2001

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SPATIAL VARIABILITY AND ISOTOPIC STUDIES OF THE PRAIRIE-FOREST TRANSITION SOIL IN LOUISIANA

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College
In partial fulfillment of the requirements for the degree of Doctor of Philosophy

In
The Department of Agronomy

by
Asfaw Bekele
B.S., Addis Ababa University, 1988
M.S., Louisiana State University, 1997
December 2001
In memory of Gerba Beyen: for her unreserved love.

To Aynalem Humna: for his mentorship and for always being there.
ACKNOWLEDGEMENTS

This dissertation could not have been written without the advice, guidance, and wisdom of Dr. Wayne H. Hudnall. I am very much grateful to him and his family for their support during my study program. I am indebted to Dr. Ray E. Ferrell, Jr., Dr. Allan E. Tiarks, Dr. Robert Downer, Mr. Jerry Daigle, and Dr. Quang V. Cao for serving on my graduate committee. I wish to thank the staff of the Department of Agronomy, LSU, for their technical assistance during my study period. I thank the Wondo Genet College of Forestry for offering me the opportunity of pursuing higher education. I would like to acknowledge the U.S. Forest Service for financially supporting this research.

I thank Phil Hyatt, and Lynn Jackson for their help in various field activities. I am thankful to Dr. Michael H. MacRoberts and Barbara R. MacRoberts for collecting and identifying plant specimens. I thank Lois West, Mark Forsyth, Steven Ward, Tracie Territo, and Kirk Hutchinson for their help in the field and laboratory part of my research. I thank Dr. Charles Lindau for isotope analysis, Calista Daigle for ICP-AES analysis, and Wanda LeBlanc for mineralogical investigation. I wish to thank Jackie Prudente, Huang Jang-Hung, and Hongxia Zhu for their friendship.

Much appreciation goes to Lulseged Ayalew, Amare Geremew, Araya Kebede, Haftay Hailu, Samuel Kidane and Cecil Dharamasri for their friendship and support. My thanks are extended to Fitsum Assefa and the rest of the Assefa family for their encouragement throughout my study program. I owe a special gratitude to my parents, sisters, and brothers for their close support.
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ABSTRACT

The calcareous prairies of Louisiana are among the most endangered ecosystems in North America. The major threat to this ecosystem is the invasion by woody and herbaceous plants, primarily eastern red cedar (*Juniperus virginiana*). The restoration and management of these rare plant communities require a thorough understanding of the soils supporting them. Geostatistical, fractal, and stable isotopic procedures were integrated to study the soil and vegetation spatial variability.

The prairie soil was alkaline, the forest soil was acidic, and the transition soil was neutral. The spherical model described the spatial variability of virtually all the soil properties considered with a spatial dependence expressed over a range of 20 to 30 m. The estimated fractal dimension for each soil property indicated short-range variation domination. Calcite was the major constituent of the soil carbonate. The $\delta^{13}C$ values of the carbonate showed that it is of secondary origin. The $\delta^{13}C$ values of soil organic matter (SOM) and pedogenic carbonate covary, indicating an isotopic equilibrium between SOM and the pedogenic carbonate. The carbon isotope data from SOM within the 0-10 cm depth suggested that the prairies are composed of a mixture of approximately equal proportions of C3 and C4 plants. The relative proportion of C3 and C4 plants varied with season. The C4 plants dominated in the summer and the C3 plants in the spring. Comparison of $\delta^{13}C$ values from the forest, transition, and prairie with depth suggested that the invasion of C3 trees and shrubs observed within the transition might not be a
recent phenomenon. SOM δ¹³C below 40-50 cm indicated that in the past a C4 community might have dominated the site.

Plant leaves from prairie, transition, and forest showed similar δ¹⁵N signals. Compared with the leaves, the soil was enriched with ¹⁵N. The order of enrichment of the 0-10 cm relative to corresponding leaves was forest soil > transition soil > prairie soil. The δ¹⁵N and Ca were significantly affected by vegetation type. The differences in the soil δ¹⁵N is a clear indication that the vegetation within the transition zone (invading woody and herbaceous plants) is altering the N cycling towards more "forest-like" conditions.
CHAPTER 1: INTRODUCTION

There is increasing concern about the loss of natural habitats and decreasing biodiversity. The native prairie ecosystem of North America is a primary example. Prior to European settlement, the prairie extended from Texas to Canada and from the Rockies to the Atlantic Ocean covering approximately 50% of the land surface area (400 million ha) (Joem and Keeler, 1995). Recent estimates show that less than 0.01% of the original native prairies remain with some of the species rare or endangered (Leach and Givnish, 1996; MacRoberts and MacRoberts, 1997a; 1997b; Noss, 1997). Habitat change is partly a natural process, but human activities have accelerated the process to the extent that natural rates of regeneration are insufficient to offset habitat loss. Anthropogenic activities such as agriculture and urban development, and fire suppression have accelerated the fragmentation and shrinking of land under prairies (Leach and Givnish, 1996). Substantial research and management efforts have been directed to understanding and restoring the ecology of the well-known Midwestern prairies. Because of their small size, Louisiana prairies have not been included in regional mapping, their ecology is poorly understood and were not included in conservation and management plans. Nevertheless, Louisiana prairies are as diverse in species composition and ecologically important as the Midwestern prairies (Smith et al., 1989; MacRoberts and MacRoberts, 1997b).

Louisiana prairies have been grouped into two types, coastal prairies and calcareous prairies (MacRoberts and MacRoberts, 1997b). The first group is located in southwestern Louisiana while the second are scattered within central
and northern Louisiana. Floristically, both types are classified as tallgrass prairies (MacRoberts and MacRoberts, 1997b). The distribution of Louisiana prairies is given in Figure 1.1. Less than 1% of the original Louisiana prairies remain now (MacRoberts and MacRoberts, 1997b). This study concentrated on the calcareous prairies of northern Louisiana since they are among the best-preserved prairie remnants in the state (MacRoberts and MacRoberts, 1997b).

The calcareous prairies exist as mosaics within short leaf pine-oak-hickory forest (Smith et al., 1989). These types of ecological configuration represent an ecotone (Gosz, 1993). Ecotones are formally defined as the “zone of transition between adjacent ecological systems, having a set of characteristics uniquely defined by space and time scale, and by the strength of interactions between adjacent ecological systems” (Castri and Hansen, 1992). Ecotones are important and deserve critical investigation and understanding because they are frequently high in biological diversity, and they serve as semipermeable barriers across which energy and nutrients flow, and consequently are sensitive to environmental change (Delcourt and Delcourt, 1992; Gehlhausen, 2000). According to Gosz (1993), ecotones are logical areas of study for research programs that utilize variability as a sensitive indicator of environmental change.

1.1 Statement of the Problem, Justification and Objectives

The current major threat to the calcareous prairies of Louisiana is the invasion of woody and herbaceous plants, primarily eastern red cedar (Juniperus virginiana). Implicated causes for invasion include overgrazing, climate change,
Figure 1.1. Distribution of Louisiana prairies (from MacRoberts and MacRoberts, 1997b).
and fire suppression. Previous studies elsewhere (Miles, 1987; Kourtev et al., 1998; Gill and Burke, 1999) show that soil is susceptible to rapid change due to changes in the overlying vegetation. Specifically, there is evidence that the invasion of grassland by woody plants is associated with an increase in soil heterogeneity; and that woody plants cause and benefit from high heterogeneity (Miles, 1987; Armesto et al., 1991; Schlesinger et al., 1996; Klebb and Wilson, 1997). Conversely, levels of soil nutrients can have a strong impact on species composition, species diversity, primary productivity, and other community and ecosystem properties thereby affecting management decisions (Bragg, 1995; Tilman, 1996; Auken and Bush, 1997). For example, certain invading plant species concentrate salts in the shoot and deposit a high salt content litter to the soil surface over time (Walker and Smith, 1997). In particular, eastern red cedar affects the soil and groundcover beneath its canopy. It raises surface soil pH (McBain, 1983) which influences species composition (Gehring and Bragg, 1992). In Nebraska, Gehring and Bragg (1992) found that groundcover of Kentucky blue grass (Poa pratensis L.) and carex (Carex spp.) increased relative to increases in eastern red cedar size. Kentucky blue grass is a non-native species to the site. Coverage of prairie species beneath eastern red cedar decreased as tree size increased. Ugarte (1987) observed massive invasions of the northeast Iowa hill prairies by eastern red cedar and predicted that the invasion may culminate in closed communities with total elimination of prairie species.

As Lubchenco et al. (1991) suggest, the effectiveness of ecological restoration projects would be increased if all pertinent information on interacting
ecological variables are gathered and a conceptual framework formulated to guide the restoration effort. Information on floristic and plant species composition of these dynamic habitats for Louisiana is being documented (MacRoberts and MacRoberts, 1995; 1996; 1997a; 1997b). However, little is known about the soils/resource levels and the influence the invading plants have on soils of these threatened habitats. On a regional scale, information on climate is necessary while on a landscape scale, understanding and quantifying soil variability is crucial (Joem and Keeler, 1995; Walker and Smith, 1997; Annen and Lyon, 1999).

Further, the detailed study of the soil characteristics supporting a remnant prairie and adjacent forest is fundamental to understanding the constraints on energy flow and nutrient cycling within this habitat. The validity of this approach is attested by the control the distribution of below ground resources has on species distribution and recruitment of individual plants (Stark, 1994).

This study was initiated by USDA Forest Service to supplement an ongoing prairie study on floristic and plant species composition within the Winn Ranger District of the Kisatchie National Forest, Louisiana. The overall goal was to develop a management plan for delineating and restoring the remnant prairies. There are many important questions related to understanding this unique habitat, whose answers are fundamental to improved management and restoration plans. This research answers the following questions: What is the soil resource level and its spatial variability of these isolated prairies? What is the effect of invading woody and herbaceous vegetation on the prairie soil spatial variability? What is the natural abundance of C and N isotopes? What plant functional forms (C3
versus C4) dominate the prairies? Are there isotopic evidences for recent shifts in
the functional forms? Can information from soil spatial variability and isotopic
studies be used to delineate the prairie?

The answers to these questions were sought by taking advantage of the
distinct differences of soil development under prairie and forest vegetation, and
the impact woody plants have on prairie soil as well as the differential C isotope
values of Soil Organic Matter (SOM) derived from C3 (trees, shrubs, and cool
season grasses) and C4 (warm season grasses) plants. Stable isotope
distribution of carbon has proven effective in identifying organic matter sources as
related to plants following either C3 or C4 photosynthetic pathways (Peterson and
Fry, 1987; Boutton, 1996). The time of European settlement defines the historic
prairie/forest boundary for this study. Anthropogenic effects, fire suppression, and
landscape fragmentation were considered minimal before European settlement
(Leach and Givinish, 1996).

The following specific objectives were formulated based on the research
questions posed:
1) to delineate the historic prairie-forest boundary based upon stable C isotope
data, and soil property gradation;
2) to map soil resource levels of the study sites;
3) to study the within-site and between-site spatial variation and resource
heterogeneity of a prairie-forest transition soil in the context of assessing the
impact of woody and herbaceous invasion on soil properties;
4) to estimate the proportion of C3 and C4 plants within the selected prairies; and
5) to suggest a management scheme that would preserve the prairie.

1.2 Dissertation Structure

Chapter one contains a brief introduction to prairie habitat change and suggested causes. In this chapter, I lay out the motivation and provide the general objectives. In chapter two, geostatistics, a spatial data analysis technique, is discussed with specific concentration on semivariograms, and kriging. The fractal concept, as applied to objectively quantifying soil variability, is considered. Since local topography often influences several soil properties, its value in understanding soil spatial variability and improving the geostatistical modeling of soil chemical properties is highlighted. In chapter three, I present the use of stable C isotopes for detecting vegetation changes, i.e., woody species encroachment to the prairie during the last 200 years. Carbonate minerals constitute the major component of prairie soils. I employ C isotope and X-ray diffraction methods to study the controls on carbonate pedogenesis of this unique habitat. The importance of vegetation influence and other processes that occur within the soil is described with respect to the formation of secondary carbonates. The use of natural N\textsuperscript{15} abundance offers an opportunity to study and understand fluxes and losses from natural systems of this limiting nutrient. In chapter four, analysis and discussion of data from N isotope is presented. In chapter five, I summarize the results obtained from the preceding chapters and offer suggestions for delineating and restoring the remnant prairies of Louisiana.

1.3 References

Transactions of the Wisconsin Academy of Sciences Arts and Letters 87: 37-50.


CHAPTER 2: SPATIAL VARIABILITY OF SOIL PROPERTIES OF THE PRAIRIE-FOREST TRANSITION IN LOUISIANA

2.1 Introduction

The lateral and vertical variability of soil properties have long been recognized by soil scientists and ecologists. Spatial variability causes uneven patterns of soil resource distribution and control species distribution and recruitment in natural systems. With the emergence of new analytical techniques, the values of studying and documenting these properties have grown recently (Robertson and Gross, 1994; Gross et al., 1995; Cross and Schlesinger, 1999). However, the study of the spatial distribution of soil properties mainly focused on the management of agricultural fields. For natural ecosystems, few data on the spatial variability of soil properties and its relation to vegetation distribution are available.

Information regarding soil pattern and variability is essential for various purposes (Wilding, 1985; Dutilleul, 1993; Legendre, 1993; Robertson and Gross, 1994; Kabrick et al., 1997): 1) for designing suitable sampling schemes and for developing an accurate soil information data base; 2) for determining the scaling behavior of soil properties and for integrating soil attributes with other ecosystem attributes; 3) for the appropriate design and analysis of field experiments; 4) for predicting soil property values at unsampled locations; and 5) for inferring processes that might be related to the causes of variability.

Traditional soil survey suffers from lack of accuracy since small scale soil variability is inherent and has been viewed as an "unavoidable nuisance"
(Webster and Burgess, 1983). Geostatistical and fractal methods offer the means to assess and quantify variability at all levels of scale. Gardner (1998) defines scale as "a change in pattern as determined by the spatial extent of measurements necessary to detect significant differences in the variability of the quantity of interest". Soil variability and its scaling behavior arise from a combination of physical and biological processes and mechanisms occurring within the soil. The study of the spatial variability of soil properties of ecologically important areas such as prairies and prairie-forest transitions is a particular concern because of the dynamic nature of these ecosystems. As Joern and Keeler (1995) emphasize, accurate characterization and estimation of the soil resource level can help in the delineation and management of the prairies. This is reasonable since species differ in terms of nutrition, metabolic rate, and the scale at which they encounter the environment. Besides, the distribution of resources in the landscape is different for each species (Miles, 1987; Milne, 1991).

Consequently, understanding scale dependent variation in resource abundance and specifying the utility of resources to each species are basic for predicting the composition of species assemblages in the landscape (Miller, 1995).

2.2 Geostatistical and Fractal Application

Geostatistics, also known as regionalized variable theory (Journel and Huijbregts, 1978), was developed originally within the mining industry and has found considerable application in soil science and other fields (Oliver and Webster, 1990). A variable that takes on values according to its spatial location is known as a regionalized variable. Geostatistics is based on the idea of spatial
autocorrelation. A variable is autocorrelated if it is possible to predict its value at a
given point in space by knowing its value at other locations. Geostatistics
assumes that the spatial variability of any variable can be expressed as the sum
of three major components:

\[ Z(s) = m(s) + \epsilon'(s) + \epsilon''(s) \]  \[1\]

Where \( Z(s) \) is a spatial variable at location \((x_i, y_i)\); \( m(s) \) is a deterministic function
describing the systematic variability of \( Z(s) \) at \((x_i, y_i)\); \( \epsilon'(s) \) denotes the random
locally varying spatially dependent residuals from \( m(s) \); and \( \epsilon''(s) \) is a spatially
independent residual having a zero mean and variance \( \sigma^2 \) (Burrough and
McDonnel, 1998). It is assumed that \( Z \) is a continuous random variable which
varies continuously through the region. The spatial correlation of \( \epsilon'(s) \) is described
by the semivariance, \( \gamma \). If \( \gamma \) is plotted as a function of the lag distance \( h \), the
semivariogram \( \gamma(h) \) is obtained. For a semivariogram to be defined, first order
stationarity or the intrinsic stationarity has to be assumed. The intrinsic hypothesis
requires that the variance of \([Z(s + h) - Z(s)]\) for all \( h \) is finite and independent of
location. In practical applications, the \( \gamma(h) \) is estimated as:

\[ \gamma(h) = \frac{1}{2 \cdot N(h)} \sum_{i} \left[ Z(s_i) - Z(s_j) \right]^2 \]  \[2\]

Where \( Z \) is a soil property (a regionalized variable), \( Z(s_i) \) is a measured sample
at point \((x_i, y_i)\), \( Z(s_j) \) is a measured sample at point with a vector separation of \( h \),
and \( N(h) \) is the number of pairs separated by distance or lag \( h \) (Isaaks and
Srivastava, 1989). The semivariogram (Figure 2.1a) has three parameters
useful for predicting and characterizing spatial dependence. These are the sill,
range and nugget. A small value of semivariance indicates that pairs of measurements for a particular separation distance are similar, or have low variability. High values of semivariance indicate that the values of measurements in the lag pairs are, on average, very dissimilar. For small values of \( h \), the semivariance is usually small if some spatial correlation is present. As the pairs of measurements become increasingly separated, the values become more dissimilar until the dissimilarity reaches a limiting value equal to the conventional population variance of the measurements called the sill, \( C_0 + C \). The sill reflects the amount of spatial variability. The distance at which the semivariogram attains the sill is termed the range. One interpretation of the range is that it defines the region of influence or spatial correlation distance of a measurement value. If one were to measure a soil property at a point \((x_i, y_i)\) in a given site, one would expect the measurement to be very close to the previous measurement if it were measured against a short distance away, relative to the range. Thus the measurement made at \((x_i, y_i)\) is a useful predictor of the soil property at points nearby. This is very important in conditions where exhaustive sampling can not be done due to time and cost as well as where minimum ecological disturbance is desired as in sensitive areas like prairies. The range can be used as a measure of homogeneity or spatial dependency (Cohen, 1994). Semivariogram ranges depend on the spatial interaction of soil processes at the sampling scale used (Trangmar et al., 1985). The value of \( \gamma(0) \) is, by definition, equal to 0. However, a value of \( \gamma(0) \) greater than 0 is known as a nugget variance, \( C_0 \). The nugget variance represents
Figure 2.1. Diagrams showing a) typical shape of a variogram with nugget, sill, and range shown, and b) nested spatial structure with multiple factors operating at different scales.
analytical error and residual variations not removed by close sampling (Webster, 1985; Cressie, 1993). The parameters from the semivariogram model provide an index of both the magnitude and scale of spatial variability in a variate (Rossi et al., 1992).

Few studies are directed to studying the spatial variability of soil properties in natural systems. Spatial variability in natural systems arises from a variety of factors. In their study of the spatial variability of pH, NO$_3$ and K in an old growth forest in Quebec, Canada, Lechowicz and Bell (1991) found a high degree of spatial dependence within a range of 2 m in all the three soil properties. They suggested that such small-scale heterogeneity in a forest understory could arise from individual tree-level effects on nutrient availability mediated through differences in stem-flow or litter deposition and decomposition. Palmer (1990) studied the spatial patterns of plant-environment relationships among hardwood stands within the Duke Forest, North Carolina. He found spatial dependence in most of the 12 soil properties measured, and most of the spatial dependence was at a scale of 10 m. He concluded that species composition in these stands varied in relation to soil calcium among plots. At the sampling scale of 4 m, Gonzalez and Zak (1994) observed spatial autocorrelation at distances of 24 m or less for forest floor mass, soil texture, pH, organic C, net N mineralization, net nitrification and available P in a secondary tropical dry forest, St. Lucia, West Indies. Because they did not find any similarity in the covariance structure between soil texture or pH and other properties, they concluded that fine scale spatial patterns of net N
mineralization and net nitrification could be driven by overstory litter inputs rather than variation in soil texture and water availability.

Multiple-scale variability is observed for many soil properties due to different processes occurring at different scales (Burrough, 1983a; Wilding, 1985). Multiple scaling is expressed by a nested semivariogram model (Figure 2.1b). Microtopography and plants induce small-scale variability (1-5 m) while parent material and climate impart large scale (landscape and regional) variability (Meyers and McSweeney, 1995). Folster and Khanna (1997) present case studies on variation in forest soil properties for various spatial scales ranging from “supra-regional” to compartmental (operational) level. They concluded that considerable heterogeneity in soil properties occurs at the scale of experimental plots.

Semivariogram estimation and its modeling from sampled data is extremely valuable for quantitative spatial analyses and is a prerequisite for interpolation by kriging. Kriging is one of several interpolation methods useful in mapping soil resource levels. Several studies showed that kriging is superior and optimal in that estimates at unsampled locations are unbiased and the estimation variance is a minimum (Cressie, 1993). Burgess and Webster (1980) describe the essential steps of the procedure as it applies to soil mapping. The kriged value for a soil property $z$ at position $s_o$ is a weighted average of the measured sample values $s_i$ in its neighborhood. It is represented as (Burgess and Webster, 1980):

$$z^*(s_o) = \sum_{i=1}^{n} \lambda_i z(s_i)$$  \[3\]
where \( n \) is the number of neighboring samples \( z(s_i) \), and \( \lambda_i \) is the weight associated with sample value \( z(s_i) \). The weights are chosen so that the estimate \( z^*(s_o) \) of the true value \( z(s_o) \) is unbiased, that is,

\[
E[z^*(s_o) - z(s_o)] = 0
\]  

[4]

and the estimation variance \( \sigma_k^2 \),

\[
\sigma_k^2 = \text{Var}[z^*(s_o) - z(s_o)] \text{ is minimized.}  
\]  

[5]

The weights placed on each neighboring sample are constrained to sum to 1.0, and their unique combination for which \( \sigma_k^2 \) is minimized can be obtained when

\[
\sum_{i=1}^{n} \lambda_i \gamma(s_i - s_i) + m = \gamma(s_o - s_i), \quad i = 1, \ldots, n.
\]  

[6]

The values \( \gamma(s_i - s_i) \) and \( \gamma(s_o - s_i) \) are the semivariances between observed locations \( s_i \) and \( s_i \) and between the observed location \( s_i \) and the interpolated location \( s_o \), respectively. These values are obtained from the semivariogram of \( Z \).

The parameter \( m \) is the Lagrangian multiplier associated with the minimization of \( \sigma_k^2 \). Solutions of the \( n + 1 \) equations of the kriging system for each \( \lambda_i \) and \( m \) enables the kriged estimate \( z^*(s_o) \) to be determined by equation 3 and the estimation variance to be determined by solving for

\[
\sigma_k^2(s_o) = \sum_{i=1}^{n} \lambda_i \gamma(s_o - s_i) + m
\]  

[7]

The set of \( n + 1 \) simultaneous equations of the kriging system is most efficiently solved using matrix methods (Isaaks and Srivastava, 1989). The estimation variance depends only on the semivariogram and the configuration of the data locations in relation to the kriged points and not on the observed values themselves (Burgess and Webster, 1980).
In heterogeneous systems, estimates of quantities such as soil properties vary with the scale at which measurements are made (Burrough, 1983a; 1983b). Scale dependence can be inferred from a nested semivariogram model (Trangamar et al., 1985; Webster, 1985), but fractal analysis provides a means for directly examining and quantifying scale-dependent variation (Milne, 1991). Mandelbrot (1967, 1982) introduced and developed the fractal concept to characterize irregularity of natural lines and surfaces. The fractal concept is suitable for modeling and describing many complex forms and patterns observed in nature that arise as a result of many interacting factors. Fractals have been used to model spatial and temporal variations in a variety of disciplines (Fan et al., 1991; Milne, 1991; Biridi, 1993; Hastings and Sugihara, 1993; Bassingthwaigte et al., 1994; Barton and La Pointe, 1995), including soil variability (Burrough, 1981; Burrough, 1983a; 1983b; Eghball et al., 1999). The key concept underlying fractals is self-similarity at all scales. Self-similarity is of two types: geometric and statistical (Bassingthwaigte et al., 1994). Geometrically self-similar objects are objects whose pieces are smaller, exact duplications of the whole object. Statistical self-similarity means that a property measured on a piece of an object at high resolution is proportional to the same property measured over the entire object at coarser resolution. Self-similarity in soil variability takes the later form. Burrough (1983a) illustrates this concept using a soil survey map produced at different scales. If the pattern of soil is mapped at a small scale, say 1:1000000, the surveyor will divide the landscape into mapping units that express the major sources of variation at that scale. However, if one part of the same area is
mapped at a larger scale, say 1:1000, new details will appear that were taken to be uniform previously. This process continues until one has reached the largest measurable scale.

