

CHEMISTRY, TESTING AND MANAGEMENT OF PHOSPHORUS AND ZINC IN
CALCAREOUS LOUISIANA SOILS

A Dissertation

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ABSTRACT

Calcareous soils make up some of the most productive agriculture lands in Louisiana. Due to their minimal occurrence little research has been done on these soils. Understanding phosphorus (P) chemistry is necessary for environmentally sound management of these soils. In this study, P speciation was investigated using several chemical fractionation procedures as well as x-ray absorption near-edge spectroscopy (XANES) coupled with principal component analysis (PCA) and least-squares linear combination fitting (LCF) on five calcareous Louisiana soils of different geological origins. Phosphorus sorption isotherm parameters were determined and their relationships with other properties were evaluated. In addition, Zinc (Zn) lability due to the interaction with P and other fertilizer nutrients was characterized and a fertilizer P and Zn response trial for corn on a calcareous Norwood silt loam soil was conducted. The results showed that these calcareous soils were dominated by Ca-P phases. All chemically defined sequential P fractions except HCl-P were significantly correlated with different Fe fractions especially amorphous Fe, indicating that Fe-oxides play an important role in P retention. A significant correlation was found between P speciation by XANES analysis and sequential P fractionation for total Ca-phosphates as well as total Fe-/Al-phosphates ($R^2 \geq 0.81$, $P \leq 0.0383$). Further, an inclusion of the NaHCO_3 extraction in chemical fractionation procedures caused a redistribution of Fe-/Al-P while Ca-P was unchanged. The evaluation on P and Zn interaction showed that the presence of PO_4^{3-} decreased where as NH_4^+ increased Zn lability, suggesting that Zn and P fertilizer placement should be separated while the simultaneous application of Zn and ammonium-N amendments could improve plant Zn availability. The field experiment exhibited a P fertilizer response

when Bray II soil test P was $< 220 \text{ mg kg}^{-1}$ while a Zn fertilizer response was dependent on P levels even when soil test Zn was very low by DTPA. It is concluded that P forms not only control P retention mechanisms for agronomic and environmental availability but also affect management of other nutrients in soils.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The majority of Louisiana soils are acidic in nature while only a handful is considered to be calcareous. Nonetheless, calcareous soils are some of the most productive agricultural soils across the state (Amacher et al., 1989). Due to the minimal occurrence of calcareous soils in Louisiana, little research in the past has focused on these soils. This lack of attention has caused the neglect of the unique chemical nature of these soils particularly when making nutrient management decisions. For example, calcareous Red River alluvial soils are commonly deficient in zinc (Zn). Nonetheless, fertilizer recommendations for Zn are non-existent in Louisiana, according to the information sheet provided by the LSU Soil Testing and Plant Analysis Laboratory (STPAL). In these same soils, phosphorus (P) management has also been problematic. For instance, these soils often fall into the “very high” soil test P classification and under the current recommendation criteria, they would not require P fertilizer application. However, corn yield responses to P fertilization in these soils have been reported (Harrell et al., 2004). The over estimation of plant available P in calcareous Louisiana soils such as these may not be uncommon. The current soil test P calibration was thought to work well for the bulk of Louisiana soils which are acidic in nature, but much of the calibration work was carried out more than 30 years ago (Byrnside and Sturgis, 1958). While the production of new crop varieties require additional calibration, a closer evaluation of soil testing P and Zn in calcareous is also important and necessary. The current soil test P extraction is Bray II (strong Bray) extractant which has a very low pH (near 1) and could

cause the release of P sorbed on CaCO₃ surfaces as well as P dissolved from stable calcium P minerals commonly found in calcareous soils (Fixen and Grove, 1990; Mallarino, 1997). It has been reported that strong acidity of the Bray II test when used in calcareous soils may cause the overestimation of available P and therefore underestimate P fertilizer recommendations (Harrell et al., 2004). On the other hand a less acid multielement soil test, Mehlich III, has been shown to extract adequate plant available P from both acid and calcareous soils (Mehlich, 1984). Regardless of what method is used, the current voids in the P and Zn soil testing calibration data for calcareous soils need to be addressed in order to help Louisiana producers to adequately manage P fertilizer amendments.

Proper management of P and Zn in calcareous Louisiana soils requires not only the knowledge of how the nutrients are applied for improving production agriculture but also the understanding of important environmental issues that nutriment amendments encompass. For example, the poultry industry in Louisiana is concentrated in the northern portion of the state. Poultry litter removed from broiler houses are often applied to agricultural fields as a fertilizer source. However, repeated applications of the poultry litter have caused the build up of P in soils such as the calcareous Quachita River alluvial soils and increase the potential for P losses due to surface runoff (Gaston et al., 2003). The P losses due to runoff have been shown as the major cause of the eutrophication of surface waters (Sharpley et al., 1996). Concentrations of Zn and other heavy metals in biosolids applied to agricultural lands are also a major environmental concern (Moore et al, 1988). Even though Zn is a plant essential micronutrient, its occurrence in high concentrations can be toxic.

Making environmentally sound P management decisions while maintaining production agriculture interests requires gathering chemical and physical information on an individual soil basis. The information on chemical forms and sorption of P is of particular interest since it reveals not only the availability of P but also the likely retention mechanisms when additional P is applied to soils. Partitioning of P into various forms such as Fe, Al, or Ca related P groups has been commonly done by using a sequence of chemical extractants that selectively solubilize each P fraction. Such sequential P fractionation procedures have been used for nearly 100 years since they were first carried out (Fraps, 1906). With the recent emergence of new technology such as x-ray adsorption near-edge spectroscopy (XANES) analysis, phosphate speciation in soils can be achieved without chemically altering the soil sample environment (Beauchemin et al., 2003). In addition to the information on P speciation, the development of working knowledge of the P fractionation methodologies is also important for accurate interpretation of P chemistry/fertility and for making nutrient management decisions.

Impact of other amendments on soil Zn may be quite different from the impact of other amendments on soil P due to the micronutrient status of Zn. Little has been documented as to how soil Zn interacts with other fertilizer nutrients when they are applied simultaneously. Even though P and Zn interaction has been studied in many soils contradictory evidence still exists in current literature (Melton et al., 1973; Shuman, 1988; McGowen et al., 2001). Therefore it is important and necessary to further explore these interactions in laboratory and field experiments especially since the deficiency of both elements have been reported in the same soil.

1.2 Objectives

This dissertation contains research focused on P and Zn in calcareous Louisiana soils from a molecular to a field scale level. The general objectives of this study are to (i) chemically speciate inorganic P in important Louisiana calcareous soils and evaluate existing relationships among the inorganic P forms, P sorption characteristics and other soil matrix components; (ii) speciate P compounds in calcareous Louisiana soils using x-ray absorption near-edge spectroscopy (XANES) and least-squares linear combination fitting; (iii) evaluate the redistribution and recovery of P in four- and six-step inorganic P fractionation procedures; (iv) examine the effect of various fertilizer cations and anions on Zn lability in calcareous and acid soils; (v) evaluate the effect of P and Zn fertilization on corn yields and nutrient uptake on a Red River alluvial Norwood silt loam soil; and (vi) establish P and Zn fertilizer recommendations for corn grown in Red River alluvial soils using common soil test P and Zn extractions.

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CHAPTER 2

FRACTIONATION AND SORPTION OF INORGANIC PHOSPHORUS IN LOUISIANA CALCAREOUS SOILS

2.1 Introduction

Proper management of phosphorus (P) fertilizer inputs is critical for maximizing agricultural crop production while minimizing potential P losses to the environment. Soil P management decisions may differ according to the alkali or acidic nature of individual soils. Ideally environmentally sound P management decisions should be made based upon a fundamental understanding of soil P chemistry coupled with site specific information which would provide insights into P availability, retention and possible loss for individual soils. Little research has been done on Louisiana calcareous soils. Calcareous soils make up approximately 13% of the total soils in Louisiana. Despite the small occurrence, they comprise some of the most highly productive agricultural soils and play a very important role in Louisiana agricultural production (Amacher et al., 1989). Providing adequate P management recommendations in these soils have proven to be problematic. For example, a recent study has shown that corn responds consistently to additional P fertilization in Red River alluvial calcareous soils with a “high” to “very high” soil test P rating (Harrell et al., 2004). On the other hand, some of calcareous Quachita river alluvial soils are impacted by poultry litter application and may be subject to potential P losses through surface water runoff (Gaston et al., 2003). The P losses due to the over application of P to agricultural soils in the form of inorganic or P-rich organic fertilizers has been considered as one of the major causes for eutrophication of surface waters (Sharpley et al., 1996; Maguire et al., 2000; Sims et al., 2000).

Inorganic P soil chemistry is an intricate system of solid and solution P phases. Various soil constituents contribute to P retention mechanisms in soils. Hydrous metal oxides, especially Fe and Al oxides are thought to retain P from soil solution through ligand exchange, sorption, and precipitation reactions (Sample et al., 1980). Aluminosilicate clays fix P through edge hydroxyls while organic matter retains P via involvement of bridging cations such as Fe^{3+} , Al^{3+} and Ca^{2+} (Wild, 1950; Sample et al., 1980). Early work based on chemical thermodynamics indicated that calcium phosphates predominate in calcareous soils while Fe and Al phosphates predominate in acidic soils (Lindsay, 1979). In calcareous soils, phosphate retention was found to relate to the surface area of soil CaCO_3 (Amer et al., 1985). Other evidence has shown that the high-energy sorption surfaces of Fe oxides were more important than CaCO_3 in P sorption reactions in calcareous soils (Holford and Mattingly, 1975; Ryan et al., 1985). Furthermore, a positive correlation was found between P sorption and non-carbonate clays at lower P concentrations while both carbonate and non-carbonate clays were related to sorbed P at higher P solution concentrations (Zhou and Li, 2001). Results of x-ray adsorption near edge structure (XANES) spectroscopy also showed that Ca phosphates existed in acid soils and Fe phosphates were present in calcareous soils (Beauchemin et al., 2003). Apparently conflicting evidence exists in current literature regarding the role of major soil matrix components in P retention in calcareous soils.

Identification of soil P compounds can provide valuable information for P management. Soil P forms are often investigated by sequential chemical fractionation procedures (Chang and Jackson, 1957; Pratt and Garber, 1963; Williams et al., 1980; Hedley et al. 1982). Sequential extraction procedures utilize the ability of various

chemical reagents to selectively solubilize the Al, Fe, or Ca phosphate phases contained in the soil. Although imperfect separation may exist, it has been shown that with careful design and interpretation chemical fractionation procedures can be very useful in revealing the controlling phases of soil P dynamics (Sui et al., 1999; Delgado and Torrent, 2000; Maguire et al., 2000). In addition to chemical fractionation, sorption characteristics have also been widely studied in order to understand P retention in soils (Agbenin and Tiessen, 1995; McDowell and Condron, 2001; Villapando and Graetz, 2001). The coupling of chemical fractionation and sorption indices have been successively employed to explain the chemical changes associated with P retention and loss in biosolids-amended soils (Maguire et al., 2000). While exact reaction mechanisms may not eluded from sorption isotherm data, statistically significant correlations can provide insight about the P retention characteristics in calcareous soils (Olsen and Watanabe, 1957).

The objectives of this study were (1) to chemically speciate and compare inorganic the P forms of some important Louisiana calcareous soils, (2) to characterize the P sorption behavior of these soils, and (3) to evaluate relationships among inorganic P fractions, soil test extractable P, P sorption isotherm parameters and soil matrix components in order to provide insight into the proper management of P in these soils.

2.2 Materials and Methods

2.2.1 Soil Selection and Characterization

Five agriculturally important calcareous soils were chosen for this study. Of these, four represent soils from different pedological origins while two were selected to represent textural differences among a similar parent material. The selected soils include

Commerce (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts; 32°39' N and 91°13' W), a Mississippi River alluvial; Jeanerette (Fine-silty, mixed, superactive, hyperthermic Typic Argiaquolls; 29°57' N and 91°55' W), a loess derived soil; Mer Rouge (Fine-silty, mixed, superactive, thermic Typic Argiudolls; 32°38' N and 91°50' W), a Ouachita River alluvial; and two Norwood (Fine-silty, mixed, superactive, hyperthermic Fluventic Eutrudepts) Red River alluvial soils, a silt loam (31°10' N and 92°24' W) and sandy loam (32°24' N and 93°38' W) respectively.

Composite soil samples were taken from each soil site at two depths representing the surface (0-15 cm) and subsurface (30-45 cm). The samples were air-dried and ground to pass through a 2-mm sieve. Soil particle size analysis was performed by the pipette method (Gee and Bauder, 1986). Organic matter (OM) content was determined by the Wakley-Black method (Walkley, 1947). Soil pH was measured in deionized water with a soil to solution ratio of 1:1. The CEC of each soil was measured by saturating the soil with 1 M NH₄OAc at pH 7 followed by distillation and titration (Soil Survey Laboratory Methods Manual, 1996). Calcium carbonate equivalent (CCE) was determined by a gravimetric method (U. S. Salinity Laboratory Staff, 1954). Mehlich-III extractable Al, Ca, Fe and Mn (Al_{M3}, Ca_{M3}, and Fe_{M3} respectively) were determined by extraction with 0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.013 M HNO₃ + 0.001 M EDTA (Mehlich, 1984). Total free iron oxide as Fe (Fe_{CBD}) was extracted with 3 M Na₃C₆H₅O₇ + 1 M NaHCO₃ + 1g Na₂S₂O₄ in a water bath heated at 85°C (Mehra and Jackson, 1960). The more reactive amorphous Fe oxide as Fe was determined by first pretreating the soil with 1 M NH₄OAc (pH 5.5) to remove carbonates, followed by extraction with 0.175 M (NH₄)₂C₂O₄ + 0.1 M H₂C₂O₄ adjusted to pH 3.0 according to

Loeppert and Inskeep (1996). Associated with this extraction, Al (Al_{AOX}) and P (P_{AOX}) were also measured. This extraction method has been used by others to characterize P and Fe oxide relations in calcareous soils (Ryan et al., 1984). Manganese oxides as Mn (Mn_{OX}) were determined by a selected dissolution procedure using 0.1 M $NH_2OH \cdot HCl$ + 0.01 M HNO_3 (Gambrell, 1996).

Clay mineralogy was determined by standard x-ray diffraction procedures (Whittig and Allardice, 1986). Oriented films were produced by smearing the clay pastes onto glass slides and x-ray diffraction patterns were obtained using a Siemens D5000 diffractometer (Bruker AXS Inc., Madison, WI) with Cu- $K\alpha$ radiation in the $2 - 36^\circ 2\theta$ range. In addition, carbonate minerals were determined by generating x-ray patterns in the $23 - 36^\circ 2\theta$ range directly from a random powder mounts of air-dry soil samples with and without carbonates removed with 3 M HCl . Differences in the 3.04 and 2.98 Å peaks in the x-ray diffractogram confirmed the occurrences of calcite and dolomite respectively.

2.2.2 Phosphorus Fractionation

A sequential fractionation procedure described by Olsen and Sommers (1982) was modified and used for characterizing different forms of inorganic P in calcareous soils. The sequence of the chemical extractions and a brief description of the targeted P forms can be seen in Table 2.01. The method was slightly modified from the original version by adding an initial $NaHCO_3$ extraction for plant available P and a complete digestion in the end for the residual P. Each extraction was carried out using a 1:50 soil to solution ratio. All soil-fractionation solution mixtures were centrifuged at 16,000 X g for 10 min. and the supernatant solution in each sequential extraction was passed through a 0.45- μm filter. The steps with washings used a 1:50 soil to solution ratio and all washings were

combined with the post extraction solutions for analysis. Subsequent separation of organic-P within each fraction was not attempted since the organic-P component of these soils was considered to be negligible and its role in P retention was likely transient (Maguire et al., 2000). In addition to P, the Fe, Al, Ca, and Mn concentration in each sequential fraction was also measured.

Besides the sequential P fractionation, direct soil test P extractions were also carried out independently. They included 0.03 M NH₄F + 0.1 M HCl (Bray and Kurtz, 1945), 0.5 M NaHCO₃ (Olsen et al., 1954), and 0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.013 M HNO₃ + 0.001 M EDTA (Mehlich, 1984) and are identified throughout as P_{Bray}, P_{Olsen}, and P_{M3} respectively.

Phosphorus concentrations in all extracts were determined by ICP-OES (SPECTRO CYRIOS^{CCD}, Spectro Analytical Instruments, Inc., Fitchburg, MA). A Scott double-pass mixing chamber and a high salts torch were used to overcome the problems associated with high salt solutions resulting from the fractionation procedure. All P extractions were replicated three times.

2.2.3 Sorption Isotherms

Phosphorus sorption experiments were carried out by equilibrating 2 g of soil with 20 mL of 0.01 M KCl containing 0, 5, 10, 25, 35, 50, 75 and 100 µg P mL⁻¹ as KH₂PO₄ in 30 mL centrifuge tubes. The samples were then shaken on a reciprocating shaker at 25±0.5°C for 24 hours. After 24 h equilibrium, the samples were centrifuged and the supernatant was passed through a 0.45-µm filter. Phosphorus concentration in the filtrate was then analyzed by ICP-OES. Sorbed P (q') was calculated by difference between initial and final solution P concentrations after equilibrium. Phosphorus sorption

Table 2.01 Sequential P fraction methodologies and resulting targeted P forms released during the chemical P fractionation procedure.

| Fraction | Extractant | Equilibration | Washing | Targeted P forms |
|--------------------------|---|--|-------------------|--|
| 1. NaHCO ₃ -P | 0.5 M NaHCO ₃ | 30 min | None | Estimate of labile P including solution P, considered to be highly plant available (Olsen et. al., 1954; Bowman and Cole, 1978). |
| 2. NaOH-P | 0.1 N NaOH + 1 M NaCl | 17 hour | 1 M NaCl | Phosphate adsorbed on mineral surfaces, phosphate released by the hydrolysis of Fe and Al phosphates and by the hydrolysis of phosphated Fe- and Al- complexes (Chang and Jackson, 1957; Delagado and Torrent, 2000) |
| 3. CB-P | 0.3 M Na ₃ C ₆ H ₅ O ₇ ·H ₂ O + 1 M NaHCO ₃ | 15 min @ 85°C | None | Phosphate re-adsorbed to carbonate surfaces during the preceeding NaOH extraction. Also extracted are the labile pedogenic Ca-rich phosphates (Williams et al., 1971; Delagado and Torrent, 2000). |
| 4. CBD-P | 0.3 M Na ₃ C ₆ H ₅ O ₇ ·H ₂ O + 1 M NaHCO ₃ + Na ₂ S ₂ O ₄ ·2H ₂ O (1g) | preheat 15 min @ 85°C after CB addition additional 15 min after dithoite addition | Saturated NaCl | Reductant-soluable P, Mostly occluded in Fe oxides. This fraction may also include a small portion of labile Ca-P not removed in the previous CB extraction (Change and Jackson, 1957; Williams et al., 1971). |
| 5. HCl-P | 1 N HCl | 1 hour | None | Stable Ca phosphates, including lithogenic apatite but excluding more labile Ca-P forms removed in the previous CB and CBD fractions (Chang and Jackson, 1957; Delagado and Torrent, 2000). |
| 6. Residual-P | Conc. H ₂ SO ₄ Conc. HF 30% H ₂ O ₂ | Variable, until complete digestion is accomplished | None | Most chemically stable inorganic and organic P forms. |

parameters were determined by fitting experimental data to the Langmuir and Freundlich models using the PROC NLIN procedure in SAS version 8.2 (SAS Institute, 1999). The Langmuir (Equation 1) and Freundlich (Equation 2) models are expressed as:

$$q = kbC/(1+kC) \quad [1]$$

and

$$q = Kd C^{1/n} \quad [2]$$

Where $q = q' + q_o$, q is the total amount of P sorbed (mg kg^{-1}), q' is the sorbed P (mg kg^{-1}) calculated by difference between the initial and the final P concentrations, q_o is the original sorbed P (mg kg^{-1}) determined by the P release at 0 initial P concentration, C is the equilibrium P concentration (mg L^{-1}), k is a constant relating to bonding strength, b is the sorption maxima, K_d is the distribution coefficient, and n is a correction factor. In addition, equilibrium P concentration (EPC_o), expressed as the final P solution concentration at which no net sorption occurred, was calculated from a linear regression of q vs. C based on the first two sorption points.

2.3 Results and Discussion

2.3.1 Basic Physical and Chemical Properties

The five calcareous soils selected for this study exhibited quite different physical and chemical characteristics (Table 2.02). The diverse geological nature of these soils can be seen by varying aluminosilicate and carbonate mineralogy in the surface samples. In general, the Mississippi River alluvial Commerce soil was dominated by smectites (78%) followed by kaolinite and clay mica (approximately 10% each). Both Quachita River alluvial Mer Rouge soil and Red River alluvial Norwood soils contained appreciable quantities of kaolinite and clay mica in addition to smectite. The losses-derived Jeanerette also included chlorite (15%). All soils

posses some randomly interstratified chlorite and smectite (6-26%) except for the Commerce which had small amount of randomly interstratified vermiculite and smectite (3%). The CCE of the soils ranged from 8.9 to 48.3 g kg⁻¹ while pH ranged from 7.2 to 8.2. Notably, these soils are only mildly calcareous as compared to those studied by others (Samadi and Gilkes, 1999; Delgado and Torrent, 2000). Nonetheless, the Commerce and Norwood sandy loam soils were dominated with dolomitic carbonates whereas the Mer Rouge with calcitic. The Jeanerette and the Norwood silt loam contained both calcite and dolomite (Table 2.02).

The Fe_{AOX} values were quite low as compared to Fe_{CBD} for almost all of the soils, suggesting that the majority of Fe oxides exist in a more crystalline form in these soils (Table 2.03). One exception to this is the Mississippi River alluvial Commerce soil where a larger Fe_{AOX} to Fe_{CBD} ratio indicated that amorphous Fe oxides were the more prevalent form. The commerce soil also contained a much larger quantity of total free Fe oxides as implied by Fe_{CBD} as compared to the other soils used in the study. In addition, the alluvial Commerce, as well as the losses-derived Jeanerette soil, contained relatively larger quantities of oxalate-extractable Al at both depths as compared to the Mer Rouge and Norwood soils. Interestingly, the Jeanerette soil also had a much larger Mn oxide content as indicated by Mn_{ox} than the four alluvial soils. Consequently, the differences in quantity and types of aluminosilicates clay minerals, carbonates and metal oxides among these calcareous soils could affect P retention and release characteristics.

2.3.2 Phosphorus Forms and Relation to Soil Matrix Components

The results of the sequential chemical P fractionation and the direct P extraction are presented in Table 2.04. Both the NaOH-P and the combined NaOH-P and CB-P as [NaOH+CB]-P are reported here. The [NaOH+CB]-P is a more accurate estimate of overall

Table 2.02 Selected chemical and physical properties for five calcareous soils at two depths[†].

| Soil | Depth | pH | Sand | Silt | Clay | OM | CCE | CEC | Clay mineralogy [‡] | | | | | Carbonate [§] | | |
|----------------------|-------|-----|-------------------------------|------|------|------|------------------------------------|-------------|------------------------------|-----|-----|-----|-----|------------------------|-----|-----|
| | | | | | | | | | Sme | Chl | Kao | Mic | ICS | IVS | Cal | Dol |
| | | cm | -----g kg ⁻¹ ----- | | | | cmol _c kg ⁻¹ | -----%----- | | | | | | | | |
| Commerce | 0-15 | 7.4 | 37 | 650 | 313 | 21.2 | 12.5 | 13.7 | 78 | - | 10 | 9 | - | 3 | 0 | 100 |
| | 30-45 | 7.5 | 7 | 466 | 524 | 12.1 | 11.1 | 35.7 | | | | | | | 0 | 100 |
| Mer Rouge | 0-15 | 7.2 | 261 | 517 | 222 | 13.2 | 8.9 | 8.3 | 32 | - | 29 | 25 | 14 | - | 100 | 0 |
| | 30-45 | 8.2 | 232 | 501 | 266 | 7.4 | 43.3 | 12.6 | | | | | | | 100 | 0 |
| Jeanerette | 0-15 | 7.9 | 83 | 609 | 308 | 9.8 | 38.0 | 17.0 | 23 | 15 | 20 | 36 | 6 | - | 66 | 34 |
| | 30-45 | 8.1 | 22 | 586 | 394 | 10.6 | 26.9 | 21.8 | | | | | | | 56 | 44 |
| Norwood (Sandy Loam) | 0-15 | 7.5 | 537 | 322 | 141 | 6.8 | 10.5 | 4.3 | 57 | - | 20 | 12 | 11 | - | 0 | 100 |
| | 30-45 | 7.7 | 253 | 405 | 343 | 4.2 | 16.4 | 17.1 | | | | | | | 0 | 100 |
| Norwood (Silt Loam) | 0-15 | 7.9 | 18 | 841 | 142 | 6.0 | 38.5 | 4.9 | 28 | - | 12 | 34 | 26 | - | 32 | 68 |
| | 30-45 | 7.9 | 20 | 818 | 162 | 1.6 | 48.3 | 8.1 | | | | | | | 38 | 62 |

[†] OM, organic matter; CEC, cation exchange capacity; CCE, calcium carbonate equivalent.

[‡]Sme, smectite; Chl, chlorite; Kao, kaolinite; Mic, clay mica (illite); ICS, Randomly stratified chlorite and smectite; IVS, randomly interstratified vermiculite and smectite.

[§]Cal, Calcite; Dol, Dolomite.

Table 2.03. Extractable Fe, Al, Mn, and Ca for five calcareous soils at two depths[†].

| Soil | Depth | Fe _{AOX} | Fe _{CBD} | Fe _{M3} | Al _{AOX} | Al _{M3} | Ca _{M3} | Mn _{OX} |
|----------------------|-------|-------------------------------|-------------------|------------------|-------------------|------------------|------------------|------------------|
| | -cm- | -----g kg ⁻¹ ----- | | | | | | |
| Commerce | 0-15 | 4.4 | 6.0 | 1.2 | 0.7 | 0.6 | 3.6 | 0.4 |
| | 30-45 | 6.6 | 8.5 | 0.6 | 0.9 | 0.7 | 4.1 | 0.3 |
| Mer Rouge | 0-15 | 0.6 | 2.2 | 0.1 | 0.4 | 0.4 | 1.5 | 0.2 |
| | 30-45 | 0.3 | 3.3 | 0.0 | 0.7 | 0.1 | 5.6 | 0.2 |
| Jeanerette | 0-15 | 0.8 | 3.8 | 0.2 | 0.6 | 0.4 | 4.8 | 0.9 |
| | 30-45 | 0.7 | 3.3 | 0.2 | 1.0 | 0.7 | 4.6 | 0.5 |
| Norwood (Sandy Loam) | 0-15 | 0.5 | 1.7 | 0.2 | 0.3 | 0.3 | 0.9 | 0.1 |
| | 30-45 | 1.9 | 3.9 | 0.2 | 0.5 | 0.4 | 2.6 | 0.2 |
| Norwood (Silt Loam) | 0-15 | 0.3 | 2.4 | 0.1 | 0.2 | 0.0 | 3.4 | 0.2 |
| | 30-45 | 0.5 | 4.1 | 0.1 | 0.4 | 0.0 | 4.6 | 0.2 |

[†]Fe_{AOX} and Al_{AOX} are ammonium oxalate extractable Fe and Al; Fe_{CBD}, citrate-bicarbonate-dithionite extractable Fe; Fe_{M3}, Al_{M3} and Ca_{M3}, are Mehlich III extractable Fe, Al, Ca, and Mn; Mn_{OX} is NH₂OH+HCl+HNO₃ extractable Mn. Data are means of two replicates. Standard error <5% for all samples (data not shown).

Fe/Al-phosphates since the CB extraction was included to recover primarily the phosphate hydrolyzed from Fe/Al-phosphates but re-adsorbed to carbonate surfaces during the proceeding NaOH extraction (Williams et al., 1971). In general, the five calcareous soils consisted of different amounts of the P fractions. Among the chemically defined fractions (disregarding the residual-P), HCl-P (primarily stable Ca-phosphates) was the dominant fraction, making up 22 to 62 % of the total P for all soils except for the Mer Rouge surface soil. The [NaOH+CB]-P was the second major fraction, accounting for 5-28% of the total P. The CBD-P, primarily the occluded P by Fe oxides, and the NaHCO₃-P were the smallest fractions, each consisting of less than 10% of the total P. The residual-P fraction, comprised of most chemically stable P forms, accounted for 25-43% of the total P. The latter was similar to those reported for other soils (Hedley et al., 1982; Sui et al., 1999).

Among five calcareous soils, the Mississippi alluvial Commerce subsurface and surface soils and the Quachita alluvial Mer Rouge surface soil contained relatively large percentages of [NaOH+CB]-P, close to or exceeding the HCl-P fraction (Table 2.04). This was probably due to very high content of amorphous Fe oxides as indicated by ammonium oxalate-extractable Fe in the Commerce surface and subsurface soils and relatively small carbonate content in the Mer Rouge surface sample (Table 2.02 and 2.03). These observations implied that the occurrence of dominant P forms may not always adhere to the simple adage that Ca-P minerals are the major P forms in alkaline soils whereas Fe and Al phosphates predominate in acid soils as suggested by thermodynamic predictions (Lindsay, 1979). Similarly, earlier studies also showed that more reactive amorphous Fe oxides were correlated with P sorption in calcareous soils (Ryan et al., 1985). Although the HCl-P has been reported as the dominant P fraction in soils containing a much higher carbonate content (CCE > 100 g kg⁻¹), contradicting evidence showed that in

heavily-fertilized soils, Al not Ca was the predominate cation associated with P in P-rich particles regardless of soil pH (Pierzynski et al., 1990). A recent study based on XANES analysis showed that Fe-, Al-, and Ca-phosphates were all present in alkaline as well as acid soils (Beauchemin et al., 2003). Our results in this study suggest that P retention in mildly calcareous soils ($CCE < 50 \text{ g kg}^{-1}$) containing large quantities of Fe oxides is likely governed by Fe oxides through the formation of Fe-P minerals. The results also imply that the stability of these Fe-P minerals may need to be examined over further pH changes in complex soil systems.

Linear regression analysis was performed on the different P fractions with various soil matrix components in order to examine their relations in these mildly calcareous soils (Table 2.05). The NaHCO_3 -P fraction, a close estimate of plant available P, was positively correlated with Fe_{AOX} and soil test Fe (Fe_{M3}) but negatively with the CCE. The negative relation between plant available P and soil CCE has been reported by others (Afif et al., 1993). Our results imply that labile Fe and amorphous Fe oxides play an important role in governing plant-available P in these mildly calcareous soils. The $[\text{NaOH}+\text{CB}]$ -P was correlated with Fe_{M3} , Fe_{AOX} , and Fe_{CBD} but not with extractable Al, Mn oxides, CCE, or clay content. This suggests that for these particular soils, the P released by NaOH is most likely derived from the hydrolysis of Fe oxides and not from Al or Mn oxides. We did not observe any significant correlations between the HCl-P fraction and any of major inorganic soil components including carbonate content (CCE). The lack of correlation between the HCl-P and the CCE implies that the HCl-P fraction was not influenced by simple carbonates. It was found, however, that the P released from this fraction was less correlated with Ca ($R^2 = 0.30$) but more strongly correlated with Mg ($R^2 = 0.54$, $P < 0.05$) associated with the fraction. The results suggest that the HCl-P from these soils were likely derived from stable minerals of phosphates such as apatite with mixed Mg-Ca phases.

The residual-P was strongly correlated with Fe_{AOX} , Fe_{CBD} and clay content, less strongly with Al_{AOX} , Al_{M3} and Fe_{M3} , but not with the CCE (Table 2.05). Regression analysis of the residual-P with other elements in the residual P digest also found very strong correlation with Fe ($R^2 = 0.78$, $P < 0.001$) and Al ($R^2 = 0.82$; $P < 0.001$) but not with Ca ($R^2 = 0.03$). In addition, Al and Fe in the residual fraction were correlated significantly ($R^2 \geq 0.78$; $P < 0.001$) with the clay content of the soils. These results suggest that the residual-P is likely stable Fe/Al P forms closely associated with soil phyllosilicate minerals.

Of the direct extractions, Olsen P was strongly correlated with Fe_{M3} ($R^2 = 0.80$; $P < 0.001$) and moderately correlated with Fe_{AOX} ($R^2 = 0.46$; $P < 0.05$) (Table 2.05). This suggested that most of the P extracted by Olsen soil test was derived from phosphates coordinated with labile Fe or adsorbed to less crystalline Fe oxides. This was further supported by the strong correlation ($R^2 = 0.94$; $P < 0.001$) between Olsen P and [NaOH+CB]-P (Table 2.06). Bray II soil test P was only moderately correlated with labile Fe ($R^2 = 0.52$; $P < 0.05$) while the commonly-used Mehlich III soil test P was only slightly correlated with labile or exchangeable Ca ($R^2 = 0.44$; $P < 0.05$) in these mildly calcareous soils (Table 2.05). It was also interesting to note that the direct ammonium oxalate-extractable P (P_{AOX}) was highly correlated with only Fe_{AOX} , Fe_{CBD} , and Fe_{M3} but not with Al_{AOX} or Al_{M3} . Since ammonium oxalate has been shown as an effective extractant of P associated with Al as compared to the CBD extraction (Wang et al., 1991), the later result further indicates the importance of Fe oxides not Al oxides in controlling P retention at existing conditions of these mildly calcareous soils. The ammonium oxalate procedure has been shown as a reliable estimator of plant-available P pool in highly weathered soils but not in calcareous soils (Guo and Yost, 1999).

All of three direct soil test-P extractions were correlated with the NaHCO_3 -P fraction, displaying the similarities among the various chemical extractants commonly used to estimate labile P (Table 2.06). As expected, the NaHCO_3 -P from the sequential fractionation procedure was most significantly ($R^2 = 0.83$; $P < 0.001$) correlated with the P_{Olsen} since the only difference between the two is the soil to solution ratio (1:50 and 1:20 respectively). Except for the moderate correlation with the NaHCO_3 -P, Mehlich III-P did not correlate with any of other sequential fractions whereas Bray II-P, in addition to NaHCO_3 -P, was correlated with $[\text{NaOH}+\text{CP}]$ -P, CBD-P as well as HCl-P (Table 2.06). The latter suggests that the strong acidity of Bray II extraction (0.1 M H^+) did extract a fraction of stable Ca-phosphates whereas Mehlich III and Olsen extractions did not. Finally, the direct ammonium oxalate-extractable P was highly correlated with the Fe oxide-related $[\text{NaOH}+\text{CP}]$ -P and CBD-P fractions (Table 2.06). The latter along with the result of lack of the correlation between P_{AOX} and HCl-P suggested that ammonium oxalate, though acidified, extracts primarily phosphates associated with Fe oxides but not stable Ca phosphates (e.g. detrital apatite) in these calcareous soils. We removed free carbonates using $1 \text{ M NH}_4\text{OAc}$ (pH 5.5) before performing the ammonium oxalate extraction (Loeppert and Inskeep, 1996).

2.3.3 Phosphorus Sorption

Phosphorus sorption isotherms for each soil at both depths can be seen in Fig. 2.01 Sorption isotherm parameters based on the Langmuir and Freundlich models are presented in Table 2.07. Sorption behavior was adequately described by both the Langmuir and Freundlich models, with R^2 values ranging from 0.96 – 0.99 and 0.97 – 1.00 respectively for nine out of ten soils. The surface soil of the Norwood silt loam had relatively lower R^2 values of 0.72 and 0.82

Table 2.04 Phosphorus fractions by several common soil test extractions and sequential fractionation scheme for five calcareous soils at two depths[†].

| Soil | Depth | Sequential P Fractionation [‡] | | | | | | | | Direct Extraction | | | | EPC ₀ |
|----------------------|-------|---|---------|-------|-------------|-------|---------|------------|-------|-------------------|-----------------|--------------------|------------------|--------------------|
| | | NaHCO ₃ -P | NaOH-P | CB-P | [NaOH+CB]-P | CBD-P | HCl-P | Residual-P | Sum-P | P _{Bray} | P _{M3} | P _{Olsen} | P _{AOX} | |
| | | -----mg kg ⁻¹ ----- | | | | | | | | | | | | |
| | | --cm-- | | | | | | | | | | | | mg L ⁻¹ |
| Commerce | 0-15 | 54(7) | 177(23) | 30(4) | 207(27) | 47(6) | 249(32) | 223(29) | 779 | 349 | 49 | 39 | 488 | 0.178 |
| | 30-45 | 39(5) | 131(18) | 22(3) | 153(20) | 61(8) | 241(32) | 253(34) | 747 | 223 | 29 | 22 | 408 | 0.120 |
| Mer Rouge | 0-15 | 32(10) | 71(21) | 22(6) | 93(28) | 14(4) | 72(22) | 123(37) | 334 | 125 | 42 | 19 | 133 | 0.056 |
| | 30-45 | 25(7) | 22(6) | 18(5) | 40(11) | 11(3) | 133(37) | 150(42) | 360 | 35 | 5 | 5 | 89 | 0.019 |
| Jeanerette | 0-15 | 22(4) | 32(6) | 25(5) | 57(11) | 32(6) | 241(46) | 171(33) | 524 | 228 | 25 | 7 | 167 | 0.138 |
| | 30-45 | 23(6) | 23(6) | 18(5) | 41(10) | 15(4) | 151(38) | 165(42) | 394 | 95 | 7 | 4 | 135 | 0.019 |
| Norwood (Sandy Loam) | 0-15 | 38(10) | 35(9) | 25(7) | 60(16) | 18(5) | 162(43) | 95(25) | 373 | 168 | 55 | 13 | 139 | 0.148 |
| | 30-45 | 33(7) | 13(3) | 19(4) | 32(7) | 19(4) | 203(44) | 172(37) | 459 | 138 | 13 | 5 | 164 | 0.207 |
| Norwood (Silt Loam) | 0-15 | 32(6) | 22(4) | 34(6) | 57(10) | 23(4) | 312(55) | 142(25) | 565 | 284 | 55 | 11 | 152 | 0.544 |
| | 30-45 | 24(5) | 6(1) | 18(4) | 23(5) | 11(2) | 293(62) | 123(26) | 475 | 141 | 5 | 3 | 127 | 0.005 |

[†] P_{Bray}, Bray II extractable P; P_{Olsen}, Olsen extractable P; P_{M3}, Mehlich III extractable P; P_{AOX}, ammonium oxalate extractable P; EPC₀, equilibrium P concentration.

[‡] Sequential P fractions according to Table 1.

Data are means of two replicates. Standard error <5% for all samples (data not shown).

Table 2.05 R^2 values for linear regressions between phosphorus fractions and various extractable Fe, Al, Mn and CCE and clay content[†].

| | Fe _{AOX} | Fe _{CBD} | Fe _{M3} | Al _{AOX} | Al _{M3} | Mn _{OX} | CCE | Clay |
|------------------------------------|-------------------|-------------------|------------------|-------------------|------------------|------------------|---------|---------|
| <i>Sequential Fractionation</i> | | | | | | | | |
| NaHCO ₃ -P [‡] | 0.44 * | 0.17 | 0.76 ** | 0.00 | 0.13 | 0.08 | -0.47 * | 0.02 |
| (NaOH+CB)-P | 0.65 ** | 0.42 * | 0.84 *** | 0.15 | 0.31 | 0.01 | 0.35 | 0.16 |
| CBD-P | 0.85 *** | 0.73 ** | 0.59 * | 0.22 | 0.35 | 0.10 | 0.18 | 0.42 * |
| HCl-P | 0.06 | 0.14 | 0.06 | 0.05 | 0.08 | 0.01 | 0.17 | 0.00 |
| Residual-P | 0.80 *** | 0.84 *** | 0.50 * | 0.52 * | 0.43 * | 0.12 | 0.07 | 0.73 ** |
| Sum-P | 0.69 ** | 0.68 ** | 0.66 ** | 0.10 | 0.13 | 0.04 | 0.04 | 0.21 |
| <i>Direct Extraction</i> | | | | | | | | |
| P _{Olsen} | 0.46 * | 0.23 | 0.80 *** | 0.04 | 0.20 | 0.01 | 0.40 | 0.04 |
| P _{M3} | 0.02 | 0.02 | 0.15 | 0.18 | 0.00 | 0.04 | 0.25 | 0.12 |
| P _{Bray} | 0.24 | 0.15 | 0.52 * | 0.01 | 0.03 | 0.04 | 0.06 | 0.00 |
| P _{AOX} | 0.83 *** | 0.66 ** | 0.90 *** | 0.20 | 0.34 | 0.02 | 0.26 | 0.29 |

[†]Fe_{AOX} and Al_{AOX} are ammonium oxalate extractable Fe and Al; Fe_{CBD}, citrate-bicarbonate-dithionite extractable Fe; Fe_{M3} and Al_{M3} are Mehlich III extractable Fe and Al; Mn_{OX} is NH₂OH+HCl+HNO₃ extractable Mn; CCE, calcium carbonate equivalent.

[‡] Minus sign "-" before R^2 value indicates negative correlation.

Data are means of two replicates. Standard error <5% for all samples (not shown).

*significant at $P < 0.05$, **significant at $P < 0.01$, *** significant at $P < 0.001$

Table 2.06 R^2 values for linear regressions between sequential P fractions and common direct P extractions[†].

| Sequential P Fraction | Direct Extractable P | | | | EPCo |
|-----------------------|----------------------|------------|-------------|-----------|------|
| | P_{M3} | P_{Bray} | P_{Olsen} | P_{AOX} | |
| NaHCO ₃ -P | 0.42 * | 0.45 * | 0.83 *** | 0.67 ** | 0.08 |
| (NaOH+CB)-P | 0.26 | 0.47 * | 0.94 *** | 0.88 *** | 0.01 |
| CBD-P | 0.11 | 0.48 * | 0.48 * | 0.82 *** | 0.04 |
| HCl-P | 0.01 | 0.43 * | 0.00 | 0.11 | 0.29 |
| Residual-P | 0.00 | 0.21 | 0.28 | 0.69 ** | 0.00 |
| Sum-P | 0.09 | 0.68 ** | 0.47 * | 0.84 *** | 0.11 |

[†] P_{Bray} , Bray II extractable P; P_{Olsen} , Olsen extractable P; P_{M3} , Mehlich III extractable P; P_{AOX} , ammonium oxalate extractable P; EPCo, equilibrium P concentration. *significant at $P < 0.05$, **significant at $P < 0.01$, *** significant at $P < 0.001$

for the Langmuir and Freundlich models respectively. Due to the lower fit, all following regressions involving sorption isotherm parameters did not include the surface soil of the Norwood silt loam.

The surface soils, in all cases, sorbed less P than the subsurface soils. Since soil test P values (P_{Bray} , P_{Olsen} , and P_{M3}) were much higher in the surface soils, possibly due to the long term use of P fertilizers, than in the subsurface, the lower P sorption by the surface soils would be expected. Among the different surface soils, the Commerce exhibited the highest Langmuir P sorption maximum (398 mg kg⁻¹) followed by Jeanerette (285 mg kg⁻¹), Mer Rouge (82 mg kg⁻¹), Norwood sandy loam (61 mg kg⁻¹), and Norwood silt loam (31 mg kg⁻¹) respectively. These P sorption maxima would correspond to a P saturation index (P_{sat}) of 10, 3, 24, 22, and 34%, respectively as defined by $P_{sat} = (P_{Olsen}/b) * 100$ due to the calcareous nature for the above surface soils (Hughes et

al., 2000; Zhou and Li, 2001). In the literature, the commonly used Mehlich III-P has been often used to assess P_{sat} (Sharpley, 1995; Zhang et al., 2005). Based on $P_{\text{sat}} = (P_{\text{M3}}/b)*100$, the P_{sat} would be calculated as 12, 51, 9, 90 and 166% for these surface soils. The P_{sat} of 25% and above has been found to correspond to the higher potential of P loss through surface water runoff (Sharpley et al., 1996). We did not perform runoff experiments on these soils to evaluate the applicability of these relations. Nonetheless, the shapes of P sorption isotherms and very low Langmuir sorption maxima (b) and Freundlich distribution coefficient (K_d) of Norwood (silt loam and sandy loam) and Mer Rouge soils seem to suggest that these three soils were near P saturation as compared to the Commerce and Jeanerette surface soils.

Linear regression was performed to determine if any relationship exists among P sorption isotherm parameters, soil matrix components, and the sequential P fractions. The Langmuir sorption maximum (b) was positively correlated with Al_{AOX} , Ca_{M3} , and clay content but surprisingly, not with Fe_{AOX} , Fe_{CBD} , Fe_{M3} , Mn_{OX} , or carbonate contents (Table 2.08). This result was similar to that reported by Solis and Torrent (1989a;b) suggesting that the role of calcium carbonates in P sorption by calcareous soils may be secondary. However, they reported stronger correlations for both CBD-P fraction and P sorption with Fe_{CBD} and weaker correlations with Al_{AOX} (Solis and Torrent, 1989a;b). On the other hand, for calcareous soils with very high CCE (e.g. $> 243 \text{ g kg}^{-1}$), calcium carbonates appeared to play a significant role in P sorption (Zhou and Li, 2001). Our results suggest that further retention of soluble P by these mildly calcareous soils is primarily controlled by labile Ca (Ca_{M3}), clays, and oxalate-extractable Al. As more phosphates are introduced, labile Ca can either directly react with phosphates to form Ca-

phosphate precipitates or serve as a bridge cation between negatively-charged clay surfaces and phosphates to form surface sorption complexes (Barrow, 1972). Since we did not observe any significant correlations ($R^2 \leq 0.16$) between labile Ca (Ca_{M3}) and clay content or CEC, this suggested that much of labile Ca was not bridging phosphates to clays as P is further sorbed, but likely it was in a precipitated form with phosphates.

The strong correlations between b and Al_{AOX} ($Y = 657.5X - 91.9$, $R^2 = 0.79$, $P = 0.002$) as well as between K_d and Al_{AOX} ($Y = 153.4X - 18.4$, $R^2 = 0.77$, $P = 0.003$) are interesting (Table 2.08). Ammonium oxalate-extractable Al has been found to account for as high as 90% of P retention in acidic andepts (Alvarado and Boul, 1985). In calcareous soils, ammonium oxalate-extractable Al is generally small and its influence to soil P retention has been often discounted (Solis and Torrent, 1989a). Our data, however, showed that although small in total quantity, ammonium oxalate-extractable Al in calcareous soils plays a very important role in further P sorption. Besides noncrystalline Al oxides or aluminosilicates, some of ammonium oxalate-extractable Al in calcareous soils could originate from the small amounts of Al extracted from clay mineral edges (Peña and Torrent, 1984; Jackson et al., 1986). We find no significant correlation between Al_{AOX} and Fe_{AOX} ($R^2 = 0.32$, $P > 0.05$). According to Peña and Torrent (1984), the lack of correlation between Al_{AOX} and Fe_{AOX} indicates that this ammonium oxalate-extractable Al was not from poorly crystalline, Al-substituted Fe oxides but possibly from the edges of aluminosilicate clays. This hypothesis appears to be supported by our observations of significant linear relations between Al_{AOX} and clay content ($Y = 0.0018X + 0.0412$, $R^2 = 0.79$, $P = 0.003$) as well as between Al_{AOX} and CEC ($Y = 0.023X + 0.23$, $R^2 = 0.72$, $P = 0.006$) for these soils. Since both clay content and CEC reflect the

apparent reactive surfaces, our results imply that the further P sorption in these soils is highly dependent upon the reactive surfaces of exposed phyllosilicate edges where P interactions with surface Al oxides occur, possibly after the sites from Fe oxides at existing soil conditions become saturated as indicated by the fractionation data. There were no significant relationships observed between the P sorption parameters and the chemically-defined P fractions.

2.4 Conclusions

The five calcareous Louisiana soils of loess and alluvial origins differed considerably in clay, carbonate mineralogy, and metal oxide content. Sequential P fractionation revealed that both the surface and subsurface soils of the Jeanerette (loess-derived) the both Norwood (Red River alluvium) soils were dominated by the HCl-P, presumably stable Ca/Mg-phosphates. The surface soils of Commerce (Mississippi River alluvium) and Mer Rouge (Quachita River alluvium) soils, however, contained large percentages of [NaOH+CB]-P, primarily Fe-bound phosphates. The latter was attributed to the very large contents of amorphous and total free Fe oxides in the Commerce surface soil and relatively small carbonate content in the Mer Rouge surface soil. The plant-available P extracted by NaHCO_3 and the reductant P by CBD were the smallest P fractions in all these calcareous soils.

All chemically-defined sequential P fractions, except for the HCl-P, were correlated with amorphous Fe (Fe_{AOX}) and labile Fe (Fe_{M3}) to a various degree. In addition, the total sum-P of all sequential P fractions was also strongly correlated with different Fe fractions. These results imply that in calcareous soils with carbonate contents < 5%, Fe oxides especially in the less amorphous forms play a very important role in P

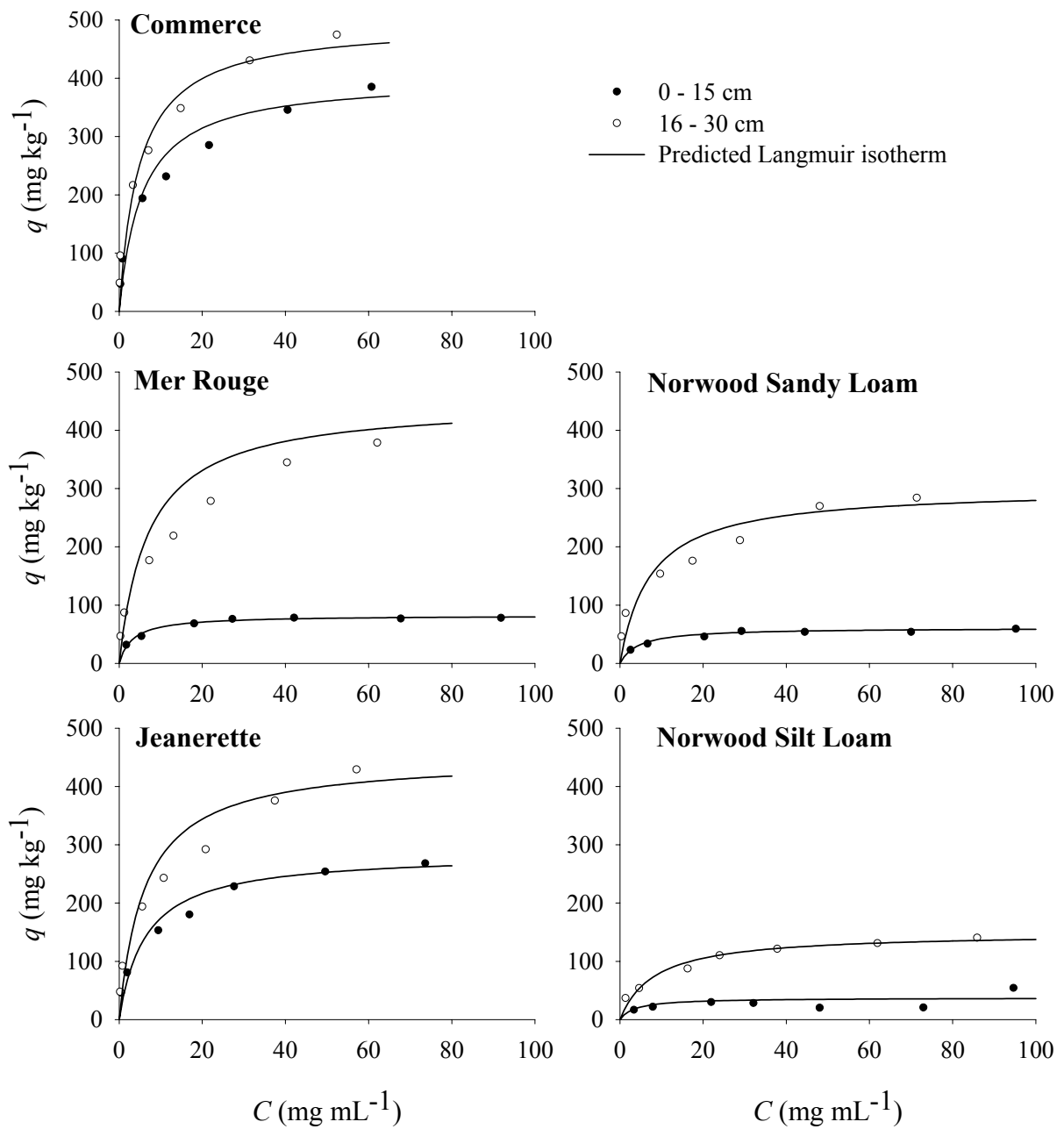


Figure 2.01 Phosphorus sorption isotherms for five calcareous Louisiana soils at two depths. Open and solid circles represent actual experimental data points. The continued line is fitted Langmuir model

Table 2.07 Langmuir and Freundlich sorption isotherm parameters with corresponding regression R^2 values[†].

| Soil | Depth | Langmuir | | | Freundlich | | |
|----------------------|--------|---------------------|--------------------|-------|--------------------|------|-------|
| | | b | k | R^2 | K_d | n | R^2 |
| | --cm-- | mg kg ⁻¹ | L kg ⁻¹ | | L kg ⁻¹ | | |
| Commerce | 0-15 | 398 | 0.16 | 0.98 | 92 | 2.79 | 0.98 |
| | 30-45 | 495 | 0.21 | 0.98 | 135 | 3.01 | 0.98 |
| Mer Rouge | 0-15 | 82 | 0.31 | 0.98 | 30 | 4.25 | 0.97 |
| | 30-45 | 496 | 0.19 | 0.97 | 124 | 2.84 | 0.98 |
| Jeanerette | 0-15 | 285 | 0.14 | 0.99 | 66 | 2.92 | 0.98 |
| | 30-45 | 463 | 0.12 | 0.98 | 98 | 2.71 | 1.00 |
| Norwood (Sandy Loam) | 0-15 | 61 | 0.23 | 0.97 | 19 | 3.82 | 0.97 |
| | 30-45 | 304 | 0.11 | 0.96 | 64 | 2.78 | 0.98 |
| Norwood (Silt Loam) | 0-15 | 33 | 1.06 | 0.72 | 12 | 4.97 | 0.82 |
| | 30-45 | 148 | 0.12 | 0.99 | 37 | 3.22 | 0.99 |

[†] b and k are Langmuir isotherm derived sorption maximum and bonding strength; K_d and n are Freundlich isotherm derived distribution coefficient and correction factor.

