LAND USE IMPACT ON SOIL GAS AND SOIL WATER TRANSPORT PROPERTIES

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LAND USE IMPACT ON SOIL GAS AND SOIL WATER TRANSPORT PROPERTIES

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Agriculture at the University of Kentucky

By
Sleem Ali Kreba

Lexington, Kentucky

Co-Directors: Dr. Ole Wendroth, Professor of Soil Physics and Dr. Mark Coyne, Professor of Soil Microbiology

Lexington, Kentucky

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ABSTRACT OF DISSERTATION

LAND USE IMPACT ON SOIL GAS AND SOIL WATER TRANSPORT PROPERTIES

The consequences of land use choices on soil water and gas transport properties are significant for gas and water flux in agricultural environments. Spatial and temporal patterns and associations of soil water and soil gas characteristics and processes in different land uses are not well understood. The objectives of this study were to 1) characterize soil structure under crop and grass systems, 2) quantify spatial patterns and associations of soil physical characteristics in crop and grass systems, and 3) quantify spatial and temporal patterns and associations of CO$_2$ and N$_2$O fluxes. The research was conducted in a 60 by 80 m field divided into grass and crop systems. Sixty sampling points were distributed in four transects with 5- and 1-m spatial intervals between measurement points. Gas fluxes were measured, at two-week time intervals, 22 times during a year. Pore size distribution was more homogeneous and more continuous pores were found in the grass than in the crop system. The spatial variability of most selected soil physical characteristics was more structured in the crop than in the grass system, which reflected the impact of land use and soil structure on their spatial patterns. CO$_2$ flux was dependent for a longer distance in the grass than in the crop system, however, the two land-use systems exhibited similar spatial ranges of N$_2$O flux. Gas fluxes were temporally dependent for a longer period in the grass than in the crop system. The spatial associations between CO$_2$ and N$_2$O fluxes and selected biochemical and physical factors depended on the flux sampling season and land use. Soil temperature was the dominant controlling factor on the temporal variability of CO$_2$ and N$_2$O fluxes but not on the spatial behavior. Considering the spatial and temporal ranges and dependency strength of soil variables helps identify efficient sampling designs that can result in better time and resource management. Spatial and temporal relationships between the selected soil variables also improve understanding soil management and sampling soil variables. This study provides the baseline and recommendations for future investigations specifically for sampling designs, soil management, and predictions of different soil processes related to gas fluxes.
LAND USE IMPACT ON SOIL GAS AND SOIL WATER TRANSPORT PROPERTIES

By

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September 2013
Dedicated to.....

the loving of my mother "Om-alsaad Alshween” whose unending love and sacrifices inspired and encouraged me, my father "Ali Kreba” who instilled in me the value of education, my sisters and brothers Ali, Ahmad, and Milad who supported me in this endeavor.
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LIST OF ABBREVIATIONS AND SYMBOLS

A  Cross-sectional area
a  Range of representativity
Ai  Soil variable
b  Intercept of a linear relationship
Bi  Soil variable
Cg  Gas (CO₂ or N₂O) concentration
C₀  Initial oxygen concentration in the diffusion chamber
c₀  Nugget variance in a semivariogram
Cᵣ  Oxygen concentration in the diffusion chamber at a specific time t
c₁  Structural component of variance in a semivariogram
CV  Coefficient of variation
DC  Dissolved carbon
D₀  Diffusion coefficient of a specific gas in the air
d₁/d₀  Difference between measurements of relative gas diffusivity at two matric potentials
Dg/D₀  Relative gas diffusion coefficient
dᵢ  Difference between predicted and measured values of relative gas diffusion coefficients
DN  Dissolved nitrogen
Dᵣ  Apparent gas diffusion coefficient
DₛT₂  Gas diffusion coefficient at temperatures T₂ (20 °C)
DₛT₁  Gas diffusion coefficient at temperatures T₁ (K)
εᵣ  Apparent permittivity
fₘᵣ  Adjusted gas flux based on sampling time
fₘᵣT  Adjusted gas flux based on soil temperature
fₘᵣᵢ  Adjusted gas flux at a particular sampling point i and time j
fₑg  Estimated gas flux using regression between soil temperature and observed flux
fₘᵣᵢ  Mean of adjusted gas flux determined for one sampling campaign consisting of two consecutive days
fₙ  Gas flux density
f\left(\frac{l}{l_c}\right)^²  Pore-continuity index
f  Reduction factor in gas diffusion due to water blocked or constricted pore
h  Lag distance
Water flux
Hydraulic conductivity at \( \psi \) matric potential
Saturated hydraulic conductivity
Length of the soil pore
Length of the soil core
TDR probe length
Mass of dry soil
Aggregate mean weight diameter
Mass of field moist soil
Number of observations
Slope of soil water retention curve
Water flow rate
Root mean square error
Radius of soil core
Rank of a variable observed at location \( i \) on date \( j \)
Standard deviation
Standard deviation of mean relative difference
Soil organic matter
Air sensor temperatures
Time domain reflectometry
Total nitrogen
Temperature
Time
Travel time through TDR probe
Oxygen sensor temperature
Optimized intercept of Troeh et al. (1982) model
Optimized slope of Troeh et al. (1982) model
Variance
Total volume of soil core
Volume of air in the gas flux chamber
Volume of the diffusion chamber
Velocity of light in a vacuum
Water volume in the soil core
Wet-aggregate stability
Soil core weight
Net weight of stable aggregates
Net weight of unstable aggregates
Proportion of the total sample weight for the corresponding aggregate size fraction
Mean diameter of each aggregate size fraction
Sampling location
\[ Y \] Number of pairs of a soil attribute
\[ Z \] Height of gas flux chamber
\[ z_i \] Observation
\[ \theta_a \] Air-filled porosity
\[ \theta_r \] Residual volumetric water contents
\[ \theta_\psi \] Soil water retention at matric potential \( \psi \)
\[ \theta_s \] Saturated volumetric water content
\[ \theta_{TDR} \] Soil water content measured using TDR
\[ \theta_{w_g} \] Soil gravimetric water content
\[ \theta_{w_v} \] Soil volumetric water content
\[ \phi \] Total porosity
\[ \rho_b \] Soil dry bulk density
\[ \rho_s \] Soil particle density
\[ \alpha \] Inverse of the air entry value of retention curve
\[ \gamma(h) \] Experimental semivariogram
\[ \hat{\gamma}(h) \] Spherical semivariogram model
\[ \Gamma(h) \] Experimental cross-semivariogram
\[ \psi \] Soil water matric potential
\[ \bar{\delta}_i \] Mean relative difference
\[ \delta_{ij} \] Relative difference
\[ \vartheta \] Pore-continuity index
\[ \Delta h \] Hydraulic gradient
\[ \Delta_{ij} \] Difference between individual measurements of a variable observed at location \( i \) on date \( j \)
CHAPTER 1: Introduction

This chapter establishes the relevance of the subject area, provides a brief background and the importance of the research, and it delivers an overview of the relevant literature. The review covers specific topics related to soil structure, spatial variability of soil properties, and spatial and temporal patterns of greenhouse-gas emissions from soils. These topics include different soil physical properties quantified to characterize soil structure in crop and grass systems such as soil bulk density, aggregate size distribution, wet-aggregate stability, and characteristics of soil hydraulic conductivity, soil water retention, soil gas diffusivity, and air-filled porosity. Basic concepts of spatial and temporal variability and their sources are also reviewed.

1.1 Soil structure

Soil structure is defined by considering different aspects. For example, in terms of the description of solid and void phases, soil structure is “the physical constitution of a soil material as expressed by the size, shape, and arrangement of the solid particles and voids, including both the primary particles to form compound particles and the compound particles themselves” (Brewer, 1964). In terms of soil aggregates and their development, another definition of soil structure can be “the arrangement of single mineral particles and organic substances to greater units known as aggregates and corresponding inter-aggregate pore system” (Horn et al., 1994). Dexter (1988) defined soil structure as “the spatial heterogeneity of the different components or properties of soil.” He stated that the aspects of soil structure were manifested at many different size scales in soil, for
example, the arrangement of colloidal clay particles in a floccule, the arrangement of clods on the surface of a tilled layer, an array of earthworm tunnels, and the variability of soil strength from one point to another.

Soil structure affects plant growth, soil water balance, and soil workability. Soil supplies water and oxygen to plant roots. Water supply to roots requires storage capacity but also the ability of the soil to transmit water to the root surfaces in response to potential gradients (Dexter, 1988). Plant roots need oxygen, which moves extremely slowly through water. Therefore, continuous air-filled pores are required for gas exchange between soil and the atmosphere. Oxygen supply to roots depends on several complex factors such as pore continuity, tortuosity, and size and spacing of air-filled pores (Dexter, 1988). Soil strength can influence plant growth by resisting root growth. Soil strength is a consequence of soil structure because it is strongly influenced by the packing of soil particles and by the cementing between the particles that can be produced by smaller particles and various inorganic and organic compounds (Dexter, 1988).

Soil structure has important impacts on soil water transport properties. Soils with sufficient pore volume let water infiltrate as fast as it is applied, which prevents run-off and erosion. Macropores including vertical earthworm channels allow water to infiltrate and bypass much of the soil matrix, so neither water nor the fertilizer it transports may be available for plant uptake. Macropores may also transport fertilizer, herbicides, pesticides, and microorganisms directly to the groundwater (White, 1985) if these chemicals applied to the soil just before a rainfall event. Micro-aggregates developed by
slaking larger aggregates and clay dispersion can eliminate larger soil pores with a significant consequent reduction in soil hydraulic conductivity (Dexter, 1988). Compacted soil layers can severely impede water infiltration; a little compaction can produce a large decrease in soil hydraulic conductivity (Dawidowski and Koolen, 1987).

Soil structural features of a given size are produced either by a combination of structural elements of lower hierarchical orders or by fragmentation of structural elements of higher hierarchical orders. Hadas (1987) introduced the concept of soil structure as a hierarchy. His hierarchical order of soil aggregation referred to the lowest hierarchical order as the combination of single mineral particles into a basic type of compound particles. The next hierarchical order was larger compound particles and so on. Compound particles of lower hierarchical order are denser than those of higher hierarchical order because each order excludes the pore spaces between the particles of the next higher order. Compound particles of lower hierarchical order also have a higher internal strength than particles of higher hierarchical order. Braunack et al. (1979) reported that aggregate tensile strength decreased with increasing aggregate size in a given soil.

Land use and soil management influence soil structure differently. Land use can influence physical, chemical, and biological factors affecting soil structure. For instance, soils under a pasture land use had higher hydraulic conductivity at -100 cm matric potential than soils under cultivated land use (Francis and Kemp, 1990; Bormann and Klaassen, 2008). Aggregate size in soils under grassland was larger and aggregates were more stable compared to aggregates in soils under cropland (John et al., 2005). Land use
can influence soil microbial activity by increasing or decreasing, for instance, carbon pool, nutrient availability, water content, and soil temperature. Soil microorganisms are fundamental to soil structure and soil formation. They can promote soil aggregation by physically binding soil particles, especially water-stable aggregates, by producing extracellular polysaccharides, glomalin, and hyphae (Hartel, 2005). Soil conservation approaches can increase aggregation by increasing the amount of carbon added to soil, decreasing the rate of carbon loss by decomposition and erosion, and conserving nutrients (Bronick and Lal, 2005).

1.2 Measurement of soil structure

Soil structure can be characterized by physical and morphological measurements. This study focuses on characterizing soil structure using soil physical properties such as soil bulk density, aggregate size distribution, wet-aggregate stability, and characteristics of soil water retention, soil hydraulic conductivity, soil gas diffusivity, air-filled porosity, and soil pore-continuity indices.

1.2.1 Soil bulk density

Soil dry bulk density is the ratio of the mass of solids to the total soil volume. The bulk density is a key physical property of any porous material and changes in response to disturbance and soil management practices (Skopp, 2002). From its definition, soil bulk density is a direct indicator of soil porosity. High bulk density reflects lower porosity and low bulk density indicates higher porosity. Bulk density can also indicate other factors such as root penetrability, soil strength, and soil compaction (Skopp, 2002), which are
strongly related to land use and soil management. Soil bulk density is influenced by soil texture; sandy soils have higher bulk density than clayey soils. The wide range of bulk density for a particular texture indicates that other factors such as organic matter and compaction status have an important influence on bulk density (Skopp, 2002). Under soil loss conditions, the bulk density can be highly labile and reflects soil structure, degree of compaction, and soil swelling and shrinkage characteristics (Hillel, 1998).

The impact of land use on soil bulk density has been evaluated in several studies (Murty et al., 2002; Bormann and Klaassen, 2008; Hu et al., 2009) in which soils under grassland had lower bulk density than soils under cropland. An accurate estimate of bulk density with a sufficient number of observations is still a challenge because bulk density exhibits high spatial variability. However, the spatial variability of bulk density under different land uses has not been studied intensively, and it is included in this study.

1.2.2 Aggregate size distribution and wet-aggregate stability

In soils containing more than 15% clay, the mineral particles tend to form structured units called aggregates (Horn et al., 1994). “An aggregate is a group of primary particles that cohere to each other more strongly than to other surrounding soil particles” (Kemper and Rosenau, 1986). Soil aggregates can be formed by aggregation and fragmentation processes. Aggregate development occurs due to a combination of soil physical, chemical, and biological processes. The widely used concept of aggregate hierarchy refers to microaggregates bound together into macroaggregates by transient binding agents (i.e., microbial- and plant-derived polysaccharides) and temporary binding agents.
(roots and fungal hyphae) (Tisdall and Oades, 1982; Six et al., 2000; John et al., 2005).

The consequences of this aggregate hierarchy are an increase in carbon concentration with increasing aggregate size due to larger aggregates being composed of smaller aggregates plus organic binding agents (Elliott, 1986; John et al., 2005).

Soil aggregate size distribution and aggregate stability are important properties in different applications of soil science. Aggregate size distribution and aggregate stability are used to quantify the impact of land use and soil management such as tillage practices and organic matter applications on soil structure, soil erosion, soil surface sealing processes, and soil productivity. Aggregate size distribution and aggregate stability are soil structural features and related to soil macropores, water infiltration and runoff, soil aeration, and root growth (Nimmo and Perkins, 2002). Aggregate properties are also used to predict soil hydraulic properties such as soil water retention and unsaturated hydraulic conductivity characteristics (Rieu and Sposito, 1991; Nimmo, 1997; Kosugi and Hopmans, 1998). Land use impacts on soil aggregate size distribution and aggregate stability were studied by John et al. (2005) who found that aggregate size distribution was affected by land use and cultivation.

Aggregate stability refers to the ability of soil aggregates to resist disruption when outside forces, usually associated with water, are applied. The stability of aggregates is affected by soil texture, the predominant type of clay, extractable iron and cations, the amount and type of organic matter, and the type and size of the microbial population. Land use affects physical, chemical, and biological factors related to aggregate stability;
the latter are considered strongly related to soil carbon and organic matter stabilization (Six et al., 1999; Shepherd et al., 2001). Bird et al. (2002) concluded that high variability of aggregate stability and soil carbon had important implications for carbon sequestration, and the multi-scale heterogeneity of aggregate stability must be considered when measuring and managing for carbon sequestration. It is commonly assumed that aggregate size distribution and aggregate stability vary randomly within the field, and the spatial structure of their variability is ignored: this assumption is evaluated in this study.

1.2.3 Soil water retention characteristics

The most fundamental characteristics of the soil water phase are the amount of water in a given amount of soil and the forces holding water in the soil matrix (Jury and Horton, 2004). The first variable (soil water content) is important for different processes in soil such as gas exchange with the atmosphere, diffusion of nutrients to plant roots, and soil temperature. The forces soil exerts on water influence different soil processes including the efficiency of water absorption by roots, the amount of drainage of water and solute occurring due to gravity, and the extent of upward water and solute movement against gravity (Jury and Horton, 2004).

The functional relationship between the soil matric potential and the soil water content is called the soil water characteristic function or the soil water retention curve. It is an important soil property related to the distribution of pore space, which is strongly influenced by soil texture, soil structure, and related factors such as soil organic matter (Or and Wraith, 2002). The soil water retention curve is required for applications related to managing and predicting water behavior in soil such as modeling water flow and
irrigation management. Jury and Horton (2004) divided the typical water retention curve into three regions; an air-entry region, a capillary region, and an adsorption region. The air-entry region corresponds to the region at saturation; the capillary region corresponds to the region where smaller pores drain progressively and air began to enter the soil; the adsorption region refers to the region where all of the water held in pores is drained and the only water remaining is that adsorbed and tightly bound to particle surfaces.

Several studies have compared the soil water retention characteristics between soils under crop and grass systems (e.g., England, 1971; Schwärzel et al., 2011). Converting native vegetation to managed land can decrease litter accumulation and soil organic matter, and improve soil water retention characteristics and soil structure (Berglund et al., 1980; Harden, 2006) because organic matter is an important binding agent and has its role in soil aggregate development and stability. Price et al. (2010) reported that variability of soil physical properties due to differences in land use were expected to result from two mechanisms. The first was direct compaction by heavy equipment. The second was variation in macropore development, organic matter, and soil structure associated with vegetation type and fauna.

Spatial heterogeneity of soil water characteristics highly affects quantifying and predicting water and solute transport in soil and leaching of solutes to the groundwater. This spatial variability is caused by the heterogeneity of soil physical properties related to the soil water characteristics and by the variability of soil water content and matric potential. To derive effective parameters for transport models at the field scale, the
spatial pattern and the spatial continuum of soil moisture state variables have to be identified (Wendroth et al., 1999). Effective sampling design to assess soil hydraulic properties is still a major challenge and direct measurements of soil surface moisture with a high spatial resolution are not feasible for large regions. Therefore, indirect methods, e.g., remote sensing techniques, have been developed and used (Wang and Choudhury, 1981; Gillies and Carlson, 1995).

1.2.4 Soil hydraulic conductivity

Soil hydraulic conductivity is a soil property affected by total porosity, the distribution of pore size, and pore geometry (e.g., tortuosity and connectivity) (Hillel, 1998). The geometry of the porous material, which is determined primarily by the mechanical composition of the solid matrix and is altered by swelling and clay dispersion, controls soil hydraulic conductivity (Bresler et al., 1984).

Land-use practices are among the most important factors influencing soil hydrology and are attributed to the effects of tillage, erosion, compaction, and pore structure evolution (Rasiah and Kay, 1995; Harden, 2006). Soils under native vegetation, such as undisturbed forest or grassland, generally feature low bulk density and high saturated hydraulic conductivity, total porosity, and macroporosity, due to ample litter cover, organic inputs, root growth and decay, and abundant burrowing fauna (Lee and Foster, 1991). On the other hand, soils exposed to human activities are often stripped of organic-rich horizons and compacted by heavy equipment or livestock, therefore the bulk density increases and infiltration rates are reduced (Celik, 2005; Li and Shao, 2006). Replacing natural
vegetation with managed land cover is associated with decreased rooting networks and faunal activity, and reduces the potential for well-developed macropore networks (Reiners et al., 1994; Schwärtz et al., 2003). For example, the rooting system of woody vegetation, such as forest plants, demonstrates substantially greater depth, diameter, dispersion, and biomass than rooting system of cultivated crops (Lee and Lauenroth, 1994; Jackson et al., 1996; Messing et al., 1997).

Quantifying the impact of different land uses on soil hydrological properties and characteristics leads to better understanding of how land-use change influences watershed hydrologic processes and for providing data for hydrologic modeling to predict hydrologic responses to land-use change. Price et al. (2010) concluded that soil modification from forest to pasture and lawn was a significant driver of the watershed hydrologic changes with increased floods and reduced base-flows. Bormann and Klaassen (2008) reported that the assumption of the constant parameterization of hydraulic models being independent from land use did not hold. They also stated that spatial variability of soil hydraulic properties and functions and the dependency on land use should be considered in these models. Bormann et al. (2007) pointed out that hydrological models were sensitive to soil parameterization related to land use, and hydrological models must be improved to consider the entire variability in soil hydraulic properties.

Soil hydraulic properties exhibit spatial and temporal variation. Van Es et al. (1999) stated that soil hydraulic properties were influenced by numerous sources of variability,
mostly related to spatial, temporal, and management factors. The variability sources of soil hydraulic properties are important due to the impact of these sources on soil hydraulic properties themselves and the impacts of the variation of these properties on the simulated processes and the simulated boundary conditions (Boesten, 1991; Holden et al., 1996). Van Es et al. (1999) reported that the variability among soil types was assumed to be the most important source of the variability of soil hydraulic properties and the significance of spatial, temporal, and management sources was not well known. Understanding the significance of variability for sources of soil hydraulic properties is important to develop efficient sampling protocols and for proper parameterization for modeling scenarios. Van Es et al. (1999) concluded that parameterization of soil hydraulic properties based on soil type may not be appropriate for agricultural lands because soil management factors were more significant. Wendroth et al. (2006) found that a pedotransfer function did not provide sufficient flexibility to describe the spatial variability observed in the field.

1.2.5 Soil gas transport characteristics

Gases move in porous media such as soil by two major mechanisms, gas convection and gas diffusion. In gas convection, the gas moves in response to the air pressure gradient. Gas diffusion is the principal mechanism for the exchange of gases between the soil and the atmosphere (Rolston and Moldrup, 2002; Jury and Horton, 2004) and it is a result of concentration gradients. The gradients can be caused by local increase or decrease of the gas concentration as a result of plant root and microbial respiration and biological reactions such as fermentation, nitrification, and denitrification.
The diffusivity in air varies with the molecular weight and diameter of the gas and depends on the temperature and pressure of the gaseous medium through which the gas diffuses (Bird et al., 1960). To eliminate the effect of specific gas properties on the diffusion processes, the measured “apparent” diffusion coefficient of a gas in soil, \(D_s\), is usually normalized with the diffusion coefficient of the same gas in air \(D_0\) at the same pressure and temperature. This ratio, the relative gas diffusivity \(D_s/D_0\), therefore depends only on soil properties. In a porous media, diffusion depends on the fractional volume of the continuous gas phase. Gas diffusivity is little influenced by the shape of the solid surface but it is affected by pore tortuosity because the mean free path of the diffusing molecules is generally much smaller than the width of the pores (Hillel, 1998). Gas diffusivity is also related to soil properties such as air-filled porosity, soil structure, bulk density, and pore tortuosity and continuity (Jin and Jury, 1996). Gas diffusivity is expected to vary spatially and temporally because it depends on spatially and temporally variable soil physical properties including soil water content, which is one of the major factors controlling the temporal and spatial patterns of soil gas diffusivity and its magnitude under different land uses.

Soil gas diffusivity and air-filled porosity are important soil properties used as indicators of soil aeration and soil structure (Troeh et al., 1982). The gas diffusion coefficient and permeability are more direct indices of soil aeration than air-filled porosity (Grable, 1971). Several processes in soil depend on gas movement. Diffusion is responsible for gas exchange between soil and the atmosphere, e.g., removing excess greenhouse gases
and volatile organic compounds from soil and providing oxygen for root and soil organism respiration. Hence, gas diffusivity and air-filled porosity are important properties of concern for various fields of soil and environmental investigation. Soil gas diffusivity and air-filled porosity vary with different land uses due to the impact of land use on soil structure and soil water status. The influence of land use on gas diffusivity and air-filled porosity is rarely investigated, therefore it is considered in this study.

Soil gas diffusivity and air-filled porosity exhibit high variation in space due to the influence of different factors such as soil water retention properties and the heterogeneity of pore size distribution and pore geometry. Predicting diffusivity from air-filled porosity is a commonly used approach to quantify gas diffusion processes for the entire field - ignoring its dependency on space. Soil gas diffusivity is strongly related to other soil physical properties, such as air-filled porosity, soil bulk density, and soil water retention properties, which are known as spatially and temporally variable properties. Relationships between gas diffusivity and different soil properties have been developed to predict gas diffusivity in different soil types (Penman, 1940; Troeh et al., 1982; Ehlers et al., 1995; Jin and Jury, 1996; Moldrup et al., 2000), however the spatial processes of gas diffusivity have rarely been investigated, and this knowledge gap is filled in this study.

Field measurements of soil gas diffusivity exhibit high variation due to error sources in the field due to difficulties associated with controlling boundary conditions (Rolston et al., 1991; Ball et al., 1994). These estimated values with uncontrolled boundaries, which are derived from field measurements and their variability in space, are usually not
discussed. Lange et al. (2009) stated that the variability of relative gas diffusivity in the field was unknown and the sample size and the spatial density of gas sampling strategy could influence the estimated variability of gas diffusivity. Lafond et al. (2011) stated that the spatial variability of soil gas diffusivity had rarely been studied because of measurement difficulties.

1.3 Spatial variability of soil properties

1.3.1 Soil variability

Soil variability is the change of a soil property as a function of space or time. Variations in soil properties tend to be correlated over space or time, for instance, two observations taken close together are more alike than two samples farther apart (Warrick et al., 1986). The variability in soil systems belongs to two broad categories: systematic (structured) and random (unstructured) (Wilding et al., 1994). The systematic variability is a gradual or marked change in a soil property as a function of physiography, geomorphology, and interactions of soil-forming factors (Wilding and Drees, 1983). In other words, if changes over short distance or time intervals are smaller than changes occurring over long intervals, the variability is structured and a range of representativity can be derived. The variation is random if the variance observed over the shortest sampling interval is in the same magnitude of the population variance (Wendroth et al., 2011).

1.3.2 Sources of soil variability

The sources for variability of soil physical properties are spatial and temporal and they are the result of intrinsic (natural) or extrinsic (cultural or management related) processes
(van Es, 2002). Natural soil variability is the result of the geological, hydrological, and biological factors that affect pedogenesis, and they are scale-dependent. Extrinsic factors include, for example, tillage, drainage, plant cover, and vehicle traffic, and they are also scale-dependent. Van Es et al. (1999) concluded that the relative significance of all sources of variability needed to be taken into account when designing soil studies because results may be seriously biased if observations were generalized over large areas, longer time domains, or multiple management practices. They also reported that the parameterization of soil hydraulic properties solely based on soil type may not be appropriate for agricultural lands because soil-management factors were more significant, and temporal factors also needed to be recognized. When sampling procedures are designed, adequate recognition should be given to soil management and temporal processes as significant sources of variability to avoid biased results by carefully selecting the scale triplet (spacing, extent, and support).

1.3.3 Auto-semivariogram

In cases where observations show structured variability, the semivariance usually increases with distance between sample locations, called lag distance, to a constant value (a plateau) or sill (total variance) at a given distance known as the range of spatial dependence (Figure 1.1). A semivariogram is inversely related to the auto-covariance and its ranges depend on the spatial interaction of soil processes affecting each property at the sampling scale used (Trangmar et al., 1985). Theoretically, the semivariance at the same location where the measurement is taken is equal to zero, but the experimental
Figure 1.1. A theoretical spherical semivariogram showing the spatial range, nugget, and sill parameters.
semivariogram frequently exhibits a discontinuity at the local scale known as the nugget variance. Nugget variance represents the variance at the sampling scale and reflects the relationship between the size of the sample and the inter-sampling distance (Russo and Bresler, 1981). The same concepts are applicable for temporal processes.

1.3.4 Cross-semivariogram

The spatial or temporal relationship (cross-semivariance behavior) of one variable with another can be quantified if the spatial or temporal variation structure and the range of representativity are identified. Cross-semivariance quantifies the spatial and temporal relationships between two variables or soil properties sampled at different spatial or temporal scales. Cross-semivariance analysis provides the opportunity to determine how far apart in space or time from each other samples can be taken to yield observations that remain related with each other if the spatial or temporal variation of two sets of measurements is known (Cassel et al., 2000).

The cross-semivariogram expresses the spatial relationship between two variables when sampled at progressively greater separation distances across the landscape (Nielsen and Wendroth, 2003). Cokriging is an interpolating procedure that takes advantage of spatial correlation between two sets of properties (Nielsen and Wendroth, 2003). It allows the possibility of interpolating values of one property from another.
1.3.5 Measurement scale

Measurement scale plays an important role in quantifying spatial and temporal variability of soil variables because the apparent variability can be different from the true natural variability and the difference is a function of the measurement scale (Blöschl, 1998). The measurement scale is an important concept of soil process predictions when the scale at which the data are collected is different from the scale at which the predictions are needed. In other words, transferring information from one scale to another is a complex task. As described by Blöschl and Sivapalan (1995), the measurement scale concept consists of the scale triplet - spacing, extent, and support. Spacing indicates the distance between samples, extent refers to the domain size, and support refers to the integration volume or area of an individual sample. The effect of spacing, extent, and support should always be viewed as relative to the scale of the natural variability (process variability) (Blöschl and Sivapalan, 1995). The process scale can be identified as the scale where observations are spatially or temporally dependent. Spatio-temporal statistical techniques are often used to identify the spatial and temporal dependency. In this data analysis, the true variance in the data will be different relative to the apparent variance because it is influenced by bias (Western and Blöschl, 1999), and the apparent variance is a function of the ratio of the true length where the observations are dependent on the measurement scale. “Large-scale measurements can only sample large-scale variability and small-scale measurements can only sample small-scale variability. As a consequence of this, large measurement scales (in terms of spacing, extent and support), compared to the process scale, will generally lead to apparent correlation lengths that are larger than the true
correlation lengths, and small measurement scales will cause an underestimation of the correlation lengths” (Western and Blöschl, 1999).

1.4 Spatial and temporal patterns of CO₂ flux

Carbon dioxide flux at the soil surface is an important component of the carbon cycle that exhibits high variation in space and with time (Hanson et al., 1993; Davidson et al., 1998; Law et al., 2001). Quantifying carbon fluxes and deriving their spatial and temporal domains of representativity is a complex task because fluxes vary at different scales and depend on many different processes and state variables. For example, nutrient dynamics (Heimann and Reichstein, 2008) and soil, and water, air, and soil temperature status strongly affect carbon transformation and respiration (Raich and Tufekcioglu, 2000; Le Mer and Roger, 2001).

Spatial variability of measured CO₂ flux is often considered to contribute to inaccuracy of its measurement, especially when the variation is spatially random (Aiken et al., 1991). In that case, many observations may be necessary to obtain a field-representative mean value of CO₂ flux (Dugas, 1993). Rochette et al. (1991) indicated that between 30 and 190 samples are needed to estimate the mean soil respiration of a one-hectare wheat plot, depending on climate, soil conditions, and the growing season. This means a large sampling effort to merely obtain the mean value and basic statistics of CO₂ flux over a relatively small domain. Studying the spatial variability of CO₂ flux would provide an opportunity to consider it as a spatial process (Wendroth et al., 2011), and to derive its spatial variability structure, range of representativity, and spatial pattern stability in time and under different soil and environmental conditions. Moreover, to relate the spatial
behavior of CO$_2$ flux to any other spatial process, it is essential that all processes involved in the description represent a spatial domain overlapping the domain represented by a CO$_2$ flux measurement. The same considerations are valid for quantifying CO$_2$ fluxes in the temporal domain. The suitability of a scheme to monitor the behavior of CO$_2$ fluxes strongly depends on their spatial and temporal variation (Fang et al., 1998) and that of associated variables.

Little is known about the space-time behavior of CO$_2$ fluxes, how their magnitude, variance, and spatial correlation lengths vary, whether spatial patterns of CO$_2$ fluxes are temporally stable, and how important statistical properties behave under different land-use systems. Herbst et al. (2009) from their study in a 14 by 14 m area concluded that quantifying the temporal behavior of CO$_2$ fluxes was less complicated than quantifying the spatial behavior, and that the spatial correlation length of CO$_2$ fluxes depended on the scale of investigation. In general, it is not known whether the spatial structure varies with season and with the magnitude of CO$_2$ fluxes in a similar way as, for example, the behavior of soil water content (Wendroth et al., 1999). In a 5 by 5 m plot, Fóti et al. (2008) noticed different magnitudes of CO$_2$ fluxes between measurements in warm and cool seasons. They also found, in general, large nugget-to-sill ratios (> 0.7). Moreover, less evidence of spatial structure, hence more random behavior of CO$_2$ fluxes, became obvious when flux was measured at times when the overall variance was relatively small. However, no consistent effect on the correlation range was found by Fóti et al. (2008) for different times and different magnitudes of CO$_2$ fluxes.
Land use is known to have a general impact on the magnitude of CO$_2$ fluxes (Emran et al., 2012). In addition to comparing different land-use systems, Iqbal et al. (2009) illustrated the strong seasonal impact of air temperature and precipitation on CO$_2$ fluxes under subtropical conditions. The overall magnitudes of trace gas fluxes they measured were influenced by soil nutrient status in the different land-use systems investigated, i.e., vegetable, upland, orchard, and pine forest. The impact of existing land-use system and spatial soil organic carbon distribution on the magnitude and the spatio-temporal dynamics of soil respiration have been noted in many studies. Raich and Tufekcioglu (2000) and Le Mer and Roger (2001) addressed the influence of land use through impact on microbial activity and soil physical conditions such as soil temperature and soil water content. Other factors such as plant photosynthesis can affect the root respiration contribution to soil respiration (Craine et al., 1999), which is also known to vary among land uses.

Scott-Denton et al. (2003) investigated seasonal changes of soil respiration rates and their spatial variances to identify possible covariation with soil temperature, soil water content, and soil carbon for upscaling respiration measurements over time and space but found severe changes in the relationships between respiration rates and covariates depending on the season. A possible explanation for this result could be a changing spatial variability structure. They concluded that variation in temperature was the primary temporal control seasonally, whereas variation in moisture was the primary temporal control inter-annually. Moreover, variation of carbon pools, especially those represented by microbial biomass, was the primary spatial control over respiration rate (Scott-Denton et al., 2003).
Although Konda et al. (2010) found strong spatial dependence of N₂O fluxes regardless of the season, CO₂ and CH₄ fluxes remained spatially uncorrelated under the conditions of that study in a 100 by 60 m field in Sumatra, Indonesia.

1.5 Spatial and temporal patterns of N₂O flux

The main sources of N₂O are microbial processes in soils, namely nitrification and denitrification (Bouwman, 1990). Nitrification is the biological oxidation of ammonia with oxygen into nitrite followed by the oxidation of nitrite into nitrate. Denitrification is a microbial process of nitrate reduction that may ultimately produce molecular nitrogen (N₂) through a series of intermediate gaseous nitrogen oxide products, NO and N₂O.

The spatial variability of N₂O emission from field soils has been recognized by several investigators (Rolston et al., 1978; Findlay et al., 1979; Matthias et al., 1980; Mosier et al., 1982). These studies and others focused on investigating the emission of N₂O from field soils and its variability under different water and fertilizer management practices. However, few studies compared the variability of N₂O emission between different land uses. The aim for these studies was to improve the efficiency of nitrogen utilization by reducing N₂O emission and to understand the global behavior of N₂O flux from soils. These studies revealed large spatial variability of the N₂O flux from field soils. Robbins et al. (1979) studied the spatial and temporal variability of N₂O flux within small areas (20 by 20 m) and reported coefficients of variation ranging from 31 to 168%. They stated that the accuracy of N₂O flux measurements was more limited by sampling problems resulting from spatial and temporal variability than by analytical problems associated
Matthias et al. (1980) concluded that the accuracy of the mean N$_2$O flux depended more on the number of flux measurements than on the accuracy of any particular flux measurement. In contrast, Folorunso and Rolston (1984) reported that the fluxes of N$_2$O measured on Yolo loam were generally spatially independent. They stated that their result was not surprising because flux integrated the activities of large population of denitrifying organisms in soil anoxic microsites as well as the complex nature of the soil properties like gaseous diffusion coefficient, soil texture, soil structure, water content, and diffusion of nutrients to the anaerobic microsites. They reported also that the lack of spatial structure made it impossible to make predictions of N$_2$O fluxes for unsampled locations using measured values at sampled locations.

Improving our knowledge of the soil and environmental factors governing N$_2$O flux should improve our ability to quantify the flux and to extrapolate to larger scales without making vast numbers of direct flux measurements. Assessing spatial and temporal variability of N$_2$O flux in relation to controlling factors helps identify the most influential factors, and this information is useful in predictive flux models (Li et al., 1992; Grant et al., 1993; Nishina et al., 2009a). Many studies have investigated the correlations between N$_2$O flux and soil moisture, soil temperature, soil pH, soil nitrate or ammonium, and soil organic matter (e.g., Denmead et al., 1979; Mosier et al., 1981; Yamulki et al., 1995). Fewer studies have looked at the influence of soil physical properties in the field on N$_2$O fluxes (Ball et al., 1988; Arah et al., 1991; Ball et al., 1997). The influences of soil physical properties and functions such as gas diffusivity, air-filled porosity, and soil water retention characteristics on N$_2$O flux and its spatial variability in different land uses
are not fully understood. An accurate quantification of the N\textsubscript{2}O emissions from different soils and under different land-use systems and a good insight into the factors that control N\textsubscript{2}O emissions from soils are needed to devise efficient strategies to mitigate and better quantifying the flux of N\textsubscript{2}O. Insight in spatial variability can be used to derive management tools to mitigate N\textsubscript{2}O fluxes especially when the spatial patterns of the flux persist in time (Velthof et al., 2000).

1.6 Objectives

This study addresses fundamental questions of how land use affects soil structure and environmental features associated with soil structure that influence gas flux and therefore influence the prediction of gas flux or its evaluation. The impacts of land use on soil structural properties and their spatial patterns in crop and grass systems are not well understood. The field-scale behavior of CO\textsubscript{2} and N\textsubscript{2}O fluxes, their change in spatial representativity, their correlation structure, their spatial pattern temporal stability in different land-use systems, and their spatial and temporal associations with biochemical and physical factors are also poorly quantified and understood. Knowing the important aspects of variability is essential to design sampling schemes and transfer information between scales. Therefore the objectives of this study were:

1. Characterizing soil structure in two land-use systems, crop and grass.
2. Quantifying spatial patterns and spatial associations of soil physical properties and characteristics in crop and grass systems.
3. Quantifying spatial and temporal patterns and associations of CO\textsubscript{2} and N\textsubscript{2}O fluxes with physical and biochemical factors in crop and grass systems.
CHAPTER 2: Materials and Methods

This chapter provides descriptions of the study area and field experiment design. It also delivers detailed depictions of field and laboratory analytical methods that were used in this study to perform the analyses and estimate and evaluate different soil water and soil gas properties. Statistical analyses used in this study are also described.

2.1 Site description

The experiment was conducted at the University of Kentucky Agricultural Experiment Station Spindletop Farm north of Lexington. The study site (38° 6' 21" N, 84° 29' 38" W) has an elevation of 300 m and a total area of 4,500 m² with two established land-use systems, grass and crop (Figures 2.1, 2.2). “The climate is mid-contiental, with moderately cold winters, warm summers, and no pronounced wet or dry seasons” (Reed et al., 2010). The annual precipitation measured approximately 15 km from the study area was 976 mm in 2010 and 1677 mm in 2011; average annual air temperature was 13.2 °C in 2010 and 13.6 °C in 2011. The study area has one soil type (Figure 2.1), Bluegrass-Maury silt loam (Typic Paleudalf), with 2-6% slope (Soil Survey Staff, 2012). The top horizon (0-30 cm depth) contains 25.4% clay, 67.3% silt, and 7.3% sand. Total carbon and total nitrogen contents in the top 10 cm depth were 3.0 and 0.18%, respectively, in the crop system, and 3.6 and 0.22% in the grass system, respectively. The crop system was under no-till and planted to winter wheat (*Triticum aestivum*). Red clover (*Trifolium spp.*) and tall fescue (*Festuca arundinacea*) were the dominant plant species in the grass system.
Figure 2.1. A soil map showing the soil type in the study area. MIB refers to Bluegrass-Maury silt loam with 2-6% slope.
Figure 2.2. Study site showing the two land-use systems (crop and grass) and 60 sampling points along four transects.
The study area was not grazed and the grass site was mowed approximately every month during the growing season between May and November every year. Wheat was grown in both years; it was planted in November 2009 and October 2010 and harvested in June 2010 and 2011. Urea ammonium nitrate (134 kg N ha\(^{-1}\)) was applied to the crop system on 17 March 2010 and urea was applied on 8 March (92 kg N ha\(^{-1}\)) and 25 April (46 kg N ha\(^{-1}\)), 2011. No fertilizer was applied to the grass system.

2.2 Field experiment design

Sixty sampling points were distributed in four transects. Forty-four of the 60 sampling points were placed at a regular interval of 5 m. In four nests, located in the middle of each transect (Figure 2.2), sampling locations were separated by 1-m distance to quantify the spatial variance of each property over distances shorter than 5 m.

2.3 Soil organic matter and total nitrogen

Soil samples were collected by horizon from each of the 60 sampling locations along the four transects using a 30 mm diameter Giddings probe. A soil core was collected to a depth of 1 m from each sampling location. The soil core was cut to 6 depths, with a 10-cm increment for the top 30 cm depth and a 20-cm increment for the deeper depths, for soil organic matter and total nitrogen analysis.

Soil samples were sent to the University of Kentucky Regulatory Services Soil Testing Laboratory for soil organic matter (SOM) and total nitrogen (TN) measurements. Total
carbon and total nitrogen were measured using a dry combustion method and organic matter was calculated as % carbon x 1.72 = % organic matter.

2.4 Soil pH, dissolved carbon, dissolved nitrogen, and oxalate-extractable iron concentrations

Soil samples, taken for aggregate size distribution and aggregate stability from sixty locations from two depths 0-15 and 15-30 cm, were used to measure soil pH, dissolved carbon, dissolved nitrogen, and oxalate-extractable iron concentrations. A pH Meter (AB15/15+, Accumet Engineering Corporation, Hudson, MA) was used to measure soil pH in a 1:1 soil to water slurry. Dissolved soil carbon and nitrogen were measured using a Total Organic Carbon Analyzer (TOC-VcPH/CPN, Shimadzu Corporation, Kyoto, Japan). The oxalate-extractable iron concentration was measured using an Atomic Absorption Spectrophotometer (AA-6800, Shimadzu Corporation, Kyoto, Japan) as described by McKeague and Day (1966).

2.5 Soil textural analysis

Soil textural analysis was performed using the pipet and sieving methods as described by Gee and Bauder (1986). A soil core was collected to a depth of 1 m from each sampling location, and cut to 7 depths, with a 10-cm increment for ≤50 cm depth and a 15-cm increment for >50 cm depth. One soil sample from each location and from each depth was used for this analysis. Each sample was air dried for 10 days and then sieved through a 2-mm sieve. Twenty grams of air-dried soil were mixed with approximately 10 ml of deionized water and then with 20 ml of 50% hydrogen peroxide (H₂O₂) applied in 5 ml
increments every 2 hours to avoid excessive effervescence. The samples were left overnight to ensure all soil organic carbon was oxidized. Once the hydrogen peroxide had destroyed the organic matter, 10 ml of 50 g L$^{-1}$ sodium hexametaphosphate was added to disperse the clay fraction. The resulting slurry was shaken for 2 hours using a shaker. The sand fraction was determined by quantitatively transferring the suspension to a graduated cylinder quantitatively through a 0.053-mm sieve which was placed on the top of the cylinder. The sand material was rinsed from the sieve into a beaker and oven dried at 105 °C for 24 hours to obtain the dry sand mass. Another 10 ml of sodium hexametaphosphate was added to the graduated cylinder, which then was brought up to volume of 1000 ml with deionized water.

A blank solution in a separate 1000 ml graduated cylinder was used to account for the sodium hexametaphosphate added to the suspension. This blank was prepared with 20 ml of 50 g L$^{-1}$ sodium hexametaphosphate and was brought up to 1000 ml volume with deionized water. A thermometer was placed inside the blank graduated cylinder to get the reference temperature at which the settling of different particle sizes occurred after ideal suspension. This was to adjust the time at which a 25 ml sample for the clay fraction <2 μm needed to be taken from the appropriate depth as described by Gee and Bauder (1986).

Before suspending the samples in the graduated cylinder, readings of the blank temperature were taken to determine the sampling time for clay for each set of samples to be analyzed. Plunging was done in 2 minutes for each sample to suspend all particles. To
account for the sodium hexametaphosphate added, a 25 ml sample was drawn from the blank and then oven-dried and weighed following the same routine as the clay fraction. The dry mass of sodium hexametaphosphate was subtracted from the clay dry mass to get the true mass of dry clay in the sample. Once the clay sample was removed, it was transferred quantitatively to a beaker and oven-dried at 105 °C for 24 hours to obtain the dry clay mass.

The silt fraction was calculated as the difference between the sand and clay fractions (100% - %sand - % clay). Because the soil texture protocol started with 20 g of an air-dried sample, a correction had to be made to account for the air-dry soil water content. Five grams of soil were oven-dried at 105 °C for 24 hours to determine the gravimetric soil water content of the air-dry soil sample. The air dry water content was used to correct the clay and sand fraction percentages.

2.6 Aggregate size distribution and wet-aggregate stability

Two disturbed soil samples were excavated from each sampling point (60 locations) at 0-15 and 15-30 cm depths. The soil samples were air-dried for ten days, and then a plastic bag containing 100 g of soil was dropped from a 1.5 m height. The aggregate size distribution analysis on this 100 g soil mass was performed using a vibratory sieve shaker (Analysette 3, Fritsch GmbH, Idar-Oberstein, Germany) with five different opening sieves. The following aggregate size classes were obtained through sieving: <0.053, 0.053-0.25, 0.25-1, 1-2, and >2 mm. The aggregate mean weight diameter (MWD) was calculated using equation 2.1 as described by Kemper and Rosenau (1986).
The water aggregate stability analysis was performed for one aggregate size class (1-2 mm) using a wet sieving apparatus (Art. no.: 08. 13, Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands) as described by Kemper and Rosenau (1986). The selection of this aggregate class was due to the equipment availability and it was recommended by others (Kemper and Rosenau, 1986). The wet-aggregate stability measurement was performed using 4 g of soil and sodium hydroxide (2 g L⁻¹) was used as a dispersing agent as recommended by Kemper and Rosenau (1986) for soils with pH <7. The wet-aggregate stability (WAS) was calculated using equation 2.2 as described by Kemper and Rosenau (1986).

\[
MWD = \sum_{i=1}^{N} \bar{x}_i w_i
\]  

(2.1)

\[
\%WAS = \frac{w_1}{w_1 + w_2} \times 100
\]

(2.2)

where \( \bar{x}_i \) refers to the mean diameter of each size fraction, \( w_i \) to the proportion of the total sample weight for the corresponding size fraction, \( w_1 \) to a net weight of stable aggregates, and \( w_2 \) to the net weight of unstable aggregates.

### 2.7 Soil gas diffusivity

Soil gas diffusivity was measured in undisturbed soil cores taken from 4-10 cm depth using a rubber-mallet-driven core sampler. Soil cores were 8.6 cm in diameter and 6.0 cm in length. These soil cores were kept at 4 °C after they were sampled. Soil gas diffusivity
was measured using a chamber method similar to that described by Rolston (1986). A diffusion chamber (2.14 L) was fabricated and a soil core was attached to the top of the chamber (Figure 2.3). One end of the soil core was open to the diffusion chamber and the other to the lab atmosphere. Oxygen diffusion was chosen as the process to estimate soil gas diffusivity. The oxygen concentration inside the chamber was initially reduced by flushing the chamber with helium. The chamber had two valves (inlet and outlet) that were used to flush the chamber and to keep atmospheric pressure inside the chamber. A small electric fan inside the chamber mixed the air before a gas sample was taken. A syringe was used to take the gas sample from the diffusion chamber and to inject it into a gas chromatograph (GC-8A with TCD detector, Shimadzu Corporation, Kyoto). The gas chromatograph was used to measure the oxygen concentration and the area under the automatically integrated oxygen peak was calibrated versus the oxygen concentration in the atmosphere (210000 ppm). The oxygen concentration inside the chamber was measured every 30 minutes for 480 minutes.