Self-similarity implies the existence of a power law scaling relationship. The spatial structure of a stationary Gaussian process can be described by the following fractal function (Eghball et al., 1999):

\[ \gamma(h) \propto kh^H, \quad 0 < H \leq 2 \]  \[8\]

where \( \gamma(h) \) is the semivariogram, \( h \) is the lag, \( H \) is the codimension, and \( k \) is a constant related to the extent of variation. This relationship is based on the variance of increments of a Weierstrass-Mandelbrot fractal function that varies as \( h^{4-2D} \) (Berry and Lewis, 1980, cited in Eghball et al., 1999). As shown by Burrough (1981), there is a mathematical relation between the first partial derivative of the semivariogram function with respect to \( h \) and \( D \). It is given by:

\[ \frac{\partial \log[\gamma(h)]}{\partial \log(h)} = 4 - 2D \]  \[9\]

Fractal dimension is calculated based on the following relationship:

\[ D = d - 1/2 H \]  \[10\]

where \( d \) is the Euclidean dimension (\( d = 1 \) for curves, \( d = 2 \) for surfaces, and \( d = 3 \) for solids). For a linear transect across a fractal area \( D = 2 - 1/2 H \). Regression of \( \log \gamma(h) \) vs. \( \log h \) provides an estimation of fractal dimension, \( D \), with \( H \) as the slope of the straight-line section of the log-log semivariogram. The fractal dimension, \( D \), is a measure of the degree to which complexity at one scale is repeated at others. Further, \( D \) is a good index of variability since it is expected to have remained constant over large time intervals on geologic time scales. Biridi
(1993) considers D analogous to the counting of rings in a tree in that any environmental changes such as weather affects both the distances between rings and the shapes. Eghball et al. (1999) suggest that differences between slopes among sites or treatments can also reflect differences between sites since slopes and D-values are related by constants.

The calculation of D using the semivariogram method is illustrated using data of pH (Site 1). The semivariance data, the semivariogram and the corresponding log-log plots are given in Appendix A. The computations were performed using GS+, version 5.1 (Gamma Design Software, 1998). The slope (H) of the linear portion of the log (distance) - log (semivariance) plot was 0.88. Equation 6 was then employed to obtain a D value of 1.56. Since H and D are linearly related confidence interval could be obtained for D similar to that for H, where H is the slope parameter of a simple regression line. Interpretation of this D value is given in the Results and Discussion section.

The knowledge of the fractal dimension of a given soil property could be useful either for a scientific description or when estimating spatial patterns or amounts of resources (Biridi, 1993). Philips (1985) presents two situations where the fractal dimension could be used in ecology: 1) to determine whether a particular factor is regular in its variability so that spatial position is a reasonable surrogate for position along an environmental gradient; and 2) to determine whether a measured gradient is 'contaminated' by deviations from the general trend serious enough to affect ecological interpretations.
The magnitude of the fractal dimension provides immediate information on the balance between long range and short range variations (Burrough, 1983b). In soil systems, long range variation arises as a result of parent material, depositional, or other effects while short range variation may arise due to individual plant effects. Simulation studies (Burrough, 1983b; Palmer 1988) established that values of D less than 1.5 imply the domination of long range variation while D values exceeding 1.5 indicate the domination of short range variation for a linear transect across a fractal area. Long-range variation implies that increments are positively correlated so that negative increments tend to be followed by negative increments and positive increments by positive increments. This phenomenon is known as persistence; that is, trends in one direction tend to persist. In contrast, short range variation implies that the increments are negatively correlated or an increasing trend in preceding increments is followed by a decreasing trend in the next and vice versa. This is antipersistence (Biridi, 1993).

Burrough (1983b) questioned the validity of kriging for antipersistent spatial phenomena (D values close to 2.0). The interpretation was that the larger the fractal dimension, the more difficult it would be to make reasonable interpolations from point data. A D value equal to 2.0 corresponds to pure nugget variance. A D value of 1.5 is representative of a Brownian motion (random walk) with an equal balance of short and long range variation. Burrough (1981), Armstrong (1986), and Culling (1986) used semivariance to determine the fractal dimension of soil properties and environmental data while Eghball et al. (1999) used it to compare
spatial variability of soil nitrate in a conventional uniform nitrogen application and variable rate nitrogen application; and to determine the effectiveness of the treatments used on reducing soil variability.

There is evidence (Burrough, 1981; 1983a; 1983b; Lam and Quattrochi, 1992) that natural phenomena including soil variability exhibit self-similarity (fractal characteristics) only over a limited range of scales. Lam and Quattrochi (1992) suggest that the existence of self-similarity over a limited range of scales could be utilized positively; as when used to identify the spatial and temporal scales of competing processes due to plant, microorganism, topographic, and other effects. Fractals are also suggested to be useful in identifying interfaces or boundaries in a pattern or distribution at a particular scale where the processes contributing to these patterns become unstable; an example is when a homogeneous pattern becomes heterogeneous and vice versa (Burrough, 1981; Lam and Quattrochi, 1992; Kenkel and Walker, 1996). This kind of combination of pattern makes up a prairie-forest transition, thereby making fractals a good tool for characterizing a prairie soil under the influence of invading woody and herbaceous plants. According to Krummel et al. (1987), identifying spatial scale ranges and transition zones can have enormous practical value in adjusting sampling and modeling schemes and the resultant interpolations.

This study was designed: 1) to document the spatial variability and scaling behavior of soil properties of three prairie remnants in Louisiana; 2) to produce soil resource maps of the prairies; and 3) to evaluate the influence of woody and herbaceous plants upon the scaling and spatial variability of soil properties.
2.3 Materials and Methods

2.3.1 Description of Study Area

The study was conducted within the Winn Ranger District of the Kitsatchie National Forest, Winn Parish, Louisiana (Figure 2.2). The dominant remnant prairies of Louisiana, also known as the Keiffer calcareous prairie/forest complex, consist of a series of natural grassland openings occurring in a mosaic with calcareous hardwood-pine forest (Smith et al., 1989). McRoberts and McRoberts (1995, 1996, 1997a, 1997b) have described the floristic composition of the prairies.

The prairie/forest complex occurs as a narrow zone that extends approximately 16 km from Couley to northeast of Calvin. The prairie openings range from less than 0.2 ha to approximately 10 ha in size (McRoberts and McRoberts, 1996). The Keiffer calcareous prairie/forest complex has developed on Eocene-age marly clays of the tertiary period (Smith et al., 1989). The sediments belong to the Jackson group (Spearing, 1995). The Keiffer prairies occur on Keiffer loam soil that has CaCO$_3$ throughout the profile. The CaCO$_3$ was formed from the remains of marine life forms (USDA, 1998). Taxonomically, the soil is classified as fine-silty, carbonatic, thermic Rendolic Eutrochrepts. Immediately adjacent to the prairies are soils of the calcareous forests dominated by Hollywood (fine, montmorillonitic, thermic Typic Pelluderts) and Oktibbeha (very-fine, montmorillonitic, thermic Vertc Hapludalfs) soils. Profile descriptions for these soil units are given in Appendix B. Vaiden (very-fine, montmorillonitic, thermic Vertc Hapludalfs) and Bellwood (very-fine, montmorillonitic, thermic...
Figure 2.2. Map showing study locations. Site 1: Milam Branch Prairie North, Site 2: White Oak Creek South Prairie, and Site 3: Coutley Church Prairie.
Aquentic Chromuderts) soils also occur adjacent to the prairies. Typical tallgrass species in Keiffer prairies include little bluestem (*Schizachyrium scoparium*), big bluestem (*Andropogon gerardii*), tall dropseed (*Sporobolus sp.*), and Indian grass (*Sorghastrum nutans*). All of the prairies have been heavily grazed and a few were farmed for short periods (Smith et al., 1989). Sites chosen for this study have not been farmed. The site receives a mean annual precipitation of 1250 mm and has a mean annual air temperature of 20 °C.

### 2.3.2 Field Methods

Three relatively undisturbed prairie/forest associations were selected for this study. The USDA Forest Service Southern Region Geographic Information System (GIS) data for Winn Ranger District was used for site selection. According to MacRoberts and MacRoberts (1997b), the largest, best-preserved and protectable prairie remnants are found within the Winn Ranger District of the Kisatchie National Forest. The criteria for site selection were established so that all the three prairies would have: 1) similar adjacent soil units derived from the same parent material; Oktibbeha and Hollywood soil units were the preferred soils adjacent to Keiffer soil; and 2) minimum disturbance (for example, roads, horse trails and history of other land use). A query that satisfied the above criteria was made using Arc View GIS, version 3.1 (ESRI, 1996). Field reconnaissance confirmed the final selection.

The selected sites were (Figure 2.2):

- **Site 1**: Milam Branch Prairie North
- **Site 2**: White Oak Creek South Prairie

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Site 3: Couley Church Prairie

The sizes of the prairie portion of the sites are approximately 0.3 ha (Site 1), 0.9 ha (Site 2), and 1.4 ha (Site 3). The sites are separated by approximately 4-5 km. Sites 2 and 3 have not been burned recently. The South side (upslope position) of site 1 was burned several times. The last burn probably occurred in 1998. The North side (downslope position) of the site has not been burned and is heavily encroached by eastern red cedar and various shrubs (MacRoberts and MacRoberts, Pers. Commun.). Plants recorded in October and March 2000 at the study sites are listed in Appendix B.

At each site four transects, long enough to encompass adjacent forest soils, were established for soil sampling. Two transects were normal and the other two were parallel to slope gradient. For Sites 1 and 3, soil samples were collected at 0-15 cm depth every 2 m within the prairie and every 4 m within the adjoining forest and transition. For site 2 similar sampling scheme was followed but with uniform sampling distance of 4 m. This decision was based on the size of the prairies and the number of samples required to perform geostatistical analysis. Semivariogram modelling require that each lag class is represented by at least 30-50 pairs of points (Journel and Huijbregts, 1978). Distance between transects varied depending on the size and shape of the prairies. For Site 1, North-South transects were separated by 10 m while East-West transects were separated by 20 m. At Site 2, North-South transects were positioned 55 m apart and East-West transects were placed 36 m apart. At Site 3, there was a 15 m distance between North-South transects and 17 m distance between East-West transects.
Measurement of relative elevation was made at each sampling location using a rod and transit. The sampling scheme and kriged three-dimensional relative elevation map for each site is presented in Figure 2.3.

2.3.3 Laboratory Methods

Soil samples were air dried for several weeks and ground to pass a 2 mm sieve. A multielement extraction of the soil samples was made using the Mehlich III extractant (Mehlich, 1984). The Mehlich III extractant is largely independent of soil type. The sum of exchangeable bases (K, Ca, Mg, Na) determined by the Mehlich III method is identical to that obtained by the ammonium acetate method. The Mehlich III extractable micronutrients (Cu, Zn, Mn, Fe) are also equivalent to those obtained by the double acid, diethylene triamine pentaacetic acid-triethanolamine (DTPA-TEA), or 0.1 M HCl methods. The Mehlich III extractable P is closely related to Bray 2, Olsen, and bicarbonate resin extractable amounts. Moreover, the Mehlich III extractant is neutralized less by carbonate compounds in soil than the other extractants (Tran and Simard, 1993).

The concentrations of K, Ca, Mg, P, Mn, and Fe were determined by inductively coupled plasma atomic emission spectroscopy (ICP). Samples were analyzed for electrical conductivity and pH (1:1 in deionized water).

2.3.4 Data Analyses

Exploratory Data Analysis (EDA) (Tukey, 1977) was performed using SAS to gain understanding of the univariate characteristics of the data and as a prerequisite to spatial data analysis (Issaks and Srivastava, 1989). The EDA
Figure 2.3. 3D representation of relative surface elevation and sampling scheme for a) Site 1, b) Site 2, and c) Site 3. Raised crosses show sampling points.
included posted maps, scatter plots, and box plots. The magnitude of between site variability of soil parameters was evaluated by a non parametric one-way ANOVA using the NPAR1WAY procedure of SAS, version 8 (SAS Institute, 1999). A Kruskal-Wallis statistic was used to test for overall significant differences between sites. The Kruskal-Wallis test compares the medians of three or more groups. This test assumes only the shapes of the distributions are identical (Freund and Wilson, 1997).

To satisfy the assumption of first-order stationarity (constant variance) required for semivariogram analysis, each soil property was examined for the presence of a trend and the trend was removed by trend surface analysis (White et al., 1997). The detrended data were then used to construct relative semivariograms to quantify the spatial dependence (heterogeneity) of cations, pH, and EC. Relative semivariograms are robust in depicting spatial continuity and are obtained by re-scaling the traditional semivariogram by the local mean (Isaaks and Srivastava, 1989). The sample sizes used for semivariogram calculation of each soil parameter for each site ranged between 138 and 153. The minimum number of pairs used to estimate the semivariance at each lag distance was greater than 90. This is greater than the 30-50 pairs minimum "rule of thumb" (Journel and Huijbregts, 1978) and is desirable in terms of statistical reliability at each distance class (Rossi et al., 1992). The linear, linear to sill, spherical, exponential and gaussian functions were investigated for the semivariogram modeling. The model with the lowest residual sum of squares and highest $R^2$ was selected following the method of Robertson (1998). The fractal dimension for each
property at each site was calculated using the semivariogram method (Burrough, 1981).

To define distinct classes of spatial dependence (autocorrelation) of the soil properties, nugget to sill ratios similar to those presented by Camberdella et al. (1994) were used. If the ratio was >25% and <75%, the variable is considered moderately spatially dependent; if the ratio was >75%, the variable is considered weakly spatially dependent. This approach allows comparison of spatial dependence among variables and sites.

Based upon a specified model, block kriging was performed to provide estimates of measured soil properties at unsampled locations between samples and for mapping the variability of each soil parameter (Burgess and Webster, 1980).

Surfer software, version 7 (Golden Software, Inc., 1999) was used for generating relative experimental semivariograms, model fitting, kriging and mapping. GS+, version 5.1 (Gamma Design Software, 1998) was used for calculating fractal dimension.

2.4 Results and Discussion

2.4.1 Exploratory Data Analysis

The soil P level was below ICP detection limit and therefore it was not considered for further analysis. Summary statistics for the measured soil attributes are given in Table 2.1. Except for electrical conductivity (EC) and relative elevation (RE) from site 2, none of the properties were normally distributed. Sites 1 and 2 Mg, K, and Fe followed a lognormal distribution as did
Site 2 EC and Mn. Soil pH and other soil parameters did not conform to a normal or log normal distribution (Table 2.1). Several authors (Grigal et al., 1991; Chien et al., 1997; Young et al., 1999) reported similar observations. Reimann and Filzmoser (1999) argue that normal and/or lognormal distribution of geochemical or environmental data are an exception and not the rule. Nevertheless, distributions of soil properties provide important information for understanding and interpreting pedogenesis (Young et al., 1999). The statistical distribution of the soil attributes among sites is demonstrated using box plots (Figure 2.4). Because of lack of symmetry in the distribution of most of the soil attributes, the median is used as a measure of central tendency. The horizontal line inside the box of the box plot represents the median. Site 1 and Site 2 had similar median pH values of 7.8 and 7.7, respectively (Figure 2.4d). Site 3 had lower median pH value (7.3). Clearly, the box plots for pH show lower pH "outliers" for Site 1 and Site 2 while a negative skewness was expressed by Site 3 pH. One of the interesting observations gleaned from these distributions is that the data that appear as "outliers" for Sites 1 and 2, and that caused skewness for Site 3 correspond to forest soil pH. The Kruskal-Wallis test indicated that there are median pH differences among the sites at the 0.05 probability level. When the samples were stratified based upon vegetation type, the pH of prairie soil was in the alkaline range (pH > 7.0), the pH of forest soil was acidic (pH < 7.0), and pH of transition soil was approximately 7.0 for Sites 1 and 2. One of the transect samples obtained from Site 3 prairie gave pH values as low as 4.7 within the prairie causing the median pH for this site to be the lowest. The pre-grouping of
Table 2.1. Summary statistics for soil properties and relative elevation of three Keiffer prairie-forest associations, Louisiana.

<table>
<thead>
<tr>
<th></th>
<th>RE# (m)</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>Ca (cmol/kg)</th>
<th>Mg (--------)</th>
<th>K (mg/kg--)</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>153</td>
<td>151</td>
<td>151</td>
<td>153</td>
<td>153</td>
<td>152</td>
<td>153</td>
<td>152</td>
</tr>
<tr>
<td>Mean</td>
<td>1.2</td>
<td>7.5</td>
<td>573</td>
<td>68.2</td>
<td>131.8</td>
<td>106.2</td>
<td>85.6</td>
<td>114.0</td>
</tr>
<tr>
<td>Median</td>
<td>1.2</td>
<td>7.8</td>
<td>573</td>
<td>55.5</td>
<td>129.2</td>
<td>101</td>
<td>71.7</td>
<td>102.1</td>
</tr>
<tr>
<td>Min</td>
<td>0</td>
<td>5.6</td>
<td>233</td>
<td>20.1</td>
<td>63.1</td>
<td>51.6</td>
<td>13.5</td>
<td>24.5</td>
</tr>
<tr>
<td>Max</td>
<td>1.95</td>
<td>8.0</td>
<td>916</td>
<td>175.3</td>
<td>228.2</td>
<td>218.9</td>
<td>289.3</td>
<td>303.3</td>
</tr>
<tr>
<td>Range</td>
<td>1.95</td>
<td>2.4</td>
<td>683</td>
<td>155.2</td>
<td>165.1</td>
<td>167.4</td>
<td>275.8</td>
<td>278.8</td>
</tr>
<tr>
<td>Variance</td>
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<td>0.3</td>
<td>15439</td>
<td>1496</td>
<td>677</td>
<td>993</td>
<td>3370</td>
<td>4044</td>
</tr>
<tr>
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<td>8</td>
<td>22</td>
<td>57</td>
<td>20</td>
<td>30</td>
<td>68</td>
<td>56</td>
</tr>
<tr>
<td>K-S**</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Site 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>96</td>
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<td>Mean</td>
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<td>627</td>
<td>78.9</td>
<td>189.7</td>
<td>163.2</td>
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<tr>
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<td>640</td>
<td>72.0</td>
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<td>157.3</td>
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</tr>
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<td>98.6</td>
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<td>439.8</td>
<td>313.7</td>
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<td>827</td>
<td>154.0</td>
<td>341.2</td>
<td>281.4</td>
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<tr>
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<td>20275</td>
<td>1572</td>
<td>3180</td>
<td>3420</td>
<td>120</td>
<td>1831</td>
</tr>
<tr>
<td>CV</td>
<td>45</td>
<td>7</td>
<td>23</td>
<td>50</td>
<td>30</td>
<td>36</td>
<td>39</td>
<td>42</td>
</tr>
<tr>
<td>K-S</td>
<td>0.09</td>
<td>&lt;0.01</td>
<td>0.13</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Site 2</td>
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</tr>
<tr>
<td>N</td>
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<td>144</td>
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<td>Mean</td>
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<td>6.9</td>
<td>216</td>
<td>58.6</td>
<td>161.3</td>
<td>165.3</td>
<td>88.8</td>
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<td>7.3</td>
<td>205</td>
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<td>167.7</td>
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<td>4.2</td>
<td>37</td>
<td>5.6</td>
<td>115.2</td>
<td>30.7</td>
<td>2.4</td>
<td>46.8</td>
</tr>
<tr>
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<td>6.2</td>
<td>577</td>
<td>117.4</td>
<td>254.3</td>
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<td>278.5</td>
<td>186.4</td>
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<td>1.0</td>
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<td>722</td>
<td>1056</td>
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<td>2141</td>
<td>2369</td>
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<tr>
<td>CV</td>
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<td>14</td>
<td>54</td>
<td>46</td>
<td>20</td>
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<tr>
<td>K-S</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

*RE: Relative Elevation; *EC: Electrical Conductivity; *CV: Coefficient of Variation; **K-S: Kolmogorov-Smirnov test p value.
Figure 2.4. Box plots showing distribution of measured soil parameters from three Keifferprairie-forest associations, Louisiana.
vegetation into prairie, transition, and forest was based upon field observation. The transition was characterized by the presence of red cedar and various shrubs and could be distinguished from the prairie and forest.

EC is a measure of total solute concentration within the soil. The median EC values were 573 μS/cm for Site 1, 640 μS/cm for Site 2, and 205 μS/cm for Site 3. These values represent a very dilute salt solution. A soil is considered saline when the EC exceeds 4000 μS/cm (Sposito, 1989). Site 3 has significantly lower EC values and the highest variability with CV of 59 %, compared to 22 % for Site 1, and 23 % for Site 2. Significant differences in median EC among sites were observed. EC had the tendency to be higher in the prairie than in the forest although the association seems to be masked by the greater effect of relative elevation on EC. Two reasons may explain why Site 3 had lower EC values. First, this site had the greatest range of relative elevation (local relief) and might be susceptible to surface flow and sediment transport thereby causing the removal to lower topographic positions of soluble salts, that were not captured in the sampling scheme. Secondly, Site 3 is among the sites that have not been burned in a long time (MacRoberts and MacRoberts, 2000). Hernandez et al. (1997) observed consistently higher EC values under burned forest soils than unburned soils.

The median Ca content was the greatest for site 2 (72 cmolc/kg) compared with Site 1 (55.5 cmolc/kg) and Site 3 (64.2 cmolc/kg). Samples from the prairie had the maximum Ca concentration. The forest soil exhibited lower Ca values. This is expected since based on field observations, free carbonates
are more abundant within 0-15 cm of the prairie soil. A similar pattern was observed for the median concentration of Mg for the three sites (Table 2.1, Figure 2.4b). For K, the median concentration was the greatest for Site 3 (167.7 mg/kg) followed by Site 2 (157.3 mg/kg) and Site 1 (101.0 mg/kg). Unlike pH and Ca, values of Mg and K do not discriminate between vegetation types. A non-parametric statistical comparison of medians of these cations showed that among-site differences existed. The observed Ca levels are considered high and are characteristic of soil Ca derived from calcareous parent materials. The Mg levels are low when compared with the range reported for temperate soils (Brady, 1990). The average K concentration in soil is about 1 % by weight (Barber, 1995), and soils derived from limestone contain relatively lower K (Sparks, 2000).

The median Fe concentration was 102.1 mg/kg for Site 1, 93.3 mg/kg for Site 2, and 92.7 mg/kg for Site 3. Manganese, with a median concentration of 71.7 mg/kg for Site 1, had the highest CV (68 %). Site 2 had the lowest median Mn concentration (25.9 mg/kg) and Site 3 had the highest (95.9 mg/kg). The median Fe concentration was not statistically significant among sites whereas differences were significant for median Mn content. Mn and Fe are similar both in chemistry and geology. The observed Fe and Mn levels were low considering their high abundance in soil (Mortvedt, 2000).

A correlation matrix among the elements, RE, pH and EC for each site is presented in Table 2.2. Correlation of pH with other parameters is relatively
consistent among sites compared with correlation among the rest of the measured variables. This is reasonable since pH controls the availability of many nutrients. pH is strongly correlated with Ca, Mg, Fe, and Mn. Pictorial examination of the correlation among the soil parameters revealed that the direction and degree of correlation differ between prairie and forest soils. The most notable ones were correlation between the pairs pH-Ca, pH-Fe, pH-Zn, and pH-EC. Figures 2.5 and 2.6 show correlation plots of pH with other soil properties after the samples were stratified based upon vegetation type representing prairie (P), transition (T), and forest (F).

Calcium is positively correlated with pH for the forest soil for all three sites (Figure 2.5b). For the prairie soil, Ca concentrations vary widely at a constant pH of around 7.5, especially for Sites 1 and 2. Based on the correlation between pH and Ca, the transition soil at Sites 1 and 3 resembles the adjoining forest soil while the transition soil of Site 2 resembles the adjoining prairie soil. When the relationship between EC and pH was examined for each site and each vegetation, these two soil parameters were positively correlated both within the forest and transition soils. For Sites 1 and 2, a slight negative or no correlation between EC and pH was apparent for the prairie soil (Figure 2.5a). Fe in the forest and transition soils were negatively correlated with pH (Figure 2.6a). This contrasting relationship among soil chemical parameters may suggest the occurrence of unique soil processes within these two adjacent habitats.
Table 2.2. Correlation among relative elevation (RE) and soil characteristics for three Keiffer prairie-forest associations, Louisiana.