Table 2.08 R^2 values for linear regression analysis between Langmuir and Freundlich sorption isotherm parameters and soil extractable Fe, Al and Mn, CCE and clay content.

| | Fe _{AOX} [†] | Fe _{CBD} | Fe _{M3} | Al _{AOX} | Al _{M3} | CCE | Mn _{OX} | Clay |
|----------------|--------------------------------|-------------------|------------------|-------------------|------------------|------|------------------|---------|
| b [‡] | 0.24 | 0.37 | 0.10 | 0.79 ** | 0.19 | 0.02 | 0.07 | 0.62 * |
| k | 0.00 | 0.04 | 0.00 | 0.04 | 0.00 | 0.27 | 0.09 | 0.04 |
| K _d | 0.33 | 0.46 * | 0.10 | 0.77 ** | 0.17 | 0.01 | 0.05 | 0.64 ** |
| n | 0.09 | 0.24 | 0.07 | 0.36 | 0.05 | 0.15 | 0.13 | 0.32 |

[†]Fe_{AOX} and Al_{AOX} are ammonium oxalate extractable Fe and Al; Fe_{CBD}, citrate-bicarbonate-dithionite extractable Fe; Fe_{M3} and Al_{M3} are Mehlich III extractable Fe and Al; Mn_{OX} is NH₂OH+HCl+HNO₃ extractable Mn; CCE, calcium carbonate equivalent.

[‡]b and k are Langmuir isotherm derived sorption maximum and bonding strength; K_d and n are Freundlich isotherm derived distribution coefficient and correction factor.

*significant at P < 0.05, **significant at P < 0.01, *** significant at P < 0.001

retention. There were no significant correlations between the HCl-P and the carbonate content of the soils or with any of other soil matrix components. Of the three soil test P extractants, only the Bray II extractable P was moderately correlated with the HCl-P fraction, suggesting that the Bray II may dissolve a portion of the more stable Ca/Mg-phosphates due to its strong acidity of the extraction solution.

The five calcareous soils exhibited different P sorption capacities with subsurface horizons having generally higher sorption than the surface horizons. Both Norwood and Mer Rouge surface soils were likely near or above the P saturation threshold based on the shapes of sorption isotherm and supported by a calculated P saturation index ($P_{sat} = (P_{Olsen}/b)*100$). Langmuir *b* and the Freundlich *K_d* were both significantly correlated with Al_{AOX}, clay content and labile Ca. The fact that Al_{AOX} alone explained 77% and

79% of the variability in the Langmuir maxima and Freundlich distribution coefficients, respectively suggests that even in calcareous soils, small quantities of Al oxides possibly from exposed aluminosilicate surfaces could be an important contributing factor for additional P retention at high P concentrations, as the available sites of Fe oxides are saturated.

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CHAPTER 3

SPECIATION OF PHOSPHORUS COMPOUNDS IN CALCAREOUS LOUISIANA SOILS USING X-RAY ABSORPTION NEAR-EDGE STRUCTURE SPECTROSCOPY

3.1 Introduction

3.1.1 Introduction

Mobility of phosphorus (P) in soils affects P availability to plants as well as environmental water quality. Non-point source pollution from agricultural lands due to the over-application of inorganic fertilizers and P-rich biosolids has been considered as one of the major contributions to eutrophication in various water bodies across the country (Sharpley et al., 1996; Maguire et al., 2000; Sims et al., 2000). Soil P mobility is controlled by an equilibrium between solution P and various solid P forms. Understanding P retention and release by the various P compounds in soils is important in order to make environmentally sound nutrient management decisions.

The three major inorganic solid P compounds in soils are Al, Fe and Ca-bound phosphates. It is generally accepted that Fe and Al bound phases control the solubility and mobility of P in acidic soils while Ca bound phases are the controlling factor in calcareous environments. However, it has been debated that Fe oxides may play an equally important role in P retention in these alkaline soils (Holford and Mattingly, 1975; Ryan et al., 1985). Investigation techniques over the past several decades have included several chemical fractionation and equilibrium techniques which have provided some insight to the question although they have also brought further controversy over the viability of the extraction procedures. For example, mineral solubility diagrams indicate that PO_4 solubility at equilibrium in alkaline soils is controlled by Ca-phosphate minerals

while phosphate solubility in acidic soils is controlled by Fe- and Al-phosphates (Lindsay, 1979). On the other hand, dispersive x-ray analysis of P-rich particles from heavily-fertilized soils indicated that Al not Ca was the predominant cation associated with P, regardless of soil pH (Pierzynski et al., 1990). Physical evidence on the chemical speciation of P in calcareous soils, such as that can be obtained from x-ray absorption near-edge structure (XANES) spectroscopy data, may prove invaluable in accepting or refuting the concept of Fe-P compounds contributing to P retention in these soils. This data may also shed light on the reliability of chemical P fractionation procedures. Recent studies have used XANES spectra to identify P species in alum amended poultry litter ($\approx 20,000 \text{ mg P kg}^{-1}$), in extremely high saturated P enriched soils ($1,223 - 2,076 \text{ mg P kg}^{-1}$), and also to partition P sorption between Fe and Al oxides (Maguire et al., 2000; Beauchemin et al., 2003; Khare et al., 2004). To date XAFS data has not been used to speciate P compounds in calcareous soils with common to moderately high total P levels ($\approx 250 - 650 \text{ mg P kg}^{-1}$). The objectives of this study were to: (i) obtain a collection of XANES spectra representing common soil P compounds; (ii) identify unique spectral features which may be used to differentiate soil P compounds; (iii) determine the P speciation of selected calcareous Louisiana soils by modeling XANES spectra using principal component analysis (PCA), target transformation, and least-squares linear combination fitting (LCF) analysis; and (iv) to compare the P speciation obtained using XANES analysis with the P speciation obtained using a sequential chemical P fractionation procedure.

3.1.2 XANES

X-ray adsorption fine structure spectroscopy (XAFS) is a powerful analytical technique which can provide information on the local chemical and structural environment of an individual elemental species. The procedure is powerful enough to probe individual elements in complex heterogeneous materials such as soils (Fendorf et al., 1994; Fendorf and Sparks, 1996). The XAFS technique has important advantages over other commonly used analytical techniques. One advantage is that it can be used on soil samples *in situ*. Although, other atomic and molecular-level techniques are also available for soil science research, those techniques are considered invasive since the experiments require modification of the sample environment such as heating, vacuum, desiccation, and particle bombardment (Sparks, 2003). Another advantage of XAFS is that it probes the local surroundings of an element which allows the study of amorphous materials and solution species which do not have long-range order (Fendorf et al., 1994). This is a limitation to the x-ray diffraction technique which requires the sample to have a highly ordered crystalline structure. Therefore, since soils contain both crystalline and amorphous mineral species this makes XAFS an important tool when examining the less crystalline soil components. Depending on the energy range of spectra analysis, XANES can be further classified into two major techniques. When only the region of a XAFS spectrum near the adsorption edge is considered the technique is referred as x-ray absorption near-edge spectroscopy (XANES) analysis. When the region of a XAFS spectrum beyond is beyond the absorption near-edge, the technique is called extended x-ray adsorption fine-structure spectroscopy (EXAFS). The use of XANES analysis is

becoming more common in soil and sediment research (Beauchemin et al., 2002; Peak et al., 2002; Beauchemin et al., 2003; Khare et al, 2004).

Good reviews on the principles of XAFS and XANES are available (Durham, 1988; Fendorf et al., 1994; Fendorf and Sparks, 1996). These reviews contain detailed information on the multiple-scattering theory. Only a brief introduction to XANES analysis will be discussed here. When x-rays strike their target, a soil sample in our case, the photon transfers its energy to an electron of the absorbing material. When the incident photon energy equals the electron binding energy of the core electron, adsorption takes place and ejects the electron from the atomic shell of the element into the continuum creating a photoelectron (Fendorf and Sparks, 1996). The energy where this occurs is often called the binding energy or the adsorption edge of the element. Every element has its unique binding energy (absorption edge). For example, the adsorption K-edge (energy need to eject an electron from the K shell, the innermost electron orbital) for phosphorus is 2149 eV. As obtaining XANES adsorption spectrum for a sample, we measure the adsorption over a range of energies which encompass the binding energy (absorption edge). A XANES spectrum contains a pre-edge and post-edge region. The pre-edge is approximately 10 eV before the edge while the post-edge region extends approximately 50 eV past the edge. The region past 50 eV is generally the focus of EXAFS analysis. The resulting XANES spectrum of the sample is a unique “fingerprint” of the element of interest. XANES is strongly sensitive to oxidation state and coordination chemistry of a selected atom. Spectral feature comparisons of unknown samples with standard spectra and linear combination fitting of XANES spectra with the

spectra of known compositions are the techniques used for the qualitative and semi-qualitative speciation of an unknown sample.

Signal detection in XANES experiments can be determined by both transmission and fluorescence modes. Transmission detection measures the x-rays which are transmitted through the sample. Transmission detection can be expressed as,

$$I_t = I_0 \exp(-\mu\chi) \quad [3.01]$$

Upon rearrangement it can be expressed as,

$$\ln\left(\frac{I_0}{I_t}\right) = \mu\chi \quad [3.02]$$

where I_t is the transmitted intensity, I_0 is the incident x-ray intensity, χ is the sample thickness, and μ is the materials absorption coefficient. Fluorescence detection measures x-rays which are emitted due to the absorption of the incident x-ray beam (Sparks, 2003). Since fluorescence detection is unaffected by the energy decay of the ring, it can be expressed as,

$$\frac{I_f}{I_0} = \mu\chi \quad [3.03]$$

Fluorescence detection is more sensitive than transmission detection and is the preferred method for characterizing elements like phosphorus which are contained in low concentrations in soils (Brown et al., 1995; Sparks, 2003).

3.2 Materials and Methods

3.2.1 Soil Sample Collection and Characterization

Chemical fractionation and XANES analysis were performed on four mildly calcareous and a near neutral poultry litter amended soil. Soil samples were collected in Louisiana and represent important agricultural soils from across the state. The calcareous

soils included: Commerce (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts; 32°39' N and 91°13' W) a Mississippi River alluvial, Norwood (Fine-silty, mixed, superactive, hyperthermic Fluventic Eutrudepts; 31°10' N and 92°24' W) a Red River alluvial, Jeanerette (Fine-silty, mixed, superactive, hyperthermic Typic Argiaquolls; 29°57' N and 91°55' W) a Loess Hills, and the Mer Rouge (Fine-silty, mixed, superactive, thermic Typic Argiudolls; 32°38' N and 91°50' W) a Ouachita River alluvial. A near neutral Savannah (Fine-loamy, siliceous, semiactive, thermic Typic Fragiudults) an upland Southern Coastal Plain soil was also included in the study. The Savannah received over ten years of poultry litter application and consequently had a very high total P concentration. The composite soil samples were taken from the A_p surface horizon at a depth of 0-15 cm. The samples were air-dried and ground to pass a 2-mm sieve before chemical analysis. Soil particle size analysis was determined by the pipette method (Gee and Bauder, 1986), organic matter (OM) content by the Walkley-Black method (Walkley, 1947), pH at a 1:1 soil/water ratio, and CEC by saturating the soil with 1 M NH₄OAc at pH 7 followed by distillation and titration (Soil Survey Laboratory Methods Manual, 1996). Phosphorus was also partitioned into various extractable P forms using a sequential P fractionation procedure (Kuo, 1996). The sequence used a 1:50 soil to solution ratio and proceeded in the following order, 0.1 N NaOH + 1 M NaCl (17 hr. shake), 0.3 M Na₃C₆H₅O₇ + 1 M NaHCO₃ + Na₂S₂O₄, 1 M HCl, and 18 M H₂SO₄ + 28.9 M HF + 30% H₂O₂. The targeted P forms were: (i) NaOH-P, representing Fe- and Al-P compounds release by hydrolysis and may also include organic P from humic compounds; (ii) CBD -P, representing reductant soluble Fe-P; (iii)

HCl-P, representing stable Ca phosphates; and (iv) Residual-P, representing inorganic and organic P forms.

3.2.2 Phosphorus Standards for X-ray Absorption Near-Edge Structure Spectroscopy

The P reference compounds were selected to represent the dominant P species commonly found in soils. The reference compounds were generally classified into five general categories representing Fe, Al, Ca, and organic-P species, as well as P sorbed to various metal oxides and carbonate surfaces. The Fe phosphates included a reagent grade FePO_4 (Sigma-Aldrich), determined to be noncrystalline by x-ray diffraction (XRD), and a more crystalline strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) which was made hydro-thermally with nitrate salts of Fe and PO_4 for 60 days (Hsu, 1982). The Al-phosphates samples included a reagent grade berlinite (AlPO_4) obtained from Sigma-Aldrich and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) synthetically made with nitrate salts of Al and PO_4 aged for 60 days (Hsu and Sikora, 1993). Calcium phosphate standards included: brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), calcium dihydrogen phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$], hydroxyapatite [$\text{Ca}_5\text{OH}(\text{PO}_4)_3$], and calcium hydroxyphosphate ($\text{H}_2\text{Ca}_{10}\text{O}_{26}\text{P}_6$) all obtained from Sigma-Aldrich and fluorapatite [$\text{Ca}_5\text{F}(\text{PO}_4)_3$] which was obtained from Wards. Organic phosphate standards included calcium phytate (National Biochemical) and sodium phytate (Sigma-Aldrich). The sorbed phosphate standards were prepared by equilibrating 2 g of the metal oxide with 20 mL of 0.01 M KCl containing 1200 $\mu\text{g P mL}^{-1}$ as KH_2PO_4 in 30 mL centrifuge tubes. The samples were then shaken on a reciprocating shaker at $25 \pm 0.5^\circ\text{C}$ for 24 hours. The metal oxides included hematite (Fe_2O_3), goethite (FeOOH), pyrolusite (MnO_2), gibbsite ($\text{Al}(\text{OH})_3$), and calcium carbonate (CaCO_3) all from Sigma-Aldrich. Ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) was obtained from a water treatment facility and was confirmed to be

two line ferrihydrite by x-ray diffraction analysis (data not shown). Potassium phosphate (KH_2PO_4), obtained from Fisher Scientific was also included in the XANES analysis. All metal oxide samples and the carbonate sample were finely ground by mortar and pestle before the sorption procedures.

3.2.3 X-Ray Absorption Near-Edge Structure Spectroscopy Analysis

The P K-XANES spectra were collected at the Double Crystal Monochromator (DCM) beamline at the Louisiana State University Center for Advanced Microstructures & Devices (CAMD) synchrotron research facility in Baton Rouge, Louisiana. The DCM was equipped with two InSb (111) crystals that were slightly detuned. The electron beam energy operated at 1.3 GeV. All samples were collected with beam current ranging from 180 – 90 mA. Phosphate standard spectra were first collected in transmission using two in-line ionization chambers equipped with Keithley 428 current amplifiers. Spectra were also collected in fluorescence mode using a Canberra 13 element ultra low energy germanium diode array detector. All spectra were detected in an enclosed He environment. The P K-XANES spectral data for standards and soil samples were collected with a resolution of 3 eV with a 2 sec. integration time over the pre- and post-edge regions (2050-2140 and 2175-2250 eV respectively), while a resolution of 0.2 eV with a 15 sec. integration time was used encompassing the P K-XANES edge (2140-2170 eV). The monochromator was calibrated by setting the energy of the maximum of the first peak of the first derivative spectrum of a reagent grade AlPO_4 (berlinite) standard to 2149 eV. Mineral and soil samples were mounted as thin films on Kapton tape. Sorbed P standards were spread on Kapton tape as a hydrated paste and covered by a second piece to prevent contamination of the fluorescence detector. After acquisition of the

initial fluorescence XANES spectral data, the data from each of the 13 fluorescence channels were averaged in Excel to produce one spectra. The resulting spectra were then background corrected using a first ordered polynomial in the pre-edge region and then normalized by setting the absorption to 1 at approximately 35 eV above the edge (2175 eV) using the WinXAS 3.02 software. Multiple scans of both standards and soil samples were collected and averaged to produce the final spectra.

3.2.4 Principal Component Analysis and Target Transformation

Principal component analysis was performed on each soil spectra in order to determine the number of orthogonal components which are mathematically adequate to reconstruct the spectra from our collection of phosphate standard spectra in a linear combination. Once PCA identified the number of orthogonal components, target transformation was used to determine the most likely species from our data set. The objective of PCA and target transformation was to quickly determine the components to use for least-squares linear combination fitting (LCF) without trying every combination of our 17 total standard P species (Beauchemin et al., 2002). Briefly, PCA defines the number of significant independent sources of variation (our set of 17 P K-XANES standards) which can be used to regenerate an experimental data set (our soil P K-XANES data). The components which are not chosen in the recombination of the spectra are considered to be noise. The PCA analysis assumes that the XANES spectra can be defined as a linear combination of the P standards with each P standard being weighted differently. The spectral soil data matrix can be expressed as the product of two matrices as seen in Equation [3.04] below:

$$D = X Y \quad [3.04]$$

where, X is the matrix of independent spectral features and Y is the matrix of the relative contributions of the independent features. The X and Y matrices are then decomposed into an abstract eigen-spectra matrix and an abstract eigenvector matrix as seen in Equation [3.05] below:

$$D = R C \quad [3.05]$$

where, R and C are purely mathematical solutions and do not have any chemical or physical meaning. The eigenspectra matrix (R) and eigenvector matrix (C) can be determined by several different mathematical algorithms. In our case PCA was done in the Sam's Interface for XAS Package (SIXPack) software which utilizes the singular value decomposition (SVD) method. Further details of PCA analysis theory and the mathematical solutions are described in detail by Malinowski (2002). The output data produced by PCA analysis includes eigenvalues, variance, cumulative variance and the factor indicator (*IND*) function. Eigenvalues correspond to the representative variance in the data matrix explained by a certain component. The *IND* function is an empirical function and can be determined according to:

$$IND = \frac{RE}{(c - n)^2} \quad [3]$$

where, *RE* is real error, *c* is columns and *n* is the number of components. The *IND* function reaches a minimum when the correct number of significant components is determined.

3.2.5 Target Transformation

Once the number of components is determined, *n*, target transformation can be used to reproduce the data matrix (D). Target transformation redefines the abstract eigenvectors and eigenspectra into chemically meaningful solution using an oblique

rotation of the axis (Beauchemin et al., 2002). Statistical output obtained from target transformation includes the χ^2 , R and *SPOIL* functions. We used the *SPOIL* value to make the final determination of the components to use in our linear combination fitting. When the *SPOIL* function is less than 1, the reproduced data matrix is improved by the component (Malinowski, 2002). A *SPOIL* function above 1 is said to “spoil” the data matrix. Generally, the larger the *SPOIL* value the more the data matrix will be “spoiled” by the target component. Malinowski (2002) defined the following *SPOIL* categories: < 1 the component is a best fit; 1 – 3 the component acceptable fit; 3 – 6 indicates a moderately acceptable component and; > 6 the component is not acceptable because it will introduce excessive error into the reproduced data matrix. Target transformation, like PCA, was also done in the SIXPack software package. Both analyses were carried out on the P K-XANES spectra from an energy range 2139 to 2169 eV.

3.2.6 Least-Squares Linear Combination Fitting

After the of the number of standard components and the acceptable standard components were determination using PCA and target transformation respectively, least-squares LCF was used to model the P K-XANES soil spectra. Least-squares LCF were done using the SIXPack software with a spectral energy range of 2139 – 2169 eV for each soil. The number of orthogonal components used in the fitting was determined by PCA. The specific P standard components used in the fitting were those components which had the lowest *SPOIL* value as determined by target transformation. The spectral data was allowed to shift during the fitting however the fits were considered unacceptable if the energy offset parameter was greater than ± 1 eV (Beauchemin et al., 2003). The data was not corrected for self absorption. Weighing factors were not allowed to be

negative and not forced to sum to one. Relative percentages of the components were determined normalizing the weighing factors to one. An equation could be written of the resulting least-squares fit. An example of a quaternary least-squares LCF could be summarized by the following general equation:

$$Y_{fit}(E) = m_1(X_1 - a_1Y_1) + m_2(X_2 - a_2Y_2) + m_3(X_3 - a_3Y_3) + m_4(X_4 - a_4Y_4) \quad [4]$$

where, $Y_{fit}(E)$ is the LCF of the P K-XANES soil spectra, X_i and Y_i are energy and the normalized absorbance of the P standard components ($i = 1 - 4$ for a quaternary fit) respectively, and m_i is the relative contribution (percentage) of each P standard component to the overall fit, and a_i is the fitted energy shift of each standard (Beuchemin et al., 2002).

The chi-square test statistic, χ^2 , was used to determine the “goodness of fit” of the fit soil spectra. The chi-square value is determined according to Equation [5] below

$$\chi^2 = \sum_{ij} \frac{(n_{ij} - E_{ij})^2}{E_{ij}} \quad [5]$$

where $i = 1, \dots, r, j = 1, \dots, c, n_{ij}$ = observed frequency for cell ij , and E_{ij} = expected frequency for cell ij . The degree of freedom is calculated by $(r - 1)(c - 1)$. The reproduced least-squares fit XANES spectrum has 100 absorbance data points from the 2139 – 2169 eV data range (rows) and 2 columns, therefore the critical value at $\alpha = 0.05$ is, $\chi^2_{0.05,99} = 123$. A χ^2 value above this critical level would reject the null hypothesis, that the least-square fit spectrum is identical to the soil spectrum and confirm that the alternative hypothesis, that the fit spectrum and the soil spectrum are different, is true.

This would indicate that the soil spectrum could not be fit with our collection of P standards. Indeed, the lower the χ^2 value the better the fit.

3.3 Results and Discussion

3.3.1 Soil Characteristics and Sequential P Fractions

The four calcareous soils and the neutral poultry litter amended soil exhibited quite different physical and chemical characteristics (Table 3.01). The pH ranged from 6.8 to 7.9. The carbonate content of the calcareous soils ranged from approximately 0.9 – 3.9 %. Indeed, these soils are only mildly calcareous in nature. The organic matter (OM) content of these soils ranged from 6 – 69 g kg⁻¹ in the A_p horizon. Notably, the Savannah soil had a much greater organic matter content as compared to the other soils in the study reflecting the numerous applications of poultry litter to this soil. The cation exchange capacity ranged from 17 – 4.9 cmol_c kg⁻¹. Notably, the Savannah soil had a lower CEC as compared to the calcareous soils which would not be expected since it contained a much larger OM content. However, the low CEC may be a reflection of the sandy texture of the Savannah soil.

The results of the sequential P fractionation procedure can be seen in Table 3.01. The number reported in the parentheses represents the percentage of the fraction from the total P removed by the fractionation procedure. The relative content of each fraction varied between soils. Generally, HCl-P fraction was the dominant P fraction in all the calcareous soils (discounting residual-P) and ranged from 42 – 65%. This would suggest that the P in these calcareous soils is primarily associated with Ca-P phases such as stable apatite like minerals and only secondarily associated with Fe-/Al-P phases. The poultry litter amended soil however, had a slightly higher CBD-P fraction content (43%), as

compared to the HCl-P fraction (38%). This suggests that the P associated with this soil is associated to a slightly higher degree to P that is interrelated with reductant soluble Fe, such as P occluded with in Fe oxide coatings.

3.3.2 XANES Analysis of P Standards

Normalized P K-XANES spectra of common phosphate minerals and phosphate sorbed to Fe, Al, and Mn oxides as well as CaCO_3 are presented in Figs. 3.01 – 3.06. The spectra of the Fe-phosphate standards (Fig. 3.01) revealed a distinctive pre-edge feature which can be found at approximately 2-3 eV before the main absorption edge. This feature was more distinct and intense in the more crystalline strengite standard as compared to the amorphous FePO_4 standard. This feature is said to represent the electron transition of a phosphorus 1s electron into an Fe (3d)-O(2p)-P(3p) antibonding molecular orbital or an Fe(4p)-O(2p) antibonding molecular orbital (Franke and Hormes, 1995; Khare et al., 2004). The Fe-phosphate standards also exhibited a large post-edge oscillation at near 2167 eV. Similar Fe phosphate XANES features were identified by others (Hesterberg, et al., 1999). The Al-phosphate samples, variscite and berlinite, both displayed two post-edge oscillations at approximately 2159 and 2167 eV, with the prior feature being less intense than the latter. The more defined post-edge oscillations were seen for the synthetically made variscite as compared to the purchased berlinite. This may suggest that the variscite, although hydrated, may be more crystalline in nature than the non-hydrated berlinite. Hesterberg and co-workers (1999) found a weak pre-edge inflection 1 eV before the edge (approximately 2148 eV), similar to the pre-edge feature of the Fe phosphate minerals. This inflection point was said to be more easily distinguishable in a first-derivative plot of the spectra. However, this inflection point was

Table 3.01 Selected chemical and physical properties for four calcareous soils and one near neutral poultry litter amended soil[†].

| Soil | Depth | pH | Sand | Silt | Clay | OM | CCE | CEC | sequential P fractions | | | |
|--------------------------------|-------|-----|-------------------------------|------|------|------|------------------------------------|------|------------------------|-----------|----------|------------|
| | | | | | | | | | NaOH-P | CBD-P | HCl-P | Residual-P |
| | cm | | -----g kg ⁻¹ ----- | | | | cmol _c kg ⁻¹ | | | | | |
| Commerce | 0-15 | 7.4 | 37 | 650 | 313 | 21.2 | 12.5 | 13.7 | 55 (9) [‡] | 139 (22) | 268 (42) | 181 (28) |
| Mer Rouge | 0-15 | 7.2 | 261 | 517 | 222 | 13.2 | 8.9 | 8.3 | 64 (21) | 23 (8) | 85 (28) | 126 (42) |
| Jeanerette | 0-15 | 7.9 | 83 | 609 | 308 | 9.8 | 38.0 | 17.0 | 9 (2) | 36 (8) | 261 (57) | 152 (33) |
| Norwood (Silt Loam) | 0-15 | 7.9 | 18 | 841 | 142 | 6.0 | 38.5 | 4.9 | 20 (4) | 29 (6) | 339 (65) | 133 (26) |
| Savannah (Poultry Litter Soil) | 0-15 | 6.8 | 525 | 343 | 132 | 69.0 | -- | 9.1 | 486 (19) | 1091 (43) | 960 (38) | -- |

[†] OM, organic matter; CEC, cation exchange capacity. Data are means of two replicates. Standard error <5% for all samples (data not shown).

[‡] The number parentheses represent the percentage of each fraction.

not seen in our Al phosphate spectra or the first-derivative spectra (Figs. 3.02 and 3.03 respectively) or in work by others (Peak et al., 2002). None the less, the two post white-line oscillations make the Al phosphate minerals easily distinguishable from the Fe phosphates. The Ca phosphates standard spectra had 3 distinct XANES spectral features (Fig 3.04). The first was a post-edge shoulder at approximately 2151 eV which is unique to the Ca-phosphate minerals. The other two post-edge oscillations (approximately 2165 and 2170 eV) are similar to the post edge-features seen in the Al-P standards however; the 2165 eV peak is much more intense in the Ca-phosphates as compared to the Al-phosphates. The position of the features found on the Ca phosphate mineral spectra are very similar to the spectra reported by others (Hesterberg, et al., 1999; Peak et al., 2002). Possible organic phosphates were represented by Na and Ca phytate and can be seen in Fig 3.05. Both phytate samples have a single post-edge feature at approximately 2167 eV similar to the Fe-P standards however, the phytate samples can be distinguished from the later since they are devoid of the unique Fe-P pre-edge feature. They are also distinguishable from the Al and Ca phosphate minerals since the organic P standard only have one post-edge oscillation. Standard spectra for phosphates sorbed to various Fe, Al, and Mn oxide minerals as well as phosphate sorbed to calcium carbonate can be seen in Fig. 3.06. All sorbed phosphate species displayed a broadened white-line peak similar to the organic phosphate standards. Each of the metal oxide sorbed phosphate species contained only one broad post-edge oscillation at 2167 eV identical to the organic P spectra. The sorbed phosphate standards can be readily distinguished from crystalline Fe, Al, and Ca-P standard spectra however they may not be distinguishable from the organic P standard spectra. Similarly, others found that quantitatively distinguishing among free

inorganic P, weakly bound P, and organic P to be difficult since they do not have any distinct spectral features (Peak et al., 2002; Toor et al., 2005). However, the phosphate sorbed to the surface of CaCO_3 , unlike the metal oxide sorbed and organic P, retained the post-edge shoulder and the two post-edge oscillations found on all crystalline Ca-phosphate minerals. These features make the CaCO_3 sorbed species distinguishable from other sorbed species. It should be pointed out however, that the pre- and post-edge features of the phosphate sorbed to CaCO_3 were not well defined as compared to the features of Ca-phosphate minerals reflecting the surface amorphous nature. A potassium phosphate spectra, was included in our group of reference standards since it was the source of the background P sorption solution (Fig 3.05). Generally, potassium phosphate had two post-edge features similar to the Al-phosphate standards although the 2165 eV oscillation was much broader and intense making it easily identifiable. The potassium phosphate spectra also differed from the phosphate sorbed metal oxides as well as the CaCO_3 sorbed species. This suggests that the spectral features of all P-sorbed species were due to the surface coordination of phosphate with other metals and not due to potassium phosphate salt itself.

3.3.3 XANES Analysis of Soils

Stacked phosphorus K-XANES spectra all soils used in this study can be seen in Fig. 3.07. Due to the combined effect of the low P concentration and interferences from other elements in the matrix, the XANES spectra of the soil samples were somewhat noisier than the pure mineral standards. The absorption signal of the poultry litter amended soil contained less noise and had a more intense white line peak as compared to the unamended soils. The cleaner signal and more intense peak are from the

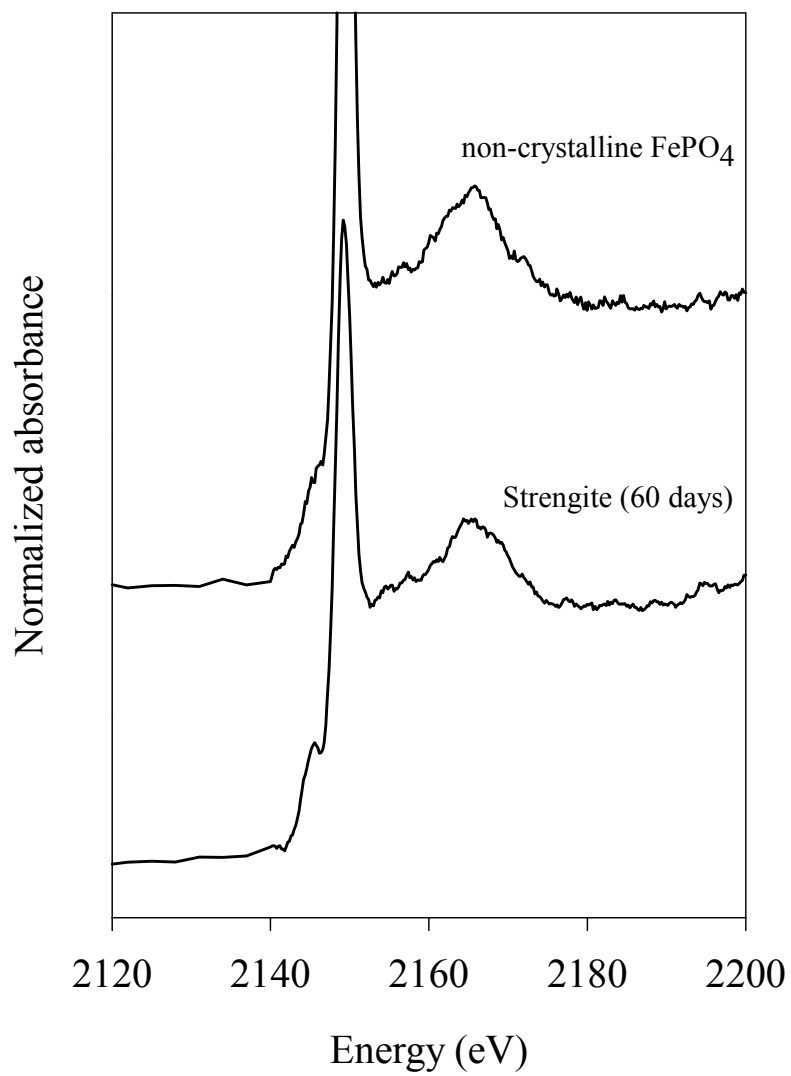


Figure 3.01 Normalized P K-XANES spectra for iron phosphate compounds.

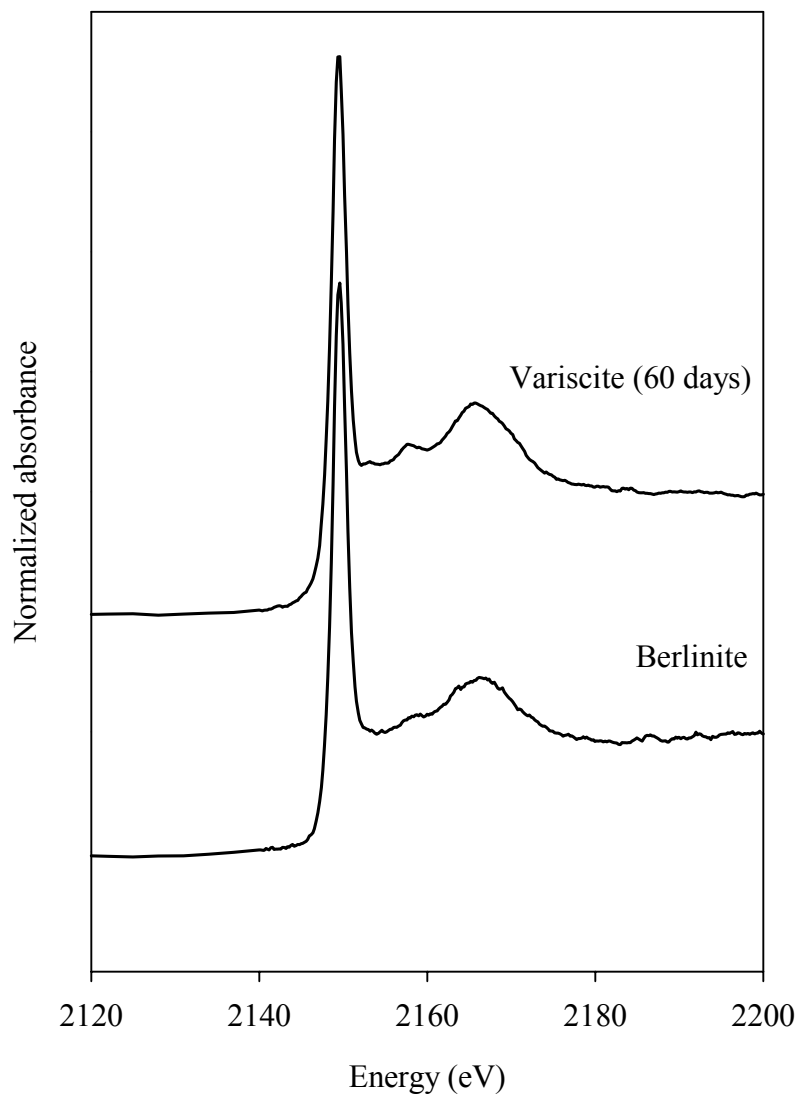


Figure 3.02 Normalized P K-XANES spectra for aluminum phosphate compounds.

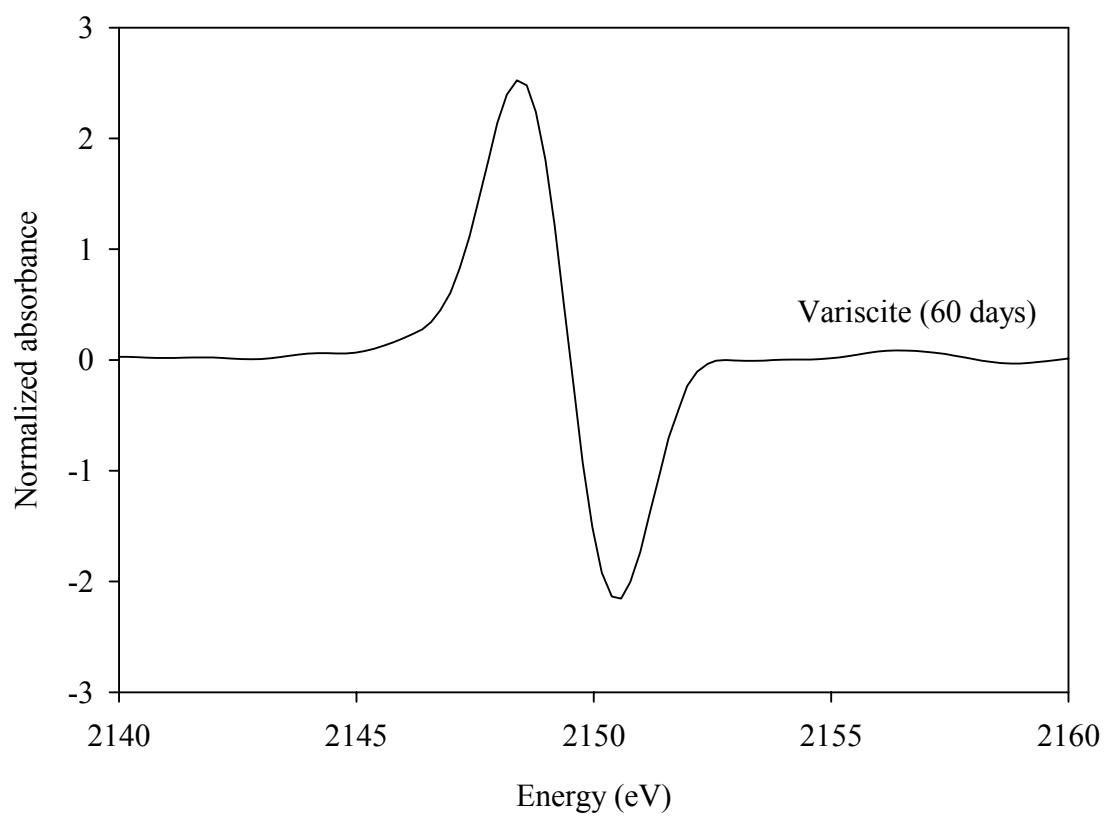


Figure 3.03 Normalized first-derivative P K-XANES spectra for variscite.

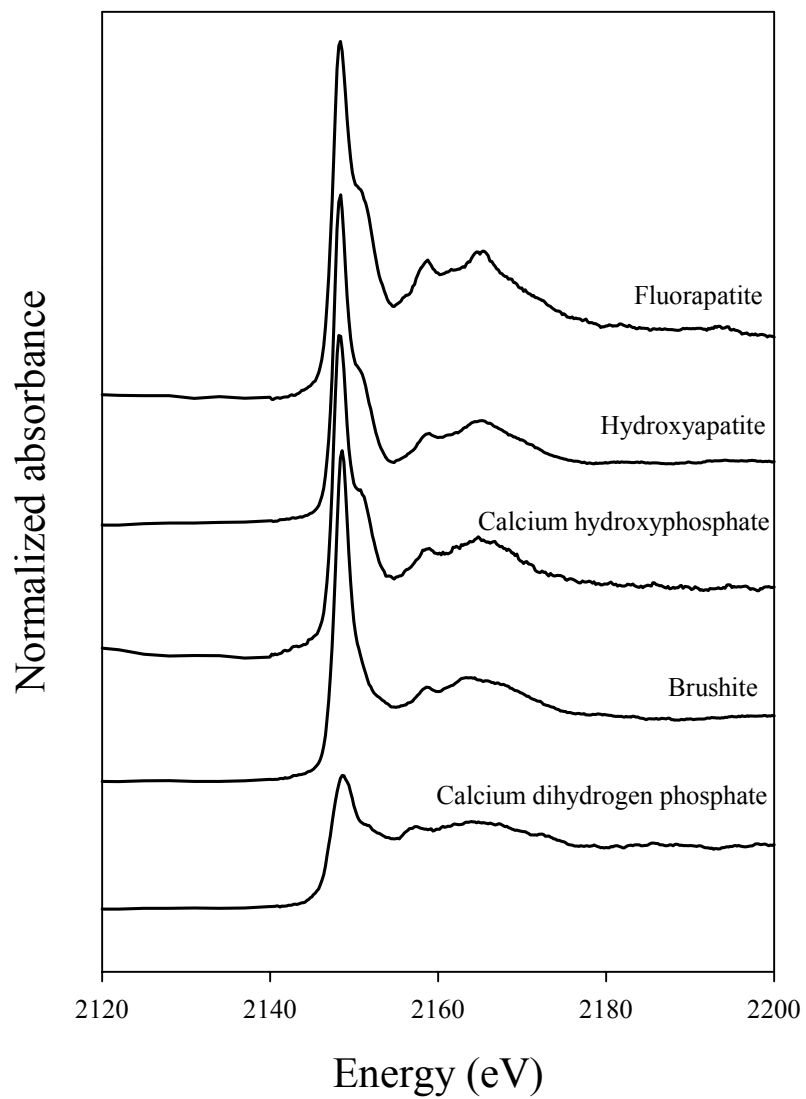


Figure 3.04 Normalized P K-XANES spectra for calcium phosphate compounds.

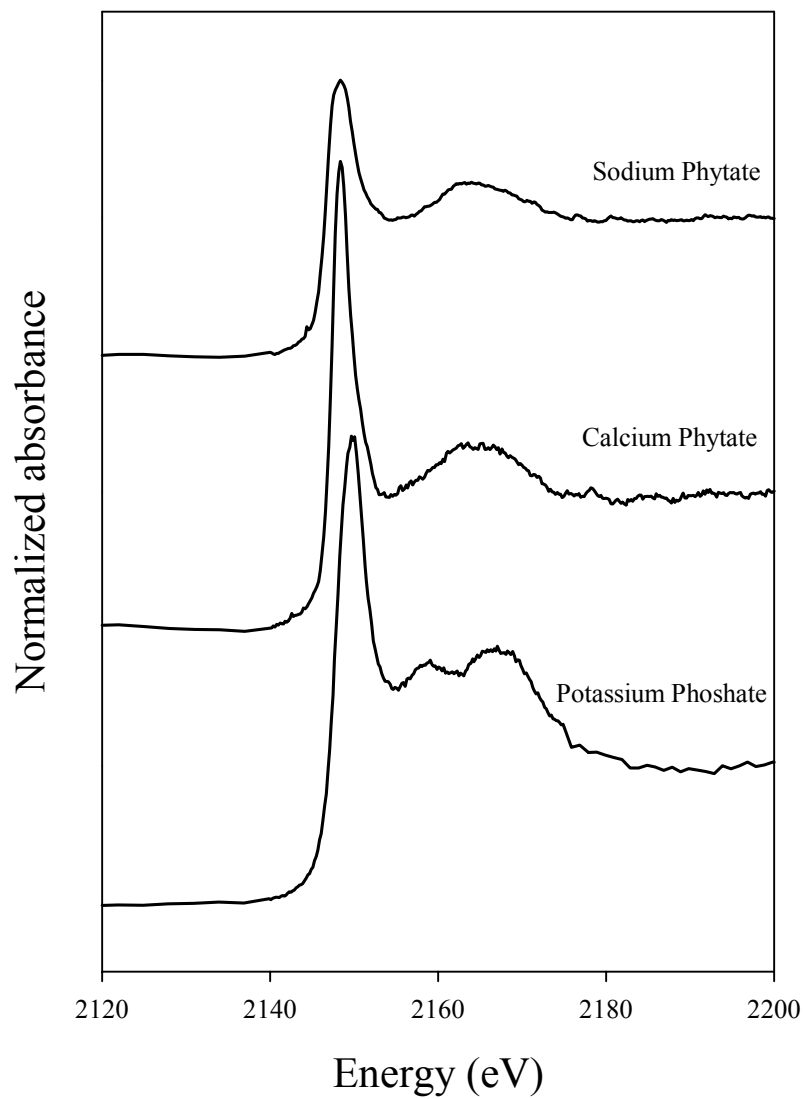


Figure 3.05 Normalized P K-XANES spectra for organic phosphate compounds and potassium phosphate.

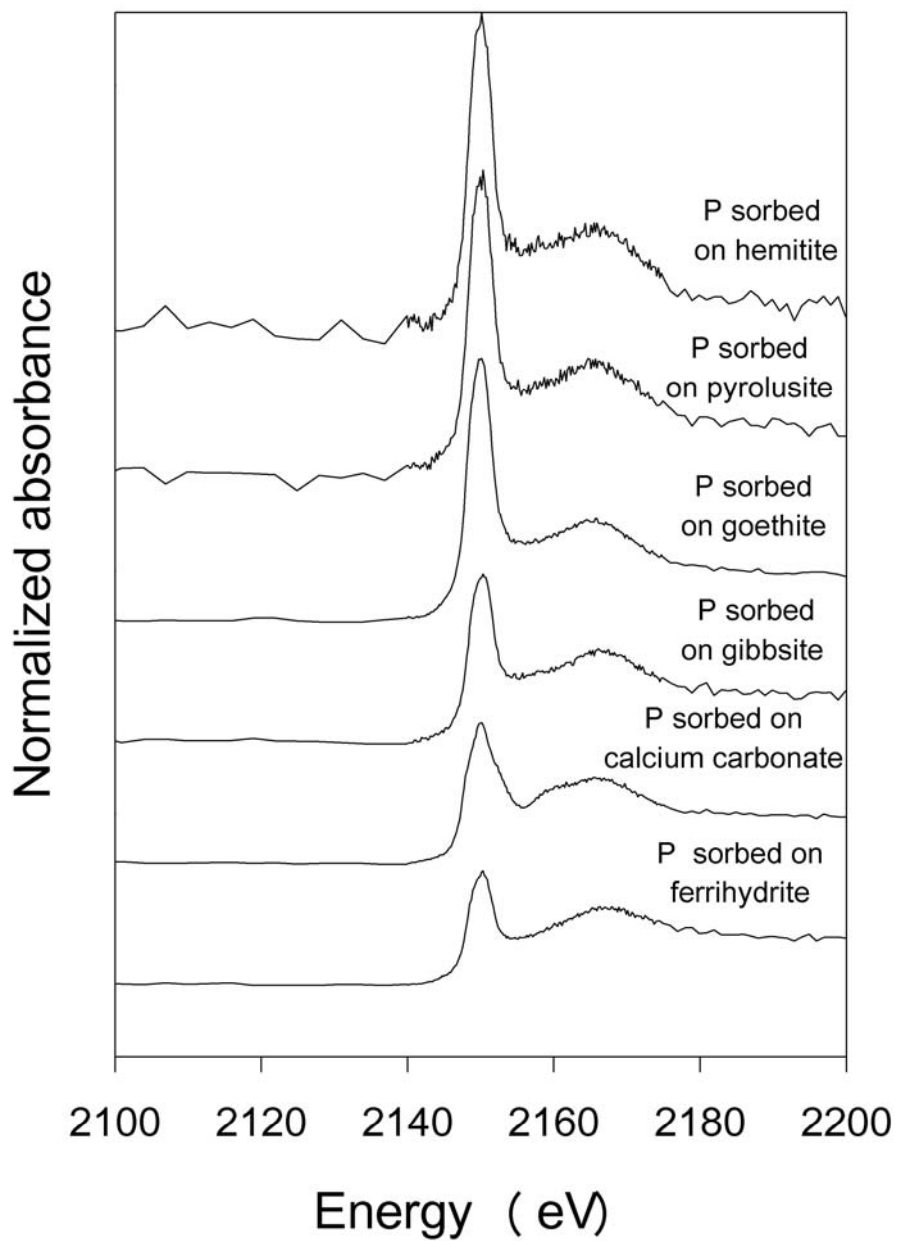


Figure 3.06 Normalized P K-XANES spectra for phosphate sorbed on various Fe and Al metal oxides along with P sorbed on calcium carbonate.

higher total P content in the Savannah soil due to the years of poultry litter application. Although noisy, subtle differences could still be seen between soil samples. For example, a possible Fe phosphate pre-edge feature could be seen for the Commerce soil at approximately 2145 eV but was not seen on the other two spectra. Also, the Norwood, Commerce and Savannah soils had a broadened white line peak as compared to the Mer Rouge and Jeanerette soils and are similar to the sorbed phosphate species suggesting that P in these soils is dominated in poorly crystalline forms.

The results of the PCA and target transformation analysis for the Jeanerette soil can be seen in Table 3.02. The *IND* variable was at a minimum after addition of the fifth orthogonal component indicating that it would take five of our standard species to adequately describe the variance of the normalized P K-XANES Jeanerette soil spectra. This was also the case for the rest of the soils in used in this experiment (data not shown). Target transformation retained almost all P standard species as acceptable fits for the soil spectra, those with *SPOIL* values < 3 . The standard representing phosphate sorbed on pyrolusite was the only P standard that was consistently considered to be only moderately acceptable via target transformation (*SPOIL* > 3). Similarly, PCA and target transformation analysis performed by others on P K-XANES of phosphorus enriched soils also found that all standards were likely components (Beauchemin et al., 2003) although, PCA and target transformation analysis was found to be adequate when working with S K-XANES spectra of humic acids (Beauchemin et al., 2002). In this study, we employed the criteria that only those species with *SPOIL* values < 1 , meaning the best fit components, were used for least-squares LCF (Malinowski, 2002). The least-squares LCF procedure was restricted to only five components suggested by PCA. In

most cases the number of species that had *SPOIL* values < 1 was five, corresponding to the five standards identified in PCA. However, in some cases there were more than five species with *SPOIL* values < 1, in these instances the standards with the lowest *SPOIL* values were used first.