The gas diffusion coefficient was calculated based on the increase of oxygen concentration in the chamber as a function of time and the difference of oxygen concentration between both open ends of the soil core (Equation 2.3) as described by Rolston (1986).

\[
\ln \frac{C_s - C_t}{C_s - C_0} = -D \frac{A t}{V l}
\] (2.3)
Figure 2.3. Gas-diffusion chamber with attached soil core used for measuring relative gas diffusivity in soil.
where $D_s$ refers to the apparent diffusion coefficient, $C_s$ to oxygen concentration in the atmosphere, $C_i$ to oxygen concentration in the diffusion chamber at a specific time $t$, $C_0$ to the initial oxygen concentration in the diffusion chamber, $A$ to the cross-sectional area of the soil core, $V$ to the volume of the diffusion chamber, and $l$ to the length of the soil core.

The oxygen diffusion coefficient and air-filled porosity were quantified at five soil water matric potential steps: -1000, -333, -100, -50, and -10 cm of water head. The soil water matric potential was controlled using a pressure plate apparatus (1600, Soil Moisture Equipment Co., Santa Barbara, CA). The soil core was satu

The gas diffusivity measurement was performed under laboratory conditions and atmospheric pressure was measured using a barometric pressure sensor (SB-100, Apogee Instruments Inc., Logan). There was little change of atmospheric pressure, which varied from 103.6 to 104.6 kPa, during the incubation period, and soil gas diffusivity was not corrected for atmospheric pressure. There was a slight change in the lab temperature with season and soil gas diffusion coefficient was expressed for a reference temperature of 20 °C using the method described by Currie (1960) (Equation 2.4). Lab temperature was not measured when soil gas diffusivity was estimated, however, an oxygen sensor (SO-100,
Apogee Instruments Inc., Logan) was attached to the gas diffusion chamber and it provided the sensor temperature that was used to estimate the air temperature (Figure 2.4). After all gas diffusion measurements were taken, the oxygen sensor temperature and the air temperature in the lab (ranging from 19.4 to 25.6 °C) were measured every minute for 5 days to develop a regression (Equation 2.5). The air temperature was measured for the regression using air temperature sensor (ST-100, Apogee Instruments Inc., Logan). This regression yielded an $R^2$ of 0.998 and was used to calculate the air temperature from the oxygen sensor temperature during the period of the soil gas diffusivity experiment.

\[ D_{sT2} = D_{sT1} \left( \frac{T_2}{T_1} \right)^{1.72} \]  

\[ T_a = 1.0145T_s - 2.1951 \]  

where $D_{sT2}$ and $D_{sT1}$ refer to gas diffusion coefficients at temperatures $T_2$ (20 °C) and $T_1$ (K), respectively, and $T_a$ and $T_s$ to air and oxygen sensor temperatures (°C), respectively.

### 2.8 Soil air-filled porosity

The soil air-filled porosity $\theta_a$ was calculated from volumetric water content $\theta_{vw}$ and total porosity $\phi$ of the soil cores used for gas diffusivity measurements. Soil water content was measured by weighing the soil core after it reached an equilibrium condition in the pressure plate apparatus. Soil porosity was calculated from dry bulk density $\rho_b$ and particle density $\rho_s$ (2.65 g cm$^{-3}$). Soil bulk density was computed from the mass of dry
Figure 2.4. A regression between lab temperature and oxygen sensor temperature.

\[ y = 1.0145x - 2.1951 \]

\[ R^2 = 0.998 \]

\[ N = 7140 \]
soil $m_s$ and total volume of the soil core $V_{core}$. The mass of dry soil was calculated from mass of field moist soil $m_w$ using soil gravimetric water content $\theta_{wg}$ (g g$^{-1}$) (Equation 2.9).

$$\theta_a = \phi - \theta_{wv}$$

(2.6)

$$\phi = 1 - \frac{\rho_b}{\rho_s}$$

(2.7)

$$\rho_b = \frac{m_s}{V_t}$$

(2.8)

$$m_s = \frac{m_w}{1 + \theta_{wg}}$$

(2.9)

### 2.9 Soil pore-continuity index

A soil pore-continuity index was also derived from soil gas transport to characterize soil structure. This index was derived from the estimated gas diffusion coefficient and air-filled porosity using the following formula described by Troeh et al. (1982) and Ehlers et al. (1995):

$$\frac{D_s}{D_0} = \theta_a f\left(\frac{l}{l_c}\right)^2$$

(2.10)

where the relative gas diffusion coefficient $\frac{D_s}{D_0}$ refers to the gas diffusion coefficient in soil $D_s$ relative to the diffusion coefficient of the specific gas in air $D_0$ (12.18 cm$^2$ min$^{-1}$
for oxygen in air), \( \theta_a \) to air-filled porosity, \( l \) to the length of soil core, \( l_c \) to the length of the pore, \( f \) to reduction in gas diffusion due to water blocked or constricted pores, and 
\[ f \left( \frac{l}{l_c} \right)^2 \]
to pore-continuity index.

### 2.10 Predicting soil gas diffusivity

Different models were tested to determine the one which best predicted relative soil gas diffusivity from air-filled porosity in both land-use systems. The root mean square error (RMSE) (Equation 2.11) was used to determine and evaluate the performance of the models and the best fit compared with the measured relative soil gas diffusivity. The RMSE is always between 0 and 1, and a perfect model gives an RMSE value of zero. The bias (Equation 2.12) was used as a measure of overestimation (positive bias) or underestimation (negative bias) of the predicted relative soil gas diffusivity.

\[
RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (d_i)^2} \quad (2.11)
\]

\[
bias = \frac{1}{N} \sum_{i=1}^{N} (d_i) \quad (2.12)
\]

where \( d_i \) refers to the difference between the predicted and the measured values of \( \frac{D}{D_0} \) at a given air-filled porosity, and \( N \) to the number of measurements.
2.11 Saturated hydraulic conductivity

Saturated hydraulic conductivity \( K_{\text{sat}} \) was estimated in the lab using a \( K_{\text{sat}} \) permeameter (Art. no.: 09.02, Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands). The saturated hydraulic conductivity was measured using the constant hydraulic head method (Reynolds and Elrick, 2002) in the same soil cores used for measuring soil gas characteristics. The soil cores were placed on the permeameter and saturated slowly from the bottom up by raising the water level in the water basin to the level above the soil core sample (Figure 2.5). The water level in the reservoir and above the soil core inside the ring was maintained in a constant level using a water pump and a siphon which was put into a drain pipe that led the water into a burette. The volumetric water flow rate through the soil was monitored from the burette readings over a time interval. The flow was allowed overnight and a rate reading was selected after obtaining three consistent consecutive readings. The hydraulic gradient was calculated from the water level in the basin and the water level above the soil core. The saturated hydraulic conductivity was calculated from the water flow rate \( Q \) and the hydraulic gradient \( \frac{\Delta h}{l} \) readings (Equations 2.13, 2.14) using Darcy’s Law (Kirkham and Powers, 1972; Marshall and Holmes, 1979; Hillel, 1980; Jury et al., 1991; Hillel, 1998).

\[
K_{\text{sat}} = \frac{Jl}{\Delta h} \quad (2.13)
\]

\[
J = \frac{Q}{A} \quad (2.14)
\]
Figure 2.5. A laboratory setup for measuring saturated hydraulic conductivity in a soil core using the $K_{sat}$ permeameter.
where $J$ refers to the water flux calculated from outflow volume as a function of time $Q$, $l$ to the soil core length, and $A$ to the soil core surface area.

2.12 Unsaturated hydraulic conductivity and soil water retention curve

Unsaturated hydraulic conductivity was measured using two methods, a double plate membrane permeameter and the evaporation method. The double plate membrane permeameter was used to obtain unsaturated hydraulic conductivity in the range close to soil water saturation (at -10, -5, and -1 cm matric potential) and the evaporation method was used to measure unsaturated hydraulic conductivity at a lower matric potential range (between -650 and -10 cm). Unsaturated hydraulic conductivity obtained by both methods was measured in the same soil cores used to estimate soil gas diffusivity and saturated hydraulic conductivity.

The soil core was placed on a double plate membrane permeameter (Figure 2.6). The double plate membrane permeameter included Mariotte devices to control the upper pressure head boundary. The soil core was allowed to slowly be saturated from the bottom up. After the saturation, both the upper and lower boundaries were set to -10 cm matric potential. U-manometers were attached to the upper and lower porous plates to verify the intended matric potential on each boundary. Once the boundaries were set; water flow across the soil core was allowed overnight. The next day, the water flux across the soil core was measured as a decrease in the water level in the water reservoir. Steady state water flux was assumed after three consistent readings of water flux were
Figure 2.6. A laboratory setup of a double plate membrane permeameter used for measuring unsaturated hydraulic conductivity at close to soil water saturation.
obtained consecutively. The same procedure was followed for -5 then -1 cm matric potentials. The unsaturated hydraulic conductivity was calculated based on Darcy’s Law (Equations 2.13, 2.14) with unit hydraulic gradient between both ends of the soil core.

Soil unsaturated hydraulic conductivity at low matric potentials and soil water retention curve were measured in the lab using the evaporation method developed by Wind (1966) and described by Wendroth and Wypler (2008). The 60 soil cores sampled from both crop and grass systems and used to measure soil gas diffusivity and soil saturated and unsaturated hydraulic conductivities at -10, -5, and -1 cm matric potentials were also used to estimate soil water retention curve and unsaturated hydraulic conductivity at a range between -650 cm of matric potential and close to soil water saturation. The evaporation method is based on measuring the decrease of soil water content and pore water matric head measured at two different depths of a soil core with time as water evaporates from the exposed upper surface of the soil core.

Fast-equilibrating tensiometers, fabricated from a round bottom straight wall ceramic cups (0652X01-B01M1, Soilmoisture Equipment Corp, Santa Barbara, CA) and pressure sensors (26PCCFA6D, Honeywell, Morristown, NJ), were used to measure soil matric heads. A multiplexer (AM16/32, Campbell Scientific, Logan, UT) and a data logger (CR10X, Campbell Scientific, Logan, UT) were used to connect and store matric potential data from 20 tensiometers inserted at two depths of a set of 10 soil cores. The tensiometers were calibrated prior to the start of the experiment using a hanging water column device and a tensimeter for matric potentials ranging between -650 and 0 cm
during the experiment. An average of five observations taken over 30 seconds was used for a matric head reading each time it was measured.

Time domain reflectometry TDR (1502C, Tektronix, Beaverton, OR) with manufactured mini probes similar to that used by Malicki et al. (1992) and Kreba and Maule (2010) was used to measure soil water content in the soil core. The length of the three-rod TDR probe was 5.5 cm and the diameter of each rod was 0.16 cm. Ten TDR probes were connected to the TDR unit using a multiplexor (TR-200, Dynamax, Houston, TX). The TDR water content readings were calculated based on the Topp et al. (1980) equation (Equations 2.15, 2.16) using commercial computer software (WinTDR version 6.1, Utah State University, Logan, UT). TDR measurements were calibrated using water content measurements taken over different times during the experiment. These volumetric water contents $\theta_w$ were obtained by weighing the soil core a few times during the evaporation process and calculated from the water volume $V_w$ in the soil core and the volume of the soil core $V_{core}$ (Equation 2.17). The water volume was calculated from the difference between the core weight $W_{core}$ and the oven dry weight of the soil core $m$, (Equations 2.18, 2.19) which was estimated after all measurements were taken. A linear relation, with $R^2$ varying between 0.925 and 0.9995 among the 60 soil cores, was observed between the TDR readings and the volumetric water contents, and was used to estimate the actual soil volumetric water content from TDR measurements. Some noise in the water content observations occurred. The cause of this noise could be because a single TDR measurement was taken each time the water content was measured in the soil core and also due to a short measuring time interval (30 min). A moving average of three
observations was used to smooth the noisy observations and ensure that the water content decreased with time during the evaporation process.

\[
\theta_{TDR} = \left( -530 + 292\varepsilon_a - 5.5\varepsilon_a + 0.043\varepsilon_a \right) / 10^4
\]  
(2.15)

\[
\varepsilon_a = \left[ v_o t / (2L) \right]^2
\]  
(2.16)

\[
\theta_{wv} = \frac{V_w}{V_{core}}
\]  
(2.17)

\[
V_w = W_{core} - m_s
\]  
(2.18)

\[
V_{core} = \pi r^2 l
\]  
(2.19)

where \( \varepsilon_a \) refers to the apparent permittivity, \( v_o \) to the velocity of light in vacuum, \( t \) to travel time through the probe, \( L \) to probe length, \( r \) to radius of soil core, and \( l \) to the length of soil core.

The undisturbed soil core (348.5 cm\(^3\)) was placed on a base plate with two cable holders to hold the two tensiometers (Figure 2.7). Two horizontal access holes, 5.5 cm length and 0.5 cm diameter, were excavated gently through the cylinder wall at 1.5 and 4.5 cm depths from the soil surface but in different angles for the tensiometer installation. After tensiometer installation, the soil core was saturated slowly from the bottom after covering the top soil surface to prevent evaporation. A plumber lute was placed on the cylinder around the tensiometer and between the bottom of the cylinder and the base plate to prevent water losses. The TDR probe was inserted into the soil vertically from the top surface. The soil core with the tensiometers and the TDR probe were left over night for
Figure 2.7. A laboratory setup for the evaporation method, with a soil core, a TDR, and a tensiometer, for unsaturated hydraulic conductivity and soil water retention curve measurements.
hydraulic equilibrium to be established. In the next days, tensiometers and TDR readings were recorded every 30 min under slow evaporation conditions until it reached a matric potential of -650 cm in the upper tensiometer.

A FORTRAN computer program was used to calculate the unsaturated hydraulic conductivity and pore water distribution relationships based on the van Genuchten (1980) function (Equation 2.20) from measured volumetric water content and matric head data. Four fitting parameters, \( \theta_r, \theta_s, \alpha, \) and \( n \) were obtained to describe the soil water retention curve.

\[
\theta_v = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha \psi)^n]^{1/(1-n)}}
\]  
(2.20)

where \( \theta_r \) and \( \theta_s \) refer to residual and saturated volumetric water contents, respectively, \( \psi \) to soil matric potential, and \( \alpha \) (cm\(^{-1}\)) and \( n \) to curve shape parameters.

Residual water content \( \theta_r \) can be estimated by extrapolating available soil water retention data because it is not always measured (van Genuchten, 1980). The \( \alpha \) parameter refers to the inverse of the air entry value and \( n \) represents the slope of the retention curve. Figure (2.8) shows that the water contents predicted with Equation (2.20) after fitting the model parameters to the data produced a very good fit with the measured data.
Figure 2.8. Measured vs. predicted water content using equation (2.20).

\[ y = 0.9965x + 0.0018 \]
\[ R^2 = 0.9976 \]
The unsaturated hydraulic conductivity was measured at a wide range, from -650 to -1 cm soil matric potential in each soil core; however it was compared among measurements at just 7 different matric potentials: -400, -200, -100, -50, -10, -5, and -1 cm in crop and grass systems. Because values of matric potential cannot be predetermined, unsaturated hydraulic conductivity value pairs were interpolated on a double-log-linear basis to obtain a value for unsaturated hydraulic conductivity at a specific matric head. Soil water content at six matric potentials: -1000, -400, -200, -100, -50, and -25 cm besides water content at saturation $\theta_s$, residual water content $\theta_r$, and shape parameters $\alpha$ and $n$ were selected to quantify soil water retention characteristics under crop and grass systems. Soil water content at -1000 cm matric potential was estimated using the pressure plate apparatus for gas diffusivity measurements.

2.13 Soil dry bulk density

Dry bulk density was estimated using the same undisturbed soil cores used for soil gas diffusivity, hydraulic conductivity, and soil water retention curve measurements. After all soil gas and soil water transport measurements were completed, the soil cores were disturbed and soils were placed in the oven under 105 °C for 24 hours. The dry mass was determined and the bulk density $\rho_b$ was calculated by dividing the dry mass $m_s$ by the total volume of the soil core $V_{core}$ (348.5 cm$^3$) (Equation 2.21).

$$\rho_b = \frac{m_s}{V_{core}}$$ (2.21)
2.14 Field measurements of CO\(_2\) and N\(_2\)O fluxes

A static chamber method was used in combination with a photoacoustic environmental gas monitor (INNOVA 1412; LumaSense Technologies, Inc., Santa Clara, CA) for gas flux measurements. At each of the 60 locations, a PVC collar was inserted 5 cm into the ground. The collar had an inner diameter of 30 cm and a height of 15 cm. A 30 cm diameter chamber with air-tight fitting was placed on top of the collar directly before the measurement (Figure 2.9). The inner height of the chamber was 8.7 cm. The total height \(Z\) (m) of airspace above the soil surface that was formed by the chamber and the collar was 18.7 cm. Carbon dioxide and N\(_2\)O concentrations were measured every minute for ten minutes at each location. The gas flux density \(f_g\) (mg CO\(_2\) or N\(_2\)O m\(^{-2}\) of soil min\(^{-1}\)) was calculated according to Rolston (1986):

\[
f_g = \frac{V_g \Delta C_g}{A \Delta t}
\]

(2.22)

where \(V_g\) is the volume of air in the chamber (m\(^3\)), \(A\) is the cross sectional soil area (m\(^2\)) within the collar over which gas flux was measured, \(\Delta C_g\) is the change in CO\(_2\) or N\(_2\)O concentration within the chamber (mg CO\(_2\) or N\(_2\)O m\(^{-3}\) of air) over a time interval \(\Delta t\) (min). Because, in our case, the gas concentration \(C_g\) increased linearly with time, the gas flux density \(f_g\) was derived from the linear relationship between \(C_g\) and \(t\):

\[
C_g = \frac{f_g t}{Z} + b
\]

(2.23)
Figure 2.9. Experimental setup for CO$_2$ and N$_2$O emission from soil, soil water content, and soil temperature measurements using a gas monitor with a collar, capacitance probe, and thermometer, respectively.
where \( b \) is the intercept of the linear relationship and therefore the theoretical initial concentration at \( t = 0 \).

As indicated by Rochette and Bertrand (2008), the gas concentration within the chamber has an immediate impact on the soil surface gas flux, and the assumption of linearity of the gas concentration-time relationship may underestimate the actual gas flux. The underestimation of closed chamber measurements due to linear regression methods has been addressed by, e.g., Hutchinson and Mosier (1981), Anthony et al. (1995), and Pederson et al. (2001). Kroon et al. (2008) stated that linear regression can be used for determination of trace gas fluxes because of the short measurement time, its easy use, and because the uncertainty introduced through spatial and temporal variation is assumed to be much larger than the bias caused by the linear regression.

At each measurement campaign, spatial measurements of gas concentration were equally split over two days approximately between 9:00 and 16:00 unless weather interfered. During the gas concentration measurement at each location, the soil temperature at 5 cm depth was recorded at a spot ≤5 cm distance from the collar. Soil water content was also measured during the gas concentration measurement at each sampling location. A capacitance probe access tube was installed 50 cm from the collar in each sampling location for the soil water content measurements. Soil water content was measured at each 10 cm depth interval for 100 cm depth using a diviner capacitance probe (Diviner 2000, Sentek Pty Ltd, Stepney, Australia). The capacitance probe readings were calibrated by developing individual linear regression equations for each soil layer (10 cm
depth) in each location using three volumetric water content measurements obtained at different water statuses in the field.

Gas fluxes, water content, and soil temperature were measured approximately every two weeks, during the period between 8 June 2010 and 8 June 2011, resulting in 22 spatial data sets of gas flux. During winter (25 November 2010 to 31 January 2011), measurements were taken approximately every month. Some data sets of gas flux were normally distributed but most sets were log$_{10}$-normally distributed. Therefore gas flux data were log-transformed for all statistical analysis. Log-transformation of CO$_2$ flux has been used in other studies (e.g., Ishizuka et al., 2005; Pringle and Lark, 2006; Herbst et al., 2009). Ln-transformation of N$_2$O fluxes has been also used by others (e.g., Ambus and Christensen, 1994; Clayton et al., 1994; Ball et al., 1997; Rover et al., 1999).

2.15 Gas flux adjustment

Parkin and Kaspar (2003) showed obvious diurnal fluctuations of gas flux field measurements at the same location in association with air and soil temperature. This behavior of gas flux was relevant for this field study inasmuch as gas flux was used for spatial data analysis which was based on the assumption that the results for a particular day had been theoretically obtained at the same time. This was technically impossible. Therefore, an adjustment of gas flux became necessary to avoid locations measured later in the day falsely suggesting gas fluxes were larger than at locations measured earlier in the day.
Two methods were used to adjust gas flux to remove the daily temporal trend of the flux. Similar to Herbst et al. (2009), gas flux was adjusted relative to the time of the day. The increasing trend of $f_{gt}$ measurements versus time between 9:00 and 16:00 was described in a linear relationship:

$$f_{gt} = st + b \quad (2.24)$$

where $s$ and $b$ denote the slope and intercept, respectively. The trend was subtracted from the measured gas flux series resulting in a series of residuals. The mean value of the measured gas flux series was then added to the residuals resulting in a series of adjusted fluxes $f_{AgT}$. The spatio-temporal analysis was based on these adjusted flux data.

A second method was based on the relationship between gas flux and soil temperature at 5 cm depth. Data analysis showed that soil temperature was the driving factor for changes in soil respiration in both daily and seasonal scales. A regression function was developed from gas flux and soil temperature measured at each sampling point at 22 times over the season. The analysis showed that linear regression best described the relationship between gas flux and soil temperature in the crop system while exponential regression was best in the grass system. The difference of soil temperature between local (sampling location) and daily average soil temperature for all locations sampled that day was used to compute estimated CO$_2$ flux $f_{eg}$ using the regression function. To adjust gas flux measurements to daily average soil temperature $f_{AgT}$, the estimated flux $f_{eg}$ was added to
or subtracted from observed flux in the field $f_g$. The estimated gas flux was added to the observed flux when the local soil temperature was lower than the daily average soil temperature, and it was subtracted from observed flux when the local soil temperature was higher than the daily average soil temperature as follows:

$$f_{AgT} = f_g \pm f_{eg}$$

(2.25)

Soil temperature variation during the day can influence not only soil biological activity but also the amount of gas dissolved in the soil solution. During the diurnal temperature increase, it is possible that gas dissolution decreases with time. This process might be one of the causes for the diurnal trend of CO$_2$ and N$_2$O fluxes with lower fluxes obtained during the morning when soil temperature is lower and more gas might be dissolved than during the afternoon. Gas dissolution processes might also explain the difference of gas fluxes between cold and warm seasons. Henry’s coefficient $K_H$ illustrates the influence of temperature on gas dissolution, and it can be used to describe solubility of gases based on measured soil temperature during the day. Henry’s constant $K_H$ describes the decreasing amount of gas solved in the solution with increasing temperature. However, in soil, the capacity of soil solution to absorb or desorb gases depends not only on the magnitude of soil temperature variation but also on soil water content and soil pH.

Shanhun et al. (2012) investigated the impact of abiotic processes on CO$_2$ flux in Antarctic soils and tested the hypotheses that, consistent with Henry’s Law, dissolution of CO$_2$ in soil water is the likely explanation for the variation of the flux. They used Henry’s
Law to predict dissolved CO₂ using soil temperature, soil moisture, soil pH, and subsurface soil CO₂ concentrations measured in different soil depths. According to their conclusion, CO₂ flux was dominated by abiotic processes, with small changes in soil temperature causing significant changes in soil CO₂ concentrations. In their study site, CO₂ flux was lower than in the current study, and they obtained positive fluxes during warm periods and negative fluxes during cold periods. Dissolution of CO₂ was significant in their soil due to lower flux and higher soil pH (10) relative to the present study.

In the current study, the dissolved CO₂ and N₂O in soil solution could not be estimated using Henry’s Law and were therefore not taken into account for adjusting the diurnal trend of the fluxes because subsurface soil CO₂ and N₂O concentrations and their partial pressures were not measured when the soil surface gas fluxes were obtained. The method for removing the daily temporal trend of the flux was therefore based on the time of measurement and it was assumed that it indirectly integrated all factors causing diurnal changes of gas fluxes including gas dissolution.

### 2.16 Descriptive statistical analysis

Descriptive statistical analysis used in this study included mean, standard deviation (SD), variance (Var), and coefficient of variation (CV) (Equations 2.26-2.29).

\[
mean = \frac{1}{N} \sum_{i=1}^{N} z_i \quad \text{(2.26)}
\]

\[
SD = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (z_i - \bar{z})^2} \quad \text{(2.27)}
\]
\[
Var = \frac{1}{N} \sum_{i=1}^{N} (z_i - \bar{z})^2
\]  
(2.28)

\[
CV(\%) = \frac{SD}{\text{mean}} \times 100
\]  
(2.29)

where \( z_i \) refers to an observation, \( N \) to number of observations.

2.17 Geostatistical analysis

The spatial and temporal processes of soil properties and their spatial associations with other soil attributes were quantified using geostatistical methods - semivariograms and cross-semivariograms. The spatial and temporal variability structures and spatial associations were quantified in experimental semivariograms and cross-semivariograms according to Journel and Huijbregts (1991) (Equations 2.30, 2.31).

\[
\gamma(h) = \frac{1}{2Y(h)} \sum_{i=1}^{Y(h)} [A_i(x_i) - A_i(x_i + h)]^2
\]  
(2.30)

\[
\Gamma(h) = \frac{1}{2Y(h)} \sum_{i=1}^{Y(h)} [A_i(x_i) - A_i(x_i + h)][B_i(x_i) - B_i(x_i + h)]
\]  
(2.31)

where \( \gamma(h) \) and \( \Gamma(h) \) refer to the experimental auto-semivariogram and cross-semivariogram, respectively, \( Y \) to the number of pairs of soil attributes \( A_i \) and \( B_i \) measured at locations \( x_i \) that are separated by lag distance \( h \). When applied in the spatial context \( x_i \) refers to a location in space and \( h \) to a spatial lag, whereas in a temporal
context they refer to an observation point in time and time lag, respectively. To characterize the variability structure, spherical semivariogram model parameters were fitted to the experimental semivariogram (Isaaks and Srivastava, 1989) (Equation 2.32):

\[
\hat{\gamma}(h) = \begin{cases} 
    c_0 + c_1 \left( \frac{3h}{2a} - 0.5 \left( \frac{h}{a} \right)^3 \right) & \ldots 0 \leq h \leq a \\
    c_0 + c_1 & \ldots h > a
\end{cases}
\]

In Equation (2.32), \(\hat{\gamma}(h)\) denotes the estimated semivariance, \(c_0\) the nugget variance, and \(c_1\) the structural component of the variance. At the range of representativity \(a\), \(c_0\) and \(c_1\) add up to the sill. The semivariogram model parameters were fitted through least squares minimization in Microsoft-Excel using Solver (Microsoft Office 2010, Microsoft Corporation, Redmond, WA). Cambardella et al. (1994) used the ratio of nugget to sill \((c_0/(c_0+c_1))\) to classify the spatial dependence: a ratio of <25% indicated strong spatial dependency, between 25 and 75% indicated moderate spatial dependence, and >75% indicated weak spatial dependence.

### 2.18 Space-time field analysis

A space-time field of a variable is a map expanded over the spatial and temporal domains. It reflects the development of spatial patterns with time, and it provides insight into the temporal behavior of particular locations or zones. For the space-time field analysis, spatial gas flux observations were arranged linearly along the spatial axis while conserving their distance to each other. The temporal development of gas flux was laid
out along the time axis. The resulting map can be understood as an ordinary map laid out in two dimensions where x- is the spatial and y- the temporal dimension. An isotropic experimental semivariogram and a semivariogram model were computed for all log_{10}-transformed gas flux data with space and time units of m and day being combined. Subsequently, gas flux was kriged and the space-time contour map developed along the spatial and temporal extension. The space-time contour map of gas flux was computed using GS+ (GS+ version 9; Gamma Design Software, Plainwell, MI).

2.19 Temporal stability analysis

Two statistical methods were used to characterize the temporal stability of spatially measured gas flux. The first method, the Spearman rank correlation, was used to determine the overall temporal persistence of gas flux. The Spearman rank correlation is a nonparametric analysis and does not require normally distributed data. The rank correlation coefficient was computed by:

\[ r_s = \frac{6 \sum_{i=1}^{N} (R_{ij} - R'_{ij})^2}{N(N^2 - 1)} \]  (2.33)

where \( R_{ij} \) refers to the rank of the gas flux \( f_{Ag} \) observed at location \( i \) on date \( j \), and \( R'_{ij} \) to the rank of \( f_{Ag} \) at the same location but on date \( j' \). The Spearman correlation coefficient was also used to quantify the relationship between two soil variables.
The second approach, the mean relative difference, was used to determine the temporal persistence of gas flux at every single location. This method is also used for opportunities to reduce the number of sampling locations when some locations show temporal stability (Vachaud et al., 1985). The methods were first described by Vachaud et al. (1985) and used by others (e.g., Grant et al., 2004; Cosh et al., 2006; Schneider et al., 2008) to determine the time stability of soil water storage. Both methods require repeated measurements. The mean relative difference method was based on the difference $\Delta_{ij}$ between an individual measurement $f_{Agij}$ at a particular sampling point $i$ and time $j$ and the mean of gas flux $\overline{f_{Agij}}$ determined for one sampling campaign consisting of two consecutive days. The equations, used to estimate the mean relative difference (MRD), were described by Vachaud et al. (1985) as follows (Equations 2.34 - 2.38):

\[
\delta_j = \frac{\Delta_{ij}}{f_{Agij}} 
\]  

(2.34)

\[
\Delta_{ij} = f_{Agij} - \overline{f_{Agij}} 
\]  

(2.35)

\[
\overline{f_{Agij}} = \frac{1}{N} \sum_{i=1}^{N} f_{Agij} 
\]  

(2.36)

\[
s_i = \sqrt{\frac{1}{N} \sum_{j=1}^{N} \left(\delta_{ij} - \overline{\delta_i}\right)^2} 
\]  

(2.37)

\[
\overline{\delta_i} = \frac{1}{N} \sum_{j=1}^{N} \delta_{ij} 
\]  

(2.38)
where $\delta_{ij}$ refers to the relative difference, $N$ to the number of observations, $s_i$ to the standard deviation of mean relative difference, and $\bar{\delta}_i$ to the mean relative difference.

Sampling locations that have mean relative difference of gas flux from the spatial mean close to zero can represent locations for the mean value of the entire field. On the other hand, locations with the highest and lowest mean relative difference from the spatial mean can represent locations for the extreme (highest or lowest) value of gas flux for the entire field.
CHAPTER 3: Characterizing Soil Structure and Relationships between Soil Variables in Crop and Grass Systems

This chapter focuses on characterizing soil structure and quantifying relationships between soil properties and functions in crop and grass systems. The first part of this chapter considers characterizing soil structure in crop and grass systems by quantifying different soil physical variables including soil bulk density, aggregate size distribution, wet-aggregate stability, soil water retention characteristics, hydraulic conductivity, soil gas diffusivity, air-filled porosity, and the soil pore-continuity index. The second part of this chapter considers quantifying relationships between soil physical characteristics and selected soil variables in crop and grass systems using the Spearman rank correlation coefficient.

Soil structure is a key factor that influences soil function, the ability to support plant and animal, and moderate environmental quality. Soil structure can be measured with different soil properties and functions. However, quantifying soil structure under different land uses using multiple measurements of three different soil phases (solid, liquid, and gas) is not usually performed. Considering only one or a few properties or functions might lead to misleading quantification of how land use affects soil structure. For example, considering only dry bulk density will not quantify the soil pore geometry and continuity and the ability of soil to conduct water and gases. Quantifying the soil pore network and its heterogeneity is difficult. Soil hydraulic conductivity, soil water retention curve, and soil gas transport functions such as relative gas diffusivity and pore continuity
are measurements that can be used to characterize soil structure and the heterogeneity of the soil pore network. However, these measurements collectively have not been compared under different land uses. Pore continuity has hardly been used as a measurement of soil structure under different land uses. Therefore, this study considers different soil measurements related to different soil phases, solid, liquid, and gas, to characterize soil structure under crop and grass systems.

Determining the correlations of soil variables used to characterize soil structure with other soil measurements is essential to understand the controlling factors on soil structure in crop and grass systems. Quantifying these relations is also important for better soil management practices. Some of these relationships have not been identified in the literature. For example, it is common that gas diffusivity is predicted from air-filled porosity and total porosity, but the relationships between gas diffusivity and other variables such as aggregate size distribution, soil water retention parameters, and hydraulic conductivity have not been well investigated. These relationships will improve predictions of soil gas and soil water transport processes under different land uses. This study shows the significant correlations between gas and water transport functions; it also shows how these relationships differ in different land uses.

**Approaches**

To meet the objectives of this chapter, 60 soil cores were taken from the field and various soil measurements were performed in the lab. Chapter 2 provides details about soil core sampling and all laboratory measurements included in this chapter.
Results and discussion

3.1 Characterizing soil structure in crop and grass systems

3.1.1 Frequency distribution

The Shapiro-Wilk normality test (Shapiro and Wilk, 1965) was used to quantify the frequency distribution of each soil measurement selected for this study. If the variable was not normally distributed, log$_{10}$-transformation was used; otherwise the original values were used for data analysis. Table A1.1 (Appendix1) shows the normal and non-normal distributed soil variables selected for this study. The non-normal or log-normal distribution reflects the high variation of the soil variable, and was mostly the consequences of multi-factorial interactions of influencing factors.

Saturated and unsaturated hydraulic conductivity measurements at all selected matric potentials were log$_{10}$-normally distributed in both land-use systems. Log$_{10}$-transformation method has been used by others (Nielsen et al., 1973; Baker and Bouma, 1976; Lauren et al., 1988) to normalize saturated and unsaturated hydraulic conductivity measurements. The retention curve parameter $\alpha$ was also log$_{10}$-normally distributed in the crop system and none normally distributed in the grass system. The other retention curve parameters $n$, $\theta_r$, and $\theta_s$ were none normally distributed in either land-use system.

3.1.2 Soil dry bulk density in crop and grass systems

The crop system had a significantly higher mean dry bulk density at 4-10 cm depth than the grass system. The bulk density in the crop system varied between 1.41 and 1.62 g cm$^{-1}$.
with an average of 1.53 g cm\(^{-3}\). On the other hand, the bulk density varied between 1.43 and 1.56 g cm\(^{-3}\) with an average of 1.49 g cm\(^{-3}\) in the grass system. The first locations in the crop system (locations from 1 to 9; Figure 2.2) exhibited lower bulk density (varied between 1.41 and 1.52 g cm\(^{-3}\)) than the rest of the sampling locations. The difference was possibly due to farming activities such as tillage that might have had been performed before establishing the experiment sites.

Despite a small difference (40 mg cm\(^{-3}\)) of the mean bulk density between crop and grass systems, this difference was significant. Because both sites had similar soil type and soil texture, significantly different values of mean bulk density obtained in crop and grass systems indicated that land use impacted soil structure. Higher bulk density in the crop system reflected lower soil porosity than the grass system. Lower bulk density in the grass system was possibly a result of higher soil organic matter, higher plant-root density, and higher microbial activity than in the crop system. These factors can cause the difference of the bulk density and the volume of pore space (Skopp, 2002).

Hu et al. (2009) found lower bulk density in a needlegrass (*stipa bungeana*) field compared to an alfalfa (*Medicago sativa*) field. Bormann and Klaassen (2008) detected a significant increase in bulk density from forest to grassland to cropland in the topsoil for two investigated soils, Podzol (Spodosol) and Stagnosol (Alfisols-Kandiaqualfs). Their result was in line with the finding of Murty et al. (2002) who stated that there was a relationship between bulk density and soil organic matter, with higher density corresponding to lower organic matter.
3.1.3 Aggregate size distribution and wet-aggregate stability in crop and grass systems

The mean of the wet-aggregate stability index was significantly higher in the grass system than in the crop system at 0-15 and 15-30 cm depths. The geometric mean of the stability index was 87.3 and 64.0% at 0-15 cm depth and 77.4% and 71.0% at 15-30 cm depth in the grass and crop systems, respectively. The geometric mean of the stability index was significantly higher at 0-15 cm depth than 15-30 cm depth in the grass system. In the crop system, the geometric mean of the stability index was significantly higher at 15-30 cm depth than at 0-15 cm depth.

The wet-aggregate stability index is an important indicator of soil structure. The stability index analysis showed that both land uses had very water stable aggregates. Bird et al. (2002) observed higher aggregate stability in the upper soil depth and stated that it was due to the positive effects of microbial activity and shallow plant roots. High aggregate stability observed in the crop site was due to no-tillage management practice, which enhanced carbon content in the upper depth of the soil profile. Soil in the crop system also had a high content of large aggregates and high wet-aggregate stability index, possibly due to no-tillage practice. Paustian et al. (1997) found an increase in carbon content under no-tillage compared to conventional tillage. They attributed this increase to reduced litter decomposition and less soil disturbance under no-tillage. Six et al. (1999) reported that carbon sequestration in no-tillage was greater than in cultivation tillage due to the slower turnover rate of macro aggregates in no-tillage. Higher stability index in the grass system than in the crop system at both depths was most probably related to soil
organic matter content. Soil organic matter in the upper 10 cm depth was significantly higher (3.64%) in the grass system than in the crop system (2.95%).

The grass system had a larger aggregate mean weight diameter than the crop system at 0-15 and 15-30 cm depths, but the difference between the two land-use systems was significant (p ≤ 0.05) only at 0-15 cm. At 0-15 cm depth, the aggregate mean weight diameter varied between 1.9 and 3.0 mm in the grass system; in the crop system, it varied between 2.0 and 2.8 mm. At 15-30 cm depth, the aggregate mean weight diameter varied between 2.1 and 3.0 mm in the grass system and between 2.1 and 2.8 mm in the crop system. The difference of the aggregate mean weight diameter between the two depths was significant in the crop system but not in the grass system. The geometric mean of the aggregate mean weight diameter was larger at 15-30 cm depth than at 0-15 cm depth in both land-use systems.

The aggregate size class >2 mm was the dominant size in both land-use systems and the aggregate content in soil decreased with decreasing aggregate size at both 0-15 and 15-30 cm depths (Figure 3.1). The grass system had higher content of large aggregates (>2 mm) than the crop system at both depths (Figure 3.1) but the difference of the mean of large aggregates between the two land uses was only significant at 0-15 cm. The 15-30 cm soil depth had more large aggregates (>2 mm) in both land-use systems, but the difference between the depths was only significant in the crop system.
Figure 3.1. Geometric mean of aggregate size distribution in crop and grass systems at two depths 0-15 and 15-30 cm.
That the large aggregate size class (>2 mm) was the most abundant size indicated that crop and grass land uses had well-developed soil structure. John et al. (2005) found significantly greater aggregate mean weight diameters in grassland and forest soils compared to maize and wheat soils, and related the difference due to tillage performed in the maize and wheat sites. In the experiment site used for the current study, the difference of aggregate size distribution is probably due to the grass system having a different land use and land management history than the crop system. The grass system had a long history of established grass. The crop system was planted to tobacco under conventional tillage before it was selected for the experiment in 2008 and converted to a corn and wheat rotation under no tillage.

The grass system had more large aggregates (>2 mm) than the crop system. There was no significant difference of the 1-2 mm aggregate size class between the two land-use systems at either depth. However, the crop system had significantly more aggregates in the 0.25-1 mm size class than the grass system at 0-15 cm depth and significantly more of the smallest selected aggregate classes, <0.053 and 0.053-0.25 mm, than the grass system at both depths. This result was because of the effect of land use and management difference between the crop and grass systems. Six et al. (2000) investigated the effect of cultivation intensity on aggregate distribution and aggregate carbon in three soils and concluded that increasing cultivation intensity led to a loss of carbon rich macro aggregates and an increase of carbon-depleted micro aggregates. The crop system was switched to no-tilled recently and the grass system was established before the crop
system and it seemed aggregates started to develop in the crop system or large aggregates broke apart to smaller aggregates.

The effect of land use (crop and grass) on soil structure, specifically on the aggregate mean weight diameter and the large aggregate size, was significant in the surface soil but not deeper. This result is probably because the organic matter in the upper depth was higher in both land uses. John et al. (2005) reported that in the upper soil, aggregate size distribution was affected by land use and cultivation as tillage destroyed large aggregates. They also observed higher aggregate contents in surface soils than in the subsoil. They also pointed out that aggregate formation was associated with increased carbon storage as carbon contents increased with aggregate size. In their soils, large aggregates (>2 mm) were the most frequent aggregate fraction in grassland and forest soils, macro aggregates (0.25-1 mm) in wheat, and micro aggregates (0.053-0.25 mm) in maize. The aggregate mean weight diameter in the grass and forest soils was significantly larger than that in wheat and maize soils. A possible reason for a significant difference in aggregate size between soil depths in the crop system (and not the grass system) could be that the surface soil was exposed to outside forces such as rainfall during seasons when there was no crop growing. In the grass system, vegetation density could protect the aggregates at the soil surface.

Several other factors might have influenced soil aggregate size distribution and stability. Bird et al. (2002) reported that soil carbon to nitrogen ratios, carbonate carbon, and easily extractable glomalin were predictors of aggregate stability. Bouajila and Gallali (2010)
found significant correlation between aggregate stability and soil organic matter and particulate organic carbon. The correlations between aggregate size and aggregate stability with other soil variables are discussed later in this chapter (Chapter 3.2).

3.1.4 Soil water retention characteristics in crop and grass systems

Soil water retention was compared between the two land uses at selected soil matric potentials varying between -1000 and -10 cm (Table 3.1). Soil water retention was measured using two methods. In the first method, soil water retention was estimated in the soil cores before they were used to determine soil gas diffusivity by placing the soil core in a pressure plate apparatus under a specific pressure until it reached equilibrium. Then the soil core was weighed to calculate the volumetric water content. The other method used TDR probes and tensiometers during the evaporation experiment. These measurements of soil water retention at selected matric potentials, -333, -100, and -50 cm, under equilibrium (obtained using the pressure plate apparatus) and evaporation (obtained using TDR probes and the evaporation method) conditions are compared in Appendix 2. The comparison showed that the measure of soil water retention differed between the evaporation experiment and the equilibrium method, with a significantly higher mean water retention for the evaporation experiment at all selected matric potentials in both land uses. Higher variations under equilibrium conditions were observed at all selected matric potentials in the crop system and at -333 and -100 cm in the grass system. The evaporation method provided more observations on the soil water retention curve than the pressure plate apparatus method.
Table 3.1. Descriptive statistics for soil water retention at different soil matric potentials in crop and grass systems measured using the evaporation method and the pressure plate apparatus. Bolded values refer to water content measured using the evaporation method.

<table>
<thead>
<tr>
<th>ψ cm</th>
<th>Crop system</th>
<th></th>
<th></th>
<th></th>
<th>Grass system</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Min.</td>
<td>Max.</td>
<td>SD</td>
<td>Mean</td>
<td>Min.</td>
<td>Max.</td>
<td>SD</td>
</tr>
<tr>
<td>-10†</td>
<td>0.40</td>
<td>0.33</td>
<td>0.45</td>
<td>0.03</td>
<td>0.42</td>
<td>0.40</td>
<td>0.45</td>
<td>0.01</td>
</tr>
<tr>
<td>-25‡</td>
<td>0.43</td>
<td>0.41</td>
<td>0.49</td>
<td>0.02</td>
<td>0.43</td>
<td>0.41</td>
<td>0.50</td>
<td>0.02</td>
</tr>
<tr>
<td>-50†</td>
<td>0.38</td>
<td>0.30</td>
<td>0.41</td>
<td>0.03</td>
<td>0.39</td>
<td>0.37</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>-50‡</td>
<td>0.42</td>
<td>0.40</td>
<td>0.48</td>
<td>0.02</td>
<td>0.42</td>
<td>0.40</td>
<td>0.49</td>
<td>0.02</td>
</tr>
<tr>
<td>-100†</td>
<td>0.36</td>
<td>0.28</td>
<td>0.40</td>
<td>0.03</td>
<td>0.37</td>
<td>0.31</td>
<td>0.44</td>
<td>0.03</td>
</tr>
<tr>
<td>-100‡</td>
<td>0.41</td>
<td>0.38</td>
<td>0.47</td>
<td>0.02</td>
<td>0.41</td>
<td>0.38</td>
<td>0.48</td>
<td>0.02</td>
</tr>
<tr>
<td>-200‡</td>
<td>0.40</td>
<td>0.37</td>
<td>0.46</td>
<td>0.02</td>
<td>0.39</td>
<td>0.37</td>
<td>0.46</td>
<td>0.02</td>
</tr>
<tr>
<td>-333†</td>
<td>0.34</td>
<td>0.26</td>
<td>0.39</td>
<td>0.03</td>
<td>0.35</td>
<td>0.28</td>
<td>0.41</td>
<td>0.02</td>
</tr>
<tr>
<td>-400‡</td>
<td>0.38</td>
<td>0.35</td>
<td>0.44</td>
<td>0.02</td>
<td>0.38</td>
<td>0.35</td>
<td>0.44</td>
<td>0.02</td>
</tr>
<tr>
<td>-1000†</td>
<td>0.31</td>
<td>0.23</td>
<td>0.35</td>
<td>0.02</td>
<td>0.32</td>
<td>0.28</td>
<td>0.35</td>
<td>0.02</td>
</tr>
</tbody>
</table>

† measured under equilibrium conditions
‡ measured under evaporation conditions
There was no significant difference of soil water retention measured using the evaporation method between the two land-use systems at any selected matric potentials between -400 and -25 cm. Soil water retention estimated using the pressure plate apparatus was significantly higher in the grass system than in the crop system at -10 and -50 cm matric potentials, but did not significantly differ between the two land uses at lower matric potentials (-100, -333, and -1000 cm).

Figure 3.2 shows six examples of soil water retention curves measured under evaporation conditions for three selected locations in the crop system (5, 10, and 16) and three in the grass system (37, 55, and 57). The selection of these locations was based on the estimated mean relative difference of soil water content measured in the field in the upper 0-10 cm. These water contents were measured in space and time as part of another experiment conducted to quantify spatial and temporal patterns of greenhouse gas fluxes (Chapters 5 and 6). These selected locations had mean relative difference values close to zero and represented the mean value of soil water content for the entire field.

Four parameters (α, n, θs, and θr) were estimated from water retention measurements using the evaporation method to describe and compare the 60 soil water retention curves in crop and grass systems. These soil water retention parameters were estimated using observations obtained using the evaporation method because more observations on the soil water retention curve were measured using this method than the pressure plate apparatus. The means of α and θs were significantly higher in the grass system than in the crop system (Table 3.2). The means of n and θr parameters were higher in the crop
Figure 3.2. Soil water content as a function of soil matric potential in the crop system (locations 5, 10, and 16, closed symbols) and the grass system (locations 37, 55, and 57, open symbols).
system than in the grass system, but the difference was not significant. There were 28 locations with an estimated value of $\theta_r$ to be zero in both land uses.