<table>
<thead>
<tr>
<th></th>
<th>RE</th>
<th>pH</th>
<th>Ca</th>
<th>K</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.21**</td>
<td>0.56***</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-0.47***</td>
<td>0.04</td>
<td>-0.27***</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>-0.03</td>
<td>-0.58***</td>
<td>-0.69***</td>
<td>0.19**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.10</td>
<td>-0.63***</td>
<td>-0.1</td>
<td>0.19**</td>
<td>0.39***</td>
<td></td>
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</tr>
<tr>
<td>Mn</td>
<td>0.12</td>
<td>-0.30***</td>
<td>-0.60***</td>
<td>0.12</td>
<td>0.79***</td>
<td>0.17*</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>-0.41***</td>
<td>0.49***</td>
<td>0.09</td>
<td>0.57***</td>
<td>-0.14</td>
<td>-0.24**</td>
<td>-0.04</td>
</tr>
<tr>
<td>pH</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.30**</td>
<td>0.45***</td>
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<td></td>
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<td>-0.33***</td>
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<td>0.05</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>-0.24**</td>
<td>-0.42***</td>
<td>-0.11</td>
<td>-0.01</td>
<td>0.05</td>
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<td></td>
</tr>
<tr>
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<td>-0.18*</td>
<td>0.01</td>
<td>0.08</td>
<td>0.60***</td>
<td>0.07</td>
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<td>0.10</td>
<td>-0.21*</td>
<td>-0.05</td>
</tr>
<tr>
<td>pH</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
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<td>0.85***</td>
<td></td>
<td></td>
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<td>0.51***</td>
<td>0.38***</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>-0.49***</td>
<td>0</td>
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<td></td>
</tr>
<tr>
<td>Mn</td>
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<td>0.56***</td>
<td>0.33***</td>
<td>0.75***</td>
<td>-0.41***</td>
<td>-0.27***</td>
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</tr>
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<td>0.35***</td>
<td>0.38***</td>
<td>0.41***</td>
<td>-0.43***</td>
<td>-0.25***</td>
<td>0.41***</td>
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</tbody>
</table>

* . **. ***Significant at 0.05, 0.01, and 0.001 probability level, respectively.
2.4.2 Semivariogram and Fractal Analysis

Semivariogram models and model parameters for the studied soil properties are shown in Table 2.3. For Site 1, the spherical model described the spatial variability of all the soil parameters except Fe where the exponential model gave a better fit. Soil pH, EC, Ca, and Mn were autocorrelated over a distance of 25 m. Soil K was autocorrelated over a shorter distance of 15 m. Semivariograms of the exponential form imply that a very continuous process is active (Joumel and Huijbregts, 1978). The nugget to sill ratio indicates that pH is highly spatially dependent with the nugget variance accounting for 14% of the maximum variance. Soil EC and Mg were moderately spatially dependent with a relative nugget of 48%. Similarly, soil Ca, K, Mn, and Fe showed moderate nugget to sill ratio (Table 2.3). Previous researchers have shown that individual trees and shrubs influence the spatial variability of soil pH and can be deduced from semivariogram shape and parameters. To evaluate the impact of invading trees and shrubs within the prairie, relative semivariograms were calculated after deleting the forest and transition soil pH data for comparison with general relative semivariogram and among sites. For Site 1 prairie, the spherical model explained the spatial variation of pH with strong autocorrelation over a distance of 6 m. When the range of spatial dependence is small or where there is no detectable spatial dependence to the variation, the variate has a homogeneous or fine-grained distribution at the scale measured (Gross et al., 1995). The fractal dimension of the properties studied also shows this. For this scale of investigation, soil pH had the lowest D (1.56), indicating a balance of short- and
Figure 2.5. Relationship between pH and other soil parameters stratified with vegetation type for three Keiffer prairie-forest associations, Louisiana. F = Forest, T = Transition, and P = Prairie.
Figure 2.6. Relationship between pH and micronutrients (Mn and Fe) stratified with vegetation type for three Keiffer prairie-forest associations, Louisiana. F = Forest, T = Transition, and P = Prairie.
Table 2.3. Spatial statistics and fractal dimension (D) for soil characteristics from three Keiffer prairie-forest associations, Louisiana.

<table>
<thead>
<tr>
<th>Site Property</th>
<th>Model</th>
<th>Co</th>
<th>Co+C</th>
<th>Range</th>
<th>Nugget %</th>
<th>D***</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>6</td>
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</tr>
<tr>
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<td>Spherical</td>
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<td>1.17</td>
<td>25</td>
<td>14</td>
<td>1.56 ± 0.15</td>
</tr>
<tr>
<td>EC</td>
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<td>1.05</td>
<td>25</td>
<td>48</td>
<td>1.77 ± 0.27</td>
</tr>
<tr>
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<td>1.1</td>
<td>25</td>
<td>31</td>
<td>1.84 ± 0.27</td>
</tr>
<tr>
<td>Mg</td>
<td>Spherical</td>
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<td>1.05</td>
<td>20</td>
<td>48</td>
<td>1.86 ± 0.29</td>
</tr>
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<td>K</td>
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<td>0.4</td>
<td>1.05</td>
<td>15</td>
<td>38</td>
<td>1.76 ± 0.26</td>
</tr>
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<td>Mn</td>
<td>Spherical</td>
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<td>1.1</td>
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<td>27</td>
<td>1.78 ± 0.27</td>
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<tr>
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<td>Exponentia</td>
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<td>20</td>
<td>24</td>
<td>1.73 ± 0.10</td>
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<td>1.72 ± 0.10</td>
</tr>
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<tr>
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<td>1.04</td>
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<td>19</td>
<td>1.81 ± 0.16</td>
</tr>
<tr>
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<td>1.05</td>
<td>15</td>
<td>19</td>
<td>1.81 ± 0.16</td>
</tr>
<tr>
<td>K</td>
<td>Spherical</td>
<td>0.25</td>
<td>1.05</td>
<td>20</td>
<td>24</td>
<td>1.81 ± 0.19</td>
</tr>
<tr>
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<td>-</td>
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<td>1.1</td>
<td>0</td>
<td>100</td>
<td>1.84 ± 0.26</td>
</tr>
<tr>
<td>Fe</td>
<td>Spherical</td>
<td>0.4</td>
<td>1.05</td>
<td>31</td>
<td>38</td>
<td>1.91 ± 0.49</td>
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<tr>
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<td>1.64 ± 0.10</td>
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<td>0</td>
<td>1.6 ± 0.11</td>
</tr>
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<td>1.75 ± 0.27</td>
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<td>1.12</td>
<td>20</td>
<td>11</td>
<td>1.65 ± 0.05</td>
</tr>
<tr>
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<td>Spherical</td>
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<td>1.04</td>
<td>20</td>
<td>57</td>
<td>1.76 ± 0.15</td>
</tr>
<tr>
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<td>Spherical</td>
<td>0.2</td>
<td>1.1</td>
<td>22</td>
<td>18</td>
<td>1.74 ± 0.20</td>
</tr>
</tbody>
</table>

*Nugget % = Co/(Co + C) X 100

**pH values from the forest and transition were deleted to calculate semivariograms.

***Fractal dimension estimated from the log-log plot of semivariograms with 90% confidence interval.
long-range variation compared with the other properties and soil pH from prairie
alone (D > 1.75) where short range variability dominated.

The sill approximately equaled the total sample variance for EC, Mg, and
K, whereas the sill was greater than the sample variance for Ca, pH, Fe, and Mn.
When the sill approximately equals the sample variance, it is an indication that
there is no spatial dependence outside the range of maximum lag (Barnes, 1991;
Robertson et al., 1993). The experimental semivariograms for pH, Ca, Fe and Mn
have a cyclic appearance beyond the range (Figures 2.7a, 2.7e, 2.8c and 2.8e).
The amplitude of these cyclic appearances is similar for these soil properties with
the trough occurring at approximately 35 and 70 m. Periodicity in semivariograms
is often related to zones of influence of a given process (Burrough, 1983a).
Individual trees impart periodicities in a soil variate with a zone of influence
equivalent to the size of their canopy (Bruckner et al., 1999). The periodicities
observed in this case did not correspond to tree or shrub canopy sizes but agree
with the shortest and longest diameter of the prairies. This is in agreement with
field observation because woody invasion towards the center of the prairie was
minimal for Site 1. In their study of the spatial patterns of soil nutrients in the
Mojave Desert shrublands, Schlesinger et al. (1996) found that the autocorrelation
ranges in the distribution of cations to be larger than the mean shrub diameter
(140 ± 40 cm). They related the observed range of influence to the average size
of intershrub spaces.
Figure 2.7. Semivariogram and log-log plots of soil pH, EC, Ca and Mg for a Keiffer prairie-forest association (Site 1), Louisiana.
Figure 2.8. Semivariogram and log-log plots of soil K, Fe and Mn for a Keiffer prairie-forest association (Site 1), Louisiana.
For Site 2, the spherical model described the variability in all the soil parameters except for Mn, which showed no spatial structure at the scale studied (Figure 2.10e). Soil Ca, Fe and pH were autocorrelated over a distance of approximately 30 m while soil EC, K, and Mg had a smaller zone of influence of 20 m, 20 m, and 15 m, respectively (Table 2.3). The general relative semivariogram for soil pH was highly spatially structured with non-detectable nugget variance. When the forest and transition soil pH data were deleted, the relative nugget variance and the range of the resulting semivariogram increased to 27% of the sill, and 35 m, respectively. The increased nugget variance implies that further small-scale variation occurs within the prairie than the whole study area. The fractal dimension for soil pH remained relatively lower and similar to Site 1 soil pH. Except for Mn and Fe, which has a moderate spatial dependence, all the soil parameters have nugget to sill ratio < 25% indicating strong spatial dependence. A cyclic pattern around the sill is clearly observed for soil EC and Fe (Figures 2.9c and 2.10c). Except for pH, the D values for all the soil parameters were greater than 1.80 (Table 2.3) showing the dominance of short-range variation.

For Site 3, the spherical model explained the spatial variability of all soil properties considered (Table 2.3). Soil pH with or without forest and transition soil data were well structured with shorter range of influence (10 m) within the prairie than the entire study site (23 m). Soil EC was weakly spatially dependent with a range of 20 m (Figure 2.11c). Similar range of influence was shown by all the soil properties except Mg with a 30 m range of influence. Semivariograms of pH and
Figure 2.9. Semivariogram and log-log plots of soil pH, EC, Ca and Mg for a Keiffer prairie-forest association (Site 2), Louisiana.
Figure 2.10. Semivariogram and log-log plots of soil K, Fe and Mn for a Keiffer prairie-forest association (Site 2), Louisiana.
Ca are similar (Figures 2.11a and 2.11e), as are those of K and Fe (Figures 2.12a and 2.12c). A cyclic pattern around the sill of the experimental semivariograms is distinct for soil K, Fe, Mg, and Mn but with varying amplitudes. In almost all cases, the experimental semivariograms decrease at a lag distance of approximately 65 m. This distance approximates the average diameter of the prairie.

Figure 2.13 presents log-log plots of soil pH semivariograms after forest and transition soil pH data were deleted. A high D value (1.93) close to 2.0 for Site 1 indicates that observations are uncorrelated and the mean pH (7.78) is representative for the entire prairie. Site 2 had an intermediate D value of 1.72 while Site 3 had the smallest, D = 1.64. These decreases in D values agree with our field observation that Site 2 and 3 had the greatest woody invasion compared with Site 1. This result is consistent with the findings of Boettcher and Kalisz (1990) and Schlesinger et al. (1996) that documented the increased heterogeneity by woody plants through the creation of "islands of fertility". Schlesinger et al. (1996) and Cross and Schlesinger (1999) observed autocorrelation of soil nutrients in desert soils dominated by shrubs at a scale similar to the size of shrubs while such autocorrelation was absent for adjacent grassland soil nutrients.

Burrough (1981) found a D value of 1.5 for soil pH while Culling (1986) obtained a higher D value (1.7-1.8) for samples representing different geographic locations. Armstrong (1986) documented similarly high values of D (1.764-1.944)
Figure 2.11. Semivariogram and log-log plots of soil pH, EC, Ca and Mg for a Keiffer prairie-forest association (Site 3), Louisiana.
Figure 2.12. Semivariogram and log-log plots of soil K, Fe and Mn for a Keiffer prairie-forest association (Site 3), Louisiana.
Figure 2.13. Semivariogram and log-log plots of soil pH for three Keiffer prairie-forest associations, Louisiana, after forest and transition data were deleted.
for the spatial variability of soil surface strength. Comparing the soil D values with those of other environmental variables such as landform, river discharge, geological sediments, and climatic data, Burrough (1983a) concluded that the variation of soil chemical properties is always more irregular. He attributes the high variability to rock weathering, biological action, microrelief, cryoturbation, erosion and deposition.

The strong spatial dependence with shorter ranges for Sites 1 and 2 imply the need for a sampling scheme with frequency equivalent to the range. This has practical implication when designing any ecological studies (Dutilleul, 1993) or monitoring, since soil nutrient pattern are known to define plant distributions and the extent of gene flow between local populations (Fitter, 1982; Lechowicz and Bell, 1991; Van Auken and Bush, 1997; Fransen et al., 1998).

### 2.4.3 Kriging Analysis

**Site 1:**

The spatial continuity of relative elevation and the soil properties studied are displayed with contour maps (Figures 2.14a-h). The relative elevation decreased from north to south. There was a clear spatial relationship between EC and relative elevation. EC was lower at the upslope position and higher in the downslope position. The spatial continuity of Ca and pH relate to vegetation type; higher pH values (> 7.0) and Ca levels (40 cmolc/kg) within the prairie than the forest. Comparison of Figures 2.14a and 2.14b show the upslope positions to exhibit lower pH values than downslope topographic positions. Soil Ca levels did
not follow the same pattern. This difference might be attributed to the relative ease and direction of movement (vertical versus lateral) of Ca\(^{2+}\) and HCO\(_3^-\) Levels of Mg were lower within the prairie compared with the adjacent forest. The spatial continuity of Mg does not correspond to that of relative elevation. The spatial pattern of K was similar to that of EC with influence from topography. The micronutrients Fe and Mn exhibited similar pattern, with lower concentration within the prairie, and higher concentration within the forest. Contour plots of kriging standard deviation for each soil property and Site are given in Appendix C, D, and E. As expected, the kriging standard deviation was lowest close to the sampling transects.

Site 2:

Contour plots of the kriged estimates for relative elevation and soil parameters are given in Figures 2.15a-g. The southern section of the study site had a more complex topography with the highest and lowest observed elevations. The prairie soil had the highest EC and relates to variation in relative elevation. Soil pH had a similar pattern to EC with greater observable uniformity within the prairie than in the forest (Figure 2.15b). The levels of Ca were higher in the prairie soil with less pronounced effect from topography. Soil Mg variability was independent of topography and had a reciprocal relationship with Ca. Soil K spatial continuity resembled that of EC and appears to be controlled by topography. The contour plot for Fe shows a patchy distribution and was inversely related to soil pH spatial pattern. The patchy distribution of Fe might be a result of invading woody and herbaceous plants. Woody and herbaceous plant
Figure 2.14. Contour maps of kriged soil properties for a Keiffer prairie-forest association (Site 1), Louisiana. RE = Relative elevation. Arrows in a) show direction of water movement.
roots may release organic acids that chelate Fe, thereby increasing Fe solubility at these spots (Miles, 1987; Fisher and Binkley, 2000).

**Site 3:**

Figures 2.16a to h provide contour plots of relative elevation and the studied soil parameters. The highest relative elevation in the landscape occurs in the northeast section of the study area. At these positions, EC, pH, Ca, K, and Mn were low while Mg and Fe were highest. Field observation showed that various shrubs and cedar trees dominated the northeast section of the study area. A close resemblance of the contour plots of EC and K is apparent (Figures 2.16c and 2.16f). The pairs pH-Fe, and Ca-Mg showed reciprocal spatial relationship. For Mn, the greatest continuity occurred in the east-west direction, similar to relative elevation.

When the three sites were compared, the range of relative elevation was greatest for Site 3. Field observation showed that the degree of invasion was in the order Site 2 > Site 3 > Site 1. For all the sites, there was close spatial association between K and EC with major topographic control. The topographic dependence of K is expected since K is very mobile in soils. Soil pH within the prairie was homogeneous for Sites 1 and 2 compared with Site 3. Except for the downslope positions, soil pH can be used for delineating the prairie and evaluating invading plant influence on the soil. Fisher and Binkley (2000) relate the topographic dependence of soil pH to the downslope movement of HCO₃⁻ that is derived from high concentration of CO₂ dissolved in soil water to produce carbonic acid (H₂CO₃). The H⁺ remains adsorbed on the soil surface while the HCO₃⁻
Figure 2.15. Contour maps of kriged soil properties for a Keiffer prairie-forest association (Site 2), Louisiana. RE = Relative elevation. Arrows in a) show direction of water movement.
Figure 2.16. Contour maps of kriged soil properties for a Keiffer prairie-forest association (Site 3), Louisiana. RE = Relative elevation. Arrows in a) show direction of water movement.
leaches downslope, subsequently reacting with H⁺ in the downslope soils that lead to higher soil pH levels. A reciprocal spatial relationship was evident between the pairs pH-Fe, and Ca-Mg. Unlike K, Ca and Mg are relatively immobile in soils (Mengel and Rehm, 2000), and may therefore be less affected by topography. The same reciprocal spatial relationship was observed between pH and Mn with possible perturbation by the interaction of topography and vegetation. Soil Fe and Mn levels in well drained soils are influenced by various factors including free CaCO₃ content, pH and organic matter content (Mengel and Rehm, 1999).

2.5 Summary and Conclusion

In this chapter, the spatial dependence and scaling behavior of soil pH, EC, and Mehlich III extractable Ca, Mg, K, Fe, and Mn within three remnant prairie-forest associations in northern Louisiana were explored. The majority of these soil properties neither followed normal nor lognormal statistical distribution. EDA indicated that the data for each site represent two populations, one representing the prairie and the other the forest. The data from the transition belonged either to the prairie or the forest depending upon the topographic position and extent of woody and herbaceous plant invasion of the prairie edge.

A non-parametric test for the equality of medians among sites showed that median values for all the soil properties differed except for soil Fe and Ca. The similarity in the median Ca content among sites is a clear indication that parent material effects are prominent. Conversely, the median soil pH values were significantly different among sites, with Site 3 showing the lowest median pH. This might be a result of greater degree of invasion of Site 3 prairie by woody
plants. This is expected since soil pH is among the soil properties that quickly respond to changes in vegetation (Birkeland, 1984; Miles, 1987).

A contrasting relationship was observed among soil properties within the prairie and forest, suggesting the existence of distinct functional boundary between these two adjacent habitats. The most notable one was the positive relationship between EC and pH for the forest soil data and the lack of such relationship for the prairie soil data.

Geostatistical and fractal assessment of the soil properties allowed an explicit description of spatial variability and scaling characteristics in the context of prairie invasion by woody and herbaceous vegetation. From a soil spatial pattern perspective, the three sites shared several common features. The spherical model described the spatial variability of virtually all the soil properties considered. Except for soil Mn at Site 2, all the soil properties exhibited a spatial dependence over a range of 20-30 m. Soil pH spatial variability was well structured as evidenced by the very low relative nugget variance. Soil EC had the highest relative nugget variance and therefore was regarded to show relatively weaker spatial structure. This is attributed to either further small-scale variation that was not captured by the sampling scheme or that there was EC instrument measurement error. But considering the relatively lower relative nugget variance of other cations such as K that was shown to be highly correlated with EC, it is unlikely that the high relative nugget variance was caused by inadequate sampling distance.
When the forest soil pH data were deleted and the semivariogram reconstructed, the semivariogram parameters changed and the change was in accordance with extent of woody invasion. Site 1 had fewer numbers of plant invaders compared with Sites 2 and 3. Site 1 prairie soil pH had a smaller range of influence and higher D values (Table 2.3) whereas Sites 2 and 3 had relatively higher range of influence and lower D values. The D values were high for the other soil properties indicating the dominance of short-range variation. But for soil pH, the short-range variability emerged when the forest soil data was deleted. This might be a consequence of the interplay between parent material and vegetation effects with dominance of one over the other with a change of scale. Theoretically, D values would have remained constant but several studies (Burrough, 1981; 1983a; 1983b; Barton and Pointe, 1995; Eghbal et al., 1999; Kravchenko et al., 1999) have shown that it is not the case for most soil and other geological properties because of the complex and competing factors causing spatial patterns.

Soil pH may be used as an index to determine prairie-forest boundary for these and similar sites derived from calcareous parent material. Soil pH ≥ 7 corresponded to soil under prairie influence while soil pH < 7 delineates the forest and transition soil. Further, the range of influence of these studied soil properties and their spatial distribution can be used as a baseline in any future management and species monitoring activities.

2.6 References


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CHAPTER 3: STABLE CARBON ISOTOPE STUDY OF PRAIRIE-FOREST TRANSITION SOIL IN LOUISIANA

3.1 Introduction

Invasion of grasslands by woody plants is among the dominant changes in Earth's vegetation during the last two centuries (Archer et al., 1995; Brown and Archer, 1999). Historical and quantitative approaches have been used to document increased woody plant abundance. Historical methods in common use are photographs, diaries, personal accounts, and government or landowner land use files (Madany and West, 1983). Quantitative methods employ soil morphological properties, soil phytolith and pollen content, aerial photographs, and isotope techniques. Information obtained based upon historical methods can be subjective. Pollen and phytolith methods are reliable only under environmental conditions that favor their preservation (Ambrose and Sikes, 1991; Boutton et al., 1998). For example, alkaline conditions do not favor pollen and phytolith preservation (Boutton et al., 1998). Data obtained from pollen records have poor spatial precision because their spatial scale depends on the dispersal properties of pollen grains and plant debris and by the nature of the depositional environment (Jackson, 1997). A method based upon aerial photography suffers from computational error.

Two factors determine whether a change in past vegetation could be determined by soil properties (Birkeland, 1984). These are the time elapsed since the vegetational change and the ability of a specific soil property to persist.
relatively unchanged under the new conditions. Properties such as pH and exchangeable bases change quickly, and thus may be important for obtaining information regarding recent changes (Ugolini et al., 1981; Birkeland; 1984). The amount and distribution of organic matter with depth would persist for a longer time enabling one to decipher clues on type of former vegetation (Quideau and Bockheim, 1996).

Isotopic investigation of soil organic matter is the most accurate and spatially explicit method for reconstructing vegetation change and understanding ecosystem function and dynamics in terms of the sources, sinks, and fluxes of C and N in the soil systems. Stable isotopes record three kinds of information that can not be obtained using other approaches (Peterson and Fry, 1987; Boutton et al., 1998): i) process information that relates to the physical and chemical reactions causing the process; ii) information regarding the rates of the processes; and iii) information regarding the origin of samples in spatially explicit manner.

The natural abundance of the stable isotopes of C, N, S, and O has been successfully applied to various ecological and environmental studies. For this study the natural abundance of C and N were found relevant. While the theory behind isotope fractionation is similar for these elements, the processes causing the fractionation is unique to the individual elements. This chapter considers fractionation processes pertaining to C while that of N is reserved for Chapter 4.
3.2 Stable Isotopes of Carbon and Isotope Fractionation: Theory

3.2.1 Isotope Ratio and Its Measurement

Carbon has two stable, naturally occurring isotopes: $^{12}$C and $^{13}$C with a natural abundance of 98.89% and 1.11%, respectively. Because of their mass differences, these isotopes have slightly different chemical and physical properties. This difference results in a mass-dependent isotope fractionation effect that has important environmental significance.

For C, the absolute stable isotope ratio ($^{13}$C/$^{12}$C) is 0.0112372 (Hoefs, 1997). Measuring an absolute isotope ratio or abundance is not practical. A relative ratio is measured with reference to a standard sample, PDB (Pee Dee Belemenite) carbonate. PDB was the internal calcite structure from a fossil *Belemnitella americana* from the cretaceous Pee Dee Formation in South Carolina. Because of the small isotopic variations, isotopic ratios in samples are reported as part per thousand (per mil, $^{9}$/oo) variations. Stable isotopes are commonly expressed in delta ($\delta$) notations as (Boutton, 1991):

$$
\delta^{13}C^{(9/oo)} = \left( \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \quad [3.1]
$$

where $\delta^{13}$C is the difference (in per mil, $^{9}$/oo) between $^{13}$C/$^{12}$C ratio of the sample and that of the standard, and R is the mass 45/44 ratio of the sample or standard CO$_2$ gas. Increases in the $\delta$ value denote increases in the relative amount of the heavy isotope component ($^{13}$C) or a reciprocal decrease in the light isotope component ($^{12}$C).
3.2.2 Isotope Fractionation

The isotopes of carbon are fractionated by a variety of natural processes, including photosynthesis and isotope exchange reactions among carbon compounds. Two main processes produce isotopic fractionations: kinetic processes and isotope exchange reactions (Peterson and Fry, 1987; Hoefs, 1997). Kinetic isotope fractionations are a result of unidirectional chemical reactions. Such reaction rates are dependent upon the ratios of the masses of the isotopes and their vibrational energies. The magnitude of a kinetic isotope fractionation depends upon the reaction pathway, the reaction rate, and the relative bond energies of the bonds being broken or formed by the reaction. Isotope fractionation of this type always shows a preferential enrichment of the lighter isotope in the reaction products. Biological processes are generally unidirectional and exhibit kinetic isotope reactions. Organisms preferentially use the lighter isotopic species because of the lower energy "costs" associated with breaking the bonds in these molecules, resulting in significant fractionations between the substrate (heavier) and the biologically mediated product (lighter). Kinetic isotopic fractionations of biologically-mediated processes vary in magnitude depending on reaction rates, concentrations of products and reactants, environmental conditions, and, in the case of metabolic transformations, species of the organism (Hoefs, 1997).

The two most important soil carbon reservoirs that are subject to isotope fractionation are soil organic carbon (SOC) and carbonate C (CC). Original SOC is a result of photosynthesis. During photosynthesis isotopic fractionation occurs.
as a result of the diffusion of CO\(_2\) to the chloroplasts and carboxylation reaction. This reaction in the cells of green plants leads to a relative enrichment by approximately 4.4 \(^\circ\text{o}/\text{o}\) in the heavier isotope and depletion in the synthesized plant material because of differences in \(^{13}\text{C}\) and \(^{12}\text{C}\) diffusion rates (Peterson and Fry, 1987). Based upon their difference in the photosynthetic pathway they follow to fix C, terrestrial plants are divided into three groups: C3, C4, and Crassulacean Acid Metabolism (CAM) (Bhagwat, 1997). Species of the C3 type constitute trees, most shrubs, and cool season grasses. Warm season grasses are categorized as C4 type and represent about 50 \(\%\) of the grasses (Bender, 1968). The CAM plants fix carbon in the dark and are mainly present in desert ecosystems (Bhagwat, 1997).