The least-squares LCF of each soil sample can be seen in Fig. 3.08. The normalized relative proportions of each phosphate standard used to fit the P K-XANES spectra for the soil samples as determined by least-squares LCF can be seen in Table 3.03. The χ^2 values, indicating the goodness of fit, ranged from 13 – 73. The critical value, $\chi^2_{0.05,99} = 123$, in all cases was not exceeded indicating that the fit was not significantly different from the soil XANES spectra. Another indication of how well the LCF predicted the soil XANES spectra is by looking at the sum of fractions before normalization to 100%, which in a perfect scenario should sum to one. Good fits were still found by others with sums as low as 0.6 and 0.7 (Manceau et al., 2000; Beauchemin, 2003). In our case, the largest deviation from the sum of one was the Jeanerette soil which had a sum of 0.69.

In Table 3.03, the fitting results were combined into three general groups of phosphates species. The first group was the total phosphate sorbed on Fe or Al oxides plus organic phosphate. These species were grouped together because, as mentioned earlier, the resulting XANES spectra for the P sorbed onto metal oxides and the organic phosphate species could not be differentiated from each other. However, these species could be distinguished from the Ca-phosphates and crystalline Al and Fe species. The insensitivity in separating these species is illustrated with the second fitting of the Commerce and Norwood soil spectra where the P sorbed ferrihydrite standard was

substituted for the P sorbed gibbsite species. As a result of these secondary fittings, the percentage of total phosphate sorbed on Fe or Al oxide plus organic P category only slightly deviated from the original. For Commerce, it decreased from 78 to 75% while for Norwood, it increased from 77 to 79%. The goodness of fit, χ^2 , increased from 32 to 73 for the Commerce soil suggesting a lesser however not a unacceptable fit. The initial Norwood soil χ^2 value of 26 stayed almost identical after the second fitting with a value of 27. The second and third groups of phosphate species found in the least-squares fit results were the crystalline Al species, only represented by variscite, and the total Ca phosphates. No crystalline Fe phosphates were found in the initial fittings which were based on the results of the target transformation.

The Commerce and Norwood soil spectra were also fitted with hydroxyapatite substituted by P sorbed on CaCO_3 as shown in the third fitting (Table 3.03). This decision was made based on the observation that both the Norwood and Commerce soils had broadened white line peaks suggesting a large content of amorphous P, likely sorbed phosphate phases. As mentioned earlier the P sorbed on CaCO_3 could be distinguished from other sorbed P species as well as from well crystalline Ca phosphate minerals such as apatites. In addition this substitution was believed valid since it did not reject the Fe and Al sorbed P species indicated in the original model (fitting 1 in Table 3.03). The total percentage of calcium phosphate minerals in the first fitting was 22% for the Commerce soil and 23% for the Norwood soil. As a result, the total Ca associated increased from 22 to 66% and from 23 to 89% for the Commerce and Norwood soils respectively. For all soils, the estimation of Ca-P by least-squares LCF of XANES spectra was greater than the estimation of Ca-P by chemical fractionation using the HCl extraction. However, there

was a highly significant correlation ($R^2 = 0.89$, $P = 0.016$) between the percentage of total Ca phosphates determined from P K-XANES spectral fitting and the HCl-P fraction from the chemical fraction procedure (Fig. 3.9). Likewise, a significant correlation ($R^2 = 0.81$, $P = 0.0383$) was also seen between the sum of relative percentages of all Fe-/Al-P (sorbed and mineral) and organic P determined by least-squares LCF and the relative percentage of NaOH-P (Fig. 3.10). In addition the correlation ($R^2 = 0.74$, $P = 0.0624$) was observed between the sum of relative percentages of all Fe-/Al-P (sorbed and mineral) and organic P determined by least-squares LCF and the sum of the relative percentage of NaOH-P and CBD-P (Fig. 3.11). In the later cases, XANES fitting results also over estimated the total Fe-/Al-P plus organic P as compared to Fe-/Al-P estimated by chemical sequential P fractionation. One explanation of this divergence may be due to the large residual-P fraction obtained by the chemical P fractionation method (Table 3.01). This residual-P fraction includes highly insoluble Fe, Al, and Ca-P minerals which were not separable into their respective groups by chemical fractionation but were separable by LCF of XANES spectra. A previous study by Beauchemin et al. (2003) also found significant correlation between Ca-P determined by least-squares fitting of P K-XANES data and HCl-P ($r = 0.87$, $P = 0.05$) and that the XANES fitting results overestimated Ca-P as compared to the chemical fractionation in soils with very high P content. They also found a high correlation between NaOH-P from chemical fractionation and the sum of P related to Fe and/or P sorbed on Al by LCF of XANES analysis ($r = 0.99$, $P = 0.001$) and that XANES also over estimated Fe and Al-P as compared to chemical P fractionation. Overall, our results suggest that even though speciation by least-squares analysis of XANES spectra may not discriminate different

metal oxide-sorbed P species, it could separate general Fe-/Al-P from Ca-P phases as compared to chemical sequential fractionation procedures, which could not identify residual P forms.

It should be pointed out that in this study we employed *SPOIL* values of < 1 as our general criteria for choosing reference standards for target transformation and further LCF analysis as discussed earlier. By doing so we eliminated of trying other possible combination of any five standard species with *SPOIL* values > 1 for the best fit of those probably acceptable standards (Malinowski, 2002). In the study conducted by Beauchemin et al. (2003), they did run all possible combinations of three reference standards for the best fit to account for the insensitivity of PCA analysis but, the *SPOIL* values reported were much higher than ours and generally in the range of 3 to 6. If all combinations of probably acceptable standards were tried for the best fit of LCF analysis, it would have to test every five species (r) combination of our 17 standards (n) for a total of 6188 possible combinations exist as determined by $\left(\frac{n!}{r!(n-r)!}\right)$. A more efficient way to statistically eliminate those improper components for the used standard species in the LCF analysis would be needed. Nonetheless, in this study by employing the criteria of the *SPOIL* value < 1 as a guideline for choosing the most statistically significant standards as fitting components, it simplified the LCF process reasonably.

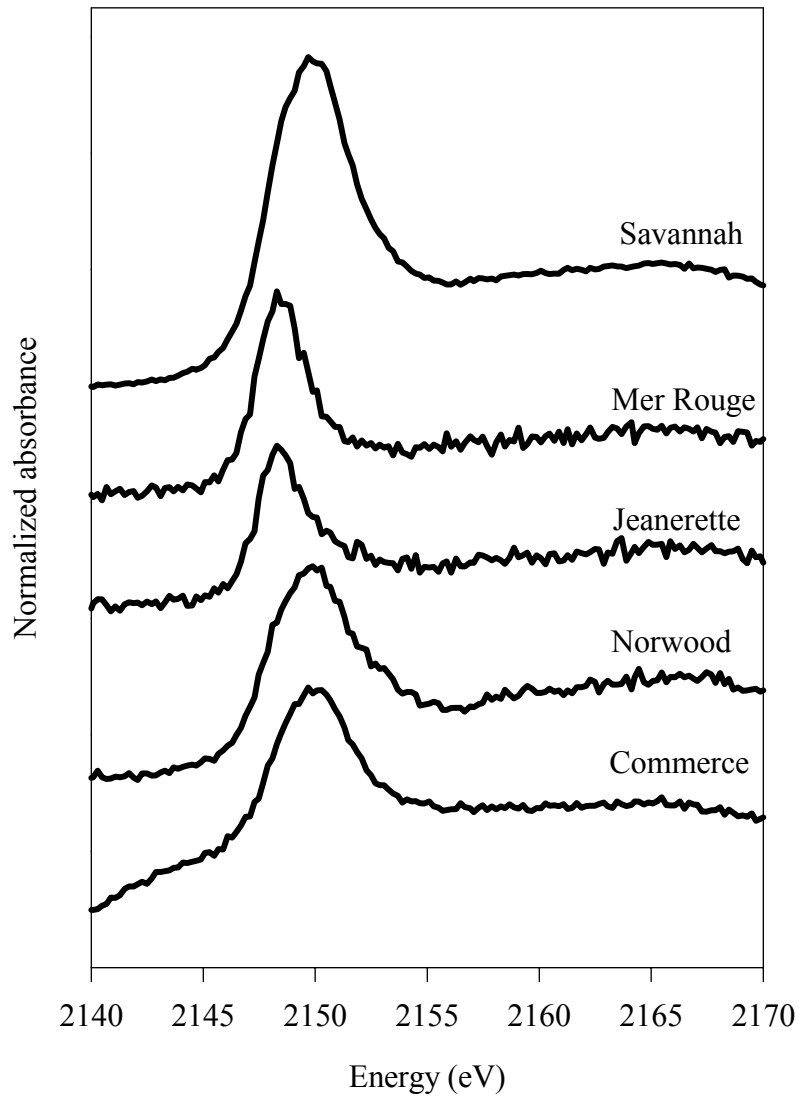


Figure 3.07 Normalized P K-XANES spectra for four calcareous soils and one poultry litter amended Savannah soil.

Table 3.02 Results of PCA and target transformation analysis for the Jeanerette spectra modeled from 2139 to 2169 eV.

| Component | PCA | | | | | target transformation | | |
|-----------|---------|-------|----------|---------|-------------------------------|-----------------------|---------|--------|
| | Eigen | Var | Cum Var. | IND | | X^2 | R | SPOIL |
| 1 | 139.174 | 0.705 | 0.705 | 0.02620 | Variscite | 0.88722 | 0.00120 | 0.0000 |
| 2 | 22.060 | 0.111 | 0.817 | 0.01753 | Fluorapatite | 1.32139 | 0.00094 | 1.3741 |
| 3 | 12.486 | 0.063 | 0.880 | 0.01200 | P sorbed on CaCO ₃ | 1.21172 | 0.00178 | 1.4500 |
| 4 | 6.773 | 0.034 | 0.915 | 0.00923 | Calcium Phytate | 0.72972 | 0.00139 | 1.3389 |
| 5 | 3.429 | 0.017 | 0.932 | 0.00894 | Brushite | 1.26391 | 0.00152 | 1.1953 |
| 6 | 2.368 | 0.012 | 0.944 | 0.00942 | P sorbed on Ferrihydrite | 1.67467 | 0.00385 | 1.7806 |
| 7 | 1.944 | 0.009 | 0.954 | 0.01026 | P sorbed on Gibbsite | 0.65135 | 0.00082 | 0.7291 |
| 8 | 1.823 | 0.009 | 0.963 | 0.01105 | P sorbed on Goethite | 1.25828 | 0.00086 | 2.6061 |
| 9 | 1.597 | 0.008 | 0.971 | 0.01192 | Hydroxyapatite | 0.56175 | 0.00066 | 0.4780 |
| 10 | 1.192 | 0.006 | 0.977 | 0.01387 | P sorbed on Hemite | 0.78719 | 0.00011 | 0.0000 |
| 11 | 1.058 | 0.005 | 0.983 | 0.01649 | Potassium phosphate | 1.47646 | 0.00211 | 2.1335 |
| 12 | 0.861 | 0.004 | 0.987 | 0.02097 | Calcium dihydrogen phosphate | 0.92171 | 0.00124 | 1.3740 |
| 13 | 0.769 | 0.003 | 0.991 | 0.02763 | Sodium Phytate | 1.11075 | 0.00304 | 0.7445 |
| 14 | 0.567 | 0.002 | 0.994 | 0.04353 | Calcium hydroxyphosphate | 0.31864 | 0.00033 | 0.0000 |
| 15 | 0.488 | 0.002 | 0.996 | 0.08319 | P sorbed on pyrolusite | 2.46818 | 0.00133 | 2.9882 |
| 16 | 0.379 | 0.001 | 0.998 | 0.27781 | Strengite | 0.97729 | 0.00309 | 1.7124 |
| 17 | 0.277 | 0.001 | 1.000 | NA | | | | |

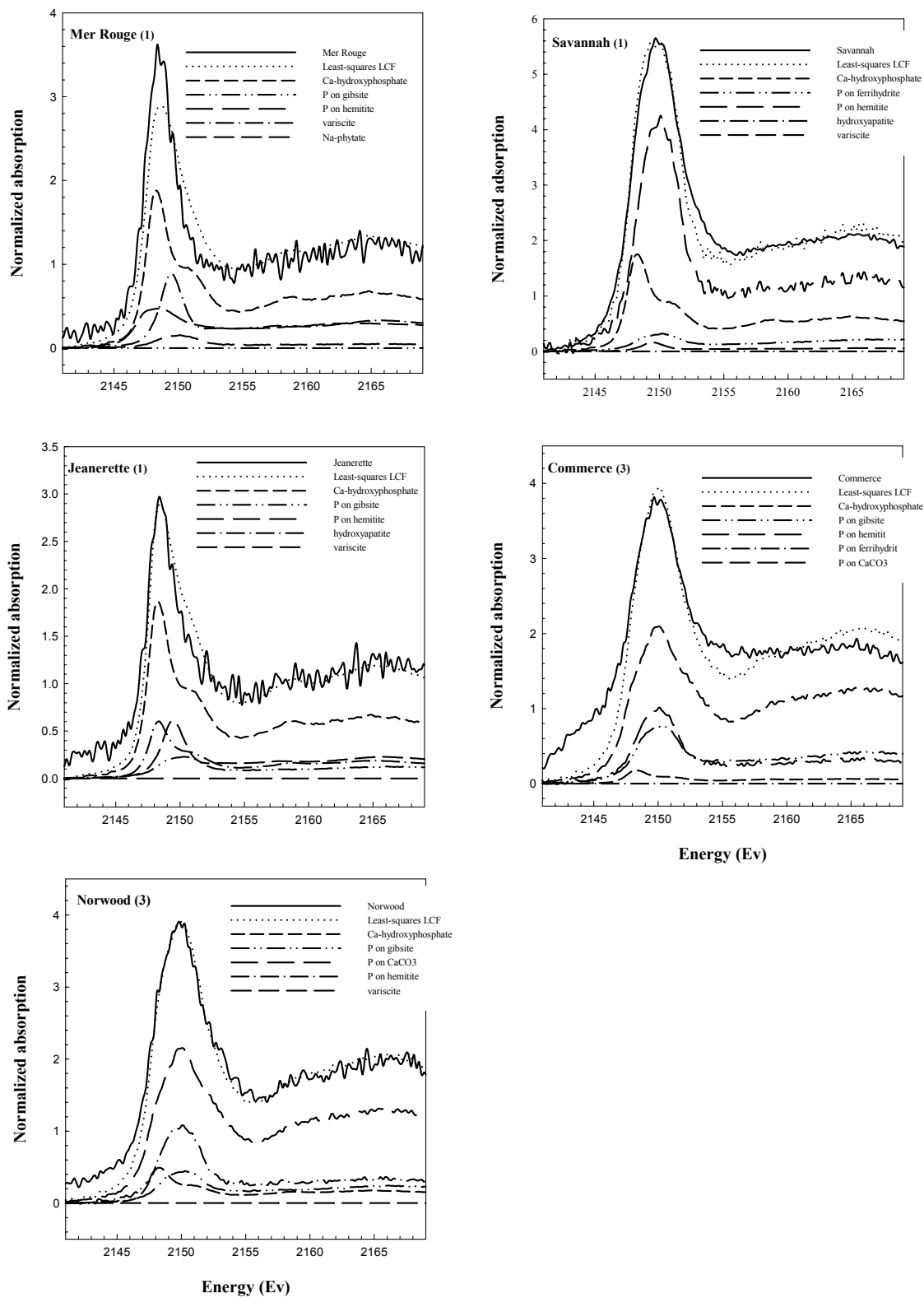


Figure 3.08 Least-squares LCF of each soil P K-XANES spectra along with the residuals of each standard species used in the fitting.

Table 3.03 Least-squares linear combination fitting results indicating the relative proportion of each phosphate standard used to fit the P K-XANES spectra for four calcareous soils and a poultry litter amended Savannah soil.

| Sample | Goodness of fit (X^2) | sum of fractions before normalization | PO ₄ sorbed on | | | | sodium phytate | Total PO ₄ sorbed on Fe or Al oxides plus Organic P | variscite | PO ₄ sorbed on CaCO ₃ | | | calcium hydroxyphosphate | Total Ca phosphates |
|------------------------|---------------------------|---------------------------------------|---------------------------|--------|----------|----------|----------------|--|-----------|---|----------|----|--------------------------|---------------------|
| | | | ferrihydrite | hemite | gibbsite | brushite | | | | hydroxyapatite | brushite | | | |
| -----% of total P----- | | | | | | | | | | | | | | |
| Commerce (1) | 32 | 1.17 | | 21 | 57 | | 78 | < 1 | | 10 | | 12 | 22 | |
| Commerce (2) | 73 | 1.07 | 63 | 12 | | | 75 | < 1 | | < 1 | | 24 | 24 | |
| Commerce (3) | 52 | 1.05 | | 8 | 25 | | 34 | < 1 | 61 | | | 5 | 66 | |
| Mer Rouge (1) | 18 | 0.82 | | 1 | < 1 | 29 | 30 | 23 | | | | 46 | 46 | |
| Jeanerette (1) | 14 | 0.69 | | < 1 | 10 | | | 19 | | 17 | | 54 | 71 | |
| Norwood (1) | 26 | 1.05 | | 5 | 72 | | 77 | < 1 | | < 1 | | 23 | 23 | |
| Norwood (2) | 27 | 1.12 | 68 | 11 | | | 79 | < 1 | | < 1 | | 22 | 22 | |
| Norwood (3) | 13 | 1.07 | | 8 | 3 | | 11 | < 1 | 87 | | | 2 | 89 | |
| Savannah (1) | 18 | 0.85 | 11 | 38 | | | 49 | 4 | | < 1 | | 48 | 48 | |

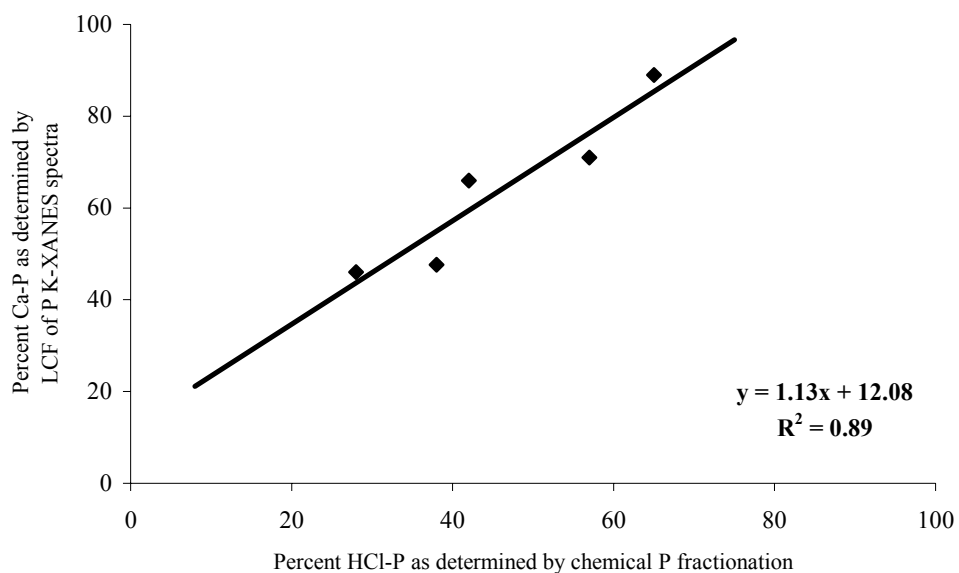


Figure 3.09 Relation between percent Ca-P determined by LCF of XANES spectra and HCl-P determined by chemical fractionation.

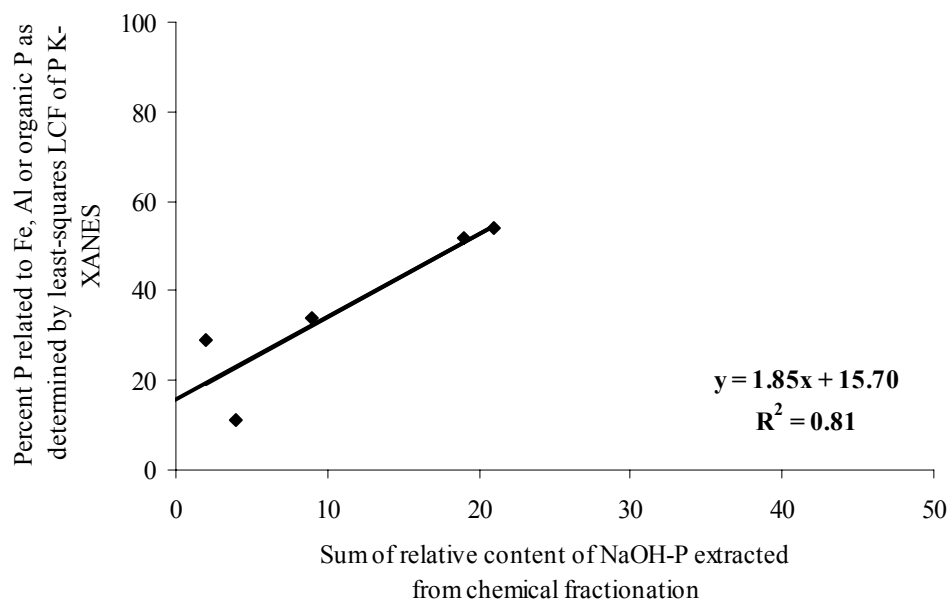


Figure 3.10 Relation between percent P related to Fe, Al or organic P determined by LCF of XANES spectra and NaOH-P determined by chemical P fractionation.

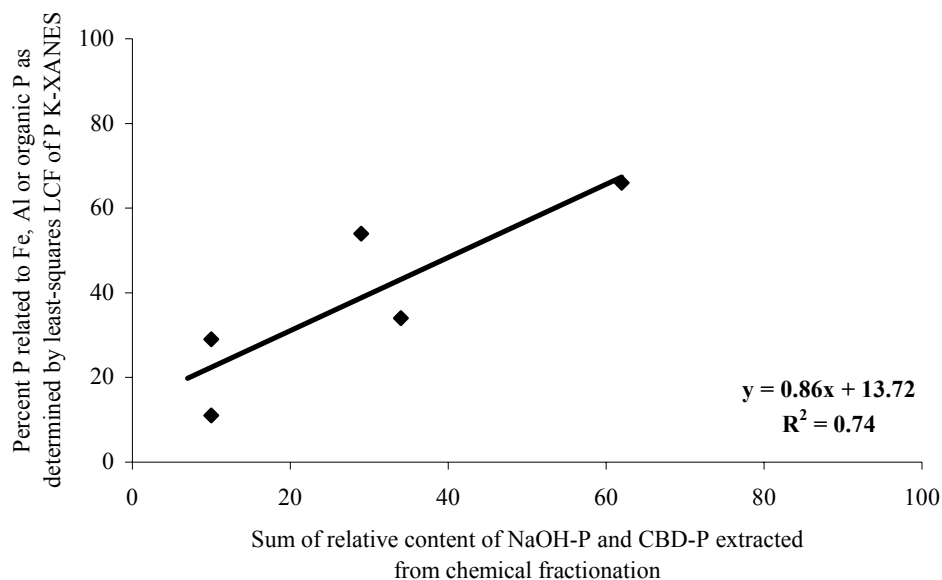


Figure 3.11 Relation between percent P related to Fe, Al or organic P determined by LCF of XANES spectra and the sum of NaOH-P and CBD-P determined by chemical P fractionation.

The P K-XANES spectra of the Savanna, Norwood and Commerce soils before and after the NaOH-P and subsequent CBD-P extractions from the chemical P fractionation procedure can be seen in Figs. 3.13 – 3.14 respectively. The resulting XANES spectra of the soils after the third chemical P fractionation, HCl-P, was not included in the stacked XANES plots because the spectra became quite noisy after removal of the Ca bound P phases. This lack of a true XANES spectra was due to the very low P concentration after the HCl-P extraction where only residual-P remained. Least-squares linear combination fitting results indicating the relative proportion of each phosphate standard used to fit the P K-XANES spectra for these soils before and after the NaOH-P and subsequent CBD-P extractions can be seen in Table 3.04. Only the original orthogonal components used in the original least-squares fitting were used in the fitting of the soil spectra after each subsequent step of the fractionation procedure. The

X^2 values for the Commerce and Savannah XANES fits after the NaOH and CBD extractions actually decreased as compared to their unaltered soil counterparts indicating an increased goodness of fit. However, the X^2 value of the Norwood XANES least-squares fit increased to 138. This X^2 value was over the critical level, $\chi_{0.05,99}^2 = 123$, indicating that a statistical valid fit of the XANES spectra for the Norwood soil after NaOH and CBD extractions could not be reproduced. Coincidentally, the Norwood soil had a lower total P concentration, as determined by the sum of the P fractions, as compared to the Commerce and the poultry litter amended Savannah soil. Since the NaOH-P extraction is targeted at removing Al and Fe oxides and the CBD-P extraction is targeted at removing reductant soluble Fe, it would be suffice to say that if the P extractions worked properly and the XANES fitting were correct, the relative proportions of the Ca phosphates estimated by LCF of the XANES spectra should increase after each extraction. This was exactly the case for the Commerce soil. The relative proportion of total phosphate sorbed on Fe and Al oxides plus organic P decreased from 34 to 12 and from 12 to 7 after the NaOH and CBD extractions respectively, while total Ca-P increased. More specifically, the phosphate sorbed on CaCO_3 increased after each extraction. While this increase could come from concentrated effect of overall Ca-P, it could also be possible that some of the soluble P extracted during the NaOH extraction of P fractionation procedures was actually resorbed to carbonate surfaces (Williams et al., 1971). However, as far as the Savannah soil, the relative proportion of total Ca phosphates as determined by LCF of XANES spectra after the NaOH-P extraction did not increase as expected. It did increase slightly after the subsequent CBD-P extraction. The exact reason for the deviation of the expected trend of the savannah soil could not be

determined. Since the Savannah soil received a large amount of poultry litter over the years and consequently contained a large amount of organic matter, it may be possible that some of the P was released by hydrolysis during the NaOH extraction and further formed a subsequent insoluble Fe-/Al-P or organic matter – Fe/Al – phosphate complex. On the other hand, this result could also be due to insensitivity of XANES analysis to differentiate P species contained in heavily organic forms (Peak et al., 2002). Further research is needed to elucidate this interesting phenomenon.

3.4 Conclusions

The P K-XANES spectra for common Fe, Al, and Ca phosphate minerals contained unique features which could be used to identify the various phosphate forms. The P K-XANES spectra for organic P as well as P sorbed on Fe and Al oxide surfaces lacked unique spectral features and could not be used to distinguish among these P species. The XANES spectra for P sorbed on CaCO₃ did however contain spectral features similar to Ca phosphates with less intensity and could be used to distinguish it from other sorbed P phases.

Principal component analysis indicated that it would take five orthogonal components to describe the variation in the XANES spectra of each soil sample. Target transformation determined that several of the 17 P standards used had *SPOIL* values < 1, indicating that they were the most probable components which could improve the fitting when included in the data matrix. Consequently, only the five P standards with the lowest *SPOIL* values determined by target transformation were generally used in the fittings. The goodness of fit, χ^2 , for all soils ranged from 13 – 73 indicating that all LCF spectra were not statistically different from the soil P K-XANES spectra. Resulting

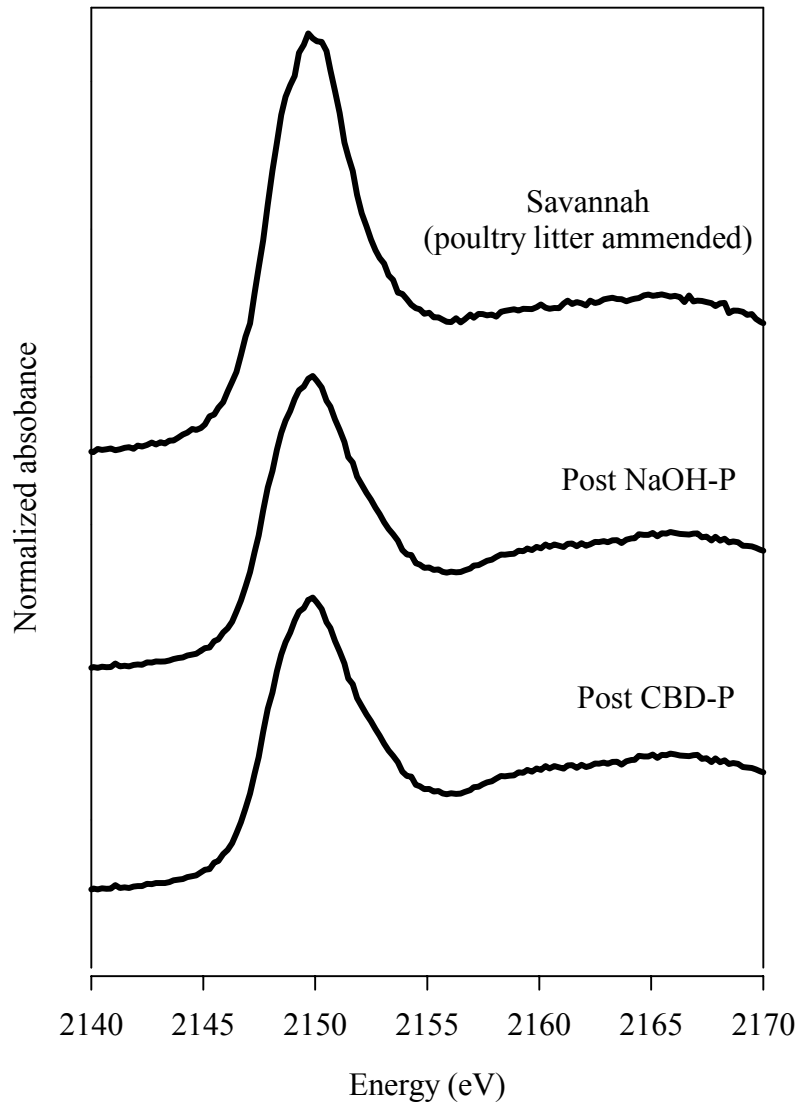


Figure 3.12 Normalized P K-XANES spectra for the poultry amended Savannah soil and the Savannah soil residue after the NaOH extraction and subsequent CBD-P extraction of the P fractionation procedure.

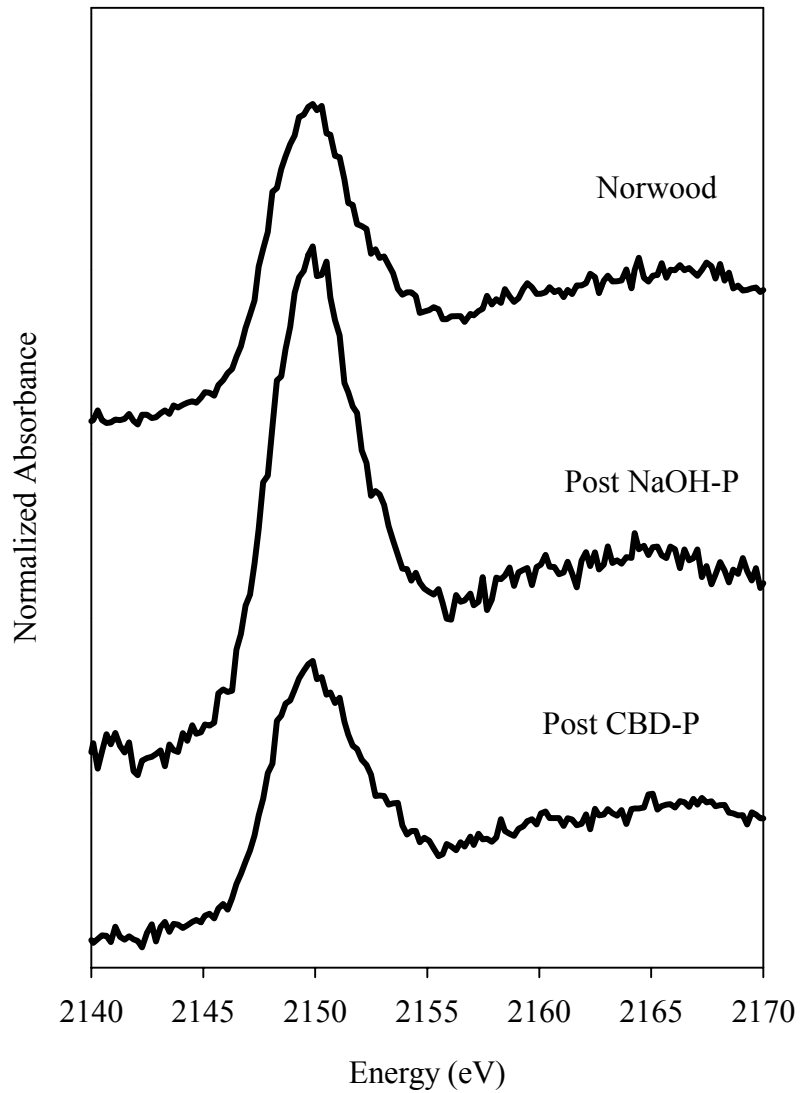


Figure 3.13 Normalized P K-XANES spectra for the poultry amended Savannah soil and the Savannah soil residue after the NaOH extraction and subsequent CBD-P extraction of the P fractionation procedure.

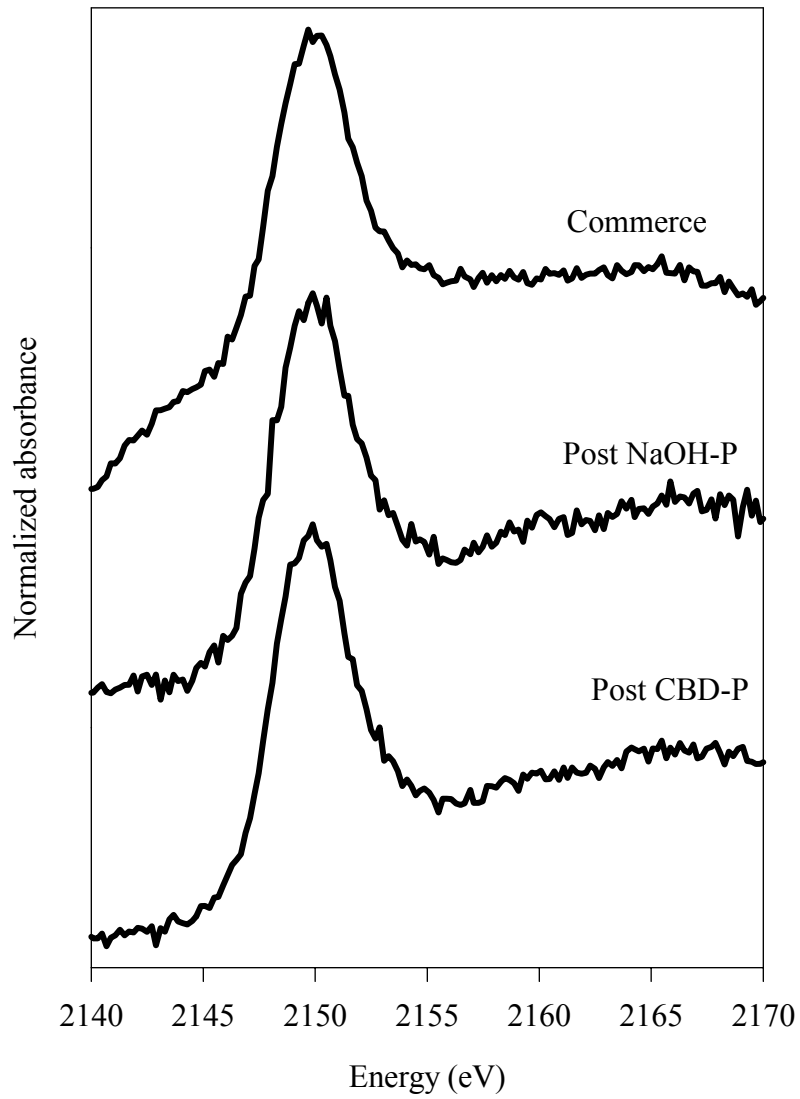


Figure 3.14 Normalized P K-XANES spectra for the Commerce soil and the Commerce soil residue after the NaOH extraction and subsequent CBD-P extraction of the P fractionation procedure.

Table 3.04 Least-squares linear combination fitting results indicating the relative proportion of each phosphate standard used to fit the P K-XANES spectra for the Commerce, Norwood and Savannah soils before and after the NaOH-P and subsequent CBD-P extractions.

| Sample | Goodness of fit (X^2) | sum of fractions before normalization | PO ₄ sorbed on | | | Total PO ₄ sorbed on Fe or Al oxides plus Organic P | PO ₄ sorbed | | | Total Ca phosphates | |
|------------------------|---------------------------|---------------------------------------|---------------------------|--------|----------|--|------------------------|----------------------|----------------|---------------------|--------------------------|
| | | | ferrihydrite | hemite | gibbsite | | variscite | on CaCO ₃ | hydroxyapatite | | calcium hydroxyphosphate |
| -----% of total P----- | | | | | | | | | | | |
| Commerce (3) | 52 | 1.05 | < 1 | 8 | 25 | 34 | | 61 | | 5 | 66 |
| post NaOH | 10 | 0.93 | < 1 | 12 | < 1 | 12 | | 87 | | 1 | 88 |
| post-CBD | 14 | 1.03 | < 1 | 7 | < 1 | 7 | | 93 | | < 1 | 93 |
| Norwood (3) | 13 | 1.07 | | 8 | 3 | 11 | < 1 | 87 | | 2 | 89 |
| post NaOH | 138 | -- | | -- | -- | -- | -- | -- | | -- | -- |
| Savannah (1) | 18 | 0.85 | 11 | 38 | | 49 | 4 | | < 1 | 48 | 48 |
| post NaOH | 11 | 1.06 | 66 | 9 | | 75 | 1 | | < 1 | 25 | 25 |
| post-CBD | 13 | 0.99 | 56 | 15 | | 71 | 0 | | < 1 | 29 | 29 |

normalized relative percentages of each standard species were summed grouped into the following categories: phosphates sorbed on Fe-/Al-oxides plus organic P, crystalline Fe-/Al-phosphates, and Ca phosphates (Ca minerals and P sorbed on CaCO₃). Nearly identical LCF results occurred when P sorbed on ferrihydrite was substituted with P sorbed on gibbsite illustrated insensitivity of XANES analysis to distinguish between the metal oxide sorbed P phases. Since the Commerce and Norwood soils contained broad white line peaks as compared to other soils, the less intense featured CaCO₃ sorbed P rather than the intense featured hydroxyapatite was used in LCF analysis. The LCF fitting of original soil XANES spectra suggests that most of the Fe-/Al-P were in sorbed forms. There was no strengite found in all soils but variscite was possibly present in Mer Rouge and Jeanerette soils. The LCF analysis also showed that the Norwood and Commerce soils contained Ca-P mostly in sorbed form associated with CaCO₃ or as Ca-hydroxyphosphate. The Mer Rouge soil contained Ca-P in the form of Ca-hydroxyphosphate while the Jeanerette contained Ca-P in both the hydroxyapatite and Ca-hydroxyphosphate forms. A highly significant correlation was found between the total Ca-P determined by least-squares LCF of P K-XANES spectra of the soils and the Ca-P determined by the HCl-P extraction of the sequential chemical fractionation procedure ($R^2 = 0.89$, $P = 0.016$). Likewise a significant correlation ($R^2 = 0.81$, $P = 0.0383$) was found between the sum of relative percentage of total Fe-/Al-P plus organic P determined by XANES fitting and the relative percentage of Fe-/Al-P from the NaOH-P fraction of the chemically sequential fractionation procedure. Generally, least-squares LCF of XANES spectra estimated more Ca-P as well as Fe-/Al-P and than was determined by chemical fractionation. Since chemical fractionation contained a large

residual-P fraction which could not be partitioned into chemically defined P forms, XANES estimates of soil total Ca-phosphates and the total Fe-/Al-P species was more effective than the chemical P fraction procedure even though XNAES could not differentiate P sorbed onto Fe or Al oxides. The LCF fitting of the Commerce soil after fractionation indicated that total Ca-P increased after the NaOH-P and CBD-P extraction as expected. However, the LCF fitting of the Savannah soil showed that total Ca-P declined after the NaOH-P extraction and then slightly increased after the subsequent CBD-P extraction. Analysis of P K-XANES spectra were limited due to the insensitivity of PCA and target transformation and the noisy soil spectra due to the low total P content in soils such as Norwood after fractionation. Although we eliminated testing all possible standard combinations by only using reference components with SPOIL values < 1, a software package allowing the simultaneous determination of the best least-squares fit of large possible standard combinations could enhance our least-squares analysis of XANES spectra data and provide additional speciation information.

3.5 References

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CHAPTER 4

EVALUATION OF FOUR- AND SIX-STEP INORGANIC CHEMICAL FRACTIONATION PROCEDURES OF PHOSPHORUS

4.1 Introduction

4.1.1 General Introduction

Identification and quantification of individual soil and sediment phosphorus (P) compounds can provide valuable information on P chemical dynamics. Direct identification and quantification of P species in soils by physical methods such as x-ray diffraction is difficult due to the overall low concentration of P in soils. Instead, chemical fractionation procedures (Kuo, 1990) are used that partition P contained in soils and sediments into associated P groups or pools. For calcareous soils, sequential chemical fractionation schemes attempt to separate soil inorganic P into discrete groups of (i) Fe-/Al-phosphates (ii) P occluded within coatings of Fe oxide and hydrated oxides and (iii) Ca associated phosphates (Olsen and Sommers, 1982). Sequential extraction procedures use various chemical reagents to selectively solubilize the Al, Fe, or Ca phosphate phases but separation of P into the broad range of detailed Al-, Fe-, and Ca-phosphate associated groups is imperfect. Even so, chemical fractionation procedures have provided valuable information in numerous soil P studies (Sui et al., 1999; Delgado and Torrent, 2000; Maguire et al., 2000).

Phosphorus fractionation procedures were first used a hundred of years ago (Fraps, 1906) and have been modified over the years (Dean, 1938; Chang and Jackson, 1957; Williams et al., 1980; Hedley et al., 1982). One of the most recent changes is the addition of an initial extraction intended to estimate plant-labile P. Labile P in inorganic and organic P fractionation procedures has been estimated using several different

extractions. The most common extractants for labile P are water (Dou et al. 2000), resin (Yang, 2000), NaHCO_3 (Zhang et al., 2004; Sharpley and Smith, 1984; Samadi and Gilkes, 1999), or a combination of resin and NaHCO_3 (Hedley et al., 1982; Sharpley et al., 1986; Beauchemin, 2003). Another change to the P fractionation schemes is the addition of the sodium citrate-sodium bicarbonate extraction (CB-P). This extraction is often inserted after the NaOH-P extraction for Ca-P and before the CBD-P fraction for reductant P (Olsen and Sommers, 1982). The purpose of the CB-P extractions is to desorb P that sorbed to CaCO_3 during the NaOH-P extraction (Williams et al., 1971a). However, little is known about the impact of these additional steps on subsequent fractions.

Analysis of solution P has been traditionally analyzed by the molybdenum blue or ascorbic acid colorimetric methods (Murphy and Riley, 1962; Olsen and Dean, 1965). For the last two decades, inductively coupled plasma argon emission spectroscopy (ICP-AES, ICP for short) has gradually replaced colorimetric methods due to its speed and ability to measure many elements simultaneously. Phosphorus chemical fractionation techniques were originally created for use with colorimetric analysis. Today P fractionation results are reported using both ICP as well as colorimetric analytical analyses. However, it has not been fully evaluated if the various background solutions yield consistent results especially in lieu of high salt matrix encountered in P fractionation procedures (Chang and Jackson, 1957; Olsen and Sommers, 1982).

The objectives of this research were to (i) determine the recovery of P in each of the common P fractionation extractions; (ii) evaluate the redistribution of P forms in soils when the NaHCO_3 -P and the CB-P extractions are added to the original P fractionation

scheme and; (iii) compare the effects of repeated extraction of each fraction on redistribution of P as determined by the original P fractionation procedure (four-step procedure) and the P fractionation procedure with the additional NaHCO_3 -P and the CB-P extractions (six-step procedure).

4.1.2 History of Chemical P Fractionation

Chemical fractionation of soil inorganic P dates from the early 1900's (Fraps, 1906; Dean, 1938). Today, the most commonly used procedure is that of Chang and Jackson (1957). The discovery that neutral NH_4F selectively dissolves Al-P without dissolving Fe-P (Turner and Rice, 1954), prompted Chang and Jackson (1957) to include NH_4F . Briefly, their procedure uses 1 *N* NH_4Cl to remove water soluble and loosely bound P, followed by neutral 0.5 *N* NH_4F to remove aluminum phosphate. Iron phosphate is then removed by 0.1 *N* NaOH , followed by Ca phosphate with 0.5 *N* H_2SO_4 . Reductant soluble Fe phosphate is extracted last by 0.3 *M* $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ and 1 g. $\text{Na}_2\text{S}_2\text{O}_4$. This procedure has been used to fractionate both acid and calcareous soils and sediments (Williams et al., 1971a; Williams et al. 1971b). It is the basis for several improved procedures (Pratt and Garber, 1964; Williams et al., 1980; Hedley et al.1982).

One early change to the Chang and Jackson fractionation procedure was increasing the buffer pH of the 0.5 *N* NH_4F extraction from 7 to 8.2 (Pratt and Garber, 1964). Further changes were proposed due to complications with the NH_4F extraction, leading to its underestimation in both acid and calcareous soils. In a study of acid soils, Williams et al. (1967) found that all of the sorbed P lost in the NH_4F extraction due to resorption by ferric compounds was recovered in the following NaOH extraction and proposed a mathematical factor of the NH_4F extracted P to correct for this discrepancy.

They also proposed replacement of 0.5 *N* H₂SO₄ extraction (used to estimate acid extractable Ca-P) with 0.5 *N* HCl to facilitate the use of the extract with the colorimetric procedure. In addition, a Na₂CO₃ fusion step was added at the end of the procedure to estimate residual inorganic P (Williams et al., 1967).

In calcareous soils, the NH₄F extractable P fraction was also compromised due to the probable formation of CaF₂ compounds during the extraction (Fife, 1959; Williams et al., 1971a; Williams et al., 1971b, Syers et al., 1972). The P dissolved during the NH₄F extraction was believed to be resorbed by both the newly formed CaF₂ and CaCO₃ (Williams et al., 1971a) resulting in the underestimation of NH₄F and NaOH extractable P (estimates of Al and Fe bound P, respectively) and the overestimation of Na₃C₆H₅O₇-NaHCO₃-Na₂S₂O₄ (CBD) extractable P (reductant soluble P) and the HCl extractable Ca-P. For this reason, the NH₄F extraction was removed from the fractionation procedure for calcareous soils and sediments, leaving only the NaOH, CBD, and HCl extractions. Although, removing NH₄F from the procedure did eliminate the formation of CaF₂, it did not prevent resorption of P by CaCO₃ during the NaOH extraction since CaCO₃ still existed. Generally, the NaOH extraction was found to be associated with Fe and Al bound P but not with Ca bound P. The bulk of the CBD extractable P was believed to be related to the recovery of P that was resorbed during the previous NaOH extraction while only a smaller portion was related to P occluded in Fe oxides (Williams et al., 1971a).

After the removal of the NH₄F extraction from the P fractionation procedure for calcareous soils, Williams et al. (1980) tested the revised procedure on several phosphate minerals to verify the P forms extracted by the procedure. In their experiment, the P fractionation procedure began with the CDB followed by the NaOH, HCl, and Na₂CO₃

fusion extraction procedures. It was found that the scheme was able to reasonably separate Al and Fe bound P (CDB plus NaOH extractable) from that of the apatite associated P (HCl extractable). In addition, they also noted that other findings were also very important to the interpretation of the extractable P fractions. First they found that vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) was extracted almost entirely by the CDB extraction (>99%). However when the vivianite was added to a sediment sample, its recovery was incomplete until the subsequent NaOH extraction. This was attributed to the resorption of CDB extractable P by other sediment components. Williams et al. (1980) hypothesized that this resorption of CBD-P may occur to some degree during the CDB extraction in any sediment containing CDB extractable P components. The second striking finding of their study was that variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) was the only mineral investigated in the study that was highly extractable by NaOH. This was attributed to the fact that the variscite is highly insoluble at a pH of <2 but are highly susceptible to hydrolysis in the presence of NaOH. Finally, they noted that the Na_2CO_3 fusion extractable P, an estimate of the residual P fraction, was the only extraction which was able to solubilize the monazite (CePO_4) and xenotime (YPO_4) minerals. Since these minerals have been found in soils (Quereshi et al., 1978), but are considered to be quite rare, it was concluded that mineral P phases such as these are the dominant components in the generally small residual P fraction.

More recent adjustments to the P fractionation procedure include introducing additional P extractions at the beginning of the procedure to estimate plant available or labile P forms and also the separation of inorganic P from organic P within each extraction (Hedley et al., 1982). Both of these adjustments were originally made to

evaluate differences in inorganic and organic P fractions between soils of different ecosystems. In the procedure described by Hedley et al. (1982), two extractions were added to estimate the more labile P forms. The first was a resin exchangeable P (resin-P) which was believed to be the most “biologically available” inorganic P (Amer et al., 1955). The next extraction, applied to the first resin-P residue, was a NaHCO₃ extractable P (NaHCO₃-P) which was believed to include both inorganic P (P_i) and organic P (P_o) sorbed on the soil surface and also some microbial P. In addition, the duplicate resin-P was pretreated with CHCl₃ followed by the NaHCO₃ extraction for removing P from lysed microbial cells. Subsequent fractionations included NaOH, HCl, and H₂SO₄-H₂O₂ digestion (Hedley et al, 1982). Separation of P_i from P_o was accomplished by treating a portion the extract from each sequential extraction (with the exception of the resin-P and HCl-P) with acidified (NH₄)₂S₂O₈. This fractionation scheme which utilizes the separation of P_i and P_o and includes initial labile P fractions is often referred to as the Hedley P fractionation scheme. To meet specific research needs the Hedley procedure has been also been modified by others. For example, in a study focused on the transformations of P fractions due to the application biosolids, Sui et al. (1999) used a H₂O extractable P instead of resin-P in the Hedley procedure because they believed that H₂O soluble P better related to bioavailable P in surface runoff than did the resin-P (Sui et al., 1999). While all these procedures have been employed to elucidate P chemistry for various soil systems, the most commonly used fractionation scheme of P for calcareous soils includes three fundamental steps: NaOH extraction for Fe-/Al-P, CBD extraction for reductant-P, and HCl extraction for Ca-P (Kuo, 1996), with or without a total digestion for residual-P.

4.2 Materials and Methods

4.2.1 Sequential P Fractionation

Two different sequential P fractionation procedures were evaluated in this study. The procedure, which will be referred to throughout as the four step P fractionation procedure, is the recommended method for calcareous soils as described by Kuo (1996). The sequence preceded in the following order: (i) NaOH-P by 0.1 *N* NaOH + 1 *M* NaCl (17 hr. shake), wash residue with 1 *M* NaCl and combine washings with extract; (ii) CBD-P by 0.3 *M* Na₃C₆H₅O₇ + 1 *M* NaHCO₃ + Na₂S₂O₄, wash with saturated NaCl, combine washings with extract and; (iii) HCl-P by 1 *M* HCl. Residual-P was also determined by digesting the remaining soil residue with 18 *M* H₂SO₄ + 28.9 *M* HF + 30% H₂O₂. The targeted P forms were: (i) NaOH-P, representing Fe- and Al-P compounds released by hydrolysis and may also include some organic P from humic compounds; (ii) CBD -P, representing reductant soluble Fe-P; (iii) HCl-P, representing stable Ca phosphates; and (iv) Residual-P, representing inorganic and organic P forms.