Higher soil water content at high matric potentials in the grass system can be evidence of the land-use impact on soil structure - specifically on soil pore size distribution. Significant differences for $\alpha$ and $\theta_s$ occurred between the crop and grass systems because these parameters are controlled by structural pores. Soil structural pores are the major controlling factor of the retention curve close to water saturation and soil textural pores are the main controlling factor in the dry range of matric potential. Water content status under dry and moist conditions (low and high matric potentials, respectively) are two processes linked by an inflection point above which mainly structural pores are emptying and below which mainly textural pores are emptying (Dexter, 2004a; Alaoui et al., 2011).

The smaller mean of the $n$ parameter in the grass system corresponded to a flatter retention curve relative to that in the crop system. In other words, the rate of decrease of water content with decreasing matric potential was smaller in the grass system than in the crop system. However, no trend or a significant difference between the land uses was found for the $n$ and $\theta_r$ parameters (estimated from the evaporation experiment), most likely because both land uses had similar soil type and soil texture. Another possible reason explaining the similarity of $n$ and $\theta_r$ means in both land uses can be that they were fitted parameters and the retention curve was limited in the dry range (lower matric potentials). In other words, no observations of water content were obtained below -650 cm matric potential because tensiometers often fail due to loss of hydraulic contact with
Table 3.2. Descriptive statistics for soil water retention curve parameters in crop and grass systems.

<table>
<thead>
<tr>
<th>Crop system</th>
<th>Grain system</th>
<th>Grass system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Mean</td>
<td>Max</td>
</tr>
<tr>
<td>α (log(cm⁻¹x10⁻³))</td>
<td>1.17</td>
<td>2.25</td>
</tr>
<tr>
<td>n</td>
<td>1.16</td>
<td>1.77</td>
</tr>
<tr>
<td>θₘ</td>
<td>0.44</td>
<td>0.51</td>
</tr>
<tr>
<td>θₜ</td>
<td>0.08</td>
<td>0.35</td>
</tr>
<tr>
<td>α (log(cm⁻¹x10⁻³))</td>
<td>1.47</td>
<td>2.43</td>
</tr>
<tr>
<td>n</td>
<td>1.11</td>
<td>1.59</td>
</tr>
<tr>
<td>θₘ</td>
<td>0.45</td>
<td>0.51</td>
</tr>
<tr>
<td>θₜ</td>
<td>0.05</td>
<td>0.33</td>
</tr>
</tbody>
</table>
the soil, or air entry into the tensiometer cup (Wendroth and Wypler, 2008). A strong relationship between \( n \) and \( \theta_r \) (\( R^2 = 0.75 \)) and a weak relationship between log-transformed \( \alpha \) and \( \theta_s \) (\( R^2 = 0.14 \)) occurred when all observations from both land uses were used. Schaap and Leij (1998) and Haverkamp et al. (2005) stated that the \( \theta_r \) is an empirical fitting parameter with an optimization error that is considerably larger than for \( \theta_s \), partly because \( \theta_r \) is extrapolated water content at infinite matric head. They also reported that the van Genuchten equations provide a relatively poor description of retention data for dry conditions (\( \psi < -1000 \) cm).

Compared to the current study, Greminger et al. (1985) observed a similar average for \( \alpha \) (0.036 cm\(^{-1}\)) and a higher average for \( n \) (3.35) in a bare Yolo loam soil. Mallants et al. (1996) reported a lower mean value for \( \alpha \) (0.007 cm\(^{-1}\)) and similar mean values for \( n \) (1.75), \( \theta_r \) (0.04 m\(^3\) m\(^{-3}\)), and \( \theta_s \) (0.42 m\(^3\) m\(^{-3}\)) in a well-drained sandy loam soil. Shouse et al. (1995) found larger means for \( n \) and \( \theta_r \) (2.34 and 0.13 m\(^3\) m\(^{-3}\), respectively), a smaller mean for \( \alpha \) (0.002), and a similar mean for \( \theta_s \) (0.47 m\(^3\) m\(^{-3}\)) in a bare silt loam soil. The differences of these curve parameters between results obtained in the current study and others can be because soils having different degrees of structure and different methods used for the measurements.

In contrast to the current study, England (1971) concluded that below -0.33 bar matric head, a row-crop cultivated Mollisol (silt loam soil) retained 40% more water and a cultivated Alfisol (silt loam soil) retained 25% more water than corresponding pastured soils. At matric potential above -0.33 bar, cultivated soils of both orders held less water.
A significant difference between the two land uses was not found in the current study compared to England’s (1971) results, possibly because he had a longer (10 years) history of established land use. Another reason can be that the cultivated soil in England’s (1971) study was tilled and he reported that the large increase in macroporosity of the cultivated Mollisols suggested that tillage improved the Mollisol surface soil structure. In contrast to England’s (1971) findings, Schwärzel et al. (2011) concluded that converting a cropped soil to pasture improved the soil structure, and soil under pasture had a more homogenous pore size distribution and a higher capacity to store plant-available water than under crop.

3.1.5 Soil hydraulic conductivity in crop and grass systems

Saturated hydraulic conductivity was higher in the grass system than in the crop system (Table 3.3) but the difference between the two land uses was not significant. Higher saturated hydraulic conductivity in the grass system indicated potentially more developed soil structure with more homogenous pore size distribution and more continuous pores in the grass than in the crop system. Three soil cores in the crop system (locations: 10, 15, and 16) exhibited saturated hydraulic conductivity values of zero. Soil in the crop system also exhibited a lower wet-aggregate stability index than in the grass system and that could be the reason why three soil cores taken from the crop site exhibited no water flow under saturation conditions. Aggregates with lower water stability can be easily dispersed and broken apart under saturation, which can significantly reduce hydraulic conductivity. Another possible explanation is that dispersed clay particles could have plugged soil pores. Dagan et al. (1983) reported that the geometry of porous material was altered by
Table 3.3. Descriptive statistics of log-transformed hydraulic conductivity at different matric potentials in crop and grass systems.

<table>
<thead>
<tr>
<th>$\psi$ cm</th>
<th>$K_{sat}$</th>
<th>Mean</th>
<th>Min.</th>
<th>Max.</th>
<th>SD</th>
<th>Mean</th>
<th>Min.</th>
<th>Max.</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Min.</td>
<td>Max.</td>
<td>SD</td>
<td>Mean</td>
<td>Min.</td>
<td>Max.</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>log(cm d(^{-1})x10(^{-3}))</td>
<td>log(cm d(^{-1})x10(^{-3}))</td>
<td>log(cm d(^{-1})x10(^{-3}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_{sat})</td>
<td>4.39</td>
<td>2.19</td>
<td>6.68</td>
<td>1.26</td>
<td>1.26</td>
<td>4.98</td>
<td>2.92</td>
<td>7.21</td>
<td>0.94</td>
</tr>
<tr>
<td>-1</td>
<td>4.03</td>
<td>1.61</td>
<td>5.25</td>
<td>0.88</td>
<td>0.88</td>
<td>4.25</td>
<td>2.90</td>
<td>5.13</td>
<td>0.17</td>
</tr>
<tr>
<td>-5</td>
<td>3.58</td>
<td>1.63</td>
<td>4.90</td>
<td>0.80</td>
<td>0.80</td>
<td>3.66</td>
<td>2.92</td>
<td>4.92</td>
<td>0.48</td>
</tr>
<tr>
<td>-10</td>
<td>2.99</td>
<td>1.74</td>
<td>4.04</td>
<td>0.54</td>
<td>0.54</td>
<td>3.16</td>
<td>2.20</td>
<td>4.04</td>
<td>0.35</td>
</tr>
<tr>
<td>-50</td>
<td>1.47</td>
<td>0.84</td>
<td>2.13</td>
<td>0.30</td>
<td>0.30</td>
<td>2.17</td>
<td>1.46</td>
<td>3.21</td>
<td>0.43</td>
</tr>
<tr>
<td>-100</td>
<td>0.90</td>
<td>0.49</td>
<td>1.32</td>
<td>0.22</td>
<td>0.22</td>
<td>1.14</td>
<td>0.69</td>
<td>1.71</td>
<td>0.23</td>
</tr>
<tr>
<td>-200</td>
<td>0.60</td>
<td>-0.22</td>
<td>1.13</td>
<td>0.28</td>
<td>0.28</td>
<td>0.76</td>
<td>0.35</td>
<td>1.03</td>
<td>0.15</td>
</tr>
<tr>
<td>-400</td>
<td>0.42</td>
<td>0.07</td>
<td>0.78</td>
<td>0.17</td>
<td>0.17</td>
<td>0.52</td>
<td>0.11</td>
<td>0.87</td>
<td>0.15</td>
</tr>
</tbody>
</table>
swelling, clay dispersion, and aggregate break down, which controls soil hydraulic conductivity. Frenkel et al. (1977) concluded that plugging of pores by dispersed clay particles was the major cause of reduced hydraulic conductivity in montmorillonitic, vermiculitic, and kaolinitic soils.

Soils in both land-use systems exhibited high saturated hydraulic conductivity coefficients that could be due to the selected sample size of the soil cores used for the measurement. Lauren et al. (1988) measured saturated hydraulic conductivity in a silty clay loam soil under a grass system using different sizes of attached columns (field measurements) and one size of detached column (laboratory measurements). They found average saturated hydraulic conductivity of 36.6 and 4296.6 cm d\(^{-1}\) from attached and detached columns, respectively. They observed a lower mean of saturated hydraulic conductivity in the field due to the larger sample size they used compared to the sample size used in the current study (348.5 cm\(^3\)). They concluded that the value of saturated hydraulic conductivity was greatly influenced by the size of the soil column used for the measurement. If a small volume of soil was used, measured saturated hydraulic conductivity was likely to be greatly biased by the presence of a single crack or conducting pores, which tended to dominate the hydraulic regime. On the other hand, large samples would average the behavior of this and other voids over a large area. They also found that measurements obtained from attached columns were much less variable compared to extremely high values of saturated hydraulic conductivity in detached columns.
The grass system had higher saturated hydraulic conductivity possibly because of larger macropores and a less heterogeneous pore size distribution and pore geometry. Beven and Germann (1982) stated that “there is no doubt that water will move through large voids under saturated conditions and that they have a very important influence on the saturated hydraulic conductivity of soils, even though they may contribute only a very small amount to the total porosity of a soil.” Francis and Kemp (1990) concluded that initial infiltration and field saturated hydraulic conductivity were least for a cultivated soil compared to a pasture soil and increased with increasing time under pasture. They stated also that greater saturated hydraulic conductivity under pasture resulted primarily from water flowing through biogenic pores connected to the surface.

The evaporation method was used to measure unsaturated hydraulic conductivity at lower ranges of matric potential, the sequence of selected soil cores for the measurement was random, and the evaporation rate depended on the laboratory conditions. The evaporation rate from the soil cores decreased with time as soil got drier and varied between 0.0005 and 1.0 cm d\(^{-1}\) and between 0.0005 and 0.76 cm d\(^{-1}\) among all soil cores taken from crop and grass systems, respectively.

Unsaturated hydraulic conductivity decreased with decreasing soil matric potential in both crop and grass systems (Figure 3.3). The mean of unsaturated hydraulic conductivity in the grass system was higher than in the crop system at all selected matric potentials (Table 3.3). The unsaturated hydraulic conductivity was significantly higher in the grass system than in the crop system at -400 to -50 cm matric potentials and not significantly
higher at higher matric potentials, -10, -5, and -1 cm. Figure 3.3 shows the unsaturated hydraulic conductivity as a function of soil matric potential and soil water content for selected six locations in the crop and grass systems. These locations were chosen based on the mean relative difference analysis of soil water content in the upper depth (0-10 cm) of the soil profile measured by capacitance probe 22 times during a year in the field. The figure shows that unsaturated hydraulic conductivity in the grass system was higher than in the crop system especially at high water content (high matric potential). The figure shows also that the unsaturated hydraulic conductivity, as a function of soil water content, exhibited a different shape in the crop system than the grass system. At higher water contents, the shape of the hydraulic conductivity-water content curve for measurements taken in the crop system differed from the grass system, with a steeper curve for the crop system measurements.

Soils in crop and grass sites had similar soil type and soil texture; however, they had different soil structure, which was evident from the hydraulic conductivity measurements. The soil water conductivity properties of unsaturated soils depended greatly on their texture and structure (Hillel, 1998). As soil get drier, the influence of soil structure on hydraulic conductivity decreases and the effect of soil texture increases, and the sensitivity of the unsaturated hydraulic conductivity becomes less significant compared to the saturated hydraulic conductivity (Bormann and Klaassen, 2008). Aggregate size distribution analysis showed that the large (>2 mm) aggregate size was the dominant class in both sites, and the grass system had significantly more large aggregates than the crop system. Large aggregates refer to a large pore size but that did not reflect the pore
Figure 3.3. Unsaturated hydraulic conductivity as a function of matric potential (a) and soil water content (b) in crop system (locations 5, 10, and 16, closed symbols) and grass system (locations 37, 55, and 57, open symbols).
geometry and pore continuity for water flow. Hydraulic conductivity measurements indicated that the grass system had not only larger but also more continuous pores to conduct water farther than the crop system. Land use can affect soil hydraulic properties and continued cropping can lead to significant reduction of soil hydraulic conductivity. Aparicio and Costa (2007) observed a reduction in unsaturated hydraulic conductivity with increasing number of years under continuous cropping and a no-tillage management condition. The unsaturated hydraulic conductivity measurements showed that the impact of land use was more obvious at high matric heads. Bormann and Klaassen (2008) compared soil hydraulic properties in three different land uses - forest, grassland, and cropland - and reported that a higher saturated hydraulic conductivity in the topsoil occurred in grassland than cropland. The highest unsaturated hydraulic conductivity was observed for forest soils followed by grassland soils and cropland soils.

3.1.6 Soil gas diffusivity, air-filled porosity, and pore-continuity index in crop and grass systems

Oxygen was used to estimate gas diffusivity in soil, but there was a possibility that soil microorganisms would affect the computed diffusivity by consuming oxygen. A laboratory experiment (Appendix 3) was conducted, to determine if respiration significantly affected the oxygen diffusion process, using one soil core attached between two diffusion chambers. The result showed that oxygen consumption rate in this soil was low and was negligible if the laboratory gas diffusion measurements using the chambers were done within a few hours. Therefore, the oxygen consumption was not corrected in this study.
The soil relative gas diffusion coefficient varied between 0.0 and 0.11; and air-filled porosity varied between 0.004 and 0.215 m$^3$ m$^{-3}$ in both land-use systems and at all selected matric potentials. For each of the five selected matric potentials, mean of relative gas diffusion coefficients was significantly higher in the grass system than in the crop system (Figure 3.4a). Mean of air-filled porosity was similar in both land-use systems at -10 cm matric potential and higher in the grass system than in the crop system at lower matric potentials (Figure 3.4b). The relative gas diffusion coefficient and air-filled porosity both increased with decreasing soil matric potential in each land-use system.

The soil pore-continuity index was significantly higher in the grass system than in the crop system at all selected soil water matric potentials (Figure 3.4c). The pore-continuity index varied between <0.01 and 0.62 in the crop system and between 0.02 and 0.75 in the grass systems at all selected soil water matric potentials. The pore-continuity index increased with decreasing soil water matric potentials in both land-use systems.

Soil relative gas diffusivity and air-filled porosity in both crop and grass systems were in the range of what has been observed by others (Lai et al., 1976; Ehlers et al., 1995; Resurreccion et al., 2007; Kuhne et al., 2012). Air-filled porosity and relative gas diffusivity increased as soil became drier and as more pores were drained and became available for gas transport. Marshall (1959) reported that available pore volume and pore continuity for gas transport change with water content. Nielson et al. (1984) also stated
Figure 3.4. Geometric mean of relative gas diffusivity (a), air-filled porosity (b), and pore-continuity index (c) in crop and grass systems at different soil matric potentials. The bars indicate standard deviation.
that gas diffusion coefficients decreased with increasing soil water contents. The grass system had higher relative gas diffusivity and air-filled porosity than the crop system possibly because the grass system had more organic matter and larger and more stable aggregates, hence, larger volume of pore space and more continuous pores. Another possible explanation can be that the root density and microbial activity also were higher in the grass system compared to that in the crop system. Roots and fauna organisms, e.g. earthworms, can develop large pores and can affect the pore geometry and continuity. The difference of relative gas diffusivity and air-filled porosity between the two land-use systems was larger when the soil was drier and larger volume of pore space was available for gas transport than at higher soil water content status (Figure 3.4).

The differences between measurements of relative gas diffusivity at each of two consecutive matric potentials computed using Equation (3.1) were also used to quantify soil structure in crop and grass systems. Overall, the geometric mean of differences of relative gas diffusivity was larger in the grass system than in the crop system (Figure 3.5). The differences of relative gas diffusivity between measurements at lower matric potentials were higher than between measurements at higher matric potentials in the crop system. In the grass system, the differences of relative gas diffusivity increased with decreasing matric potentials from -10 to -333 cm but it was lower between -1000 and -333 cm than between -333 and -100 cm matric potentials.

\[
d_{D_2/D_0} = \left( \frac{D_2}{D_0(\varphi_2)} - \frac{D_1}{D_0(\varphi_1)} \right)
\]  

(3.1)
Figure 3.5. Differences between measurements of relative gas diffusivity at each of two matric potentials in crop and grass systems.
where \( d_{\psi_1/\psi_0} \) refers to the difference between measurements of relative gas diffusivity \( D_\psi/D_0 \) at two matric potentials \( \psi_1 \) and \( \psi_2 \), and \( \psi_1 > \psi_2 \).

The differences between measurements of relative gas diffusivity estimated at each two consecutive matric potentials were larger at dry water content status than in wet conditions possibly because large pores contributed to gas diffusion process at high water content status but both small and large pores contributed to the diffusion process when the soil was drier. Ehlers et al. (1995) stated that in soil with well-defined aggregates, bigger pores contribute to effective gas diffusivity through smaller pores.

### 3.1.7 Soil gas diffusivity as a function of air-filled porosity

Soil gas diffusivity as a function of air-filled porosity in the crop and the grass systems measured at different soil water matric potentials ranging from -1000 to -10 cm are in Figure 3.6a. Soil gas diffusivity corresponded to air-filled porosity differently in the crop than in the grass system. For the same air-filled porosity, relative gas diffusivity was lower in the crop than in the grass system. At low ranges of air-filled porosity (\(<0.012 \text{ m}^3 \text{ m}^{-3}\) ), more observations of air-filled porosity and relative gas diffusivity were obtained in the crop than in the grass system. Figure 3.6a also shows that relative gas diffusivity as a function of air-filled porosity exhibited a higher and steeper slope in the grass than in the crop system. Figure 3.6b shows the relationship of relative gas diffusivity with the pore-continuity index for all 60 soil cores. Relative gas diffusivity corresponded well to the pore-continuity index in the crop system but not well at high pore-continuity index values in the grass system. Figure 3.6c shows that there was a relationship between pore
Figure 3.6. Relative gas diffusivity as a function of air-filled porosity (a), relative gas diffusivity as a function of pore-continuity index (b), and air-filled porosity as a function of pore-continuity index (c) in two different land-use systems measured at five different soil matric potentials: -1000, -333, -100, -50, and -10 cm.
continuity and air-filled porosity but this relationship was not strong in either land-use system. This result indicated that air-filled porosity was not the main factor controlling pore continuity in crop and grass systems. To date, the relationship of pore-continuity to relative gas diffusivity and air-filled porosity has not been reported in the literature. Janse and Bolt (1960) and Gradwell (1960) stated that the relationship between gas diffusivity and air-filled porosity provided information on the arrangement and the continuity of pores. Figure 3.6a shows that more observations of air-filled porosity and relative gas diffusivity were found in the low range of air-filled porosity (<0.012 m$^3$ m$^{-3}$) in the crop system relative to the grass system, possibly because the crop system had a larger volume of small pores than the grass system. Pore continuity and pore tortuosity are important factors controlling gas transport in soils. The relative gas diffusivity as a function of air-filled porosity (Figure 3.6a) exhibited a smaller slope and a flatter curve in the grass system than in the crop system. This indicated that the pore volume and continuity in the grass system were higher relative to the crop system. The result of higher diffusivity in the grass system than in the crop system at the same air-filled porosity indicated that the pore size distribution and pore geometry in the grass system were more homogenous than in the crop system. The grass system had a higher index of pore-continuity than the crop system. Relative gas diffusivity was controlled by both air-filled porosity and pore continuity; however, air-filled porosity did not exhibit a strong relationship with pore-continuity index (Figure 3.6c). The pore geometry in the crop system was more tortuous compared to that in the grass system, and soils with tortuous pores exhibit lower gas diffusivity than soils with better-developed structure.
Bruckler et al. (1989) indicated that there was no unique relationship between the gas diffusion coefficient and air-filled porosity for porous media because this relationship was highly dependent on several different properties such as pore size, pore continuity, morphology, and tortuosity. Hence, the existing relationships between gas diffusivity and air-filled porosity should be tested for different soil types and soils from different land use systems. The result of predicting soil gas diffusivity indicated that the optimized Troeh et al. (1982) (figure 3.6a) model gave the best predicted relative gas diffusivity at a wide range of air-filled porosity in both land-use systems. The model did not give the best prediction at low air-filled porosity (ranging from 0.01 to 0.17 m$^3$ m$^{-3}$) in the crop system. The relationship between relative gas diffusivity and air-filled porosity in the crop system exhibited a higher and steeper slope relative to the grass system. Higher and steeper slopes indicated greater heterogeneity of pore size distribution and pore continuity.

### 3.1.8 Predicting soil gas diffusivity

Relationships have been developed to predict relative gas diffusivity using easily measured parameters such as soil air-filled porosity and soil bulk density. The differences among these relationships were based on the range of water content and the soil type used to develop the model. These relationships have not been extensively evaluated for different land uses. Table 3.4 shows the root mean square error (RMSE) calculated from measured and predicted relative gas diffusion coefficients using ten widely used simple models in two land-use systems, crop and grass, and at different soil matric potentials. Gas diffusivity was predicted using air-filled porosity and total porosity. The gas
Table 3.4. The root mean square error (RMSE) of models used to predict soil gas diffusivity in crop and grass systems at different soil water matric potentials. The bolded values indicate the lowest RME at each matric potential.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Models</th>
<th>Crop system</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Buckingham (1904)</td>
<td>( \frac{D}{D_0} = \theta_a^2 )</td>
<td>0.022</td>
<td><strong>0.003</strong></td>
<td>0.006</td>
<td>0.012</td>
<td>0.025</td>
<td>0.040</td>
<td>0.035</td>
<td>0.007</td>
<td>0.016</td>
<td>0.023</td>
</tr>
<tr>
<td>Penman (1940)</td>
<td>( \frac{D}{D_0} = 0.66\theta_a )</td>
<td>0.032</td>
<td>0.025</td>
<td>0.032</td>
<td>0.036</td>
<td>0.033</td>
<td>0.032</td>
<td>0.024</td>
<td>0.018</td>
<td>0.026</td>
<td>0.031</td>
</tr>
<tr>
<td>Millington and Quirk (1961a)</td>
<td>( \frac{D}{D_0} = \theta_a^{10/3} \phi^{-2} )</td>
<td>0.016</td>
<td>0.004</td>
<td><strong>0.005</strong></td>
<td>0.009</td>
<td>0.018</td>
<td>0.028</td>
<td>0.028</td>
<td>0.007</td>
<td>0.013</td>
<td>0.018</td>
</tr>
<tr>
<td>Millington and Quirk (1961b)</td>
<td>( \frac{D}{D_0} = \theta_a^2 \phi^{1/3} )</td>
<td>0.028</td>
<td><strong>0.003</strong></td>
<td>0.009</td>
<td>0.017</td>
<td>0.033</td>
<td>0.050</td>
<td>0.042</td>
<td>0.009</td>
<td>0.019</td>
<td>0.029</td>
</tr>
<tr>
<td>Lai et al. (1976)</td>
<td>( \frac{D}{D_0} = \theta_a^{5/3} )</td>
<td>0.014</td>
<td>0.005</td>
<td><strong>0.008</strong></td>
<td><strong>0.005</strong></td>
<td>0.015</td>
<td>0.025</td>
<td>0.024</td>
<td><strong>0.015</strong></td>
<td><strong>0.015</strong></td>
<td>0.032</td>
</tr>
<tr>
<td>Ball (1981)</td>
<td>( \frac{D}{D_0} = \theta_a^b )</td>
<td>0.031</td>
<td>0.004</td>
<td>0.010</td>
<td>0.019</td>
<td>0.036</td>
<td>0.056</td>
<td>0.045</td>
<td>0.009</td>
<td>0.020</td>
<td>0.030</td>
</tr>
<tr>
<td>Troeh et al. (1982)</td>
<td>( \frac{D}{D_0} = \left( \frac{\theta_a - u}{1 - u} \right)^{\frac{3}{2}} )</td>
<td><strong>0.013</strong></td>
<td>0.004</td>
<td>0.007</td>
<td>0.019</td>
<td><strong>0.012</strong></td>
<td><strong>0.015</strong></td>
<td><strong>0.013</strong></td>
<td><strong>0.006</strong></td>
<td><strong>0.009</strong></td>
<td>0.030</td>
</tr>
<tr>
<td>Xu et al. (1992)</td>
<td>( \frac{D}{D_0} = \theta_a^{2.51} \phi^{-3} )</td>
<td>0.016</td>
<td>0.004</td>
<td><strong>0.005</strong></td>
<td>0.010</td>
<td>0.019</td>
<td>0.027</td>
<td>0.028</td>
<td>0.008</td>
<td>0.015</td>
<td>0.020</td>
</tr>
<tr>
<td>Moldrup et al. (2000)</td>
<td>( \frac{D}{D_0} = 0.66\theta_a \left( \frac{\theta_a}{\phi} \right)^3 )</td>
<td>0.030</td>
<td><strong>0.003</strong></td>
<td>0.010</td>
<td>0.018</td>
<td>0.035</td>
<td>0.054</td>
<td>0.044</td>
<td>0.009</td>
<td>0.020</td>
<td>0.030</td>
</tr>
<tr>
<td>Moldrup et al. (2005)</td>
<td>( \frac{D}{D_0} = \phi \left( \frac{\theta_a}{\phi} \right)^{x_{100}} )</td>
<td>0.025</td>
<td><strong>0.003</strong></td>
<td>0.008</td>
<td>0.015</td>
<td>0.030</td>
<td>0.046</td>
<td>0.039</td>
<td>0.008</td>
<td>0.018</td>
<td>0.026</td>
</tr>
</tbody>
</table>

\( ^\dagger b = 3.7 \) for crop system, \( ^\dagger b = 3.2 \) for grass system, \( ^\dagger x_{100} = 2 + \frac{\log(\theta_a^{1/100})}{\log(\theta_a^{1/100} / \phi)} \), \( \theta_a \) is air-filled porosity, \( \phi \) is total porosity.
diffusivity was predicted from each measurement of air-filled porosity and total porosity in crop and grass systems. Using the entire range of air-filled porosity, 0.01-0.22 m$^3$ m$^{-3}$ in the crop system and 0.00-0.20 m$^3$ m$^{-3}$ in the grass system, and total porosity, 0.40-0.48 in the crop system and 0.43-0.48 in the grass system, all models gave low root mean square error values for each land-use system and lower root mean square error in the crop system than in the grass system except for the Penman (1940) model. The optimized Troeh et al. (1982) model gave a similar and the lowest root mean square error values in both crop and grass systems. The optimization was performed through the least squares minimization procedure described in Chapter 2.17. The optimized intercepts $u$ of the Troeh et al. (1982) model were similar (0.013 and 0.012 m$^3$ m$^{-3}$ in crop and grass systems, respectively); however, the optimized slopes $v$ were different (1.43 and 1.3 in crop and grass systems, respectively).

When the air-filled porosity was used, all models overestimated the relative gas diffusivity in both land-use systems except the Penman (1940) model. The optimized Troeh et al. (1982) model overestimated relative gas diffusivity in both land-use systems (bias of 0.003 and 0.00002 in the crop and grass systems, respectively) when the entire range of air-filled porosity was used. The Troeh et al. (1982) model gave the lowest root mean square error at -1000 and -333 cm matric potentials in the crop system and at -100, -50, and -10 cm in the grass system. The model underestimated the diffusivity at all five selected matric potentials except at -333 cm in the crop system, and overestimated it at all selected matric potentials in the grass systems. At -10 cm matric potential, four models, i.e. Buckingham (1904), Millington and Quirk (1961b), Moldrup et al. (2000), and
Moldrup et al. (2005), gave the lowest root mean square error (0.003) with positive biases in the crop system. Three models, Millington and Quirk (1961a), Lai et al. (1976), and Xu et al. (1992), had the lowest root mean square error in the crop system at -50 cm matric potential. The Lai et al. (1976) model gave the lowest root mean square error at 100 cm matric potential in both crop and grass systems.

3.2 Relationships between soil physical characteristics and soil variables in crop and grass systems

In this chapter, the relationships between different soil physical properties and functions that were quantified to characterize soil structure and different soil variables were evaluated using the Spearman rank correlation coefficient. Selected soil physical attributes previously mentioned in this chapter and selected soil measurements included soil texture, soil organic matter (SOM), total nitrogen (TN), dissolved carbon (DC), dissolved nitrogen (DN), and oxalate-extractable iron concentrations.

3.2.1 Soil measurements in crop and grass systems

Although crop and grass systems had a similar soil type and soil texture in the upper 0-10 cm depth, soil in the grass system had a significantly higher average sand content and significantly lower average clay content than in the crop system. The differences of average silt content and C/N between soils in the two land uses were not significant. Soil in the grass system also had significantly higher mean soil organic matter (SOM), total dissolved carbon (DC), and total soil nitrogen (TN) than the crop system at 0-10 cm depth. The averages of total dissolved nitrogen (DN) concentrations, however, were
significantly higher in crop than in grass system at 0-10 cm depth. Table 3.5 shows descriptive statistics of the selected soil measurements in crop and grass systems.

3.2.2 Relationships between dry bulk density, aggregate size distribution, and aggregate stability and selected soil variables in crop and grass systems

Dry bulk density $\rho_b$ did not significantly correlate with any of the selected soil variables in the crop system (Table 3.6). In the grass system, on the other hand, the bulk density was significantly negatively correlated with soil organic matter, total soil nitrogen, total dissolved carbon, and total dissolved nitrogen. The result of significant correlations between bulk density and soil organic matter and dissolved carbon showed that soil carbon played important roles in soil structure development in the grass system. Increasing soil carbon contributed to increasing soil porosity and improving soil structure in the grass system, but these impacts were not significant in the crop system, which reflected the influence of land use on soil structure. Kay et al. (1997) reported that bulk density decreased with increasing organic carbon content and the magnitude of the decrease decreased with increasing clay content in three different textural agricultural soils, sandy loam, loam, and clay loam. A significant relation between soil organic matter and bulk density was not found in the crop system possibly due to a narrower range of measured soil organic matter (Table 3.6), but may also reflect fundamental differences in the behavior of different land uses.
Table 3.5. Descriptive statistics for different soil variables measured at 0-10 cm depth in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>Crop system</th>
<th></th>
<th>Grass system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Min.</td>
<td>Max.</td>
<td>SD</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>7.20</td>
<td>2.45</td>
<td>11.02</td>
<td>1.75</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>22.70</td>
<td>7.40</td>
<td>26.34</td>
<td>3.49</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>70.10</td>
<td>65.70</td>
<td>85.56</td>
<td>4.12</td>
</tr>
<tr>
<td>SOM (%)</td>
<td>2.94</td>
<td>2.24</td>
<td>3.78</td>
<td>0.36</td>
</tr>
<tr>
<td>TN (%)</td>
<td>0.18</td>
<td>0.14</td>
<td>0.22</td>
<td>0.02</td>
</tr>
<tr>
<td>C/N</td>
<td>9.31</td>
<td>8.48</td>
<td>10.88</td>
<td>0.60</td>
</tr>
<tr>
<td>Fe† (g kg⁻¹)</td>
<td>8.0</td>
<td>2.4</td>
<td>17.0</td>
<td>3.3</td>
</tr>
<tr>
<td>DC‡ (g kg⁻¹)</td>
<td>0.09</td>
<td>0.06</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>DN‡ (g kg⁻¹)</td>
<td>0.03</td>
<td>0.01</td>
<td>0.06</td>
<td>0.01</td>
</tr>
</tbody>
</table>

† Oxalate-extractable iron
‡ Total dissolved carbon C or nitrogen N
Table 3.6. The Spearman correlation coefficients between bulk density, different aggregate size classes, mean weight diameter, and aggregate stability and different soil measurements in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>$\rho_b$</th>
<th>&gt;2 mm</th>
<th>2-1 mm</th>
<th>1-0.25 mm</th>
<th>0.25-0.053 mm</th>
<th>&lt;0.053 mm</th>
<th>MWD</th>
<th>WAS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crop system</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>0.13</td>
<td>0.18</td>
<td>-0.17</td>
<td>-0.14</td>
<td>-0.09</td>
<td>-0.12</td>
<td>0.13</td>
<td>0.35</td>
</tr>
<tr>
<td>Clay</td>
<td>0.17</td>
<td>-0.28</td>
<td>0.06</td>
<td>0.37*</td>
<td>0.20</td>
<td>0.29</td>
<td>-0.26</td>
<td>0.09</td>
</tr>
<tr>
<td>Silt</td>
<td>-0.16</td>
<td>0.08</td>
<td>0.06</td>
<td>-0.18</td>
<td>-0.07</td>
<td>-0.11</td>
<td>0.09</td>
<td>-0.30</td>
</tr>
<tr>
<td>SOM</td>
<td>-0.15</td>
<td>0.16</td>
<td>-0.30</td>
<td>-0.09</td>
<td>-0.09</td>
<td>-0.11</td>
<td>0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>TN</td>
<td>0.07</td>
<td>-0.03</td>
<td>-0.17</td>
<td>0.11</td>
<td>0.08</td>
<td>0.12</td>
<td>-0.05</td>
<td>0.17</td>
</tr>
<tr>
<td>C/N</td>
<td>-0.19</td>
<td>0.33</td>
<td>-0.28</td>
<td>-0.29</td>
<td>-0.22</td>
<td>-0.31</td>
<td>0.31</td>
<td>0.08</td>
</tr>
<tr>
<td>DC</td>
<td>-0.10</td>
<td>0.36</td>
<td>-0.01</td>
<td>-0.40*</td>
<td>-0.32</td>
<td>-0.39*</td>
<td>0.40*</td>
<td>0.30</td>
</tr>
<tr>
<td>DN</td>
<td>-0.14</td>
<td>-0.25</td>
<td>0.04</td>
<td>0.31</td>
<td>0.10</td>
<td>0.18</td>
<td>-0.26</td>
<td>-0.30</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.18</td>
<td>0.21</td>
<td>0.01</td>
<td>-0.16</td>
<td>-0.25</td>
<td>-0.33</td>
<td>0.22</td>
<td>0.29</td>
</tr>
<tr>
<td><strong>Grass system</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>-0.08</td>
<td>0.03</td>
<td>-0.03</td>
<td>-0.04</td>
<td>-0.04</td>
<td>-0.08</td>
<td>0.03</td>
<td>0.21</td>
</tr>
<tr>
<td>Clay</td>
<td>0.31</td>
<td>0.56**</td>
<td>-0.48**</td>
<td>-0.56**</td>
<td>-0.56**</td>
<td>-0.51**</td>
<td>0.57**</td>
<td>-0.15</td>
</tr>
<tr>
<td>Silt</td>
<td>-0.28</td>
<td>-0.50**</td>
<td>0.38*</td>
<td>0.50**</td>
<td>0.53**</td>
<td>0.49**</td>
<td>-0.50**</td>
<td>0.05</td>
</tr>
<tr>
<td>SOM</td>
<td>-0.43*</td>
<td>-0.22</td>
<td>0.19</td>
<td>0.28</td>
<td>0.21</td>
<td>0.17</td>
<td>-0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>TN</td>
<td>-0.50**</td>
<td>-0.29</td>
<td>0.22</td>
<td>0.33</td>
<td>0.29</td>
<td>0.27</td>
<td>-0.31</td>
<td>0.30</td>
</tr>
<tr>
<td>C/N</td>
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<td>0.14</td>
<td>-0.09</td>
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<td>-0.15</td>
<td>-0.16</td>
<td>0.16</td>
<td>0.08</td>
</tr>
<tr>
<td>DC</td>
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<td>-0.05</td>
<td>0.00</td>
<td>0.05</td>
<td>0.12</td>
<td>0.16</td>
<td>-0.07</td>
<td>0.27</td>
</tr>
<tr>
<td>DN</td>
<td>-0.45*</td>
<td>-0.15</td>
<td>0.10</td>
<td>0.14</td>
<td>0.20</td>
<td>0.26</td>
<td>-0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.03</td>
<td>0.16</td>
<td>-0.02</td>
<td>-0.13</td>
<td>-0.25</td>
<td>-0.22</td>
<td>0.16</td>
<td>-0.004</td>
</tr>
</tbody>
</table>

** Correlation is significant at 0.01 levels
* Correlation is significant at 0.05 levels
Dexter (2004b) reported that “part of the soil physical benefit attributed in the literature to soil organic matter is due to other factors such as the associated increased crop rooting intensity and reduced machinery impacts when, for example, grass is grown.”

The aggregate mean weight diameter MWD positively correlated with dissolved carbon in the crop system and with clay content in the grass system, but negatively correlated with silt content in the grass system. Aggregate size classes correlated with different soil variables (Table 3.6) and all classes correlated with clay and silt contents in the grass system. It should be noted that the largest aggregate size class (>2 mm) had positive correlations with clay content in the grass system, however, the smaller aggregate size classes negatively correlated with clay content. The opposite behavior was true with silt content. Aggregate stability did not show any significant correlations with any of the selected soil variables in either land use.

The significant impacts of soil texture on large aggregates indicated the influence of these soil variables on soil structure. Clay and silt contents had different influence on aggregate development in the grass system. Increasing clay content led to increasing content of large aggregates. Increasing silt content led to increasing content of smaller aggregates. Clay has larger surface area and higher negative charge than silt which are important factors in aggregate development.

Soil organic matter did not significantly correlate with aggregate size distribution, but others have found a significant impact of soil carbon on aggregate development and
aggregate stability with soil carbon being an important binding agent. John et al. (2005) concluded that aggregate formation was associated with increased carbon storage because carbon contents increased with aggregate size. Bouajila and Gallali (2010) also found significant correlations between soil organic carbon and the aggregate mean diameter and aggregate stability in three land uses: forest, pasture, and cropland. No significant correlations were found between aggregate stability and different soil variables in the current study, but others have observed some correlations. For example, Shouse et al. (1990) concluded that aggregate stability was not correlated to texture in a conventionally tilled field but correlated with silt and clay in a native pasture. Bird et al. (2002) stated that the carbon to nitrogen ratio had a significant correlation with aggregate stability in grassland. The reasons why no significant correlations between aggregate size distribution and aggregate stability and soil carbon were found in either land use can possibly be due to the narrower range of soil organic matter observations and because soil carbon was not measured in the aggregates but was measured in soils sampled within 50 cm distance from the location where the aggregates were sampled. This could be because between and within aggregates there could be a difference between the quantity and quality of soil organic matter (Handayani et al., 2010).

### 3.2.3 Relationships between soil water retention characteristics and selected soil attributes in crop and grass systems

The Spearman correlation coefficient was calculated between each of the soil water retention characteristic parameters and selected soil variables (Table 3.7). A significant impact of bulk density on retention curve parameters $\alpha$ and $\theta_s$ in the crop system and not
Table 3.7. The Spearman correlation coefficients between soil water retention characteristics and different soil properties and soil measurements in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>Soil water retention characteristics</th>
<th>Crop system</th>
<th>Grass system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>n</td>
<td>$\theta_s$</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>-0.47**</td>
<td>-0.07</td>
<td>-0.43*</td>
</tr>
<tr>
<td>&gt;2 mm</td>
<td>0.18</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>1-2 mm</td>
<td>0.06</td>
<td>-0.21</td>
<td>0.01</td>
</tr>
<tr>
<td>0.25-1 mm</td>
<td>-0.27</td>
<td>-0.15</td>
<td>-0.36*</td>
</tr>
<tr>
<td>0.053-0.25 mm</td>
<td>-0.37*</td>
<td>0.03</td>
<td>-0.34</td>
</tr>
<tr>
<td>&lt;0.053 mm</td>
<td>0.37*</td>
<td>0.28</td>
<td>0.07</td>
</tr>
<tr>
<td>MWD</td>
<td>0.24</td>
<td>0.22</td>
<td>0.05</td>
</tr>
<tr>
<td>WAS</td>
<td>-0.06</td>
<td>0.22</td>
<td>-0.15</td>
</tr>
<tr>
<td>Sand</td>
<td>0.43*</td>
<td>-0.17</td>
<td>0.31</td>
</tr>
<tr>
<td>Clay</td>
<td>-0.23</td>
<td>0.09</td>
<td>-0.23</td>
</tr>
<tr>
<td>Silt</td>
<td>0.37*</td>
<td>-0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>SOM</td>
<td>-0.18</td>
<td>-0.02</td>
<td>-0.13</td>
</tr>
<tr>
<td>DC</td>
<td>-0.23</td>
<td>0.38*</td>
<td>0.11</td>
</tr>
<tr>
<td>C/N</td>
<td>0.02</td>
<td>0.13</td>
<td>0.14</td>
</tr>
</tbody>
</table>

** Correlation is significant at 0.01 levels
* Correlation is significant at 0.05 levels

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in the grass system reflected the influence of land use on soil porosity and soil water retention characteristics especially at high water content. Zhang et al. (2006) found that water retention curves for silt loam soils from two sites and two depths were significantly influenced by soil compaction. In the crop system, bulk density had negative correlations with water retention close to saturation and positive relations with water content at relatively dry conditions. This behavior was also found by others (Ferrero and Lipiec, 2000) who showed that compaction resulted in a decrease of water content at high matric potentials (-100 to 0 cm) and an increase of water content at low matric potentials (-15500 to -2500 cm).

Sand content had different impacts on the soil water retention curve’s slope \( n \) in the crop compared to the grass systems, with a positive relation observed in the crop and a negative relation in the grass system. The results showed also that increasing sand content in the grass system led to decreasing residual water content \( \theta_r \) and soil water retention at -50 and -25 cm matric heads. The parameter \( \alpha \) had strong relations with the texture variables in the crop system and with the soil carbon in the grass system.

The residual water content parameter \( \theta_r \) correlated with just one soil property in each land use. Luckner et al. (1989), Tietje and Tapkenhinrichs (1993), and Haverkamp et al. (2005) reported that the physical interpretation of \( \theta_r \) has not been completely resolved, and it poorly correlated with other soil properties. Haverkamp et al. (2005) stated that the shape parameters \( \alpha \) and \( n \) were closely related to soil texture, while the scale parameters \( \theta_r \) and \( \theta_s \) exhibited far less correlation with soil texture. The current study showed that \( \alpha \)
correlated with sand and silt contents in the crop system and \( n \) correlated with sand content in both land use systems.

Rawls et al. (2003) studied the effects of soil organic carbon and soil texture on soil water retention. They concluded that soil water retention at -33 cm matric potential was affected more strongly by the organic carbon than water retention at -1500 cm, and they explained this behavior by postulating that the structure-forming effect of organic matter was affecting the water retention at water contents close to field capacity to a larger extent than water retention close to the wilting point. They found also that the relationship between soil water retention and organic carbon content was affected by the proportions of textural components. At low carbon contents, an increase in carbon content led to an increase in water retention in coarse soils and to a decrease in water retention in fine-textured soils. At high carbon contents, an increase in carbon contents resulted in an increase in water retention of all textures. However, their comparison did not include silt loam soils. Hollis et al. (1977) also found significant impacts of soil organic carbon, bulk density, silt, and clay contents on soil water retention properties in 77 soil profiles that had sandy and loamy drift soils and were located in five areas mostly under grass.

3.2.4 Relationships between soil hydraulic conductivity and selected soil variables in crop and grass systems

Log-transformed saturated hydraulic conductivity negatively correlated with dry bulk density and the smallest aggregate size classes (<0.053 and 0.053-0.25 mm) in the crop system but it did not significantly correlate with any of the selected variables in the grass
Saturated hydraulic conductivity positively correlated, but the correlation was not significant, with large aggregates (>2 mm) in either land use.

Dry bulk density was one of the major factors that controlling saturated hydraulic conductivity in the crop system because increasing bulk density reflected a decrease of soil porosity and pore space available for water flow. Arvidsson (1997) reported that a small increase in bulk density may decrease the conductivity by several orders of magnitude. Increasing the amount of small aggregates in the crop system led to decreasing saturated hydraulic conductivity possibly because more small size aggregates led to a decrease of macropores that are known to be an important factor influencing saturated hydraulic conductivity (Mallants et al., 1997; Azevedo et al., 1998). Increasing the number of large aggregates increased saturated hydraulic conductivity and that seemed to be reflected in positive correlations between the large aggregate class and saturated hydraulic conductivity. However, these correlations were not significant in either land use. The difference between the two land uses in terms of relationships between saturated hydraulic conductivity and the selected soil measurements indicated the impact of land use on soil structural properties and their relations.