C3 plants reduce CO\(_2\) to a three-carbon compound and generally exhibit \(\delta^{13}\text{C}\) values ranging from -32 \(^\circ\text{o}/\text{o}\) to -20 \(^\circ\text{o}/\text{o}\), with a mean of -27 \(^\circ\text{o}/\text{o}\). The C4 plants reduce CO\(_2\) to four-carbon compounds and show \(\delta^{13}\text{C}\) values ranging between -17 \(^\circ\text{o}/\text{o}\) and -9 \(^\circ\text{o}/\text{o}\) with a mean of -13 \(^\circ\text{o}/\text{o}\) (Boutton, 1996). CAM plants exhibit \(\delta^{13}\text{C}\) values intermediate between those of C3 and C4 plants. Both C4 and CAM plants are believed to have evolved from C3 plants under changing atmospheric conditions (Ehleringer and Monson, 1993).

C4 plants are generally capable of higher rates of CO\(_2\) uptake than are C3 plants; especially at a low intercellular CO\(_2\) concentration. Low CO\(_2\) concentrations commonly occur under the environmental conditions of high irradiance, high temperature, and water stress (Ehleringer and Monson, 1993). Geographically C4 plants occupy warmer and more arid areas. For North
America, the proportion of C4 plants increase from north to south and from east to west (Ehleringer et al., 1997; Collatz et al., 1998). Where C3 and C4 plants occur in the same ecological system, they are segregated along specific microenvironments controlled by local soil conditions and topography (Tieszen and Steuter, 1991). Barnes et al. (1983) observed that C4 plants tend to occur on nutrient poor topographic positions. Generally C4 plants are competitive under harsh environmental conditions and possess greater resource use efficiency (Ode et al., 1980; Ehleringer and Monson, 1993; Bhagwat, 1997). Ode et al. (1980) examined the temporal dynamics of C3 and C4 plants in a landscape composed of mixed prairie. A notable result from their study was the functional displacement in time of these two plant types. C4 plants were more productive in summer while C3 plants dominate in spring and fall. At a regional scale C3 versus C4 temporal dynamics depend upon the interaction between temperature and precipitation while soil conditions and topography become determining factors at the landscape scale (Barnes et al., 1983; Ehleringer et al., 1987).

3.2.3 C Isotope Signature and Vegetation Change

The systematic isotopic variation between C3 and C4 plants allows one to study plant community compositions and temporal trends. The $\delta^{13}C$ values of soil organic carbon in the upper soil profile (0-20 cm) for a given site is similar to that of the plant community at the site (Boutton, 1998). Thus, changes in the relative proportions of C3 and C4 plants can be detected by a measured difference between the isotopic composition of the current plant community and that of the soil organic matter. Isotopic signals from antecedent vegetation persist deeper in
the soil profile. Older organic matter found deeper in the soil profile has δ¹³C values that are generally 1-3 ‰ greater than those for organic carbon in the upper profile (Balesdent et al., 1987). Balesdent et al. (1987) offered three explanations as to why δ¹³C of soil organic carbon change with age (depth): i) the δ¹³C decrease in atmospheric CO₂ over the last 200 years; ii) different decay rates of organic components with differing δ¹³C; and iii) isotope fractionation within the soil caused mainly by microbial respiration.

Several studies (Balesdent et al., 1987; Amundson et al., 1988; Boutton, 1991; 1996; Wang et al., 1993; Archer, 1995; Boutton et al., 1998; Kindscher and Tieszen, 1998; Sinton, 2000) employed the C isotope technique for documenting vegetation change and understanding the C dynamics in an ecosystem where C₃ and C₄ plants coexist.

The proportion of organic carbon derived from C₄ sources in the soil samples can be estimated by a mass balance equation (Boutton, 1996):

\[ x = \frac{\delta^{13}C_{\text{soil}} - \delta^{13}C_{C_3}}{\delta^{13}C_{C_4} - \delta^{13}C_{C_3}} \]  [3.2]

Where δ¹³C_soil is the δ¹³C of soil organic matter samples, δ¹³C_C₄ is the average δ¹³C value of C₄ plants (-13 ‰ ), x is the proportion of carbon from C₄ plant sources, δ¹³C_C₃ is the average δ¹³C value of C₃ plants (-27 ‰ ). The proportion of carbon derived from C₃ plant sources is 1-x.
3.2.4 Carbonate Equilibria and Isotope Fractionation

Isotope exchange reactions occur when the reactants and products remain in contact such that reverse reactions can occur and chemical equilibrium can be established. During equilibrium reactions, the heavier isotope preferentially accumulates in the species or compound with the higher oxidation state (Hoefs, 1997). This process takes place during the dissolution and precipitation of CaCO$_3$ in an aqueous solution open to CO$_2$ gas. The equilibrium reaction is given by (Nordt et al., 1996):

\[
\text{CO}_2 (g) \leftrightarrow \text{CO}_2 (aq)
\]

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-
\]

\[
\text{CaCO}_3(\text{lithogenic}) + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-
\]

\[
\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{CO}_2(g) + \text{H}_2\text{O} + \text{CaCO}_3(\text{pedogenic})
\]

Lithogenic inorganic C is inherited from soil parent materials such as limestone and calcareous glacial outwash, eolian deposits, and alluvium (Nordt et al., 1999). Pedogenic carbonates are secondary derivatives of the parent material through the process of dissolution and precipitation. LeChatellier's principle (McQuarrie and Rock, 1991) dictates that increased CO$_2$ partial pressure and moisture favor the dissolution of CaCO$_3$. Precipitation occurs either from a reduction in soil partial pressure or from reduced moisture. Therefore, the process of carbonate precipitation is enhanced by evaporation and by removal of soil water by plants, and retarded by the maintenance of high CO$_2$ in the soil atmosphere due to respiration of roots and soil microbes. Greater accumulation of pedogenic carbonate is expected under grasses than beneath forest or...
invading shrub canopies because of reduced evaporation rates under forest than grasses.

During the dissolution of carbonates, a distinction is made between open and closed systems. In an open system, CaCO$_3$ reacts with water in contact with a gas phase of fixed CO$_2$ partial pressure. In a closed system the water first equilibrates with a CO$_2$ reservoir, is subsequently isolated from the reservoir, and finally reacts with the carbonates (Salomons and Mook, 1986). In an open system, the CO$_2$ in the equilibrium reaction originates from the atmosphere or from soil (microbial respiration and organic matter decomposition) having distinct $\delta^{13}$C values (Figure 3.1). Mermut et al. (1999) distinguish between soil CO$_2$ and soil respired CO$_2$ because of its influence on the resulting $\delta^{13}$C values of pedogenic carbonate. The surface flux of CO$_2$, which is considered a measure of the biological activity within the soil, is called soil respired CO$_2$. The CO$_2$ that remains in the soil’s atmosphere and partly dissolved in soil water is known as soil CO$_2$ (Mermut et al., 1999). Cerling et al. (1991) have shown that the carbon isotopic composition of soil CO$_2$ differs from the isotopic composition of carbon in soil-respired CO$_2$. Because of the difference in diffusion coefficients for $^{12}$CO$_2$ and $^{13}$CO$_2$, the isotopic composition of soil CO$_2$ is at least 4.4 $\%_\text{o}$ enriched relative to soil respired CO$_2$ or soil organic matter. Cerling (1991) confirmed this value for soils from North America.

Research shows that most soils behave as open systems because the flux of CO$_2$(g) is orders of magnitude greater than both the amount of dissolved carbon species in solution and the rate of carbonate dissolution or precipitation.
Figure 3.1. Relationship among δ¹³C of C3 and C4 plants, atmospheric CO₂, and pedogenic carbonate in an open soil system. D = fractionation due to diffusion (+ 4.4 ‰), and E = fractionation due to equilibria reaction (+ 10 ‰). (From Nordt et al., 1996)
(Cerling, 1984; McFadden et al., 1991). Under such conditions, pedogenic carbonate precipitates in isotopic equilibrium with soil CO$_2$(g) where dissolving parent carbonate has no influence on the stable C isotope composition of HCO$_3^-$ or the precipitating carbonate (Cerling, 1984).

If the rate of soil respiration is high, soil CO$_2$ can have nearly the same $\delta^{13}C$ values as the plants and organic matter derived from them (Cerling, 1984). Vogel (1970), and Broecker and Olsson (1961) observed a $\delta^{13}C$ value of -23.4 °/oo and -24.9 °/oo for CO$_2$ above soil in temperate forests (cited in Salomons and Mook, 1986). Direct determination of the CO$_2$ in the soil atmosphere show a range of $\delta^{13}C$ values from -10 to -28 °/oo depending on whether C3 or C4 vegetation dominates (Deines, 1980). In areas of very low biological activity, atmospheric CO$_2$ ($\delta^{13}C$ of -6 to -7 °/oo) diffuses down into the profile, causing the $\delta^{13}C$ of the soil CO$_2$ to be much greater than that of the plants (Pendall and Amundson, 1990).

By employing the theory of molecular diffusion, Cerling (1984) developed a one dimensional steady state model to predict the $\delta^{13}C$ of soil CO$_2$ with depth. Nordt et al. (1996) summarize important results from this model as follows: i) soil CO$_2$ is always enriched in $^{13}C$ relative to soil respired CO$_2$ because of molecular diffusion and atmospheric mixing; ii) $\delta^{13}C$ values are 4 to 5 °/oo greater for soil CO$_2$ below a depth of 20 cm than for soil respired CO$_2$ even in soils with high CO$_2$ production rates (>4 mmol m$^{-2}$ hr$^{-1}$); iii) soils with high CO$_2$ production rates show minimal isotopic gradient below 20 cm because of reduced atmospheric mixing below that depth; iv) soils with low CO$_2$ production rates show a measurable
isotopic gradient to a depth of at least 50 cm because of atmospheric mixing; and
v) the boundary conditions imposed produce a $\delta^{13}C$ range for soil CO$_2$ of between
-22.6 $\%$ (with no atmospheric mixing) and -8 $\%$ (when in equilibrium with the
present day atmosphere).

Lithogenic inorganic C has $\delta^{13}C$ value of approximately 0 $\%$ (Hoefs, 1997;
West et al., 1988) whereas pedogenic inorganic C has $\delta^{13}C$ values ranging from
+3 to -10 $\%$. The sources of CO$_2$ largely determine the $\delta^{13}C$ values of pedogenic
carbonate (Figure 3.1). Carbonate reprecipitation under the influence of
atmospheric CO$_2$ ($\delta^{13}C = -7 $ $\%$) would give a $\delta^{13}C$ value of about +3 $\%$, a slight
enrichment with respect to the parent carbonate. If the CO$_2$ is derived from the
decay of C4 vegetation, the pedogenic carbonate gives a $\delta^{13}C$ signal of -2 $\%$.
Pedogenic carbonate formed under C3 vegetation has $\delta^{13}C$ value of about -7 $\%$.
In general, the following relationship is used to estimate the $\delta^{13}C$ value of
pedogenic carbonate end-member (Nordt et al, 1998):

$$\delta^{13}C_{\text{pedogenic carbonate}} = \delta^{13}C_{\text{SOM}} + \Delta_{\text{CO}_2\text{ diffusion}} + \Delta_{\text{CO}_2\text{-CaCO}_3}$$  \[3.3\]

Where $\delta^{13}C_{\text{SOM}}$ is measured from soil organic matter, $\Delta_{\text{CO}_2\text{ diffusion}}$ is the $\delta^{13}C$
difference between $^{12}$CO$_2$ and $^{13}$CO$_2$, and $\Delta_{\text{CO}_2\text{-CaCO}_3}$ is the $\delta^{13}C$ difference
between C in carbonate and CO$_2$ occurring during equilibrium reactions. Equation
3.2 ensures that the $\delta^{13}C$ values of pedogenic carbonate differ predictably from
the parent carbonate and provides evidence for carbonate pedogenesis.

When theoretical values for fractionation due to diffusion effect ($\Delta_{\text{CO}_2\text{ diffusion}}$
= 4.4 $\%$) and CO$_2$-CaCO$_3$ equilibrium effect ($\Delta_{\text{CO}_2\text{-CaCO}_3} = 12 \%$ at 0 °C and 9 $\%$
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at 25 °C) are used, the expected δ13C difference between pedogenic carbonate and SOM ranges between 13.4 ‰ and 16.4 ‰. Deviations from these theoretical values were reported in the literature (Rabenhorst et al., 1984; Wang and Anderson, 1998) and these deviations were related to local conditions.

The turnover rate for carbonate (~1000 yrs) is slower than that of the bulk SOM. Because of the relationship between δ13C of SOM and that of carbonate, a change of C4 and C3 plants within an ecosystem in the past can also be detected using the δ13C of soil carbonate (Wang et al., 1993). Pedogenic carbonate exists in the field either as nodules, pendants, and laminar coatings or as disseminated forms. Many grassland soils possess carbonates of the later type making their field identification very difficult (Kelly et al., 1991; Nordt et al., 1998). The use of δ13C values not only facilitate to distinguish pedogenic carbonate from lithogenic carbonate but also to estimate the relative proportion of each within a soil using simple mass balance equation (Salomons and Mook, 1976):

\[
\text{% pedogenic carbonate} = \left( \frac{\delta^{13}C_{\text{soil}} - \delta^{13}C_{\text{parent}}}{\delta^{13}C_{\text{pedogenic}} - \delta^{13}C_{\text{parent}}} \right) \times 100
\]

where \( \delta^{13}C_{\text{soil}} \) is the \( \delta^{13}C \) of the bulk soil; \( \delta^{13}C_{\text{pedogenic}} \) is the \( \delta^{13}C \) of pedogenic carbonates separated from the soil as nodules; and \( \delta^{13}C_{\text{parent}} \) is the \( \delta^{13}C \) value of the parent rock. The bulk soil carbonate is a mixture of parent and pedogenic carbonate components.

This approach has been found powerful to understand and quantify the rates of soil carbonate weathering, C sequestration, and as indicators of vegetation and climate change (Salomons and Mook, 1976; Cerling, 1984; Kelly
et al., 1991; Wang et al., 1993; Nordt et al., 1998; Khademi and Mermut, 1999). Nordt et al. (1998) compared the isotopic method with other quantitative methods such as binocular light microscope point counts, thin-section point counts, and quantitative estimates conducted by field morphology and found the isotopic method to be superior.

The objectives of this study were: to reconstruct the vegetation history of the Keiffer prairies, Louisiana, using the natural abundance of C isotope; to document the proportion of C3 and C4 plants within the prairie; and to investigate carbonate pedogenesis.

3.3 Materials and Methods

3.3.1 Description of Study Area

The study was conducted within the Winn Ranger District of the Kitsatchie National Forest, Winn Parish, Louisiana. The dominant remnant prairies of Louisiana, also known as the Keiffer calcareous prairie/forest complex, consist of a series of natural grassland openings occurring in a mosaic with calcareous hardwood-pine forest (Smith et al., 1989).

The Keiffer calcareous prairie/forest complex has developed on Eocene-age marly clays of the Tertiary period (Smith et al., 1989). The sediments belong to the Jackson group (Spearing, 1995). The Keiffer prairies occur on Keiffer loam soil that has CaCO₃ throughout the profile. The CaCO₃ was formed from the remains of marine life forms (USDA, 1998). Taxonomically, the soil is classified as fine-silty, carbonatic, thermic Rendolic Eutrochrepts. Immediately adjacent to the prairies are soils of the calcareous forests dominated by Hollywood (fine,
montmorillonitic, thermic Typic Pelluderts) and Oktibbeha (very-fine, montmorillonitic, thermic Vertc Hapludalfs) soils. Vaiden (very-fine, montmorillonitic, thermic Vertc Hapludalfs) and Bellwood (very-fine, montmorillonitic, thermic Aquentic Chromuderts) soils also occur adjacent to the prairies. All of the prairies have been heavily grazed and a few were farmed for short periods (Smith et al., 1989). Sites chosen for this study have not been farmed. The sites have not been burned in a long time and are invaded by eastern red cedar and other herbaceous and woody plants. The sites receive mean annual precipitation of 1250 mm and have a mean annual air temperature of 20 °C.

3.3.2 Field Methods

Soil samples were collected from each site using a push probe at 10 cm increments to a depth of 1 m. Two sets of samples were collected from each of prairie, transition, and forest, each representing contrasting slope positions (Figure 3.2). Carbonate nodules were sampled separately to obtain $\delta^{13}C$ of pedogenic carbonate. Rock fragments and carbonate samples from the lower portion of the profiles from each site were collected to obtain $\delta^{13}C$ estimate for the parent material (lithogenic carbonate). For stable C isotope analysis, plant specimens were collected from the prairie, transition, and forest using a 1 m x 1 m quadrat in the prairie, and 5 m x 5 m quadrat in the transition and forest.
3.3.3 Laboratory Methods

All soil samples were air dried for several weeks and ground to pass a 2 mm sieve. Soil samples from each depth were divided into two portions. One portion was used for the analysis of soil organic matter (SOM) $\delta^{13}C$ and the second for the carbonate $\delta^{13}C$. Samples for SOM $\delta^{13}C$ analysis were treated with 1 N HCl at 25 °C for three days to remove carbonate C. Samples for carbonate $\delta^{13}C$ analysis were treated with 5 % NaOCl solution for three days to remove organic matter (Boutton, 1991). Each set of samples was washed with distilled water to neutrality, to remove excess chloride, dried, and pulverized with a ball mill. SOM $\delta^{13}C$ was measured using Thermal Ionization Mass Spectrometer (Finnigan MAT 262). Duplicate measurement of the same sample was within the error range of the instrument ($\pm 0.2$). All the $\delta^{13}C$ values are reported relative to the international standard Pee Dee Belemnite (PDB).

Organic C and inorganic C were analyzed with a CHN analyzer (EA 1108 Elemental Analysis, Fison Instruments). The mineralogy of the carbonates was identified by X-ray diffraction (XRD) analysis. Oriented sample slides were prepared by spreading the ground samples on a glass slide. The analysis was carried out with a Siemens D5000 diffractometer using CuK$\alpha$ (40 KV, 30 mA) at a scanning speed of 1° /50 sec and a sampling step of 0.02°.

3.3.4 Data Analysis

The data were analyzed as a split-split plot design using the PROC MIXED procedure of SAS (SAS Institute, 1999). The split-split plot design was used
Figure 3.2. Idealized schematic showing an isolated prairie enclosed by forest. The transition is composed of eastern red cedar and various shrubs. The transition range from approximately 10 m in the upslope position to 15 m at the downslope position. Stars show push probe sampling locations.
because of the randomization restriction associated with this type of study. The statistical model used was:

\[ y_{ijkl} = \mu + \alpha_i + \beta_j + e_i^A + \gamma_k + (\beta \gamma)_{jk} + e_{ijk}^B + \delta_l + (\beta \delta)_{jl} + (\gamma \delta)_{kl} + (\beta \gamma \delta)_{jkl} + e_{ijkl}^C \]

where \( \mu \) is the overall mean of a given soil property, \( \alpha_i \) is the random block (site) effect, \( \beta_j \) is the vegetation (main plot) effect, \( \gamma_k \) is the landscape position (subplot) effect, and \( \delta_l \) is the depth (sub-subplot) effect. Thus, site*vegetation \( (e_i^A) \) was the error term used for testing the main effect of vegetation, site*vegetation*landscape position \( (e_{ijk}^B) \) was the error term used for testing the effects of landscape position and vegetation x landscape position interaction. Site was considered random because the selected sites would represent other Keiffer prairies in Louisiana. Smith et al. (1989) reported the presence of 45 Keiffer prairies.

The LSMEANS option was used to separate main effects of vegetation; and where soil depth*vegetation interaction was significant, the SLICE option was used to compare soil depth for each vegetation type and vice versa. The SLICE option evaluates the simple effects of vegetation at each depth, and the simple effects of depth for each vegetation (Littell et al., 1996). This is useful since I wish to investigate the impact of recent vegetation on soil properties at each depth. The proportion of organic carbon derived from C4 sources in the soil samples was estimated using equation 3.2 while equation 3.4 was used to estimate the proportion of pedogenic carbonate at each depth.
3.4 Results and Discussion

3.4.1 Soil Organic C (SOC) and $\delta^{13}$C of SOM and Plants

There was no significant difference in SOC content due to vegetation and landscape position (Table 3.1). Figure 3.3 shows the vertical distribution of SOC for the three vegetation types. Mean SOC within the 0-10 cm depth was slightly higher for the forest (3.55 % by weight), followed by transition (3.35 %), and the prairie (3.16 %). Statistical significance was observed with depth for SOC but no vegetation by depth interaction was revealed indicating that the vertical distribution of SOC is similar among the three vegetation types. Other studies (Vitousek et al., 1987; Boutton and Archer, 1998; San Jose et al., 1998; Gill and Burke, 1999) showed increased SOC following woody invasion. Vitousek et al. (1987) attribute the increased SOC to N-fixing capability of the invading plant where the additional N increased net primary production. The lack of significant increase in SOC at the transition where the vegetation is exclusively invasive suggests that these woody and herbaceous vegetation may not be N-fixing.

There was significant depth effect of $\delta^{13}$C of SOM (Table 3.1). Vegetation (p value = 0.08) and vegetation X depth effects (p value = 0.09) were marginally significant. Since there was no significant difference in $\delta^{13}$C of SOM from the two topographic positions, the values were pooled together for plotting and discussion purposes.

The mean $\delta^{13}$C of SOM within the 0-10 cm depth of the forest soil was -25.9 \(^\circ\)oo (Figure 3.4). The values increased to -18.6 \(^\circ\)oo at the 40-50 cm depth and decreased to -22.2 \(^\circ\)oo at a depth of 80-90 cm. The mean $\delta^{13}$C of SOM
within 0-10 cm depth of the prairie soil was -19.7 °/oo. The value increased to -16.5 °/oo at a depth of 30-40 cm and decreased to -20.0 °/oo at 80-90 cm depth. As expected, the vertical distribution of δ¹³C of SOM at transition lies between that of the forest and the prairie (Figure 3.4). The mean values were -22.1 °/oo at 0-10 cm depth, increased to -17.5 °/oo up to the 40-50 cm depth and decreased to -20.9 °/oo at the depth of 90-100 cm. The increase with depth of SOM δ¹³C is a common trend (Balesdent et al., 1990; Kindscher and Tieszen, 1998; Boutton et al., 1999). The increasing age and degree of decay of organic carbon partly explain this enrichment in the heavier isotope with depth. Because organic matter migrates downwards as it decays, the relative proportion of old carbon increases with depth and thus is larger in the subsoil compared to the surface (Balesdent et al., 1990).

The δ¹³C of above ground plant samples gave a value of -28.9 ± 0.2 °/oo (Mean ± 1SD, n = 6) for the forest, -28.0 ± 0.7 °/oo for the transition, and -27.0 ± 1.1 °/oo for the prairie for samples collected in late March 2000. Plant samples were re-sampled in late August 2000 and δ¹³C value of -22.6 ± 1.9 °/oo was observed for the prairie while there was no change for the forest and transition zones. Similar to this observation, Ode et al. (1980) and Tieszen and Steuter (1991) documented a variation in δ¹³C values from around -26 °/oo in early spring to around -20 °/oo in late summer for the Ordway Prairie, north-central South Dakota. This shows that prairie SOM δ¹³C is a time integrated signal and provides evidence on the temporal C3 and C4 community dynamics where these plant communities co-exist.
Table 3.1. Analysis of variance table showing the effect of vegetation (VEGE), landscape position (LSPN), soil depth (DEPTH) and interaction terms on δ¹³C of SOM, δ¹³C of soil carbonate, organic C (OC) content and carbonate C (CC) from three Keiffer prairie-forest associations, Louisiana.

