

EFFECTS OF A PRESCRIBED FIRE ON SOIL NUTRIENT POOLS
IN THE PINE ROCKLAND FOREST ECOSYSTEM

By

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To all those who supported and inspired me these past four years

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LIST OF ABBREVIATIONS

AB-DTPA	Ammonium Bicarbonate - Diethylene Triamine Pentaacetic Acid
C	Carbon
CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
DCP	Dicalcium Phosphate
DCPD	Dicalcium Phosphate Dihydrate
DDI Water	Double Deionized Water
DI Water	Deionized Water
DNRA	Dissimilation Nitrate Reduction to Ammonium
DRIS	Diagnosis and Recommendation Integrated System
EC	Electrical Conductivity
EDTA	Ethylene Diamine Tetraacetic Acid
ET	Evapotranspiration
FAWN	Florida Automated Weather Network
HA	Hydroxyapatite
HID	Hole-in-the Donut
ICB	Initial Calibration Blank
ICV	Initial Calibration Verification
IS	Ionic Strength
LOI	Loss of Ignition
MCP	Monocalcium Phosphate
MSE	Mean Standard Error
N	Nitrogen
NEDD	N-(1-naphthyl) –Ethelenediamine Dihydrochloride
NPP	Normal Probability Plot

OCP	Octacalcium Phosphate
OM	Organic Matter
P	Phosphorus
QA	Quality Assurance
QC	Quality Control
SI	Saturated Index
SOM	Soil Organic Matter
TAI	Total Aluminum
TC	Total Carbon
TCa	Total Calcium
TCP	Tricalcium Phosphate
TCu	Total Copper
TFe	Total iron
TK	Total Potassium
TM	Total Metal
TMg	Total Magnesium
TMn	Total Manganese
TN	Total Nitrogen
TP	Total Phosphorus
TREC	Tropical Research and Education Center
TZn	Total Zinc
USDA	U.S Department of Agriculture
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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The Pine Rockland forest originated from limestone substrates is listed as one of the most endangered ecosystems in the United States, and has harbored the South Florida slash pine (*Pinus elliottii* var. *densa*). Ecological roles of fire to the Pine Rockland forest are to control relative dominance of hardwood plants to understory vegetation, and to promote rapid regrowth of native plants and germination of pine seedlings. Changes of fire regime and landscape fragmentation have caused a declination of this habitat. In order to evaluate fully nutrient status and role of fire on soil nutrient pools, the objectives of this research were to (1) determine P limitation and effects of prescribed fire on nutrient availability; (2) determine impacts of fire intensity and soil moisture on soil nutrient pools; and (3) predict availability of P in calcareous soils under the Pine Rockland after a fire.

Results of analysis of foliar nutrient contents and DRIS indices indicated that P is the most limiting factor in the Pine Rockland forest. Prescribed fire impacted significantly soil pH, EC, and soil nutrient pools at the top 0-5cm soil. The fire increased immediately soil pH, EC, and extractable P, Mg, K, Mn after 14 days, and extractable Fe and Ca in 270 and 360 days respectively, but not for extractable Cu and Zn. Increases in soil C and N pools occurred in 14

days after the fire, and returned their pre-burn levels in 30 days. Soil NH_4^+ pool significantly increased immediately after the fire, whereas soil NO_3^- pool was increased in post-fire 180 days.

An increase in burn temperature decreased significantly TC, TN, and TK contents in residual ash, but not for TP, TCa, TMg, TFe, TMn, and TZn. The burn temperature significantly impacted pH, EC, and water-soluble P, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, K, Mn, and Zn in ash, but their responses along the burn temperature gradient were very variously. The burn temperature significantly affected to soil nutrient pools. Increasing in the burn temperature resulted in an increase of soil pH and extractable contents of Mg, K, Fe, Cu, but decreased the extractable $\text{NH}_4\text{-N}$, Mn, and Zn. The highest extractable contents of $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, and EC were produced at 350°C .

Soil moisture content didn't impact soil extractable contents of Mg, K, Mn, Zn, and Cu; however, it significantly changed soil pH, EC, and availability of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, and Fe. An increment of soil moisture content increased soil pH and extractable $\text{NH}_4\text{-N}$, and decreased the extractable $\text{PO}_4\text{-P}$. Extractable $\text{NO}_3\text{-N}$ and soil EC had their maximum values at soil water content of 70% field capacity, whereas this soil moisture content produced the lowest extractable Fe content. Time after burn didn't influence extractable Fe and soil pH, but it significantly changed extractable contents of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, P, Mg, K, Mn, Zn, Cu, and EC. An increase of the time caused a linear reduction of extractable $\text{NH}_4\text{-N}$ and an increase of $\text{NO}_3\text{-N}$ concentration. Significant alterations of soil EC and availability of P, Mg, K, Mn, Zn, and Cu occurred concurrently at 120 days after the fire.

The interaction between soil moisture content and burn temperature varied significantly soil extractable contents of some nutrient elements. The burn temperature of 350°C and soil water content of 35% field capacity produced the highest extractable P; whereas the interaction between the burn temperature of 350°C or 550°C and 70% field capacity created the highest NO_3^- content.

The highest EC occurred when heating to 450⁰C and 70% field capacity. Soil extractable Fe was substantially produced at 550⁰C and 100% field capacity.

HPO_4^{2-} , H_2PO_4^- , FeHPO_4 (aq), MgHPO_4 (aq), CaHPO_4 (aq), MnHPO_4 (aq), $\text{FeH}_2\text{PO}_4^+$, $\text{CaH}_2\text{PO}_4^+$, and CaPO_4^- were major compounds of P in the soil solution of the Pine Rockland calcareous soils. Prescribed fire significantly increased extractable concentrations of these P compounds after 14 days, except for $\text{FeH}_2\text{PO}_4^+$. Within a relatively low P availability, solubility of P in the soil solution was controlled by vivianite and MnHPO_4 , and undersaturated with Ca/Mg-P minerals. Changes of ionic activities in the soil solution following the fire shifted equilibrium of P between vivianite and MnHPO_4 . A predictive model for determination of a long-term effect of fire on P availability was exemplified by an equation:

$$Y = 3.38 - 27.19 * M + 0.06579 * T - 0.000143 * D^2 - 0.000115 * T^2 + 0.05008 * M * D + 0.03983 * M * T$$

Where Y is extractable P (mg/kg soil), M is the soil moisture content (v/v), T is fire temperature (⁰C), and D is day after a fire (days).

CHAPTER 1 INTRODUCTION

Pine Rockland Ecosystem

The Pine Rockland is a unique upland ecosystem originated from limestone substrates, and is one of the most endangered forest types in the world (Florida Natural Area Inventory, 2008). In addition to three intact remnant regions in South Florida (Figure 1-1a) including the Long Pine Key in the Everglades National Park, the Big Pine Key in the Florida Lower Keys, and a part of the Big Cypress National Preserve, the Pine Rockland is also found in the Bahamas and Cuba (Snyder, 1986; U.S Fish and Wildlife Service, 2007). Soils under the South Florida Pine Rockland are characterized as entisols order, which is less developed mineral soil without natural genetic horizons and absent of distinct pedogenic horizons (Collins, 2002).

Presence of fragments of limestone (calcium carbonate) in soil surface of the Pine Rockland creates high soil pH ranging from 7.4 to 8.4 (Li, 2001). The soil surface is often irregular with solution holes accumulated by organic matter and humus. Soils in the surface layer range from dark grayish brown to brown fine sands or fine sandy loams whereas the subsurface layers are light gray to yellowish-red fine sand and brown to reddish-brown sandy or clay loams (Snyder, 1986). Drainage of soil often occurs quickly due to the porosity of limestone substrates; however, many areas of Pine Rockland are wet for a short period after heavy rains. During the rainy season, some of the Pine Rockland areas may be shallowly inundated by very slow-flowing surface water (U.S. Fish and Wildlife Service, 2007).

The Pine Rockland forest is a monospecific stand of the South Florida slash pine (*Pinus elliottii* var. *densa*), with a diverse understory of palms, hardwoods, and herbs (Snyder, 1986). *Pinus elliottii* var. *densa* differs from the typical variety, which is known as *Pinus elliottii* var. *elliottii*, not only in geographical location, but in seedling development and wood density as well

(Newton et al., 2005). The South Florida slash pine has longer needles and smaller cones than the typical variety. Additionally, it has a denser wood and a thicker, longer taproot than those of the typical pine variety (Hill, 2001). It can also be distinguished from loblolly pine or other pines by the characteristics of its needles, cones, barks, and fruits. Needles of the South Florida slash pine have brooms at ends of rough twigs. These needles are approximately from 12 to 28 cm in length. Its cones range from 12.5 to 20 cm in length. Plates of bark of the slash pine are large, flat and orange-brown. The fruit is a dark-brown woody cone that is 12 to 20 cm long (Hill, 2001).

The Pine Rockland forest is listed as one of the major endangered ecosystems in the United States (Florida Natural Area Inventory, 2008). It is rated as G1 on the global conservation scale, which represents the most critically imperiled habitats because of extreme rarity or extreme vulnerability to extinction due to some natural or man-made factors. More than 20% of 225 native plant species in the Pine Rockland forest are found nowhere else in the world (Ross, 1995). Several plants and animals that are native to the Pine Rockland forest are listed on Florida's environmentally endangered species list as threatened or endangered (U.S. Fish and Wildlife Service, 2007). Human activities, land-use change, and natural disasters such as hurricanes have caused a habitat degradation of the Pine Rockland forest ecosystem since the late 1800's. The biggest loss of the Pine Rockland habitat occurred in Miami-Dade County, where approximately 98.5% of Pine Rockland was converted into urban and suburban areas by changes of land use during the last century (Figure 1-1b).

The Pine Rockland ecosystem is a fire-dependent habitat, and is maintained by fires in every 3 to 10 years for continued health of endemic plants (Snyder et al., 1990). Historically, lightning was a primary source of fire which usually burned the understory of the Pine Rockland forest with a minimal effect on the pine canopy. Natural fires benefited the Pine Rockland

ecosystem by increasing contents of nutrients, decreasing competition of hardwood species with herbaceous plants, helping germination of pine seeds (Snyder, 1986), controlling exotic species, and creating more light for understory native plants (U.S. Fish and Wildlife Service, 2007). However, alterations in fire regime and landscape fragmentation caused by humans have made the Pine Rockland ecosystem highly vulnerable. Rock plowing during the 1950s destroyed a large area of the Pine Rockland forest in Long Pine Key, called Hole-in-the Donut (HID), that has promoted a favorable environment for a rapid invasion of exotic plant species, particularly Brazilian pepper (Li and Norland, 2001). The presence of massive amounts of Brazilian pepper in the HID is a threat to undisturbed Pine Rockland habitat in the Long Pine Key.

Fire Intensity and Severity

A commonly accepted term used to describe ecological effects of fire is fire severity (Neary et al., 2005). Fire severity has been defined as the qualitative effect which fire has on the soil and water system, and has been used to describe individual fires and fire regimes (Govender et al., 2006; Neary et al., 1999; Simard, 1991). While fire severity is largely dependent upon the nature and characteristics of fuels available for burning, fire intensity has been more narrowly defined as rate of energy released by an individual fire or temperature of burning environment (Govender et al., 2006; Neary et al., 1999). It is determined as $I = H \times W \times R$, where I is fire intensity, H is heat yield (kJ g^{-1}), W is mass of fuel combusted (g m^{-2}), and R is spread rate of heat fire front (m s^{-1}) (Bilgili et al., 2003; DeBano et al., 1998).

Fire regime describes general characteristics of fire that occurs within a specific vegetation type or ecosystem. Three basic kinds of fire regime expressing levels of fire severity are understory fire regime, stand replacement, and mixed fire regime (Neary et al., 2005). Of fire behavior characteristics, spread rate of fire intensity is related to both fuel loading and fuel moisture (Bilgili

et al., 2003). Direct effect of fire on belowground systems is a result of fire severity, which integrates aboveground fuel loading (live and dead), soil moisture and subsequent soil temperature, and duration of fire. Time for recovery of belowground systems not only depends on burning intensity, but also on previous disturbance and recruitment of organisms (Neary et al., 1999). The season of the fire influences rates of fuel consumption and fire intensity (Sparks et al., 2002), and a short fire interval drastically decreases biomass (Enslin et al., 2000; McCaw et al., 2002).

Fire intensity is often affected by burning season and fire frequency, but not depend on burning techniques (micro-plot burn and macro-plot burn) (Smith et al., 1993), and can be determined by some different methods. Henig-Sever et al. (2001) estimated wildfire intensity based on ash pH and the soil micro-arthropod community. They found that ash accumulation and an increase of ash layer pH were directly related to fire intensity, and there was a positive correlation between fire intensity and ash layer pH and minimum diameter of burned branches, whereas a negative correlation was found between size of micro-arthropod community and fire intensity. Gill et al. (2000) who used a model of PIP (Probability of Ignition at a Point) to determine effects of fire regimes over 15 years in the Kakadu National Park in Australia found that early dry season fires had lower intensity than late dry season fires. Govender et al. (2006) used fuel loads, fuel moisture contents, rates of fire spread, and heat yields of fuel to compute fire intensity in 21 years with five different return intervals (1, 2, 3, 4 and 6 years) and five different months/year (Feb, Apr, Aug, Oct, Dec). Their results showed that fire season had a significant effect on fire intensity, but no significant difference of fire intensity between annual burns and burns in the biennial, triennial, quadrennial categories. They also found that fuel loads were significantly different between annual, 2, 3, 4 year burns, and increased with increasing rainfall over two previous years.

The vegetation community dominated by slash pine in the Pine Rockland forest can be considered as a vegetation type with an understory fire regime (Snyder et al., 1990). Fires in the Pine Rockland forests are surface fires that consume only litter and understory vegetation because the pine canopy is usually too open to support a crown fire (Sah et al., 2004 & 2006). Accumulation of pine needles on or near the ground associated with an open canopy of the pine trees allows for rapid drying of fuels that is favorable for fires (Snyder, 1986). Fires did not result in significant changes in species composition in the Pine Rockland forest because almost all species are perennials that survive and recover in place (Gunderson and Snyder, 1997).

Ecological Role of Prescribed Fire in the Pine Rockland Forest

Fire is a dynamic process that influences composition, structure, and patterns of a vegetation community and soil (Boerner, 1982). Not only does fire burn vegetation, residues, and microorganisms in aboveground layers, but it also heats belowground environments (DeBano et al., 1998). Fire can significantly influence physical, chemical, and biological properties of soil (Certini, 2005; Neary et al., 2005). Soil properties can experience short-term, long-term or permanent fire-induced changes, depending primarily on types of property, severity and frequency of fires, and post-fire climatic conditions. Fire can cause alterations of soil biogeochemical cycles, consume soil organic matter, ephemerally increase soil pH, and change availability of nutrients in soil (González-Pérez et al., 2004; Neill et al., 2007; Prieto-Fernandez et al., 1993). Consequently, it can shift the competitive balance between plant species, especially between native plants and invasive plants.

Prescribed fire is defined as fire that is purposely set under specific weather conditions to reduce natural buildup of vegetation and litter in a fire-adapted habitat (Knapp et al., 2009; Wade et al., 1980). It is an effective tool to decrease fuel accumulation, to manage wildlife habitats, to

control an invasion of exotic plant species, and to maintain natural plant communities. Prescribed fires having low to moderate fire intensity often promote a renovation of dominant plant species by eliminating undesired species, whereas severe fires (wildfires) have negative impacts on soil because they cause a loss of organic matter and nutrients through volatilization, damage soil structure and porosity, and change microbial composition (Certini, 2005; DeBano et al., 1998; Neary et al., 2005).

Fire is an important component and is required to maintain and to control, at least in part, the relative dominance of hardwood plants in understory of the Pine Rockland forest (Snyder et al., 1990). In absence of fire, pine canopy is likely to be replaced by dense hardwoods, resulting in loss of the characteristic herb flora (U.S Fish and Wildlife Service, 2007). Three major sources of fire associated with the Pine Rockland forest are prescribed fire, human-caused wildfire, and lightning-caused fire (Gunderson and Snyder, 1997). Lightning-caused fires usually occur during the rainy season from May through October. In contrast, human-caused wildfires mostly happen in the dry season from November through May. Prescribed burnings in the Pine Rockland forest, so far, have often been done from November to April by mild burning conditions. In history, however, the main fire season was carried out by the growing season (March-October) (Knapp et al., 2009). The obvious ecological impact of fires on the Pine Rockland forest is to promote rapid regrowth and to increase flowering of the native vegetation communities in the understory of the pine trees (Wade et al., 1980). According to our observation in the field-burning experiment, most of the native plants and herbs in the understory grew and flowered as rapidly as in three months after the fire, and all species could survive and recover in place after the fire.

Prescribed fire is one of the most widespread management actions in South Florida's natural areas, where the Department of the Interior managers are responsible for the vast majority

of the remaining Pine Rockland forests (USGS, 2000). Responses of vegetation communities in the Pine Rockland forest ecosystem with seasons and intervals of prescribed burns were reported by some studies. Snyder (1986) utilized prescribed fire to burn two different sites of Pine Rockland in Long Pine Key in two different seasons (dry and wet). Site 1 was higher, more frequently burned pinelands while site 2 was lower, less frequently burned pinelands. In his research results, fire intensity in wet season was lower than that in dry season in both site 1 and site 2. By conducting summer-burned and winter-burned experiments in the Big Pine Key, Snyder et al. (2005) showed summer burns had more intense fires than winter burns. Sah et al. (2006) used char height and temperature-sensitive paints to determine fuel consumption of fire in the Pine Rockland, and showed that surface fuel consumption was higher in summer than in winter. In another study, Sah et al. (2010) assessed mortality of South Florida slash pine after fire, and reported that the rate of mortality of pine trees after a summer burn was not different from that after a winter burn.

Effects of Prescribed Fire on Soil Properties

Fire is a fundamental, dynamic process that plays a dominant role in recycling organic matter (DeBano et al., 1998) and influences the composition, structure, and pattern of vegetation community and soil (Neary et al., 2005; Knapp et al., 2009). Immediate responses of soil components to a fire happen as a result of chemical release from ash produced from biomass combustion (Hernandez et al., 1997; Monleon et al., 1997). Long-term impacts, which are usually subtle and can persist for years following a fire, occur as a consequence of changes in soil biogeochemical cycles (DeBano et al., 1998 & 2005) or arises from a relationship between hydrology, fire, soils, nutrient cycling, and site productivity (Monleon et al., 1996 & 1997; Neary et al., 1999). Fire influences comprehensively on soil physical, chemical, mineralogical, and biological properties. Physical properties that are impacted by fire include soil texture, clay content, soil structure, bulk density, and porosity

(Certini, 2005; DeBano et al., 2005; Ulery and Graham; 1993a). The most common chemical components affected by fire include soil organic matter and carbon (C), soil organic nitrogen (N), soil pH buffer capacity, cation exchange capacity, and availability of nutrient elements (Knoepp et al., 2005), whereas biological components most affected by fire are microbial and invertebrate biomass and community composition (Busse and DeBano, 2005). Figure 1-2 describes temperature thresholds of typical soil components usually affected by a fire.

Soil Physical Properties

Soil texture and structure: Soil texture is defined as the relative proportion of different – sized inorganic components that are found in the 0.08-inch mineral fraction of soils (Brady and Weil, 2002; DeBano, 2000b). Components of soil texture are often not impacted by fire because of relatively high temperature thresholds. Clay, the finest textural fraction, can only be changed by soil heating temperature of about 400⁰C and is completely destroyed at soil temperatures of 700⁰C to 800⁰C, but these temperatures can rarely reach beyond several centimeters below the soil surface (Certini, 2005; DeBano et al., 2005). However, humus, an essential component of soil organic matter which acts as a glue to hold mineral soil particles together to form aggregates of soil structure (Brady and Weil, 2002), can be easily broken down as a result of combustion of soil organic matter at low and moderate temperatures (DeBano et al., 1998; Giovannini et al., 1988).

Bulk density and porosity: Bulk density is defined as the mass of dry soil per unit bulk volume expressed in g/cm³, and is related to porosity which is the volume of pores in a soil sample divided by bulk volume of the sample (Brady and Weil, 2002). Heating associated with fire often causes a collapse of soil structure that affects both porosity and pore size distribution in the surface soil. As a result, fire increases bulk density and reduces soil porosity of organic horizons (Neill et al., 2007), and promotes rapid runoff and erosion (DeBano et al., 1998 &

2005). Additionally, black carbon or charcoal created at temperatures between 250 and 500⁰C from an incomplete combustion of woody residues also contribute to the increase of bulk density in soil (Giovannini et al., 1988).

Water repellency: The important physical process associated with fire in the Pine Rockland is water repellency. Heat transferring downward into the soil surface during a fire creates water repellency. The water repellency is often caused by changes of SOM structure resulting from drying of organic matter and coating of mineral soil particles (DeBano, 2000a & b). Erosion is a natural process that involves three different components: detachment, transport, and deposition. A decrease in cover due to combustion of aboveground vegetation and litter during fire promotes a higher rate of erosion (DeBano et al., 2005).

Chemical Properties

Fire not only directly impacts soil organic matter (SOM), C, N, P, S, nutrient cations, pH, and electrical conductivity (EC), but it also indirectly influences the exchange of cations absorbed on the surface of mineral soil particles and humus (DeBano et al., 1998; Knoepp et al., 2005; Neary et al., 2005). Fire-induced changes of nutrient elements in soil solution mainly derive from changes of soil pH, cation exchange capacity, and C/N ratio following a fire. Fire never makes an increase to the total amount of nutrients in soil, but it can transform these elements making nutrients more available for plant and microorganism uptake. In the following sections, focus on reviewing literature about changes of soil pH, P, C, N, SOM, and nutrient elements.

Soil pH and EC

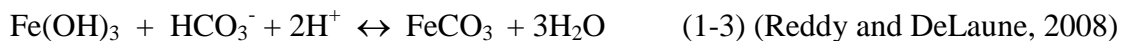
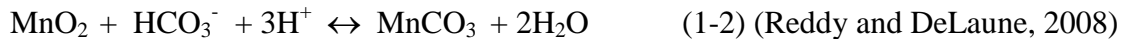
Soil pH is one of the most important factors influencing availability of soil nutrients ;fire-induced changes of soil pH in turn promote alteration of nutrient availability. (DeBano et al., 1998; Ubeda et al., 2005). Nutrient cations (Ca, Mg, and K) released by combustion of fuels and

organic matter tend to move downward into soils, and result in elevation of surface soil pH (Dikici and Yilmax, 2006; Murphy et al., 2006a). In general, fire increases quickly soil pH resulting from combustions of SOMs and plant residues, and denaturation of organic acids in soils. Nevertheless, this increment only occurs when fire temperature is greater than 450°C and fuels are absolutely burned to create white ash (Arocena and Opio, 2003; Macadam, 1987; Qian et al., 2009a & b), and is temporary because increasing in soil pH depends on original pH buffer in soils, composition and amount of cations produced, and soil moisture content (Knoepp et al., 2005). Khanna et al. (1994) assessed that capacity of ash to neutralize soil acidity was well correlated with sum of concentrations of K, Ca, and Mg in ash itself. By analyzing a series of soils developed on different lithologies and under *Q. engelmannii*, *P. ponderosa* and mixed conifers forest, Ulery et al. (1993b) found that the topsoil pH could increase as much as 3 units immediately after fire. This rise was essentially due to production of K and Na oxides, hydroxides, and carbonates from the fire. In contrast, fire-induced changes of soil pH are negligible in calcareous soils where have a high pH buffer (Motavalli et al., 1995).

In addition, anions in ash are also important for neutralizing acidity of soil. Durgin et al. (1984) showed that concentrations of anions (CO_3^{2-} , HCO_3^- , OH^- , SO_4^{2-}) dominant in black ash and grey ash increased alkalinity, and that EC and concentrations of these anions were higher in grey ash than in black ash. Of these anions, CO_3^{2-} and HCO_3^- played an essential role in neutralizing soil acidity because of their abundance in ash products. After being released into soils, anions associated with ash go downward into soil by rain water. In soil solutions, these anions are hydrolyzed and neutralize H^+ ions resulting in an increase of soil pH. Hydrolysis of CO_3^{2-} in water that results in releasing hydroxyl ions (OH^-) (Equation 1-1) as well as OH^- ions produced from combustion contribute chiefly to the increase of soil pH after a fire.



Manganese oxide (MnO_2) and iron hydroxide ($\text{Fe}(\text{OH})_3$) are abundant in acidic soils. Reactions between HCO_3^- and MnO_2 and $\text{Fe}(\text{OH})_3$ (Equations 1-2 & 1-3) consume a large amount of H^+ ions that causes reduction of activity of H^+ ions in soil solution and increases considerably soil pH in acidic soils.



Soil Organic Carbon

Soil organic matter, which is defined as a wide range of organic substances, comprises of intact plant and animal tissues; organisms; dead roots and other recognizable plant residues; and humus (Brady and Weil, 2002; Essington, 2004). Organisms (macrofauna, mesofauna, and microorganisms) living in soil and organic compounds associated with them are collectively called microbial biomass. Humus, 60 to 80% of SOM, is composed of aromatic ring-type structures with a molecular weight from about 2,000 to 300,000, and is split into humic and nonhumic substances. Ill-defined, complex, resistant compounds are called humic substances, whereas nonhumic substances refer to the group of identifiable biomolecules that are mainly produced by microbial action and are generally less resistant to breakdown. Furthermore, humic substances are classified into fulvic acid and humic acid, based on their solubility in acid and alkali (Figure 1-3).

Soil organic matter is an important component of soil because it serves a key role not only in soil chemistry such as cation exchange capacity, cycling of nutrients, and water retention but also in soil physical and biological properties (Certini, 2005; DeBano et al., 1998). Fire causes reduction of SOM content (Covington and Sackett, 1984; Gonzales-Perez et al., 2004) and

alterations of chemical characteristics of SOM (Gonzales –Perez et al., 2004; Knicker, 2007). Depending on fire severity, SOM can be slightly distilled, partly charred, or completely oxidized (Hatten and Zabowski, 2009 & 2010). In a laboratory experiment, by heating the 10cm of topsoil of *Pinus sylvestris* forest at four different temperatures of 150, 220, 350, and 490°C, Fernandez et al. (1999) found that SOMs were not affected by the lowest temperature, but were completely burned by the highest temperature, whereas 37% of SOM were lost at 220°C. Approximately 85% of SOMs were destroyed at between 220°C and 350°C. In addition, Neary et al. (2005) showed that about 99% of SOMs were exclusively demolished at 450°C for 2 hours or at 500°C for a half hour.

Fire frequency also influences SOMs because it diminishes accumulation of aboveground material layers (Johnson and Curtis, 2001; Neary et al., 2005). Bird et al. (2000) reported that a low frequency burning (every 5 years) resulted in an increase in soil C of approximately 10% compared with that of high frequency burning (every year). Along a gradient of fire frequency (every 1-4 years) over a 12-year period in spring burns and summer burns, Neill et al. (2007) demonstrated that soil organic horizon thickness was decreased more in summer burns than in spring burns, and only summer burning every 1-2 years reduced soil organic horizons. Recovery of SOM after fire generally is due to net primary productivity of secondary ecological successions. Fernandez et al. (1999) showed that SOM's content was totally recovered in two years after fire.

Nitrogen

Immediate response of N pool to fire is loss of organic N in the forest floor through volatilization during combustion (Wan et al., 2001; Vose et al., 1999). High fire temperature rapidly oxidizes components of N in organic matter, volatilizes organic N compounds contained in forest floor and soil organic matter, and thereafter releases NH₄-N (Christensen and Muller, 1975; Kutiel et al., 1989; Marion et al., 1991). In general, the total amount of volatilized organic

N is directly proportional to the amount of SOM destroyed during fire. Soil organic N is reduced as a result of combustion; however, contents of inorganic N ions increase considerably following fire (Choromanska and Deluca, 2001; Knoepp and Swank, 1993; Raison et al., 1985).

Fire-induced production of $\text{NH}_4\text{-N}$ is related to the decomposition of secondary amide groups and amino acids in soils. By analyzing thermal decomposition of proteins and N-rich organic matter, Russel et al. (1974) proved that production of $\text{NH}_4\text{-N}$ was involved in the decomposition of secondary amide groups and amino acids which were easily decomposed at heating temperatures above 100°C , and heat-resistant N compounds can be volatilized up to 400°C . In addition, ash produced from aboveground combustion also contains a substantial amount of $\text{NH}_4\text{-N}$ (Qian et al., 2009 a & b). Its downward movement into soils results in increasing content of $\text{NH}_4^+ \text{- N}$ in soil solution (Lavoie et al., 2010; Monleon et al., 1997; Schoch and Binkley, 1986). Unlike ammonium, fire-induced increase of soil NO_3^- was small immediately after fire, but could reach a maximum of approximately threefold of its preburn level within 0.5-1 year after fire, and then decreased thereafter (Bauhus et al., 1993; Covington and Sackett, 1992; Wan and Luo, 2001).

Prieto-Fernandez et al. (1993) demonstrated that total inorganic N was increased in both the surface layer (0-5cm) and subsurface layer (5-10cm) under *P. pinaster* forest one month after fire while soil NO_3^- content was only increased in the subsurface layer. Choromanska et al. (2001) showed that concentrations of mineralizable N and $\text{NH}_4\text{-N}$ in surface soil (0-10cm) of Ponderosa pine forest were significantly increased immediately after fire, and the mineralizable N was significantly reduced after nine months. On other research, Weston and Attiwill (1990) quantified concentration of fire-induced inorganic N in the topsoil of *E. regnans* forest in which inorganic N reached three times as much as its original concentration over the first 205 days, but returned to its pre-fire level after 485 days.

Fire intensity and fire frequency also has impact on soil N pool. Combustion of soil organic N starts at temperature above 100°C, but its loss really occurs at temperature of about 200°C and organic N components are entirely volatilized at temperature above 500°C. While 75 to 100% of N is lost at temperatures of 400 to 500°C, temperatures of 300 to 400°C can cause loss of 50 to 75% of N, and between 25 to 50% of N is volatilized at temperatures of 200 to 300°C (Knoepp et al., 2005). Total amounts of NH₄-N and NO₃-N produced as a result of fire are generally increasing with increase in fire intensity. In a collection of eight studies, Neary et al. (2005) showed that the more severe a fire was, the higher the inorganic N content produced. Total amounts of inorganic N produced by low severity is less than 10 ppm (mg N kg⁻¹ soil), but soil inorganic N amounts reach from 16 ppm to 43 ppm with medium and high fire severity (Figure 1-4). Covington and Sackett (1986), who conducted a study of repeated burning at 1-, 2-, and 5-year intervals in the Ponderosa pine forest in the Northern Arizona, expressed that there were no significant differences in TN among treatments of burning frequencies, but available concentrations of inorganic N were higher on the repeated burning sites than on unburned controls. Monleon et al. (1996) conducted burns on Ponderosa pine sites at three burn-return intervals of 4 months, 5 years, and 12 years. Only surface soils (0-5cm) had a significant response to changes of N, with increases of inorganic N and soil C:N ratio in the 4-month burned sites, reduction of total N and soil C:N ratio at the 5-year burned sites, and without response of soil C:N ratio at the 12-year burned sites.

After entering into soil solution, ammonium and nitrate participate in processes of N biogeochemical cycle (Figures 1-5) where fate of soil NH₄-N is different from NO₃-N. Ammonium is oxidized into nitrate by bacterial oxidation, absorbed into negatively charged surfaces of minerals by cation exchange, fixed in clay colloids by fixation process, volatilized to

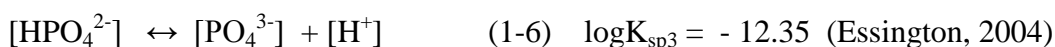
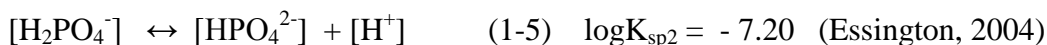
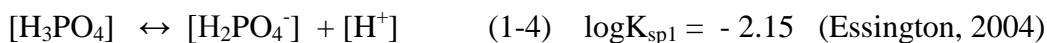
the air as ammonia, immobilized into soil biomass through microbial activities, or leached into groundwater or surface flow (Cleemput, 1998; Megonigal et al., 2004). Bio-availability of nitrate almost depends on the soil microbial community. Nitrate is converted back into ammonium by dissimilation nitrate reduction to ammonium (DNRA) (Burgin and Hamilton, 2007), denitrified into nitrogen gas (Korom, 1992), or leached into groundwater.

Phosphorus

Phosphorous is probably the second most limiting nutrient in natural forest ecosystems after N. Common compounds of P often fall into one of two following main groups: those containing calcium; and those containing iron and aluminum. Calcium-phosphate compounds become more soluble as soil pH decreases; hence, they tend to dissolve and disappear in acid soils. These compounds are quite stable and very insoluble at higher pH, and so become dominant forms of P compounds present in neutral and alkaline soils. Solubility of calcium-phosphate compounds are in order of monocalcium-P > Dicalcium-P > octacalcium-P > tricalcium-P > oxy apatite > hydroxyl apatite > carbonate apatite > flourapatite (Brady and Weil, 2002; Pierzynski et al., 2005). In contrast, hydroxyl phosphate minerals of iron and aluminum, such as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), have very low solubility in strongly acidic soils and become more soluble as soil pH rises. These minerals are unstable in alkaline soils, but they are prominent in acid soils (Brady and Weil, 2002; Pierzynski et al., 2000). In both acid and alkali soils, P tends to undergo sequential reactions that produce P-containing compounds of lower solubility and less bioavailability for plant uptake

Orthophosphate, which is defined as inorganic P ions including H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} , is a bio-available form of P in soil solution. Speciation of these ions in soil solution is a function that is dependent on soil pH (Figure 1-6) and is characterized by three equilibrium

constants (Equations 1-4, 1-5 & 1-6). Of these ions, H_2PO_4^- and HPO_4^{2-} are two dominant species of orthophosphate in natural forest soils. While H_2PO_4^- is a dominant form of orthophosphate in soils of pH range of 4 to 7.2, HPO_4^{2-} is only present in alkaline soils with pH greater than 7.2 (Pierzynski et al., 2005).



Fire has a significant impact on increasing contents of P in soils. Not only does fire supply a large amount of orthophosphate into soil from ash (Durgin et al., 1984; Khanna et al., 1994; Qian et al., 2009b), but it also converts soil organic P into orthophosphate as well (Cadenun et al., 2002; Certini, 2005; Sharpley and Moyer, 2000). This results in an increase of P bio-availability in soils after fire (Giardina et al., 2000; Knoepp et al., 2005; Romanya et al., 1994; Serrasolsas, 1995b). Residence time of inorganic P ions after fire depends entirely on presence of cations (Al, Fe, Ca, Mg, Mn) in soil solution. Figure 1-6 describes possible pathways relating to the fate of inorganic P ions in soil solution after fire. Precipitation with cations of Al, Fe, Ca, Mg, and Mn and adsorption of P ions on surface of soil particles are two main processes that respond immediately to the availability of inorganic P ions in soil solution. In acidic soils, inorganic P ions bind to Al, Fe, and Mn oxides through chemisorptions, whereas in neutral or alkaline soils, it binds to Ca/Mg-minerals or precipitates as discrete Ca/Mg-phosphate minerals (Brady and Weil, 2002; Neary et al., 2005; Pierzynski et al., 2000).

Precipitation of P can be defined as the formation of discrete, insoluble compounds in soils, and can be viewed as the reverse of mineral dissolution. The most commonly precipitated P compounds are constituted by reactions among orthophosphates and cations of Ca, Al, and Fe.

In alkali soils, HPO_4^{2-} ions quickly react with calcium to form dicalcium phosphate dehydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) which later reverts to other, more stable, Ca phosphates such as octacalcium phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 2.5\text{H}_2\text{O}$), and then to fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$). In acidic soils, reactions of H_2PO_4^- ions with dissolved cations (Fe^{3+} , Al^{3+} , and Mn^{4+}) form hydroxyl phosphate precipitates. In addition to precipitation, amorphous or crystalline oxides which are dominant in acidic soils are capable of absorbing inorganic P ions, fixing them on the soil surface, and creating discrete solid phases of Fe-P and Al-P. Phosphate fixation processes mostly occur when H_2PO_4^- reacts with or is adsorbed to the surfaces of insoluble oxides of iron, aluminum, and manganese, such as gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and goethite ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), and 1:1 type silicate clays. H_2PO_4^- ions are attracted to positive charges on the surfaces of iron and aluminum oxides or on the broken edges of kaolinite clays to form outer-sphere complexes or may replace a structural hydroxyl to form an inner-sphere complex with surfaces of oxides (or clays).

Other Nutrients

Many recent studies have reported that fires (prescribed fire and wildfire) significantly increased cation contents, especially Ca, K, Mg, Na (Gray and Dighton, 2006; Groechl et al., 1993; Grove et al., 1986; Marion et al., 1991; Soto et al., 1993). These studies mostly focused on determining alterations of nutrient cations in acidic and neutral soils. Brais et al. (2000) found that exchangeable Ca and Mg contents following a light/moderate burn increased in the 0-10cm mineral layer of boreal forest in Northwest Quebec. Grove et al. (1986) demonstrated that extractable nutrients (Ca, Mg, K, Na) at the top 3 cm immediately increased after the fire, whereas only extractable K concentration was increased at the lower depths. In a study of the *Q. rubra* and *P. grandidentata* forest, Adams and Boyle (1980) proved that availabilities of Ca, Mg, and K were significantly higher than pre-burn levels after one month, but they went back their

pre-burn levels in three months. Tomkins et al. (1991) described that changes on concentrations of K and Mg in surface soil of *Eucalyptus* forest lasted up to 6 months after fire. In other studies, however, Neill et al. (2007) showed that fire had no significant effect on exchangeable Ca, Mg, and K in Cape Cod Oak-pine forest, and Vose et al. (1999) showed that there was no response of soil chemistry to burning in the Southern Appalachian pine-hardwood ecosystems.

Ash produced from fuel combustion contains a large amount of cations (DeBano and Conrad, 1978; Qian et al., 2009b) that contribute to increasing in activity of cations in soil solution (DeBano et al., 1998). Fire-induced increases of ionic activities in soil solution are strictly dependent on types of cations, soil properties (Blank et al., 2007; Kutiel and Shaviv, 1992), accumulation of fuel loading (Snyder, 1986), and degree of combustion (Durgin et al., 1984, Raison et al., 1985). By comparing availability of nutrient elements in two different kinds of soils, Blank et al. (2007) concluded that fire-induced increasing in availability of K, Ca, Mg, and Fe differed from Nevada soils and Utah soils, which was explained by differences in soil moisture and elevation. By analyses of plant ash, Durgin et al. (1984) proved that contents of Ca, Mg, and K were higher in grey ash than in black ash. Moreover, Raison et al. (1985) showed that Ca, Mg, and K were dominant cations in the plant ash, and concentrations of these cations were greater in fine ashes (grey and white ash) than in partly combusted material.

Fire-induced transformation of elements was described by Boerner (1982), which included loss through volatilization during fire, deposition as ashes, and remaining in incompletely burned vegetation or detritus. Similar to N and P, after deposited into soil solution, macro- and micro-nutrients undergo processes in their biogeochemical cycles. Figure 1-7 expresses main pathways relating to fate of nutrient elements in soil solution. Their fate often relates to processes of precipitation with orthophosphates, adsorption by colloids through cation exchanges, loss by leach

or/and runoff, and redox changes. Behaviors of these elements mostly involve reactions with nitrates and orthophosphates produced from fire or in the soil solution.

Research Objectives

Previous studies showed that fire has played an important role in changes of nutrient contents in mineral and organic soils with acidic or neutral pH. Fire reduces contents of TC and TN in both soil and forest floor as a consequence of combustion of SOM and aboveground vegetation. Losses of C and N pools are proportional to an increase in fire intensity. However, fire increases contents of inorganic N, orthophosphate, Ca, Mg, K, and other elements. Ash production and nutrient elements associated with residual ash have important impacts on changes of nutrient availability in soil solution. Effects of fire on vegetation and acidic soils in pine forests have been well documented in many recent studies: pine-oak mixed forest (Kuddes-Fisher and Arthur, 2002; Hubbard et al., 2004), loblolly pine (Schoch and Binkley, 1986; Binkley et al., 1992; Waldrop et al., 1992), longleaf pine (Wilson et al., 2002; Boring et al., 2004; Glitzenstein et al., 2003), longleaf pine –slash pine (Abrahamson and Abrahamson, 1996; Lavoie et al., 2010).

The Pine Rockland slash pine in South Florida is a nutrient-poor and fire-dependent forest ecosystem (U.S Fish and Wildlife Service, 2007; USGS, 2000), and is calcareous soil with a high pH buffer and abundance of calcium, magnesium, iron, and manganese. Effects of fire on soil chemistry of the Pine Rockland ecosystem may differ from those of fire in acidic/neutral soils. Although ecological roles of fire on vegetation recovery in the Pine Rockland forest ecosystem were evaluated by some studies (Ross et al., 2003; Sah et al., 2004 and 2006; Snyder 1986; Snyder et al., 2005), effects of fire on soil chemistry have not been documented. Research questions for this study were: (i) What is a status of P in the Pine Rockland forest: (ii) How will prescribed fire impact the availability of P, N and other elements in calcareous soils under the

Pine Rockland ecosystem? (iii) How can soil moisture and burning temperature affect availability of P, N, and other elements following prescribed fire? (iv) What are the main forms of phosphate compounds and their concentrations following prescribed fire? We hypothesized that P was a limiting factor in the Pine Rockland forest, prescribed fire would improve availability of P and other nutrients, and soil moisture was an important factor which contributed to availability of P, N, and nutrient elements after prescribed fire.

The overall objective of my research was to evaluate impacts of fire on availability of nutrients in calcareous soils under the Pine Rockland forest. Specific objectives were:

1). Determining the status of P in the Pine Rockland slash pine forest, C:N:P ratios in soil and pine foliar, and how prescribed fire could improve availability of P and other nutrient elements (Chapter 2). Limitation of P was determined by comparing foliar critical P values of slash pine forests published in previous studies with pine foliar P contents of the Pine Rockland forest. In addition to the comparison, a method of Diagnosis and Recommendation Integrated System index was applied for estimating foliar P index based on a dynamic relationship with other nutrients in order to provide more evidence for P limitation. To evaluate effects of fire on soil chemistry, a field burning experiment was conducted in the Long Pine Key in Everglades National Park to determine changes of soil pH, EC, and soil C, N, and nutrient pools following prescribed fire.

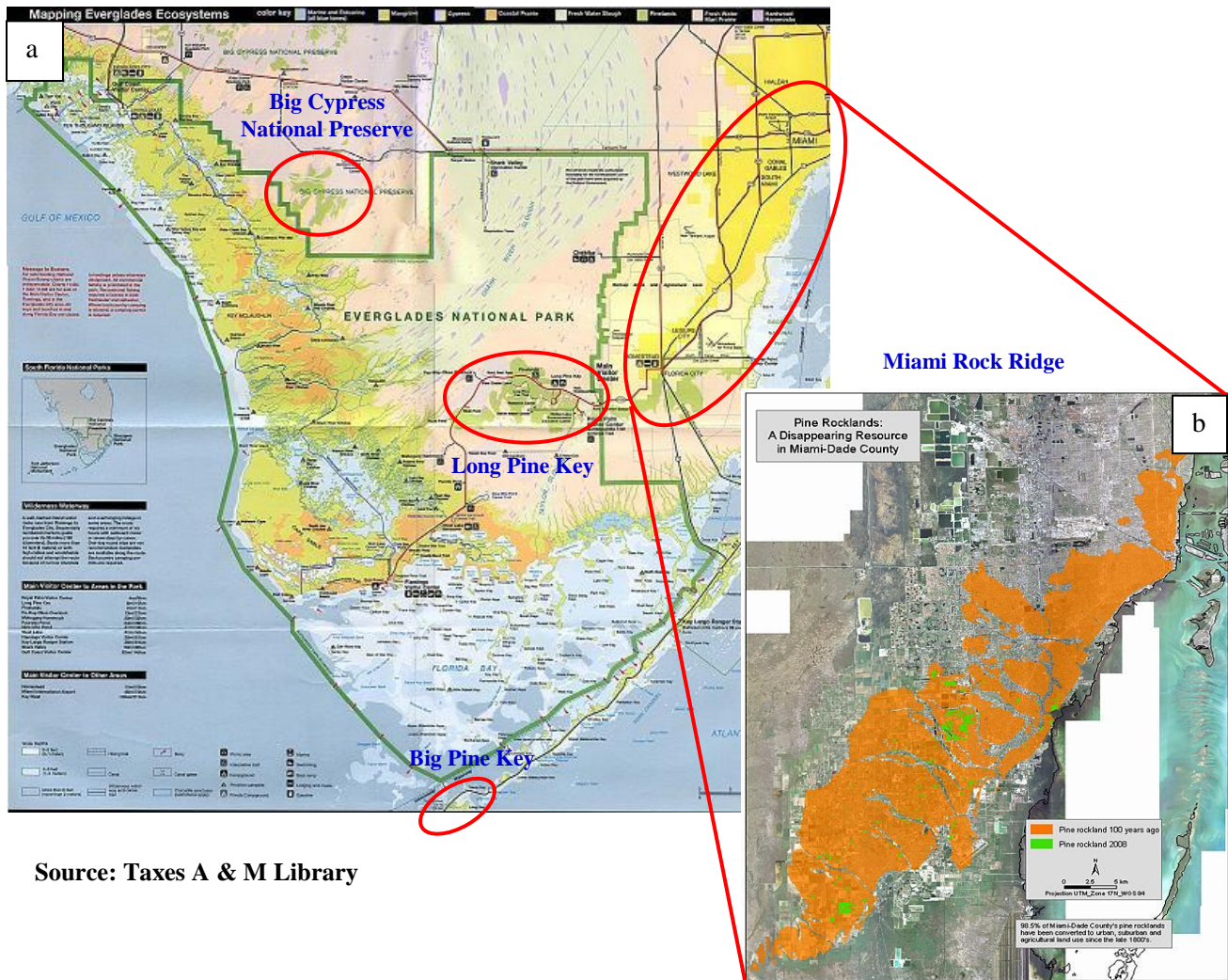
2). Determining how fire intensity and soil moisture affect available contents of P and soil nutrient pools, and to estimate a fire temperature for the field burning experiment (Chapter

3). Alterations of inorganic P, N, and nutrient concentrations were examined by laboratory incubation experiment with four burn temperatures, three levels of soil moistures, and six different incubation times. Field fire temperature was estimated based on a relationship between contents of Ca, Mg, P, Fe, and Mg associated with residual ash and heating temperatures in the

laboratory experiment. This work aimed to answer how soil moisture and fire intensity could impact on soil nutrient availability.

3). Simulating P species and their contents following the fire, determine solubility of phosphate minerals after the fire, construct a best-fit curve of soil moisture content for Pine Rockland's calcareous soils, and establish a predictive model for determination of fire long-term effect on P availability (Chapter 4).

Stability diagrams of P were established to describe a relationship between soil pH and phosphate minerals to phosphate solubility following a fire. Ionic activities simulated from Minteq were applied for establishment of these diagrams. A best-fit curve of soil moisture content constructed from experimental data for Pine Rockland calcareous soils was fit by Retention Curve (Retc) model. Data obtained in the laboratory incubation experiment was used to establish a predictive model to predict P availability following a fire. The predictive model was developed based on multiple linear regression method within predictor variables of soil moisture content and fire intensity, and verified with data collected at the TREC's Pine Rockland burn experiment.



Source: Taxes A & M Library

Source: Fairchild Tropical Botanic Garden, 2008

Figure 1-1: (a) Distribution of the Pine Rockland forests in South Florida, and (b) loss of the Pine Rockland Area in the Miami-Dade County during the 1900s

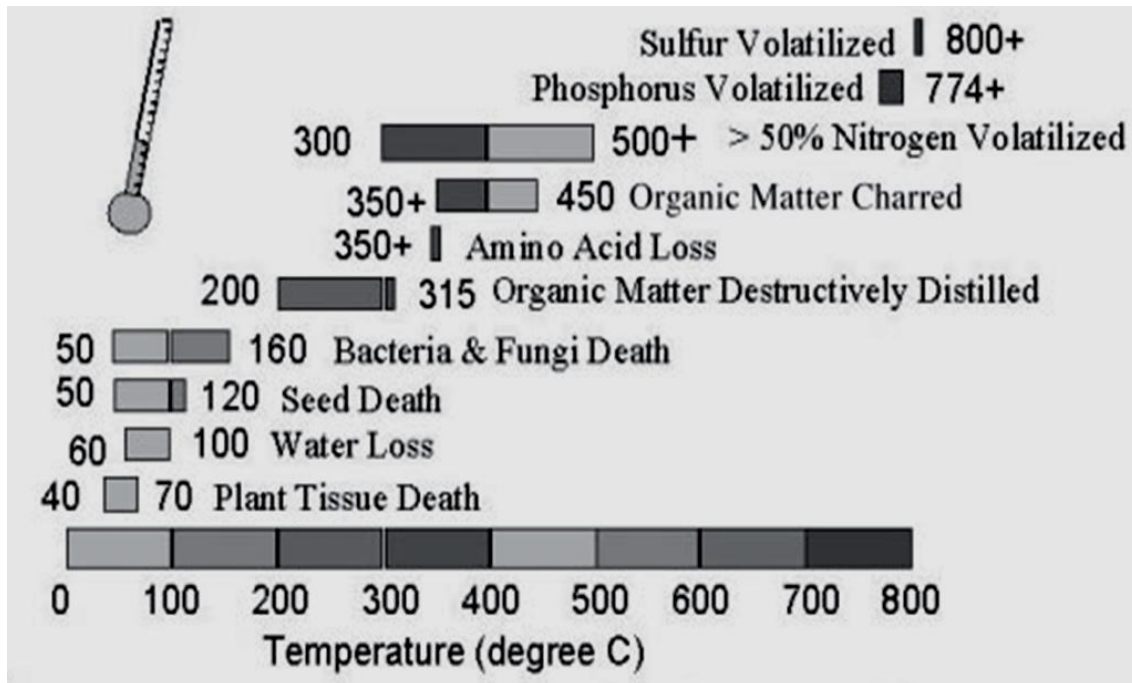


Figure 1-2: Temperature thresholds of typical soil components (Neary et al., 2005)

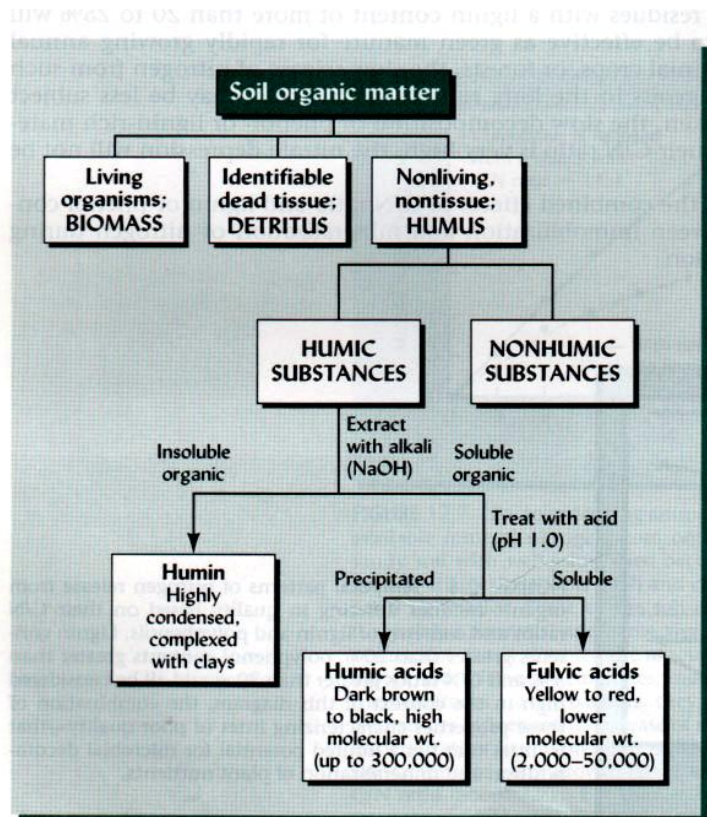
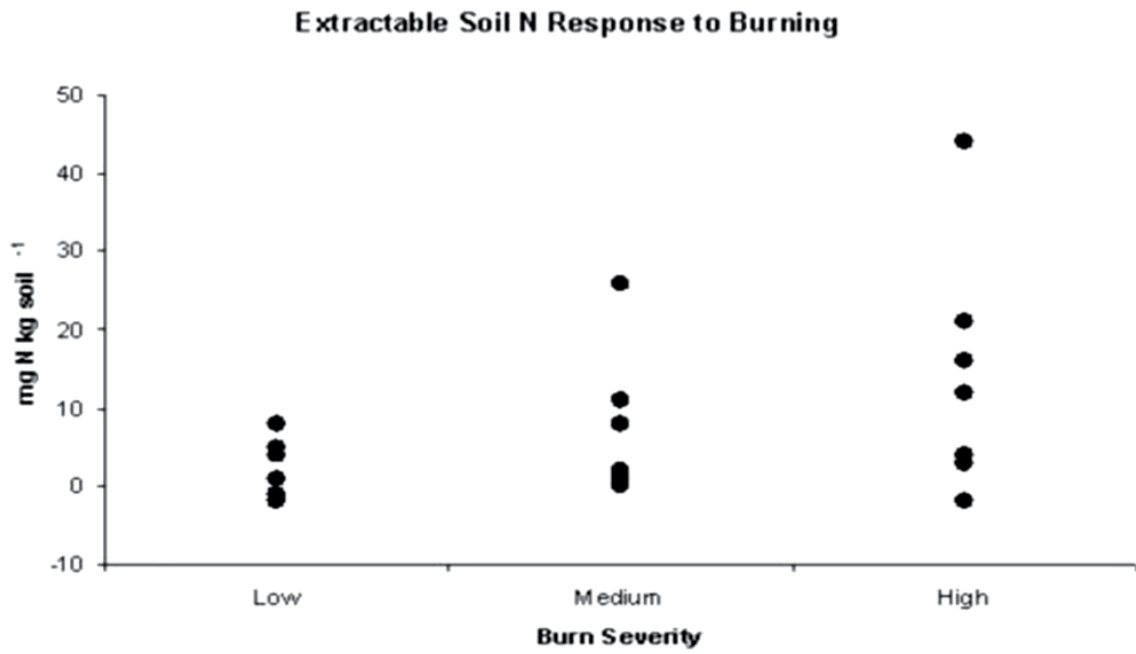


Figure 1-3: Pool of soil organic matter (Brady and Weil, 2002)



Source: Neary et al., 2005

Figure 1-4: Variations of soil extractable N to fire severity gathered by eight studies

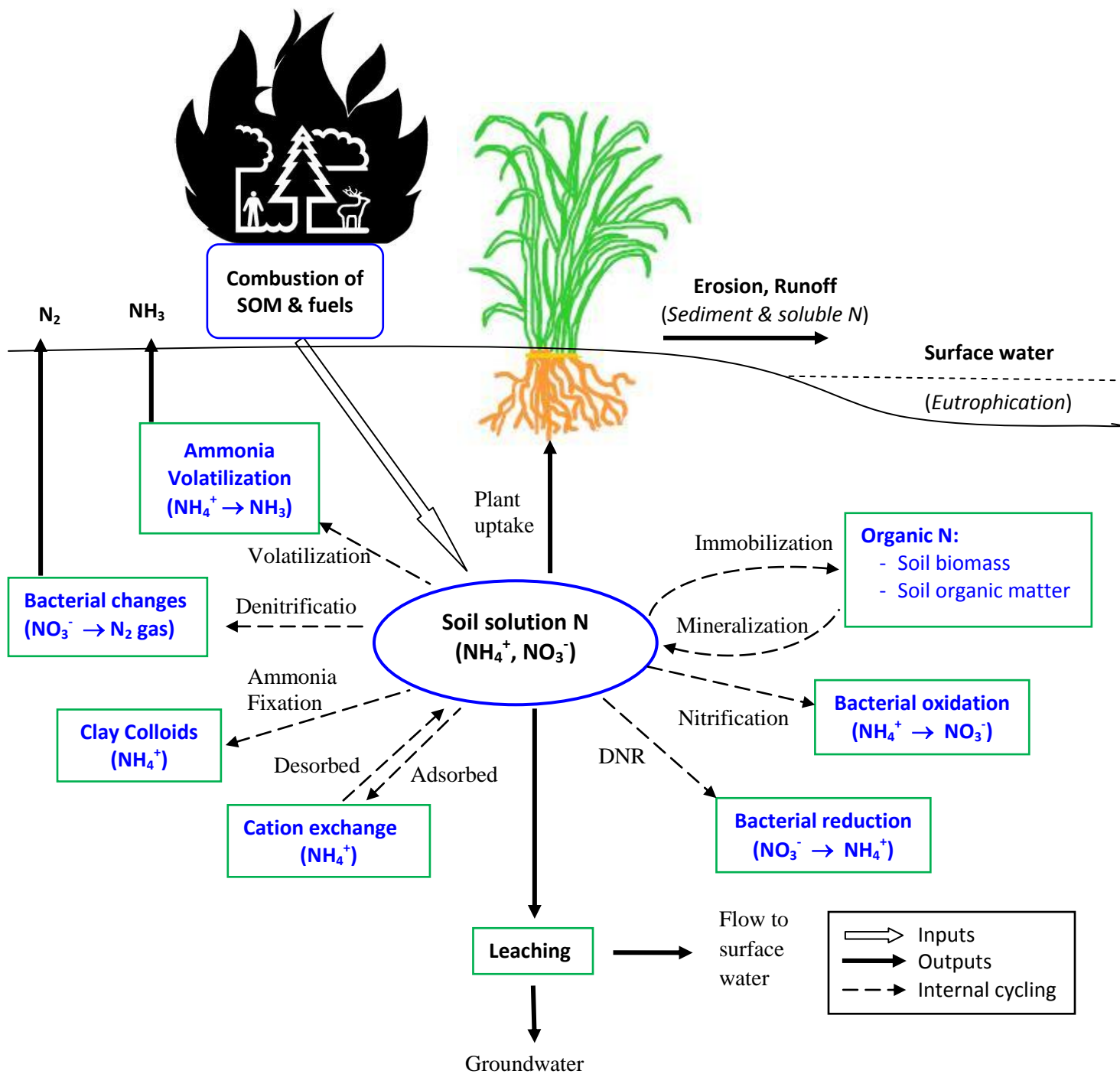


Figure 1-5: Possible pathways relating to fate of NH_4^+ and NO_3^- after a fire (Modified from Pierzynski et al., 2000, p. 103)

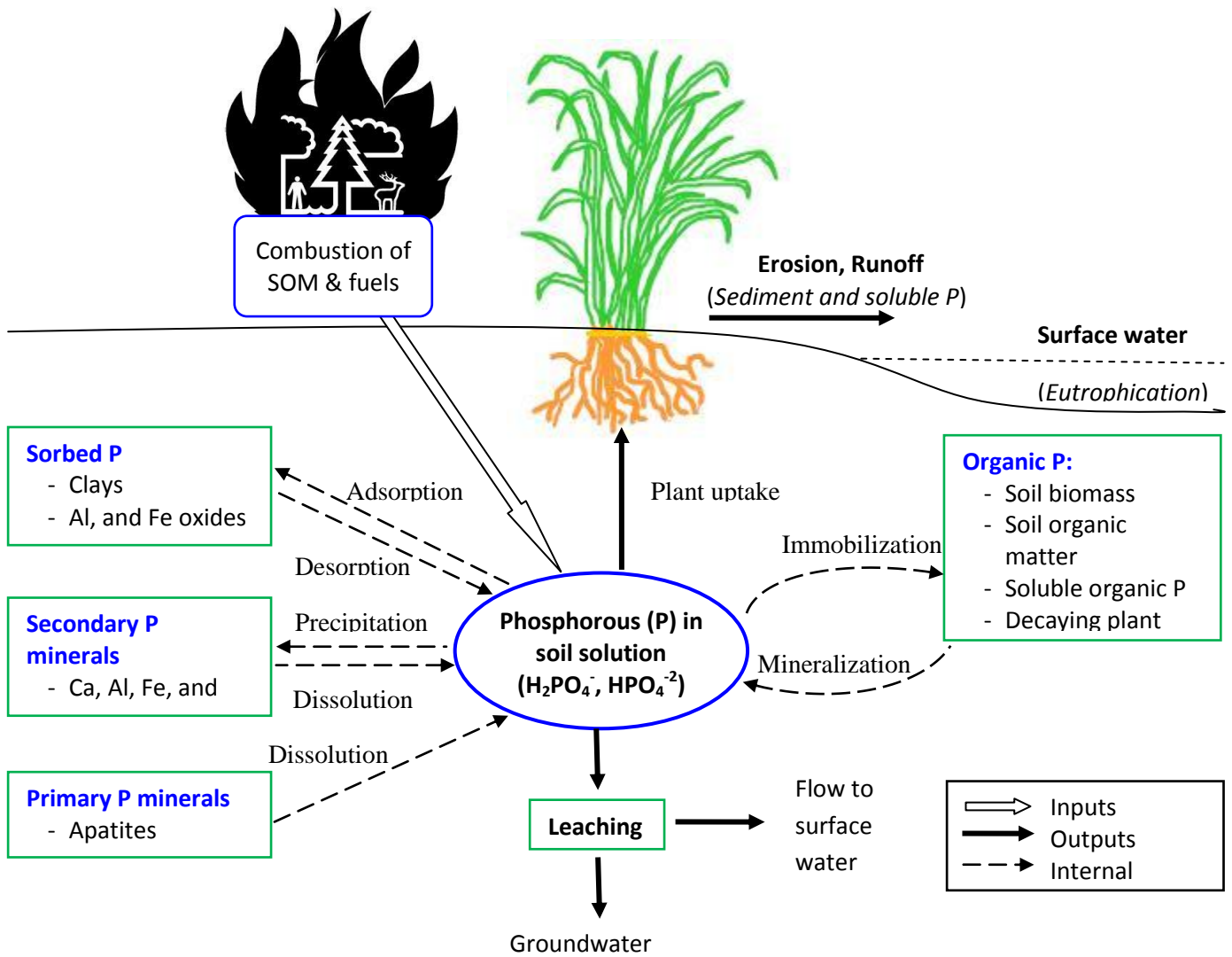


Figure 1-6: Possible pathways relating to fate of ortho-phosphate after a fire (Modified Pierzynski et al., 2000)

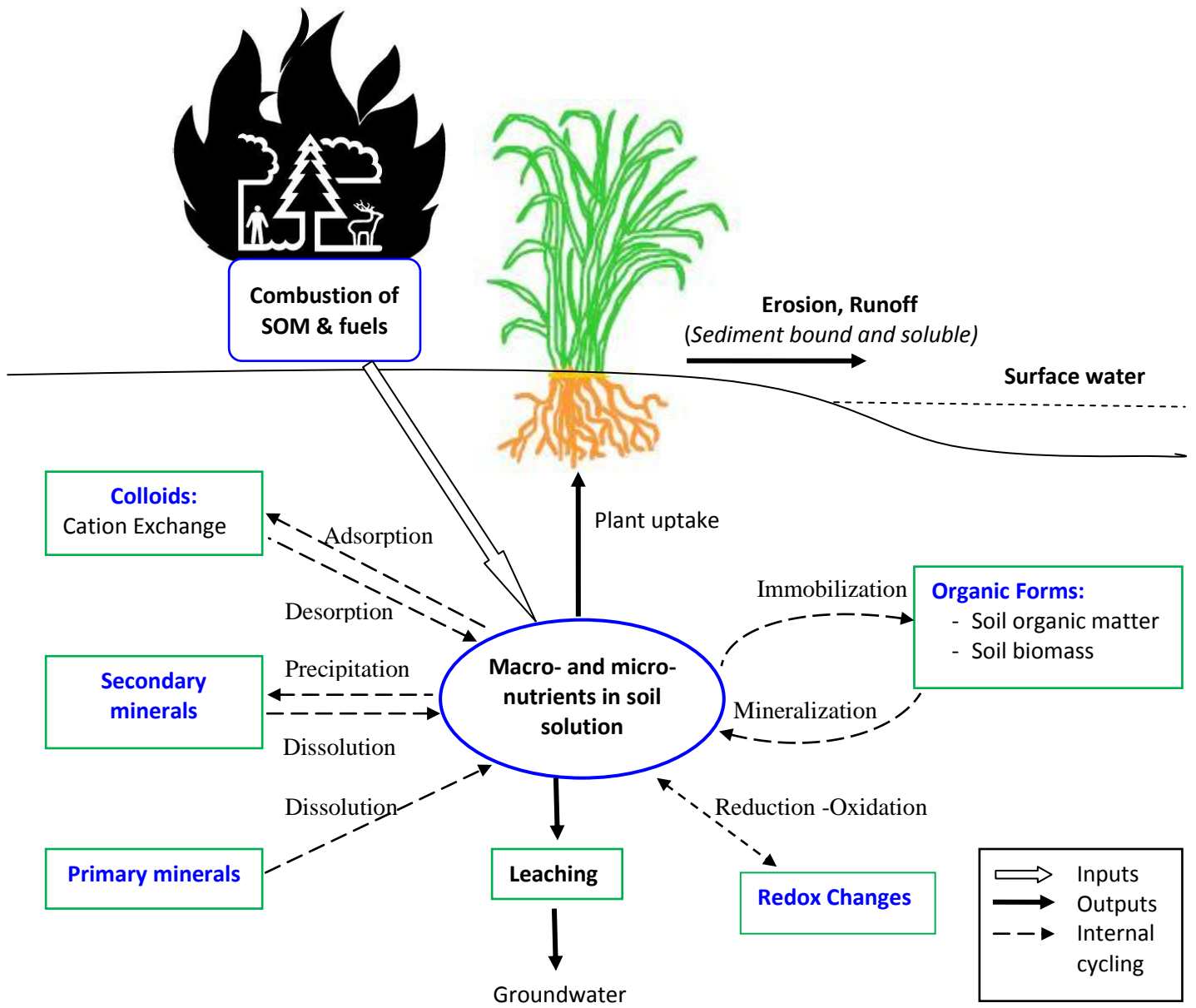


Figure 1-7: Possible pathways relating to fate of nutrient cations after a fire (Modified Pierzynski et al., 2000)

CHAPTER 2
PHOSPHORUS LIMITATION IN THE PINE ROCKLAND FOREST ECOSYSTEM
AND NUTRIENT AVAILABILITY AFTER A PRESCRIBED FIRE

Introduction

Phosphorus and Nitrogen Limitations in Natural Forest Ecosystems

Three basic methods were used in diagnosing deficiencies of nitrogen (N) and phosphorus (P) in forest ecosystems by foliar analysis, namely, 1) regressing nutrient concentration versus growth and defining a critical level, 2) adjusting critical levels for stand age or development, and 3) evaluating a nutrient balance (Comerford and Fisher, 1984). Approaches of regression and the adjustment evaluate critical levels of a single nutrient while nutrient balance approach assesses the sufficiency level of one nutrient in relation to other nutrients (Sumner, 1977). Adjusting the method of critical N and P levels for stand age is often implemented experimentally by adding N and/or P fertilizers in order to determine optimum growth contents of N and P for a certain ecosystem. In the nutrient balance approach, optimum N and P contents of growth are determined by a dynamic relationship with other nutrients. The Diagnosis and Recommendation Integrated System (DRIS) is an effective tool utilized to evaluate sufficiency of N and P.

Atmospheric N deposition often leads to N saturation and P constraint in natural forest ecosystems (Aber et al., 1989; Asner et al., 1997). Many studies have determined limitations of N and P as well as symptoms of N saturation in different forests (de Visser et al., 1994; Fenn et al., 1996; Tessier and Raynal, 2003; Vitousek and Howarth, 1991). Deriving from the Redfield ratio (C:N:P = 106:16:1) for phytoplankton, many studies have developed experiments in greenhouses by adding N and P fertilizers to determine N and/or P limitations for natural forest ecosystems through foliar N:P ratios. In experimental studies, it is assumed that under conditions

of low P supply and high N supply, plants will take up relatively more N than P resulting in a higher foliar N:P ratio. Under conditions of low N supply and high P supply, in contrast, plants will take up relatively more P and, therefore, the N:P ratio in the plant tissue will be relatively low. Based on values of foliar N and P for optimal growth, conclusions can be drawn regarding critical values of foliar N and P or the critical N:P value for forest ecosystems or crops.

The N:P ratio has been widely used to determine nutritional limitations of N and P in terrestrial ecosystems throughout the world. This ratio is used as a diagnostic indicator of N saturation (Fenn et al., 1996) and nutrient limitation of vegetative growth (Chaneton et al., 1996). N:P ratio has been not only utilized to detect N saturation (Fenn et al., 1996; Fenn et al., 1998; Williams et al., 1996), but it has been also applied to indentify thresholds of P limitation in different terrestrial ecosystems (Gusewell et al., 2003; Koerselman and Meuleman, 1996; Verhoeven et al., 1996). The foliar N:P ratio is usually considered as a sensitive index of P limitation to vegetation growth, and an effective tool for ecological managers to determine N saturation and P limitation in forest ecosystems (Tessier and Raynal, 2003). Primary symptoms of N excess include a higher N:P ratio in foliage and a lower C:N ratio in soil (Fenn et al., 1998).