The bulk density had negative correlations with unsaturated hydraulic conductivity close to saturated water content, -10, -5, and -1 cm matric heads, and positive, but not significant, correlations under dry conditions, -400 and -200 cm matric potentials, in the crop system. On the other hand, none of the correlations between unsaturated hydraulic conductivity at all selected matric potentials and bulk density were significant in the grass
Table 3.8. The Spearman correlation coefficients between hydraulic conductivity $K_{(ψ)}$ and different soil properties and soil measurements in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>$K_{\text{sat}}$</th>
<th>$K_{(-1)}$</th>
<th>$K_{(-5)}$</th>
<th>$K_{(-10)}$</th>
<th>$K_{(-50)}$</th>
<th>$K_{(-100)}$</th>
<th>$K_{(-200)}$</th>
<th>$K_{(-400)}$</th>
</tr>
</thead>
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<td><strong>Crop system</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho_b$ &gt;2 mm</td>
<td>-0.44*</td>
<td>0.33</td>
<td>0.44*</td>
<td>-0.19</td>
<td>-0.01</td>
<td>0.02</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>1-2 mm</td>
<td>-0.17</td>
<td>-0.15</td>
<td>-0.22</td>
<td>-0.17</td>
<td>-0.08</td>
<td>-0.36*</td>
<td>-0.31</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.25-1 mm</td>
<td>-0.36</td>
<td>-0.43*</td>
<td>-0.47**</td>
<td>-0.36</td>
<td>-0.34</td>
<td>-0.40*</td>
<td>-0.29</td>
<td></td>
</tr>
<tr>
<td>0.053-0.25 mm</td>
<td>-0.41*</td>
<td>-0.45*</td>
<td>-0.55**</td>
<td>-0.37*</td>
<td>-0.18</td>
<td>-0.24</td>
<td>-0.25</td>
<td>-0.11</td>
</tr>
<tr>
<td>&lt;0.053 mm</td>
<td>-0.46*</td>
<td>-0.49**</td>
<td>-0.53**</td>
<td>-0.34</td>
<td>-0.20</td>
<td>-0.26</td>
<td>-0.25</td>
<td>-0.14</td>
</tr>
<tr>
<td>MWD</td>
<td>0.33</td>
<td>0.36*</td>
<td>0.46*</td>
<td>0.30</td>
<td>0.25</td>
<td>0.31</td>
<td>0.29</td>
<td>0.19</td>
</tr>
<tr>
<td>Sand</td>
<td>0.12</td>
<td>-0.03</td>
<td>-0.09</td>
<td>-0.13</td>
<td>-0.33</td>
<td>-0.28</td>
<td>-0.37*</td>
<td>-0.29</td>
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<tr>
<td>Clay</td>
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<td>-0.26</td>
<td>-0.23</td>
<td>-0.21</td>
<td>-0.53**</td>
<td>-0.46*</td>
<td>-0.38*</td>
<td>-0.46*</td>
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<tr>
<td>Silt</td>
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<td>0.27</td>
<td>0.28</td>
<td>0.57**</td>
<td>0.44*</td>
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<td>0.26</td>
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<tr>
<td>SOM</td>
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<td>-0.02</td>
<td>0.07</td>
<td>-0.38*</td>
<td>-0.26</td>
<td>-0.26</td>
<td>-0.18</td>
</tr>
<tr>
<td>C/N</td>
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<td>0.34</td>
<td>0.37*</td>
<td>0.38*</td>
<td>0.31</td>
<td>0.41*</td>
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<tr>
<td>$\rho_b$ &gt;2 mm</td>
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<td>0.08</td>
<td>-0.17</td>
<td>-0.19</td>
<td>-0.02</td>
</tr>
<tr>
<td>1-2 mm</td>
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<td>0.17</td>
<td>0.21</td>
<td>0.33</td>
<td>0.09</td>
<td>-0.17</td>
<td>-0.22</td>
<td>-0.23</td>
</tr>
<tr>
<td>0.25-1 mm</td>
<td>-0.06</td>
<td>-0.04</td>
<td>-0.08</td>
<td>-0.34</td>
<td>-0.11</td>
<td>0.14</td>
<td>0.22</td>
<td>0.17</td>
</tr>
<tr>
<td>0.053-0.25 mm</td>
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<td>-0.14</td>
<td>-0.17</td>
<td>-0.31</td>
<td>-0.09</td>
<td>0.16</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>&lt;0.053 mm</td>
<td>-0.21</td>
<td>-0.25</td>
<td>-0.30</td>
<td>-0.31</td>
<td>-0.06</td>
<td>0.17</td>
<td>0.17</td>
<td>0.24</td>
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<tr>
<td>MWD</td>
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<td>0.17</td>
<td>0.22</td>
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<td>0.07</td>
<td>-0.19</td>
<td>-0.22</td>
<td>-0.23</td>
</tr>
<tr>
<td>WAS</td>
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<td>-0.14</td>
<td>-0.16</td>
<td>0.08</td>
<td>-0.13</td>
<td>-0.32</td>
<td>-0.40*</td>
<td>-0.31</td>
</tr>
<tr>
<td>Sand</td>
<td>-0.03</td>
<td>-0.09</td>
<td>-0.06</td>
<td>-0.37*</td>
<td>-0.44*</td>
<td>-0.42*</td>
<td>-0.38*</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>0.08</td>
<td>0.23</td>
<td>0.30</td>
<td>0.17</td>
<td>-0.08</td>
<td>-0.22</td>
<td>-0.11</td>
<td>-0.07</td>
</tr>
<tr>
<td>Silt</td>
<td>-0.16</td>
<td>-0.20</td>
<td>-0.26</td>
<td>-0.21</td>
<td>0.21</td>
<td>0.38*</td>
<td>0.28</td>
<td>0.29</td>
</tr>
<tr>
<td>SOM</td>
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<td>-0.03</td>
<td>-0.09</td>
<td>0.01</td>
<td>-0.06</td>
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<td>-0.20</td>
</tr>
<tr>
<td>C/N</td>
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<td>-0.01</td>
<td>0.23</td>
<td>0.12</td>
<td>-0.37</td>
<td>-0.31</td>
<td>-0.33</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

* Correlation is significant at 0.05 levels
** Correlation is significant at 0.01 levels
system. The large aggregate class (>2 mm) showed positive correlations and the smaller aggregate classes had negative correlations with unsaturated hydraulic conductivity at water content close to saturation in the crop system (Table 3.8). Sand contents showed negative correlations with hydraulic conductivity at matric potentials -400 to -50 cm in the grass system and its correlations with unsaturated hydraulic conductivity were not significant in the crop system. The clay content negatively correlated with hydraulic conductivity at -400 to -50 cm matric potentials in the crop system and was not significantly correlated in the grass system. The silt content was positively correlated with hydraulic conductivity at -100 and -50 cm matric heads in the crop system and at -100 cm water head in the grass system.

The result showed that increasing soil porosity led to a significant increase of unsaturated hydraulic conductivity at water content close to saturation and insignificant impact on unsaturated hydraulic conductivity under relatively dry conditions in the crop system. Similar to saturated hydraulic conductivity, the unsaturated hydraulic conductivity at close to saturation in the crop system increased with increasing large aggregate content and decreased with increasing smaller aggregate content. That can be because the large aggregates associated with large pores and small aggregates most likely dispersed and plugged pores, which influenced hydraulic conductivity especially at water content close to saturation. The wet-aggregate stability analysis was performed only for 1-2 aggregate size class. Interestingly, the clay content was the main controlling factor on unsaturated hydraulic conductivity at relatively dry conditions in the crop system and the sand content was the main controlling factor in the grass system. It seemed that bulk density
and aggregate size distribution had a significant impact on unsaturated hydraulic conductivity at close to saturation and soil texture had significant correlations at low matric potentials. This illustrates that soil structural properties were the main controlling factor on saturated hydraulic conductivity and unsaturated hydraulic conductivity at close to saturation water content, and soil texture was the main factor on unsaturated hydraulic conductivity in dry conditions (Dexter, 2004a). The difference of these relationships between the crop and grass systems reflected the influence of land use on soil structural properties such as hydraulic conductivity at high matric potentials and their relations. The result shows also that under more developed structure soil (grass system) the sand content had more influence on unsaturated hydraulic conductivity at relatively dry conditions, and on the other hand, the clay content was more influential under less developed structure soil (crop system).

3.2.5 Relationships between soil gas transport characteristics and selected soil variables in crop and grass systems

The Spearman rank correlation coefficient was calculated between relative gas diffusivity, air-filled porosity, and the pore-continuity index at selected matric potentials and selected soil variables (Table 3.9). Bulk density had significantly negative correlations with relative gas diffusivity at all selected matric potentials in the crop system and at matric heads lower than -50 cm in the grass system. Aggregate size classes significantly correlated with relative gas diffusivity at -333, -100, and -50 cm matric potentials in the grass system. Dry bulk density had negative correlations with air-filled porosity at all selected matric potentials in both land-use systems (Table 3.9). Aggregate
size classes significantly correlated with pore-continuity indices at -333, -50, and -10 cm matric potentials in the grass system and these significant relations were not obtained in the crop system (Table 3.9).

Soil bulk density was the main factor controlling gas diffusivity and air-filled porosity in each land use. In other words, increasing soil porosity led to increasing air-filled porosity and gas diffusivity at all selected water content statuses, but that did not mean increasing pore continuity for air transport in each land use. Aggregate size distribution was another important factor influencing gas diffusivity and pore continuity for gas transport in the grass system. Increasing the content of the large aggregates and the aggregate mean weight diameter led to increasing gas diffusivity at moderate water content status in the grass system, most likely because large aggregates were associated with larger pore volume, which influenced gas transport in soil. Nielson et al. (1984) stated that gas diffusion coefficients increased with median pore diameter. Similar relations were found in the grass system between aggregate size distribution and pore continuity at all selected water heads except at -333 cm water head, which indicated that increasing the pore volume in soil was related to increasing pore continuity for air transport. The impact of large aggregates on gas diffusivity and pore continuity was not significant in the crop system, but was significant in the grass system, which reflected the difference of pore arrangement and geometry between crop and grass systems.

Grable and Siemer (1968) stated that bulk density and aggregate size greatly influenced soil gas diffusivity in a silty clay loam cropland soil. They obtained low relative gas
Table 3.9. The Spearman correlation coefficients between relative gas diffusivity, air-filled porosity, and pore continuity index and different soil properties and soil measurements in crop and grass systems.

| $\psi$ (cm) |作物系统 | $D_r/D_0$ | $\rho_b$ | $\rho$ | $\phi$ | $\chi$ | $\psi$ | $C/N$ | $\rho_b$ | $\rho$ | $\phi$ | $\chi$ | $\psi$ | $C/N$ |
|-------------|--------|----------|-------|-------|-----|-----|-----|------|-------|-------|-----|-----|-----|-----|------|
| -10 | -0.41* | -0.71* | -0.50* | -0.79* | -0.70* | -0.56* | -0.75* | -0.81* | -0.82* | -0.82* | 0.05 | -0.27 | -0.26 | -0.39* | -0.13 |
| -50 | 0.21 | 0.22 | 0.25 | 0.28 | 0.05 | 0.27 | 0.15 | 0.19 | 0.22 | 0.25 | 0.04 | 0.14 | 0.13 | 0.22 | -0.14 |
| -100 | -0.17 | -0.05 | -0.15 | -0.08 | 0.04 | -0.22 | -0.05 | 0.00 | -0.05 | -0.06 | -0.17 | -0.14 | -0.11 | -0.18 | -0.01 |
| -333 | -0.25 | -0.30 | -0.31 | -0.41* | -0.10 | -0.19 | -0.13 | -0.22 | -0.26 | -0.29 | -0.06 | -0.29 | -0.21 | -0.35 | 0.12 |
| -1000 | -0.25 | -0.33 | -0.30 | -0.40* | -0.15 | -0.36* | -0.26 | -0.32 | -0.34 | -0.35 | 0.01 | -0.18 | -0.12 | -0.30 | 0.14 |
| <0.053 mm | -0.25 | -0.29 | -0.20 | -0.36 | -0.18 | -0.33 | -0.27 | -0.29 | -0.32 | -0.33 | 0.02 | -0.06 | -0.03 | -0.21 | 0.08 |
| MWD | 0.19 | 0.26 | 0.26 | 0.32 | 0.05 | 0.30 | 0.18 | 0.22 | 0.25 | 0.27 | -0.04 | 0.13 | 0.12 | 0.22 | -0.16 |
| WAS | -0.07 | 0.18 | 0.06 | 0.05 | 0.15 | 0.06 | 0.09 | 0.08 | 0.04 | 0.01 | -0.18 | -0.19 | 0.03 | 0.05 | 0.13 |
| Sand | -0.28 | -0.29 | -0.08 | -0.26 | -0.31 | -0.29 | -0.40* | -0.36* | -0.35 | -0.35 | 0.00 | -0.20 | -0.01 | 0.07 | -0.06 |
| Clay | 0.04 | -0.02 | -0.05 | -0.17 | -0.20 | 0.30 | 0.11 | 0.04 | 0.01 | -0.04 | -0.15 | -0.17 | -0.05 | -0.06 | -0.08 |
| Silt | 0.10 | 0.18 | 0.19 | 0.29 | 0.27 | -0.11 | 0.11 | 0.17 | 0.21 | 0.23 | 0.11 | 0.26 | 0.14 | 0.04 | 0.04 |
| SOM | 0.23 | -0.05 | -0.11 | -0.09 | 0.11 | 0.30 | 0.19 | 0.10 | 0.07 | 0.14 | 0.04 | 0.02 | -0.27 | -0.10 | 0.11 |
| C/N | 0.32 | 0.28 | 0.49* | 0.25 | 0.41* | 0.10 | 0.13 | 0.10 | 0.06 | 0.14 | 0.04 | 0.30 | 0.43* | 0.29 | 0.40* |

| $\psi$ (cm) |作物系统 | $D_r/D_0$ | $\rho_b$ | $\rho$ | $\phi$ | $\chi$ | $\psi$ | $C/N$ | $\rho_b$ | $\rho$ | $\phi$ | $\chi$ | $\psi$ | $C/N$ |
|-------------|--------|----------|-------|-------|-----|-----|-----|------|-------|-------|-----|-----|-----|-----|------|
| -10 | -0.18 | -0.25 | -0.37* | -0.38* | -0.41* | -0.55* | -0.69* | -0.60* | -0.72* | -0.76* | 0.00 | -0.03 | 0.01 | 0.10 | 0.05 |
| -50 | 0.23 | 0.61* | 0.56* | 0.56* | 0.27 | 0.11 | 0.30 | 0.30 | 0.26 | 0.11 | 0.40* | 0.63* | 0.33 | 0.46* | 0.24 |
| -100 | -0.26 | -0.59* | -0.55* | -0.50* | -0.25 | 0.02 | -0.30 | -0.30 | -0.27 | -0.15 | -0.42* | -0.58* | -0.30 | -0.39* | -0.18 |
| -333 | -0.27 | -0.65* | -0.57* | -0.58* | -0.30 | 0.12 | -0.30 | -0.30 | -0.26 | -0.11 | -0.42* | -0.67* | -0.35 | -0.48* | -0.27 |
| -1000 | -0.13 | -0.49* | -0.44* | -0.52* | -0.21 | 0.14 | -0.25 | -0.27 | -0.22 | -0.07 | -0.27 | -0.52* | -0.26 | -0.45* | -0.23 |
| <0.053 mm | -0.15 | -0.44* | -0.36 | -0.41* | -0.10 | 0.18 | -0.19 | -0.16 | -0.08 | 0.06 | -0.35 | -0.51* | -0.24 | -0.40* | -0.19 |
| MWD | 0.22 | 0.59* | 0.53* | 0.54* | 0.25 | -0.12 | 0.28 | 0.28 | 0.23 | 0.08 | 0.39* | 0.62* | 0.32 | 0.46* | 0.24 |
| WAS | 0.25 | 0.07 | 0.17 | 0.16 | 0.08 | 0.27 | 0.13 | 0.19 | 0.10 | 0.05 | 0.12 | 0.14 | -0.03 | 0.09 | 0.02 |
| Sand | 0.30 | 0.20 | 0.20 | 0.33 | 0.23 | 0.21 | 0.33 | 0.28 | 0.14 | 0.23 | 0.46* | 0.19 | -0.02 | 0.10 | 0.05 |
| Clay | 0.07 | 0.34 | 0.29 | 0.15 | -0.03 | -0.21 | 0.12 | 0.07 | 0.02 | -0.07 | 0.19 | 0.29 | 0.27 | 0.23 | 0.06 |
| Silt | -0.16 | -0.38* | -0.33 | -0.31 | -0.09 | 0.23 | -0.16 | -0.14 | -0.03 | 0.00 | -0.35 | -0.37* | -0.29 | -0.34 | -0.15 |
| SOM | 0.09 | -0.14 | 0.03 | 0.01 | 0.10 | 0.40* | 0.16 | 0.21 | 0.21 | 0.26 | -0.03 | -0.15 | -0.03 | -0.08 | 0.01 |
| C/N | 0.05 | 0.08 | 0.06 | 0.08 | 0.11 | 0.16 | 0.11 | 0.03 | 0.04 | 0.06 | 0.06 | 0.02 | 0.19 | 0.14 | 0.21 |
diffusivity in the smallest aggregates and most compacted soil. Kay et al. (1997) found a negative relation between clay content and air-filled porosity in agricultural soil with three different texture types; sandy loam, loam, and clay loam.

Some models (Millington and Quirk, 1961a; Millington and Quirk, 1961b; Xu et al., 1992; Moldrup et al., 2000; Moldrup et al., 2005) used total porosity with air-filled porosity to predict relative gas diffusivity. However, the current study showed that the relationship between bulk density (soil porosity) and relative gas diffusivity in the crop system differed from that in the grass system. Bulk density did not significantly correlate with relative gas diffusivity at high matric potentials in the grass system. Hence, land use should be considered when bulk density or porosity is included in modeling gas diffusivity. Aggregate size distribution is another important factor to be considered for modeling gas diffusivity especially at moderate water content status in a grass system for similar soils (Table 3.9).

Tables 3.10 and 3.11 show the Spearman correlation coefficients for soil gas transport properties and water retention characteristics in crop and grass systems, respectively. Significant positive correlations were found between α and relative gas diffusivity and air-filled porosity at all selected matric potentials except at -10 cm in the crop system, and no significant relations were found in the grass system. Water content at saturation $\theta_s$ positively correlated with relative gas diffusivity at -1000, -333, and -50 cm matric heads.
Table 3.10. The Spearman correlation coefficients between relative gas diffusivity, air-filled porosity, and pore continuity index and soil water retention characteristics in a crop system.

<table>
<thead>
<tr>
<th></th>
<th>D_s/D_0</th>
<th></th>
<th>Air-filled porosity</th>
<th></th>
<th>Pore-continuity index</th>
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<tr>
<td></td>
<td>-10</td>
<td>-50</td>
<td>-100</td>
<td>-333</td>
<td>-1000</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>-10</td>
<td>-50</td>
<td>-100</td>
<td>-333</td>
<td>-1000</td>
</tr>
<tr>
<td>α†</td>
<td>0.11</td>
<td>0.58*</td>
<td>0.44*</td>
<td>0.60*</td>
<td>0.45*</td>
</tr>
<tr>
<td></td>
<td>-0.02</td>
<td>-0.06</td>
<td>0.09</td>
<td>-0.03</td>
<td>-0.12</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>0.51*</td>
<td>0.26</td>
<td>0.55*</td>
<td>0.53*</td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>0.03</td>
<td>0.10</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>0.11</td>
<td>0.19</td>
<td>0.23</td>
<td>0.45*</td>
<td>-0.42*</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>0.30</td>
<td>0.08</td>
<td>0.31</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>-0.28</td>
<td>-0.37*</td>
<td>-0.22</td>
<td>-0.16</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>-0.02</td>
<td>-0.03</td>
<td>-0.30</td>
<td>-0.14</td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>-0.29</td>
<td>-0.45*</td>
<td>-0.36</td>
<td>-0.29</td>
<td>-0.17</td>
</tr>
<tr>
<td></td>
<td>-0.14</td>
<td>-0.22</td>
<td>-0.38*</td>
<td>-0.31</td>
<td>-0.17</td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>-0.27</td>
<td>-0.47*</td>
<td>-0.41*</td>
<td>-0.21</td>
</tr>
<tr>
<td></td>
<td>-0.27</td>
<td>-0.42*</td>
<td>-0.32</td>
<td>-0.32</td>
<td>-0.18</td>
</tr>
<tr>
<td></td>
<td>-0.09</td>
<td>-0.24</td>
<td>-0.44*</td>
<td>-0.41*</td>
<td>-0.19</td>
</tr>
<tr>
<td></td>
<td>-0.27</td>
<td>-0.39*</td>
<td>-0.31</td>
<td>-0.33</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

interpreted as

|                  | 0.47*   | 0.38*          | 0.18               | 0.11            | 0.08                  |
|                  | -0.45*  | 0.20           | 0.43*              | 0.26            | 0.08                  |
|                  | 0.19    | 0.33           | 0.34               | 0.44*           | 0.19                  |
|                  | 0.36    | 0.33           | 0.34               | 0.02            | 0.34                  |
|                  | 0.02    | 0.19           | 0.33               | 0.34            | 0.34                  |
|                  | 0.15    | 0.00           | 0.04               | 0.23            | 0.22                  |
|                  | -0.03   | -0.07          | 0.15               | 0.26            | 0.15                  |
|                  | -0.10   | -0.03          | 0.06               | 0.06            | 0.06                  |
|                  | 0.00    | -0.07          | -0.38*             | -0.16           | 0.07                  |
|                  | 0.23    | 0.00           | 0.16               | 0.29            | 0.29                  |
|                  | 0.00    | 0.04           | -0.31              | -0.33           | -0.18                 |
|                  | 0.22    | 0.00           | 0.17               | 0.45*           | -0.41*                |
|                  | 0.05    | 0.04           | -0.31              | -0.33           | -0.18                 |
|                  | 0.22    | 0.00           | 0.17               | 0.45*           | -0.41*                |
|                  | 0.03    | 0.17           | 0.45*              | 0.22            | 0.03                  |

† Soil water retention measured using the pressure plate apparatus
‡ Soil water retention measured the evaporation method
* Correlation is significant at 0.05 levels
Table 3.11. The Spearman correlation coefficients between relative gas diffusivity, air-filled porosity, and pore continuity index and soil water retention characteristics in a grass system.

<table>
<thead>
<tr>
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</tr>
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<tbody>
<tr>
<td></td>
<td>-10</td>
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<td>-100</td>
<td>-333</td>
<td>-1000</td>
<td>-10</td>
<td>-50</td>
<td>-100</td>
<td>-333</td>
<td>-1000</td>
<td>-10</td>
<td>-50</td>
<td>-100</td>
</tr>
<tr>
<td>α†</td>
<td>0.06</td>
<td>-0.08</td>
<td>0.08</td>
<td>0.13</td>
<td>0.11</td>
<td>0.14</td>
<td>0.22</td>
<td>0.20</td>
<td>0.18</td>
<td>0.24</td>
<td>0.16</td>
<td>-0.09</td>
<td>-0.08</td>
</tr>
<tr>
<td>n†</td>
<td>-0.26</td>
<td>0.07</td>
<td>-0.02</td>
<td>0.09</td>
<td>0.15</td>
<td>-0.27</td>
<td>-0.18</td>
<td>-0.14</td>
<td>0.02</td>
<td>-0.06</td>
<td>-0.23</td>
<td>0.09</td>
<td>0.13</td>
</tr>
<tr>
<td>θ₁†</td>
<td>0.10</td>
<td>0.16</td>
<td>0.19</td>
<td>0.20</td>
<td>0.14</td>
<td>0.02</td>
<td>0.17</td>
<td>0.09</td>
<td>0.19</td>
<td>0.14</td>
<td>0.13</td>
<td>0.19</td>
<td>0.17</td>
</tr>
<tr>
<td>θ₂†</td>
<td>-0.08</td>
<td>0.04</td>
<td>0.02</td>
<td>0.09</td>
<td>0.10</td>
<td>-0.09</td>
<td>-0.11</td>
<td>-0.07</td>
<td>0.02</td>
<td>-0.01</td>
<td>-0.09</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>θ⁽(c-10)⁾†</td>
<td>-0.05</td>
<td>-0.06</td>
<td>-0.01</td>
<td>0.00</td>
<td>-0.09</td>
<td>-0.42*</td>
<td>-0.09</td>
<td>-0.05</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.18</td>
<td>0.13</td>
</tr>
<tr>
<td>θ⁽(c-25)⁾†</td>
<td>0.11</td>
<td>0.16</td>
<td>0.11</td>
<td>-0.01</td>
<td>-0.04</td>
<td>0.01</td>
<td>-0.03</td>
<td>-0.04</td>
<td>0.07</td>
<td>0.01</td>
<td>0.03</td>
<td>0.26</td>
<td>0.15</td>
</tr>
<tr>
<td>θ⁽(c-50)⁾†</td>
<td>-0.37*</td>
<td>-0.57*</td>
<td>-0.58*</td>
<td>-0.54*</td>
<td>-0.32</td>
<td>-0.45*</td>
<td>-0.68*</td>
<td>-0.53*</td>
<td>-0.42*</td>
<td>-0.36</td>
<td>-0.30</td>
<td>-0.26</td>
<td>-0.21</td>
</tr>
<tr>
<td>θ⁽(c-100)⁾†</td>
<td>0.15</td>
<td>0.17</td>
<td>0.15</td>
<td>-0.02</td>
<td>-0.11</td>
<td>0.05</td>
<td>0.00</td>
<td>-0.01</td>
<td>0.03</td>
<td>-0.02</td>
<td>0.05</td>
<td>0.26</td>
<td>0.19</td>
</tr>
<tr>
<td>θ⁽(c-2000)⁾†</td>
<td>0.19</td>
<td>0.16</td>
<td>0.11</td>
<td>0.00</td>
<td>-0.14</td>
<td>0.13</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.04</td>
<td>0.03</td>
<td>0.26</td>
<td>0.13</td>
</tr>
<tr>
<td>θ⁽(c-333)⁾†</td>
<td>-0.21</td>
<td>0.18</td>
<td>0.15</td>
<td>0.02</td>
<td>-0.11</td>
<td>0.09</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>-0.03</td>
<td>-0.01</td>
<td>0.24</td>
<td>0.15</td>
</tr>
<tr>
<td>θ⁽(c-400)⁾†</td>
<td>-0.09</td>
<td>-0.18</td>
<td>-0.31</td>
<td>-0.33</td>
<td>-0.36</td>
<td>-0.30</td>
<td>-0.54*</td>
<td>-0.81*</td>
<td>-0.82*</td>
<td>-0.77*</td>
<td>0.00</td>
<td>0.02</td>
<td>0.41*</td>
</tr>
<tr>
<td>θ⁽(c-1000)⁾†</td>
<td>0.31</td>
<td>0.17</td>
<td>0.16</td>
<td>0.00</td>
<td>-0.15</td>
<td>0.26</td>
<td>0.10</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
<td>0.07</td>
<td>0.20</td>
<td>0.13</td>
</tr>
</tbody>
</table>

† Soil water retention measured using the evaporation method
‡ Soil water retention measured using the pressure plate apparatus
* Correlation is significant at 0.05 levels
and with the pore-continuity index at -333 and -50 cm matric heads in the crop system and these correlations were not significant in the grass system. In the grass system soil water retention at -50 cm matric potential negatively correlated with relative gas diffusivity at all selected matric heads except at -1000 cm. In the grass system, soil water retention at -100 cm matric head negatively correlated with relative gas diffusivity at -333 and -100 cm water heads. Water content at relatively low matric potential (-1000 cm) correlated to relative gas diffusivity at the same matric potential.

Air-filled porosity at all selected matric heads negatively correlated with soil water retention measured under equilibrium conditions at matric heads lower than -10 cm in both land uses. Air-filled porosity at all selected matric heads except at -10 cm negatively correlated with soil water content measured under evaporation conditions at matric heads lower than -50 cm in the crop system and no similar correlations were found in the grass system.

Gas diffusivity and air-filled porosity in both land uses correlated more significantly with soil water retention measured under equilibrium conditions than measured under evaporation conditions possibly because they were measured under equilibrium conditions. Gas diffusivity, air-filled porosity, and pore continuity had different relationships with water retention characteristics in the crop system than in the grass system, which reflected the influence of land use on soil pore size distribution and pore geometry. Moldrup et al. (2000) used soil water content at -100 cm matric potential with air-filled porosity to predict relative gas diffusivity. However, in this study, soil water
retention significantly correlated to relative gas diffusivity at just -100 and -50 cm matric potentials in the crop system and only at -1000 and -333 cm matric potentials in the grass system. The results indicated that the inverse of air entry value $\alpha$ and $\theta_s$ can be used, besides other factors such as air-filled porosity, to predict relative gas diffusivity in cropland and similar soils.

The relationships between soil gas transport properties and hydraulic conductivity for the same soils were also quantified (Table 3.12). Saturated hydraulic conductivity and hydraulic conductivity at high matric potentials, -10, -5, and -1 cm, had significantly positive correlations with relative gas diffusivity and air-filled porosity at all selected matric potentials in the crop system. Saturated hydraulic conductivity significantly correlated with relative gas diffusivity at all water heads except -10 and -100 cm in the grass system.

Saturated hydraulic conductivity positively correlated with the pore-continuity index at -333 and -100 cm matric potentials, and did not correlate with the pore-continuity index in the grass system. The pore-continuity index at -333, -100, and -50 cm matric heads positively correlated with unsaturated hydraulic conductivity at -10, -5, and -1 cm matric potentials in the crop system.

Significant relations between hydraulic conductivity and gas transport functions were found in the crop but not in the grass system possibly because soil structure in the grass system was more developed with larger pore volume and more continuous pores than in the crop system. Hydraulic conductivity at close to saturation water status, relative gas
Table 3.12. The Spearman correlation coefficients between relative gas diffusivity, air-filled porosity, and pore continuity index and soil hydraulic conductivity $K(\psi)$ in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>$K(\psi)$</th>
<th>-10</th>
<th>-50</th>
<th>-100</th>
<th>-333</th>
<th>-1000</th>
<th>Air-filled porosity</th>
<th>-10</th>
<th>-50</th>
<th>-100</th>
<th>-333</th>
<th>-1000</th>
<th>Pore-continuity index</th>
<th>-10</th>
<th>-50</th>
<th>-100</th>
<th>-333</th>
<th>-1000</th>
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<td></td>
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<td>D/D$_0$</td>
<td></td>
<td></td>
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<tr>
<td>$K_{sat}$</td>
<td></td>
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</tr>
<tr>
<td>$K_{(1)}$</td>
<td>0.70**</td>
<td>0.48*</td>
<td>0.52**</td>
<td>0.64**</td>
<td>0.48*</td>
<td>0.40*</td>
<td>0.40*</td>
<td>0.42*</td>
<td>0.44*</td>
<td>0.42*</td>
<td>0.33</td>
<td>0.22</td>
<td>0.41*</td>
<td>0.55**</td>
<td>0.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{(5)}$</td>
<td>0.47**</td>
<td>0.68**</td>
<td>0.62**</td>
<td>0.80**</td>
<td>0.74**</td>
<td>0.24</td>
<td>0.51**</td>
<td>0.55**</td>
<td>0.60**</td>
<td>0.56**</td>
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**Crop system**

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</table>

* Correlation is significant at 0.05 levels

**Correlation is significant at 0.01 levels**
diffusivity, and air-filled porosity were strongly affected by land use and soil structure as was discussed earlier in this chapter. To date, the relationships between gas transport functions and hydraulic conductivity under different land uses have not been reported in the literature.

3.3 Summary and conclusions

Soil structure was characterized by assessing selected soil physical properties and important characteristics at different degrees of soil water saturation in crop and grass systems. The results showed that land use affected soil structure; more developed soil structure and more continuous pores were found in the grass than in the crop system. Significantly higher porosity and larger aggregate mean weight diameter at the upper depth (0-15 cm) were found in the grass than in the crop system. The difference of aggregate mean weight diameter between upper and deeper depths was significant in the crop but not in the grass system with larger geometric mean was obtained at the deeper depth. The large aggregate class >2 was the dominant size in both land uses, and the grass system had higher content of large aggregates at the upper depth than the crop system. Soil water retention curve parameters, \( \alpha \) and \( \theta_s \), which are controlled by structural pores, were significantly higher in the grass than in the crop system. Soil water content was significantly higher in the grass than in the crop system at high matric potentials (-50 and -10 cm) but did not significantly differ between the two land uses at lower matric potentials. Water transport characteristics showed differences between the two land uses, with higher hydraulic conductivity in the grass system relative to that in the crop system. Hydraulic conductivity measurements indicated that the grass system had not only larger
but also more continuous pores to conduct water farther than the crop system. Gas transport functions showed that the grass system had significantly higher relative gas diffusivity and pore continuity for gas transport than the crop system. For each of the five selected matric potentials, mean relative gas diffusion coefficient and pore continuity index were significantly higher in the grass than in the crop systems.

The results indicated that structural pores controlled water transport properties at high water content and textural pores controlled water transport at low soil water content status. Pore geometry, continuity, and size distribution are the most important factors controlling water and gas transport processes in soil. The pore continuity index has not been considered as an indicator of soil structure. It provided an important estimation of the influence of land use on pore geometry and pore continuity for gas diffusion processes.

In this chapter, relationships between selected soil physical properties and functions and selected soil variables were also examined using the Spearman correlation coefficients in crop and grass systems. Some, but not all, of these relationships were significant in one or both land use systems. These relations showed the effective factors which can significantly impact soil structure under crop and grass systems. Soil organic matter, total nitrogen, and total dissolved carbon and nitrogen significantly correlated with bulk density only in the grass system. Clay and silt contents had significant correlation with aggregate size classes also only in the grass system. The soil water retention curve parameter $\alpha$ significantly correlated with sand and silt contents in the crop system and
with soil organic matter and total dissolved carbon in the grass system. Hydraulic conductivity at low matric potentials (between -400 and -50 cm) had significant relationship with clay contents in the crop system and with sand contents in the grass system. Bulk density and small aggregate size classes showed significant relationships with hydraulic conductivity at high matric potentials (between -10 and -1 cm) only in the crop system. Bulk density also significantly correlated with relative gas diffusivity and air-filled porosity in crop and grass system. Aggregate size classes also showed significant relationships with relative gas diffusivity and pore continuity index only in the grass system. An explanation for non-significant relationships could be that a narrower range of measurements existed, but may also reflect fundamental differences in the behavior of different land uses. Soil variables with a narrow range of observations and low variation might show no correlations.

Quantifying these relationships helps better determining factors affecting soil structure and answering questions related to how land use affects structural properties and processes. Understanding these relationships was also important for predicting soil water and soil gas transport behaviors. However, how these soil attributes are associated to each other in space is still an important question, which will be answered in the next chapter. Results of quantifying soil structure under different land uses and relations between variables that influenced by land uses obtained in this study are applicable for predicting similar processes and behaviors under similar conditions of soil type, land use, and soil management. Furthermore, future work of modeling these processes under different conditions of soil type and land use and management is recommended.
CHAPTER 4: Quantifying Spatial Patterns of Soil Physical Properties and Characteristics and Their Spatial Associations with Selected Soil Variables in Crop and Grass Systems

Soil physical properties and functions exhibit high spatial variability. Quantifying the spatial patterns of these variables is essential to better understand their spatial processes and associations. The field-scale spatial patterns and associations of soil physical variables and the impact of land use on these patterns and relationships are not well understood. The spatial associations and the controlling factors on the spatial variability of soil physical variables are rarely investigated. Quantifying the spatial variability of these soil variables is essential to enable characterizing their spatial relationships with CO$_2$ and N$_2$O fluxes, which are considered in the next chapters (Chapters 5 and 6).

Therefore, the objectives of this chapter were to characterize the spatial patterns of different soil physical properties and processes in crop and grass systems, and to quantify the spatial associations of these soil physical variables with selected soil variables. These soil attributes included: soil bulk density, soil aggregate size distribution, wet-aggregate stability, soil water retention characteristics, soil hydraulic conductivity, soil gas diffusivity, air-filled porosity, and the pore-continuity index. The spatial associations between these soil variables and other selected variables such as soil texture, soil organic matter, and dissolved carbon and nitrogen were also quantified in crop and grass systems. This investigation will contribute to the knowledge of improving field-scale sampling design protocols and modeling soil physical processes such as dynamics of soil transport coefficients as a function of soil water or air content under crop and grass systems.
Approaches

To meet the objectives of this chapter, 60 soil cores were taken from the field at 4-10 cm depth and different soil measurements were performed in the lab. Chapter 2 provides details about the soil core sampling and all laboratory measurements included in this chapter. Semivariogram and cross-semivariogram analysis were used in this chapter to quantify the spatial patterns and spatial associations between soil variables, respectively.

Results and discussion

4.1 Spatial patterns of soil physical properties and characteristics in crop and grass systems

4.1.1 Spatial patterns of soil bulk density in crop and grass systems

Spatial variation of soil bulk density, estimated by the coefficient of variation (CV), was low in the crop and grass systems. The CV was higher in the crop (3.5%) than in the grass system (2.2%). Spatial variability of soil bulk density was structured in both crop and grass systems based on the semivariogram analysis (Figure 4.1). Both land uses exhibited low nugget semivariance but the grass system had one order of magnitude lower nugget semivariance \((2.9 \times 10^{-5} \text{ g cm}^{-3})^2\) than the crop system \((2.5 \times 10^{-4} \text{ g cm}^{-3})^2\). Both land uses also exhibited a low nugget-to-sill ratio (0.07 and 0.03 for crop and grass systems, respectively). The crop system also showed a longer spatial correlation length (30.9 m) than the grass system (7.9 m).
Figure 4.1. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of soil bulk density in crop (b) and grass (c) systems.
Strong spatial dependency was obtained in both land-use systems as was indicated from low nugget-to-sill ratios. A strong spatial dependency of bulk density corresponded to low coefficients of variation in both land uses. Measurements of bulk density were correlated for longer distance in the crop system than in the grass system because crop and grass systems exhibited different soil structure (Chapter 3.1). The grass system had more developed soil structure with higher porosity than the crop system. For the sake of comparison, Anderson and Cassel (1986) found a higher CV (16%) for bulk density in a limited drainage Portsmouth sandy loam soil relative to CVs found in the current study. They obtained a correlation length of <4 m in a 50-cm distance interval transect. Gajem et al. (1981) estimated a spatial range of bulk density of 3.4 m in a 30-cm distance interval transect and concluded that the spatial range strongly depended on the domain size and distance between samples, with larger intervals and longer transects tending to give greater values of the spatial range. The differences between their results and the result from the current study indicate that soil type (Typic Torrifluvent clay loam) and measurement scale are important in determining the spatial range of bulk density.

4.1.2 Spatial patterns of soil aggregate size distribution and wet-aggregate stability in crop and grass systems

Spatial variability of aggregate size distribution and aggregate stability was quantified at two depths (0-15 and 15-30 cm). The CVs of aggregate size classes and the aggregate mean weight diameter were higher in the grass than in the crop system at both depths (Figure 4.2). At the 0-15 cm depth, the CV increased with decreasing aggregate size in the grass system, and the difference of CVs between the two land-use systems was larger.
Figure 4.2. Coefficients of variation (CV) of aggregate-size classes and of the aggregate mean weight diameter MWD in crop and grass systems at 0-15 and 15-30 cm depths.
for smaller than for larger aggregate size classes. The CV of aggregate size classes corresponded to the content of aggregates. For instance, the large aggregate-size class (>2 mm) was the most abundant size and it had the lowest CV in both land uses and both depths. The CV of the wet-aggregate stability index was higher in the crop than in the grass system at both depths. In the crop system, the CV of the stability index was higher at 0-15 cm (20.0%) than at 15-30 cm (15.5%). On the other hand, it was higher at 15-30 cm (10.5%) than at 0-15 cm (5.5%) in the grass system. This suggested that the mechanisms promoting aggregate stability differed in the crop from the grass system (Chapter 3.1.3 and 3.2.2).

The semivariogram analysis showed that the spatial variability of the mean weight diameter at 0-15 cm depth was structured in crop and grass systems with stronger spatial dependency in the grass but longer spatial range in the crop system (Figures 4.3). The spatial variability of only the large aggregate-size classes 1-2 and >2 mm in the crop were structured at 0-15 cm depth (Figures 4.4-4.8). In the grass system, the spatial variability of all selected aggregate-size classes except 1-2 mm was structured at 0-15 cm depth. At the 15-30 cm depth, the spatial variability of all selected aggregate-size classes in both land uses was random. The spatial variability of the wet-aggregate stability index was random in both land-use systems and at both depths (Figure 4.9). The nugget-to-sill ratio indicated that, in the crop system, the spatial structure of the large aggregate-size class (>2 mm) was moderate while it was strong for the 1-2 mm class at 0-15 cm depth (Table 4.1). The spatial dependency was strong for all selected aggregate-size classes which showed structured variability in the grass system at 0-15 cm depth. Among the selected
Figure 4.3. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of the aggregate mean weight diameter MWD at two depths in crop (b) and grass (c) systems.
Figure 4.4. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of aggregate size >2 mm at two depths in crop (b) and grass (c) systems.
Figure 4.5. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of aggregate size 1-2 mm at two depths in crop (b) and grass (c) systems.
Figure 4.6. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of aggregate size 0.25-1 mm at two depths in crop (b) and grass (c) systems.
Figure 4.7. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of aggregate size 0.053-0.25 mm at two depths in crop (b) and grass (c) systems.
Figure 4.8. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of aggregate size <0.053 mm at two depths in crop (b) and grass (c) systems.
Figure 4.9. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of wet-aggregate stability index at two depths in crop (b) and grass (c) systems.
Table 4.1. Semivariogram parameters for the aggregate mean weight diameter, aggregate-size classes, and wet-aggregate stability at 0-15 cm depth in crop and grass systems.

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aggregate fractions, the large aggregate class (>2 mm) exhibited the highest nugget semivariance at both depths and land uses. The difference of spatial patterns of large aggregate-size distribution between crop and grass systems was a reflection of the land use impact on soil aggregation. The grass system had more developed soil structure with a larger mean weight diameter and higher contents of large aggregates than the crop system.

Spatial behavior of soil aggregate size distribution and aggregate stability has rarely been investigated. Shouse et al. (1990) studied the spatial distribution of aggregate stability index in conventionally tilled, transition between conventional and non-tillage regimes, and native pasture fields in 36- by 84-m grids with 0.3 m as the shortest lag distance. Compared to what was found in the current study, they found a lower stability index but similar CVs of 10.3 and 6.2% in a conventionally tilled field and a pasture field, respectively. The spatial variability of their stability index was structured with a spatial correlation range of 45.7 m in the conventionally tilled field and 7.6 m in the native pasture field. They also concluded that the spatial variability of the aggregate stability index seemed to increase in fields that have been tilled. Their unexpected result - a longer spatial range of the aggregate stability index in the conventionally tilled field than in the pasture field - was possibly their semivariogram was unbounded, and due to their selection of larger spacing (20 m) than the current study. In semivariogram analysis, the semivariance usually increases with separation distance (lag distance) to a constant value (sill) at a given distance, which is the range of spatial dependence. Shukla et al. (2007) studied the spatial variability of water stability and the aggregate mean weight diameter.
besides other variables associated with soil aggregation at unmined and mined sites reclaimed at different times. They reported CVs of 22 and 29% for aggregate stability and the aggregate mean weight diameter, respectively, in the unmined site. They found a spatial range of 41 m for wet-aggregate stability and 159 m for the aggregate mean weight diameter in the unmined site and concluded that reclamation initially reduced the variability of both variables but variability increased as time increased. In other words, the variability increased as soil structure developed. They obtained structured variability of aggregate stability and longer spatial ranges of the aggregate mean weight diameter because of the longer separation distance they selected (20 m) and a larger spatial domain (300- by 60-m). Their results corresponded to the results obtained from the current study in which more developed soil structure in the grass system was more related to higher and unstructured spatial variability of aggregate size and stability than the crop system.

4.1.3 Spatial behavior of soil water retention characteristics in crop and grass systems

Soil water retention properties at selected matric potentials used for this data analysis were measured using the evaporation method except at -1000 cm water head, which was measured under equilibrium conditions (Chapter 2). The CV of soil water content increased slightly with decreasing matric potentials in both land-use systems (Figure 4.10). The increase of the spatial variation with decreasing matric potentials was more obvious in the crop than in the grass system. The crop system had higher CVs than the grass system at all selected matric potentials except at -50 cm and the difference of CVs between the two land uses was more obvious under dry conditions than at higher matric
Figure 4.10. Coefficient of variation (CV) of soil water retention characteristics in crop and grass systems.
potentials. The crop system had higher CVs for $\alpha$, $n$, and $\theta_s$ and a slightly lower CV for $\theta_r$ than the grass system (Figure 4.10). The coefficient of variation of residual water content was extremely large compared to that for water content at saturation in both land uses. Residual water content is an empirical fitting parameter with an optimization error that is considerably larger than for $\theta_s$, partly because $\theta_r$ is extrapolated water content at infinite matric head.

The soil water retention data showed greater spatial variation at lower matric heads in both land uses in comparison with retention data at higher matric potentials. This result implies that more observations of soil water content should be taken when the soil is dry than wet. Similar observations were reported by Warrick and Nielsen (1980) and Greminger et al. (1985) for a field drainage experiment and by Shouse et al. (1995) for laboratory data obtained from small soil cores. Mallants et al. (1996) observed the same behavior of increasing spatial variability with decreasing the matric head and reported that the increased spatial variability of retention data in dry conditions had important implications for sampling density. They concluded that more samples were needed when the soil became drier to accurately estimate the mean water content.

In general, the CV values for $n$ and $\theta_s$ in the current study were very similar to results obtained by Russo and Bresler (1981) and Shouse et al. (1995). Mallants et al. (1996) reported a larger CV for $\alpha$ (45%) and similar values for $n$ (22%) and $\theta_s$ (7.2%); and smaller value for $\theta_r$ (58%). However, they found a CV value of 156% for $\theta_r$ for soil cores taken from 25-55 cm depth and attributed the higher CV to some values being zero,
whereas the next lowest value was 0.0016. There were 28 locations with an estimated value of $\theta_r$ to be zero in both land uses in the current study. The same behavior of large CV for $\theta_r$ due to some values being zero was obtained by Shouse et al. (1995). Higher variability of $\alpha$ in the crop system relative to that in the grass system can be interpreted as heterogeneity of pore sizes in the crop system. The shape parameter $n$ displayed less heterogeneity in the grass system in comparison with the crop system.

The semivariogram analysis (Figures 4.11-4.14) showed that the spatial variability of soil water retention was structured in the crop system at all selected matric potentials except at -1000 cm. In the grass system, on the other hand, it was only structured at -400, -200, and -100 cm matric potentials. The spatial variability of retention curve parameters $\alpha$ and $\theta_s$ was only structured in the crop system, and was only structured in the grass system for the other curve parameters $n$ and $\theta_r$. Soil water content at selected matric potentials and the retention curve parameters exhibited low nugget semivariance in both land uses. The nugget semivariance of soil water content was larger at low than at high matric potential in the crop system, and it was similar for water content at all selected matric potentials in the grass system. This behavior corresponded to the CV value which was also larger at low than at high matric potentials. The spatial dependency of soil water retention and retention curve parameters that showed structured variability was strong in both land uses except for water content at -200 and -100 cm matric potentials in the grass system, which showed moderate structure. Table 4.2 provides semivariogram parameters for soil water retention at different matric potentials and retention curve parameters in crop and grass systems.
Figure 4.11. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of $\alpha$ and $n$ in crop (b) and grass (c) systems.
Figure 4.12. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of $\theta_s$ and $\theta_r$ in crop (b) and grass (c) systems.
Figure 4.13. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of soil water content at -25, -50, and -100 cm matric heads in crop (b) and grass (c) systems.
Figure 4.14. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of soil water content at -1000, -400, and -200 cm matric heads in crop (b) and grass (c) systems.
Table 4.2. Semivariogram parameters for soil water retention curve parameters and soil water content at different matric potentials in crop and grass systems.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Crop system</th>
<th>Grass system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range (m)</td>
<td>Nugget</td>
</tr>
<tr>
<td>$\alpha$ (log(cm$^{-1}$x10$^{-3}$))</td>
<td>22.7</td>
<td>1x10$^{-2}$</td>
</tr>
<tr>
<td>$n$</td>
<td>-</td>
<td>1x10$^{-3}$</td>
</tr>
<tr>
<td>$\theta_s$ (m$^3$ m$^{-3}$)</td>
<td>14.3</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_r$ (m$^3$ m$^{-3}$)</td>
<td>-</td>
<td>1x10$^{-2}$</td>
</tr>
<tr>
<td>$\theta_{(0.25)}$ (m$^3$ m$^{-3}$)</td>
<td>10.8</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{(0.50)}$ (m$^3$ m$^{-3}$)</td>
<td>10.7</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{(100)}$ (m$^3$ m$^{-3}$)</td>
<td>9.8</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{(200)}$ (m$^3$ m$^{-3}$)</td>
<td>9.8</td>
<td>2x10$^{-5}$</td>
</tr>
<tr>
<td>$\theta_{(400)}$ (m$^3$ m$^{-3}$)</td>
<td>10.6</td>
<td>2x10$^{-5}$</td>
</tr>
<tr>
<td>$\theta_{(1000)}$ (m$^3$ m$^{-3}$)</td>
<td>-</td>
<td>1x10$^{-3}$</td>
</tr>
</tbody>
</table>
The spatial variability of water content at -1000 cm matric potential was random in both land-use systems possibly because it was measured under equilibrium conditions. Soil water retention curve measured under equilibrium conditions exhibited lower values of water content and higher variation than measured using the evaporation method (Appendix 2). Land use impact on soil structural properties such as soil water retention characteristics discussed in Chapter 3 can explain the difference of spatial patterns of these functions between crop and grass systems. Based on soil water retention measurements (Chapter 3.1.4), the grass system exhibited a more homogeneous soil pore size distribution than the crop system.