<table>
<thead>
<tr>
<th>Effect</th>
<th>DF</th>
<th>δ¹³C (SOM)</th>
<th>δ¹³C (CC)</th>
<th>OC</th>
<th>CC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Pr &gt; F)</td>
<td>(Pr &gt; F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VEGE</td>
<td>2</td>
<td>4.98[0.08]</td>
<td>1.45[0.28]</td>
<td>0.31[0.74]</td>
<td>2.25[0.22]</td>
</tr>
<tr>
<td>LSPN</td>
<td>1</td>
<td>0.11[0.75]</td>
<td>0.02[0.90]</td>
<td>0[0.95]</td>
<td>2.02[0.30]</td>
</tr>
<tr>
<td>DEPTH</td>
<td>9</td>
<td>9.45[&lt;0.001]</td>
<td>10.00[&lt;0.001]</td>
<td>86.2[&lt;0.001]</td>
<td>11.5[&lt;0.001]</td>
</tr>
<tr>
<td>VEGE*LSPN</td>
<td>2</td>
<td>0.56[0.59]</td>
<td>0.03[0.96]</td>
<td>0.11[0.90]</td>
<td>1.99[0.21]</td>
</tr>
<tr>
<td>VEGE*DEPTH</td>
<td>18</td>
<td>1.53[0.09]</td>
<td>0.83[0.64]</td>
<td>0.98[0.48]</td>
<td>0.91[0.57]</td>
</tr>
<tr>
<td>VEGE<em>LSPN</em>DEPTH</td>
<td>27</td>
<td>0.48[0.98]</td>
<td>0.29[0.99]</td>
<td>0.73[0.83]</td>
<td>0.92[0.58]</td>
</tr>
</tbody>
</table>
Figure 3.3. Vertical distribution of Soil Organic C (SOC) of prairie, transition and forest vegetation in Keiffer prairies, Louisiana. Error bars represent standard error from three sites and two topographic positions that did not differ statistically.
Figure 3.4. $\delta^{13}$C values of plant, soil organic matter (filled symbols), and carbonate (blank symbols) of prairie, transition and forest vegetation in Keiffer prairies, Louisiana. Error bars represent standard error from three sites and two topographic position that did not differ statistically. Plant $\delta^{13}$C from prairie represent two seasonal values.
The 0-10 cm SOM was enriched with the heavier isotope ($^{13}$C) relative to the plant samples by approximately 3 °/oo for the forest, 6 °/oo for the transition, and an average of 5.1 °/oo for the prairie considering the seasonal differences. These differences are a consequence of several factors including differences in $\delta^{13}$C of plant parts, litter chemistry, and decomposition rates among plant species. Generally, leaves are depleted in the heavier isotope compared to roots (von Fischer and Tieszen, 1995). Litter derived from trees and shrubs contains high concentrations of lignin and secondary compounds that retard decomposition rates (Wedin et al., 1995). von Fischer and Tieszen (1995) reported that cellulose was enriched an average of 1.3 °/oo while lignin was depleted by approximately similar amount for four forest types in Luquillo, Puerto Rico. Wedin et al. (1995) analyzed changes in the isotopic composition of aboveground and belowground plant tissues of C3 and C4 grass species and associated changes in lignin concentration and isotopic composition during decomposition. Lignin fractions were consistently depleted in $^{13}$C compared to bulk tissues (3.6 parts °/oo more negative on average). The large enrichment observed for this study may be a result of any combination of: i) greater contribution of roots to the SOM within the prairie and transition compared with the forest; ii) selective preservation of cellulose and other enriched components within the soil; iii) isotope fractionation by decomposer organisms, and iv) the isotopic depletion of atmospheric CO$_2$, approximately 1.5 °/oo in the last two centuries (Balesdent et al., 1990; von Fischer and Tieszen, 1995; Boutton, 1996). The greater contribution of roots to the SOM within the prairie and transition compared with the forest is consistent with the...
result from a study by Gill and Jackson (2000) where they showed greater root turnover rates for shrubs and grasses compared with forests.

Figure 3.5 presents relative mean $\delta^{13}$C enrichment ($\Delta\delta$) with depth with reference to $\delta^{13}$C at 0-10 cm depth for SOM derived from the prairie, transition, and forest. The maximum enrichment that can be obtained due to a combination of recent atmospheric $^{13}$C depletion (1.5 °/oo) and isotope fractionation by decomposer organisms (1.0 °/oo in the upper profile and 3.0 °/oo at maximum depth) was estimated to vary between 2.5 °/oo in the upper profile and 4.5 °/oo at maximum depth. Further enrichment was interpreted as the occurrence of major vegetation shift, in this case the predominance in the past of C4 vegetation.

The approximate proportion of soil organic C sources at each depth within prairie, transition, and forest is presented in Figure 3.6. The isotope signal observed for the forest soil in the upper 10 cm depth was typical of C3 predominant communities. For the prairie, approximately 52 % of the SOM within the 0-10 cm depth was derived from C4 vegetation, while for the transition, the C4 contribution was 35 %. The proportion of C4 contribution increased with depth reaching approximately 75 % at the 30-40 cm depth for the prairie, 65 % for the transition, and 60 % for the forest at the 40-50 cm depth. Below 40-50 cm depth, the prairie, transition, and forest were similar in vegetation composition with a slight decrease in C4 contribution to a depth of 80-90 cm. The statistical test from the SLICES option for the vegetation X depth effect ($p = 0.09$) on SOM $\delta^{13}$C gave significant differences among vegetation types only for the 0-10 cm, 10-20 cm, 20-30 cm, and 30-40 cm depths (Table 3.2). This indicates that the invasion
of C3 trees and shrubs at the transition may not be a recent phenomenon because recent vegetation changes would have been restricted to the upper soil layer.

The SOM in the upper 10 cm layer is indicative of a recent vegetation, approximately 200 years (Boutton, 1996). Kindscher and Tieszen (1998) suggested that based upon their study of native prairies of northeast Kansas, the carbon isotopic signal at a depth around 25 cm is representative of an undisturbed prairie signal with the assumption that turnover at this depth is slower than that near the surface. Given the climatic differences between Kansas and Louisiana, I expect the turnover rate to be higher within Louisiana prairies. If Kindscher and Tieszen's (1998) suggestion is correct, the carbon isotope signal at a depth of 40-50 cm may represent an undisturbed prairie signal for the Keiffer prairies. This depth is also where δ¹³C values of the prairie, transition, and forest converge suggesting that in the past the forest site may have been dominated by C4 vegetation. This depth may also be indicative of middle Holocene (6000 - 4500 yr B. P.) climatic conditions. Radiocarbon data for SOM from central Texas (Nordt et al., 1994) revealed the prevalence of maximum temperatures and minimum precipitation and therefore greater productivity of C4 plants during the middle Holocene. Humphrey and Ferring (1994) used similar methods to obtain evidence for more humid early Holocene (greater C3 productivity), drier middle Holocene similar to the results of Nordt et al. (1994), and more humid early Holocene for north-central Texas. These historic climatic fluctuations determine the C3/C4
Figure 3.5. Mean $\delta^{13}C$ enrichment relative to the 0-10 cm depth of SOM derived from prairie, transition, and forest vegetation in Keiffer prairies, Louisiana. The broken line show approximate enrichment caused by a combination of $\delta^{13}C$ decrease (1.5 $^\circ/oo$) of atmospheric CO$_2$ over the last two centuries and isotope fractionation due to decomposer organisms (1.0 $^\circ/oo$ at the upper profile and 3.0 $^\circ/oo$ at maximum depth).
Figure 3.6. Approximate proportion of soil organic carbon derived from C4 vegetation within prairie, transition, and forest in Keiffer prairies, Louisiana.
productivity (Ehleringer, 1997) and therefore partly explain the fluctuation with depth of the carbon isotope signature of SOM.

3.4.2 Carbonate Mineral Identification

Mineralogical analysis by XRD of the soil samples from selected depths and from the three sites indicated that calcite with a major peak at 0.303 nm is the dominant component (Figures 3.7, 3.8, 3.9). A quartz peak (0.334 nm), generally less intense than the calcite one, is present in most XRD patterns, thus confirming that quartz is the second most abundant mineral. The parent material from Site 1 clearly exhibits a siderite peak with a d-value of 0.279 nm. Although field observations suggested the presence of siderite higher in the profile, no siderite was detected by XRD methods. No Mg bearing carbonates could be detected by XRD.

3.4.3 Soil Carbonate Content and $\delta^{13}$C of Carbonate C

The Keiffer soil has a calcic B-horizon and exhibits a general profile horizonation of A/Bk/Bkss. The calcic horizon is defined by the NRCS as "an illuvial horizon in which secondary calcium carbonate, or other carbonates have accumulated to a significant extent" (Soil Survey Staff, 1998). Calcic horizons must be $\geq 15$ cm thick, neither indurated nor cemented, $\geq 15\%$ CaCO$_3$ by weight, and either $\geq 5\%$ CaCO$_3$ by weight than the underlying horizon or $\geq 5\%$ secondary carbonates by volume (Soil Survey Staff, 1998).

Field observation revealed the presence of various sizes of carbonate nodules throughout the profile. Nodules are considered the most robust form of
Table 3.2. Simple effects of vegetation on the $\delta^{13}$C of SOM at each depth as evaluated by the SLICE option of SAS.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>F</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>8.7</td>
<td>0.0031</td>
</tr>
<tr>
<td>10-20</td>
<td>7.2</td>
<td>0.0066</td>
</tr>
<tr>
<td>20-30</td>
<td>5.4</td>
<td>0.0154</td>
</tr>
<tr>
<td>30-40</td>
<td>4.2</td>
<td>0.0367</td>
</tr>
<tr>
<td>40-50</td>
<td>0.6</td>
<td>0.5652</td>
</tr>
<tr>
<td>50-60</td>
<td>1.4</td>
<td>0.2757</td>
</tr>
<tr>
<td>60-70</td>
<td>1.4</td>
<td>0.2748</td>
</tr>
<tr>
<td>70-80</td>
<td>0.5</td>
<td>0.6297</td>
</tr>
<tr>
<td>80-90</td>
<td>1.6</td>
<td>0.2210</td>
</tr>
<tr>
<td>90-100</td>
<td>1.5</td>
<td>0.2521</td>
</tr>
</tbody>
</table>
pedogenic carbonate, because they typically are not influenced by parent material, ground water or soil age (Birkeland, 1984; Pal et al., 1999).

The carbonate content at each depth was estimated by multiplying the carbonate C content of the respective depth by 100/12 (formula weight of CaCO₃ divided by atomic weight of C) assuming that CaCO₃ was the dominant source of inorganic C. The upper 0-20 cm depth of the forest soil contained very low amounts of carbonate and was not determined. Below 20 cm depth, the carbonate content in the forest soil ranged between 17 and 49 %. The carbonate content of the prairie soil was within the range of 32-65 % while the transition had values ranging from 22-55 % (Table 3.3). There was no statistical difference in carbonate content due to vegetation and landscape position whereas significant effect was observed due to depth (Table 3.1). West et al. (1988) found that topographic effects are much less pronounced if the parent material is calcareous.

Similar to soil carbonate content, only depth influenced (p < 0.0001) δ¹³C of carbonate C (Table 3.1). Figure 3.10 shows the relationship between mean δ¹³C values of organic matter and carbonate. The pedogenic carbonate zone was obtained by a 14-16 ‰ increase in δ¹³C relative to that of soil organic matter. Pedogenic carbonate formed under an exclusively C₃ vegetation is expected to exhibit δ¹³C values ranging between -13 ‰ and -11 ‰; whereas δ¹³C values between 1 ‰ to 3 ‰ is expected for pedogenic carbonate formed under C₄ vegetation (Cerling, 1984). The pedogenic zone for the studied samples were calculated based on profile mean δ¹³C value and was approximated at -20 ‰. A 14-16 ‰ offset gives values within the range -6 ‰ and -4 ‰. The mean δ¹³C of
Figure 3.7. X-ray diffraction patterns of soil carbonate samples from Site 1, Keiffer prairie, Louisiana.
Figure 3.8. X-ray diffraction patterns of soil carbonate samples from Site 2, Keiffer prairie, Louisiana.
Figure 3.9. X-ray diffraction patterns of soil carbonate samples from Site 3, Keiffer prairie, Louisiana.
carbonate nodules fall within this pedogenic zone. This indicates that the pedogenic carbonate were formed in equilibrium with soil CO$_2$ produced from a mixture of C3 (57 %) and C4 (43 %) vegetation. The observed $\delta^{13}C$ increase with depth and the relatively more negative $\delta^{13}C$ values at the shallower depth is characteristic of high respiration soils where the effect of atmospheric CO$_2$ on carbonate equilibria was low. Estimate of CO$_2$ production for these soils using the equation proposed by Raich and Schlesinger (1992) gave a value of approximately 7.7 mmol CO$_2$ m$^{-2}$ h$^{-1}$. The equation is based on a positive linear relationship between soil respiration rate as a dependent variable and mean annual temperature and mean annual precipitation as independent variables. The estimated respiration rate is considered high (Nordt et al., 1998) and confirms the observed $\delta^{13}C$ pattern.

The $\delta^{13}C$ of the parent material gave a mean value of -4.6 $\%_o$. Carbonate parent material of marine origin of Cambrian to Tertiary age is expected to have $\delta^{13}C$ values within the range of -2 to $+2 \%_o$ (Salomons and Mook, 1976; Faure, 1977). Pendall and Amundson (1990) obtained $\delta^{13}C$ of -3.83 $\pm$ 0.35 $\%_o$ for carbonate parent material from the Punjab, Pakistan, while Kelly et al. (1991) reported $\delta^{13}C$ of carbonate parent material ranging between -4 and -5 $\%_o$ for Holocene grassland soils of the northern Great Plains of the USA. These authors attributed the more negative $\delta^{13}C$ values to preweathering of the carbonate prior to deposition. Estimated pedogenic carbonate is presented in Table 3.3. The carbonate within the upper 0-40 cm is exclusively pedogenic and decreased with depth suggesting that it had undergone several dissolution and precipitation.
Table 3.3. $\delta^{13}$C of Carbonate C, carbonate content and proportion of carbonate that is pedogenic in forest, transition, and prairie soils of Keiffer prairies, Louisiana.

<table>
<thead>
<tr>
<th>Vegetation</th>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>$\delta^{13}$C-Carbonate ($^{\circ}/_{oo}$)</th>
<th>Carbonate °</th>
<th>Pedogenic* %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest</td>
<td>A</td>
<td>0-10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Bw</td>
<td>20-30</td>
<td>-6.56</td>
<td>17</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Bk1</td>
<td>30-40</td>
<td>-5.91</td>
<td>34</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40-50</td>
<td>-5.25</td>
<td>41</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>Bk2</td>
<td>50-60</td>
<td>-5.12</td>
<td>36</td>
<td>56</td>
</tr>
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<td></td>
<td></td>
<td>70-80</td>
<td>-4.23</td>
<td>47</td>
<td>0</td>
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<td></td>
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<td></td>
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<td>-4.51</td>
<td>48</td>
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<tr>
<td>Transition</td>
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</tr>
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<td>Bw</td>
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<td>30</td>
<td>100</td>
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<td>55</td>
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<td>-5.15</td>
<td>45</td>
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<td></td>
<td>Bkss</td>
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<td>-4.22</td>
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<td>0-10</td>
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<td></td>
<td>Bw</td>
<td>10-20</td>
<td>-7.16</td>
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<td></td>
<td>Bk1</td>
<td>20-30</td>
<td>-6.59</td>
<td>41</td>
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<td>30-40</td>
<td>-5.71</td>
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<td>Bk2</td>
<td>40-50</td>
<td>-5.42</td>
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<td>50-60</td>
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<td></td>
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<td>-5.17</td>
<td>44</td>
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*Mean measured $\delta^{13}$C of parent carbonate from three sites = $-4.64 \pm 0.9$ (n = 3), and of carbonate nodules = $-5.5 \pm 1.0$ (n = 6).
Figure 3.10. Mean $\delta^{13}C$ values of organic matter and carbonate from three Keiffer prairie-forest associations, Louisiana. The solid line is the profile mean $\delta^{13}C$ value. The pedogenic carbonate zone was obtained by a 14-16 $^\infty/_{oo}$ increase in $\delta^{13}C$ relative to that of soil organic matter.
cycles. Dissolution is favored in horizons higher in the profile because of the relatively higher CO$_2$ partial pressure.

Chadwick and Graham (2000) consider a mechanism of carbonate precipitation in a well-drained soil where water flux is downward. In well drained soils organic matter decomposition in the A horizon produces a high CO$_2$ partial pressure. The high CO$_2$ partial pressure yields a relatively large amount of CO$_2$ dissolved in soil solution, producing HCO$_3^-$ and Ca$^{2+}$ and HCO$_3^-$ are transported with soil water to a depth at which calcite precipitates (Bk horizon). According to Chadwick and Graham (2000), this depth is determined by decreased CO$_2$ partial pressure below the zone of major biological activity and by the soil solution being concentrated as it enters the dry subsoil and is depleted by evapotranspiration. Field observation at these study sites showed that the prairie soils get saturated with water occasionally during the rainy season while soil cracks at the surface were common during the dry season. This indicates that the high clay content in the Bkss horizon may be retarding the vertical movement of water thereby providing time for the carbonate dissolution process to start, reach equilibrium, and finally precipitate as it dries out. In general, the depth to carbonate precipitation is smaller within the prairie soil compared with the forest suggesting greater leaching within the forest than the prairie. In grassland soils, evaporation is the major mechanism for water loss while leaching dominates in forest soils because of the canopy effect (Fisher and Binkley, 2000).

If the morphological classification developed by Birkeland (1984) is applied, this calcareous prairie soil would be placed in stage II. Stage II means that few to
common nodules exist and constitutes about 10-15 % CaCO₃ in whole sample and 15-75 % in nodules. This morphological classification is based on six stages each reflecting a distinct evolutionary pedogenic carbonate development. At the earliest stage, calcite precipitates as filaments in root pores, then as soft masses. At the later stage, formation of petrocalcic horizon (stages IV or greater) ensues with eventual plugging of the horizon with carbonate (50-75 % carbonate).

3.5 Summary and Conclusion

This study explored the carbonate mineralogy, the vertical distribution of soil carbonate, SOC, and the δ¹³C from SOM and soil carbonate from three remnant calcareous isolated prairies enclosed by forest in north-central Louisiana.

SOC varied with depth but variation due to vegetation and landscape position were not statistically significant. Mean SOC at the 0-10 cm was 3.6 ± 0.7 for the forest soil, 3.4 ± 0.3 for the transition soil, and 3.2 ± 0.3 for the prairie soil. The δ¹³C values of SOM with soil depth served as a signal of the temporal vegetation dynamics. The mean δ¹³C of SOM within 0-10 cm depth was -25.9 ± 0.9 °/oo for the forest soil, -22.1 ± 3.0 °/oo for the transition soil, and -19.7 ± 3.2 °/oo for the prairie soil. Live leaf samples gave values of -28.9 ± 0.6 °/oo for the forest, -28.0 ± 1.1 for the transition, and two seasonal values for the prairie, -27.0 ± 1.7 °/oo in spring and -22.6 ± 2.6 °/oo in the fall. These δ¹³C signatures show that while the forest is exclusively C3, the transition and the prairie are composed of a mixture of C3 and C4 plant functional forms. The C4 contribution to the 0-10 cm SOM pool within the prairie was 52 % whereas C4 contribution to the SOM at a similar depth was lower (35 %) in the transition soil. The δ¹³C of SOM increased
with depth with proportional increase in C4 productivity for each vegetation, and almost converged at a depth of 40-50 cm. The observation that the isotope signature spacing of prairie-transition and forest-transition up to the of 40-50 cm depth suggest that the transition has been stable for some centuries. This depth was also indicative that the entire site was occupied by a predominantly C4 vegetation. This interpretation agrees with radio isotopic data from central Texas that revealed conditions of maximum temperatures and minimum precipitation favoring the expansion of C4 vegetation during the middle Holocene, 6000 - 4500 yr B. P. A radio isotopic dating of SOM sample from the 40-50 cm depth would provide the age of the plant remains that might be equivalent to the time of major vegetation shift.

The soil carbonate was calcite and was predominantly pedogenic. In general, the proportion of soil carbonate was greater in the prairie compared with the forest. A good agreement was found between $\delta^{13}C$ of SOM and soil carbonate indicating that the carbonate pedogenesis was controlled by CO$_2$ derived from the vegetation. This result has implications for carbon cycling, atmospheric C sequestration and management of this ecosystem.

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CHAPTER 4: \(^{15}\)N NATURAL ABUNDANCE AND THE DEPTH DISTRIBUTION OF SOIL NUTRIENTS OF THE PRAIRIE-FOREST TRANSITION IN LOUISIANA

4.1 Introduction

The differential soil development under grasses and forest, as expressed by their differing morphological and chemical characteristics, is a commonly cited example to illustrate the effect of vegetation on soil genesis (Jenny, 1980; Birkeland, 1984; Anderson, 1987). These differences are largely related to the distinct differences between trees and grasses in nutrient acquisition, biomass allocation, and cycling. Compared with trees and shrubs, grasses occupy nutrient poor sites and have greater turnover rates. Trees generally produce more aboveground biomass per kg of nutrients taken up. These differences, through their effect on nutrient redistribution in the soil system, influence the vertical stratification of N and other nutrients (Trudgill, 1988).

For natural systems, nutrient inputs occur through weathering, rainfall, dryfall, and nitrogen fixation. Nutrient outputs occur via leaching, surface runoff, volatilization, and the removal of plant biomass (Trudgill, 1988). Because these processes differ for prairie and forest, the rate of nutrient input and output, or nutrient cycling, for grasses and trees are expected to be different. Likewise, invasive plants may have an effect on levels of a particular nutrient if that nutrient is limiting or if it is not utilized at the same level by native and invasive species (Walker and Smith, 1997; Burke et al., 1998). The consequence is possible disruption of the nutrient cycling and subsequent interference with ecosystem
function (Archer et al., 1988). This arises because levels of soil nutrients can have a strong impact on species composition, species diversity, primary productivity, and other community and ecosystem properties (Walker and Smith, 1997). For example, tree invasion enriches the upper soil layers in certain plant nutrients thereby allowing the invasion of selective plant species with high nutrient requirements (Luken, 1990).

As Walker and Smith (1997) suggest, prior to making management decisions concerning invasive plants, one must establish that the invasive plant is altering the availability of one or more soil nutrients. The study of the distribution of the natural abundance of the stable N isotope, $\delta^{15}$N (Shearer and Kohl, 1986; Vitousek et al., 1989; Garten, 1993; Hogberg, 1997) and soil nutrients with depth (Trudgill, 1988; Jobbagy and Jackson, 2001) yields insight into the patterns and processes of nutrient cycling through time. The $\delta^{15}$N values of soil and plant systems reflect the relative importance of different nitrogen sources and the major processes in the nitrogen cycle. Thus, $\delta^{15}$N values can be used as a proxy to infer whether nitrogen dynamics differ among prairie, transition, and forest. Any significant departure in depth distribution of soil nutrients of the transition from the prairie would indicate the influence of plant invasion on the prairie. According to Jobbagy and Jackson (2001), nutrients most cycled by plants such as P and K are expected to be concentrated in the upper 20 cm. If the rates of nutrient cycling differ between trees and grasses, and considerable time had elapsed since invading trees and shrubs occupied a formerly grass occupied site, it must be possible to observe differences in the depth distribution of nutrients under prairie,
transition, and forest. In this chapter, I compare and document the depth
distribution of soil nutrients and the $\delta^{15}$N natural abundance of these contiguous
habitats.

4.2 $\delta^{15}$N Natural Abundance

4.2.1 Fractionation and Application

Nitrogen has two stable isotopes, $^{14}$N and $^{15}$N with a natural abundance of
99.6336 % and 0.3664 %, respectively. Isotopic composition ($\delta^{15}$N) is expressed
in parts per thousand (‰) deviations from the atmospheric N as defined by the
following equation (Shearer and Kohl, 1986):

$$\delta^{15}\text{N}(\text{‰}) = \left( \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \quad [4.1]$$

where $R$ is $^{15}$N/$^{14}$N of the sample or the standard. Atmospheric N has an
invariant $^{15}$N/$^{14}$N ratio and is used as a standard in measuring the isotope ratio of
samples. A $\delta^{15}$N value greater than zero means that the substance is enriched in
the heavier isotope ($^{15}$N) relative to atmospheric N. Negative $\delta^{15}$N values are
interpreted as a depletion in the heavier isotope and an enrichment in the lighter
isotope ($^{14}$N).

Two factors determine the $\delta^{15}$N values of soil-plant systems (Hubner,
1986): i) variations in the $\delta^{15}$N of the N source (input), and ii) the processes of N
transformation within soil-plant systems. For natural systems, N inputs occur
through atmospheric N fixation, rainfall, and dryfall. The processes of N
transformation include: N fixation, N mineralization, ammonia volatilization,
nitrification, denitrification, ion exchange, diffusion, and mass flow (Hogberg, 1997). These processes largely constitute the N cycle (Schlesinger, 1991).

A close examination of the nitrogen cycle reveals the occurrence of various kinetic and equilibrium processes leading to isotopic fractionation. Nitrogen fixation, assimilation of inorganic N, nitrification, denitrification, ammonification, and other processes of N metabolism cause kinetic isotope fractionation of varying degree (Hoefs, 1997). Ammonia volatilization is the major equilibrium process that causes the fractionation of N isotopes. Atmospheric N with δ15N of zero is the major N input to the soil-plant systems under natural conditions. During the conversion of atmospheric nitrogen into various forms, isotopic discrimination occurs.

Nitrogen fixation, the conversion of N2 gas into a plant usable form (NH4+), is the major pathway through which atmospheric N enters the biosphere. Because nitrogen fixed from the atmosphere has the same δ15N as the atmosphere, N-fixing plants have δ15N values close to zero. Nitrification is the oxidation of NH4+ via nitrite (NO2−) to nitrate (NO3−). Nitrification discriminates against the heavier isotope; that is, less δ15N would be found in NO3− compared with the starting material (NH4+). Because NO3− is the most mobile N form in soil, it can be lost via leaching leaving the soil profile enriched with 15N. Denitrification occurs under conditions of low oxygen concentration where nitrate is reduced via nitrite to nitric oxide (NO), nitrous oxide (N2O) and/or dinitrogen (N2). Denitrification tends to increase δ15N. During ammonia volatilization, the lighter isotope is lost from a soil system, so the remainder is enriched in the heavier
isotope (Hogberg, 1997). Thus, in a soil system, the $\delta^{15}$N value is determined by one or more of these processes. Non nitrogen fixing plants, which derive their entire N from the soil N pool, are expected to be isotopically heavier than nitrogen fixing plants, which derive some of their N directly from the atmosphere. The lighter (more negative $\delta^{15}$N) the plant material with respect to soil N, the better its N-fixing ability. This difference forms the basis for the $^{15}$N natural abundance technique of estimating symbiotic N (Boddey et al., 2000).