Spatial and temporal variations have impacts on N saturation and P limitation because content of nutrients may be altered in the growing season, or by wet deposition and soil type. By the studying distribution and dynamics of N and P in grazed and ungrazed grasslands in Argentina over winter –spring seasons, Chaneton et al. (1996) found that shoot N:P ratios were high in the early winter and low in the late spring across two areas, and the system were relatively more P-limited in early winter, but more N-limited in late spring. Fourqurean and Zieman (1992) determined variations of C, N, P contents on seagrass at two spatial scales: locally (10-100m) and regionally (10-100km) through the Florida Bay. Their results showed that ratios of C:P and N:P

greatly varied both locally and regionally while C:N ratios showed less variation, and the seagrass ecosystem was P-limited with leaf N:P ratio greater than 58.6 and N-saturated with leaf C:N ratio smaller than 18.5. Carlyle and Nambiar (2001) evaluated effects of three typical soils on N saturation and P limitation at the same age of a *Pinus radiata* plantation in Australia. Results of Carlyle and Nambiar (2001) showed that litter C:N ratios indicating to N saturation were 53.2, 60.6, 82.6 for Yellow podsolic, Krasnozern, Siliceous sand soil types, whereas soil C:N ratios for N saturation in these soils were 31.3, 34.1, 37.7. Soil N:P ratios for P limitation ranged from 13 to 18.8 and did not differ much among three types of soils in both litter and soil.

Fenn et al. (1998) used both foliar C:N and soil C:N ratios to evaluate N saturation of the mixed forest (Pine, Oak, Fern) in the San Gabriel Mountains, Northeast Los Angeles, CA. Indications for N saturation in the mixed forest were from 24 to 48 for foliar C:N and from 18.8 to 26.6 for soil C:N. Egli and Quayle (1986) applied different C:N ratios of the inflowing medium to microbes to determine constraints of C and N in soils. Accumulation of C and N in microbial cells corresponded to restrictions of C and N in soils. The high cell-protein content and low cell-carbohydrate content in which C:N ratio of the inflowing medium was less than 12 resulted in C-limited growth, whereas the N-limited growth inferred from the low cell-protein content and high cell-carbohydrate content had C:N ratio greater than 31. McGroddy et al. (2004) estimated global nutrient ratios for limitation of N and P in terrestrial ecosystems based on molar basis as described by Redfield (1934 and 1958), and reported that global C:N:P ratios for limitations of N and P were 1212:28:1 for foliage and 3007:45:1 for litter.

In addition to foliar critical values, the Diagnosis and Recommendation Integrated System (DRIS) index has been widely applied for determining nutrient limitations of different ecosystems. It has been shown to bestow considerable advantages on its utilization (Sumner,

1977, 1979). DRIS index is used to assess limitations of not only N or P but also the extent of other elements. It utilizes a dynamic relationship and a wide range of ratios among nutrient elements in order to evaluate the sufficiency status of each single nutrient (Bailey et al., 2000; Bailey et al., 1997a & b; Baldock and Schulte, 1996; Bangroo et al., 2010). The status of an individual nutrient is diagnosed based on at least two and as many as eight other plant nutrients (Walworth and Sumner, 1987). The DRIS index which takes into account of a nutrient balance within plant tissues is determined from ratio functions of foliar nutrient contents.

The DRIS approach has been successfully used to interpret results of nutrient sufficiency or deficiency of many different crops such as corn, maize, potato, sweet potato, sugarcane, rice (Bangroo et al., 2010). The biggest advantage of the DRIS method is that it ranks automatically excesses or deficiencies of nutrients in order of importance (Walworth and Sumner, 1987). However, this method also has disadvantages because a DRIS norm needs to be established for each ecosystem. In each ecosystem, DRIS indexes of nutrients are estimated from its own DRIS norm. Since a norm is usually determined easier for agronomic crops than for natural forests, the DRIS method is not popularly used for natural forest ecosystems. Only one DRIS norm has been established for a plantation forest of Loblolly pine in Georgia and the Carolinas (M.E. Sumner, personal communication, 2011).

The DRIS method (Bailey et al., 1997a; Bangroo et al., 2010; Bethlenfalway et al., 1990; Elwali et al., 1985; Needham et al., 1990) calculates DRIS index for each nutrient element which is the mean of deviation of a ratio containing a given nutrient from its respective optimum or DRIS norm (Bailey et al., 1997a & b). The norm obtained as the mean value for a particular form of expression for a high-yielding or desirable population and it has its respective coefficient of variation (Bangroo et al., 2010). DRIS indices range from negative values to positive values,

but sum to zero. Negative values indicate a deficiency, whereas positive values refer to a sufficiency of nutrients (Bangroo et al., 2010).

Effects of Fire on Nutrient Availability in Calcareous Soils

A major factor controlling P availability in calcareous soils is the abundance of calcium. Availability of P is relatively low in calcareous soils, ranging from 2.1 mg P/kg soil in natural forests to 35.7 mg P/kg soil in agricultural areas with fertilizations (Afif et al., 1993; Chien et al., 2009; von Wandruszka, 2006; Yang et al., 2002). Effects of fire on availability of P and nutrient elements in calcareous soils have been evaluated in some studies. Ubeda et al. (2005) conducted a study on a grassland ecosystem developed on calcareous bedrock, and found that soil pH, total C and N, and extractable potassium in the topsoil 0-5cm were significantly increased immediately after fire, and that contents of C and N were still higher than their pre-burn levels in one year after fire while soil pH and extractable K returned to their pre-burn values after one year. Hernandez et al. (1997) conducted five burning experiments with different fire temperatures and soil textures on calcareous soils in *Pinus halepensis* and *Pinus pinaster* forests. Their results showed that soil pH values of five burned sites were slightly higher than their unburned counterparts, whereas contents of extractable P, K, NH₄-N, and NO₃-N in burned sites were significantly higher than those in unburned sites. In particular, available P contents in burned sites of 300⁰C and 350⁰C reached 120% compared with their unburned controls.

The Pine Rockland forest developed on limestone bedrock is a nutrient-poor and fire-dependent ecosystem. It is thought that P is a limiting factor in this ecosystem, and bio-availability of micro-nutrients may be relatively low as well. Limitations of P and micronutrients in calcareous soils under the Pine Rockland forest are mainly due to abundances of Ca, Mg, Fe, and Mn. The ecological role of fire in the Pine Rockland has been recently tested (Ross et al.,

2003; Sah et al., 2004 and 2006; Snyder, 1986; Snyder et al., 2005) but the effects of fire on soil chemistry of this ecosystem have not been well documented. Therefore, a study that comprehensively assesses nutrient status and the role of fire on nutrient availability in the Pine Rockland is necessary. Two specific objectives of this study were (i) to confirm P limitation based on analysis of pine foliage, and (ii) to evaluate effects of fire on changes in soil pH, EC, and soil nutrients following a prescribed fire.

Materials and Methods

Description of Study Site

This study was conducted in the Long Pine Key in Everglades National Park. South Florida slash pine (*Pinus elliottii* var. *densa*) trees (Appendix A) are dominant in the overstory of the Pine Rockland, and have an average canopy height ranging from 20 to 24 m (Snyder et al., 1990) and their density is reported from 453 to 1,179 pines/ha (Snyder, 1986). The lower-story contains a diverse assemblage of native plants and a rich herbaceous layer including saw palmettos, locust berry, willow bastic, beauty berry, broom grasses, and silver palms (U.S. Fish and Wildlife Service, 2007). Terrain of the Long Pine Key is flat and moderately to well-drained with an average elevation of approximately 2m above sea level (Snyder, 1990). Surface soils are very shallow because limestone bedrock is at or near the surface. Most sites in this area are only wet for a short period following heavy-rain events, but some sites may be inundated by very slow flowing surface water during the rainy season (U.S. Fish and Wildlife Service, 2007).

Soils in the Long Pine Key were formed with Miami oolitic limestone (Snyder, 1986; U.S. Fish and Wildlife Service, 2007) with various depths from less than one cm (mostly rock outcrop) to over 10 cm. When deep soil more looks like mineral soil with a reddish-brown color and contains a small amount of organic matter, soils in rock outcropping area often were dominated by

organic matter. The hydroperiod in the Long Pine Key ranges from about 20 to 60 days/year. Annual average rainfall and temperature in this area are approximately 143 cm and 25⁰C, respectively (Weather Channel, 2008). Average water table is 0.6 to 2.0 m below the soil surface in the dry season and 0.3 to 1.0 m below the surface in the wet season (Olmsted et al., 1983).

Brazilian-pepper (*Schinus terebinthifolius*) and Burma reed (*Neyraudia reynaudiana*) are the two most widespread invaders in the area. The exotic Brazilian-pepper has entirely occupied the Hole-in-the-Donut, and has threatened the Pine Rockland on the Long Pine Key. The Burma reed which can be tolerant to fire has established slightly in the Pine Rockland of the Long Pine Key (U.S. Fish and Wildlife Service, 2007). Currently, the Everglades National Park is carrying out an ongoing program of prescribed burning to control invasive plants in the Long Pine Key (Olmsted et al., 1983). Although prescribed fire was usually done in winter in the Pine Rockland in the past, the Park has begun to use a summer-burning program since 1981 (Doren et al., 1993).

Determination of P Limitation and C:N:P ratio

A literature search for critical P value in slash pine forests as well as critical P values for P limitation in upland ecosystems was performed using the following key-words: nitrogen content, nitrogen concentration, nitrogen deficiency, nitrogen limitation, phosphorus content, phosphorus concentration, phosphorus deficiency, phosphorus limitation, N:P, N/P, N:P ratio, N/P ratio, N to P ratio, nutrient concentration, nutrient content, nutrient deficiency, nutrient limitation, nitrogen fertilization and phosphorus fertilization (Tessier and Raynal, 2003). The results were tabulated for a generalized determination of global P limitation in upland ecosystems, and for a specific determination of critical P value in slash pine forests.

Determination of global P restriction aimed to providing a broad view of P limitation that could occur in upland forest ecosystems. Limitation of P in the Pine Rockland forest ecosystems were

determined based on comparisons between the foliar P contents of the Pine Rockland slash pine and published critical values of pine foliage P in slash pine forests.

Additionally, DRIS indices were established for P based on the DRIS norm created for the Loblolly pine forest in the Southeastern United States. Although the DRIS norms for Loblolly may not be exactly that of slash pine, they are closely related species with similar geographical distributions. Needham et al. (1990) established the DRIS norms for N, P, K, Ca, and Mg for the Loblolly pine forest (Table 2-5). Relying on these norms, DRIS indices of N, P, K, Ca, and K for the Pine Rockland slash pine were calculated by the following two steps (Bangroo et al., 2010; Walworth and Sumner, 1987):

First, construction of functions for each nutrient-ratio pair:

$$F(A/B) = \left(\frac{A/B}{a/b} - 1 \right) \frac{100}{CV} \quad \text{if } A/B \text{ is greater or equal to } a/b$$

$$F(A/B) = \left(1 - \frac{a/b}{A/B} \right) \frac{100}{CV} \quad \text{if } A/B \text{ is smaller than } a/b$$

Where A/B is a nutrient ratio of pine foliage to be diagnosed such as ratios among N, P, Mg, Ca, and K; a/b is the optimum value or norm for the given ratio obtained from the Loblolly pine forest; CV is the coefficient of variation associated with the norm.

Secondly, calculation of DRIS index for each nutrient:

$$N \text{ index} = [f(N/P) + f(N/K) + f(N/Ca) + f(N/Mg)]/4$$

$$P \text{ index} = [f(P/N) + f(P/K) + f(P/Ca) + f(P/Mg)]/4$$

$$K \text{ index} = [f(K/N) + f(K/P) + f(K/Ca) + f(K/Mg)]/4$$

$$Mg \text{ index} = [f(Mg/N) + f(Mg/P) + f(Mg/K) + f(Mg/Ca)]/4$$

$$Ca \text{ index} = [f(Ca/N) + f(Ca/P) + f(Ca/K) + f(Ca/Mg)]/4$$

Indices of these five nutrients were listed in an increasing order. Negative index value of a nutrient would demonstrate a deficiency of the given nutrient, whereas positive index value of a

nutrient would prove a sufficiency of the given nutrient.

Field-Burning Experiment and Sample Collection

Three sites (management blocks I1, I2, and Boy Scout Camp) within the Long Pine Key (Figure 2-1) were selected for sampling. The geographic coordinates of these blocks are approximately 25° 23' 27'' N and 80° 38' 57'' W. A field burning experiment was conducted at the Boy Scout block which was entirely burned on November 19, 2008. Absence of fire for five years and drought associated with the event in the 2007-2008 La Nina provided favorable conditions for fire. Prescribed fire was started at noon and completed approximately two hours after burning. The air temperatures averaged 28°C during the fire, and a slight precipitation occurred approximately one week prior to burning (Figure 2-5).

Soil samples were randomly collected at topsoil 0-5cm within nine different sampling dates, including pre-burn, and 14, 30, 90, 180, 270, 360, 450, and 540 days following the fire. Twenty soil samples were collected at each sampling period, and four samples were mixed together for each replicate (in total, five replicates for each sampling period). A 50 x 50 cm sampling frame (Appendix A) was used to collect fuel loads and residual ash with ten replicates. Fuel loads including litter, residues, and understory vegetation were randomly collected one day before the fire in order to determine content of nutrients in fuel loads. Ash products created by combustion were immediately gathered after the fire by a vacuum machine. Twenty samples of pine foliage were randomly collected from twenty different pine trees (average heights of 8-10 m) in unburned blocks of I1 and I2 in January (Appendix A), beginning of the pine growing season (Harley et al., 2011).

Sample Preparation

Soil samples were air-dried, ground, and sieved at 2 mm screen. Plant roots and rocks were removed before sieving through 2 mm. Fuel samples and pine needles were cut into 1 to 2 cm segments, dried in oven at 65⁰C for 5 days, and ground before nutrient analysis.

Chemical Analysis

Electrical conductivity (EC), pH, NH₄-N, NO₃-N, PO₄-P, total P (TP), total C (TC), total N (TN), and other elements were measured. Soil and ash pH and EC were measured using a pH/Conductivity meter. Soil P was extracted by 0.5M NaHCO₃ (Olsen et al., 1954), and measured using a spectrophotometer with the automated colorimetric method. Ammonium and nitrate were extracted with 2M KCl, and measured using a discrete auto-analyzer (AQ2, Seal Analytical, Mequon, WI) with USEPA methods of 350.1 and 353.2, respectively. Other nutrients (Ca, K, Na, Fe, Mg, Mn, Zn, and Cu) were extracted by the Ammonium Bicarbonate- Diethylene Triamine Pentaacetic Acid (AB-DTPA) method, and measured on an Atomic Absorption spectrophotometer (AA6300, Shimadzu Scientific Instruments, Columbia, MD). Total C and N in soil, fuel load, and pine foliage were automatically measured by CNS auto-analyzer (vario Max, Elementar Americas, InC., Mt. Laurel, NJ). Total P in soil, pine foliage, and fuel load were dry-ashed, dissolved in 6M HCl acid, and measured using a spectrophotometer. Analytical methods of these soil components and their detection limits were summarized in Table 2-1. Procedures of chemical analysis and QA/QC methods in laboratory for analyses of these chemical components are presented in Appendix B. Procedures for preparation of standard solutions and standard calibration curves obtained from laboratory analyses are shown in Appendix C.

Statistical Analysis

Repeated Measures method was used to determine significant effects of prescribed fire on

nutrient contents. Significant differences at confidence levels of $p < 0.05$; $p < 0.01$, and $p < 0.001$ were evaluated. Tukey's multiple comparison technique was also utilized to determine significant differences by time for each nutrient component. Plots of residuals versus fitted values were performed to evaluate homogeneity of variances for nutrient components. If there was a variance inequality of any nutrient component, the data were transformed to obtain an equality of variances.

Selection of a suitable model from analysis of within-subject covariance structure is the most important step in ANOVA analysis by the Repeated Measures method. Analysis of covariance structure within subjects ensures that inferences about the mean are valid. Compound symmetry and 1st-order autoregressive covariance-structure models were used for the ANOVA analysis. The compound symmetry model assumes that any two measurements on the same subject have the same covariance regardless of length of time between measurements. The 1st-order autoregressive model assumes that observations on the same subject that are closer in time are more highly correlated than measurements at times that are farther apart. Correlation between two measurements in the 1st-order autoregressive model decreases exponentially with increasing in length of time between two measurements. The most appropriate covariance structure was selected by comparing Akaike's Information Criterion (AIC) and Schwarz's Bayesian Criterion (SBC) in two covariance-structure models. A model with the smallest values of AIC and SBC was deemed the best. Results of ANOVA analyses by the Repeated Measures are exhibited in Appendix D.

Results and Discussion

Phosphorus limitation in Pine Foliage and Fuel Load

Results of a literature search on nutrient limitation indicated that, in general, most of upland ecosystems are limited by P (Table 2-2). Published N:P ratios of plant tissues in upland forest ecosystems ranged from 7 to 16 for N limitation, whereas P limitation was approximately

from 14.17 to 29.41. However, results showed also that some upland forest ecosystems were limited by both N and P. Additionally, results of a literature search on critical N and P values of slash pine forests revealed that critical N value of pine foliage ranged from 0.87% to 1.30% (averagely 1.0%) (Table 2-3), and critical P value of pine foliage was from 0.07% to 0.125% (averagely 0.09%) (Table 2-4). By pine foliar analysis, N and P contents of the Pine Rockland forest were 0.81% and 0.045%, respectively (Table 2-6). These findings indicated that P is a limited factor in the Pine Rockland forest, whereas N is marginal to limitation or may be saturated in this forest ecosystem where has a high amount of atmospheric N deposition associated with the high lightning intensity (Li et al., 2002).

On analysis of a dynamic relationship among pine foliar nutrients, DRIS indices of P, K, N, Mg, and Ca for the Pine Rockland slash pine were - 46.13, - 10.77, - 0.89, 8.71, and 49.05, respectively (Table 2-5). Negative value of DRIS index associated with a nutrient indicated that the given nutrient was deficient while positive value of DRIS index expressed sufficiency of a given nutrient. The higher the negative value of DRIS index, the more deficient the nutrient is. Obviously, result of DRIS index analysis proved that P is the most limiting nutrient and K is the second limiting nutrient in the Pine Rockland ecosystem. The negative value (-0.89) of N index close to zero could confirm that N is marginal limiting. Results of other nutrient analyses in pine foliage and fuel load (forest floor and understory vegetation) are presented in Table 2-6. Generally, contents of other nutrients in pine foliage were higher than those in fuel load, except for Ca and Fe. Content of carbon was decreased from 51.7% in pine foliage to 46.6% in fuel load. Contents of N and P in pine foliage (0.81% and 0.045%) were approximately twice N and P contents in fuel load (respectively 0.475% and 0.02%). Contents of Mg, K, Mn, and Zn in pine foliage were similar to those in fuel load. The results indicate that the release rates of C, N,

P, Mg, K, Mn, and Zn in the forest floor due to decomposition process are different (Knoepp et al., 2005b). Release and retention of nutrients in litters are driven by biological, physical, and chemical processes, in which N, Ca, and Mg in litters are being regulated by biological processes while K release is a physical process (Laskowski et al., 1995).

C:N:P Ratios in Pine Foliage, Fuel Load, and Soil

C:N:P ratios were 1162.5 : 17.9 : 1 for pine foliage, 2361.2 : 23.8 : 1 for fuel load, and 920 : 30.3 : 1 for soil. Figures 2-2, 2-3, 2-4 showed ratios of C:N, N:P, and C:P in soil, fuel load, and pine foliage. The order of C:N was fuel load (99:1) > pine foliage (65:1) > soil (30:1).

Photosynthesis creates a large amount of carbon in plant tissue, and provides carbon for soil C pool through turnover (Binkley et al., 1992; González-Pérez et al., 2004). Although soil contains a large amount of N, most of soil N exist in organic forms that are not available for plant uptake. Ammonia and nitrate are the only two major forms of inorganic N which are bio-available for plant uptake. In natural forest ecosystems, availability of ammonia and nitrate is often limited because two these forms of N are mostly dependent on processes of microbial mineralization, nitrogen biological fixation, or atmospheric deposition. Consequently, C:N ratios in pine foliage (65:1) and fuel load (99.2:1) were higher than soil C:N ratio (30.4:1). Since a large portion of N in plant tissues disappears during decay while abundance of carbon still remained in plant tissues, C:N ratio in fuel load was higher than that in pine foliage.

Soil N:P ratio of 30.3:1 was greater than N:P ratios of pine foliage (17.9:1) and fuel load (23.8:1); whereas soil C:P ratio of 920:1 was lower than pine foliar C:P ratio (1162.5:1) and fuel load C:P ratio (2361.2:1). Higher N:P ratio and lower C:N ratio in soil to those in fuel load and pine foliage could also indicate that N may not be limited in the Pine Rockland. This inference was suitable with results of some previous studies in which soil C:N ratios for N saturation in three

typical soils (Siliceous sand, Yellow podsollic, and Krasnozern) of pine plantation forest in Australia were 31.3, 34.1, and 37.7 (Carlyle and Nambiar, 2001), and soil C:N ratio for N saturation in the mixed forest (Pine, Oak, Fern) in California was about 26.6 (Fenn et al., 1998).

Pools of C and N in Fuel Load after Fire

Prescribed fire did not affect the canopy of pine trees, but significantly decreased the understory biomass and pools of C and N in fuel load, at least immediately after the fire (Table 2-7). Approximately 90.2 % of aboveground and understory biomass were consumed by the fire. Fire volatilized approximately 80% and 92% of N and C contents in fuel loads. Losses of NH_4^+ and NO_3^- associated with volatilization of fuel-load N pool were 86% and 48%.

The result showed that considerable amounts of fuel loads accumulated in the understory aboveground biomass over the fire interval were lost. The amount of biomass consumed by the fire was higher than percentage of fuel consumption in dry-season burn reported by Snyder (1986). This might be due to differences in nature of initial conditions and burning frequency before fire. Volatilizations of C and N pools in fuel loads were linearly to loss of biomass. Higher rate of C loss and lower rate of N loss were similar to results from the simulation experiment in laboratory.

Changes of Soil pH and EC after Fire

Prescribed fire impacted significantly on pH ($p < 0.05$) and EC ($p < 0.001$) at the 0 - 5 cm depth (Table 2-8). Soil EC increased dramatically after the fire, from 333 $\mu\text{S}/\text{cm}$ in the pre-burn to 698 $\mu\text{S}/\text{cm}$ in 14 days after the fire, and maintained a high value until 30 days, before returning to its pre-fire level after 90 days (Table 2-9). Although soils in the Pine Rockland forest have high pH, prescribed fire slightly increased soil pH, from 7.55 in pre-burn to 7.82 in 14 days after the fire before returning to its original value in 30 days later (Table 2-9).

Fire-induced increases in soil pH and EC in calcareous soils found here were similar to those of Ubeda et al. (2005). Soil pH was close to the value reported by Snyder (1986). Release of inorganic ions from fuel combustion led to considerable increases in EC (Hernández et al., 1997; Kutiel and Shaviv, 1992). Increase in pH, the so-called liming effect, could be attributed not only to accumulation of K- and Na-hydroxides, and Mg- and Ca-carbonates in post-fire ash (Knicker, 2007), but also due to the destruction of acid group in organic matter during the fire (Dumontet et al., 1996; Giovannini et al., 1988). Rainfall was a primary factor contributing to increases in soil pH and EC as a result of leaching of inorganic ions from the ash into the surface soil. Figure 2-5 showed changes of soil pH and EC along with rainfall events in one year following the fire. The ephemeral rise of soil pH following fire actually occurred after the first rainfall event.

Changes of Soil C, N, and P Pools after Fire

Prescribed fire significantly affected soil C ($p < 0.01$) and N contents ($p < 0.01$) (Table 2-8). Although the fire virtually removed the pools of C and N in the forest floor and understory vegetation through volatilization, C and N pools in the surface soil 14 days after the fire were measured as result of residual-ash deposition. Comparisons in soil C, N, and P contents over time by Tukey's method which are presented in Table 2-9 indicate that prescribed fire significantly changed pools of soil C and N, but not soil P. Contents of TC and TN at 0-5cm depth significantly increased in 14 days after the fire. Content of TN was 0.95% in pre-burn and increased to 1.42% after 14 days. Pre-fire content of TC was 24% and its content was 40% after 14 days. Contents of TC and TN reached their original values in 30 days after the fire; nevertheless, these contents continued to decrease thereafter and had the lowest contents after 90 days. Although content of TP in soil was increased from 0.032% in pre-burn to 0.042% in 14 days later, the difference was not statistically significant. According to our observations, most of the native plants and vegetation

under pine grew rapidly and bloomed in 90 days, and finished their cycles in 180 to 360 days following the fire. Therefore, nitrogen demands for development and blooming of understory vegetation were very high during 90 days after the fire. This caused a dramatic decline in soil TN contents at 90 days after the fire, and made pools of soil N stable after 360 days.

Increase in TC and TN following the fire did not affect the soil C:N ratio, but it significantly altered soil C:P and N:P ratios (Table 2-8). Alterations of soil C:P and N:P ratios fluctuated with changes of soil C and N contents after the fire (Figures 2-6 and 2-7). Ratios of soil C:P and N:P following the fire increased at 14 days, tended to decrease gradually until 90 days, went up and reached a peak at 270 days, and then declined to its original values in 540 days. With a confidence level of 95%, significant difference of soil N:P and C:P ratios actually occurred between 90 and 270 days after the fire.

Ammonium and nitrate were two major components contributing to increase in soil N pool after the fire. Prescribed fire increased extractable contents of NH_4^+ ($p < 0.001$) and NO_3^- ($p < 0.001$) significantly (Table 2-8). Extractable NH_4^+ concentration increased immediately after the fire, which remained until 30 days, and then declined thereafter. While content of ammonium in soil was raised immediately due to the direct release of ash products during the fuel combustion, an increase of nitrate resulted from nitrification. NO_3^- concentration was not changed immediately after the fire, but increased significantly in the post 180 days. Soil NH_4^+ pool was 40.6 mg kg^{-1} soil in pre-burn, increased approximately twofold after 14 days (99.6 mg kg^{-1} soil), and then declined to the pre-fire level after 30 days (53.6 mg kg^{-1} soil). Although fire immediately increased soil NO_3^- , from 8.1 mg kg^{-1} soil in pre-burn to 11.3 mg kg^{-1} soil in 14 days later, it was not significantly. Soil NO_3^- pool increased at post-fire 180 days to approximately 25.1 mg kg^{-1} soil, which was a tripling of its pre-fire value. Changes in soil NH_4^+ and NO_3^- pools

in this study were similar to the meta-analysis results of Wan et al. (2001) which assessed the fire's effects on N pools in terrestrial ecosystems. Significant increase in soil NO_3^- content after 180 days was followed by heavy rainfall (Nardoto and Bustamante, 2003) which promoted the nitrification process, and resulted in a reduction of NH_4^+ (Covington and Sackett, 1992; DeLuca and Zouhar, 2000; Knicker, 2007).

Effects of Fire on Other Soil Nutrients

Analysis of ANOVA by Repeated Measures indicated that there were significant differences in extractable contents of Ca, Fe ($p < 0.05$), Mg, Mn, $\text{PO}_4\text{-P}$ ($p < 0.001$), and K ($p < 0.01$) in soil after the fire, except for Cu and Zn (Table 2-8). Effects of fire on soil nutrient pools were variable. Table 2-9 shows a comparison of extractable nutrient contents over time by Tukey's method. Prescribed fire significantly increased extractable concentrations of Olsen-P, K, Mg, and Mn after 14 days, but extractable Fe and Ca increased after 270 and 360 days, respectively. Olsen-P content increased from 4.2 mg/kg soil in pre-burn to 13.4 mg/kg soil after 14 days. AB-DTPA extractable K, Mg, and Mn increased immediately from 52 to 144 mg/kg soil (Mg), from 165 to 277 mg/kg soil (K), and from 69 to 256 mg/kg soil (Mn) in comparison between pre-fire and 14 days after the fire. Extractable Fe was 178 mg/kg soil in pre-burn, and increased into 289 mg/kg soil after 270 days, whereas Ca increased from 1060 mg/kg soil in pre-burn to 1162 mg/kg soil at 360 days after the fire.

Prescribed fire was very effective for increasing the pool size and contents of extractable K, Ca, Mg, Mn, and Fe (Blank et al., 2007; Lavoie et al., 2010) in the Pine Rockland forests, except for Cu and Zn. Olsen-P content measured in the Pine Rockland forest was in a reported range of Olsen-P concentration for calcareous soils (Afif et al., 1993b; Ryan et al., 1985a & b). As described in Figure 2-5, rainfall played an important role in changes in soil nutrient pools

following the fire. The rainy season started after 180 days and lasted until 360 days after the fire. Since soils have high organic matter, they often saturated and became anaerobic for a short period after continuous rainfall events during the rainy season. Under the anaerobic conditions, forms of Fe (III) such as $\text{Fe}(\text{OH})_3$, goethite ($\text{FeOOH}\cdot\text{H}_2\text{O}$), FeCO_3 , and hematite (Fe_2O_3) were reduced into Fe (II) forms (Brady and Weil, 2002, p. 611; Reddy and Delaune, 2008, p. 409) which resulted in increases of extractable Fe^{2+} after 270 days.

Conclusions

This study employed both foliar critical value and DRIS indices methods to determine status of P and other nutrients in the Pine Rockland forest. The finding indicated that P is the most limiting factor in the Pine Rockland forest. The restriction of P led to elevation in pine foliar N:P ratio (17.9) which was higher than foliar N:P critical level (14-15) of slash pine forests reported by Comerford and Fisher (1984). However, pine foliar N:P ratio was lower than those in soil (30.3) and in fuel load (23.8). C:N:P ratios were 1162.5:17.9:1 for pine foliage, 2361.2:23.8:1 for fuel load, and 920:30.3:1 for soil. Lower C:N ratio and higher N:P ratio in soil than those in pine foliage and fuel load could provide evidence that N may be sufficient in the Pine Rockland forest.

Prescribed fire impacted significantly soil pH, EC, and soil nutrient pools at 0-5cm soil depth of the Pine Rockland forest. The fire increased immediately soil pH, EC, and extractable contents of P, Mg, K, Mn in post-fire 14 days, but increased extractable content of Fe in post-fire 270 days and that of Ca in post-fire 360 days. However, the fire did not influence available contents of Cu and Zn. Increases of Fe and Ca contents depended on more rainfall events. Prescribed fire increased significantly contents of TC and TN, but did not change TP content. Increases of TC and TN occurred in post-fire 14 days, and they returned to their pre-fire levels in

30 days. Effects of fire on soil inorganic N pools were variable. Soil NH_4^+ pool significantly increased immediately after the fire, whereas soil NO_3^- pool was increased in post-fire 180 days, corresponding with a dramatic decline of NH_4^+ production. Increases of soil C and N pools did not vary soil C:N ratio, however; significant differences were observed for ratios of N:P and C:P.

Table 2-1: A summary of analytical methods in the laboratory

Parameter	Method	Instrument	Detection limit[†]
pH and EC (ash)	Ash : water = 1:50	pH/conductivity meter	0.1
pH (soil)	Soil : water = 1:2.5	pH/conductivity meter	0.1
EC (soil)	Soil : water= 1:2	pH/conductivity meter	0.1
NH ₄ -N (soil)	Soil: 2M KCl = 1:10	discrete auto-analyzer	0.02
NO ₃ -N (soil)	Soil: 2M KCl = 1:10	discrete auto-analyzer	0.006
NH ₄ -N (ash)	Ash: water = 1:20	discrete auto-analyzer	0.02
NO ₃ -N (ash)	Ash: water = 1:20	discrete auto-analyzer	0.006
TC	Combustion	CNS auto-analyzer	0.3
TN	Combustion	CNS auto-analyzer	0.06
Extractable P (soil)	Olsen-P	Spectrophotometer	0.01
Soluble P (ash)	Ash: water = 1:20	Spectrophotometer	0.01
Total P	Ashing and 6N HCl	Spectrophotometer	0.01
Extractable cations	AB-DTPA	Spectrophotometer	0.001-0.02

[†]μS/m for EC and mg/L for nutrients.

Table 2-2: Thresholds of foliar N and P limitations in upland ecosystems

Studies	Systems	Locations	Addition	N:P ratio	Limitation by
Aerts et al. (1988)	Heath	The Netherlands	N & P	29.41	P
Alan et al. (2000)	<i>Carica papaya</i>	Laboratory	N & P	7	N & P
Bobbink (1991)	Chalk grassland	The Netherlands	N & P	16.08	N & P
Bowman (1994)	Alpine dry meadow	Colorado	N & P	13	N
Bowman (1994)	Alpine wet meadow	Colorado	N & P	14	P
Clarholm et al. (1995)	<i>Picea abies</i> plantation	Sweden	N & P	9.8	N & P
de Visser et al. (1994)	Coniferous forest	Europe	N	7–14.5	Not N
Herbert et al. (1995)	Montane forest	Hawaii	N & P	13.83	P
Jacobson et al. (2001)	<i>Picea abies</i> stand	Sweden	N & P	7.54	N
Jacobson et al. (2001)	<i>Pinus sylvestris</i> stand	Sweden	N & P	8.96	N
Ljungstrom et al. (1995)	Beech forest	Europe	P	14.17	At least P
Mohren et al. (1986)	Douglas fir forest	The Netherlands	N & P	22 -25	P
Mohren et al. (1986)	Douglas fir forest	The Netherlands	N & P	8	N
Tessier et al. 2003	Catskill Mountains	New York, USA	N & P	17.71	P
Valentine et al. (1990)	Pine plantation	North Carolina	N & P	10.42	N & P

Modified from Tessier et al. (2003)

Table 2-3: Critical foliar N contents of slash pine forests (*Pinus elliottii* var *elliottii*)

Studies	Locations	Slash pine (<i>Pinus elliottii</i> var <i>elliottii</i>)
		Critical foliar N content ----- (%) -----
Barron-Gafford et al. (2003)	Southeastern Georgia, USA	0.9 – 1.2
Comerford et al. (1984)	Southeastern Coastal Plain sites, USA	0.96 - 1.01
Dickens et al. (2003)	Southeastern Coastal Plain, Georgia	1.0
Fisher et al. (2000)	Southeastern Georgia, USA	1.0
Gholz et al. (1985)	Northern Florida, USA	0.87 – 1.03
McGarvey et al. (2004)	Putnam and Levy Counties, Florida, USA	1.19 - 1.24
Richards et al. (1972)	Australia	0.9
Teskey et al. (1994)	Northeastern Florida, USA	0.93 – 1.16
Will et al. (2001)	Southeastern, USA	0.95 - 1.30
Xu et al. (1995)	Australia	0.94 – 1.19

Table 2-4: Critical foliar P contents and N:P ratio of slash pine forests

Studies	Locations	Slash pine (<i>Pinus elliottii</i> var <i>elliottii</i>)	
		Critical foliar P content ----- (%) -----	Critical foliar N:P ratio -----
Barron-Gafford et al. (2003)	Southeastern Georgia, USA	0.095 – 0.125	
Comerford et al. (1984)	Southeastern Coastal Plains, USA	0.07	14 -15
Dickens et al. (2003)	Southeastern Coastal Plain, Georgia	0.09	
Fisher et al. (2000)	Southeastern Georgia, USA	0.09	
Gholz et al. (1985)	Northern Florida, USA	0.055 – 0.085	
Richards et al. (1972)	Australia	0.075 – 0.08	
Teskey et al. (1994)	Northeastern Florida, USA	0.072 – 0.097	

Table 2-5: DRIS indices of N, P, K, Ca, and Mg in the South Florida slash pine

	N/P	P/K	Ca/P	Mg/P	N/K	Ca/N	Mg/N	Ca/Mg	Ca/K	Mg/K
----- DRIS norm of Loblolly pine forest -----										
Mean [†]	10.426	0.227	1.589	0.696	2.361	0.154	0.066	2.355	0.362	0.158
C.V. [†]	11.6	16.6	28.4	28.5	18.1	24.5	24.5	25.25	35.2	31.9
----- Foliar nutrient ratios of South Florida slash pine -----										
Mean	17.907	0.296	9.144	3.228	5.303	0.509	0.181	2.835	2.727	0.954
f(A/B)	6.19	1.84	167.42	12.77	6.89	9.42	7.10	0.81	18.56	15.79
----- DRIS Index of South Florida slash pine -----										
Nutrient	P	K	N	Mg	Ca					
Index	-46.13	-10.77	-0.86	8.71	49.05					

[†] Source from Needham et al. (1990) and the norm and coefficient of variation (C.V.) of the Loblolly pine forest

Table 2-6: Nutrient contents of pine foliage and fuel load in the Pine Rockland forest

Parameter	C	N	P	Ca	Mg	K	Fe	Mn	Zn
	----- Pine foliage (% of dry mass) -----								
Mean	51.7	0.805	0.045	0.405	0.144	0.156	0.0045	0.0024	0.0017
SD	0.42	0.102	0.006	0.099	0.022	0.030	0.0011	0.0009	0.0007
SE	0.09	0.023	0.001	0.022	0.005	0.007	0.0002	0.0002	0.0002
Min	51.0	0.703	0.036	0.263	0.103	0.101	0.0028	0.0011	0.0009
Max	52.8	1.040	0.059	0.611	0.191	0.215	0.0064	0.0044	0.0036
	----- Fuel load (% of dry mass) -----								
Mean	46.6	0.475	0.020	0.640	0.131	0.172	0.0086	0.0023	0.0009
SD	0.43	0.053	0.003	0.127	0.055	0.026	0.0027	0.0011	0.0003
SE	0.15	0.019	0.001	0.040	0.017	0.008	0.0009	0.0003	0.0001
Min	46.1	0.435	0.018	0.510	0.085	0.143	0.0060	0.0014	0.0005
Max	47.3	0.600	0.025	0.905	0.277	0.210	0.0135	0.0052	0.0014

Where “SD” is the standard deviation; “SE” is the standard error; “Min” is the minimum value; and “Max” is the maximum value

Table 2-7: Loss of biomass and pools of C and N in forest floor and understory vegetation (fuel load) due to fire

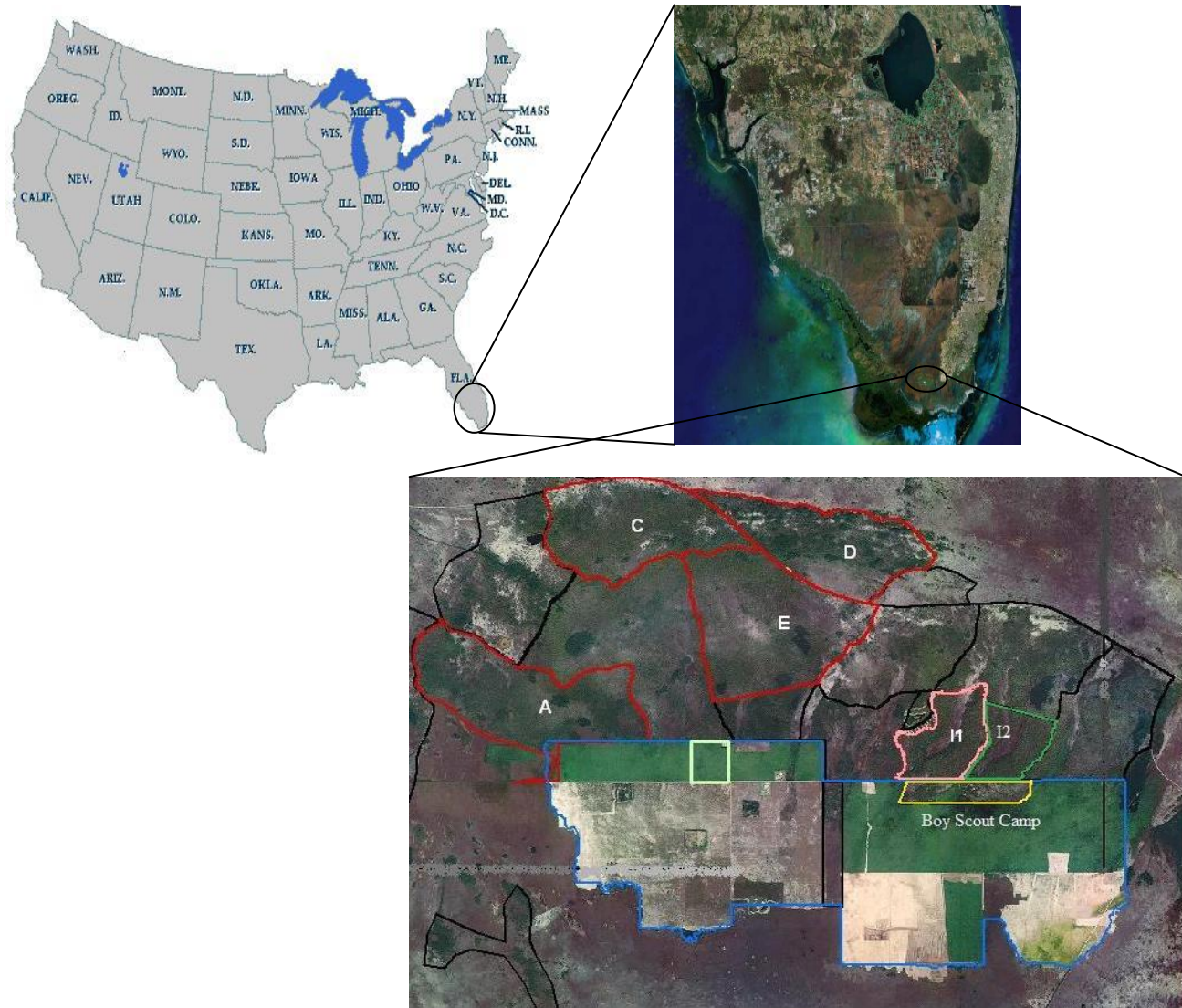
Parameter	Biomass	TN	TC	NH₄⁺	NO₃⁻
	----- % loss -----				
Mean	90.19	80.13	91.59	86.44	48.21
SD	2.24	2.87	0.40	1.52	11.06
SE	0.71	1.17	0.16	0.62	4.52
Min	86.47	74.71	91.16	84.16	34.28
Max	93.82	83.08	92.02	88.36	64.98

Table 2-8: Results of ANOVA analysis of soil nutrient pools following prescribed fire

ANOVA analysis by Repeated Measures method								
Variables	Pr > F	Significant level	Variables	Pr > F	Significant level	Variables	Pr > F	Significant level
Ca ²⁺	0.0497	*	Fe ²⁺	0.0122	*	TC	0.0015	**
Mg ²⁺	< .0001	***	Mn ²⁺	< .0001	***	TN	0.0048	**
K ⁺	0.0011	**	Zn ²⁺	0.0989	NS	TP	0.1139	NS
PO ₄ -P	< .0001	***	Cu ²⁺	0.2317	NS	C:N	0.2532	NS
NH ₄ -N	< .0001	***	pH	0.0187	*	N:P	0.0334	*
NO ₃ -N	< .0001	***	EC	< .0001	***	C:P	0.0277	*

Table 2-9: Results of Tukey's pairwise comparison on content of nutrients between different times after the fire

Days after fire	Average pH, EC, TP, TN, TC, NH ₄ ⁺ , NO ₃ ⁻ , and extractable contents of nutrient elements following the fire														
	Ca ²⁺	Mg ²⁺	K ⁺	Fe ²⁺	Mn ²⁺	Zn ²⁺	Cu ²⁺	PO ₄ -P	NH ₄ ⁺	NO ₃ ⁻	TP	TN	TC	EC	pH
	mg/kg soil										%			μS/cm	
0	1060ab	52b	165bc	178ab	69b	3.5a	3.4a	4.2b	40.6bc	8.1b	0.0322a	0.93abc	24abc	333c	7.55ab
14	905b	144a	277a	153b	256a	5.1a	4.1a	13.4a	99.6a	11.3ab	0.0423a	1.42a	40a	698a	7.82a
30	1035ab	80b	193abc	207ab	89b	5.4a	3.1a	4.4b	53.6b	2.4b	0.0301a	0.91abc	25abc	544ab	7.48b
90	972ab	40b	188abc	170ab	47b	3.3a	3.8a	1.2b	23.1bc	5.2b	0.0347a	0.69c	15c	370bc	7.45b
180	1094ab	54b	236ab	158b	53b	5.3a	3.8a	4.0b	31.2bc	25.1a	0.0340a	0.84bc	23bc	383bc	7.56ab
270	989ab	56b	122c	289a	89b	4.2a	3.6a	3.2b	21.6bc	8.5b	0.0277a	0.98abc	28abc	348bc	7.48b
360	1162a	53b	145bc	173ab	73b	5.3a	4.2a	4.6b	22.1bc	2.6b	0.0377a	1.28ab	34ab	328c	7.57ab
450	1049ab	62b	160bc	197ab	114b	4.0a	4.0a	2.7b	23.0bc	2.7b	0.0337a	0.96abc	33ab	453bc	7.72ab
540	972ab	34b	137bc	223ab	59b	2.4a	3.8a	3.0b	11.4c	10.5b	0.0317a	0.79bc	20bc	332c	7.58ab



Source: Everglades National Park
Figure 2-1: Blocks of Pine Rockland in the Long Pine Key

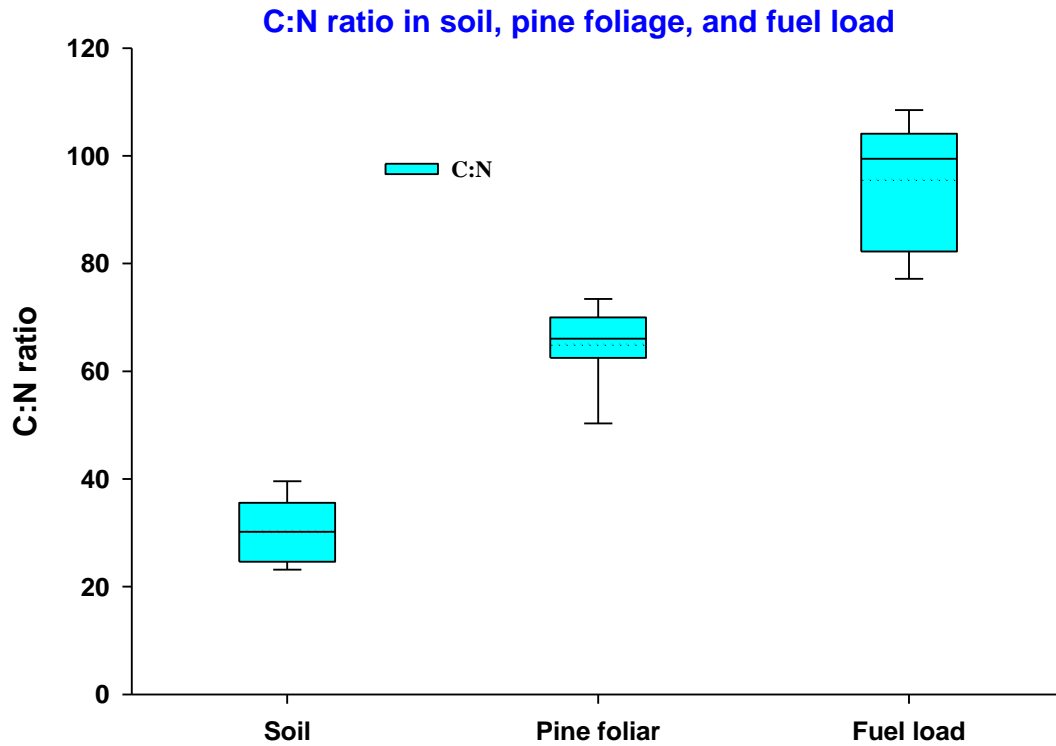


Figure 2-2: C:N ratios in soil, pine foliage, and fuel load of the Pine Rockland forests

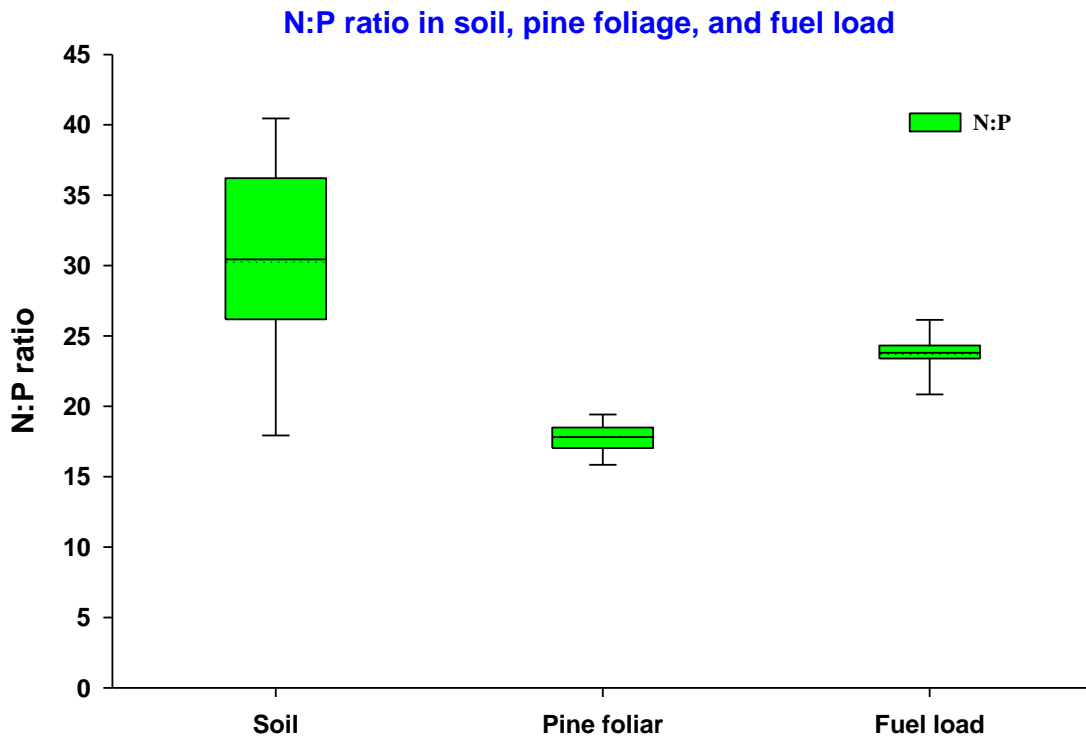
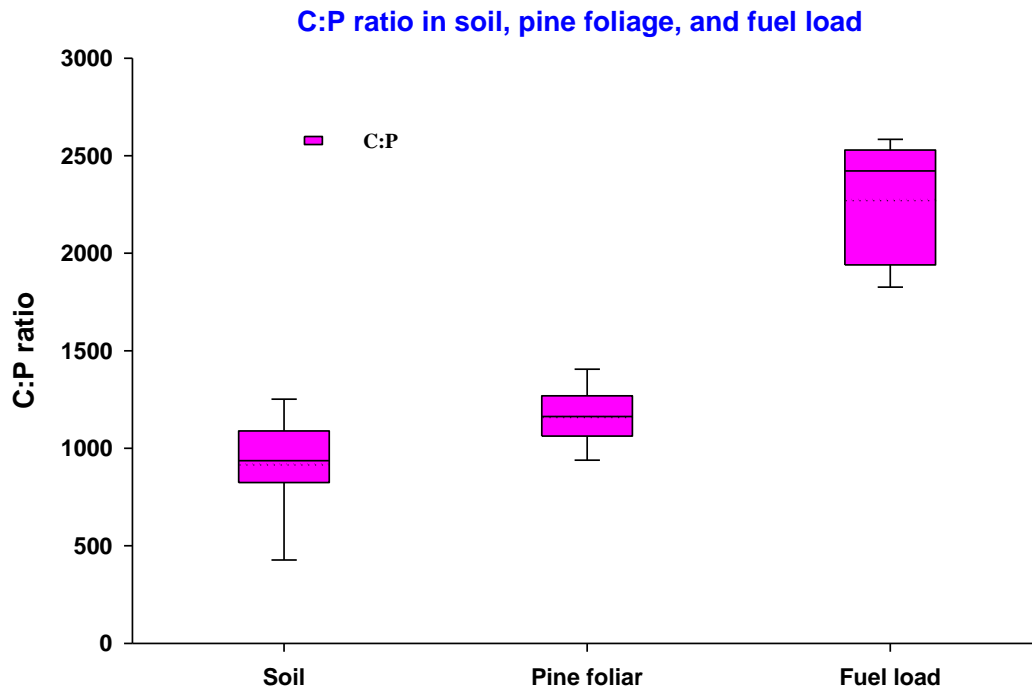


Figure 2-3: N:P ratios in soil, pine foliage, and fuel load of the Pine Rockland forests



The lower and upper whisker caps are 10th and 90th percentiles; the lower and upper boundaries of the box are 25th and 75th percentiles; solid lines are medians of ratios; and dotted lines are means of ratios.

Figure 2-4: C:P ratios in soil, pine foliage, and fuel load of the Pine Rockland forests

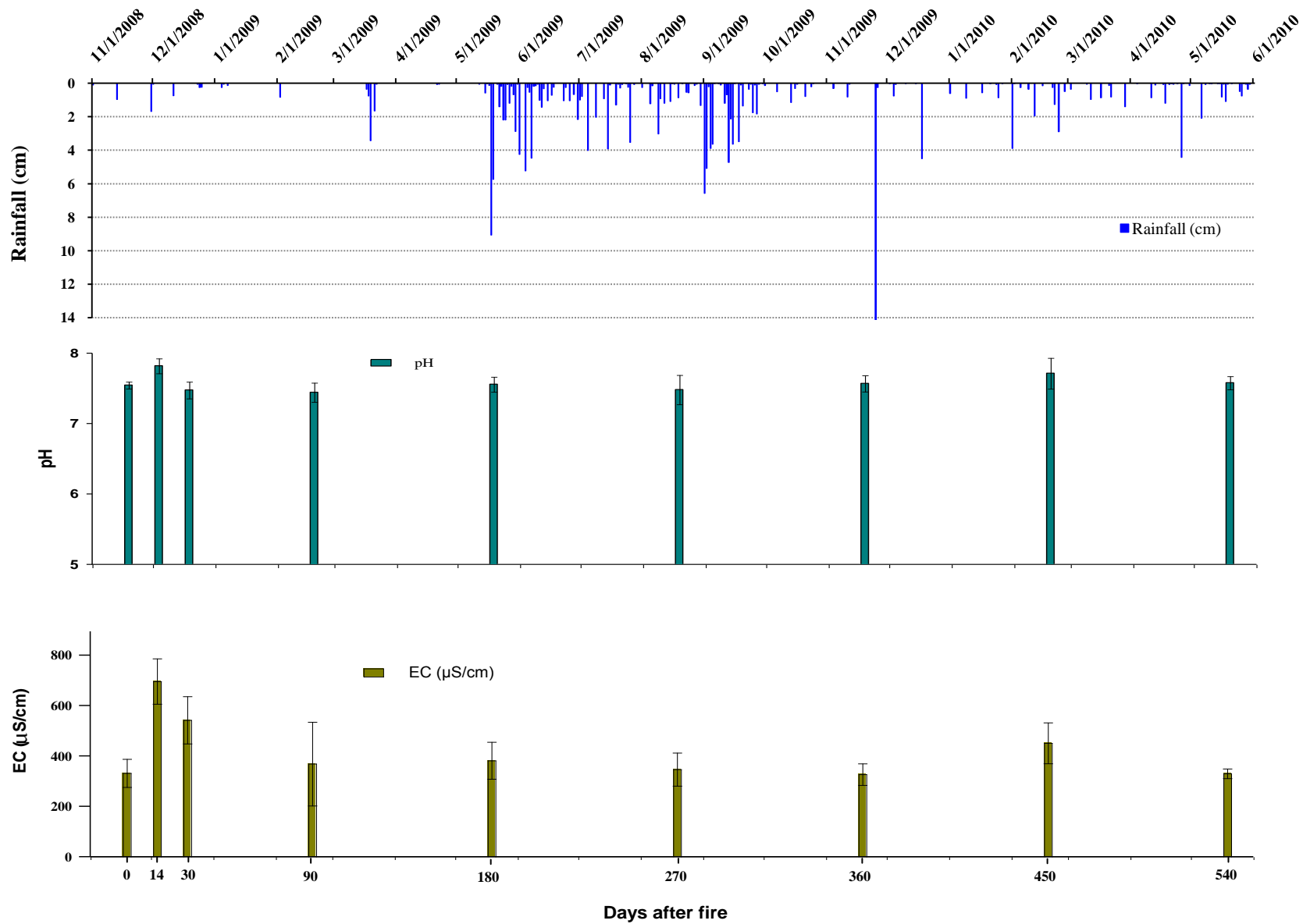


Figure 2-5: Rainfall and changes of pH and EC along with rainfall after the fire

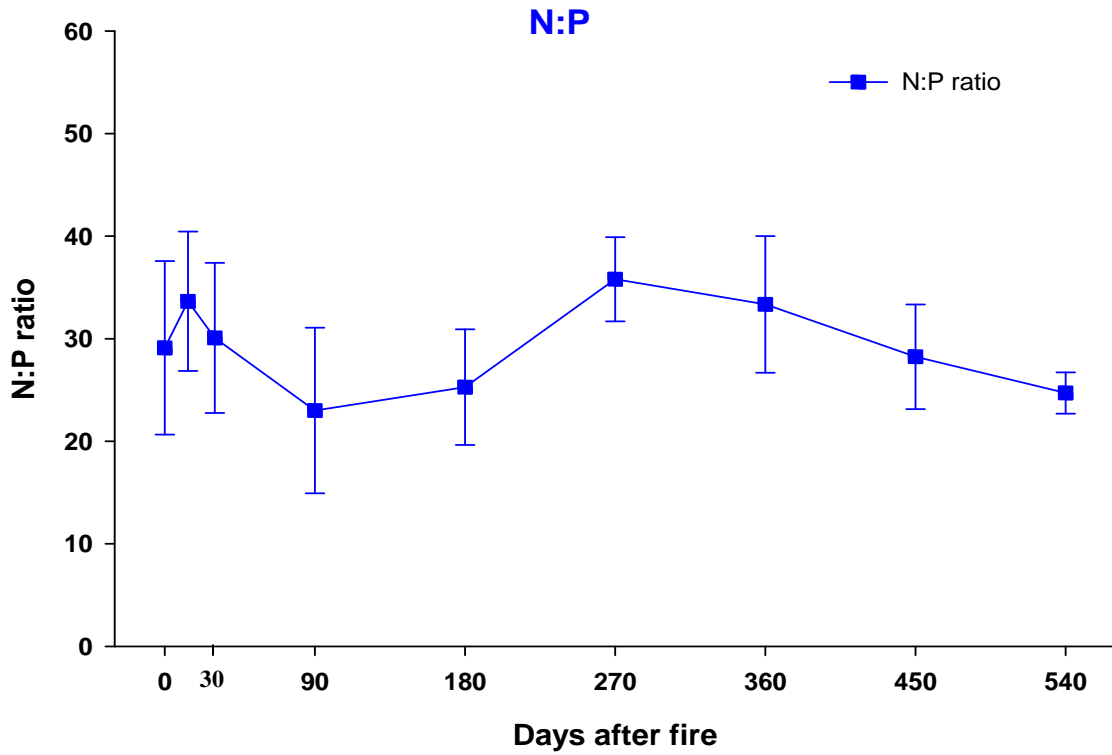


Figure 2-6: Changes of soil N:P ratio by following the fire

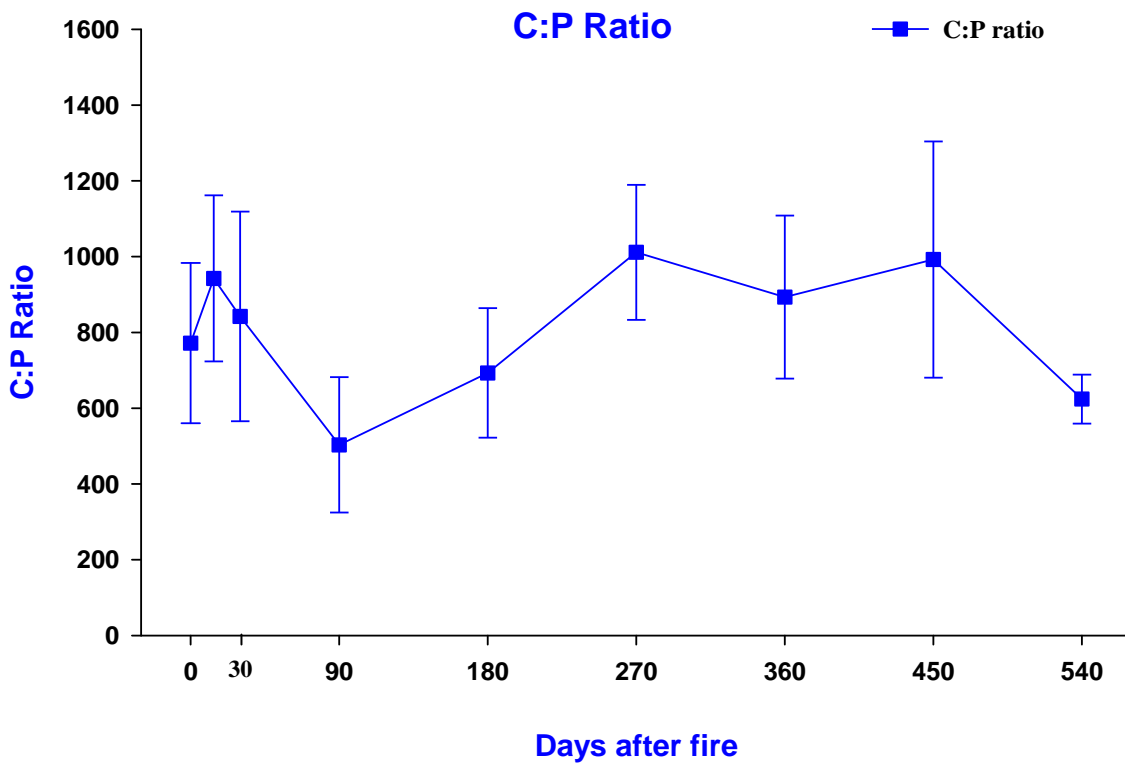


Figure 2-7: Changes of soil C:P ratios by following the fire

CHAPTER 3

BURNING TEMPERATURE AND SOIL MOISTURE AFFECTED NUTRIENT POOLS IN CALCAREOUS SOILS UNDER THE PINE ROCKLAND FOREST ECOSYSTEM

Introduction

Post-fire plant ash derived from both wildfire and prescribed fire is an important factor in the balance and cycling of nutrients in natural ecosystems (Wan et al., 2001; Yermakov and Rothstein, 2006). Composition and availability of ash nutrients depend entirely on fire intensity (fire temperature), plant species, nutrient enrichment of habitat, and accumulation of fuels (Qian et al., 2009b). During a fire, a portion of nutrient elements accumulated in vegetation or surface soil can be transferred to the atmosphere (Raison et al., 1985; Cachier et al., 1995); however, a large amount of nutrients remain in residual ash and deposit downward to the soil surface (Neary et al., 2005; Marion et al., 1991). Environmental factors including wind, rainfall, runoff, erosion, or leaching can contribute to deposition and/or redistribution of ash nutrients into soil.

Deposition of residual ashes results in increased nutrient contents which may have important effects on nutrient status of soils after a fire. Increases of post-fire nutrient contents in soils have been recently observed in several studies (DeBano and Conrad, 1978; Lavoie et al., 2010; Murthy et al., 2006a; Ubeda et al., 2005; Ulery and Graham, 1993a). Ulery et al. (1993b) showed that soil pH was increased by approximately three units due to large amounts of basic cations in wood ashes deposited into soil, whereas Badia and Marti (2003) pointed out that soil pH, carbon (C): nitrogen (N) ratio, available content of nutrients, and soil organic matter were increased with addition of ashes. Basic cations [potassium (K), magnesium (Mg), calcium (Ca)] accumulated in ashes also result in increasing in surface soil pH (Murphy et al., 2006a; Murphy et al., 2006b). A study conducted by Khanna et al. (1994) found that neutralization of soil acidity correlated well with contents of K, Ca, Mg in residual ashes.

One important factor influencing nutrient availability after a fire is fire intensity (Certini, 2005; Neary et al., 2005), which is generally defined as fire temperature and duration (Govender et al., 2006; Neary et al., 1999). Available contents of elements depend on volatilization points of elements and fuel consumption caused by fire temperature. Sulfur (S), C, and N are often oxidized completely at high burning temperatures ($> 400^{\circ}\text{C}$) due to their relatively low vaporization points (Neary et al., 2005; Gray and Dighton, 2006). In contrast, elemental phosphorus (P) and metals having relatively high vaporization points (e.g., 1484°C for Ca and 1091°C for Mg) are not impacted by fire temperature. Loss of P in a field burn was reported by Raison et al (1985), but under controlled laboratory conditions all contents of P were accumulated in ashes possibly due to limited air movement (Gray and Dighton, 2006).

Responses of plants to fire with regard to nutrient availability in residual ashes vary among species as well as ecosystems, which are attributed to differences in structure and composition of vegetation. Miao et al. (1997) showed that allocation of nutrients after a fire varied within species growing along a nutrient gradient in the Everglades. Moreover, translocation of nutrients during leaf senescence also constituted lower nutrient contents in dead leaves than in live leaves (Miao, 2004), whereas litter created more nutrients available than the same amount of plant tissues before burning (Debano and Conrad, 1978). By conducting a laboratory burn experiment with fire intensity ranging from 150 to 550°C , Qian et al. (2009b) demonstrated that availability of ash nutrients in the sawgrass and cattail ecosystems in the Everglades was significantly affected by fire intensity. There was more labile inorganic P remaining in sawgrass ashes than in cattail ashes; contents of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ followed the same pattern with total N (TN) showing a significantly decreasing trend with the lowest contents at 450 and 550°C ; there was a significant increase of ash pH along the temperature gradient;

availability of different metals varied with the fire intensity; but contents of total P (TP), total Ca (TCa), total Mg (TMg), and total aluminum (TAI) were not changed by burning temperatures. In another study, by assessing loss of nutrients in ashes between two different burn seasons under uncontrolled field conditions, Snyder (1986) proved that TP, TCa, and TMg contents were not impacted by both wet-season burn and dry-season burn, whereas a significant loss of total K (TK) occurred in the wet-season burn, but there was no loss of TK in the dry-season burn.

Other factor determining availability of soil nutrients is soil water content. Soil moisture is an important characteristic of soil that affects chemical reactions in soil solution and provides nutrients for plant uptake. Availability of nutrient sources in the rhizosphere depends on soil water content (Dunham and Nye, 1976) because the concentration and mobility of nutrients in soil solution as well as ion exchange from solid phases are influenced by soil water content. In natural forest conditions, soil moisture fluctuates with temperature, rainfall, and aboveground vegetation. Fluctuations of soil moisture can change soil solution chemistry and regulate the availability of nutrients in the soil solution and the distribution of plant species as well.

Limitations of bio-available forms of several plant nutrients have created severe problems for plant growth on calcareous soils. Some plants don't grow successfully on these soils because of deficiencies of P and/or other micro-nutrients (Tyler, 1992). Phosphorus uptake by plants mainly controlled by P depletion and diffusion rates in rhizosphere is greatly affected by soil moisture in calcareous soils (Gahoonia et al., 1994). The soil moisture content considerably influences mineral nutrient contents in soil solutions and their uptake by plants (Misra and Tyler, 1999). Moreover, bicarbonate (HCO_3^-) ion, mostly constituted from calcite (CaCO_3), is relatively high in calcareous soil solution. An increase in soil moisture causes an increase in HCO_3^- concentration (Inskeep and Bloom, 1986; Mengel et al., 1984). The presence of bicarbonate ions in soil solution can control

activities of other ions, especially cations. Bicarbonate ions are not only considered as a primary factor responsible for plant chlorosis (Mengel, 1994; White and Robson, 1990), but they also interfere with plant uptake of other nutrients such as K and Mg (Misra and Tyler, 1999). The effect of soil moisture levels on content of nutrients in calcareous soil and in plant biomass was evaluated by Misra and Tyler (1999). They tested seven soil moisture levels, ranging from 35 to 85% of water holding capacity, and showed that extractable Ca, Mg, and Zn decreased while soil pH, solution HCO_3^- , P and Mn increased with increasing soil moisture; potassium had the highest concentration at 50-70% of water holding capacity; contents of P, Zn, and Mn which had relatively low solubility and availability in calcareous soils varied in different plant species.

Pine Rockland is one of the major endangered ecosystems in the United States, and rated as G1 on the global conservation scale which represents the most critically imperiled habitats globally because of extreme rarity or because of extreme vulnerability to extinction due to some natural or man-made factors (Florida Natural Area Inventory, 2008; Snyder et al., 1990). The Pine Rockland forest ecosystem originated on limestone substrates and has been influenced by anthropogenic activities and fire suppression. Since the European settlement, approximately 98.5% of the Pine Rockland area in Miami-Dade County were converted into urban, suburban, and agricultural areas (Fairchild Tropical Botanic Garden, 2008). Intact ecosystems of the Pine Rockland currently exist in three remnant regions in South Florida include the Long Pine Key in the Everglades National Park, the Big Pine Key in the Florida Lower Keys, and a part of the Big Cypress National Preserve (Snyder et al., 2005; U.S Fish and Wildlife Service, 2007).

Anthropogenic activities have led to significant changes of the Pine Rockland ecosystem in geographic extent (e.g., fragmentation of habitats), environmentally driven factors (e.g., wildfire), biodiversity (e.g., invasion of exotic species), and nutrient biogeochemical cycling. In

particular, limitations of available P and micro-nutrients (Mn, Cu, and Zn) are threatening to biodiversity of native plant communities in this ecosystem. Hundreds of hectares historically originated from the Pine Rockland forest have been abandoned or replaced entirely by Brazilian pepper (*Schinus terebinthifolius*) in the Hole-in-the-Donut (Loope and Dunevitz, 1981). Recent interests in preservation of intact Pine Rockland ecosystems, the Everglades National Park has resulted in the use of prescribed fire to manage the Pine Rockland forests (Olmsted et al., 1983). The Park has focused on controlling exotic plant species and appropriating fire management regimes with respect to maintenance, protection, restoration, and enhancement of the Pine Rockland forest ecosystem.