Mallants et al. (1996) also found structured spatial variability for $\alpha$ and $\theta_s$, but a pure nugget for $n$ and $\theta_r$ parameters, which indicated random variation, in undisturbed soil columns taken from grassland with sandy loam soil. They found moderate spatial dependence (nugget-to-sill ratio of 0.65) and a correlation length of <5 m for all retention curve parameters that showed a clear spatial dependence. They reported that the high nugget was probably caused by experimental uncertainties and/or the presence of non-optimal parameter estimates and not due to microheterogeneity at distances smaller than 0.1 m. The nugget semivariance represents measurement errors besides short-scale variation and sampling errors (Isaaks and Srivastava, 1989). The reason they observed random variability for some retention parameters, shorter spatial range, and weak spatial dependence compared to the current study can be the fact that they selected a smaller transect size (31 m), a shorter sampling interval (10 cm), and smaller sample size (100 cm$^3$). Shouse et al. (1995) also found structured spatial variability for retention curve
parameters estimated for a bare silt loam soil with spatial ranges similar to those found in the current study in the crop system, and the spatial dependence was moderate for their $\alpha$, $\theta_r$, and $n$ parameters and weak for $\theta_s$.

4.1.4 Spatial patterns of soil hydraulic conductivity in crop and grass systems

Saturated and unsaturated hydraulic conductivity exhibited high spatial variation in crop and grass systems. The spatial CV of untransformed saturated hydraulic conductivity was high in both land-use systems and higher in the grass than in the crop system. The CV of saturated hydraulic conductivity was 254 and 311% in crop and grass systems, respectively. The CV of unsaturated hydraulic conductivity was similar at high matric potentials, -10, -5, and -1 cm, and was lower at lower matric potentials in the crop system (Figure 4.15). In the grass system, on the other hand, it was the highest at -5 cm and the lowest at -200 cm matric potential. It should be noted that hydraulic conductivity at -10, -5, and -1 cm matric potentials was measured using the double plate membrane permeameter, and the evaporation method was used to measure hydraulic conductivity at lower matric potentials (Chapter 2).

Semivariogram analysis showed that spatial variability of log-transformed saturated hydraulic conductivity was only structured in the crop system (Figure 4.16). The saturated hydraulic conductivity in the grass system exhibited higher nugget semivariance than in the crop system. The spatial dependency of saturated hydraulic conductivity in the crop system was strong, with a spatial range of 9.2 m (Table 4.3).
Figure 4.15. Coefficients of variation (CV) of unsaturated hydraulic conductivity $K(\psi)$ measured at different matric heads $\psi$ in crop and grass systems.
Figure 4.16. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of saturated hydraulic conductivity at different matric potentials in crop (b) and grass (c) systems.
Figure 4.17. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of unsaturated hydraulic conductivity at different matric potentials in crop (b) and grass (c) systems.
Figure 4.18. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of unsaturated hydraulic conductivity at different matric potentials in crop (b) and grass (c) systems.
Table 4.3. Semivariogram parameters for saturated and unsaturated hydraulic conductivity $K_{(ψ)}$ at different soil matric potentials in crop and grass systems.

<table>
<thead>
<tr>
<th>$K_{(ψ)}$</th>
<th>Range (m)</th>
<th>Nugget (log(cm d$^{-1}$x10$^{-3}$))$^2$</th>
<th>Nugget/sill</th>
<th>Range (m)</th>
<th>Nugget (log(cm d$^{-1}$x10$^{-3}$))$^2$</th>
<th>Nugget/sill</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{sat}$</td>
<td>9.2</td>
<td>0.41</td>
<td>0.25</td>
<td>-</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>$K_{(-1)}$</td>
<td>4.7</td>
<td>0.35</td>
<td>0.42</td>
<td>6.9</td>
<td>0.06</td>
<td>0.25</td>
</tr>
<tr>
<td>$K_{(-5)}$</td>
<td>-</td>
<td>0.43</td>
<td>1.0</td>
<td>-</td>
<td>0.06</td>
<td>1.0</td>
</tr>
<tr>
<td>$K_{(-10)}$</td>
<td>13.3</td>
<td>0.12</td>
<td>0.35</td>
<td>-</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>$K_{(-50)}$</td>
<td>20.5</td>
<td>0.04</td>
<td>0.42</td>
<td>-</td>
<td>0.10</td>
<td>1.0</td>
</tr>
<tr>
<td>$K_{(-100)}$</td>
<td>12.4</td>
<td>0.02</td>
<td>0.44</td>
<td>-</td>
<td>3x10$^{-3}$</td>
<td>1.0</td>
</tr>
<tr>
<td>$K_{(-200)}$</td>
<td>10.7</td>
<td>0.00</td>
<td>0.03</td>
<td>-</td>
<td>3x10$^{-3}$</td>
<td>1.0</td>
</tr>
<tr>
<td>$K_{(-400)}$</td>
<td>3.5</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>9x10$^{-4}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Bormann and Klaassen (2008) measured saturated hydraulic conductivity in forest, grassland, and cropland soils and found higher spatial variability of $K_{\text{sat}}$ for the cropland. Lauren et al. (1988) also found a high CV of 1496% for saturated hydraulic conductivity measured in detached columns (884 cm$^3$) in the lab and a lower CV (36%) for saturated hydraulic conductivity measured in the field in silty clay loam soil columns. They compared the magnitude of saturated hydraulic conductivity measured in the field and its spatial variability behavior among different column sizes. They found structured spatial variability of saturated hydraulic conductivity of their soil; the structured variability was a function of the sample (column) size. Sample size affected the spatial variation of saturated hydraulic conductivity and the CV increased with decreasing sample size. They observed a longer correlation length because of their larger sampling domain (370 m), longer sampling distance interval (10 m), and larger sample size relative to the current study.

Semivariogram analysis of log-transformed unsaturated hydraulic conductivity showed that its spatial variability was structured at all selected matric heads, except -5 cm, in the crop system (Figures 4.17, 4.18). In the grass system, on the other hand, the spatial variability of hydraulic conductivity was only structured at -1 cm matric potential with strong spatial dependency. The nugget values of hydraulic conductivity were larger at high, -10, -5, and -1 cm than at lower matric potentials in both land uses except at -50 cm water head in the grass system (Table 4.3). In the crop system, the spatial dependency of hydraulic conductivity was strong at low, -400 and -200 cm, matric potentials and moderate at the other selected water heads that showed structured variability.
The spatial range of hydraulic conductivity varied among the selected matric potentials with the longest range obtained at -50 cm in the crop system (Table 4.3). Thus, samples taken within the correlation length (spatial range) or less would be statistically dependent, and samples taken outside the spatial range would be independent. Bormann and Klaassen (2008) reported that the variability of unsaturated hydraulic conductivity in forest, grassland, and cropland soils was very high but the difference between the land uses was not significant. They pointed out that the variability of unsaturated hydraulic conductivity was increased by the high sensitivity of the evaporation method to determination of unsaturated hydraulic conductivity at lower soil suctions. Mohanty et al. (1994) measured saturated and unsaturated hydraulic conductivity in a corn field under no-tillage management at -15, -6, and -3 cm soil water tensions and reported that the highest CV (125%) occurred at saturation - $K_{sat}$. However, they found a random spatial variability (pure nugget) of saturated and unsaturated hydraulic conductivity. Logsdon and Jaynes (1996) in cropped land with loam soil found structured spatial variability, varying between 6.6 and 16.8 m, with similar spatial ranges to those found in the current study for unsaturated hydraulic conductivity at -15 cm water tension, and a spatial range of <1 m for saturated hydraulic conductivity. They found shorter spatial range of saturated hydraulic conductivity than those found in the current study possible because their site was tilled. They reported that tillage destroyed the inherent soil properties but did not reduce the variability of hydraulic conductivity. These studies showed different results relative to the current study mainly because different measurement scales were selected.
4.1.5 Spatial patterns of relative gas diffusivity, air-filled porosity, and the pore-continuity index in crop and grass systems

The relative gas diffusion coefficient, air-filled porosity, and the pore-continuity index exhibited high spatial variation in both land-use systems. The CVs of relative gas diffusion coefficients, air-filled porosity, and the pore-continuity index were higher in the crop than in the grass system at all selected soil matric potentials (Figure 4.19). The CVs for the relative gas diffusion coefficient and air-filled porosity decreased with decreasing soil matric potential in both land-use systems.

Semivariogram analysis showed that the spatial variability of relative gas diffusion coefficients was structured at all selected soil water matric potentials in crop and grass systems (Figures 4.20-4.22). The nugget semivariance values of relative gas diffusivity were low in both land-use systems at all selected soil matric potentials. The nugget-to-sill ratio of the relative gas diffusivity was lower in the crop than in the grass system at all selected matric potentials. In the crop system, the spatial dependence of relative gas diffusivity was strong at all selected matric potentials except at -1000 cm. On the other hand, the spatial structure of relative gas diffusivity varied between moderate and strong among the selected matric potentials in the grass system (Table 4.4). The spatial correlation lengths (ranges) of the relative gas diffusion coefficients were longer in the grass (varied between 7.0 and 30.4 m) than in the crop system (varied between 4.4 and 8.1 m) at all selected soil water matric potentials (Table 4.4).
Figure 4.19. Spatial coefficient of variation of relative gas diffusion coefficient (a), air-filled porosity (b), and the pore-continuity index (c) in crop and grass systems at different soil matric potentials.
Figure 4.20. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of soil gas diffusivity in crop (b) and grass (c) systems at -0.1 and -0.5 m soil matric potentials.
Figure 4.21. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of soil gas diffusivity in crop (b) and grass (c) systems at -3.33 and -1 m soil matric potentials.
Figure 4.22. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of relative apparent soil gas diffusivity in crop (b) and grass (c) systems at -10 m soil matric potentials.
Table 4.4. Spatial semivariogram parameters of relative gas diffusivity, air-filled porosity, and the pore-continuity index in crop and grass systems at different soil water matric potential.

<table>
<thead>
<tr>
<th>ψ (cm)</th>
<th>Range (m)</th>
<th>Nugget</th>
<th>Nugget/sill</th>
<th>Range (m)</th>
<th>Nugget</th>
<th>Nugget/sill</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crop system</td>
<td></td>
<td></td>
<td>Grass system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>--------</td>
<td>-------------</td>
<td>-------------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>-10</td>
<td>4.7</td>
<td>0.0</td>
<td>0.0</td>
<td>22.5</td>
<td>4x10^{-5}</td>
<td>0.34</td>
</tr>
<tr>
<td>-50</td>
<td>6.4</td>
<td>0.0</td>
<td>0.0</td>
<td>7.0</td>
<td>3.6x10^{-5}</td>
<td>0.39</td>
</tr>
<tr>
<td>-100</td>
<td>4.4</td>
<td>0.0</td>
<td>0.0</td>
<td>30.4</td>
<td>1.2x10^{-5}</td>
<td>0.07</td>
</tr>
<tr>
<td>-333</td>
<td>8.1</td>
<td>0.0</td>
<td>0.0</td>
<td>12.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>-1000</td>
<td>8.0</td>
<td>1x10^{-4}</td>
<td>0.44</td>
<td>15.3</td>
<td>2x10^{-4}</td>
<td>0.67</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Relative gas diffusivity D/D₀</th>
<th></th>
<th></th>
<th>Air-filled porosity (m³ m⁻³)</th>
<th></th>
<th></th>
<th>Pore-continuity index</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>17.5</td>
<td>2x10^{-4}</td>
<td>0.55</td>
<td>-</td>
<td>2x10^{-4}</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-50</td>
<td>12.8</td>
<td>4x10^{-4}</td>
<td>0.60</td>
<td>5.3</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-100</td>
<td>16.1</td>
<td>3x10^{-4}</td>
<td>0.37</td>
<td>-</td>
<td>5x10^{-4}</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-333</td>
<td>11.7</td>
<td>3x10^{-4}</td>
<td>0.38</td>
<td>-</td>
<td>2x10^{-4}</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1000</td>
<td>16.8</td>
<td>4x10^{-4}</td>
<td>0.43</td>
<td>7.1</td>
<td>2x10^{-4}</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10</td>
<td>9.0</td>
<td>3x10^{-3}</td>
<td>0.39</td>
<td>5.3</td>
<td>1x10^{-3}</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-50</td>
<td>4.0</td>
<td>0.0</td>
<td>0.0</td>
<td>4.1</td>
<td>3x10^{-3}</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-100</td>
<td>5.5</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>8x10^{-3}</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-333</td>
<td>2.4</td>
<td>0.0</td>
<td>0.0</td>
<td>12.5</td>
<td>5x10^{-3}</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1000</td>
<td>-</td>
<td>2x10^{-2}</td>
<td>1.0</td>
<td>-</td>
<td>1x10^{-4}</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The spatial variability of air-filled porosity was also structured at all selected soil water matric potentials in the crop system (Figures 4.23-4.25). In the grass system, on the other hand, the spatial variability of air-filled porosity was structured only at -1000 and -50 cm matric potentials. Semivariogram analysis showed that air-filled porosity in both land-use systems exhibited low nugget semivariance values at all selected soil matric potentials. The spatial dependence of air-filled porosity was moderate at all selected water heads in the crop system, and it was strong at -50 cm and moderate at -1000 cm matric potential in the grass system (Table 4.4). The spatial correlation length of air-filled porosity was longer in the crop than in the grass system at -1000 and -50 cm matric potentials which showed structured semivariograms.

The spatial variability of the pore-continuity index was structured at all selected soil water matric potentials except -1000 cm in the crop system and except -1000 and -100 cm in the grass system (Figures 4.26-4.28). The nugget semivariance of the pore continuity was low in both land-use systems and at all selected matric potentials. The nugget-to-sill ratio of pore continuity followed the same patterns of the nugget semivariance in the crop system with strong spatial dependence obtained at all selected matric potentials except -10 cm (Table 4.4). The spatial dependence of pore continuity varied between weak and strong among the selected matric potentials in the grass system. The result showed that the spatial range, which provided the maximum distance over which pairs of soil pore continuity measurements remain correlated, varied among the selected soil water matric potentials in both land-use systems (Table 4.4).
Figure 4.23. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of air-filled porosity in crop (b) and grass (c) systems at -0.1 and -0.5 m matric potentials.
Figure 4.24. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of air-filled porosity in crop (b) and grass (c) systems at -1 and -3.33 m matric potentials.
Figure 4.25. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of air-filled porosity in crop (b) and grass (c) systems at -10 m matric potential.
Figure 4.26. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of the pore-continuity index in crop (b) and grass (c) systems at -0.1 and -0.5 m matric potentials.
Figure 4.27. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of the pore-continuity index in crop (b) and grass (c) systems at -1 and -3.33 m matric potentials.
Figure 4.28. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of the pore-continuity index in crop (b) and grass (c) systems at -10 m matric potential.
Relative gas diffusivity and air-filled porosity exhibited higher CVs in the crop than in the grass system which indicated that more measurements were required in the crop system to estimate the mean. However, the coefficient of variation does not provide much knowledge about how the variability and continuity of relative gas diffusivity and air-filled porosity behave with distance. The differences of spatial process between the two land-use systems were because the grass system exhibited more developed soil structure and higher soil aeration status than the crop system (Chapter 3). The grass system also had a more homogeneous pore size distribution and more continuous pores than the crop system (Chapter 3). Spatial variability of gas diffusivity and air-filled porosity has rarely been studied. Compared to what was obtained in the current study, Resurreccion et al. (2007) found similar spatial correlation lengths of 10 to 20 m for relative gas diffusivity and air-filled porosity in a cattle pasture field. They measured relative gas diffusivity and air-filled porosity in 100 cm$^3$ undisturbed soil cores sampled from a 117-m transect with 3-m spatial intervals. Poulsen et al. (2001) also reported a similar spatial correlation range of 10 to 20 m for air-filled porosity on a 70-m transact with 2-m spatial sampling intervals. Grevers and Jong (1994) used image analysis with geostatistical analysis to characterize soil macroporosity and its continuity in compacted and subsoiled soils. They found a spatial correlation length, that varied with pore size, between 12 and 25 m and concluded that there was a greater degree of spatial continuity in the subsoiled soils especially in the largest size of macropores.

The spatial processes of air-filled porosity and the pore-continuity index showed that the variability of the overall spatial domain of air-filled porosity and pore continuity
determined by the CV gave different results compared to multi-scale variability quantified by semivariogram analysis. The CVs of air-filled porosity and pore continuity were higher in the crop than in the grass system and decreased with decreasing soil matric potential in both land-use systems. However, the semivariogram analysis showed that the variability of air-filled porosity and pore continuity in both land-use systems was structured at more matric potentials in the crop than in the grass system. The semivariogram analysis has the advantage of providing the semivariance for each lag distance (different scales) and the range of the spatial continuity where measurements are dependent.

Much work has been done regarding the prediction of relative gas diffusivity from air-filled porosity; however, the results showed that air-filled porosity exhibited different spatial behavior than the relative gas diffusivity. Lange et al. (2009) reported that the variability of relative gas diffusivity within the soil profile could not be explained by the variability of air-filled porosity, volumetric water content, total porosity, or bulk density. Understanding the field-scale variability of relative gas diffusivity and air-filled porosity helps to better interpret results related to quantifying soil structure and soil aeration in different land-use systems than considering only the mean values. Air-filled porosity has been widely studied and used to characterize soil aeration and predict soil gas transport such as gas diffusivity, but the spatial variability was not taken into account. The current study showed that air-filled porosity exhibited different spatial patterns than the gas diffusivity and it differed between crop and grass systems. To date, the field-scale spatial
variability of gas diffusivity and air-filled porosity in crop and grass systems has not been investigated.

The spatial variability of some selected soil physical variables was random (as apparent from unstructured semivariograms) (e.g. Figures 4.3, 4.4, 4.6-4.8, 4.14, 4.18) and their semivariance did not increase with lag distance. The lack of structured semivariograms was because of high semivariance obtained for <5 m lag distances. These lags were the separation distances for observations located in the nests. It seemed that the sampling distance interval influenced the spatial variations of soil physical variables, with higher semivariance obtained for separation distance interval of 1-m than 5-m. Gajem et al. (1981) investigated the influence of the separation distance on spatial variation of different soil physical variables. They measured the soil variables along 9 transects at 0.2, 2, and 20 m distance intervals. They concluded that the standard deviation and the zone of influence increased with spacing and the spatial domain. Another reason caused the high semivariance for lag distances <5 m can be that half of observations included in obtaining the semivariance for these lags were located in the transition zone between the crop and grass systems. The variability of soil physical variables tended to be higher in the transition zones between the two land uses relative to that for observations obtained in the rest of the field.

4.2 Spatial associations between soil physical variables in crop and grass systems

The remaining part of this chapter focuses on quantifying spatial relationships between different selected soil properties and functions in crop and grass systems. The spatial
variability of these soil properties was quantified previously in this chapter and these physical variables were used to characterize soil structure in crop and grass systems (Chapter 3). Cross-semivariogram analysis was used to quantify the spatial associations between the selected soil variables. The objective of this data analysis was to determine the controlling factors on the spatial variability of soil physical properties and functions in crop and grass systems.

4.2.1 Spatial variability of selected soil variables

To calculate the spatial cross-semivariogram for two variables, the spatial variability of both variables must be structured. Therefore, the spatial variability of soil variables used for this data analysis was quantified first. Nine soil variables, besides the soil physical properties used to characterize soil structure, were selected to quantify their spatial associations. These soil variables included: sand, silt, clay, soil organic matter (SOM), total nitrogen (TN), the carbon to nitrogen ratio (C/N), dissolved carbon (DC), and dissolved nitrogen (DN). The CVs of the selected soil variables are shown in Figure 4.29. Dissolved carbon and dissolved nitrogen concentrations exhibited the highest CVs among the selected soil variables and the silt content and the carbon to nitrogen ratio exhibited the lowest CVs. The crop system had higher CVs for sand, silt, C/N, and dissolved nitrogen than the grass system. On the other hand, the grass system had higher CVs for clay contents, soil organic matter, total nitrogen, and dissolved carbon than the crop system.

The semivariogram analysis (Figures 4.30-4.32) showed that the spatial variability of all selected soil variables was structured except for C/N and dissolved carbon in the crop
Figure 4.29. Spatial coefficients of variation (CV) for different soil measurements in crop and grass systems.
Figure 4.30. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of sand, silt, and clay contents in crop (b) and grass (c) systems.
Figure 4.31. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of soil organic matter (SOM), total nitrogen (TN), and carbon to nitrogen ratio (C/N) in crop (b) and grass (c) systems.
Figure 4.32. Spatial distribution (a) and experimental (dots) and fitted spherical (line) semivariograms of dissolved carbon (DC) and dissolved nitrogen (DN) in crop (b) and grass (c) systems.
system and C/N and clay content in the grass system. Therefore, the spatial associations for C/N, dissolved carbon, and clay contents with the soil physical variables were not considered in this study. In the crop system, the spatial dependence, as indicated from the nugget-to-sill ratio, was strong for soil textural fractions, soil organic matter, and dissolved nitrogen, moderate for total nitrogen, and weak for C/N and dissolved carbon. On the other hand, spatial dependency in the grass system was strong for all selected soil variables except for clay contents and C/N, which exhibited weak spatial dependency (Table 4.5).

Therefore, soil physical variables considered for this data analysis included only soil bulk density, relative gas diffusivity at -1000 and -10 cm matric potentials, air-filled porosity at -1000 cm matric potential, and the pore-continuity index at -10 cm water head. The spatial variability of these physical variables was structured in crop and grass systems. Other soil physical variables, such as aggregate size distribution, soil water retention characteristics, and hydraulic conductivity, were not included because their spatial variability was not structured in both land-use systems. The spatial associations of the selected physical variables were quantified with selected soil variables for which their spatial variability was also structured in both land uses. These soil variables included soil organic matter, total nitrogen, dissolved nitrogen, sand, and silt.
<table>
<thead>
<tr>
<th></th>
<th>Crop system</th>
<th></th>
<th>Grass system</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Range (m)</strong></td>
<td><strong>Nugget</strong></td>
<td><strong>Nugget/sill</strong></td>
<td><strong>Nugget</strong></td>
</tr>
<tr>
<td>Sand (%)</td>
<td>9.0</td>
<td>0.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>15.0</td>
<td>0.0</td>
<td>35.9</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>14.4</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>SOM (%)</td>
<td>4.7</td>
<td>0.22</td>
<td>5.1</td>
</tr>
<tr>
<td>TN (%)</td>
<td>19.1</td>
<td>0.0</td>
<td>5.9</td>
</tr>
<tr>
<td>C/N</td>
<td>-</td>
<td>0.44</td>
<td>-</td>
</tr>
<tr>
<td>DC (g kg(^{-1}))</td>
<td>-</td>
<td>2x10(^{-4})</td>
<td>4.4</td>
</tr>
<tr>
<td>DN (g kg(^{-1}))</td>
<td>12.4</td>
<td>0.0</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 4.5. Semivariogram parameters for different soil variables in crop and grass systems.
4.2.2 *Spatial associations between soil bulk density and selected soil variables in crop and grass systems*

The cross-semivariogram analysis showed that soil dry bulk density exhibited spatial relationships with sand content, total nitrogen, and dissolved nitrogen in the crop system and with only silt content in the grass system (Figures A4.1-A4.3 in Appendix 4). The cross-semivariance increased with lag distance for all variables that exhibited spatial associations with bulk density except dissolved nitrogen in the crop system. This result indicated that bulk density exhibited an inverse relationship with dissolved nitrogen in the crop system. The spatial structure, as indicated from the nugget-to-sill ratio, of the associations for bulk density was strong with sand content and total nitrogen and moderate with dissolved nitrogen in the crop system. In the grass system, the spatial dependency of the relationship between bulk density and silt contents was moderate. Sand and total nitrogen contents exhibited strong associations with bulk density but the sand content correlated with the density for a longer distance (spatial range) (Table 4.6). This result implied that among the selected soil measurements, and with more developed soil structure in the grass system, silt was the only factor that controlled the spatial variability of bulk density. On the other hand, sand and soil nitrogen dominated the spatial variability of bulk density in the crop system.

The cross-semivariogram gave different results compared to the Spearman correlation analysis (Chapter 3). Bulk density was significantly correlated with soil organic matter in the grass system, but the spatial relationship, quantified using the cross-semivariogram, between these two variables was weak. In the crop system, on the other hand, there were
Table 4.6. Cross-semivariogram parameters for bulk density $\rho_b$ with different soil variables in crop and grass systems.

<table>
<thead>
<tr>
<th>$\rho_b$ vs.</th>
<th>Crop system</th>
<th>Grass system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (%)</td>
<td>17.6</td>
<td>1x10^{-3}</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>2x10^{-2}</td>
<td>0.05</td>
</tr>
<tr>
<td>SOM (%)</td>
<td>0.0</td>
<td>9x10^{-3}</td>
</tr>
<tr>
<td>TN (%)</td>
<td>9.1</td>
<td>3x10^{-4}</td>
</tr>
<tr>
<td>DN (g kg^{-1})</td>
<td>8.8</td>
<td>2x10^{-5}</td>
</tr>
</tbody>
</table>
no significant correlations observed between bulk density and other soil variables, however, the cross-semivariogram analysis showed that bulk density spatially correlated with sand, total nitrogen, and dissolved nitrogen. The cross-semivariogram analysis not only provided the strength of the spatial association between bulk density and the selected variables but also the distance over which these two variables remained correlated. It also illustrated the continuity of the relationship at different scales. However, the Spearman correlation coefficient provided the statistical dependence between two variables in the overall domain. The literature on the spatial associations between soil bulk density and other soil properties is not very abundant. For example, Carroll and Oliver (2005) also found spatial association between bulk density and sand content with a spatial range of approximately 60 m in a silty clay loam soil under arable land use.

4.2.3 Spatial associations of soil gas diffusivity, air-filled porosity, and pore continuity with selected soil measurements in crop and grass systems

Relative gas diffusivity at -10 cm matric potential was spatially associated with all selected soil measurements in both land uses (Figures A4.4-A4.6). Relative gas diffusivity at -10 cm matric potential exhibited an inverse relationship with bulk density and sand contents in both land uses as indicated from decreased cross-semivariance with lag distance. An inverse spatial association between relative gas diffusivity at -10 cm matric potential and silt content was obtained only in the grass system. Higher bulk density and sand contents reflects lower soil porosity, and the latter has positive impacts on relative gas diffusivity. The different influence of silt content on relative gas diffusivity between crop and grass systems can be because of the difference of soil
structure between the two land uses. The difference of silt contents between crop and grass systems was not significant but the grass system exhibited more developed soil structure with higher porosity and more continuous pores than the crop system. The nugget-to-sill ratio indicated that the spatial structure of the relationship between relative gas diffusivity at -10 cm water head was strong with bulk density and moderate with sand and silt contents in the crop system and moderate with all selected soil measurements in the grass system (Table 4.7).

Relative gas diffusivity at -1000 cm matric potential was also spatially associated with bulk density and sand contents in the crop system and with bulk density and silt contents in the grass system (Figures A4.7-A4.9). Relative gas diffusivity at -1000 cm matric potential also exhibited inverse relationships with all selected variables which showed structured cross-semivariograms with relative gas diffusivity. The spatial relations of relative gas diffusivity at -1000 cm matric potential with bulk density and sand exhibited strong spatial continuity in the crop system and strong and moderate dependency with bulk density and silt, respectively in the grass system (Table 4.7).

Different factors can control soil gas diffusivity such as soil structure, soil texture, and soil water status. Soil bulk density controlled the spatial variability of relative gas diffusivity in crop and grass systems, and the relationship differed under high from low water content status. The spatial ranges of the association between relative gas diffusivity and bulk density were longer at -1000 than -10 cm matric potential in both land uses. Soil bulk density and soil texture reflected soil porosity and the latter influenced the spatial
Table 4.7. Cross-semivariogram parameters for relative gas diffusivity $D_s/D_{0(\psi)}$, air-filled porosity $\theta_a(\psi)$, and pore continuity $\vartheta(\psi)$ with different soil variables in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>Crop system</th>
<th></th>
<th>Grass system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range (m)</td>
<td>Nugget</td>
<td>Nugget/sill</td>
</tr>
<tr>
<td>$\rho_b$ (g cm$^{-3}$)</td>
<td>8.7 4x10^{-5}</td>
<td>0.23</td>
<td>8.8 5x10^{-5}</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>8.5 1x10^{-3}</td>
<td>0.32</td>
<td>2.9 6x10^{-3}</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>9.9 6x10^{-3}</td>
<td>0.34</td>
<td>14.4 5x10^{-3}</td>
</tr>
<tr>
<td>$\rho_b$ (g cm$^{-3}$)</td>
<td>27.4 0.0</td>
<td>0.0</td>
<td>9.6 2x10^{-4}</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>10.5 0.0</td>
<td>0.0</td>
<td>- 1x10^{-3}</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>- 4x10^{-3}</td>
<td>1.0</td>
<td>7.2 2x10^{-2}</td>
</tr>
<tr>
<td>$\rho_b$ (g cm$^{-3}$)</td>
<td>22.4 0.0</td>
<td>0.00</td>
<td>6.6 0.0</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>8.0 5x10^{-3}</td>
<td>0.16</td>
<td>- 1x10^{-2}</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>19.2 9x10^{-3}</td>
<td>0.17</td>
<td>- 3x10^{-3}</td>
</tr>
<tr>
<td>$\rho_b$ (g cm$^{-3}$)</td>
<td>4.0 6x10^{-4}</td>
<td>0.36</td>
<td>3.1 1x10^{-4}</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>- 1x10^{-1}</td>
<td>0.51</td>
<td>- 2x10^{-2}</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>11.2 5x10^{-3}</td>
<td>0.07</td>
<td>9.5 1x10^{-2}</td>
</tr>
</tbody>
</table>
variability of soil gas diffusivity. A stronger spatial relationship, with lower nugget-to-sill ratio and longer spatial range, between relative gas diffusivity at -1000 cm matric potential and bulk density obtained in the crop system was because the grass system exhibited more developed soil structure with higher soil porosity and more continuous soil pores for gas transport than the crop system.

The spatial relationships between air-filled porosity and selected soil properties such as bulk density, sand, and silt were only quantified at -1000 cm matric potential in crop and grass systems. Air-filled porosity at -1000 cm water head spatially associated with all selected soil properties in the crop system and with only bulk density in the grass system (Figures A4.10- A4.12). Air-filled porosity exhibited an inverse relationship with bulk density in both land uses and with sand contents in the crop system as indicated from a decrease of cross-semivariance with lag distance. These inverse relationships reflected the positive relationship of total porosity with air-filled porosity. The spatial structure of the association between air-filled porosity and the selected variables was strong in both land uses (Table 4.7). The spatial range of the relationship between air-filled porosity and bulk density was longer in the crop (lower porosity) than in the grass (higher porosity) system.

The pore-continuity index at -10 cm matric potential spatially related with all selected measurements except sand content in both land uses (Figures A4.13-A4.15). The pore-continuity index at -10 cm matric potential exhibited inverse relations with bulk density and silt contents in crop and grass systems, respectively. The spatial associations for pore
continuity with bulk density and silt differed between crop and grass systems because soil structure also differed between these land uses. The grass system exhibited higher porosity and more continuous pores as indicated from lower bulk density and higher pore continuity than the crop system. The nugget-to-sill ratio showed that the spatial dependency of the associations of pore continuity at -10 cm matric potential was strong, with silt contents and moderate with bulk density and sand contents in the crop system, and strong with bulk density and silt in the grass system (Table 4.7). The spatial association of silt content with pore continuity exhibited a strong structure in both land uses but this relationship exhibited a longer spatial range in the crop than in the grass system. Land use influenced the spatial associations between soil gas characteristics and the selected soil variables. The spatial relationships between relative gas diffusivity and selected measurements also depended on soil water status.

The spatial associations between soil variables are influenced by scale triplet (spacing, extent, and support), and considering a different measurement scale can lead to different results (Chapter 1.3.5). For structured cross-semivariograms, the cross-semivariance increased or decreased with lag distance, indicating that the spatial relationship between the two selected variables is a subject of the measurement scale. It should be noted that, for some structured spatial cross-semivariograms, the cross-semivariance decreased with separating distance or exhibited a different sign for <5-m lags distances from longer lags. For example, Figure A4.9c shows the cross-semivariogram for relative gas diffusivity at -1000 cm matric potential with silt contents. The cross-semivariance for the first 3 lags was positive and negative for longer lags. Another example can be Figure A4.6b, which
shows that the cross-semivariance was negative for the first 4 lags and positive for the longer lags. This behavior was most likely because the <5 m lags were the separation distances for observations located in the nests. This result can be an indication of the influence of spacing on cross-semivariogram analysis. It seemed that a constant distance interval should be selected for cross-semivariogram analysis. Another reason can be that the <5 m lags were the separation distance for sampling points located in the transition zone between the crop and grass systems. The variation of soil physical variables tended to be higher in the transition zone than in the rest of the field.

4.3 Summary and conclusions

The spatial variability of selected soil physical properties and functions was quantified by geostatistical analysis. The spatial processes of these soil physical variables in the crop system differed from the grass system. Soils in the crop system exhibited stronger spatial dependency of bulk density than in the grass system. The spatial variability was structured for only large aggregate-size classes in the crop system and for most of the classes in the grass system in the upper depth. The spatial variability of the selected aggregate-size classes, the mean weight diameter, and the wet-aggregate stability was random in the deeper depth in both land-use systems. The spatial variation of soil water content increased with decreasing matric potentials indicating that more measurements should be taken as soil became drier to accurately obtain the mean. Spatial variability of most of the soil water retention exhibited stronger spatial dependency in the crop than in the grass system. The spatial continuity for the retention curve parameters $\alpha$ and $\theta_r$ was structured only in the crop system and for $n$ and $\theta_r$ was structured only in the grass system. Measurements of soil hydraulic conductivity were dependent in space in the crop
system, with stronger spatial continuity at low than at high matric potentials, and their statistical description must incorporate the spatial structure of the properties. On the other hand, the spatial variability of hydraulic conductivity, except at -1 cm matric potential, was random in the grass system. The spatial variability of relative gas diffusivity, air-filled porosity, and pore continuity has not been quantified in different land-use systems. The variability of relative gas diffusivity was structured in both land uses, with stronger dependency being obtained in the crop system. Air-filled porosity and pore continuity exhibited structured and stronger spatial continuity at more matric potentials in the crop than in the grass systems. Spatial processes should be considered when soil gas diffusivity is predicted from air-filled porosity because their spatial variability was not random and they had different spatial patterns.

Land use influenced the spatial variability of all selected soil physical characteristics with stronger spatial continuity obtained in the crop than in the grass system. A possible reason for this result is that soils in the grass system exhibited higher porosity and more continuous pores than soils in the crop system. Understanding the field-scale variability of the selected soil physical properties and characteristics helps to better interpret results related to quantifying soil structure in different land-use systems than considering only the mean values. Land use and its impact on field-scale spatial continuity should be taken into account for sampling designs, quantifying spatial associations, and modeling soil physical processes.
The cross-semivariogram analysis can be a better alternative approach for quantifying relationships between different physical properties in space. A search in the literature showed that the cross-semivariogram analysis has not been used to quantify spatial associations between soil gas transport properties, such as relative gas diffusivity, air-filled porosity, and the pore-continuity index, with other soil properties and in different land uses. The cross-semivariogram analysis provides not only the strength of the relationship but also the spatial range where the two variables are correlated. The cross-semivariogram analysis showed that land use influenced the spatial associations between the selected soil attributes. Soil structure and the arrangement of soil pores and pore geometry influenced the spatial processes of the selected soil physical variables and their spatial associations with the selected soil measurements, which was evident from the difference between the two land uses. The spatial relationships of the selected soil physical functions with other soil properties depended on soil water status. Spatial associations between soil attributes and the influence of land use on these relationships should be considered for modeling important soil physical processes and designing sampling protocols.
CHAPTER 5: Spatial and Temporal Patterns and Associations of CO₂ Flux in Crop and Grass Systems

This chapter focuses on quantifying spatial and temporal patterns of soil surface CO₂ flux in crop and grass systems. The spatial and temporal behaviors of soil respiration were studied using different statistical methods. An investigation of the temporal stability of spatial patterns of soil respiration was also included. This chapter also emphasizes investigating the controlling factors for CO₂ flux and the spatial and temporal associations between soil respiration and biochemical and physical factors in crop and grass systems.

Soil respiration is highly variable in space and time, but the influence of land use on this variability is not well understood. Although the relationships between soil respiration and biotic and abiotic factors have been intensively studied, the roles of soil physical factors on spatial variability of soil respiration have not. Temporal behavior of CO₂ flux and the influence of land use on the temporal stability of spatial patterns of soil respiration have rarely been investigated. Correlation coefficients are commonly used to quantify the spatial and temporal relationships for soil respiration with other variables. Geostatistical approaches such as the semivariogram analysis are not commonly used to quantify the spatial and temporal variability of soil respiration and under different land uses. For example, cross-semivariograms have not been used to quantify spatial and temporal associations for CO₂ fluxes with biotic, abiotic, and physical factors under different land uses. Cross-semivariogram analysis has the advantage that it provides the cross-
semivariance for each lag separation and the influence zone where (or when) the two variables are remained correlated. The objectives of the studies underling this chapter were: 1) to characterize spatial and temporal variability structure of CO₂ fluxes in a field soil under two land-use systems and its change throughout a year; 2) to evaluate the temporal stability of their spatial patterns; 3) to quantify relationships with biotic, abiotic, and physical factors in crop and grass systems. These objectives are relevant prerequisites for identifying the drivers of CO₂ fluxes.

**Approaches**

The description of site, sampling locations, sampling protocol, and data analysis are as previously described in Chapter 2.

**Results and discussion**

5.1 **Spatial and temporal patterns of CO₂ flux in crop and grass systems**

5.1.1 **Adjustments of CO₂ flux**

Gas flux is a diurnal phenomenon. Dugas (1993) reported no CO₂ flux in the early morning and after sunset, with the flux maximum near midday. In the current study on most measurement days, CO₂ flux increased with time presumably because of increased soil temperature during the day. For example, Figure 5.1 shows CO₂ flux increasing with time during the day for measurements taken in summer (16 and 17 August 2010), and little change of flux during the day in winter (31 January and 1 February 2011). Carbon dioxide flux increased with time on 16 August 2010 (crop system) and 17 August 2010 (grass system) yielding slopes of 3 and 7%, respectively. Soil temperature also increased
Figure 5.1. Comparison of CO₂ flux distribution with time (space) during the day in two land-use systems taken on two different dates - summer and winter. Fluxes from the crop system were measured first, then from the grass system the next day.
with time on those two days providing slopes of 4 and 6% in crop and grass systems, respectively. In contrast, CO₂ flux measurements taken on 31 January (crop system) and 1 February 2011 (grass system) did not show much change, yielding slopes of 0.06 and 0.09%, respectively. Soil temperature also did not change much in the first day yielding a slope of 0.2% but there was some change in the second day providing a slope of 2%.

To investigate the spatial behavior of CO₂ flux, the flux had to be adjusted to remove its temporal trend caused by the diurnal temperature patterns. The two methods used, adjusting flux to daily mean soil temperature and adjusting flux to sampling time (described in Chapter 2) removed the diurnal trend without great influence on the overall daily average magnitude and the small scale variation of CO₂ flux (Figure 5.2). However, Table 5.1 shows that adjusting the flux to sampling time yielded a more similar magnitude of mean and small scale variation to the measured CO₂ flux than adjusting to daily mean soil temperature for both land-use systems. Adjusting to sampling time gave more similar semivariograms to the measured CO₂ flux than adjusting to daily mean soil temperature (Figure 5.3), which indicated that adjusting to sampling time had no significant influence on the small scale variability of CO₂ flux.

The flux adjusted to daily average soil temperature was more variable with space than adjusted to sampling time and the original measured flux because adjusting flux to daily average soil temperature was based on a regression between CO₂ flux and soil temperature measured in different times during the study period. The relationship between CO₂ flux and soil temperature tended to be influenced by soil water status and
Figure 5.2. Measured and adjusted CO$_2$ fluxes to sampling time and daily mean soil temperature on 16 and 17 August 2010 in two land-use systems.
Table 5.1. Descriptive statistics comparing two methods to adjust CO$_2$ flux to diurnal fluctuations - adjusting flux to daily mean soil temperature and to sampling time during the day - for the measured CO$_2$ flux from the crop and grass systems (n = 22 sampling periods).

<table>
<thead>
<tr>
<th></th>
<th>Observed</th>
<th>Adjusted to soil temperature</th>
<th>Adjusted to time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crop</td>
<td>Grass</td>
<td>Crop</td>
</tr>
<tr>
<td>Mean</td>
<td>1.0-14.6</td>
<td>1.8-26.8</td>
<td>0.3-15.5</td>
</tr>
<tr>
<td>Max.†</td>
<td>2.1-25.3</td>
<td>2.9-37.8</td>
<td>5.2-29.2</td>
</tr>
<tr>
<td>Min.‡</td>
<td>-0.1-9.6</td>
<td>-0.1-16.2</td>
<td>-10.4-8.2</td>
</tr>
<tr>
<td>CV</td>
<td>0.2-1.1</td>
<td>0.1-0.7</td>
<td>0.2-8.8</td>
</tr>
<tr>
<td>Var.§</td>
<td>0.2-37.3</td>
<td>0.5-55.2</td>
<td>6.5-50.5</td>
</tr>
<tr>
<td>SD</td>
<td>0.5-6.1</td>
<td>0.7-7.4</td>
<td>2.6-7.1</td>
</tr>
</tbody>
</table>

†maximum ‡minimum §variance
Figure 5.3. Fitted spherical semivariograms of measured, adjusted to sampling time, and adjusted to daily average soil temperature CO₂ fluxes for measurements taken on 28 and 29 March 2011 from the entire field.
varied with season (Davidson et al., 1998). Other factors such as plant photosynthesis can affect root respiration (Craine et al., 1999) and these factors were not taken into account in adjusting flux by the soil temperature method.

Adjusting flux to sampling time was based on a regression between CO₂ flux and sampling time for the same day and under the same climatic and soil water conditions. Adjusting to sampling time was a more conservative approach to evaluate the observed flux. Hence, data of CO₂ flux used for this study were adjusted to sampling time. These methods give the opportunity to remove the diurnal trend of CO₂ flux only when the flux measurements are performed for a period that is long enough to show an obvious increase of flux with time. Adjustment to sampling time has been used by other investigators (e.g., Herbst et al., 2009). Consequently, for the current study adjusted CO₂ flux was used in all data analysis.

5.1.2 Field observations of CO₂ flux

The adjusted CO₂ flux varied between 0.0 and 36.7 mg CO₂ m⁻² min⁻¹ among all sampling locations during the study period (Figure 5.4b). Carbon dioxide flux was slightly higher in the grass system than in the crop system, with differences more pronounced when it was warm-moist than when it was cold-wet. The spatial mean of CO₂ flux varied with time between 1.7 and 25.5 mg m⁻² min⁻¹ in the grass system and between 1.1 and 16.8 mg m⁻² min⁻¹ in the crop system (Figure 5.4b). The magnitude of CO₂ flux was similar to previous reports. For example, Aiken et al. (1991) found soil CO₂ flux rates of 4.1 mg m⁻² min⁻¹ in a wheat system and 12.0 mg m⁻² min⁻¹ in a grass system. Ham
Figure 5.4. Daily precipitation and air temperature (a), mean (b), variance (c), and coefficient of variation (d) of CO₂ fluxes measured in different times during a year in crop and grass systems.
and Knapp (1998) reported CO₂ fluxes of 12.4 mg m⁻² min⁻¹ in a prairie ecosystem. Mielnick and Dugas (2000) reported fluxes between 0 and 15 mg m⁻² min⁻¹ in a tallgrass prairie. The treatment differences (i.e. land use) can probably be attributed to greater plant biomass and soil organic matter content in the grass system sampling locations (Aiken et al., 1991) and to soil physical conditions such as soil gas diffusivity and air-filled porosity. The factors controlling CO₂ flux will be discussed in detail in this chapter.

5.1.3 Spatial behavior of CO₂ flux

The lowest and the highest mean of CO₂ fluxes in the crop system occurred on 31 January 2011 and 19 July 2010, respectively, and on 31 January 2011 and 21 June 2010, respectively in the grass system (Figure 5.4b). The spatial variance of CO₂ flux was in good agreement with the mean of soil respiration in both land-use systems (Figure 5.4c). The highest variance of CO₂ flux occurred when the flux was high during the warm-moist period and the lowest observed when the flux was low during the cold-moist period in both land-use systems. Carbon dioxide fluxes were spatially more variable in the crop system than in the grass system as indicated by the average coefficient of variation (CV) depicted with time (Figure 5.4d). Moreover, the spatial CV of CO₂ flux proceeded at lower levels during warm-moist periods with higher fluxes than in warm-dry or cold-wet periods, with lower fluxes in both land-use systems (Figure 5.4b and d).

The CV and variance exhibited an inverse relationship because the mean of the flux changed with season in both land-use systems. For example, the spatial variance of CO₂ flux was low during winter and the mean was low also, which caused large CV values.
Similar to results in the present study (Figure 5.4d), Ohashi and Gyokusen (2007) found higher CVs (42%) for CO$_2$ flux in winter than summer (26%) in a forest ecosystem. Han et al. (2007) observed CV values between 28 and 55% in a maize field and determined the local scale effects as major causes of variation, i.e., CO$_2$ flux measured near plants was generally higher than between plants and in inter-rows. Fang et al. (1998) found CVs of 55% in a 25 by 25 m pine plantation. Besides the impact of land use, the magnitude of the variation strongly depended on the components of the scale triplet (Blöschl and Sivapalan, 1995), i.e., the domain size, the sampling density (Parkin and Kaspar, 2004), and the support size or sample volume, which in our case was the cross-sectional area of the collar.

For both land-use systems, experimental semivariograms and their respective models of log$_{10}$-transformed CO$_2$ flux showed a pronounced spatial variability structure throughout the study period as obvious from the nugget-to-sill ratio (Figure 5.5b). On the two dates, lacking structure in the crop system (2 September and 15 October 2010), CO$_2$ flux was much smaller than its mean over the entire study period. In addition, due to a small spatial average CO$_2$ flux, the highest CV value (115%) was observed over the entire period in the crop system occurred on 15 October. In the grass system, CO$_2$ flux appeared spatially uncorrelated only on 28 April 2011.