The second P fractionation procedure, which will be referred to throughout as the six step P fractionation procedure, contains the original three extractions as described above and also contains two additional extractions. The first additional extraction is targeted at removing labile-P by extracting with 0.5 *M* NaHCO₃ and shaking for 30 min. (Olsen, 1954). The second was a CB-P extraction (0.3 *M* Na₃C₆H₅O₇ + 1 *M* NaHCO₃, no wash) added after the NaOH-P extraction and before the CBD-P extraction. The CB-P extraction is targeted at recovering P which was dissolved but then sorbed to the surface of CaCO₃ during the NaOH-P extraction (Williams et al., 1971a). The P contained in the CB-P extraction is normally added to the NaOH-P fraction ([NaOH+CB]-P) in order to

correctly estimate Fe- and Al-P. A more precise explanation of the chemical extractions used and a brief description of the targeted P forms can be seen in Chapter 2 (Table 2.01).

Each extraction procedure was carried out using a 1:50 soil to solution ratio. All soil-fractionation solution mixtures were centrifuged at 16,000 X *g* for 10 min. and the supernatant solution in each sequential extraction was passed through a 0.45- μ m filter. The steps with washings used a 1:50 soil to solution ratio and all washings were combined with the post extraction solutions for analysis. Each extraction was done in triplicate.

4.2.2 Spike Recovery of Phosphate in Sequential Fractionation Matrix

A spike recovery of a known amount P was determined after each sequential P extraction on a soil by soil basis. This was carried out by spiking a 9 mL aliquot of the soil extract with 1 mL of a P solution with a known concentration to yield a final concentration of approximately 150 – 200% of the P in each sequential extraction solution. Spike recovery determination was duplicated for each extraction of the sequential fractionation for each soil.

In addition to the spiking recovery of P in the sequential extraction of each soil, a recovery test was also conducted to determine if using a washing salt solution in the sequential fractionation procedure caused any interference with ICP-OES analysis. A series of dilutions were made to the NaOH extracting solution by adding 1 *M* NaCl until the final concentration of 1 *M* NaCl in the NaOH extraction solution was 0, 10, 25 and 50%. A series of dilutions were also made to the CBD extracting solution by adding a saturated NaCl solution until the final concentration of the saturated NaCl in the CBD extracting solution was 0, 10, 25 and 50%. Both the 1 *M* NaCl and saturated NaCl were

used as washings in NaOH and CBD extractions respectively to promote flocculation and enhance centrifugation (Jackson et al., 1986). Nine mL of each salt-extracting solution mixture was spiked with 1 mL of a $20 \mu\text{g mL}^{-1}$ phosphate solution. Each spiked sample was replicated three times.

Phosphorus concentrations in all extracts were determined at wavelength of 213 nm by ICP-OES (SPECTRO CYRIOS^{CCD}, Spectro Analytical Instruments, Inc., Fitchburg, MA) calibrated with P standards made in a 2 % HNO₃ matrix. A Scott double-pass mixing chamber and a high salts torch were used in ICP determination. The high salt torch was designed to overcome the problems associated with high salt solutions.

4.2.3 Soil Selection and Characterization

The soils used in this study include Commerce, Mer Rouge, Jeanerette and two Norwood (a silt loam and a sandy loam) soils. Each soil was sampled at two depths, 0 – 15 and 30 – 45 cm, representing the A_p and the sub-soil horizons respectively. A complete description of the soils including geological history and sampling sites can be seen in Chapter 2 of this dissertation. Basic chemical and physical properties can be seen in Table 2.02.

4.3 Results and Discussion

4.3.1 Phosphorus Spike Recovery

The mean spike P recovery determined after each sequential extraction from both the four- and six-step calcareous P fractionation procedures are given in Table 4.01. The P spike recovery varied among the different extractions due to individual matrix effect of each sequential extraction step. Recovery was close to 100% for the NaHCO₃-P, CB-P,

HCl-P and Residual-P extraction solution matrices. However, considerably lower spike recoveries of 81 and 61% were seen for the NaOH-P and CBD-P extractions respectively. These low recoveries were observed for both soil and pure extracts suggesting a significant matrix effect due to these two sequential extractions. As a result, a simple correction to the NaOH-P and CBD-P results were made by adjusting the data based on 81 and 61 % recovery respectively. Due to the fact that both the NaOH-P and CBD-P extraction procedures required a post extraction washing with a salt solution (1 *M* NaCl for NaOH-P and saturated NaCl for CBD-P) which was combined with the original extract before ICP analysis, we suspected that this “washing” may be the reason for the poor recovery of P in the NaOH-P and CBD-P extractions by ICP.

In order to determine if this was the case, P recovery was determined for the NaOH-P and CBD-P extraction solutions with various mixtures of their respective washing salt solution. Phosphorus recovery in the NaOH-P extraction solution decreased with an increasing percentage of the 1 *M* NaCl solution (Fig. 4.01). Eighty-one percent of the variation in P recovery in the NaOH-P solution could be explained by increasing the 1 *M* NaCl concentration in the final NaCl-NaOH mixture on a percent by volume basis as indicated by the linear relationship. Since the NaOH-P extraction in the sequential fractionation procedure requires washing the soil residue with an equal volume of 1 *M* NaCl, note that nearly identical P recoveries were found in the actual NaOH-P extraction (81%) and the subsequent P recovery experiment at the 50% of 1 *M* NaCl in final solution of NaOH (83%; Fig. 4.01). These results clearly suggest that the loss of P recovery in the NaOH-P extraction by ICP analysis was not due to the NaOH extraction solution itself but to the addition of the 1 *M* NaCl washing solution.

The effect of the saturated NaCl content on the P recovery in the CBD solution can be seen in Fig 4.02. Similarly, as the content of the saturated NaCl solution increased in the CBD solution the P recovery decreased. Linear regression indicated that 98 % of the variation in P recovery in the CBD solution could be explained by the effect of the saturated NaCl in the final NaCl-CBD mixture. In the CBD-P extraction of the sequential fractionation procedure, we also washed the soil residue with an equal volume of saturated NaCl. The same P recovery (61%) was also observed in the actual CBD-P extraction (Table 4.01) and in the subsequent recovery test experiment at the 50% saturated NaCl in the final NaCl-CBD mixture (Fig. 4.02). These results further confirmed that the loss of P recovery by ICP analysis of the CBD-P extraction was due to the use of saturated NaCl as a washing solution and not the CBD extraction itself.

It is uncertain if a loss of P recovery due to the use of the NaCl washing solutions in the NaOH-P and CBD-P extractions occurs when the P concentration is determined calorimetrically. However, work by others using a similar P fractionation scheme which did not include washing the residue, showed that there were no significant differences ($\alpha = 0.05$) between results from spectroscopic analysis and ICP analysis of selected P fractions of manure samples (Duo et al., 2000). Moreover, high P recoveries were found for each of the P fractions (91 – 109 %) when the washing solution was not used (Duo et al., 2000). It should be pointed out that the effect of high salt concentration on ICP determination of other metals has been reported before (Hislop and Hornbeck, 2002). Often the use of a high salt torch was recommended in these circumstances (Spectro Analytical Instruments, Inc., Fitchburg, MA). However in this study, we did use a high salt torch which was supposed to overcome the problems associated with samples of high

salt concentration. Our results clearly suggest that even with a high salt torch, P determination with ICP could still be impacted and care should be taken to assure accurate measurement of these P fractionation solutions that contain washings using various concentrations of NaCl.

Table 4.01 Mean P spike recoveries and method detection limits for each sequential P extraction in both the four-step and six-step calcareous P fractionation procedures across all soils and depths.

| | NaHCO ₃ -P | NaOH-P | CB-P | CBD-P | HCl-P | Residual-P |
|------------------|--------------------------------|--------|--------|--------|---------|------------|
| | -----%----- | | | | | |
| Mean | | | | | | |
| Recovery | 98 ± 4 [†] | 81 ± 4 | 95 ± 2 | 61 ± 3 | 100 ± 3 | 94 ± 4 |
| | -----mg kg ⁻¹ ----- | | | | | |
| MDL [‡] | 9.0 | 3.1 | 7.0 | 2.1 | 0.5 | 4.7 |

[†] numner following ± repersents the standard deviation

[‡] MDL is method detection limit

4.3.2 Comparison of Sequential Phosphorus Fractionations

The results of the four-step P fractionation procedure and the four-step P fractionation procedure with replicated extractions can be seen in Table 4.02 and 4.03 respectively. The results of the six-step P fractionation procedure and the six-step fractionation procedure with replicated extractions can be seen in Table 4.04 and 4.05 respectively. All pair-wise comparisons of the relative percentages of the NaHCO₃-P, NaOH-P, CB-P, CBD-P, HCl-P and Residual-P fractions extracted by each procedure with and without replication can be seen in Tables 4.06 – 4.11.

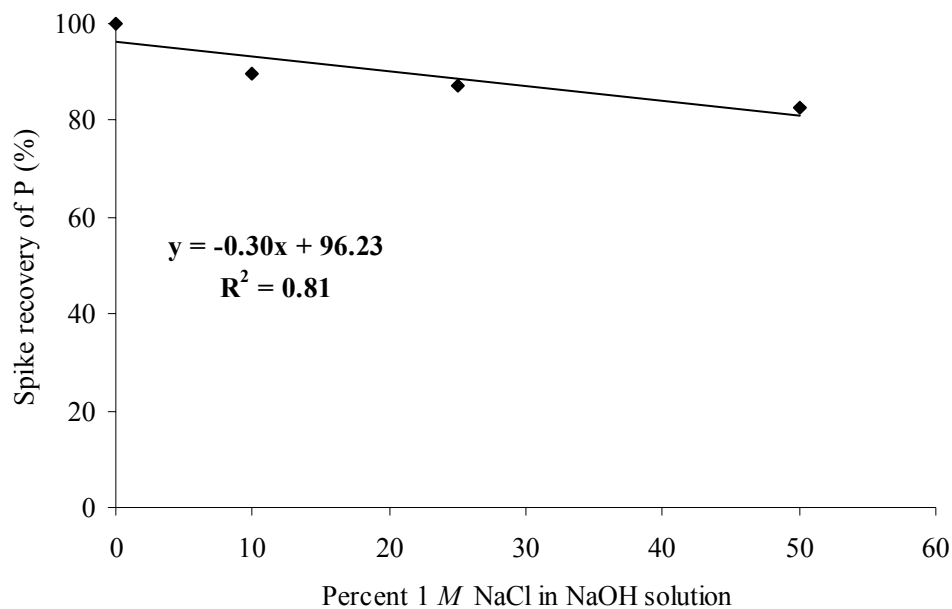


Figure 4.01 Relationship between the spike P recovery by ICP and the percentage of 1 M NaCl in the NaOH extraction solution.

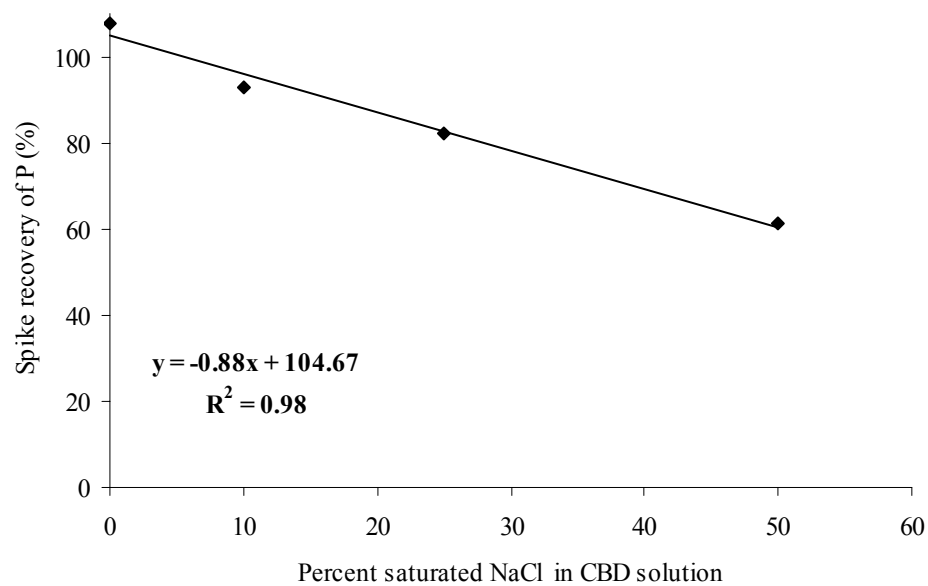


Figure 4.02 Relationship between the spike P recovery by ICP and the percentage of saturated NaCl in the CBD extraction solution.

Repeating each extraction from the four step fractionation procedure resulted in more P being extracted from all soils as determined by the sum of P fractions. Although higher, the sum of P fractions in the four step P fraction procedure with repeated extractions was highly correlated ($R^2 = 0.97$) with the sum of P fractions from the unrepeated four step procedure (Tables 4.02 and 4.03). Similarly, more P was extracted by the six-step P fractionation procedure with repeated extractions as compared to the normal non-repeated six-step procedure in all soils as illustrated by the sum of P fractions. Again, a high correlation ($R^2 = 0.96$) was seen between the sum of P fractions from the six-step P fractionation procedure and the six-step fractionation procedure with repeated extractions. More P was extracted by the six-step P fractionation procedure, with and with-out replicated extractions as compared to the four-step procedure with and with-out repeated extractions as determined by the sum of P fractions. Nonetheless, the sum of P fractions in both the six- and four-step procedures were highly correlated ($R^2 = 0.97$ and $R^2 = 0.98$). These results suggest that repeated extractions as well as the addition of the $\text{NaHCO}_3\text{-P}$ and CB-P in the six-step procedure as compared to the four-step procedure alter the trend of the total P extracted.

Although total P extracted did not vary considerably between P fractionation methods, the partitioning of P into various P fractions may vary considerably. The $\text{NaHCO}_3\text{-P}$ fraction is the first extraction of the six-step P fraction procedure and is not used in the four-step procedure. The $\text{NaHCO}_3\text{-P}$ fraction made up between 4 – 10 % of the extracted P from the six-step P fractionation procedure (Table 4.06). Although, the relative percentage of the $\text{NaHCO}_3\text{-P}$ is low, the extent of the impact of the extraction was seen in the subsequent NaOH-P extraction. The NaOH-P fraction in the six-step

procedure was higher as compared to the NaOH-P fraction in the four-step procedure in the Jeanerette and Mer Rouge soils and considerably higher in the Commerce soil (Tables 4.02 and 4.04). On a relative percentage basis, the dramatic impact of NaHCO₃ on the subsequent percentage of NaOH-P was primarily observed with the Commerce soil (Table 4.07). Coincidentally, the Commerce, soil had a higher ammonium oxalate extractable Fe and Al (Fe_{AOX} and Al_{AOX}) values as compared to the rest of the soils used in this study (Chapter 2, Table 2.03). These results suggest that in some way the NaHCO₃-P extraction may alter the chemistry of P associated with the Fe- or Al-oxides and enhance P release from the hydrolysis of these oxides by the subsequent NaOH-P extraction. In fact, low concentrations of alkaline solutions such as Na₂CO₃, are often used to dissolve alumina cements, cleaning mineral grains and dispersing clays. It is believed that repeated alkaline extractions with Na₂CO₃ have a moderate solvent effect on some alumina (Jackson et al., 1986). Similarly, NaCO₃ has been shown to be a good reagent for the dissolution of non-crystalline Al oxides (Tokashiki and Wada, 1975; Jackson et al., 1986). Like Na₂CO₃, the NaHCO₃ extraction is also a weak alkaline solution and could produce similar results.

The general mechanism of the removal of phosphate by the NaHCO₃-P extraction is by anion replacement. Thus the phosphate sorbed to the surface of CaCO₃ and Fe and Al oxides is replaced by the bicarbonate ion (Kamprath and Watson, 1980; Olsen et al., 1954). Further, since the NaHCO₃-P extraction is buffered at pH 8.5, the OH⁻ in the solution could hydrolyze Al-P and to some extent Fe-P to release P (Kamprath and Watson, 1980; Tyner and Davide, 1962). Additional effect of NaHCO₃ could come from

Na⁺ has been reported to increase P release with increasing soil saturation of Na⁺ (Kamprath and Watson, 1980).

The CB-P fraction is the second extraction added to the six-step fractionation procedure that is not seen in the four-step procedure. The CB-P fraction accounted for 3 – 6 % of the P removed from the six-step procedure and this percentage nearly doubled when a second CB-P extraction was applied (Table 4.08). The CB-P fraction is included in the six-step P fractionation procedure to desorb P that was sorbed during the NaOH-P extraction. This P is added to the NaOH-P fraction as [NaOH+CB]-P and is believed to represent a better estimate of the NaOH-P fraction (Williams et al., 1980). The P removed by the CBD-P extraction in the six-step procedure as compared to the CBD-P from the four-step procedure is, therefore, affected not only by the initial NaHCO₃-P extraction but also by the CB-P extraction. Generally, the P removed by the six-step CBD-P extraction is much smaller as compared to the P removed by the four-step CBD-P extraction except for the Norwood silt soil. Furthermore, on a relative basis, the percentage of P removed by the CBD-P extraction in the four-step procedure is greater in four out of the five soils than the CBD-P from the six-step procedure and five out of five soils when the extraction is repeated (Table 4.09). This may be a direct effect of the P removed from the CB-P extraction in the six-step procedure since when the CB-P is added to the CBD-P ([CBD+CB]-P) it is slightly higher than that of the four-step procedure with the exception of the Commerce soil.

The absolute amount of P extracted by the HCl-P fraction from the six-step procedure as compared to the four-step procedure was very similar (Tables 4.02 and 4.04). In fact, linear regression between the absolute values between the HCl-P of the

six-step and four-step procedures indicated that the relationship was highly significant ($R^2 = 0.99$, $P < 0.0001$). Repeating the HCl extraction did remove more P, however, the amount of removed P was minimal as compared to the initial HCl extraction. Moreover, when the two HCl-P extractions are summed (Tables 4.03 and 4.05) for both the six- and four-step fractionation procedures the values were almost identical in had a highly significant linear regression ($R^2 = 1.00$, $P < 0.0001$). These results suggest that the P removed by the HCl extraction was very similar regardless of the addition of the NaHCO_3 and CB extractions used in the six-step procedure as compared to the four-step procedure or whether or not each extraction was repeated. The lack of variation between all HCl-P fractions indicates that the HCl extraction tends to remove a stable pool of P, presumably stable Ca phosphates, as opposed to the preceding extractions.

The P extracted in the residual-P fraction, like the HCl-P fraction, was also very similar when comparing the six- and four-step fractionation procedures with the exception of the Commerce A_p sample (Tables 4.02 and 4.04) and when comparing the six- and four-step repeated procedures (Tables 4.03 and 4.05). Repeating extractions caused residual-P content to decrease in both the six- and four-step procedures as compared to non-repeated procedures. This may indicate that the increase in the P extracted by repeated extractions preceding HCl-P fraction could actually be derived from Fe-/Al-phosphates of the residual-P fraction.

4.4 Conclusions

The matrix effect of P analysis by ICP was minimal in the presence of the NaHCO_3 , CB, HCl extraction or $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ digestion background solutions. The spiked recovery of P was 81 and 61 % in the NaOH and CBD extractions respectively.

Table 4.02 Phosphorus fractionation by four sequential extractions.

| Soil | Depth | NaOH-P [†] | CBD-P [‡] | HCl-P | Residual-P | Sum of P Fractions |
|----------------------|---------|--------------------------------|--------------------|----------|------------|--------------------|
| | -cm- | -----mg kg ⁻¹ ----- | | | | |
| Commerce | 0 - 15 | 68 ± 6 [§] | 228 ± 22 | 268 ± 1 | 181 ± 2 | 745 |
| Commerce | 30 - 45 | 42 ± 2 | 196 ± 16 | 250 ± 15 | 232 ± 3 | 720 |
| Mer Rouge | 0 - 15 | 78 ± 3 | 38 ± 3 | 85 ± 1 | 126 ± 4 | 326 |
| Mer Rouge | 30 - 45 | 7 ± 2 | 18 ± 3 | 142 ± 4 | 144 ± 2 | 310 |
| Jeanerette | 0 - 15 | 11 ± 1 | 59 ± 3 | 261 ± 9 | 152 ± 1 | 484 |
| Jeanerette | 30 - 45 | 7 ± 4 | 37 ± 14 | 167 ± 4 | 172 ± 9 | 382 |
| Norwood (sandy loam) | 0 - 15 | 41 ± 6 | 18 ± 3 | 182 ± 21 | 105 ± 6 | 345 |
| Norwood (sandy loam) | 30 - 45 | 9 ± 2 | 11 ± 7 | 202 ± 10 | 150 ± 1 | 373 |
| Norwood (silt loam) | 0 - 15 | 25 ± 2 | 48 ± 16 | 339 ± 11 | 133 ± 0 | 545 |
| Norwood (silt loam) | 30 - 45 | 7 ± 2 | 26 ± 1 | 295 ± 4 | 113 ± 1 | 442 |

[†] NaOH-P values were corrected based on a recovery of 81%

[‡] CBD-P values were corrected based on a recovery of 61%

[§] number following ± represents the standard deviation

Table 4.03 Phosphorus fractionation by four sequential extractions with each extraction being repeated before proceeding to the next extraction.

| Soil | Depth | NaOH-P_1 [†] | NaOH-P_2 | Sum NaOH-P | CBD-P_1 [‡] | CBD-P_2 | Sum CBD-P | HCl-P_1 | HCl-P_2 | Sum HCl-P | Residual-P | Sum of P Fractions |
|----------------------|---------|--------------------------------|----------|---------------|----------------------|---------|--------------|----------|---------|--------------|------------|-----------------------|
| | | -----mg kg ⁻¹ ----- | | | | | | | | | | |
| | | -cm- | | | | | | | | | | |
| Commerce | 0 - 15 | 72 ± 1 [§] | 60 ± 3 | 132 | 178 ± 10 | 18 ± 4 | 196 | 237 ± 20 | 15 ± 4 | 252 | 169 ± 15 | 749 |
| Commerce | 30 - 45 | 48 ± 2 | 58 ± 1 | 105 | 154 ± 10 | 42 ± 6 | 195 | 250 ± 9 | 20 ± 1 | 270 | 153 ± 14 | 724 |
| Mer Rouge | 0 - 15 | 76 ± 3 | 42 ± 6 | 117 | 38 ± 3 | 11 ± 8 | 49 | 79 ± 2 | 8 ± 4 | 87 | 117 ± 4 | 370 |
| Mer Rouge | 30 - 45 | 14 ± 2 | 31 ± 2 | 45 | 25 ± 1 | 7 ± 4 | 32 | 134 ± 15 | 8 ± 2 | 142 | 132 ± 2 | 351 |
| Jeanerette | 0 - 15 | 16 ± 2 | 38 ± 4 | 54 | 74 ± 2 | 38 ± 0 | 112 | 227 ± 17 | 14 ± 5 | 242 | 142 ± 7 | 549 |
| Jeanerette | 30 - 45 | 10 ± 1 | 34 ± 1 | 44 | 42 ± 0 | 24 ± 1 | 67 | 139 ± 8 | 11 ± 1 | 151 | 124 ± 5 | 385 |
| Norwood (sandy loam) | 0 - 15 | 45 ± 1 | 35 ± 8 | 79 | 46 ± 3 | 35 ± 9 | 80 | 164 ± 11 | 6 ± 3 | 170 | 91 ± 0 | 421 |
| Norwood (sandy loam) | 30 - 45 | 18 ± 2 | 29 ± 2 | 47 | 45 ± 3 | 29 ± 1 | 75 | 188 ± 3 | 9 ± 5 | 197 | 136 ± 2 | 455 |
| Norwood (silt loam) | 0 - 15 | 34 ± 1 | 22 ± 8 | 56 | 60 ± 3 | 39 ± 1 | 99 | 296 ± 5 | 9 ± 1 | 305 | 95 ± 2 | 556 |
| Norwood (silt loam) | 30 - 45 | 14 ± 3 | 6 ± 8 | 19 | 26 ± 3 | 23 ± 3 | 49 | 276 ± 8 | 10 ± 2 | 286 | 109 ± 1 | 464 |

[†] NaOH-P values were corrected based on a recovery of 81%

[‡] CBD-P values were corrected based on a recovery of 61%

[§] number following ± represents the standard deviation

Table 4.04 Phosphorus fractionation by six sequential extractions.

| Soil | Depth | NaHCO ₃ -P | NaOH-P [†] | CB-P [‡] | CBD-P | HCl-P | Residual-P | Sum of P Fractions |
|----------------------|---------|--------------------------------|---------------------|-------------------|---------|----------|------------|--------------------|
| | -cm- | -----mg kg ⁻¹ ----- | | | | | | |
| Commerce | 0 - 15 | 54 ± 7 [§] | 219 ± 6 | 30 ± 2 | 77 ± 7 | 249 ± 7 | 223 ± 0 | 851 |
| Commerce | 30 - 45 | 39 ± 3 | 162 ± 4 | 22 ± 1 | 100 ± 8 | 241 ± 7 | 253 ± 1 | 817 |
| Mer Rouge | 0 - 15 | 32 ± 2 | 88 ± 2 | 22 ± 1 | 23 ± 1 | 72 ± 2 | 123 ± 2 | 359 |
| Mer Rouge | 30 - 45 | 25 ± 3 | 28 ± 3 | 18 ± 0 | 18 ± 2 | 133 ± 6 | 150 ± 0 | 372 |
| Jeanerette | 0 - 15 | 22 ± 3 | 40 ± 1 | 25 ± 4 | 53 ± 7 | 242 ± 11 | 171 ± 4 | 552 |
| Jeanerette | 30 - 45 | 23 ± 1 | 29 ± 1 | 18 ± 0 | 24 ± 4 | 151 ± 5 | 165 ± 8 | 409 |
| Norwood (sandy loam) | 0 - 15 | 38 ± 3 | 43 ± 2 | 25 ± 0 | 29 ± 5 | 162 ± 6 | 95 ± 2 | 393 |
| Norwood (sandy loam) | 30 - 45 | 33 ± 3 | 17 ± 2 | 19 ± 0 | 31 ± 0 | 203 ± 8 | 172 ± 2 | 474 |
| Norwood (silt loam) | 0 - 15 | 32 ± 1 | 28 ± 1 | 34 ± 1 | 37 ± 5 | 312 ± 9 | 142 ± 6 | 585 |
| Norwood (silt loam) | 30 - 45 | 24 ± 3 | 7 ± 4 | 18 ± 0 | 18 ± 1 | 293 ± 4 | 123 ± 4 | 483 |

[†] NaOH-P values were corrected based on a recovery of 81%

[‡] CBD-P values were corrected based on a recovery of 61%

[§] number following ± represents the standard deviation

Table 4.05 Phosphorus fractionation by six sequential extractions with each extraction being repeated before proceeding to the next extraction.

| Soil | Depth | NaHCO ₃ -P ₁ | NaHCO ₃ -P ₂ | Sum NaHCO ₃ -P | NaOH-P ₁ [†] | NaOH-P ₂ | Sum NaOH-P | CB-P ₁ [‡] | CB-P ₂ | Sum CB-P | CBD-P ₁ | CBD-P ₂ | Sum CBD-P | [NaOH+CB]-P | HCl-P ₁ | HCl-P ₂ | Sum HCl | Residual-P | Sum of P Fractions |
|----------------------|---------|------------------------------------|------------------------------------|------------------------------|----------------------------------|---------------------|---------------|--------------------------------|-------------------|-------------|--------------------|--------------------|--------------|-------------|--------------------|--------------------|------------|------------|-----------------------|
| | -cm- | -----mg kg ⁻¹ ----- | | | | | | | | | | | | | | | | | |
| Commerce | 0 - 15 | 54 ± 7 [§] | 32 ± 10 | 86 | 171 ± 5 | 19 ± 1 | 190 | 29 ± 1 | 20 ± 0 | 49 | 63 ± 4 | 28 ± 1 | 92 | 141 | 238 ± 11 | 22 ± 3 | 260 | 184 ± 6 | 861 |
| Commerce | 30 - 45 | 39 ± 3 | 26 ± 3 | 65 | 143 ± 6 | 20 ± 3 | 162 | 23 ± 1 | 19 ± 1 | 42 | 86 ± 4 | 42 ± 5 | 128 | 170 | 222 ± 4 | 21 ± 3 | 243 | 184 ± 1 | 825 |
| Mer Rouge | 0 - 15 | 32 ± 2 | 24 ± 9 | 56 | 83 ± 4 | 20 ± 5 | 103 | 21 ± 1 | 18 ± 1 | 39 | 25 ± 8 | 16 ± 4 | 42 | 80 | 67 ± 3 | 4 ± 2 | 71 | 37 ± 11 | 338 |
| Mer Rouge | 30 - 45 | 25 ± 3 | 19 ± 4 | 44 | 27 ± 4 | 14 ± 1 | 41 | 20 ± 0 | 16 ± 1 | 35 | 17 ± 5 | 14 ± 1 | 31 | 67 | 124 ± 4 | 10 ± 4 | 134 | 49 ± 2 | 334 |
| Jeanerette | 0 - 15 | 22 ± 3 | 22 ± 5 | 44 | 37 ± 2 | 15 ± 1 | 52 | 29 ± 0 | 23 ± 0 | 52 | 44 ± 5 | 25 ± 1 | 70 | 122 | 208 ± 7 | 18 ± 4 | 226 | 126 ± 5 | 580 |
| Jeanerette | 30 - 45 | 23 ± 1 | 18 ± 9 | 41 | 30 ± 2 | 17 ± 1 | 48 | 20 ± 0 | 16 ± 0 | 36 | 30 ± 6 | 20 ± 2 | 50 | 86 | 141 ± 4 | 12 ± 5 | 154 | 123 ± 6 | 454 |
| Norwood (sandy loam) | 0 - 15 | 38 ± 3 | 31 ± 6 | 69 | 40 ± 2 | 23 ± 6 | 63 | 26 ± 1 | 21 ± 0 | 47 | 32 ± 11 | 19 ± 3 | 50 | 98 | 150 ± 5 | 4 ± 2 | 154 | 82 ± 6 | 465 |
| Norwood (sandy loam) | 30 - 45 | 33 ± 3 | 20 ± 3 | 53 | 21 ± 3 | 20 ± 5 | 40 | 19 ± 2 | 18 ± 0 | 37 | 38 ± 7 | 23 ± 2 | 61 | 98 | 187 ± 6 | 11 ± 2 | 198 | 102 ± 7 | 490 |
| Norwood (silt loam) | 0 - 15 | 32 ± 1 | 27 ± 1 | 59 | 29 ± 2 | 22 ± 4 | 51 | 32 ± 2 | 26 ± 0 | 57 | 34 ± 1 | 34 ± 2 | 68 | 126 | 254 ± 6 | 7 ± 1 | 261 | 129 ± 9 | 625 |
| Norwood (silt loam) | 30 - 45 | 24 ± 3 | 25 ± 10 | 48 | 9 ± 2 | 24 ± 7 | 33 | 17 ± 1 | 17 ± 1 | 35 | 20 ± 2 | 12 ± 12 | 33 | 67 | 267 ± 4 | 7 ± 3 | 275 | 119 ± 9 | 542 |

[†] NaOH-P values were corrected based on a recovery of 81%

[‡] CBD-P values were corrected based on a recovery of 61%

[§] number following ± represents the standard deviation

Table 4.06 Comparison of relative percentage of $\text{NaHCO}_3\text{-P}$ extracted by the six step fractionation procedure with and with out repeated extractions.

| Soil | Depth | 6 extractions | |
|----------------------|---------|---|---------------------------------------|
| | | Non-Repeated $\text{NaHCO}_3\text{-P}$ | Repeated $\text{NaHCO}_3\text{-P}$ |
| | -cm- | -----%----- | |
| Commerce | 0 - 15 | 6 | 10 |
| Commerce | 30 - 45 | 5 | 8 |
| Mer Rouge | 0 - 15 | 9 | 16 |
| Mer Rouge | 30 - 45 | 7 | 13 |
| Jeanerette | 0 - 15 | 4 | 8 |
| Jeanerette | 30 - 45 | 6 | 9 |
| Norwood (sandy loam) | 0 - 15 | 10 | 15 |
| Norwood (sandy loam) | 30 - 45 | 7 | 11 |
| Norwood (silt loam) | 0 - 15 | 5 | 9 |
| Norwood (silt loam) | 30 - 45 | 5 | 9 |

Table 4.07 Comparison of relative percentage of NaOH-P extracted by the four and six step fractionation procedures with and with out repeated extractions.

| Soil | Depth | 4 extractions | | 6 extractions | | | |
|----------------------|---------|---------------------------------|-----------------------------|---------------------------------|-----------------------------|--|--|
| | | Non-Repeated NaOH-P | Repeated NaOH-P | Non-Repeated NaOH-P | Repeated NaOH-P | Non-Repeated [NaOH+CB]- P | Repeated [NaOH+CB]- P |
| | -cm- | -----%----- | | | | | |
| Commerce | 0 - 15 | 9 | 18 | 26 | 22 | 29 | 28 |
| Commerce | 30 - 45 | 6 | 15 | 20 | 20 | 23 | 25 |
| Mer Rouge | 0 - 15 | 24 | 32 | 24 | 30 | 30 | 41 |
| Mer Rouge | 30 - 45 | 2 | 13 | 7 | 12 | 12 | 23 |
| Jeanerette | 0 - 15 | 2 | 10 | 7 | 9 | 12 | 18 |
| Jeanerette | 30 - 45 | 2 | 11 | 7 | 11 | 11 | 18 |
| Norwood (sandy loam) | 0 - 15 | 12 | 19 | 11 | 13 | 17 | 24 |
| Norwood (sandy loam) | 30 - 45 | 2 | 10 | 3 | 8 | 7 | 16 |
| Norwood (silt loam) | 0 - 15 | 5 | 10 | 5 | 8 | 11 | 17 |
| Norwood (silt loam) | 30 - 45 | 2 | 4 | 1 | 6 | 5 | 12 |

Table 4.08 Comparison of relative percentage of CB-P extracted by the six step fractionation procedure with and with out repeated extractions.

| Soil | Depth | 6 extractions | |
|----------------------|---------|----------------------|------------------|
| | | Non-Repeated CB-P | Repeated CB-P |
| | -cm- | -----%----- | |
| Commerce | 0 - 15 | 4 | 6 |
| Commerce | 30 - 45 | 3 | 5 |
| Mer Rouge | 0 - 15 | 6 | 11 |
| Mer Rouge | 30 - 45 | 5 | 11 |
| Jeanerette | 0 - 15 | 5 | 9 |
| Jeanerette | 30 - 45 | 4 | 8 |
| Norwood (sandy loam) | 0 - 15 | 6 | 10 |
| Norwood (sandy loam) | 30 - 45 | 4 | 7 |
| Norwood (silt loam) | 0 - 15 | 6 | 9 |
| Norwood (silt loam) | 30 - 45 | 4 | 6 |

Table 4.09 Comparison of relative percentage of CBD-P extracted by the four and six step fractionation procedures with and with out repeated extractions.

| Soil | Depth | 4 extractions | | 6 extractions | | | |
|----------------------|---------|-----------------------|-------------------|-----------------------|-------------------|----------------------------|------------------------|
| | | Non-Repeated CBD-P | Repeated CBD-P | Non-Repeated CBD-P | Repeated CBD-P | Non-Repeated [CBD+CB]-P | Repeated [CBD+CB]-P |
| | -cm- | -----%----- | | | | | |
| Commerce | 0 - 15 | 31 | 26 | 9 | 11 | 13 | 16 |
| Commerce | 30 - 45 | 27 | 27 | 12 | 16 | 15 | 21 |
| Mer Rouge | 0 - 15 | 12 | 13 | 6 | 12 | 12 | 23 |
| Mer Rouge | 30 - 45 | 6 | 9 | 5 | 9 | 10 | 20 |
| Jeanerette | 0 - 15 | 12 | 20 | 10 | 12 | 14 | 21 |
| Jeanerette | 30 - 45 | 10 | 17 | 6 | 11 | 10 | 19 |
| Norwood (sandy loam) | 0 - 15 | 5 | 19 | 7 | 11 | 14 | 21 |
| Norwood (sandy loam) | 30 - 45 | 3 | 16 | 6 | 12 | 10 | 20 |
| Norwood (silt loam) | 0 - 15 | 9 | 18 | 6 | 11 | 12 | 20 |
| Norwood (silt loam) | 30 - 45 | 6 | 11 | 4 | 6 | 7 | 12 |

Table 4.10 Comparison of relative percentage of HCl-P extracted by the four and six step fractionation procedures with and with out repeated extractions.

| Soil | Depth | 4 extractions | | 6 extractions | |
|----------------------|---------|-----------------------|-------------------|-----------------------|-------------------|
| | | Non-Repeated HCl-P | Repeated HCl-P | Non-Repeated HCl-P | Repeated HCl-P |
| | -cm- | -----%----- | | | |
| Commerce | 0 - 15 | 36 | 34 | 29 | 30 |
| Commerce | 30 - 45 | 35 | 37 | 29 | 29 |
| Mer Rouge | 0 - 15 | 26 | 24 | 20 | 21 |
| Mer Rouge | 30 - 45 | 46 | 41 | 36 | 40 |
| Jeanerette | 0 - 15 | 54 | 44 | 44 | 40 |
| Jeanerette | 30 - 45 | 44 | 39 | 37 | 34 |
| Norwood (sandy loam) | 0 - 15 | 53 | 40 | 41 | 33 |
| Norwood (sandy loam) | 30 - 45 | 54 | 43 | 43 | 40 |
| Norwood (silt loam) | 0 - 15 | 62 | 55 | 53 | 42 |
| Norwood (silt loam) | 30 - 45 | 67 | 62 | 61 | 51 |

Table 4.11 Comparison of relative percentage of Residual-P extracted by the four and six step fractionation procedures with and with out repeated extractions.

| Soil | Depth | 4 extractions | | 6 extractions | |
|----------------------|---------|-------------------------|---------------------|-------------------------|---------------------|
| | | Non-Repeated Residual-P | Repeated Residual-P | Non-Repeated Residual-P | Repeated Residual-P |
| | -cm- | -----%----- | | | |
| Commerce | 0 - 15 | 24 | 23 | 26 | 21 |
| Commerce | 30 - 45 | 32 | 21 | 31 | 22 |
| Mer Rouge | 0 - 15 | 39 | 31 | 34 | 11 |
| Mer Rouge | 30 - 45 | 46 | 38 | 40 | 15 |
| Jeanerette | 0 - 15 | 31 | 26 | 31 | 22 |
| Jeanerette | 30 - 45 | 45 | 32 | 40 | 27 |
| Norwood (sandy loam) | 0 - 15 | 30 | 22 | 24 | 18 |
| Norwood (sandy loam) | 30 - 45 | 40 | 30 | 36 | 21 |
| Norwood (silt loam) | 0 - 15 | 24 | 17 | 24 | 21 |
| Norwood (silt loam) | 30 - 45 | 26 | 24 | 26 | 22 |

The reductions in P recovery were not attributed to the NaOH and CBD extraction solution matrices themselves but to the subsequent salt washing solutions used in the sequential fractionation procedure. The higher the content of 1 M NaCl in the NaOH extraction or the higher the saturated NaCl in the CBD extraction, the lower the P recovery of the spiked sample. The results suggest that correction may need to be made to NaOH-P and CBD-P when 1 M NaCl or saturated NaCl is used in the fractionation procedure and P measurement is carried out by ICP even when a high salt torch is used.

The use of repeated extractions increased the total P removed by both the six- and four-step P fractionation procedures. The addition of the NaHCO₃ extraction for labile P enhanced P release in the subsequent NaOH-P extraction of the six-step fractionation procedure. This effect was especially significant in soils that were very high in

amorphous Fe or Al oxide. Similar concentrations were seen between the NaHCO₃-P extraction of the six-step procedure and the NaOH-P of the four-step procedure. These results were attributed to the fact that the NaHCO₃ extraction, like the NaOH extraction, could also hydrolyze Al and Fe oxides. The addition of the CB extraction removed < 6 % of the total P by the six-step fractionation procedure. Subsequently, the P removed by the CBD extraction in the six-step fractionation procedure was lower than the P removed by the four-step CBD extraction. This suggested that some of the P that would normally be removed by the CBD-P fraction in the four-step procedure was redistributed to the CB-P fraction in the six-step procedure. Very similar amounts of HCl-P was removed by both the six- and four step P fractionation procedures with and with out repeated extractions. This indicated that the P removed by the HCl-P fraction was very stable and was generally unaffected by the inclusion of the NaHCO₃ fraction, CB-P fraction as well as by repeated extractions. The residual-P fraction was higher in the six-step procedure as compared to the four-step procedure but was generally unaltered by repeating extractions. The percentage of the residual-P fraction with repeated extractions was, however, lower than those of non-repeated extraction in both four- and six-step fractionation procedures.

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CHAPTER 5

EFFECT OF FERTILIZER ANIONS AND CATIONS ON ZINC SORPTION AND LABILITY IN SELECTED CALCAREOUS AND ACID SOILS

5.1 Introduction

Applications of biosolids as fertilizer amendments which are rich in zinc (Zn) as well as other heavy metals have caused considerable concern over impacts on environmental soil and water quality (Alloway and Jackson, 1991; Moore et al., 1998). Zinc is an essential micronutrient for plants as well as animals. High soil concentrations of Zn can be toxic to plants and animals and therefore has prompted Zn as a subject in various studies. Nonetheless, our current understanding of the process involved in Zn chemical reactions in soils especially when applied with other fertilizer elements (inorganic sources or biosolids) is limited (Kabata-Pendias and Pendias, 2001).

The mobility and bioavailability of Zn in soils is likely controlled by its sorption behavior (McBride, 1989). Soil Zn sorption capacity correlates with aluminosilicate clays, metal oxides, and carbonates (Udo et al., 1970; Reddy et al., 1974; Kalbasi et al., 1978; Brümmer et al., 1983). Aluminosilicate clays affect Zn sorption mainly through their effects on soil cation exchange capacity (McBride, 1989). The interactions between Zn and Fe- or Al-oxides through the formation of a covalent bond with surface aquo and/or hydroxo groups have been thought to be the major mechanism of Zn retention by acid soils (Kalbasi et al., 1978; McBride, 1989), whereas Zn sorption by CaCO_3 and precipitation of Zn hydroxides or Zn hydroxi-carbonates are the mechanisms controlling Zn solubility in calcareous soils (Papadopoulus and Rowell, 1989). Soil organic matter can influence Zn sorption behavior by forming both soluble and insoluble Zn-humic substance complexes, although the role of organic matter on Zn sorption appears to be

less significant in soils relative to other heavy metals such as Cu and Cd (Elliot et al., 1986; Catlett et al., 2002).

Soil solution pH, ionic strength and composition also affect Zn sorption. Increasing soil pH increases the total number of negative sites of clay minerals and organic matter, and therefore increases the capacity for Zn sorption (Harter, 1983; McBride, 1989). The soil pH also influences Zn speciation. An increase in pH from 4.8 to 7.1 in acid soils decreased exchangeable Zn from 42 to 2 %, with associated increase in inorganically complexed and oxide-bound Zn (Sims and Kline, 1991). Increasing ionic strength decreased Zn retention in acid soils but did not cause any significant effect on Zn sorption in calcareous soils (Elrashidi and O'Connor, 1982; Shuman, 1986). At a similar ionic strength, Ca^{2+} inhibited Zn sorption more effectively in sandy soils than did Mg^{2+} and K^+ (Zhu and Alva, 1993). However, no difference was observed among Ca^{2+} , K^+ and Na^+ ions in their ability to desorb soil Zn in Andepts (Pardo and Guadalix, 1996). Sulfate increased Zn sorption capacity in acid soils (Shuman, 1986) but had no effect on Zn sorption in calcareous soils as compared to NO_3^- and Cl^- (Elrashidi and O'Connor, 1982). On the other hand, depending on accompanying cations, SO_4^{2-} may have different effects on Zn retention (Pulford, 1986). Previous studies focused primarily on total Zn sorption and little effort was made to reveal the fate of sorbed soil Zn under different chemical environments.

The interaction between Zn and other fertilizer components such as NH_4^+ and PO_4^{3-} salts or N- and P-rich biosolids is not well understood. Very little literature is available on how NH_4^+ affects Zn behavior in soil, although application of nitrogen as certain NH_4^+ salts has been reported to yield higher wheat tissue Zn content (Spratt,

1973). Although different ionic species may be present in soils (Kabata-Pendias and Pendias, 2001), free Zn ion is known to form a complex with NH_3 (Evangelou, 1998), which could be generated from application of NH_4^+ salts or biosolids (Fenn and Hossner, 1985; Sims and Wolf, 1994). An antagonistic relationship between P and Zn was often observed for plant uptake (Burlison et al., 1961; Stukenholtz et al., 1966). While this antagonistic relationship was attributed by some to P toxicity rather than Zn deficiency (Stukenholtz et al., 1966; Loneragan et al., 1979), it is much less clear how P interacts with Zn in soils (Norvell et al., 1987). An early study reported conditions favorable for Zn-phosphate precipitation in aqueous solution, and suggested that similar reactions could also occur in soils (Jurinak and Inouye, 1962). However, this hypothesis was rejected based on a thermodynamic equilibrium evaluation (Lindsay, 1979). Other evidence showed that increasing soil phosphate did not affect soil Zn buffering capacity and only slightly affected Zn intensity (Norvell et al., 1987; Pasricha et al., 1987). Additional studies showed that treating soils with KH_2PO_4 changed existing soil Zn from a less-available form, such as that co-existing with Fe/Mn oxides, to a more available and exchangeable form (Shuman, 1988). In contrast, phosphate application reduced Zn mobility in agricultural and contaminated soils (Melton et al., 1973; McGowen et al., 2001). Clearly, contradicting evidence exists in the literature and further study is necessary to clarify P-Zn interactions in soils.

Recent studies show that many Louisiana soils are deficient in Zn (Harrell et al., 2004; Wang et al., 2004a). Early work reported that as high as 86.4% of total Zn in certain Louisiana soils was in a residual mineral fraction (Sedberry and Reddy, 1976). Because of the wide distribution of different soils, a clear understanding of Zn behavior,

especially its lability, as impacted by other fertilizer elements is necessary to better manage these soils. Therefore, the objective of this study was to investigate the effect of NH_4^+ , K^+ , NO_3^- , H_2PO_4^- , and other background ions on Zn sorption and lability in selected calcareous and acid Louisiana soils.

5.2 Materials and Methods

5.2.1 Soil Samples and Basic Characterization

Surface samples (0-15 cm) of three acid and four calcareous soils collected from Louisiana were used for this study. The three acid soils included Calloway (fine-silty, mixed, active, thermic Aquic Fraglossudalfs), Crowley (fine, smectitic, hyperthermic Typic Albaqualfs), and Dundee (fine-silty, mixed, active, thermic Typic Endoaqualfs). The four calcareous soils included Commerce (fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts), Jeanerette (fine-silty, mixed, superactive, hyperthermic Typic Argiaquolls), MerRouge (fine-silty, mixed, superactive, thermic Typic Argiudolls), and Norwood (fine-silty, mixed, superactive, hyperthermic Fluventic Eutrudepts). The soil samples were air-dried and ground to pass through a 2-mm sieve before use. The chemical and physical characteristics of the soils are presented in Table 5.01. Soil particle size distribution was determined by the pipette method (Gee and Bauder, 1986), organic matter (OM) content by the Wakley-Black method (Wakley, 1947), and pH was determined at a 1:1 soil/water ratio. Soil exchangeable Ca, Mg and K were determined by 1 M NH_4OAc extraction (Thomas, 1982) and CEC by saturating the soil with 1 M NH_4OAc at pH 7 followed by distillation and titration (Soil Survey Laboratory Methods Manual, 1996). Soil P was extracted by 0.03 M NH_4F -0.1 M HCl (Bray and Kurtz, 1945) and Fe, Mn and Zn by DTPA-TEA (Lindsay and Norvell, 1978).

Soil calcium carbonate content was determined by the gravimetric method (US Salinity Laboratory Staff, 1954) and amorphous Fe by ammonium oxalate extraction in the dark (Loeppert and Inskeep, 1996).

5.2.2 Zinc Sorption Isotherms

The sorption experiment was conducted by equilibrating 2 g soil samples with 20 mL of a series of different electrolyte solutions containing 0, 0.5, 1.0, 2.0, 5.0, and 10.0 mM of ZnSO₄ in 30-mL centrifuge tubes (pre-weighed) for 24 hours on a reciprocating shaker. A relatively large initial Zn concentration range was used in this study so that the results would be also analogous to the situation of high water-soluble Zn levels resulting from certain biosolid applications (Epstein, 2003). A preliminary experiment indicated that the large initial Zn concentration range was also necessary to evaluate soils with high Zn sorption capacities. Eight 50 mM electrolyte background solutions were used in the study and they were KCl, KNO₃, KH₂PO₄, NH₄NO₃, and NaNO₃. The cation effect was evaluated by comparing Zn sorption in nitrate salts of Na⁺, K⁺, and NH₄⁺ whereas the anion effect was evaluated in K⁺ salts of Cl⁻, NO₃⁻, and H₂PO₄⁻ backgrounds. Use of 50 mM background solutions was to insure that effects of cations and anions were evaluated at a dominant and constant ionic strength. After equilibrium, samples were centrifuged and the supernatant was filtered through a Whatman No. 42 filter paper. Two replicates were used for collecting each data point. Zinc concentration in the supernatant was analyzed by ICP-OES (Perkin Elmer Optima 3000, Boston, MA) at a wavelength of 213.8 nm. The amount of Zn sorbed was calculated by difference between the initial concentration and the final concentration after equilibration.

Table 5.01 Basic properties of surface soils used for this study[†].

| Soil | pH | Sand | Silt | Clay | CaCO ₃ | Am. Fe | OM | CEC | Extractable | | | | |
|-------------------|-----|-------------------------------|------|------|-------------------|--------|------------------------------------|--------------------------------|-------------|-----|------|-----|-----|
| | | | | | | | | | P | K | Ca | Mg | Zn |
| | | -----g kg ⁻¹ ----- | | | | | cmol _c kg ⁻¹ | -----mg kg ⁻¹ ----- | | | | | |
| <i>Acidic</i> | | | | | | | | | | | | | |
| Calloway | 6.3 | 40 | 695 | 265 | -- | 4.68 | 10 | 8.5 | 253 | 91 | 1066 | 251 | 0.6 |
| Crowley | 5.4 | 110 | 640 | 250 | -- | 2.87 | 20 | 10.4 | 38 | 144 | 1302 | 322 | 0.9 |
| Dundee | 5.4 | 210 | 630 | 160 | -- | 1.40 | 10 | 5.4 | 49 | 131 | 1043 | 166 | 0.6 |
| <i>Calcareous</i> | | | | | | | | | | | | | |
| Commerce | 7.4 | 37 | 650 | 313 | 12 | 4.45 | 21 | 13.7 | 349 | 166 | 3044 | 568 | 2.0 |
| MerRouge | 7.2 | 261 | 517 | 222 | 9 | 0.58 | 13 | 8.3 | 125 | 74 | 1296 | 222 | 2.4 |
| Jeanerette | 7.9 | 83 | 609 | 308 | 38 | 0.80 | 10 | 17.0 | 228 | 86 | 3968 | 482 | 0.4 |
| Norwood | 7.9 | 20 | 860 | 120 | 38 | 0.26 | 6 | 4.9 | 284 | 157 | 2422 | 124 | 0.2 |

[†]Am. Fe, amorphous Fe; OM, organic matter; CEC, cation exchange capacity; Extractable P by Bray 2; Extractable K, Ca and Mg by ammonium acetate; Extractable Zn by DTPA-TEA.

Zinc sorption parameters were obtained by fitting experimental data to the Langmuir model using the Proc nonlinear procedure with SAS statistical software package version 8.02 (SAS Institute, 1999):

$$q = \frac{bkC}{(1 + kC)} \quad [5.01]$$

where q is the sorbed Zn amount in mg kg^{-1} , C equilibrium solution concentration in mg kg^{-1} , b sorption maximum and k bonding energy constant in L kg^{-1} (Langmuir, 1918). A higher bonding energy constant (k) indicates that a larger sorption of a solute by the solid surface exists at very low equilibrium solute concentrations (Olsen and Watanabe, 1957). Use of the Langmuir model offers a simple advantage in managing sorption data (Harter, 1984), even though reaction mechanism inferred from Langmuir fitting alone for a specific set of experimental data may need further independent confirmation (Veith and Sposito, 1977).