Several recent studies have focused on evaluating effects of fire on restoration of understory vegetation in the Pine Rockland forests (Knapp et al., 2009; Robbin and Myers, 1992; Ross et al., 1994 and 2003; Sah et al., 2004 and 2006; Sah et al., 2010; Snyder et al., 2005; Sparks et al., 2002). Snyder (1986) assessed effects of prescribed fire to restoration of mass and nutrients in the understory vegetation in the Pine Rockland during two different burn seasons (dry-season and wet-season burns), and showed that the mass and nutrient contents of the understory vegetation varied with the burn season. This implied that there might have been changes of soil nutrient contents after the fire relating to differences in soil moisture content between two burn seasons. With limited information regarding the content of nutrients in plant ashes and post-fire soil nutrient status, it is essential to quantify availability of nutrients in fire-induced plant ashes, and to assess impacts of soil moisture and fire intensity on post-fire soil nutrient status for the fire-dependent Pine Rockland ecosystem. This initiates a better understanding of biogeochemical processes associated with a fire. This is particularly important for determining the role of a prescribed fire in P biogeochemical process because P is the most limiting factor in the Pine Rockland ecosystem.

The main objective of this chapter was to assess effects of prescribed fire on nutrient availability in soil during different burn seasons simulated under controlled condition of laboratory incubation. Specific tasks included: 1) determining effects of burn temperatures on pH, EC, and nutrient contents in residual ashes; 2) determining a relationship between burn temperature and extractable concentration of soil nutrients; 3) determining whether this relationship is affected by soil moisture content; 4) determining whether the relationship is impacted by time after burn; and 5) estimating a field-fire temperature based on laboratory simulated results.

Materials and Methods

Incubation Experiment

A burn experiment was conducted under a controlled condition of laboratory incubation to determine how fire intensity and soil water content impact on soil nutrient pools after a fire. Treatments consisted of four burn temperatures (250, 350, 450, and 550⁰C), three levels of soil moisture (35, 70, and 100% of soil field capacity), six different lengths of incubation time (14, 30, 60, 90, 120, and 180 days). There were three replicates of each treatment combination. Soil samples were put into plastic bottles (approximately 800 cm³; 10cm of length x 8cm of width x 10cm of height), and were incubated at 25⁰C in above intervals of incubation time. The incubation temperature was the average annual temperature in the Everglades National Park over fifty years (The Weather Channel, 2008).

The four burn temperatures of fuel-load samples were based on burned-temperatures reported by many previous studies and soil chemical properties, i.e., nitrogen (N) starts to volatilize at temperatures above 200⁰C (Certini, 2005; Neary et al., 2005), plant tissues and litters are entirely burned and converted into white ashes at temperatures from 500 to 550⁰C (Gray and Dighton, 2006; Qian et al., 2009b). The three soil moisture levels were selected, representing a

range that can be found in Pine Rockland throughout the year.

The Long Pine Key in the Everglades National Park where was burned in five years ago was chosen for collecting samples. A sampling frame of 30 x 30 cm was used to collect soil samples and fuel-load samples in the field. The fuel load was defined as aboveground and understory of pine trees, including forest floor, dead standing, dead pine needle, herbaceous plants and grasses, and small shrubs (palms). All plants, litter, and residues inside the frame were gathered for the fuel-load samples. Soils at the top 0-5cm depth in the same frame with the fuel-load samples were collected. Twenty four samples were collected for the incubation experiment. Soils in each sampling-frame sample were divided into nine subsamples corresponding nine bottle samples in the laboratory incubation experiment. Additionally, six other sampling-frame samples of soils and fuel loads were collected for determination nutrient contents in the fuel-load samples and developing a soil moisture curve and determination of soil field capacity.

Soil samples were air-dried, ground, and sieved through a 2 mm screen. Plants, litter, and residues of fuel loads were cut into approximately 1-2 cm pieces, and dried in oven at 65⁰C for 5 days. Mixed soils (150g) were put into plastic bottles for the incubation experiment. Subsamples were used to develop the soil moisture curve and determination of the field capacity.

Approximately 28g of oven-dried, mixed tissues and residues were put into 500 ml-glass beakers, and heated for 6 hours at the four temperatures.

Residual ashes produced by heating were weighed to calculate percentages of ash production for the given temperature. Ashes at the same heating temperature were mixed well, and then divided into fifty-four equal parts and placed on top of soil in the bottle samples. Deionized water was applied to soil samples at each soil-water content. During the incubation, while the bottles were covered with plastic Ziploc bags, bottle caps were left open. Ziploc bags were opened and

closed immediately every 24 hours. This provided oxygen to ensure an aerobic condition for soils inside the bottles. A procedure for the laboratory incubation experiment is shown in Appendix E.

Soil-Water Field Capacity

Soil field capacity was estimated by a gravimetric method. Four replicates of 100 g air-dried, sieved soil were put into 250-ml plastic cups with small holes in the bottom. Soils in these cups were repacked and continuously flooded with tap water for 2 hours. The flooded soils were then drained for 24 hours under laboratory conditions. The drained soils were weighed to determine weight of the soil. Thereafter, the drained soils were dried in Oven at 105°C for 24 hours, cooled to room temperature, and reweighed to determine the weight of oven-dried soil for each replicate (Brady and Weil, 2002; Liu et al., 2007). Calculation of the amount of water for each soil-water content treatment is shown in Appendix F.

Estimation of a Field-Fire Temperature

Fire temperatures during a field fire can be computed based on a relationship between nutrient contents in laboratory residual ashes and nutrient contents in field ashes. Qian et al. (2009b) used piecewise equations and contents of TC, TN, and TP in residual ashes from both the laboratory simulation and the field to estimate the field-fire temperature. Because of relatively high vaporization points of elemental P (774⁰C), Ca (1484⁰C), Mg (1091⁰C), and Fe (2862⁰C) (Wikipedia, 2010), contents of TP, TCa, TMg, and TFe in residual ashes are not impacted by fire temperatures (Qian et al., 2009b; Snyder, 1986). In addition, inorganic P ions are capable of binding to compounds of Fe, Ca, and Mg; therefore, residual-ash TP, TCa, TMg, and TFe were selected as predictor variables for an estimation of a field-fire temperature.

Regression models with 1st, 2nd, and 3rd order were fitted based on burn temperature (response variable) and content of TP, TCa, TMg, or TFe in residual ashes (independent variable)

resulting from the laboratory simulation. A field fire temperature was estimated from the selected regression models for each independent variable and content of TP, TCa, TMg, or TFe in ashes collected from the field. The field ash was the ash which was collected in the field study as described in Chapter 2. Fire temperatures for predictor variables were computed by substituting contents of TP, TCa, TMg, and TFe in the field ashes into their own selected regression models. A fire field temperature was an average value of estimated temperatures from the regression models. Furthermore, ANOVA analyses of TP/TCa, TP/TMg, and TP/TFe in field and laboratory ashes were performed to check if there was any loss of P, Ca, Mg, and Fe in field ashes (Appendix I).

Chemical Analysis

Soil chemical components in this chapter were analyzed using the same methods described in the section of chemical analysis in Chapter 2.

Statistical Analysis

The method of multiple regression analysis using the PROC GLM procedures (SAS Institute Inc., Cary, North Carolina) was used for evaluating effects of soil moisture, burn temperature, incubation time, and interactions among these factors on soil nutrient pools. The analysis results were reported by values of F test from type I of hypothesis test. The multiple regression analysis was firstly carried out by fitting a full model with main effects, two-way and three-way interactions for each chemical component. If there was no significant difference of any two-way or three-way interaction in the full model, a reduced model was fitted without the insignificant interactions in the full model. In addition, a plot of residuals versus predicted values, a normal probability plot (NPP), and Durbin-Watson test were done simultaneously with the regression analyses to check homogeneity of error variances, normal distribution of error variances, and independence of the errors for analytical components, respectively. If there was any

heterogeneity of error variances for an independent variable, the data were transformed to obtain an equality of error variances. Methods of influence analysis such as DFFITS, Covariance Ratio, and Cook's D were performed to determine outliers of the data that could affect results of the multiple regression analysis. All results of multiple regression analysis are shown in Appendix G.

The method of linear regression analysis using the PROC GLM procedures was utilized to assess effects of burn temperature on ash pH, electrical conductivity (EC), and total and water-soluble nutrients in laboratory residual-ashes. Results of linear regression analyses are shown in Appendix H. The method of a stepwise, multiple linear regression with 1st, 2nd, and 3rd order was used to fit regression models between burn temperature and contents of residual-ash TP, TCa, TFe, or TMg in laboratory simulation. Selection criteria for choosing the best models to estimate a field-fire temperature were the highest R-square, lowest coefficient of variation, and lowest root MSE (mean standard error). Results of fitting multiple regression models are shown in Appendix I.

Results and Discussion

Biomass and Total Nutrients in Residual Ashes

Significant differences were observed for effects of heating temperatures on losses of biomass, and TN and TC contents in the fuel loads (Table 3-1 and Figure 3-1). Most of the fuel-load biomass, TN, and TC were lost via volatilization at 450 and 550⁰C. At two these temperatures, the fuel-load materials were converted into white ash (Appendix E) with an average ash production of 8.3% at 450⁰C compared with 6.7% of ash products constituted at 550⁰C. Black ash (charcoal) was generated at 350⁰C with an average ash production of 19.1%, whereas heating to 250⁰C produced approximately 43.6% of a reddish-black ash. Volatilization of TC and TN was proportional to biomass loss. Volatilization of TN ranged from 24.5% at 250⁰C to 91.8% at 550⁰C. Approximately 33.4% of TN was lost by heating to 350⁰C while loss

of TN was about 81% at 450⁰C. Volatilization of TC ranged from 51.2 to 96.1% at 250 and 550⁰C, respectively, whereas up to 81 and 94.3% of TC lost at 350 and 450⁰C, respectively.

Results of the linear regression analysis revealed that increasing in burn temperatures did not impact on total contents of nutrients in ashes, except for TC ($p < 0.001$), TN ($p < 0.001$), and TK ($p < 0.001$) (Table 3-1). With comparatively low concentration in soils, Cu could not be determined in residual ashes because of being below the detection limit. Due to their relatively high melting points (over 600⁰C), high heat of vaporization (over 128 kJ/mol), and limited air movement in the muffle furnace, contents of TP, TCa, TMg, TFe, TMn, and TZn in term of dry fuel-load content did not decrease with increasing burning temperature. This indicated that TP, TCa, TMg, TFe, TMn, and TZn accumulated in residual ashes within an increase in burning temperature. Nevertheless, because of the low melting point (63.38⁰C) and heat of vaporization (76.9kJ/mol) (Wikipedia, 2010), TK content was significantly reduced as burn temperature increased in term of dry fuel-load content. Contents of TK significantly decreased between 250, 350 and 450⁰C, but no decrease was observed for contents of TK at heating to 550⁰C (Figure 3-2).

The dry mass of the fuel loads ($\sim 331 \text{ g/m}^2$) was in the range of dry mass of pre-burn aboveground vegetation in a dry-season burn described by Snyder (1986), which was from 200 to 491 g/m^2 . Significant impacts of burn temperatures were observed on TC and TN contents in plant ashes. A high burn temperature (over 450⁰C) resulted in removal of substantial amounts of C and N pools in the fuel loads. Our results were similar to the rate of biomass loss reported by Snyder (1986) and Gillon et al. (1995), and the rates of volatilized C and N due to increasing burn temperatures (Qian et al., 2009b). No evidence was found for effects of the burn temperature on TP, TCa, TMg, TFe, TMn, and TZn contents, which were due to their relatively high volatilization temperatures. However, the significant decrease of TK as burn temperatures increased may be due

to its relatively low melting point and the nature of understory vegetation. A significant loss of K in post-burn field ashes in the Pine Rockland was also quantified by Snyder (1986). Raison et al. (1985) showed that the order magnitude of volatilization was $N > K > P > Ca$, in which significant loss of non-particulate K could occur at high temperature. Qian et al. (2009b) pointed out that field-collected ashes contained 76% less total K compared with laboratory-burned ashes at temperatures over 450⁰C with dead cattail leaves. Moreover, loss of K ($p < 0.01$) due to an increased temperature under controlled condition in laboratory was found by Gillon et al. (1995).

pH, EC, and Water-Soluble Nutrients in Residual Ashes

Results of linear regression analysis indicated that pH, EC, and the water-soluble nutrient contents in residual ashes significantly varied with burn temperatures, except for water-soluble Ca and Mg (Table 3-1). Ash pH and EC had an increasing trend along the temperature gradient. Ash pH significantly increased from acid with heating temperatures at or below 250⁰C to alkaline at temperatures greater than or equal to 350⁰C (Figure 3-3c). The average pH in was 5.4 at 250⁰C, significantly increased to 8.1 at 350⁰C, and finally stabilized at 450 and 550⁰C. No significant difference was found for ash EC below or at 250⁰C (~ 214.3 $\mu\text{S}/\text{cm}$); however, value of EC was significantly increased at 350⁰C (813.3 $\mu\text{S}/\text{cm}$), continued to increase at 450⁰C (1090 $\mu\text{S}/\text{cm}$), and reached a peak at 550⁰C (1253.3 $\mu\text{S}/\text{cm}$) (Figure 3-3d). Residual-ash pH and EC were inexorably increased by increases of heating temperatures as a result of inorganic ion releases from the fuel combustion. Significant increases in residual-ash pH and EC were similar to results of recent studies (Certini, 2005; Qian et al., 2009b). These increases were attributed to releases of base cations from an organic-matter combustion which could change soil pH and EC and impact the availabilities of soil nutrient pools (DeBano et al., 1998; Knoepp et al., 2005; Murphy et al., 2006a). Nevertheless, significant increases of ash pH and EC occurred only at

high temperatures ($\geq 350^{\circ}\text{C}$) which coincided with a complete fuel combustion (Arocena and Opio, 2003; Qian et al., 2009b).

Significant effects of burn temperatures were observed on water-soluble N and P in residual ashes (Table 3-1). Concentrations of $\text{NH}_4\text{-N}$ were significantly reduced along the temperature gradient from 250 to 550°C , with the lowest concentrations at 450 and 550°C (Figure 3-3a). Heating to 250°C produced $13.25 \mu\text{g NH}_4\text{-N/g}$ of dry fuel load, whereas $1.09 \mu\text{g NH}_4\text{-N/g}$ of dry fuel loads after heating to 550°C . Approximately 10.95 and $2.74 \mu\text{g}$ of $\text{NH}_4\text{-N}$ were produced at heating temperatures of 350 and 450°C , respectively. Concentrations of $\text{NO}_3\text{-N}$ in residual ashes significantly reduced at a heating temperature of 350°C , from $2.4972 \mu\text{g/g}$ at 250°C to $0.3743 \mu\text{g/g}$ at 350°C . No significance was observed for $\text{NO}_3\text{-N}$ in ashes at burn temperatures greater than or equal to 350°C (Figure 3-3b). The decline of the water-soluble $\text{NH}_4\text{-N}$ as burn temperature increased indicated that ammonia oxidized during heating, and lost through volatilization. The significant reduction of the water-soluble $\text{NO}_3\text{-N}$ only at 350°C was different from results of some other studies such as Gray and Dighton (2006) and Qian et al. (2006b). This may be attributed to differences in compositions of understory species (Lavoie et al., 2010).

Burning at high temperatures (350, 450, and 550°C) had significantly less water-soluble P than that at lower temperatures (Figure 3-3a). The water-soluble P contents were $60.55 \mu\text{g/g}$ dry fuel load at 250°C , $17.48 \mu\text{g/g}$ dry fuel load at 350°C , $2.32 \mu\text{g/g}$ dry fuel load at 450°C , and $0.36 \mu\text{g/g}$ dry fuel load at 550°C . The significant decrease of the water-soluble P at the higher burn temperatures ($\geq 450^{\circ}\text{C}$) was similar to results reported by Qian et al. (2009b). This implied that a low-fire intensity generally could produce more available P than an intense fire. With increasing burn temperatures, inorganic P ions tended to bind to basic oxides (Ca, Mg, Fe, Mn) in residual ashes, and then formed insoluble phosphates (Raison et al., 1985). Additionally, a dramatic

increase in ratio of TP to water-soluble P in residual ashes at higher temperatures (2.8, 10, 75, and 524 at 250, 350, 450, and 550⁰C respectively) indicated that inorganic phosphate became unavailable with an intense fire (Gray and Dighton, 2006).

Burn temperature significantly affected water-soluble metals in ashes, but responses of each metal along the temperature gradient in term of dry fuel-load content were very different. Concentration of water-soluble K was significantly lower at 250⁰C than at 350, 450, and 550⁰C. The water-soluble K was 429.9 µg/g at 250⁰C, whereas K concentrations were 737.5, 950.8, and 955.4 µg/g at 350, 450, and 550⁰C, respectively (Figure 3-3b). The water-soluble Mn and Zn were gradually reduced as burn temperatures increased, but Zn concentration was not significantly different between 350, 450, and 550⁰C (Figure 3-3b) while no difference was observed for the water-soluble Mn between 450 and 550⁰C (Figure 3-3a). Differences in melting points, boiling points, and heat of vaporization of plant nutrients generally resulted in different responses to concentrations of water-soluble nutrients in residual ashes as burn temperatures increased. The fuel combustion converted organic compounds into basic cations and basic oxides (Qian et al., 2009b; Ulery et al., 1993a & b; Ulery et al., 1995).

Interactions of Soil Nutrient Pools

Results of the multiple regression analysis showed that the three-way interaction among soil moisture, burn temperature, and incubation time were not significant; however, the two-way interaction among these factors was significant for some nutrients (Table 3-2). The interaction between incubation time (or period) and soil moisture significantly affected extractable NH₄-N ($p < 0.001$), PO₄-P, K, Fe ($p < 0.05$), and Zn ($p < 0.01$). The interaction between soil moisture and burn temperature was significantly for soil EC ($p < 0.01$), extractable NO₃-N, PO₄-P, Fe ($p <$

0.001), and Mn ($p < 0.05$) while the interaction between incubation time and burn temperature was only significant for extractable Mn ($p < 0.01$).

Under the controlled condition of laboratory incubation, the extractable Mn concentration was significantly higher at 250⁰C than at 350, 450, and 550⁰C at the same as incubation time (Figure 3-4). Increasing in the incubation time resulted in reduction of extractable Mn. There was no statistical significance effect of temperatures on the extractable Mn after 180 days. Extractable P concentration decreased not only with increasing incubation time but also with increasing soil moisture (Figure 3-5a). The highest P concentration of 8.4 mg/kg was observed at soil water content of 35% field capacity in 30 days, whereas the lowest P was 4.0 mg/kg at 100% of field capacity after 180 days. The extractable NH₄⁺ concentrations increased with an increase in the soil water content, but it decreased when the incubation time was increased, especially after 30 days (Figure 3-5c). Concentration of NH₄⁺ reached a peak (184 mg/kg soil) at a soil water content of 100% field capacity in 14 days, and its lowest concentration (38 mg/kg soil) occurred at the soil water content of 35% field capacity after 120 days. Responses of K, Fe, and Zn to the soil moisture over time were variable. The extractable K was significantly reduced after 120 days and dramatically increased after 180 days with the same soil moisture (Figure 3-5b). Changes of the extractable Fe fluctuated with soil moisture and time. In general, the extractable Fe was higher at 35 and 100% of field capacity than at 70% of field capacity at the same length of incubation time (Figure 3-5d). Concentration of extractable Zn did not change until 120 days, but significantly decreased after 180 days (Figure 3-5e).

The burn temperature at 350⁰C and 35% of field capacity had the highest extractable P (10.6 mg/kg), whereas the lowest concentration (2.9 mg/kg) occurred at 550⁰C and 100% of field capacity (Figure 3-6a). At the same soil moisture, burn temperature of 350⁰C always produced a

higher concentration of P. The combined effect of burn temperature and soil moisture to the extractable NO_3^- was different from those of P. The soil water content of 70% field capacity always constituted greater amount of $\text{NO}_3\text{-N}$ when the temperature was kept constant. The highest NO_3^- (approximately 203 mg/kg) occurred at temperatures 350 or 550⁰C with soil water content of 70% field capacity (Figure 3-6b). Responses of Fe and Mn to the interaction effect of burn temperature and soil moisture altered variously. A significant increase of extractable Mn only occurred at the burn temperature of 250⁰C with all soil water contents. The extractable Mn concentration at 250⁰C reached approximately 70 mg/kg soil, whereas Mn concentration ranged from 46 to 52 mg/kg soil at other burn temperatures (Figure 3-6c). The extractable Fe content was highest at 550⁰C and 100% of field capacity with 201.5 mg/kg, and lowest at 250⁰C and 70% of field capacity with 148.5 mg/kg soil (Figure 3-6d). Similarly, changes of EC showed the same pattern as $\text{NO}_3\text{-N}$. The interaction of burn temperature of 450⁰C and 70% of field capacity resulted in the highest EC, whose value was 1265.9 $\mu\text{S/cm}$ (Figure 3-6e).

Effects of Burn Temperature on Soil Nutrient Pools

Results of multiple regression analysis showed that the burn temperature significantly impacted soil pH, extractable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, P, K, Fe, Mn, Zn, Cu ($p < 0.001$), EC ($p < 0.01$), and extractable Mg ($p < 0.05$) (Table 3-2). As a result of availability of the water-soluble nutrients in residual ashes at different burn temperatures, changes of pH, EC, and extractable concentrations of soil $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, P, K, Mg, Fe, Mn, Zn, and Cu along the temperature gradient had generally the same pattern as those of the water-soluble nutrients in the laboratory residual-ash.

The burn temperature significantly increased extractable Mg, K, Fe, Cu, and soil pH. Generally, the burn temperature at or over 450⁰C, sometimes significantly, produced more bioavailable Mg, K (Figure 3-7a), Fe, Cu (Figure 3-7b), and led to an increase of soil pH (Figure 3-

7c). The extractable Mg was around 65 mg/kg at or below 350⁰C, and approximately 70.8 mg/kg at or higher 450⁰C. The extractable K was significantly different among 250, 350, and 450⁰C, but no significance was found between 450 and 550⁰C. The extractable K concentrations were 339.7, 401.2, 415.9, and 421.0 mg/kg soil at the burn temperatures of 250, 350, 450, and 550⁰C, respectively. Responses of soil extractable Fe and pH to the burn temperatures had the same trend as those of extractable K. The concentrations of Fe were 158.9, 166.2, 180.2, and 181.8 mg/kg soil with respect to the burn temperature gradient, whereas soil pH was 7.45, 7.58, 7.65, 7.67 at burn temperatures of 250, 350, 450, and 550⁰C, respectively. Extractable Cu increased linearly with the burn temperature, ranging from 2 mg/kg at 250⁰C to 2.78 mg/kg at 550⁰C. In contrast, an increase in burn temperatures resulted in a reduction of extractable NH₄-N, Mn, and Zn (Figure 3-7d). The significant reduction of NH₄-N occurred when the burn temperature increased from 350 to 450⁰C. No significant change was observed for NH₄-N contents between 250 and 350⁰C or 450 and 550⁰C. The concentrations of NH₄-N ranged from 102 to 104.9 mg/kg soil at or below 350⁰C, and were approximately 91 mg/kg soil at or over 450⁰C. The extractable Zn content which linearly decreased as burn temperatures increased were 4.01, 3.75, 3.56, 3.09 mg/kg when heating to 250, 350, 450, and 550⁰C, respectively. The burn temperature significantly decreased the extractable Mn after heating to 350⁰C while no significant difference was found for extractable Mn between 350, 450 and 550⁰C.

Changes of extractable PO₄-P, NO₃-N (Figure 3-7e), and EC (Figure 3-7f) along the burn temperature gradient were different from other soil nutrient elements, whose concentrations had the highest values at 350⁰C. The extractable P with respect to the burn temperature was 7.2 mg/kg at 250⁰C, reached its maximum concentration of 9.04 mg/kg at 350⁰C, and decreased gradually to 6.06 and 3.31 mg/kg at 450 and 550⁰C, respectively. The extractable NO₃-N

produced at 350⁰C was 168 mg/kg while those of NO₃-N were 122.2, 132.0, and 129.6 mg/kg soil at 250, 450, and 550⁰C, respectively. The highest value of EC was 1134.1 μS/cm at 350⁰C, whereas the values of EC were 959.2, 1089.1 and 1040.8 μS/cm which corresponded to the burn temperatures of 250, 450, and 550⁰C.

Various responses of soil nutrient pools along the temperature gradient depended on availability of nutrients in the residual ash which were attributable to differences of their melting points, boiling points, and heating points of vaporization. Unlike in a field fire, leaching and plant uptake didn't influence the soil nutrient pools under the controlled condition in the laboratory, alterations of soil nutrient pools with respect to the burn temperature trended to be the same as their changes in the residual ash. Thus, changes of the nutrient pools were directly related to the amount of nutrients in ashes deposited into soils (Badia and Marti, 2003).

Effects of Soil Water Content on Soil Nutrient Pools

Overall, soil moisture significantly impacted soil pH, EC ($p < 0.01$), and extractable NH₄-N, NO₃-N, PO₄-P, Fe ($p < 0.001$), but no significant difference was founded for extractable Mg, K, Mn, Zn, or Cu (Table 3-2). Under the controlled condition of laboratory incubation, extractable P significantly decreased with an increase in soil moisture (Figure 3-8a). The highest P concentration was 7.36 mg/kg occurring with 35% of field capacity, whereas the lowest P was 5.39 mg/kg with 100% of field capacity. The soil moisture of 70% field capacity resulted in 6.46 mg/kg extractable P. However, an increase in the soil moisture significantly increased extractable NH₄⁺ (Figure 3-8b). The greatest concentration of NH₄-N was 119.3 mg/kg when the soil moisture was 100% of field capacity, whereas its lowest concentration was 71.7 mg/kg occurred at the soil water content of 35% field capacity. The soil with water content of 70% field capacity had 101.3 mg NH₄-N/kg soil.

Responses of $\text{NO}_3\text{-N}$ and EC to soil moisture each showed the same tendency. Soil extractable $\text{NO}_3\text{-N}$ and EC reached a peak at 70% of field capacity. The extractable NO_3^- concentration was 128.4 mg/kg with soil moisture content of 35% field capacity, significantly increased to 188.7 mg/kg at 70% of field capacity, thereafter decreased to 96.7 mg/kg when the soil water content increased into the 100% of field capacity (Figure 3-8c). The EC values were 976.3 and 988.2 $\mu\text{S/cm}$ with soil water content of 35 and 100% field capacity, respectively, whereas its value was 1202.8 $\mu\text{S/cm}$ at 70% field capacity (Figure 3-8d). On the other hand, changes of soil pH and extractable Fe due to the soil moisture were opposite to those of EC and $\text{NO}_3\text{-N}$. Extractable Fe was significantly lower a soil water content of 70% field capacity (162.2 mg/kg) than at the soil moisture contents of 35% (169.9 mg/kg) and 100% field capacity (183.3 mg/kg) (Figure 3-8e). Although soil pH at soil water content of 70% field capacity was lower than that at 35% of field capacity, there was no significant difference in soil pH between these soil water contents (Figure 3-8f). Soil pH significantly increased at 100% field capacity due to increasing CO_2 concentration under anaerobic condition (Glinski et al., 1992; Yan et al., 1996).

The soil water content of 100% field capacity had the highest concentrations of extractable $\text{NH}_4\text{-N}$ and Fe, and pH. The high soil moisture promoted a denitrification process which only occurred at the soil moisture greater than 60% of air-filled pore space (van Cleemput, 1998). When soils become more anaerobic due to an increase in soil water content, the high soil moisture was favorable for Fe^{2+} -oxidizing bacteria to enhance Fe^{3+} reduction and produce more Fe^{2+} (Megonigal et al., 2004). Nitrate was accumulated over time as a result of the nitrification process (Misra and Tyler, 1999; Tyler, 1996); however, availability of $\text{NO}_3\text{-N}$ in term of soil moisture regime was also dependent on Fe^{2+} concentration because an increase of Fe^{2+} content in soil solution could enhance the rate of nitrate reduction (van Cleemput, 1998). Therefore, the

concentration of $\text{NO}_3\text{-N}$ was considerably reduced at soil water content of 100% field capacity as a result of an increase in the concentration of Fe^{2+} . On the other hand, comparatively high concentrations of P at the low soil moisture denoted that higher soil moisture favored reactions among P with Ca and Mg to form Ca/Mg-P precipitates.

Effects of Incubation Time on Soil Nutrient Pools

Results of multiple regression analysis showed that the incubation time (or period) significantly impacted soil EC and extractable $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Mg, K, Mn, Cu, and Zn ($p < 0.001$), but not for extractable Fe and soil pH (Table 3-2). Ammonia content linearly declined over the time, and stabilized after 120 days. Conversely, a reduction of NH_4^+ resulted in an increase of extractable $\text{NO}_3\text{-N}$ which was positively correlated with incubation time (Figure 3-9a). Significant changes of soil EC and extractable P, Mg, K, Mn, Zn, and Cu actually occurred at 120 days or thereafter. The extractable $\text{PO}_4\text{-P}$, Zn (Figure 3-9b) and Mg, Mn (Figure 3-9c) were significantly decreased when the incubation time was raised from 120 to 180 days while the extractable Cu (Figure 3-9b) was increased after 120 days. The extractable K was greatly reduced at 120 days compared to 90 days, but higher than its original value after 180 days (Figures 3-9c). Soil EC was significantly higher at 120 days compared to its original value at 14 days, and then stable after that time (Figure 3-9d).

Increasing in incubation time resulted in a reduction of extractable P, $\text{NH}_4\text{-N}$, Mg, Mn, and Zn, and an increment of soil EC and extractable K, Cu, and $\text{NO}_3\text{-N}$. A variation of soil pH, EC, and extractable nutrients occurred comprehensively at or after 120 days indicated that time is an important factor contributing to availability of soil nutrient pools following a fire. Soil nutrient concentrations changed simultaneously at 120 days expressed that there was a dynamic interaction among soil chemical components and biogeochemical reactions at this time.

Estimation of Field-Fire Temperature from Residual Ashes

Although there were slight variations among ratios of TP/TCa, TP/TMg, and TP/TFe in ashes along laboratory simulated temperatures and field ashes, no significant effect of fire temperature was observed for these ratios. This indicated that P, Ca, Mg, and Fe were accumulated in both laboratory simulated ashes and in ashes collected from the field. Hence, contents of TP, TCa, TFe, and TMg in residual ashes could be utilized as predictor variables for estimating field-fire temperatures. Figure 3-10 showed contents of TP, TCa, TMg, and TFe accumulated in laboratory residual-ashes and in the field ash. Accumulation of residual-ash TP, TCa, TMg, and TFe increased as burn temperatures increased. The TP was 0.30 mg/g at 250⁰C and increased to 2.6 mg/g at 550⁰C. The TFe content was 0.48 mg/g at 250⁰C and 4.8 mg/g at 550⁰C. Calcium had the highest concentration in residual ashes with 20.2 mg/g ash at 250⁰C and 155.89 mg/g ash at 550⁰C, whereas Mg content was lower than that of Ca, having 1.6 mg/g ash at 250⁰C and 12.0 mg/g ash after heating to 550⁰C. Concentrations of TP, TCa, TMg, and TFe in the field ashes were 1.11, 76.96, 6.15, and 1.82 mg/g ash (Table 3-3).

Fitted linear regression models of TP, TCa, TMg, and TFe selected for prediction of a field fire temperature were presented in Table 3-3. These models demonstrated a good relationship between heated temperatures and fitted temperatures with R-square values over 0.95 (Figure 3-11). From simulated temperatures as presented in Table 3-3, an average field-fire temperature was estimated to be approximately 370⁰C. The high R-square values in the goodness-of-fit models and no significant difference observed in ratios of TP/TCa, TP/TMg, and TP/TFe indicated that contents of P, Ca, Mg, and Fe in ashes were good indicators for predicting a field-fire temperature. The estimated temperature of the field fire was similar to the results reported by Qian et al. (2009b) and Snyder (1986), but was higher than the temperature measured by Sah et al. (2006) and lower

than the temperature determined by Snyder et al. (2005). The difference of fire temperatures was due to differences in understory vegetation communities and the burned seasons among studies. The fire experiments of Snyder et al. (2005) and Sah et al. (2006) were carried out in July and December and conducted in the Big Pine Key and the National Deer Refuge in the Florida Keys, respectively, where was dominated by West Indian tropical hardwoods and a diverse herb layer. On the other hand, this study which was implemented in the Long Pine Key in October was mostly predominated by grasses and palm trees in the understory vegetation.

Conclusions

Results of the study showed that the burn temperature, soil moisture content, and time after burn had significant impacts on soil nutrient pools following a fire. The interaction among incubation time, soil moisture content, and burn temperature did not impact on availability of the nutrients; however, the interaction between soil moisture and burn temperature significantly affected soil EC, extractable $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, Fe, and Mn while the interaction effect between incubation time and burn temperature was only significant for extractable Mn. A burn temperature of 350°C and soil water content of 35% field capacity resulted in the highest extractable P. The highest NO_3^- concentration occurred at or over 350°C and 70% field capacity. The interaction between the burn temperature of 350°C or higher and 70% field capacity resulted in the highest EC. The highest extractable Fe was substantially produced at or over 450°C and 100% field capacity. The burn temperature at below 350°C produced the greater concentration of extractable Mn over soil moisture and time after burn.

The increase along the burn temperature gradient which modified the quantity of elemental nutrients in residual ashes significantly changed soil nutrient pools. An increase in the burn temperature resulted in an increase of soil pH and extractable Mg, K, Fe, Cu, and the decrease of

extractable $\text{NH}_4\text{-N}$, Mn, and Zn, whereas the burn temperature of 350^0C constituted the highest concentrations of $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, and EC. The soil water content had no effect on the extractable Mg, K, Mn, Zn, and Cu; however, it significantly changed soil pH, EC, and availability of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$. Increasing in the soil water content increased the soil pH and availability of $\text{NH}_4\text{-N}$, and decreased the availability of $\text{PO}_4\text{-P}$. The extractable $\text{NO}_3\text{-N}$ and soil EC were highest at soil water content of 70% field capacity, whereas this moisture produced the lowest extractable Fe. Incubation time did not influence extractable Fe and soil pH, but it significantly changed the extractable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, P, Mg, K, Mn, Zn, Cu, and EC. The increase of incubation time caused a linear reduction of extractable $\text{NH}_4\text{-N}$ and an increase of $\text{NO}_3\text{-N}$. Significant alterations of soil EC and availability of P, Mg, K, Mn, Zn, and Cu occurred at or after 120 days of burning in which the extractable P, Mg, Mn, and Zn were decreased while those of K and Cu were increased.

The burn temperature significantly impacted extractable contents of all soil nutrients indicated that difference of fire temperatures between different burn seasons will produce different availabilities of soil nutrient pools after a fire. The significant effects of the interactions between soil water content and burn temperature on extractable $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, Fe, and between incubation time and burn temperature on extractable Mn implied that soil moisture and time after a fire plays an important role in availability of soil nutrient pools following a fire. The dramatic increase in ratio of TP to inorganic P in residual ash as fire intensity raised indicated that a low-fire intensity generally can produce more available P content than a high intense fire because inorganic P ions tend to bind to basic oxides (Ca, Mg, Fe, Mn) in residual ashes, and then form insoluble phosphates when the fire intensity increases. The reduction in extractable P content as an increase in the soil moisture indicated that a higher soil moisture favored for reactions among P with Ca and Mg or Fe and Mn to form Ca/Mg-P precipitates or Fe/Mn-P hydroxyl compounds.

Table 3-1: Results of linear regression analysis on pH, electrical conductivity (EC), and total and water-soluble nutrients in laboratory residual-ashes

Effects of burn temperatures on ash pH, EC, total and water-soluble contents in terms of dry fuel-load content					
Total (T)	Sig. level	Water soluble	Sig. level	pH	EC
N	***	NH ₄ -N	***	**	***
C	***	NO ₃ -N	**		
P	NS	PO ₄ -P	***		
Ca	NS	Ca	NS		
Mg	NS	K	***		
K	***	Mg	NS		
Fe	NS	Mn	***		
Mn	NS	Zn	***		
Zn	NS				

* p < 0.05, ** p < 0.01, *** p < 0.001, NS: not significant

Table 3-2: Results of multiple regression analysis on incubation time (or period), soil moisture, burn temperature, and their interactions

Variables	Main effects			Interactions			
	Period (P)	Moisture (M)	Temperature (T)	P*M	M*T	P*T	P*M*T
pH	NS	**	***	NS	NS	NS	NS
EC	***	**	**	NS	**	NS	NS
NH ₄ -N	***	***	***	***	NS	NS	NS
NO ₃ -N	***	***	***	NS	***	NS	NS
PO ₄ -P	***	***	***	*	***	NS	NS
Mg	***	NS	*	NS	NS	NS	NS
K	***	NS	***	*	NS	NS	NS
Fe	NS	***	***	*	***	NS	NS
Mn	***	NS	***	NS	*	**	NS
Zn	***	NS	***	**	NS	NS	NS
Cu	***	NS	***	NS	NS	NS	NS

* p < 0.05, ** p < 0.01, *** p < 0.001, NS: not significant

Table 3-3: Estimation of a field-fire temperature from laboratory and field residual ashes

Predictor variables	The fitted linear regression models were selected for prediction of P availability after a fire	Field-burning ashes	
		Content μg g ⁻¹	Simulated T °C
TP	$Y^{\dagger} = 171.26 + 0.30356*TP - 0.00014573*(TP)^2 + 3.2363E-8*(TP)^3$	1110.2	372.9
TCa	$Y = 214.04 + 0.00199*TCa$	76964.2	367.2
TFe	$Y = 240.22 + 0.063*TFe$	1821.8	355.0
TMg	$Y = 154.2 + 0.07195*TMg - 0.000008*(TMg)^2 + 3.9495E-10*(TMg)^3$	6149.5	385.9
Average field-fire temperature			370°C

[†] Y is a function of the laboratory heated temperatures, or a burn temperature, with independent variable of TP, TCa, TFe, or TMg (μg g⁻¹ of ash) from ash products; T is a temperature

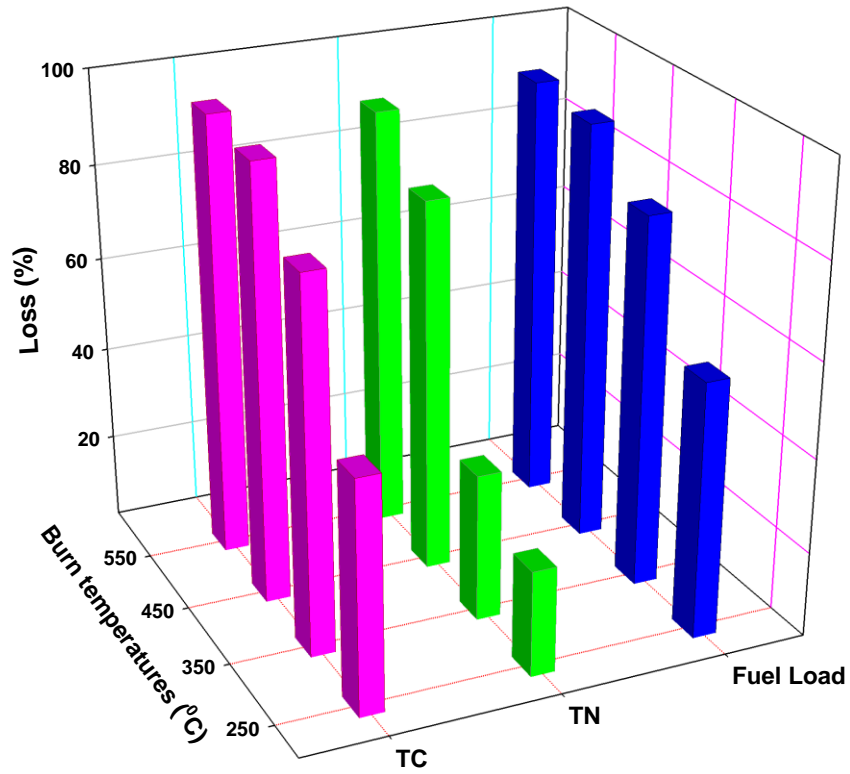


Figure 3-1: Losses of total carbon (TC), total nitrogen (TN), and biomass in fuel load at different burn temperatures

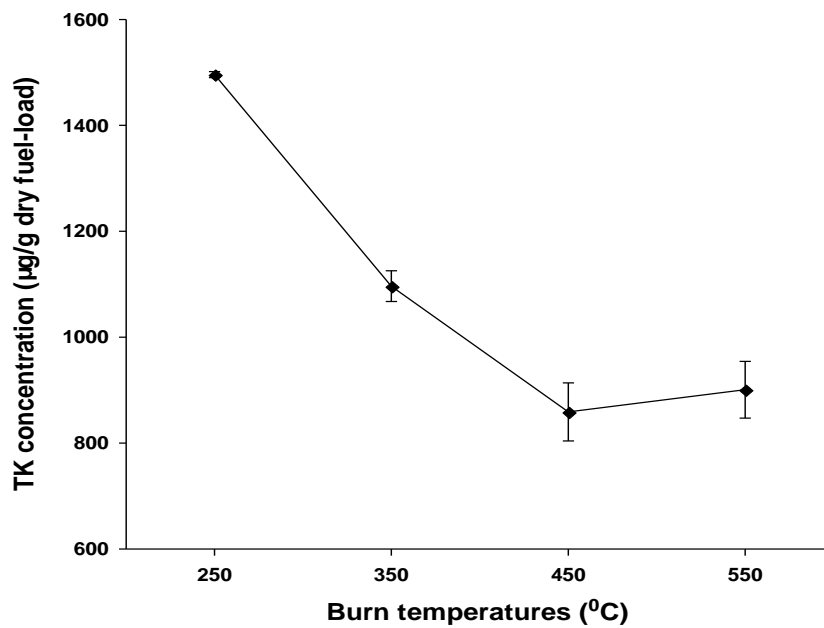


Figure 3-2: Effects of burn temperature on total K in residual ash in term of dry fuel load

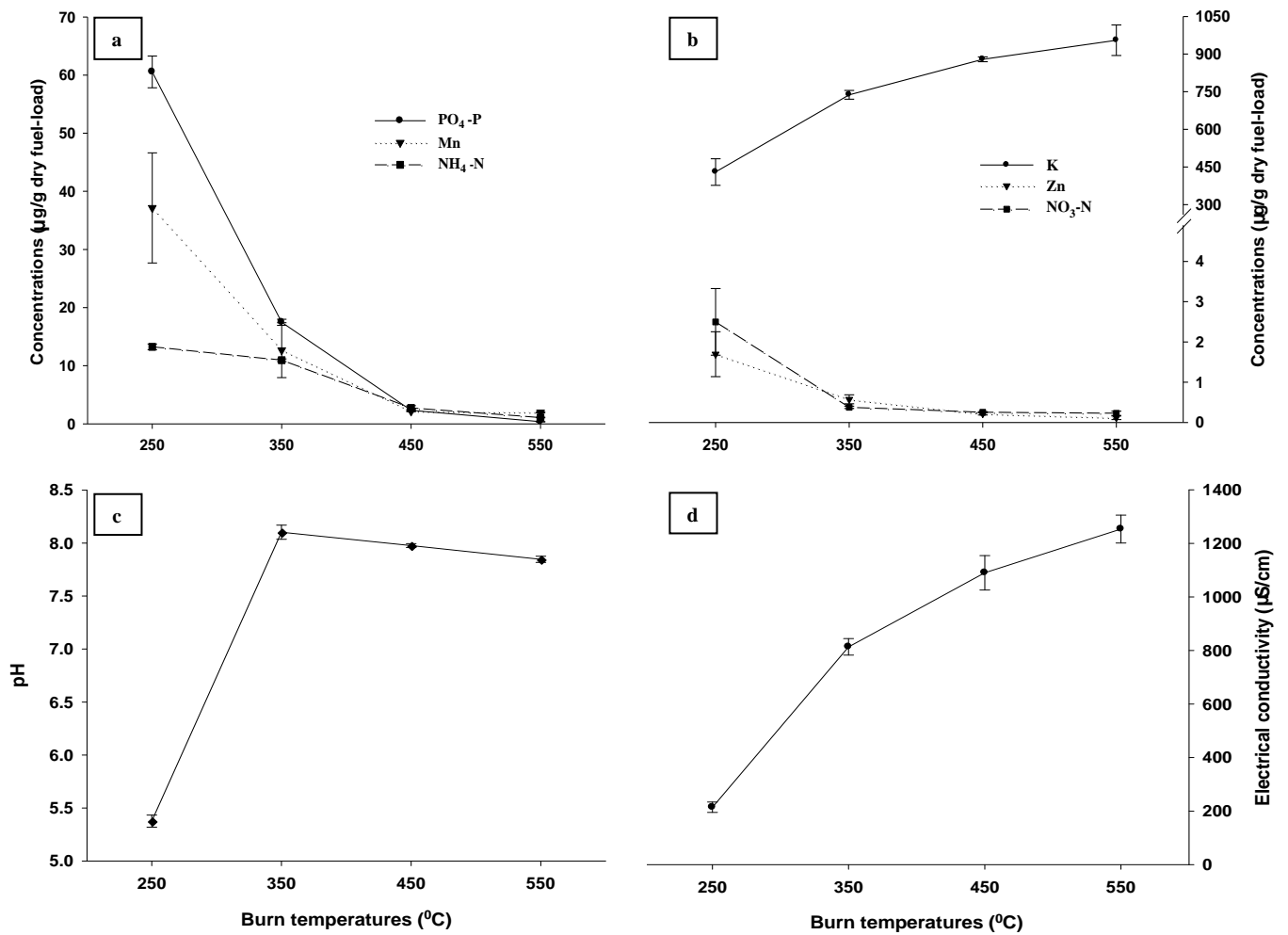


Figure 3-3: Effects of burn temperatures on water-soluble nutrients in residual ash in term of dry fuel load: (a) PO₄-P, NH₄-N, Mn; (b) NO₃-N, K, Zn; (c) pH; and (d) EC

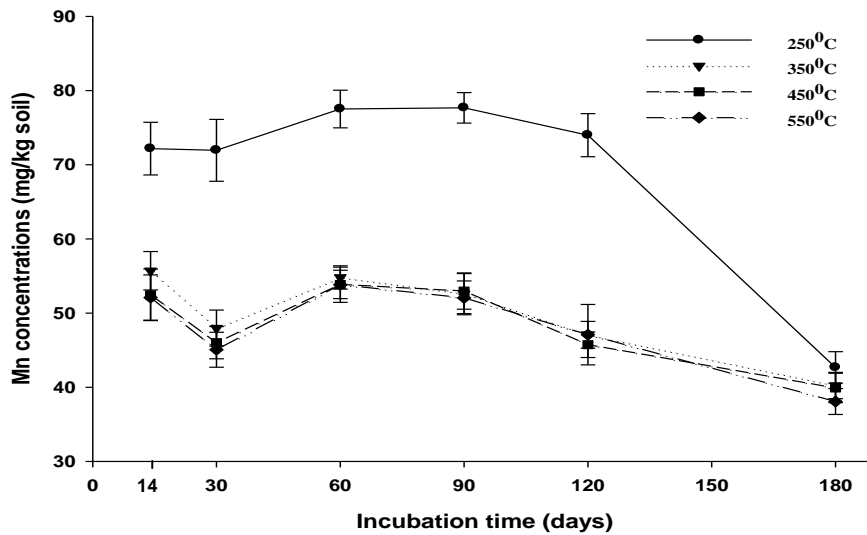


Figure 3-4: The interaction of burn temperature and incubation time on soil extractable Mn

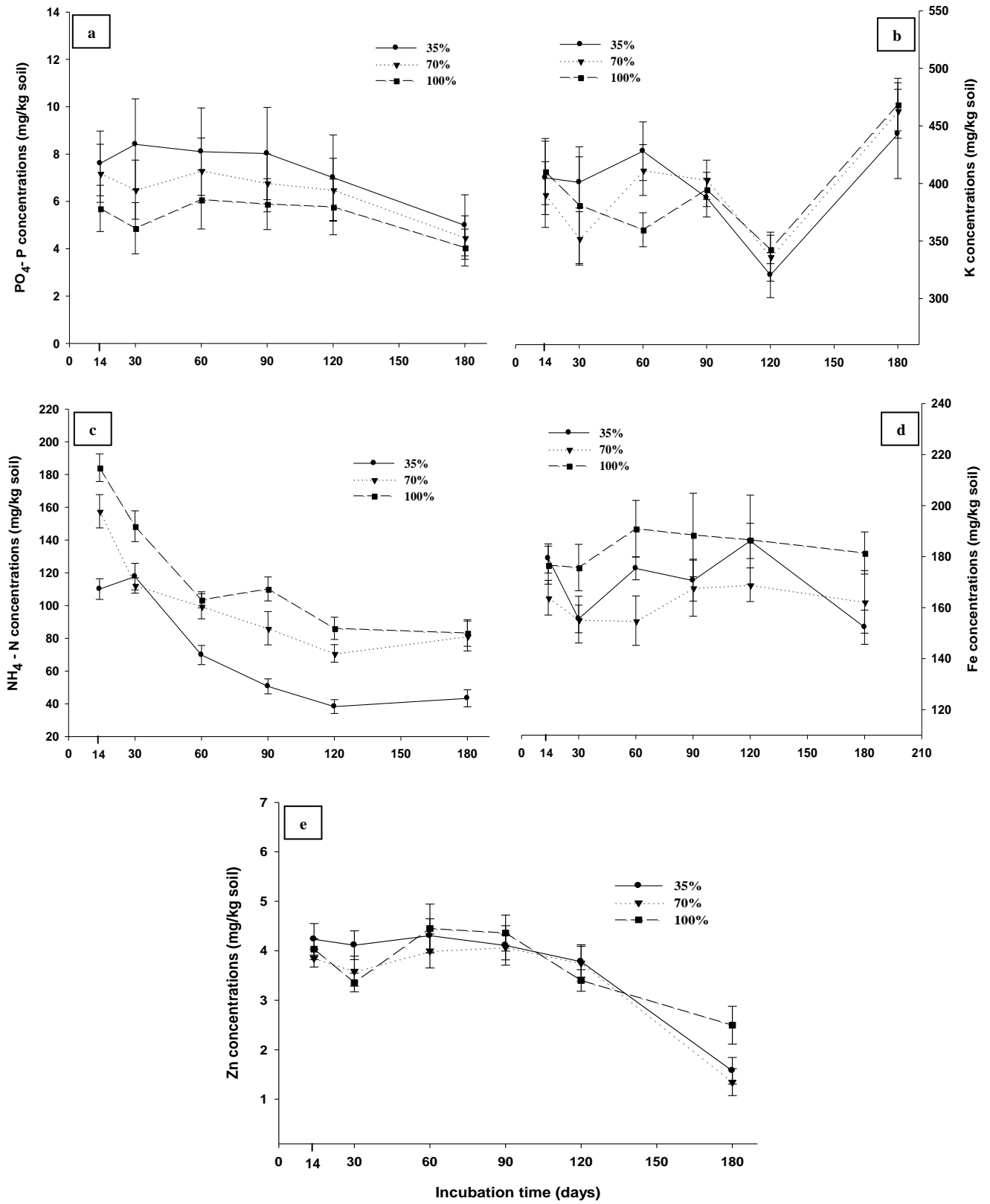


Figure 3-5: The interaction of soil moisture and incubation time on soil extractable nutrients: (a) PO₄-P, (b) K, (c) NH₄-N, (d) Fe, (e) Zn

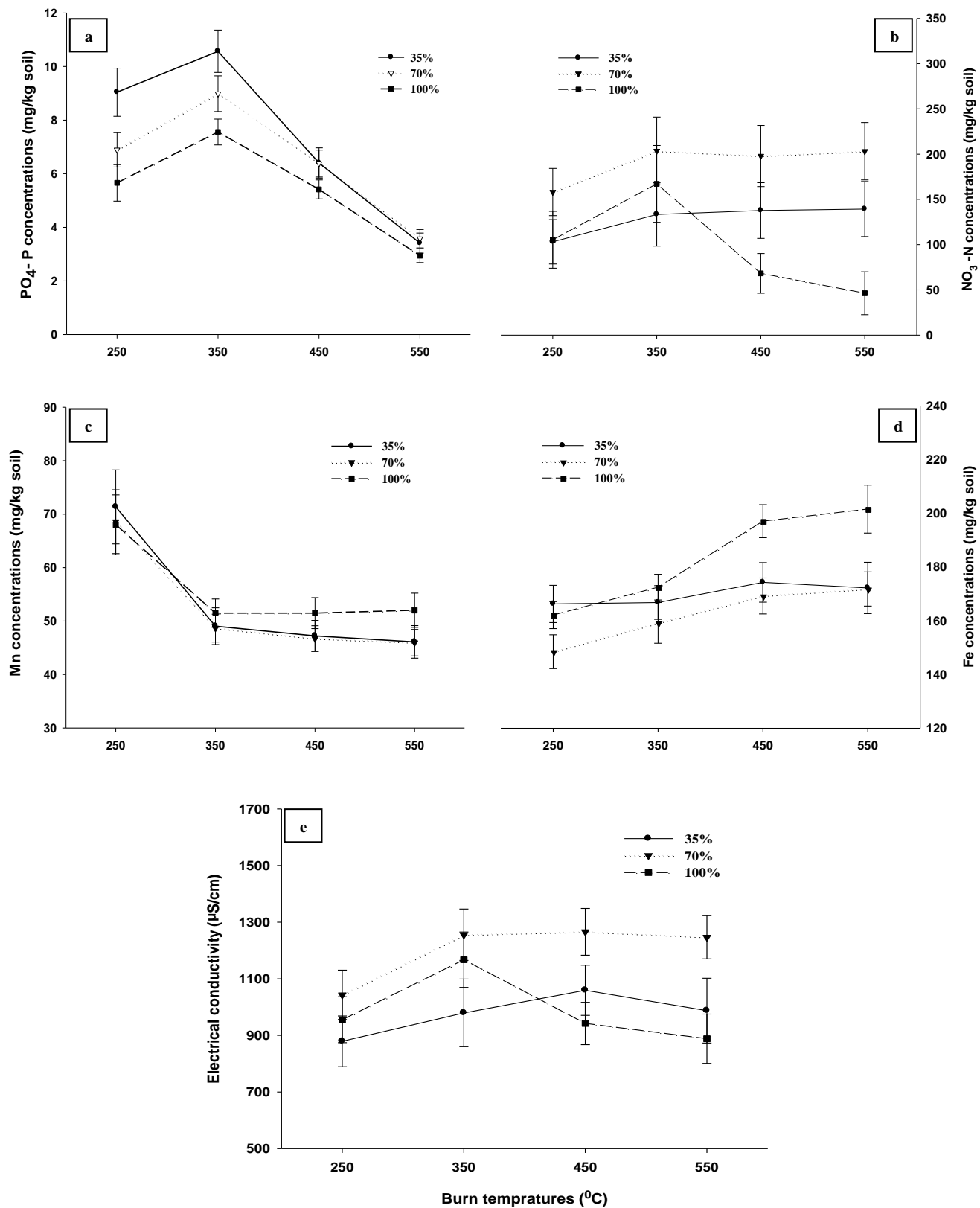


Figure 3-6: The interaction of soil moisture and burn temperature on soil extractable nutrients: (a) PO₄-P, (b) NO₃-N, (c) Mn, (d) Fe, (e) EC

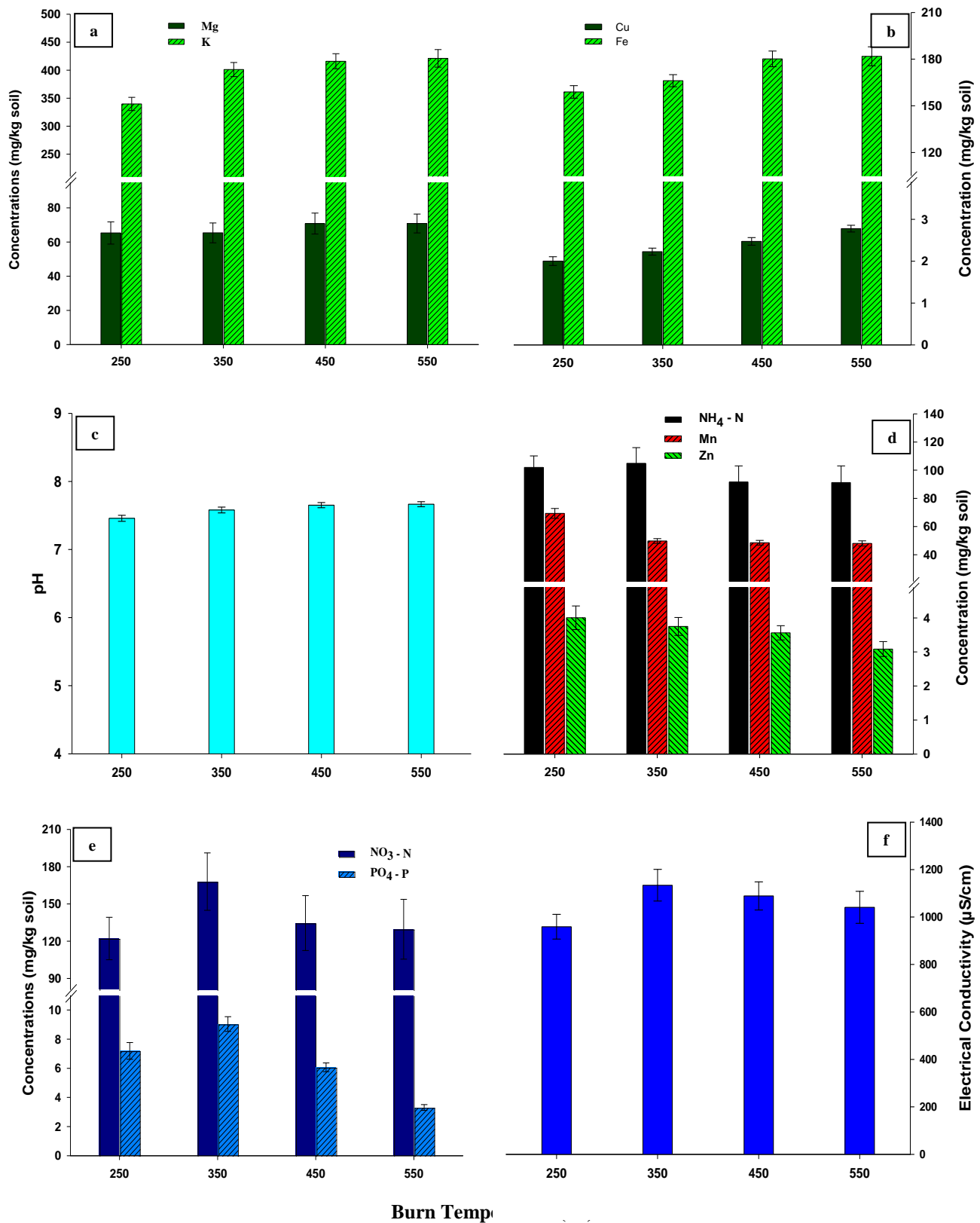


Figure 3-7: Effects of burn temperature on extractable concentration of soil nutrients: (a) Mg, K; (b) Fe, Cu; (c) pH; (d) NH₄-N, Mn, Zn; (e) PO₄-P, NO₃-N; and (f) EC

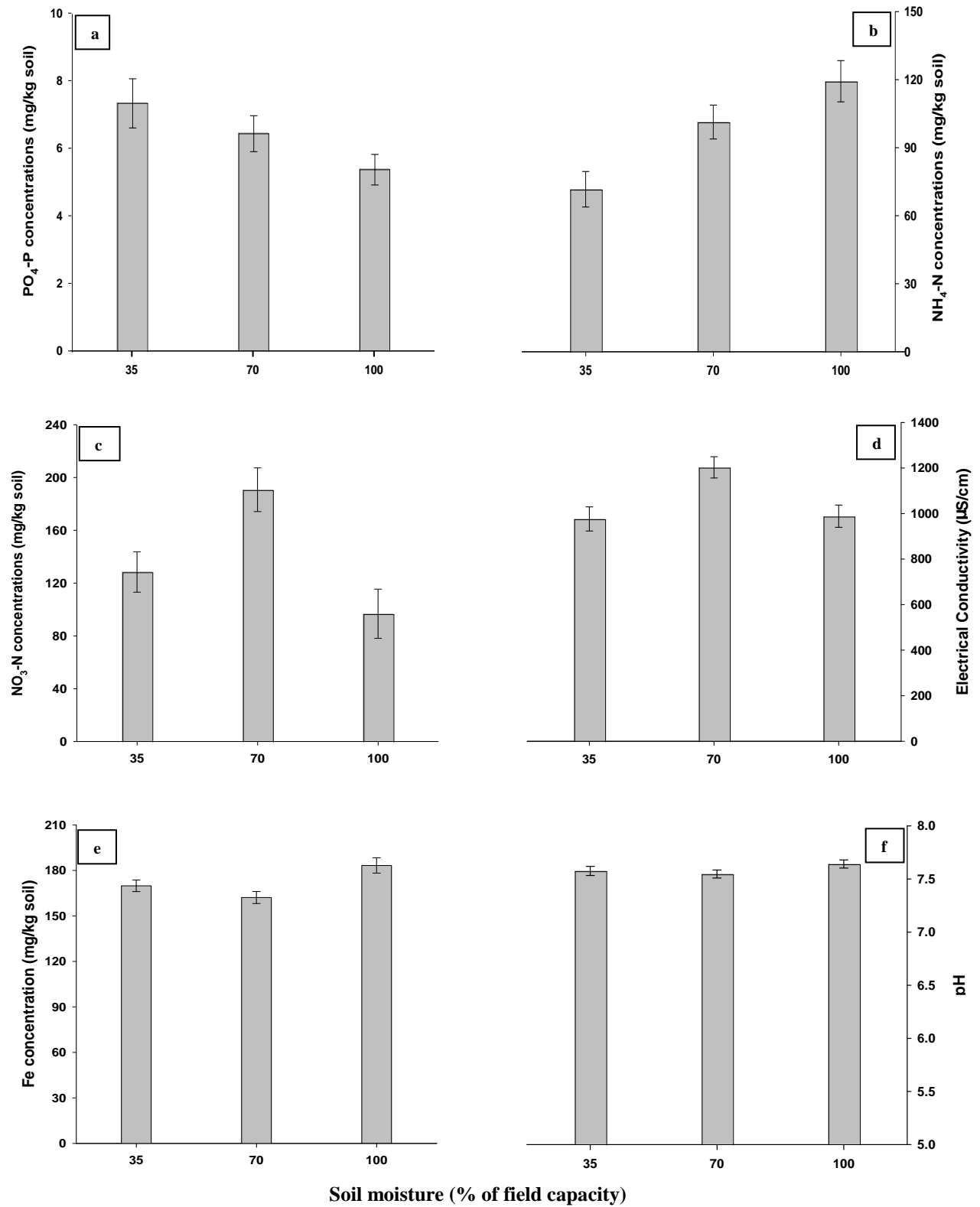


Figure 3-8: Effects of soil moisture on extractable concentrations of soil nutrients: (a) PO₄-P, (b) NH₄-N, (c) NO₃-N, (d) EC, (e) Fe, and (f) pH

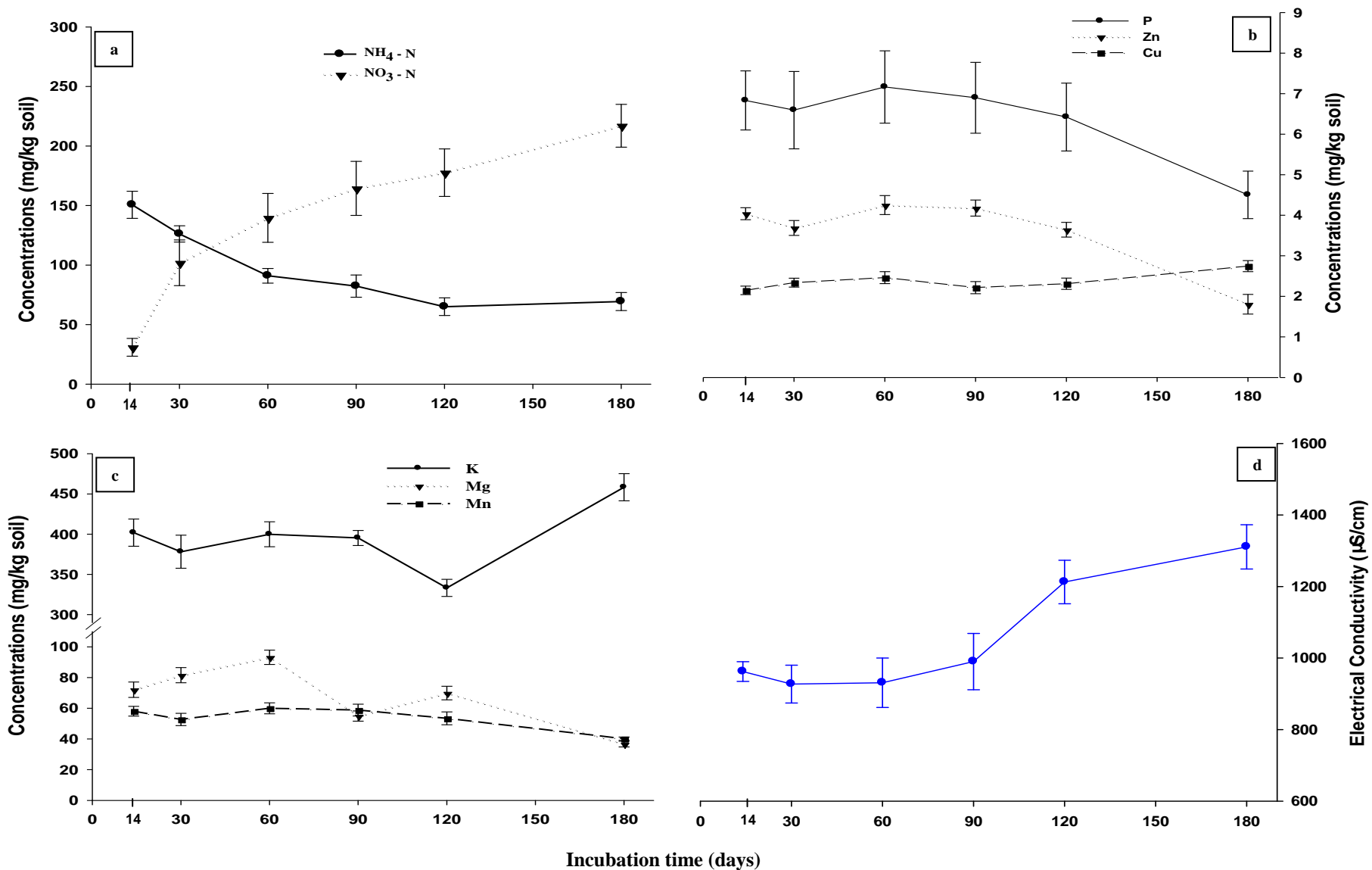


Figure 3-9: Effects of incubation time on extractable concentration of soil nutrients: (a) NH₄-N and NO₃-N; (b) PO₄-P, Zn, and Cu; (c) K, Mg, and Mn; and (d) EC

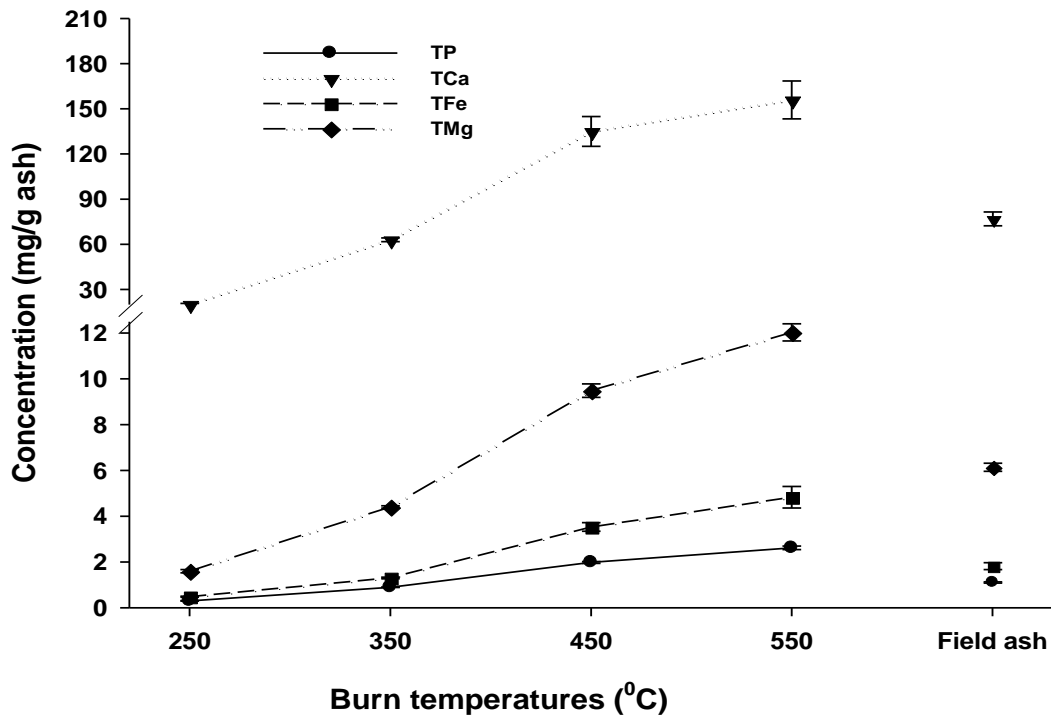


Figure 3-10: Concentrations of TP, TCa, TMg, and TFe in laboratory and field ashes

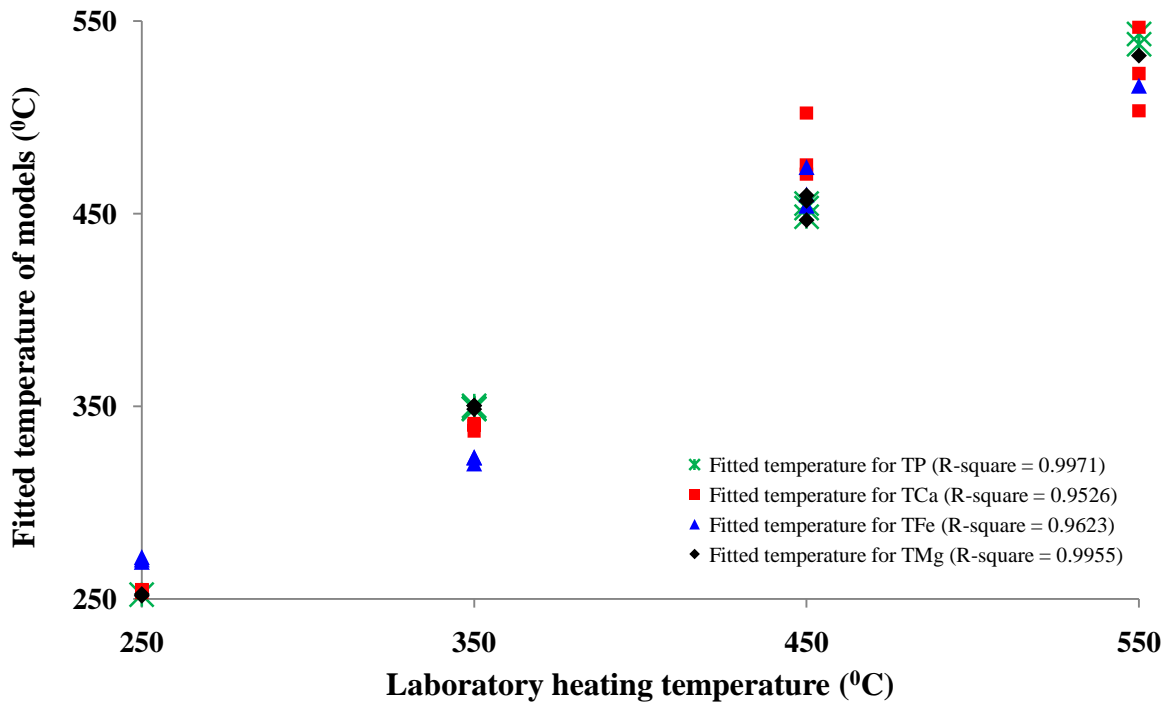


Figure 3-11: Goodness-of-fit models for fire-temperature prediction based on TP, TCa, TMg, and TFe in residual ash

CHAPTER 4

PREDICTING PHOSPHORUS AVAILABILITY IN CALCAREOUS SOILS UNDER THE PINE ROCKLAND FOREST AFTER A PRESCRIBED FIRE

Introduction

Phosphorous (P) is probably the second most limiting nutrient in natural forest ecosystems after nitrogen (N) (DeBano et al., 1998; Pierzynski et al., 2000). Common inorganic compounds of P in soils often fall into one of two following main groups: those containing calcium; and those containing iron and aluminum (Brady and Weil, 2002). Calcium-phosphate compounds become more soluble as soil pH decreases; hence, they tend to dissolve and disappear in acid soils. These compounds are quite stable and less insoluble at higher pH, and become dominant forms of P compounds present in neutral and alkaline soils. In contrast to calcium phosphates, hydroxyl phosphate minerals of iron and aluminum, strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), have very low solubility in strongly acid soils and become more soluble as soil pH rises. These minerals are unstable in alkaline soils, but they are predominant in acid soils. In both acid and alkali soils, therefore, phosphorus tends to undergo sequential reactions that produce P-containing compounds of lower solubility and less bioavailability for plant uptake. Moreover, phosphate minerals, as means of reducing P bio-availability in soils, are described in more detail by Pierzynski et al. (2005).