Most higher plants growing on nutrient poor soils are associated with mycorrhizal fungi for an enhanced nutrient uptake (Fisher and Binkley, 2000). Observations by Hogberg (1997), Schmidt and Stewart (1997), and Hobbie et al. (1999), revealed that mycorrhizal fungi preferentially transfer $^{14}$N to their host plants. Hogberg et al. (1996), in their study of $^{15}$N abundance of surface soils, roots and mycorrhizas in European forest soils, observed that the fungal portion of mycorrhizal root tips was 2.4 to 6.4 $^\%$ enriched relative to the plant portion of the root. Although alkaline soil conditions severely inhibit mycorrhizal colonization (Fisher and Binkley, 2000), almost all the dominant prairie plant species form mycorrhizal associations (Hartnett and Keeler, 1995).

The $^{15}$N natural abundance technique has been used for evaluating forest health (Gebauer and Schulze, 1991; Gebauer et al., 1994). Needles from a healthy Norway spruce ($Picea abies$) stand were more depleted in $^{15}$N than those from a declining stand receiving increased atmospheric N and S depositions. The authors attributed this observation to increased soil $\delta^{15}$N caused by atmospheric deposition. Increased $\delta^{15}$N is observed in vegetation following long term
fertilization (Hogberg, 1990; 1991; Hogberg and Johannisson, 1993; Johannisson and Hogberg, 1994). The enrichment with the heavier isotope following fertilization was related to increased N-pool sizes, cycling of N and to preferential losses of the lighter isotope, $^{14}$N (Johannisson and Hogberg, 1994).

In forests, high soil $\delta^{15}$N values have been related to their high nitrification potential (Koba et al., 1998). Garten (1993) observed a positive correlation between foliar $^{15}$N abundance and net nitrification potential in a study designed to investigate topographic variation of $^{15}$N natural abundance. Nitrogen saturation (availability) of an ecosystem is accompanied by higher $^{15}$N natural abundance because of the more open N-cycle and the associated loss of $^{14}$N (Hogberg, 1990; Garten, 1993; Martinelli et al. 1999). Agren and Bosatta (1988) define N saturation of forest soil as a condition whereby N input from N mineralization plus atmospheric input exceeds the systems retention capacity and NO$_3^-$ begins to be leached out of the system. Tamm (1990) consider N saturation of an ecosystem as "where the physiological N demand of the primary producers is satisfied and where considerable nitrate leaching occurs".

Martinelli et al. (1999) tested the hypothesis that N in most tropical forests is relatively more available than N in most temperate forests based upon a survey of foliar and soil $\delta^{15}$N values. Foliar $\delta^{15}$N values from tropical forests averaged 6.5 $\%$ higher than from temperate forests. Within the tropics, ecosystems with relatively low N availability were significantly more depleted in $^{15}$N than other tropical forests. Mean $\delta^{15}$N values for tropical soils were 8 $\%$ higher than temperate forest soils.
Vitousek (1999) demonstrated the control of other limiting nutrients on N-fixation and consequently on δ¹⁵N in natural systems. He observed an increase in foliar δ¹⁵N from a range of -10.8 to -11.1 ‰ to -8.1 to -9.3 ‰ after amendment with P and other essential nutrients. The observed pattern was attributed to enhanced N-fixation, because newly fixed N would have a δ¹⁵N near 0 ‰. His result was corroborated with increased nitrogenase activity in nutrient amended plots compared with the control.

4.2.2 δ¹⁵N-Soil Depth Relations

The δ¹⁵N values in the top few centimeters of a mineral soil are similar to those of plant litter. The general trend of δ¹⁵N with depth under natural and managed systems is that of enrichment with ¹⁵N at greater depths. Nattelhoffer and Fry (1988) obtained average δ¹⁵N values of -3.8 ‰ for leaf litter and -1.6 ‰ for root litter inputs in two oak (Quercus spp.) forests in Madison, WI. They observed soil δ¹⁵N value of +5.9 ‰ within the 10-20 cm depth. Their laboratory incubation experiment confirmed their conclusion that ¹⁵N enrichment was caused by decomposition. Their conclusion was in good agreement when compared with results for non-plowed soils from France, Japan, and Australia.

Similarly, Koba et al. (1998) observed an increase with depth of δ¹⁵N from a mean of +1.0 ‰ within the 0-5 cm depth to +6.8 ‰ within the 30-50 cm depth within a Japanese red cedar (Cryptomeria japonica D. Don) forest in Japan. Preservation of ¹⁵N enriched materials, illuviation of ¹⁵N enriched materials from shallower to deeper soil layers, and decomposition were considered responsible
for the observed $^{15}$N enrichment. Hogberg (1997) related the positive change in
$\delta^{15}$N with depth to N limitation and to low rates of nitrification. Connin et al. (2001)
observed $\delta^{15}$N increase by 1.2 °/oo within big blue stem (Schizachyrium gerardii)
litter, a C4 grass species, in a 5 yr long litter bag decomposition experiment. They
found higher $^{15}$N enrichment (2.6 °/oo) for the hard wood varital (Drypetes glauca)
while small and inconsistent variations were recorded for slash pine (Pinus elliotti)
roots. The enrichment was attributed to microbially mediated fractionation or the
preferential retention of $^{15}$N enriched substrates.

Relatively few studies reported decreased $\delta^{15}$N values with increasing soil
depth. Karamanos and Rennie (1980) observed such a decrease in well-drained
depressional profiles and constant $\delta^{15}$N with depth in upper slope positions in
Canada. Their findings demonstrated the general relationship between $\delta^{15}$N and
landscape position. They suggested that $\delta^{15}$N of total N might provide clues to
long term pedogenic processes when landscape position is considered as a
pedogenic factor. In some situations high N inputs promote nitrification leading to
the production of $^{15}$N enriched NH$_4^+$. Some plants preferentially use NH$_4^+$ as a N
source and progressively enrich the soil surface via litter fall decomposition.
Under such conditions NO$_3^-$ depleted in $^{15}$N is readily lost from the upper part of
the soil profile, and might be partly retained deeper in the soil profile (Hogberg,
1997). Hogberg (1997) further suggests that higher $\delta^{15}$N in the deeper soil layers
indicate higher rates of nitrification, which under humid conditions correlate with
loss of N from the system.
4.3 **Plant Control on Vertical Distribution of Soil Nutrients**

Four major mechanisms shape the vertical distribution of soil nutrients. These are weathering, atmospheric deposition, leaching, and biological cycling (Trudgill, 1988). Weathering and atmospheric deposition are the major sources of nutrients and therefore affect the depth at which nutrient inputs occur (Kirby, 1985). The input of nutrients released by weathering depend upon their original content in the parent rock, and the stability of the minerals in which they are contained. For example, granitic rocks have more K but much less P and Ca than basaltic rocks (Anderson, 1988). The significance of the contribution of these nutrients to nutrient cycling in influenced by vegetation and landscape position, among other factors.

Leaching moves nutrients downward and may increase nutrient concentrations with depth. Biological cycling generally moves nutrients upwards because some proportion of the nutrients absorbed by plants are transported above ground and then recycled to the soil surface by litter fall and through fall (Stark, 1994). The extent with which these occur differ among plants because of differences in tissue chemistry, above- and below-ground allocation, rooting depth and distributions, and turnover rates (Finer et al., 1997). Woody plants tend to have deeper and more widely spreading root systems than grasses (Lee and Lauenroth, 1994). Consequently, grasses and woody plants derive nutrients and water from different depths within a profile, with grasses exploiting the upper soil layer (20-35 cm) and trees and some shrubs exploiting the deeper soil layer (> 50 cm depth) (Akpo, 1997; Weltzin and McPherson, 1997; Le Roux and Bariac,
1998; Yoder et al., 1998; Boutton et al., 1999). According to Weltzin and McPherson (1997), such resource partitioning may facilitate the stable coexistence of mature trees and grasses in a temperate savanna. Yoder et al. (1998) suggest that woody and herbaceous plants are able to invade grasslands because of their greater access to and more rapid utilization of deeper soil water.

There is substantial evidence concerning the detectable effect of individual trees on soil chemical characteristics and nutrient cycling (Zinke, 1962; Challinor, 1968; Lodhi, 1977; Turner and Franz, 1985; Boettcher and Kalisz, 1990; Dahlgren et al., 1991; Barton and Wallenstein, 1997). Dahlgren et al. (1991) examined the soil forming processes and the effect of Japanese oak (Quercus serrata Thunb.) tree invasion on soils developed under Japanese pampas grass (Miscanthus sinensis Anders.). A 50 yr Invasion by oak vegetation resulted in a lowering of soil solution pH and a subsequent increase in Al concentration. Further, they observed that the oak vegetation appeared to have promoted the greater cycling of Ca, Mg, K, and Cl in the upper 20 cm of the soil profile. Barton and Wallenstein (1997) studied soil next to eastern red cedar of different ages and sizes and at varying distances from these trees and in early successional savanna sites versus late succession forest sites in southeastern Pennsylvania. They were able to test the hypothesis that savanna invasion by eastern red cedar modifies soil conditions in a way that may promote conversion to forest. Mineral soil depth and litter depth increased with size of and proximity to trees, and from savanna to forest, suggesting that eastern red cedar exerts strong effects on soil development at the
tree scale that lead to similar changes at the stand level. Individual eastern red
cedar also increased organic matter and Ca:Mg ratio.

Nitrogen is the most limiting element to net primary production of soils for
many ecosystems (Vitousek and Farrington, 1997). Wedin and Tilman (1990) and
Tilman and Wedin (1991) showed for subhumid grasslands that variation among
plant species in biomass and nutrient allocation may cause significant variation in
N availability. Dodd et al. (2000) observed that the available and total N was the
greatest in the surface soil layer (0-10 cm) and decreased substantially with depth
for a Colorado short grass steppe dominated by both shrubs and grasses.
Jobbagy and Jackson (2001) studied the vertical distribution of nutrients at a
global scale and concluded that soil nutrients that are most limiting for plants have
the shallowest average distributions. Moreover, nutrients most cycled by plants,
such as P and K were more concentrated within the 0-20 cm zone than were
nutrients less limiting plant growth.

The objectives of this study were to compare and contrast the depth
distributions of $\delta^{15}$N, total N, C/N ratio, P, K, Mg, Ca, Fe, and Mn; and the
variability of pH and electrical conductivity (EC) within profiles of prairie, transition,
and forest soils of three prairie-forest associations invaded by eastern red cedar
and other herbaceous and woody plants in Louisiana.

4.4 Materials and Methods

4.4.1 Description of Study Area

The study was conducted within the Winn Ranger District of the Kitsatchie
National Forest, Winn Parish, Louisiana. The dominant remnant prairies of
Louisiana, also known as the Keiffer calcareous prairie/forest complex, consist of a series of natural grassland openings occurring in a mosaic with calcareous hardwood-pine forest (Smith et al., 1989).

The Keiffer calcareous prairie/forest complex has developed on Eocene-age marly clays of the Tertiary period (Smith et al., 1989). The sediments belong to the Jackson group (Spearing, 1995). The Keiffer prairies occur on Keiffer loam soil that has CaCO$_3$ throughout the profile. The CaCO$_3$ was formed from the remains of marine life (USDA, 1998). Taxonomically, the soil is classified as a fine-silty, carbonatic, thermic Rendolic Eutrochrepts. Immediately adjacent to the prairies are soils of the calcareous forests dominated by Hollywood (fine, montmorillonitic, thermic Typic Pelluderts) and Oktibbeha (very-fine, montmorillonitic, thermic Vertc Hapludalfs) soils. Vaiden (very-fine, montmorillonitic, thermic Vertc Hapludalfs) and Bellwood (very-fine, montmorillonitic, thermic Aquentic Chromuderts) soils also occur adjacent to the prairies. All of the prairies have been heavily grazed and a few were farmed for short periods (Smith et al., 1989). Sites chosen for this study have not been farmed. The sites have not been burned in a long time and are invaded by eastern red cedar and other herbaceous and woody plants. The sites receive mean annual precipitation of 1250 mm and have a mean annual air temperature of 20 °C.

4.5.2 Field Methods

Soil samples were collected from each site using a push probe at 10 cm increments to a depth of 1 m. Two sets of samples were collected from each of
prairie, transition, and forest, each representing contrasting slope positions. Plant specimens were collected for $\delta^{15}N$ analysis from the prairie, transition, and forest using a $1 \text{ m} \times 1 \text{ m}$ quadrat in the prairie, and $5 \text{ m} \times 5 \text{ m}$ quadrat in the transition and forest.

### 4.5.3 Laboratory Methods

All soil samples were air dried for several weeks and ground to pass a 2 mm sieve. Soil samples for $\delta^{15}N$ analysis were pulverized with a ball mill. The $\delta^{15}N$ was measured using Thermal Ionization Mass Spectrometer (Finnigan MAT 262). Duplicate measurements of the same sample were within the error range of the instrument ($\pm 0.2$). All the $\delta^{15}N$ values are reported relative to atmospheric N$_2$.

Total N and organic C were analyzed with a CHN analyzer (EA 1108 Elemental Analysis, Fison Instruments). A multielement extraction of the soil samples was made using the Mehlich III extractant (Mehlich, 1984). The concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP). Samples were analyzed for electrical conductivity and pH (1:1 in deionized water).

### 4.5.4 Data Analysis

The data were analyzed as a split-split plot design using the PROC MIXED procedure of SAS (SAS Institute, 1999). The split-split plot design was used because of the randomization restriction associated with this type of study. The statistical model used was:

$$y_{ijkl} = \mu + \alpha_i + \beta_j + \epsilon_{ij} + \gamma_k + (\beta \gamma)_{jk} + \delta_l + (\beta \delta)_j + (\gamma \delta)_k + (\beta \gamma \delta)_{jk} + \epsilon_{ijkl}$$
where $\mu$ is the overall mean of a given soil property, $\alpha_i$ is the random block (site) effect, $\beta_j$ is the vegetation (main plot) effect, $\gamma_k$ is the landscape position (subplot) effect, and $\delta_l$ is the depth (sub-subplot) effect. Thus, site*vegetation ($e_{ij}^A$) was the error term used for testing the main effect of vegetation, site*vegetation*landscape position ($e_{ijk}^B$) was the error term used for testing the effects of landscape position and vegetation x landscape position interaction. Site was considered random because the selected sites would represent other Keiffer prairies in Louisiana. Smith et al. (1989) reported the presence of 45 Keiffer prairies.

The LSMEANS option was used to separate main effects of vegetation; and where soil depth*vegetation interaction was significant, the SLICE option was used to compare soil depth for each vegetation type and vice versa. The SLICE option evaluates the simple effects of vegetation at each depth, and the simple effects of depth for each vegetation (Littell et al., 1996). This is useful since I wish to investigate the impact of recent vegetation on soil properties at each depth.

4.6 Results and Discussion

4.6.1 Soil and Plant $\delta^{15}N$

The mean $\delta^{15}N$ values of plant foliage from prairie, transition, and forest lie within a narrow range. The prairie vegetation ($\delta^{15}N = -1.1 \pm 0.6 \%\text{oo}$) was slightly more enriched in $^{15}N$ compared with the forest ($\delta^{15}N = -1.6 \pm 0.6 \%\text{oo}$) and transition ($\delta^{15}N = -1.3 \pm 0.7 \%\text{oo}$). These values are within the range reported for foliage $\delta^{15}N$ values from temperate forest ecosystems (Martinelli et al., 1999).

The $\delta^{15}N$ depth profiles are given in Figure 4.1. There was significant vegetation effect on soil $\delta^{15}N$ ($p=0.066$). There was no effect of landscape
position, depth, or interaction terms on the soil δ¹⁵N (Table 4.1). The mean soil δ¹⁵N value within the 0-10 cm depth was +4.0 ± 0.9 ‰ for the forest, +3.4 ± 0.2 ‰ for the transition, and +2.5 ± 0.4 ‰ for the prairie. These values correspond to enrichment relative to the foliage of 5.5 ‰ for the forest soil, 4.7 ‰ for the transition soil, and 3.6 ‰ for the prairie soil. Although not statistically significant, a general enrichment with depth with the heavier isotope was observed (Figure 4.1). For the forest soil, the greatest enrichment (+6.7 ‰) occurred within the depth of 30-40 cm. The variability with depth was smaller for transition soil and prairie soil compared with the forest soil. The prairie soil consistently had more depleted ¹⁵N values compared with the transition and forest soil. Pairwise comparison of means for the significant effect of vegetation showed that the mean soil δ¹⁵N of the prairie (+3.5 ± 0.2 ‰) was significantly (p = 0.0008) less than both the mean transition soil δ¹⁵N (+4.9 ± 0.2 ‰) and mean forest δ¹⁵N (+5.4 ± 0.2 ‰). The differences in the mean soil δ¹⁵N of the forest and transition were not statistically significant (p = 0.194).

The lack of significant depth enrichment implies that the loss of ¹⁴N via nitrate leaching and ammonia volatilization is minimal (Hogberg, 1997). Although ammonia volatilization from unfertilized soils is small (Warneck, 1988), some is expected to occur in alkaline conditions. The NH₄⁺ produced during soil organic matter decomposition is in equilibrium with NH₃, with the amount of NH₃ increasing at pH >7. This process is expected to more likely occur within the prairie soil and cause ¹⁵N enrichment. If this process occurs under a dense forest canopy, much of the NH₃ may be reabsorbed by the foliage and retained within
Figure 4.1. Depth profiles of $\delta^{15}$N for leaves and soil of prairie, transition, and forest in Keiffer prairies, Louisiana. Error bars represent standard error ($n = 6$).
Table 4.1. Analysis of variance table showing the effect of vegetation (VEGE), landscape position (LSPN), soil depth (DEPTH) and interaction terms on $\delta^{15}$N and other soil chemical characteristics from three Keiffer prairie-forest associations, Louisiana. Asterisks show significant difference at the 10% probability level.

<table>
<thead>
<tr>
<th>Effect</th>
<th>DF</th>
<th>$\delta^{15}$N</th>
<th>N</th>
<th>C/N</th>
<th>P</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(---)</td>
<td></td>
<td></td>
<td>F[Pr &gt; F]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.5[0.32]</td>
<td>0.9[0.46]</td>
<td>6.1[0.02]*</td>
<td>1.1[0.40]</td>
<td>1.5[0.33]</td>
</tr>
<tr>
<td>LSPN</td>
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<td>0.3[0.59]</td>
<td>1.6[0.25]</td>
<td>3.8[0.05]</td>
<td>0.0[0.92]</td>
<td>6.4[0.03]</td>
<td>7.2[0.04]*</td>
<td>0.0[1.0]</td>
</tr>
<tr>
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<td>1.1[0.35]</td>
<td>23.0[&lt;0.001]*</td>
<td>16.8[&lt;0.001]*</td>
<td>2.5[0.01]*</td>
<td>2.2[0.03]*</td>
</tr>
<tr>
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<td>1.1[0.38]</td>
<td>0.7[0.47]</td>
<td>2.3[0.10]*</td>
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<td>1.7[0.26]</td>
<td>0.6[0.57]</td>
</tr>
<tr>
<td>VEGE*DEPTH</td>
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<td>0.8[0.66]</td>
<td>1.3[0.21]</td>
<td>0.5[0.96]</td>
<td>0.8[0.69]</td>
<td>2.4[0.003]*</td>
<td>0.9[0.61]</td>
</tr>
<tr>
<td>LSPN*DEPTH</td>
<td>9</td>
<td>0.5[0.88]</td>
<td>1.3[0.28]</td>
<td>0.5[0.89]</td>
<td>0.8[0.66]</td>
<td>1.15[0.34]</td>
<td>0.5[0.90]</td>
<td>0.6[0.79]</td>
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<tr>
<td>VEGE<em>LSPN</em>DEPTH</td>
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<td>0.7[0.83]</td>
<td>0.6[0.91]</td>
<td>0.4[0.99]</td>
<td>1.0[0.45]</td>
<td>1.0[0.51]</td>
<td>0.5[0.93]</td>
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(table con'd.)
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<thead>
<tr>
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<th>Mn</th>
<th>EC</th>
<th>pH</th>
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<td>(Pr &gt; F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VEGE</td>
<td>2</td>
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<td>0.9[0.47]</td>
<td>0.6[0.61]</td>
<td>0.8[0.50]</td>
</tr>
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<td>0.1[0.75]</td>
<td>0.0[0.98]</td>
<td>1.6[0.26]</td>
</tr>
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<td>5.5[&lt;0.001]</td>
<td>2.1[0.04]</td>
<td>18.1[&lt;0.001]</td>
</tr>
<tr>
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<td>1.0[0.44]</td>
<td>0.2[0.83]</td>
<td>1.6[0.28]</td>
</tr>
<tr>
<td>VEGE*DEPTH</td>
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<td>4.0[&lt;0.001]</td>
<td>0.9[0.55]</td>
<td>1.1[0.39]</td>
<td>3.1[&lt;0.001]</td>
</tr>
<tr>
<td>LSPN*DEPTH</td>
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<td>0.4[0.92]</td>
<td>0.4[0.95]</td>
<td>0.6[0.8]</td>
<td>0.9[0.50]</td>
</tr>
<tr>
<td>VEGE<em>LSPN</em>DEPTH</td>
<td>27</td>
<td>0.6[0.89]</td>
<td>1.4[0.13]</td>
<td>0.6[0.9]</td>
<td>1.1[0.36]</td>
</tr>
</tbody>
</table>
the ecosystem (Tamm, 1990). Another avenue for N loss from an ecosystem is via periodic burning. Fire causes the direct loss of volatile N compounds and the indirect loss of N through NO₃⁻ leaching after conversion of N to nitrate form. The ecological significance of these losses depends on the fire intensity, and on the distribution of N between biomass and soil, among others (Tamm, 1990). Almost all the N in the aboveground biomass, litter and top organic horizon can be lost during very intensive fires. Because trees and shrubs store large proportions of their N in biomass and organic soil horizons, they are exposed to a great risk of losing N after fires, especially if the fires recur frequently (Tamm, 1990).

Frequently burned prairies lose a large quantity of N-store through volatilization. Hobbs et al. (1991) predicted for a tallgrass prairie that twice as much N is lost in a single fire as enters the system yearly in rainfall or by N fixing organisms. Burning results in ¹⁵N enrichment (Hogberg, 1997). Grogan et al. (2000) studied fire effects on N cycling in a Californian bishop pine (Pinus muricata D. Don) forest. They reported that ¹⁵N natural abundance was enriched (≥ +2 °/oo) and similar in plants and in bulk soil organic matter (0-10 cm depth) at the burned site. For an unburned site, plant δ¹⁵N was more negative (approx. -2 °/oo) and contrasted markedly with the ¹⁵N enrichment observed within the soil (approx. + 5 °/oo). As expected, the data from Keiffer prairies show the absence of fire from this ecosystem.

The similarity in δ¹⁵N of foliage from prairie, transition, and forest may suggest that these plants have similar N sources. The δ¹⁵N values close to zero imply that atmospheric N is probably the main N source. Shearer and Kohl (1988)
suggested that species that draw N from the atmosphere are expected to have δ15N values close to zero, whereas species that depend on N uptake from the soil typically show positive values. This observation is reasonable since legumes were the third most abundant plant forms constituting the Keiffer prairies (Smith et al., 1989). Wedin and Tilman (1990), however, suggest that N fixation is not common in prairies. This suggestion was supported by Vitousek and Howarth's (1991) proposition that the high requirements for energy and the needs for high concentrations of other nutrients such as P, make N fixation a very costly process. This argument collaborates the observation by Wedin and Tilman (1990) that the dominant C4 grasses have the highest N use efficiencies and are able to persist under low N conditions. Seastedt (1995) notes that nitrogen fixing species would become dominant only if N became essentially unavailable as happens following many years of fires. The Keiffer prairies have not been burned frequently in recent years and hence N loss and limitation is unlikely.

The greater enrichment of forest and transition soil relative to their corresponding foliage compared with the prairie might be a consequence of one or more of the following factors (Nadelhoffer and Fry, 1988; Hogberg, 1997): i) differences in preservation of 15N enriched plant component from trees and grasses; ii) differences in the type of N forms taken up (primarily NO3−, depleted in 15N, versus NH4+, relatively enriched in 15N) and rooting depth; and iii) mycorrhizal fractionation.

The δ15N values of cultivated soils are often higher than that of forest soils as a result of higher losses of 15N depleted N from cultivated soils via fertilization.
with $^{15}$N enriched animal manure and activation of processes that lead to losses of $^{15}$N depleted N (Hogberg, 1997; Koerner et al., 1999). The consistently lower $\delta^{15}$N values that were observed with depth within the prairie soil compared with the forest soil may be evidence and supportive of historical accounts (MacRoberts and MacRoberts, pers. Comm.) that these prairies have not been farmed in the past.

### 4.6.2 Soil N, C/N ratio and P

Only depth influenced the variability in total soil N (Table 4.1). The mean value within the 0-10 cm depth was 0.29 ± 0.03 %. These values sharply decreased to 0.07 ± 0.01 % within the 40-50 cm depth and reached a value of 0.03 ± 0.01 % at the maximum depth sampled (1.0 m). The pattern was described by a logarithmic decay function fitted to mean values ($R^2 = 0.985$, Figure 4.2). The observed range of N contents within these soils are similar to soil N levels reported for previously uncultivated old-growth oak forests in the prairie-forest region of north central USA (Natelhoffer and Fry, 1988).