All pHs of initial experimental solutions as well as soil-sorption solution mixtures after equilibration were measured and presented in Table 2. A chemical equilibrium simulation using GEOCHEM-PC (Parker et al., 1995) based on published stability constants was carried out and the results indicated that there was no precipitation in the initial pure experimental solutions between Zn and background electrolytes at all Zn concentrations and pH ranges.

5.2.3 Lability of Sorbed Zn

Availability status of sorbed Zn was evaluated at the end of sorption experiment by conducting a DTPA-TEA extraction (Lindsay and Norvell, 1978). A 20 mL DTPA-TEA solution was added to each centrifuge tube containing Zn-sorbed samples from the sorption experiment. The tubes were then shaken for 2 hrs on the reciprocating shaker to

extract Zn. After 2-hr extraction, the samples were centrifuged, and the supernatant solutions were filtered and analyzed for Zn content by ICP-OES. The amount of Zn extracted by DTPA-TEA at the end of Zn sorption experiment was corrected for Zn concentration in the interstitial solution based on pre-weighed tubes, soil weight and added solution weight. The corrected DTPA-TEA extractable Zn was designated as the portion of sorbed Zn retained in the labile pool whereas Zn un-extractable by DTPA-TEA was attributed to soil Zn in the non-labile pool. All sorption isotherm and DTPA-TEA extraction experiments were conducted at 295.2 ± 0.2 °K.

Table 5.02 Measured range of pH values for initial experimental solution and for each soil-sorption solution mixture after 24 hr equilibrium in different electrolyte solutions.

| Medium | NH ₄ NO ₃ | NaNO ₃ | KNO ₃ | KCl | KH ₂ PO ₄ |
|-------------------------|---------------------------------|-------------------|------------------|-----------|---------------------------------|
| Experimental solution | 5.0 - 4.7 | 5.2 - 5.0 | 5.8 - 5.5 | 6.0 - 5.6 | 4.7 - 4.4 |
| <i>Acid soils</i> | | | | | |
| Calloway | 5.9 - 5.2 | 6.1 - 5.4 | 5.9 - 5.4 | 5.9 - 5.5 | 5.3 - 4.6 |
| Crowley | 4.9 - 4.7 | 5.2 - 4.9 | 4.9 - 4.7 | 4.9 - 4.7 | 4.8 - 4.4 |
| Dundee | 4.9 - 4.7 | 5.2 - 4.8 | 4.9 - 4.7 | 4.8 - 4.7 | 4.7 - 4.3 |
| <i>Calcareous soils</i> | | | | | |
| Commerce | 6.7 - 6.0 | 6.9 - 6.1 | 6.7 - 6.1 | 6.7 - 6.2 | 5.4 - 5.0 |
| MerRouge | 7.0 - 6.3 | 7.1 - 6.4 | 6.9 - 6.2 | 7.2 - 6.3 | 5.5 - 4.8 |
| Jeanerette | 7.6 - 7.2 | 8.0 - 7.3 | 7.8 - 7.2 | 7.7 - 7.2 | 5.7 - 5.0 |
| Norwood | 7.7 - 7.0 | 8.2 - 6.9 | 8.0 - 6.9 | 8.0 - 6.9 | 5.8 - 4.9 |

5.3 Results and Discussion

5.3.1 Effect on Total Zn Sorption

Data in Figs. 1 and 2 showed that both cations and anions had large effects on Zn sorption, especially at high Zn concentrations. Total amount of Zn sorbed within the experimental concentration range was larger in calcareous soils than in acid soils. Zinc sorption in calcareous soils was more dominated by specific site sorption as suggested by generally larger Langmuir bonding energy constant (k) values than those in acid soils (Tables 5.03 and 5.04). Of the three cations, the greatest Zn sorption was in the Na^+ background followed by K^+ and NH_4^+ backgrounds. There was little difference in total Zn sorption behavior in K^+ or NH_4^+ background solutions. This trend held true for both acid and calcareous soils.

The differences in total Zn sorption caused by different cations were generally reflected in Langmuir sorption maxima for all soils except for Jeanerette (Table 5.03). The strong Zn sorption nature of the Jeanerette soil made it difficult to fit the Langmuir model and calculate b and k values for the Na^+ background within the Zn experimental concentration range, although it is clear that Na^+ background yielded the largest Zn sorption by the soil (Fig. 5.01). The large total Zn sorption in the Na^+ background as opposed to that in either K^+ or NH_4^+ backgrounds could be due to the less competitive nature of Na^+ with Zn for sorption sites as compared to K^+ and NH_4^+ . The Na^+ , due to its large hydrated ionic size, forms only outer-sphere complexes with clay mineral surfaces whereas K^+ and possibly NH_4^+ are able to form inner-sphere complexes with mineral surfaces (Sposito, 1984). The inhibitory effect of K^+ on Zn sorption as compared to Na^+ has been previously reported for acid sandy soils and Andepts (Zhu and Alva, 1992;

Pardo and Guadalix, 1996). Our results (Fig. 5.02) clearly showed that K^+ also reduced Zn sorption in calcareous soils, although the extent of this inhibitory effect appeared to be relatively small, possibly due to generally large Zn sorption capacity in calcareous soils. It is interesting to note that K^+ and NH_4^+ greatly decreased the bonding energy parameter of Zn sorption in two out of four calcareous soils and one out of three acid soils (Table 5.03). This reduction in the Langmuir bonding energy constant could suggest that Zn sorption by specific site was somewhat restricted by the presence of K^+ and NH_4^+ as opposed to the presence of Na^+ .

The NH_4^+ was thought to resemble K^+ in cation exchange reactions in soils due to their similar ionic size and charge (Rich and Black, 1964; Sposito, 1984). Recent evidence, however, suggests that NH_4^+ and K^+ have different impacts on the interlayer surfaces of certain clay minerals, such as vermiculites (Lumbanraja and Evangelou, 1990). Ammonium ion induced expansion, rather than collapse, of the interlayer of vermiculite as opposed to K^+ (Lumbanraja and Evangelou, 1990). The expansion of the clay mineral interlayer by NH_4^+ would suggest higher Zn sorption in the presence of NH_4^+ . Further, it is well known that application of NH_4^+ fertilizer may cause the evolution of NH_3 even in slightly acid soils (Fenn and Hossner, 1985), and NH_3 could complex with Zn as $Zn(NH_3)^{2+}$ (Evangelou, 1998). We did not characterize the clay mineralogy for the soils used in this study but previous studies with similar soils showed that the acid soils contained appreciable quantities of vermiculites (Tassin, 1966; Wang et al., 2004b). The results shown in Figs. 1 and 2 indicated that the difference, if any, in NH_4^+ and K^+ interaction with clay mineral interlayers or in complex with Zn^{2+} yielded very small difference in total Zn sorption except for MerRouge soil where the Zn sorption

was slightly larger in the presence of K^+ than NH_4^+ at high Zn solution concentrations (Fig. 5.02). The latter was similar to that observed for Cd sorption in presence of K^+ as opposed to NH_4^+ by illite and bentonite (Evangelou, 1998). Nonetheless, the small or negligible difference in total Zn sorption as influenced by K^+ and NH_4^+ appears to be well reflected in generally similar Langmuir sorption maxima and bonding energy parameters (Table 5.03).

The effects of anions on total amounts of Zn sorbed were different between acid and calcareous soils (Figs. 5.01 and 5.02). In acid soils, the largest Zn sorption was observed in the $H_2PO_4^-$ background followed by that in Cl^- and NO_3^- , whereas in calcareous soils the presence of $H_2PO_4^-$ decreased Zn sorption with the exception of the Commerce soil. The overwhelming increase in total Zn sorption in the $H_2PO_4^{2-}$ background shown in Fig. 5.01 for acid soils is consistent with results reported for Hawaiian acid soils (Saeed and Fox, 1979). It has been shown that oxyanions such as PO_4^{3-} and AsO_4^{3-} can form inner-sphere surface complexes with iron and aluminum oxides that increase negative surface charges (Bolland et al., 1977; Bolan et al., 1999). The predominance of Fe/Al oxides in acid soils (Table 1) may explain our observation of higher Zn sorption caused by the presence of $H_2PO_4^-$ in acid soils.

It is interesting to note that for calcareous soils, the presence of $H_2PO_4^-$ decreased total Zn sorption in the MerRouge, Jeanerette and Norwood soils but not in the Commerce soil (Fig. 5.02). This result of $H_2PO_4^-$ lowering total Zn sorption differed from previous work which found that adding P reduced both the soluble Zn concentration and the Zn concentration ratio ($[Zn^{2+}]/[Ca^{2+} + Mg^{2+}]$) in alkaline and calcareous soils (Norvell et al., 1987). In the present study, the result of lowering Zn sorption by $H_2PO_4^-$

in calcareous soils may be explained by the pH difference between H_2PO_4^- and the other electrolyte solutions. The pH ranges of soil-sorption solution mixtures were generally similar for a soil among NH_4NO_3 , NaNO_3 , KNO_3 , and KCl except for KH_2PO_4 (Table 5.02). This was especially true in calcareous soils. Strong buffering by KH_2PO_4 maintained relative lower pH ranges in its soil-solution mixtures than the other electrolytes. We propose that the strong acidity of H_2PO_4^- could dissolve a certain quantity of CaCO_3 in these soils, which could not only decrease the total carbonate surface for Zn sorption but also release more Ca ions to compete with Zn for surface sites of aluminosilicate clays (McBride, 1989; Zhu and Alva, 1993). In addition, increased H^+ may also compete with Zn for negative charged clay surface sites. All these could constitute the cause for low total Zn sorption observed for Jeaneratte, MerRouge, and Norwood soils, which contained 3.8%, 0.9%, and 3.8% CaCO_3 , respectively (Table 5.01).

The Commerce soil, which contained 1.2% CaCO_3 , behaved differently from other calcareous soils; however, it contained 8-10 times more amorphous oxide-Fe than the other three calcareous soils (Table 5.01). Note also the relationship between the amount of total Zn sorption (at the highest initial Zn concentration) and the amorphous Fe as shown in Fig. 5.03 for soils used in this study. The regression equation ($Y=914.3x + 3306$, $R^2=0.988$) obtained for the three acid soils indicated that approximately 98.8% of the variation in total sorbed Zn could be explained by the amorphous Fe oxide content. The calcareous Commerce soil apparently followed this relationship for the acid soils whereas other calcareous soils, Jeanerette, MerRouge and Norwood did not. Clearly, the integrated effect of very high amorphous Fe oxide content and low CaCO_3 content caused

an increased, rather than decreased, Zn sorption by the presence of H_2PO_4^- in Commerce soil. This result has an important implication. It means that even in calcareous soil, the interaction between P and Fe oxides can still significantly influence Zn sorption characteristics. This interaction could be a major mechanism in controlling Zn mobility in calcareous soils with high Fe oxide contents. It may also explain some of contradictory behavior observed for P-Zn interactions for calcareous soils reported in previous studies (Adams, 1980; Norvell et al., 1987).

Langmuir sorption parameters showed that in acid soils, the presence of H_2PO_4^- increased Zn sorption maxima as well as the bonding energy value (Table 5.04). The latter indicated that H_2PO_4^- enhanced specific Zn sorption as opposed to Cl^- or NO_3^- background. In calcareous soils, H_2PO_4^- decreased specific Zn sorption as seen by the large drop in k values except for amorphous Fe oxide-rich Commerce soil. It is interesting to note, however, that Langmuir sorption maxima were actually increased by H_2PO_4^- as opposed to Cl^- and NO_3^- although within the experimental Zn concentration range, Zn sorption was clearly decreased by H_2PO_4^- in Jeanerette, MerRouge and Norwood soils (Table 5.04 vs. Fig. 5.02). It should be pointed out that the Langmuir model was employed to predict the overall sorption capacity beyond experimental concentration range. Limitations of using the Langmuir model have been discussed elsewhere (Veith and Sposito, 1977; Harter, 1984). Nonetheless, a small k bonding energy constant generally yields a less sharp initial slope of the sorption curve, which is consistent with a low-affinity (non-specific) sorption (Langmuir, 1918; Harter, 1984). The results (Fig. 5.02 and Table 5.04) clearly demonstrate the impact of H_2PO_4^- (as opposed to Cl^- and NO_3^-) on the shape and description of Zn sorption isotherms using the

Langmuir model. Although the intrinsic sorption mechanisms involved may require further examination, the Langmuir parameters indicated that the presence of H_2PO_4^- may increase the non-specific sorption capacity of Zn in calcareous soils.

There was no difference in Zn sorption caused by the presence of Cl^- and NO_3^- (Figs. 5.01 and 5.02). This result was true for both acid and calcareous soils. The similar effect of Cl^- and NO_3^- on total Zn sorption was consistent with those reported by others for an alkaline sandy soil (Elrashidi and O'Connor, 1982) and for two acid coastal plain soils (Shuman, 1986). On the other hand, Zn sorption on goethite was enhanced by Cl^- and not by NO_3^- at low pH conditions, possibly due to specific sorption of Zn-Cl complex ions (Padmanabham, 1983; Shuman, 1986). In the present study for acid soils, there was no difference between the Cl^- and NO_3^- effect in the specificity of sorption as seen by equal Langmuir bonding energy parameters for acid soils (Table 5.04). For calcareous soils, Cl^- did increase k values as compared to NO_3^- for the Jeanerette, Mer Rouge and Norwood soils but not for the Commerce soil. Predicted Zn sorption maxima by the best-fit Langmuir model were similar in general for all acid and calcareous soils in the presence of Cl^- and NO_3^- although some slight differences existed (Table 5.04).

5.3.2 Effect on Lability of Sorbed Zinc

The sorbed Zn was partitioned into labile and non-labile pools by extracting with DTPA-TEA at the end of sorption experiment. The DTPA-TEA extraction was originally developed for extracting plant-available Zn in neutral and alkaline soils (Lindsay and Norvell, 1978). Analysis using isotopic exchange and dilution techniques showed that this extraction was able to characterize the labile pool of Zn in both acid and calcareous soils (Sinaj et. al., 1999). For this reason, we chose DTPA-TEA extraction to fractionate

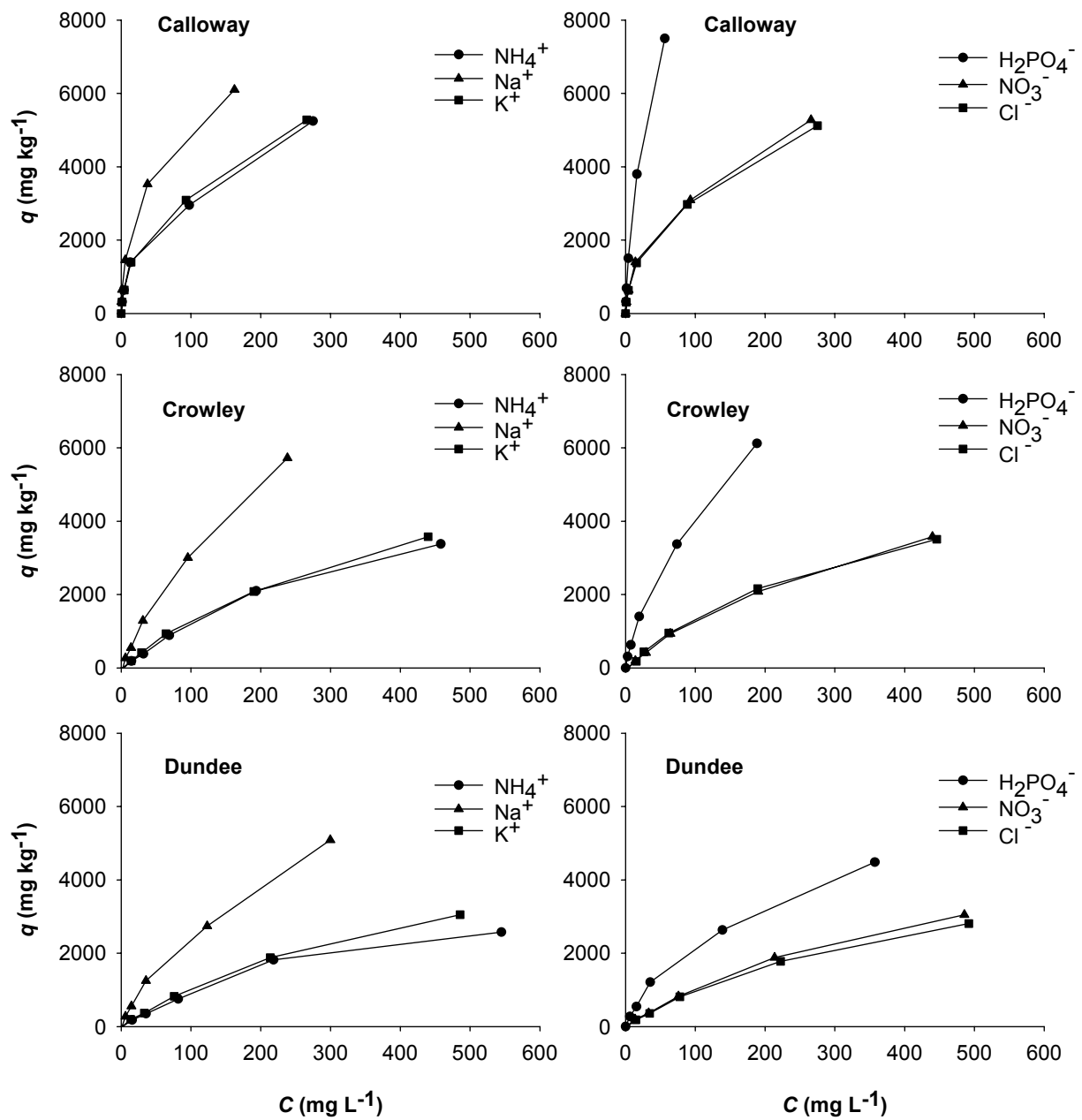


Figure 5.01 Zinc adsorption on selected acid soils as affected by differing anionic and cationic background solutions.

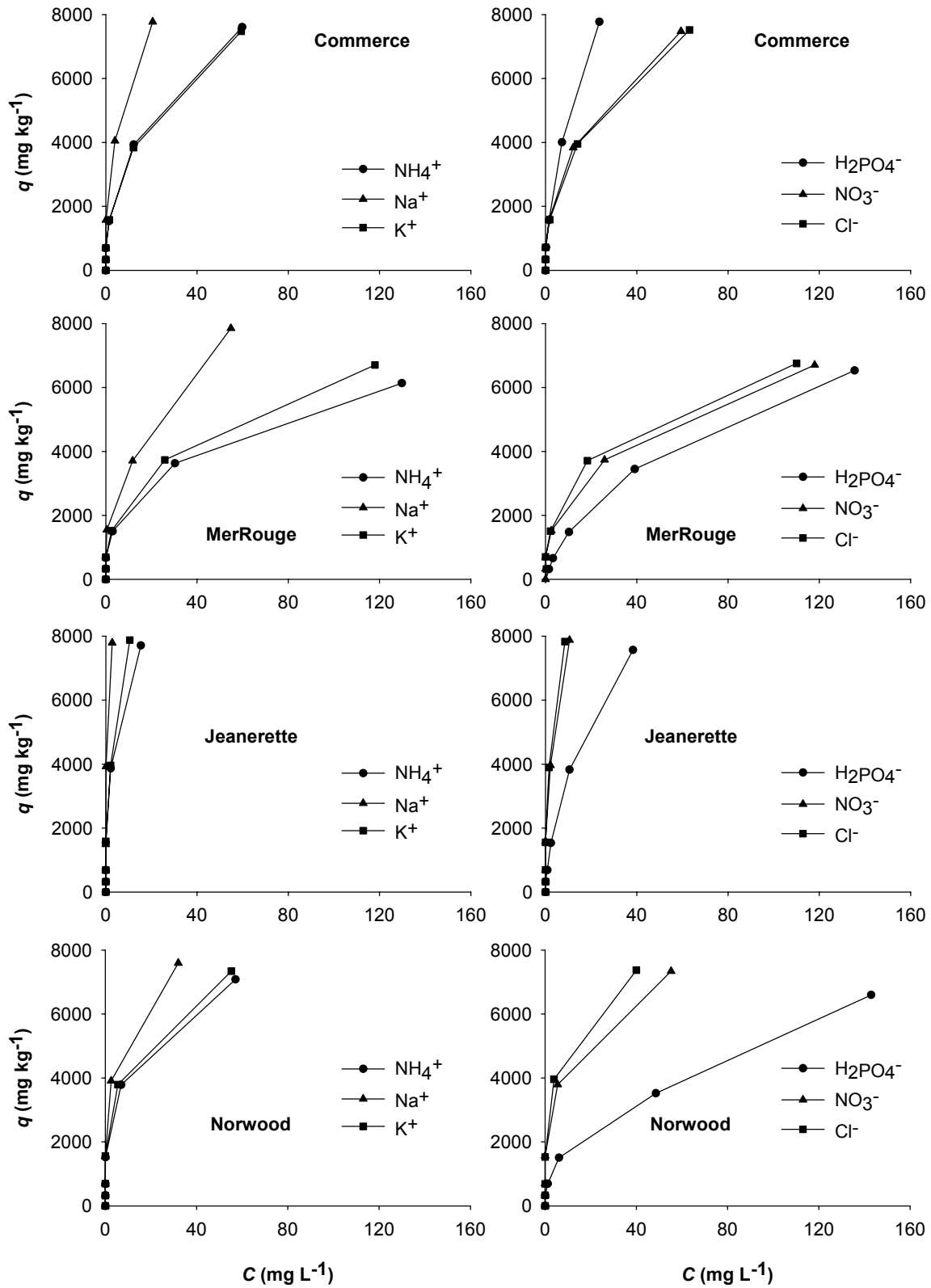


Figure 5.02 Zinc adsorption on selected calcareous soils as affected by differing anionic and cationic background solutions.

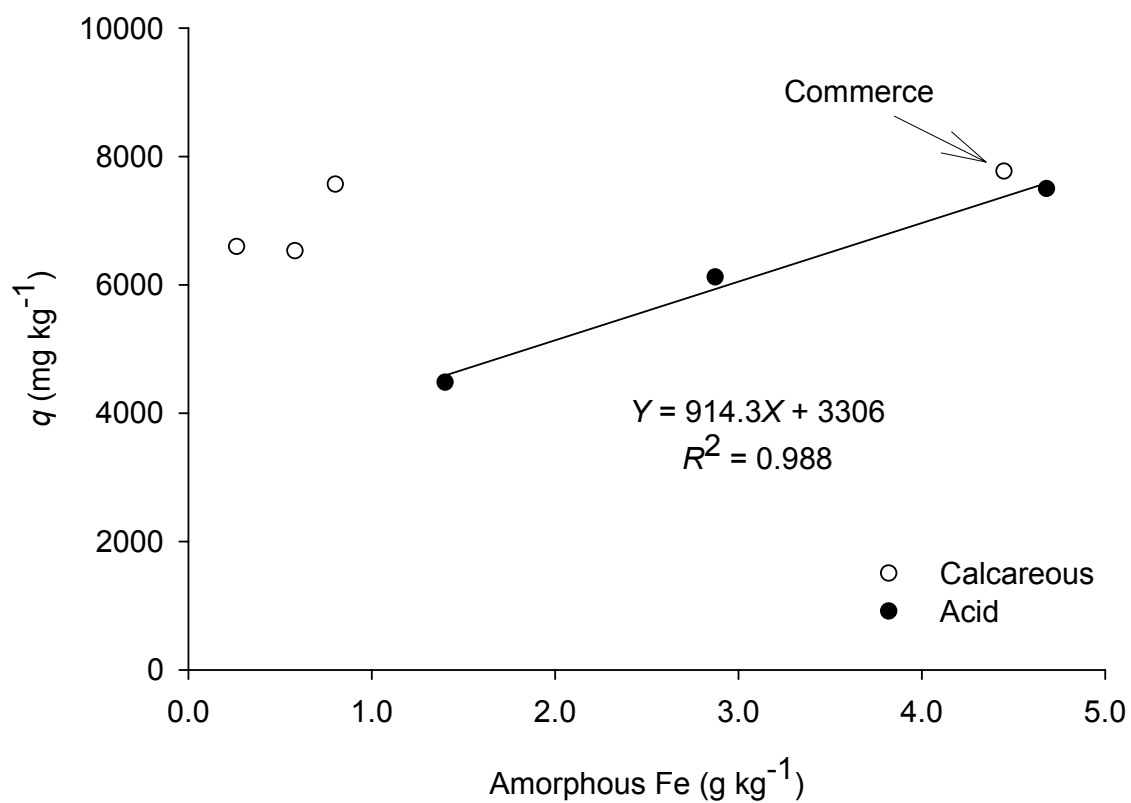


Figure 5.03 Relationship between the total Zn sorption (at the highest initial Zn concentration in KH_2PO_4 background) and the amorphous Fe content for acid and calcareous soils.

Table 5.03. Langmuir sorption isotherm parameters and correlation coefficient for total Zn sorption by selected acid and calcareous soils in differing cationic solutions of nitrate salts.

| Soil | Background | Langmuir | | |
|-------------------|------------------------------|---------------------|--------------------|----------------|
| | | <i>b</i> | <i>k</i> | R ² |
| | | mg kg ⁻¹ | L kg ⁻¹ | |
| <i>Acid</i> | | | | |
| Calloway | NH ₄ ⁺ | 6856 | 0.010 | 0.959 |
| | Na ⁺ | 7201 | 0.030 | 0.983 |
| | K ⁺ | 6737 | 0.012 | 0.973 |
| Crowley | NH ₄ ⁺ | 6318 | 0.003 | 0.999 |
| | Na ⁺ | 13280 | 0.003 | 0.998 |
| | K ⁺ | 7265 | 0.002 | 0.999 |
| Dundee | NH ₄ ⁺ | 4060 | 0.004 | 0.990 |
| | Na ⁺ | 10249 | 0.003 | 0.995 |
| | K ⁺ | 6022 | 0.002 | 0.999 |
| <i>Calcareous</i> | | | | |
| Commerce | NH ₄ ⁺ | 9419 | 0.07 | 0.969 |
| | Na ⁺ | 9730 | 0.19 | 0.940 |
| | K ⁺ | 9278 | 0.07 | 0.967 |
| MerRouge | NH ₄ ⁺ | 7056 | 0.04 | 0.955 |
| | Na ⁺ | 10820 | 0.05 | 0.941 |
| | K ⁺ | 7988 | 0.04 | 0.957 |
| Jeanerette | NH ₄ ⁺ | 9226 | 0.33 | 0.924 |
| | Na ⁺ | -- | -- | -- |
| | K ⁺ | 10550 | 0.28 | 0.924 |
| Norwood | NH ₄ ⁺ | 7996 | 0.13 | 0.920 |
| | Na ⁺ | 8265 | 0.35 | 0.922 |
| | K ⁺ | 8192 | 0.16 | 0.915 |

Table 5.04. Langmuir sorption isotherm parameters and correlation coefficient for total Zn sorption by selected acid and calcareous soils in differing anionic solutions of potassium salts.

| Soil | Background | Langmuir | | |
|-------------------|---|---------------------|--------------------|----------------|
| | | <i>b</i> | <i>k</i> | R ² |
| | | mg kg ⁻¹ | L kg ⁻¹ | |
| <i>Acid</i> | | | | |
| Calloway | H ₂ PO ₄ ⁻ | 11626 | 0.032 | 0.997 |
| | NO ₃ ⁻ | 6737 | 0.012 | 0.973 |
| | Cl ⁻ | 6490 | 0.012 | 0.978 |
| Crowley | H ₂ PO ₄ ⁻ | 11263 | 0.006 | 0.997 |
| | NO ₃ ⁻ | 7265 | 0.002 | 0.999 |
| | Cl ⁻ | 6267 | 0.003 | 0.999 |
| Dundee | H ₂ PO ₄ ⁻ | 6960 | 0.005 | 0.995 |
| | NO ₃ ⁻ | 6022 | 0.002 | 0.999 |
| | Cl ⁻ | 5295 | 0.002 | 0.999 |
| <i>Calcareous</i> | | | | |
| Commerce | H ₂ PO ₄ ⁻ | 12078 | 0.075 | 0.986 |
| | NO ₃ ⁻ | 9278 | 0.066 | 0.967 |
| | Cl ⁻ | 9457 | 0.058 | 0.969 |
| MerRouge | H ₂ PO ₄ ⁻ | 9564 | 0.016 | 0.996 |
| | NO ₃ ⁻ | 7988 | 0.040 | 0.957 |
| | Cl ⁻ | 7653 | 0.060 | 0.969 |
| Jeanerette | H ₂ PO ₄ ⁻ | 11180 | 0.054 | 0.993 |
| | NO ₃ ⁻ | 10550 | 0.279 | 0.924 |
| | Cl ⁻ | 10092 | 0.405 | 0.925 |
| Norwood | H ₂ PO ₄ ⁻ | 9812 | 0.014 | 0.962 |
| | NO ₃ ⁻ | 8192 | 0.156 | 0.915 |
| | Cl ⁻ | 8143 | 0.240 | 0.920 |

the total sorbed Zn into labile and non-labile pools. The results of this fractionation in the presence of different background electrolytes for the acid Dundee and calcareous Norwood soils are shown in Figs. 5.04 and 5.05, respectively. Similar results were also observed for other acid and calcareous soils (Data not shown).

The majority of total sorbed Zn was labile (as defined by DTPA-TEA extraction for 2 hr of equilibration; Figs. 5.04 and 5.05), suggesting that much of the sorbed Zn was readily bioavailable. This was true for all soils regardless of what background ions were present although the amount of labile Zn differed among certain ionic backgrounds. On average, about 60-96% of the total sorbed Zn by all soils was labile (Table 5.05). The effect of the three cations on the lability of the total sorbed Zn was very similar in calcareous soils, whereas in acid soils, NH_4^+ appeared to yield a slightly higher percentage of labile Zn (by 4-12% higher) than K^+ (Fig. 5.04 and Table 5.05). The latter result was unlikely due to the pH effect since NH_4^+ and K^+ salts yielded generally similar pH values in soil-solution mixtures (Table 5.02). It is known, however, that these acid soils contain predominately fully and partially expandable clay minerals such as montmorillonite and vermiculite (Tassin, 1966; Wang et al., 2004b). Since the hydrated ionic size of Zn is smaller than those of K^+ and NH_4^+ , the difference between NH_4^+ and K^+ in influencing interlayer expansion or collapse of these minerals as suggested by Lumbanraja and Evangelou (1990) could affect the accessibility of sorbed Zn for DTPA-TEA extraction. Incorporation of Zn into hydroxyl-Al interlayered phyllosilicates was recently confirmed in an acid subsoil of a contaminated site by X-ray absorption spectroscopy (Scheinost et al., 2002). The results in Table 5.05, along with those shown in Table 5.03 and Figs. 5.01 and 5.02, indicate that although K^+ and NH_4^+ did not differ

in competing with Zn for total sorption sites, although they may differ in their affect on the lability of sorbed Zn in acid soils.

The difference among the three anions in influencing lability of total sorbed Zn was small (<8%) in acid soils but relatively large (>10%) in calcareous soils (Table 5.05). In general, the presence of H_2PO_4^- caused 10-25% more nonlabile Zn than Cl^- or NO_3^- depending on the individual calcareous soil. This result is very interesting considering that within the experimental concentration range, the presence of H_2PO_4^- decreased initial Zn sorption in three out of four calcareous soils (Fig. 5.02). This suggests that although total Zn sorption was decreased due to lower pH effect of H_2PO_4^- , the sorbed Zn was less labile and possibly less available for plant uptake. Nonlability of a metal ion in soil has been generally attributed to the entrapment of the metal into small pores of particle aggregates or clay mineral structures, the strong surface adsorption by oxides, and/or the formation of insoluble metal precipitates (McBride, 1989; Hamon et al., 2002). All these reactions (especially the latter) may account for the loss of lability in certain fractions of sorbed Zn in the present study.

It should be pointed that in this study, we did not measure carbonate ions in soil-solution mixtures for both acid and calcareous soils. It is possible that carbonate ions in calcareous soils with low P concentrations could react with Zn to form ZnCO_3 precipitates (Papadopoulos and Rowell, 1989). However, it is unlikely that ZnCO_3 would be present as a stable compound even in calcareous soils since it is generally more soluble than “Soil-Zn”, an undefined Zn mineral (Lindsay, 1979). Precipitation as Zn hydroxylcarbonate, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, was proposed in calcareous soils (Papadopoulos and Rowell, 1989). Other research suggests that the formation of Zn-Fe precipitates such

as ZnFe_2O_4 (franklinite) may occur in both acid and calcareous soils (Pulford, 1986; Catlett et al., 2002; Scheinost et al., 2002). In the presence of H_2PO_4^- , we speculate that the increase in the non-labile fraction of sorbed Zn in calcareous soils may be largely due to the formation of Zn-phosphate precipitates such as $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (hopeite). This was indirectly supported by the results of thermodynamic equilibrium modeling using GEOCHEM-PC based on initial Zn and H_2PO_4^- concentrations and the observed pH ranges of sorption soil-solution mixtures for the calcareous soils. However, it may not be valid to assume equilibrium without further defining solid surfaces in the system (McBride, 1989; Parker et al., 1995). Earlier, Lindsay (1979) pointed out that the formation of hopeite was not likely because H_2PO_4^- could be fixed by strengite-soil-Fe at low pH and by $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and other Ca-phosphates or carbonates at higher pHs. However, recent evidence suggests that in Zn-contaminated soils the addition of KH_2PO_4 may indeed lead to the formation of hopeite (McGowen et al., 2001) and an increase in the nonlabile pool (irreversible sorption) of soil Zn as confirmed by isotopic exchange and dilution techniques (Hamon et al., 2002). The results of the present study using Zn and P concentrations commonly found in localized soil environments with or without applications of inorganic P and/or Zn fertilizers or P- and Zn-rich biosolids are consistent with such studies.

5.4 Conclusions

The present study clearly demonstrates various effects of background K^+ , Na^+ , NH_4^+ cations and H_2PO_4^- , Cl^- , NO_3^- anions on Zn sorption characteristics and lability in acid and calcareous soils. The labile fraction of total sorbed Zn does not necessarily correspond to the amount of total Zn sorption observed in the presence of

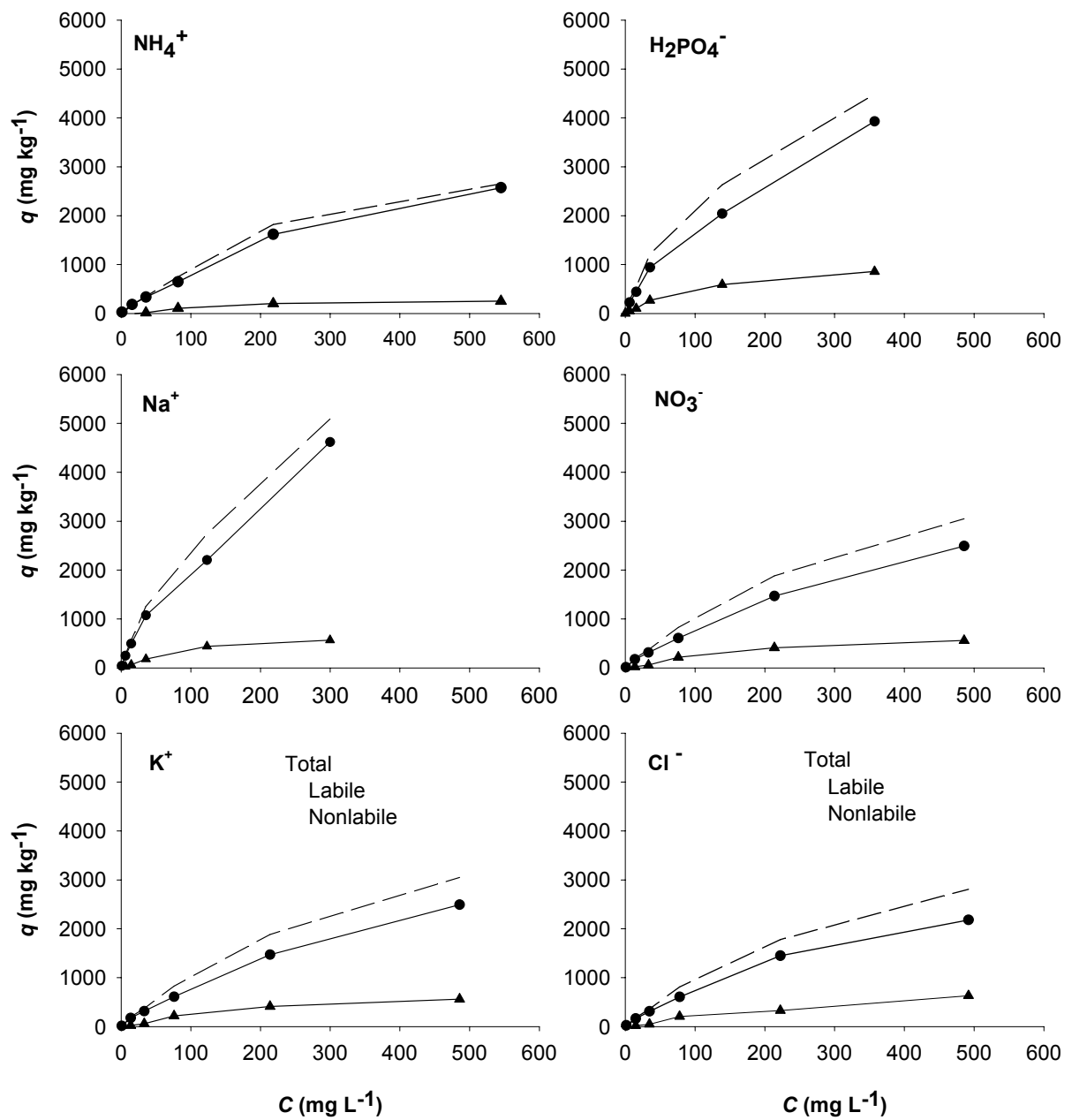


Figure 5.04 Sorption isotherms for total, labile, and non-labile Zn sorption for an acid Dundee soil as affected by different background cationic and anionic species.

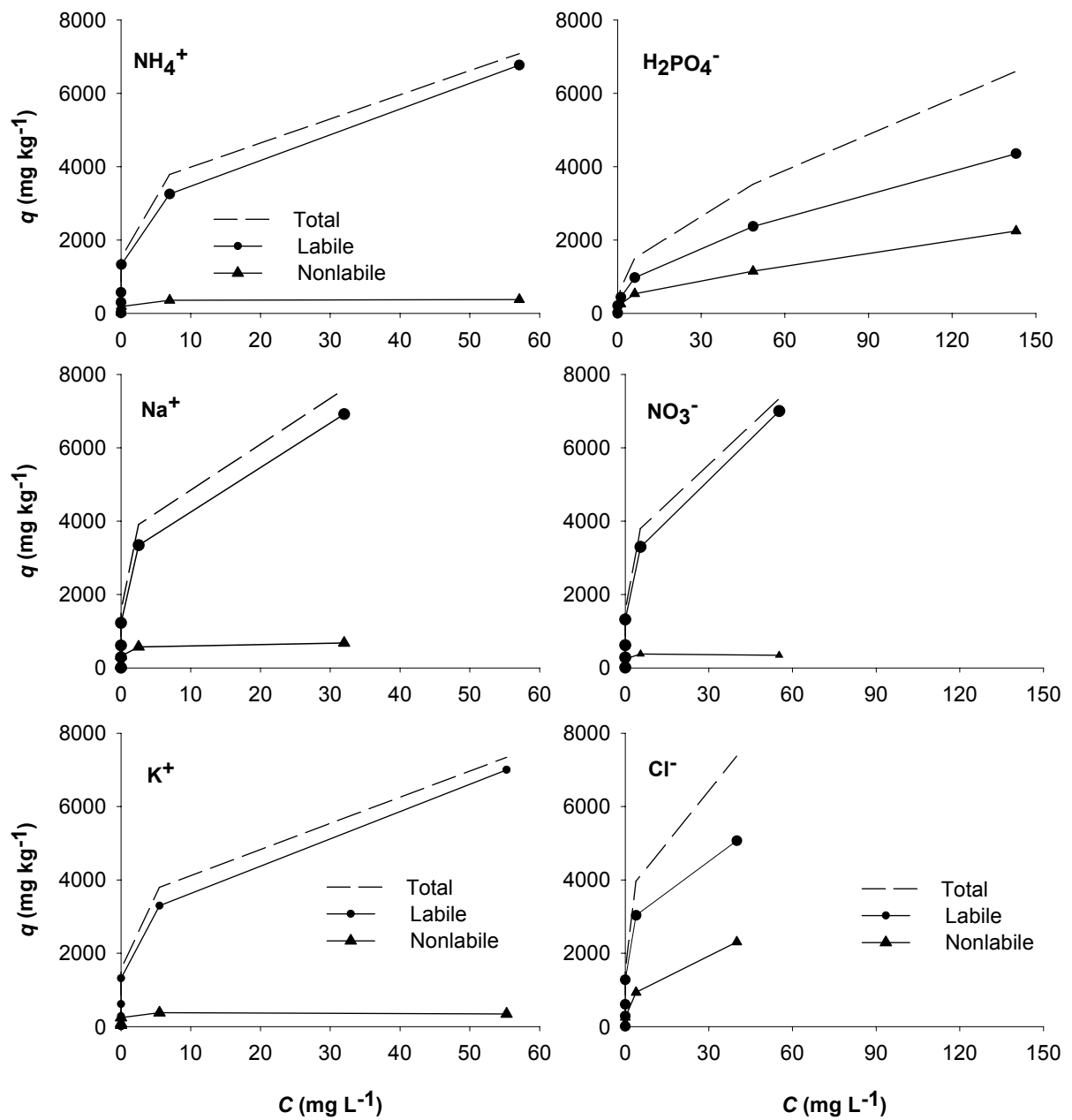


Figure 5.05 Sorption isotherms for total, labile, and non-labile Zn sorption for a calcareous Norwood soil as affected by different background cationic and anionic species.

Table 5.05 Average percentage (mean \pm SE) of labile pool of the total sorbed Zn in the presence of different cations and anions[†].

| Soil | Cations | | | Anions | | |
|-------------------|----------------|-----------------|------------------------------|---|-----------------|------------------------------|
| | K ⁺ | Na ⁺ | NH ₄ ⁺ | H ₂ PO ₄ ⁻ | Cl ⁻ | NO ₃ ⁻ |
| Acid | | | | | | |
| Calloway | 87.2 \pm 1.5 | 89.9 \pm 1.5 | 91.9 \pm 1.3 | 80.4 \pm 2.5 | 88.1 \pm 1.8 | 87.2 \pm 1.5 |
| Crowley | 90.5 \pm 3.2 | 96.4 \pm 1.6 | 96.3 \pm 1.3 | 83.1 \pm 2.9 | 88.2 \pm 3.4 | 90.5 \pm 3.2 |
| Dundee | 81.6 \pm 2.6 | 87.4 \pm 2.0 | 93.8 \pm 2.6 | 81.1 \pm 1.8 | 81.9 \pm 2.7 | 81.6 \pm 2.6 |
| Calcareous | | | | | | |
| Commerce | 88.4 \pm 1.7 | 90.2 \pm 2.3 | 93.4 \pm 1.7 | 65.5 \pm 1.3 | 84.2 \pm 2.6 | 88.4 \pm 1.7 |
| Jeanerette | 85.2 \pm 1.8 | 83.9 \pm 1.4 | 88.3 \pm 2.4 | 60.6 \pm 2.1 | 83.1 \pm 1.3 | 85.2 \pm 1.8 |
| MerRouge | 90.9 \pm 1.8 | 89.8 \pm 1.9 | 94.3 \pm 1.6 | 80.2 \pm 1.6 | 91.3 \pm 1.9 | 90.9 \pm 1.8 |
| Norwood | 88.4 \pm 1.8 | 85.8 \pm 1.9 | 88.5 \pm 2.1 | 65.0 \pm 0.7 | 80.5 \pm 3.5 | 88.4 \pm 1.8 |

[†]Zinc in labile pool was determined by DTPA-TEA extraction at the end of adsorption experiment. Average percentage of labile Zn was calculated from all concentration levels of adsorption.

these ions, with important implications for managing nutrient interactions. The presence of NH₄⁺ or K⁺ similarly reduced total Zn sorption as compared to Na⁺. Ammonium, however, was able to maintain slightly more sorbed Zn in the labile pool as opposed K⁺ in acid soils. The latter suggests that in acid soils a more efficient application Zn would occur with co-application of NH₄, not K, salt fertilizers. The presence of H₂PO₄⁻ enhanced Zn sorption in acid soils but decreased Zn sorption in three out of four calcareous soils when compared to Cl⁻ or NO₃⁻ backgrounds. Higher total Zn sorption

caused by H_2PO_4^- in one calcareous soil, Commerce, was attributed to its high amorphous Fe oxide content. This result indicates that even in calcareous soils, Zn-P interaction could be greatly influenced by Fe oxides. Furthermore, although in acid soils total Zn sorption was enhanced by the presence of H_2PO_4^- , the sorbed Zn was generally labile, implying a greater mobility and availability. On the other hand, although in three out of four calcareous soils total Zn sorption was decreased by H_2PO_4^- , a larger percentage of the sorbed Zn was associated with the nonlabile pool. Overall, the presence of these various cations and anions changed both the capacity and specificity characteristics of Zn sorption in acid and calcareous soils.

5.5 References

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CHAPTER 6

MANAGEMENT OF PHOSPHORUS AND ZINC FOR CORN GROWN IN A CALCAREOUS RED RIVER ALLUVIAL SOIL: A THREE YEAR FERTILIZER STUDY

6.1 Introduction

An accurate soil testing program can take a soil sample and estimate the essential plant available nutrients and provide proper fertilizer recommendations to producers in order to maximize agronomic yields. A soil testing program includes an accurate analytical laboratory procedure as well as the appropriate correlation and calibration data for recommending the correct fertilization practices (Sabbe and Marx, 1987). The current soil test phosphorus (P) extraction method in Louisiana is the Bray II extraction. The Bray II extraction is strongly acidic and has a pH near 1. It has been reported that the strong acidity of the extraction solution may lead to the overestimation the plant available P from calcareous soils (Fixen and Grove, 1990; Mallarino, 1997; Harrell et al., 2004). The Red River alluvial soils have a high soil test P, but may actually be deficient in labile (plant available) P. Recent observations suggest that this could be the case where yield responses in corn (*Zea Mays* L.) due to P fertilization occurred in calcareous Red River alluvial soils where normally P fertilization would not be recommended (Moore and Wilcott, unpublished data). This information leads us to believe that a problem exists with the LSU P extraction procedure and/or with associated calibration data for these calcareous Red River soils. Zinc (Zn) deficiency is also a problem in these soils.

Zinc deficiencies are commonly found in calcareous Red and Mississippi River alluvial soils that contain high levels of P. Zinc deficient soils can cause reduced agronomic yields and thus profits if not corrected early in the growing season. There is

currently very little information on Zn fertility recommendations in Louisiana. Other research has found that when both P and Zn are marginal or limiting in soil, P fertilization can promote plant growth and cause dilution in tissue Zn levels which may further complicate or induce Zn deficiency (Singh et al. 1988; Goh et al., 1997). Little documented information exists on the extent of the P and Zn deficiencies in these particular calcareous Louisiana alluvial soils.

Red River alluvial soils make up some of the most productive agricultural soils in the state of Louisiana. The importance of these soils to Louisiana agriculture and the current void of knowledge on the P and Zn problems with respect to these soils prompted initiation of the current research. Specifically, the research objectives are to (i) evaluate the effect of Zn and P fertilization on corn yields and nutrient uptake on a Red River alluvial Norwood silt loam soil; (ii) establish critical levels for common soil test Zn and P extractions where significant yield responses due to P and Zn fertilization occur; and (iii) to formulate P and Zn fertilizer recommendations for corn grown in Red River alluvial soils using common soil test P and Zn extractions.

6.2 Materials and Methods

A field experiment conducted to study the response of corn to P and Zn fertilization was established at the Dean Lee Louisiana Research Station in Alexandria, Louisiana in the spring of 2002. The study was moved to separate locations within the research station in 2003 and again in 2004 for a total of three site-years. The soil at each site was a Red River alluvial Norwood silt loam (fine-silty, mixed, calcareous, superactive, hyperthermic Fluventic Eutrudepts). The experimental design was a randomized block consisting of 4 blocks (replications). Six rates of P (0, 34, 67, 101,

135, and 359 kg P₂O₅ ha⁻¹) and 6 rates of Zn (0, 1.12, 2.24, 3.36, 4.48, and 6.73 kg Zn ha⁻¹) were used in the design. Each block contained a total of 36 P and Zn treatment combinations for a total of 144 plots (n = 144). Plots were 15.2 m long and contained 4 rows with a 96.52 cm row spacing in 2002 and 2003. In 2004 plot length was reduced to a length of 7.6 m to facilitate the available field size. Planting depth was approximately 5 cm with plant spacing of approximately 15.2 cm. A 'Dekalb 697' corn variety was used in 2002 and 2004 while a 'Pioneer 34B23' variety was used in 2003. Planting dates were April 18, 2002, April 18, 2003 and April 2, 2004. Zinc was applied in furrow during planting as zinc sulfate (ZINC-GRO[®] Mini Granular, TETRA Micronutrients, Woodlands, TX). Phosphorus was banded seven days after planting each year as triple super phosphate (46% P₂O₅) at a distance of 24.3 cm from the furrow and a depth of 5 cm using a modified Hege grain drill. All plots received nitrogen applied as ammonium nitrate at a rate of 224 kg ha⁻¹ and potash applied as K₂O at a rate of 67.2 kg ha⁻¹. Weed and pest management included the use of Dual, Atrazine, Counter, Aztec, Prowl, and Clarity products applied at the recommended application rates.

Corn was harvested on September 6, September 10, and August 24 for the 2002, 2003 and 2004 years respectively. Yield was determined with only the middle two rows of each plot. Plots were trimmed by hand prior to harvesting to a length of approximately 10.64 m in 2002 and 2003. In 2004 the plots were trimmed to a length of 6.08 m.

Soil samples were taken at a depth of 0 to 15 cm from each plot prior to the initiation of the fertilizer treatments and also after harvesting each year to determine extractable P and Zn levels. The samples were air-dried and ground to pass through a 2-mm sieve. Extractable P was determined by three soil test extraction methods including:

i) Mehlich III, determined by extracting 2 g of soil with 20 mL of 0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.013 M HNO₃ + 0.001 M EDTA and shaking for 5 min (Mehlich, 1984); ii) Olsen, determined by extracting 1 g of soil with 20 mL of 0.5 M NaHCO₃ and shaking for 30 min. (Olsen et al., 1954) and iii) Bray II, determined by extracting 2 g of soil with 40 mL of 0.03 M NH₄F + 0.1 M HCl and shaking for 15 min (Bray and Kurtz, 1945). Extractable Zn was determined by two soil testing procedures including i) DTPA-TEA Zn (DTPA), determined by extracting 10 g of soil with 20 mL of 0.0005 M DTPA + 0.01 M CaCl₂ + 0.1 M C₆H₁₅NO₃ adjusted to pH 7 and shaking for 2 hours (Lindsay and Norvell, 1978) and ii) Mehlich III Zn extracted simultaneously with P as described above.

Plant tissue samples were taken approximately seven weeks after planting each year in order to estimate nutrient Zn and P uptake. Sampling dates were June 14, 2002, June 13, 2003 and June 9, 2004. The third leaf from the top of the corn plant taken for analysis each year. The leaf was then dried at 60°C for 48 h in a forced-air oven and homogeneously ground in a Cyclone 1093 Sample Mill (Tecator, Hoganas, Sweden). The tissue samples were then digested with concentrated HNO₃ and 30% H₂O₂ according to Jones and Case (1990) and analyzed for P and Zn by ICP-OES.