Orthophosphate which consist of H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} is a bioavailable P form in soil solution. The presence of these ions in soil solution is a function of soil pH (Brady and Weil, 2002). H_2PO_4^- and HPO_4^{2-} are two dominant P species in most natural forest soils. Species of H_2PO_4^- are predominant in soils with neutral pH ranging from 4 to 7.2, whereas HPO_4^{2-} is dominantly present in soils with pH greater than 7.2 (Pierzynski et al., 2005).

Fire often produces a substantial amount of P for soils not only by providing

orthophosphate ions from ash residual deposit during a fire but also converting soil organic P compounds into orthophosphate as well (Cade-Menun et al., 2002; Certini, 2005; Sharpley and Moyer, 2000). Ashes released from fuel combustion contain a large amount of orthophosphate (Khanna et al., 1994; Durgin and Vogelsang, 1984) resulting in an increase of P bioavailable contents in acidic soils (Giardina et al., 2000; Knoepp et al. 2005; Serrasolsas, 1995b) and in calcareous soils (Ubeda et al., 2005; Hernandez et al., 1997). Quality and quantity of orthophosphate in residual ashes depend wholly on fire intensity during a fire. Romanya et al. (1994) pointed out that content of soil extractable P after the fire was higher than its pre-fire level.

Surface reactions and precipitation are two main mechanisms responding immediately to the fate of orthophosphate ions in calcareous soils after a fire (von Wandruszka, 2006). Main products of surface reactions are dicalcium phosphate (DCP) and octacalcium phosphate (OCP). In calcareous soils, calcium carbonate (calcite) plays an essential role in P retention when concentration of P is relatively high in soil solution, but non-carbonate clays are important to retention of P at lower P concentration (von Wandruszka, 2006; Zhou and Li, 2001). Afif et al. (1993) found that P availability in calcareous soils is negatively correlated to the amount of lime, whereas Castro and Torrent (1994) indicated that P retention increased with the ratio of Fe oxides to CaCO_3 . Hamad et al. (1992) reported that 1.6 % of a coating rate between Fe_2O_3 and calcite increased P retention by 9-fold. By comparing a relative importance of surface reaction and precipitation in P retention, Tunesi et al. (1999) concluded that precipitation was a dominant mechanism in reduction of P availability in soils with high exchangeable cations.

Precipitation of phosphorus can be defined as a formation of discrete, insoluble P compounds in soils, and can be viewed as a reverse of mineral dissolution. With a high pH in calcareous soils, P binds to Ca/Mg-minerals or precipitates as discrete Ca/Mg-phosphate (Brady

and Weil, 2002; Knoepp et al., 2005). Abundance of soluble Ca ions controls activities of inorganic P ions in soil solution after a fire resulting in formation of dicalcium phosphate dehydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) which later reverts to others more stable Ca phosphates such as octacalcium phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), then hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{-}(\text{OH})$), and finally transform into apatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$). Additionally, soil moisture content, which influences soil solution chemistry, also contributes considerably to availability of P after a fire. Under a field condition, soil water content often fluctuates with rainfall and air temperature. Fluctuations of soil moisture result in availability of nutrients in calcareous soils (Gahoonia et al., 1994; Misra and Tyler, 1999). Calcareous soils are generally characterized by high contents of calcite (CaCO_3) and bicarbonate ions (HCO_3^-). Increasing soil moisture causes an increase in concentrations of soil solution HCO_3^- ions (Inskeep and Bloom, 1986; Mengel et al., 1984).

A soil moisture curve is a useful tool in determining hydraulic properties of an unsaturated soil. It describes a relationship between soil water content (θ) and soil water potential (ψ), and is often utilized to predict soil-water storage and plant-water supply, especially effectively determining soil field capacity and wilting point of a given soil. Water holding capacity of soil is dependent on soil porosity and nature of bonding in soils; therefore, soil moisture curve is specific to different types of soils, and depends on soil texture and structure, organic matter content, and composition of solution phase (Muñoz-Carpena et al., 2002; Pham and Fredlund, 2008). Although shape of a water retention curve can be characterized by several models, the Mualem-van Genuchten model is known as fitting well in different soils (Schaap and van Genuchten, 2006).

Availability of P in calcareous soils depends on persistence of metastable calcium-phosphate minerals (Fixen et al., 1983). By continuously applying fertilizers in two different calcareous soils in Colorado through three years, Fixen et al. (1983) proved that solubility of P was

controlled by octacalcium phosphate (OCP) if concentration of Olsen-P exceeded 35 mg/kg soil, whereas in a range of 10 to 25 mg Olsen-P/kg soil, tricalcium phosphate (TCP) inhibited solubility of P. In calcareous soils, transformation of Ca-P minerals derives from monocalcium phosphate (MCP) to hydroxyl apatite (HA); therefore, a solubility order of Ca-P minerals are MCP > dicalcium phosphate dihydrate (DCPD) > TCP > HA (Brady and Weil, 2002, p. 612; Pierzynski, et al., 2005). However, kinetics of Ca-P transformation could be influenced by several factors. Transformation of DCPD to OCP can slow with the presence of magnesium (Bell and Black, 1970), and decreases with the existence of soluble organic matter (Moreno et al., 1960).

The Pine Rockland soils have a low content of carbonate clay and a high content of non-carbonate clay. According to the classification of a USDA soil survey in 1958, the pineland Rockdale soil contained approximately 96% of non carbonate clay and 4% of carbonate clay. Zhou and Li (2001) quantified that the Pine Rockland soil contained the total clay of approximately 730 g/kg soil in which the content of non-carbonate clay was 707 g/kg soil and the amount of carbonate clay was 23 g/kg soil. Because of relatively low clay content, clay minerals are not significant in adsorption of P, but precipitation among P with Ca and Mg is the dominant process affecting retention of P in calcareous soils in the Pine Rockland (Zhang et al., 2001). In addition, since available contents of Fe and Mn are rather high in calcareous soils in South Florida (Hanlon et al., 1996; Zinati et al., 2001), reactions between orthophosphate ions with dissolved Fe and Mn ions forming hydroxyl phosphate precipitates also control availability of P in the Pine Rockland's calcareous soils.

Identification of phosphate minerals as a result of weathering P bearing minerals in parent materials has been documented by previous studies (Lindsay et al., 1989; Karathanasis, 1991). A direct determination of naturally occurring phosphate minerals in calcareous soils under the Pine Rockland forests is generally very difficult because of the relatively low P content and complexity

of phosphate minerals. Minteq, a geochemical assessment tool for environment systems, applies equilibrium speciation models to simulate species of soil chemical components and their concentrations. A notable advantage of Minteq's geochemical models is the capability of determining a magnitude order of phosphate minerals controlling availability of P in soil solution (Allison et al., 1991). A phosphate solubility diagram, which is constructed from ionic activities simulated from Minteq's geochemical models, is an effective tool for depicting solubility of phosphate minerals in soil environments. The diagram is particularly useful for determining a relative stability of phosphate compounds and minerals in soils at various pH values. Not only is P equilibrium a function of pH in the diagram, but it also depends on the ionic activities of Ca^{2+} , Mg^{2+} , Mn^{2+} , and Fe^{2+} in soil solution (Karathanasis, 1991). In calcareous soils, phosphate-mineral solubility is mostly controlled by Ca/Mg-P minerals (Fixen et al., 1983; Zhang et al., 2001). Although Mn-P equilibrium relationships are often super-saturations with respect to MnHPO_4 and $\text{MnPO}_4 \cdot 1.5\text{H}_2\text{O}$, these minerals could also participate in controlling solubility of P in calcareous soils when soil solution concentration of P is very low (Karathanasis, 1991, Lindsay et al., 1989).

Effects of prescribed fire on vegetation in the Pine Rockland forest have been well documented (Ross et al., 2003; Sah et al., 2004 and 2006; Snyder 1986; Snyder et al., 2005). Results of these studies showed that the fire regime, fuel loads, fire intensity, and burn season significantly impacted on the post-fire recovery of the understory vegetation, but were inconclusive for soil P dynamics. The main objective of this study was to predict a long-term impact of fire on P availability in calcareous soils under the Pine Rockland forest. Specific tasks included: 1) determining concentrations of P compounds following a fire using Minteq's equilibrium speciation program; 2) describing a relationship of soil pH and phosphate minerals to phosphate solubility after a fire by establishing stability diagrams of phosphorus; 3) modeling

a best-fit curve of soil water retention for Pine Rockland's calcareous soils; and 4) establishing a predictive model for prediction of P availability after a fire.

Materials and Methods

Simulation of Extractable Concentration of P compounds after the Fire

Results from the field burning experiment as described in Chapter 2 were utilized to simulate concentrations of P compounds and construct stability diagrams of phosphorus after the fire. Table 4-1 presented soil chemical components used to characterize P compounds and their extractable concentrations in soil solution after the fire using the Minteq's equilibrium speciation model. These components comprised soil pH, ionic strength (IS), and concentrations of extracted $\text{PO}_4\text{-P}$, Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Fe^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. Aluminum was excluded because of its low concentration in high pH. Ionic strength (IS) was estimated from electrical conductivity (EC) using Marion-Babcock equation: $\text{Log (IS)} = 1.159 + \text{Log (EC)}$, where IS is in unit of mol/m^3 , and EC is in dS/m or mS/cm (Essington, 2004).

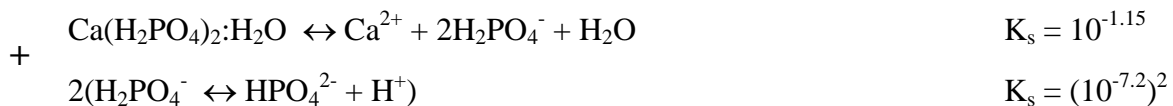
The simulation process was carried out three primary steps including (i) specification of CO_2 partial pressure; (ii) specification of possible solid species included into the speciation models; and (iii) input of extracted concentrations of solution components. The atmospheric CO_2 partial pressure was at 0.00038 atm or -3.42 for a logarithm of CO_2 partial pressure, which is recommended by Minteq's speciation model. This pressure is the most suitable in equilibrium between calcite and CO_2 (gas) at high soil pH, especially in calcareous soils. The possible solid species were tricalcium-phosphate ($\text{Ca}_3(\text{PO}_4)_2$ - am1, am1, beta), octocalcium-phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$), monetite (CaHPO_4); dicalcium-phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3), hydroxyapatite, $\text{Mg}_3(\text{PO}_4)_2$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mn}_3(\text{PO}_4)_2$, MnHPO_4 , strengite, and vivianite, which could be involved in a speciation of P compounds and in controlling

availability of P as well. The extracted solution components, as described in Table 4-1, were cations and anions in soil solution participating directly to speciation processes. The initial input for the speciation process is displayed in Appendix J.

A total of forty-five data collectives for each solution components were input into Minteq's speciation model. All simulation processes were carried out at 25⁰C, the average temperature in the Everglades National Park over 30 years. Extractable concentrations of P compounds were computed by basing on their percentage distributions with respect to the extracted P contents, which resulted from the equilibrium speciation model. Additionally, ionic activities of soil solution components and saturation indices of Ca/Mg/Mn/Fe-P minerals were obtained from results of the speciation process.

Construction of Stability Diagrams of Phosphorus after the Fire

Table 4-2 presented relevant information for eleven phosphate minerals and two orthophosphate ions that are potential in calcareous soils. Equilibrium reactions and solubility product constants of Ca-P minerals were obtained from Pierzynski et al. (2005), whereas those of other minerals were received from the Minteq geochemical program. Relationships among the activity of HPO₄²⁻ with activities of H⁺, Ca²⁺, Mg²⁺, Fe²⁺, and Mn²⁺ for the selected minerals were established basing on equilibrium reactions and solubility product constants. Calculations of these relationships are fully described in Appendix K. The following example showed steps how to compute a relationship between activities of HPO₄²⁻ and Ca²⁺ for the monocalcium-P mineral.



$$K_s = 10^{-15.55} = \frac{(\text{Ca}^{2+})(\text{HPO}_4^{2-})^2(\text{H}^+)^2(\text{H}_2\text{O})}{(\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O})}$$

$$\leftrightarrow -15.55 = \log(\text{Ca}^{2+}) + 2\log(\text{HPO}_4^{2-}) + 2\log(\text{H}^+)$$

$$\leftrightarrow 15.55 = \text{pCa}^{2+} + 2\text{pHPO}_4^{2-} + 2\text{pH}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 7.775 - 0.5\text{pCa}^{2+} - \text{pH}$$

Stability diagrams of phosphorus plotted between pHPO_4^{2-} versus pH with presence of the selected phosphate minerals were constructed using average values of ionic activities of HPO_4^{2-} , Ca^{2+} , Fe^{2+} , Mg^{2+} , and Mn^{2+} in soil solution following the fire. These ionic activities used to develop the diagrams were obtained from Minteq's equilibrium speciation process. In addition, a correlation matrix among $\text{pH} + \text{pHPO}_4^{2-}$, $\text{pH} - 1/2\text{pFe}^{2+}$, $\text{pH} - 1/2\text{pMn}^{2+}$, $\text{pH} - 1/2\text{pCa}^{2+}$, and $\text{pH} - 1/2\text{pMg}^{2+}$ was also considered to determine a further relationship among pH and activity of HPO_4^{2-} with ionic activities of Ca^{2+} , Mg^{2+} , Fe^{2+} , and Mn^{2+} in soil solution.

Soil Moisture Curve for the Pine Rockland Soils

Determination of the soil moisture curve for the Pine Rockland soil was conducted in the laboratory. The Tempe cell and Richard plate methods were used to measure water amount in soils at different suctions. Fourteen different pressures (suctions), which included 0, 0.49, 0.98, 1.47, 2.45, 3.43, 4.90, 6.67, 14.71, 29.41, 58.82, 98.04, 500, and 800 kPa, were applied for determination of soil moisture curve. A Tempe-cell method was applied at lower suctions (less than 100 kPa), whereas a Richard-plate method was used at higher suction (higher than 100 kPa). The soil moisture curve was fitted by the Retention curve (Retc) model based on volumetric water content (the amount of water per cubic unit of soil) and soil suction or matrix potential (the amount of water held by capillarity against gravity force) (Muñoz-Carpena et al., 2006; vanGenuchten et al., 1991). Procedures for a measurement of the volumetric water content in the laboratory are described in Appendix L.

The shape and equation of the soil-water retention curve which were fitted by the Retention curve (Retc) model was mainly characterized by the Mualem –van Genuchten equation:

$$\theta(\psi) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha|\psi|)^n]^{1-1/n}}, \text{ Where } \theta(\psi) \text{ is a water retention curve (L}^3/\text{L}^3), |\psi| \text{ is}$$

suction pressure (cm of water), θ_s is saturated water content (L^3/L^3), and θ_r is residual water content, α is related to inverse of air entry suction, and n is a measure of pore-size distribution (vanGenuchten et al., 1991). Initial characterization of soil for the Retc model was a sandy loam (Al-Yahyai et al., 2006). Hydraulic properties of an unsaturated soil in the Retc model were based on the modified Mualem-van Genuchten formulation as described by Schaap and vanGenuchten (2005). The observed water content from the laboratory experiment and the fitted water content from the model are presented in Appendix M, and results and parameters used to fit the water retention curve are shown in Appendix N.

A goodness-of-fit of model was examined by three different methods: (i) coefficient of determination; (ii) coefficient of efficiency; and (iii) index of agreement (Legates and McCabe, 1999; Krause et al., 2005). Coefficient of determination (R^2) is defined as a square of a Pearson's correlation coefficient, and expresses a proportion of a total variance in the observation data which can be explained by the model. Coefficient of determination was obtained from a linear regression between the observational data (O) and the fitted data (P). Coefficient of efficiency (E) is a ratio of a mean square error to variance in observation data, subtracted from unity

(Legates and McCabe, 1999), and expressed as: $E = 1.0 - \frac{\sum_{i=1}^N (O_i - P_i)^2}{\sum_{i=1}^N (O_i - \bar{O})^2}$, where \bar{O} is an

observational mean. Index of agreement (d) represents a ratio of a mean square error and

potential error (Krause et al., 2005), and is described as: $d = 1 - \frac{\sum_{i=1}^N (O_i - P_i)^2}{\sum_{i=1}^N (|P_i - \bar{O}| + |O_i - \bar{O}|)^2}$. Higher

values of R^2 , d , and E indicate a better agreement of model.

Modeling for Prediction of P Availability after the Fire

Data received from results of the laboratory simulation experiment in Chapter 3 were

used to establish a predictive model for prediction of P availability after a fire. Data set of the soil moisture content (35, 70, 100% of field capacity), the burn temperature of fuel loads or fire intensity (250, 350, 450, 550⁰C) and the incubation time or time after burn (14, 30, 60, 90, 120, and 180 days) were utilized to develop a multiple regression model for evaluating a long-term effect of fire on P availability. Extractable P concentration was assigned as a response variable, whereas predictors (independent variables) consisted of soil moisture content, burn temperature, and incubation time. The method of a stepwise, multiple regression analysis using PROC GLM procedures (SAS Institute Inc., Cary, North Carolina) were applied for fitting the predictive models of P availability. Fitting of the regression models was based on a combination of orders (1st, 2nd, 3rd), two-way and three-way interactions among three selected predictors.

A full regression model of each combination was fitted to determine significant components to be included the model. A reduced model would be considered if there was any component in the full model that was not significant. The reduced model was fitted by only significant components in a full model. Insignificant components were determined by F-values and $Pr > |F|$ of each component at $\alpha = 0.05$ in the fitted models. If an intercept was not significantly important in the full model, a full model without the intercept was also fitted. Selection criteria for choosing the best model to predict availability of phosphorus after a fire was based on a model having a highest R-square value, and lowest values of variation coefficient and root MSE (mean standard error). Results of fitting of multiple regression models were enclosed in Appendix O. In addition, three basic assumptions of multiple regression analysis regarding to constant variance, normality of errors, and independence of errors were examined to validate a selected predictive model. A plot of predicted values versus residuals was performed to check homogeneity of variance for the selected model. A NPP plot, which is a normal

probability plot of residuals, was used to detect non-normality of errors. Independence of errors was checked by a Durbin-Watson test statistic (Appendix P). The selected predictive model was further evaluated by analysis of goodness-of-fit measures. The goodness-of-fit measures for the selected model was assessed by three various methods as described in the previous section.

In efforts to verify the selected model, a field-burning experiment was carried out on the Pine Rockland forest at the Tropical Research and Education Center (TREC), University of Florida, Homestead, FL. A 5-acre plot of Pine Rockland forest was burned on May 5th, 2010. Post-fire ash production was collected immediately after the fire to analyze contents of TN and TC in the ashes. Post-fire soil samples were collected at 7, 14, 21, 30, 60, and 90 days with 20 replicates for each sampling time in order to measure extractable P concentrations. Moreover, a rain-gauge was also installed into the burned location to record precipitation after the fire. Contents of ash TN and TC were used to estimate a field-fire temperature (Qian et al., 2009b), whereas rainfall data recorded from rain-gauge was used to estimate soil moisture content following the fire.

The fire temperature of the TREC's Pine Rockland burning experiment was estimated by contents of TN and TC in ashes (Qian et al., 2009b) and a linear regression relationship between contents of TN and TC and heating temperatures of the laboratory incubation experiment described in Chapter 3. The soil moisture contents in 0-5cm topsoil at the sampling periods after the fire were computed from differences of water amounts between precipitation recorded from the rain-gauge and evapotranspiration (ET) obtained from the website of the Florida Automated Weather Network (FAWN) at TREC (FAWN, 2011). The soil moisture content was calculated from a daily rain event. If the water amount of the daily rain event is higher than the water amount of soil field capacity estimated from the soil retention curve, water amount at the field capacity was counted for that day. Detailed information of calculation of soil moistures is described in Appendix Q.

Statistical Analysis

Significant differences on concentrations of P compounds and ionic activities of solution components following the fire were examined by the Repeated Measures method as described in Chapter 2. The method of Tukey's multiple comparison was used to evaluate a significant difference of extractable concentrations of P compounds following the fire. Additionally, a regression correlation matrix among activities of solution nutrient elements and among $\text{pH} + \text{pHPO}_4^{2-}$, $\text{pH} - 1/2\text{pFe}^{2+}$, $\text{pH} - 1/2\text{pMn}^{2+}$, $\text{pH} - 1/2\text{pCa}^{2+}$, and $\text{pH} - 1/2\text{pMg}^{2+}$ using the method of principle components in the multivariate analysis were performed to check correlation relationship among them in soil solution.

Results and Discussion

Phosphorus Speciation after the Fire

Minteq program showed fifteen different P compounds in which nine P species exhibited dominantly in the calcareous soils including two orthophosphate species of HPO_4^{2-} and H_2PO_4^- , and seven other species of FeHPO_4 (aq), MgHPO_4 (aq), CaHPO_4 (aq), MnHPO_4 (aq), $\text{FeH}_2\text{PO}_4^+$, $\text{CaH}_2\text{PO}_4^+$, and CaPO_4^- . Simulation concentrations of these species were significantly different after the fire, except $\text{FeH}_2\text{PO}_4^+$ ($p = 0.1756$) (Table 4-3). Extractable concentrations of HPO_4^{2-} , H_2PO_4^- , and ortho-phosphate simulated from the Minteq were shown in Figure 4-1. Contents of HPO_4^{2-} following the fire, which were always much higher than those of H_2PO_4^- , largely fluctuated with changes of extractable P content; whereas the concentration of H_2PO_4^- was less varied along with extractable P concentration. The concentration of HPO_4^{2-} was 0.23 mg/kg soil for pre-burn significantly increased to 0.72 mg/kg soil at 14 days after the fire, and returned to its pre-burn value in 30 days. Especially, content of HPO_4^{2-} , 0.073 mg/kg soil, significantly reduced in 90 days which was closely to content of H_2PO_4^- . Orthophosphate content, which is defined as

a sum of HPO_4^{2-} and H_2PO_4^- , also varied the same pattern as extractable P content.

Table 4-3 presented the average concentrations and results of the multiple comparisons of P compounds associated with Ca, Mg, Fe, and Mn following the fire. Most of these species were significantly increased in 14 days and decreased to their pre-fire values in 30 days; however concentration of $\text{CaH}_2\text{PO}_4^+$ only significantly reduced in 90 days, and returned back its initial value in 180 days after the fire. Among these species, FeHPO_4 (aq) and CaHPO_4 (aq) were two predominant compounds of P in soils with pre-burn contents of 1.57 mg/kg soil for FeHPO_4 (aq) and 1.44 mg/kg soil for CaHPO_4 (aq). Although the pre-burn concentration of MnHPO_4 (aq) was 0.4 mg/kg soil, it reached to 3.68 mg/kg soil in 14 days which was the highest content compared to the content of other P compounds at this time.

The fire significantly impacted on contents of orthophosphate and primary P compounds associated with Ca, Mg, Fe, and Mn. Although both HPO_4^{2-} and H_2PO_4^- exist in the soils, species of HPO_4^{2-} is dominant in the soil solution. This result was suitable with the Pine Rockland calcareous soils having soil pH greater than 7.2 (Pierzynski et al., 2005). Obviously, the deposit of ash production contributed to increasing in the concentrations of orthophosphate and other P compounds, resulting in rising in the extractable P content in 14 days after the fire (Hernandez et al., 1997). In contrast, a rapid development of understory plant communities which demanded a large amount of orthophosphate in the soil solution caused a dramatic reduction of HPO_4^{2-} and H_2PO_4^- contents in post-fire 90 days.

Soil Solution Chemistry after the Fire

Ionic activities of nutrient elements in soil solution following the fire were obtained from Minteq's speciation program. Results of ANOVA analysis and average ionic activities of these elements are shown in Table 4-4, where "p" is notated for a negative logarithm of ionic activities

of nutrient elements. Results showed that the fire significantly affected the activities of nutrient elements, excluding pZn^{2+} ($p = 0.1043$). Fire significantly increased the ionic activities of Mg^{2+} , K^+ , Mn^{2+} , and NH_4^+ in post-fire 14 days and activity of NO_3^- in post-fire 180 days, but significantly decreased the activities of Cu^{2+} , HPO_4^{2-} , and $H_2PO_4^-$ in 14 days after the fire. The activities of Ca^{2+} and Fe^{2+} fluctuated with time as a consequence of seasonal variations. Ionic activities of nutrient elements in soil solution highly correlated with their extracted concentrations. Significant changes of the activities of these elements almost occurred concurrently the same time as those of their extracted contents. The results showed that the activity of P was very low in the soil solution (around 10 for $pHPO_4^{2-}$ and 10.5 for $pH_2PO_4^-$, respectively). In contrast, activities of Ca^{2+} ($pCa^{2+} \sim 1.75$), Mg^{2+} ($pMg^{2+} \sim 2.95$), Fe^{2+} ($pFe^{2+} \sim 2.7$), and Mn^{2+} ($pMn^{2+} \sim 3.24$) were very high. This result indicated that the activity of P in soil solution of the Pine Rockland calcareous soils was strongly controlled by not only solubility of Ca/Mg-phosphate minerals but also solubility of iron- and manganese-phosphate minerals.

Table 4-5 showed a correlation matrix among ionic activities of the nutrient elements in the soil solution. Coefficients of a regression correlation among the ionic activities were similar to results reported by Zhang et al. (2001), which had a negative correlation among pH with activities of Ca^{2+} , Mg^{2+} , Mn^{2+} , and K^+ , and a positive correlation among pH with activities of Fe^{2+} and phosphate ionic species. Soil solution pH was highly correlated with pCu^{2+} , $pHPO_4^{2-}$, and $pH_2PO_4^-$ (0.931, 0.620, and 0.871, respectively). The positive correlation between pH and pFe^{2+} (0.279) and the negative correlations among pH with pCa^{2+} (-0.062), pMg^{2+} (-0.356), and pMn^{2+} (-0.445) indicated that increasing in soil pH reduces the activity of Fe^{2+} and raises the activities of Ca^{2+} , Mg^{2+} , and Mn^{2+} . $pHPO_4^{2-}$, which are the dominant phosphate ionic species in the Pine Rockland calcareous soils, positively correlated with pCa^{2+} (0.342) and pH, but negatively correlated with

$p\text{Mg}^{2+}$ (-0.185), $p\text{Fe}^{2+}$ (-0.427), and $p\text{Mn}^{2+}$ (-0.645). This result suggests that changes in phosphate are controlled by calcium-phosphate minerals if the pH is raised (Zhang et al., 2001). Furthermore, a higher correlation between $p\text{Mn}^{2+}$ and $p\text{HPO}_4^{2-}$ than those among $p\text{Ca}^{2+}$, $p\text{Mg}^{2+}$, and $p\text{Fe}^{2+}$ with $p\text{HPO}_4^{2-}$ demonstrated that manganese has the most magnitude on solubility of phosphate ionic species in the soil solution of the Pine Rockland forest.

Phosphate Phase Equilibria after the Fire

Initial solubility relationships between the activity of HPO_4^{2-} and the activities of Ca^{2+} , Fe^{2+} , Mg^{2+} , and Mn^{2+} for the selected Ca/Mg/Fe/Mn- P minerals are presented in Table 4-6. The activity of HPO_4^{2-} in the soil solution controlled by minerals of monocalcium-P, tricalcium-P (beta), octacalcium-P, hydroxyapatite, vivianite, $\text{Mg}_3(\text{PO}_4)_2$, and $\text{Mn}_3(\text{PO}_4)_2$ was dependent on soil pH; whereas relationships among activity of HPO_4^{2-} with monetite, dicalcium dihydrate -P, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, and MnHPO_4 were independent on soil pH. A high regression correlation between $p\text{HPO}_4^{2-}$ and pH revealed that P equilibrium in soils was a function of soil pH. Additionally, solution parameters including Ca, Mg, Fe, and Mn could play a significant role in controlling P solubility in soil (Karathanasis, 1991) because they are exemplified by the strong regression relationships among $\text{pH} + p\text{HPO}_4^{2-}$ with $\text{pH} - 1/2p\text{Fe}^{2+}$ (0.954), $\text{pH} - 1/2p\text{Mn}^{2+}$ (0.898), $\text{pH} - 1/2p\text{Ca}^{2+}$ (0.819), and $\text{pH} - 1/2p\text{Mg}^{2+}$ (0.758) (Table 4-7).

Solubility diagrams are particularly useful for determining a relative stability of phosphate compounds and minerals in soils at different pH values (Essington, 2004). Figures 4-2, 4-3, 4-4, 4-5, and 4-6 showed compositions in the soil solution with relation to a stability of phosphate minerals in calcareous soils of the Pine Rockland in pre-burn, and in 14, 30, 90, and 180 days after the fire. These stability diagrams expressed a relationship between $p\text{HPO}_4^{2-}$ versus pH with presence of the selected phosphate minerals. Monocalcium-P mineral disappeared from

diagrams because it doesn't exist in the soil solution with the high soil pH. These diagrams were developed using the activities of Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , HPO_4^{2-} , and pH as reported in Table 4-4. Red diamond points on the diagrams displayed solubility of P relating to the phosphate minerals. The point plotted above a mineral solubility isotherm indicated that solubility of P was supersaturated with respect to the given mineral, and solution conditions could form stable or meta-stable states of the given mineral. The point plotted below a solubility isotherm of a certain mineral described that P solubility was under-saturated relative to the given mineral. The point plotted on or very near a solubility line of a certain mineral showed that P solubility was in equilibrium with the given mineral.

Generally, solubility of P was under-saturated with Ca/Mg-P minerals including monetite, DCPD, TCP, OCP, HA, $\text{Mg}_3(\text{PO}_4)_2$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{Mn}_3(\text{PO}_4)_2$. The fire shifted solubility of P in equilibrium between vivianite and MnHPO_4 . Pre-burn solubility of P was in equilibrium with vivianite and under-saturated with MnHPO_4 (Figure 4-2), but the soil solution was in equilibrium with MnHPO_4 and under-saturated with vivianite in post-fire 14 days (Figure 4-3). Particularly, there was a shift between two minerals of $\text{Mn}_3(\text{PO}_4)_2$ and $\text{Mg}_2(\text{PO}_4)_2$ in 14 days after the fire. The solution was in equilibrium with both vivianite and MnHPO_4 in 30 days after the fire (Figure 4-4). Although solubility of P returned to its pre-burn state in 90 days after the fire (Figure 4-5), the diagram of P solubility in post-fire 180 days was exactly the same as that in pre-burn condition (Figure 4-6). The role of Mn and Fe on P solubility seemed to be important in the Pine Rockland calcareous soils, where there is a very low P concentration and high soil pH. Increases in the activities of HPO_4^{2-} after the fire promoting to form precipitates between P with Mn^{2+} and Fe^{2+} resulted in shifting the equilibrium between vivianite and MnHPO_4 . This was similar to the result of Zhang et al. (2001), where MnHPO_4 in the soil

solution was closely in equilibrium without the application of fertilizers, and saturated after applying fertilizers. Precipitations between P with Ca and Mg to form Ca-P and Mg-P minerals were not likely to occur after the fire because the solubility points of P always fell below the solubility lines of Ca- and Mg-P minerals.

The pattern of the stability diagrams was similar to results of previous studies (Fixen et al., 1982; Karathanasis, 1991; Zhang et al., 2001). The magnitude order controlling solubility of P as increasing in the activity of P in the soil solution included vivianite > MnHPO_4 > HA > TCP > OCP > Monetite > DCPD > $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ > $\text{Mg}_3(\text{PO}_4)_2$, > $\text{Mn}_3(\text{PO}_4)_2$. The magnitude was demonstrated by saturation indices (SI) of these minerals as shown in Table 4-8. These SI values were obtained from the Minteq's speciation program. Minteq does not have octacalcium-P mineral ($\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$), instead $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$; therefore, the saturation index of the octacalcium-P mineral was not presented in Table 4-8. The positive, negative, and zero values of SI indicated oversaturation, undersaturation, and equilibrium, respectively. A given mineral with a lower negative SI value has a higher priority to react with orthophosphate species in order to form precipitation. Equilibrium will shift to other mineral having a higher negative SI value after the given mineral reaches in equilibrium and becomes oversaturation.

Modeling a Soil-Water Characteristic Curve for the Pine Rockland forest

Soil-water characteristic curve represents a relationship between volumetric water content and matric suction. Parameters of the Retc model utilized to express soil-water characteristics of the Pine Rockland soils are presented in Table 4-9. The fitted values of the saturated water content (θ_s), the residual water content (θ_r), α , n, and m were 0.41, 0.07, 0.08, 1.89, and 0.87, respectively. Figure 4-7 showed the shape and equation of the fitted soil-water retention curve

with R-squared value of 0.9214. The relationship between the volumetric water content and the suction for the Pine Rockland soils was described by the following equation:

$$y = - 0.064\ln(x) + 0.6454, \text{ where } y \text{ is the volumetric water content (v/v); and } x \text{ is suction (kPa).}$$

The fitted parameters and shape of the curve were very similar to the results of Al-Yahyai et al. (2005) and Muñoz-Carpena et al. (2002), which described soil-water characteristics of Krome calcareous soil in the agricultural areas in the South Florida. However, there was a shifting of the volumetric water content. Al-Yahyai et al. (2005) and Muñoz-Carpena et al. (2002) showed that the volumetric water content (v/v) ranged from 0.15 to 0.50, whereas the volumetric water content in this study was from 0.22 to 0.66. This shift could be explained that the Pine Rockland forest soils contained more organic matters than the Krome very gravelly loam soil. Therefore, the Pine Rockland soils exhibited a higher water-holding capacity at low suction and a lower water-holding capacity at high suction than those of the calcareous rock-plowed soil (Krome soil). Effects of organic matter and bulk density on performance of the soil-water retention curve were documented by Cornelis et al. (2001). Stuffs of the Pine Rockland forest floor were accumulated for five years; hence, the Pine Rockland soils contained a high content of organic matter, approximately 46.6% which was not reported in this study. Bulk density of the repacked soil used for determination of the retention curve was 1.1 g cm^{-3} , which was in a range of from 1.0 to 1.4 g cm^{-3} for the rocky outcrop soils reported by USDA Soil Survey of Dade County (1996).

Evaluation of a goodness-of-fit measure was a useful criterion used to express how good between fitted data and observation data was (Al-Yahyai et al., 2006; Cornelis et al., 2001; Regalado et al., 2005). It can be observed from Figure 4-8 that there was a good relationship of regression correlation between the observed volumetric water content and the fitted volumetric water content with determination coefficient (R^2) of 99.4%. Moreover, coefficient of efficiency (E)

and index of agreement (d) were recognized very high, 0.994 for E and 0.998 for d (Table 4-9). It could be said that the Retention Curve model with the modified Mualem-van Genuchten formulation as described by Schaap and van-Genuchten (2005) performed very well with the sandy loam soils of the Pine Rockland forests.

Modeling for Prediction of P Availability after the Fire

Table 4-10 showed a meta-analysis and results of the stepwise, multiple regression analysis of the fitted models, where “*” denotes an interaction between two predictors and “x” shows components included in the models. Among twenty-four fitted models, the model 17 which included intercept, the 1st order of soil moisture and burning temperature, the 2nd order of time (days after a fire) and burning temperature, and the interactions between soil moisture and time and between soil moisture and burning temperature was selected for a predictive model of P availability after a fire. As shown in Table 4-10, the chosen model performed the most appropriate one, which had the highest determination coefficient of 0.8523, the lowest coefficient of variation (15.76%), and the smallest RMSE value (1.009). The relationship between extractable P content after a fire and predictors was formulated by the following equation:

$$\text{Extractable P content} = 3.38 - 27.19*M + 0.06579*T - 0.000143*D^2 - 0.000115*T^2 + 0.05008*M*D + 0.03983*M*T$$

where “M” is the soil moisture content (v/v); “T” is the fire temperature (°C); and “D” is the time or day after fire.

Issues accompanied with a multiple regression analysis are its initial assumptions. A normal probability plot having a straight line demonstrated that the developed model had a normality of errors. Although the vertical spread of residuals did not equally distribute in both sides of the zero line, there was no evidence for an inequality of variances for the chosen model. The expected value of Durbin-Watson (D) is approximately 2.0 for independence of errors, but an

acceptable range for D value is from 1.5 to 2.5. A critical value of D test statistic of the selected model was 1.41, which was very closely to the acceptable range. Therefore, the developed model basically met three initial assumptions of a multiple regression analysis.

Assessment of performance ability of a model is an important step in modeling. Relative error measure or “goodness-of-fit” is a statistical technique that is usually used to assess the simulation capacity of a model in reality. Correlation-based measure to evaluate an effectiveness of model is often oversensitivity to outliers that can lead to a bias toward extreme events (Legates and Davis, 1997). Goodness-of-fit measures for the developed model were investigated by three different statistical methods including coefficient of determination (R^2), coefficient of efficiency (E), and index of agreement (d) in order to give a better assessment of the predictive model. Correlation-based R^2 value of the predictive model was 0.8523 (Figure 4-9), whereas values of E and d were 0.8523 and 0.9588, respectively (not shown in this study).

A final goal of modeling is to obtain a good prediction of a developed model. Verification of model is to confirm a relative performance of a model with respect to observational data in the real world. It proves precision and accuracy of fit of a model (Oreskes et al., 1994). Based on a relationship of contents of TN and TC in ashes between the laboratory incubation experiment and the TREC’s field-burning experiment, an average fire temperature of the burning experiment at TREC’s Pine Rockland was 520°C (Table 4-11). Average volumetric water contents, observed P contents, and simulated P concentrations in six different times of sampling in the TREC’s burning experiment are shown in Table 4-12. By comparing simulation data with observation data, it was found that contents of simulated P agreed well with concentrations of measured P with R-square value of 0.8119 (Figure 4-10). Relatively high values of coefficients implied that the developed model fitted very well with observational data, and could perform a good simulation for available P

content following a fire. Comparison of agreement index (d) with E and R^2 revealed that a higher value of d was attributable to overcoming an insensitivity of E and R^2 to differences in the fitted and observed means and variances (Krause et al., 2005).

Conclusions

Phosphorus is the most limiting nutrient in the Pine Rockland ecosystem due to abundance of Ca and high contents of Mg, Fe, and Mn. Availability of P in this ecosystem is dependent on persistence of metastable Ca-P minerals and phosphate minerals of Mg, Fe, and Mn as well. Of sixteen P compounds resulted from simulation of Minteq's equilibrium speciation, HPO_4^{2-} , H_2PO_4^- , FeHPO_4 (aq), MgHPO_4 (aq), CaHPO_4 (aq), MnHPO_4 (aq), $\text{FeH}_2\text{PO}_4^+$, $\text{CaH}_2\text{PO}_4^+$, and CaPO_4^- were majority compounds of P in the soil solution of the Pine Rockland calcareous soils. The prescribed fire had a significant impact on contents of these P compounds in soil solution, except for $\text{FeH}_2\text{PO}_4^+$. HPO_4^{2-} were predominant species of orthophosphate in the Pine Rockland soils. Its contents fluctuated with extractable P concentrations following a fire, and significantly increased in 14 days after the fire.

The prescribed fire greatly impacted soil solution chemistry. It significantly increased ionic activities of Mg^{2+} , K^+ , Mn^{2+} , and NH_4^+ in post-fire 14 days and activity of NO_3^- in post-fire 180 days, but significantly decreased activities of Cu^{2+} , HPO_4^{2-} , and H_2PO_4^- in 14 days after the fire. Activities of Ca^{2+} and Fe^{2+} which was not influenced by fire fluctuated with time as a result of seasonal variations. Soil solution pH was highly correlated with pCu^{2+} , pHPO_4^{2-} , and pH_2PO_4^- . The positive correlation between pH and pFe^{2+} and the negative correlations among pH with pCa^{2+} , pMg^{2+} , and pMn^{2+} indicated that increasing in soil pH reduces the activity of Fe^{2+} and raises activities of Ca^{2+} , Mg^{2+} , and Mn^{2+} . Findings indicated that the activity of orthophosphate ions in the soil solution was mainly controlled by solubility of vivianite and MnHPO_4 minerals.

Solubility of P was generally under-saturated with Ca/Mg-P minerals. The prescribed fire shifted solubility of P in equilibrium between vivianite and MnHPO_4 . The magnitude order controlling solubility of P as an increase of P activity in the soil solution included vivianite > MnHPO_4 > HA > TCP > OCP > Monetite > DCPD > $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ > $\text{Mg}_3(\text{PO}_4)_2$, > $\text{Mn}_3(\text{PO}_4)_2$.

The soil-water characteristic curve of the Pine Rockland calcareous soils fitted very well with the modified Mualem-van Genuchten model. The relationship between volumetric water content and suction in the Pine Rockland soils was expressed by the equation as follows:

$y = -0.064 \ln(x) + 0.6454$, where y is a volumetric water content (v/v) and x is a suction (kPa). A

long-term effect of a fire on availability of P was modeled by results of simulation from the laboratory incubation experiment with three predictors of soil moisture, fire intensity, and time after the fire. Results of multiple regression analysis showed that the following predictive model could perform the best prediction for P availability following a fire:

$$\text{Extractable P content} = 3.38 - 27.19 * \mathbf{M} + 0.06579 * \mathbf{T} - 0.000143 * \mathbf{D}^2 - 0.000115 * \mathbf{T}^2 + 0.05008 * \mathbf{M} * \mathbf{D} + 0.03983 * \mathbf{M} * \mathbf{T}$$

Table 4-1: Average extracted concentration of soil nutrient elements, pH, and ionic strength after the fire used for Minteq's equilibrium speciation model

Days after fire	pH	EC (µS/cm)	IS [†] (mol/L)	mg/kg soil										
				PO ₄ -P	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Fe ²⁺	Mn ²⁺	Zn ²⁺	Cu ²⁺	NH ₄ ⁺	NO ₃ ⁻
0	7.55 ab [‡]	333 c	0.0048 c	4.2 b	1060 ab	52 b	165 bc	291 bc	178 ab	69 b	3.5 a	3.4 a	40.6 bc	8.1 b
14	7.82 a	698 a	0.0101 a	13.4 a	905 b	144 a	277 a	359 a	153 b	256 a	5.1 a	4.1 a	99.6 a	11.3 ab
30	7.48 b	544 ab	0.0078 ab	4.4 b	1035 ab	80 b	193 abc	358 ab	207 ab	89 b	5.4 a	3.1 a	53.6 b	2.4 b
90	7.45 b	370 bc	0.0053 bc	1.2 b	972 ab	40 b	188 abc	310 abc	170 ab	47 b	3.3 a	3.8 a	23.1 bc	5.2 b
180	7.56 ab	383 bc	0.0055 bc	4.0 b	1094 ab	54 b	236 ab	277 c	158 b	53 b	5.3 a	3.8 a	31.2 bc	25.1 a
270	7.48 b	348 bc	0.0050 bc	3.2 b	989 ab	56 b	122 c	301 abc	289 a	89 b	4.2 a	3.6 a	21.6 bc	8.5 b
360	7.57 ab	328 c	0.0047 c	4.6 b	1162 a	53 b	145 bc	278 c	173 ab	73 b	5.3 a	4.2 a	22.1 bc	2.6 b
450	7.72 ab	453 bc	0.0065 bc	2.7 b	1049 ab	62 b	160 bc	313 abc	197 ab	114 b	4.0 a	4.0 a	23.0 bc	2.7 b
540	7.58 ab	332 c	0.0048 c	3.0 b	972 ab	34 b	137 bc	307 abc	223 ab	59 b	2.4 a	3.8 a	11.4 c	10.5 b

[†]IS (Ionic strength) was calculated from EC (electrical conductivity) described by Marion-Babcock equation: $\text{Log (IS)} = 1.159 + \text{Log (EC)}$, where IS is in units of mol/m³, and EC is in dS/m or mS/cm (Essington, 2004).

[‡] Means followed by the same letter within the same column are not significant different

Table 4-2: Solubility product constants and stoichiometry of Ca/Mg/Fe/Mn-P minerals

Name	Stoichiometry	K _s
Monetite	$\text{CaHPO}_4 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{H}_2\text{PO}_4^-$	$10^{0.30}$
Monocalcium-P	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	$10^{-1.15}$
Dicalcium dihydrate-P	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O}$	$10^{0.63}$
Tricalcium-P (beta)	$\text{Ca}_3(\text{PO}_4)_2 \text{ (beta)} + 4\text{H}^+ \leftrightarrow 3\text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^-$	$10^{10.18}$
Octacalcium-P	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O} + 5\text{H}^+ \leftrightarrow 4\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + 2.5\text{H}_2\text{O}$	$10^{11.76}$
Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3\text{(OH)} + 7\text{H}^+ \leftrightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	$10^{14.46}$
Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \leftrightarrow 3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$	$10^{-37.76^\dagger}$
Mg ₃ (PO ₄) ₂	$\text{Mg}_3(\text{PO}_4)_2 \leftrightarrow 3\text{Mg}^{2+} + 2\text{PO}_4^{3-}$	$10^{-23.28^\dagger}$
MgHPO ₄ ·3H ₂ O	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \leftrightarrow \text{Mg}^{2+} + \text{PO}_4^{3-} + \text{H}^+ + 3\text{H}_2\text{O}$	$10^{-18.175^\dagger}$
Mn ₃ (PO ₄) ₂	$\text{Mn}_3(\text{PO}_4)_2 \leftrightarrow 3\text{Mn}^{2+} + 2\text{PO}_4^{3-}$	$10^{-23.827^\dagger}$
MnHPO ₄	$\text{MnHPO}_4 \leftrightarrow \text{Mn}^{2+} + \text{PO}_4^{3-} + \text{H}^+$	$10^{-25.4^\dagger}$
H ₂ PO ₄ ⁻	$\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+$	$10^{-7.2^\dagger}$
HPO ₄ ²⁻	$\text{HPO}_4^{2-} \leftrightarrow \text{H}^+ + \text{PO}_4^{3-}$	$10^{-12.35^\dagger}$

Source: Peirzynski et al. (2005); “†” from Minteq’s geochemical model; K_s is solubility product constant of minerals

Table 4-3: Results of ANOVA analysis and simulated concentrations of P compounds associated with Ca, Mg, Fe, and Mn after the fire

Days after fire	FeH ₂ PO ₄ ⁺	FeHPO ₄ (aq)	MgHPO ₄ (aq)	MnHPO ₄ (aq)	CaHPO ₄ (aq)	CaH ₂ PO ₄ ⁺	CaPO ₄ ⁻
	Results of ANOVA analysis						
	NS	***	***	***	***	*	***
Simulated concentration (mg kg ⁻¹ soil)							
0	0.096 a	1.57 b	0.17 b	0.40 b	1.44 bc	0.034 a	0.15 b
14	0.132 a	3.46 a	1.16 a	3.68 a	3.20 a	0.043 a	0.65 a
30	0.100 a	1.42 b	0.27 b	0.62 b	1.40 bc	0.037 a	0.14 b
90	0.031 a	0.43 b	0.05 b	0.09 b	0.45 c	0.012 b	0.04 b
180	0.072 a	1.20 b	0.20 b	0.29 b	1.59 bc	0.038 a	0.17 b
270	0.132 a	1.51 b	0.10 b	0.30 b	0.81 bc	0.026 a	0.07 b
360	0.087 a	1.49 b	0.20 b	0.43 b	1.74 b	0.039 a	0.20 b
450	0.043 a	0.93 b	0.12 b	0.38 b	0.85 bc	0.014 a	0.17 b
540	0.076 a	1.32 b	0.07 b	0.23 b	0.94 bc	0.021 a	0.11 b

“*”, “**”, “***”: Significant levels at α = 0.05, α = 0.01, and α = 0.001

Table 4-4: Results of ANOVA analysis and ionic activities of elements after the fire obtained from Minteq’s speciation model

Days after fire	pH	pCa ²⁺	pMg ²⁺	pK ⁺	pFe ²⁺	pMn ²⁺	pZn ²⁺	pCu ²⁺	pNH ₄ ⁺	pNO ₃ ⁻	pHPO ₄ ²⁻	pH ₂ PO ₄ ⁻
	Result of ANOVA analysis											
	*	**	***	*	**	***	NS	**	***	***	***	**
Result of Tukey’s multiple comparison												
0	7.55 ab	1.75 ab	2.95 a	2.46 ab	2.70 ab	3.24 a	4.48 a	5.13 ab	2.75 bc	3.97 bc	9.99 c	10.32 b
14	7.82 a	1.83 a	2.43 b	2.21 c	2.79 a	2.55 b	4.37 a	5.47 a	2.36 d	3.91 bc	10.47 a	11.09 a
30	7.48 b	1.75 ab	2.65 ab	2.35 abc	2.62 ab	3.00 ab	4.28 a	5.11 b	2.60 cd	4.50 a	10.16 abc	10.44 b
90	7.45 b	1.75 ab	3.02 a	2.36 abc	2.68 ab	3.23 a	4.49 a	4.95 b	2.95 b	4.17 ab	10.01 bc	10.26 b
180	7.56 ab	1.70 b	2.86 a	2.27 bc	2.72 a	3.19 a	4.27 a	5.08 b	2.83 bc	3.54 c	10.03 bc	10.39 b
270	7.48 b	1.74 ab	2.79 ab	2.55 a	2.44 b	2.94 ab	4.48 a	5.02 b	2.97 b	3.98 bc	10.38 ab	10.66 ab
360	7.57 ab	1.67 b	2.81 ab	2.47 ab	2.67 ab	3.07 ab	4.28 a	5.06 b	2.98 ab	4.44 a	10.08 bc	10.46 b
450	7.72 ab	1.74 ab	2.78 ab	2.43 ab	2.62 ab	2.87 ab	4.43 a	5.28 ab	2.96 b	4.43 a	10.32 abc	10.84 ab
540	7.58 ab	1.75 ab	2.99 a	2.49 a	2.55 ab	3.12 ab	4.64 a	5.09 b	3.25 a	3.86 bc	10.26 abc	10.65 ab

*, **, ***: Significant levels at $\alpha = 0.05$, $\alpha = 0.01$, and $\alpha = 0.001$; “p” notates for negative logarithm of ionic activities of Ca²⁺, Mg²⁺, Mn²⁺, Fe²⁺, and HPO₄²⁻

Table 4-5: Correlation matrix of ionic activities of nutrient elements obtained from the Minteq’s speciation program (n = 45)

	pH	pCa ²⁺	pMg ²⁺	pK ⁺	pFe ²⁺	pMn ²⁺	pZn ²⁺	pCu ²⁺	pNH ₄ ⁺	pNO ₃ ⁻	pHPO ₄ ²⁻
pCa²⁺	-0.062										
pMg²⁺	-0.356	-0.101									
pK⁺	-0.180	-0.132	0.495								
pFe²⁺	0.279	-0.227	-0.449	-0.523							
pMn²⁺	-0.445	-0.455	0.623	0.268	-0.028						
pZn²⁺	-0.102	0.160	0.005	0.116	0.035	-0.008					
pCu²⁺	0.931	0.067	-0.448	-0.226	0.321	-0.491	-0.109				
pNH₄⁺	-0.220	-0.505	0.445	0.474	-0.230	0.498	0.214	-0.395			
pNO₃⁻	-0.078	-0.086	-0.208	0.128	-0.016	-0.104	-0.009	-0.033	0.024		
pHPO₄²⁻	0.620	0.342	-0.185	0.122	-0.427	-0.645	-0.039	0.553	-0.218	-0.018	
pH₂PO₄⁻	0.871	0.184	-0.287	-0.010	-0.133	-0.619	-0.074	0.796	-0.243	-0.049	0.926

Table 4-6: Stoichiometry between activity of HPO_4^{2-} and activities of Ca^{2+} , Fe^{2+} , Mg^{2+} , Mn^{2+} for the selected Ca/Mg/Fe/Mn- P minerals

Name	Stoichiometry
Monetite	$\text{pHPO}_4^{2-} = 6.9 - \text{pCa}^{2+}$
Monocalcium-P	$\text{pHPO}_4^{2-} = 7.775 - 0.5\text{pCa}^{2+} - \text{pH}$
Dicalcium dihydrate -P	$\text{pHPO}_4^{2-} = 6.57 - \text{pCa}^{2+}$
Tricalcium-P (beta)	$\text{pHPO}_4^{2-} = 2.11 - 1.5\text{pCa}^{2+} + \text{pH}$
Octacalcium-P	$\text{pHPO}_4^{2-} = 3.28 - 4/3\text{pCa}^{2+} + 2/3\text{pH}$
Hydroxyapatite	$\text{pHPO}_4^{2-} = 2.38 - 5/3\text{pCa}^{2+} + 4/3\text{pH}$
Vivianite	$\text{pHPO}_4^{2-} = 6.53 - 1.5\text{pFe}^{2+} + \text{pH}$
$\text{Mg}_3(\text{PO}_4)_2$	$\text{pHPO}_4^{2-} = -0.71 - 1.5\text{pMg}^{2+} + \text{pH}$
$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	$\text{pHPO}_4^{2-} = 5.825 - \text{pMg}^{2+}$
$\text{Mn}_3(\text{PO}_4)_2$	$\text{pHPO}_4^{2-} = -0.4365 - 1.5\text{pMn}^{2+} + \text{pH}$
MnHPO_4	$\text{pHPO}_4^{2-} = 13.05 - \text{pMn}^{2+}$

“p” notates for negative logarithm of ionic activities of Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , and HPO_4^{2-}

Table 4-7: Correlation relationships among $\text{pH} + \text{pHPO}_4^{2-}$, $\text{pH} - 1/2\text{pFe}^{2+}$, $\text{pH} - 1/2\text{pMn}^{2+}$, and $\text{pH} - 1/2\text{pCa}^{2+}$ in soil solution (n = 45)

Solution variables	Correlation matrix among solution variables			
	$\text{pH} + \text{pHPO}_4^{2+}$	$\text{pH} - 1/2\text{pFe}^{2+}$	$\text{pH} - 1/2\text{pMn}^{2+}$	$\text{pH} - 1/2\text{pCa}^{2+}$
$\text{pH} - 1/2\text{pFe}^{2+}$	0.9544			
$\text{pH} - 1/2\text{pMn}^{2+}$	0.8975	0.8394		
$\text{pH} - 1/2\text{pCa}^{2+}$	0.8191	0.8783	0.8539	
$\text{pH} - 1/2\text{pMg}^{2+}$	0.7576	0.7231	0.9098	0.8610

Table 4-8: Saturation index (SI) for phosphate minerals in the Pine Rockland soils following the fire obtained from simulation results of the Minteq speciation program

Days after fire	Saturation Index (SI) [†] for P minerals in Pine Rockland soils following a fire								
	Vivianite	MnHPO ₄	HA	β-TCP	Monetite	DCPD	MgHPO ₄ ·3H ₂ O	Mg ₃ (PO ₄) ₂	Mn ₃ (PO ₄) ₂
0	0.000	-0.102	-1.407	-4.037	-4.899	-5.180	-7.091	-14.948	-15.114
14	-0.574	0.000	-2.097	-4.637	-5.409	-5.690	-7.092	-14.021	-13.878
30	0.000	-0.006	-1.849	-4.925	-5.206	-6.271	-6.921	-14.593	-14.981
90	0.000	-0.147	-1.641	-4.112	-4.815	-5.096	-7.082	-15.250	-15.576
180	0.000	-0.146	-1.100	-3.841	-4.814	-5.094	-7.007	-14.756	-15.304
270	0.000	-0.243	-2.603	-4.777	-5.183	-5.464	-7.316	-15.513	-15.426
360	0.000	-0.082	-1.125	-3.876	-4.859	-5.140	-7.080	-14.876	-15.011
450	0.000	-0.122	-1.477	-4.189	-5.133	-5.414	-7.247	-14.866	-14.622
540	0.000	-0.356	-2.021	-4.454	-5.119	-5.400	-7.462	-15.820	-15.632

[†]SI = logarithm of the ratio of the ionic activity product (IAP) to equilibrium solubility product constant (K_s), SI = log(IAP) – log(K_s); positive, negative, and zero SI values indicate oversaturation, undersaturation, and equilibrium, respectively. Saturation index of each variable at time point was an average value of replicates at the given time point.