The temporal behavior of the spatial nugget semivariance was strongly associated with the CV. In both land-use systems, larger nugget semivariances were observed on days when the land use average of CO$_2$ flux was relatively small (Figure 5.4b and 5.5a). The
Figure 5.5. Spatial semivariogram parameters: Nugget (a), nugget-to-sill ratio (b), and range (c) of log_{10}-transformed CO₂ fluxes measured in different times during a year in crop and grass systems.
nugget-to-sill ratio in this study indicated moderate spatial dependence and behaved similarly (varied between 0.01 and 1.0) in both land-use systems (Figure 5.5b). In an area of 182 m², Herbst et al. (2011) measured respiration in a 2-m grid and found a large contribution of the nugget to the total or sill variance (approximately >0.75) at a variance level comparable to our observations made on 8 June 2010 in the crop system (Figure 5.5b). In their field experiment, a relatively large local variability coinciding with a shorter sampling distance and a smaller sample support size might have caused the larger nugget-to-sill ratio than in this study. From the semivariograms in Fóti et al.’s (2008) study, nugget-to-sill ratios of approximately 0.70 and higher were derived. The less pronounced structure of variation in their study could have been caused by the smaller sample support compared to this study, and the relatively small sampling domain of 15 by 15 m, although spatial distances were relatively short at 0.2 m. Compared to findings reported in the literature, the current study emphasizes the relevance of the scale-triplet for planning experiments and sampling protocols. For example, a large correlation length is expected if the selected measurement scale is larger than the process scale. On the other hand, large-scale variability will not be captured and will be underestimated if the sampling domain is smaller than the process variability.

In both land-use systems, CO₂ flux exhibited relatively long spatial correlation ranges (Figure 5.5c) while the range parameter was generally larger under the grass than under the crop system. Over the 22 spatial sampling campaigns, the range varied between 5.5 and 55.8 m with an average of 23.0 m in the crop system and between 3.2 and 70.4 m with an average of 33.0 m in the grass system. No obvious relationship existed between
the behavior of the spatial range over time and the mean of CO$_2$ flux or other variance characteristics such as the CV or the nugget semivariance. Kosugi et al. (2007) found spatial ranges of soil respiration between 4.4 and 24.7 m in a 50 by 50 m forest soil domain. Both these ranges and the CVs observed for the respiration measurements were similar to findings obtained from the present study despite the different land use and their smaller sample support size. Aiken et al. (1991) did not detect a range of spatial representativeness of soil respiration in their 18 by 18 m field for a 3-m sampling interval in grass and crop plots of silt loam soil. They explained the pure nugget effect to be caused by analytical error and by their selection of a sampling interval exceeding the scale of spatial correlation. Further reasons for the lack of spatial structure in their study and the obvious existence of spatial structure in the present study can be based on the smaller sampling domain in Aiken et al.’s (1991) study and their considerably smaller sample support than in our study. Fóti et al. (2008) found a relatively longer spatial range during summer water stress and fall senescence periods than under well-watered conditions in grasslands. In the present study, an association between season and spatial range could not be observed (Figure 5.4a and 5.5c) and that could be due to a higher precipitation recorded in our site relative to what Fóti et al. (2008) reported. The relationship between soil respiration and soil water content will be discussed later in this chapter.

5.1.4 Temporal behavior of CO$_2$ flux

In Figure 5.6a, CO$_2$ flux was presented as an average over time for each location, i.e., across both land-use systems together. The temporal mean, variance, and CV proceeded at a higher level in the grass than in the crop system (Figure 5.6a and b). The CV was
Figure 5.6. Temporal mean (a), variance and coefficient of variation (b), temporal nugget and nugget-to-sill ratio (c), and temporal correlation length (d) of \( \log_{10} \)-transformed CO\(_2\) fluxes measured in crop and grass systems.
larger under both land-use systems in the temporal domain than in the spatial domain (Figure 5.4d). In other words, the variation relative to the mean was larger with time for any location than it was in space at any time.

Semivariograms calculated over time for each of the 60 locations revealed temporal structure of log$_{10}$-transformed CO$_2$ flux for all sampling points in both land-use systems. For two sampling locations (29 and 58, not shown), unbounded temporal semivariograms were found for which no nugget-to-sill ratio or correlation length could be calculated. These two sampling points were located in the nests of the spatial transition zone between the crop and grass systems. Location 58 showed the lowest mean of CO$_2$ flux and one of the highest CVs in the entire field. Although there was a tendency of the Gaussian semivariogram model to fit the experimental semivariograms in the grass system slightly better than a spherical model, the latter fitted semivariograms better in the crop system and was chosen to describe temporal semivariograms in both land-use systems in general. Only a uniform model type allows for comparing semivariogram parameters and the nugget-to-sill ratio. The temporal nugget semivariance proceeded at a relatively low magnitude across the locations in both land-use systems (Figure 5.6c). It was higher and more variable over the locations in the crop system than over those in the grass system. The nugget-to-sill ratio was generally small in both land-use systems and more variable in the crop system (Figure 5.6c). The magnitude of the nugget-to-sill ratio varied between 0.0 and 0.33 in the crop system and between 0.0 and 0.45 in the grass system, and indicated a strongly structured temporal variability of CO$_2$ flux in both land-use systems.
Between the two land-use systems, the grass system exhibited longer temporal ranges of CO₂ flux representativity than the crop system (Figure 5.6d) and the ranges fluctuated more in the latter. Temporal semivariogram analysis has rarely been applied to CO₂ flux data in the past. Parkin and Kaspar (2004) investigated the temporal behavior of CO₂ flux and computed the difference between cumulative CO₂ fluxes based on hourly measured CO₂ flux and less frequently sampled CO₂ flux. In their study, increasing the sampling interval from 1 day to 12 days substantially increased the variance.

5.1.5 Space-time field of CO₂ flux

A space-time field of a variable is a map expanded over the spatial and temporal domains. It reflects the development of spatial patterns with time, and it provides insight into the temporal behavior of particular locations or zones. The space-time field analysis gives the opportunity to combine soil respiration observations taken in both space and time domains. Phenomena or patterns can be obscured in a space-time field if the variance in one domain is more pronounced than in the other domain (Wendroth et al., 1999). Therefore, besides using space-time fields to investigate the variability dynamics of log₁₀-transformed CO₂ flux, space-time field of standardized relative differences from the mean of ln(CO₂ flux+1) were also computed. The relative difference of ln(CO₂ flux+1) was calculated from the spatial mean of each land use separately. The data was transformed to ln(CO₂ flux+1) because some observations were close to zero when they were log₁₀-transformed, which led to extremely small relative difference values.
The space-time fields consisted of 1320 values of log$_{10}$-transformed CO$_2$ flux or relative differences to the spatial mean of ln(flux +1), respectively (Figure 5.7a and b). The variation of log$_{10}$-transformed CO$_2$ flux was more pronounced in time than in space during the year. In both land-use systems the temporal variability of CO$_2$ flux was most obvious between December 2010 and March 2011, a period with relatively low CO$_2$ flux. During this cold period, the variation of CO$_2$ flux was more pronounced in the crop system than in the grass system. During warmer periods, the temporal stability of CO$_2$ flux was more obvious than in cooler periods in the crop system (Figure 5.7a). For the grass system, on the other hand, temporal stability was more pronounced in cooler than in warmer periods. In both land-use systems, relative differences of CO$_2$ flux from the mean were most variable during colder months in both space and time. The relative difference of CO$_2$ flux was most variable during the period between 16 September and 31 December 2010 in the crop system and between 1 December 2010 and 1 April 2011 in the grass system. However, during the warmer periods between 8 June and 16 September 2010 and between 1 April and 8 June 2011, the variability of relative differences was more pronounced in space than in time, which was evidence of existing temporal stability of spatial patterns of relative difference of soil respiration. This result indicated that soil respiration variability should be considered in both spatial and temporal domains for designing effective sampling schemes and for predicting soil respiration. The relative difference from the mean provided a better insight of the space-time field of soil respiration than CO$_2$ flux.
Figure 5.7. Space-time field of $\log_{10}$-transformed CO$_2$ flux (a) and relative difference of $\ln$(CO$_2$ flux+1) (b) in two land-use systems. The space-time field of $\log_{10}$-transformed CO$_2$ flux was computed passed on the isotropic model (c).
5.1.6 Temporal stability of spatially measured CO\textsubscript{2} flux

The mean relative difference from the spatial average of CO\textsubscript{2} flux was applied to determine locations that could support identifying the mean CO\textsubscript{2} flux for the entire field. Fluxes measured at locations with low standard deviation of the mean relative difference are temporally stable. The determination of relative differences of log\(_{10}\)-transformed CO\textsubscript{2} flux was based on the median of spatially measured CO\textsubscript{2} flux rather than the mean. Graf et al. (2011) also used the median to determine the relative differences of soil respiration. One third (20 locations) of all sampling locations would support estimating the mean CO\textsubscript{2} flux for the entire field. Seven sampling locations from the crop system (2, 6, 7, 13, 16, 17, and 21) and 13 sampling locations from the grass system (29, 30, 32, 41, 42, 43, 45, 46, 47, 51, 52, 53, and 54) had mean relative differences less than ±0.1 (Figure 5.8). It should be noted that mean relative differences close to zero were not only observed for individual sampling locations but also for some local zones. For instance, there were two sets of sampling points in the grass system (locations between 41 and 47 and between 51 and 54) that were spatially consecutive with mean relative difference less than ±0.1. Sampling locations 58 and 34 (Figure 5.8) gave the lowest and the highest CO\textsubscript{2} flux for the entire field, respectively. The high variability of soil respiration rate in space and over time explains the wide range of mean relative differences and a large standard deviation of mean relative differences. This same method was used by Herbst et al. (2009) and Graf et al. (2011) to identify sampling points that behave similar to the field average of CO\textsubscript{2} flux. Herbst et al. (2009) found that there were 17 sampling points in their field with a mean relative difference < ±0.1 that would support identifying the field areal average of
Figure 5.8. Spatially measured CO$_2$ flux ranked by temporal relative deviation from the median. Vertical bars refer to associated standard deviation of relative differences.

Numbers refer to measuring locations.
CO₂ flux. The results also indicated that both the number of samples and the measurement locations are important and should be chosen carefully (Herbst et al., 2009).

During the period between 8 June and 16 September 2010, the Spearman rank correlation coefficient showed that log₁₀-transformed CO₂ flux was temporally stable within a period of 100 days during the summer for the entire field, and the rank correlation between sampling dates was significant for eight consecutive measurement dates during that period (Table 5.2). During this period, CO₂ flux was highest with an average varying between 9.4 and 17.1 mg m⁻² min⁻¹. At the end of the experiment, when the flux was higher than 10 mg m⁻² min⁻¹ on 28 April and 8 June 2011, a significant rank correlation was observed between these two consecutive sampling dates. Interestingly, there were significant correlations between sampling dates of CO₂ flux during the end and the beginning of the experiment. For example, a significant correlation was observed between measurements taken on 8 June 2011 and measurements taken during the period between 8 June and 16 September 2010 (Table 5.2). The same correlations were found between measurements taken on 28 April and 13 April 2011 and seven sampling dates in the beginning of the experiment in 2010. Temporal stability of spatial patterns of CO₂ fluxes revealed that geostatistics can be used for fluxes measured at any time during that period.

5.2 Controlling factors on CO₂ flux and their spatial and temporal associations in crop and grass systems

Besides microbial activities, soil surface CO₂ flux seemed to be influenced by parameters related to: (1) soil biochemical properties such as soil organic matter, soil nitrogen, and
Table 5.2. The Spearman rank correlation coefficients between sampling dates of log$_{10}$-transformed CO$_2$ flux for the entire field.

| Mean | 1.2 | 1.3 | 1.0 | 1.3 | 1.1 | 1.1 | 0.9 | 0.8 | 0.6 | 0.6 | 0.5 | 0.4 | 0.4 | 0.3 | 0.1 | 0.3 | 0.4 | 0.8 | 0.6 | 0.9 | 1.0 | 1.0 |
| 6/8 | 1.0* | 1.0* | 7/6 | 0.7* | 0.8* | 1.0* | 7/19 | 0.8* | 0.6* | 0.8* | 1.0* | 8/2 | 0.8* | 0.8* | 0.8* | 1.0* | 8/16 | 0.8* | 0.7* | 0.7* | 0.8* | 1.0* |
| 9/2 | 0.7* | 0.7* | 0.6* | 0.6* | 0.6* | 0.5* | 1.0* | 9/16 | 0.3* | 0.5* | 0.6* | 0.4* | 0.6* | 0.5* | 0.4* | 1.0* | 9/30 | 0.3* | -0.2 | 0.0 | -0.1 | -0.1 | -0.1 | -0.2 | 0.4* | 1.0* |
| 10/15 | 0.0 | 0.2 | 0.1 | -0.1 | 0.1 | 0.2 | 0.0 | 0.3 | 0.5* | 1.0* | 10/28 | 0.1 | 0.2 | 0.2 | 0.1 | 0.3* | 0.3 | 0.0 | 0.5* | 0.5* | 0.5* | 1.0* |
| 11/11 | 0.1 | 0.2 | 0.1 | 0.1 | 0.3 | 0.1 | 0.1 | 0.4* | 0.3* | 0.3* | 0.7* | 1.0* | 11/25 | 0.2 | 0.1 | 0.2 | 0.2 | 0.3* | 0.3* | 0.1 | 0.4* | 0.3* | 0.2 | 0.6* | 0.5* | 1.0* |
| 12/31 | -0.4* | -0.3* | -0.2 | -0.3* | -0.3 | -0.2 | -0.2 | 0.2 | 0.5* | 0.4* | 0.3* | 0.2 | 0.4* | 1.0* | 1/31 | 0.6* | 0.5* | 0.4* | 0.5* | 0.6* | 0.5* | 0.4* | 0.3* | 0.4* | 0.4* | -0.2 | 1.0* |
| 2/15 | 0.5* | 0.5* | 0.3* | 0.2 | 0.5* | 0.4* | 0.4* | -0.2 | 0.1 | 0.3* | 0.4* | 0.2 | 0.0 | 0.6* | 1.0* | 3/1 | -0.0 | -0.1 | -0.1 | 0.0 | 0.0 | 0.0 | 0.4* | 0.3* | 0.2 | 0.5* | 0.5* | 0.4* | 0.6* | 0.3 | 0.3* | 1.0* |
| 3/17 | 0.3* | 0.1 | 0.1 | 0.3* | 0.3 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.3* | 0.4* | 0.4* | 0.2 | 0.6* | 0.5* | 0.5* | 0.5* | 1.0* | 3/28 | -0.6* | -0.5* | -0.5* | -0.6* | -0.5* | -0.5* | -0.5* | -0.1 | 0.3* | 0.3* | 0.2 | 0.2 | 0.0 | 0.7* | -0.2 | 0.1 | 0.6* | 0.3* | 1.0* |
| 4/13 | 0.3* | 0.3* | 0.3* | 0.3* | 0.3* | 0.2 | 0.3* | 0.3* | 0.1 | 0.1 | 0.3* | 0.4* | 0.2 | 0.1 | 0.4* | 0.5* | 0.5* | 0.5* | 0.4* | 0.2 | 1.0* | 4/28 | 0.7* | 0.5* | 0.4* | 0.5* | 0.5* | 0.6* | 0.4* | 0.1 | -0.5* | -0.1 | 0.0 | 0.0 | 0.1 | -0.5* | 0.4* | 0.4* | -0.3* | 0.1 | -0.5* | -0.1 | 1.0* |
| 6/8 | 0.6* | 0.6* | 0.6* | 0.6* | 0.5* | 0.6* | 0.6* | 0.3* | -0.3* | -0.2 | -0.1 | 0.0 | 0.0 | -0.4* | 0.5* | 0.3* | -0.2 | 0.1 | -0.6* | 0.1 | 0.5* | 1.0* |

*Correlation is significant at the 0.05 level
The mean was calculated from log$_{10}$-transformed CO$_2$ flux (log(mg m$^{-2}$ min$^{-1}$))
soil carbon cycles; (2) soil physical properties such as soil temperature, soil moisture, soil texture, soil density, soil air-filled porosity, and soil gas diffusivity; (3) environmental conditions such as rainfall and air temperature related to seasons; (4) crop management such as fertilization, tillage, and manure applications (Allaire et al., 2012). This chapter focuses on quantifying the relationships for soil respiration with selected soil physical and soil biochemical factors and their spatial and temporal associations in crop and grass land-use systems.

5.2.1 Relationships of CO₂ flux with soil temperature and soil water content in crop and grass systems

Soil temperature measured at 5 cm depth varied between 0.3 and 35.5 °C in the crop system and between -0.3 and 36.6 °C in the grass system among all sampling dates and sampling locations. The spatial average of soil temperature varied between 1.2 and 28.7 °C with a mean of 16.8 °C in the crop system and between 3.9 and 29.0 °C with a mean of 17.4 °C in the grass system but the difference of the mean between the two land uses was not significant. Soil temperature in both land-use systems varied with season. The highest soil temperature was observed in the period between 8 June and 25 September 2010 besides 8 June 2011 in both land-use systems. The lowest soil temperature was recorded on 31 January 2011 in both land-use systems. Figure 5.9 shows the space-time field of soil temperature in crop and grass systems measured during a year from 8 June 2010 to 8 June 2011. The average soil water content at 0-30 cm depth varied between 0.09 and 0.36 m³ m⁻³ in the crop system and between 0.02 and 0.40 m³ m⁻³ in the grass system among all sampling dates and sampling locations. The selection of the upper 30
Figure 5.9. Space-time field of soil temperature measured at 5 cm depth in crop and grass systems.
cm depth was based on the assumption that it was the active depth for soil microorganisms and plant roots. Allaire et al. (2012) concluded that the entire upper 35 cm depth of the soil profile contributed to soil surface CO$_2$ flux because significant correlations were obtained with parameters measured at 25-35 cm depth. Figure 5.10 shows the space-time field of average soil water content at 0-30 cm depth in crop and grass systems measured from 8 June 2010 to 8 June 2011. Average soil water content differed between the crop and grass systems more obviously during summer and fall seasons between 8 June and 15 November 2010 than during other seasons. During this period, soil water content was higher in the crop system than in the grass system, most likely because wheat was harvested in July 2010 and there were no growing plants in the crop site between July and November 2010. On the other hand, grass was continuously growing and removing water from soil during the study period in the grass site. Assuming a higher root density in the grass compared with the crop system, a higher transpiration rate can be expected. Choudhary et al. (2002) also observed lower soil water content in grassland than in cropland and stated that lower water content in grassland could be due to high transpiration rate from the growing pasture.

Soil temperature was the most controlling factor on CO$_2$ flux in crop and grass systems. Increasing soil temperature led to an increase of CO$_2$ flux in both land uses. Several studies found strong positive correlations between CO$_2$ flux and temperature (Fang and Moncrieff, 2001; Hashimoto et al., 2007; Herbst et al., 2009; Allaire et al., 2012). The relationship between CO$_2$ flux and soil temperature exhibited a steeper slope in the crop
Figure 5.10. Space-time field of average soil water content at 0-30 cm depth in crop and grass systems.
system relative to the slope in the grass system. Figure 5.11 shows that at low soil
temperature, a wider scatter of CO$_2$ flux was observed in the crop than in the grass
system. On the other hand, at higher soil temperature, higher CO$_2$ flux was obtained in
the grass than in the crop system. The wide scatter of CO$_2$ flux was most likely caused by
the spatial variability of fluxes, of the flux-temperature relationships, and by seasonal
effects.

Soil water is essential for soil microorganisms. Without some water, there is no microbial
activity in soil; soil water affects gas exchange and various soil chemical reactions; soil
water plays an important role in nutrient availability for soil microorganisms and plant
roots. However, weak relationships between soil water content and soil respiration were
obtained in crop and grass systems (Figure 5.12). There was greater scatter in the
relationship between CO$_2$ flux and soil water content than between CO$_2$ flux and soil
temperature. Others have also found this behavior (Grahammer et al., 1991; Davidson et
al., 1998; Mielnick and Dugas, 2000). The relationship between soil water content
measured at 0-30 cm depth and CO$_2$ flux was more obvious in the grass system than in
the crop system (Figure 5.12). A reason for this behavior could be that low soil water
contents were more frequently obtained in the grass than in the crop system. Moreover,
average soil water content values did not vary much over seasons in the crop relative to
the grass system. The greater amount of scatter of soil respiration as a function of soil
water content in the grass than in the crop system could be because soil water was
averaged for the upper 30 cm depth of the soil profile which was a shallow depth
compared to the potential rooting capacity in the grass system. Singh et al. (1998)
Figure 5.11. CO$_2$ flux as a function of soil temperature at 5 cm depth in crop and grass systems. The flux and temperature were measured in each of 60 locations every two weeks for a year except during winter when they measured every month. Each symbol represents a particular flux vs. temperature measurement for a particular location and at a particular time.
Figure 5.12. CO₂ flux as a function of average soil water content at 0-30 cm depth in crop and grass systems. The flux and water content were measured in each of 60 locations every two weeks for a year except during winter when they measured every month. Each symbol represents a particular flux vs. moisture measurement for a particular location and at a particular time.
reported that wetter soil conditions at greater depths may buffer the effects of near-surface soil water deficits on CO$_2$ flux.

The relationships for CO$_2$ flux with soil temperature and soil water content are complex and the impact of the two driving factors on soil respiration cannot be studied independently (Herbst et al., 2009). Soil temperature and soil water content are inextricably linked and soil temperature is influenced by soil water content status. Soil water content can impact soil temperature because water has a high specific heat. At high water content status, soils have higher heat capacity than at low soil water status. The volumetric heat capacity of a substance is “the quantity of heat required to raise a unit volume of the substance” (Jury and Horton, 2004). Van Wijk and de Vries (1963) showed that heat capacity increased from 0.3 to 0.7 cal cm$^{-3}$ °C$^{-1}$ when soil water content increased from 0.0 to 0.4 m$^3$ m$^{-3}$ in sandy and clayey soils. Figures 5.11 and 5.12 show that soil temperature and soil water content had different relationships with soil respiration in both crop and grass systems.

Therefore, to quantify the roles of soil temperature and soil water content on soil respiration, a contour map was plotted using all observations of log-transformed CO$_2$ flux, soil temperature, and total soil water storage at 0-30 cm depth in crop and grass systems (Figure 5.13a and b). The contour map provided better insight in understanding the influence of soil temperature and soil water storage on surface CO$_2$ fluxes in crop and grass systems. Total soil water storage was chosen for this analysis to scale up the unit of
Figure 5.13. Contour maps show CO$_2$ flux as a function of soil temperature measured at 5 cm depth and total soil water storage measured at 30 cm depth in crop (a) and grass (b) systems.
soil moisture in the contour map. Contour maps of soil respiration as a function of soil temperature and soil water storage at 0-30 cm depth show that soil temperature was the dominant factor controlling soil respiration in both land-use systems in the time domain. In the crop system, the highest CO$_2$ flux was observed at high soil temperature, and the influence of soil temperature on CO$_2$ flux was more obvious at high than at low soil water storage. In the grass system, on the other hand, the highest CO$_2$ flux occurred at high soil water storage and high soil temperature and soil water storage did not influence the relation between flux and soil temperature as was obtained in the crop system. Soil respiration increased with increasing soil temperature from -0.3 °C to approximately 29.0 °C then it decreased with further increase of soil temperature in the grass system. The difference of the influence of soil temperature on soil respiration at different soil water storage conditions between the two land uses was because there were few observations of low soil water content obtained in the crop system relative to that in the grass system (Figures 5.10 and 5.12). CO$_2$ flux was highest under high soil temperature and relatively high soil water storage in both land-use systems because it was the optimum condition for soil-organism and plant-root growths and activities.

Herbst et al. (2009) also reported that soil temperature was the main factor controlling soil respiration under high water content conditions. Webster et al. (2008) studied the relationship between soil respiration and both soil temperature and soil water content in a forest soil and stated that most of the variance (48%) was explained by an exponential response to soil temperature and the remainder of the variance (9%) could be explained by a quadratic response to soil moisture. Xu and Qi (2001) reported that soil respiration
was less sensitive to soil temperature under lower soil moisture conditions. They found similar results of a negative correlation between soil respiration and soil moisture at high soil water content and stated that under high water content conditions, the relationship between CO\textsubscript{2} flux and soil moisture was confounded by soil temperature. The negative effect of soil moisture on CO\textsubscript{2} flux at high water content status can be due to the availability of oxygen in the soil pore space, which is an important factor driving microbial and plant-root activities.

The Spearman correlation analysis showed that spatially measured soil temperature significantly correlated with spatially measured CO\textsubscript{2} flux on only three dates in the crop system and they did not significantly correlate in the grass system (Figure 5.14a). Similarly, spatially measured soil water content significantly correlated with CO\textsubscript{2} flux measured on only two dates in the crop system, and they did not significantly correlate in the grass system (Figure 5.14b). Significant temporal correlations were obtained between CO\textsubscript{2} flux and soil temperature for all sampling locations in crop and grass systems. Soil water content significantly correlated with CO\textsubscript{2} flux only at one sampling point, which was located in the transition zone between the crop and grass systems (Figure 5.14c). Scott-Denton et al. (2003) also found that soil temperature was the primary control on soil respiration seasonally, and biotic factors were the major spatial controlling factors.
Figure 5.14. The spatial correlation coefficients for CO$_2$ flux with soil temperature at 5 cm depth (a), soil water content at 0-30 cm depth (b), and temporal correlation coefficient for CO$_2$ flux with soil temperature and soil moisture (c) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
5.2.2 Relationships between CO₂ flux and biochemical factors in crop and grass systems

The relationships between CO₂ flux measured on 22 sampling dates during the study period and selected soil biochemical factors in crop and grass systems were quantified using the Spearman rank correlation analysis. The selected factors included soil organic matter, total nitrogen, the carbon-to-nitrogen ratio, and soil pH. Totals of soil organic matter, total nitrogen, and the carbon to nitrogen ratio in the upper 30 cm depth of the soil profile were used for this data analysis. The magnitudes and the spatial distributions of soil organic matter, total nitrogen, and the carbon to nitrogen ratio were described in Chapters 3 and 4, respectively, in the crop and grass systems. Soils in the grass system had significantly higher average soil pH (6.0) than in the crop system (5.4). Soil pH in the crop system varied between 4.1 and 6.6 with a standard deviation of 0.5 in the crop system and between 5.4 and 6.8 with a standard deviation of 0.3 in the grass system.

Data analysis using the Spearman correlation showed that soil organic matter positively correlated with CO₂ flux measured on 8 June 2010 (summer season) when the flux was high in the crop system and on 31 January 2011 (winter season) when the flux was low in the grass system (Figure 5.15a). However, this relation was not obtained for all measuring dates in summer and winter seasons. Soil organic matter is an important factor driving CO₂ flux, as soil respiration represents decomposition of soil organic matter, and soil microbes use residue components as substrates for energy and also as carbon sources in the synthesis of new cells. Total nitrogen positively correlated with CO₂ flux measured on 8 June 2010 in the crop system and on 8 June 2010 and 31 January 2011 in the grass
Figure 5.15. The Spearman correlation coefficients for CO$_2$ flux with soil organic matter (a), total nitrogen (b), C/N (c), and soil pH (d) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
system (Figure 5.15b). It seemed that total nitrogen had a similar role to soil organic matter on soil respiration with significant and positive relationships found during the summer season when the flux was high in both land uses and during the winter season when the flux was low in the grass system. Nitrogen is an essential nutrient for plants and soil microorganisms as they need protein to build their cells. Tewary et al. (1982) stated that total nitrogen augmented soil respiration rates by providing a source of protein for microbial and plant growth. Xu and Qi (2001) and Joshi (1994) also found an increase of soil respiration with an increase of total nitrogen and organic matter in a young ponderosa pine plantation soils. Konda et al. (2010) reported that CO$_2$ flux significantly and positively related to total carbon and total nitrogen in a wet season (March 2006) and to only total carbon during a dry season (August 2005).

The carbon to nitrogen ratio did not significantly correlate with CO$_2$ flux in the crop system; on the other hand, it positively correlated with CO$_2$ flux measured on seven dates in summer and fall in the grass system (Figure 5.15c). It was an interesting result that the carbon to nitrogen ratio had significant relationships with CO$_2$ flux only in the grass system even though there was not a significant difference of the carbon to nitrogen ratio between the two land-use systems. Therefore, the difference was most likely because CO$_2$ flux was higher in the grass system than in the crop system. The carbon to nitrogen ratio has been identified as an important biotic factor for soil respiration but to a lesser extent than abiotic factors such as soil temperature and soil water content (Reth et al., 2005). Allaire et al. (2012) found a significant negative correlation between CO$_2$ flux measured during the spring season and the carbon to nitrogen ratio in an agricultural field. They
found a significant relation in their agricultural field most likely because their soil had different texture (sandy soil) compared to the soil used for the present study.

Soil respiration did not significantly correlate with soil pH in the crop system and negatively correlated with soil pH in the grass system for flux measurements taken during the fall season (2 August 2010) (Figure 5.15d). Xu and Qi (2001) also found negative relationship between CO₂ flux and soil pH in a forest soil. Soil pH was significantly correlated with CO₂ flux in the grass system but was not significantly correlated with CO₂ flux in the crop system, possibly because soils in the grass system had significantly higher average pH (6.0) than in the crop system (5.4). Soil pH significantly correlated with CO₂ flux in the grass system when soil respiration was high during the fall season when the soil was warm and moist. It seemed that the correlation of CO₂ flux with the selected soil biochemical factors varied with the flux measuring time, possibly because of the temperature and soil water status variations with season during the study period. Schimel and Holland (2005) stated that climate was the most important factor controlling soil respiration rates, with substrate quality second.

5.2.3 Relationships between CO₂ flux and soil physical factors in crop and grass systems

The relationships between CO₂ flux and selected soil physical properties and functions in crop and grass systems were quantified using the Spearman rank correlation analysis. These selected soil physical factors included: soil texture fractions (sand, silt, and clay), dry bulk density, aggregate mean weight diameter, largest aggregate size class (>2 mm),
smallest aggregate size class (<0.053 mm), soil water retention characteristics (α, n, θs, and θ(-1000)), relative gas diffusivity, air-filled porosity, and the pore-continuity index. Averages of soil texture fractions (sand, silt, and clay) at 0-30 cm depth were used for this analysis as was relative gas diffusivity, air-filled porosity, and the pore-continuity index measured at 5 selected soil water matric potentials. The quantification and spatial distributions of soil texture fractions, aggregate size distribution, soil water retention characteristics, soil gas diffusivity, air-filled porosity, and the pore-continuity index were described in Chapters 3 and 4, respectively, for each land-use system.

The relationship between soil texture and soil respiration has rarely been investigated. The relationships between CO2 flux and soil texture fractions were more obvious in the crop system with a greater number of significant correlations than in the grass system (Figure 5.16). During the fall season when the flux was high, sand and clay had significantly positive but silt had negative correlations with CO2 flux in the crop system.

Soil organic matter did not significantly correlate with CO2 fluxes; however it might influence the relationships between CO2 flux and other factors. To eliminate the impact of soil organic matter on the relationships of CO2 flux with soil texture fractions and soil pH, the flux measurements were normalized by computing the flux to organic matter ratio. Figures 5.16 and 5.17 show that normalizing the flux influenced the relationships of soil respiration with silt and clay contents only during the warm and moist period when the flux was high. During summer and fall seasons, the relationships of the normalized flux with silt and clay contents were significant for more measuring dates.
Figure 5.16. The Spearman correlation coefficients for CO$_2$ flux with sand (a), silt (b), and clay (c) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
Figure 5.17. The Spearman correlation coefficients for CO$_2$ flux to organic matter ratio with sand (a), clay (b), silt (c), and soil pH (d) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
than for non-normalized fluxes. The relationships of the normalized fluxes with silt and clay contents were similar in crop and grass systems during the summer and fall seasons. The relationships of the normalized fluxes were significantly positive with the clay content and significantly negative with the silt content because silt and clay contents had an inverse relationship. This analysis indicated the soil organic matter controlled the relationships of CO$_2$ fluxes with clay and silt contents especially during warm and moist seasons when the flux was high.

Dry bulk density negatively correlated with CO$_2$ flux measured during spring (17 March 2011) in the crop system and did not significantly correlate with CO$_2$ flux in the grass system (Figure 5.18a). Xu and Qi (2001) also found a negative correlation between CO$_2$ flux and soil bulk density in a forest soil. De Figueiredo Brito et al. (2009) measured higher CO$_2$ flux with lower soil bulk density and interpreted this as a consequence of higher soil porosity. This relationship indicated the importance of pore space for microbial and plant-root activities (Elliot et al., 1980). Soil pores play a major role in water and air movement, which are also important factors influencing plant-root and microbial activities in soil, besides providing habitat for soil microorganisms.

The relationships between CO$_2$ flux and aggregate size distributions were more obvious in the grass system with a greater number of significant correlations than in the crop system (Figure 5.18b, c, and d). The aggregate mean weight diameter and the large aggregate class significantly and positively correlated with CO$_2$ flux, but the small aggregate class negatively correlated with flux measured mostly during the fall season.
The Spearman correlation coefficients for CO$_2$ flux with bulk density (a), the aggregate mean weight diameter (b), large aggregate class (>2 mm) (c), and small aggregate class (<0.053 mm) (d) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
only in the grass system. The results showed that aggregate size had a significant influence on microbial and plant-root activities during the warm-moist period. Aggregate size is associated with soil porosity and soil organic matter content, and the latter have important relations with soil respiration with providing favorable conditions of aeration, moisture, and substrate for plant-roots and soil organisms. The relationship between the aggregate size and soil respiration was more obvious in the grass than in the crop system, most likely because the grass system had more developed soil structure with higher content of large aggregates, higher porosity, and more continuous pores (Chapter 3).

The role of soil water content on soil respiration has been intensively investigated; however, relationships between soil water retention curve parameters and soil respiration have not been studied. The relations of soil water retention curve parameters $\alpha$ and $n$ with soil respiration were more obvious in the crop than in the grass system. The $\alpha$ and $n$ parameters were significantly negatively correlated with CO$_2$ flux measured in fall and spring seasons, respectively, only in the crop system (Figure 5.19a and b). Soil water content at saturation did not significantly correlate with CO$_2$ flux in either system; however, soil water content at -1000 cm matric potential positively correlated with flux measured in the fall season in the grass system and negatively with flux measured in the spring season in the crop system (Figure 5.18c and d). Soil water retention characteristics are measurements of soil pore size distribution. The negative correlation between the inverse of the air entry point $\alpha$ and CO$_2$ flux reflected the importance of soil aeration to soil respiration. In other words, the air entry value positively related with soil aeration and therefore soil respiration. The slope of the soil water retention curve reflects the
Figure 5.19. The Spearman correlation coefficients for CO$_2$ flux with soil water retention characteristics, $\alpha$ (a), $n$ (b), $\theta_s$ (c), and $\theta_{(-1000)}$ (d) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
homogeneity of soil pore size distribution; a less steep slope indicates more homogeneous pore size distribution and more developed soil structure. The negative correlation between \( n \) and flux indicated that soil respiration was higher when soil exhibited more homogeneous pore size distribution. More significant correlations found in the crop than in the grass system were not expected because the grass system exhibited more developed soil structure with more homogenous pore size distribution than the crop system. In contrast to the result obtained from this study, Allaire et al. (2012) found a strong relationship between water content at saturation and soil respiration in an agricultural field. They obtained a significant correlation with water content at saturation possibly because their soil had different texture (sandy soil).

The relation between relative gas diffusivity and soil respiration was more obvious in the grass than in the crop system, with more significant correlations and higher correlations in the grass system especially during the summer and fall seasons when the flux was high (Figure 5.20). It seemed that the relationship between gas diffusivity and soil respiration varied with flux measuring time during the year. That can be because the range of \( \text{CO}_2 \) flux and its spatial variation varied with seasons. Relative gas diffusivity at -333, -100, and -50 cm matric potentials exhibited significantly positive correlation with soil respiration in the grass system and significantly negative correlation in the crop system. The relationship between gas diffusivity and soil respiration was stronger and more obvious in the grass system because it exhibited more developed soil structure with higher gas diffusivity than the crop system. Soil in the grass system also exhibited higher porosity, more homogeneous pore size distribution, and more continuous pores than in
Figure 5.20. The Spearman correlation coefficients for CO$_2$ flux with relative gas diffusivity at -10, -50, -100, -333, and -1000 cm matric potentials in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
the crop system. All these factors controlled the relationships between gas diffusivity and soil respiration because they influenced soil aeration and gas transport in soil.

A few significant correlations of air-filled porosity at higher matric potentials (-100, -50, and -10 cm) with soil respiration were obtained in the crop system and no significant correlation was found in the grass system (Figure 5.21). The relationship between pore continuity and soil respiration was more obvious in the grass system with more significant correlations than in the crop system (Figure 5.22). The pore-continuity index at -333, -100, and -50 cm matric potentials was significantly positively correlated with CO₂ flux in the grass system and negatively in the crop system. The significant correlations between pore continuity and soil respiration in the grass system were obtained mostly during the summer and fall seasons when the flux was high. Pore continuity is an important factor controlling soil aeration and gas transport in soil, therefore the exchange of oxygen and other gases between soil and the atmosphere. The grass system exhibited more and stronger correlations with CO₂ flux most likely because it exhibited more developed soil structure with more continuous pores than the crop system. The relationship between pore continuity and soil respiration varied with flux measuring time most likely because the range of the soil respiration rate and its variation also varied with seasons.

Allaire et al. (2012) found a significant negative correlation for soil respiration measured during spring with gas diffusivity and air-filled porosity estimated from field-soil moisture in an agricultural field. No study was found in the literature demonstrating the
Figure 5.21. The Spearman correlation coefficients for CO₂ flux with air-filled porosity at -10, -50, -100, -333, and -1000 cm matric potentials in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
Figure 5.22. The Spearman correlation coefficients for CO$_2$ flux with the pore-continuity index at -10, -50, -100, -333, and -1000 cm matric potentials in crop and grass systems.

The dashed line refers to the significance at 0.05 levels, either positive or negative.
relationship between soil respiration and the pore-continuity index. In summary, the results of significant correlations showed that gas diffusivity and pore continuity for gas transport played important roles in gas exchange between soils and the atmosphere in crop and grass systems during the period when fluxes were high. Gas diffusivity is essential for providing oxygen to plant-roots and soil microorganisms and releasing CO₂ from the soil. The relationships between these gas transport properties depended on the magnitude of these properties (matric potential), the range of CO₂ flux observations (measuring season), and the land use. The differences between the two land uses in terms of the relationships between these gas transport properties and soil respiration rates were because the grass system exhibited more developed soil structure than the crop system and the magnitude of CO₂ flux also differed between the two land uses. It should be noted that the effect of each of these factors may not be individually explained because these factors were often strongly inter-correlated and co-vary with soil organic matter and root respiration (Xu and Qi, 2001).

5.2.4 Temporal associations for CO₂ flux with soil temperature and soil water content in crop and grass systems

The temporal relationships of soil respiration with soil temperature and soil water content were quantified using cross-semivariogram analysis for three sampling locations in the crop system (locations 7, 13, and 16; Figure 2.2) and three sampling locations in the grass system (locations 41, 47, and 51). The selection of these six locations was based on the mean relative difference values of CO₂ flux (Figure 5.8). Sampling locations with a mean relative difference from the average close to zero tend to be representative locations for
the mean value for the entire field (Vachaud et al., 1985). Soil temperature and soil water content were the only variables measured in space and over time besides gas fluxes. To compute the temporal cross-semivariograms for CO$_2$ flux with soil temperature and soil water content, the structure of the temporal variability of these considered variables had to be quantified. The temporal variability of CO$_2$ flux measured at the selected locations in the crop and grass systems was structured as was discussed earlier in this chapter. Temporal semivariograms for soil temperature and soil water content for the selected measuring locations in both land-use systems were computed to quantify the temporal variability of these variables.

The temporal coefficient of variation of soil temperature varied between 47 and 60% with an average of 47% in the crop system and between 43 and 54% with an average of 49% in the grass system among all sampling locations. The temporal variability of soil temperature for all selected locations was structured and semivariograms for all selected locations were unbounded, so the temporal correlation length and sill values for these selected locations were not obtained (Figure A5.1 in Appendix 5). Soil temperature measured at the selected locations in the grass systems exhibited larger nugget values than in the crop system (Table 5.3).

The temporal coefficient of variation of average soil water content at 0-30 cm varied between 1 and 39% with an average of 8% in the crop system and between 7 and 49% with an average of 24% in the grass system among all sampling locations. The temporal variability of the average soil water content was structured for all selected measuring
Table 5.3. Temporal semivariogram parameters for soil temperature and soil water content at 0-30 cm depth measured at selected locations in crop and grass systems.

<table>
<thead>
<tr>
<th>Locations</th>
<th>Soil temperature</th>
<th>Soil water content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crop system</td>
<td>Grass system</td>
</tr>
<tr>
<td></td>
<td>Range (day)</td>
<td>Nugget (°C)²</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>16</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>41</td>
<td>-</td>
<td>13.48</td>
</tr>
<tr>
<td>47</td>
<td>-</td>
<td>5.50</td>
</tr>
<tr>
<td>51</td>
<td>-</td>
<td>3.23</td>
</tr>
</tbody>
</table>

| Nugget (m³ m⁻³)² | 2x10⁻⁵ | 2x10⁻⁴ | 2x10⁻⁴ | 0.0 | 0.0 | 1x10⁻⁴ |
| Nugget/sill    | 0.04   | 0.27   | 0.28   | 0.0 | 0.0 | 0.03   |
locations in both land-use systems (Figure A5.2). Soil water content in the grass system exhibited longer temporal correlation lengths than in the crop system for the selected measuring locations (Table 5.3). Soil water content in both land uses exhibited a strong temporal structure and the nugget-to-sill ratios were lower for the selected locations in the grass than in the crop system.

The cross-semivariogram analysis showed that there existed a strong temporal relationship between CO₂ flux and soil temperature measured at 5 cm depth for all selected measuring locations in crop and grass systems (Figures A6.1, A6.2 in Appendix 6). The temporal ranges of the association between CO₂ flux and soil temperature were longer in the crop than in the grass system (Table 5.4). Nugget-to-sill ratios showed that the dependency of the temporal relationship was strong for all selected locations.

The cross-semivariogram analysis also showed that CO₂ flux temporally related to average soil water content at 0-30 cm depth for the selected measuring locations in the crop system (Figures A6.3-A6.4). In the grass system, on the other hand, cross-semivariogram for only one measuring location (47) was structured, indicating that CO₂ flux temporally related to soil water content. The temporal cross-semivariance decreased with lag distance for all selected locations in the crop system indicating an inverse relationship. On the other hand, the temporal association in the grass system in location 47 was positive but weak. The negative impact of soil moisture on the temporal variability of soil respiration in the crop system can be because soil temperature dominated the control on its temporal variation. The range of average soil moisture
Table 5.4. Temporal cross-semivariogram parameters for CO$_2$ flux with soil temperature and average soil moisture at 0-30 cm depth measured at different locations in crop and grass systems.

<table>
<thead>
<tr>
<th>Locations</th>
<th>Crop system</th>
<th>Grass system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>Range (day)</td>
<td>CO$_2$ flux vs. soil temperature</td>
<td>255</td>
</tr>
<tr>
<td>Nugget</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Nugget/Sill</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Range (day)</td>
<td>CO$_2$ flux vs. soil water content</td>
<td>181</td>
</tr>
<tr>
<td>Nugget</td>
<td>1x10$^{-3}$</td>
<td>3x10$^{-3}$</td>
</tr>
<tr>
<td>Nugget/Sill</td>
<td>0.18</td>
<td>0.27</td>
</tr>
</tbody>
</table>
values in the crop system was smaller relative to that in the grass system which might explain the difference of the temporal relations in crop and grass systems. The temporal correlation lengths for the temporal association between CO$_2$ flux and soil water content varied between 173 and 181 days in the crop system (Table 5.4). The temporal range obtained from one cross-semivariogram for sampling location 47 in the grass system was 57 days. A lower nugget-to-sill ratio was found for selected locations in the crop than in the grass system indicating stronger temporal association structure in the crop system. The result showed that despite the spatial variability for both CO$_2$ flux and soil water content being more structured in the grass than the crop system, the temporal relationship between soil respiration and soil water content was stronger in the crop than in the grass system. Longer correlation ranges and smaller nugget-to-sill ratios of the relationship between CO$_2$ flux and water content were obtained in the crop system.

The temporal associations of CO$_2$ flux were quantified with only soil temperature and soil water content and the results showed that soil temperature had a stronger temporal relationship with soil respiration than with soil water content in the crop and grass systems. The temporal relationships between soil respiration and soil temperature have been demonstrated in several studies. For instance, Fang et al. (1998) reported that soil temperature was the most influential factor controlling soil respiration rate and its temporal variation in forest soils. The high temporal correlation between soil respiration and soil temperature was in general agreement with many previous reports (e.g., Oberbauer et al., 1992; Bridgham and Richardson, 1992). However, cross-semivariogram
analysis has not been used by others to quantify the temporal associations for CO₂ flux with soil temperature and soil water content.

5.2.5 Spatial associations for CO₂ flux with soil temperature and soil water content in crop and grass systems

The spatial relationships of CO₂ flux with soil temperature and soil water content in crop and grass systems were quantified using cross-semivariogram analysis for selected data sets of CO₂ flux measured on four sampling dates that represented four different seasons. These selected sampling dates were 8 June 2010 (summer), 28 October 2010 (fall), and 17 March 2011 (spring). The 31 December 2010 was the fourth sampling date for the crop system and 31 January 2011 was the fourth date in the grass system and both represented winter. Different sampling dates were selected for the winter in crop and grass systems because semivariograms for CO₂ flux measured on 31 December 2010 and 31 January 2011 in the grass and crop systems, respectively, were unbounded. The spatial variability of CO₂ flux measured on these four selected sampling dates was structured in both land uses as was shown earlier in this chapter. To quantify the spatial associations for CO₂ flux with soil temperature and soil water content, the spatial dependencies of soil temperature and soil moisture were quantified first.

The spatial coefficient of variation CV of soil temperature varied between 6 and 117% with an average of 25% in the crop system and between 5 and 116% with an average of 19% in the grass system among the 22 sampling dates. The spatial variability of soil temperature was structured only for measurements taken on 31 January 2011 in the grass
systems (Figure A7.1 in Appendix 7). The semivariogram analysis showed that the spatial range of soil temperature measured on 31 January 2011 in the grass system was 24.3 m with nugget and nugget-to-sill ratio of 0 which indicted a strong spatial dependency. Allaire et al. (2012) found spatial correlation lengths of 19.4 and 23.5 m and nugget-to-sill ratios of 0.62 and 0.60 (moderate spatial structure) for soil temperature measured in 0-15 cm in two agricultural fields.

The spatial variation of average soil water content at 0-30 cm depth as estimated by CV varied between 4 and 15% with an average of 8% in the crop system and between 6 and 30% with an average of 12% in the grass system among the 22 sampling dates. The semivariogram analysis showed that the spatial variability of average soil water content was structured only on 31 December 2010 in the crop system and on all selected dates in the grass system (Figure A7.2). The structured variability of average water content measured in the winter in the crop system exhibited a spatial range of 9.6 m and nugget-to-sill ratio of 0.81. The spatial correlation length for soil water content varied between 23.7 and 33.6 m in the grass system among the selected sampling dates. The spatial dependency of average water content as estimated from the nugget-to-sill ratio was strong in summer and fall and moderate in winter and spring seasons in the grass system.