Prior to the initiation of the 2002 field experiment, during the site selection process, a composite soil sample was taken at the Dean Lee Research Station (31°10' N and 92°24' W) at two depths representing the surface (0-15 cm) and subsurface (30-45 cm). The samples were used to gather selected physical and chemical information of the Norwood series (Table 6.01). The data includes soil particle size analysis performed by the pipette method (Gee and Bauder, 1986). Organic matter (OM) content was

determined by the Walkley-Black method (Walkley, 1947). Soil pH was measured in deionized water with a soil to solution ratio of 1:1. The CEC was measured by saturating the soil with 1 M NH₄OAc at pH 7 followed by distillation and titration (Soil Survey Laboratory Methods Manual, 1996). Calcium carbonate equivalent (CCE) was determined by a gravimetric method (U. S. Salinity Laboratory Staff, 1954). Total free iron oxide as Fe (Fe_{CBD}) was extracted with 3 M Na₃C₆H₅O₇ · 2H₂O + 1 M NaHCO₃ + 1 g Na₂S₂O₄ in a water bath heated at 85°C (Mehra and Jackson, 1960). The more reactive amorphous Fe oxide as Fe (Fe_{AOX}) was determined by first pretreating the soil with 1 M (NH₄)₂C₂O₄ (pH 5.5) to remove carbonates, followed by extraction with 0.175 M (NH₄)₂C₂O₄ + 0.1 M H₂C₂O₄ adjusted to pH 3.0 according to Loeppert and Inskeep (1996).

Clay mineralogy was determined by standard x-ray diffraction procedures (Whittig and Allardice, 1986). The <2 µm clay size fraction was collected by dispersing the soil particles using 0.01% Na-hexametaphosphate (NaHMP). Sand and silt fractions were allowed to settle out and the suspended clay particles were siphoned from the suspension. This was repeated several times to remove the entire clay fraction from the initial sample. The clay fraction was centrifuged and oriented films were produced by smearing the clay pastes onto glass slides. X-ray diffraction patterns were obtained using a Siemens D5000 diffractometer (Bruker AXS Inc., Madison, WI) with Cu-Kα radiation in the 2 – 36° 2θ range. Along with air-dried samples, X-ray patterns were also obtained for ethylene glycol solvated, 300°C and 550°C heat-treated samples. X-ray patterns were normalized at the quartz 4.23Å peak and peak areas were obtained using a Pearson VII function in MacDiff 4.2.5 (Petschick, 2000).

Table 6.01 Selected physical and chemical properties of the Norwood soil at two depths.

| Depth | pH | Particle size analysis | | | OM | CCE | CEC | Clay mineralogy [†] | | | | | | Carbonate [§] | | Iron Oxides | |
|-------|-----|-------------------------------|------|------|-----|------|------------------------------------|------------------------------|-----|-----|-----|-----|-----|-------------------------------|-----|-------------------|-------------------|
| | | Sand | Silt | Clay | | | | Sme | Chl | Kao | Mic | ICS | IVS | Cal | Dol | Fe _{AOX} | Fe _{CBD} |
| cm | | -----g kg ⁻¹ ----- | | | | | cmol _c kg ⁻¹ | -----%----- | | | | | | -----g kg ⁻¹ ----- | | | |
| 0-15 | 7.9 | 18 | 841 | 142 | 6.0 | 38.5 | 4.9 | 28 | - | 12 | 34 | 26 | - | 32 | 68 | 263 | 2439 |
| 30-45 | 7.9 | 20 | 818 | 162 | 1.6 | 48.3 | 8.1 | | | | | | | 38 | 62 | 482 | 4144 |

[†] OM, organic matter; CEC, cation exchange capacity; CCE, calcium carbonate equivalent.

[‡] Sme, smectite; Chl, chlorite; Kao, kaolinite; Mic, clay mica (illite); ICS, Randomly stratified chlorite and smectite; IVS, randomly interstratified vermiculite and smectite.

[§] Cal, Calcite; Dol, Dolomite.

Peak height percentages (PHP) were used to determine a quantitative representation (QR) of the phyllosilicate clay minerals present in the sample according to Equation [6.01]

$$PHP = \left(\frac{Int\alpha}{Int\alpha + Int\beta} \right) * 100 \quad [6.01]$$

where Int = peak intensity (area) of mineral of interest (α , β). The PHP represents only a QR of the clay minerals present in each sample and is not intended to be a precise measure of absolute mineral quantities in the sample (Hughes et al., 1994; Aparicio and Ferrell, 2001).

Mineralogical analysis of carbonates was determined by generating x-ray patterns in the $23 - 36^{\circ}2\theta$ range directly from a random powder mount of air-dry soil samples with and without carbonates removed. Carbonates were removed by treating the samples with 3 M HCl. Differences in the 3.04 and 2.98 Å peaks in the x-ray diffractogram confirmed the occurrences of calcite and dolomite respectively (Figs. 6.01 and 6.02). A quantitative estimation of each carbonate mineral was also determined according to Equation [6.01] above.

Statistical analysis was conducted using the SAS software package. Analysis of Variance was calculated using PROC GLM. The MODEL statements compared yield means with Zn, P, and Zn*P fertilizer application interactions. Other MODEL statements compared tissue Zn and tissue P concentrations with Zn, P, and Zn*P fertilizer interactions. Significant effects found in the ANOVA were further analyzed by Duncan's multiple range test in order to evaluate where a significant difference would lie between treatment means.

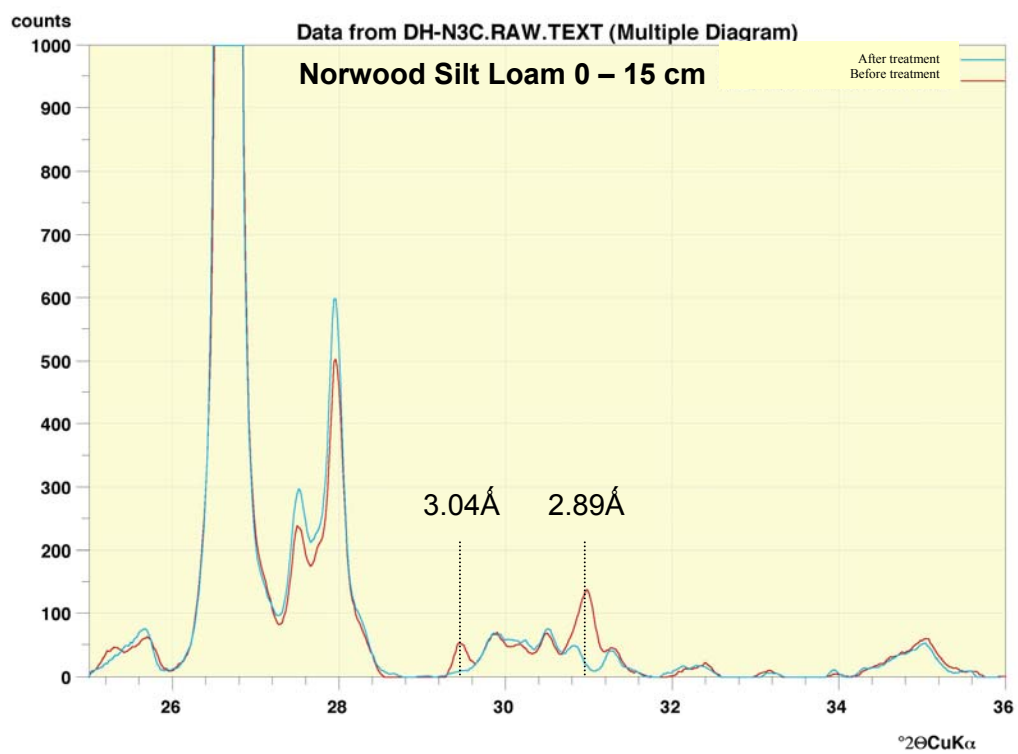


Figure 6.01 X-ray diffractogram of the 0 – 15 cm depth of the Norwood silt loam soil before and after carbonate removal by 3 M HCl.

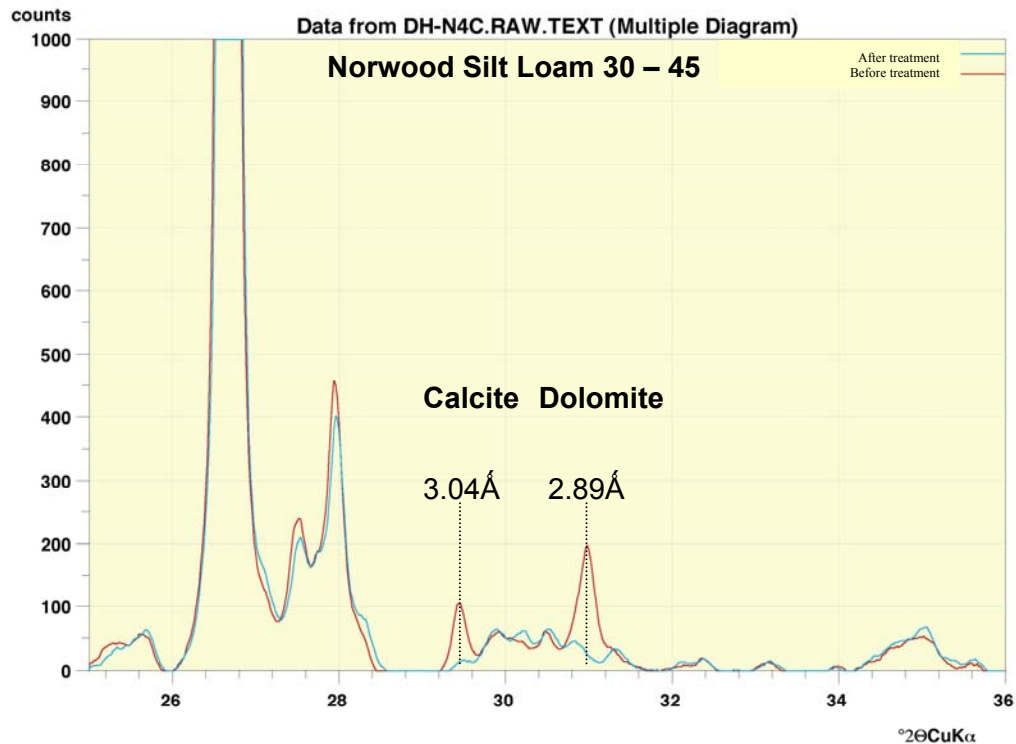


Figure 6.02 X-ray diffractogram of the 30 – 45 cm depth of the Norwood silt loam soil before and after carbonate removal by 3 M HCl.

6.3 Results and Discussion

6.3.1 Physical and Chemical Characteristics of the Norwood Soil

Selected physical and chemical data for the Norwood soil at two depths can be seen in Table 6.01. In general, Norwood soils are geologically young carbonate containing soils that normally occupy the lower positions of the natural levee at the highest elevations of the Red River flood plains. The Norwood soils at the Dean Lee Research Station fit this general description as indicated by the alkaline pH and the moderate calcium carbonate content (CCE) of both the surface (A_p) and subsurface soil. Particle size analysis indicates that the soil texture is classified a silt loam. The

mineralogy of the clay fraction is in the general order of clay mica > smectite > interstratified chlorite-smectite > kaolinite. Norwood soils also have a distinguishing reddish-brown color which is characteristic of geological sediments of the Permian age which originate from the eastern slope of the Rocky Mountains (Lytle, 1968). This reddish color may also reflect the soils' moderately high reductant soluble Fe (Fe_{CBD}) content. Only a small portion of this Fe is in the more amorphous, less crystalline form (Fe_{AOX}).

Table 6.02 Mean soil test extractable P and Zn values for each site-year.

| Year | P | | | Zn | |
|------|--------------------------------|---------|-------|--------------------------------|-------------|
| | Mehlich III | Bray II | Olsen | DTPA | Mehlich III |
| | -----mg kg ⁻¹ ----- | | | -----mg kg ⁻¹ ----- | |
| 2002 | 53 | 270 | 15.1 | 0.44 | 1.32 |
| 2003 | 14 | 178 | 7.6 | 0.40 | 0.81 |
| 2004 | 54 | 251 | 11.9 | 0.36 | 1.44 |

Mean soil test P and Zn values taken before planting each year can be seen in Table 6.02. Labile Zn as determined by the DTPA soil test was nearly identical for each site-year. Mehlich III extractable Zn at the 2003 experimental site was slightly lower than those at the 2001 and 2004 sites. Using the current Louisiana DTPA Zn soil test rating criteria (Table 6.03), these soils would fall into the “low” soil test category and a

Table 6.03 Current soil test Zn ratings for all agronomic crops used by the LSU Soil Testing and Plant Analysis Laboratory.

| Soil Test Level | Texture | | Fertilizer Recommendation |
|-----------------|----------------------------|--|---------------------------|
| | All | | |
| | DTPA | | Zn |
| | ---mg kg ⁻¹ --- | | --lbs ac ⁻¹ -- |
| L | <0.5 | | ----- |
| M | 0.5-1.25 | | ----- |
| H | >1.25 | | ----- |

Table 6.04 Current soil test P ratings and fertilizer recommendations for corn grown on alluvial soils used by the LSU Soil Testing and Plant Analysis Laboratory.

| Soil Test Level | Texture | | Fertilizer Recommendation |
|-----------------|------------------------------|--------------------|-------------------------------|
| | sicl,cl,sic,c | ls,sl,fsl,vfsl,sil | |
| | Bray II soil test P | | P ₂ O ₅ |
| | ---(mg kg ⁻¹)--- | | --(lbs/ac)-- |
| VL | <50 | <40 | 100 |
| L | 50-70 | 40-60 | 80 |
| M | 71-140 | 61-120 | 60 |
| H | 141-160 | 121-140 | 0 |
| VH | >160 | >140 | 0 |

Zn fertilizer response would be expected. However, Zn fertilizer recommendations are not currently available for Louisiana soils. Initial soil test P values for the field study sites-years indicated that two general scenarios existed. At the 2002 and 2004

experimental sites the soils contained mean Bray II P values of 270 and 251 mg kg⁻¹, putting them well above the 140 mg kg⁻¹ threshold of the “very high” soil test category (Table 6.04) currently used by the Louisiana Soil Testing and Plant Analysis Laboratory. The 2003 Bray II P soil test value was also above the “very high” threshold however, it was approximately 92 – 72 mg kg⁻¹ less than the values for the 2002 and 2004 years respectively. In both scenarios using the current Bray II calibration and recommendation criteria a P fertilizer response would not be expected and P fertilizer would not be recommended for these soils.

6.3.2 Yield and Plant Tissue Results for 2002

Corn yields ranged from approximately 4.7 to 9.8 Mg ha⁻¹. Analysis of variance of the effects of P and Zn fertilization on corn yields for the 2002 site-year can be seen in Table 6.05. Phosphorus fertilization did not significantly increase or decrease yields. A histogram showing the effects of P fertilization rates on corn yields indicated that plots receiving the highest P rate of 359 kg P₂O₅ ha⁻¹ actually had the lowest mean yield of all P rates (Fig. 6.03). Zinc fertilizer application did significantly increase corn yields from 6.5 to > 7 Mg ha⁻¹ respectively, comparing the 0 to the 6.7 kg Zn ha⁻¹ application rates. The Duncan multiple range test indicated that the significant increase in corn yields due to Zn fertilization occurred only between the 0 and 1.1 kg ha⁻¹ rates (Fig. 6.03). Treatment means for all P*Zn interactions on corn yields can be seen in Table 6.06. There was no significant P*Zn interaction effect on corn yields.

Plant uptake of P and Zn was estimated by determining the P concentration in the third leaf from the top of the corn plant. Plant tissue P ranged from 2.1 – 4.5 g kg⁻¹. Analysis of variance of the effect of P and Zn fertilization on tissue P concentration can

be seen in Table 6.07. Phosphorus fertilization had a highly significant effect on tissue concentration. A histogram illustrating the effect of P fertilization rate on tissue P concentration clearly shows that as P fertilizer application increased, tissue P concentration increases (Fig. 6.06). The Duncan test indicated that the significant difference occurred between the 135 and 359 kg P₂O₅ ha⁻¹ P application rate. Interpretation of plant analysis elemental values often includes the use of a critical value (Jones et al., 1990). The critical value is frequently defined as the value that is correlated with a 10% decrease in yield or as the concentration where visual deficiency symptoms occur. Research by Melsted et al. (1969) found the critical value for P in the corn ear leaf at tassel to be 2.5 g kg⁻¹. Our tissue P values were clearly over this critical value even when no P was applied (Fig. 6.06). The tissue P and yield results for 2002 suggests that an initial Bray II soil test P level of 270 mg kg⁻¹ (Table 6.02) is more than adequate to supply the P needs for corn growth. Zinc fertilizer application rate also had a significant effect on P tissue concentration. A histogram illustrating the effect of Zn fertilization rate on tissue P concentration indicates that as Zn fertilizer application increased, tissue P concentration decreased (Fig. 6.07). The Duncan multiple range test indicated that plants receiving 0 and 1.1 kg ha⁻¹ Zn application rate contained a significantly higher plant tissue P concentration as compared to all other Zn rates. Furthermore, where Zn was applied at the 6.7 kg ha⁻¹ rate tissue P concentration was significantly lower than any other Zn application rate. Treatment means for all P*Zn interactions on tissue P concentration can be seen in Table 6.08. There was no significant effect of the P*Zn treatment interaction on tissue P concentration at the $P < 0.05$ level. However, a histogram visually representing the P*Zn interaction on tissue P concentration, indicates

that tissue P concentrations increase with decreasing Zn rate and further increase with increasing P rate (Fig. 6.08). Since tissue P is above the critical in all cases and considered to be non-limiting, this antagonistic relationship is noteworthy even though it had no negative effect on corn yields.

Plant tissue Zn in 2002 ranged from 7.7 – 26.6 mg kg⁻¹. Analysis of variance of the effect of P and Zn fertilization on tissue Zn concentration can be seen in Table 6.09. Phosphorus fertilizer application rates did not have a significant effect on tissue Zn concentration. Although it is non-significant, a histogram of the effect of P rate on tissue Zn concentration does indicate that as P rate increases tissue Zn concentration decreases from approximately 15 mg kg⁻¹ at the 0 rate to 13.5 mg kg⁻¹ at the 358.7 kg P₂O₅ ha⁻¹ rate (Fig. 6.09). Work by Melsted et al. (1969) established a critical value of 15.0 mg kg⁻¹ for tissue Zn concentration of the corn ear leaf taken at the tassel stage. Using this critical value it is evident that when P is applied at a rate of over 100.9 kg P₂O₅ ha⁻¹, tissue Zn concentration drops well below this critical value. Zinc fertilizer application rate had a highly significant effect on tissue Zn concentration. The Duncan multiple range test indicated that the significant difference between Zn application rates occurred between the 1.1 kg ha⁻¹ and higher Zn rates (Fig. 6.09). Applying the critical level, we can see that the 15.0 mg kg⁻¹ tissue Zn level was not achieved until at least 3.4 kg ha⁻¹ of Zn fertilizer is applied. The treatment means for all P*Zn interactions on tissue Zn concentration can be seen in Table 6.10. There was no significant effect of the P*Zn treatment interaction on tissue Zn concentration. The lack of a significant interaction between P and Zn rates is also visually evident by the large variability in the histogram of the combined effects (Fig. 6.11).

Table 6.05 ANOVA of the effect of P and Zn fertilization on corn yield for the 2002 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|-------|------|------|--------|
| Block | 3 | 6.23 | 2.08 | 2.38 | 0.0742 |
| P Rate | 5 | 3.67 | 0.73 | 0.84 | 0.5244 |
| Zn Rate | 5 | 24.07 | 4.81 | 5.51 | 0.0002 |
| P Rate*Zn Rate | 25 | 13.17 | 0.53 | 0.60 | 0.9268 |

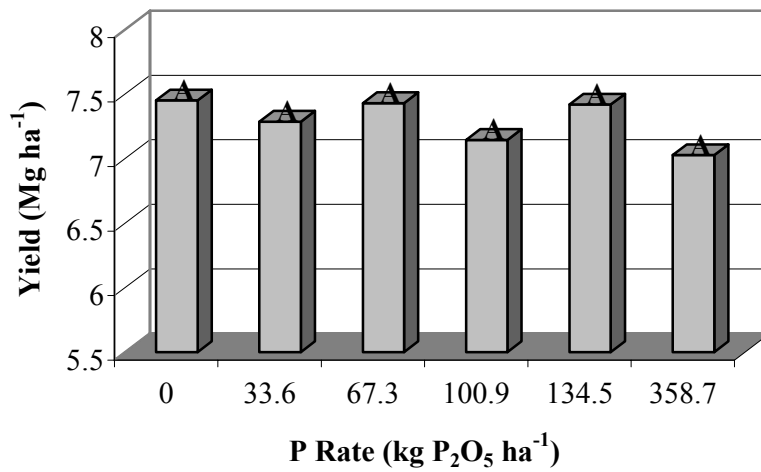


Figure 6.03 Histogram of the effect of P fertilizer rate on corn yield for the 2002 site-year.

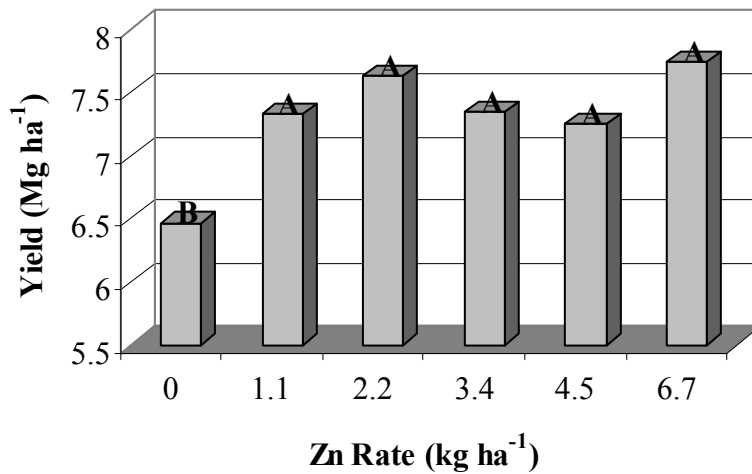


Figure 6.04 Histogram of the effect of Zn fertilizer rate on corn yield for the 2002 site-year.

Table 6.06 Treatment means for all P*Zn interactions on corn yield for the 2002 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|------|------|------|------|------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 7.19 | 6.15 | 6.16 | 6.14 | 6.71 | 6.47 |
| 1.1 | 7.30 | 7.08 | 7.76 | 7.23 | 7.52 | 7.11 |
| 2.2 | 7.31 | 7.99 | 7.34 | 7.87 | 7.60 | 7.66 |
| 3.4 | 6.89 | 7.67 | 8.00 | 7.29 | 7.56 | 6.62 |
| 4.5 | 7.78 | 7.13 | 7.58 | 7.10 | 7.14 | 6.76 |
| 6.7 | 8.25 | 7.70 | 7.75 | 7.23 | 7.98 | 7.55 |

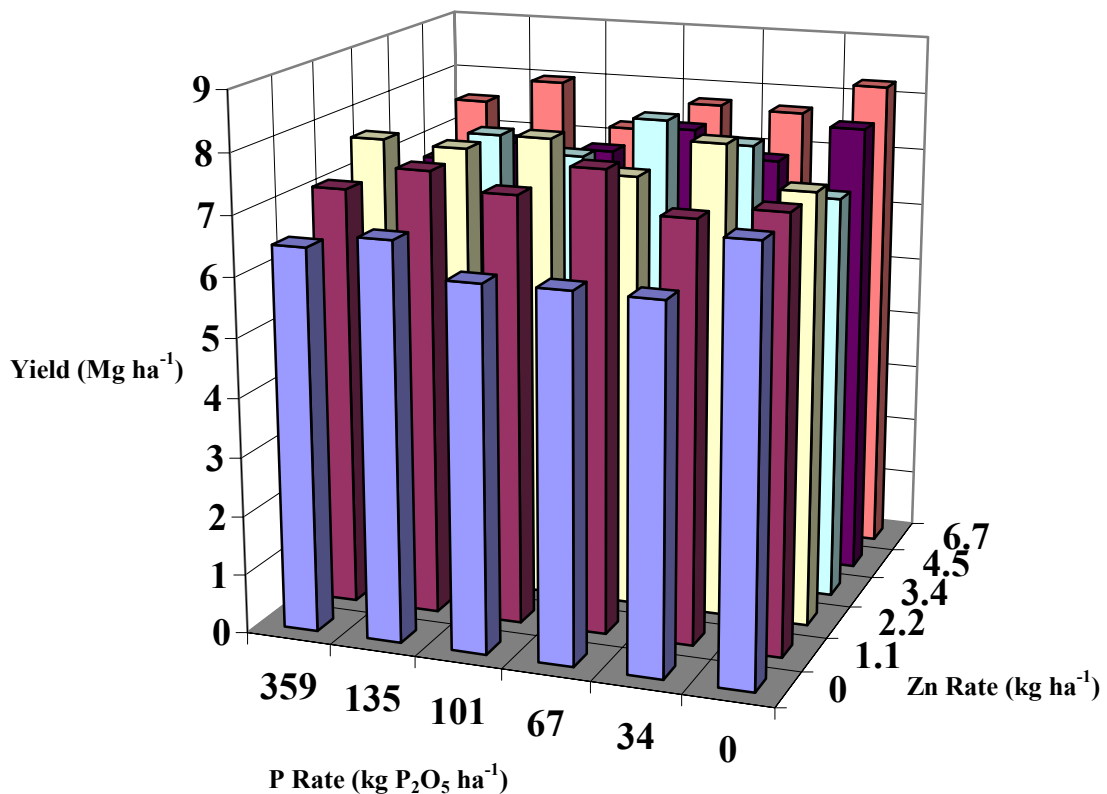


Figure 6.05 Histogram of the combined effects of P and Zn fertilization on corn yield for the 2002 site-year.

Table 6.07 ANOVA of the effect of P and Zn fertilization on tissue P concentration.

| Source | DF | SS | MS | F | P |
|----------------|----|------|------|------|---------|
| Block | 3 | 1.21 | 0.40 | 5.73 | 0.0011 |
| P Rate | 5 | 2.74 | 0.55 | 7.81 | <0.0001 |
| Zn Rate | 5 | 0.84 | 0.17 | 2.38 | 0.0431 |
| P Rate*Zn Rate | 25 | 2.25 | 0.09 | 1.28 | 0.1917 |

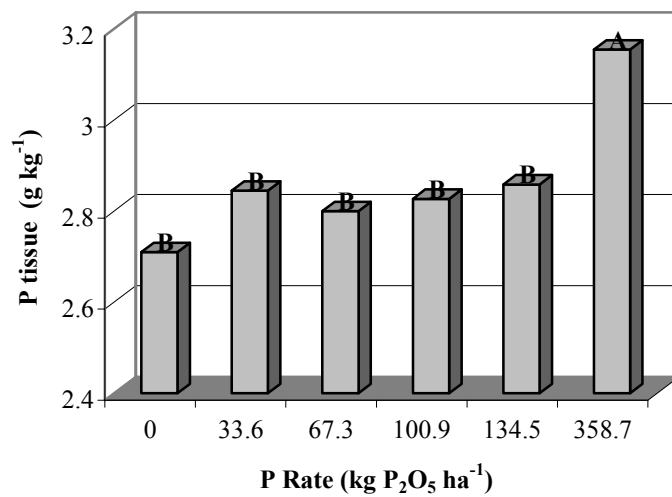


Figure 6.06 Histogram of the effect of P fertilization on tissue P concentration for the 2002 site year.

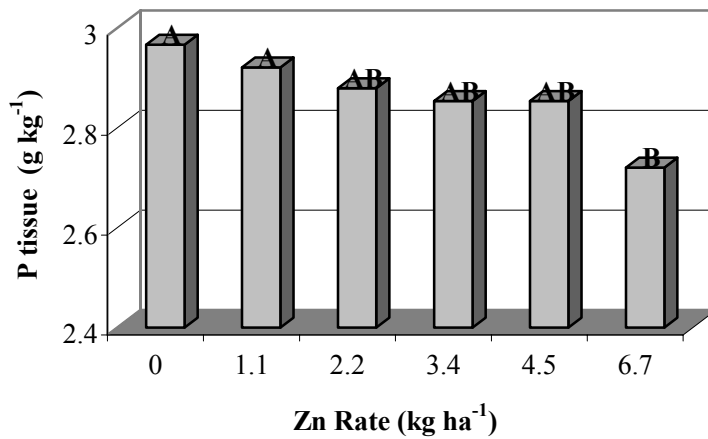


Figure 6.07 Histogram of the effect of P fertilization on tissue Zn concentration for the 2002 site-year.

Table 6.08 Treatment means for all P*Zn interactions on tissue P concentration for the 2002 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|------|------|------|------|------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 2.68 | 3.02 | 2.98 | 2.92 | 2.97 | 3.23 |
| 1.1 | 2.80 | 2.81 | 2.99 | 2.93 | 2.56 | 3.44 |
| 2.2 | 2.73 | 2.88 | 2.74 | 2.87 | 2.87 | 3.18 |
| 3.4 | 2.77 | 2.83 | 2.63 | 2.61 | 2.91 | 3.38 |
| 4.5 | 2.68 | 2.86 | 2.80 | 2.87 | 2.91 | 3.01 |
| 6.7 | 2.61 | 2.68 | 2.67 | 2.77 | 2.93 | 2.69 |

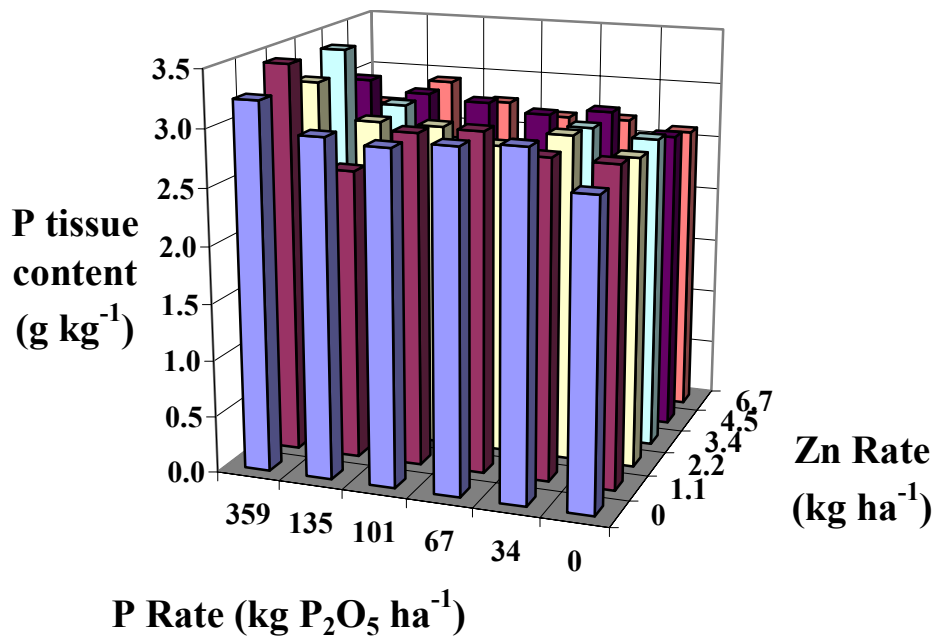


Figure 6.08 Histogram of the combined effects of P and Zn fertilization on tissue P concentration for the 2002 site-year.

Table 6.09 ANOVA of the effect of P and Zn fertilization on tissue Zn concentration for the 2002 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|--------|-------|------|---------|
| Block | 3 | 279.49 | 93.16 | 8.94 | <0.0001 |
| P Rate | 5 | 70.35 | 14.07 | 1.35 | 0.2493 |
| Zn Rate | 5 | 149.86 | 29.97 | 2.88 | 0.0179 |
| P Rate*Zn Rate | 25 | 369.90 | 14.80 | 1.42 | 0.1128 |

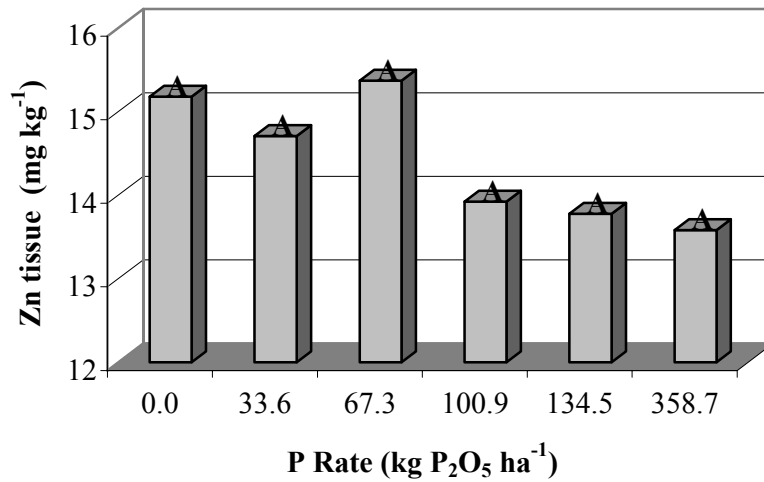


Figure 6.09 Histogram of the effect of P fertilization on tissue Zn concentration for the 2002 site-year.

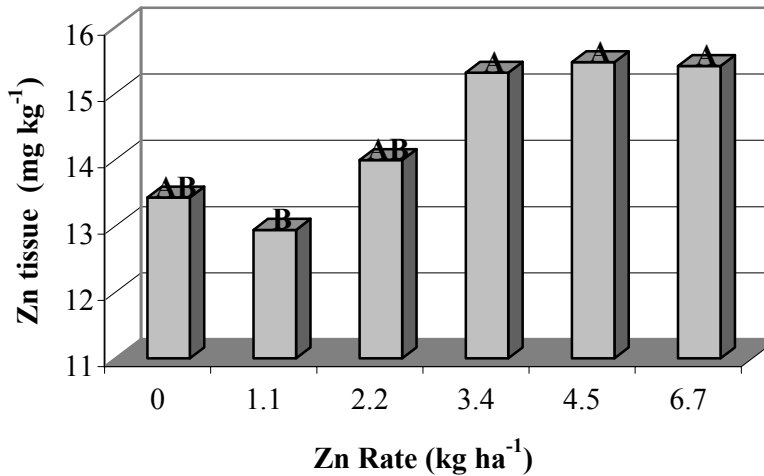


Figure 6.10 Histogram of the effect of Zn fertilization on tissue Zn concentration for the 2002 site-year.

Table 6.10 Treatment means for all P*Zn interactions on tissue Zn concentration for the 2002 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|-------|-------|-------|-------|-------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 14.90 | 13.09 | 12.38 | 11.86 | 11.66 | 16.67 |
| 1.1 | 14.52 | 13.22 | 13.82 | 10.61 | 14.96 | 10.50 |
| 2.2 | 15.51 | 14.17 | 14.25 | 14.05 | 11.72 | 14.26 |
| 3.4 | 14.19 | 14.05 | 15.68 | 17.80 | 17.81 | 12.32 |
| 4.5 | 16.70 | 15.92 | 17.88 | 14.85 | 12.63 | 14.84 |
| 6.7 | 15.28 | 17.81 | 18.23 | 14.38 | 13.89 | 12.90 |

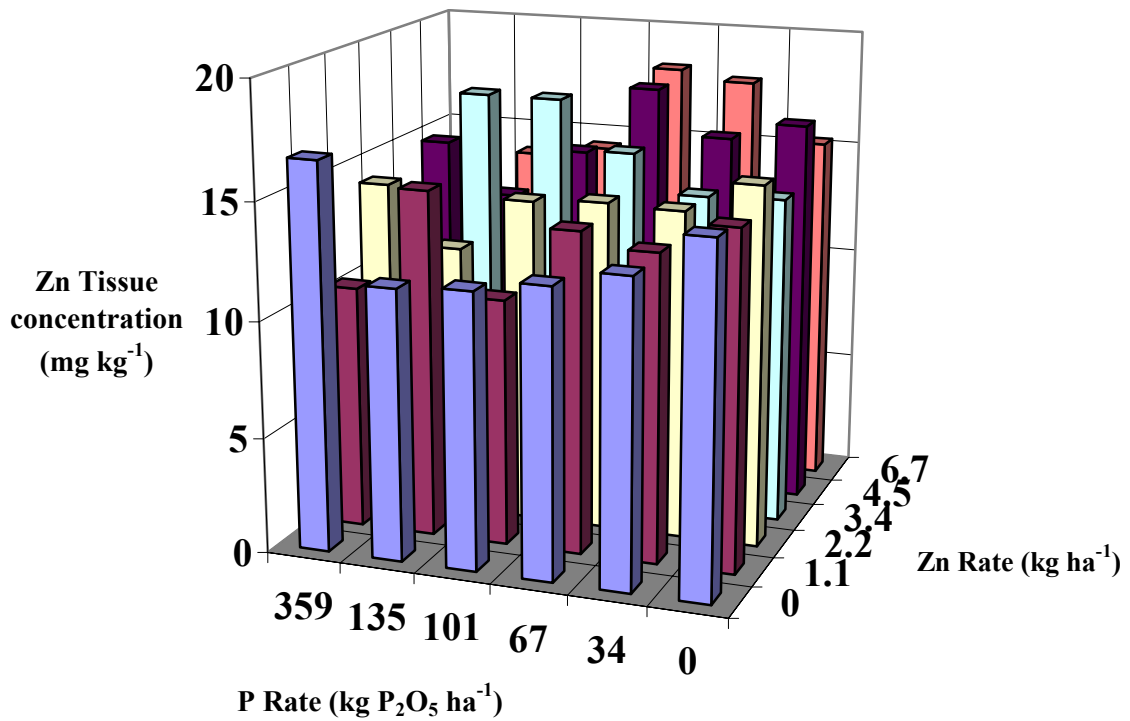


Figure 6.11 Histogram of the combined effects of P and Zn fertilization on tissue Zn concentration for the 2002 site-year.

6.3.3 Yield and Plant Tissue Results for 2003

Corn yields at the 2003 site year ranged from 0.7 to 6.6 Mg ha⁻¹. Analysis of variance of the effect of P and Zn fertilization on corn yields in 2003 can be seen in Table 6.11. Phosphorus fertilization had a highly significant effect on corn yield. A histogram of the effect of P fertilization rates on corn yields illustrated that as P rate increased yields increased from approximately 1.5 Mg ha⁻¹ at the 0 kg P₂O₅ ha⁻¹ rate to nearly 5 Mg ha⁻¹ at the 359 kg P₂O₅ ha⁻¹ (Fig. 6.12). The Duncan multiple range test indicated that significant increases in yield due to P fertilization occurred between 0 and 32, 32 and 67, and 135 and 359 kg P₂O₅ ha⁻¹. Zinc fertilization did not significantly affect corn yields at the 2003 experimental site. Treatment means of yields were almost identical between all Zn fertilization rates (Fig. 6.13). There was no significant treatment interaction effect between P and Zn fertilization on corn yields. Treatment means for all P*Zn interactions can be seen in Table 6.12. A histogram of the P*Zn interaction visually shows the increase of corn yields with increasing P rate and a clear lack of response due to Zn fertilization (Fig. 6.14).

Corn leaf tissue P concentration ranged from a low of 0.5 to a high 2.5 g kg⁻¹. Phosphorus fertilization rate had a significant effect on plant tissue P content (Table 6.13). Plant tissue P increased with increasing P fertilization rate (Fig. 6.15). The Duncan post hoc test indicated that with the exception of the 101 kg P₂O₅ ha⁻¹ rate, a significant increase in corn yields was seen between each incremental P fertilization rate. When applying the critical value of 2.5 g kg⁻¹, we saw that even at the highest P rate of 359 g kg⁻¹ this critical value was not met. However, it is important to point out that the two most significant factors to consider when interpreting plant analysis results are: (i)

the influence of the applied fertilizers and (ii) possible varietal effects on element composition (Jones et al., 1990). Since the variety of corn used in 2003 (Pioneer 34B23) differed from the variety used in 2002 and 2004 (Dekalb DK697) the lower tissue P levels may simply reflect differences in the corn varieties and therefore may not be P deficient based on the 2.5 g kg^{-1} critical level. Moreover, Therman et al. (1972) reported a critical level of 1.4 g kg^{-1} for whole corn tops at 8 weeks of age. This critical level for tissue P was generally met in after $67 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ is applied (Fig. 6.15). Zinc fertilization rate was not significantly related to leaf tissue P concentration. A histogram of the effect of Zn fertilization rate on plant tissue P indicated that the treatment means across all Zn fertilization rates were almost identical. Zinc rate treatment means had values near 1.5 g kg^{-1} , well below the published critical value of 2.5 g kg^{-1} found in literature (Melsted et al., 1969). There were no significant P*Zn fertilization rate interactions on plant tissue P. Treatment means for all P*Zn interactions can be seen in Table 6.14. An increase in tissue P concentration with increasing P rate along with the lack of a tissue P response due to Zn fertilization can be clearly seen in the histogram of the P*Zn fertilization response on tissue P (Fig 6.17).

Corn tissue Zn concentration ranged from 10.7 to 31.2 mg kg^{-1} . Phosphorus fertilization did not significantly effect plant tissue Zn concentration (Table 6.15). Treatment means of yields across P fertilization rates were nearly identical to or slightly above the 15 g kg^{-1} plant tissue Zn critical value. Zinc fertilization rate had a significant effect on tissue Zn concentration at only the $P = 0.0829$ level. The Duncan test indicated that the significant differences were found between the 3.4 and the 0 and also between the 3.4 and 1.1 kg ha^{-1} Zn fertilization rates (Fig. 6.19). The histogram of the effect of Zn

fertilization on tissue Zn concentration indicated that all Zn treatment means were near or above the plant tissue Zn critical level. There was no significant effect of P by Zn fertilization rate interaction on plant tissue Zn concentration. Treatment means for all P*Zn treatment interactions can be seen in Table 6.16. A histogram of the combined effects of P and Zn fertilization visually shows the lack of response across all Zn and most P fertilizer application rates (Fig. 6.20).

Table 6.11 ANOVA of the effect of P and Zn fertilization on corn yield for the 2003 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|--------|-------|------|---------|
| Block | 3 | 4.14 | 1.38 | 1.88 | 0.1371 |
| P Rate | 5 | 153.28 | 30.66 | 41.8 | <0.0001 |
| Zn Rate | 5 | 3.76 | 0.75 | 1.02 | 0.4072 |
| P Rate*Zn Rate | 25 | 9.09 | 0.36 | 0.50 | 0.9769 |

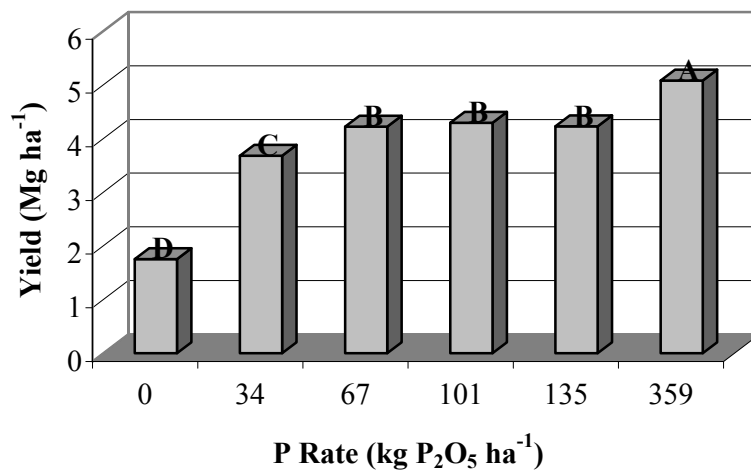


Figure 6.12 Histogram of the effect of P fertilization on corn yield for the 2003 site-year.

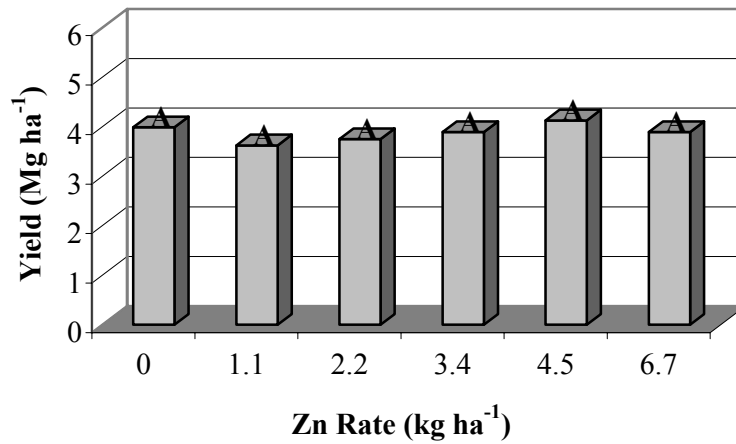


Figure 6.13 Histogram of the effect of Zn fertilization on corn yield for the 2003 site-year.

Table 6.12 Treatment means for all P*Zn interactions on corn yield for the 2003 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|------|------|------|------|------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 2.13 | 3.52 | 4.44 | 4.58 | 4.42 | 4.82 |
| 1.1 | 1.80 | 3.86 | 3.85 | 3.88 | 3.68 | 4.65 |
| 2.2 | 1.74 | 3.22 | 4.10 | 4.06 | 4.22 | 5.15 |
| 3.4 | 1.68 | 4.06 | 4.14 | 4.41 | 4.01 | 5.04 |
| 4.5 | 1.61 | 3.74 | 4.10 | 4.52 | 7.89 | 5.89 |
| 6.7 | 1.58 | 3.66 | 4.71 | 4.31 | 4.17 | 4.92 |

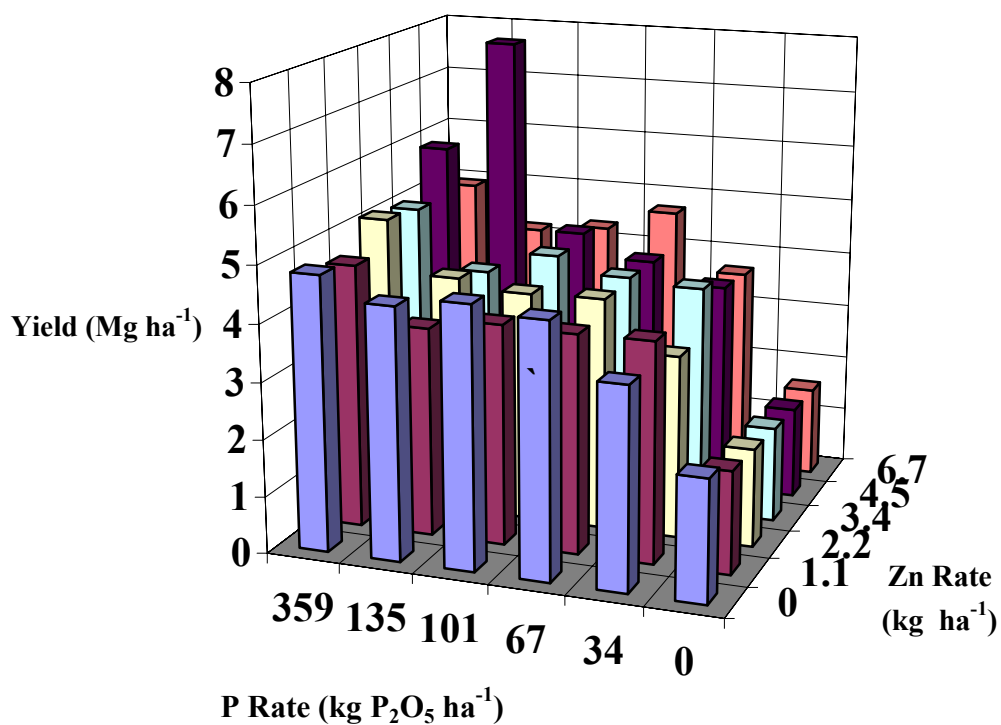


Figure 6.14 Histogram of the combined effects of P and Zn fertilization on corn yield for the 2003 site-year.

Table 6.13 ANOVA of the effect of P and Zn fertilization on tissue P concentration for the 2003 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|-------|------|-------|---------|
| Block | 3 | 1.96 | 0.65 | 7.12 | 0.0002 |
| P Rate | 5 | 19.89 | 3.98 | 43.32 | <0.0001 |
| Zn Rate | 5 | 0.17 | 0.03 | 0.37 | 0.8685 |
| P Rate*Zn Rate | 25 | 1.02 | 0.04 | 0.45 | 0.9887 |

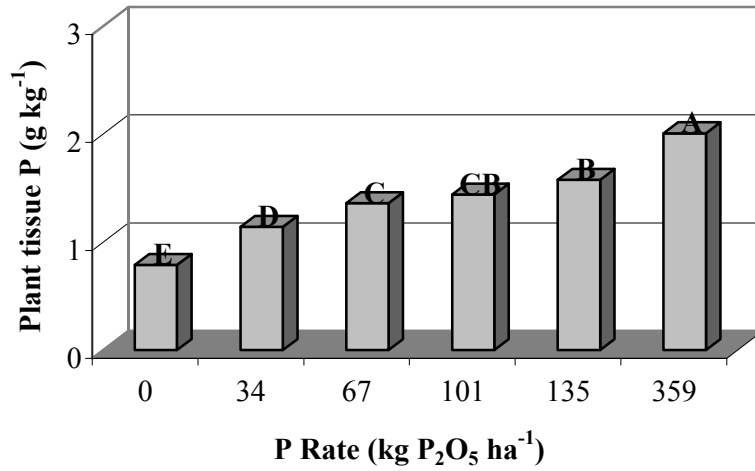


Figure 6.15 Histogram of the effect of P fertilization rate on tissue P concentration for the 2003 site-year.

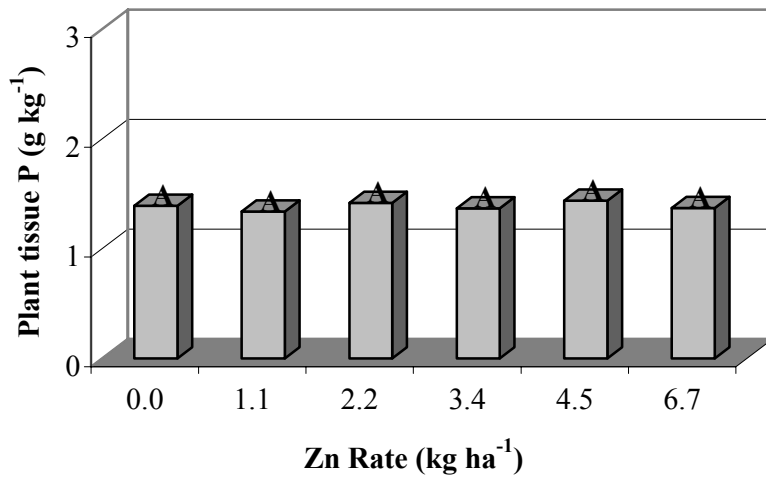


Figure 6.16 Histogram of the effect of Zn fertilization rate on tissue P concentration for the 2003 site-year.