There was no significant effect of vegetation, depth, and interaction terms on soil C/N ratio (Table 4.1). The mean C/N ratio was significantly lower ($p = 0.070$) at the downslope landscape position (C/N = 12.1 ± 0.5) compared with the upslope landscape position (C/N = 12.9 ± 0.5). Although not statistically significant, the C/N ratio was greater for the forest soil up to the depth of 40-50 cm where it converged with the C/N ratio for prairie and transition soil (Figure 4.3). Both prairie and transition soil exhibited similar and constant C/N ratio (10 to 13) depth patterns. This observation is consistent with C/N ratio profiles for other
$N (\%) = -0.0913 \ln(\text{Depth}) + 0.4299$

$R^2 = 0.985$, $p < 0.001$

Figure 4.2. Logarithmic decay function fitted to mean total soil N of prairie, transition, and forest in Keiffer prairies, Louisiana. Error bars represent standard error ($n = 18$)

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Figure 4.3. Depth profiles of soil C/N ratio of prairie, transition and forest in Keiffer prairies, Louisiana. Error bars represent standard error (n = 6).
grasslands (Fenton, 1983). The C/N ratio is a useful indication of the degree of decomposition of organic matter in soils. It narrows with increasing modification. Well-decomposed soil humus has a C/N ratio of approximately 12 to 13 for humid temperate soils (Buol et al., 1997). A decrease in C/N ratio is often related to greater degree of decomposition. Thus, ideally, decomposition increases with increasing depth and, consequently, the C/N ratio decreases. This depth dependence explains the observation for the forest soil; this also implies that the quality of organic matter and degrees of recalcitrancy differ for the forest compared with the prairie and transition sites. The relatively uniform C/N ratio despite low levels of N within the prairie and transition is an indication that turnover rate is higher within the prairie. Garten (1993) reported similar topographic trend for C/N ratio (mean ± SD, 14 ± 2 for valley bottom, and 17 ± 2 for ridgetop) for Walker Branch Watershed, Tennessee.

Exploration of correlation between C/N ratio and δ¹⁵N or δ¹³C gives insight to the relationship between decomposition and isotope fractionation. Figure 4.4a shows no relationship between δ¹⁵N and C/N ratio. Selles et al. (1984), and Kitayama and Iwamoto (2001) demonstrated an inverse relationship between these two soil properties. Lack of correlation implies that the isotopic composition of soil N may be primarily a function of the natural ¹⁵N abundance of plant N deposited both on the soil surface by plant tops and within the soil profile by plant roots (Selles et al., 1984). The C/N ratio and δ¹³C are negatively correlated for the forest soil implying the strong bearing of decomposition upon δ¹³C. The narrow
Figure 4.4. Correlation plots of a) soil $\delta^{15}$N versus C/N ratio, and b) soil organic matter $\delta^{13}$C versus $\delta^{15}$N, and soil organic matter $\delta^{13}$C versus C/N ratio of prairie, transition, and forest in Keiffer prairies, Louisiana.
range in C/N ratio may be partly responsible for the weak correlation with $\delta^{13}\text{C}$ for the transition and prairie soil. The $\delta^{13}\text{C}-\delta^{15}\text{N}$ correlation for the prairie soil contrasts with the forest soil (Figure 4.4b). Soil organic matter $\delta^{13}\text{C}$ increased with increasing soil $\delta^{15}\text{N}$ for the forest soil. The opposite trend was observed for the prairie soil. This difference might be ascribed to differences in responses to isotope fractionation between different plant functional forms (C3 versus C4).

Only depth affected the variation in soil P content ($p < 0.0001$). The profile distribution of P is given in Figure 4.5. The mean P content was $9.3 \pm 1.1$ mg/kg for the 0-10 cm depth, and $6.4 \pm 0.8$ mg/kg within the 10-20 cm depth. The mean P content decreased as a logarithmic function of depth. Variability was higher in the upper 0-40 cm depth as shown by the greater standard errors compared with the lower depths (Figure 4.5). This is expected since carbonate content and soil pH (Figure 4.6), which are known to control P availability, are high and equivalent in all the three vegetation types below the 40-50 cm depth. Maximum availability of soil P occurs at slightly acid to neutral pH range. A highly carbonated insoluble hydroxyapatite precipitates in calcareous soils (Stevenson and Cole, 1999). This compound is not a good source of P for plants.

4.6.3 Soil pH and EC

There was a significant depth ($p < 0.0001$) and vegetation by depth interaction ($p < 0.0001$) effect on soil pH (Table 4.1). The mean soil pH within the 0-10cm depth was $6.6 \pm 0.2$ for the forest soil, 7.0 for transition soil, and 7.2 for the prairie soil. Within the prairie and transition, the soil pH increased with depth to a mean of 7.5 and remained approximately constant thereafter. In the forest,
Figure 4.5. Logarithmic decay function fitted to mean Mehlich III extractable soil P of prairie, transition, and forest in Keiffer prairies, Louisiana. Error bars represent standard error (n=18).
the soil was moderately acidic to the 20-30 cm depth. Below this depth, the pH was greater than 7.0 and similar to that of the prairie and transition soils (Figure 4.6). When the error bars at each depth were compared among the vegetation types, the greater variability for forest soil pH was noticeable. The test for the simple effect of vegetation at each depth showed statistical significance for the depths 0-10, 10-20, and 20-30 cm (Table 4.2). The test for the simple effect of depth at each vegetation type showed that there were significant depth differences of soil pH for the forest (p < 0.0001) and transition (p < 0.057) but not for the prairie (p = 0.153). This suggests that the soil profiles under prairies are homogeneous with respect to pH compared with the transition and forest soil and that invasion by woody and herbaceous vegetation tend to create depth dependent changes in the profile.

Only depth influenced soil EC (Table 4.1). The mean EC was 631 ± 107 μS/cm within the 0-10 cm depth. The EC linearly decreased with depth to 365 ± 49 μS/cm within the 80-90 cm depth (Figure 4.7). This shows that soluble salts are low, and leaching is insignificant; supporting the conclusion drawn from δ¹⁵N data. The high standard errors for soil EC show that this soil property is highly variable. A similar conclusion was drawn regarding soil EC from the spatial variability study (CHAPTER 2).

4.6.4 Soil Ca, Mg, and K

There was significant effect of vegetation (p = 0.041), landscape position (p = 0.033) and depth (p < 0.0001) on soil Ca (Table 4.1). Figure 4.8 presents
Figure 4.6. Depth profiles of soil pH of prairie, transition and forest in Keiffer prairies, Louisiana. Error bars represent standard error (n = 6).
Table 4.2. Results from tests of the simple effect of depth at each vegetation type and the simple effect of vegetation type at each depth determined from significant vegetation by depth interaction terms. Asterisks show significant difference at the 10% probability level.

<table>
<thead>
<tr>
<th>Vegetation</th>
<th>Depth (cm)</th>
<th>pH</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>(--------- F [Pr &gt; F] -----------)</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>14.2 [0.002]*</td>
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</tr>
<tr>
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<td>5.0 [0.05]*</td>
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</table>
Figure 4.7. Depth profile of soil EC of prairie, transition, and forest in Keiffer prairies, Louisiana. Error bars represent standard error (n=18).
Figure 4.8. Depth profiles of Mehlich III extractable Ca of prairie, transition, and forest soil in Keiffer prairies, Louisiana. Error bars represent standard error (n = 6).
extractable Ca depth profiles of prairie, transition, and forest. The mean values within the 0-10 cm depth were 39 ± 8 cmolc/kg for the forest soil, 70 ± 12 cmolc/kg for the transition soil, and 79 ± 7 cmolc/kg for the prairie soil. Calcium content increased to 133 ± 20 cmolc/kg for the forest soil, to 156 ± 11 cmolc/kg for the transition soils, and to 165 ± 6 cmolc/kg for the prairie soil at the 40-50 cm depth. Below this depth, the Ca contents were statistically similar among the three vegetation types (Figure 4.8). The mean Ca content at the maximum depth was approximately 150 ± 14 cmolc/kg. The forest soil contained consistently lower Ca levels compared with the transition and prairie soils. The upper landscape position contained significantly greater Ca (141 ± 6 cmolc/kg) compared with the lower landscape position (116 ± 7 cmolc/kg).

There was no significant effect of vegetation on extractable Mg. Significant effects due to landscape position (p = 0.042), depth (0.013), and vegetation by depth interaction (p = 0.0034) were observed (Table 4.1). Mean extractable Mg at the upslope landscape position was greater (135 ± 5 mg/kg) than the downslope landscape position (124 ± 5). The mean Mg content within the 0-10 cm depth was 133 ± 10 mg/kg and decreased to 118 ± 9 mg/kg at the 20-30 cm depth, and increased again to 140 ± 12 mg/kg at 90-100 cm depth. Since Mg variability with depth was greater for the forest and transition soil compared with the prairie soil, a significant vegetation by depth interaction was observed (Figure 4.9, Table 4.2).

Only depth influenced the variability in extractable K (Table 4.1). The mean extractable K was 249 ± 25 mg/kg within the 0-10 cm depth. The K content decreased with depth and reached the minimum of 175 ± 22 mg/kg at the 80-90
Figure 4.9. Depth profiles of Mehlich III extractable Mg of prairie, transition, and forest soil in Keiffer prairies, Louisiana. Error bars represent standard error (n = 6).
cm depth. Although not statistically significant, the prairie soil contained greater K to the 60-70 cm depth (Figure 4.10).

Processes such as weathering, cation exchange, and leaching govern the cycles of Ca, Mg, and K in natural ecosystems. The calcareous parent material and presence of secondary calcium carbonate explain the high Ca content and the observed increased with depth. Soil K is primarily derived from primary minerals such as micas and potassium feldspar (Brady, 1990). For natural systems, nutrients taken up by plants are either incorporated into aboveground biomass, recycled to the soil via litter fall or root death, or leach from leaves or roots (Fisher and Binkley, 2000). These cycling processes differ among plant forms, and nutrients. When compared with grasses, trees promote greater cycling of Ca, Mg, and K in the upper soil profile (Dahlgren et al., 1991). This was observed for soil Mg by a relatively uniform depth distribution for the prairie and a decrease with depth for the forest (Figure 4.9). A significant vegetation by depth interaction for Mg implies that the trees and shrubs may have greater demand for Mg and that invading plants may eventually compete with the prairie grasses for this soil nutrient. The decreasing depth profile of cations under forest is caused by the accumulation in the aboveground tree parts. The moderate depth gradient within the prairie is consistent with the greater underground biomass allocation of grasses. Loss of K via foliage leaching from trees and shrubs is an important mechanism (Tamm, 1990; Fisher and Binkley, 2000) and may explain the relatively lower soil K in the forest and transition soil than the prairie soil.
Figure 4.10. Depth profiles of Mehlich III extractable K of prairie, transition, and forest soil in Keiffer prairies, Louisiana. Error bars represent standard error (n = 6).
4.6.5 Soil Fe and Mn

The profile distribution of Fe is given in Figure 4.11. Vegetation did not significantly affect soil Fe. There was significant depth (p = 0.002), and vegetation by depth interaction effect (p < 0.0001). The Fe content was greatest in the forest soil within the upper 0-30 cm depth (108 ± 7 to 99 ± 11 mg/kg). The Fe content at this depth ranged between 83 ± 15 to 65 ± 16 mg/kg for the transition soil and between 49 ± 6 to 40 ± 3 for the prairie soil. Below a depth of 50-60 cm, the relative abundance switches with the prairie soil containing greater Fe than the forest (Figure 4.11). The transition maintained intermediate content and low variability with depth. At 40-60 cm depth, the prairie, transition, and forest soil Fe content converge.

Two mechanisms by which Fe content could increase below a depth of 50-60 cm within the prairie soil are (Fanning and Fanning, 1989; Chadwick and Graham, 2000): i) leaching and subsequent accumulation of organic matter complexed Fe to this depth by a process known as podzolization; or ii) the occurrence of anaerobic conditions and presence of a readily oxidizable organic matter such that Fe is reduced and becomes more available below the 50-60 cm depth. Podzolization is accompanied by the presence of a bleached E horizon, but field observation revealed that these soils lack the E horizon. Podzolization is characteristic of forest soils and not of prairie soils. Podzolization is inhibited by high levels of Ca by directly preventing mobilization as well as by promoting microbial activity that decomposes soluble organic matter so that it is not available for complexation and subsequent leaching (Chadwick and Graham, 2000).
Figure 4.11. Depth profiles of Mehlich III extractable Fe of prairie, transition, and forest soil in Keiffer prairies, Louisiana. Error bars represent standard error (n = 6).
Anaerobic conditions do not occur in these soils; thus ruling out the occurrence of Fe reduction. The most likely explanation is that increased Fe content is due to siderite (FeCO₃) weathering (Hudnall, pers. commun.). This is supported by the presence of siderite (FeCO₃) in the prairie soil. X-ray diffraction analysis of the soil samples confirmed the presence of siderite in the parent material (see section 3.4.2). Reducing conditions are required for the formation of siderite (Doner and Lynn, 1989). But the siderite in these soils is probably a product of the parent material (Hudnall, pers. commun.).

Only depth significantly affected the variability of extractable Mn (Table 4.1). The mean Mn content was 50 ± 7 mg/kg within the 0-10 cm depth. Mean soil Mn content decreased to 19 ± 2 mg/kg up to the 40-50 cm depth and remained nearly constant thereafter (Figure 4.12). Mn and Fe share several chemical characteristics. Redox conditions and pH control their availability (Shuman, 1991). Although not as obvious as for Fe, a slight increase in Mn content was observed below the 50-60 cm depth within the prairie soil. A large percentage of soil Mn is associated with organic components, thus explaining the relatively higher Mn content within the 0-10 cm depth. The lack of similarity in depth patterns of Fe and Mn supports the contention that reduction is not a mechanism for increased Fe content within the prairie soil.

4.7 Summary and Conclusion

This study was concerned with the depth profiles of δ¹⁵N, soil pH, soil EC, and Mehlich III extractable nutrients of three remnant prairie-forest associations of Louisiana. These prairies are threatened by the invasion of woody and
Figure 4.12. Depth profiles of Mehlich III extractable Mn of prairie, transition, and forest soil in Keiffer prairies, Louisiana. Error bars represent standard error (n = 6).
herbaceous plants. The study was designed to gain full understanding of this ecosystem prior to embarking on management and restoration activities.

Plant leaves from prairie, transition, and forest showed similar $\delta^{15}$N signals, and mean values ranged between -1.6 $\%_{\text{o}}$ and -1.1 $\%_{\text{o}}$. Compared with the leaves, the soil was enriched with $^{15}$N. The order of enrichment of the 0-10 cm depth relative to corresponding leaves was forest soil > transition soil > prairie soil. This is an indication that trees and shrubs are associated with N loss or have more mycorrhizal mediated N uptake compared with the grasses. As a whole, N loss seems to be minimal and the ecosystem exhibits a tight N cycling with major contribution from the atmosphere.

The depth patterns of total N and P were similar and were not affected by vegetation type. The mean measured values within the 0-10 cm depth were 0.29 ± 0.03 % by weight for total N and 9.3 ± 1.1 mg/kg for P. The dichotomy in the results of $\delta^{15}$N and total N regarding vegetation type effects might be related to the fact that total soil N is not a good measure of plant available N (Binkley, 1986). Both N and P decreased as a logarithmic function of depth (Figures 4.2 and 4.5).

Both the prairie and transition soil had similar C/N ratios (10 to 13). For the forest soil, although not statistically different from the prairie and transition soils, the C/N ratio was higher (13 to 16) within the 0-40 cm depth. Irrespective of the vegetation type, the soil C/N ratio and $\delta^{15}$N were poorly correlated. The soil C/N ratio and $\delta^{13}$C were negatively correlated for prairie and forest soils. This correlation was stronger for the forest soil showing that under pure C3 community, decomposition affected the $\delta^{13}$C signal more than it did $\delta^{15}$N. The poor correlation...
observed for the prairie soil might be partly related to differences in decomposition patterns of C3 and C4 plants that co-exist and whose proportions change with season. A similar explanation may hold for the transition soil.

The forest soil was slightly acidic (pH = 6.6 ± 0.2), the transition soil was neutral (pH = 7.0), and the prairie soil was slightly alkaline (pH = 7.2) within the 0-10 cm depth. These differences were not statistically significant at 10% probability level. However, a significant depth and vegetation by depth interaction was noted for soil pH. The soil pH variability with depth was greater for the forest, and least for the prairie soil. Soil pH was similar for the three vegetation types below the 30-40 cm depth. The maximum recorded pH was (7.5 ± 0.1) below the 30-40 cm depth. Only depth affected soil EC. The mean EC decreased from 631 ± 107 μS/cm at the 0-10 cm depth to 365 ± 49 μS/cm at the 80-90 cm depth. These EC values are considered very low.

Among the Mehlich III extractable cations, Ca was the most abundant, owing to the Ca bearing parent material. Vegetation type, landscape position, and depth influenced soil Ca. Within the 0-10 cm depth, Ca was greatest for the prairie soil (79 ± 7 cmol/kg), intermediate for the transition soil (70 ± 12 cmol/kg), and lowest for the forest soil (39 ± 8 cmol/kg). The Ca content increased with depth and a maximum of 165 ± 7 cmol/kg was recorded in the prairie soil. Unlike Ca, Mg was not affected by vegetation type. But there was significant variation due to landscape position, depth, and vegetation by depth interaction. The upslope position contained greater Mg (135 ± 5 mg/kg) compared with the downslope landscape position (124 ± 5 mg/kg). Soil K content was similar among
vegetation types. A decrease from 249 ± 25 mg/kg within the 0-10 cm depth to 175 ± 22 mg/kg within the 80-90 cm depth was observed.

Similar to soil pH and Mg, soil Fe was not significantly affected by vegetation type. The soil Fe depth profile was characterized by significant depth, vegetation by depth interaction effects. Compared with the prairie soil, the forest soil contained greater Fe within the 0-30 cm depth, but lower Fe below the 50-60 cm depth. The transition soil contained intermediate Fe levels relative to the forest and prairie soil. The processes of localized reduction in the prairie and differences in rooting depth between trees/shrubs and grasses may partly explain the observed trends. Similar to EC and K, only depth affected the variability in soil Mn. Because large percentage of Mn is associated with the organic components, greater Mn was found within the 0-10 cm depth.

In this study I consider soil properties with significant effects from vegetation type, landscape position, vegetation by depth interaction, and vegetation by landscape position interaction to offer clues regarding the impact of invading plants on the prairie soil properties. Landscape position was considered because field observation and previous reports (MacRoberts and MacRoberts, 1997; Smith et al., 1989) showed that greater invasion by woody and herbaceous plants is more concentrated in the lower landscape position than the upper landscape position.

Among the soil properties studied, δ¹⁵N and Ca were significantly affected by vegetation type. The differences in the soil δ¹⁵N are a clear indication that the vegetation at transition (invading woody and herbaceous plants) is altering the N
cycling towards more “forest-like” conditions. This might be a consequence of changes in decomposition patterns of organic matter (D'Antonio and Vitousek, 1992). Significant effects due to landscape position were observed for soil C/N ratio, soil Ca, and soil Mg whereas vegetation by depth interaction effects were observed for soil pH, Mg, and Fe. While the changes in soil Ca may not be of primary concern, because of the very high supply of this nutrient, changes in the other soil properties call for preparing appropriate management and restoration plans for these and similar prairies.

4.8 References


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CHAPTER 5: CONCLUSION

5.1 Summary

This dissertation integrated statistical/geostatistical, fractal, and isotopic procedures to study the effect of invading woody and herbaceous vegetation on soil properties of three prairie-forest associations, known as Keiffer prairies, in Louisiana. Statistical procedures were used to analyze for differences in soil properties among vegetation types (prairie, transition, and forest), landscape position, and soil depth. The transition is where greater invasion of woody and herbaceous vegetation was observed. The prairies were colonized by eastern red cedar at varying degrees from one site to the other. Geostatistical and fractal procedures were used to characterize the spatial variability of soil properties, to identify the scale of influence of invading plants on the soil properties, i.e., short and long range variations, and to produce maps of soil pH, EC, extractable Ca, Mg, K, Mn, and Fe. The isotopic technique established the vegetational history of the site and described the temporal C3/C4 dynamics of the prairie, the processes of soil carbonate pedogenesis, and the nitrogen dynamics of this endangered habitat. The approach emanated from the belief that the delineation and management of ecologically important sites would greatly benefit from accurate characterization and estimation of the soil resource level (Joem and Keeler, 1995; Walker and Smith, 1997).

The first study examined the spatial variability of surface soil (0-10 cm depth) pH, electrical conductivity (EC), and Mehlich III extractable Ca, Mg, K, Fe, and Mn. A contrasting relationship was observed among these soil properties
within the prairie and forest, suggesting the existence of distinct functional boundary between these two adjacent habitats. The most notable one was the positive relationship between EC and pH for the forest soil data and the lack of such relationship for the prairie soil data. The prairie soil was alkaline (pH > 7.0), the forest soil was acidic (pH < 7.0), and the transition soil was intermediate and near neutral (pH = 7). The invading plants are altering the soil pH towards reducing the alkalinity of the prairie soil. This was expected since soil pH is among the soil properties that quickly responds to changes in vegetation (Birkeland, 1984; Miles, 1987).

The spherical model described the spatial variability of virtually all the soil properties considered. Except for soil Mn at Site 2, all the soil properties exhibited a spatial dependence over a range of 20 to 30 m. Soil pH spatial variability was well structured as evidenced by the very low relative nugget variance. Soil EC had the highest relative nugget variance and therefore was regarded to show relatively weaker spatial structure. When the forest soil pH data were deleted and the semivariogram reconstructed, the semivariogram parameters changed and the change was in accordance with extent of woody invasion. Site 1 had fewer numbers of plant invaders compared with Sites 2 and 3. Site 1 prairie soil pH had a smaller range of influence and higher D values (Table 2.3) whereas Sites 2 and 3 had relatively higher ranges of influence and lower D values. The D values were high for the other soil properties indicating the dominance of short-range variation. But for soil pH, the short-range variability emerged when the forest soil data were deleted. This was considered a consequence of the interplay between parent
material and vegetation effects with dominance of one over the other with a change of scale. Based upon the semivariogram models, kriged estimates of the soil properties were provided for each site. These data are useful for designing future ecological researches that consider controlling soil spatial variability within the prairie. For example, adequate information may be gained from soil sampling procedures carried out at 20-30 m distance intervals with adjustments made with reference to semivariograms of soil properties of interest. Permanent plots may be positioned in a similar manner to aid in long-term species inventory and monitoring activities, especially concerning rare species specific to Louisiana.

The second study focused on the vertical distribution of soil organic carbon (SOC), soil carbonate abundance and mineral composition, and the natural abundance of carbon isotope ($\delta^{13}C$) from soil organic matter (SOM) and soil carbonate. SOC varied with depth but variation due to vegetation and landscape position were not statistically significant. Although not statistically different from one another, there was an increase in mean SOC within the 0-10 cm depth from prairie (Mean ± SE, 3.2 ± 0.3), to transition (3.4 ± 0.3), and to forest (3.6 ± 0.7). The $\delta^{13}C$ values of SOM with soil depth served as a signal of the temporal vegetation dynamics. The mean $\delta^{13}C$ of SOM within 0-10 cm depth was -25.9 ± 0.9 ‰ for the forest soil, -22.1 ± 3.0 ‰ for the transition soil, and -19.7 ± 3.2 ‰ for the prairie soil. New growth leaf samples gave values of -28.9 ± 0.6 ‰ for the forest, -28.0 ± 1.1 for the transition, and two seasonal values for the prairie, -27.0 ± 1.7 ‰ for the spring and -22.6 ± 2.6 ‰ for the fall. These $\delta^{13}C$ signatures show that while the forest is exclusively C3, the transition and the prairie are
composed of a mixture of C3 and C4 plant functional forms. The C4 contribution to the 0-10 cm SOM pool within the prairie was 52% whereas C4 contribution to the SOM at a similar depth was lower (35%) in the transition soil. The δ¹³C of SOM increased with depth with proportional increase in C4 productivity for each vegetation, and almost converged at a depth of 40-50 cm. The observation that the isotope signature spacing of prairie-transition and forest-transition up to the 40-50 cm depth suggest that the transition has been stable for some centuries. This depth was also indicative that the entire site was occupied by a predominantly C4 vegetation. This interpretation agrees with radio isotopic data from central Texas that revealed conditions of maximum temperatures and minimum precipitation favoring the expansion of C4 vegetation during the middle Holocene, 6000 - 4500 yr B. P. (Nordt et al., 1994). A radio isotopic dating of SOM sample from the 40-50 cm depth would provide the age of the plant remains that might be equivalent to the time of major vegetation shift. The soil carbonate is predominantly pedogenic calcite. The proportion of soil carbonate was greater in the prairie compared with the forest. A good agreement was found between δ¹³C of SOM and soil carbonate indicating that the carbonate pedogenesis was controlled by CO₂ derived from the vegetation.