Because of the leak of structured spatial variability of soil temperature for the selected measuring dates, the spatial association of soil respiration with soil temperature was not quantified, and the spatial association between soil moisture and soil respiration quantified only for flux measured in winter. The cross-semivariograms for CO₂ flux with
average soil water content measured in the winter was structured only in the grass systems (Figure A8.1). This spatial relation between soil respiration and average water content in the grass system exhibited spatial range of 2.6 m and nugget-to-sill ratio of 0.89.

Herbst et al. (2009) investigated the impacts of soil temperature and soil water content on soil respiration from bare soils and concluded that the temporal evolution of soil respiration was driven by soil temperature and soil water content. They stated that the temporal variability of soil variability of CO₂ flux depended strongly on temperature for wet soils, soil water content was the main factor controlling the spatial variability of soil respiration, and the variation of soil water content was one order of magnitude higher than the variation of soil temperature. They found different results of higher spatial variation for soil water content than soil temperature relative to the current study, possibly because they measured both temperature and moisture at a different depth (15 cm) than depths selected for this study, and because they used bare soil. Fóti et al. (2008) also studied CO₂ flux in grassland and concluded that soil respiration depended on soil water content and soil temperature as the main governing factors. They stated that the actual spatial pattern of soil respiration depended on soil water content, soil temperature, and plant-root biomass, but mainly on soil water content, especially under water stress conditions. It can be concluded that the current study showed that soil temperature and soil water content were not the controlling factors on spatial variability of soil respiration in crop and grass systems.
5.2.6 Spatial associations for CO$_2$ flux with soil biochemical factors in crop and grass systems

The spatial relationships for CO$_2$ flux with selected soil biochemical properties included soil organic matter, total nitrogen, and soil pH were quantified in crop and grass systems. The cross-semivariogram analysis was used to quantify these spatial relationships for CO$_2$ flux measured on four selected sampling dates represented four different seasons. The spatial variability of soil organic matter and total nitrogen were discussed in Chapter 4. The spatial variability of soil organic matter and total nitrogen was structured in both crop and grass systems. The spatial variability of the carbon to nitrogen ratio was random; therefore the cross-semivariograms for CO$_2$ flux with the carbon to nitrogen ratio was not computed.

The coefficient of variation of soil pH was higher in the crop system (9%) than in the grass system (5%). The spatial variability of soil pH was structured in crop and grass systems as was indicated from structured semivariograms of soil pH (Figure A7.3). The spatial correlation length for soil pH was longer in the grass (24.6 m) than in the crop (13.2 m) system. The nugget-to-sill ratio indicated that the spatial dependence of soil pH was strong in the crop system and moderate in the grass system.

Total soil organic matter in the upper 30 cm of the soil profile was spatially associated with soil respiration measured on all selected sampling dates in both crop and grass systems as it was quantified using cross-semivariogram analysis (Figure A9.1). The nugget-to-sill ratio indicated that the spatial dependency of the relationship between CO$_2$
flux and soil organic matter was strong in the crop system and moderately to strongly varied among the selected flux sampling dates in the grass systems (Table 5.5). It seemed that soil organic matter was more spatially associated with soil respiration when the latter was low in the grass system. This behavior was obvious when this spatial relationship was compared between the two land-use systems, with longer spatial range obtained in the crop system due to lower respiration rates in the crop than in the grass system.

Total soil nitrogen at 0-30 cm depth also spatially related with CO$_2$ flux measured on all selected sampling dates except 8 June 2010 in the crop system (Figure A9.2). The spatial dependency of the relationship between total nitrogen and soil respiration varied between weak and strong among the selected flux sampling dates in both land-use systems as indicated from the nugget-to-sill ratio (Table 5.5). Longer correlation lengths of the spatial relationship between total nitrogen and CO$_2$ flux were obtained in the crop than in the grass system for all selected flux sampling dates except 8 June 2010 in the crop system.

Similar to what was found for the spatial relationship between soil organic matter and CO$_2$ flux, the spatial range of the spatial relationship between total nitrogen and CO$_2$ flux was longer when the respiration rate was lower and shorter when the flux was higher among the climatic seasons and between the crop and grass systems. Another possible reason why obviously longer correlation lengths were obtained in the crop system relative to that in the grass system can be that soil organic matter and total nitrogen exhibited lower CVs and longer spatial ranges in the crop system.
Table 5.5. Spatial cross-semivariogram parameters for CO$_2$ flux measured on four selected dates with soil organic matter, total nitrogen, total mineral nitrogen, and pH in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>Crop system</th>
<th></th>
<th>Grass system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Range (m)</td>
<td>33.8</td>
<td>23.4</td>
<td>32.3</td>
<td>5.9</td>
</tr>
<tr>
<td>Nugget</td>
<td>0.0</td>
<td>1x10$^{-2}$</td>
<td>1x10$^{-2}$</td>
<td>3x10$^{-2}$</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.0</td>
<td>0.15</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>CO$_2$ flux vs. SOM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>28.3</td>
<td>39.4</td>
<td>30.6</td>
</tr>
<tr>
<td>Nugget</td>
<td>1x10$^{-6}$</td>
<td>4x10$^{-4}$</td>
<td>1x10$^{-3}$</td>
<td>8x10$^{-4}$</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>0.10</td>
<td>0.29</td>
<td>0.22</td>
</tr>
<tr>
<td>CO$_2$ flux vs. TN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>-</td>
<td>8.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Nugget</td>
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<td>0.0</td>
<td>5x10$^{-2}$</td>
<td>5x10$^{-2}$</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>1.0</td>
<td>0.37</td>
<td>0.54</td>
</tr>
</tbody>
</table>
Soil pH measured in the upper 15 cm was spatially correlated with soil respiration in the grass system. In the crop system, soil pH was spatially negatively associated with soil respiration only in winter and spring (Figure A9.4). The spatial dependency of the relationship between pH and CO$_2$ flux was moderate in both land uses and among the selected measuring dates that showed structured cross-semivariograms (Table 5.5).

5.2.7 Spatial associations between CO$_2$ flux and soil physical factors in crop and grass systems

The spatial associations between soil respiration and selected soil physical variables such as soil textural fractions, bulk density, relative gas diffusivity at -1000 and -10 cm matric potential, air-filled porosity at -1000 cm matric potential, and the pore-continuity index at -10 cm matric potential were quantified in crop and grass systems using cross-semivariogram analysis. These spatial relationships were quantified for CO$_2$ flux measured on four selected sampling dates representing four different seasons. The spatial structure of these physical properties and functions was quantified in Chapter 4. The spatial variability of these soil physical factors was structured in crop and grass systems.

Only sand and silt contents were considered for this data analysis because the spatial variability of clay contents was not structured in both land uses. The cross-semivariogram analysis showed that average sand content at 0-30 cm depth spatially correlated with CO$_2$ flux measured on the selected sampling dates in crop and grass systems (Figure A9.5). The spatial relationship between sand and soil respiration was positive in summer and fall and negative in winter and spring in the crop system. This behavior can be because the flux was higher and exhibited lower CVs in summer and fall than in winter and spring.
The nugget-to-sill ratio indicated that the spatial dependency of the relationship between the sand content and CO\textsubscript{2} flux was moderate in both land-use systems and among all selected flux sampling dates (Table 5.6). The difference of the spatial relation between soil respiration and sand between the two land uses was most likely due to the differences of the spatial variability of CO\textsubscript{2} flux between the land uses because the spatial variability of the sand content was similar in crop and grass systems (Chapter 4).

Average silt content at 0-30 cm depth spatially negatively correlated with CO\textsubscript{2} flux measured on only fall and winter in the grass system (Figure A9.5). On the other hand, silt contents spatially positively related to soil respiration in fall and spring and negatively in summer and winter in the crop system. In summer and winter, silt negatively related, while in fall and spring, silt negatively correlated with CO\textsubscript{2} flux in the crop system. The spatial dependency as indicated from the nugget-to-sill ratio of the spatial relationships for soil respiration with silt contents varied between moderate and strong in the crop system and between weak and moderate in the grass system among the flux sampling dates. The correlation lengths of the spatial relations for soil respiration with silt contents were longer in the crop system than in the grass system for all selected flux measuring dates (Table 5.6).

The cross-semivariogram analysis showed that soil dry bulk density spatially negatively associated with CO\textsubscript{2} flux only measured in spring in the crop system and with flux measured on all selected sampling dates in the grass systems (Figure A9.6). The inverse relationship between bulk density and soil respiration reflected the positive influence of
Table 5.6. Spatial cross-semivariogram parameters for CO₂ flux measured on four selected dates with sand and silt contents in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>Crop system</th>
<th></th>
<th>Grass system</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>2010</td>
<td>2010</td>
<td>2010</td>
<td>2011</td>
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<td></td>
<td>2010</td>
<td>2010</td>
<td>2011</td>
<td>2011</td>
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<tr>
<td>CO₂ flux vs. sand</td>
<td>Range (m)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>2.0</td>
<td>5.6</td>
<td>8.8</td>
<td>13.6</td>
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<tr>
<td></td>
<td>5x10⁻²</td>
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<td>5x10⁻²</td>
<td>1x10⁻²</td>
</tr>
<tr>
<td></td>
<td>Nugget</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5x10⁻²</td>
<td>5x10⁻²</td>
<td>1x10⁻²</td>
<td>4x10⁻²</td>
</tr>
<tr>
<td></td>
<td>Nugget/sill</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.46</td>
<td>0.31</td>
<td>0.47</td>
<td>0.27</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CO₂ flux vs. silt</td>
<td>Range (m)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>6.1</td>
<td>-</td>
<td>4.7</td>
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<tr>
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<tr>
<td></td>
<td>Nugget</td>
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<tr>
<td></td>
<td>6x10⁻²</td>
<td>2x10⁻²</td>
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<tr>
<td></td>
<td>Nugget/sill</td>
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<tr>
<td></td>
<td>0.50</td>
<td>-</td>
<td>0.47</td>
<td>0.0</td>
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253
total porosity on CO₂ flux. The nugget-to-sill ratio showed that the spatial dependency of the relationship between bulk density and CO₂ flux was strong in the spring in the crop system and varied between moderate and strong among the selected flux sampling dates in the grass system (Table 5.7). In the spring, the spatial correlation length for the spatial relationship between bulk density and CO₂ flux was longer in the crop than in the grass system. The grass system exhibited spatial correlations between soil respiration and bulk density for more selected measuring dates than the crop system, most likely because grass had more developed soil structure with higher soil porosity. The influence of bulk density on the spatial variability of soil respiration has been quantified by others. For instance, Fiener et al. (2012) concluded that soil bulk density was one of the factors having the most consistent effect on the spatial variability of heterotrophic soil respiration in a crop system with silt loam soils.

Relative gas diffusivity at -10 cm matric potential spatially associated with CO₂ flux measured only in summer and spring in the crop system and only in fall in the grass system (Figures A9.7). The relationship between soil respiration and relative gas diffusivity at -10 cm matric potential was negative in the grass system (in fall), and it was negative in summer and positive in spring in the crop system. The spring season was wetter than the summer season which might be the reason why soil respiration was positively influenced by gas diffusivity in spring and negatively in summer in the crop system. The spatial dependency of this relation was moderate for all seasons that showed structured cross-semivariograms in both land uses (Table 5.7). Relative gas diffusivity at -1000 cm matric potential spatially associated with soil respiration on all selected
Table 5.7. Spatial cross-semivariogram parameters for CO$_2$ flux measured on four selected dates with bulk density, relative gas diffusivity (D$_s$/D$_{0(\psi)}$), air-filled porosity ($\theta_{af(1000)}$), and the pore-continuity index ($\theta_{c(10)}$) in crop and grass systems.

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</tr>
<tr>
<td><strong>Grass system</strong></td>
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<td></td>
</tr>
<tr>
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<td>23.6</td>
<td>23.6</td>
<td>23.6</td>
<td>23.6</td>
<td>23.6</td>
<td>23.6</td>
<td>23.6</td>
</tr>
<tr>
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<td>2x10$^{-4}$</td>
<td>1x10$^{-3}$</td>
<td>1x10$^{-3}$</td>
<td>1x10$^{-3}$</td>
<td>1x10$^{-3}$</td>
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</tr>
<tr>
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<td>1.0</td>
<td>1.0</td>
<td>0.17</td>
<td>0.54</td>
<td>0.39</td>
<td>0.18</td>
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</tr>
<tr>
<td><strong>CO$_2$ flux vs. D$<em>s$/D$</em>{0(\psi)}$</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
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<td>10.9</td>
<td>16.9</td>
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<td>4.9</td>
<td>-</td>
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<td>1x10$^{-3}$</td>
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<td>9x10$^{-5}$</td>
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<td>Nugget/sill</td>
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<td>0.43</td>
<td>0.30</td>
<td>0.50</td>
<td>0.53</td>
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<td>0.45</td>
</tr>
<tr>
<td><strong>CO$<em>2$ flux vs. $\theta</em>{af(1000)}$</strong></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>5.9</td>
<td>11.3</td>
<td>-</td>
<td>7.1</td>
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<td>11.0</td>
<td>-</td>
<td>21.1</td>
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<td>6x10$^{-4}$</td>
<td>8x10$^{-4}$</td>
<td>2x10$^{-3}$</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.49</td>
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<td>1.0</td>
<td>0.39</td>
<td>0.6</td>
<td>0.51</td>
<td>1.0</td>
<td>0.41</td>
</tr>
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<td><strong>CO$<em>2$ flux vs. $\theta</em>{c(10)}$</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>3.1</td>
<td>7.6</td>
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<td></td>
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<td>5x10$^{-4}$</td>
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<td>0</td>
<td>1x10$^{-2}$</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.47</td>
<td>1.0</td>
<td>0.53</td>
<td>0.0</td>
<td>0.48</td>
</tr>
</tbody>
</table>
measuring dates except in fall in the crop system and in winter in the grass system (Figure A9.8). These spatial relationships were positive in the crop and negative in the grass system, and that was due to soil structure difference between land-use systems. The spatial dependency of this relationship was moderate for all seasons that showed structured cross-semivariograms in both land uses (Table 5.7).

The spatial variability of air-filled porosity at -10 cm matric potential in the grass system and the pore-continuity index at -1000 cm matric potential in crop and grass systems was random (Chapter 4). Therefore, the spatial associations of soil respiration and air-filled porosity were quantified at only -1000 cm matric potential and with pore-continuity index at only -10 cm matric potential. The air-filled porosity at -1000 cm matric potentials was spatially positively associated with soil respiration measured on all selected flux sampling dates except for flux measured in the winter in both land uses (Figure A9.9). The spatial structure as indicated from the nugget-to-sill ratio for the spatial relationship between CO₂ flux and air-filled porosity at -1000 cm matric potential varied between weak and strong in the crop system and between weak and moderate in the grass system among the selected flux measuring dates. The spatial range of the relation between respiration rate and air-filled porosity at -1000 cm matric potential was longer or similar in the grass than in crop system (Table 5.7).

The pore-continuity index at -10 cm matric potential spatially related with CO₂ flux measured only in spring in the crop and on all sampling dates except 8 June 2010 in the grass systems (Figure A9.10). These spatial relationships were negative in both land uses
except in winter in the grass system. The spatial dependency for the relationship between
the pore-continuity index at -10 cm water head and CO₂ flux was moderate in the crop
system and varied between moderate and strong in the grass system among the selected
flux sampling dates that showed structured cross-semivariograms (Table 5.7). In the
spring the spatial association between the pore-continuity index at -10 cm matric
potential and soil respiration exhibited longer spatial range in the grass than in the crop
system.

Overall, the results showed that climatic factors such as soil temperature controlled the
temporal variability of soil respiration and the soil biochemical and physical processes
dominated the spatial variability of soil respiration. In the crop system, soil organic
matter and total nitrogen were the main factors controlling the spatial variability of soil
respiration on all selected dates. Dry bulk density, air-filled porosity at -1000 cm water
head, and silt also exhibited strong spatial associations with CO₂ flux measured in the
spring and fall in the crop system. In the grass system, on the other hand, bulk density
and pore continuity at -10 cm water head were the main controlling factor on soil
respiration measured in winter while soil organic matter and total nitrogen were the
dominant factors controlling the spatial variability of soil respiration in winter and spring
(cool and moist).

Xu and Qi (2001) studied CO₂ flux in a young ponderosa pine plantation and reported
results similar to those obtained in the present study. They concluded that soil moisture
and its interaction with soil temperature had a strong influence on the temporal variation
of soil respiration, especially during the summer when soil moisture was low. They also stated that soil properties, especially total nitrogen, bulk density, and organic matter content, had strong impacts on the spatial variability of soil respiration.

Similar to those found for soil physical properties and functions (Chapter 4), for some structured spatial cross-semivariograms, the cross-semivariance decreased with separating distance or exhibited a different sign for <5-m lags distances from longer lags. For example, Figure A9.3c shows the cross-semivariogram for soil respiration with soil pH in the grass system. The cross-semivariance became smaller as lag distance increased, and it was negative for the first lags and positive for longer lags. Another example can be Figure A9.4c, which shows that the cross-semivariance was positive for the first lags and negative for the longer lags. This behavior was most likely because the <5 m lags were the separation distance for sampling points located in the transition zone between the crop and grass systems. The variation of soil respiration and the selected factors tended to be higher in the transition zone than in the rest of the field. Another reason can be because the <5 m lags were the separation distances for observations located in the nests. This behavior is an indication of the influence of sampling interval on cross-semivariogram analysis. It seemed that a constant distance interval should be selected for cross-semivariogram analysis.

Spatial correlations between soil respiration and some selected soil properties were not found or were weak, possibly because the scale of variability for soil respiration rate and the selected property were different. Correlations between variables may be
misinterpreted if their scales of variability are ignored in the presence of scale-dependent processes and relationships (Biswas and Si, 2009; Riveros-Iregui and McGlynn, 2009). Allaire et al. (2012) concluded that stronger correlations between soil respiration and soil properties were obtained when statistical analyses considered different scales rather than total variability, and more parameters were significantly correlated with CO$_2$ flux when differentiated for scales than when not.

Cross-semivariogram analysis has been used to identify spatially dependent relationships between hydraulic parameters and soil physical properties (e.g., Biswas and Si, 2009), but no other studies were found in the literature that investigated the spatial associations of soil respiration rates with other soil properties using cross-semivariogram analysis. Correlation coefficients have been used to quantify the controls on the spatial variability of soil respiration in other studies (Scott-Denton et al., 2003; Allaire et al., 2012; Fiener et al., 2012). In the present study, the Spearman correlation analysis gave different results relative to the cross-semivariogram analysis. For example, the Spearman correlation analysis showed that soil relative gas diffusivity and air-filled porosity at -1000 cm water head did not significantly correlate with soil respiration rates on any of the flux sampling dates in the crop system. In contrast, the cross-semivariogram analysis showed that these factors were spatially associated with soil respiration rates in the crop system. The same lack of significant Spearman correlation coefficients was found between soil respiration rates and clay content, bulk density, air-filled porosity at -1000 cm matric potentials in the grass system, but spatial associations were obtained using the cross-semivariogram analysis between soil respiration and these factors in the grass system. The cross-
semivariogram analysis has the advantage that it not only provides a measure of the strength of the spatial association between soil respiration and the considered factor but it also shows how the relationship changes with distance (scale) and provides the cross-semivariance and the spatial range where these two variables are significantly correlated, indicating they should be sampled within this distance range.

The results from this study were useful for identifying and understanding controlling factors on the behavior of CO₂ flux along temporal and spatial scales in different land-use systems. It is also important for understanding how various ecosystem processes respond to the shifts in climate patterns and management regimes. CO₂ flux from the soil surface is a key component of the carbon cycle of any ecosystem. Quantifying soil surface CO₂ flux and understanding the factors that underlie the spatial and temporal variation in its magnitude in different land-use systems are fundamental to our understanding of the behavior of the ecosystem as a whole and to our ability to predict the likely consequences of climatic change (Rayment and Jarvis, 2000). The diversity of factors influencing soil respiration explained some of the reasons behind the extreme heterogeneity of soil respiration in crop and grass systems. It should be noted that these different biochemical and physical factors might influence each other and their control on soil respiration. Fang et al. (1998) studied the effects of different factors influencing the spatial variability of CO₂ flux in forest soils and concluded that different factors influenced CO₂ flux but no single factor could explain adequately or dominate the spatial heterogeneity of CO₂ flux of their site.
5.3 Summary and conclusions

Soil respiration was quantified in two land-use systems with the highest soil respiration observed during a warm-moist period and the lowest during a cold-wet period. The grass system had slightly higher CO$_2$ flux than the crop system. Although soil respiration exhibited high variation in space and time, its spatial and temporal variability was structured. Land use had notable impacts on spatial and temporal variability of soil respiration, and respiration was correlated over longer times and spatial distances in the grass system than in the crop system. The heterogeneity of soil respiration was more pronounced in time than in space in both land-use systems. Temporal stability analysis showed that the variability of soil respiration was temporally structured and spatial patterns of CO$_2$ flux were temporally stable for 100 days. The temporal stability of CO$_2$ flux patterns was more obvious during the warm-moist period when the flux was higher than lower. It is recommended to consider the spatial and temporal correlation ranges (23 m and 144 days in the crop system, and 33 m and 155 days in the grass system) obtained from this study for designing field experiments under similar measurement scale, land use, soil type, and environmental conditions.

Cross-semivariogram analysis has not been used for quantifying spatial and temporal relationships of soil respiration with biochemical and physical factors. It provided important knowledge about how correlations between CO$_2$ fluxes and the selected factors changed at different spatial and temporal scales and the length where or when the flux and the controlling factors remained correlated. The effect of soil temperature on soil respiration was only observed over the temporal but not the spatial domain. Spatial
relations between CO₂ flux and the selected biochemical and physical factors depended on land use and varied with the flux sampling time, and the range of measurements. Biochemical factors, specifically soil organic matter and total nitrogen, besides soil physical factors such as bulk density, air-filled porosity at -1000 cm matric potential, and silt content were the dominant factors controlling the spatial variability of CO₂ flux in the crop system. On the other hand, bulk density, pore continuity at -10 cm matric potential, organic matter, and total nitrogen were the dominant factor controlling the spatial variability of CO₂ flux in the grass system. This result of relations between soil respiration and different biochemical and physical factors provided important knowledge for improving prediction of soil carbon dioxide flux under different land uses and sampling design schemes.
CHAPTER 6: Spatial and Temporal Patterns of N\textsubscript{2}O Flux and Its Associations in Crop and Grass Systems

This chapter focuses on quantifying spatial and temporal patterns of soil surface N\textsubscript{2}O flux in crop and grass systems. The spatial and temporal behaviors of N\textsubscript{2}O fluxes were studied using different statistical methods. An investigation of the temporal stability of spatial patterns of N\textsubscript{2}O flux was also included. It also emphasizes investigating the controlling factors and the spatial and temporal associations between N\textsubscript{2}O flux and selected biochemical and physical factors in crop and grass systems.

Nitrous oxide flux is an important component of the nitrogen cycle and it is essential to quantify its spatial and temporal patterns under different land uses. Besides CO\textsubscript{2} and CH\textsubscript{4}, N\textsubscript{2}O is one of the most important greenhouse gases because of its influence on ozone. The quantification of CO\textsubscript{2} flux and its spatial and temporal patterns were in the previous chapter; in this chapter, the same data analysis was performed for N\textsubscript{2}O flux in crop and grass systems.

N\textsubscript{2}O flux exhibits high variation in space and time and its spatial and temporal behaviors and temporal stability under different land uses such as crop and grass are not well understood. One of the major reasons why N\textsubscript{2}O flux exhibits high variation in space and time is because there are different factors that control the flux. The effects of biochemical and environmental factors on N\textsubscript{2}O flux have been extensively studied. However, the influence of physical factors on the spatial variability of N\textsubscript{2}O flux and under different
land uses is not well understood. Cross-semivariogram analysis has not been used by others for quantifying associations of N\textsubscript{2}O flux with controlling factors. Therefore, the objectives of this chapter were to quantify the spatial and temporal variability of N\textsubscript{2}O flux in crop and grass systems, and to identify the controlling factors on these spatial and temporal patterns.

**Methods**

The description of site, sampling locations, sampling protocol, and data analysis are as previously described in Chapter 2.

**Results and Discussion**

6.1 Spatial and temporal patterns of N\textsubscript{2}O flux in crop and grass systems

6.1.1 Field observations of N\textsubscript{2}O flux in crop and grass systems

A trend was obtained for measured N\textsubscript{2}O flux with time during the day of measurement. Figure 6.1 shows two examples of flux measurements performed on 6 July 2010 and 8 June 2011 in crop and grass systems. The measurements were performed in the crop system on the first day and in the grass system the next day. An increase of N\textsubscript{2}O flux with time during the day was observed in both land-use systems. Therefore, the measured N\textsubscript{2}O flux was adjusted to measuring time as was described in Chapter 2.15. After the flux observations were adjusted, they were ln-transformed. More sets of N\textsubscript{2}O flux were normally distributed when N\textsubscript{2}O flux was ln-transformed. Because a few flux observations were negative, a constant (one) was added to the flux values before they were ln-transformed. Ln-transformation of N\textsubscript{2}O fluxes has been used by others (e.g., Ambus and
Figure 6.1. Two sets of N$_2$O fluxes measured on two dates showing the trend of flux with time in crop and grass systems.
Christensen, 1994; Clayton et al., 1994; Ball et al., 1997; Rover et al., 1999). The ln-normal distribution reflects the high spatial variation of N\textsubscript{2}O production processes and the subsequent N\textsubscript{2}O transport through the soil profile to the surface (Rover et al., 1999). Aitchinson and Brown (1957) stated that the ln-normal distribution patterns were mostly the consequences of multi-factorial interactions of influencing factors.

Nitrous oxide flux varied between -0.04 and 0.029 mg m\textsuperscript{-2} min\textsuperscript{-1} in the crop system and between -0.014 and 0.045 mg m\textsuperscript{-2} min\textsuperscript{-1} in the grass system among all sampling locations and sampling dates. The magnitude of N\textsubscript{2}O flux was similar to that reported in the literature (Ambus and Christensen, 1994; Clayton et al., 1994; van den Pol-van Dasselaar et al., 1998). Soils in the grass system had a higher maximum and a wider range of N\textsubscript{2}O flux than in the crop system, but the difference of the mean flux between the two land-use systems was not significant. Ball et al. (1997) detected a lower range of N\textsubscript{2}O flux relative to the current study, and higher N\textsubscript{2}O flux in fertilized grassland than in fertilized cropland and the flux varied between 0.0 and 0.0018 mg m\textsuperscript{-2} min\textsuperscript{-1} in the cropland and between 0.0 and 0.0093 mg m\textsuperscript{-2} min\textsuperscript{-1} in the grassland. Unlike CO\textsubscript{2}, N\textsubscript{2}O concentrations inside the chamber decreased with time during the 10 minute measurement period most often for flux measurements obtained during the morning (e.g. Figure 6.2). During the morning when the soil temperature and the flux were low, N\textsubscript{2}O was most likely dissolved or reduced to N\textsubscript{2}. Figure 6.3b shows that the mean of N\textsubscript{2}O flux varied with seasons with the highest mean observed during summer and the lowest obtained during winter in crop and grass systems. In the crop system, the lowest spatial average of N\textsubscript{2}O flux (\(-5\times10^{-5}\) mg m\textsuperscript{-2} min\textsuperscript{-1}) was obtained on 31 January 2011 and the highest (\(1\times10^{-2}\) mg m\textsuperscript{-2} min\textsuperscript{-1}) was
Figure 6.2. As an example, cumulative concentrations of CO$_2$ (a) and N$_2$O (b) inside the chamber as a function of sampling time measured in locations 1 and 58 at 9:10 and 14:22 on 2 and 3 September 2010, respectively.
obtained on 21 June and 2 August 2010. On the other hand in the grass system, the lowest spatial average of N\textsubscript{2}O flux (-2x10\textsuperscript{-3} mg m\textsuperscript{-2} min\textsuperscript{-1}) was obtained on 30 September 2010 and the highest (2x10\textsuperscript{-2} mg m\textsuperscript{-2} min\textsuperscript{-1}) was observed on 6 July 2010. The spatial mean of N\textsubscript{2}O flux was similar in crop and grass systems when it was low during winter and varied between land uses when it was higher during summer (Figure 6.3b).

6.1.2 Spatial patterns of N\textsubscript{2}O flux in crop and grass systems

Overall and in both land-use systems, the highest N\textsubscript{2}O fluxes were several orders of magnitude greater than the mean, indicating that extensive sampling was needed. The coefficients of variation of not transformed N\textsubscript{2}O fluxes were large in both land-use systems (Figure 6.3c) and reflected their high spatial variability. Extremely large coefficients of variation were obtained as a result of hot spots in both land-use systems. High spatial coefficients of variation of N\textsubscript{2}O flux were also reported by other investigators (e.g., Mosier et al., 1981; Folorunso and Rolston, 1984; Rover et al., 1999; Choudhary et al., 2002). The highest coefficient of variation of N\textsubscript{2}O flux was obtained during winter and the lowest during summer when the flux was high in both land-use systems. Spatial coefficients of variation of N\textsubscript{2}O flux were similar for crop and grass systems when the flux was high during summer and differed between the two land-use systems when the flux was low during winter (Figure 6.3c). Ambus and Christensen (1995) compared the spatial variability among N\textsubscript{2}O fluxes from different land uses and found higher CVs for fluxes measured from abandoned farmland (617%) than from coastal grassland (400%). They found that the coefficient of variation values were the highest when N\textsubscript{2}O flux was high during summer and the lowest when the flux was low.
Figure 6.3. Daily precipitation and air temperature (a), mean (b), coefficient of variation (c), and variance (d) of N₂O fluxes measured in different times during a year in two land-use systems.
during winter in both land-use systems. Choudhary et al. (2002) observed higher variation of N\textsubscript{2}O flux during winter than during summer and fall in crop and grass systems. They stated that the higher variation of N\textsubscript{2}O flux during winter could be triggered by wet weather, which was more frequent and intense, creating favorable conditions for denitrification. In the current study, spatial variance of N\textsubscript{2}O flux behaved differently than the coefficient of variation in both land-use systems (Figure 6.3d). The highest spatial variance was obtained during fall, and the lowest was observed during winter in both land-use systems. The coefficient of variation of N\textsubscript{2}O flux was low during summer due to large mean values, and it was high during winter because of small mean values observed at the same period.

Spatial experimental semivariograms and their respective spherical models showed that the spatial variability of ln-transformed N\textsubscript{2}O fluxes was structured in only 8 measuring dates in the crop system and 10 in the grass system. Unstructured semivariograms for N\textsubscript{2}O fluxes showed nugget-to-sill ratios of 1.0 (Figure 6.4b). The nugget-to-sill ratios indicated that the spatial structure of N\textsubscript{2}O flux variability varied from weak to strong in crop and grass systems. Nugget semivariance of N\textsubscript{2}O flux was the highest during summer and fall and the lowest during the winter (Figure 6.4a). The spatial correlation length of N\textsubscript{2}O fluxes varied with time in both land uses (Figure 6.4c). Two measuring dates in the spring showed the longest spatial range in the grass system. No trend between the spatial range of N\textsubscript{2}O flux and seasonality was observed. In contrast, Turner et al. (2008) found a longer correlation length (73 m) for flux measured in February (summer) than spatial range (51 m) for flux measured in April (fall) in irrigated pasture in Australia. They
Figure 6.4. Spatial semivariogram parameters, nugget (a), nugget-to-sill ratio (b), and range (c), of N\textsubscript{2}O fluxes measured in different times during a year in two land-use systems.
found different results between seasons possibly because water filled pore space was higher in April (69-100%) than in February (35-100%) but soil temperature was higher in February (26 °C) than in April (19 °C). They found a higher/lower difference of spatial range between seasons unlike the present study most likely because their experimental site was irrigated and fertilized.

Spatial dependency of N₂O fluxes from managed grasslands may range from a few meters up to 100 m (Ambus and Christensen, 1994; Clayton et al., 1994; Van den Pol-van Dasselaar et al., 1998). Ball et al. (1997) reported that N₂O fluxes were highly spatially variable but not strongly spatially autocorrelated. They found a spatial structure of N₂O flux with a spatial correlation length of 10 to 15 m in fertilized grassland and random spatial variability in fertilized cropland. Velthof et al. (1996a) showed that N₂O fluxes from grassland were spatially dependent for a distance of less than 6 m. Velthof et al. (2000) investigated the spatial variability of N₂O flux measured during four consecutive days along a transect (400 m) on a fertilized sloping grassland soil. They stated that all variograms showed clear spatial dependency of ln-transformed N₂O fluxes with a spatial range of approximately 22 m. The application of nitrogen fertilizer just before the study period possibly disturbed the nature of spatial pattern of N₂O fluxes and decreased the distance of spatial dependency of the flux. Konda et al. (2010) found a strong spatial dependence of N₂O flux with a range of about 18 m in drier and wetter seasons in a 60 by 100 m plots measured at 10-m intervals in forest soil.
Other studies showed that the spatial variability of N$_2$O flux was weak or not structured in agricultural, grassland, and forest soils (Folorunso and Rolston, 1984; Clemens et al., 1999; Weitz et al., 1999; Ishizuka et al., 2005). Rover et al. (1999) found no spatial structure of N$_2$O flux in arable soil in a field plot site of 60 by 63 m where 7 m and 1 m (nested design) were the shortest sampling distances between the sampling locations. They stated that there was high micro-scale variability below 1.0 m distances, which emphasized the importance of microsites as sources of N$_2$O. Similarly, Ambus and Christensen (1994) found a spatial range <1 m in a 45 by 45 m grid designed for N$_2$O flux measurements from fertilized grassland. They reported that the high nugget variance and also emphasized the importance of soil microsites as sources of N$_2$O. The difference between the spatial range determined in the present study and that reported by others was due to the difference of selected measurement scales (scale triplet, Chapter 1.3.5) among these studies. A longer spatial range was expected for a larger measurement scale.

Results obtained in the present study in comparison to findings reported in the literature emphasized the relevance of the scale-triplet for planning experiments and sampling protocols. All considered semivariogram parameters are scale dependent, and comparing results obtained from experiments with different measuring scales can lead to wrong conclusions. Results from previous investigations and initial measurements help to determine the efficient sampling design but the measurement scale has to be similar to that for the compared investigations.
6.1.3 Temporal patterns of N$_2$O flux in crop and grass systems

N$_2$O fluxes in the crop system exhibited a higher average of coefficients of temporal variation than in the grass system but the difference was not significant. The coefficients of temporal variation of N$_2$O flux varied between 72 and 893% with an average of 167% in the crop system and between 108 and 238% with an average of 154% in the grass system. The average temporal variance of N$_2$O flux was significantly higher in the grass system than in the crop system. The temporal variance of N$_2$O flux varied between $8.1 \times 10^{-6}$ and $1.1 \times 10^{-4}$ mg m$^{-2}$ min$^{-1}$ among all measuring locations in the crop system and between $1.3 \times 10^{-5}$ and $1.1 \times 10^{-4}$ mg m$^{-2}$ min$^{-1}$ among all measuring locations in the grass system. The spatial behavior of the temporal variance was associated with the spatial behavior of the temporal mean of N$_2$O flux (Figure 6.5a and b). The seasonal variability of N$_2$O flux was a result of the influence of climatic factors such as rainfall and temperature.

The semivariogram analysis showed that the temporal variability of ln-transformed N$_2$O flux was structured in all sampling points except 5 locations in the crop and 4 locations in the grass system. Unstructured temporal semivariograms exhibited nugget-to-sill ratios of 1.0 (Figure 6.5c). It should be noted that 4 sampling points located in the transition zone between the crop and grass systems exhibited unstructured temporal variability. Sampling points located in the transition zones tended to exhibit higher variation of N$_2$O flux than in the rest of the field. The grass system had slightly higher nugget values than the crop system (Figure 6.5c). The nugget-to-sill ratio indicated that the temporal structure of N$_2$O
Figure 6.5. Temporal mean (a) variance and coefficient of variation (b), nugget and nugget-to-sill ratios (c), and temporal correlation length (d) of N₂O fluxes measured in crop and grass systems.
flux variability varied between weak and strong among the sampling locations in crop and grass systems (Figure 6.5c).

N₂O flux in the crop system exhibited a significantly longer average of a temporal correlation length than in the grass system. The temporal correlation length of N₂O flux varied between 55 and 220 days with an average of 129 days in the crop system and between 28 and 187 days with an average of 97 days in the grass system (Figure 6.5d). The results of temporal semivariogram parameters obtained in this study could not be compared with other studies because this type of analysis has not been used to quantify the temporal variability of N₂O fluxes.

6.1.4 Space-time field of N₂O flux in crop and grass systems

Figure 6.6a shows the space-time field of N₂O flux in crop and grass systems. It shows that the variation of N₂O flux was more pronounced in time than in space in both land-use systems. This pronunciation of the temporal variation was more obvious during summer and early fall when the soil was warm and moist. During winter, on the other hand, the temporal variation was more stable in both land-use systems. The space-time field analysis showed also that the spatial patterns of N₂O flux were temporally stable in both land-use systems. These temporally stable patterns were more obvious during winter than the other times of the year.
Figure 6.6. Space-time field (a) computed based on the isotropic model (b) of spatially and temporally measured and ln-transformed N$_2$O flux.
The results indicated that N₂O flux varied in space and time during summer when the flux was high with more pronunciation in time than in space during these periods in crop and grass systems. Velthof et al. (2000) used a space-time variogram to show that the variability of N₂O flux in space was much higher than the variability in time. Their results differ from the present study most likely because they estimated the flux in a smaller temporal domain size (four days) and they measured the flux in sloping and fertilized grassland. Topography and soil management (fertilizer applied just before the experimental period) possibly influenced the nature of spatial and temporal patterns of N₂O fluxes.

### 6.1.5 Temporal stability of spatially measured N₂O flux in crop and grass systems

The temporal stability of N₂O flux was quantified using the mean relative difference analysis. Figure 6.7 shows the estimated mean relative difference of N₂O flux from the mean for all sampling locations in crop and grass systems. Overall, N₂O fluxes exhibited high mean relative differences in crop and grass systems. One sampling location (location 2) in the crop system and two sampling locations (locations 29 and 32) in the grass system showed mean relative difference <0.2. It should be noted that sampling point 29 was located in the transition zone between the crop and grass systems. These sampling points can provide the mean value of N₂O flux for the entire field. It should be noted also that these three sampling locations (2, 29, and 32) had mean relative differences of CO₂ flux less than ±0.1 (Figure 5.8). Sampling locations 9 and 10 gave the lowest and the highest N₂O fluxes (mean relative differences), respectively for the entire field.
Figure 6.7. Spatially measured N$_2$O flux ranked by temporal relative deviation from the median. Vertical bars refer to associated standard deviation of relative differences.

Numbers refer to measuring locations.
The Spearman rank correlation analysis was used to quantify the temporal stability of N₂O flux. The Spearman correlation coefficient was calculated to determine the correlation between two spatial sets of N₂O flux measured at different times during the year. There were significant correlations between fluxes measured on five consecutive sampling dates from 16 August to 15 October 2010 (Table 6.1). It indicated that N₂O flux was temporally stable for 60 days during fall when the flux was high. Another set of three consecutive sampling dates from 1st March to 28 March 2011 showed significant correlations of N₂O flux, which indicated that N₂O flux was temporally stable for 27 days during spring. Temporal stability of spatial patterns of N₂O fluxes revealed that geostatistics can be used for quantifying and predicting behaviors of fluxes measured at any time during that period. Velthof et al. (2000) stated that the geostatistical analysis of fluxes measured at different times only provided accurate information about spatial patterns when both the magnitude of the flux and the spatial pattern of the fluxes did not change in time.

Ambus and Christensen (1994), Clayton et al. (1994), and Velthof et al. (1996b) also found a persistent spatial pattern of N₂O fluxes from grassland in a period of a few days to three weeks. Van Kessel et al. (1993) stated that denitrification rates in soil might fluctuate in time but its spatial patterns may persist up to a whole growing season. Others have used the Spearman rank correlation to quantify the temporal stability of N₂O flux in different land uses. For example, Ambus and Christensen (1995) calculated the Spearman correlation coefficients between measuring dates of N₂O fluxes in different land uses and found temporal stability of the flux from only coastal grassland. Ambus and Christensen
Table 6.1. The Spearman rank correlation coefficients between sampling dates of ln-transformed N$_2$O flux for the entire field.

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*Correlation is significant at the 0.05 level
(1994) also found temporal stability of N₂O fluxes from fertilized grassland as indicated from significant Spearman correlations between sampling dates. Christensen et al. (1996) stated that the spatial distribution of hot spots of denitrification activity persisted for periods ranging from days to weeks. They obtained the temporal stability of N₂O flux from 30 locations measured 8 times by ranking the sampling locations in order of increasing activity on each of the eight sampling dates. Also they used the Spearman rank correlation to compare ranks of denitrification rates between sampling days.

6.2 Biochemical and physical factors controlling N₂O fluxes in crop and grass systems

This sub-chapter focuses on the relationships between N₂O flux and different biochemical and physical factors in crop and grass systems. It also emphasizes the spatial and temporal associations between N₂O fluxes and biochemical and physical factors in crop and grass systems.

6.2.1 Relationships of N₂O flux with soil temperature and soil water content in crop and grass systems

The spatial and temporal distribution of soil temperature at 5 cm depth and average soil water content at 0-30 cm depth in crop and grass systems were described in Chapter 5 (Section 5.2.1). Soil temperature influenced N₂O flux in crop and grass systems. Figure 6.8 shows the relationship between soil temperature and N₂O flux in crop and grass systems. An increase of soil temperature led to increasing N₂O flux in both land-use systems. The relationship between soil temperature and N₂O flux was similar in both
land-use systems at low soil temperature but a wider scatter was observed in the grass system at higher soil temperature than in the crop system.

The relationship between soil temperature and \( \text{N}_2\text{O} \) flux exhibited a steeper slope in the grass system than in the crop system (Figure 6.8). The relationship between \( \text{N}_2\text{O} \) flux and soil temperature accounted for approximately 50 and 40% of \( \text{N}_2\text{O} \) flux variability in the crop and grass systems, respectively (Figure 6.8).

The relationships between the average of soil water content and \( \text{N}_2\text{O} \) flux in crop and grass systems are shown in Figure 6.9. The influence of soil water content on \( \text{N}_2\text{O} \) flux was more obvious in the grass than in the crop system. \( \text{N}_2\text{O} \) flux increased with increasing soil water content then it decreased with further increase of soil water content in both land-use systems. It seemed that the activity of nitrification peaked then declined as the soil became anaerobic. Davidson (1991) reported that if the water content was less than field capacity, nitrification was the main source of \( \text{N}_2\text{O} \), and denitrification was the main source if water content was higher than the field capacity.

Similar to the data analysis performed for \( \text{CO}_2 \) flux (Chapter 5), the influences of both soil temperature and soil water storage on \( \text{N}_2\text{O} \) flux were investigated using contour maps. Figure 6.10 shows contour maps for kriged ln-transformed \( \text{N}_2\text{O} \) fluxes with soil temperature measured at 5 cm and soil water storage at 0-30 cm depth in crop and grass systems. These contour maps provided a better insight to understand the influence of soil temperature and soil water storage together on surface \( \text{N}_2\text{O} \) fluxes in crop and grass systems. They showed that \( \text{N}_2\text{O} \) flux was low under low soil temperature and low soil
Figure 6.8. \( \text{N}_2\text{O} \) flux as a function of soil temperature at 5 cm depth in crop and grass systems. The flux and temperature were measured in each of 60 locations every two weeks for a year except during winter when they measured every month. Each symbol represents a particular flux vs. temperature measurement for a particular location and at a particular time.
Figure 6.9. N₂O flux as a function of average soil water content at 0-30 cm depth in crop and grass systems. The flux and water content were measured in each of 60 locations every two weeks for a year except during winter when they measured every month. Each symbol represents a particular flux vs. moisture measurement for a particular location and at a particular time.
water storage conditions in both land-use systems. In the crop system, soil temperature had more obvious impacts on N$_2$O flux than soil water storage (Figure 6.10a). The highest N$_2$O flux occurred under high soil temperature and high soil water storage conditions in the crop system. At the highest measured soil temperature, N$_2$O flux decreased with increasing soil water storage then increased to maximum as soil water storage further increased in the crop system. This behavior can be an indication that the nitrification process was the main source of N$_2$O under high temperature and low soil water storage and denitrification was the main source under high temperature and high soil water storage in the crop system. In the grass system, on the other hand, there was no clear impact of soil water storage on N$_2$O flux under low soil temperature but the influence of soil water storage was more obvious under high soil temperature (Figure 6.10b). The highest N$_2$O flux occurred under high soil temperature and low soil water storage conditions and decreased as soil water storage increased in the grass system. The observation of the highest N$_2$O flux under low soil water storage and high soil temperature indicated that nitrification was the main source of N$_2$O in the grass system.

The Spearman correlation analysis showed that N$_2$O fluxes spatially positively and negatively correlated with soil temperature and only correlated positively with average water contents on a few measuring dates in crop and grass systems (Figure 6.11a and b). Temporal correlations showed that soil temperature positively influenced N$_2$O fluxes at all sampling points in crop and grass systems except two located in the transition zone between the two land uses (Figure 6.11c). Average water contents temporally correlated with N$_2$O fluxes at a few measuring locations only in the crop system.
Figure 6.10. Contour maps show \( \text{N}_2\text{O} \) flux as a function of soil temperature measured at 5 cm depth and total soil water storage measured at 0-30 cm depth in crop (a) and grass (b) systems.
Figure 6.11. The spatial correlation coefficients for N₂O flux with soil temperature at 5 cm depth (a), soil water content at 0-30 cm depth (b), and temporal correlation coefficient for N₂O flux with soil temperature and soil moisture (c) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
Similar to most biological processes in soil and within a particular range of temperature, microbial activities such as nitrification and denitrification increase with increasing soil temperature. Other studies have shown a relationship between N₂O flux and soil temperature. For example, Mummey et al. (1997) found that N₂O flux was limited by low temperature during winter. In contrast, other studies found significant N₂O production under cold conditions (e.g., Sommerfeld et al., 1993) which indicated that other factors and their reaction with soil temperature such as soil moisture influenced the N₂O flux.

The influence of soil water content on N₂O flux was more obvious in the grass than in the crop system because there was a wider range of soil water content at 0-30 cm depth in the grass than in the crop system (Figure 5.11). Soil water content was lower in the grass than in the crop system during the growing season, most likely because the transpiration rate was higher because the plant-roots being denser and deeper in the grass system. Soil water content could control the emission of N₂O because nitrification tends to occur under aerobic environment while denitrification tends to occur under anaerobic environments in soils. Diffusion of NH₄⁺ and NO₂⁻ and movement of nitrifiers are also affected by soil water content. Besides the impact of soil water on gas exchange and a variety of soil chemical reactions, soil moisture also can play an important role on nutrient availability for soil microorganisms. Stark and Firestone (1995) reported that in moist soil, a decrease of nitrification rates can be due to either not enough oxygen or not enough NH₄ being available in soil. They stated that in dry soil, nitrification rates might decrease due to the effect of dehydration on the nitrifying bacteria.
Soil water content can influence oxygen diffusion and oxygen is important factor controlling denitrification. For example, Velthof et al. (2000) obtained a significant correlation between soil water content and N$_2$O flux in a fertilized sloping grassland soil. They observed higher fluxes on the wettest parts of a transect. Choudhary et al. (2002) observed that the lowest N$_2$O flux occurred when soil water content was low in crop and grass systems and tended to increase with higher soil water content. Konda et al. (2010) reported that N$_2$O flux showed a clear seasonal difference, with significantly higher flux in the wetter season than in the drier season.