Table 6.14 Treatment means for all P*Zn interactions on tissue P concentration for the 2003 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|------|------|------|------|------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 0.82 | 1.13 | 1.43 | 1.38 | 1.44 | 2.16 |
| 1.1 | 0.83 | 1.16 | 1.31 | 1.31 | 1.57 | 1.86 |
| 2.2 | 0.75 | 1.16 | 1.32 | 1.35 | 1.72 | 2.20 |
| 3.4 | 0.82 | 1.14 | 1.40 | 1.58 | 1.36 | 1.91 |
| 4.5 | 0.77 | 1.17 | 1.40 | 1.55 | 1.74 | 2.00 |
| 6.7 | 0.77 | 1.10 | 1.32 | 1.47 | 1.64 | 1.92 |

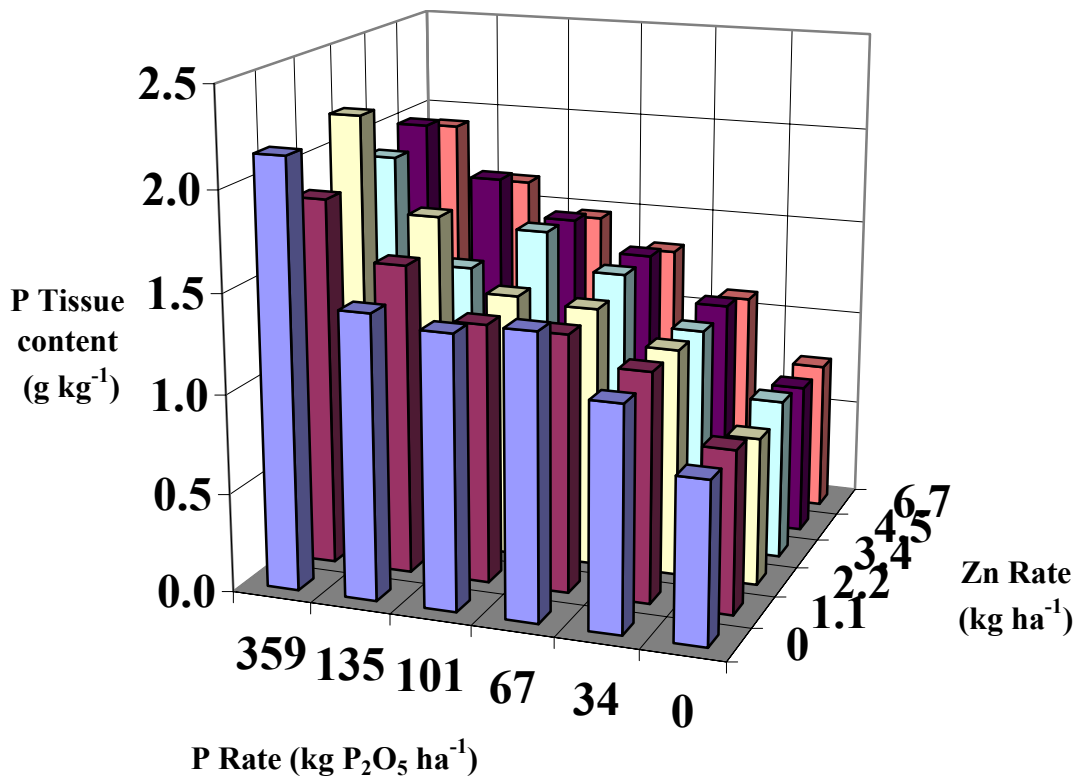


Figure 6.17 Histogram of the combined effects of P and Zn fertilization on tissue P concentration for the 2003 site-year.

Table 6.15 ANOVA of the effects of P and Zn fertilization on tissue Zn concentration for the 2003 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|--------|--------|-------|---------|
| Block | 3 | 308.50 | 102.83 | 11.69 | <0.0001 |
| P Rate | 5 | 48.60 | 9.72 | 1.1 | 0.3623 |
| Zn Rate | 5 | 88.50 | 17.70 | 2.01 | 0.0829 |
| P Rate*Zn Rate | 25 | 279.07 | 11.16 | 1.27 | 0.2015 |

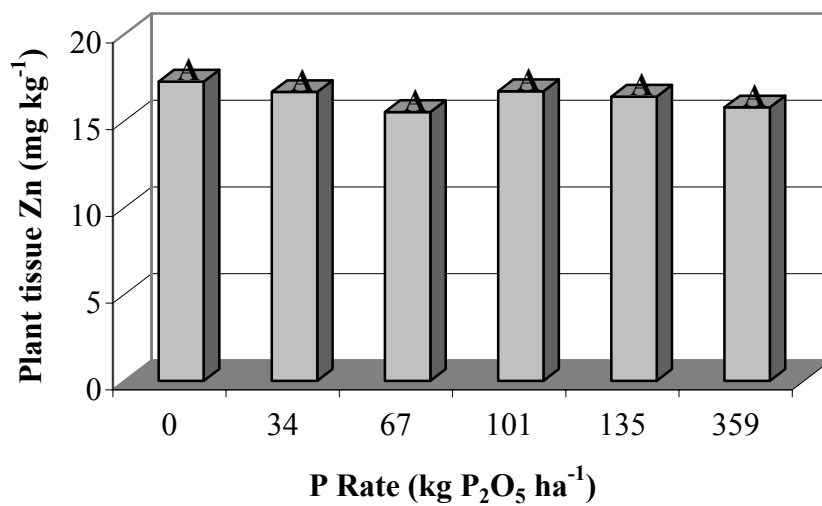


Figure 6.18 Histogram of the effect of P fertilization rate on tissue Zn concentration for the 2003 site-year.

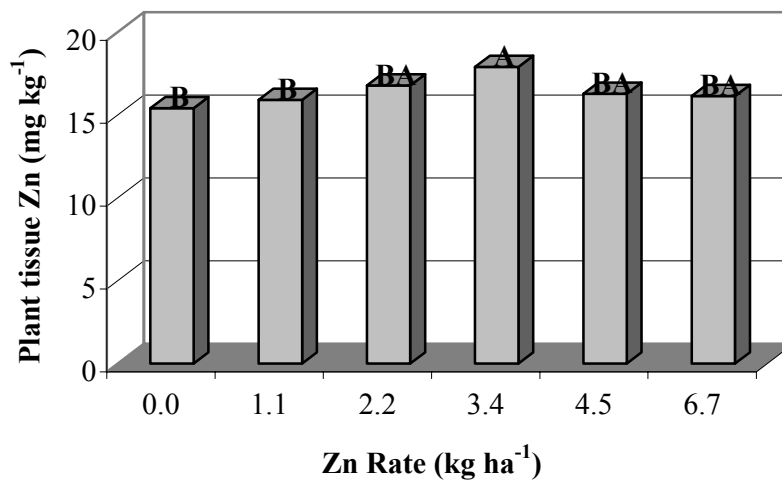


Figure 6.19 Histogram of the effect of Zn fertilization on tissue Zn concentration for the 2003 site-year.

Table 6.16 Treatment means for all P*Zn interactions on tissue Zn concentration for the 2003 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|-------|-------|-------|-------|-------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 16.21 | 18.34 | 14.09 | 13.81 | 14.72 | 15.17 |
| 1.1 | 16.55 | 15.90 | 14.79 | 14.07 | 17.06 | 17.03 |
| 2.2 | 18.42 | 17.61 | 14.55 | 17.29 | 17.57 | 15.17 |
| 3.4 | 18.11 | 16.37 | 16.30 | 23.60 | 17.26 | 15.67 |
| 4.5 | 16.30 | 15.94 | 17.00 | 16.48 | 16.22 | 15.62 |
| 6.7 | 17.98 | 15.82 | 16.33 | 15.02 | 15.55 | 16.03 |

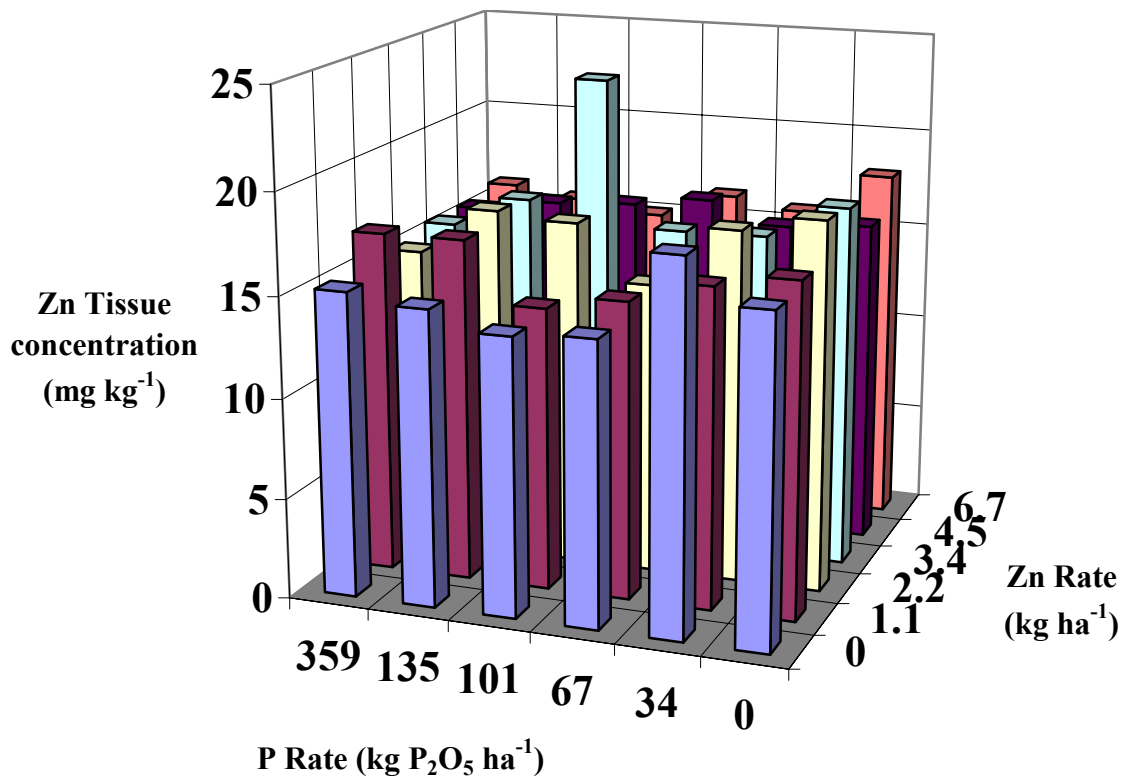


Figure 6.20 Histogram of the combined effects of P and Zn fertilization on tissue Zn concentration for the 2003 site-year.

6.3.4 Yield and Plant Tissue Results for 2004

Corn yields for the 2004 site-year ranged from 0 – 7.4 kg ha⁻¹. Analysis of variance of the effect of P and Zn fertilization rates on corn yields can be seen in Table 6.17. Phosphorus fertilization did not have a statistically significant effect on corn yields. A histogram showing the effect of P fertilization rates on corn yields indicated that yields across all P application rates were similar ranging from approximately 2.6 to 3.0 kg ha⁻¹ (Fig. 6.14). Zinc fertilization rate had a highly significant effect on corn yields. Corn yields increased with increasing Zn fertilization rate (Fig. 6.22). The Duncan mean separation post hoc test indicated that the increase in yield due to Zn fertilization occurred between no Zn fertilization and the 1.1 kg ha⁻¹ Zn application rate. The yield of the plots 3.3 kg ha⁻¹ Zn application rate was approximately three fold higher than those plots receiving no Zn fertilizer. A significant increase in yields was also seen between the 4.5 and 6.7 kg ha⁻¹ Zn fertilizer application rate. There was no statistically significant P*Zn interaction on corn yields. Treatment means for all P*Zn fertilizer rate interactions on corn yields can be seen in Table 6.18. A 3-dimensional histogram of the combined effects of P and Zn fertilization on corn yields visually shows the increase in corn yields with increasing Zn fertilizer application and the lack of response of corn yields across P fertilization (Fig. 6.23).

Analysis of variance of the effect of P and Zn fertilization rate on corn tissue P concentration can be seen in Table 6.19. Phosphorus fertilization rate did not significantly alter the plant tissue concentration of the corn leaves. Plant tissue P values ranged from 1.3 to 4.9 g kg⁻¹. A histogram comparing the average effects of P fertilization rate on tissue P showed that tissue P concentration across all P fertilization

rates were close to or slightly above 2.0 g kg^{-1} (Fig. 6.24). These average P values are above the critical level of 1.4 g kg^{-1} established by Terman et al. (1972). Zinc fertilization had a highly significant effect on plant tissue P concentration (Table 6.19, Fig. 6.25). Tissue P concentration decreased with increasing Zn fertilization across the first three application rates (Fig. 6.25). The Duncan multiple range test indicated that the significant decrease in plant tissue P concentration occurred between no Zn fertilization and the 1.12 kg ha^{-1} Zn application rate (Fig. 6.25). Plant tissue P content was above the 1.4 g kg^{-1} critical across all Zn fertilization rates. There was no significant P*Zn fertilization interaction effect on plant tissue P concentration (Table 6.20).

Corn leaf Zn concentration ranged from a low of 5.2 to a high of 13.9 mg kg^{-1} . Analysis of variance of the effect of P and Zn fertilization on tissue Zn concentration can be seen in Table 6.21. Phosphorus fertilization did not statistically alter the tissue Zn concentration. The histogram of the effect of P fertilization rate on tissue Zn concentration indicated that the tissue Zn concentration across all P fertilizer application rates was approximately 8.8 mg kg^{-1} , well below the 15 mg kg^{-1} commonly sited critical value (Fig. 6.27). Zinc fertilizer application had statistically significant effect on plant tissue Zn concentration. Zinc fertilization increased leaf tissue Zn content. The Duncan multiple range test indicated that the significant increases in tissue Zn concentration occurred between the 2.2 and 3.4 kg ha^{-1} treatments and also between the 4.5 and 6.7 kg ha^{-1} Zn treatments. The critical level of 15 mg kg^{-1} was not reached even at the highest Zn fertilization rate of 6.7 kg ha^{-1} . There was no significant effect of P*Zn rate interaction on plant tissue Zn concentration. Treatment means for all P*Zn interactions on tissue Zn concentration can be seen in Table 6.22. A histogram comparing the

treatment means for all P*Zn fertilization rate combinations visually shows the increase in tissue Zn concentration with increasing Zn fertilization rate and the lack of a P and a P*Zn fertilizer rate response (Fig. 6.29).

Table 6.17 ANOVA of the effect of P and Zn fertilization on corn yield for the 2004 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|-------|-------|-------|---------|
| Block | 3 | 46.50 | 15.50 | 13.94 | <0.0001 |
| P Rate | 5 | 2.32 | 0.46 | 0.42 | 0.8353 |
| Zn Rate | 5 | 62.74 | 12.55 | 11.28 | <0.0001 |
| P Rate*Zn Rate | 25 | 16.32 | 0.65 | 0.59 | 0.9367 |

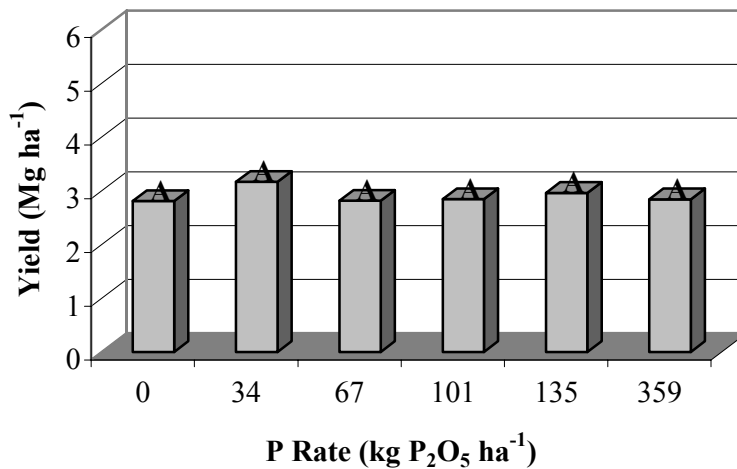


Figure 6.21 Histogram of the effect of P fertilization rate on corn yield for the 2004 site-year.

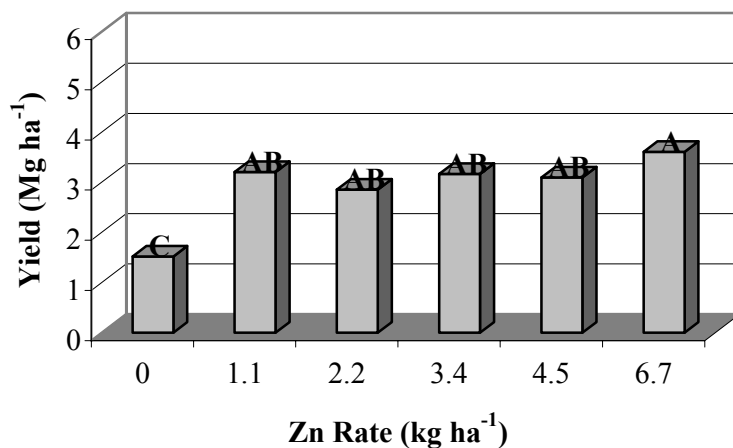


Figure 6.22 Histogram of the effect of Zn fertilization rate on corn yield for the 2004 site-year.

Table 6.18 Treatment means for all P*Zn interactions on corn yield for the 2004 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|------|------|------|------|------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 0.89 | 1.91 | 1.07 | 1.23 | 2.33 | 1.66 |
| 1.1 | 2.88 | 3.48 | 3.55 | 2.73 | 3.13 | 3.43 |
| 2.2 | 3.10 | 2.90 | 2.48 | 2.82 | 2.85 | 2.96 |
| 3.4 | 2.74 | 3.33 | 3.35 | 3.62 | 2.87 | 3.07 |
| 4.5 | 3.15 | 3.54 | 3.04 | 2.94 | 2.64 | 3.27 |
| 6.7 | 4.09 | 3.85 | 3.38 | 3.73 | 3.93 | 2.66 |

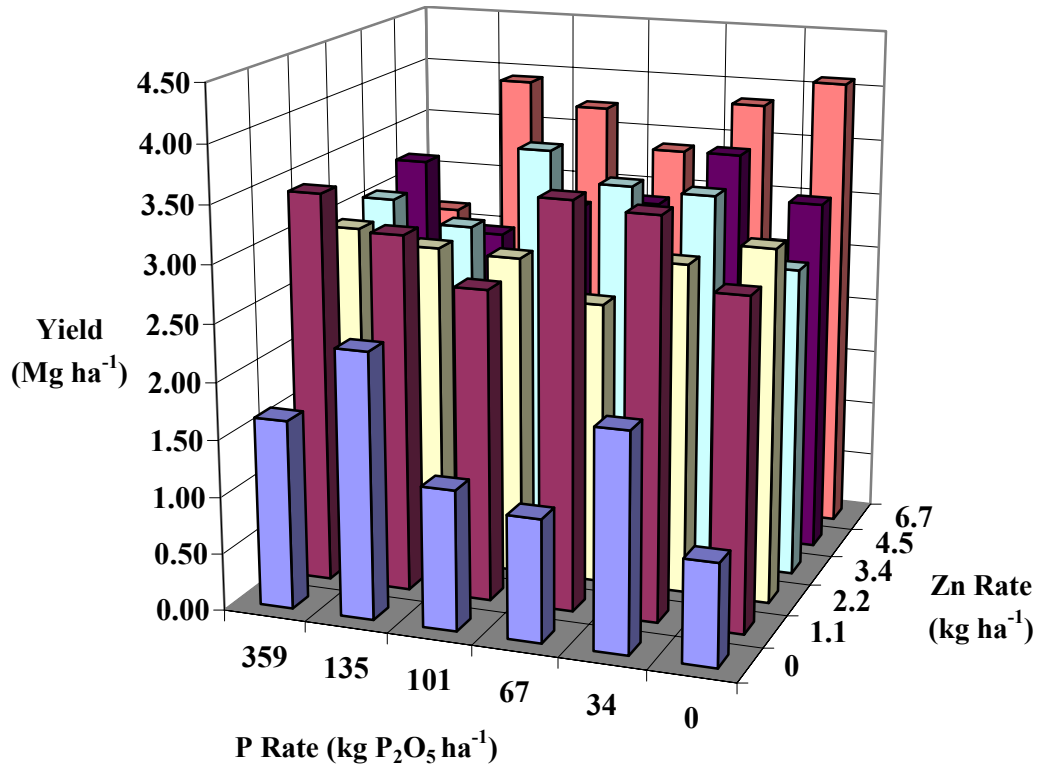


Figure 6.23 Histogram of the combined effects of P and Zn fertilization on corn yield for the 2004 site-year.

Table 6.19 ANOVA of the effect of P and Zn fertilization on tissue P concentration for the 2004 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|-------|------|-------|---------|
| Block | 3 | 0.66 | 0.22 | 0.98 | 0.4074 |
| P Rate | 5 | 1.21 | 0.24 | 1.07 | 0.3819 |
| Zn Rate | 5 | 20.53 | 4.11 | 18.17 | <0.0001 |
| P Rate*Zn Rate | 25 | 2.23 | 0.09 | 0.40 | 0.9952 |

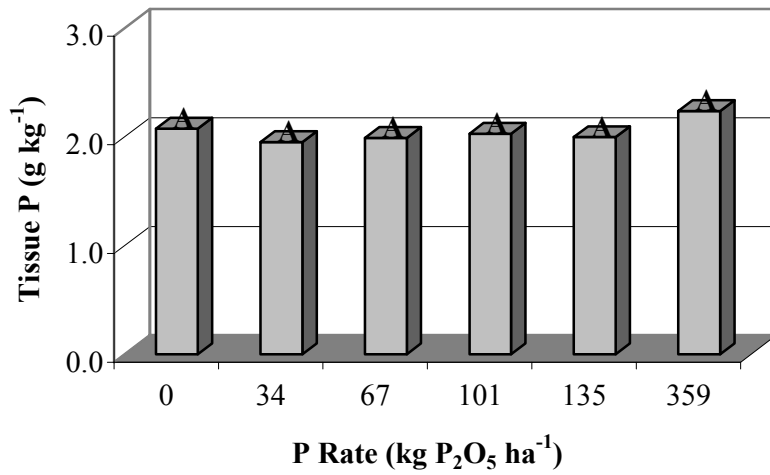


Figure 6.24 Histogram of the effect of P fertilization rate on tissue P concentration for the 2004 site-year.

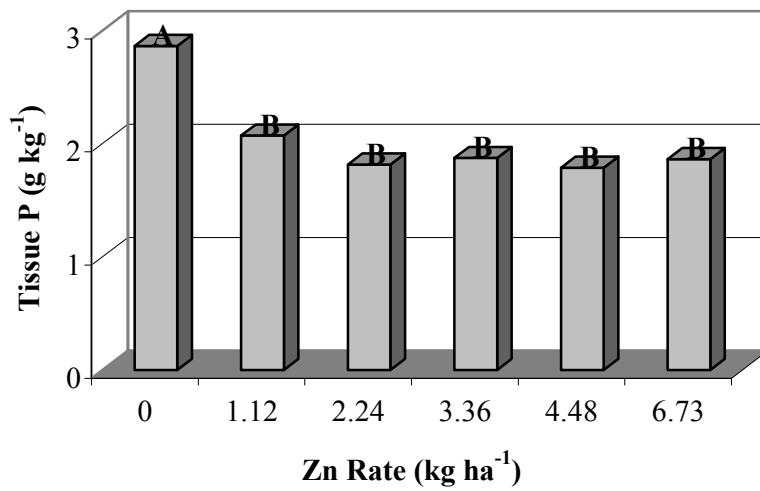


Figure 6.25 Histogram of the effect of Zn fertilization rate on tissue P concentration for the 2004 site-year.

Table 6.20 Treatment means for all P*Zn interactions on tissue P concentration for the 2004 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|------|------|------|------|------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 2.95 | 2.65 | 2.89 | 2.96 | 2.53 | 3.21 |
| 1.1 | 1.97 | 1.96 | 2.04 | 1.80 | 2.45 | 2.30 |
| 2.2 | 1.86 | 1.71 | 1.68 | 1.90 | 1.70 | 2.05 |
| 3.4 | 1.87 | 1.84 | 1.90 | 1.95 | 1.69 | 2.01 |
| 4.5 | 1.76 | 1.70 | 1.73 | 1.72 | 1.78 | 2.03 |
| 6.7 | 2.02 | 1.85 | 1.71 | 1.84 | 1.95 | 1.82 |

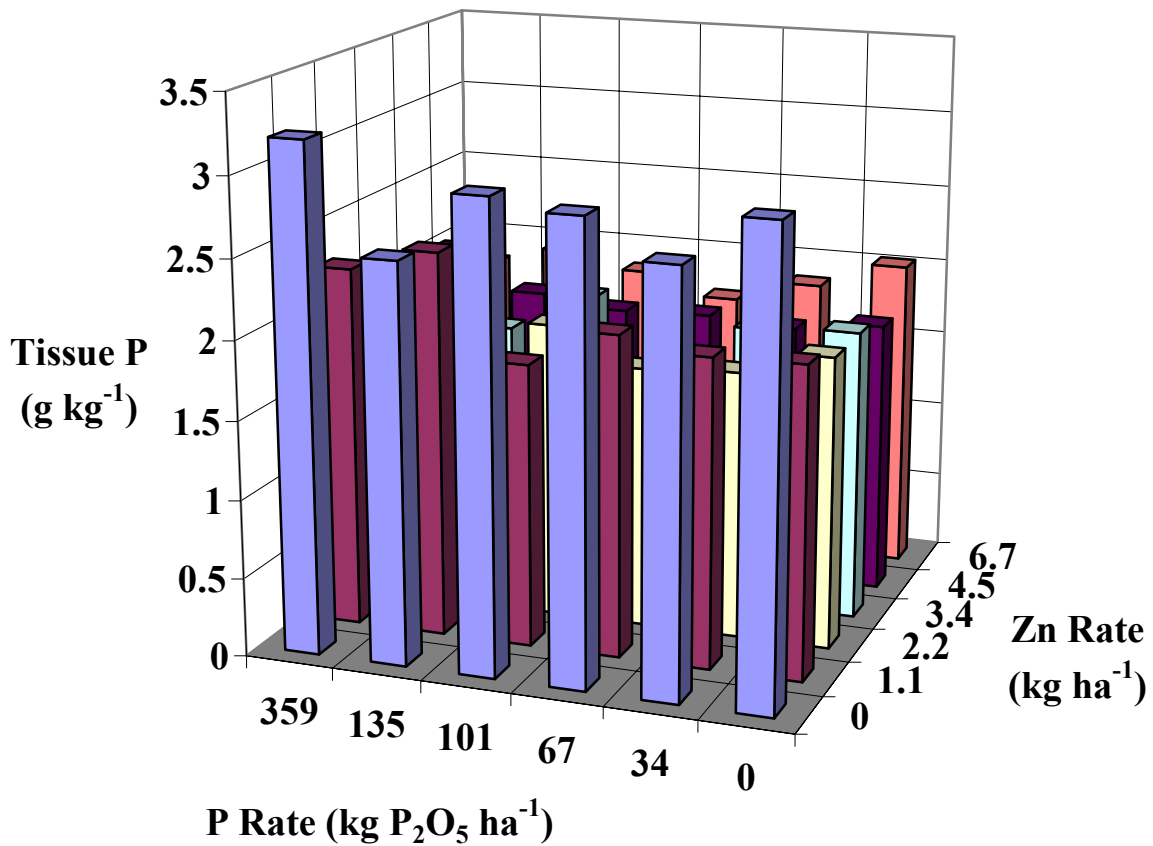


Figure 6.26 Histogram of the combined effects of P and Zn fertilization rate on tissue P concentration for the 2004 site-year.

Table 6.21 ANOVA of the effect of P and Zn fertilization on tissue Zn concentration for the 2004 site-year.

| Source | DF | SS | MS | F | P |
|----------------|----|--------|-------|-------|---------|
| Block | 3 | 77.80 | 25.93 | 14.76 | <0.0001 |
| P Rate | 5 | 1.66 | 0.33 | 0.19 | 0.9664 |
| Zn Rate | 5 | 291.12 | 58.22 | 33.15 | <0.0001 |
| P Rate*Zn Rate | 25 | 36.41 | 1.46 | 0.83 | 0.6970 |

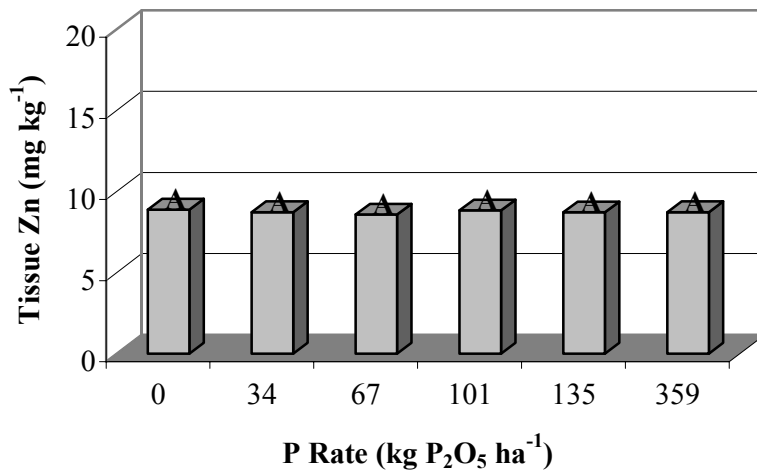


Figure 6.27 Histogram of the effect of P fertilization rate on tissue Zn concentration for the 2004 site-year.

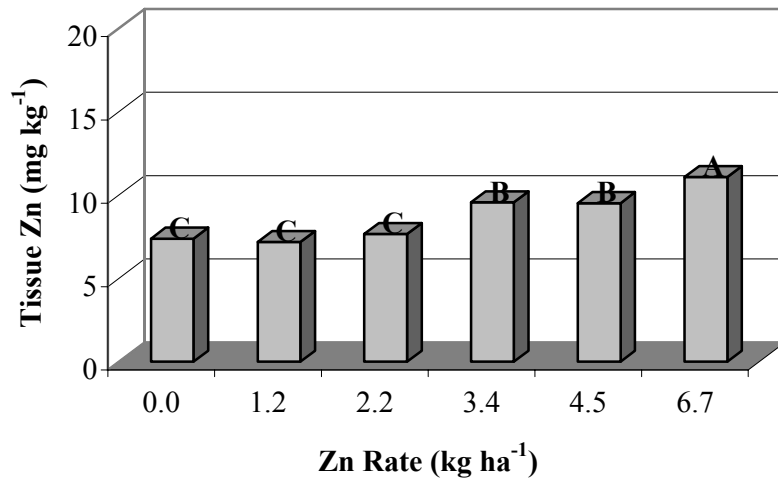


Figure 6.28 Histogram of the effect of Zn fertilization rate on tissue Zn concentration for the 2004 site-year.

Table 6.22 Treatment means for all P*Zn interactions on tissue Zn concentration for the 2004 site-year.

| Zn Rate (kg ha ⁻¹) | P Rate (kg P ₂ O ₅ ha ⁻¹) | | | | | |
|-----------------------------------|---|-------|-------|-------|-------|-------|
| | 0 | 34 | 67 | 101 | 135 | 359 |
| | -----kg ha ⁻¹ ----- | | | | | |
| 0 | 7.05 | 7.54 | 7.00 | 6.83 | 6.83 | 7.56 |
| 1.1 | 7.40 | 7.67 | 7.12 | 7.35 | 7.35 | 6.84 |
| 2.2 | 7.44 | 8.16 | 7.85 | 7.37 | 7.37 | 7.91 |
| 3.4 | 9.31 | 8.60 | 9.71 | 10.69 | 10.69 | 9.78 |
| 4.5 | 10.70 | 9.61 | 8.90 | 9.49 | 9.49 | 9.85 |
| 6.7 | 11.38 | 10.74 | 10.84 | 11.25 | 11.25 | 10.42 |

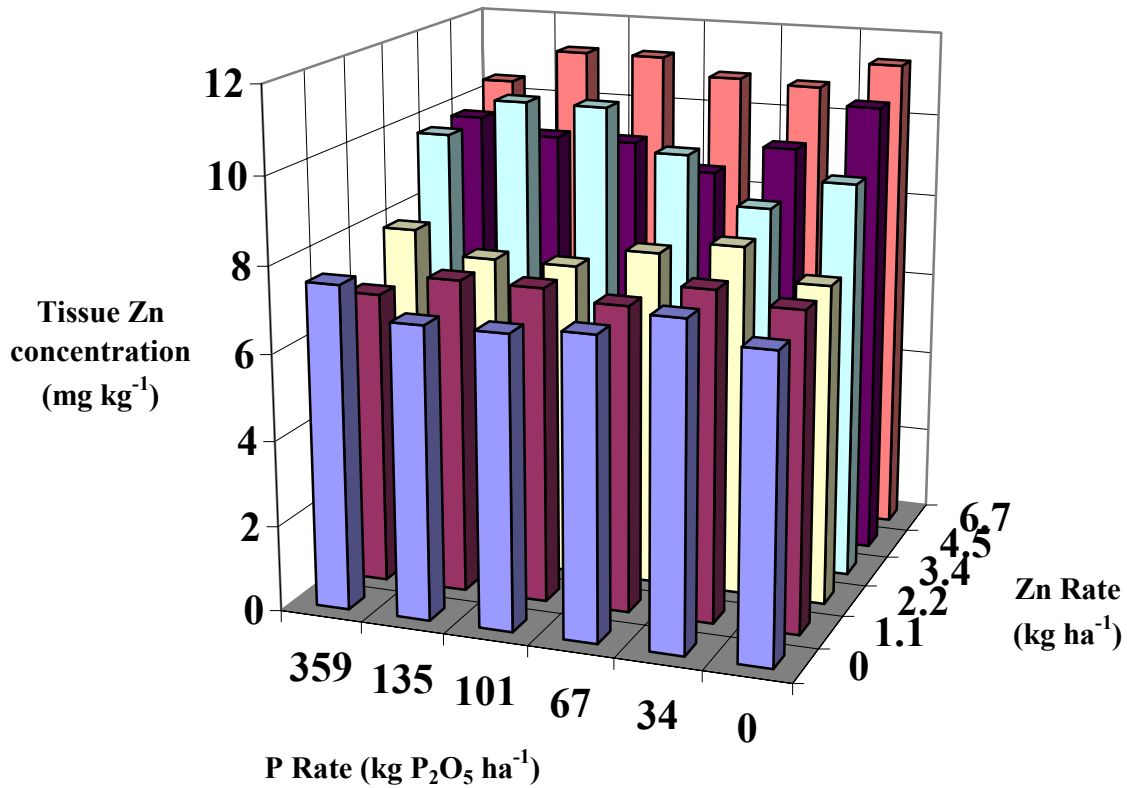


Figure 6.29 Histogram of the combined effects of P and Zn fertilization rate on tissue Zn concentration for the 2004 site-year.

6.3.5 Soil Test Correlation and Calibration

The overall goal of a soil test is to determine the plant available nutrient status of the soil. The soil test extraction provides data which can be used to identify the potential need for fertilizer additions. Once a need is accessed, a soil test also provides assistance in developing fertilizer recommendations. Soil test extraction methods that can accurately determine the plant nutrient status and provide fertilizer recommendations based on positive crop response data are often referred to as calibrated or fully developed soil tests. Dahnke and Olson (1990) provided a good overview of the procedures needed to develop a functional soil test. According to Dahnke and Olson, soil test development procedures often require three major steps: (i) correlation, (ii) calibration, and (iii)

interpretation of data to develop recommendations. This section will focus on correlation and calibration based on yield data generated from 2002 – 2004.

Soil test correlation is often defined as the process of determining whether a relationship exists between plant uptake or yield and the amount of nutrient extracted by a soil test. In other words correlation is determining the best soil test extraction method for a given set of soils. Soil test calibration can be defined as the process of determining a meaning from the soil test results in terms of crop response. In doing so, the soil test values are categorized into response categories in order to simplify the fertilizer recommendation process. The typical response categories used by most soil testing laboratories are: *Very Low*, where <50% of crop yield potential (CYP) is expected without additional nutrient application; *Low*, where 50 – 75% CYP is expected without additional nutrient application; *Medium*, where 75 – 100% CYP is expected without additional nutrient application; *High*, where a yield increase due to fertilization is not expected because the soil can provide all plant nutrient requirements; and *Very High*, where a yield increase due to fertilization is not expected because the soil can provide much more than crop requirements and additional nutrient application may cause detrimental environmental problems (Hanlon, 2001).

This study focuses on determining P and Zn fertilizer recommendations of selected soil test extraction methods for calcareous Red River alluvial soils with initial soil test values similar to those seen in Table 6.02. However, due to the production of new crop varieties, it was necessary to verify the current soil test correlation and calibrations for soil test extractable P and Zn methods prior to calculating fertilizer recommendations. More specifically, we wanted to verify the critical soil test level. In

general, the critical soil test level separates the soil test values into two categories, those that are likely to respond to fertilization and those that are unlikely to respond to fertilization (Dahnke and Olson, 1990). In practice, the critical value is also the division between the *Medium* and *High* soil test response categories. In this study a soil specific approach was employed to attempt correlation and calibration simultaneously by plotting relative yield against post season soil test values generated from the 2002 – 2004 year field experiments. Relative yield was defined as:

$$\text{Relative Yield (\%)} = \frac{\text{Yield from the test plot}}{\text{Maximum plot yield}} \quad [6.02]$$

The data in the resulting graph was separated into two linear portions. The first line had a sharp slope and represented the portion of the curve that would most likely respond to fertilization, the second line has no slope and represents the portion of the curve that most likely would not respond to fertilization. The critical level (value) was estimated at the intersection of the two linear lines. The Bray II, Mehlich III, and Olsen soil tests were calibrated for P while the DTPA and Mehlich III soil test were calibrated for Zn.

The relationship between corn yield and soil test P for the Bray, Olsen, and Mehlich soil tests can be seen in Figs. 6.30, 6.31, and 6.32 respectively. Only the 2003 season was used for the determination of the critical level since this was the only year that a fertilizer P response was seen. The critical level for the Bray II-P extraction was estimated at approximately 220 mg kg⁻¹ (Fig. 6.30). This critical value is much greater than the critical value of 120 mg kg⁻¹ currently used by in Louisiana for corn grown in alluvial silt loam soils (Table 6.03). The 100 mg kg⁻¹ disparity between the two critical levels suggests that the Bray II-P critical level of 120 mg kg⁻¹ currently used for Louisiana soils may not be accurate for the calcareous Red River alluvial soils. It has

been reported that the acidic nature of the Bray II soil test causes the dissolution of CaCO_3 and release of CaCO_3 bound P and thereby overestimating the plant available P in these calcareous soils (Fixen and Grove, 1990; Mallarino, 1997; Harrell et al., 2004).

The critical level for the Olsen P soil test extraction for the Norwood soil was estimated at approximately 8 mg kg^{-1} (Fig. 6.31). This critical level is very close to the critical level of 10 mg kg^{-1} previously originally established for cotton, wheat, and alfalfa (Olsen et al., 1954). The tight grouping of the data points and a clear distinction of the two linear portions of Fig. 6.31 indicated that a high correlation exists between relative yield and Olsen extractable P. The high correlation made the determination of the critical level much easier for the Olsen P soil test as compared to the Bray II extraction. This also suggests that the Olsen P soil test may be a better soil test extraction for calcareous Red River alluvial soils than the Bray II extraction.

The less clear-cut distinction between the two linear portions of the Mehlich III extractable P and relative yield data made the estimation of a critical level difficult. Nonetheless, a critical level of approximately 40 mg kg^{-1} was determined after much consideration. This critical level is slightly smaller than critical levels currently being used by the state soil testing laboratories of North Carolina (53.5 mg kg^{-1}) and Arkansas (50 mg kg^{-1}) however, but it is larger than the critical level used by Kentucky (30 mg kg^{-1}) and Oklahoma (32.5 mg kg^{-1}) (Hanlon, 2001).

Zinc fertilization rate was found to have a significant yield response in both 2002 and 2004. Due to the similarities of the 2002 and 2004 data, only the relationship between relative yield and the post harvest soil test extractable Zn for the 2004 year is

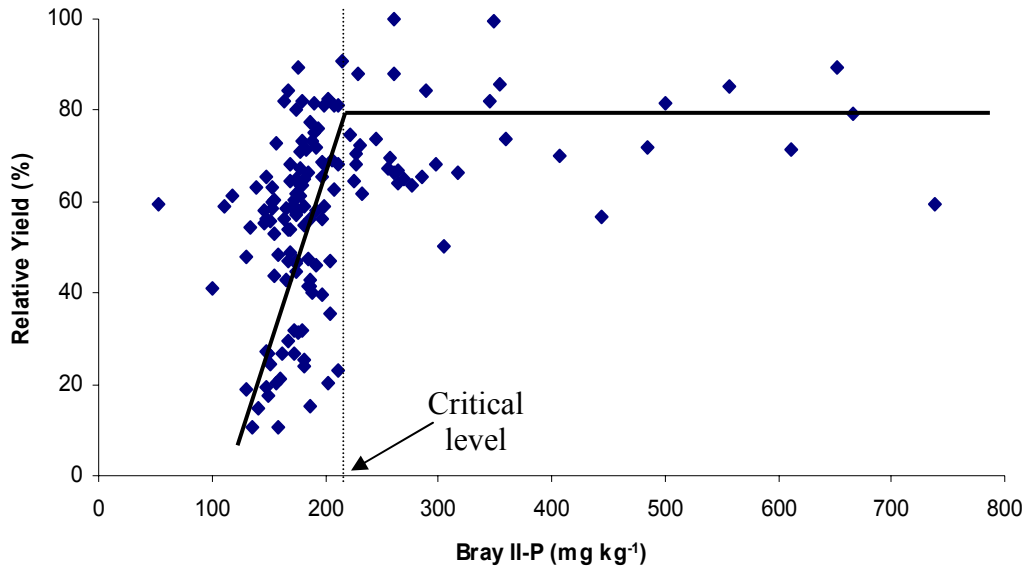
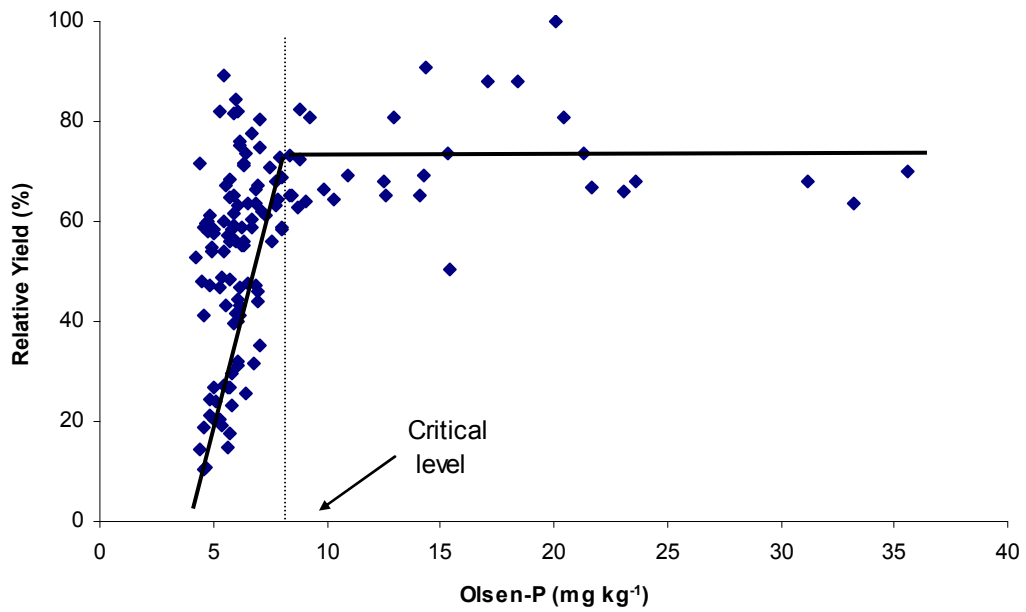


Figure 6.30 Relationship between relative yield and the post harvest Bray P soil test values for the 2003 site-year.



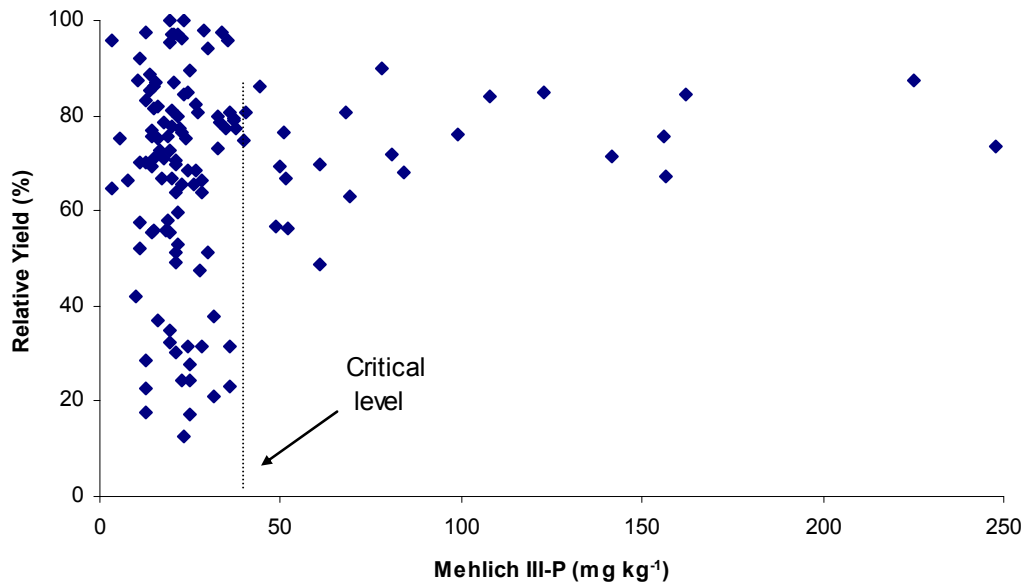


Figure 6.32 Relationship between relative yield and the post harvest Mehlich P soil test values for the 2003 site-year.

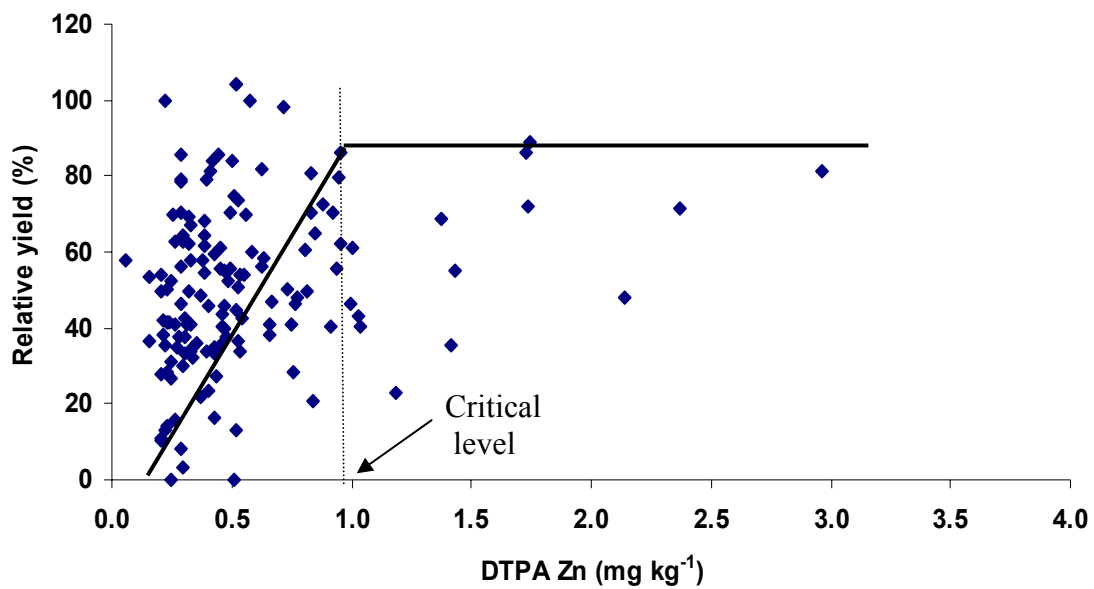


Figure 6.33 Relationship between relative yield and the post harvest DTPA Zn soil test values for the 2004 site-year.

shown. This relationship for the DTPA and Mehlich III soil test extractions can be seen in Figs. 6.33 and 6.34 respectively. The Zn critical level determination was difficult for the DTPA test since the intersection between the two linear portions of the scatter plot were not clear cut. Nonetheless, a critical level for the DTPA soil test extraction was estimated at approximately 1 mg kg^{-1} . This critical level is very close to the high end of the medium rating, 1.25 mg kg^{-1} , of the DTPA Zn soil test currently used in Louisiana (Fig. 6.03) and also the average critical level of 0.8 mg kg^{-1} used in many other parts of the USA (Cox, 1987). This suggests that the currently used soil test rating for Zn is correct and that only Zn fertilizer recommendations for each soil testing category need to be determined.

The estimation of the Mehlich III extractable Zn critical level was also difficult to determine strictly from the scatter plot of relative yield and extractable Zn (Fig. 6.34). Since the current Louisiana DTPA soil testing calibration is most likely correct as discussed previously, we used the linear regression relationship between Mehlich III extractable Zn and DTPA extractable Zn for the collective 2002 and 2004 post harvest soil samples to help determine the Mehlich III Zn critical level. This regression between the Mehlich III and DTPA soil test extractions can be seen in Fig. 6.35. The resulting regression equation was determined: $\text{Mehlich III Zn} = 1.647 * \text{DTPA Zn} + 0.616$. This linear relationship is very similar to the one reported for more than 300 soils across Louisiana (Wang et al., 2004). Substituting the DTPA critical level of $1.00 - 1.25 \text{ mg kg}^{-1}$, we found the Mehlich III critical Zn level to be approximately between 2.25 and 2.65 mg kg^{-1} (Fig. 3.34).

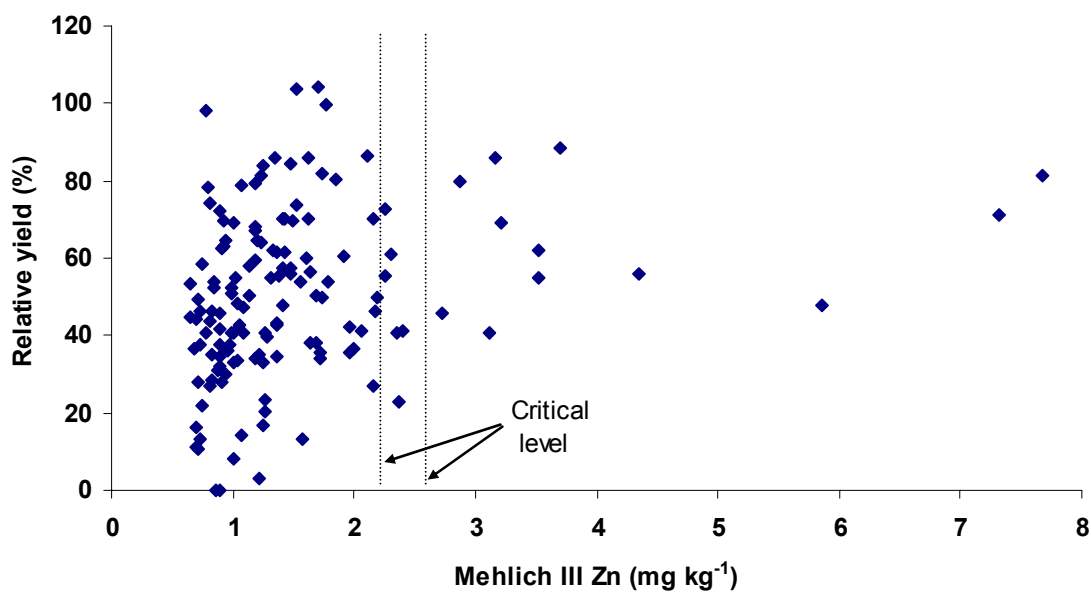


Fig. 6.34 Relationship between relative yield and the post harvest Mehlich Zn soil test values for the 2004 site-year.