Table 4-9: Fitted parameters of Retc model used to describe soil-water characteristics of the Pine Rockland calcareous soils, and coefficients used to evaluate a goodness-of-fit of model

Retention curve model		Measures of goodness-of-fit of model	
Parameter [†]	Value	Coefficient [‡]	Value
θ_s	0.41	R²	0.994
θ_r	0.07	E	0.994
α	0.08	d	0.998
n	1.89		
m	0.47		

[†] θ_s is the saturated water content; θ_r is the residual water content; α , n, and m are the model fitting parameters

[‡] R² is the coefficient of determination; E is the coefficient of efficiency; and d is the index of agreement

Table 4-10: A summary of parameters of regression models fitted by response variable of extractable P and three predictors

Model	Day (D)			Moisture (M)			Temperature (T)			D	D	M	D	I	Parameters from fitted models				Components having insignificant differences at $\alpha = 0.05$ in the model
	1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd	*	*	*	*		R ²	CV	RMSE	Pr > F	
1	x			x			x							x	0.5715	26.65	1.7064	<.0001	
2	x			x			x			x	x	x		x	0.6180	25.35	1.6227	<.0001	D*T
3	x			x			x			x		x		x	0.6180	25.29	1.6189	<.0001	
4	x			x			x			x	x	x	x	x	0.6191	25.37	1.6243	<.0001	D*M, D*T, D*M*T
5	x			x			x					x		x	0.6088	25.53	1.6343	<.0001	
6		x			x			x						x	0.6562	23.88	1.5286	<.0001	
7		x			x			x		x	x	x		x	0.7429	20.79	1.3311	<.0001	
8		x			x			x		x	x	x	x	x	0.7450	20.76	1.3290	<.0001	D*M*T
9			x			x								x	0.7068	22.05	1.4116	<.0001	
10			x			x				x	x	x		x	0.7598	20.10	1.2868	<.0001	D*M
11			x			x					x	x		x	0.7595	20.06	1.2845	<.0001	
12			x			x				x	x	x	x	x	0.7619	20.06	1.2843	<.0001	D*M, D*T, D*M*T
13			x			x						x		x	0.7503	20.39	1.3056	<.0001	
14	x	x		x	x		x	x						x	0.8090	17.93	1.1476	<.0001	M, M*M
15	x	x					x	x						x	0.7124	21.89	1.4013	<.0001	
16	x	x		x	x		x	x		x	x	x		x	0.8554	15.71	1.0055	<.0001	I, D, M*M, D*T
17		x		x			x	x		x		x		x	0.8523	15.76	1.0090	<.0001	
18	x	x		x	x		x	x		x	x	x	x	x	0.8565	15.69	1.0042	<.0001	D, M*M, D*T, D*M*T
19	x	x	x	x	x	x	x	x	x					x	Model could not be fitted by 3 rd order of moisture				
20	x	x	x	x	x		x	x	x					x	0.8566	15.60	0.9990	<.0001	D, M, D*D, M*M, D*D*D
21							x	x	x					x	0.6468	24.20	1.5492	<.0001	
22	x	x	x	x	x		x	x	x	x	x	x		x	0.9031	12.92	0.8272	<.0001	D, D*D, M*M, D*D*D, D*T
23				x			x	x	x	x		x		x	0.8279	17.01	1.0890	<.0001	
24	x	x	x	x	x		x	x	x	x	x	x	x	x	0.9042	12.88	0.8247	<.0001	D, D*D, M*M, D*D*D, D*T, D*M*T

RMSE: Root mean square error, R²: R-Square; CV: Coefficient of Variation; 1st, 2nd, 3rd: orders in the linear regression; I: Intercept
 “*” denotes the interactions among factors; “x” denotes components including in the model

Table 4-11: Estimation of a fire temperature for burning experiment at the TREC's Pine Rockland forest

Variables	The fitted models from the laboratory residual ashes	Field collected ashes	
		Content %	Simulated T ⁰ C
TC	$Y^{\dagger} = 75.27233 - 0.0897*(T)$	1.02	521.3
TN	$Y = - 4.16540 + 0.03148*(T) - 0.00004139*(T)^2$	28.53	518.9
			Average simulated T: 520⁰C

[†] concentrations of TN (%) and TC (%) in ash production simulated from the laboratory incubation with independent variable of heating temperature (T)

Table 4-12: Observation and simulation data of extractable P content after the fire at the TREC's Pine Rockland forest

Days after fire	Average volumetric water content at 5cm topsoil	Simulated P content	Observed P content
	----- v/v -----	----- mg/kg soil -----	-----
7	0.00000	6.52	9.16
14	0.02555	6.35	6.98
21	0.07011	6.08	6.55
30	0.14230	5.69	6.77
60	0.08632	5.71	4.85
90	0.11078	5.15	3.51

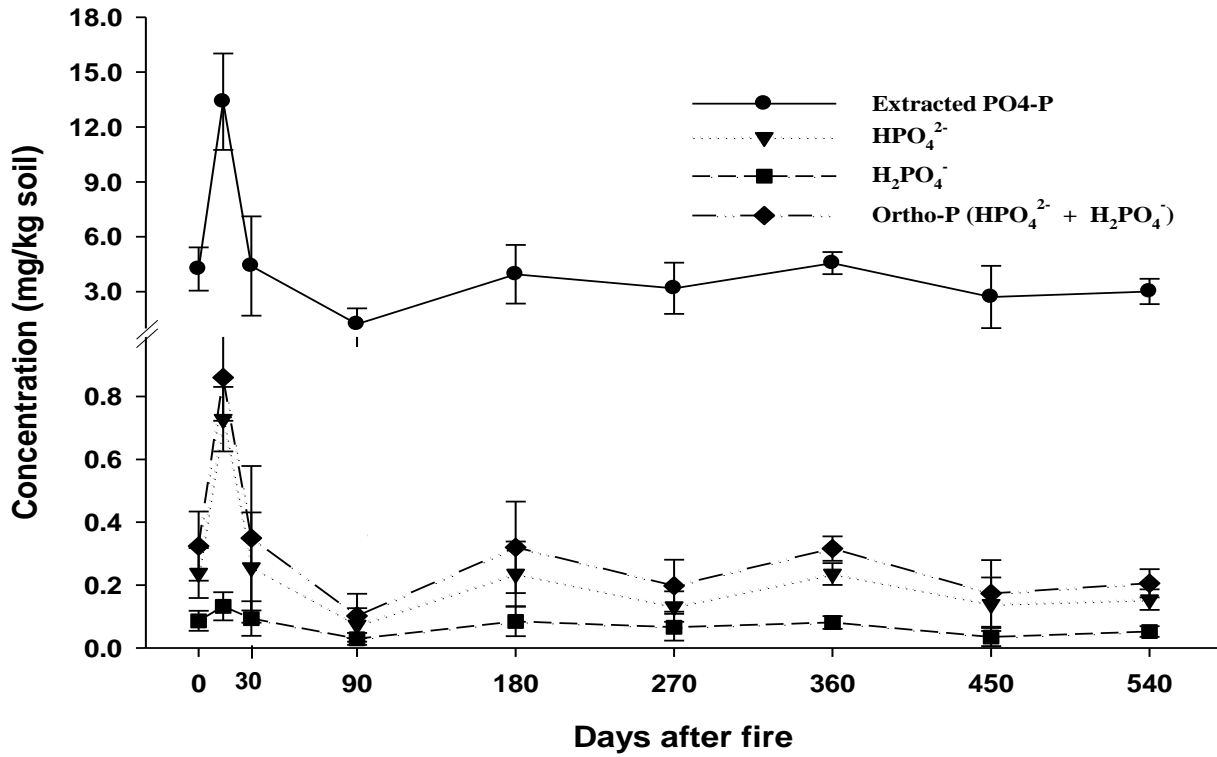


Figure 4-1: Concentrations of ortho-P species after the fire, relatively Olsen-P contents

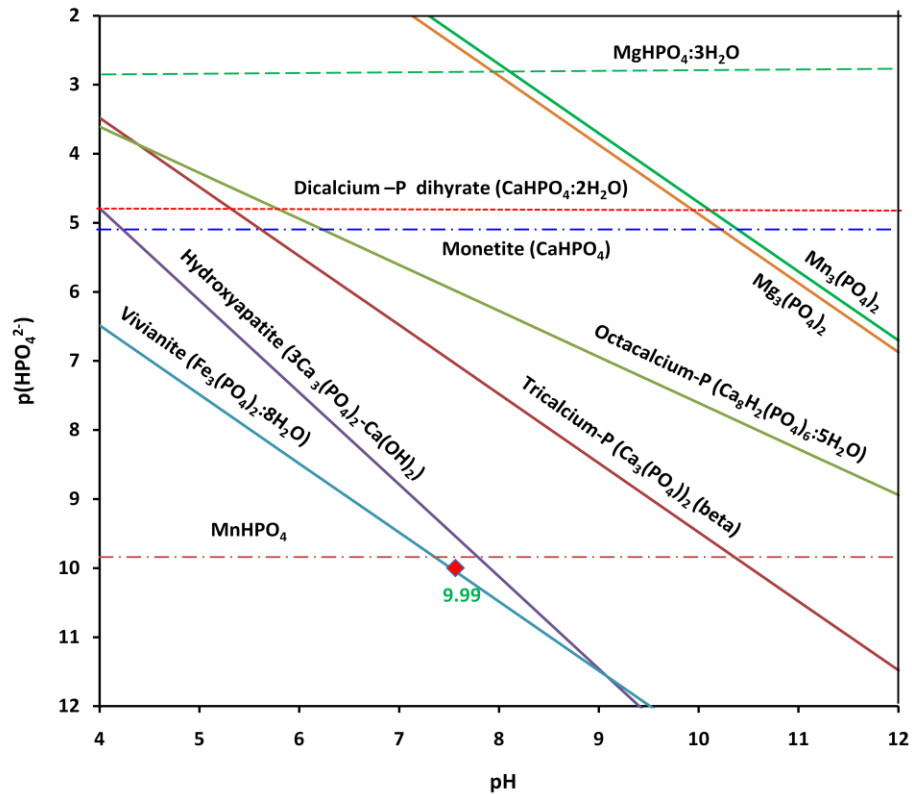


Figure 4-2: Relationship of pH and phosphate mineral stability in soil solution before fire

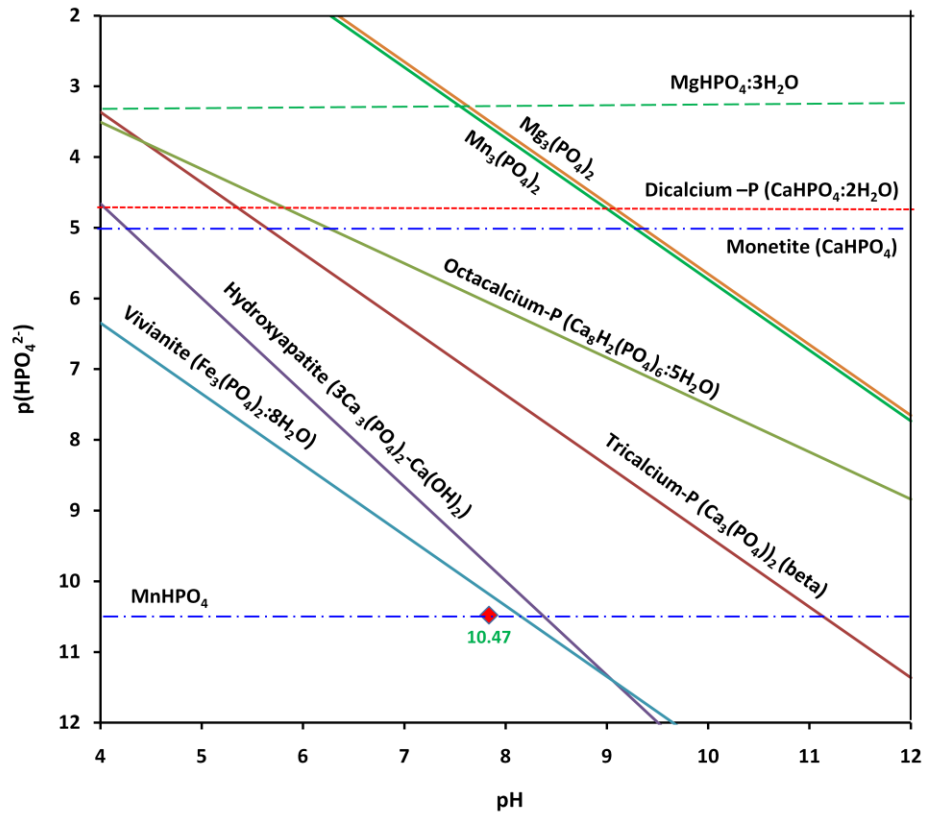


Figure 4-3: Relationship of pH and phosphate mineral stability in 14 days after fire

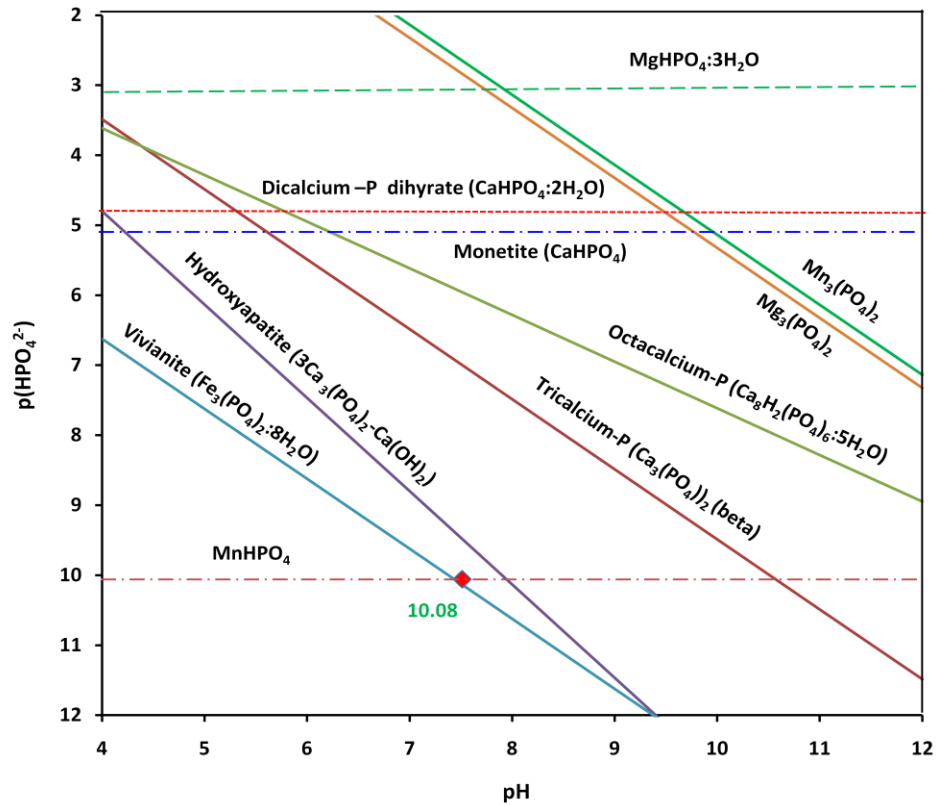


Figure 4-4: Relationship of pH and phosphate mineral stability in 30 days after fire

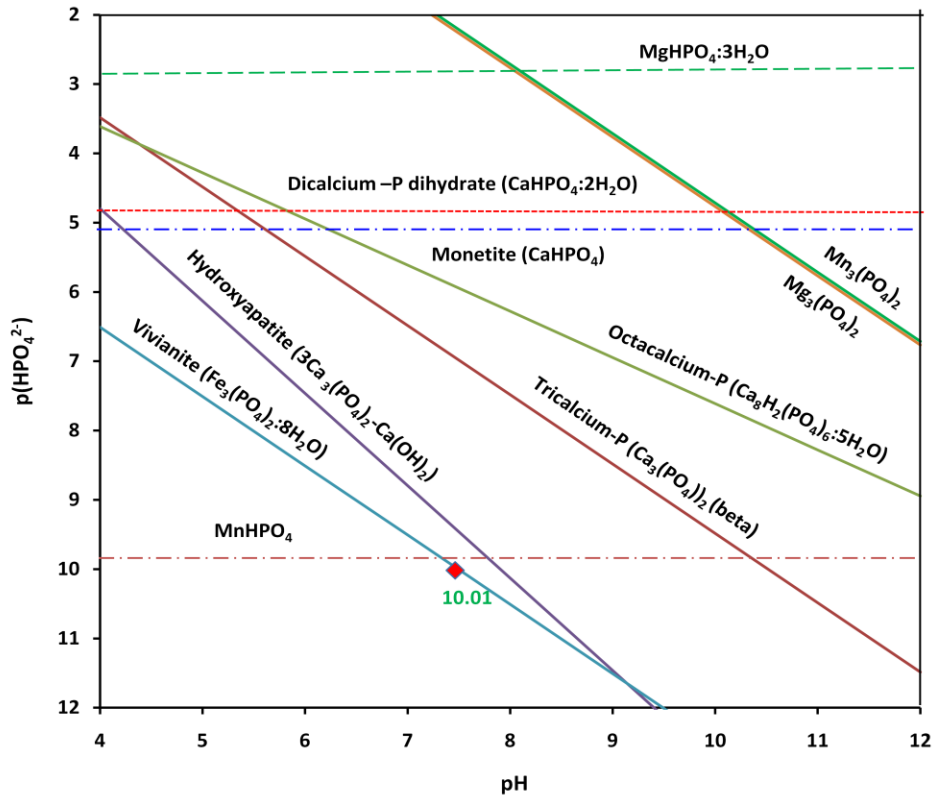


Figure 4-5: Relationship of pH and phosphate mineral stability in 90 days after fire

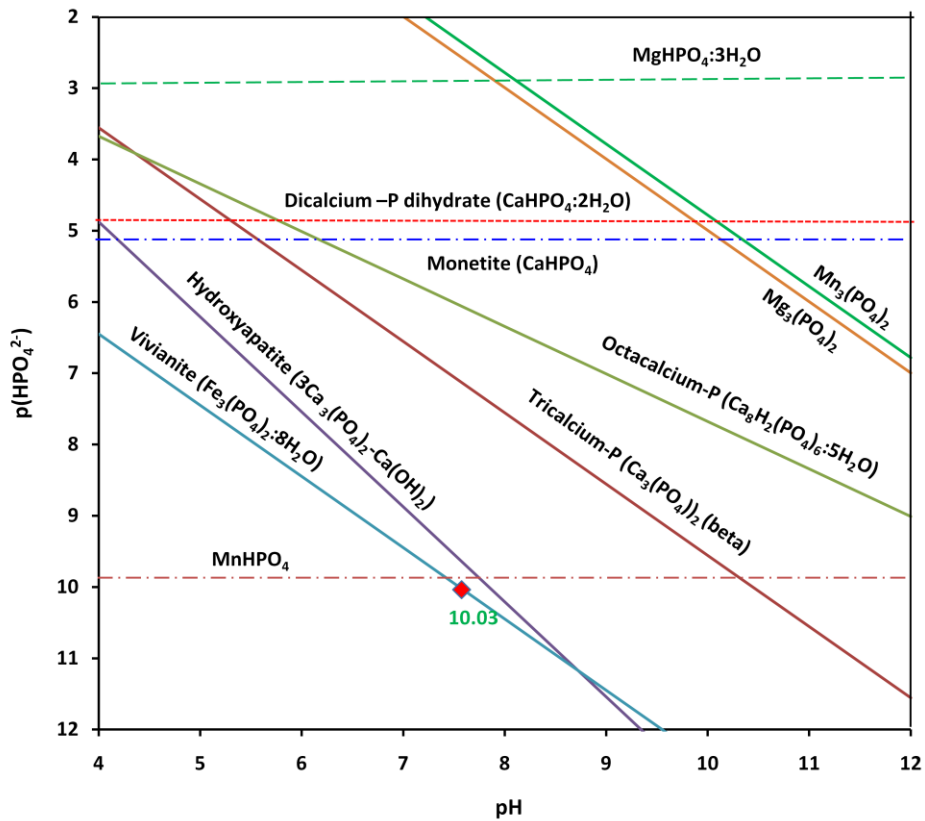


Figure 4-6: Relationship of pH and phosphate mineral stability in 180 days after fire

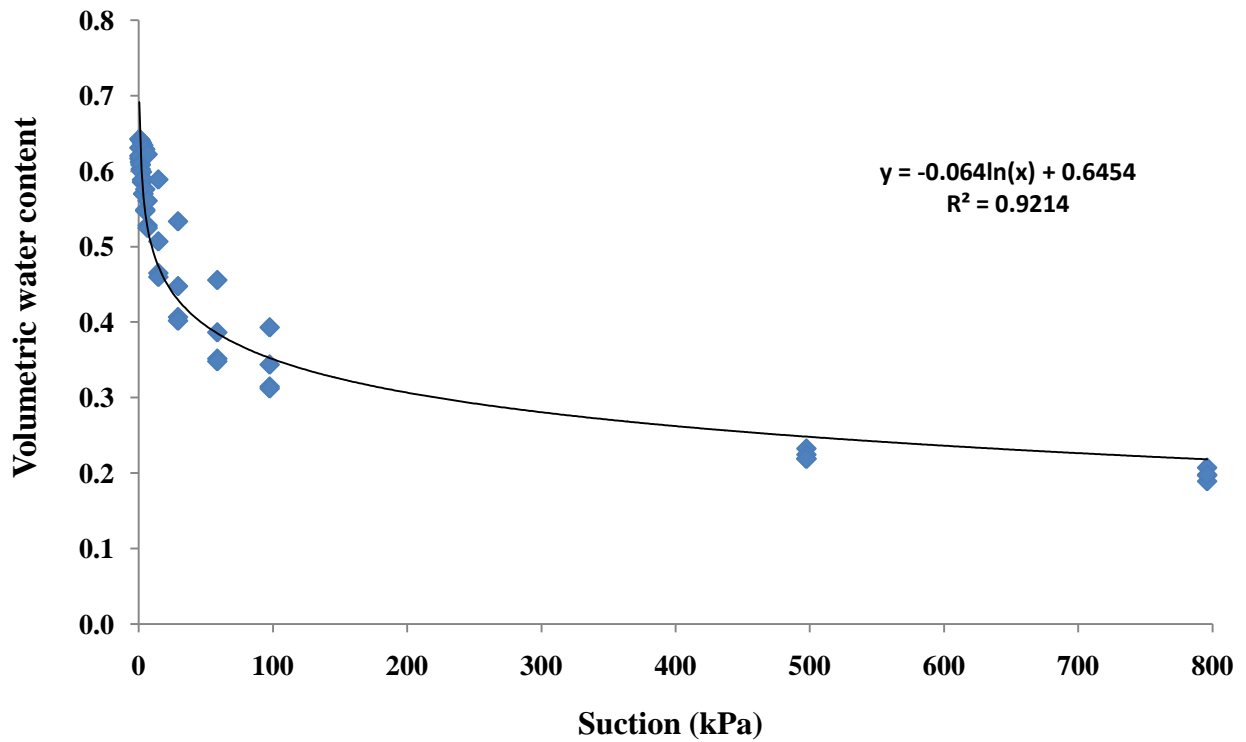


Figure 4-7: Soil moisture curve of the Pine Rockland fitted by the Retc model

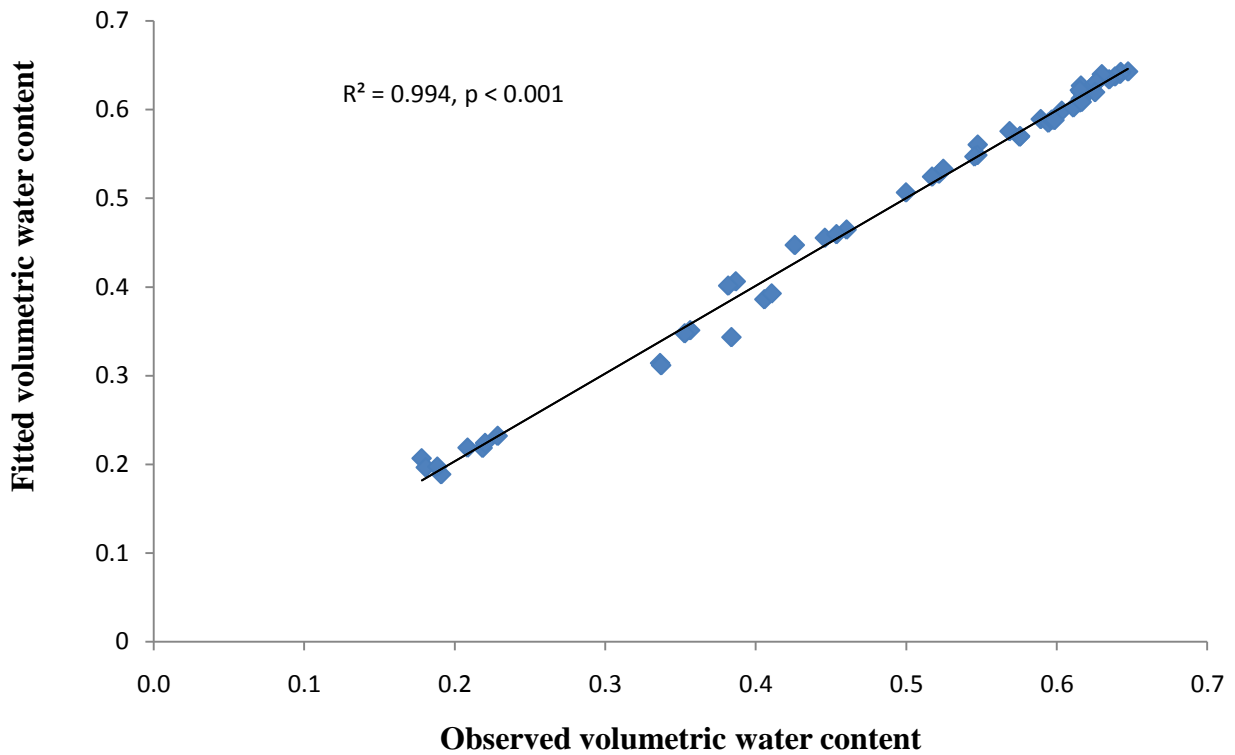


Figure 4-8: A goodness-of-fit model for soil moisture curve of the Pine Rockland forest

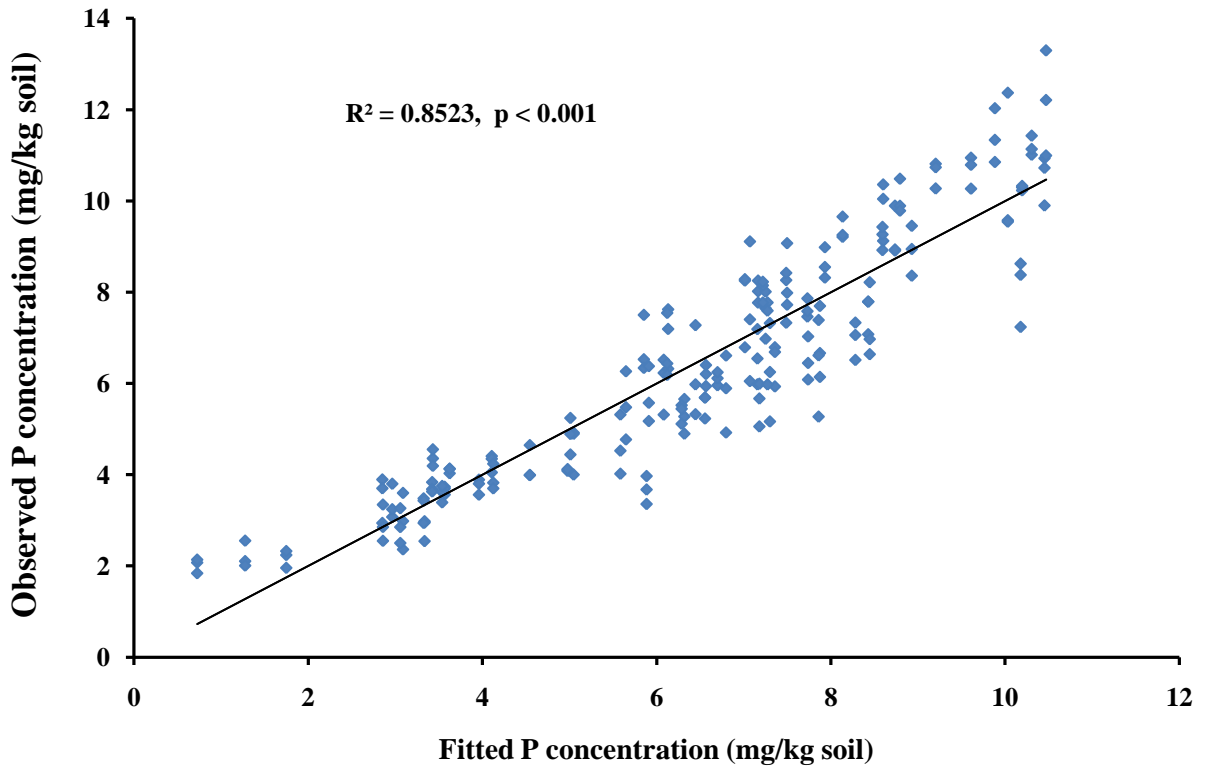


Figure 4-9: A goodness-of-fit for the predictive model of P availability after the fire

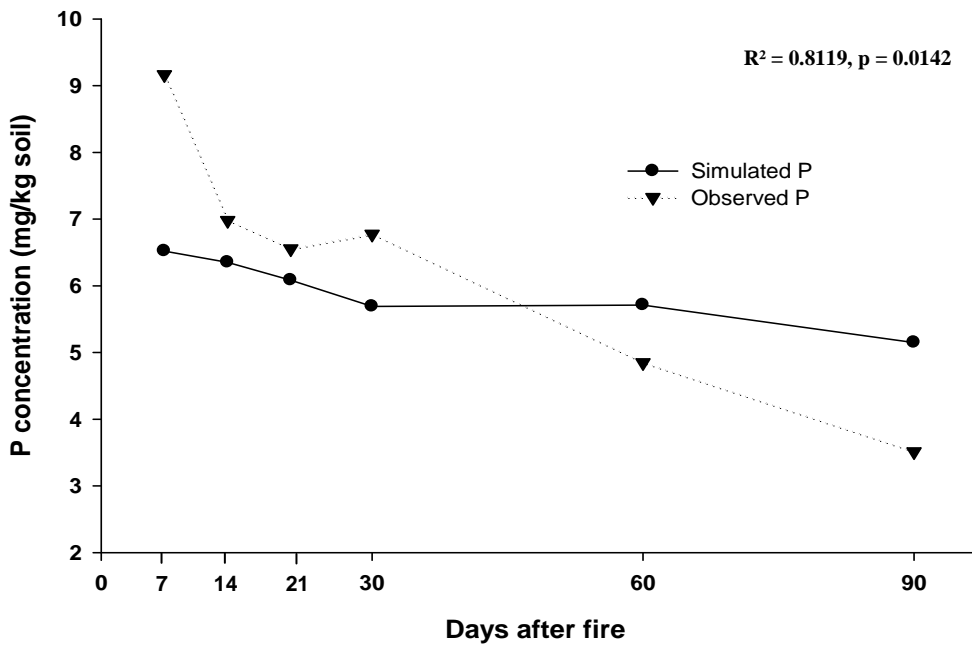


Figure 4-10: Verification of the predictive model for P prediction after the fire

CHAPTER 5 SUMMARY

The Pine Rockland forest is a unique upland ecosystem originated from limestone substrates, and preserved one of the most endangered forest types in the world – South Florida slash pine (*Pinus elliottii* var. *densa*), with a diverse native plants in the understory vegetation (Snyder et al., 1990). It is found in three remnant regions in South Florida including the Long Pine Key in the Everglades National Park, the Big Pine Key in the Florida Lower Keys, and a part of the Big Cypress National Preserve (Snyder, 1986). The increasing influence of human activities on the landscape has changed many critical ecosystem processes, particularly on the hydrological balance, fire regime, and rapid invasion of exotic species.

The Pine Rockland forest is a poor-nutrient and fire-dependent ecosystem (U.S Fish and Wildlife Service, 2007; USGS, 2000) which is often maintained by fires in every 3 to 10 years for a continued health of endemic plants (Snyder et al., 1990). Fire is an environmentally important factor that requires for controlling, at least a part, relative dominance of hardwood plants in understory of the Pine Rockland forest. The importance of fire as a part of this ecosystem has long been recognized (Snyder et al., 2005; Wade et al., 1980). The ecological roles of fire on vegetation recovery in the Pine Rockland forest have been recently evaluated (Knapp et al., 2009; Robbin and Myers, 1992; Ross et al., 1994 & 2003; Sah et al., 2004 & 2006; Sah et al., 2010; Snyder, 1986; Sparks et al., 2002); however, effects of fire on soil nutrient pools have not been documented. The overall goal of this study was to evaluate effects of prescribed fire on soil nutrient pools in the Pine Rockland forest ecosystem. We hypothesized that phosphorus (P) is a limiting factor, and prescribed fire would improve deficiency of P and create more availability of soil nutrient elements in the Pine Rockland forest. The specific objectives and summary of results are outlined below.

Objective 1

It was to determine whether P is limited in the Pine Rockland ecosystem due to abundance of calcium in calcareous soils, and evaluate how prescribe fire could improve availability of soil nutrient pools. The specific tasks of this objective were to 1) determine P limitation basing on pine foliar P and other nutrients, and foliar DRIS indices; 2) evaluate effects of fire on pools of C and N in fuel-load and soil; 3) assess impacts of fires on soil pH, EC, and soil nutrient pools; and 4) compare C:N:P ratios among pine foliage, fuel load, and soil. To achieve these specific tasks, a field-burning experiment was conducted in the Long Pine Key in the Everglades National Park on November 19th, 2008. In addition, samples of pine foliage were collected at the beginning of the growing season of pine tree, and fuel-load samples were collected in one day before the burning experiment.

Determination of P restriction was based on comparisons between the foliar P of the Pine Rockland slash pine and published critical values of pine foliage P in slash pine forests as well as on pine foliar DRIS indices. The foliar P concentration in the Pine Rockland was 0.045 % of dry biomass while the published critical P concentration of slash pine forest was from 0.07% to 0.125% of dry biomass. The foliar N concentration in the Pine Rockland was approximately 0.81% of dry biomass which was closely to the critical N concentration of the slash pine forest, ranging from 0.87% to 1.3% of dry biomass. DRIS indices of P, K, N, Mg, and Ca in the Pine Rockland slash pine were - 46.13, - 10.77, - 0.89, 8.71, and 49.05, respectively. These results demonstrated that P is the most limiting factor and N is marginal to limitation or may be saturated in the Pine Rockland forest ecosystem.

The P limitation led to rise the pine foliar N:P ratio of 17.9 that was higher than the critical foliar N:P ratio of the Slash pine forest. The C:N:P ratios of pine foliage and fuel load were 1162.5:17.9:1 and 2361.2:23.8:1 respectively, whereas those of soil were 920:30.3:1. The lower

C:N ratio and higher N:P ratio in soil than those in pine foliage could provide more evidence that N is sufficient in the Pine Rockland forest ecosystem. The fire did not impact on soil C:N ratio, but it significantly altered soil C:P and N:P ratios. The soil C:P and N:P ratios fluctuated with changes of soil C and N concentrations after the fire. Alterations of the soil C:P and N:P ratios depended on more the growing season of pine trees and seasonal variation than the fire.

The fire consumed approximately 90.2% of the forest floor and understory biomass, caused losses of 80% of N pool and 92% of C pool in the forest floor and understory biomass, and volatilized 86% of NH_4^+ pool and 48% of NO_3^- pool that associated with the N pool in the forest floor and understory biomass. In contrast, the prescribed fire significantly affected on soil C and N pools at the top 0-5cm soil from 0.95 to 1.42% for TN and from 24 to 40% for TC in 14 days after the fire, respectively. Although the concentrations of TC and TN reached their original values in 30 days after the fire, these concentrations continued to decrease thereafter and had the lowest values after 90 days. Ammonium and nitrate were two major components contributing to increase in soil N pool after the fire. The extractable NH_4^+ in the top 0-5cm soil increased immediately after the fire, remained until 30 days, and then declined in thereafter. However, the extractable NO_3^- was not changed immediately after the fire, but increased significantly in the post-fire 180 days as a result of the nitrification process.

The fire-induced increases in soil EC, pH, and the extractable concentrations of P, Mg, K, and Mn occurred concurrently in 14 days after the fire, whereas the increase in the extractable Ca and Fe occurred in 270 days and 360 days, respectively, as a result of the variation on soil moisture content between the dry season and the rainy season.

Objective 2

It was to assess the effect of the fire to soil nutrient pools following by different burn seasons on calcareous soils in the Pine Rockland forest ecosystem. The specific tasks of this study included 1) determining effects of different fire temperatures on pH, EC, and nutrients in residual ashes; 2) determining a relationship between burn temperature and soil nutrient pools in the calcareous soils; 3) determining if the relationship is affected by soil moisture content; 4) assessing if the relationship is impacted by time after burn; and 5) estimating a fire temperature for the field burning experiment basing on concentrations of TP, TMg, TCa, TFe in residual ashes. The burning experiment was conducted under the controlled condition of laboratory incubation to determine how burn temperature and soil moisture content influenced on soil nutrient pools after the fire. Four burning temperatures of fuel loads which included 250, 350, 450, and 550⁰C used to determine effects of burn temperature on nutrient concentrations in ashes and soils. The soil moisture content consisted of 35, 100, and 70% of soil field capacity, representing a range of soil moisture that can be found in the Pine Rockland throughout the year. Soil samples were incubated at 25⁰C in six different time intervals of 14, 30, 60, 90, 120, and 180 days.

Increase in burn temperatures significantly impacted on TC, TN, and TK in ashes in term of dry fuel-load, but did not change concentrations of TP, TCa, TMg, TFe, TMn, and TZn due to their relatively high volatilization temperatures. Losses of TN and TC via volatilization occurred mostly at 450 and 550⁰C, and were proportional to biomass loss. Concentration of TK significantly decreased at the burn temperatures of 350 and 450⁰C, but no further decrease was found for concentration of TK at heating to 550⁰C. The volatilizations of TN and TK in the residual ash along the burn temperature gradient resulted in significant changes of the water-soluble concentrations of NH₄-N, NO₃-N, and K in the residual ash. The water-soluble

concentration of $\text{NH}_4\text{-N}$ significantly reduced as the burn temperature increased. In contrast, the concentrations of $\text{NO}_3\text{-N}$ in residual ashes significantly increased at 250°C , but no significance was observed at or greater than 350°C . The water-soluble K was significantly lower in 250°C than those in 350, 450, and 550°C .

The temperature-induced changes of water dissolved pH and EC, and the water-soluble nutrients in residual ashes were significantly along the burn temperature gradient. The ash pH significantly increased from acidic with burn temperatures at or below 250°C to alkaline at the temperatures at or over 350°C . Although no significant difference was found for ash EC with the temperature at or below 250°C , the EC was linearly increased as the burn temperature increased above 250°C . However, the water-soluble P decreased when heating to 350°C or higher. Responses of water-soluble concentrations of other nutrient elements along the temperature gradient in term of dry fuel-load were very variously. The water-soluble Ca and Mg reached their highest values at 350°C , whereas the water-soluble Mn and Zn were gradually reduced as the burn temperature increased.

The different availability of nutrients in the ash resulted in significant changes of soil pH, EC, and extractable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, P, Mg, K, Fe, Mn, Zn, Cu. Generally, the burn temperature at or over 450°C led to an increase of soil pH, and produced more available Mg, K, Fe, and Cu. On the other hand, an increase in the burn temperatures caused a decline of extractable $\text{NH}_4\text{-N}$, Mn, and Zn. The extractable P, $\text{NO}_3\text{-N}$, and EC with respect to the burn temperatures reached a peak after heating to 350°C .

The soil moisture content significantly impacted on soil pH, EC, and extractable $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, P, and Fe, but was not for extractable Mg, K, Mn, Zn, and Cu. Under the controlled condition in the laboratory, extractable P decreased with an increase in the soil moisture.

Increasing in the soil moisture increased in the extractable NH_4^+ . Responses of $\text{NO}_3\text{-N}$ and EC to the soil moisture had the same tendency that reached a peak with the soil water content of 70% field capacity. However, soil pH and extractable Fe varied in the opposite pattern to those of EC and $\text{NO}_3\text{-N}$ from which their lowest values were on the soil water content of 70% field capacity.

The time after the fire significantly influenced on soil EC and extractable P, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Mg, K, Mn, Cu, and Zn, but not for extractable Fe and pH. Ammonia was linearly declined with an increase of the time, and stabilized after 120 days. Conversely, the reduction of NH_4^+ concentration resulted in the increase of $\text{NO}_3\text{-N}$ concentration through the nitrification process. Significant changes of soil EC and extractable P, Mg, K, Mn, Zn, and Cu actually occurred at 120 days or thereafter.

Non-significant difference of TP/TCa, TP/Mg, and TP/TFe in residual ashes indicated that TP, TCa, TMg, and TFe were good predictors for precisely estimating a field-fire temperature. Based on the regression relationship between the simulation temperatures and concentrations of TP, TCa, TMg, and TFe in residual ashes, the fire temperature for the field burning experiment was estimated to be approximately 370°C .

Objective 3

The goal was to predict long-term impacts of fire on P availability in calcareous soils under the Pine Rockland forest. Four specific tasks consisted of 1) determining P species following a fire using Minteq's equilibrium speciation model; 2) describing a relationship of soil pH and phosphate minerals to phosphate solubility after a fire by establishing stability diagrams of phosphorus; 3) modeling soil-water characteristic curve for Pine Rockland's calcareous soils by applying the Retention Curve (Retc) model; and 4) Modeling a predictive model for prediction of P availability after a fire. The P species and the solubility diagrams of P were

determined basing on the results from the field burning experiment while the predictive model was fitted from the simulation results in the laboratory experiment with predictors of soil moisture content, burn temperature, and incubation time.

The result of simulation from the Minteq's speciation exhibited that HPO_4^{2-} , H_2PO_4^- , FeHPO_4 (aq), MgHPO_4 (aq), CaHPO_4 (aq), MnHPO_4 (aq), $\text{FeH}_2\text{PO}_4^+$, $\text{CaH}_2\text{PO}_4^+$, and CaPO_4^- are the dominant P compounds in the Pine Rockland calcareous soils. Concentrations of these species were significantly different following the fire, except $\text{FeH}_2\text{PO}_4^+$. HPO_4^{2-} was a predominant species of orthophosphate, and fluctuated with Olsen-P concentrations. In general, these species significantly increased in 14 days and returned to their pre-burn values in 30 days after the fire. Nevertheless, concentrations of HPO_4^{2-} , CaHPO_4 (aq), and $\text{CaH}_2\text{PO}_4^+$ continued to decrease until 90 days after the fire.

Ionic activities of nutrients in soil solution highly correlated with their extracted concentrations. The fire significantly affected the activities of nutrient elements, excluding pZn^{2+} . Fire significantly increased the ionic activities of Mg^{2+} , K^+ , Mn^{2+} , and NH_4^+ in post-fire 14 days and activity of NO_3^- in post-fire 180 days, but significantly declined the activities of Cu^{2+} , HPO_4^{2-} , and H_2PO_4^- in 14 days after the fire. The activities of Ca^{2+} and Fe^{2+} fluctuated with time as the consequence of seasonal variations. Ionic activities of nutrient elements in soil solution highly correlated with their extracted concentrations. The solution pH had a negative correlation with activities of Ca^{2+} , Mg^{2+} , Mn^{2+} , and K^+ , and a positive correlation with activities of Fe^{2+} and orthophosphate species.

The activity of HPO_4^{2-} in the soil solution controlled by minerals of MCP, β -TCP, OCP, HA, vivianite, $\text{Mg}_3(\text{PO}_4)_2$, and $\text{Mn}_3(\text{PO}_4)_2$ was dependent on soil pH; whereas relationships among activity of HPO_4^{2-} with monetite, DCDP, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, and MnHPO_4 were

independent on soil pH. The activity of orthophosphate ions in the soil solution was mainly controlled by solubility of vivianite and MnHPO_4 minerals. The solubility of P in the soil solution was expressed by the magnitude order of vivianite > MnHPO_4 > HA > TCP > OCP > Monetite > DCPD > $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ > $\text{Mg}_3(\text{PO}_4)_2$, > $\text{Mn}_3(\text{PO}_4)_2$.

The soil-water characteristic curve of the Pine Rockland calcareous soils was expressed by the equation: $y = -0.064 \ln(x) + 0.6454$, where y is a volumetric water content (v/v) and x is suction (kPa). A long-term effect of fire on availability of P could predict by the following model:

$$\text{Extractable P} = 3.38 - 27.19 * \mathbf{M} + 0.06579 * \mathbf{T} - 0.000143 * \mathbf{D}^2 - 0.000115 * \mathbf{T}^2 + 0.05008 * \mathbf{M} * \mathbf{D} + 0.03983 * \mathbf{M} * \mathbf{T}$$

where “M” is the soil moisture content (v/v); “T” is the fire temperature ($^{\circ}\text{C}$); and “D” is the time or day after a fire (days).

Research Synthesis

The bioavailability of P in the Pine Rockland forest ecosystem is very low due to the nature of the calcareous soils. Phosphorus is the most limiting factor in this ecosystem with the average Olsen-P concentration of 4.2 mg/kg soil. The prescribed fire could increase threefold in available P (13.4 mg/kg soil) in the top 0-5cm soil in 14 days after the fire. Because of its relatively low concentration in the soil solution, the solubility of P in the soil solution is in equilibrium with the vivianite mineral and undersaturated with all Ca/Mg-P minerals. The prescribe fire shifted the equilibrium from the vivianite into MnHPO_4 in 14 days after the fire and returned its original equilibrium status in 60 days. A dramatic increase in ratio of TP to inorganic P in residual ash as fire intensity raised implied that low-fire intensity generally can produce more available P than high intense fire because inorganic P ions tend to bind to basic cations (Ca, Mg, Fe, Mn) in residual ashes, and then form insoluble phosphates when the fire intensity is increased. The reduction in Olsen-P as an increase in the soil moisture indicated that

higher soil moisture favored for reactions among P with Ca and Mg or Fe and Mn to form Ca/Mg-P precipitates or Fe/Mn-P hydroxyl compounds.

The higher N:P ratio and lower C:N ratio in soil to those in pine foliage could indicate that N may not be limited in the Pine Rockland forest where have had a high rate of nitrogen deposition associated with the high lightning intensity. Although the fire virtually removed a large amount of N pool in the forest floor and understory vegetation, it increased soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ pools. However, the concentration of $\text{NH}_4\text{-N}$ in soil trended to reduce with an increase in the fire intensity and was higher at the high soil moisture content, whereas the nitrification process promoted the increase in the soil $\text{NO}_3\text{-N}$ pool which could occur in several months after a fire.

The prescribe fire could rise availability of Mn, Zn, and Cu. The high fire-intensity created less the available Mn and Zn and more availability of Cu than the low fire-intensity. The soil moisture content didn't impact on the availability of Mn, Zn, and Cu; nevertheless, time after the fire could cause a reduction of soil extractable Mn, and Zn, and increment of soil extractable Cu. The relatively high correlation between the pH and the activity of Cu in soil solution demonstrated that availability of Cu depends considerably on the high soil pH of the Pine Rockland forest.

Significance of This Study and Suggestions of Further Study

This study provided basic information for predicting a dynamics of soil nutrient pools after a fire in calcareous soils under the Pine Rockland forest ecosystems in South Florida. The findings can also be used for similar ecosystems elsewhere. The following are the major contributions from my study:

- The highest negative value of DRIS index of P and much lower foliar P compared to critical P concentrations reported for slash pine has indicated that phosphorus is the most limiting nutrient in the Pine Rockland forest, which has not been documented. Modeling tools provide an opportunity to predict a long-term impact of a prescribed fire on P

availability in calcareous soil of the Pine Rockland forests.

- Although many studies have evaluated the role of prescribed fire on restoration of the understory vegetation of the Pine Rockland forest ecosystem, this is the first time that such a detailed study involved in exploring how fire intensity affects on availability of P and other nutrients in post-fire ash and soil. Findings on an inorganic P reduction in residual ash as an increase in fire intensity as well as a decrease of soil extractable P after a fire due to an increment of soil moisture content would be beneficial to ecological fire managers, who could choose a suitable burn season to produce a maximum bio-available P amount for plant uptake.
- It is being thought that phosphate solubility is mainly controlled by Ca/Mg-P minerals in calcareous soils; however, this study found that the solubility of P in the Pine Rockland soil is controlled by Fe/Mn-P minerals, particularly vivianite mineral, due to relatively low P concentration and a high content of iron. This is also the first time that solubility of P was evaluated for the Pine Rockland calcareous soil. This finding could help soil scientists to have a broader view on predicting solubility of phosphate minerals in calcareous soils.

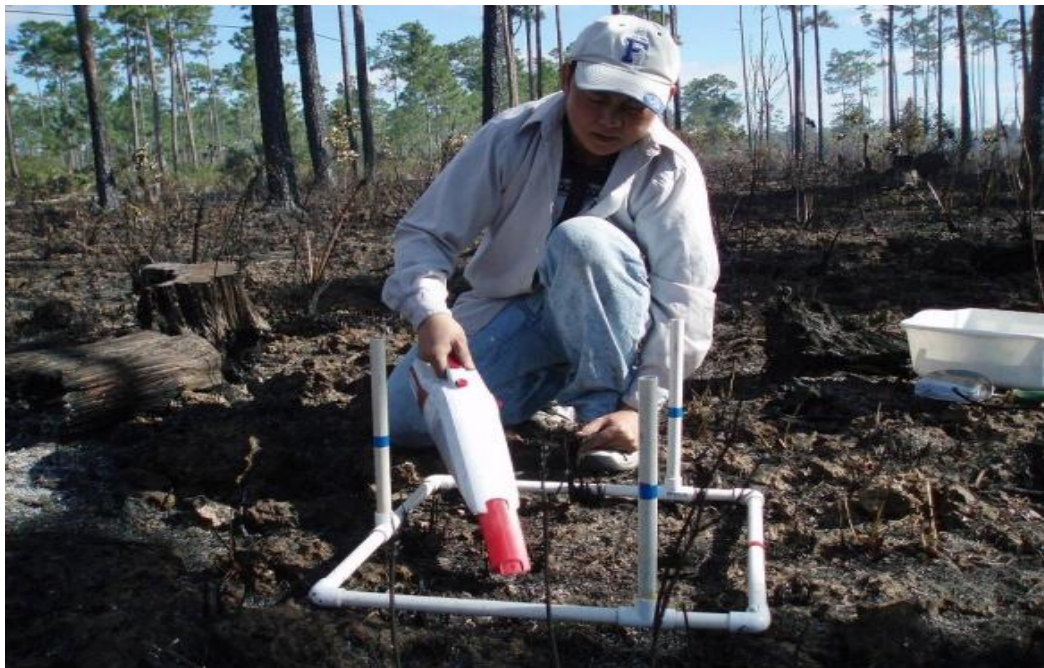
The Pine Rockland forest is the nutrient-poor ecosystem. Low availability of micro-nutrients, particularly Zn and Cu, can cause a growth limitation for the vegetation communities and the slash pine in the Pine Rockland forest as well. Although the field burning study showed that the prescribed fire did not influence availability of Zn and Cu, the laboratory study demonstrated that fire intensity significantly impacted extractable Zn and Cu. Additionally fire intensity and soil moisture content also significantly affected extractable Fe and Mn. This study did not include evaluation of response of plant community to prescribed fire. For sure, changes of P and other nutrients after fire directly affect survival and growth of plants. Therefore, a further study which has a linkage between fire-induced change of soil micro-nutrients and post-fire responses of understory vegetation to these nutrients should be carried out.

APPENDIX A
STUDY SITE AND SAMPLING PROCEDURES

Pine Rockland Forest in the Long Pine Key, Everglades National Park



A 50 x 50cm Sampling Frame Used to Collect Ashes after the Fire



APPENDIX B

PROCEDURES OF CHEMICAL ANALYSIS AND QA/QC METHODS IN LABORATORY

pH

Procedures: Soil and ash pH were measured using the AR-60 Dual Channel pH/Conductivity meter. Soil pH was extracted with rate of 10g soil and 25ml DDI water. 10 g of soils were weighted into 50-ml plastic bottles and 25 ml DDI water added followed by shaking at 180 oscillations per minute for 15 minutes by a reciprocating shaker. The shaking solutions were filtered through a Whatman paper No. 42. Similarly, ash pH was determined by extracting 1g ash and 50 ml DDI water (Qian et al., 2009a & b).

Calibration of pH meter: pH meter was calibrated daily using three pH-buffer standard solutions of 4.0, 7.0, and 10.0 at ambient temperature of 25⁰C before measurement. Calibration curve method was the first order with a calibrated slope of approximately 99.6% (an acceptable range of slope from 98.0% to 100%).

Quality Assurance (QA)/quality control (QC) method: Three methods for controlling quality included repeated measurement of soil samples, NSI standard QC solution, and pH-buffer standard solution. After every 20 samples, a duplicate of the 20th sample, standard QC solution, and pH buffer solution were measured to check the meter. The QC standard solution received from the NSI company had value of 7.20 (an acceptable range from 7.00 to 7.40). The pH buffer solution applied for the QA/QC was 7.0.

Electrical Conductivity

Procedures: Electrical conductivity was measured on a 1:2 dilution (10g soil: 20 ml DDI water) for soil and 1:50 dilution (1g ash: 50 ml DDI water) for ash on the AR-60 Dual Channel pH/Conductivity meter. 10 g of soil samples were weighed in 50-ml plastic bottles, and then added by 20 ml DDI water. Solutions were shaken in 10 minutes, allowed suspension to stand for

2 hours, thereafter filtered through a Whatman paper No. 42. A similar method was used for measurement of EC on ash samples (Qian et al., 2009b).

Calibration of conductivity meter: A reference standard solution of 1,412 $\mu\text{S}/\text{cm}$ from the NSI was used to calibrate conductivity meter before measurement daily. Standard settings of the instrument were cell constant of 1.0/cm, default temperature of 25⁰C, and temperature coefficient of 0.00%/⁰C. If the meter is set up with cell constant of 1.001/cm or 0.9999/cm and temperature coefficient of 0.00%/⁰C, calibration process meets the standard criteria for the instrument.

QA/QC method: Similarly to pH measurement, EC was controlled by three measurements: duplicates of every 20th sample; standard QC reference solution of EC, and calibrated standard solution. After every 20 samples were measured, repetition of the 20th sample, standard QC reference solution of 349 $\mu\text{S}/\text{cm}$ (an acceptable range from 310 to 387 $\mu\text{S}/\text{cm}$), and calibrated standard solution of 1,412 $\mu\text{S}/\text{cm}$ were performed to check the conductivity meter.

Ammonium

Procedures: Ammonium in soils was extracted by 2M KCl extracting solution, and measured by the AQ2 discrete auto-analyzer. An extracting solution of 2M KCl was created by adding 149.1g KCl into a 1000-ml volumetric flask with 900ml DDI water, stirring the solution until KCl completely dissolved, and then diluted volume into 1000 ml with DDI water. After 2g of soils were weighed into 50-ml plastic bottles, 20 ml of the extracting solution were added into the bottles, shaken at 180 oscillations per minute for 30 minutes, and then filtered through Whatman paper No. 42 (Mulvaney, 1996). Filtrate solutions were used to measure extractable concentrations of ammonium and nitrate. A similar procedure was used for ash samples, but extraction rate of 2g ash and 40 ml DDI water and a shaking time of 2 hours at 180 oscillations per minute (Qian et al., 2009b).

The USEPA standard method of 350.1 was used to measure extractable $\text{NH}_4\text{-N}$ in soil and ash. Principle of this method is that alkaline phenol and hypochlorite react with ammonia to form indophenol blue. Blue color is intensified by sodium nitroprusside, and measured at wavelength of 650-660 nm on the AQ2 discrete auto-analyzer. The range of this method is from 0.02 to 2.0 mg $\text{NH}_4\text{-N L}^{-1}$, with a level of detection of 0.007 mg $\text{NH}_4\text{-N L}^{-1}$.

Preparation of color reagents: Four color reagents applying for $\text{NH}_4\text{-N}$ measurement by the AQ2 auto-analyzer consisted of EDTA buffer, sodium phenate, sodium hypochlorite, and sodium nitroprusside. EDTA (ethylenediamine tetraacetic acid) buffer reagent is used to prevent interferences associated with precipitation problems due to high contents of Ca and Mg in sample solutions. The other reagents are used to develop blue color for standard solutions and sample solutions. Procedures for color reagent preparation are described more details in the USEPA method of 350.1.

Calibration method: An auto-standard concentration of 2 mg $\text{NH}_4\text{-N L}^{-1}$ was placed at the cup position # 1 on the roundtable of the AQ2 instrument. A standard calibration curve was set up daily at nine target concentrations of 0%, 2.5%, 5%, 10%, 25%, 50%, 75%, and 100% of the standard concentration (2mg $\text{NH}_4\text{-N L}^{-1}$). The establishment of calibration curve was based on the relationship between observed absorbances and the target concentrations (Appendix C).

QA/QC method: QA/QC was set up with two auto bracketing controls. The first one was CCV (continuing calibration verification) and CCB (continuing calibration blank). The concentration of CCV was 1 mg $\text{NH}_4\text{-N L}^{-1}$, and the CCB is DDI water. The CCV and CCB were performed after every ten samples measured and after completion of calibration setup. Acceptable ranges of CCV and CCB were 0.9 – 1.1 mg $\text{NH}_4\text{-N L}^{-1}$ and – 0.1 to 0.1 mg $\text{NH}_4\text{-N L}^{-1}$. The other controls included duplicates and spikes which were checked within a frequency of

every 20 samples measured. Concentration of ammonium added into spike samples was 0.5 mg $\text{NH}_4\text{-N L}^{-1}$ received from a spiking stock concentration of 20 mg $\text{NH}_4\text{-N/L}^{-1}$ which was set up at the position # 57 of the roundtable of the AQ2 instrument.

Nitrate

Procedures: Nitrate extraction was the same method as described for the $\text{NH}_4\text{-N}$ extraction. The USEPA standard method of 353.2 was used to measure nitrate for samples. Principle of this method is that nitrate reacts with sulfanilamide to form a diazonium compound which couples with N-(1-naphthyl) –ethelenediamine dihydrochloride (NEDD) to create a reddish-purple azo dye. This color is measured spectrophotometrically at a wavelength of 520 nm. The range of this method is from 0.03 to 4.5 mg $\text{NO}_3\text{-N L}^{-1}$ with a detection limit level of 0.006 mg $\text{NO}_3\text{-N L}^{-1}$.

Preparation of color reagents: Working buffer and sulfanilamide –NEDD are two main color reagents used for nitrate measurement by the AQ2 discrete auto-analyzer. Preparation of these reagents is described step by step in the USEPA method of 353.2. The working buffer reagent is a mixed solution containing EDTA which can prevent interferences of iron, copper, and other metals in sample solutions. The sulfanilamide –NEDD reagent is also a mixed solution comprising of sulfanilamide and NEDD that are used to develop color for nitrate.

Calibration method: An auto-standard concentration of 5 mg $\text{NO}_3\text{-N L}^{-1}$ was put at the cup position # 1 on the roundtable of the AQ2 instrument. A calibration curve was set up daily based on a relationship between nine target concentrations and their observed absorbances. The target concentrations included 0, 0.0333, 0.05, 0.1333, 0.25, 1.25, 2.5, 5, and 0 mg $\text{NO}_3\text{-N L}^{-1}$ created from percentages of the standard concentration of 5 mg $\text{NO}_3\text{-N L}^{-1}$ (Appendix C).

QA/QC method: Procedures of QA/QC for nitrate measurement was established the same as the ammonium measurement. But concentration of CCV was $1 \text{ mg NO}_3\text{-N L}^{-1}$, and concentration adding for spike sample was $0.5 \text{ mg NO}_3\text{-N L}^{-1}$ from a spiking stock concentration of $50 \text{ mg NO}_3\text{-N L}^{-1}$ which was set up at the position # 57 of the roundtable.

Concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ were calculated as follows:

$$[\text{NH}_4^+] \text{ or } [\text{NO}_3^-] (\text{mg kg}^{-1} \text{ soil or ash}) = \frac{X \text{ mg}}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{Y \text{ ml}}{2 \text{ g soil or ash}} \times \frac{1000 \text{ g soil or ash}}{1 \text{ kg soil or ash}} \quad (2-1)$$

where X is a content of $\text{NH}_4\text{-N}$ or $\text{NO}_3\text{-N}$ obtained from AQ2 auto-analyzer, Y is a volume of the extracting solution or DDI water added into soil samples (20 ml) or ash samples (40 ml).

Extractable Phosphorus

Tests for soil P availability are mainly based on understanding of chemical P forms existing in soils. Some chemical solutions have been widely used to extract potential P forms in soils. Bray and Kurtz (1945), so-called Bray P-1 test, developed a method for P extraction in the acid-to-neutral soils. Mehlich (1953) developed a P test, which is called Mehlich-1, for soils with low CEC in the South and Mid-Atlantic. Soltanpour and Workman (1979) developed AB-DTPA (Ammonium Bicarbonate - Diethylene Triamine Pentaacetic Acid) to extract P in calcareous soils. In addition, Olsen-P test (Olsen et al. 1954) and Mehlich-3 test (Mehlich, 1984) were utilized to extract soil P within a wider range of soil including acid soils and alkaline soils.

Four basic reactions can remove P from the solid phase of soil (Elrashidi, 2009), including (i) dissolving actions of acids; (ii) anion replacement to enhance desorption; (iii) complexing of cations binding P; and (iv) hydrolysis of cations binding P. Selection of a P test must take into account the chemical forms of P in soils. Calcium and magnesium phosphates are the major P minerals in calcareous soils. Tests of AB-DTPA, Olsen-P, and Mehlich 3 can be applied to extract soil P in calcareous soils (Elrashidi, 2009; Kamprath et al., 2000); however,

Olsen-P test is primarily recommended for P extraction in calcareous soils because of its own advantages (Orphanos, 1978; Vucāns et al., 2008). The Olsen-P test contains a single extractant of sodium bicarbonate (NaHCO_3). This extractant reduces calcium in solution through precipitation of calcium carbonate, controls dissolution of Ca-phosphates, and removes dissolved and absorbed P on calcium carbonate and Fe-oxide surfaces (Elrashidi, 2009). Although the AB-DTPA test contains ammonium bicarbonate, this test also includes a multi-element extractant (DTPA). This multi-element extractant often causes an interference of P extraction and gives an underestimation of results.

Bates (1990) used five different extractants (NaHCO_3 , AB-DTPA, Bray-Kurtz P1, Bray-Kurtz P2, and Mehlich 3) to test P availability. Availability of P was tested on 88 different soil types having soil pH range from 5.0 to 7.6. Results of Bates (1990) showed that two alkaline extractants (NaHCO_3 and AB-DTPA) were equally effective and superior in P availability to three acidic extractants (Bray-Kurtz P1, Bray-Kurtz P2, and Mehlich 3). Correlation coefficients (r^2 values) of extractable P to plant P uptake were 0.74, 0.73, 0.54, 0.65, and 0.66 for NaHCO_3 , AB-DTPA, Bray-Kurtz P1, Bray-Kurtz P2, and Mehlich 3, respectively. Prediction of plant P uptake was improved after adding soil pH into regression models, resulting in R^2 values of 0.80, 0.80, 0.70, 0.73, and 0.75 for NaHCO_3 , AB-DTPA, Bray-Kurtz P1, Bray-Kurtz P2, and Mehlich 3, respectively.

Comparing P availability by three different extractants (Olsen test, AB-DTPA test, Pi test) in the same soil and environmental conditions, Ahmad et al. (2006) showed that the Olsen test had the highest available P content (16.43 mg/kg), the Pi test (P extracted by Fe-impregnated filter paper after 16h of shaking) had 10.6 mg P/kg, whereas the AB-DTPA method gave the lowest available P contents (6.37 mg/kg). Nevertheless, Olsen test may underestimate or

overestimate availability of P in calcareous soils. Chien et al. (2009) found that Olsen-P was underestimated when calcareous soils contained more than 20% of gypsum, whereas Castro and Torrent (1995) proved that the Olsen-P test overestimated P availability in soils relatively rich in carbonate and poor in noncarbonate clay and Fe oxides.

Soils in the Pine Rockland forest have high contents of noncarbonate clay and Fe oxides and low carbonate content. Content of carbonate clay was from 10.4 to 36.0 g/kg soil and noncarbonate clay content was 699 to 715 g/kg soil (Zhou and Li, 2001). According to the USDA soil survey (1958), the Pine Rockland soils contained 16.5 g of carbonate clay/kg soil and 447 g of noncarbonate clay/kg soil. Gypsum content is relatively low in the Pine Rockland because sulfate in the Pine Rockland is derived mostly from wet deposition. In this study, Olsen-P test (Olsen et al., 1954) was chosen for assessing P availability in calcareous soils under the Pine Rockland forests.

Procedures: Soil P was extracted by 0.5M NaHCO₃ solution (Olsen et al., 1954) using a ratio of 2g soil to 40 ml 0.5M NaHCO₃ solution, and measured by the Beckman DU-640 spectrophotometer with an automated colorimetric method. The 0.5M NaHCO₃ extracting solution was prepared by placing 42g of NaHCO₃ into a 1000-ml volumetric flask containing 950ml DDI water. After NaHCO₃ was completely dissolved by stirring, pH of extracting solution was adjusted into 8.5 by adding 4M NaOH, and diluted the solution to volume of 1 liter. 2g of soils were weighed in 50-ml plastic bottles. 1g of activated carbon was also added into sample bottles to remove dark-brown color created from reactions between charcoal in soil samples and the extracting solution. Blank samples and blank samples with activated carbon were performed repeatedly after every 20 soil samples measured for QA/QC checking. 40 ml of the extracting solution were added into soil samples and blank samples. These bottles were shaken at 180

oscillations per minute for 30 minutes, and filtered by Whatman paper No. 42 (Kuo, 1996).

Filtrates were used to measure extractable P contents. A similar method was used to extract P from ash samples with rate of 2g ash and 40 ml DDI water (Qian et al., 2009b).

Preparation of P standard solutions: Seven P standard solutions preparing for calibration of spectrophotometer included 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg P L⁻¹. Volumes of 0, 0.5, 1, 2, 3, 4, 5 ml of 10mg P L⁻¹ stock standard solution were transferred into 50-ml flash, and diluted to the volume by blank solution (0.5M NaHCO₃ extracting solution) to make above P standard solutions.

Preparation of color reagent: Color reagent was prepared by the following steps:

- (1) Slowly transferring 152.8 ml concentrated H₂SO₄ to a 1-liter beaker with 400ml DDI water,
- (2) Putting 20g of ammonium molybdate into 1000-ml flash with 300 ml DDI water,
- (3) Slowly transferring (1) into (2),
- (4) Adding 100 ml of Antimony Potassium Tartrate (5%) into (3),
- (5) Diluting (4) into 1 liter by DDI water.

Color reagent was daily prepared by adding L-ascorbic acid to the mixed solution at rate of 1.5g of L-ascorbic acid to 100ml of the mixed solution.

Calibration curve method and determination of P concentration: 5ml of standard solutions and filtrates (sample solutions) were transferred into 20-ml vials, followed by addition of 1 drop of P-Nitrophenol and 0.5 ml of 5M H₂SO₄. 0.61ml of the color reagent (rate of 1 ml color reagent: 9 ml sample solution) to develop the blue color for standard and sample solutions. After adding color reagent, the blue color in standard and sample solutions which was stabilized after 45 minutes was measured at 880 nm by spectrophotometer. Calibration curve was established basing a linear relationship between known concentrations of seven standard solutions and their obtained absorbances (Appendix C). Concentrations of P in sample solutions (mg P L⁻¹) were

calculated from standard calibration curve and absorbance obtained from sample solutions.

Contents of P in soil or ash samples were estimated as follows:

$$P \text{ (mg P kg}^{-1} \text{ soil or ash)} = \left(\frac{X \text{ mg}}{1 \text{ L}} - \frac{Y \text{ mg}}{1 \text{ L}} - \frac{Z \text{ mg}}{1 \text{ L}} \right) \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{40 \text{ ml}}{2 \text{ g soil or ash}} \times \frac{1000 \text{ g soil or ash}}{1 \text{ kg soil or ash}} \quad (2-2)$$

where X is the concentration of P in the filtrates of soil or ash samples, Y is the average P content of the blank samples with activated carbon, and Z is the average P concentrations of the blank samples without activated carbon.

QA/QC method: Since blue color in sample solutions is stable from 45 to 60 minutes after adding the color reagent, only twenty samples were measured at the same time. In addition to duplicates and blank samples, the blank standard solution was also measured after every 20 samples in order to recalibrate the instrument.

Extractable Metals

Melich-1, Melich-3, and AB-DTPA are currently three methods widely applied to extract plant-available contents of metals. AB-DTPA method developed by Soltanpour and Workman (1979) is globally utilized to extract macro- and micro-nutrients in calcareous soils. AB-DTPA extractant with pH buffer of 7.6 works very well with calcareous soils, and is recommended by the UF/IFAS Extension Soil Testing Laboratory to extract plant-available contents of macro- and micro-nutrients for calcareous soils in South Florida. The AB-DTPA extracting solution contains two main components including ammonium bicarbonate which is used to extract chiefly macronutrients, and DTPA, a chelating agent, which is used to extract micronutrients.

Many studies reported that the AB-DTPA method has given good results on extractable contents of K, Fe, Mn, Cu, and Zn (Havlin and Soltanpour, 1981; Leggett and Argyle, 1983; O'Connor, 1988; Soltanpour and Workman, 1979). Moreover, the AB-DTPA extracting solution was also assessed to be good for extracting calcium and magnesium. By comparing effectiveness

of the AB-DTPA method with other traditional methods in different types of calcareous soils, Lucena and Bascones (1993) concluded that AB-DTPA extractant was not only valid for micronutrients but also good for calcium extraction in calcareous soils. By evaluating the effective capacity of AB-DTPA method in extraction of nutrient elements in South Florida calcareous soils using compost amendments, Hanton et al. (1996) proved that nutrients and heavy metals could be monitored successfully using AB-DTPA extractant, and AB-DTPA extractant was a good indicator to measure Ca and Mg in the South Florida calcareous soils. In this study, therefore, AB-DTPA method was selected to extract contents of nutrient elements.

Preparation for AB-DTPA extracting solution: 1.25 ml of NH_4OH added into a 2500-ml glass bottle containing 1750 ml of DDI water. Approximately 4.925 g of DTPA was added into the bottle, and swirled the solution until DTPA was completely dissolved. Approximately 197.65g of NH_4HCO_3 was added into the solution, swirled the solution to dissolve NH_4HCO_3 and brought the volume into 2500 ml by DDI water. The mixed solution (the AB-DTPA extracting solution) was adjusted to pH of 7.6 by adding either concentrated hydrochloric acid if the solution pH was higher than 7.6 or concentrated ammonium hydroxide if the buffer pH of the extracting solution was lower than 7.6 (Reed and Martens, 1996).

Extraction procedures: 10g of soil samples were weighed and put into 50-ml plastic bottles. 20ml of the AB-DTPA extracting solution were dispensed into the bottles. The solution bottles were shaken for 15 minutes at 180 rpm by a reciprocating shaker, and then filtered through a filter paper of Whatman No. 42. 5 ml of the filtrate was transferred into another 50-ml plastic bottle, added 0.5 ml of concentrated HNO_3 into the bottle (10 ml extracted solution:1 ml HNO_3), and thereafter diluted it into 50 ml by DDI water. The solution acidified by HNO_3 was analyzed by the AA-6300 Atomic Absorption Spectrophotometer to measure contents of

elements (Ca, Mg, K, Na, Fe, Mn, Cu, and Zn). Ash samples were extracted by DDI water with 2g ash and 40 ml DDI water (Qian et al., 2009b). These samples were shaken in 2 hours at 180 rpm, and filtered by Whatman No. 42. Other extraction steps were similar to soil extraction.

Preparation of blank solution: Blank solution for AB-DTPA method was prepared by adding 25 ml of concentrated HNO₃ and 250 ml of the AB-DTPA extracting solution into a 2500-ml plastic bottle, and then diluting it into the volume of 2500 ml by DDI water.

Instrument calibration: Standard calibration curve and standard addition are two major methods which can be applied to calibrate the AA-6300 Atomic Absorption Spectrophotometer. It is recommended that method of standard calibration curve shows a good linearity in the low concentration area; therefore, method of the 1st – order calibration curve was utilized to calibrate the instrument for each element measured. Objective of the calibration curve method is to use known standard concentrations of an element to obtain target concentrations of unknown solutions from soil samples. The 1st – order calibration curve for each element measurement was established by five different standard solutions. The standard solutions were prepared from a stock standard solution of 10 mg L⁻¹ and blank solution. A stock standard solution (1000 mg L⁻¹) of each element was diluted into a stock standard solution of 100 mg L⁻¹ by DDI water, and the 100 mg L⁻¹ standard solution was then diluted into a stock standard solution of 10 mg L⁻¹ by DDI water. Since concentrations of Ca, Mg, K, Na, Fe, Mn, Zn, and Cu in filtrate solutions were relatively different, concentrations of five standard solutions for each element were applied at different standard concentrations (Appendix C). Basing on specific concentrations of five standard solutions for each element, different volumes of the 10 mg L⁻¹ standard solution were added into 50-ml flashes, and then diluted into 50 ml by the blank solution.

QA/QC method: Setting of QA/QC aimed to validate a created calibration curve and

verify effects of pretreatment and liquid properties. Validation of the created calibration curve was carried out by ICV, ICB, CCV, CCB, and re-slope of the calibration curve. Spike test and duplicate were applied to verify influences of the pretreatment after every 20 samples were measured. ICV (initial calibration verification) and ICB (initial calibration blank) were performed immediately after the calibration curve was created. ICB occurred after ICV performance was intended to check that blank value decreased exactly. CCV (continuing calibration verification) and CCB (continuing calibration blank) were automatically performed with a frequency of every 20 samples measured. Concentrations of ICV and CCV were different from the standard concentrations used to create the calibration curve, but were in a concentration range of the calibration curve. Measured values of ICV, ICB, CCV, and CCB which ranged between 90% and 110% of their prepared concentrations were met with the EPA's acceptance criteria. Measurement was stopped if CRDL (Contract required detection limit) was exceeded the criteria. This action was implemented by establishment of "Out of Control Action" for ICV, ICB, CCV, and CCB. In addition, re-slope of the calibration curve was also established in frequency of every 20 samples measured. Re-slope measurement was carried out at the highest standard concentration used to constitute the calibration curve. The re-slope was the sensitivity correction measurement, and slope of the calibration curve was corrected basing on measured absorbance.

Establishment of measurement time: Pre-pray time, integration time, and response time are three important factors that impact on QA/QC and measurement results. The pre-pray time is time between two measurements, or interval of time that sampler of the instrument is rinsed by DDI water. The pre-pray time was set up at 18 seconds (5 seconds by default in the instrument). Eighteen seconds was enough time to clean all residuals of previous solution. The integration time is time that needs for sampler to take sample solution and pray the solution into burner, or

time that needs to measure a sample. The integration time was set up at 8 seconds (6 seconds by default). The response time is the repeated number of the integration. The integration was repeated in two times. Concentration of each sample was average value of two integration times.

Concentrations of nutrient elements in soils were calculated by the following equation:

$$\text{Ca (mg Ca kg}^{-1}\text{ soil)} = \frac{X \text{ mg}}{1\text{L}} \times \frac{1\text{L}}{1000 \text{ ml}} \times \frac{20 \text{ ml}}{10 \text{ g soil}} \times \frac{50 \text{ ml}}{5 \text{ ml}} \times \frac{1000 \text{ g soil}}{1 \text{ kg soil}} \quad (2-3)$$

Where X is a concentration of Ca obtained from the atomic absorbance spectrophotometer.

Concentrations of other elements were estimated as same as Ca calculation.

Total Nitrogen and Total Carbon

Contents of TC and TN were automatically measured by the Elemental CNS auto-analyzer. 200 mg (0.2g) of soil, ash, or plant tissue samples were weighed in crucibles, and put in roundtable of the CNS instrument in order. Sampler of the instrument picked up crucibles, and measured automatically contents of TC and TN.

Calibration of CNS instrument: CNS instrument was daily calibrated, and performed before samples measured. A standard calibration was set up by seven standard samples including three blanks (three empty crucibles) and four standards (four crucibles with 250mg of glutamic acid). The glutamic acid with 9.52% N and 40.78% C is a standard chemical used to calibrate the instrument and to check QA/QC during the measurement.

QA/QC setup: CNS operation is mainly depended on combustion process to measure contents of TC and TN. During the combustion process, CNS instrument uses a chemical mixture installed into a reduction tube of the instrument to burn all of soil or plant tissues at approximately 1000⁰C to measure carbon and nitrogen. QA/QC setup aimed to check out of the chemical mixture in the reduction tube. Duplicates of samples and Runin samples (250 mg of glutamic acid) were performed in every 20 samples measured in order to check existence of the chemical mixture. If

there is no more chemical in the reduction tube, TN (%) in Runin sample is higher than 9.52 %, and TN (%) in duplicate is also higher than that of the same sample of duplicate.

Total Phosphorus and Total Metal

Procedures of digestion: The dry-ashed method was applied to digest soil, ash, and plant tissue samples. 0.5 g of samples were weighed in 50-ml glass beakers and heated in a muffle furnace. Heating process was followed by heating samples at 250⁰C in 30 minutes, and continuing to increase temperature to 550⁰C and maintaining at this temperature for 4 hours, thereafter reducing temperature below 100⁰C before removing samples from the furnace. Burned soil samples were digested by 6M HCl following eight steps: firstly moistening burned soil samples in beakers by 3 drops of DDI water; secondly adding 20ml of 6M HCl into the beakers and placing them on a hot plate at a controlled temperature (from 100 to 120⁰C) until dry, approximately 3 hours; thirdly after the beakers were dried, heating the beakers on the hot plate at a high temperature (260 ÷ 280⁰C) for 30 minutes; fourthly removing the beakers from the hot plate and allowing them cool down to room temperature; fifthly moistening the soil in beakers with 2-3 ml of DDI water, and then adding 2.25 ml of 6M HCl; sixthly putting simultaneously four beakers into the hot plate with the high temperature, and removing them out the plate when boiling was started; seventhly, transferring solutions in the beakers into 50-ml volumetric flasks, washing the beakers at least three times with DDI water, and bring the flasks into 50 ml by DDI water; finally filtering the solution with Whatman paper No. 42. The filtrates were used to measure contents of phosphorus and metals. For ash and plant tissue samples, digestion process was similar to soil digestion, except for steps of 2, 3, 4, and 6.