The third study addressed the depth profiles of δ¹⁵N, soil pH, soil EC, and Mehlich III extractable nutrients. Plant leaves from prairie, transition, and forest showed similar δ¹⁵N signals. Compared with the leaves, the soil was enriched with ¹⁵N. The order of enrichment of the 0-10 cm relative to corresponding leaves was forest soil > transition soil > prairie soil. This is an indication that trees and shrubs
are associated with N loss or have more mycorrhizal mediated N uptake compared with the grasses. In general, N loss seems to be minimal and the ecosystem follows a tight N cycling. Among the soil properties studied, δ^{15}N and Ca were significantly affected by vegetation type. The differences in the soil δ^{15}N is a clear indication that the vegetation within the transition zone (invading woody and herbaceous plants) is altering the N cycling towards more "forest-like" conditions. Significant effects due to landscape position were observed for soil C/N ratio, soil Ca, and soil Mg whereas vegetation by depth interaction effects were observed for soil pH, Mg, and Fe.

5.2 Limitations

Although this study is the first major attempt to understand the soil properties of these rare natural communities, practical limitations and unanswered questions remain for future investigation. The restoration and management of these prairies would be facilitated if the boundaries of the prairies were georeferenced with a GPS (Global Positioning System). I was not able to accomplish this because of the small sizes of these prairies, and the low spatial resolution of the GPS available compounded by the interference by tree canopies on the GPS signal.

The stable isotopes of C and N were used as tracers and indicators of plant-soil processes and ecosystem function. While the information derived from stable C isotope is reliable and very useful, it only provides relative temporal information. The measurement of ¹⁴C would provide additional information concerning the absolute age of the prairies. Further, the spatio-temporal dynamics of the prairie plants (in terms of species diversity, productivity, and nutrient concentrations in
the above ground biomass) must be coupled with that of the soil resources to better understand soil-plant interaction within these prairies. The relatively high annual mean rainfall received by these prairies may suggest that water is not limiting the productivity of these prairies, but periodic soil moisture deficits may occur thereby affecting their productivity. Although the prairies selected for this study were not burned recently, fire remains an important component of the prairie ecosystem. Several authors (Hulbert, 1988; Turner et al., 1997; Eom et al., 1999; Marafa and Chau, 1999) investigated the effects of fire on soil properties and other grassland ecosystem components. Bragg (1995), however, cautions generalization since the effects of fire on the soil properties often occur in a site-specific manner. Thus, future research must establish the effects of fire on soil properties and the natural abundance of C and N for these habitats.

5.3 Prairie Management Recommendations

The material in this section heavily draws on literature review relevant to the control of eastern red cedar invasion of prairies. The growing body of evidence suggest that eastern red cedar affect species composition of prairies by directly altering the soil environment (Gehring and Bragg, 1992; Joy and Young, 1996) or indirectly by serving as a nurse tree, i.e., by facilitating the establishment of other woody and herbaceous plants (Meiners and Gorchov, 1998). Thus, if rare prairie species are to be saved from possible loss, prairies must be protected from invasion by eastern red cedar and other woody and herbaceous plants.

Chemical application, grazing, cutting, and burning are among the methods commonly used to manage grasslands and suppress the spread of invasive plant
species (Luken, 1990). Herbicide applications take the form of foliar and stem sprays, soil application, basal application, or injection. Most herbicides are ineffective for controlling red cedar (Converse, Undated).

Herbivores are an important component of the prairie ecosystem. They cause considerable damage to woody vegetation by browsing. The intensity and timing of grazing must be considered when used as a management technique (Hartnet and Keeler, 1995). For example, overgrazing has been implicated to altering the species composition of grasslands (Gillard, 1969; Collins et al., 1995) and facilitating invasion by woody and herbaceous plants (Schlesinger et al., 1990).

A combination of cutting and prescribed fires is the easiest and most cost-effective control for red cedar (Owensby et al., 1972). Burning controls small trees and opens the area for large tree removal by cutting. The effectiveness of burning to control red cedar depends upon tree height, crown density, stand density, amount of herbaceous fuel, and fire weather conditions (Converse, Undated). Timing of the burn is also very important for obtaining the desired response. In order to damage invading plants, burning must occur when they are actively growing or has buds above the soil surface. Spring burns (March through May) usually kill trees up to about one meter tall. Larger trees up to 6.0 m occasionally are killed by fires (Owensby et al., 1993). Smith et al. (1989) studied the effect of winter burns on the flora of two Keiffer prairies. They concluded that application of late-winter fire causes a decline in the number of intermediate size stems (1-4 cm diameter) but an increase in small stems. They also observed that many larger stems (> 4 cm) were not eliminated by single or two consecutive late-winter burns.
Their observation is suggestive of the need to use both burning and mechanical methods to control woody plant invasion of these prairies. Stritzke and Bidwell (1987) provide ambient conditions required for a successful burn. These are: air temperature (15-27 °C), relative humidity (30-50 %), wind speed (8-16 km/h), fire fuel loading (2242 kg/ha), and soil moisture (top 15 cm moist).

Fire at different times favors different species groups in tallgrass prairie. Winter and early spring burns favor C3 plants while mid- to late spring burns favor C4 grasses. Cognizant of this fact, Smith et al. (1989) suggest that the Keiffer prairies should be burned on a random seasonal schedule from late winter/early spring to late spring. They stress that individual prairies should not be burned at the same time of year to simulate the historic random timing of natural fires in the prairies and to benefit the existence of a wider range of species. For the three prairies considered in this study as well as similar prairies, a management approach suggested by Smith et al. (1989) and MacRoberts and MacRoberts (1997) should be followed since their recommendation was based up on a preliminary study on the effects of winter burn and information gained from visits made to other southeastern prairies (i.e., Mississippi, Texas, and Arkansas).

Although no comprehensive recommendation can be made because of the site-specific nature of controlling plant invasion (Wallace and Dyer, 1995), the following suggestions are put forward concerning the three prairies this study investigated. Red cedar and other woody plants were dominant at the edges of the prairies. This transition zone can easily be identified in the field and ranges in size from 5 to 10 m depending up on the landscape position and site. To reduce
edge effect, this zone should be freed from red cedar and other woody plants. Given the sizes of some of the red cedar trees, a combination of cutting and burning seems. Larger trees must be cut and removed while the stump and smaller trees can easily be destroyed by burning. At site 1 prairie, the western side was dominated by many small red cedar trees that need to be removed if the prairie is to be enlarged. But closeness to the highway (Hwy 156) and a trail that passes through the prairie may make its management very difficult. At prairie sites 2 and 3, not only did the invading plants dominate the edges, but they encroached to the center and divided the prairies into two. Such a fragmentation is not favorable for the existence of the prairies and they should be opened up.

A comprehensive recommendation depends on a complete understanding of this ecosystem. Along this line, Smith et al. (1989) posed important research questions that have not been addressed. These questions remain important for an effective prairie management and restoration and are reiterated as below: i) What is the actual time of year of most natural fires in the Keiffer prairie area and the random frequency with which they occurred?, ii) What are the long term effects of annual and other yearly schedules of burning on indigenous biota?, and iii) What effect does seasonal variation of fire have on the various biotic components and prairie community dynamics?

5.4 References


APPENDIX A. Illustration of the steps followed in the calculation of the fractal dimension using the
semivariogram method. Data used is soil pH (Site 1).

<table>
<thead>
<tr>
<th>Separation Distance (m)</th>
<th>Semivariance</th>
<th>Log(Separation distance)</th>
<th>Log(semivariance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10</td>
<td>0.03</td>
<td>0.32</td>
<td>-1.54</td>
</tr>
<tr>
<td>5.15</td>
<td>0.08</td>
<td>0.71</td>
<td>-1.12</td>
</tr>
<tr>
<td>9.75</td>
<td>0.08</td>
<td>0.99</td>
<td>-1.09</td>
</tr>
<tr>
<td>13.58</td>
<td>0.13</td>
<td>1.13</td>
<td>-0.90</td>
</tr>
<tr>
<td>17.53</td>
<td>0.14</td>
<td>1.24</td>
<td>-0.86</td>
</tr>
<tr>
<td>21.40</td>
<td>0.28</td>
<td>1.33</td>
<td>-0.55</td>
</tr>
<tr>
<td>25.63</td>
<td>0.27</td>
<td>1.41</td>
<td>-0.56</td>
</tr>
<tr>
<td>29.75</td>
<td>0.31</td>
<td>1.47</td>
<td>-0.51</td>
</tr>
<tr>
<td>33.69</td>
<td>0.32</td>
<td>1.53</td>
<td>-0.49</td>
</tr>
<tr>
<td>37.71</td>
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<td>1.58</td>
<td>-0.47</td>
</tr>
<tr>
<td>41.79</td>
<td>0.35</td>
<td>1.62</td>
<td>-0.46</td>
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<td>45.70</td>
<td>0.43</td>
<td>1.66</td>
<td>-0.37</td>
</tr>
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<td>49.68</td>
<td>0.49</td>
<td>1.70</td>
<td>-0.31</td>
</tr>
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<td>53.74</td>
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<td>1.73</td>
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<td>61.74</td>
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<td>0.44</td>
<td>1.87</td>
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</tr>
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<td>77.43</td>
<td>0.47</td>
<td>1.89</td>
<td>-0.33</td>
</tr>
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<td>81.43</td>
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<td>1.91</td>
<td>-0.35</td>
</tr>
<tr>
<td>85.35</td>
<td>0.46</td>
<td>1.93</td>
<td>-0.34</td>
</tr>
</tbody>
</table>

For a linear transect across a fractal area, $D = 2 - 1/2H$, where $D$ is the fractal dimension, and $H$ is the slope of the linear part of the log-log plot. For soil pH (Site 1), $H = 0.88$, $D = 2 - 1/2(0.88) = 1.56$. 
APPENDIX B. Soil profile descriptions.

Profile description for Keiffer loam soil.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth, cm</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0-13</td>
<td>Very dark grayish brown (2.5Y 3/2) loam; weak medium granular structure; firm, very plastic, sticky, common fine roots, few fine rounded nodules of calcium carbonate; moderately alkaline, strongly effervescent; clear smooth boundary.</td>
</tr>
<tr>
<td>Bk1</td>
<td>13-46</td>
<td>Light olive brown (2.5Y 5/6) loam, common medium distinct yellowish brown (10YR 5/4) mottles, moderate medium subangular blocky structure; firm, very plastic, very sticky, few fine roots; common fine and medium rounded nodules of calcium carbonate; moderately alkaline, strongly effervescent; gradual wavy boundary.</td>
</tr>
<tr>
<td>Bk2</td>
<td>46-89</td>
<td>Light yellowish brown (10YR 6/4) silt loam; common medium distinct yellowish brown (10YR 5/6) mottles; moderate medium subangular blocky structure, firm, very plastic, very sticky; common medium rounded nodules of calcium carbonate; moderately alkaline, strongly effervescent; gradual wavy boundary.</td>
</tr>
<tr>
<td>Bk3</td>
<td>89-137</td>
<td>Light yellowish brown (10YR 6/4) clay loam; common medium distinct yellowish brown (10YR 5/8) mottles; moderate medium subangular blocky structure; firm, very plastic, very sticky; few coarse and common medium rounded nodules of calcium carbonate; moderately alkaline, strongly effervescent; gradual wavy boundary.</td>
</tr>
<tr>
<td>Bkss</td>
<td>137-183</td>
<td>Light yellowish brown (10YR 6/4) clay loam; common medium distinct yellowish brown (10YR 5/8) mottles; moderate medium subangular blocky structure; firm, very plastic, very sticky; few slickensides; common medium rounded nodules of calcium carbonate; moderately alkaline, strongly effervescent.</td>
</tr>
</tbody>
</table>
Profile description for Oktibbeha silt loam soil.
Taxonomic classification: Very-fine, montmorillonitic, thermic Vertic Hapludalfs.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth, cm</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0-10</td>
<td>Dark brown (10YR 3/3) silt loam; weak medium granular structure; very friable; common fine and medium roots; common fine and medium brown concretions; moderately acid; clear smooth boundary.</td>
</tr>
<tr>
<td>Btss1</td>
<td>10-36</td>
<td>Yellowish red (5YR 4/6) clay; moderate medium subangular blocky structure; very firm, very plastic, very sticky; common fine and medium roots; few fine brown concretions; shiny ped faces; few slickensides; very strongly acid; gradual smooth boundary.</td>
</tr>
<tr>
<td>Btss2</td>
<td>36-66</td>
<td>Yellowish red (5YR 4/6) clay; common medium prominent yellowish brown (10YR 5/4) mottles; moderate medium subangular blocky structure; very firm, very plastic, very sticky; common fine and medium roots, shiny ped faces; few slickensides; few fine brown concretions; strongly acid, gradual smooth boundary.</td>
</tr>
<tr>
<td>Btss3</td>
<td>66-81</td>
<td>Mottled yellowish red (SYR 5/6) and yellowish brown (10YR 5/4) clay; few medium distinct light brownish yellow (10YR 6/4) mottles; moderate medium subangular blocky structure; very firm, very plastic, very sticky; few fine roots; shiny ped faces; few slickensides; slightly acid; clear wavy boundary.</td>
</tr>
<tr>
<td>Ckss</td>
<td>81-155</td>
<td>Light yellowish brown (2.5YR 6/4) clay; common fine, medium, and coarse distinct yellowish brown (10YR 5/6) and light olive brown (2.5Y 5/6) mottles; massive; very firm, very plastic, very sticky; common black stains; small pockets of powdery calcium carbonate; common fine and medium concretions of calcium carbonate; slightly alkaline.</td>
</tr>
</tbody>
</table>
Profile description for Hollywood silty clay loam soil.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth, cm</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0-15</td>
<td>Black (10YR 2/1) silty clay loam: moderate medium granular structure, friable; slightly sticky, very plastic; few coarse roots and many fine and medium roots; slightly acid, clear wavy boundary.</td>
</tr>
<tr>
<td>A2</td>
<td>15-56</td>
<td>Very dark gray (10YR 3/1) clay, common fine distinct brown mottles (10YR 4/4); moderate medium blocky structure; firm, very plastic, slightly sticky; few coarse roots and common fine and medium roots; common medium brown and black concretions; common shiny pressure faces, neutral gradual wavy boundary.</td>
</tr>
<tr>
<td>A3</td>
<td>56-74</td>
<td>Very dark gray (10YR 3/1) clay; many medium distinct yellowish brown (10YR 5/4 and 10YR 5/6) mottles, moderate medium blocky structure; very firm, very plastic, slightly sticky, few fine and medium roots; common fine and medium brown and black concretions; common shiny pressure faces; moderately alkaline; clear wavy boundary.</td>
</tr>
<tr>
<td>ACkss1</td>
<td>74-132</td>
<td>Light olive brown (2.5Y 5/4) clay; common medium distinct yellowish brown (10YR 5/4) mottles and few fine faint grayish brown (10YR 5/2) mottles; very firm, slightly plastic, slightly sticky; few fine roots; common fine brown and black concretions; many fine and medium concretions of calcium carbonate; few pockets of powdery calcium carbonate, common intersecting slickensides; moderately alkaline; gradual wavy boundary.</td>
</tr>
<tr>
<td>ACkss2</td>
<td>132-183</td>
<td>Light olive brown (2.5Y 5/4) clay; many fine and medium distinct light brownish gray (2.5Y 6/2) mottles, few medium prominent yellowish brown (10YR 5/8) mottles, and common medium distinct brown (10YR 5/3) mottles; very firm, slightly plastic, slightly sticky, few fine roots; common fine brown and black concretions; common shiny pressure faces; many concretions of calcium carbonate; few pockets of powdery calcium carbonate; common intersecting slickensides; moderately alkaline.</td>
</tr>
</tbody>
</table>
APPENDIX C. Plants recorded at the study sites from prairie, transition, and forest.

<table>
<thead>
<tr>
<th>Site</th>
<th>Location/Date</th>
<th>Plants</th>
</tr>
</thead>
</table>
| 1**    | Prairie (October 7, 2000) | Solidago nitida (Small shiny goldenrod)  
Carex microdonta (Littletooth sedge)  
Silphium laciniatum (Compass plant)  
Hedyotis nigricans (Diamond flowers)  
Gaura longiflora (Longflower beeblossom)  
Netptunia lutea (Yellow puff)  
Diodia teres (Poor joe)  
Heliotropium tenellum (Pasture heliotrope)  
Schizachyrium scoparium (Little bluestem)  
Dickanthelium sp.  
Euphorbia bicolor (Snow on the prairie)  
Ruellia humilis (Carolina wild petunia)  
Salvia azurea (Azure blue sage)  
Smilax bona-nox (Greenbriar)  
Sporobolus junceus (Pineywoods dropseed)  
Aster patens (Late purple aster)  
Helenium autumnale (common sneezeweed)  
Sorghastrum nutans (Indian grass)  
Onosmodium hispidissimum (softhair marbleseed)  
Panicum anceps (Beaked panicgrass)  
Liatris squarruiosa (Appalachian blazing star)  
Paspalum L. (Crowngrass)  
Solidago nitida (Small shiny goldenrod)  
Agalinis sp.  
Dalea L. (Prairie clover) |
| Transition (March 27, 2000) | Liquidambar styraciflua* (Sweetgum)  
Cornus drummondii (Swamp dogwood)  
Berchemia scandens (Rattan)  
Juniperus virginiana (Eastern redcedar)*  
Rubus sp. (Dewberry)  
Ulmus americana (American elm)  
Cornus florida (Flowering dogwood)*  
Acer barbatum (Southern sugar maple)  
Rhamnus caroliniana (Carolina buckthorn)  
Aesculus pavia (Red buckeye)  
Sassafras albidum (Sassafras)  
Viburnum rufidulum (Rusty blackhaw)  
Pinus taeda (Loblolly pine)  
Fraxinus sp. (Ash)  
Smilax bona-nox (Greenbriar)  
Lonicera japonica (Japanese honeysuckle) |
Forest (March 27, 2000)

Cornus florida (Flowering dogwood)*
Quercus alba (White oak)*
Ulmus americana (American elm)

Prairie (October 7, 2000)

Schizachyrium scoparium (Little bluestem)
Andropogon gerardii (Big bluestem)
Glandularia canadensis (Rose mock vervain)
Solidago nitida (Small shiny goldenrod)
Salvia azurea (Azure blue sage)
Echinacea pallida (Blacksamson echinacea)
Galactia sp.

Eragrostis spectabilis (Purple lovegrass)
Hedyotis purpurea (Venus’ pride)
Carex microdonta (Littletooth sedge)
Sorghastrum nutans (Indiangrass)
Berchemia scandens (Alabama supplejack)
Ambrosia
Setaria geniculata (Marsh bristlegrass)
Aster hemisphericus (Southern prairie aster)
Sporobolus junceus (Pineywoods dropseed)
Silphium laciniatum (Compassplant)
Liatris pycnostachya (Prairie blazing star)
Liatris squarrulosa (Appalachian blazing star)
Desmodium sp.
Mimosa sp.
Eupatorium sp.
Andropogon glomeratus (Purple bluestem)

Transition (March 28, 2000)

Berchemia scandens (Alabama supplejack)
Juniperus virginiana* (Eastern redcedar)
Pinus taeda (Loblolly pine)
Rubus sp.
Rhamnus caroliniana (Carolina buckthorn)
Gleditsia sp.
Ulmus americana (American elm)
Smilax bona-nox (Greenbriar)
Ilex decidua (Possumhaw)
Cercis canadensis (Eastern redbud)
Cornus drummondii (Swamp dogwood)
Viburnum L. (Viburnum)
Carya (Hickory)
Chionanthus virginicus (White fringetree)
Aesculus L. (Buckeye)
Callicarpa L. (beautyberry)
Acer barbatum (Southern sugar maple)*
Salvia lyrata (Lyreleaf sage)
Salvia azurea (Azure blue sage)
Liquidambar L. (Sweetgum)
Cornus florida (Flowering dogwood)
Glandularia canadensis (Rose mock vervain)
Hypoxis L. (Star-grass)
Solidago nitida (Small shiny goldenrod)
Crataegus L. (Hawthorn)

Rhamnus caroliniana (Carolina buckthorn)
Ulmus americana (American elm)
Pinus taeda (Loblolly pine)
Quercus sp. (Oak)
Cornus florida (Flowering dogwood)
Pinus echinata (Shortleaf pine)*
Acer barbatum (Southern sugar maple)*
Carya (Hickory)
Cornus drummondii (Swamp dogwood)
Viburnum rufidulum (Rusty blackhaw)
Liquidambar L. (Sweetgum)
Gleditsia triacanthos (Honeylocust)
Solidago nitida (Small shiny goldenrod)
Carex microdonta (Littletooth sedge)
Crataegus sp. (Hawthorn)
Berchemia scandens (Alabama supplejack)
Ilex decidua (Deciduous Holly/Winterberry)

Sporobolus R. Br. (Dropseed)
Salvia azurea (Azure blue sage)
Liatris squarrosa (Appalachian blazing star)
Aster hemisphericus (Southern prairie aster)
Dalea L. (Prairie clover)
Paspalum L. (Crowngrass)
Carex microdonta (Littletooth sedge)
Galactia P. Br. (Milkpea)
Dichanthelium sp.
Hedyotis nigricans (Diamondflowers)
Eupatorium sp.
Dichondra sp.
Aster patens (Late purple aster)
Desmodium sp.
Smilax bona-nox (Greenbriar)
Panicum anceps (Beaked panicgrass)
Onosmodium hispidissimum (Soft hair marbleseed)
Schizachyrium scoparium (Little bluestem)
Aristida L. (Threeawn)
Eryngium yuccifolium (Button eryngo)
Scleria sp.

Transition
(March 28, 2000)
Rhus radicans (Poison ivy)
Parthenocissus Planch. (Creeper)
Chasmanthium sessiliflorum (Longleaf woodoats)
Cacalia ovata (Ovateleaf cacalia)
Agrimonia microcarpa (Smallfruit agrimon)
Ulmus americana (American elm)
Cornus florida (Flowering dogwood)
Juniperus virginiana (Eastern redcedar)
Rhamnus sp.
Cercis canadensis (Eastern redbud)
Smilax bona-nox (Greenbriar)
Pinus taeda (Loblolly pine)
Chasmanthium L. (Woodoats)
Liquidambar L. (Sweetgum)
Ilex decidua (Deciduous Holly /Winterberry)
Viburnum rufidulum (Rusty blackhaw)
Berchemia scandens (Rattan)

Forest
(March 28, 2000)
Quercus sp. (Oak)
Comus florida (Flowering dogwood)*
Cercis canadensis (Eastern redbud)
Comus drummondii (Swamp dogwood)*
Pinus echinata (Shortleaf pine)
Ulmus americana (American elm)
Acer rubrum (Red maple )* 
Acer barbatum (Southern sugar maple)*
Carya (Hickory)
Viburnum rufidulum (Rusty blackhaw)

*Dominant plants
** The South side (up slope position) of site 1 was burned several times. The last burn probably occurred in 1998. The North side (down slope position) of the site has not been burned and is heavily encroached by Juniperus & various shrubs.
APPENDIX D. Contour plots of kriging standard deviation of soil properties for Keiffer prairie-forest transition (Site 1), Louisiana.

- a) pH
- b) EC (uS/cm)
- c) Ca (cmolc/kg)
- d) Mg (mg/kg)
- e) K (mg/kg)
- f) Fe (mg/kg)
- g) Mn (mg/kg)
APPENDIX E. Contour plots of kriging standard deviation of soil properties for Keiffer prairie-forest transition (Site 2), Louisiana.

a) pH

b) EC (µS/cm)

c) Ca (cmolc/kg)

d) Mg (mg/kg)

e) K (mg/kg)

f) Fe (mg/kg)

Easting (m)

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APPENDIX F. Contour plots of kriging standard deviation of soil properties for Keiffer prairie-forest transition (Site 3), Louisiana.

a) pH

b) EC (uS/cm)

c) Ca (cmol+/kg)

d) Mg (mg/kg)

e) K (mg/kg)

f) Fe (mg/kg)

g) Mn (mg/kg)
Asfaw Bekele was born in 1967 in Nekemte, Ethiopia. He earned a bachelor of science degree in chemistry in 1988 from the Addis Ababa University, Ethiopia. He began his career in September 1988 as a graduate assistant at the Wondo Genet College of Forestry, Ethiopia. There, he taught Chemistry and Soil Science courses until July 1995. He served the college as dean of students for three years where he was exposed to challenging, yet rewarding experience of working with people of diverse interests. In July 1995, Asfaw left the college on a Fulbright fellowship to pursue a master of science degree at Louisiana State University, U. S. A. He obtained his master of science degree in Agronomy with Soil Science major in December 1997.

Asfaw started his doctoral program in the Department of Agronomy at Louisiana State University in January 1998. In June 2000, he was accepted by the Department of Experimental Statistics at Louisiana State University into a dual degree program to pursue a master of science degree in Applied Statistics. He expects to receive both degrees in December 2001. Asfaw is a member of Sigma Xi, Gamma Sigma Delta, International Soil Science Congress, Soil Science Society of America, and American Society of Agronomy.
Candidate:  Asfaw Bekele

Major Field:  Agronomy

Title of Dissertation:  Spatial Variability and Isotopic Studies of the Prairie-Forest Transition Soil in Louisiana

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

August 31, 2001