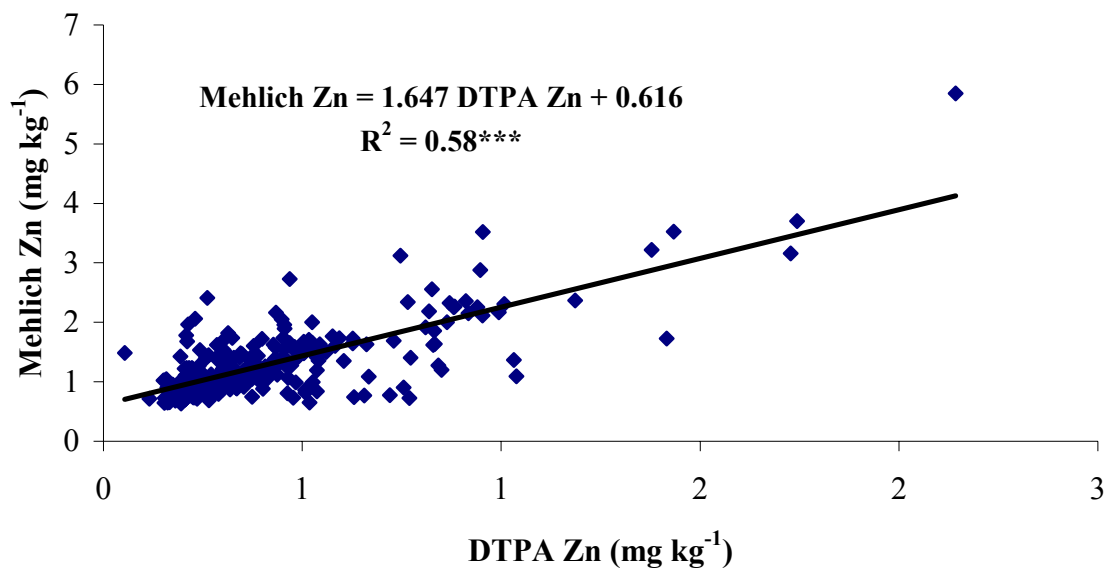


Fig. 6.35 Comparison of extractable Zn by the Mehlich III and DTPA soil test extractions for the combined 2002 and 2004 post harvest data.

6.3.6 Soil Test Recommendations

The third and final step in the development of soil test procedure is the interpretation and determination of fertilizer recommendations from field study data (Dahnke and Olson, 1990). Several models can be used to interpret field study results in order to develop fertilizer recommendations. The three most common models include: yield response, linear-plateau, and the Mitscherlich-Bray model. The Mitscherlich-Bray model was used to determine the P and Zn fertilization recommendations for this study.

Mitscherlich and other early scientists observed that when plants were supplied with sufficient amounts of all but one nutrient, their growth was proportional to the amount of the limiting nutrient that was supplied to the soil. Moreover, plant growth increased with increasing fertilization of the limiting nutrient but the amount of the increase declined with each successive addition of the nutrient (Tisdale et al., 1993; Sonar and Babhulkar, 2002). This prompted Mitscherlich to develop the following exponential mathematical model:

$$\frac{dy}{dx} = (A - y)c \quad [6.03]$$

where dy = the increase in yield resulting from an increment of fertilizer nutrient dx , A = the maximum yield obtained by supplying all nutrients in optimum but not excessive amounts, y is the yield obtained after any given quantity of nutrient x has been applied, and c = proportionality constant dependent on the nutrient often considered as a fertilizer nutrient efficiency factor.

When it is assumed that $y = 0$ and $x = 0$ for all the yield contributed from the fertilizer nutrient, Equation 6.03 can be integrated to:

$$y = A(1 - 10^{-cx}) \quad [6.04]$$

The exponential function above can also be stated as the integral of Equation [6.04] using common logarithms:

$$\log(A - y) = \log A - cx \quad [6.05]$$

The Mitcherlich equation was further modified by Bray to include the initial soil test value (b) and a soil test nutrient efficiency factor (c_1) (Bray, 1952). The following equation is referred to as the Mitcherlich-Bray equation:

$$\log(A - y) = \log A - c_1 b - cx \quad [6.06]$$

When A , y , c_1 , and c are determined from field study results, the equation can provide two important pieces of information: (i) the sufficiency level itself and (ii) the amount of fertilizer required to achieve optimum yields if soil test levels fall below the sufficiency level (Eckert, 1987). The utility of the equation was one of the determining factors for its use in the present study.

Calculation of the Mitcherlich parameters were determined by first determining a theoretical yield in lieu of an absolute max yield by plotting $\log y$ against $1/x$. An example of the theoretical maximum yield determination during the 2003 season can be seen in Fig. 6.36. Next, c_1 and c_2 were determined separately by solving for c_1 and c from the original equation resulting in Equations 6.07 and 6.08 respectively.

$$c_1 = \frac{\log A - \log(A - y)}{b} \quad [6.07]$$

where y = mean yield obtained from check plots

$$c = \frac{\log(A - c_1 b) - \log(A - yx)}{x} \quad [6.08]$$

where yx = yield obtained at fertilizer rate x .

Finally, the site specific fertilizer recommendations were determined by solving for x resulting in Equation 6.09.

$$x = \frac{\log (A - c_1 b_1) - \log (A - yx)}{c} \quad [6.09]$$

Corn yield results and calculated coefficients for the Mitscherlich-Bray model for Zn and P recommendation can be seen in Tables 6.38 – 6.40. Since a response to Zn fertilization was seen during 2002 and 2004 and a P response was seen during the 2003 season, the parameters were solved using the DTPA and Mehlich III initial soil test Zn values for the 2002 and 2004 seasons and solved for Bray, Olsen and Mehlich III initial soil test P values for the 2003 season. The c_1 values for DTPA were much larger than the Mehlich III extractable c_1 values for both the 2002 and 2004 seasons. This is an indication that the soil test Zn extracted by DTPA has a larger contribution to corn growth than does the Zn extracted by Mehlich III. Conversely, a smaller c_1/c ratio for the Mehlich extraction as compared to the DTPA extraction indicates the same. Comparisons of the P soil test extraction coefficients found that the large extractable P values by the Bray II soil test had a c_1 value that was 10 fold less efficient than both the Mehlich III and Olsen extracted P. In general the c_1/c ratio for the three tests was in the order of Olsen > Mehlich III > Bray suggesting the order of soil test P efficiency (accuracy).

Fertilizer P_2O_5 recommendations based on the three different soil tests were further determined using the calculated c_1 and c values for the 2003 season. Since calculation of the P fertilization recommendations via the Mitscherlich-Bray equation required all soil test P values and P fertilization values to be in an equivalent unit

Figure 6.36 Determination of the theoretical maximum corn yield for the 2003 site-year.

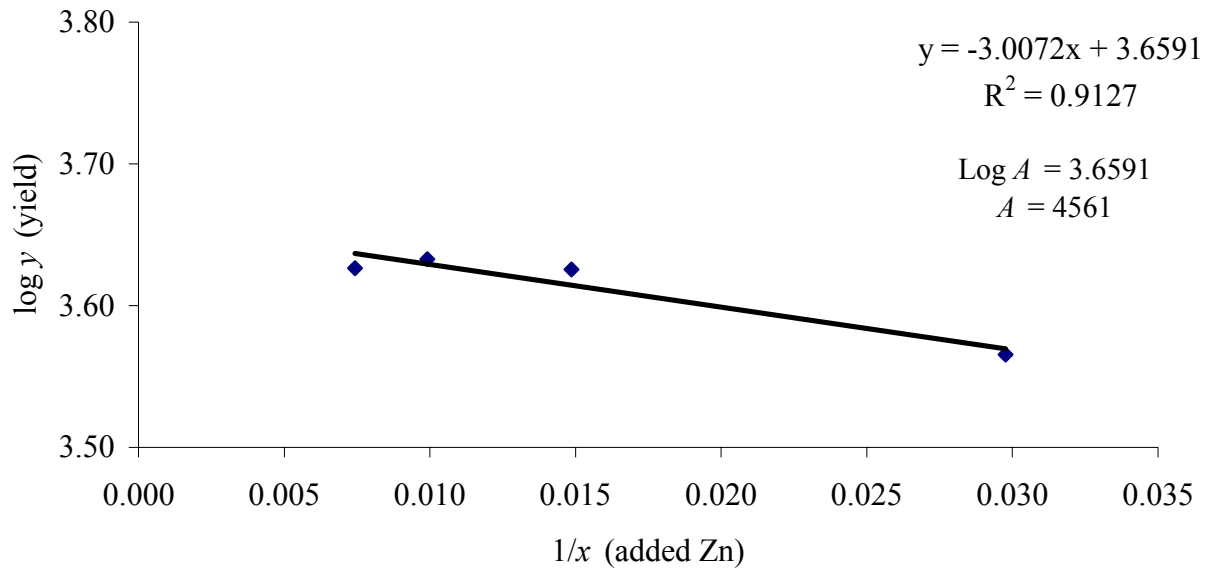


Table 6.23 Calculated Mitscherlich-Bray efficiency coefficients for DTPA and Mehlich III extractable Zn for the 2002 site-year.

| Zn applied kg/ha | Corn Yield Calculated | | 1/x | DTPA | | | Mehlich III | | |
|------------------------|-----------------------|-------|-------|----------------|---------|-------------------|----------------|-------|-------------------|
| | (y) kg/ha | log y | | C ₁ | C | C ₁ /C | C ₁ | C | C ₁ /C |
| 0 | 6467 | --- | --- | 0.747 | --- | | 0.248 | --- | |
| 1.1 | 7330 | 3.87 | 0.909 | | 0.34994 | | | 0.350 | |
| 2.2 | 7627 | 3.88 | 0.455 | | 0.30788 | | | 0.308 | |
| 3.4 | 7340 | 3.87 | 0.294 | | 0.11517 | | | 0.115 | |
| 4.5 | 7247 | 3.86 | 0.222 | | 0.07310 | | | 0.073 | |
| 6.7 | 7743 | 3.89 | 0.149 | | 0.13168 | | | 0.132 | |
| Mean | --- | --- | --- | 0.747 | 0.19556 | 4 | 0.248 | 0.196 | 1.270 |
| Theoretical max. yield | 7936 | | | | | | | | |

Table 6.24 Calculated Mitscherlich-Bray efficiency coefficients for DTPA and Mehlich III extractable Zn for the 2004 site-year.

| Zn applied kg/ha | Corn Yield (y) kg/ha | Claculated log y | 1/ x | DTPA | | | Mehlich III | | |
|------------------------|-----------------------------|-----------------------|--------|-------|-------|---------|-------------|-------|---------|
| | | | | C_1 | C | C_1/C | C_1 | C | C_1/C |
| 0 | 1514 | --- | --- | 0.307 | --- | | 0.078 | --- | |
| 1.1 | 3200 | 3.51 | 0.909 | | 0.805 | | | 0.805 | |
| 2.2 | 2852 | 3.46 | 0.455 | | 0.231 | | | 0.231 | |
| 3.4 | 3161 | 3.50 | 0.294 | | 0.242 | | | 0.242 | |
| 4.5 | 3095 | 3.49 | 0.222 | | 0.163 | | | 0.163 | |
| 6.7 | 3603 | 3.56 | 0.149 | | -- | | | -- | |
| Mean | --- | --- | --- | 0.307 | 0.360 | 0.9 | 0.078 | 0.360 | 0.216 |
| Theoretical max. yield | 3453 | | | | | | | | |

basis (kg ha^{-1}), soil test P values and P fertilization rates were converted into mg kg^{-1} and lbs. ac^{-1} respectively, in order to simplify the reading of the recommendation table.

The P_2O_5 fertilizer recommendations for Norwood and other calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and Mehlich III initial soil test values can be seen Table 6.26. Based on the initial soil test reading of 14 mg kg^{-1} of Mehlich III extractable P, it would take approximately 85 lbs. ac^{-1} of P_2O_5 fertilizer to achieve 95% of the maximum corn yield, 61 lbs. ac^{-1} of P_2O_5 fertilizer to achieve 90% of the maximum yield, and 30 lbs. ac^{-1} of P_2O_5 fertilizer to achieve 75% of the maximum yield. Fertilizer recommendations made by the Mitscherlich-Bray concept provide the producer with a choice for choosing a target yield goal in accordance with current and future financial aspects and thus provide a dual benefit (Sonar and Babhulkar, 2002). In this study it took approximately 24 lbs. ac^{-1} of P_2O_5 fertilizer to increase only 5% of the maximum yield (from 90 – 95%). Therefore, it may be more economical choice to apply P fertilizer at the 90% maximum yield level. It should be pointed out that the

Table 6.25 Calculated Mitscherlich-Bray efficiency coefficients for Mehlich III, Bray and Olsen extractable P for the 2003 site-year.

| P ₂ O ₅ applied kg/ha | Corn Yield Calculated (y) kg/ha | log y | 1/x | Mehlich III | | | Bray | | | Olsen | | |
|---|------------------------------------|-------|-------|----------------|-------|-------------------|----------------|-------|-------------------|----------------|-------|-------------------|
| | | | | C ₁ | C | C ₁ /C | C ₁ | C | C ₁ /C | C ₁ | C | C ₁ /C |
| 0.0 | 1757 | --- | --- | 0.0029 | --- | | 0.0002 | --- | | 0.005 | --- | |
| 33.6 | 3678 | 3.566 | 0.030 | | 0.015 | | | 0.015 | | | 0.015 | |
| 67.3 | 4222 | 3.626 | 0.015 | | 0.014 | | | 0.014 | | | 0.014 | |
| 100.9 | 4292 | 3.633 | 0.010 | | 0.010 | | | 0.010 | | | 0.010 | |
| 134.5 | 4230 | 3.626 | 0.007 | | 0.007 | | | 0.007 | | | 0.007 | |
| 358.7 | 5078 | 3.706 | 0.003 | | -- | | | -- | | | -- | |
| Mean | --- | --- | --- | 0.0029 | 0.011 | 0.259 | 0.0002 | 0.011 | 0.020 | 0.005 | 0.011 | 0.475 |
| Theoretical max. yield | 4561 | | | | | | | | | | | |

Mitscherlich-Bray equation and other curvilinear models tend to recommend too much fertilizer to obtain the maximum yield (Dahnke and Olsen, 1990). State laboratories traditionally adopt yield goals at the 95% of maximum yield level (Eckert, 1987) however, in this case, the 90% maximum yield goal may be the most appropriate.

The P_2O_5 fertilizer recommendations for Norwood and other calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and Bray II initial soil test P values can be seen Table 6.27. Our initial Bray soil test extractable P value of 178 mg kg^{-1} would require between 60 and 64 lbs of P_2O_5 fertilizer to obtain 90% of the maximum yield. It is interesting to note that according to the Mitscherlich-Bray calculations, P_2O_5 fertilizer would still be recommended at the 90% maximum yield goal level even when soils which have an initial Bray soil test P value of 700 mg kg^{-1} . This can easily be explained by the extremely large quantities of P extracted by the Bray II soil test in these calcareous and the resulting low soil test P efficiency coefficient (c_1). The Bray II soil test extracted approximately an average of 910 kg ha^{-1} of plant available P as compared to 72 and 39 kg ha^{-1} of plant available P by the Mehlich III and Olsen soil test extractions for the 2002 site soil. This gross overestimation of the plant available P by the Bray soil test was even larger than $358.7 \text{ kg ha}^{-1} P_2O_5$, the highest fertilizer rate used in this study. As a result, soil test P efficiency coefficient was calculated at approximately 0.02%, ten times less than the efficiencies of the Mehlich III and Olsen soil test values (see previous discussion). The calculation of the fertilizer requirements therefore remained high even when the Bray soil test values were high. Clearly, this implies that the Bray II soil test extracts much more P than is actually plant available in these calcareous Red River alluvial soils and causes the subsequent inability of the

Mitscherlich-Bray equation to predict unrealistic fertilizer recommendations based on these overestimated soil test P values.

The P_2O_5 fertilizer recommendations for Norwood and other calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and Olsen initial soil test P values can be seen Table 6.28. Based on the initial soil test reading of 7.6 mg kg^{-1} of Olsen extractable P, it would take approximately 85 lbs. ac.^{-1} of P_2O_5 fertilizer to achieve 95% of the maximum corn yield, 61 lbs. ac.^{-1} of P_2O_5 fertilizer to achieve 90% of the maximum yield, and 30 lbs. ac.^{-1} of P_2O_5 fertilizer to achieve 75% of the maximum yield.

Zinc fertilizer recommendations for Norwood and other calcareous Red River alluvial soils based on the Mitscherlich-Bray concept for the DTPA and Mehlich III soil test extractions can be seen in Tables 6.44 and 6.45 respectively. Since the a Zn fertilizer response was seen in two different years (2002 and 2004), the fertilizer recommendations were calculated based on mean c_1, c , and soil test values. Based on the results of the fertilizer recommendation calculations and the initial DTPA and Mehlich III soil test Zn levels of 0.44 and 1.32 mg kg^{-1} in 2002 it would require approximately $2.6 \text{ lbs. ac.}^{-1}$ of Zn fertilizer to achieve 95% of the maximum corn yield, $1.6 \text{ lbs. ac.}^{-1}$ of Zn fertilizer to achieve 90% of the maximum yield, and $0.7 \text{ lbs. ac.}^{-1}$ of Zn fertilizer to achieve 75% of the maximum yield. In 2004 initial DTPA and Mehlich III soil test Zn levels were 0.36 and 1.44 mg kg^{-1} which would require approximately $2.8 \text{ lbs. ac.}^{-1}$ of Zn fertilizer to achieve 95% of the maximum corn yield, $1.9 \text{ lbs. ac.}^{-1}$ of Zn fertilizer to achieve 90% of the maximum yield, and $0.6 \text{ lbs. ac.}^{-1}$ of Zn fertilizer to achieve 75% of the maximum yield.

Table 6.26 P₂O₅ fertilizer recommendations for calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and Mehlich III initial soil test P values.

| Soil Available Mehlich III P ₂ O ₅ | Percent theoretical max yield | | | | | Soil Available Mehlich III P | Percent theoretical max yield | | | | |
|--|--|----|----|----|-----|---------------------------------|--|----|----|----|----|
| | 50 | 75 | 80 | 90 | 95 | | 50 | 75 | 80 | 90 | 95 |
| kg ha ⁻¹ | Fertilizer P ₂ O ₅ , kg ha ⁻¹ | | | | | mg kg ⁻¹ | Fertilizer P ₂ O ₅ , lbs ac. ⁻¹ | | | | |
| 25 | 20 | 46 | 55 | 81 | 108 | 5 | 18 | 41 | 49 | 73 | 96 |
| 50 | 14 | 40 | 48 | 75 | 101 | 10 | 12 | 36 | 43 | 67 | 90 |
| 75 | 7 | 33 | 42 | 68 | 95 | 15 | 6 | 30 | 37 | 61 | 85 |
| 100 | 1 | 27 | 36 | 62 | 88 | 20 | 1 | 24 | 32 | 55 | 79 |
| 125 | 0 | 21 | 29 | 55 | 82 | 24 | 0 | 18 | 26 | 50 | 73 |
| 150 | | 14 | 23 | 49 | 75 | 29 | | 13 | 20 | 44 | 67 |
| 175 | | 8 | 16 | 43 | 69 | 34 | | 7 | 14 | 38 | 62 |
| 200 | | 1 | 10 | 36 | 63 | 39 | | 1 | 9 | 32 | 56 |
| 225 | | 0 | 3 | 30 | 56 | 44 | | 0 | 3 | 26 | 50 |
| 250 | | | 0 | 23 | 50 | 49 | | | 0 | 21 | 44 |
| 275 | | | | 17 | 43 | 54 | | | | 15 | 39 |
| 300 | | | | 10 | 37 | 59 | | | | 9 | 33 |
| 325 | | | | 4 | 30 | 63 | | | | 3 | 27 |
| 350 | | | | 0 | 24 | 68 | | | | 0 | 21 |
| 375 | | | | | 17 | 73 | | | | | 15 |
| 400 | | | | | 11 | 78 | | | | | 10 |
| 425 | | | | | 4 | 83 | | | | | 4 |
| 450 | | | | | 0 | 88 | | | | | 0 |

Table 6.27 P₂O₅ fertilizer recommendations for calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and Bray II initial soil test P values.

| Soil Available Bray II P ₂ O ₅ | Percent theoretical max yield | | | | | Soil Available Bray II P | Percent theoretical max yield | | | | |
|--|--|----|----|----|-----|-----------------------------|--|----|----|----|-----|
| | 50 | 75 | 80 | 90 | 95 | | 50 | 75 | 80 | 90 | 95 |
| kg ha ⁻¹ | Fertilizer P ₂ O ₅ , kg ha ⁻¹ | | | | | mg kg ⁻¹ | Fertilizer P ₂ O ₅ , lbs ac. ⁻¹ | | | | |
| 0 | 26 | 53 | 61 | 88 | 114 | 0 | 24 | 47 | 55 | 78 | 102 |
| 200 | 22 | 49 | 57 | 84 | 110 | 39 | 20 | 44 | 51 | 75 | 98 |
| 400 | 18 | 45 | 53 | 80 | 106 | 78 | 16 | 40 | 48 | 71 | 95 |
| 600 | 14 | 41 | 49 | 76 | 102 | 117 | 13 | 36 | 44 | 68 | 91 |
| 800 | 10 | 37 | 45 | 72 | 98 | 156 | 9 | 33 | 40 | 64 | 87 |
| 1000 | 6 | 32 | 41 | 67 | 94 | 195 | 5 | 29 | 37 | 60 | 84 |
| 1200 | 2 | 28 | 37 | 63 | 90 | 234 | 2 | 25 | 33 | 57 | 80 |
| 1400 | 0 | 24 | 33 | 59 | 86 | 273 | 0 | 22 | 29 | 53 | 77 |
| 1600 | | 20 | 29 | 55 | 82 | 312 | | 18 | 26 | 49 | 73 |
| 1800 | | 16 | 25 | 51 | 78 | 351 | | 14 | 22 | 46 | 69 |
| 2000 | | 12 | 21 | 47 | 74 | 390 | | 11 | 18 | 42 | 66 |
| 2200 | | 8 | 17 | 43 | 69 | 429 | | 7 | 15 | 38 | 62 |
| 2400 | | 4 | 12 | 39 | 65 | 468 | | 4 | 11 | 35 | 58 |
| 2600 | | 0 | 8 | 35 | 61 | 507 | | 0 | 7 | 31 | 55 |
| 2800 | | | 4 | 31 | 57 | 546 | | | 4 | 27 | 51 |
| 3000 | | | 0 | 27 | 53 | 585 | | | 0 | 24 | 47 |
| 3200 | | | | 23 | 49 | 624 | | | | 20 | 44 |
| 3400 | | | | 19 | 45 | 663 | | | | 17 | 40 |
| 3600 | | | | 14 | 41 | 702 | | | | 13 | 36 |
| 3800 | | | | 10 | 37 | 741 | | | | 9 | 33 |

Table 6.28 P₂O₅ fertilizer recommendations for calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and Olsen initial soil test P values.

| Soil Available Olsen P ₂ O ₅ | Percent theoretical max yield | | | | | Soil Available Olsen P | Percent theoretical max yield | | | | |
|--|--|----|----|----|-----|---------------------------|--|----|----|----|-----|
| | 50 | 75 | 80 | 90 | 95 | | 50 | 75 | 80 | 90 | 95 |
| kg ha ⁻¹ | Fertilizer P ₂ O ₅ , kg ha ⁻¹ | | | | | mg kg ⁻¹ | Fertilizer P ₂ O ₅ , lbs ac. ⁻¹ | | | | |
| 0 | 26 | 53 | 61 | 88 | 114 | 0 | 24 | 47 | 55 | 78 | 102 |
| 15 | 19 | 46 | 54 | 81 | 107 | 3 | 17 | 41 | 48 | 72 | 96 |
| 30 | 12 | 39 | 47 | 74 | 100 | 6 | 11 | 34 | 42 | 66 | 89 |
| 45 | 5 | 32 | 40 | 66 | 93 | 9 | 5 | 28 | 36 | 59 | 83 |
| 60 | 0 | 24 | 33 | 59 | 86 | 12 | 0 | 22 | 29 | 53 | 77 |
| 75 | | 17 | 26 | 52 | 79 | 15 | | 15 | 23 | 47 | 70 |
| 90 | | 10 | 19 | 45 | 72 | 18 | | 9 | 17 | 40 | 64 |
| 105 | | 3 | 12 | 38 | 64 | 20 | | 3 | 10 | 34 | 58 |
| 120 | | 0 | 4 | 31 | 57 | 23 | | 0 | 4 | 28 | 51 |
| 135 | | | 0 | 24 | 50 | 26 | | | 0 | 21 | 45 |
| 150 | | | | 17 | 43 | 29 | | | | 15 | 38 |
| 165 | | | | 9 | 36 | 32 | | | | 8 | 32 |
| 180 | | | | 2 | 29 | 35 | | | | 2 | 26 |
| 195 | | | | 0 | 22 | 38 | | | | 0 | 19 |
| 210 | | | | | 15 | 41 | | | | | 13 |
| 225 | | | | | 7 | 44 | | | | | 7 |
| 240 | | | | | 0 | 47 | | | | | 0 |

Table 6.29 Zinc fertilizer recommendations for calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and DTPA initial soil test Zn values.

| Soil Available DTPA Zn | Percent theoretical max yield | | | | | | Soil Available DTPA Zn | Percent theoretical max yield | | | | | |
|------------------------------|-------------------------------|-----|-----|-----|-----|-----|------------------------------|-------------------------------|-----|-----|-----|-----|-----|
| | 50 | 75 | 80 | 85 | 90 | 95 | | 50 | 75 | 80 | 85 | 90 | 95 |
| kg ha ⁻¹ | Zn, kg ha ⁻¹ | | | | | | mg kg ⁻¹ | Zn, lbs ac. ⁻¹ | | | | | |
| 0.00 | 1.1 | 2.2 | 2.5 | 3.0 | 3.6 | 4.7 | 0.00 | 1.0 | 1.9 | 2.2 | 2.6 | 3.2 | 4.2 |
| 0.15 | 0.8 | 1.9 | 2.2 | 2.7 | 3.3 | 4.4 | 0.07 | 0.7 | 1.7 | 2.0 | 2.4 | 3.0 | 3.9 |
| 0.30 | 0.5 | 1.6 | 1.9 | 2.4 | 3.0 | 4.1 | 0.13 | 0.5 | 1.4 | 1.7 | 2.1 | 2.7 | 3.7 |
| 0.45 | 0.2 | 1.3 | 1.7 | 2.1 | 2.7 | 3.8 | 0.20 | 0.2 | 1.2 | 1.5 | 1.9 | 2.5 | 3.4 |
| 0.60 | 0.0 | 1.0 | 1.4 | 1.8 | 2.5 | 3.5 | 0.27 | 0.0 | 0.9 | 1.2 | 1.6 | 2.2 | 3.2 |
| 0.75 | | 0.7 | 1.1 | 1.5 | 2.2 | 3.3 | 0.33 | | 0.7 | 1.0 | 1.4 | 1.9 | 2.9 |
| 0.90 | | 0.5 | 0.8 | 1.3 | 1.9 | 3.0 | 0.40 | | 0.4 | 0.7 | 1.1 | 1.7 | 2.7 |
| 1.05 | | 0.2 | 0.5 | 1.0 | 1.6 | 2.7 | 0.47 | | 0.2 | 0.5 | 0.9 | 1.4 | 2.4 |
| 1.20 | | 0.0 | 0.2 | 0.7 | 1.3 | 2.4 | 0.54 | | 0.0 | 0.2 | 0.6 | 1.2 | 2.1 |
| 1.35 | | | 0.0 | 0.4 | 1.0 | 2.1 | 0.60 | | | 0.0 | 0.4 | 0.9 | 1.9 |
| 1.50 | | | | 0.1 | 0.8 | 1.8 | 0.67 | | | | 0.1 | 0.7 | 1.6 |
| 1.65 | | | | 0.0 | 0.5 | 1.6 | 0.74 | | | | 0.0 | 0.4 | 1.4 |
| 1.80 | | | | | 0.2 | 1.3 | 0.80 | | | | | 0.2 | 1.1 |
| 1.95 | | | | | 0.0 | 1.0 | 0.87 | | | | | 0.0 | 0.9 |
| 2.10 | | | | | | 0.7 | 0.94 | | | | | | 0.6 |
| 2.25 | | | | | | 0.4 | 1.00 | | | | | | 0.4 |
| 2.40 | | | | | | 0.1 | 1.07 | | | | | | 0.1 |
| 2.55 | | | | | | 0.0 | 1.14 | | | | | | 0.0 |

Table 6.30 Zinc fertilizer recommendations for calcareous Red River alluvial soils based on the Mitscherlich-Bray concept and Mehlich III initial soil test Zn values.

| Soil Available Mehlich III Zn | Percent theoretical max yield | | | | | | Soil Available Mehlich III Zn | Percent theoretical max yield | | | | | |
|-------------------------------------|-------------------------------|-----|-----|-----|-----|-----|-------------------------------------|-------------------------------|-----|-----|-----|-----|-----|
| | 50 | 75 | 80 | 85 | 90 | 95 | | 50 | 75 | 80 | 85 | 90 | 95 |
| kg ha ⁻¹ | Zn, kg ha ⁻¹ | | | | | | mg kg ⁻¹ | Zn, lbs ac. ⁻¹ | | | | | |
| 0.00 | 1.1 | 2.2 | 2.5 | 3.0 | 3.6 | 4.7 | 0.00 | 1.0 | 1.9 | 2.2 | 2.6 | 3.2 | 4.2 |
| 0.50 | 0.8 | 1.9 | 2.2 | 2.7 | 3.3 | 4.4 | 0.22 | 0.7 | 1.7 | 2.0 | 2.4 | 3.0 | 3.9 |
| 1.00 | 0.5 | 1.6 | 1.9 | 2.4 | 3.0 | 4.1 | 0.45 | 0.4 | 1.4 | 1.7 | 2.1 | 2.7 | 3.7 |
| 1.50 | 0.2 | 1.3 | 1.6 | 2.1 | 2.7 | 3.8 | 0.67 | 0.2 | 1.1 | 1.5 | 1.9 | 2.4 | 3.4 |
| 2.00 | 0.0 | 1.0 | 1.3 | 1.8 | 2.4 | 3.5 | 0.89 | 0.0 | 0.9 | 1.2 | 1.6 | 2.2 | 3.1 |
| 2.50 | | 0.7 | 1.0 | 1.5 | 2.1 | 3.2 | 1.12 | | 0.6 | 0.9 | 1.3 | 1.9 | 2.9 |
| 3.00 | | 0.4 | 0.8 | 1.2 | 1.8 | 2.9 | 1.34 | | 0.4 | 0.7 | 1.1 | 1.6 | 2.6 |
| 3.50 | | 0.1 | 0.5 | 0.9 | 1.5 | 2.6 | 1.56 | | 0.1 | 0.4 | 0.8 | 1.4 | 2.3 |
| 4.00 | | 0.0 | 0.2 | 0.6 | 1.2 | 2.3 | 1.79 | | 0.0 | 0.1 | 0.5 | 1.1 | 2.1 |
| 4.50 | | | 0.0 | 0.3 | 1.0 | 2.0 | 2.01 | | | 0.0 | 0.3 | 0.9 | 1.8 |
| 5.00 | | | | 0.0 | 0.7 | 1.7 | 2.23 | | | | 0.0 | 0.6 | 1.6 |
| 5.50 | | | | | 0.4 | 1.5 | 2.46 | | | | | 0.3 | 1.3 |
| 6.00 | | | | | 0.1 | 1.2 | 2.68 | | | | | 0.1 | 1.0 |
| 6.50 | | | | | 0.0 | 0.9 | 2.90 | | | | | 0.0 | 0.8 |
| 7.00 | | | | | | 0.6 | 3.13 | | | | | | 0.5 |
| 7.50 | | | | | | 0.3 | 3.35 | | | | | | 0.2 |
| 8.00 | | | | | | 0.0 | 3.57 | | | | | | 0.0 |

In addition to fertilizer recommendations determined by the Mitscherlich-Bray concept, recommendations were also determined by using polynomial regression between corn yield response and fertilizer application rates. The resulting regression between Zn fertilizer rate and relative yield during the 2002 and 2003 years can be seen in Figs. 6.37 and 6.38 respectively. In 2002, 58 percent of the variation in relative corn yields could be explained by Zn fertilization. The first derivative calculation indicated that the relative maximum corn yield was achieved after approximately 5.68 kg ha⁻¹ of Zn fertilizer was applied. In 2004, 68 percent of the variation of relative corn yields could be explained by Zn fertilization rate. Solving for the first derivative of the equation indicated that the relative maximum corn yield was achieved after 5.76 kg ha⁻¹ of Zn fertilizer was applied. The regression between P fertilization rate and relative yield

during the 2003 year can be seen in Fig. 6.39. Approximately 82 percent of the variation of corn yield could be explained by P fertilizer rate. The calculation of the first derivative of the regression equation indicated that relative maximum yield was achieved after approximately 235 kg ha⁻¹ P fertilizer was applied. The 359 kg ha⁻¹ P rate is an extremely high P fertilization rate which would normally not be applied to an agricultural field. The excessive rate was only included in the study to assure maximum corn yield due to P fertilization. Unexpectedly, corn yields were statistically higher for the 359 kg ha⁻¹ as compared to the 135 kg ha⁻¹ P rate (Fig. 6.12) during the 2003 season. Nonetheless, when the 359 kg ha⁻¹ P rate is excluded from the regression (Fig. 6.40) approximately 97 percent of the variability in corn yield can be explained by P fertilizer rate and the relative maximum yield was obtained after approximately 63 kg ha⁻¹ of fertilizer P was applied.

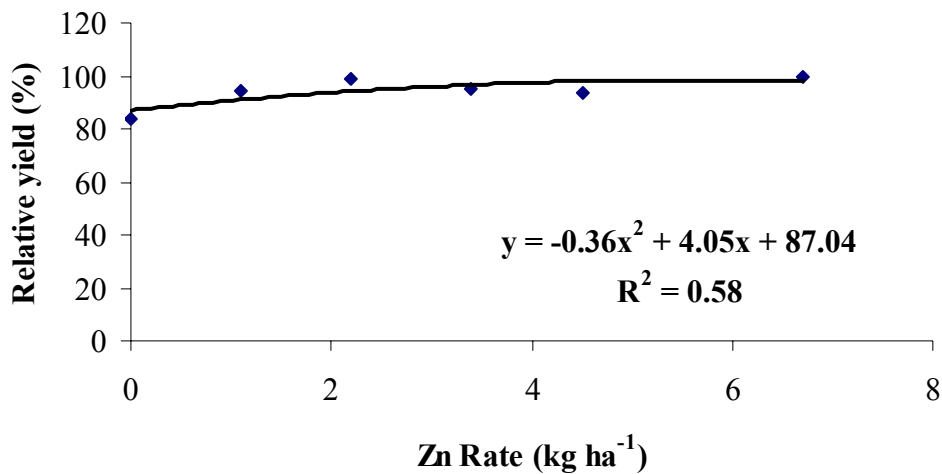


Figure 6.37 Polynomial regression between Zinc fertilizer rate and relative corn yield for the 2002 site-year.

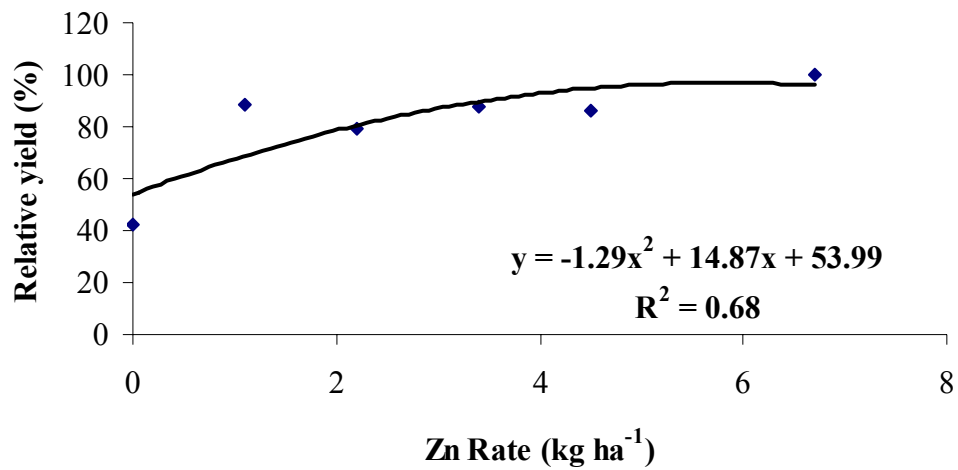


Figure 6.38 Polynomial regression between Zinc fertilization rate and relative corn yield for the 2004 site-year.

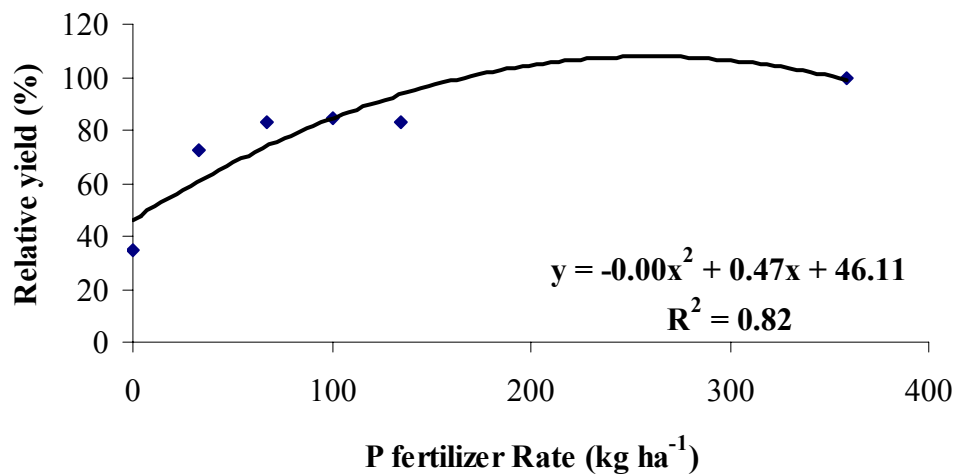


Figure 6.39 Polynomial regression between P fertilizer rate and relative yield for the 2003 site-year.

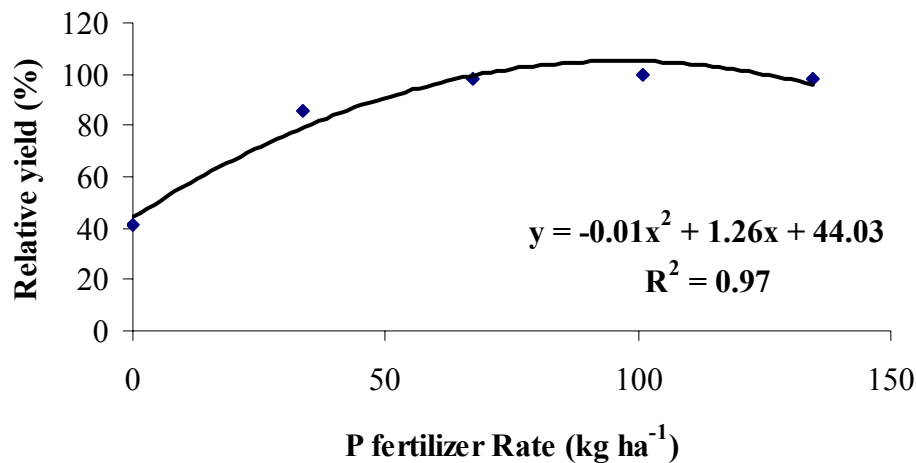


Figure 6.40 Polynomial regression between P fertilizer rate and relative yield for the 2003 site-year excluding the 359 kg ha⁻¹ P rate.

6.4 Discussion and Conclusions

This field study was conducted, in part, to determine the effect of P and Zn fertilization on corn growth and plant tissue P and Zn concentrations in a calcareous Red River alluvial Norwood soil which initially tested *High to Very High* in Bray II extractable P. Secondly, site specific P and Zn fertilization recommendations using several common soil test extraction procedures were conceived where increases in corn yields occurred due to P or Zn fertilization. The work presented herein provides further insights into the management of P and Zn for corn grown in a Norwood Red River alluvial soil and may also be used to help manage P and Zn inputs for other crops grown in calcareous alluvial Louisiana soils.

As a result of conducting the P and Zn fertility experiment at three separate sites during the three year tenure of the study, although the soil at each site was a calcareous Red River alluvial Norwood soil, two very different scenarios occurred. In the first scenario (A), a significant increase in corn yield in 2002 and 2004 was attributed to Zn fertilization and not P fertilization. During the 2003 season, scenario (B), a significant

increase in corn yields was seen due to P but not Zn fertilizer application. The fertilization response between the two scenarios was quite different, and the result could be explained by examining the soil test P and Zn results taken prior to planting each season. Initial mean soil test Zn results were very similar during all three years ranging from 0.36 – 0.44 DTPA extractable Zn and from 0.81 – 1.44 Mehlich III extractable Zn. Consequently, soil test P mean initial soil test values were quite different for the scenario B year as compared to the scenario A years. Bray II initial soil test P values were 270 and 251 mg kg⁻¹ for the 2002 year and the 2004 year (scenario A), and 178 mg kg⁻¹ for the 2003 year (scenario B). Under the current calibration for the Bray II soil test for corn grown on an alluvial silt loam soil in both, cases these soils would be classified as *Very High* in plant available P and the probability of seeing a yield response due to P fertilization would be negligible. In fact, under the current calibration, a response to P fertilization should not be seen when a soil tests above 120 mg kg⁻¹ (Peevy, 1972). The mere occurrence of a P fertilization response, as seen in scenario B, confirm our initial hypothesis that the currently used Bray II soil P test may not be accurate for these calcareous soils possibly due to P overestimation from the dissolution of calcium-P phases. Further proof of the strong acidity of the Bray II extraction leading to the overestimation of P from the dissolution of calcium-P minerals in calcareous soils was described in Chapter 2 (a significant correlation existed between the Bray II extractable P and the HCl-P fraction while no relationship existed with Mehlich III or Olsen extractable P and the HCl-P fraction).

The fact that corn yield response took place in scenario B but not in scenario A suggested that the critical level of the Bray II soil test extraction would lie somewhere

between the 178 and 251 mg kg⁻¹ level for these Norwood Red River calcareous soils. Consequently, based on the post harvest soil test data, the critical level of the Bray II soil test was estimated at approximately 220 mg kg⁻¹. Mehlich III and Olsen P critical levels were estimated at 40 and 8 mg kg⁻¹ respectively, and were very similar to ones published in literature (Olsen et al., 1954; Hanlon, 2001). Phosphate fertilizer recommendations, based on the Mitscherlich-Bray equation, were determined for the Bray II, Mehlich III and Olsen soil test extractions. It was calculated that with an initial soil test of 178 mg kg⁻¹ Bray II extractable P and a 90% yield goal it would require approximately 60 to 64 lbs. P₂O₅ fertilizer per acre.

Initial Zn soil test values at three different sites of this study indicated that based on the current DTPA soil test rating, these soils would be classified as *Low Zn* containing soils and that a yield response due to Zn fertilization would be highly probable. This was the case for scenario A, but not for scenario B. These results suggest that response of corn to Zn fertilization may be dependant not only on the Zn fertility status of the soil but also on the status of soil P. The high soil P levels tend to induce Zn deficiency (Moraghan, 1984; Adams, 1986; Grant and Baily, 1989). It has been reported that P induced Zn deficiency occurs not in the soil but in the plants (Elsokkary, 1981; Singh et al., 1988). The results from this study appear to support this negative interaction. Increasing P rates generally decreased plant tissue Zn concentration and vice versa. The study indicates that soil P level has to be considered when making a decision on Zn fertilization even when soil test Zn is very low.

Critical levels for the DTPA and Mehlich III soil tests using post harvest soil test data were estimated at 1.00 and 2.25 mg kg⁻¹ respectively. The DTPA critical level was

close to the published average of 0.80 mg kg⁻¹ (Cox, 1987). Zinc fertilizer recommendations based on the Mitscherlich-Bray equation were determined for the DTPA and Mehlich III Zn soil test extractions. It was found that with an initial Zn soil test of 0.44 mg kg⁻¹ in 2002 and 0.36 mg kg⁻¹ in 2004, it would take approximately 1.6 lbs. and 1.9 lbs. of Zn fertilizer per acre respectively achieve a yield goal of 90%.

This research established critical levels for several P and Zn soil test extractions and P and Zn fertilizer recommendations for corn grown on calcareous Red River alluvial soils. Future work in Louisiana is needed to further evaluate these soil test critical levels under other soil types and conditions, especially as the state is switching from the Bray II to the Mehlich III extraction.

6.5 References

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CHAPTER 7

CONCLUSIONS

Understanding phosphorus-soil interactions is necessary for environmentally sound management of P. The focus of this study was to first characterize the P forms and sorption properties of Louisiana calcareous soils and to investigate any existing relationships between these parameters and soil matrix properties. Five mildly calcareous soils (calcium carbonate equivalent ranged from 8.9-48.3 g kg⁻¹) of different geological origins at two depths were characterized. Soil P forms were sequentially fractionated by NaHCO₃, NaOH, citrate bicarbonate (CB), citrate-bicarbonate-dithionate (CBD) and HCl. Direct extractable P by Olsen, Bray II, Mehlich III and ammonium oxalate were also determined. Phosphorus sorption was carried out with a 1:10 soil to solution ratio and sorption parameters were derived from best-fit Langmuir and Freundlich models to the experimental data. Norwood (Red River alluvium) and Jeanerette soils (loess-derived) were dominated at both depths with the HCl-P, presumably stable Ca/Mg-phosphates whereas the Commerce surface soil (Mississippi River alluvium) and the Mer Rouge surface (Quachita River alluvium) contained also large percentages of [NaOH+CB]-P, primarily Fe phosphates. All chemically-defined sequential P fractions, except for the HCl-P, were significantly ($R^2 = 0.42-0.85$; $P = 0.03-0.0002$) correlated with different Fe fractions especially amorphous Fe and labile Fe. The HCl-P did not correlate with carbonates or with any other major soil matrix components. Both the Langmuir sorption maximum (b) and the Freundlich distribution coefficient (K_d) were significantly correlated with ammonium oxalate-extractable Al, clay content, and labile Ca ($R^2 = 0.47-0.79$; $P = 0.02-0.003$). Overall, this study indicates a strong influence

of Fe in P chemistry of mildly calcareous soils. It also reveals the importance of labile Ca and surface Al oxides (at exposed edges of aluminosilicate clays) for further P sorption, possibly after available sites of Fe oxides in the calcareous soils are saturated.

The subsequent study used XANES analysis for P speciation in the same calcareous soils and one poultry litter amended Savannah soil. The K-XANES spectra for various common Fe, Al, and Ca phosphate minerals contained unique spectral features which could be used to distinguish between species. The spectra of organic phosphate standards or phosphate sorbed to Fe and Al oxide standards could not be distinguished from each other however, phosphate sorbed on CaCO₃ did contain spectral features similar to Ca phosphate minerals. Principal component analysis (PCA) indicated that five orthogonal components could best describe the variation in the XANES soil spectra. The five standards with *SPOIL* values < 1, were generated from target transformation analysis were selected as data matrix components for least squares linear combination fitting (LCF) of each soil spectra. Based on goodness of fit criteria, χ^2 , the reproduced LCF spectra were determined not to be significantly different from the soil K-XANES spectra. In all soils, Ca related phosphates (including phosphate sorbed on CaCO₃), were the dominate P forms in all the calcareous soils while the Savannah soil contained more P in the organic and Fe-/Al-oxide sorbed P form. A highly significant linear correlation was found between the relative percentage of Ca-P determined by XANES analysis and relative percentage of HCl-P from chemical sequential P fractionation ($R^2 = 0.89$, $P = 0.016$). Similarly, a significant linear correlation was also found between the relative percentage of P related to Fe-/Al-P and organic P by XANES

analysis and the relative percentage of the NaOH-P from the sequential P fractionation procedure (Fe-/Al-P) ($R^2 = 0.81$; $P = 0.0383$).

In the succeeding experiment, the variability associated with common chemical sequential P fractionation procedures recommended for calcareous was evaluated. The focus of the evaluation was the matrix effect of each sequential extraction, the impact of additional NaHCO₃ and CB steps on the subsequent fractions, and the effect of repeated extraction on P fractions of each extraction step. A phosphorus recovery 81 and 61 % was determined in the NaOH-P and CBD-P extractions respectively. The loss of recovery was determined to originate from the use of 1 M NaCl and saturated NaCl soil residue “washing” solutions, used in the NaOH-P and CBD-P extractions respectively. Repeated extractions (double) increased each P fraction as opposed to non-repeated extraction (single) in both the four- and six-step fractionation procedures. The inclusion of the NaHCO₃-P extraction before the NaOH-P extraction in the commonly used four-step fractionation procedure greatly increased the P extracted by NaOH. Since the NaHCO₃-P extraction could cause the hydrolysis of Fe and Al oxides, it removes some of the P which would normally be removed during the NaOH-P. Furthermore, the inclusion of NaHCO₃-P appears to yield an “open-up” effect that caused the P removed during the subsequent NaOH-P fraction to increase. Similar amounts of HCl-P were seen observed both the six- and four-step P fractionation procedures, with and with out repeated extractions indicating that the HCl-P fraction may be unaffected by the addition of the NaHCO₃ or CB-P extractions in the six-step procedure.

This experiment was also conducted to investigate the effect of common fertilizer cations and anions on Zn sorption and lability. Zinc sorption isotherms were conducted

on three acid and four calcareous soils in NH_4^+ , K^+ , and Na^+ and H_2PO_4^- , NO_3^- and Cl^- backgrounds. The acid soils were included in this portion of the study as a reference for comparison. Lability of the sorbed Zn was evaluated by DTPA following sorption. Calcareous soils sorbed more Zn than did acid soils. Predicted Langmuir maxima for Zn sorption differed among the various ionic backgrounds. A majority of the total sorbed Zn (60-96%) was recoverable in the labile fraction. Both NH_4^+ and K^+ equally decreased Zn sorption as opposed to Na^+ in acid and calcareous soils, however NH_4^+ yielded 4-12% more of sorbed Zn into the labile pool than did K^+ in acid soils. Zinc sorption was enhanced by H_2PO_4^- as opposed to Cl^- or NO_3^- in acid soils, but it was decreased in three out of four calcareous soils. The effect of H_2PO_4^- on the lability of the sorbed Zn in acid soils was similar to that of Cl^- or NO_3^- , but in calcareous soils the phosphate held 10-25% more of the sorbed Zn in the non-labile pool. It seems that even in calcareous soil total Zn sorption could be impacted by phosphate-Fe oxide interactions. Furthermore, the effect of background fertilizer ions on the lability of sorbed Zn varies between acid and calcareous soils.

Finally, a fertilizer P and Zn response field trial for corn was conducted to reevaluate the soil test P critical level and establish Zn recommendations for calcareous soils. The experiment was carried out for three years at three different sites and all sites were calcareous Norwood silt loam soils. Initial soil test soil test results indicated that all sites were determined to be “very high” in P and “low” in Zn using the current soil test calibration data. A Zn response was seen in 2002 and 2004, while a P response was seen in 2003. Based on the P fertilization responses and with post harvest soil test correlation data a Bray II soil test P critical level was estimated at 220 mg kg^{-1} . Olsen and Mehlich

soil test P critical levels were estimated at 8 and 40 mg kg⁻¹ respectively. Phosphate fertilizer recommendations for P using the Mitscherlich-Bray equation at a 90% yield goal at an initial Bray II soil test level of 178 mg kg⁻¹ would require approximately 60 – 64 lbs. P₂O₅ per acre. Critical levels for Zn using the DTPA and Mehlich III soil tests were estimated at 1.00 and 2.25 respectively. Zinc fertilizer recommendations calculated using the Mitscherlich-Bray equation indicated that it would take approximately 1.6 and 1.9 lbs per acre of Zn fertilizer to achieve a yield goal of 90% for the 2002 and 2004 seasons respectively when applied in furrow at planting.

In conclusion, calcareous soils comprise some of the most productive agriculture lands even though they make up only a small portion of the total acreage in Louisiana. Phosphorus within these calcareous soils is dominated by Ca-P phases, yet Fe-/Al-oxides also tend to play a very important role in P retention and further sorption, which appear to be confirmed by speciation by XANES analysis and sequential P fractionation. Understanding the difference between the methodologies of P fractionation can help better interpret P chemistry and fertility in calcareous soils. Phosphorus and Zn fertilizer interactions in calcareous soils can cause a loss of Zn lability therefore, P and Zn fertilizer placement should be separated where as the lability of Zn may be improved when Zn fertilizers are applied with ammonium-N amendments. The soil testing calibration and correlation data determined from this study for corn grown on a calcareous Norwood silt loam soil may provide a foundation for managing P and Zn fertilizer amendments in mildly calcareous soils of Louisiana.

VITA

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