Blank solution, standard solutions, and measurement of TP and TM: Blank solution was created by adding 112.5 ml 6M HCl into a 2500-ml plastic bottle, and bringing to volume of the

bottle with DDI water. Preparation of standard solutions for TP and TM was the same steps as described by sections of extractable P and extractable metals, but the above blank solution was used to create standard solutions for TP and TM measurements. Total contents of P and metals were determined by methods as presented in QA/QC sections of extractable P and metals.

QA/QC method: In addition to QA/QC setup for P measurement as described in the section of extractable P, a standard soil of SQCO-019 from NSI was applied for QA/QC in TP measurement. The standard soil sample having a standard concentration of 1040 mg P kg⁻¹ soil, in companion with duplicate and blank sample, was checked after every 20 samples measured.

QA/QC setup for TM measurement was similar to section of extractable metals.

APPENDIX C
CALIBRATION CURVES OBTAINED FROM LABORATORY ANALYSES, AND
STANDARD SOLUTIONS USED FOR METAL MEASUREMENT

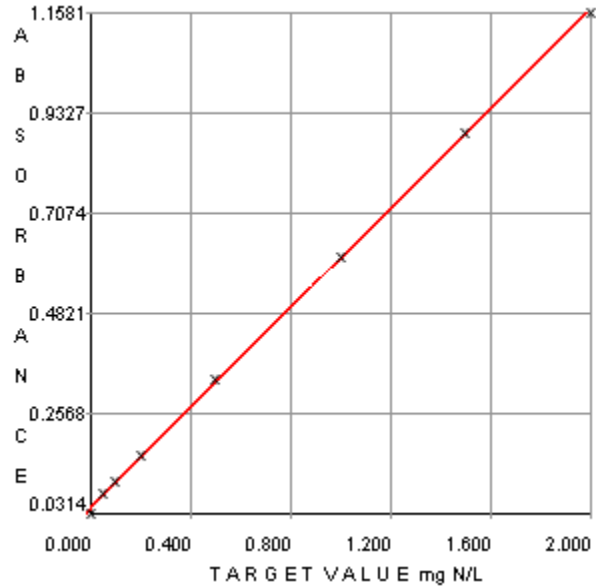
Calibration Chart and Curve Obtained from NH₄-N Measurement by AQ2

Calibration Chart

Type	Observed	Calculated	Target	% Error
S1	0.0314	-0.0228	0.0000	
S90	0.0731	0.0516	0.0500	3.2250
S91	0.1026	0.1044	0.1000	4.3537
S92	0.1597	0.2065	0.2000	3.2354
S93	0.3298	0.5106	0.5000	2.1118
S94	0.6062	1.0045	1.0000	0.4506
S95	0.8858	1.5043	1.5000	0.2884
S96	1.1581	1.9910	2.0000	-0.4521
S0	0.0328	-0.0204	0.0000	

Polynomial Order: 1
 Correlation Coefficient: 0.9999
 Carryover: 0.1
 Date & Time: Wed May 05 13:53:18 2010

Calibration Graph



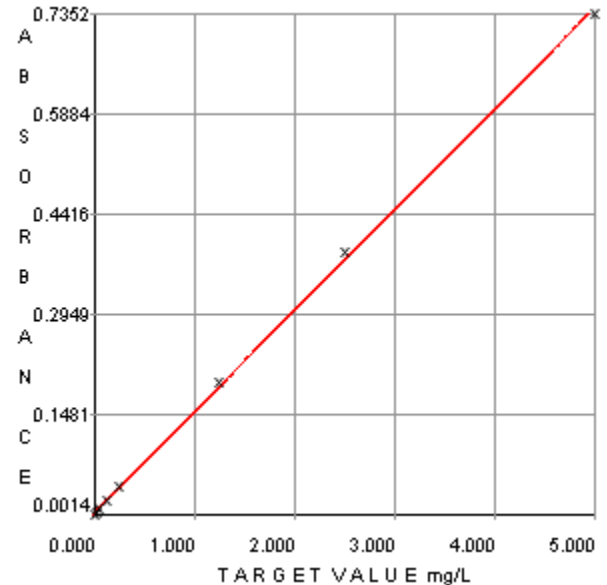
Calibration Chart and Curve Obtained from NO₃-N Measurement by AQ2

Calibration Chart

Type	Observed	Calculated	Target	% Error
S1	0.0014	-0.0215	0.0000	
S90	0.0050	0.0029	0.0333	-91.3896
S91	0.0102	0.0384	0.0500	-23.2672
S92	0.0212	0.1129	0.1333	-15.3413
S93	0.0436	0.2646	0.2500	5.8429
S94	0.1941	1.2839	1.2500	2.7089
S95	0.3867	2.5879	2.5000	3.5154
S96	0.7352	4.9477	5.0000	-1.0455
S0	0.0047	0.0009	0.0000	

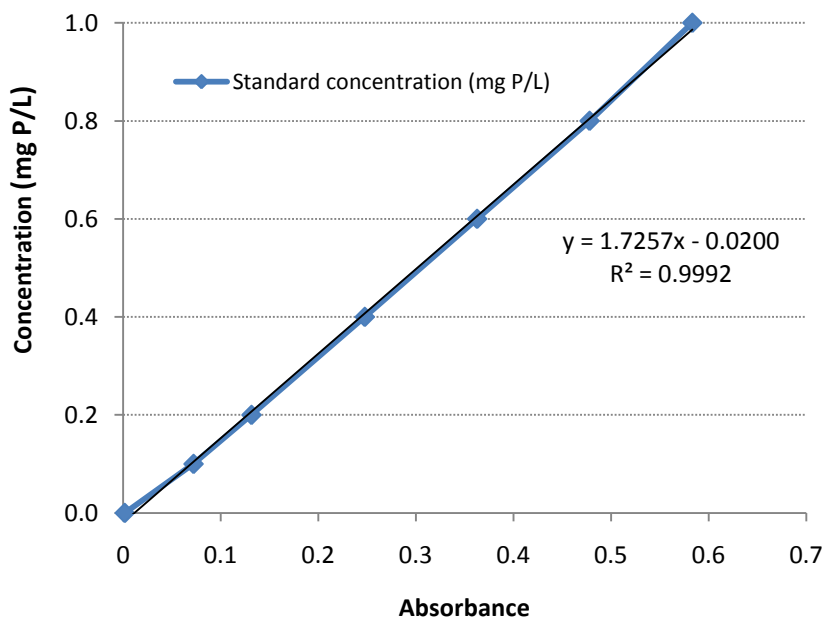
Polynomial Order: 1
 Correlation Coefficient: 0.9997
 Carryover: 0.5
 Date & Time: Wed Apr 21 08:03:37 2010

Calibration Graph



Standard Solutions and Calibration Curve Obtained from P Measurement by Spectrophotometer

Absorbance	Standard concentration (mg P/L)
0.0017	0.0
0.0722	0.1
0.1316	0.2
0.2477	0.4
0.3628	0.6
0.4781	0.8
0.5834	1.0



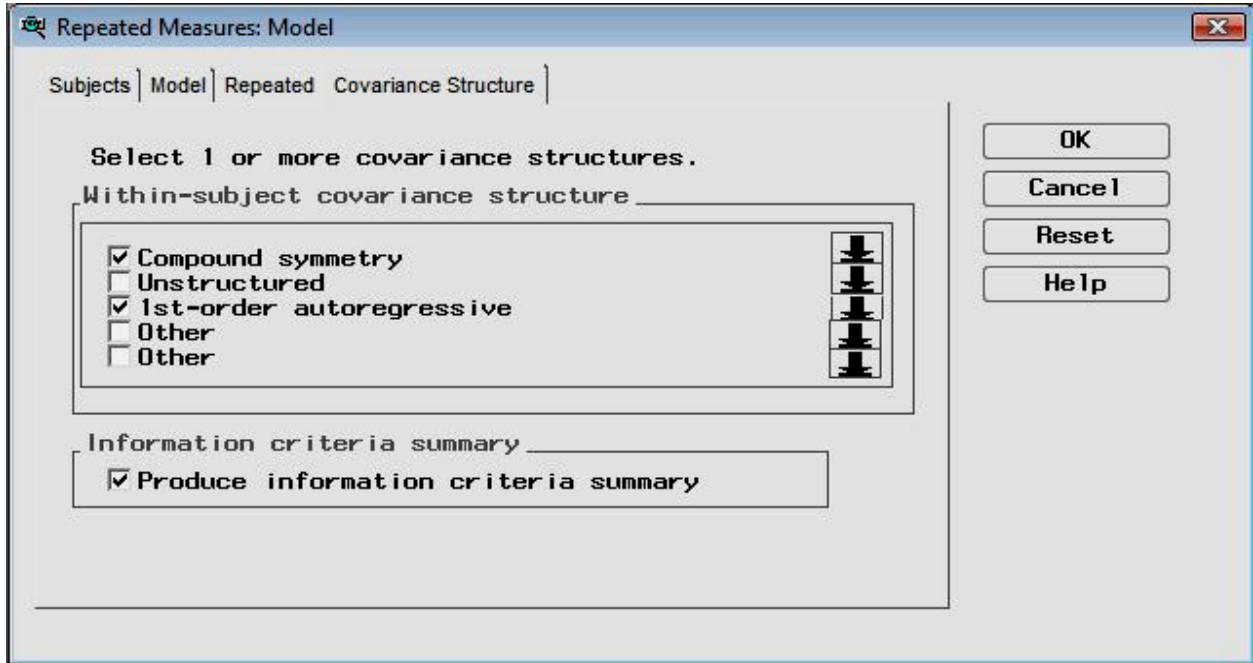
Standard Solutions and Detection Limits Used for Metal Measurement

Elements	Standard concentrations applied for calibration curve method										Detection limit
	0	0.2	0.4	0.5	0.6	0.8	1.0	2.0	3.0	5.0	
	----- mg L -----										
Ca	x			x			x		x	x	0.02
K	x			x			x		x	x	0.0025
Na	x			x			x		x	x	0.001
Fe	x			x			x		x	x	0.025
Mg	x			x			x	x	x		0.001
Mn	x			x			x	x	x		0.01
Zn	x	x	x		x	x					0.002
Cu	x	x	x		x	x					0.008

Where "x" are the standard concentrations of elements applied for calibration curve methods

APPENDIX D
COVARIANCE STRUCTURE MODELS AND ANOVA RESULTS BY REPEATED MEASURES ANALYSIS AND TUKEY'S COMPARISON RESULTS

Covariance Structure Models Applied for ANOVA Analysis by Repeated Measures



Results of ANOVA Analysis by Repeated Measures Method and Tukey's Comparison

Ca²⁺

The Mixed Procedure
Model Information

Data Set	WORK.CN2
Dependent Variable	Ca
Covariance Structure	Compound Symmetry
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
 Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 449.1
 AIC (smaller is better) 453.1
 AICC (smaller is better) 453.5
 BIC (smaller is better) 452.4

Type 3 Tests of Fixed Effects

Effect	Num	Den	F Value	Pr > F
	DF	DF		
Time	8	32	2.25	0.0497

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	1059.76	48.4434	32.9	21.88	<.0001
Time	14	904.61	48.4434	32.9	18.67	<.0001
Time	30	1035.04	48.4434	32.9	21.37	<.0001
Time	90	972.20	48.4434	32.9	20.07	<.0001
Time	180	1094.06	48.4434	32.9	22.58	<.0001
Time	270	988.70	48.4434	32.9	20.41	<.0001
Time	360	1161.85	48.4434	32.9	23.98	<.0001
Time	450	1048.94	48.4434	32.9	21.65	<.0001
Time	540	971.95	48.4434	32.9	20.06	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for Ca2_

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
 Error Degrees of Freedom 36
 Error Mean Square 11733.83
 Critical Value of Studentized Range 4.66279
 Minimum Significant Difference 225.88

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	1161.85	5	360
B A	1094.06	5	180
B A	1059.76	5	0
B A	1048.94	5	450
B A	1035.04	5	30
B A	988.70	5	270
B A	972.20	5	90
B A	971.95	5	540
B	904.61	5	14

Mg²⁺

The Mixed Procedure
Model Information

Data Set WORK.CN2
Dependent Variable Mg
Covariance Structure Autoregressive
Subject Effect Subject
Estimation Method REML
Residual Variance Method Profile
Fixed Effects SE Method Model-Based
Degrees of Freedom Method Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 346.9
AIC (smaller is better) 350.9
AICC (smaller is better) 351.2
BIC (smaller is better) 350.1

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	23.3	9.75	<.0001

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	52.1450	11.6969	28.5	4.46	0.0001
Time	14	143.66	11.6969	28.5	12.28	<.0001
Time	30	80.1241	11.6969	28.5	6.85	<.0001
Time	90	40.2032	11.6969	28.5	3.44	0.0018
Time	180	53.6432	11.6969	28.5	4.59	<.0001
Time	270	55.6509	11.6969	28.5	4.76	<.0001
Time	360	53.4054	11.6969	28.5	4.57	<.0001
Time	450	61.7985	11.6969	28.5	5.28	<.0001
Time	540	33.7322	11.6969	28.5	2.88	0.0074

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for Mg2_

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	688.3541
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	54.71

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	143.66	5	14
B	80.12	5	30
B	61.80	5	450
B	55.65	5	270
B	53.64	5	180
B	53.41	5	360
B	52.15	5	0
B	40.20	5	90
B	33.73	5	540

K⁺

The Mixed Procedure
Model Information

Data Set	WORK.CN2
Dependent Variable	K
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	398.4
AIC (smaller is better)	402.4
AICC (smaller is better)	402.7
BIC (smaller is better)	401.6

Type 3 Tests of Fixed Effects

Effect	Num	Den	F Value	Pr > F
	DF	DF		
Time	8	22.1	5.14	0.0011

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	164.79	22.8170	33.5	7.22	<.0001
Time	14	277.33	22.8170	33.5	12.15	<.0001
Time	30	193.48	22.8170	33.5	8.48	<.0001
Time	90	187.56	22.8170	33.5	8.22	<.0001
Time	180	236.42	22.8170	33.5	10.36	<.0001
Time	270	121.79	22.8170	33.5	5.34	<.0001
Time	360	144.82	22.8170	33.5	6.35	<.0001
Time	450	159.86	22.8170	33.5	7.01	<.0001
Time	540	136.82	22.8170	33.5	6.00	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for K_

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	2609.794
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	106.53

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	277.33	5	14
B A	236.42	5	180
B A C	193.48	5	30
B A C	187.56	5	90
B C	164.79	5	0
B C	159.86	5	450
B C	144.82	5	360
B C	136.82	5	540
C	121.79	5	270

Fe²⁺

The Mixed Procedure

Model Information

Data Set	WORK.CN2
Dependent Variable	Fe
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
 Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 406.7
 AIC (smaller is better) 410.7
 AICC (smaller is better) 411.1
 BIC (smaller is better) 410.0

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	22.3	3.31	0.0122

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	177.87	25.5837	33.8	6.95	<.0001
Time	14	153.31	25.5837	33.8	5.99	<.0001
Time	30	207.18	25.5837	33.8	8.10	<.0001
Time	90	169.80	25.5837	33.8	6.64	<.0001
Time	180	158.06	25.5837	33.8	6.18	<.0001
Time	270	288.91	25.5837	33.8	11.29	<.0001
Time	360	172.77	25.5837	33.8	6.75	<.0001
Time	450	196.97	25.5837	33.8	7.70	<.0001
Time	540	222.59	25.5837	33.8	8.70	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for Fe2_

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
 Error Degrees of Freedom 36
 Error Mean Square 3284.141
 Critical Value of Studentized Range 4.66279
 Minimum Significant Difference 119.5

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	288.91	5	270
B A	222.59	5	540
B A	207.18	5	30
B A	196.97	5	450
B A	177.87	5	0
B A	172.77	5	360
B A	169.80	5	90
B	158.06	5	180
B	153.31	5	14

Mn²⁺

The Mixed Procedure
Model Information

Data Set WORK.CN2
Dependent Variable Mn
Covariance Structure Autoregressive
Subject Effect Subject
Estimation Method REML
Residual Variance Method Profile
Fixed Effects SE Method Model-Based
Degrees of Freedom Method Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 375.5
AIC (smaller is better) 379.5
AICC (smaller is better) 379.9
BIC (smaller is better) 378.7

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	19.1	16.04	<.0001

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	69.2158	17.0049	30.5	4.07	0.0003
Time	14	256.37	17.0049	30.5	15.08	<.0001
Time	30	89.2194	17.0049	30.5	5.25	<.0001
Time	90	46.9500	17.0049	30.5	2.76	0.0097
Time	180	53.1232	17.0049	30.5	3.12	0.0039
Time	270	89.3215	17.0049	30.5	5.25	<.0001
Time	360	72.6488	17.0049	30.5	4.27	0.0002
Time	450	113.92	17.0049	30.5	6.70	<.0001
Time	540	58.8743	17.0049	30.5	3.46	0.0016

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for Mn2_

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	1444.268
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	79.247

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	256.37	5	14
B	113.92	5	450
B	89.32	5	270
B	89.22	5	30
B	72.65	5	360
B	69.22	5	0
B	58.87	5	540
B	53.12	5	180
B	46.95	5	90

Zn²⁺

The Mixed Procedure
Model Information

Data Set	WORK.CN2
Dependent Variable	Zn
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

The Mixed Procedure
Fit Statistics

-2 Res Log Likelihood	154.1
AIC (smaller is better)	158.1
AICC (smaller is better)	158.5
BIC (smaller is better)	157.4

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
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Time 8 21.1 1.99 0.0989

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	3.4637	0.7582	35.1	4.57	<.0001
Time	14	5.1102	0.7582	35.1	6.74	<.0001
Time	30	5.3852	0.7582	35.1	7.10	<.0001
Time	90	3.2660	0.7582	35.1	4.31	0.0001
Time	180	5.3352	0.7582	35.1	7.04	<.0001
Time	270	4.1550	0.7582	35.1	5.48	<.0001
Time	360	5.2907	0.7582	35.1	6.98	<.0001
Time	450	4.0349	0.7582	35.1	5.32	<.0001
Time	540	2.3814	0.7582	35.1	3.14	0.0034

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for Zn2_

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
 Error Degrees of Freedom 36
 Error Mean Square 2.880462
 Critical Value of Studentized Range 4.66279
 Minimum Significant Difference 3.5391

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	5.385	5	30
A	5.335	5	180
A	5.291	5	360
A	5.110	5	14
A	4.155	5	270
A	4.035	5	450
A	3.464	5	0
A	3.266	5	90
A	2.381	5	540

Cu²⁺

The Mixed Procedure

Model Information

Data Set WORK.CN2
 Dependent Variable Cu
 Covariance Structure Autoregressive
 Subject Effect Subject
 Estimation Method REML
 Residual Variance Method Profile
 Fixed Effects SE Method Model-Based
 Degrees of Freedom Method Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
 Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 89.7
 AIC (smaller is better) 93.7
 AICC (smaller is better) 94.1
 BIC (smaller is better) 92.9

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	20.5	1.46	0.2317

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	3.4427	0.3086	35.5	11.16	<.0001
Time	14	4.1178	0.3086	35.5	13.34	<.0001
Time	30	3.0644	0.3086	35.5	9.93	<.0001
Time	90	3.8265	0.3086	35.5	12.40	<.0001
Time	180	3.8131	0.3086	35.5	12.36	<.0001
Time	270	3.5783	0.3086	35.5	11.59	<.0001
Time	360	4.2436	0.3086	35.5	13.75	<.0001
Time	450	3.9561	0.3086	35.5	12.82	<.0001
Time	540	3.7901	0.3086	35.5	12.28	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for Cu2_

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
 Error Degrees of Freedom 36
 Error Mean Square 0.476144
 Critical Value of Studentized Range 4.66279
 Minimum Significant Difference 1.4389

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	4.2436	5	360
A	4.1178	5	14
A	3.9561	5	450
A	3.8265	5	90
A	3.8131	5	180
A	3.7901	5	540
A	3.5783	5	270
A	3.4427	5	0
A	3.0644	5	30

PO4-P

The Mixed Procedure
Model Information

Data Set WORK.CN2
 Dependent Variable P
 Covariance Structure Compound Symmetry
 Subject Effect Subject
 Estimation Method REML
 Residual Variance Method Profile
 Fixed Effects SE Method Model-Based
 Degrees of Freedom Method Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
 Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 158.6
 AIC (smaller is better) 162.6
 AICC (smaller is better) 163.0
 BIC (smaller is better) 161.9

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	32	16.19	<.0001

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	4.2394	0.8289	33.8	5.11	<.0001
Time	14	13.3829	0.8289	33.8	16.15	<.0001
Time	30	4.4067	0.8289	33.8	5.32	<.0001
Time	90	1.2249	0.8289	33.8	1.48	0.1488
Time	180	3.9528	0.8289	33.8	4.77	<.0001
Time	270	3.1879	0.8289	33.8	3.85	0.0005
Time	360	4.5643	0.8289	33.8	5.51	<.0001
Time	450	2.7131	0.8289	33.8	3.27	0.0025
Time	540	3.0140	0.8289	33.8	3.64	0.0009

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for PO4_P

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	3.435366
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	3.865

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	13.383	5	14
B	4.564	5	360
B	4.407	5	30
B	4.239	5	0
B	3.953	5	180
B	3.188	5	270
B	3.014	5	540
B	2.713	5	450
B	1.225	5	90

NH4-N

The Mixed Procedure Model Information

Data Set	WORK.CN2
Dependent Variable	NH4_N
Covariance Structure	Compound Symmetry
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	316.7
AIC (smaller is better)	320.7
AICC (smaller is better)	321.1
BIC (smaller is better)	319.9

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	32	12.98	<.0001

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	40.5855	7.2474	35.3	5.60	<.0001
Time	14	99.5711	7.2474	35.3	13.74	<.0001
Time	30	53.5506	7.2474	35.3	7.39	<.0001
Time	90	23.0816	7.2474	35.3	3.18	0.0030
Time	180	31.2149	7.2474	35.3	4.31	0.0001
Time	270	21.6083	7.2474	35.3	2.98	0.0052
Time	360	22.1453	7.2474	35.3	3.06	0.0043
Time	450	22.9957	7.2474	35.3	3.17	0.0031
Time	540	11.3979	7.2474	35.3	1.57	0.1247

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for NH4_N

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	262.6211
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	33.793

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	99.57	5	14
B	53.55	5	30
C B	40.59	5	0
C B	31.21	5	180
C B	23.08	5	90
C B	23.00	5	450
C B	22.15	5	360
C B	21.61	5	270
C	11.40	5	540

NO3-N

The Mixed Procedure

Model Information

Data Set	WORK.CN2
Dependent Variable	NO3_N
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
 Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 256.2
 AIC (smaller is better) 260.2
 AICC (smaller is better) 260.6
 BIC (smaller is better) 259.4

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	21.6	5.22	0.0010

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	8.1121	3.1089	35.9	2.61	0.0131
Time	14	11.3295	3.1089	35.9	3.64	0.0008
Time	30	2.4052	3.1089	35.9	0.77	0.4442
Time	90	5.1645	3.1089	35.9	1.66	0.1054
Time	180	25.1373	3.1089	35.9	8.09	<.0001
Time	270	8.5222	3.1089	35.9	2.74	0.0095
Time	360	2.6389	3.1089	35.9	0.85	0.4016
Time	450	2.7202	3.1089	35.9	0.87	0.3874
Time	540	10.5369	3.1089	35.9	3.39	0.0017

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for N03_N

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
 Error Degrees of Freedom 36
 Error Mean Square 48.33865
 Critical Value of Studentized Range 4.66279
 Minimum Significant Difference 14.498

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	25.137	5	180
B A	11.330	5	14
B	10.537	5	540
B	8.522	5	270
B	8.112	5	0
B	5.165	5	90
B	2.720	5	450
B	2.639	5	360
B	2.405	5	30

EC

The Mixed Procedure
Model Information

Data Set	WORK.CN2
Dependent Variable	EC
Covariance Structure	Compound Symmetry
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	444.8
AIC (smaller is better)	448.8
AICC (smaller is better)	449.2
BIC (smaller is better)	448.0

Type 3 Tests of Fixed Effects

	Num	Den		
Effect	DF	DF	F Value	Pr > F
Time	8	32	8.27	<.0001

Least Squares Means

			Standard			
Effect	Time	Estimate	Error	DF	t Value	Pr > t
Time	0	333.33	42.8200	35.5	7.78	<.0001
Time	14	697.64	42.8200	35.5	16.29	<.0001
Time	30	543.84	42.8200	35.5	12.70	<.0001
Time	90	370.08	42.8200	35.5	8.64	<.0001
Time	180	383.34	42.8200	35.5	8.95	<.0001
Time	270	348.22	42.8200	35.5	8.13	<.0001
Time	360	328.16	42.8200	35.5	7.66	<.0001
Time	450	452.72	42.8200	35.5	10.57	<.0001
Time	540	331.50	42.8200	35.5	7.74	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for EC

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	9167.775
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	199.66

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	697.64	5	14
B A	543.84	5	30
B C	452.72	5	450
B C	383.34	5	180
B C	370.08	5	90
B C	348.22	5	270
C	333.33	5	0
C	331.50	5	540
C	328.16	5	360

pH

The Mixed Procedure Model Information

Data Set	WORK.CN2
Dependent Variable	pH
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	-18.1
AIC (smaller is better)	-14.1
AICC (smaller is better)	-13.7
BIC (smaller is better)	-14.8

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	21.7	3.04	0.0187

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	7.5480	0.06889	36	109.57	<.0001
Time	14	7.8220	0.06889	36	113.54	<.0001
Time	30	7.4780	0.06889	36	108.55	<.0001
Time	90	7.4460	0.06889	36	108.09	<.0001
Time	180	7.5600	0.06889	36	109.74	<.0001
Time	270	7.4840	0.06889	36	108.64	<.0001
Time	360	7.5720	0.06889	36	109.91	<.0001
Time	450	7.7160	0.06889	36	112.01	<.0001
Time	540	7.5820	0.06889	36	110.06	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for pH

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	0.023732
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	0.3212

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	7.82200	5	14
B A	7.71600	5	450
B A	7.58200	5	540
B A	7.57200	5	360
B A	7.56000	5	180
B A	7.54800	5	0
B	7.48400	5	270
B	7.47800	5	30
B	7.44600	5	90

TP (%)

The Mixed Procedure

Model Information

Data Set	WORK.CN2
Dependent Variable	TP
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read 45
 Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 423.1
 AIC (smaller is better) 427.1
 AICC (smaller is better) 427.5
 BIC (smaller is better) 426.3

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	20.6	1.60	0.1845

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	321.82	31.8915	34.7	10.09	<.0001
Time	14	422.93	31.8915	34.7	13.26	<.0001
Time	30	301.09	31.8915	34.7	9.44	<.0001
Time	90	347.14	31.8915	34.7	10.88	<.0001
Time	180	340.12	31.8915	34.7	10.66	<.0001
Time	270	276.50	31.8915	34.7	8.67	<.0001
Time	360	376.98	31.8915	34.7	11.82	<.0001
Time	450	337.04	31.8915	34.7	10.57	<.0001
Time	540	316.92	31.8915	34.7	9.94	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for TP_____

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
 Error Degrees of Freedom 36
 Error Mean Square 0.000051
 Critical Value of Studentized Range 4.66279
 Minimum Significant Difference 0.0149

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	0.042293	5	14
A	0.037698	5	360
A	0.034714	5	90
A	0.034012	5	180
A	0.033704	5	450
A	0.031182	5	0
A	0.031692	5	540
A	0.030109	5	30
A	0.027650	5	270

TN (%)

The Mixed Procedure Model Information

Data Set	WORK.CN2
Dependent Variable	TN_____
Covariance Structure	Compound Symmetry
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45
Number of Observations Not Used	0

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	19.9
AIC (smaller is better)	23.9
AICC (smaller is better)	24.2
BIC (smaller is better)	23.1

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	32	3.55	0.0048

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	0.9303	0.1189	34.4	7.83	<.0001
Time	14	1.4151	0.1189	34.4	11.91	<.0001
Time	30	0.9056	0.1189	34.4	7.62	<.0001
Time	90	0.6896	0.1189	34.4	5.80	<.0001
Time	180	0.8386	0.1189	34.4	7.06	<.0001
Time	270	0.9835	0.1189	34.4	8.28	<.0001
Time	360	1.2838	0.1189	34.4	10.80	<.0001
Time	450	0.9575	0.1189	34.4	8.06	<.0001
Time	540	0.7871	0.1189	34.4	6.62	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for TN_____

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	0.070635
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	0.5542

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	1.4151	5	14
B A	1.2838	5	360
B A C	0.9835	5	270
B A C	0.9575	5	450
B A C	0.9517	5	0
B A C	0.9056	5	30
B C	0.8386	5	180
B C	0.7871	5	540
C	0.6896	5	90

TC (%)

The Mixed Procedure Model Information

Data Set	WORK.CN2
Dependent Variable	TC (%)
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	263.3
AIC (smaller is better)	267.3
AICC (smaller is better)	267.6
BIC (smaller is better)	266.5

Type 3 Tests of Fixed Effects

Num	Den
-----	-----

Effect	DF	DF	F Value	Pr > F
Time	8	21.5	4.89	0.0015

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	24.1156	3.4326	35.8	7.03	<.0001
Time	14	39.4621	3.4326	35.8	11.50	<.0001
Time	30	25.2949	3.4326	35.8	7.37	<.0001
Time	90	15.0340	3.4326	35.8	4.38	<.0001
Time	180	22.9942	3.4326	35.8	6.70	<.0001
Time	270	28.0598	3.4326	35.8	8.17	<.0001
Time	360	33.7697	3.4326	35.8	9.84	<.0001
Time	450	32.9431	3.4326	35.8	9.60	<.0001
Time	540	19.8249	3.4326	35.8	5.78	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for TC_____

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	58.93609
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	16.009

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	39.462	5	14
B A	33.770	5	360
B A	32.943	5	450
B A C	28.060	5	270
B A C	25.295	5	30
B A C	28.516	5	0
B C	22.994	5	180
B C	19.825	5	540
C	15.034	5	90

Soil C:N ratio

The Mixed Procedure

Model Information

Data Set	WORK.CN2
Dependent Variable	C_N_ratio
Covariance Structure	Compound Symmetry
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540

Subject 5 1 2 3 4 5

Number of Observations

Number of Observations Read 45
Number of Observations Used 45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood 249.8
AIC (smaller is better) 253.8
AICC (smaller is better) 254.2
BIC (smaller is better) 253.1

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	32	1.36	0.2532

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	26.8136	2.8571	35.5	9.38	<.0001
Time	14	28.1136	2.8571	35.5	9.84	<.0001
Time	30	29.2028	2.8571	35.5	10.22	<.0001
Time	90	21.9202	2.8571	35.5	7.67	<.0001
Time	180	27.3310	2.8571	35.5	9.57	<.0001
Time	270	28.2735	2.8571	35.5	9.90	<.0001
Time	360	26.7711	2.8571	35.5	9.37	<.0001
Time	450	34.7003	2.8571	35.5	12.15	<.0001
Time	540	25.3755	2.8571	35.5	8.88	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for C_N_ratio

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha 0.05
Error Degrees of Freedom 36
Error Mean Square 40.81496
Critical Value of Studentized Range 4.66279
Minimum Significant Difference 13.322

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	34.700	5	450
A	29.203	5	30
A	28.274	5	270
A	28.114	5	14
A	27.331	5	180
A	26.814	5	0
A	26.771	5	360

A	25.375	5	540
A	21.920	5	90

Soil N:P ratio

The Mixed Procedure
Model Information

Data Set	WORK.CN2
Dependent Variable	N_P_ratio
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	253.0
AIC (smaller is better)	257.0
AICC (smaller is better)	257.3
BIC (smaller is better)	256.2

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Time	8	19.3	2.74	0.0334

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	29.1075	3.1579	28.8	9.22	<.0001
Time	14	33.6452	3.1579	28.8	10.65	<.0001
Time	30	30.0741	3.1579	28.8	9.52	<.0001
Time	90	22.9960	3.1579	28.8	7.28	<.0001
Time	180	25.2722	3.1579	28.8	8.00	<.0001
Time	270	35.7968	3.1579	28.8	11.34	<.0001
Time	360	33.3465	3.1579	28.8	10.56	<.0001
Time	450	28.2369	3.1579	28.8	8.94	<.0001
Time	540	24.7085	3.1579	28.8	7.82	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for N_P_ratio

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	49.94508
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	14.737

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	35.797	5	270
B A	33.645	5	14
B A	33.346	5	360
B A	30.074	5	30
B A	29.108	5	0
B A	28.237	5	450
B A	25.272	5	180
B A	24.709	5	540
B	22.996	5	90

Soil C:P ratio

The Mixed Procedure
Model Information

Data Set	WORK.CN1
Dependent Variable	C_P_ratio
Covariance Structure	Autoregressive
Subject Effect	Subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
Time	9	0 14 30 90 180 270 360 450 540
Subject	5	1 2 3 4 5

Number of Observations

Number of Observations Read	45
Number of Observations Used	45

Convergence criteria met.

Fit Statistics

-2 Res Log Likelihood	509.8
AIC (smaller is better)	513.8
AICC (smaller is better)	514.2
BIC (smaller is better)	513.1

Type 3 Tests of Fixed Effects

	Num	Den		
Effect	DF	DF	F Value	Pr > F
Time	8	20.7	2.82	0.0277

Least Squares Means

Effect	Time	Estimate	Standard Error	DF	t Value	Pr > t
Time	0	771.83	106.55	34.5	7.24	<.0001
Time	14	942.59	106.55	34.5	8.85	<.0001
Time	30	842.29	106.55	34.5	7.91	<.0001
Time	90	503.21	106.55	34.5	4.72	<.0001
Time	180	693.08	106.55	34.5	6.50	<.0001
Time	270	1011.41	106.55	34.5	9.49	<.0001
Time	360	893.09	106.55	34.5	8.38	<.0001
Time	450	992.34	106.55	34.5	9.31	<.0001
Time	540	624.15	106.55	34.5	5.86	<.0001

The ANOVA Procedure

Tukey's Studentized Range (HSD) Test for C_P_ratio

This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	36
Error Mean Square	56925.29
Critical Value of Studentized Range	4.66279
Minimum Significant Difference	497.52

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	Time
A	1011.4	5	270
B A	992.3	5	450
B A	942.6	5	14
B A	893.1	5	360
B A	842.3	5	30
B A	771.8	5	0
B A	693.1	5	180
B A	624.2	5	540
B	503.2	5	90

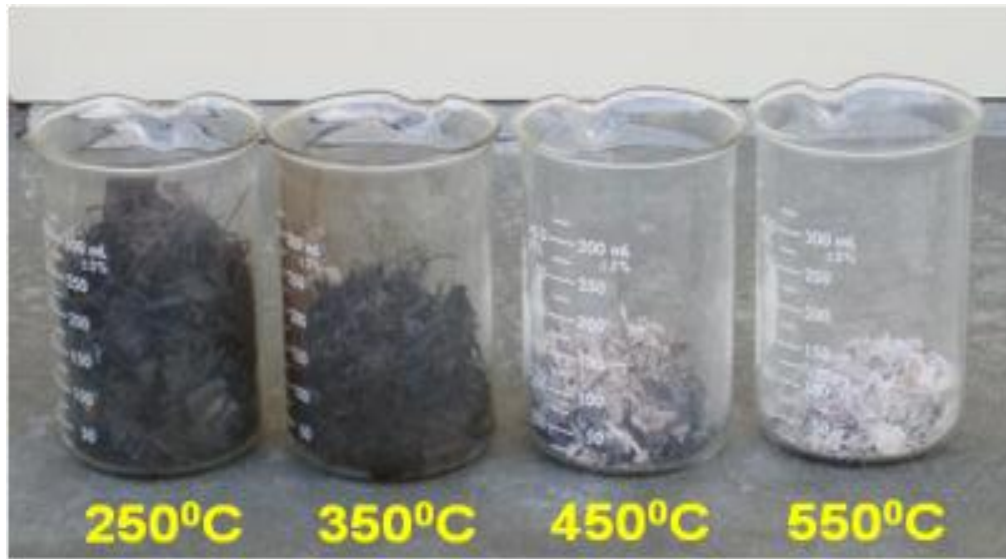
APPENDIX E
PROCEDURES FOR THE LABORATORY INCUBATION EXPERIMENT
A 30 x 30cm Sampling Frame Used to Collect Fuel-Load and Soil Samples



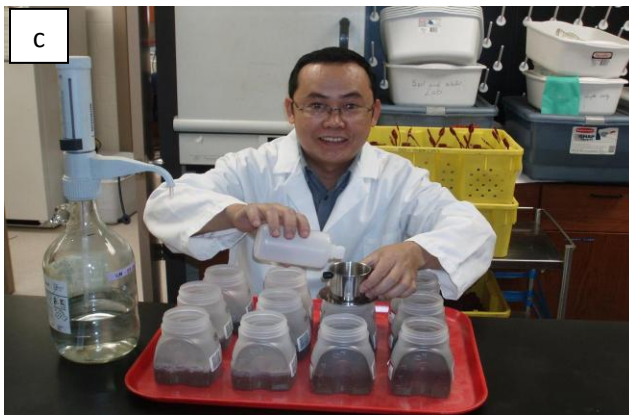
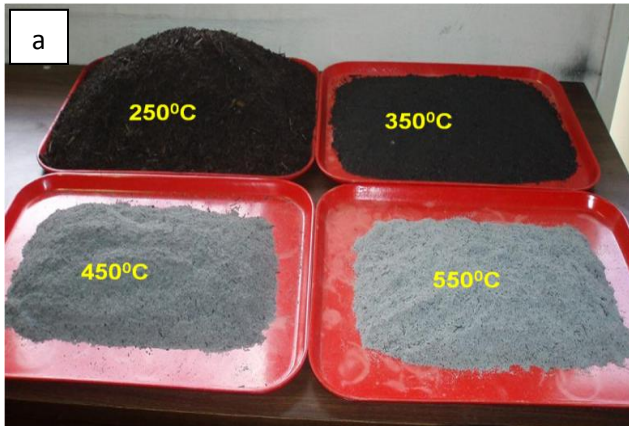
Preparation for Preparation: (a) Soils, (b) Fuel-Loads, (c) Bottles, and (d) Muffle Furnace



Ash Production at Different Heating Temperatures



Procedures for Incubation: (a) Mixing Ash Products, (b) Applying Ashes into Samples, (c) Applying DI Water for Soil Water Content, and (d) Incubating oil Samples



APPENDIX F
PROCEDURES FOR DETERMINATION OF SOIL FIELD CAPACITY

Replicates	Air-dried weight (g)	Drained soil weight (g)	Oven-dried soil weight (g)	Field capacity (%)	Water content in air-dry soil (%)
	a	b	c	$d = (b-c)*100/c$	$e = (a-c)*100/c$
1	100.09	199.57	88.04	126.68	13.69
2	100.04	199.07	88.14	125.86	13.50
3	100.06	192.17	83.78	129.37	19.43
4	100.03	193.02	86.83	122.30	15.20
Average	100.1	196.0	86.7	126.1	15.5

The water amounts at 35%, 70%, and 100% of field capacity applied for the incubation experiment were calculated as follows:

- Water amount in 150g air-dried soil: $150\text{g soil} \times 15.5\% = 23.25\text{ ml H}_2\text{O}$
- 150 g air-dried soil contains: $126.75\text{ g oven-dried soil} + 23.25\text{ ml H}_2\text{O}$
- 35% of field capacity: $126.1\% \times 35\% = 44.1\%$
- 70% of field capacity: $126.1\% \times 70\% = 88.27\%$
- 100% of field capacity: $126.1\% \times 100\% = 126.1\%$
- Water amount added into 150g air-dried soil samples at 35% of field capacity:
 $44.1\% \times 126.75\text{ g soil} - 23.25\text{ ml H}_2\text{O} = 33\text{ ml}$
- Water amount added into 150g air-dried soil samples at 70% of field capacity:
 $88.27\% \times 126.75\text{ g soil} - 23.25\text{ ml H}_2\text{O} = 88\text{ ml}$
- Water amount added into air-dried soil samples at 100% of field capacity:
 $126.1\% \times 126.75\text{ g soil} - 23.25\text{ ml H}_2\text{O} = 136\text{ ml}$

APPENDIX G
RESULTS OF MULTIPLE REGRESSION ANALYSES BY PROC GLM PROCEDURES
FOR THE LABORATORY INCUBATION EXPERIMENT

The GLM Procedure

Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	891.880275	127.411468	48.29	<.0001
Error	208	548.790959	2.638418		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P Mean
0.619073 25.37268 1.624321 6.401850

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Period	1	107.0590408	107.0590408	40.58	<.0001
Moisture	1	137.8747888	137.8747888	52.26	<.0001
Temperature	1	578.4344802	578.4344802	219.24	<.0001
Period*Moisture	1	13.1956077	13.1956077	5.00	0.0264
Moisture*Temperature	1	53.7227858	53.7227858	20.36	<.0001
Period*Temperature	1	0.0403640	0.0403640	0.02	0.9017
Period*Moistu*Temper	1	1.5532081	1.5532081	0.59	0.4438

Dependent Variable: P P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	890.327067	148.387845	56.35	<.0001
Error	209	550.344167	2.633226		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P Mean
0.617995 25.34770 1.622722 6.401850

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Period	1	107.0590408	107.0590408	40.66	<.0001
Moisture	1	137.8747888	137.8747888	52.36	<.0001
Temperature	1	578.4344802	578.4344802	219.67	<.0001
Period*Moisture	1	13.1956077	13.1956077	5.01	0.0262
Moisture*Temperature	1	53.7227858	53.7227858	20.40	<.0001
Period*Temperature	1	0.0403640	0.0403640	0.02	0.9016

Dependent Variable: P P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	890.286703	178.057341	67.94	<.0001
Error	210	550.384531	2.620879		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P Mean
0.617967 25.28820 1.618913 6.401850

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Period	1	107.0590408	107.0590408	40.85	<.0001
Moisture	1	137.8747888	137.8747888	52.61	<.0001
Temperature	1	578.4344802	578.4344802	220.70	<.0001
Period*Moisture	1	13.1956077	13.1956077	5.03	0.0259
Moisture*Temperature	1	53.7227858	53.7227858	20.50	<.0001

The GLM Procedure

Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: NH4 NH4

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	251552.4944	35936.0706	86.33	<.0001
Error	208	86579.0761	416.2456		
Corrected Total	215	338131.5705			

R-Square 0.743949 Coeff Var 20.94201 Root MSE 20.40210 NH4 Mean 97.42185

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	82518.9500	82518.9500	198.25	<.0001
Period	1	156699.0187	156699.0187	376.46	<.0001
Temperature	1	5586.9453	5586.9453	13.42	0.0003
Moisture*Period	1	6131.3155	6131.3155	14.73	0.0002
Moisture*Temperature	1	1.8245	1.8245	0.00	0.9473
Period*Temperature	1	425.7091	425.7091	1.02	0.3130
Moistu*Period*Temper	1	188.7313	188.7313	0.45	0.5015

Dependent Variable: NH4 NH4

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	251363.7631	41893.9605	100.91	<.0001
Error	209	86767.8074	415.1570		
Corrected Total	215	338131.5705			

R-Square 0.743390 Coeff Var 20.91461 Root MSE 20.37540 NH4 Mean 97.42185

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	82518.9500	82518.9500	198.77	<.0001
Period	1	156699.0187	156699.0187	377.45	<.0001
Temperature	1	5586.9453	5586.9453	13.46	0.0003
Moisture*Period	1	6131.3155	6131.3155	14.77	0.0002
Moisture*Temperature	1	1.8245	1.8245	0.00	0.9472
Period*Temperature	1	425.7091	425.7091	1.03	0.3124

Dependent Variable: NH4 NH4

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
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Model	4	250936.2295	62734.0574	151.81	<.0001
Error	211	87195.3410	413.2481		
Corrected Total	215	338131.5705			

R-Square Coeff Var Root MSE NH4 Mean
0.742126 20.86647 20.32850 97.42185

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	82518.9500	82518.9500	199.68	<.0001
Period	1	156699.0187	156699.0187	379.19	<.0001
Temperature	1	5586.9453	5586.9453	13.52	0.0003
Moisture*Period	1	6131.3155	6131.3155	14.84	0.0002

The GLM Procedure

Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: N03 N03

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	746665.373	106666.482	32.77	<.0001
Error	208	677062.137	3255.106		
Corrected Total	215	1423727.510			

R-Square Coeff Var Root MSE N03 Mean
0.524444 41.36232 57.05354 137.9360

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	27599.8311	27599.8311	8.48	0.0040
Period	1	646375.5199	646375.5199	198.57	<.0001
Temperature	1	510.3588	510.3588	0.16	0.6925
Moisture*Period	1	255.7087	255.7087	0.08	0.7795
Moisture*Temperature	1	64287.6899	64287.6899	19.75	<.0001
Period*Temperature	1	1506.5502	1506.5502	0.46	0.4971
Moistu*Period*Temper	1	6129.7148	6129.7148	1.88	0.1715

Dependent Variable: N03 N03

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	740535.659	123422.610	37.76	<.0001
Error	209	683191.852	3268.861		
Corrected Total	215	1423727.510			

R-Square Coeff Var Root MSE N03 Mean
0.520139 41.44962 57.17395 137.9360

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	27599.8311	27599.8311	8.44	0.0041
Period	1	646375.5199	646375.5199	197.74	<.0001
Temperature	1	510.3588	510.3588	0.16	0.6932
Moisture*Period	1	255.7087	255.7087	0.08	0.7800
Moisture*Temperature	1	64287.6899	64287.6899	19.67	<.0001

Period*Temperature	1	1506.5502	1506.5502	0.46	0.4980
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Dependent Variable: NO3 NO3

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	738773.400	184693.350	56.89	<.0001
Error	211	684954.110	3246.228		
Corrected Total	215	1423727.510			

R-Square	Coeff Var	Root MSE	NO3 Mean
0.518901	41.30587	56.97568	137.9360

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	39788.1244	39788.1244	12.26	0.0006
Period	1	646375.5199	646375.5199	199.12	<.0001
Temperature	1	52047.3065	52047.3065	16.03	<.0001
Moisture*Temperature	1	64287.6899	64287.6899	19.80	<.0001

The GLM Procedure

Number of Observations Read	216
Number of Observations Used	216

Dependent Variable: Mg Mg

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	43113.9441	6159.1349	20.71	<.0001
Error	208	61867.6150	297.4405		
Corrected Total	215	104981.5591			

R-Square	Coeff Var	Root MSE	Mg Mean
0.410681	25.33742	17.24646	68.06717

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	147.79143	147.79143	0.50	0.4817
Period	1	40944.17542	40944.17542	137.66	<.0001
Temperature	1	1318.37570	1318.37570	4.43	0.0365
Moisture*Period	1	42.37133	42.37133	0.14	0.7062
Moisture*Temperature	1	49.10095	49.10095	0.17	0.6849
Period*Temperature	1	414.05598	414.05598	1.39	0.2394
Moistu*Period*Temper	1	198.07330	198.07330	0.67	0.4154

Dependent Variable: Mg Mg

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	42915.8708	7152.6451	24.09	<.0001
Error	209	62065.6883	296.9650		
Corrected Total	215	104981.5591			

R-Square	Coeff Var	Root MSE	Mg Mean
0.408794	25.31716	17.23267	68.06717

Source	DF	Type I SS	Mean Square	F Value	Pr > F
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Moisture	1	147.79143	147.79143	0.50	0.4813
Period	1	40944.17542	40944.17542	137.88	<.0001
Temperature	1	1318.37570	1318.37570	4.44	0.0363
Moisture*Period	1	42.37133	42.37133	0.14	0.7060
Moisture*Temperature	1	49.10095	49.10095	0.17	0.6847
Period*Temperature	1	414.05598	414.05598	1.39	0.2390

Dependent Variable: Mg Mg

		Sum of			
Source	DF	Squares	Mean Square	F Value	Pr > F
Model	3	42410.3426	14136.7809	47.90	<.0001
Error	212	62571.2166	295.1472		
Corrected Total	215	104981.5591			

R-Square Coeff Var Root MSE Mg Mean
0.403979 25.23955 17.17985 68.06717

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	147.79143	147.79143	0.50	0.4800
Period	1	40944.17542	40944.17542	138.72	<.0001
Temperature	1	1318.37570	1318.37570	4.47	0.0357

The GLM Procedure

Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: K K

		Sum of			
Source	DF	Squares	Mean Square	F Value	Pr > F
Model	7	232723.7821	33246.2546	13.42	<.0001
Error	208	515350.5578	2477.6469		
Corrected Total	215	748074.3399			

R-Square Coeff Var Root MSE K Mean
0.311097 12.61950 49.77597 394.4368

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	803.6009	803.6009	0.32	0.5696
Period	1	33001.7488	33001.7488	13.32	0.0003
Temperature	1	180391.6127	180391.6127	72.81	<.0001
Moisture*Period	1	10530.4672	10530.4672	4.25	0.0405
Moisture*Temperature	1	106.7017	106.7017	0.04	0.8358
Period*Temperature	1	494.3652	494.3652	0.20	0.6556
Moistu*Period*Temper	1	7395.2857	7395.2857	2.98	0.0855

Dependent Variable: K K

		Sum of			
Source	DF	Squares	Mean Square	F Value	Pr > F
Model	6	225328.4964	37554.7494	15.01	<.0001
Error	209	522745.8435	2501.1763		
Corrected Total	215	748074.3399			

R-Square Coeff Var Root MSE K Mean

0.301211 12.67928 50.01176 394.4368

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	803.6009	803.6009	0.32	0.5714
Period	1	33001.7488	33001.7488	13.19	0.0004
Temperature	1	180391.6127	180391.6127	72.12	<.0001
Moisture*Period	1	10530.4672	10530.4672	4.21	0.0414
Moisture*Temperature	1	106.7017	106.7017	0.04	0.8366
Period*Temperature	1	494.3652	494.3652	0.20	0.6571

Dependent Variable: K K

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	224727.4296	56181.8574	22.65	<.0001
Error	211	523346.9103	2480.3171		
Corrected Total	215	748074.3399			

R-Square Coeff Var Root MSE K Mean
 0.300408 12.62630 49.80278 394.4368

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	803.6009	803.6009	0.32	0.5698
Period	1	33001.7488	33001.7488	13.31	0.0003
Temperature	1	180391.6127	180391.6127	72.73	<.0001
Moisture*Period	1	10530.4672	10530.4672	4.25	0.0406

The GLM Procedure

Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: Fe Fe

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	32383.33717	4626.19102	17.48	<.0001
Error	208	55042.04072	264.62520		
Corrected Total	215	87425.37789			

R-Square Coeff Var Root MSE Fe Mean
 0.370411 9.469961 16.26730 171.7779

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	5771.52855	5771.52855	21.81	<.0001
Period	1	14.45253	14.45253	0.05	0.8154
Temperature	1	18468.35837	18468.35837	69.79	<.0001
Moisture*Period	1	1049.12153	1049.12153	3.96	0.0478
Moisture*Temperature	1	6185.11206	6185.11206	23.37	<.0001
Period*Temperature	1	758.26269	758.26269	2.87	0.0920
Moistu*Period*Temper	1	136.50145	136.50145	0.52	0.4734

Dependent Variable: Fe Fe

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
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Model	6	32246.83572	5374.47262	20.36	<.0001
Error	209	55178.54217	264.01216		
Corrected Total	215	87425.37789			

R-Square Coeff Var Root MSE Fe Mean
0.368850 9.458985 16.24845 171.7779

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	5771.52855	5771.52855	21.86	<.0001
Period	1	14.45253	14.45253	0.05	0.8152
Temperature	1	18468.35837	18468.35837	69.95	<.0001
Moisture*Period	1	1049.12153	1049.12153	3.97	0.0475
Moisture*Temperature	1	6185.11206	6185.11206	23.43	<.0001
Period*Temperature	1	758.26269	758.26269	2.87	0.0916

Dependent Variable: Fe Fe

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	31488.57303	6297.71461	23.64	<.0001
Error	210	55936.80486	266.36574		
Corrected Total	215	87425.37789			

R-Square Coeff Var Root MSE Fe Mean
0.360177 9.501054 16.32071 171.7779

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	5771.52855	5771.52855	21.67	<.0001
Period	1	14.45253	14.45253	0.05	0.8160
Temperature	1	18468.35837	18468.35837	69.33	<.0001
Moisture*Period	1	1049.12153	1049.12153	3.94	0.0485
Moisture*Temperature	1	6185.11206	6185.11206	23.22	<.0001

The GLM Procedure

Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: Mn Mn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	18161.76282	2594.53755	37.50	<.0001
Error	208	14390.60068	69.18558		
Corrected Total	215	32552.36350			

R-Square Coeff Var Root MSE Mn Mean
0.557925 15.43393 8.317787 53.89287

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	175.24893	175.24893	2.53	0.1130
Period	1	5356.27765	5356.27765	77.42	<.0001
Temperature	1	11448.86482	11448.86482	165.48	<.0001
Moisture*Period	1	106.70997	106.70997	1.54	0.2157
Moisture*Temperature	1	385.46962	385.46962	5.57	0.0192

Period*Temperature	1	647.42388	647.42388	9.36	0.0025
Moistu*Period*Temper	1	41.76794	41.76794	0.60	0.4380

Dependent Variable: Mn Mn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	18119.99489	3019.99915	43.73	<.0001
Error	209	14432.36862	69.05440		
Corrected Total	215	32552.36350			

R-Square 0.556641
 Coeff Var 15.41929
 Root MSE 8.309897
 Mn Mean 53.89287

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	175.24893	175.24893	2.54	0.1127
Period	1	5356.27765	5356.27765	77.57	<.0001
Temperature	1	11448.86482	11448.86482	165.79	<.0001
Moisture*Period	1	106.70997	106.70997	1.55	0.2152
Moisture*Temperature	1	385.46962	385.46962	5.58	0.0191
Period*Temperature	1	647.42388	647.42388	9.38	0.0025

Dependent Variable: Mn Mn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	18013.28491	3602.65698	52.04	<.0001
Error	210	14539.07859	69.23371		
Corrected Total	215	32552.36350			

R-Square 0.553363
 Coeff Var 15.43930
 Root MSE 8.320680
 Mn Mean 53.89287

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	175.24893	175.24893	2.53	0.1131
Period	1	5356.27765	5356.27765	77.37	<.0001
Temperature	1	11448.86482	11448.86482	165.37	<.0001
Moisture*Temperature	1	385.46962	385.46962	5.57	0.0192
Period*Temperature	1	647.42388	647.42388	9.35	0.0025

The GLM Procedure

Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: Zn Zn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	120.8635977	17.2662282	34.07	<.0001
Error	208	105.3983368	0.5067228		
Corrected Total	215	226.2619345			

R-Square 0.534176
 Coeff Var 19.77035
 Root MSE 0.711845
 Zn Mean 3.600567

Source	DF	Type I SS	Mean Square	F Value	Pr > F
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Moisture	1	0.00862878	0.00862878	0.02	0.8963
Period	1	90.57580624	90.57580624	178.75	<.0001
Temperature	1	23.44641073	23.44641073	46.27	<.0001
Moisture*Period	1	5.04079205	5.04079205	9.95	0.0018
Moisture*Temperature	1	0.13988819	0.13988819	0.28	0.5999
Period*Temperature	1	1.29992540	1.29992540	2.57	0.1107
Moistu*Period*Temper	1	0.35214631	0.35214631	0.69	0.4054

Dependent Variable: Zn Zn

		Sum of			
Source	DF	Squares	Mean Square	F Value	Pr > F
Model	6	120.5114514	20.0852419	39.70	<.0001
Error	209	105.7504831	0.5059832		
Corrected Total	215	226.2619345			

R-Square 0.532619
 Coeff Var 19.75592
 Root MSE 0.711325
 Zn Mean 3.600567

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.00862878	0.00862878	0.02	0.8962
Period	1	90.57580624	90.57580624	179.01	<.0001
Temperature	1	23.44641073	23.44641073	46.34	<.0001
Moisture*Period	1	5.04079205	5.04079205	9.96	0.0018
Moisture*Temperature	1	0.13988819	0.13988819	0.28	0.5996
Period*Temperature	1	1.29992540	1.29992540	2.57	0.1105

Dependent Variable: Zn Zn

		Sum of			
Source	DF	Squares	Mean Square	F Value	Pr > F
Model	4	119.0716378	29.7679094	58.60	<.0001
Error	211	107.1902967	0.5080109		
Corrected Total	215	226.2619345			

R-Square 0.526256
 Coeff Var 19.79546
 Root MSE 0.712749
 Zn Mean 3.600567

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.00862878	0.00862878	0.02	0.8964
Period	1	90.57580624	90.57580624	178.30	<.0001
Temperature	1	23.44641073	23.44641073	46.15	<.0001
Moisture*Period	1	5.04079205	5.04079205	9.92	0.0019

The GLM Procedure

Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: Cu Cu

		Sum of			
Source	DF	Squares	Mean Square	F Value	Pr > F
Model	7	22.72708882	3.24672697	36.38	<.0001
Error	208	18.56494385	0.08925454		
Corrected Total	215	41.29203267			

R-Square Coeff Var Root MSE Cu Mean
 0.550399 12.60532 0.298755 2.370071

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.02681326	0.02681326	0.30	0.5842
Period	1	4.41933481	4.41933481	49.51	<.0001
Temperature	1	17.90643658	17.90643658	200.62	<.0001
Moisture*Period	1	0.17778274	0.17778274	1.99	0.1596
Moisture*Temperature	1	0.13881834	0.13881834	1.56	0.2138
Period*Temperature	1	0.00088223	0.00088223	0.01	0.9209
Moistu*Period*Temper	1	0.05702086	0.05702086	0.64	0.4250

Dependent Variable: Cu Cu

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	22.67006795	3.77834466	42.41	<.0001
Error	209	18.62196471	0.08910031		
Corrected Total	215	41.29203267			

R-Square Coeff Var Root MSE Cu Mean
 0.549018 12.59442 0.298497 2.370071

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.02681326	0.02681326	0.30	0.5839
Period	1	4.41933481	4.41933481	49.60	<.0001
Temperature	1	17.90643658	17.90643658	200.97	<.0001
Moisture*Period	1	0.17778274	0.17778274	2.00	0.1593
Moisture*Temperature	1	0.13881834	0.13881834	1.56	0.2134
Period*Temperature	1	0.00088223	0.00088223	0.01	0.9208

Dependent Variable: Cu Cu

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	22.35258464	7.45086155	83.40	<.0001
Error	212	18.93944803	0.08933702		
Corrected Total	215	41.29203267			

R-Square Coeff Var Root MSE Cu Mean
 0.541329 12.61114 0.298893 2.370071

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.02681326	0.02681326	0.30	0.5844
Period	1	4.41933481	4.41933481	49.47	<.0001
Temperature	1	17.90643658	17.90643658	200.44	<.0001

The GLM Procedure

Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: EC EC

Sum of

Source	DF	Squares	Mean Square	F Value	Pr > F
Model	7	4571017.69	653002.53	18.79	<.0001
Error	208	7227531.94	34747.75		
Corrected Total	215	11798549.63			

R-Square 0.387422
 Coeff Var 17.65571
 Root MSE 186.4075
 EC Mean 1055.792

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	19336.360	19336.360	0.56	0.4565
Period	1	4061714.949	4061714.949	116.89	<.0001
Temperature	1	107900.023	107900.023	3.11	0.0795
Moisture*Period	1	34147.301	34147.301	0.98	0.3227
Moisture*Temperature	1	286682.223	286682.223	8.25	0.0045
Period*Temperature	1	24052.440	24052.440	0.69	0.4064
Moistu*Period*Temper	1	37184.391	37184.391	1.07	0.3021

Dependent Variable: EC EC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	4533833.30	755638.88	21.74	<.0001
Error	209	7264716.33	34759.41		
Corrected Total	215	11798549.63			

R-Square 0.384270
 Coeff Var 17.65867
 Root MSE 186.4388
 EC Mean 1055.792

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	19336.360	19336.360	0.56	0.4566
Period	1	4061714.949	4061714.949	116.85	<.0001
Temperature	1	107900.023	107900.023	3.10	0.0796
Moisture*Period	1	34147.301	34147.301	0.98	0.3228
Moisture*Temperature	1	286682.223	286682.223	8.25	0.0045
Period*Temperature	1	24052.440	24052.440	0.69	0.4064

Dependent Variable: EC EC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	4475633.56	1118908.39	32.24	<.0001
Error	211	7322916.07	34705.76		
Corrected Total	215	11798549.63			

R-Square 0.379338
 Coeff Var 17.64504
 Root MSE 186.2948
 EC Mean 1055.792

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	305914.342	305914.342	8.81	0.0033
Period	1	4061714.949	4061714.949	117.03	<.0001
Temperature	1	381998.978	381998.978	11.01	0.0011
Moisture*Temperature	1	286682.223	286682.223	8.26	0.0045

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: pH pH

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	1.54419845	0.22059978	9.54	<.0001
Error	208	4.80867887	0.02311865		
Corrected Total	215	6.35287731			

R-Square 0.243071 Coeff Var 2.003844 Root MSE 0.152048 pH Mean 7.587824

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.13799103	0.13799103	5.97	0.0154
Period	1	0.01659215	0.01659215	0.72	0.3979
Temperature	1	1.33492676	1.33492676	57.74	<.0001
Moisture*Period	1	0.03874446	0.03874446	1.68	0.1969
Moisture*Temperature	1	0.00000387	0.00000387	0.00	0.9897
Period*Temperature	1	0.00006768	0.00006768	0.00	0.9569
Moistu*Period*Temper	1	0.01587250	0.01587250	0.69	0.4083

Dependent Variable: pH pH

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	1.52832595	0.25472099	11.03	<.0001
Error	209	4.82455136	0.02308398		
Corrected Total	215	6.35287731			

R-Square 0.240572 Coeff Var 2.002341 Root MSE 0.151934 pH Mean 7.587824

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.13799103	0.13799103	5.98	0.0153
Period	1	0.01659215	0.01659215	0.72	0.3975
Temperature	1	1.33492676	1.33492676	57.83	<.0001
Moisture*Period	1	0.03874446	0.03874446	1.68	0.1966
Moisture*Temperature	1	0.00000387	0.00000387	0.00	0.9897
Period*Temperature	1	0.00006768	0.00006768	0.00	0.9569

Dependent Variable: pH pH

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	1.48950994	0.49650331	21.64	<.0001
Error	212	4.86336738	0.02294041		
Corrected Total	215	6.35287731			

R-Square 0.234462 Coeff Var 1.996105 Root MSE 0.151461 pH Mean 7.587824

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Moisture	1	0.13799103	0.13799103	6.02	0.0150
Period	1	0.01659215	0.01659215	0.72	0.3960
Temperature	1	1.33492676	1.33492676	58.19	<.0001

APPENDIX H

RESULTS OF LINEAR REGRESSION ANALYSIS ON ASH pH, EC, TOTAL AND WATER-SOLUBLE NUTRIENTS IN LABORATORY RESIDUAL ASHES

The GLM Procedure
 Number of Observations Read 12
 Number of Observations Used 12

Dependent Variable: pH pH

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	7.95704167	7.95704167	10.82	0.0082
Error	10	7.35205000	0.73520500		
Corrected Total	11	15.30909167			

R-Square 0.519759 Coeff Var 11.70435 Root MSE 0.857441 pH Mean 7.325833

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	7.95704167	7.95704167	10.82	0.0082

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	4.412500000	0.91950299	4.80	0.0007
Temperature	0.007283333	0.00221390	3.29	0.0082

Dependent Variable: EC EC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	1727546.017	1727546.017	107.20	<.0001
Error	10	161144.233	16114.423		
Corrected Total	11	1888690.250			

R-Square 0.914679 Coeff Var 15.06290 Root MSE 126.9426 EC Mean 842.7500

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	1727546.017	1727546.017	107.20	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-514.7166667	136.1307711	-3.78	0.0036
Temperature	3.3936667	0.3277644	10.35	<.0001

Dependent Variable: Ca Ca

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	271458.100	271458.100	2.51	0.1445
Error	10	1083216.982	108321.698		
Corrected Total	11	1354675.082			

R-Square 0.200386 Coeff Var 101.6885 Root MSE 329.1226 Ca Mean 323.6576

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	271458.0996	271458.0996	2.51	0.1445

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	861.7610600	352.9446882	2.44	0.0348
Temperature	-1.3452586	0.8497909	-1.58	0.1445

Dependent Variable: K K

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	442760.5605	442760.5605	85.10	<.0001
Error	10	52029.7890	5202.9789		
Corrected Total	11	494790.3495			

R-Square	Coeff Var	Root MSE	K Mean
0.894845	9.611067	72.13168	750.5064

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	442760.5605	442760.5605	85.10	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	63.28162428	77.35260654	0.82	0.4324
Temperature	1.71806201	0.18624319	9.22	<.0001

Dependent Variable: Mg Mg

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	2927.16979	2927.16979	0.85	0.3769
Error	10	34239.42369	3423.94237		
Corrected Total	11	37166.59348			

R-Square	Coeff Var	Root MSE	Mg Mean
0.078758	52.82394	58.51446	110.7726

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	2927.169791	2927.169791	0.85	0.3769

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	166.6502868	62.74977071	2.66	0.0241
Temperature	-0.1396942	0.15108369	-0.92	0.3769

Dependent Variable: Mn Mn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	2019.922713	2019.922713	33.03	0.0002
Error	10	611.602143	61.160214		
Corrected Total	11	2631.524857			

R-Square	Coeff Var	Root MSE	Mn Mean
0.767586	57.96844	7.820500	13.49096

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	2019.922713	2019.922713	33.03	0.0002

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	59.90845976	8.38655152	7.14	<.0001
Temperature	-0.11604375	0.02019244	-5.75	0.0002

Dependent Variable: Zn Zn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	3.88962675	3.88962675	29.73	0.0003
Error	10	1.30810550	0.13081055		
Corrected Total	11	5.19773225			

R-Square 0.748331
 Coeff Var 55.53474
 Root MSE 0.361677
 Zn Mean 0.651263

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	3.88962675	3.88962675	29.73	0.0003

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	2.688156930	0.38785581	6.93	<.0001
Temperature	-0.005092234	0.00093385	-5.45	0.0003

Dependent Variable: NH4 NH4

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	299.7569696	299.7569696	123.34	<.0001
Error	10	24.3024330	2.4302433		
Corrected Total	11	324.0594026			

R-Square 0.925006
 Coeff Var 22.25270
 Root MSE 1.558924
 NH4 Mean 7.005548

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	299.7569696	299.7569696	123.34	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	24.88684491	1.67175949	14.89	<.0001
Temperature	-0.04470324	0.00402512	-11.11	<.0001

Dependent Variable: NO3 NO3

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	7.20895014	7.20895014	14.79	0.0032
Error	10	4.87267081	0.48726708		
Corrected Total	11	12.08162095			

R-Square 0.596687
 Coeff Var 83.30160
 Root MSE 0.698045
 NO3 Mean 0.837973

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	7.20895014	7.20895014	14.79	0.0032

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	3.610976511	0.74857007	4.82	0.0007
Temperature	-0.006932508	0.00180234	-3.85	0.0032

Dependent Variable: Ext_P Ext-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	5746.024625	5746.024625	43.81	<.0001
Error	10	1311.697690	131.169769		
Corrected Total	11	7057.722315			

R-Square 0.814147
 Coeff Var 56.76776
 Root MSE 11.45294
 Ext_P Mean 20.17507

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	5746.024625	5746.024625	43.81	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	98.46359568	12.28190679	8.02	<.0001
Temperature	-0.19572131	0.02957136	-6.62	<.0001

Dependent Variable: Biomass_____ Biomass (%)

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	2231.136240	2231.136240	53.63	<.0001
Error	10	416.038427	41.603843		
Corrected Total	11	2647.174667			

R-Square 0.842837
 Coeff Var 8.001949
 Root MSE 6.450104
 Biomass_____ Mean 80.60667

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	2231.136240	2231.136240	53.63	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	31.82266667	6.91696603	4.60	0.0010
Temperature	0.12196000	0.01665410	7.32	<.0001

Dependent Variable: TN_____ TN (%)

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.51695640	0.51695640	112.06	<.0001
Error	10	0.04613026	0.00461303		
Corrected Total	11	0.56308667			

R-Square 0.918076
 Coeff Var 23.64038
 Root MSE 0.067919
 TN_____ Mean 0.287302

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	0.51695640	0.51695640	112.06	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	1.029878613	0.07283529	14.14	<.0001
Temperature	-0.001856442	0.00017537	-10.59	<.0001

Dependent Variable: TC_____ TC (%)

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	1171.505481	1171.505481	40.02	<.0001
Error	10	292.737411	29.273741		
Corrected Total	11	1464.242892			

R-Square 0.800076 Coeff Var 50.14524 Root MSE 5.410521 TC_____ Mean 10.78970

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	1171.505481	1171.505481	40.02	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	46.13946621	5.80213773	7.95	<.0001
Temperature	-0.08837441	0.01396991	-6.33	<.0001

Dependent Variable: TP TP

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	23.86685765	23.86685765	4.01	0.0732
Error	10	59.56438879	5.95643888		
Corrected Total	11	83.43124644			

R-Square 0.286066 Coeff Var 1.404285 Root MSE 2.440582 TP Mean 173.7954

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	23.86685765	23.86685765	4.01	0.0732

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	168.7497940	2.61723226	64.48	<.0001
Temperature	0.0126140	0.00630155	2.00	0.0732

