: 0L, 2P	1.00	25.78	80	10.19	1798.16
T2: 0L, 2P	1.00	25.20	100	16.97	2090.83
T2: 0L, 2P	1.00	25.03	150	44.30	2644.21
T2: 0L, 2P	1.00	25.07	200	76.41	3094.08
T2: 0L, 2P	1.00	25.00	400	220.49	4486.32
T3: 2L, 0P	1.00	25.08	0	0.10	-2.45
T3: 2L, 0P	1.00	25.02	20	0.35	491.51
T3: 2L, 0P	1.00	25.02	50	3.24	1169.55
T3: 2L, 0P	1.00	25.03	80	10.64	1734.39
T3: 2L, 0P	1.00	25.47	100	18.87	2065.79
T3: 2L, 0P	1.00	25.00	150	45.41	2614.68
T3: 2L, 0P	1.00	25.43	200	77.51	3111.81
T3: 2L, 0P	1.00	25.07	400	227.74	4318.07
T4: 2L, 2P	1.00	25.05	0	0.11	-2.70
T4: 2L, 2P	1.00	25.02	20	0.43	489.39
T4: 2L, 2P	1.00	25.03	50	3.93	1152.98
T4: 2L, 2P	1.00	25.00	80	11.74	1705.61
T4: 2L, 2P	1.00	25.03	100	20.11	1998.45
T4: 2L, 2P	1.00	25.00	150	48.13	2545.82
T4: 2L, 2P	1.00	25.03	200	82.60	2938.01
T4: 2L, 2P	1.00	25.20	400	223.27	4450.95

**Table B-2. Phosphorus released from the soil plug equilibrated with 400 mg P L<sup>-1</sup> is shown per round and also as a cumulative number.**

Treatment	Round	Desorbed P	
		Per Round	Cumulative
		mg P g <sup>-1</sup>	mg P kg <sup>-1</sup>
T1: 0L, 0P	1	0.61	
T1: 0L, 0P	2	0.26	
T1: 0L, 0P	3	0.16	
T1: 0L, 0P	4	0.12	
T1: 0L, 0P	5	0.10	1232.71
T2: 0L, 2P	1	0.63	
T2: 0L, 2P	2	0.25	
T2: 0L, 2P	3	0.16	
T2: 0L, 2P	4	0.11	
T2: 0L, 2P	5	0.10	1251.75
T3: 2L, 0P	1	0.63	
T3: 2L, 0P	2	0.26	
T3: 2L, 0P	3	0.17	
T3: 2L, 0P	4	0.10	
T3: 2L, 0P	5	0.10	1265.91
T4: 2L, 2P	1	0.65	
T4: 2L, 2P	2	0.26	
T4: 2L, 2P	3	0.17	
T4: 2L, 2P	4	0.13	
T4: 2L, 2P	5	0.10	1316.47

**Table B-3. Fractionation results showing P in solution after sequential chemical extraction of four treated soils from a greenhouse project.**

Treatment	Labile P	Al- and Fe- P	Organic P	Ca- and Mg- P	Residual P
	mg P kg <sup>-1</sup>				
T1: 0L, 0P	0.00	5.47	26.83	66.20	1047.56
T1: 0L, 0P	0.07	2.89	25.22	66.10	756.04
T1: 0L, 0P	0.07	3.33	25.18	64.10	905.76
T1: 0L, 0P	0.08	4.20	23.40	55.70	1148.56
T2: 0L, 2P	0.08	4.25	25.94	64.90	1431.40
T2: 0L, 2P	0.07	4.25	29.75	63.30	1037.69
T2: 0L, 2P	0.07	4.21	26.62	64.10	1522.47
T2: 0L, 2P	0.11	3.42	25.10	68.90	1298.65
T3: 2L, 0P	0.10	2.53	26.25	49.30	1124.70
T3: 2L, 0P	0.08	2.68	28.81	52.00	1068.87
T3: 2L, 0P	0.15	2.47	26.31	57.00	1103.73
T3: 2L, 0P	0.18	3.27	31.31	56.10	1082.65
T4: 2L, 2P	0.25	4.71	35.84	51.80	1104.46
T4: 2L, 2P	0.18	4.85	23.86	62.30	1055.89
T4: 2L, 2P	0.17	4.29	28.61	69.10	1041.43
T4: 2L, 2P	0.25	2.87	34.36	62.70	1049.27