Dependent Variable: TCa TCa

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	3049.260	3049.260	0.01	0.9288
Error	10	3437782.296	343778.230		
Corrected Total	11	3440831.556			

R-Square 0.000886 Coeff Var 4.975485 Root MSE 586.3260 TCa Mean 11784.30

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	3049.260167	3049.260167	0.01	0.9268

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	11727.26890	628.7646332	18.65	<.0001
Temperature	0.14258	1.5138873	0.09	0.9268

Dependent Variable: TFe TFe

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	642.654225	642.654225	1.78	0.2114
Error	10	3604.009713	360.400971		
Corrected Total	11	4246.663939			

R-Square 0.151332
 Coeff Var 6.941913
 Root MSE 18.98423
 TFe Mean 273.4726

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	642.6542254	642.6542254	1.78	0.2114

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	247.2905784	20.35831813	12.15	<.0001
Temperature	0.0654550	0.04901707	1.34	0.2114

Dependent Variable: TK TK

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	613953.7554	613953.7554	38.74	<.0001
Error	10	158498.2924	15849.8292		
Corrected Total	11	772452.0478			

R-Square 0.794811
 Coeff Var 11.57171
 Root MSE 125.8961
 TK Mean 1087.964

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	613953.7554	613953.7554	38.74	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	1897.213207	135.0085317	14.05	<.0001
Temperature	-2.023123	0.3250623	-6.22	<.0001

Dependent Variable: TMg TMg

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	2255.62677	2255.62677	2.80	0.1253
Error	10	8059.04145	805.90414		
Corrected Total	11	10314.66822			

R-Square 0.218681
 Coeff Var 3.279768
 Root MSE 28.38845
 TMg Mean 865.5627

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	2255.626766	2255.626766	2.80	0.1253

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	914.6136899	30.44322202	30.04	<.0001
Temperature	-0.1226275	0.07329867	-1.67	0.1253

Dependent Variable: TMn TMn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.2208524	0.2208524	0.02	0.8966
Error	10	124.3686407	12.4368641		
Corrected Total	11	124.5894931			

R-Square	Coeff Var	Root MSE	TMn Mean
0.001773	7.995175	3.526594	44.10903

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	0.22085242	0.22085242	0.02	0.8966

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	44.59439038	3.78185056	11.79	<.0001
Temperature	-0.00121340	0.00910563	-0.13	0.8966

Dependent Variable: TZn TZn

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	2.96681365	2.96681365	3.49	0.0913
Error	10	8.49959201	0.84995920		
Corrected Total	11	11.46640567			

R-Square	Coeff Var	Root MSE	TZn Mean
0.258740	12.36420	0.921932	7.456465

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature	1	2.96681365	2.96681365	3.49	0.0913

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	5.677532034	0.98866227	5.74	0.0002
Temperature	0.004447332	0.00238042	1.87	0.0913

APPENDIX I

RESULTS OF FITTING REGRESSION MODELS AND ANOVA ANALYSIS ON TP, TCa, TMg, AND TFe IN RESIDUAL ASHES

Results of ANOVA Analysis on TP/TCa, TP/TMg, TP/TFe in Residual Ashes

Variables	Average values of TP/TCa, TP/TMg, TP/TFe						ANOVA result	
	65 ⁰ C	250 ⁰ C	350 ⁰ C	450 ⁰ C	550 ⁰ C	Field ash	Pr > F	Sig. level
TP/TCa	0.0165 a	0.0149 a	0.0142 a	0.0147 a	0.0168 a	0.0197 a	0.3680	NS
TP/TMg	0.1863 a	0.1885 a	0.2028 a	0.2087 a	0.2177 a	0.1889 a	0.0695	NS
TP/TFe	1.2194 a	0.6273 a	0.6849 a	0.5616 a	0.5457 a	0.9039 a	0.1105	NS

Results of Fitting of Regression Models with 1st, 2nd, and 3rd order among Burn Temperature (Response Variable) and Content of TP, TCa, TFe, or TMg in Laboratory Simulation Ashes (Explanatory Variable)

- Linear regression model for TP with

The REG Procedure
Dependent Variable: Temperature Temperature

Number of Observations Read 12
Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	147781	147781	666.03	<.0001
Error	10	2218.85073	221.88507		
Corrected Total	11	150000			

Root MSE 14.89581 R-Square 0.9852
Dependent Mean 400.00000 Adj R-Sq 0.9837
Coeff Var 3.72395

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	222.54987	8.10979	27.44	<.0001
TP	TP	1	0.12254	0.00475	25.81	<.0001

- Quadratic regression model for TP

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	147807	73903	303.28	<.0001
Error	9	2193.13084	243.68120		
Corrected Total	11	150000			

Root MSE 15.61029 R-Square 0.9854
 Dependent Mean 400.00000 Adj R-Sq 0.9821
 Coeff Var 3.90257

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	218.90934	14.06407	15.57	<.0001
TP	TP	1	0.13063	0.02540	5.14	0.0006
TP_2	2nd power of TP	1	-0.00000277	0.00000852	-0.32	0.7527

- Cubic regression model for TP

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	149560	49853	905.58	<.0001
Error	8	440.41061	55.05133		
Corrected Total	11	150000			

Root MSE 7.41966 R-Square 0.9971
 Dependent Mean 400.00000 Adj R-Sq 0.9960
 Coeff Var 1.85491

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	171.26427	10.76967	15.90	<.0001
TP	TP	1	0.30356	0.03294	9.22	<.0001
TP_2	2nd power of TP	1	-0.00014573	0.00002566	-5.68	0.0005
TP_3	3rd power of TP	1	3.236256E-8	5.735489E-9	5.64	0.0005

- Linear regression model for TCa

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	142892	142892	201.04	<.0001
Error	10	7107.50412	710.75041		
Corrected Total	11	150000			

Root MSE 26.65990 R-Square 0.9526
 Dependent Mean 400.00000 Adj R-Sq 0.9479
 Coeff Var 6.66498

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	214.03657	15.20667	14.08	<.0001
TCa	TCa	1	0.00199	0.00014024	14.18	<.0001

- Quadratic regression model for TCa

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	142898	71449	90.54	<.0001
Error	9	7102.43012	789.15890		
Corrected Total	11	150000			

Root MSE 28.09197 R-Square 0.9527
 Dependent Mean 400.00000 Adj R-Sq 0.9421
 Coeff Var 7.02299

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	215.83354	27.54952	7.83	<.0001
TCa	TCa	1	0.00192	0.00081046	2.37	0.0416
TCa_2	2nd power of TCA	1	3.55409E-10	4.432363E-9	0.08	0.9378

- Cubic regression model for TCa

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	144007	48002	64.08	<.0001
Error	8	5993.02001	749.12750		
Corrected Total	11	150000			

Root MSE	27.37019	R-Square	0.9600
Dependent Mean	400.00000	Adj R-Sq	0.9451
Coeff Var	6.84255		

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	177.39808	41.44888	4.28	0.0027
TCa	TCa	1	0.00419	0.00202	2.07	0.0721
TCa_2	2nd power of TCA	1	-3.09069E-8	2.604977E-8	-1.19	0.2695
TCa_3	3rd power of TCA	1	1.18099E-13	9.70459E-14	1.22	0.2583

- Linear regression model for TFe

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	144343	144343	255.18	<.0001
Error	10	5656.50831	565.65083		
Corrected Total	11	150000			

Root MSE	23.78342	R-Square	0.9623
Dependent Mean	400.00000	Adj R-Sq	0.9585
Coeff Var	5.94585		

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	240.21913	12.13193	19.80	<.0001
TFe	TFe	1	0.06300	0.00394	15.97	<.0001

- Quadratic regression model for TFe

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	145100	72550	133.26	<.0001
Error	9	4899.80275	544.42253		
Corrected Total	11	150000			

Root MSE 23.33286 R-Square 0.9673
 Dependent Mean 400.00000 Adj R-Sq 0.9601
 Coeff Var 5.83322

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	223.27192	18.66269	11.96	<.0001
TFe	TFe	1	0.08515	0.01918	4.44	0.0016
TFe_2	2nd power of TFE	1	-0.00000415	0.00000352	-1.18	0.2686

- Cubic regression model for TFe

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	146935	48978	127.86	<.0001
Error	8	3064.62438	383.07805		
Corrected Total	11	150000			

Root MSE 19.57238 R-Square 0.9796
 Dependent Mean 400.00000 Adj R-Sq 0.9719
 Coeff Var 4.89309

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	176.96912	26.31742	6.72	0.0001
TFe	TFe	1	0.17762	0.04521	3.93	0.0044
TFe_2	2nd power of TFE	1	-0.00004372	0.00001832	-2.39	0.0441
TFe_3	3rd power of TFE	1	4.635843E-9	2.118035E-9	2.19	0.0600

- Linear regression model for TMg

The REG Procedure
Dependent Variable: Temperature Temperature

Number of Observations Read 12
Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	147118	147118	510.46	<.0001
Error	10	2882.06965	288.20697		
Corrected Total	11	150000			

Root MSE 16.97666 R-Square 0.9808
Dependent Mean 400.00000 Adj R-Sq 0.9789
Coeff Var 4.24416

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	214.53110	9.56060	22.44	<.0001
TMg	TMg	1	0.02696	0.00119	22.59	<.0001

- Quadratic regression model for TMg

The REG Procedure
Dependent Variable: Temperature Temperature

Number of Observations Read 12
Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	147122	73561	230.04	<.0001
Error	9	2878.00185	319.77798		
Corrected Total	11	150000			

Root MSE 17.88234 R-Square 0.9808
Dependent Mean 400.00000 Adj R-Sq 0.9765
Coeff Var 4.47058

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	216.18294	17.77404	12.16	<.0001
TMg	TMg	1	0.02620	0.00684	3.83	0.0040
TMg_2	2nd power of TMG	1	5.549943E-8	4.92077E-7	0.11	0.9127

- Cubic regression model for TMg

The REG Procedure
 Dependent Variable: Temperature Temperature

Number of Observations Read 12
 Number of Observations Used 12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	149332	49777	596.18	<.0001
Error	8	667.95165	83.49396		
Corrected Total	11	150000			

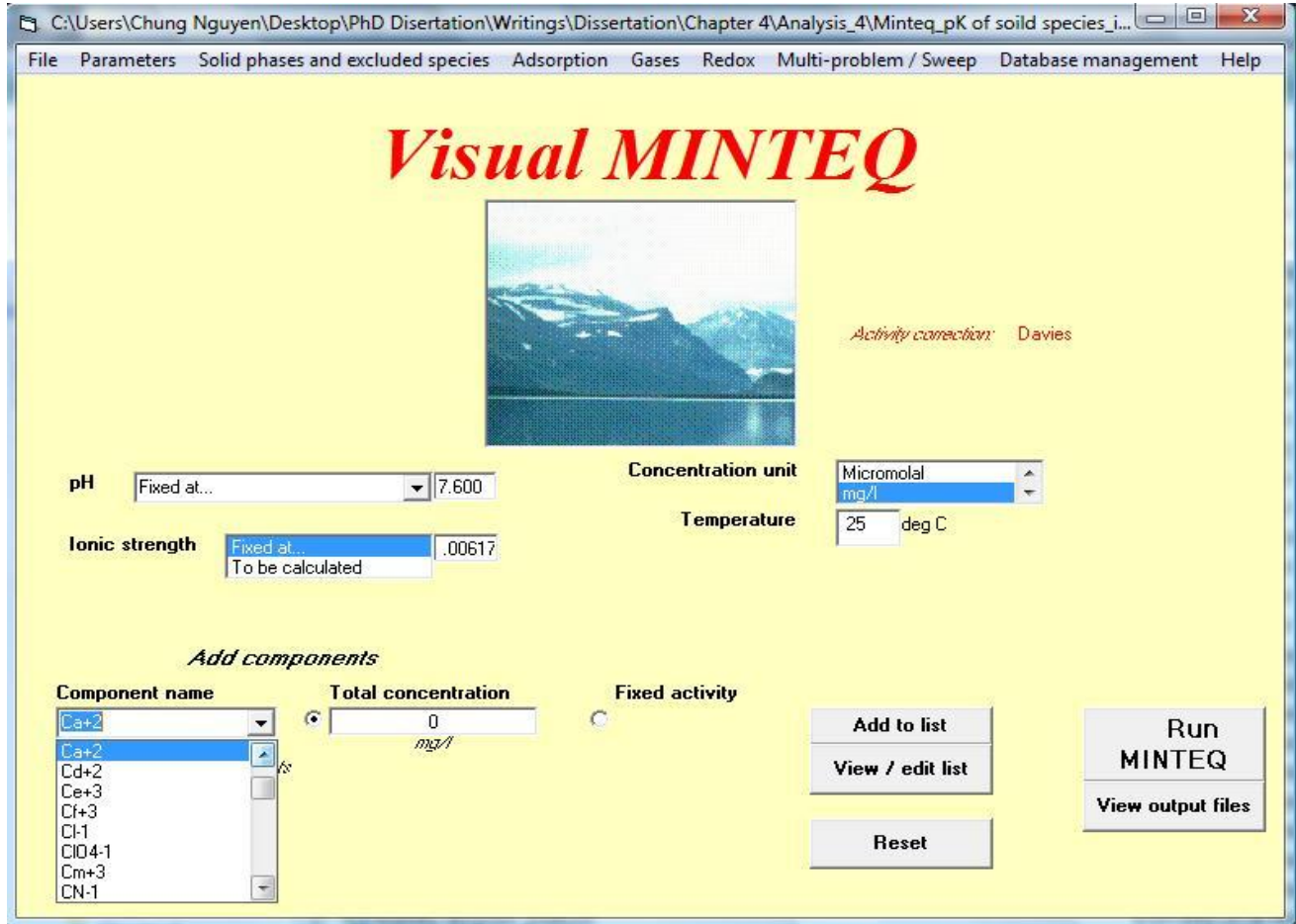
Root MSE 9.13750 R-Square 0.9955
 Dependent Mean 400.00000 Adj R-Sq 0.9939
 Coeff Var 2.28438

Parameter Estimates

Variable	Label	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	Intercept	1	154.20021	15.08735	10.22	<.0001
TMg	TMg	1	0.07195	0.00956	7.53	<.0001
TMg_2	2nd power of TMG	1	-0.00000802	0.00000159	-5.05	0.0010
TMg_3	3rd power of TMG	1	3.94955E-10	7.6767E-11	5.14	0.0009

APPENDIX J
PROCEDURES FOR MINTEQ'S EQUILIBRIUM SPECIATION MODEL

The Main Interface of the Minteq's Program



**Initial Species Input into the Minteq's Equilibrium Speciation Model:
 (a) Fixed Species, (b) Possible Solid Species, and (c) Main Solution Components**

Visual MINTEQ

a White solids - Visual MINTEQ

Fixed species in the present problem

<i>Species name</i>	<i>Adjusted log K**</i>	<i>ΔH of reaction*</i>	<i>Log Partial pressure</i>	
H+1	7.600	0		Delete this species
CO2 (g)	18.149	-10	-3.42021640338319	Delete this species

b White solids - Visual MINTEQ

Possible species in the present problem

<i>Species name</i>	<i>Adjusted log K**</i>	<i>ΔH of reaction*</i>	
Ca3(PO4)2 (am1)	25.5	94	Delete this species
Ca3(PO4)2 (am2)	28.25	87	Delete this species
Ca3(PO4)2 (beta)	28.92	-54	Delete this species
Ca4H(PO4)3·3H2O	47.95	105	Delete this species
CaHPO4	19.275	-31	Delete this species
CaHPO4·2H2O	18.995	-23	Delete this species
Calcite	8.48	8	Delete this species
Hydroxyapatite	44.333	0	Delete this species
Mg3(PO4)2	23.28	0	Delete this species
MgHPO4·3H2O	18.175	0	Delete this species
Mn3(PO4)2	23.827	-8.8701	Delete this species
MnHPO4	25.4	0	Delete this species
Strengite	26.4	9.3601	Delete this species
Vivianite	37.76	-5.06	Delete this species

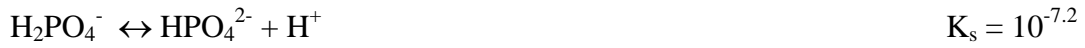
c List of components - Visual MINTEQ

Components in the present problem

<i>Component name</i>	<i>Total concentration*</i>	<i>Act guess?*</i>	
H+1	1E-16	✓	Delete this component
Ca+2	1187.4	✓	Delete this component
PO4-3	4.02	✓	Delete this component
Mg+2	85.3	✓	Delete this component
Mn+2	151.5	✓	Delete this component
K+1	230.7	✓	Delete this component
Na+1	338	✓	Delete this component
Zn+2	3.46	✓	Delete this component
Cu+2	4.65	✓	Delete this component
Fe+2	235.3	✓	Delete this component
NH4+1	58	✓	Delete this component
NO3-1	9.86	✓	Delete this component
CO3-2	1E-16	✓	Delete this component
Fe+3	1E-16	✓	Delete this component

APPENDIX K
CALCULATION OF STOICHIOMETRY FOR ACTIVITY OF HPO_4^{2-} FROM
Ca/Mg/Fe/Mn-P MINERALS

Monetite



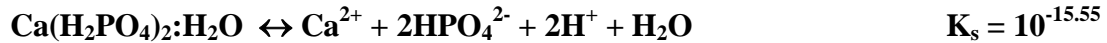
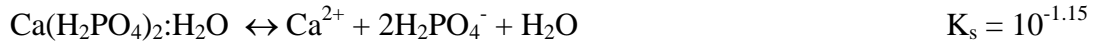
$$K_s = 10^{-6.9} = \frac{(\text{Ca}^{2+})(\text{HPO}_4^{2-})}{(\text{CaHPO}_4)}$$

$$\leftrightarrow -6.9 = \log(\text{Ca}^{2+}) + \log(\text{HPO}_4^{2-})$$

$$\leftrightarrow 6.9 = \text{pCa}^{2+} + \text{pHPO}_4^{2-}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 6.9 - \text{pCa}^{2+} \quad (4-1)$$

Monocalcium-P



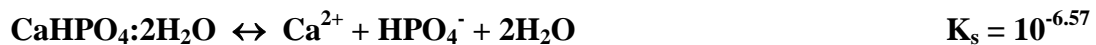
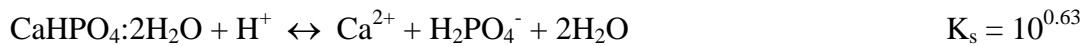
$$K_s = 10^{-15.55} = \frac{(\text{Ca}^{2+})(\text{HPO}_4^{2-})^2(\text{H}^+)^2(\text{H}_2\text{O})}{(\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O})}$$

$$\leftrightarrow -15.55 = \log(\text{Ca}^{2+}) + 2\log(\text{HPO}_4^{2-}) + 2\log(\text{H}^+)$$

$$\leftrightarrow 15.55 = \text{pCa}^{2+} + 2\text{pHPO}_4^{2-} + 2\text{pH}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 7.775 - 0.5\text{pCa}^{2+} - \text{pH} \quad (4-2)$$

Dicalcium-P

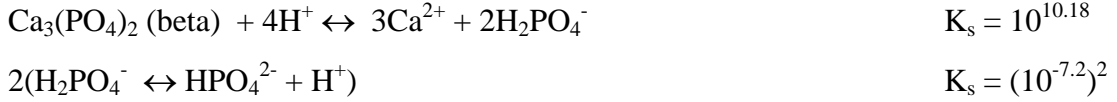


$$K_s = 10^{-6.57} = \frac{(\text{Ca}^{2+})(\text{HPO}_4^{2-})(\text{H}_2\text{O})^2}{(\text{CaHPO}_4 \cdot 2\text{H}_2\text{O})}$$

$$\leftrightarrow -6.57 = \log(\text{Ca}^{2+}) + \log(\text{HPO}_4^{2-})$$

$$\begin{aligned} \leftrightarrow 6.57 &= \text{pCa}^{2+} + \text{pHPO}_4^{2-} \\ \leftrightarrow \text{pHPO}_4^{2-} &= 6.57 - \text{pCa}^{2+} \end{aligned} \quad (4-3)$$

Tricalcium-P



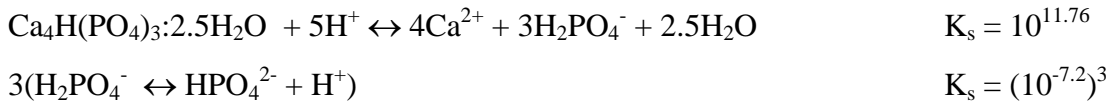
$$K_s = 10^{-4.22} = \frac{(\text{Ca}^{2+})^3 (\text{HPO}_4^{2-})^2}{(\text{H}^+)^2 (\text{Ca}_3(\text{PO}_4)_2)}$$

$$\leftrightarrow -4.22 = 3\log(\text{Ca}^{2+}) + 2\log(\text{HPO}_4^{2-}) - 2\log(\text{H}^+)$$

$$\leftrightarrow 4.22 = 3\text{pCa}^{2+} + 2\text{pHPO}_4^{2-} - 2\text{pH}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 2.11 - 1.5\text{pCa}^{2+} + \text{pH} \quad (4-4)$$

Octacalcium-P



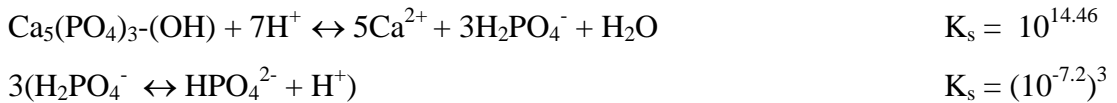
$$K_s = 10^{-9.84} = \frac{(\text{Ca}^{2+})^4 (\text{HPO}_4^{2-})^3 (\text{H}_2\text{O})^{2.5}}{(\text{H}^+)^2 (\text{Ca}_4(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O})}$$

$$\leftrightarrow -9.84 = 4\log(\text{Ca}^{2+}) + 3\log(\text{HPO}_4^{2-}) - 2\log(\text{H}^+)$$

$$\leftrightarrow 9.84 = 4\text{pCa}^{2+} + 3\text{pHPO}_4^{2-} - 2\text{pH}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 3.28 - 4/3\text{pCa}^{2+} + 2/3\text{pH} \quad (4-5)$$

Hydroxyapatite

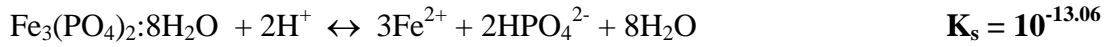
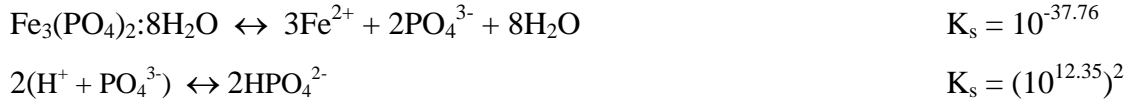


$$K_s = 10^{-7.14} = \frac{(\text{Ca}^{2+})^5 (\text{HPO}_4^{2-})^3 (\text{H}_2\text{O})}{(\text{H}^+)^4 (\text{Ca}_5(\text{PO}_4)_3\text{-(OH)})}$$

$$\leftrightarrow -7.14 = 5\log(\text{Ca}^{2+}) + 3\log(\text{HPO}_4^{2-}) - 4\log(\text{H}^+)$$

$$\begin{aligned} \leftrightarrow 7.14 &= 5\text{pCa}^{2+} + 3\text{pHPO}_4^{2-} - 4\text{pH} \\ \leftrightarrow \text{pHPO}_4^{2-} &= 2.38 - 5/3\text{pCa}^{2+} + 4/3\text{pH} \end{aligned} \quad (4-6)$$

Vivianite



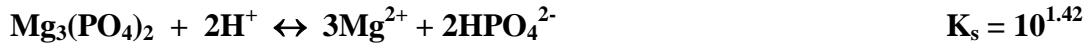
$$K_s = 10^{-13.06} = \frac{(\text{Fe}^{2+})^3 (\text{HPO}_4^{2-})^2 (\text{H}_2\text{O})^8}{(\text{H}^+)^2 (\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})}$$

$$\leftrightarrow -13.06 = 3\log(\text{Fe}^{2+}) + 2\log(\text{HPO}_4^{2-}) - 2\log(\text{H}^+)$$

$$\leftrightarrow 13.06 = 3\text{pFe}^{2+} + 2\text{pHPO}_4^{2-} - 2\text{pH}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 6.53 - 1.5\text{pFe}^{2+} + \text{pH} \quad (4-7)$$

Mg₃(PO₄)₂



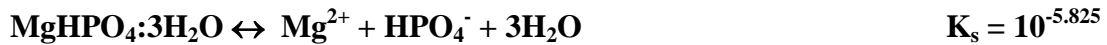
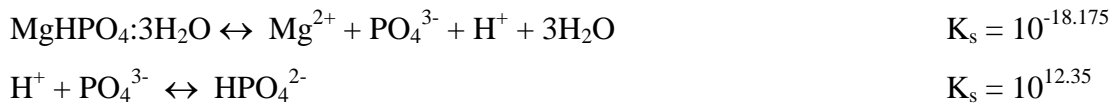
$$K_s = 10^{1.42} = \frac{(\text{Mg}^{2+})^3 (\text{HPO}_4^{2-})^2}{(\text{H}^+)^2 (\text{Mg}_3(\text{PO}_4)_2)}$$

$$\leftrightarrow 1.42 = 3\log(\text{Mg}^{2+}) + 2\log(\text{HPO}_4^{2-}) - 2\log(\text{H}^+)$$

$$\leftrightarrow -1.42 = 3\text{pMg}^{2+} + 2\text{pHPO}_4^{2-} - 2\text{pH}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = -0.71 - 1.5\text{pMg}^{2+} + \text{pH} \quad (4-8)$$

MgHPO₄·3H₂O



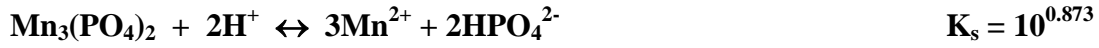
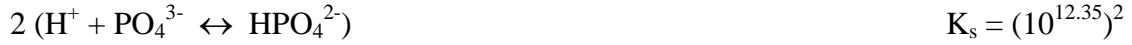
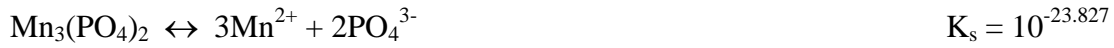
$$K_s = 10^{-5.825} = \frac{(\text{Mg}^{2+})(\text{HPO}_4^{2-})(\text{H}_2\text{O})^3}{(\text{MgHPO}_4 \cdot 3\text{H}_2\text{O})}$$

$$\leftrightarrow -5.825 = \log(\text{Mg}^{2+}) + \log(\text{HPO}_4^{2-})$$

$$\leftrightarrow 5.825 = \text{pMg}^{2+} + \text{pHPO}_4^{2-}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 5.825 - \text{pMg}^{2+} \quad (4-9)$$

Mn₃(PO₄)₂



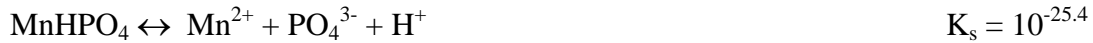
$$K_s = 10^{0.873} = \frac{(\text{Mn}^{2+})^3(\text{HPO}_4^{2-})^2}{(\text{H}^+)^2(\text{Mn}_3(\text{PO}_4)_2)}$$

$$\leftrightarrow 0.873 = 3\log(\text{Mn}^{2+}) + 2\log(\text{HPO}_4^{2-}) - 2\log(\text{H}^+)$$

$$\leftrightarrow -0.873 = 3\text{pMn}^{2+} + 2\text{pHPO}_4^{2-} - 2\text{pH}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = -0.4365 - 1.5\text{pMn}^{2+} + \text{pH} \quad (4-10)$$

MnHPO₄



$$K_s = 10^{-13.05} = \frac{(\text{Mn}^{2+})(\text{HPO}_4^{2-})}{(\text{MnHPO}_4)}$$

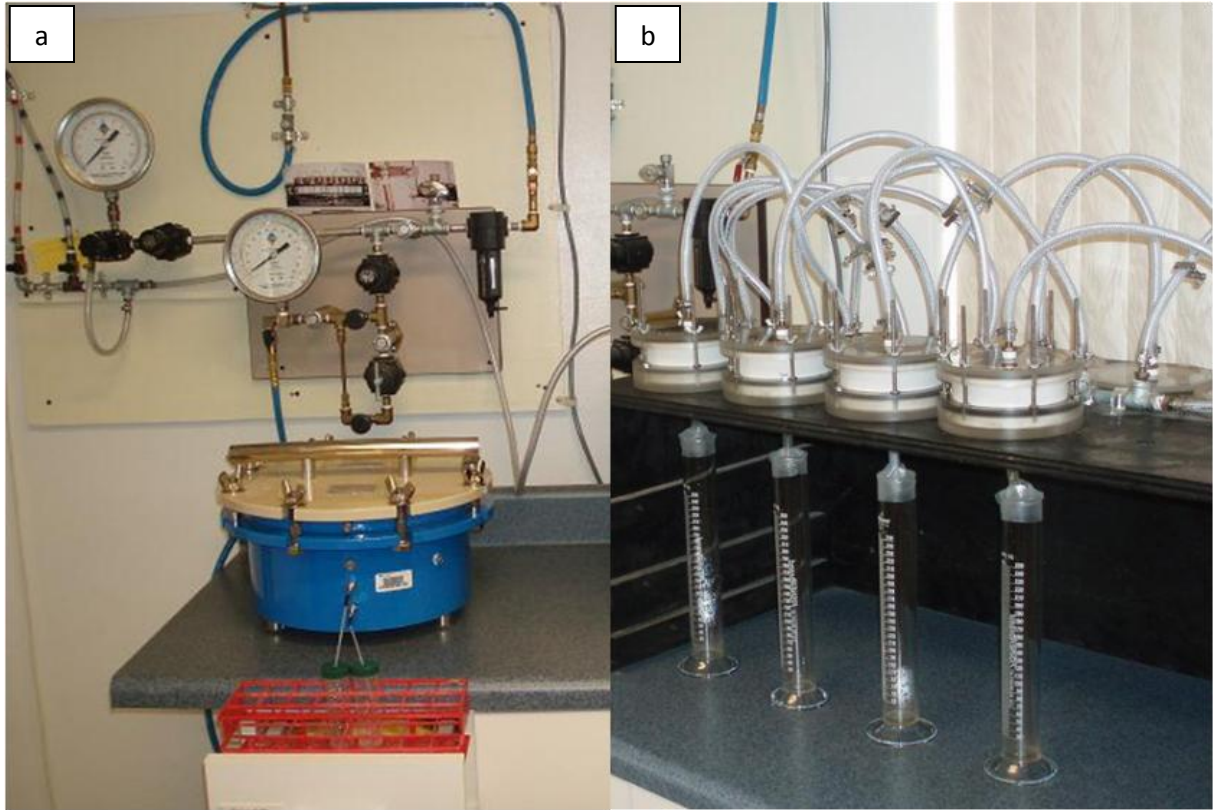
$$\leftrightarrow -13.05 = \log(\text{Mn}^{2+}) + \log(\text{HPO}_4^{2-})$$

$$\leftrightarrow 13.05 = \text{pMn}^{2+} + \text{pHPO}_4^{2-}$$

$$\leftrightarrow \text{pHPO}_4^{2-} = 13.05 - \text{pMn}^{2+} \quad (4-11)$$

APPENDIX L
EXPERIMENT FOR DETERMINATION OF SOIL-WATER CHARACTERISTIC CURVE

Establishment of the Experiment: (a) Richard Plates and (b) Tempe Cells



Procedures for the Experiment

The 1-bar, 1400/1405-100 Tempe pressure cells, core cylinders, and 1-bar ceramic plates were utilized to determine volumetric water amount with pressures less than 1 bar (1020 cm H₂O). The volume of the core cylinder was approximately 415.7 cm³ with height of 53 mm and diameter of 100 mm. The height of the selected cylinder corresponded to height of soil in the field. The bottom of the cylinder was secured by mesh cloth and rubber band to prevent loss of soil. Air-dried soils were repacked into cores of cylinders using a layering approach to prevent uneven distribution of soil bulk density.

Sample preparation: Cores with soils were put into a container, and soaked with a mixed

solution of 0.005M Calcium Sulfate Di-hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and Thymol (0.25 g Thymol/L). This solution aimed to reduce biological activities in soils. Since soils contained a high organic content, cores with soils were soaked for one week. Soil was slowly wet by placing a shallow solution, increased gradually height of the mixed solution in the container in every day, eventually soaked with the mixed solution just below the top of the core in last day. A gradual soakage avoided to immerse suddenly soils which could cause a compressed gas and disrupt soil structure.

Tempe cell setup: The “O” ring cylinder seals and ceramic plates were also soaked in one day before setting up Tempe cell. While submerged in the mixed solution, a ceramic plate was placed in bottom piece of Tempe cell, and then the core was placed on the ceramic plate. After the “O” ring applied with a thin film of grease was inserted into the cell, the core was placed in upside down position on the plate so that the mesh cloth was on the top and removed from the core. There should be no bubbles visible on the bottom of the Tempe cell. If any bubble was present in the bottom of the Tempe cell, process of Tempe cell setup was repeated from the first step. Tempe cells were put on a Tempe cell stand with graduate cylinders placed underneath (Figure 4-3b). The top of Tempe cells were covered by wet paper towels to prevent evaporative loss of water while soils in cores were drained to reach equilibrium, and graduated cylinders were also covered by parafilm to prevent evaporation. After water was no longer draining from soils, the cores were secured by Tempe cell top and the “O” ring (Figure 4-3b).

Pressures applied for Tempe cell method were 0, 0.49, 0.98, 1.47, 2.45, 3.43, 4.90, 6.67, 14.71, 29.41, 58.82, 98.04 kPa. The experiment started with the lowest pressure and increased gradually with higher pressures. Total amount of water at each pressure was determined when water was no longer fallen from Tempe cells, and measured by a water manometer. Graduated cylinders were empty after water volumes of a given pressure were recorded. Soils removed after

the last pressure were used for Richard plate method with higher pressures. Fifteen-bar Richard plates were moistened at least one day before the experiment of Richard plate started. Twelve rings with a height of 0.5 cm and diameter of 3 cm were placed together on each plate, and then put above soils into the rings (Figure 4-3c). Three Richard plates were installed simultaneously into a compressor with a secured seal. The plates were connected to outside by tubes from which water amount could be measured at each pressure applied. Pressures used for Richard plate method were 500, and 800 kPa (5 and 8 bars, respectively). After removing from the last pressure, soils were dried in Oven at 105⁰C for 24 hours. Weight of soils before and after drying was also recorded to measure water amount remained in soils after applying the 8-bar pressure.

APPENDIX M
VOLUMETRIC WATER CONTENTS OF PINE ROCKLAND SOIL OBTAINED FROM
OBSERVATION EXPERIMENT AND FROM RETENTION CURVE MODEL

Suction (pressure)		Volumetric water content from observation				Volumetric water content fitted by Retention Curve model (RETC)			
cm H ₂ O	kPa	R1	R2	R3	R4	R1	R2	R3	R4
5	0.49	0.6177	0.6160	0.6425	0.6261	0.6167	0.6202	0.6425	0.6308
10	0.98	0.6160	0.6160	0.6420	0.6254	0.6126	0.6114	0.6415	0.6198
15	1.47	0.6153	0.6109	0.6420	0.6165	0.6081	0.6025	0.6403	0.6088
25	2.45	0.6032	0.5943	0.6386	0.5984	0.5988	0.5853	0.6374	0.5883
35	3.43	0.5893	0.5753	0.6348	0.5756	0.5894	0.5695	0.6342	0.5702
50	4.90	0.5686	0.5472	0.6249	0.5453	0.5758	0.5488	0.6289	0.5472
68	6.67	0.5474	0.5217	0.6153	0.5171	0.5606	0.5278	0.6221	0.5245
150	14.71	0.4998	0.4604	0.5965	0.4536	0.5067	0.4648	0.5887	0.4596
300	29.41	0.4260	0.3867	0.5246	0.3817	0.4474	0.4064	0.5333	0.4016
600	58.82	0.4057	0.3564	0.4459	0.3528	0.3862	0.3513	0.4555	0.3478
1000	98.04	0.3839	0.3365	0.4106	0.3372	0.3435	0.3143	0.3928	0.3118
5099	500.00	0.2286	0.2186	0.2202	0.2086	0.2322	0.2186	0.2242	0.2189
8159	800.00	0.1781	0.1809	0.1911	0.1885	0.2069	0.1967	0.1889	0.1975

Where "R1, R2, R3, R4" are replicates

APPENDIX N
RESULTS OF FITTING OF VOLUMETRIC WATER CONTENT BY RETENTION CURVE
MODEL

Replicate 1

```
*****
*
*   Analysis of soil hydraulic properties
*
*   Example 1: Forward Problem
*
*   Mualem-based restriction, M=1-1/N
*   Analysis of retention data only
*   MType= 3   Method= 3
*
*****
```

INITIAL values of the coefficients

```
=====
```

No	Name	INITIAL value	Index
1	ThetaR	.0650	1
2	ThetaS	.4100	1
3	Alpha	.0750	1
4	n	1.8900	1
5	m	.4709	0
6	l	.5000	0
7	Ks	1.0000	0

Observed data

```
=====
```

Obs. No.	Pressure head	Water content	Weighting coefficient
1	.000	.6203	1.0000
2	5.000	.6177	1.0000
3	10.000	.6160	1.0000
4	15.000	.6153	1.0000
5	25.000	.6032	1.0000
6	35.000	.5893	1.0000
7	50.000	.5686	1.0000
8	68.000	.5474	1.0000
9	150.000	.4998	1.0000
10	300.000	.4260	1.0000
11	600.000	.4057	1.0000
12	1000.000	.3839	1.0000
13	5099.000	.2286	1.0000
14	8158.000	.1781	1.0000

NIT	SSQ	ThetaR	ThetaS	Alpha	n
0	1.39291	.0650	.4100	.0750	1.8900
1	.58235	.2551	.6473	.0947	1.0050
2	.51816	.0474	.6461	.2056	1.0077
3	.50709	.0197	.6458	.2242	1.0080
4	.50177	.0068	.6457	.2331	1.0082
5	.49916	.0005	.6456	.2375	1.0083

wcr is less then 0.001: Changed to fit with wcr=0.0

NIT	SSQ	ThetaS	Alpha	n
0	1.78016	.4100	.0750	1.8900
1	.28994	.5314	.0066	1.0050
2	.17330	.6117	.3071	1.1371
3	.02750	.6494	.0922	1.1210
4	.02320	.6536	.0796	1.1291
5	.02005	.6560	.0702	1.1365
6	.01767	.6572	.0626	1.1431
7	.01259	.6465	.0304	1.1620
8	.01039	.6311	.0123	1.2029
9	.00378	.6202	.0104	1.2426
10	.00367	.6196	.0105	1.2464
11	.00367	.6197	.0106	1.2460
12	.00367	.6198	.0106	1.2460
13	.00367	.6198	.0106	1.2459

Correlation matrix

```

=====
          Theta      Alpha      n
          1          2          3
1      1.0000
2      .6713      1.0000
3     -.4030     -.8614      1.0000

```

RSquared for regression of observed vs fitted values = .98711721

Nonlinear least-squares analysis: final results

```

=====
                                     95% Confidence limits
Variable      Value      S.E.Coeff.      T-Value      Lower      Upper
ThetaS        .61977      .00900        68.90        .6000      .6396
Alpha         .01057      .00263         4.02        .0048      .0164
n              1.24595      .02218        56.18        1.1971     1.2948

```

Observed abd fitted data

```

=====
NO          P          log-P      WC-obs      WC-fit      WC-dev
1      .1000E-04      -5.0000      .6203      .6198      .0005
2      .5000E+01        .6990      .6177      .6167      .0010
3      .1000E+02        1.0000      .6160      .6126      .0034
4      .1500E+02        1.1761      .6153      .6081      .0072
5      .2500E+02        1.3979      .6032      .5988      .0044
6      .3500E+02        1.5441      .5893      .5894     -.0001
7      .5000E+02        1.6990      .5686      .5758     -.0072
8      .6800E+02        1.8325      .5474      .5606     -.0132
9      .1500E+03        2.1761      .4998      .5067     -.0069
10     .3000E+03        2.4771      .4260      .4474     -.0214
11     .6000E+03        2.7782      .4057      .3862      .0195
12     .1000E+04        3.0000      .3839      .3435      .0404
13     .5099E+04        3.7075      .2286      .2322     -.0036
14     .8158E+04        3.9116      .1781      .2069     -.0288

```

Sum of squares of observed versus fitted values

```

=====
          Unweighted      Weighted
Retention data      .00367      .00367

```

Cond/Diff data	.00000	.00000
All data	.00367	.00367

Soil hydraulic properties (MType = 3)

=====

WC	P	logP	Cond	logK	Dif	logD
.0016	-.3312E+13	12.520	.1045E-28	-28.981	.8904E-13	-13.050
.0032	-.1978E+12	11.296	.1659E-25	-25.780	.4218E-11	-11.375
.0063	-.1181E+11	10.072	.2632E-22	-22.580	.1998E-09	-9.699
.0126	-.7050E+09	8.848	.4176E-19	-19.379	.9465E-08	-8.024
.0190	-.1356E+09	8.132	.3111E-17	-17.507	.9041E-07	-7.044
.0253	-.4210E+08	7.624	.6626E-16	-16.179	.4484E-06	-6.348
.0316	-.1699E+08	7.230	.7106E-15	-15.148	.1552E-05	-5.809
.0379	-.8096E+07	6.908	.4937E-14	-14.307	.4283E-05	-5.368
.0443	-.4326E+07	6.636	.2542E-13	-13.595	.1010E-04	-4.996
.0506	-.2514E+07	6.400	.1051E-12	-12.978	.2124E-04	-4.673
.0569	-.1557E+07	6.192	.3678E-12	-12.434	.4091E-04	-4.388
.0632	-.1014E+07	6.006	.1128E-11	-11.948	.7354E-04	-4.133
.0696	-.6886E+06	5.838	.3106E-11	-11.508	.1250E-03	-3.903
.0759	-.4834E+06	5.684	.7834E-11	-11.106	.2029E-03	-3.693
.0822	-.3491E+06	5.543	.1835E-10	-10.736	.3168E-03	-3.499
.0885	-.2583E+06	5.412	.4034E-10	-10.394	.4785E-03	-3.320
.0949	-.1951E+06	5.290	.8401E-10	-10.076	.7025E-03	-3.153
.1012	-.1501E+06	5.176	.1669E-09	-9.778	.1006E-02	-2.997
.1075	-.1173E+06	5.069	.3179E-09	-9.498	.1410E-02	-2.851
.1138	-.9295E+05	4.968	.5837E-09	-9.234	.1938E-02	-2.713
.1202	-.7461E+05	4.873	.1037E-08	-8.984	.2619E-02	-2.582
.1265	-.6056E+05	4.782	.1790E-08	-8.747	.3485E-02	-2.458
.1328	-.4966E+05	4.696	.3006E-08	-8.522	.4573E-02	-2.340
.1391	-.4110E+05	4.614	.4930E-08	-8.307	.5925E-02	-2.227
.1455	-.3430E+05	4.535	.7910E-08	-8.102	.7589E-02	-2.120
.1518	-.2884E+05	4.460	.1244E-07	-7.905	.9618E-02	-2.017
.1581	-.2443E+05	4.388	.1920E-07	-7.717	.1207E-01	-1.918
.1644	-.2082E+05	4.319	.2914E-07	-7.536	.1502E-01	-1.823
.1708	-.1786E+05	4.252	.4353E-07	-7.361	.1854E-01	-1.732
.1771	-.1540E+05	4.188	.6410E-07	-7.193	.2271E-01	-1.644
.1834	-.1335E+05	4.125	.9311E-07	-7.031	.2761E-01	-1.559
.1897	-.1163E+05	4.065	.1336E-06	-6.874	.3336E-01	-1.477
.1960	-.1017E+05	4.007	.1893E-06	-6.723	.4006E-01	-1.397
.2024	-.8936E+04	3.951	.2655E-06	-6.576	.4783E-01	-1.320
.2087	-.7881E+04	3.897	.3684E-06	-6.434	.5679E-01	-1.246
.2150	-.6977E+04	3.844	.5062E-06	-6.296	.6710E-01	-1.173
.2213	-.6198E+04	3.792	.6894E-06	-6.162	.7891E-01	-1.103
.2277	-.5523E+04	3.742	.9307E-06	-6.031	.9238E-01	-1.034
.2340	-.4937E+04	3.693	.1246E-05	-5.904	.1077E+00	-.968
.2403	-.4426E+04	3.646	.1656E-05	-5.781	.1251E+00	-.903
.2466	-.3979E+04	3.600	.2185E-05	-5.660	.1447E+00	-.840
.2530	-.3586E+04	3.555	.2863E-05	-5.543	.1668E+00	-.778
.2593	-.3239E+04	3.510	.3727E-05	-5.429	.1917E+00	-.717
.2656	-.2933E+04	3.467	.4822E-05	-5.317	.2195E+00	-.659
.2719	-.2662E+04	3.425	.6201E-05	-5.208	.2507E+00	-.601
.2783	-.2421E+04	3.384	.7930E-05	-5.101	.2854E+00	-.544
.2846	-.2206E+04	3.344	.1009E-04	-4.996	.3242E+00	-.489
.2909	-.2013E+04	3.304	.1277E-04	-4.894	.3672E+00	-.435
.2972	-.1841E+04	3.265	.1608E-04	-4.794	.4149E+00	-.382
.3036	-.1686E+04	3.227	.2016E-04	-4.696	.4678E+00	-.330
.3099	-.1547E+04	3.189	.2516E-04	-4.599	.5263E+00	-.279

.3162	-.1421E+04	3.153	.3127E-04	-4.505	.5909E+00	-.228
.3225	-.1307E+04	3.116	.3871E-04	-4.412	.6621E+00	-.179
.3289	-.1204E+04	3.081	.4774E-04	-4.321	.7406E+00	-.130
.3352	-.1111E+04	3.046	.5865E-04	-4.232	.8269E+00	-.083
.3415	-.1026E+04	3.011	.7181E-04	-4.144	.9218E+00	-.035
.3478	-.9480E+03	2.977	.8763E-04	-4.057	.1026E+01	.011
.3542	-.8772E+03	2.943	.1066E-03	-3.972	.1140E+01	.057
.3605	-.8124E+03	2.910	.1293E-03	-3.889	.1266E+01	.102
.3668	-.7531E+03	2.877	.1563E-03	-3.806	.1403E+01	.147
.3731	-.6987E+03	2.844	.1885E-03	-3.725	.1554E+01	.191
.3794	-.6487E+03	2.812	.2266E-03	-3.645	.1719E+01	.235
.3858	-.6027E+03	2.780	.2719E-03	-3.566	.1899E+01	.279
.3921	-.5602E+03	2.748	.3254E-03	-3.488	.2097E+01	.322
.3984	-.5211E+03	2.717	.3886E-03	-3.411	.2313E+01	.364
.4047	-.4849E+03	2.686	.4630E-03	-3.334	.2549E+01	.406
.4111	-.4513E+03	2.654	.5505E-03	-3.259	.2809E+01	.448
.4174	-.4203E+03	2.624	.6534E-03	-3.185	.3092E+01	.490
.4237	-.3914E+03	2.593	.7742E-03	-3.111	.3403E+01	.532
.4300	-.3646E+03	2.562	.9157E-03	-3.038	.3744E+01	.573
.4364	-.3396E+03	2.531	.1081E-02	-2.966	.4119E+01	.615
.4427	-.3164E+03	2.500	.1275E-02	-2.894	.4530E+01	.656
.4490	-.2947E+03	2.469	.1502E-02	-2.823	.4981E+01	.697
.4553	-.2744E+03	2.438	.1767E-02	-2.753	.5479E+01	.739
.4617	-.2554E+03	2.407	.2077E-02	-2.683	.6027E+01	.780
.4680	-.2376E+03	2.376	.2439E-02	-2.613	.6633E+01	.822
.4743	-.2210E+03	2.344	.2861E-02	-2.543	.7303E+01	.864
.4806	-.2053E+03	2.312	.3355E-02	-2.474	.8047E+01	.906
.4870	-.1906E+03	2.280	.3932E-02	-2.405	.8873E+01	.948
.4933	-.1768E+03	2.247	.4607E-02	-2.337	.9794E+01	.991
.4996	-.1637E+03	2.214	.5398E-02	-2.268	.1082E+02	1.034
.5059	-.1514E+03	2.180	.6326E-02	-2.199	.1198E+02	1.079
.5123	-.1397E+03	2.145	.7416E-02	-2.130	.1329E+02	1.123
.5186	-.1287E+03	2.110	.8699E-02	-2.061	.1476E+02	1.169
.5249	-.1182E+03	2.073	.1021E-01	-1.991	.1644E+02	1.216
.5312	-.1083E+03	2.035	.1201E-01	-1.921	.1836E+02	1.264
.5376	-.9889E+02	1.995	.1414E-01	-1.850	.2058E+02	1.314
.5439	-.8989E+02	1.954	.1668E-01	-1.778	.2316E+02	1.365
.5502	-.8131E+02	1.910	.1974E-01	-1.705	.2619E+02	1.418
.5565	-.7310E+02	1.864	.2344E-01	-1.630	.2978E+02	1.474
.5628	-.6523E+02	1.814	.2795E-01	-1.554	.3410E+02	1.533
.5692	-.5766E+02	1.761	.3351E-01	-1.475	.3938E+02	1.595
.5755	-.5035E+02	1.702	.4046E-01	-1.393	.4598E+02	1.663
.5818	-.4327E+02	1.636	.4930E-01	-1.307	.5443E+02	1.736
.5881	-.3637E+02	1.561	.6083E-01	-1.216	.6564E+02	1.817
.5945	-.2960E+02	1.471	.7639E-01	-1.117	.8126E+02	1.910
.6008	-.2289E+02	1.360	.9848E-01	-1.007	.1047E+03	2.020
.6071	-.1610E+02	1.207	.1328E+00	-.877	.1444E+03	2.160
.6134	-.9001E+01	.954	.1971E+00	-.705	.2322E+03	2.366
.6166	-.5096E+01	.707	.2646E+00	-.577	.3475E+03	2.541
.6182	-.2903E+01	.463	.3320E+00	-.479	.4932E+03	2.693
.6191	-.1386E+01	.142	.4177E+00	-.379	.7372E+03	2.868
.6197	-.2179E+00	-.662	.6014E+00	-.221	.1664E+04	3.221
.6198	-.3432E-01	-1.464	.7353E+00	-.134	.3203E+04	3.506
.6198	.0000E+00		.1000E+01	.000		

End of problem

=====

Replicate 2

```
*****
*
*   Analysis of soil hydraulic properties
*
*   Example 1: Forward Problem
*
*   Mualem-based restriction, M=1-1/N
*   Analysis of retention data only
*   MType= 3   Method= 3
*
*****
```

INITIAL values of the coefficients

```
=====
```

No	Name	INITIAL value	Index
1	ThetaR	.0650	1
2	ThetaS	.4100	1
3	Alpha	.0750	1
4	n	1.8900	1
5	m	.4709	0
6	l	.5000	0
7	Ks	1.0000	0

Observed data

```
=====
```

Obs. No.	Pressure head	Water content	Weighting coefficient
1	.000	.6160	1.0000
2	5.000	.6160	1.0000
3	10.000	.6160	1.0000
4	15.000	.6109	1.0000
5	25.000	.5943	1.0000
6	35.000	.5753	1.0000
7	50.000	.5472	1.0000
8	68.000	.5217	1.0000
9	150.000	.4604	1.0000
10	300.000	.3867	1.0000
11	600.000	.3564	1.0000
12	1000.000	.3365	1.0000
13	5099.000	.2286	1.0000
14	8158.000	.1781	1.0000

NIT	SSQ	ThetaR	ThetaS	Alpha	n
0	1.22174	.0650	.4100	.0750	1.8900
1	.63378	.2351	.6374	.0760	1.0050
2	.56150	.0117	.6361	.1809	1.0078
3	.55845	.0044	.6361	.1854	1.0079
4	.55695	.0008	.6360	.1876	1.0080
5	.55676	.0004	.6360	.1879	1.0080

wcr is less then 0.001: Changed to fit with wcr=0.0

NIT	SSQ	ThetaS	Alpha	n
0	1.58104	.4100	.0750	1.8900

1	.32522	.5304	.0081	1.0050
2	.12561	.6084	.5078	1.1143
3	.03525	.6422	.1639	1.1088
4	.02766	.6486	.1411	1.1189
5	.02221	.6536	.1228	1.1279
6	.01825	.6571	.1084	1.1358
7	.01532	.6594	.0968	1.1428
8	.01310	.6606	.0873	1.1490
9	.00825	.6500	.0467	1.1665
10	.00519	.6355	.0231	1.2002
11	.00179	.6272	.0209	1.2238
12	.00176	.6273	.0211	1.2251
13	.00176	.6272	.0211	1.2251
14	.00176	.6272	.0211	1.2251

Correlation matrix

```

=====
      Theta      Alpha      n
      1         2         3
1  1.0000
2  .7328    1.0000
3  -.4187   -.8394    1.0000

```

RSquared for regression of observed vs fitted values = .99411768

Nonlinear least-squares analysis: final results

```

=====
                                95% Confidence limits
Variable      Value      S.E.Coeff.      T-Value      Lower      Upper
ThetaS        .62724      .00742        84.57        .6109      .6436
Alpha         .02113      .00371         5.69        .0130      .0293
n              1.22511      .01239        98.91        1.1978     1.2524

```

Observed abd fitted data

```

=====
NO      P      log-P      WC-obs      WC-fit      WC-dev
1      .1000E-04      -5.0000      .6160      .6272      -.0112
2      .5000E+01      .6990      .6160      .6202      -.0042
3      .1000E+02      1.0000      .6160      .6114      .0046
4      .1500E+02      1.1761      .6109      .6025      .0084
5      .2500E+02      1.3979      .5943      .5853      .0090
6      .3500E+02      1.5441      .5753      .5695      .0058
7      .5000E+02      1.6990      .5472      .5488      -.0016
8      .6800E+02      1.8325      .5217      .5278      -.0061
9      .1500E+03      2.1761      .4604      .4648      -.0044
10     .3000E+03      2.4771      .3867      .4064      -.0197
11     .6000E+03      2.7782      .3564      .3513      .0051
12     .1000E+04      3.0000      .3365      .3143      .0222
13     .5099E+04      3.7075      .2286      .2186      .0100
14     .8158E+04      3.9116      .1781      .1967      -.0186

```

Sum of squares of observed versus fitted values

```

=====
                Unweighted      Weighted
Retention data      .00176      .00176
Cond/Diff data      .00000      .00000

```

All data .00176 .00176

Soil hydraulic properties (MType = 3)

```
=====
```

WC	P	logP	Cond	logK	Dif	logD
.0016	-.1567E+14	13.195	.1012E-30	-30.995	.4402E-14	-14.356
.0032	-.7207E+12	11.858	.2706E-27	-27.568	.2707E-12	-12.568
.0064	-.3315E+11	10.521	.7234E-24	-24.141	.1664E-10	-10.779
.0128	-.1525E+10	9.183	.1934E-20	-20.714	.1023E-08	-8.990
.0192	-.2518E+09	8.401	.1955E-18	-18.709	.1139E-07	-7.944
.0256	-.7015E+08	7.846	.5170E-17	-17.286	.6293E-07	-7.201
.0320	-.2603E+08	7.416	.6558E-16	-16.183	.2370E-06	-6.625
.0384	-.1158E+08	7.064	.5227E-15	-15.282	.7002E-06	-6.155
.0448	-.5840E+07	6.766	.3023E-14	-14.520	.1750E-05	-5.757
.0512	-.3227E+07	6.509	.1382E-13	-13.859	.3870E-05	-5.412
.0576	-.1912E+07	6.282	.5284E-13	-13.277	.7791E-05	-5.108
.0640	-.1197E+07	6.078	.1753E-12	-12.756	.1457E-04	-4.836
.0704	-.7841E+06	5.894	.5189E-12	-12.285	.2567E-04	-4.591
.0768	-.5327E+06	5.727	.1397E-11	-11.855	.4306E-04	-4.366
.0832	-.3733E+06	5.572	.3476E-11	-11.459	.6928E-04	-4.159
.0896	-.2686E+06	5.429	.8081E-11	-11.093	.1076E-03	-3.968
.0960	-.1977E+06	5.296	.1772E-10	-10.751	.1621E-03	-3.790
.1024	-.1484E+06	5.171	.3696E-10	-10.432	.2379E-03	-3.624
.1088	-.1134E+06	5.055	.7369E-10	-10.133	.3411E-03	-3.467
.1152	-.8795E+05	4.944	.1413E-09	-9.850	.4791E-03	-3.320
.1216	-.6917E+05	4.840	.2614E-09	-9.583	.6607E-03	-3.180
.1280	-.5508E+05	4.741	.4688E-09	-9.329	.8962E-03	-3.048
.1344	-.4434E+05	4.647	.8170E-09	-9.088	.1198E-02	-2.922
.1408	-.3606E+05	4.557	.1388E-08	-8.858	.1579E-02	-2.802
.1472	-.2960E+05	4.471	.2302E-08	-8.638	.2057E-02	-2.687
.1536	-.2450E+05	4.389	.3737E-08	-8.427	.2649E-02	-2.577
.1600	-.2043E+05	4.310	.5948E-08	-8.226	.3376E-02	-2.472
.1664	-.1716E+05	4.235	.9298E-08	-8.032	.4263E-02	-2.370
.1728	-.1451E+05	4.162	.1429E-07	-7.845	.5335E-02	-2.273
.1792	-.1235E+05	4.091	.2162E-07	-7.665	.6624E-02	-2.179
.1856	-.1056E+05	4.024	.3225E-07	-7.492	.8162E-02	-2.088
.1920	-.9083E+04	3.958	.4745E-07	-7.324	.9986E-02	-2.001
.1984	-.7850E+04	3.895	.6893E-07	-7.162	.1214E-01	-1.916
.2048	-.6815E+04	3.833	.9898E-07	-7.004	.1466E-01	-1.834
.2112	-.5942E+04	3.774	.1405E-06	-6.852	.1761E-01	-1.754
.2176	-.5202E+04	3.716	.1975E-06	-6.704	.2104E-01	-1.677
.2240	-.4572E+04	3.660	.2748E-06	-6.561	.2501E-01	-1.602
.2304	-.4032E+04	3.606	.3790E-06	-6.421	.2958E-01	-1.529
.2368	-.3568E+04	3.552	.5180E-06	-6.286	.3484E-01	-1.458
.2432	-.3167E+04	3.501	.7022E-06	-6.154	.4085E-01	-1.389
.2496	-.2820E+04	3.450	.9444E-06	-6.025	.4771E-01	-1.321
.2560	-.2518E+04	3.401	.1261E-05	-5.899	.5552E-01	-1.256
.2624	-.2254E+04	3.353	.1672E-05	-5.777	.6436E-01	-1.191
.2688	-.2024E+04	3.306	.2202E-05	-5.657	.7436E-01	-1.129
.2752	-.1821E+04	3.260	.2881E-05	-5.540	.8564E-01	-1.067
.2816	-.1642E+04	3.215	.3748E-05	-5.426	.9832E-01	-1.007
.2880	-.1484E+04	3.171	.4847E-05	-5.315	.1126E+00	-.949
.2944	-.1344E+04	3.128	.6235E-05	-5.205	.1285E+00	-.891
.3008	-.1219E+04	3.086	.7978E-05	-5.098	.1463E+00	-.835
.3072	-.1108E+04	3.045	.1016E-04	-4.993	.1662E+00	-.779
.3136	-.1009E+04	3.004	.1287E-04	-4.890	.1883E+00	-.725
.3200	-.9206E+03	2.964	.1624E-04	-4.790	.2129E+00	-.672

.3264	-.8410E+03	2.925	.2039E-04	-4.691	.2402E+00	-.619
.3328	-.7694E+03	2.886	.2550E-04	-4.593	.2705E+00	-.568
.3392	-.7049E+03	2.848	.3177E-04	-4.498	.3040E+00	-.517
.3456	-.6467E+03	2.811	.3943E-04	-4.404	.3410E+00	-.467
.3520	-.5940E+03	2.774	.4876E-04	-4.312	.3819E+00	-.418
.3584	-.5462E+03	2.737	.6009E-04	-4.221	.4271E+00	-.369
.3648	-.5028E+03	2.701	.7380E-04	-4.132	.4768E+00	-.322
.3712	-.4634E+03	2.666	.9036E-04	-4.044	.5316E+00	-.274
.3776	-.4274E+03	2.631	.1103E-03	-3.957	.5920E+00	-.228
.3840	-.3945E+03	2.596	.1343E-03	-3.872	.6584E+00	-.182
.3904	-.3645E+03	2.562	.1630E-03	-3.788	.7314E+00	-.136
.3968	-.3370E+03	2.528	.1973E-03	-3.705	.8116E+00	-.091
.4032	-.3118E+03	2.494	.2383E-03	-3.623	.8999E+00	-.046
.4096	-.2886E+03	2.460	.2872E-03	-3.542	.9969E+00	-.001
.4160	-.2673E+03	2.427	.3453E-03	-3.462	.1103E+01	.043
.4224	-.2476E+03	2.394	.4142E-03	-3.383	.1221E+01	.087
.4288	-.2295E+03	2.361	.4960E-03	-3.305	.1350E+01	.130
.4352	-.2128E+03	2.328	.5928E-03	-3.227	.1492E+01	.174
.4416	-.1973E+03	2.295	.7074E-03	-3.150	.1648E+01	.217
.4480	-.1829E+03	2.262	.8427E-03	-3.074	.1820E+01	.260
.4544	-.1696E+03	2.229	.1003E-02	-2.999	.2010E+01	.303
.4608	-.1572E+03	2.197	.1191E-02	-2.924	.2220E+01	.346
.4672	-.1457E+03	2.163	.1413E-02	-2.850	.2452E+01	.389
.4736	-.1350E+03	2.130	.1676E-02	-2.776	.2709E+01	.433
.4800	-.1250E+03	2.097	.1985E-02	-2.702	.2994E+01	.476
.4864	-.1157E+03	2.063	.2349E-02	-2.629	.3311E+01	.520
.4928	-.1069E+03	2.029	.2778E-02	-2.556	.3664E+01	.564
.4992	-.9876E+02	1.995	.3286E-02	-2.483	.4059E+01	.608
.5056	-.9110E+02	1.960	.3885E-02	-2.411	.4503E+01	.653
.5120	-.8391E+02	1.924	.4593E-02	-2.338	.5001E+01	.699
.5184	-.7715E+02	1.887	.5433E-02	-2.265	.5564E+01	.745
.5248	-.7079E+02	1.850	.6429E-02	-2.192	.6204E+01	.793
.5312	-.6479E+02	1.812	.7615E-02	-2.118	.6933E+01	.841
.5376	-.5913E+02	1.772	.9031E-02	-2.044	.7770E+01	.890
.5440	-.5377E+02	1.731	.1073E-01	-1.969	.8738E+01	.941
.5504	-.4869E+02	1.687	.1277E-01	-1.894	.9865E+01	.994
.5568	-.4387E+02	1.642	.1525E-01	-1.817	.1119E+02	1.049
.5632	-.3929E+02	1.594	.1827E-01	-1.738	.1277E+02	1.106
.5696	-.3492E+02	1.543	.2198E-01	-1.658	.1467E+02	1.166
.5760	-.3074E+02	1.488	.2660E-01	-1.575	.1700E+02	1.230
.5824	-.2673E+02	1.427	.3243E-01	-1.489	.1992E+02	1.299
.5888	-.2287E+02	1.359	.3991E-01	-1.399	.2367E+02	1.374
.5952	-.1913E+02	1.282	.4977E-01	-1.303	.2865E+02	1.457
.6016	-.1549E+02	1.190	.6320E-01	-1.199	.3562E+02	1.552
.6080	-.1190E+02	1.076	.8252E-01	-1.083	.4609E+02	1.664
.6144	-.8312E+01	.920	.1129E+00	-.947	.6392E+02	1.806
.6208	-.4592E+01	.662	.1710E+00	-.767	.1035E+03	2.015
.6240	-.2573E+01	.410	.2331E+00	-.632	.1555E+03	2.192
.6256	-.1451E+01	.162	.2964E+00	-.528	.2212E+03	2.345
.6266	-.6842E+00	-.165	.3781E+00	-.422	.3310E+03	2.520
.6272	-.1042E+00	-.982	.5591E+00	-.252	.7432E+03	2.871
.6272	-.1590E-01	-1.799	.6969E+00	-.157	.1413E+04	3.150
.6272	.0000E+00		.1000E+01	.000		

End of problem

=====

Replicate 3

```
*****
*
*   Analysis of soil hydraulic properties
*
*   Example 1: Forward Problem
*
*   Mualem-based restriction, M=1-1/N
*   Analysis of retention data only
*   MType= 3   Method= 3
*
*****
```

INITIAL values of the coefficients

```
=====
```

No	Name	INITIAL value	Index
1	ThetaR	.0650	1
2	ThetaS	.4100	1
3	Alpha	.0750	1
4	n	1.8900	1
5	m	.4709	0
6	l	.5000	0
7	Ks	1.0000	0

Observed data

```
=====
```

Obs. No.	Pressure head	Water content	Weighting coefficient
1	.000	.6473	1.0000
2	5.000	.6425	1.0000
3	10.000	.6420	1.0000
4	15.000	.6420	1.0000
5	25.000	.6386	1.0000
6	35.000	.6348	1.0000
7	50.000	.6249	1.0000
8	68.000	.6153	1.0000
9	150.000	.5965	1.0000
10	300.000	.5246	1.0000
11	600.000	.4459	1.0000
12	1000.000	.4106	1.0000
13	5099.000	.2286	1.0000
14	8158.000	.1781	1.0000

NIT	SSQ	ThetaR	ThetaS	Alpha	n
0	1.82937	.0650	.4100	.0750	1.8900
1	.32231	.1971	.5334	.0052	1.0050
2	.30930	.0314	.5345	.0091	1.0075
3	.30688	.0082	.5345	.0100	1.0078
4	.30631	.0029	.5345	.0102	1.0079
5	.30603	.0003	.5345	.0103	1.0080

wcr is less then 0.001: Changed to fit with wcr=0.0

NIT	SSQ	ThetaS	Alpha	n
0	2.26798	.4100	.0750	1.8900

1	.47893	.4768	.0374	1.1716
2	.20402	.5174	.0136	1.1581
3	.06753	.5754	.0053	1.1720
4	.00400	.6431	.0039	1.3016
5	.00091	.6432	.0033	1.3640
6	.00077	.6431	.0033	1.3703
7	.00077	.6431	.0033	1.3701
8	.00077	.6431	.0033	1.3701

Correlation matrix

```
=====
      Theta   Alpha   n
      1       2       3
1  1.0000
2  .5335   1.0000
3  -.3107  -.8575   1.0000
```

RSquared for regression of observed vs fitted values = .99768288

Nonlinear least-squares analysis: final results

```
=====
                                     95% Confidence limits
Variable   Value   S.E.Coeff.   T-Value   Lower   Upper
ThetaS     .64310   .00324       198.19    .6360   .6502
Alpha      .00333   .00027        12.18     .0027   .0039
n          1.37009 .01572        87.18    1.3355  1.4047
```

Observed abd fitted data

```
=====
NO      P      log-P   WC-obs   WC-fit   WC-dev
1      .1000E-04  -5.0000  .6473   .6431   .0042
2      .5000E+01   .6990   .6425   .6425   .0000
3      .1000E+02   1.0000   .6420   .6415   .0005
4      .1500E+02   1.1761   .6420   .6403   .0017
5      .2500E+02   1.3979   .6386   .6374   .0012
6      .3500E+02   1.5441   .6348   .6342   .0006
7      .5000E+02   1.6990   .6249   .6289   -.0040
8      .6800E+02   1.8325   .6153   .6221   -.0068
9      .1500E+03   2.1761   .5965   .5887   .0078
10     .3000E+03   2.4771   .5246   .5333   -.0087
11     .6000E+03   2.7782   .4459   .4555   -.0096
12     .1000E+04   3.0000   .4106   .3928   .0178
13     .5099E+04   3.7075   .2286   .2242   .0044
14     .8158E+04   3.9116   .1781   .1889   -.0108
```

Sum of squares of observed versus fitted values

```
=====
                Unweighted   Weighted
Retention data   .00077       .00077
Cond/Diff data  .00000       .00000
All data        .00077       .00077
```

Soil hydraulic properties (MType = 3)

```
=====
      WC      P      logP      Cond      logK      Dif      logD
.0016  -.3050E+10  9.484   .2320E-21  -21.635   .1166E-08  -8.933
```

.0033	-.4688E+09	8.671	.5557E-19	-19.255	.2145E-07	-7.669
.0066	-.7204E+08	7.858	.1331E-16	-16.876	.3948E-06	-6.404
.0131	-.1107E+08	7.044	.3189E-14	-14.496	.7267E-05	-5.139
.0197	-.3701E+07	6.568	.7861E-13	-13.105	.3993E-04	-4.399
.0262	-.1701E+07	6.231	.7638E-12	-12.117	.1338E-03	-3.874
.0328	-.9309E+06	5.969	.4456E-11	-11.351	.3416E-03	-3.466
.0394	-.5688E+06	5.755	.1883E-10	-10.725	.7350E-03	-3.134
.0459	-.3750E+06	5.574	.6368E-10	-10.196	.1405E-02	-2.852
.0525	-.2614E+06	5.417	.1830E-09	-9.738	.2462E-02	-2.609
.0591	-.1901E+06	5.279	.4642E-09	-9.333	.4039E-02	-2.394
.0656	-.1430E+06	5.155	.1068E-08	-8.972	.6289E-02	-2.201
.0722	-.1105E+06	5.044	.2268E-08	-8.644	.9388E-02	-2.027
.0787	-.8738E+05	4.941	.4512E-08	-8.346	.1353E-01	-1.869
.0853	-.7038E+05	4.847	.8495E-08	-8.071	.1895E-01	-1.722
.0919	-.5760E+05	4.760	.1526E-07	-7.816	.2587E-01	-1.587
.0984	-.4780E+05	4.679	.2633E-07	-7.580	.3458E-01	-1.461
.1050	-.4014E+05	4.604	.4387E-07	-7.358	.4537E-01	-1.343
.1116	-.3407E+05	4.532	.7085E-07	-7.150	.5855E-01	-1.232
.1181	-.2918E+05	4.465	.1113E-06	-6.953	.7447E-01	-1.128
.1247	-.2521E+05	4.402	.1708E-06	-6.768	.9350E-01	-1.029
.1312	-.2194E+05	4.341	.2562E-06	-6.591	.1160E+00	-.935
.1378	-.1922E+05	4.284	.3769E-06	-6.424	.1425E+00	-.846
.1444	-.1694E+05	4.229	.5447E-06	-6.264	.1734E+00	-.761
.1509	-.1502E+05	4.177	.7744E-06	-6.111	.2092E+00	-.679
.1575	-.1338E+05	4.126	.1085E-05	-5.965	.2503E+00	-.601
.1641	-.1197E+05	4.078	.1499E-05	-5.824	.2975E+00	-.527
.1706	-.1076E+05	4.032	.2045E-05	-5.689	.3511E+00	-.455
.1772	-.9710E+04	3.987	.2758E-05	-5.559	.4119E+00	-.385
.1837	-.8794E+04	3.944	.3680E-05	-5.434	.4805E+00	-.318
.1903	-.7990E+04	3.903	.4861E-05	-5.313	.5576E+00	-.254
.1969	-.7283E+04	3.862	.6361E-05	-5.196	.6439E+00	-.191
.2034	-.6657E+04	3.823	.8253E-05	-5.083	.7403E+00	-.131
.2100	-.6102E+04	3.785	.1062E-04	-4.974	.8474E+00	-.072
.2166	-.5607E+04	3.749	.1356E-04	-4.868	.9663E+00	-.015
.2231	-.5165E+04	3.713	.1720E-04	-4.764	.1098E+01	.040
.2297	-.4768E+04	3.678	.2167E-04	-4.664	.1243E+01	.094
.2362	-.4410E+04	3.644	.2712E-04	-4.567	.1402E+01	.147
.2428	-.4087E+04	3.611	.3374E-04	-4.472	.1578E+01	.198
.2494	-.3795E+04	3.579	.4175E-04	-4.379	.1770E+01	.248
.2559	-.3530E+04	3.548	.5138E-04	-4.289	.1980E+01	.297
.2625	-.3288E+04	3.517	.6292E-04	-4.201	.2210E+01	.344
.2691	-.3068E+04	3.487	.7667E-04	-4.115	.2460E+01	.391
.2756	-.2867E+04	3.457	.9302E-04	-4.031	.2733E+01	.437
.2822	-.2682E+04	3.428	.1124E-03	-3.949	.3029E+01	.481
.2887	-.2512E+04	3.400	.1352E-03	-3.869	.3351E+01	.525
.2953	-.2356E+04	3.372	.1620E-03	-3.790	.3701E+01	.568
.3019	-.2212E+04	3.345	.1935E-03	-3.713	.4079E+01	.611
.3084	-.2079E+04	3.318	.2302E-03	-3.638	.4489E+01	.652
.3150	-.1956E+04	3.291	.2730E-03	-3.564	.4932E+01	.693
.3216	-.1842E+04	3.265	.3227E-03	-3.491	.5411E+01	.733
.3281	-.1736E+04	3.239	.3804E-03	-3.420	.5928E+01	.773
.3347	-.1637E+04	3.214	.4470E-03	-3.350	.6486E+01	.812
.3412	-.1545E+04	3.189	.5239E-03	-3.281	.7088E+01	.851
.3478	-.1459E+04	3.164	.6125E-03	-3.213	.7738E+01	.889
.3544	-.1379E+04	3.140	.7142E-03	-3.146	.8438E+01	.926
.3609	-.1304E+04	3.115	.8308E-03	-3.081	.9193E+01	.963
.3675	-.1234E+04	3.091	.9642E-03	-3.016	.1001E+02	1.000

.3740	-.1168E+04	3.067	.1117E-02	-2.952	.1088E+02	1.037
.3806	-.1106E+04	3.044	.1291E-02	-2.889	.1183E+02	1.073
.3872	-.1047E+04	3.020	.1489E-02	-2.827	.1285E+02	1.109
.3937	-.9923E+03	2.997	.1715E-02	-2.766	.1394E+02	1.144
.4003	-.9404E+03	2.973	.1971E-02	-2.705	.1513E+02	1.180
.4069	-.8915E+03	2.950	.2262E-02	-2.646	.1640E+02	1.215
.4134	-.8452E+03	2.927	.2591E-02	-2.586	.1778E+02	1.250
.4200	-.8014E+03	2.904	.2965E-02	-2.528	.1926E+02	1.285
.4265	-.7598E+03	2.881	.3388E-02	-2.470	.2087E+02	1.320
.4331	-.7205E+03	2.858	.3866E-02	-2.413	.2261E+02	1.354
.4397	-.6830E+03	2.834	.4406E-02	-2.356	.2449E+02	1.389
.4462	-.6475E+03	2.811	.5016E-02	-2.300	.2652E+02	1.424
.4528	-.6136E+03	2.788	.5706E-02	-2.244	.2873E+02	1.458
.4594	-.5813E+03	2.764	.6483E-02	-2.188	.3113E+02	1.493
.4659	-.5506E+03	2.741	.7361E-02	-2.133	.3374E+02	1.528
.4725	-.5212E+03	2.717	.8352E-02	-2.078	.3658E+02	1.563
.4790	-.4931E+03	2.693	.9471E-02	-2.024	.3967E+02	1.599
.4856	-.4662E+03	2.669	.1073E-01	-1.969	.4306E+02	1.634
.4922	-.4404E+03	2.644	.1216E-01	-1.915	.4677E+02	1.670
.4987	-.4156E+03	2.619	.1377E-01	-1.861	.5085E+02	1.706
.5053	-.3919E+03	2.593	.1559E-01	-1.807	.5534E+02	1.743
.5119	-.3690E+03	2.567	.1766E-01	-1.753	.6031E+02	1.780
.5184	-.3470E+03	2.540	.2000E-01	-1.699	.6580E+02	1.818
.5250	-.3258E+03	2.513	.2265E-01	-1.645	.7192E+02	1.857
.5315	-.3054E+03	2.485	.2568E-01	-1.590	.7876E+02	1.896
.5381	-.2856E+03	2.456	.2912E-01	-1.536	.8643E+02	1.937
.5447	-.2664E+03	2.426	.3306E-01	-1.481	.9509E+02	1.978
.5512	-.2478E+03	2.394	.3757E-01	-1.425	.1049E+03	2.021
.5578	-.2297E+03	2.361	.4276E-01	-1.369	.1162E+03	2.065
.5644	-.2121E+03	2.327	.4875E-01	-1.312	.1291E+03	2.111
.5709	-.1949E+03	2.290	.5572E-01	-1.254	.1442E+03	2.159
.5775	-.1781E+03	2.251	.6387E-01	-1.195	.1620E+03	2.209
.5840	-.1616E+03	2.209	.7347E-01	-1.134	.1831E+03	2.263
.5906	-.1454E+03	2.163	.8488E-01	-1.071	.2088E+03	2.320
.5972	-.1293E+03	2.112	.9863E-01	-1.006	.2405E+03	2.381
.6037	-.1133E+03	2.054	.1155E+00	-.938	.2808E+03	2.448
.6103	-.9735E+02	1.988	.1365E+00	-.865	.3338E+03	2.524
.6169	-.8118E+02	1.909	.1636E+00	-.786	.4069E+03	2.610
.6234	-.6460E+02	1.810	.2001E+00	-.699	.5154E+03	2.712
.6300	-.4719E+02	1.674	.2534E+00	-.596	.6978E+03	2.844
.6365	-.2795E+02	1.446	.3449E+00	-.462	.1098E+04	3.041
.6398	-.1670E+02	1.223	.4323E+00	-.364	.1626E+04	3.211
.6415	-.1003E+02	1.001	.5126E+00	-.290	.2301E+04	3.362
.6424	-.5124E+01	.710	.6057E+00	-.218	.3460E+04	3.539
.6430	-.9528E+00	-.021	.7762E+00	-.110	.8228E+04	3.915
.6431	-.1774E+00	-.751	.8763E+00	-.057	.1730E+05	4.238
.6431	.0000E+00		.1000E+01	.000		

End of problem

=====

Replicate 4

 *
 * Analysis of soil hydraulic properties *

```

*
* Example 1: Forward Problem
*
* Mualem-based restriction, M=1-1/N
* Analysis of retention data only
* MType= 3 Method= 3
*
*****

```

INITIAL values of the coefficients

```

=====
No      Name      INITIAL value  Index
1      ThetaR      .0650         1
2      ThetaS      .4100         1
3      Alpha       .0750         1
4      n           1.8900        1
5      m           .4709         0
6      l           .5000         0
7      Ks          1.0000        0

```

Observed data

```

=====
Obs. No.  Pressure head  Water content  Weighting coefficient
1          .000          .6299          1.0000
2          5.000          .6261          1.0000
3         10.000          .6254          1.0000
4         15.000          .6165          1.0000
5         25.000          .5984          1.0000
6         35.000          .5756          1.0000
7         50.000          .5453          1.0000
8         68.000          .5171          1.0000
9        150.000          .4536          1.0000
10       300.000          .3817          1.0000
11       600.000          .3528          1.0000
12      1000.000          .3372          1.0000
13      5099.000          .2286          1.0000
14     8158.000          .1781          1.0000

```

```

NIT      SSQ      ThetaR  ThetaS  Alpha  n
0    1.22998  .0650  .4100  .0750  1.8900
1    .69231  .2346  .6491  .0744  1.0050
2    .61262  .0032  .6477  .1836  1.0078
3    .61178  .0013  .6477  .1848  1.0079
4    .61136  .0004  .6477  .1854  1.0079
5    .61125  .0002  .6477  .1855  1.0079

```

wcr is less then 0.001: Changed to fit with wcr=0.0

```

NIT      SSQ      ThetaS  Alpha  n
0    1.58773  .4100  .0750  1.8900
1    .34390  .5354  .0076  1.0050
2    .11414  .6135  .5331  1.1088
3    .03896  .6464  .1914  1.1062
4    .03745  .6509  .0454  1.1334
5    .02715  .6389  .0139  1.2040
6    .00334  .6379  .0248  1.2070
7    .00198  .6402  .0265  1.2183

```

8	.00198	.6400	.0262	1.2191
9	.00198	.6400	.0263	1.2190
10	.00198	.6400	.0263	1.2190
11	.00198	.6400	.0263	1.2190

Correlation matrix

```

=====
      Theta   Alpha   n
      1       2       3
1  1.0000
2  .7468   1.0000
3  -.4153  -.8306   1.0000

```

RSquared for regression of observed vs fitted values = .99368809

Nonlinear least-squares analysis: final results

```

=====
                                95% Confidence limits
Variable      Value      S.E.Coeff.      T-Value      Lower      Upper
ThetaS        .64004      .00830      77.12      .6218      .6583
Alpha         .02625      .00484      5.43      .0156      .0369
n             1.21904      .01208      100.88     1.1924     1.2456

```

Observed abd fitted data

```

=====
NO      P      log-P      WC-obs      WC-fit      WC-dev
1      .1000E-04  -5.0000      .6299      .6400      -.0101
2      .5000E+01   .6990      .6261      .6308      -.0047
3      .1000E+02   1.0000      .6254      .6198      .0056
4      .1500E+02   1.1761      .6165      .6088      .0077
5      .2500E+02   1.3979      .5984      .5883      .0101
6      .3500E+02   1.5441      .5756      .5702      .0054
7      .5000E+02   1.6990      .5453      .5472      -.0019
8      .6800E+02   1.8325      .5171      .5245      -.0074
9      .1500E+03   2.1761      .4536      .4596      -.0060
10     .3000E+03   2.4771      .3817      .4016      -.0199
11     .6000E+03   2.7782      .3528      .3478      .0050
12     .1000E+04   3.0000      .3372      .3118      .0254
13     .5099E+04   3.7075      .2286      .2189      .0097
14     .8158E+04   3.9116      .1781      .1975      -.0194

```

Sum of squares of observed versus fitted values

```

=====
                        Unweighted   Weighted
Retention data         .00198       .00198
Cond/Diff data        .00000       .00000
All data              .00198       .00198

```

Soil hydraulic properties (MType = 3)

```

=====
      WC      P      logP      Cond      logK      Dif      logD
.0033  -.1111E+13  12.046  .7055E-28  -28.151  .1096E-12  -12.960
.0065  -.4693E+11  10.671  .2237E-24  -24.650  .7339E-11  -11.134
.0131  -.1982E+10   9.297  .7094E-21  -21.149  .4914E-09  -9.309
.0196  -.3113E+09   8.493  .7924E-19  -19.101  .5748E-08  -8.240
.0261  -.8372E+08   7.923  .2249E-17  -17.648  .3291E-07  -7.483

```

.0327	-.3023E+08	7.480	.3014E-16	-16.521	.1274E-06	-6.895
.0392	-.1315E+08	7.119	.2513E-15	-15.600	.3849E-06	-6.415
.0457	-.6505E+07	6.813	.1509E-14	-14.821	.9805E-06	-6.009
.0522	-.3536E+07	6.549	.7133E-14	-14.147	.2204E-05	-5.657
.0588	-.2065E+07	6.315	.2807E-13	-13.552	.4502E-05	-5.347
.0653	-.1277E+07	6.106	.9558E-13	-13.020	.8530E-05	-5.069
.0718	-.8263E+06	5.917	.2896E-12	-12.538	.1521E-04	-4.818
.0784	-.5554E+06	5.745	.7967E-12	-12.099	.2578E-04	-4.589
.0849	-.3854E+06	5.586	.2021E-11	-11.694	.4189E-04	-4.378
.0914	-.2748E+06	5.439	.4786E-11	-11.320	.6566E-04	-4.183
.0980	-.2005E+06	5.302	.1068E-10	-10.972	.9978E-04	-4.001
.1045	-.1493E+06	5.174	.2262E-10	-10.646	.1476E-03	-3.831
.1110	-.1132E+06	5.054	.4578E-10	-10.339	.2132E-03	-3.671
.1176	-.8723E+05	4.941	.8900E-10	-10.051	.3015E-03	-3.521
.1241	-.6815E+05	4.833	.1669E-09	-9.777	.4186E-03	-3.378
.1306	-.5392E+05	4.732	.3031E-09	-9.518	.5713E-03	-3.243
.1372	-.4315E+05	4.635	.5347E-09	-9.272	.7681E-03	-3.115
.1437	-.3489E+05	4.543	.9185E-09	-9.037	.1019E-02	-2.992
.1502	-.2848E+05	4.455	.1540E-08	-8.812	.1334E-02	-2.875
.1567	-.2345E+05	4.370	.2527E-08	-8.597	.1727E-02	-2.763
.1633	-.1946E+05	4.289	.4063E-08	-8.391	.2212E-02	-2.655
.1698	-.1627E+05	4.211	.6413E-08	-8.193	.2807E-02	-2.552
.1763	-.1369E+05	4.136	.9947E-08	-8.002	.3529E-02	-2.452
.1829	-.1160E+05	4.064	.1519E-07	-7.819	.4401E-02	-2.356
.1894	-.9878E+04	3.995	.2285E-07	-7.641	.5446E-02	-2.264
.1959	-.8460E+04	3.927	.3389E-07	-7.470	.6691E-02	-2.175
.2025	-.7282E+04	3.862	.4964E-07	-7.304	.8165E-02	-2.088
.2090	-.6298E+04	3.799	.7183E-07	-7.144	.9902E-02	-2.004
.2155	-.5471E+04	3.738	.1028E-06	-6.988	.1194E-01	-1.923
.2221	-.4772E+04	3.679	.1455E-06	-6.837	.1431E-01	-1.844
.2286	-.4179E+04	3.621	.2039E-06	-6.691	.1707E-01	-1.768
.2351	-.3673E+04	3.565	.2831E-06	-6.548	.2027E-01	-1.693
.2416	-.3240E+04	3.510	.3895E-06	-6.409	.2395E-01	-1.621
.2482	-.2866E+04	3.457	.5315E-06	-6.275	.2817E-01	-1.550
.2547	-.2544E+04	3.406	.7194E-06	-6.143	.3300E-01	-1.481
.2612	-.2265E+04	3.355	.9665E-06	-6.015	.3852E-01	-1.414
.2678	-.2022E+04	3.306	.1289E-05	-5.890	.4478E-01	-1.349
.2743	-.1809E+04	3.258	.1708E-05	-5.768	.5189E-01	-1.285
.2808	-.1623E+04	3.210	.2248E-05	-5.648	.5993E-01	-1.222
.2874	-.1460E+04	3.164	.2940E-05	-5.532	.6899E-01	-1.161
.2939	-.1316E+04	3.119	.3823E-05	-5.418	.7919E-01	-1.101
.3004	-.1189E+04	3.075	.4943E-05	-5.306	.9064E-01	-1.043
.3070	-.1076E+04	3.032	.6358E-05	-5.197	.1035E+00	-.985
.3135	-.9755E+03	2.989	.8137E-05	-5.090	.1178E+00	-.929
.3200	-.8862E+03	2.948	.1036E-04	-4.985	.1338E+00	-.874
.3266	-.8064E+03	2.907	.1313E-04	-4.882	.1516E+00	-.819
.3331	-.7350E+03	2.866	.1657E-04	-4.781	.1715E+00	-.766
.3396	-.6709E+03	2.827	.2083E-04	-4.681	.1935E+00	-.713
.3461	-.6133E+03	2.788	.2606E-04	-4.584	.2179E+00	-.662
.3527	-.5614E+03	2.749	.3249E-04	-4.488	.2450E+00	-.611
.3592	-.5146E+03	2.711	.4035E-04	-4.394	.2750E+00	-.561
.3657	-.4723E+03	2.674	.4994E-04	-4.302	.3081E+00	-.511
.3723	-.4339E+03	2.637	.6159E-04	-4.210	.3446E+00	-.463
.3788	-.3990E+03	2.601	.7572E-04	-4.121	.3850E+00	-.415
.3853	-.3674E+03	2.565	.9281E-04	-4.032	.4294E+00	-.367
.3919	-.3385E+03	2.530	.1134E-03	-3.945	.4785E+00	-.320
.3984	-.3122E+03	2.494	.1382E-03	-3.859	.5324E+00	-.274

.4049	-.2881E+03	2.460	.1680E-03	-3.775	.5919E+00	-.228
.4115	-.2661E+03	2.425	.2036E-03	-3.691	.6573E+00	-.182
.4180	-.2459E+03	2.391	.2463E-03	-3.609	.7294E+00	-.137
.4245	-.2273E+03	2.357	.2971E-03	-3.527	.8087E+00	-.092
.4310	-.2103E+03	2.323	.3578E-03	-3.446	.8960E+00	-.048
.4376	-.1946E+03	2.289	.4299E-03	-3.367	.9921E+00	-.003
.4441	-.1801E+03	2.255	.5156E-03	-3.288	.1098E+01	.041
.4506	-.1667E+03	2.222	.6173E-03	-3.210	.1215E+01	.085
.4572	-.1543E+03	2.188	.7378E-03	-3.132	.1344E+01	.128
.4637	-.1429E+03	2.155	.8806E-03	-3.055	.1486E+01	.172
.4702	-.1323E+03	2.121	.1050E-02	-2.979	.1643E+01	.216
.4768	-.1224E+03	2.088	.1249E-02	-2.903	.1817E+01	.259
.4833	-.1132E+03	2.054	.1486E-02	-2.828	.2010E+01	.303
.4898	-.1047E+03	2.020	.1765E-02	-2.753	.2225E+01	.347
.4964	-.9677E+02	1.986	.2096E-02	-2.679	.2464E+01	.392
.5029	-.8935E+02	1.951	.2486E-02	-2.604	.2730E+01	.436
.5094	-.8241E+02	1.916	.2949E-02	-2.530	.3028E+01	.481
.5160	-.7592E+02	1.880	.3497E-02	-2.456	.3362E+01	.527
.5225	-.6984E+02	1.844	.4147E-02	-2.382	.3739E+01	.573
.5290	-.6413E+02	1.807	.4919E-02	-2.308	.4165E+01	.620
.5355	-.5877E+02	1.769	.5838E-02	-2.234	.4648E+01	.667
.5421	-.5372E+02	1.730	.6934E-02	-2.159	.5200E+01	.716
.5486	-.4896E+02	1.690	.8247E-02	-2.084	.5835E+01	.766
.5551	-.4447E+02	1.648	.9825E-02	-2.008	.6568E+01	.817
.5617	-.4023E+02	1.604	.1173E-01	-1.931	.7424E+01	.871
.5682	-.3620E+02	1.559	.1404E-01	-1.853	.8431E+01	.926
.5747	-.3238E+02	1.510	.1687E-01	-1.773	.9630E+01	.984
.5813	-.2874E+02	1.458	.2036E-01	-1.691	.1108E+02	1.044
.5878	-.2527E+02	1.403	.2472E-01	-1.607	.1285E+02	1.109
.5943	-.2194E+02	1.341	.3022E-01	-1.520	.1507E+02	1.178
.6009	-.1875E+02	1.273	.3732E-01	-1.428	.1793E+02	1.254
.6074	-.1566E+02	1.195	.4669E-01	-1.331	.2174E+02	1.337
.6139	-.1266E+02	1.102	.5951E-01	-1.225	.2706E+02	1.432
.6204	-.9707E+01	.987	.7800E-01	-1.108	.3506E+02	1.545
.6270	-.6763E+01	.830	.1072E+00	-.970	.4871E+02	1.688
.6335	-.3724E+01	.571	.1634E+00	-.787	.7901E+02	1.898
.6368	-.2080E+01	.318	.2239E+00	-.650	.1189E+03	2.075
.6384	-.1170E+01	.068	.2858E+00	-.544	.1693E+03	2.229
.6394	-.5493E+00	-.260	.3662E+00	-.436	.2535E+03	2.404
.6400	-.8287E-01	-1.082	.5460E+00	-.263	.5685E+03	2.755
.6400	-.1253E-01	-1.902	.6845E+00	-.165	.1077E+04	3.032
.6400	.0000E+00		.1000E+01	.000		

End of problem

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APPENDIX O
RESULTS OF FITTING OF MULTIPLE REGRESSION MODELS FOR PREDICTION OF
P AVAILABILITY AFTER THE FIRE

Model 1:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	823.368310	274.456103	94.26	<.0001
Error	212	617.302924	2.911806		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P04_P Mean
0.571517 26.65482 1.706402 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	107.0590408	107.0590408	36.77	<.0001
Moisture	1	137.8747888	137.8747888	47.35	<.0001
Temperature	1	578.4344802	578.4344802	198.65	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	15.34402853	0.55156361	27.82	<.0001
Day	-0.01253608	0.00206743	-6.06	<.0001
Moisture	-7.13426676	1.03678368	-6.88	<.0001
Temperature	-0.01463677	0.00103848	-14.09	<.0001

Model 2:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	890.327067	148.387845	56.35	<.0001
Error	209	550.344167	2.633226		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P04_P Mean
0.617995 25.34770 1.622722 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	20.4034436	20.4034436	7.75	0.0059
Moisture	1	117.5023736	117.5023736	44.62	<.0001
Temperature	1	191.0766954	191.0766954	72.56	<.0001
Day*Moisture	1	13.1956077	13.1956077	5.01	0.0262
Day*Temperature	1	0.0403640	0.0403640	0.02	0.9016
Moisture*Temperature	1	53.7227858	53.7227858	20.40	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	20.93804965	1.34782249	15.53	<.0001
Day	-0.02472916	0.00888386	-2.78	0.0059
Moisture	-26.30277588	3.93751576	-6.68	<.0001
Temperature	-0.02629133	0.00308640	-8.52	<.0001
Day*Moisture	0.03930053	0.01755609	2.24	0.0262
Day*Temperature	0.00000218	0.00001758	0.12	0.9016
Moisture*Temperature	0.03983191	0.00881852	4.52	<.0001

Model 3:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	890.286703	178.057341	67.94	<.0001
Error	210	550.384531	2.620879		
Corrected Total	215	1440.671234			

R-Square 0.617967
Coeff Var 25.28820
Root MSE 1.618913
P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	50.9016376	50.9016376	19.42	<.0001
Moisture	1	117.5023736	117.5023736	44.83	<.0001
Temperature	1	241.6569864	241.6569864	92.20	<.0001
Day*Moisture	1	13.1956077	13.1956077	5.03	0.0259
Moisture*Temperature	1	53.7227858	53.7227858	20.50	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	20.86634822	1.21420373	17.19	<.0001
Day	-0.02385830	0.00541374	-4.41	<.0001
Moisture	-26.30277588	3.92827359	-6.70	<.0001
Temperature	-0.02611208	0.00271935	-9.60	<.0001
Day*Moisture	0.03930053	0.01751488	2.24	0.0259
Moisture*Temperature	0.03983191	0.00879783	4.53	<.0001

Model 4:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	891.880275	127.411468	48.29	<.0001
Error	208	548.790959	2.638418		
Corrected Total	215	1440.671234			

R-Square 0.619073
Coeff Var 25.37268
Root MSE 1.624321
P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
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Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Day	1	9.66825839	9.66825839	3.66	0.0570
Moisture	1	57.12702555	57.12702555	21.65	<.0001
Temperature	1	95.63806239	95.63806239	36.25	<.0001
Day*Moisture	1	4.74425117	4.74425117	1.80	0.1814
Day*Temperature	1	1.52372996	1.52372996	0.58	0.4481
Moisture*Temperature	1	26.62311568	26.62311568	10.09	0.0017
Day*Moistur*Temperat	1	1.55320811	1.55320811	0.59	0.4438

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	22.08227729	2.01102670	10.98	<.0001
Day	-0.03862667	0.02017832	-1.91	0.0570
Moisture	-30.27450141	6.50620885	-4.65	<.0001
Temperature	-0.02915190	0.00484198	-6.02	<.0001
Day*Moisture	0.08754011	0.06528224	1.34	0.1814
Day*Temperature	0.00003692	0.00004858	0.76	0.4481
Moisture*Temperature	0.04976123	0.01566511	3.18	0.0017
Day*Moistur*Temperat	-0.00012060	0.00015718	-0.77	0.4438

Model 5:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	877.091096	219.272774	82.09	<.0001
Error	211	563.580138	2.670996		
Corrected Total	215	1440.671234			

R-Square 0.608807
Coeff Var 25.52884
Root MSE 1.634318
P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	107.0590408	107.0590408	40.08	<.0001
Moisture	1	104.4456910	104.4456910	39.10	<.0001
Temperature	1	241.6569864	241.6569864	90.47	<.0001
Moisture*Temperature	1	53.7227858	53.7227858	20.11	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	19.93415203	1.15177493	17.31	<.0001
Day	-0.01253608	0.00198010	-6.33	<.0001
Moisture	-23.06703217	3.68878268	-6.25	<.0001
Temperature	-0.02611208	0.00274523	-9.51	<.0001
Moisture*Temperature	0.03983191	0.00888154	4.48	<.0001

Model 6:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	945.315822	315.105274	134.86	<.0001

Error	212	495.355412	2.336582
Corrected Total	215	1440.671234	

R-Square	Coeff Var	Root MSE	P04_P Mean
0.656163	23.87729	1.528588	6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day	1	142.0247409	142.0247409	60.78	<.0001
Moisture*Moisture	1	138.8002245	138.8002245	59.40	<.0001
Temperatu*Temperatur	1	664.4908564	664.4908564	284.39	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	11.68408692	0.28861199	40.48	<.0001
Day*Day	-0.00007279	0.00000934	-7.80	<.0001
Moisture*Moisture	-12.53415352	1.62626176	-7.71	<.0001
Temperatu*Temperatur	-0.00001949	0.00000116	-16.86	<.0001

Model 7:

The GLM Procedure

Number of Observations Read	216
Number of Observations Used	216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	1070.312331	178.385388	100.67	<.0001
Error	209	370.358903	1.772052		
Corrected Total	215	1440.671234			

R-Square	Coeff Var	Root MSE	P04_P Mean
0.742926	20.79375	1.331184	6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day	1	85.4132351	85.4132351	48.20	<.0001
Moisture*Moisture	1	170.5524952	170.5524952	96.25	<.0001
Temperatu*Temperatur	1	344.8446432	344.8446432	194.60	<.0001
Day*Moisture	1	10.6065295	10.6065295	5.99	0.0153
Day*Temperature	1	9.6659175	9.6659175	5.45	0.0205
Moisture*Temperature	1	86.1242099	86.1242099	48.60	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	12.45439184	0.26756274	46.55	<.0001
Day*Day	-0.00016818	0.00002422	-6.94	<.0001
Moisture*Moisture	-47.48169427	4.83988921	-9.81	<.0001
Temperatu*Temperatur	-0.00003781	0.00000271	-13.95	<.0001
Day*Moisture	0.03120982	0.01275683	2.45	0.0153
Day*Temperature	0.00002647	0.00001133	2.34	0.0205
Moisture*Temperature	0.04394971	0.00630422	6.97	<.0001

Model 8:

The GLM Procedure

Number of Observations Read	216
Number of Observations Used	216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	1073.297359	153.328194	86.81	<.0001
Error	208	367.373875	1.766221		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P04_P Mean
0.744998 20.75951 1.328992 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day	1	75.4488083	75.4488083	42.72	<.0001
Moisture*Moisture	1	157.0445674	157.0445674	88.92	<.0001
Temperatu*Temperatur	1	331.4466333	331.4466333	187.66	<.0001
Day*Moisture	1	10.0224914	10.0224914	5.67	0.0181
Day*Temperature	1	11.4659949	11.4659949	6.49	0.0116
Moisture*Temperature	1	73.4397442	73.4397442	41.58	<.0001
Day*Moistur*Temperat	1	2.9850282	2.9850282	1.69	0.1950

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	12.12467517	0.36834631	32.92	<.0001
Day*Day	-0.00018867	0.00002887	-6.54	<.0001
Moisture*Moisture	-50.47681190	5.35307004	-9.43	<.0001
Temperatu*Temperatur	-0.00003894	0.00000284	-13.70	<.0001
Day*Moisture	0.05851896	0.02456582	2.38	0.0181
Day*Temperature	0.00004217	0.00001655	2.55	0.0116
Moisture*Temperature	0.04975136	0.00771546	6.45	<.0001
Day*Moistur*Temperat	-0.00008630	0.00006639	-1.30	0.1950

Model 9:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	1018.225111	339.408370	170.33	<.0001
Error	212	422.446123	1.992670		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P04_P Mean
0.706771 22.05019 1.411620 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day*Day	1	156.1173849	156.1173849	78.35	<.0001
Moistu*Moistu*Moistu	1	135.4036843	135.4036843	67.95	<.0001
Temper*Temper*Temper	1	726.7040422	726.7040422	364.69	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	10.43604988	0.20863393	50.02	<.0001
Day*Day*Day	-0.00000041	0.00000005	-8.85	<.0001
Moistu*Moistu*Moistu	-26.43362465	3.20670650	-8.24	<.0001
Temper*Temper*Temper	-0.00000003	0.00000000	-19.10	<.0001

Model 10:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	1094.609720	182.434953	110.18	<.0001
Error	209	346.061514	1.655797		
Corrected Total	215	1440.671234			

R-Square 0.759791 Coeff Var 20.10009 Root MSE 1.286778 P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day*Day	1	79.8725036	79.8725036	48.24	<.0001
Moistu*Moistu*Moistu	1	126.2504032	126.2504032	76.25	<.0001
Temper*Temper*Temper	1	355.4645854	355.4645854	214.68	<.0001
Day*Moisture	1	0.4243149	0.4243149	0.26	0.6132
Day*Temperature	1	6.8894035	6.8894035	4.16	0.0426
Moisture*Temperature	1	56.2336509	56.2336509	33.96	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	9.67979570	0.22142435	43.72	<.0001
Day*Day*Day	-0.00000065	0.00000009	-6.95	<.0001
Moistu*Moistu*Moistu	-69.21044644	7.92608585	-8.73	<.0001
Temper*Temper*Temper	-0.00000005	0.00000000	-14.65	<.0001
Day*Moisture	0.00579373	0.01144506	0.51	0.6132
Day*Temperature	0.00001930	0.00000946	2.04	0.0426
Moisture*Temperature	0.02837741	0.00486943	5.83	<.0001

Model 11:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	1094.185405	218.837081	132.63	<.0001
Error	210	346.485829	1.649933		
Corrected Total	215	1440.671234			

R-Square 0.759497 Coeff Var 20.06447 Root MSE 1.284497 P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day*Day	1	84.3509834	84.3509834	51.12	<.0001
Moistu*Moistu*Moistu	1	134.0385060	134.0385060	81.24	<.0001
Temper*Temper*Temper	1	417.0538749	417.0538749	252.77	<.0001
Day*Temperature	1	13.1976723	13.1976723	8.00	0.0051
Moisture*Temperature	1	58.8949651	58.8949651	35.70	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
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Intercept	9.67340578	0.22067246	43.84	<.0001
Day*Day*Day	-0.00000063	0.00000009	-7.15	<.0001
Moistu*Moistu*Moistu	-68.00201588	7.54466722	-9.01	<.0001
Temper*Temper*Temper	-0.00000005	0.00000000	-15.90	<.0001
Day*Temperature	0.00002201	0.00000778	2.83	0.0051
Moisture*Temperature	0.02873462	0.00480949	5.97	<.0001

Model 12:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	1097.596108	156.799444	95.06	<.0001
Error	208	343.075126	1.649400		
Corrected Total	215	1440.671234			

R-Square 0.761864
Coeff Var 20.06123
Root MSE 1.284290
P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day*Day	1	59.4819993	59.4819993	36.06	<.0001
Moistu*Moistu*Moistu	1	104.7684755	104.7684755	63.52	<.0001
Temper*Temper*Temper	1	342.0956488	342.0956488	207.41	<.0001
Day*Temperature	1	0.6711644	0.6711644	0.41	0.5242
Moisture*Temperature	1	29.6361113	29.6361113	17.97	<.0001
Day*Moisture	1	1.0532899	1.0532899	0.64	0.4251
Day*Moistur*Temperat	1	2.9863880	2.9863880	1.81	0.1799

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	10.08294676	0.37229831	27.08	<.0001
Day*Day*Day	-0.00000060	0.00000010	-6.01	<.0001
Moistu*Moistu*Moistu	-65.94604742	8.27439800	-7.97	<.0001
Temper*Temper*Temper	-0.00000005	0.00000000	-14.40	<.0001
Day*Temperature	0.00000805	0.00001261	0.64	0.5242
Moisture*Temperature	0.02429144	0.00573067	4.24	<.0001
Day*Moisture	-0.01568610	0.01962926	-0.80	0.4251
Day*Moistur*Temperat	0.00007592	0.00005642	1.35	0.1799

Model 13:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	1080.987733	270.246933	158.53	<.0001
Error	211	359.683501	1.704661		
Corrected Total	215	1440.671234			

R-Square 0.750336
Coeff Var 20.39452
Root MSE 1.305627
P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day*Day*Day	1	156.1173849	156.1173849	91.58	<.0001
Moistu*Moistu*Moistu	1	139.5177658	139.5177658	81.84	<.0001
Temper*Temper*Temper	1	414.2182889	414.2182889	242.99	<.0001
Moisture*Temperature	1	62.7626218	62.7626218	36.82	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	9.79398200	0.22007666	44.50	<.0001
Day*Day*Day	-0.00000041	0.00000004	-9.57	<.0001
Moistu*Moistu*Moistu	-69.25775473	7.65548451	-9.05	<.0001
Temper*Temper*Temper	-0.00000005	0.00000000	-15.59	<.0001
Moisture*Temperature	0.02960266	0.00487865	6.07	<.0001

Model 14:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	1165.443025	194.240504	147.50	<.0001
Error	209	275.228210	1.316881		
Corrected Total	215	1440.671234			

R-Square 0.808958
Coeff Var 17.92536
Root MSE 1.147555
P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	20.8431431	20.8431431	15.83	<.0001
Moisture	1	0.2778930	0.2778930	0.21	0.6464
Temperature	1	199.0061665	199.0061665	151.12	<.0001
Day*Day	1	55.8088432	55.8088432	42.38	<.0001
Moisture*Moisture	1	1.2033288	1.2033288	0.91	0.3402
Temperatu*Temperatur	1	285.0625427	285.0625427	216.47	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-3.214021277	1.35954371	-2.36	0.0190
Day	0.021556683	0.00541843	3.98	<.0001
Moisture	-2.330572324	5.07337626	-0.46	0.6464
Temperature	0.077266972	0.00628541	12.29	<.0001
Day*Day	-0.000177825	0.00002732	-6.51	<.0001
Moisture*Moisture	-8.491978829	8.88362226	-0.96	0.3402
Temperatu*Temperatur	-0.000114880	0.00000781	-14.71	<.0001

Model 15:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	1026.364907	256.591227	130.68	<.0001

Error	211	414.306327	1.963537
Corrected Total	215	1440.671234	

R-Square	Coeff Var	Root MSE	P04_P Mean
0.712421	21.88840	1.401263	6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	20.8431431	20.8431431	10.62	0.0013
Temperature	1	199.0061665	199.0061665	101.35	<.0001
Day*Day	1	55.8088432	55.8088432	28.42	<.0001
Temperatu*Temperatur	1	285.0625427	285.0625427	145.18	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-4.696756889	1.46997719	-3.20	0.0016
Day	0.021556683	0.00661637	3.26	0.0013
Temperature	0.077266972	0.00767503	10.07	<.0001
Day*Day	-0.000177825	0.00003335	-5.33	<.0001
Temperatu*Temperatur	-0.000114880	0.00000953	-12.05	<.0001

Model 16:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	9	1232.401782	136.933531	135.44	<.0001
Error	206	208.269452	1.011017		
Corrected Total	215	1440.671234			

R-Square	Coeff Var	Root MSE	P04_P Mean
0.855436	15.70629	1.005493	6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	1.7259669	1.7259669	1.71	0.1928
Moisture	1	18.4410492	18.4410492	18.24	<.0001
Temperature	1	129.4842234	129.4842234	128.07	<.0001
Day*Day	1	55.8088432	55.8088432	55.20	<.0001
Moisture*Moisture	1	1.2033288	1.2033288	1.19	0.2766
Temperatu*Temperatur	1	285.0625427	285.0625427	281.96	<.0001
Day*Moisture	1	13.1956077	13.1956077	13.05	0.0004
Day*Temperature	1	0.0403640	0.0403640	0.04	0.8418
Moisture*Temperature	1	53.7227858	53.7227858	53.14	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	2.37999984	1.41806469	1.68	0.0948
Day	0.00936359	0.00716647	1.31	0.1928
Moisture	-21.49908144	5.03391953	-4.27	<.0001
Temperature	0.06561241	0.00579771	11.32	<.0001
Day*Day	-0.00017782	0.00002393	-7.43	<.0001
Moisture*Moisture	-8.49197883	7.78387640	-1.09	0.2766
Temperatu*Temperatur	-0.00011488	0.00000684	-16.79	<.0001
Day*Moisture	0.03930053	0.01087835	3.61	0.0004

Day*Temperature	0.00000218	0.00001090	0.20	0.8418
Moisture*Temperature	0.03983191	0.00546426	7.29	<.0001

Model 17:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	1227.885799	204.647633	201.01	<.0001
Error	209	212.785435	1.018112		
Corrected Total	215	1440.671234			

R-Square 0.852301
 Coeff Var 15.76131
 Root MSE 1.009015
 P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Moisture	1	130.9220413	130.9220413	128.59	<.0001
Temperature	1	133.3864201	133.3864201	131.01	<.0001
Day*Day	1	103.4381905	103.4381905	101.60	<.0001
Temperatu*Temperatur	1	285.0625427	285.0625427	279.99	<.0001
Moisture*Day	1	30.7664605	30.7664605	30.22	<.0001
Moisture*Temperature	1	53.7227858	53.7227858	52.77	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	3.37854726	1.24132498	2.72	0.0070
Moisture	-27.19046962	2.39777336	-11.34	<.0001
Temperature	0.06579166	0.00574795	11.45	<.0001
Day*Day	-0.00014309	0.00001420	-10.08	<.0001
Temperatu*Temperatur	-0.00011488	0.00000687	-16.73	<.0001
Moisture*Day	0.05008224	0.00911051	5.50	<.0001
Moisture*Temperature	0.03983191	0.00548340	7.26	<.0001

Model 18:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	10	1233.954990	123.395499	122.37	<.0001
Error	205	206.716244	1.008372		
Corrected Total	215	1440.671234			

R-Square 0.856514
 Coeff Var 15.68574
 Root MSE 1.004177
 P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	0.1173653	0.1173653	0.12	0.7333
Moisture	1	18.4200832	18.4200832	18.27	<.0001
Temperature	1	102.2390278	102.2390278	101.39	<.0001
Day*Day	1	55.8088432	55.8088432	55.35	<.0001
Moisture*Moisture	1	1.2033288	1.2033288	1.19	0.2759

Temperatu*Temperatur	1	285.0625427	285.0625427	282.70	<.0001
Day*Moisture	1	4.7442512	4.7442512	4.70	0.0312
Day*Temperature	1	1.5237300	1.5237300	1.51	0.2204
Moisture*Temperature	1	26.6231157	26.6231157	26.40	<.0001
Day*Moistur*Temperat	1	1.5532081	1.5532081	1.54	0.2160

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	3.52422749	1.68986423	2.09	0.0383
Day	-0.00453391	0.01328964	-0.34	0.7333
Moisture	-25.47080697	5.95946512	-4.27	<.0001
Temperature	0.06275184	0.00623201	10.07	<.0001
Day*Day	-0.00017782	0.00002390	-7.44	<.0001
Moisture*Moisture	-8.49197883	7.77368836	-1.09	0.2759
Temperatu*Temperatur	-0.00011488	0.00000683	-16.81	<.0001
Day*Moisture	0.08754011	0.04035837	2.17	0.0312
Day*Temperature	0.00003692	0.00003004	1.23	0.2204
Moisture*Temperature	0.04976123	0.00968438	5.14	<.0001
Day*Moistur*Temperat	-0.00012060	0.00009717	-1.24	0.2160

Model 19:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	8	1234.106902	154.263363	154.59	<.0001
Error	207	206.564332	0.997895		
Corrected Total	215	1440.671234			

R-Square 0.856619
Coeff Var 15.60404
Root MSE 0.998947
P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	0.75341303	0.75341303	0.76	0.3859
Moisture	0	0.00000000	.	.	.
Temperature	1	97.19754369	97.19754369	97.40	<.0001
Day*Day	1	0.13954545	0.13954545	0.14	0.7088
Moisture*Moisture	0	0.00000000	.	.	.
Temperatu*Temperatur	1	84.60988180	84.60988180	84.79	<.0001
Day*Day*Day	1	0.28931306	0.28931306	0.29	0.5908
Moistu*Moistu*Moistu	0	0.00000000	.	.	.
Temper*Temper*Temper	1	68.37456463	68.37456463	68.52	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-49.88253197 B	5.78155920	-8.63	<.0001
Day	0.01355201	0.01559659	0.87	0.3859
Moisture	-2.33057232 B	4.41637799	-0.53	0.5983
Temperature	0.46265629	0.04687846	9.87	<.0001
Day*Day	-0.00007320	0.00019575	-0.37	0.7088
Moisture*Moisture	-8.49197883 B	7.73320010	-1.10	0.2734
Temperatu*Temperatur	-0.00112134	0.00012178	-9.21	<.0001
Day*Day*Day	-0.00000036	0.00000067	-0.54	0.5908
Moistu*Moistu*Moistu	0.00000000 B	.	.	.

Temper*Temper*Temper 0.0000084 0.0000010 8.28 <.0001

The X'X matrix has been found to be singular, and a generalized inverse was used to solve the normal equations. Terms whose estimates are followed by the letter 'B' are not uniquely estimable.

Model 20:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	8	1234.106902	154.263363	154.59	<.0001
Error	207	206.564332	0.997895		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P04_P Mean
 0.856619 15.60404 0.998947 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	0.75341303	0.75341303	0.76	0.3859
Moisture	1	0.27789305	0.27789305	0.28	0.5983
Temperature	1	97.19754369	97.19754369	97.40	<.0001
Day*Day	1	0.13954545	0.13954545	0.14	0.7088
Moisture*Moisture	1	1.20332876	1.20332876	1.21	0.2734
Temperatu*Temperatur	1	84.60988180	84.60988180	84.79	<.0001
Day*Day*Day	1	0.28931306	0.28931306	0.29	0.5908
Temper*Temper*Temper	1	68.37456463	68.37456463	68.52	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-49.88253197	5.78155920	-8.63	<.0001
Day	0.01355201	0.01559659	0.87	0.3859
Moisture	-2.33057232	4.41637799	-0.53	0.5983
Temperature	0.46265629	0.04687846	9.87	<.0001
Day*Day	-0.00007320	0.00019575	-0.37	0.7088
Moisture*Moisture	-8.49197883	7.73320010	-1.10	0.2734
Temperatu*Temperatur	-0.00112134	0.00012178	-9.21	<.0001
Day*Day*Day	-0.00000036	0.00000067	-0.54	0.5908
Temper*Temper*Temper	0.00000084	0.00000010	8.28	<.0001

Model 21:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	931.871588	310.623863	129.43	<.0001
Error	212	508.799646	2.399998		
Corrected Total	215	1440.671234			

R-Square Coeff Var Root MSE P04_P Mean
 0.646832 24.19914 1.549193 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Temperature	1	97.19754369	97.19754369	40.50	<.0001
Temperatu*Temperatur	1	84.60988180	84.60988180	35.25	<.0001
Temper*Temper*Temper	1	68.37456463	68.37456463	28.49	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-51.48846470	8.91350881	-5.78	<.0001
Temperature	0.46265629	0.07270032	6.36	<.0001
Temperatu*Temperatur	-0.00112134	0.00018886	-5.94	<.0001
Temper*Temper*Temper	0.00000084	0.00000016	5.34	<.0001

Model 22:

The GLM Procedure
Number of Observations Read 216
Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	1301.065660	118.278696	172.84	<.0001
Error	204	139.605574	0.684341		
Corrected Total	215	1440.671234			

R-Square 0.903097 Coeff Var 12.92203 Root MSE 0.827249 P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	0.00678248	0.00678248	0.01	0.9208
Moisture	1	18.44104915	18.44104915	26.95	<.0001
Temperature	1	92.22631556	92.22631556	134.77	<.0001
Day*Day	1	0.13954545	0.13954545	0.20	0.6521
Moisture*Moisture	1	1.20332876	1.20332876	1.76	0.1863
Temperatu*Temperatur	1	84.60988180	84.60988180	123.64	<.0001
Day*Day*Day	1	0.28931306	0.28931306	0.42	0.5163
Temper*Temper*Temper	1	68.37456463	68.37456463	99.91	<.0001
Day*Moisture	1	13.19560773	13.19560773	19.28	<.0001
Day*Temperature	1	0.04036402	0.04036402	0.06	0.8084
Moisture*Temperature	1	53.72278578	53.72278578	78.50	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-44.28851086	4.82948654	-9.17	<.0001
Day	0.00135892	0.01365013	0.10	0.9208
Moisture	-21.49908144	4.14155457	-5.19	<.0001
Temperature	0.45100173	0.03884965	11.61	<.0001
Day*Day	-0.00007320	0.00016211	-0.45	0.6521
Moisture*Moisture	-8.49197883	6.40402547	-1.33	0.1863
Temperatu*Temperatur	-0.00112134	0.00010085	-11.12	<.0001
Day*Day*Day	-0.00000036	0.00000055	-0.65	0.5163
Temper*Temper*Temper	0.00000084	0.00000008	10.00	<.0001
Day*Moisture	0.03930053	0.00894994	4.39	<.0001
Day*Temperature	0.00000218	0.00000896	0.24	0.8084
Moisture*Temperature	0.03983191	0.00449561	8.86	<.0001

Model 23:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	1192.822173	198.803696	167.64	<.0001
Error	209	247.849061	1.185881		
Corrected Total	215	1440.671234			

R-Square 0.827963
 Coeff Var 17.01042
 Root MSE 1.088981
 P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Moisture	1	79.89154185	79.89154185	67.37	<.0001
Temperature	1	92.33296905	92.33296905	77.86	<.0001
Temperatu*Temperatur	1	84.60988180	84.60988180	71.35	<.0001
Temper*Temper*Temper	1	68.37456463	68.37456463	57.66	<.0001
Moisture*Day	1	69.35301091	69.35301091	58.48	<.0001
Moisture*Temperature	1	53.72278578	53.72278578	45.30	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-44.84300652	6.30550181	-7.11	<.0001
Moisture	-20.37940853	2.48291396	-8.21	<.0001
Temperature	0.45118098	0.05113201	8.82	<.0001
Temperatu*Temperatur	-0.00112134	0.00013275	-8.45	<.0001
Temper*Temper*Temper	0.00000084	0.00000011	7.59	<.0001
Moisture*Day	-0.03264320	0.00426855	-7.65	<.0001
Moisture*Temperature	0.03983191	0.00591797	6.73	<.0001

Model 24:

The GLM Procedure
 Number of Observations Read 216
 Number of Observations Used 216

Dependent Variable: P04_P P04-P

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	12	1302.618868	108.551572	159.62	<.0001
Error	203	138.052366	0.680061		
Corrected Total	215	1440.671234			

R-Square 0.904175
 Coeff Var 12.88156
 Root MSE 0.824658
 P04_P Mean 6.401850

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Day	1	0.39638915	0.39638915	0.58	0.4461
Moisture	1	18.42008325	18.42008325	27.09	<.0001
Temperature	1	90.84309497	90.84309497	133.58	<.0001
Day*Day	1	0.13954545	0.13954545	0.21	0.6510
Moisture*Moisture	1	1.20332876	1.20332876	1.77	0.1849
Temperatu*Temperatur	1	84.60988180	84.60988180	124.42	<.0001
Day*Day*Day	1	0.28931306	0.28931306	0.43	0.5150
Temper*Temper*Temper	1	68.37456463	68.37456463	100.54	<.0001

Day*Moisture	1	4.74425117	4.74425117	6.98	0.0089
Day*Temperature	1	1.52372996	1.52372996	2.24	0.1360
Moisture*Temperature	1	26.62311568	26.62311568	39.15	<.0001
Day*Moistur*Temperat	1	1.55320811	1.55320811	2.28	0.1323

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-43.14428321	4.87353178	-8.85	<.0001
Day	-0.01253858	0.01642333	-0.76	0.4461
Moisture	-25.47080697	4.89407723	-5.20	<.0001
Temperature	0.44814116	0.03877419	11.56	<.0001
Day*Day	-0.00007320	0.00016160	-0.45	0.6510
Moisture*Moisture	-8.49197883	6.38396743	-1.33	0.1849
Temperatu*Temperatur	-0.00112134	0.00010053	-11.15	<.0001
Day*Day*Day	-0.00000036	0.00000055	-0.65	0.5150
Temper*Temper*Temper	0.00000084	0.00000008	10.03	<.0001
Day*Moisture	0.08754011	0.03314341	2.64	0.0089
Day*Temperature	0.00003692	0.00002467	1.50	0.1360
Moisture*Temperature	0.04976123	0.00795308	6.26	<.0001
Day*Moistur*Temperat	-0.00012060	0.00007980	-1.51	0.1323

APPENDIX P
CHECKING OF ASSUMPTIONS FOR THE SELECTED PREDICTIVE MODEL

Independence of Errors: Durbin-Watson Test

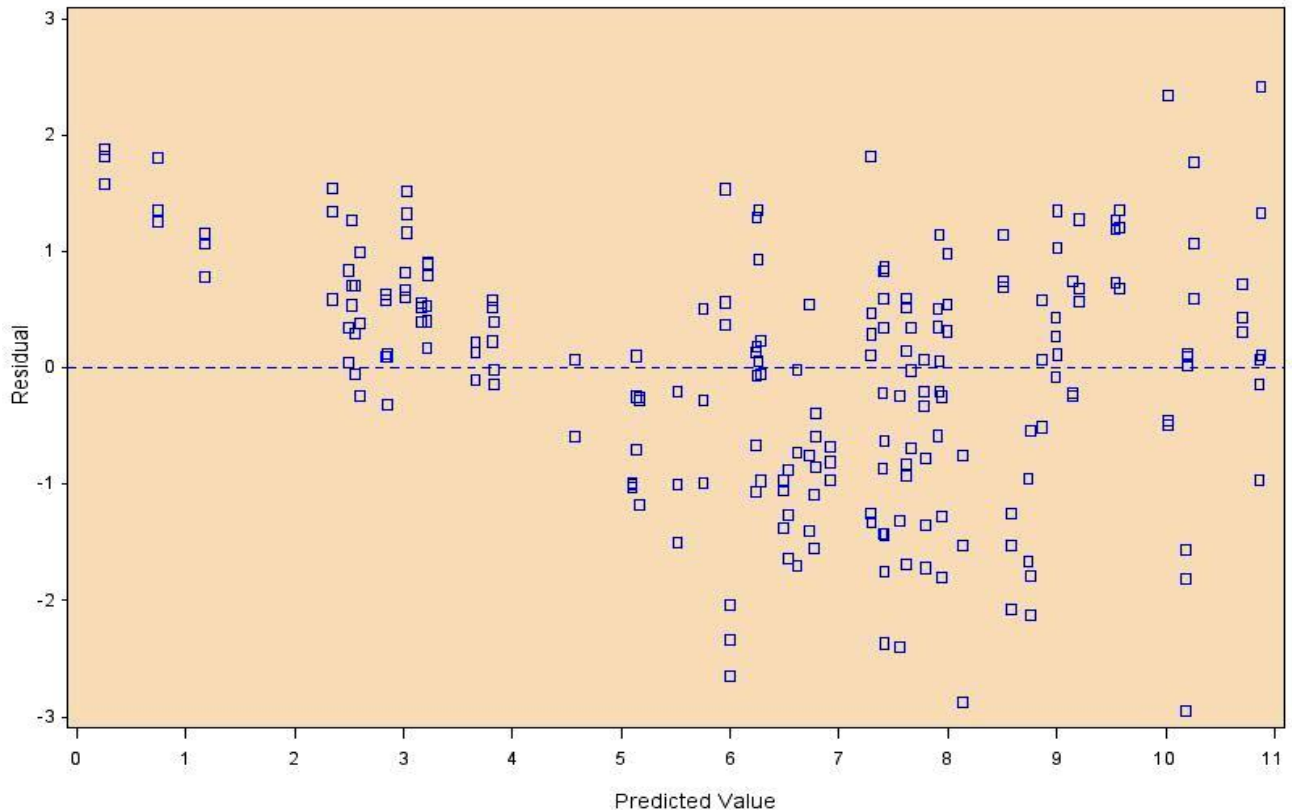
The REG Procedure
 Dependent Variable: P04_P P04-P
 Collinearity Diagnostics

-----Proportion of Variation-----							
Number	Intercept	Temperature	Moisture	Moist_Temp	Moist_Day	Day_Day	Temp_Temp
1	0.00008524	0.00002564	0.00022310	0.00024555	0.00145	0.00195	0.00008093
2	0.00010072	0.00007496	0.00016935	0.00053986	0.02072	0.08372	0.00041671
3	0.00012887	0.00038304	0.01015	0.00401	0.03007	0.06736	0.00317
4	0.01372	0.00006541	0.00245	0.01229	0.02478	0.00253	0.00565
5	0.00236	0.00056044	0.01966	0.04342	0.87712	0.80488	0.00185
6	0.06632	0.00155	0.89584	0.85790	0.04576	0.03948	0.10901
7	0.91730	0.99734	0.07150	0.08159	0.00009101	0.00007800	0.87983

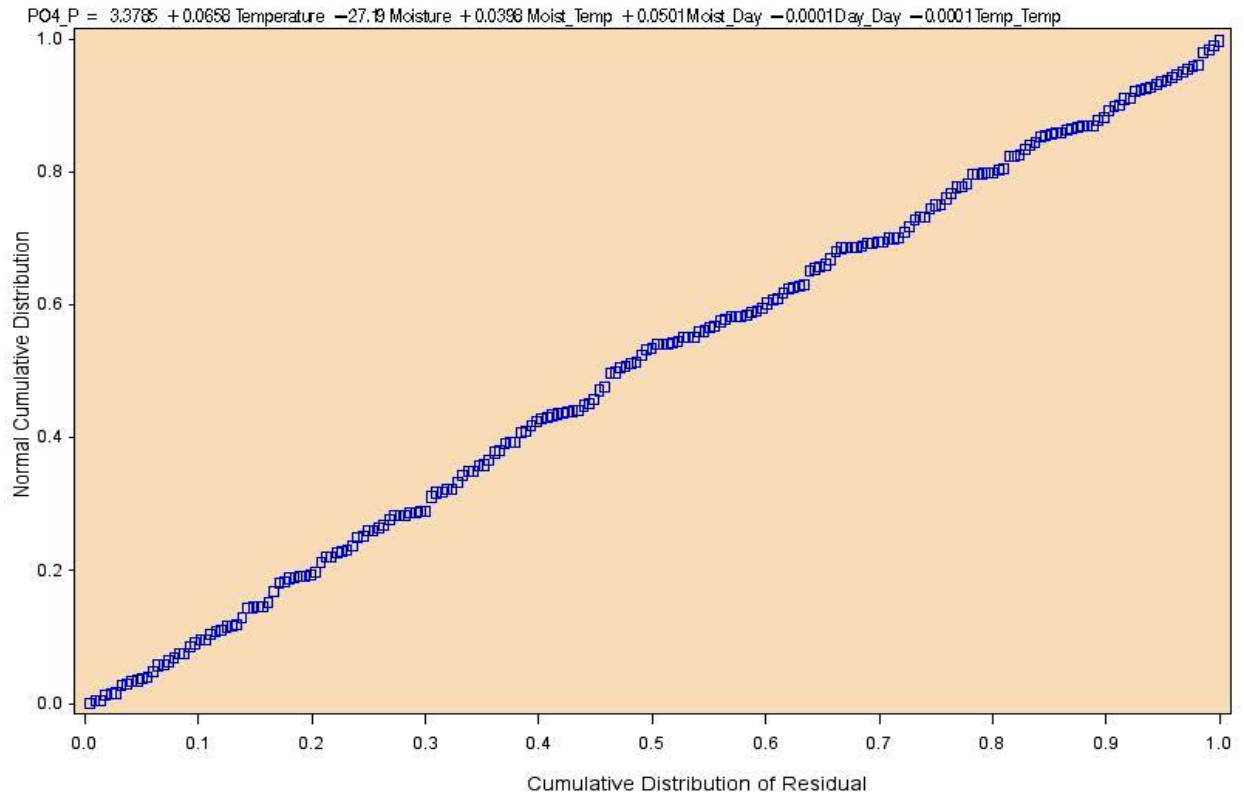
The REG Procedure
 Dependent Variable: P04_P P04-P

Durbin-Watson D 1.410
 Number of Observations 216
 1st Order Autocorrelation 0.269

Plot of Predicted Values versus Residuals



Normal Probability Plot of Residuals



APPENDIX Q

RESULTS OF ESTIMATION OF SOIL MOISTURE CONTENT FOR TREC'S PINE ROCKLAND SOILS AFTER THE FIRE

Where:

- ET: Evapotranspiration; FC: field capacity; and SWC: soil water content
- 0.421 is the volumetric water content (v/v) at field capacity of the Pine Rockland soil estimated from the soil moisture curve at suction of 1/3 bar (33.3 cbar or 33.3 kPa).
- 2.1049 is the water amount (cm) of field capacity at 5cm topsoil (0.421 x 5 cm = 2.1049 cm)

Days after fire	Date	Rainfall (cm)	ET (cm)	FC (cm)	SWC (cm)	FC at 5cm topsoil (%)	Adjusted FC at 5 cm topsoil (%)	Volumetric water content (v/v)
		a	b	c = 2.1049 if a > 2.1049 c = a if a < 2.1049	d = c-b	e = 100*d/ 5cm	f(1) = e if c = 2.1 f(1) = e + 100*(c-b)/5cm if c < 2.1 f(2) = f1 + 100*(c1-b1)/5cm f(3) = f2 + 100*(c2-b2)/5cm	g = f*0.421/100
	4/20/10	0.4064	0.30	0.4064	0.1016	2.03	0	
	4/21/10	0.1524	0.33	0.1524	0	0	0	
	4/22/10	0	0.39	0	0	0	0	
	4/23/10	0	0.28	0	0	0	0	
	4/24/10	0	0.39	0	0	0	0	
	4/25/10	0	0.39	0	0	0	0	
	4/26/10	4.4958	0.18	2.1049	1.9220	38.44	38.44	
	4/27/10	0	0.39	0	0	0	30.72	
	4/28/10	0	0.37	0	0	0	23.40	
	4/29/10	0	0.18	0	0	0	19.75	
	4/30/10	0.1524	0.30	0.1524	0	0	16.70	
	5/1/10	0	0.30	0	0	0	10.60	
	5/2/10	0	0.35	0	0	0	3.69	
	5/3/10	0	0.37	0	0	0	0	
	5/4/10	0	0.41	0	0	0	0	
Burned	5/5/10	0.0762	0.41	0.0762	0	0	0	0
	5/6/10	0.0254	0.28	0.0254	0	0	0	0
	5/7/10	0	0.37	0	0	0	0	0
	5/8/10	0	0.33	0	0	0	0	0
	5/9/10	0	0.45	0	0	0	0	0
	5/10/10	0.02	0.43	0.02	0	0	0	0
	5/11/10	0.3	0.30	0.3	0	0	0	0
7days	5/12/10	0	0.41	0	0	0	0	0
	5/13/10	0	0.41	0	0	0	0	0
	5/14/10	0	0.35	0	0	0	0	0

	5/15/10	0	0.37	0	0	0	0	0
	5/16/10	0	0.30	0	0	0	0	0
	5/17/10	0.16	0.30	0.16	0	0	0	0
	5/18/10	5.26	0.28	2.1049	1.8204	36.41	36.41	0.153272
14days	5/19/10	0.02	0.20	0.02	0	0	32.74	0.137847
	5/20/10	0	0.41	0	0	0	24.62	0.103630
	5/21/10	0	0.43	0	0	0	16.08	0.067702
	5/22/10	0	0.43	0	0	0	7.55	0.031774
	5/23/10	0	0.45	0	0	0	0	0
	5/24/10	0	0.39	0	0	0	0	0
	5/25/10	6.64	0.33	2.1049	1.7798	35.60	35.60	0.149850
21days	5/26/10	0.56	0.35	0.56	0.2146	4.29	39.89	0.167915
	5/27/10	0	0.41	0	0	0	31.76	0.133698
	5/28/10	1.04	0.43	1.04	0.6133	12.27	44.02	0.185334
	5/29/10	0.2	0.37	0.2	0	0	40.71	0.171378
	5/30/10	0	0.37	0	0	0	33.39	0.140582
	5/31/10	0	0.39	0	0	0	25.67	0.108076
	6/1/10	0.1	0.33	0.1	0	0	21.17	0.089121
30days	6/2/10	0.56	0.28	0.56	0.2755	5.51	26.68	0.112319
	6/3/10	0.02	0.43	0.02	0	0	18.55	0.078075
	6/4/10	0	0.45	0	0	0	9.61	0.040436
	6/5/10	2.22	0.43	2.1049	1.6782	33.56	43.17	0.181732
	6/6/10	0.28	0.33	0.28	0	0	42.27	0.177933
	6/7/10	0.06	0.39	0.06	0	0	35.74	0.150478
	6/8/10	7.72	0.39	2.1049	1.7188	34.38	34.38	0.144718
	6/9/10	0.02	0.43	0.02	0	0	26.24	0.110474
	6/10/10	0.18	0.41	0.18	0	0	21.71	0.091412
	6/11/10	1.24	0.33	1.24	0.9149	18.30	40.01	0.168441
	6/12/10	0	0.30	0	0	0	33.92	0.142778
	6/13/10	0.06	0.39	0.06	0	0	27.39	0.115323
	6/14/10	3.04	0.28	2.1049	1.8204	36.41	36.41	0.153272
	6/15/10	0.14	0.39	0.14	0	0	31.49	0.132553
	6/16/10	0	0.45	0	0	0	22.55	0.094914
	6/17/10	3.62	0.33	2.1049	1.7798	35.60	35.60	0.149850
	6/18/10	5.12	0.22	2.1049	1.8814	37.63	37.63	0.158405
	6/19/10	0	0.45	0	0	0	28.69	0.120766
	6/20/10	0	0.47	0	0	0	19.34	0.081416
	6/21/10	0	0.00	0	0	0	19.34	0.081416
	6/22/10	0.18	0.47	0.18	0	0	13.59	0.057221
	6/23/10	0.16	0.47	0.16	0	0	7.45	0.031343
	6/24/10	0	0.47	0	0	0	0	0

	6/25/10	0	0.00	0	0	0	0	0
	6/26/10	0.46	0.33	0.46	0.1349	2.70	2.70	0.011356
	6/27/10	0.04	0.41	0.04	0	0	0	0
	6/28/10	0	0.41	0	0	0	0	0
	6/29/10	0	0.41	0	0	0	0	0
	6/30/10	0.02	0.35	0.02	0	0	0	0
	7/1/10	0	0.43	0	0	0	0	0
60days	7/2/10	0.14	0.26	0.14	0	0	0	0
	7/3/10	1.12	0.26	1.12	0.8558	17.12	17.12	0.072058
	7/4/10	0.72	0.22	0.72	0.4965	9.93	27.05	0.113860
	7/5/10	0.8	0.22	0.8	0.5765	11.53	38.58	0.162397
	7/6/10	0	0.39	0	0	0	30.85	0.129891
	7/7/10	0.2	0.39	0.2	0	0	27.13	0.114224
	7/8/10	0.28	0.37	0.28	0	0	25.42	0.107003
	7/9/10	0	0.39	0	0	0	17.70	0.074497
	7/10/10	0.68	0.33	0.68	0.3549	7.10	24.79	0.104376
	7/11/10	0	0.47	0	0	0	15.45	0.065026
	7/12/10	0	0.43	0	0	0	6.91	0.029098
	7/13/10	3.16	0.33	2.1049	1.7798	35.60	35.60	0.149850
	7/14/10	3.12	0.24	2.1049	1.8611	37.22	37.22	0.156694
	7/15/10	1.52	0.39	1.52	1.1339	22.68	37.22	0.156694
	7/16/10	0.12	0.28	0.12	0	0	33.93	0.142845
	7/17/10	0	0.35	0	0	0	27.02	0.113761
	7/18/10	3.78	0.35	2.1049	1.7595	35.19	35.19	0.148139
	7/19/10	0	0.37	0	0	0	27.87	0.117344
	7/20/10	0.96	0.39	0.96	0.5739	11.48	39.35	0.165666
	7/21/10	0	0.43	0	0	0	30.82	0.129738
	7/22/10	0	0.45	0	0	0	21.88	0.092099
	7/23/10	10.36	0.24	2.1049	1.8611	37.22	37.22	0.156694
	7/24/10	0.14	0.45	0.14	0	0	31.08	0.130842
	7/25/10	0.12	0.39	0.12	0	0	25.76	0.108439
	7/26/10	0	0.39	0	0	0	18.04	0.075933
	7/27/10	0	0.47	0	0	0	8.69	0.036583
	7/28/10	0	0.43	0	0	0	0.16	0.000655
	7/29/10	0	0.39	0	0	0	0	0
	7/30/10	2.68	0.35	2.1049	1.7595	35.19	35.19	0.148139
	7/31/10	0	0.41	0	0	0	27.06	0.113922
	8/1/10	4.54	0.37	2.1049	1.7391	34.78	34.78	0.146429
90days	8/2/10	3.04	0.24	2.1049	1.8611	37.22	37.22	0.156694
	8/3/10	0.16	0.37	0.16	0	0	33.11	0.139370

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BIOGRAPHICAL SKETCH

Chung Tan Nguyen was born in the middle part of Vietnam and grew up in the countryside where is exposed to various agricultural activities. He graduated from the University of Agriculture and Forestry (UAF), located in HoChiMinh City (formerly Sai Gon city), with Bachelor of Science in Forestry in 2000. He worked for the Center for Information and Technology of the UAF from 2000 to 2001. He has been a lecturer at the University of Agriculture and Forestry since 2001. Additionally, he served as the assistant of vice President and the secretary of the Wetland Management project in the Mekong River Basin from 2001 to 2004. Chung Nguyen was awarded a full scholarship from the Vietnamese government for studying the Master program in the United States in 2004, and completed the Master degree in Environmental Sciences from the University of Colorado at Denver in 2006. After obtaining the M.Sc. degree, he was appointed as the assistant President of the University of Agriculture and Forestry from 2006 to 2007. He was granted a four-year match assistantship from the School of Natural Resources and Environment, and a two-year fellowship from the Vietnam Education Foundation for studying the Ph.D. program in Interdisciplinary Ecology at the University of Florida in 2007. Chung will be an assistant professor at the University of Agriculture and Forestry after he gets the Ph.D. degree.