### 6.2.2 Relationships of N$_2$O flux with soil biochemical properties in crop and grass systems

Biochemical properties and processes considered for this data analysis included CO$_2$ flux, soil organic matter, total nitrogen, carbon to nitrogen ratio, and soil pH. Soil surface CO$_2$ flux can be a representative factor of soil microbial populations and activities. Figure 6.12 shows that CO$_2$ flux was related to N$_2$O flux in both land-use systems with increasing N$_2$O flux when CO$_2$ flux increased. The figure shows also that the relationship between CO$_2$ and N$_2$O fluxes was more scattered in the grass than in the crop system especially when CO$_2$ flux was high. This can be because N$_2$O flux exhibited a wider range in the grass than in the crop system. The relationship between CO$_2$ and N$_2$O fluxes exhibited a steeper slope in the crop than in the grass system.

The Spearman correlation analysis was used to quantify the influence of the other soil biochemical factors on N$_2$O fluxes in crop and grass systems. It should be noted that
Figure 6.12. N$_2$O flux as a function of CO$_2$ flux in crop and grass systems. The fluxes were measured in each of 60 locations every two weeks for a year except during winter when they were measured every month. Each symbol represents a particular N$_2$O flux vs. CO$_2$ flux for a particular location and at a particular time.

\[ y = 0.0037x^2 + 0.0031x - 0.0018 \]
\[ R^2 = 0.3725 \]

\[ y = 0.0053x^2 + 0.0022x - 0.0009 \]
\[ R^2 = 0.4032 \]
these biochemical properties were measured once in soils sampled on 22 July 2010. Total soil organic matter and total nitrogen at 0-30 cm depth did not significantly correlate with N$_2$O flux measured during any season in the crop system. On the other hand, soil organic matter significantly and positively correlated with N$_2$O fluxes measured during summer and fall in the grass system (Figure 6.13a). Soil nitrogen negatively influenced N$_2$O fluxes measured during fall and winter in the grass system. The carbon-to-nitrogen ratio at 0-30 cm depth significantly and positively correlated with N$_2$O fluxes measured only during winter in the crop system and only during fall in the grass system. Soil pH significantly and negatively correlated with N$_2$O fluxes measured on different sampling dates during summer and fall seasons in the crop system, but did not significantly correlate with N$_2$O flux in the grass system (Figure 6.13d).

The correlations between the selected soil biochemical properties and N$_2$O fluxes varied with season because the range of observations and the spatial variation of N$_2$O fluxes varied with season. A relationship between CO$_2$ and N$_2$O fluxes was obtained in both land-use systems because nitrifiers gained carbon by the fixation of CO$_2$ (Coyne, 1999). Another explanation can be that increasing CO$_2$ flux was related to increased mineralization and as a result increased NH$_4$ which was used by nitrifiers. Ball et al. (1997) reported significant positive correlation between N$_2$O and CO$_2$ concentrations in grassland and stated that soil respiration was creating a suitably anaerobic environment for denitrification. Soil organic matter was an important factor because it is an essential source of mineral nitrogen for soil microorganisms. Soil organic matter and total nitrogen significantly influenced N$_2$O flux in the grass system and not in the crop system.
Figure 6.13. The Spearman correlation coefficients for N$_2$O flux with soil organic matter (a), total nitrogen (b), C/N (c), and soil pH (d) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
likely because soil organic matter and total nitrogen were higher in the grass than in the crop system. Denitrification strongly depends on carbon availability. Electrons would be unavailable to further reduce N$_2$O if carbon was limited. Coyne (2008) reported that denitrification in soil was associated with organic matter and water-soluble carbon accounted for 71% of the denitrification potential. He also stated that because organic matter distribution in soil was extremely variable, denitrification in soil was expected also to be extremely variable in space. Ambus and Christensen (1994) reported a several-fold increase in N$_2$O flux in response to glucose application in fertilized grassland and stated that it was an indication that denitrification was the main source of N$_2$O.

Other studies have shown positive correlations between N$_2$O flux and total nitrogen and between N$_2$O emission and total carbon (Kosugi et al., 2007; Konda et al., 2008; Nishina et al., 2009b). Konda et al. (2010) also found a negative correlation between N$_2$O flux and total nitrogen content in forest soil. Choudhary et al. (2002) stated that the spatial variability of N$_2$O fluxes in grassland and cropland could be attributed to hot-spots associated with soil organic matter and nitrate level. Christensen and Tiedje (1998) and Clemens et al. (1999) reported that the formation of these hot-spots was governed by the creation of anaerobic conditions due to increasing respiration following an application of organic matter to the soil in their study. Yanai et al. (2003) stated that soil organic matter and soil pH were the main determining factors for N$_2$O fluxes in a cropped field.

Soil pH significantly influenced N$_2$O emission in the crop system and its correlation with the flux was not significant in the grass system, possibly because the mean of soil pH was
significantly higher in the grass than in the crop system. High soil pH can inhibit NO$_2^-$ oxidizers and low pH can inhibit NH$_4^+$ oxidizers. Schmidt (1982) reported that nitrification was most rapid in natural to alkaline soils, and nitrification rates fall markedly below pH 6 and became negligible below pH 5. Nitrous oxide reductase was acid sensitive and low pH affected its activity (Coyne, 1999). Ball et al. (1997) reported a significant negative correlation between N$_2$O concentration and soil pH in grassland but not in cropland.

6.2.3 Relationships of N$_2$O flux with soil physical properties in crop and grass systems

The Spearman correlation analysis was also used to quantify relationships between soil physical factors and N$_2$O fluxes in crop and grass systems. Soil physical properties and functions considered in this analysis included soil texture fractions, soil bulk density, aggregate size distribution, soil water retention characteristics, gas diffusivity, air-filled porosity, and the pore-continuity index functions.

Sand and silt contents significant positively correlated with N$_2$O flux in the grass system and negatively in the crop system in some measuring dates during summer and fall when the flux was high (Figure 6.14a and b). Different relations for N$_2$O flux with sand and silt contents in crop from grass system were most likely due to soil structure difference between the two land uses. Over all, the clay content had more positive correlations with N$_2$O fluxes in the crop and more negative correlations in the grass system, and it was significantly negatively correlated with the flux in the grass system during summer (Figure 6.14c). Soil texture can play an important role of N$_2$O flux by influencing soil
Figure 6.14. The Spearman correlation coefficients for N$_2$O flux with average sand (a), silt (b), and clay (c) at 0-30 cm depth in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
water content, soil organic matter and nutrient availability, soil porosity, and soil gas transport properties. The influence of soil texture on N$_2$O fluxes was indirect and it was related to the interaction of soil porosity with soil organic matter and nutrient and to soil structure.

Soil dry bulk density had a significant and positive influence on N$_2$O fluxes measured on only a few dates during summer, fall, and spring in the crop system but did not significantly correlate with the N$_2$O fluxes in the grass system (Figure 6.15a). Konda et al. (2010) also found a positive correlation between N$_2$O flux and bulk density in forest soil. Bulk density reflects soil porosity and the latter is important for soil microorganisms and their activities. The difference of the relationship of N$_2$O flux with bulk density between the two land uses was because the grass system had higher soil porosity than the crop system.

Overall, N$_2$O flux had more positive correlations with the aggregate mean weight diameter and the large aggregate-size class (>2 mm) in the grass system and more negative correlations in the crop system (Figure 6.15a and b). However, the flux had more positive correlations with small aggregate class (<0.053 mm) in the crop system and more negative correlations in the grass system (Figure 6.15c). The aggregate mean weight diameter and the large aggregate-size class (>2 mm) significantly correlated with N$_2$O flux measured during warm and moist seasons when the flux was high. The small aggregate-size class (<0.053 mm) significantly correlated with N$_2$O fluxes measured in all seasons. Large aggregate size is associated with large pores and the latter is an
Figure 6.15. The Spearman correlation coefficients for N$_2$O flux with bulk density (a), the aggregate mean weight diameter (b), large aggregate class (>2 mm) (c), and small aggregate class (<0.053 mm) (d) at 0-15 cm depth in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
important controlling factor on gas emission from soil. Large aggregate size contains more organic matter than small aggregates and organic matter has an influence on microbial activities especially on denitrification in soil. The difference of the relationships between aggregate size distribution and N$_2$O fluxes between crop and grass systems was because the grass system had more developed soil structure with larger aggregate mean weight diameter and larger content of large aggregates than the crop system.

The inverse air entry of the soil water retention curve $\alpha$ negatively correlated with N$_2$O flux measured during summer and fall in the crop system and positively correlated with fluxes measured during fall in the grass system (Figure 6.16a). The slope of the retention curve $n$ negatively correlated with N$_2$O flux measured only on 2 September 2010 in the crop system and did not significantly correlate with the flux in the grass system. Soil water content at saturation $\theta_s$ negatively correlated with N$_2$O fluxes measured during summer and spring in the crop system and did not significantly correlate with the flux in the grass system. Soil water content at -1000 cm matric potential positively correlated with N$_2$O flux measured on 25 November 2010 in the crop system and negatively correlated with the flux measured on 13 April 2011 in the grass system. Soil water retention characteristics are measurements of soil pore size distribution. The significant relations between these characteristics and N$_2$O flux reflected the influence of soil structure and soil physical factors on the flux. The negative correlations of $\alpha$, $n$, and $\theta_s$ and positive correlation of $\theta_\text{-1000}$ with N$_2$O fluxes indicated the importance of soil aeration and oxygen availability for the production of N$_2$O.
Figure 6.16. The Spearman correlation coefficients for N$_2$O flux with soil water retention characteristics, $\alpha$ (a), $n$ (b), $\theta_s$ (c), and $\theta(-1000)$ (d) in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
Relative gas diffusivity at different soil aeration status, except at -10 matric potential in the crop system, significantly and negatively influenced N$_2$O flux in the crop system and positively correlated with N$_2$O flux in the grass system. The significant correlations between relative gas diffusivity and N$_2$O fluxes were obtained during different seasons in both land-use systems (Figure 6.17). Significant and negative correlations were obtained between air-filled porosity at all selected matric potentials and N$_2$O flux measured on 25 November 2010 in the crop system (Figure 6.18). Air-filled porosity at lower matric potentials, -1000, -333, and -100 cm, also negatively correlated with flux measured on 28 April 2011 in the crop system (Figure 6.18). In the grass system, on the other hand, air-filled porosity at -10 and -50 cm matric potentials positively correlated with N$_2$O fluxes measured during summer and fall. Air-filled porosity at low water content statuses did not significantly correlate with N$_2$O fluxes in the grass system. Over all, N$_2$O fluxes had more positive correlation with the pore-continuity index in the grass system and more negative correlations in the crop system (Figure 6.19). At high matric potentials, -50 and -10 cm, the pore-continuity index significantly correlated with N$_2$O fluxes only in the grass system. The pore-continuity index at -1000 cm matric potential did not significantly correlate with N$_2$O fluxes in either land-use system.

Gas transport characteristics were important factors influencing N$_2$O flux because they controlled gas (N$_2$O, CO$_2$, and O$_2$) exchange between soil and the atmosphere. Oxygen is important to nitrification because chemoautotrophic nitrifiers are obligate aerobes (Coyne, 1999). Oxygen is the most controlling factor for denitrification in soils by inhibiting denitrifying enzyme synthesis and electron flow to denitrifying enzymes.
Figure 6.17. The Spearman correlation coefficients for N$_2$O flux with relative gas diffusivity at -10, -50, -100, -333, and -1000 cm matric potentials in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
Figure 6.18. The Spearman correlation coefficients for N₂O flux with air-filled porosity at -10, -50, -100, -333, and -1000 cm matric potentials in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
Figure 6.19. The Spearman correlation coefficients for N$_2$O flux with the pore-continuity index at -10, -50, -100, -333, and -1000 cm matric potentials in crop and grass systems. The dashed line refers to the significance at 0.05 levels, either positive or negative.
(Coyne, 1999). McTaggar et al. (2002) also found strong relationships between N$_2$O fluxes and air-filled porosity and relative gas diffusivity in four different types of soil with different soil texture.

N$_2$O flux did not significantly correlate with some of the selected soil biochemical and physical factors on some dates possibly due to the complex reactions among different factors which can affect the production of N$_2$O in soil. Beauchamp (1997) stated that “the complexity of physical, chemical, and biological factors and their interacting effects on N$_2$O-producing processes in soils, and the uncertainties about measurements have made the development of global N$_2$O budgets very tentative”.

The relationships between N$_2$O fluxes and some of the selected controlling factors were not significant, and others were significant for fluxes measured on some dates and not significant for fluxes measured on others. Poor relationships between N$_2$O flux and different soil variables were also found by others (e.g., Ambus and Christensen, 1995; Velthof et al., 1996a). Van den Pol-van Dasselaar et al. (1998) found poor relationships between N$_2$O fluxes and different controlling factors and stated that the poor relationships could be because soil processes and properties were determined using soil cores with a surface area 18-fold magnitude smaller than the area where the N$_2$O emission was measured. They stated that the volume of the soil cores may not have fully represented the spatial and temporal distribution of the soil processes and properties. Another reason they reported weak relations was that the soil processes and properties were measured at the top 20 cm of the soil profile while N$_2$O emission integrated the activity of the whole
soil profile. For example, Christensen et al. (1996) found the main N$_2$O producing layers just above the groundwater at a depth of 1 m. Another reason for the observed poor relationships can be because measuring soil processes and properties using soil cores did not accurately represent the integrated effect of multi interactions of factors in soil microsites controlling N$_2$O emissions.

6.2.4 Temporal associations of N$_2$O flux with soil temperature, soil water content, and CO$_2$ flux in crop and grass systems

To quantify the temporal relationships between N$_2$O flux and soil temperature and between N$_2$O flux and soil water content using cross-semivariogram analysis, three measuring locations in the crop system (4, 20, and 27) and three measuring locations in the grass system (32, 35, and 43) were selected. These six measuring locations showed mean relative differences from the mean of N$_2$O flux close to zero and small standard deviations (<10) (Figure 6.7). Locations with mean relative differences close to zero can provide the mean N$_2$O flux for the entire field.

The temporal variability of N$_2$O fluxes measured at the selected locations was structured in both land-use systems (Figure 6.5). The semivariogram analysis showed that the temporal variability of soil temperature and average soil water content at 0-30 cm measured at the selected locations in the crop and grass systems was structured (Figures A10.1, A10.2 in Appendix 10). All semivariograms for soil temperature were structured for the selected locations in both land-use systems. The temporal nugget semivariance for soil temperature was smaller in the grass than in the crop system for the selected
measuring locations (Table 6.2). Semivariograms of soil water content measured at the selected locations exhibited longer temporal correlation lengths in the grass system relative to the crop system (Table 6.2). The nugget-to-sill ratio indicated that the spatial structure of soil water content was strong for all selected locations in both land-use systems.

The cross-semivariogram analysis showed that N$_2$O flux was temporally associated with soil temperature measured at all selected locations in crop and grass systems (Figures A11.1, A11.2 in Appendix 11). The temporal structure of the association between N$_2$O flux and soil temperature was strong for all selected locations in crop and grass systems as indicated by the nugget-to-sill ratios (Table 6.3).

N$_2$O flux was temporally associated with average soil water content measured at all selected locations in crop and grass systems as indicated from structured cross-semivariograms (Figures A11.3, A11.4). Only one cross-semivariogram for location 20 was unbounded. The temporal association between N$_2$O flux and water content was positive in the grass system and negative in the crop system. That can be due to the impact of soil structure and soil organic matter on soil moisture, and because of a wider range of soil water content obtained in the grass relative to the crop system. The dependency of the temporal relationship between N$_2$O flux and soil water content as indicated by nugget-to-sill ratios was strong for all selected locations with bounded cross-semivariograms (Table 6.3).
Table 6.2. Temporal semivariogram parameters for soil temperature and average soil water content at the upper 0-30 cm measured at selected locations in crop and grass systems.

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<th>Grass system</th>
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<td>Range (day)</td>
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<td>Nugget (°C)^2</td>
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<tr>
<td>Nugget/sill</td>
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<td>-</td>
</tr>
<tr>
<td>Range (day)</td>
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</tr>
<tr>
<td>Nugget (m^3 m^-3)^2</td>
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<tr>
<td>Nugget/sill</td>
<td>0.26</td>
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Table 6.3. Temporal cross-semivariogram parameters for N$_2$O flux with soil temperature, average soil moisture at 0-30 cm depth, and CO$_2$ flux measured at different locations in crop and grass systems.

<table>
<thead>
<tr>
<th>Locations</th>
<th>Crop system</th>
<th>Grass system</th>
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<tr>
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</tr>
<tr>
<td>Range (day)</td>
<td>247.9</td>
<td>208.5</td>
</tr>
<tr>
<td>Nugget</td>
<td>$8 \times 10^{-3}$</td>
<td>0.0</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.09</td>
<td>0.0</td>
</tr>
</tbody>
</table>

N$_2$O flux vs. soil water content

| Range (day) | 155.2 | - | 128.8 | 121.0 | 125.0 | 103.4 |
| Nugget | $2 \times 10^{-5}$ | $1 \times 10^{-5}$ | $2 \times 10^{-6}$ | $4 \times 10^{-5}$ | $4 \times 10^{-5}$ | $8 \times 10^{-5}$ |
| Nugget/sill | 0.24 | - | 0.12 | 0.21 | 0.13 | 0.20 |

N$_2$O flux vs. CO$_2$ flux

| Range (day) | 241.4 | 235.2 | - | 180.3 | 180.1 | 131.9 |
| Nugget | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nugget/sill | 0.0 | 0.0 | - | 0.0 | 0.0 | 0.0 |
N\textsubscript{2}O and CO\textsubscript{2} fluxes were temporally associated for all selected measuring locations in crop and grass systems (Figures A11.5, A11.6). The temporal structure of the association between N\textsubscript{2}O and CO\textsubscript{2} fluxes was strong for all selected locations in crop and grass systems with longer temporal ranges found for locations in the crop than in the grass systems (Table 6.3).

Strong temporal associations for N\textsubscript{2}O flux with soil temperature and soil water content indicated that these factors had a significant influence on the temporal variability of N\textsubscript{2}O fluxes in crop and grass systems. The strong temporal relationship between N\textsubscript{2}O and CO\textsubscript{2} fluxes indicated the influence of nitrogen mineralization on N\textsubscript{2}O flux. Soil respiration reflected microbial activity and nitrogen mineralization in soil. The relationships between N\textsubscript{2}O emission and soil temperature, soil water content, and CO\textsubscript{2} flux have been a concern for other investigators; however the cross-semivariogram analysis has not been used before by others to quantify these relationships.

6.2.5 Spatial associations for N\textsubscript{2}O flux with soil temperature and soil water content in crop and grass systems

The spatial relationships for N\textsubscript{2}O flux with soil temperature and soil water content were quantified using data sets of these three variables measured in three different seasons, 21 June, 31 December 2010, and 17 March 2011. The spatial variability of soil temperature and average soil water content measured on all selected measuring dates was structured in crop and grass systems (Chapter 5, Figure A12.1). The spatial variability of average
water content measured on 21 June 2010 was structured only in the grass system (Figure A12.1), therefore its relationship with N₂O fluxes was quantified only in the grass system. The spatial variability of N₂O fluxes measured on the selected dates also was structured in both land-use systems as shown earlier in this chapter. The spatial relationships between N₂O fluxes and other variables were not quantified in the fall because the spatial variability of the flux was not structured in either land use during this season (Figure 6.4).

The cross-semivariogram analysis showed that N₂O flux was spatially associated with soil temperature only in spring in the crop system and in winter and spring in the grass system (Figure A12.2). The spatial relationship between N₂O flux and soil temperature was inverse in the crop system and positive in the grass system. The spatial association between N₂O flux and soil temperature measured in spring exhibited a longer spatial correlation length in the crop than in the grass system (Table 6.4). The structure of the spatial association between N₂O flux and soil temperature was moderate for all structured cross-semivariograms in crop and grass systems.

N₂O flux and average soil water content were spatially associated as quantified using the cross-semivariograms in crop and grass systems only in spring in the crop system and in summer and spring in the grass system (Figure A12.3). The spatial relationship between N₂O flux and soil moisture was negative in the crop system and negative in summer and positive in spring in the grass system. The spatial correlation length for the spatial
Table 6.4. Spatial cross-semivariogram parameters for N\textsubscript{2}O flux with soil temperature and average soil moisture at 0-30 cm measured at different dates in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>Crop system</th>
<th></th>
<th>Grass system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21-Jun-10</td>
<td>31-Dec-10</td>
<td>17-Mar-11</td>
<td>21-Jun-10</td>
</tr>
<tr>
<td>N\textsubscript{2}O flux vs. soil temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>14.4</td>
<td>-</td>
<td>8.2</td>
</tr>
<tr>
<td>Nugget</td>
<td>2x10\textsuperscript{-3}</td>
<td>3x10\textsuperscript{-4}</td>
<td>1x10\textsuperscript{-3}</td>
<td>6x10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>1.0</td>
<td>0.28</td>
<td>1.0</td>
</tr>
<tr>
<td>N\textsubscript{2}O flux vs. soil water content</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>34.5</td>
<td>20.2</td>
<td>-</td>
</tr>
<tr>
<td>Nugget</td>
<td>-</td>
<td>3x10\textsuperscript{-6}</td>
<td>1x10\textsuperscript{-6}</td>
<td>4x10\textsuperscript{-6}</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>-</td>
<td>1.0</td>
<td>0.11</td>
<td>0.09</td>
</tr>
</tbody>
</table>
relationship between N\textsubscript{2}O flux and soil water content measured in spring was longer in the crop than in the grass system (Table 6.4). The spatial dependence of the relationship between N\textsubscript{2}O flux and soil water content, as was indicated from the nugget-to-sill ratio, was strong for all structured cross-semivariograms in both land uses. N\textsubscript{2}O fluxes were spatially associated with soil temperature and average water content in both land-use systems in the spring possibly because they exhibited the longest spatial range, strong spatial dependency, and low nugget semivariance especially in the grass system.

### 6.2.6 Spatial associations between N\textsubscript{2}O flux and biochemical properties in crop and grass systems

Cross-semivariogram analysis was also used to quantify the spatial relationships between N\textsubscript{2}O flux and soil biochemical properties in crop and grass systems. Soil biochemical properties included soil organic matter, total nitrogen, and soil pH. The spatial variability of these selected biochemical properties was structured in both land-use systems (Chapters 4 and 5).

The cross-semivariograms for N\textsubscript{2}O fluxes with soil organic matter were structured when fluxes were measured in winter and spring in the crop system and only in spring in the grass system (Figure A13.1). A structured cross-semivariogram indicated a spatial relationship between soil organic matter and N\textsubscript{2}O flux. The structure of the spatial association between N\textsubscript{2}O flux and soil organic matter varied between moderate and strong in the crop system and was moderate in the grass system as indicated from the nugget-to-sill ratio (Table 6.5). Soil total nitrogen was also spatially associated with N\textsubscript{2}O
flux measured in only winter and spring in crop and grass systems, respectively, with strong spatial structure in both land-use systems (Figure A13.2).

The result showed that the spatial associations of N$_2$O fluxes with total nitrogen and between N$_2$O flux and soil organic matter were similar in winter and spring in crop and grass systems, respectively, with similar nugget-to-sill ratios and spatial ranges. The coefficient of variation and variance of soil organic matter and N$_2$O fluxes (except for flux measured on 31 December 2010) were larger in the grass system than in the crop system, which might explain the differences of the spatial relationship of N$_2$O flux with soil organic matter between crop and grass systems.

The cross-semivariogram analysis showed that N$_2$O flux was spatially associated with soil pH in summer and winter in the crop system and only in spring in the grass system (Figure A13.3). The spatial relationship between N$_2$O flux and soil pH was negative in the crop system and positive in the grass system. The spatial structure of the association between N$_2$O flux and soil pH was moderate and strong in the crop system and moderate in the grass system (Table 6.5). Soil pH exhibited larger coefficient of variation and variance in the crop system than in the grass system, however N$_2$O flux showed higher spatial variation in the grass system than in the crop system except for flux measured in winter. N$_2$O flux was spatially associated with CO$_2$ flux measured on all selected sampling dates with strong spatial dependence as indicated from nugget-to-sill ratios in crop and grass systems (Figure A13.4). The results showed that N$_2$O fluxes spatially correlated with all selected biochemical properties in winter (low flux) in the crop system
Table 6.5. Spatial cross-semivariogram parameters for N$_2$O flux with selected soil biochemical properties in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>Crop system</th>
<th></th>
<th>Grass system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>26.4</td>
<td>27.7</td>
<td>-</td>
</tr>
<tr>
<td>Nugget</td>
<td>2x10^{-4}</td>
<td>0.0</td>
<td>1x10^{-4}</td>
<td>3x10^{-4}</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>0.0</td>
<td>0.38</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>N$_2$O flux vs. SOM</td>
<td>N$_2$O flux vs. TN</td>
<td>N$_2$O flux vs. pH</td>
<td>N$_2$O flux vs. CO$_2$ flux</td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>28.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nugget</td>
<td>0.0</td>
<td>1x10^{-6}</td>
<td>0.0</td>
<td>2x10^{-5}</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>0.05</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Range (m)</td>
<td>9.7</td>
<td>11.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nugget</td>
<td>5x10^{-4}</td>
<td>1x10^{-4}</td>
<td>3x10^{-5}</td>
<td>5x10^{-5}</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.23</td>
<td>0.33</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Range (m)</td>
<td>4.3</td>
<td>12.4</td>
<td>14.6</td>
<td>36.7</td>
</tr>
<tr>
<td>Nugget</td>
<td>0.0</td>
<td>1x10^{-6}</td>
<td>2x10^{-5}</td>
<td>4x10^{-5}</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.0</td>
<td>0.01</td>
<td>0.13</td>
<td>0.08</td>
</tr>
</tbody>
</table>
and in spring (moderate flux) in the grass system. \( \text{N}_2\text{O} \) flux exhibited the lowest variance in the winter season, when the flux was low and soil was cool and moist, and the highest variance in the summer season, when the flux was high and soil was warm and moist, in both land uses. \( \text{N}_2\text{O} \) flux exhibited the longest spatial range and strong spatial dependency in the spring season.

### 6.2.7 Spatial associations between \( \text{N}_2\text{O} \) flux and soil physical factors in crop and grass systems

Soil physical factors considered for this data analysis included soil texture fractions, soil bulk density, relative gas diffusivity at -100 and -10 cm matric potentials, air-filled porosity at -1000 cm matric potential, and the pore-continuity index at -10 cm matric potential. The selection of these physical factors was based on their structured spatial variability (Chapter 4). The spatial association between \( \text{N}_2\text{O} \) flux and clay contents was not quantified because the spatial variability of clay contents was not structured in both land uses. The sand content was spatially associated with \( \text{N}_2\text{O} \) flux for all selected flux measuring dates in crop and grass systems (Figure A14.1). The spatial relationship between \( \text{N}_2\text{O} \) flux and sand was positive in summer and spring in the crop system and only in summer in the grass system, and negative in the other seasons in both land uses. The nugget-to-sill ratios indicated that the spatial structure for the relationship between sand contents and \( \text{N}_2\text{O} \) fluxes was moderate in the crop system and varied between moderate and strong among the measuring dates in the grass system. The correlation length of the spatial association between \( \text{N}_2\text{O} \) flux and sand contents was longer in the grass than in the crop system in summer and spring (Table 6.6).
Table 6.6. Spatial cross-semivariogram parameters for N$_2$O flux with soil texture fractions in crop and grass systems.

<table>
<thead>
<tr>
<th></th>
<th>21-Jun-10</th>
<th>31-Dec-10</th>
<th>17-Mar-11</th>
<th>21-Jun-10</th>
<th>31-Dec-10</th>
<th>17-Mar-11</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>N$_2$O flux vs. sand content</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>6.6</td>
<td>7.8</td>
<td>5.6</td>
<td>33.1</td>
<td>3.2</td>
<td>31.3</td>
</tr>
<tr>
<td>Nugget</td>
<td>3x10$^{-3}$</td>
<td>2x10$^{-4}$</td>
<td>3x10$^{-4}$</td>
<td>0.0</td>
<td>7x10$^{-4}$</td>
<td>5x10$^{-4}$</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.40</td>
<td>0.28</td>
<td>0.56</td>
<td>0.0</td>
<td>0.42</td>
<td>0.17</td>
</tr>
<tr>
<td><strong>N$_2$O flux vs. silt content</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>29.8</td>
<td>2.8</td>
<td>-</td>
<td>24.4</td>
<td>17.7</td>
</tr>
<tr>
<td>Nugget</td>
<td>1x10$^{-3}$</td>
<td>6x10$^{-4}$</td>
<td>8x10$^{-4}$</td>
<td>0.0</td>
<td>6x10$^{-4}$</td>
<td>8x10$^{-4}$</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>0.34</td>
<td>0.40</td>
<td>1.0</td>
<td>0.65</td>
<td>0.36</td>
</tr>
</tbody>
</table>
The N₂O flux spatially associated with silt contents in winter and spring in crop and grass systems (Figure A14.2). The spatial relationship between N₂O flux and silt was negative in both seasons in the crop system and only in winter in the grass system. The spatial structure of the association between N₂O flux and silt contents varied between weak and moderate in both land uses (Table 6.6). The spatial range of the relationship between N₂O flux and silt contents was longer in winter than in spring in both land uses (Table 6.6).

Overall, sand contents exhibited stronger spatial relationships with N₂O fluxes in the grass than in the crop system. On the other hand, and for the structured cross-semivariograms, silt contents exhibited stronger spatial associations with N₂O fluxes in the crop than in the grass system. Sand contents had the largest CV and silt contents had the smallest CV in both land-use systems among the texture fractions. The strongest spatial relationship between N₂O flux and sand content was obtained when the flux was high with smaller CV in summer and spring in the grass system. On the other hand, the strongest spatial relationships between N₂O fluxes and silt contents were obtained when the flux was low with higher CV in winter in the crop system.

Soil bulk density was spatially associated with N₂O flux measured in summer and spring in the crop system and did not correlate with the flux in the grass system (Figure A14.3). The spatial relationship between N₂O flux and bulk density was positive in summer and negative in spring in the crop system. The spatial structure of the association between
Table 6.7. Spatial cross-semivariogram parameters for \( \text{N}_2\text{O} \) flux with bulk density, relative gas diffusivity \( \text{D}_s/\text{D}_0 \), air-filled porosity \( \theta_a \), and the pore-continuity index \( \vartheta \) in crop and grass systems.

<p>| | | | | | | | | | |</p>
<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crop system</td>
<td>Grass system</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{N}_2\text{O} ) flux vs. ( \rho_b )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>7.1</td>
<td>13.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget</td>
<td>( 2 \times 10^{-4} )</td>
<td>0.0</td>
<td>( 5 \times 10^{-6} )</td>
<td>0.0</td>
<td>( 1 \times 10^{-5} )</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.29</td>
<td>1.0</td>
<td>0.15</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} ) flux vs. ( \text{D}_s/\text{D}_0(-10) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18.4</td>
<td>14.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget</td>
<td>( 1 \times 10^{-6} )</td>
<td>0.0</td>
<td>0.0</td>
<td>( 1 \times 10^{-6} )</td>
<td>( 2 \times 10^{-6} )</td>
<td>( 2 \times 10^{-6} )</td>
<td>1.0</td>
<td>0.37</td>
<td>0.19</td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} ) flux vs. ( \text{D}_s/\text{D}_0(-1000) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>4.5</td>
<td>-</td>
<td>11.7</td>
<td>23.5</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget</td>
<td>( 6 \times 10^{-7} )</td>
<td>0.0</td>
<td>( 7 \times 10^{-6} )</td>
<td>0.0</td>
<td>( 1 \times 10^{-5} )</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.01</td>
<td>1.0</td>
<td>0.37</td>
<td>0.11</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} ) flux vs. ( \theta_a(-1000) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>7.4</td>
<td>-</td>
<td>12.1</td>
<td>6.2</td>
<td>34.2</td>
<td>21.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget</td>
<td>( 6 \times 10^{-5} )</td>
<td>( 4 \times 10^{-6} )</td>
<td>0.0</td>
<td>( 6 \times 10^{-6} )</td>
<td>( 9 \times 10^{-6} )</td>
<td>( 4 \times 10^{-5} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>0.28</td>
<td>1.0</td>
<td>0.0</td>
<td>0.08</td>
<td>0.47</td>
<td>0.34</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} ) flux vs. ( \vartheta(-10) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range (m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget</td>
<td>0.0</td>
<td>( 8 \times 10^{-6} )</td>
<td>( 4 \times 10^{-6} )</td>
<td>( 8 \times 10^{-5} )</td>
<td>( 9 \times 10^{-5} )</td>
<td>( 4 \times 10^{-5} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nugget/sill</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
$N_2O$ flux and bulk density was strong for the structured cross-semivariograms in the crop system (Table 6.7).

Relative gas diffusivity at -10 cm matric potentials was spatially negatively associated with $N_2O$ fluxes in winter and spring seasons in the grass system and did not correlate with the flux in the crop system (Figure A14.4). Relative gas diffusivity at -1000 cm matric potential was spatially associated with $N_2O$ fluxes in summer and spring in the crop system and only in summer in the grass system (Figure A14.5). The spatial dependency of the spatial relation between relative gas diffusivity at -1000 cm water head and $N_2O$ flux measured in the summer was strong in both land uses with longer spatial range in the grass than in the crop system (Table 6.7). December 2010 was the only measuring time when the $N_2O$ flux exhibited larger spatial variability (higher CV) in the crop than in the grass system. Air-filled porosity at -1000 cm water head spatially related with $N_2O$ flux measured on all selected dates in crop and grass systems except on 31 December 2010 in the crop system (Figure A14.6). The spatial relationship between $N_2O$ flux and air-filled porosity at -1000 cm water head was positive in grass system and negative in the crop system in summer. Cross-semivariograms showed that the spatial dependency of the relationship between air-filled porosity at -1000 cm matric potential and $N_2O$ fluxes varied between weak and strong in the crop system and moderate and strong in the grass system. The correlation length of the spatial relation between air-filled porosity at -1000 cm water head and $N_2O$ flux was similar in summer and longer in spring in the grass than in the crop system (Table 6.7). The pore-continuity index at -10 cm matric potential did not spatially associate with $N_2O$ flux in either land-use system.
The cross-semivariograms for the pore-continuity index at -10 cm water head and N$_2$O flux were not structured and showed nugget-to-sill ratios of 1.0 (Table 6.7).

The results showed not only the controlling factors on the spatial variability of N$_2$O flux, but also showed the influence of land use (crop and grass) on the spatial associations for N$_2$O flux with biochemical and physical factors. The spatial and temporal relationships between N$_2$O flux and the selected factors in the crop system differed from the grass system because the grass system had more developed soil structure than the crop system (Chapter 3) and also because the grass system had higher contents of soil organic matter and higher microbial population and activities (Chapter 5).

Spatial associations between N$_2$O fluxes and different biochemical and physical factors in crop and grass systems were quantified using the cross-semivariogram analysis, and these spatial relationships varied among seasons and between land uses. In summer, a strong spatial association with the longest spatial range was obtained for N$_2$O flux with soil pH in the crop and with CO$_2$ flux in the grass system. Different physical and biochemical factors exhibited spatial relationships with N$_2$O flux with long spatial ranges in winter but the strongest dependency was obtained for the association of flux with soil organic matter and total nitrogen in the crop system and with air-filled porosity at -1000 cm matric potential in the grass system. In spring, average soil water contents at 0-30 cm depth exhibited a strong spatial relationship with N$_2$O flux with the longest spatial range in the crop system and soil organic matter and total nitrogen in the grass system. It seemed that,
in summer and winter, biochemical factors had the dominant influence of the spatial variability of N$_2$O flux in the crop system, and soil physical factors controlled the spatial variability of the flux in the grass system. On the other hand in spring, soil water content was the main factor controlling the spatial variability of N$_2$O flux in the crop system while biochemical factors controlled in the grass system.

Similar to those found for soil physical characteristics (Chapter 4) and soil respiration (Chapter 5), the cross-semivariance decreased with separating distance or exhibited a different sign for <5-m lags distances from longer lags for some structured spatial cross-semivariograms. For example, Figures A13.2c, A13.3c, and A14.6b show the cross-semivariogram for N$_2$O fluxes with selected soil variables. The cross-semivariance was negative for the first lags and positive for longer lags. Other examples can be Figures A13.3b and A14.5c which show that the cross-semivariance was positive for the first lags and negative for the longer lags. This behavior was most likely because the <5 m lags were the separation distances for observations located in the nests. This behavior is an indication of the influence of sampling interval on cross-semivariogram analysis, and a constant distance interval should be selected for cross-semivariogram analysis. Another reason can be because the <5 m lags were the separation distance for sampling points located in the transition zone between the crop and grass systems. The variation of N$_2$O flux and the selected factors tended to be higher in the transition zone than in the rest of the field.
6.3 Summary and conclusions

Spatial and temporal variability of N$_2$O fluxes was quantified in crop and grass systems. Nitrous oxide flux was highest during summer and lowest during winter in both land-use systems. In some measuring dates, negative N$_2$O fluxes were obtained in the morning when soil temperature and flux were low due to N$_2$O was most likely dissolved or reduced to N$_2$. Nitrous oxide fluxes exhibited high variation in space and time and the spatial variability was structured on 8 measuring dates in the crop and 10 dates in the grass systems. The two land-use systems exhibited similar spatial correlation lengths of N$_2$O flux. The temporal variability of N$_2$O fluxes was structured at most of the sampling locations in crop and grass systems. Overall, the temporal correlation length of N$_2$O flux was longer in the crop than in the grass system. The variation of N$_2$O flux was more pronounced in time than in space in both land-use systems, and this manifestation of the temporal variation was more obvious during summer and early fall when the soil was warm and moist. During winter the temporal variation was more stable in both land-use systems. Correlations between N$_2$O flux measurements taken on different dates during a year indicated that N$_2$O flux was temporally stable for 60 days during the fall season when the flux was high.

Soil temperature and soil water content had significant influence on the temporal variability of N$_2$O fluxes in crop and grass systems. The spatial associations between N$_2$O fluxes and soil physical and biochemical factors varied among the flux measuring dates and between land-use systems. In the crop system, soil organic matter, total nitrogen, soil pH, bulk density, relative gas diffusivity and air-filled porosity at -1000 cm matric
potential exhibited strong spatial associations with N$_2$O flux. On the other hand in the grass system, sand contents, relative gas diffusivity at -1000 and -10 cm matric potentials, and air-filled porosity at -1000 cm water head controlled the spatial variability of N$_2$O flux. Quantifying spatial and temporal variability of N$_2$O flux and its controlling factors over space and time is essential for efficient sampling design and effective soil nitrogen management. The obtained spatial and temporal ranges and semivariance in this study, and the determination of the effective controlling factors on N$_2$O fluxes can be used for designing other field experiments and predicting nitrogen loses under similar measurement scale, land use, soil type, and environmental conditions.
CHAPTER 7: Conclusions-Recommendations for Future Work

In this study, the impact of land use on soil properties and functions was investigated. The influence of land use on soil structure and on spatial patterns of different soil physical properties and characteristics was shown. The grass system exhibited more developed soil structure with higher soil porosity and a more continuous soil pore system than the crop system. Measurements of all selected soil physical properties and characteristics showed the influence of land use on soil structure. Measurements of relative gas diffusion coefficients and air-filled porosity were used to compute the soil pore-continuity index which indicated that soil in the grass system exhibited more continuous pore networks than in the crop system. For most of the selected soil physical properties and characteristics, soil in the crop system exhibited stronger spatial continuity and more structured spatial variability than in the grass system. Based on this result, sampling design protocols should be different between crop and grass systems. The strength of the spatial dependency and its range for each of the selected variables in crop and grass systems should be considered for sampling designs, however these spatial parameters are scale dependent and influenced by the measurement scale (spacing, extent, and support).

Land use influenced spatial and temporal variability of gas fluxes. Carbon dioxide and nitrous oxide fluxes proceeded at higher levels during warm-moist periods than in cold-wet periods in both land-use systems. Carbon dioxide and nitrous oxide fluxes were slightly higher in the grass system than in the crop system, with differences more
pronounced when it was warm-moist than when it was cold-wet. Soil respiration was correlated over longer periods and spatial distances in the grass than in the crop system. Nitrous oxide flux was more variable in space and time and less temporally stable than CO$_2$ flux in crop and grass systems. Unlike for CO$_2$ flux, the spatial variability of N$_2$O flux was structured in a few measuring dates in both land uses, and it was correlated over a longer period in the crop than in the grass system. Understanding the spatial and temporal patterns and the temporal stability of CO$_2$ and N$_2$O fluxes and their spatial and temporal associations help to not only select efficient design for sampling protocols but also better determine carbon and nitrogen losses from soil systems. Soil temperature was the dominant factor controlling the temporal variability of CO$_2$ and N$_2$O fluxes in crop and grass systems. Soil biochemical and physical factors controlled the spatial variability of CO$_2$ and N$_2$O fluxes, and the relationships between the fluxes and controlling factors varied between the land uses and among the measuring dates.

This study provides the base lines and recommendations for future investigations specifically for sampling designs, soil management, and predictions of different soil processes. Considering the spatial and temporal ranges and dependency strength of the selected soil variables helps select efficient sampling designs which can result in better time and resource management without losing important information. Although modeling of soil processes was not considered in this study, spatial and temporal processes and relationships between the selected soil gas and soil water characteristics obtained in this study help improve understanding soil management and improve different models for different soil processes.
Recommendations towards improving methods of sampling and measurements and thus confirming the results include:

1. Determining the effects of scale dependency. The spatial and temporal processes of different soil properties and processes considered in this study are scale dependent (Chapter 1.3.5). Quantifying these spatial and temporal processes at different scales might lead to different results and conclusions of spatial and temporal patterns of soil variables and their associations. Considering different components of the scale triplet (spacing, extent, and support) is expected to provide different semivariogram parameters. In other words, large-scale measurements can only sample large-scale variability and small-scale measurements can only sample small-scale variability. For example, under the same conditions of soil type, land use, soil management, and climate, a larger scale will exhibit a larger spatial range than a small scale.

2. Assessing whether these spatial relationships exist at deeper depths of the soil profile and under different land use types such as forest soils. The cross-semivariogram analysis and the Spearman correlation coefficients were used to quantify the correlations and the spatial associations between soil properties which were sampled only from the upper depth of the soil profile in crop and grass systems.

3. Spatial associations between soil physical variables showed that spatial modeling of soil processes should include the spatial associations of soil properties used in the model and the land use factor.

4. The correlations between soil properties showed that besides bulk density and air-filled porosity, there were other parameters such as aggregate size distribution and
retention curve parameters that should be used for predicting soil gas diffusivity in different land uses.

5. More work regarding the comparison between two methods of determining soil water retention using different soils is recommended. Soil water retention curves were estimated using the evaporation method, which provided soil water content as a function of soil water matric potential during evaporation experiments. However, the soil water characteristic curve describes the functional relationship between soil water content and matric potential under equilibrium conditions (as a definition). A comparison between water retention estimated under equilibrium and non-equilibrium (evaporation) conditions was provided in the appendix and showed that soil water retention measured using the evaporation method was significantly higher than using the pressure plate apparatus. The comparison showed also that the spatial variation of soil water retention was higher when it was estimated under equilibrium conditions. It is also recommended that water retention curve be estimated under equilibrium conditions for a wide range of matric potential depending on the soil type.

6. To my knowledge, hysteresis of gas transport in soil and under different land uses has not been investigated. Relative gas diffusivity was measured at high matric potential starting with a sequence of from the highest (-10 cm) to the lowest (-1000 cm). However, performing the measurement in the opposite direction (starting with the lowest to the highest) might lead to different results of the magnitude of the gas transport coefficient and its variability. Such an analysis will reveal whether hysteresis effects are still obvious in the gas diffusivity – air-filled porosity relationship.
7. The correlations between gas (CO$_2$ and N$_2$O) fluxes and selected soil measurements and soil properties and their spatial associations in crop and grass systems were tested in this study. However, other factors that can influence gas fluxes, and might have spatial relationships, should be considered in future investigations. These factors are, for example, root biomass, microbial biomass, mineral nitrogen, soil phosphorus, EC, and air temperature.

8. The relations between soil temperature and these fluxes should be quantified for soil temperature measured at different depths of the soil profile. Soil temperature measured at 5 cm depth of the soil profile was the main factor controlling the magnitude and the temporal variability of soil surface CO$_2$ and N$_2$O fluxes.

9. Soil macroporosity and convective gas flux should be considered as other factors that may influence soil surface CO$_2$ and N$_2$O fluxes and its spatial variability in crop and grass systems. Lang et al. (2009) and Deurer et al. (2009) showed the importance of macroporosity and convective flux on greenhouse gas emissions from soil surface.

10. The spatial and temporal variations of soil respiration should be decomposed into different scales rather than using the total variation to better understand the spatial and temporal correlations of CO$_2$ or N$_2$O flux with the selected factors, using the correlation coefficients.

11. Statistical analysis of relationships between soil properties and soil processes should consider different scales of spatial and temporal distributions rather than total variability. Cross-semivariogram analysis provided more knowledge and better understanding of the spatial and temporal relationships between soil variables than correlation coefficients. The cross-semivariogram analysis provided the cross-
semivariance for different lag distances or time (different scales) and for what extent the two considered variables are remained correlated.

12. Other studies have shown that topography was the most common element influencing the spatial dependence of gas fluxes on a field scale. Therefore, topography should be considered as another factor that might control the spatial structure of CO\textsubscript{2} and N\textsubscript{2}O emissions in crop and grass systems.

13. Land use significantly influenced gas fluxes and their relations with selected factors. It is recommended that a land-use factor should be included in modeling CO\textsubscript{2} and N\textsubscript{2}O fluxes.

14. It is recommended that spatial and temporal observations of gas fluxes should be used to refine prediction of carbon and nitrogen loses under different scenarios of land use, soil type, and climate.

15. Temporal stability analysis of gas fluxes gave the opportunity to better understand the behaviors of gas fluxes in space and time and should be considered for future studies. The temporal stability analysis contributes to the effort of developing strategies to minimize the number of observations without significant loss of information.

16. Dissolved CO\textsubscript{2} and N\textsubscript{2}O in soil solution should be estimated using Henry’s Law. Dissolved CO\textsubscript{2} and N\textsubscript{2}O were not taken into account for adjusting the diurnal trend of the fluxes because subsurface soil CO\textsubscript{2} and N\textsubscript{2}O concentrations and their partial pressures were not measured when the soil surface gas fluxes were obtained.
APPENDIXES

Appendix 1: Frequency distribution

Table A1.1. Soil variables which are normally distributed (Yes) or not normally distributed (No) measured at 0-10 cm depth in crop and grass systems.

<table>
<thead>
<tr>
<th>Variable</th>
<th>CROP</th>
<th>GRASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_b$</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>&gt;2 mm</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>2-1 mm</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>1-0.25 mm</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>0.25-0.053 mm</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>&lt;0.053 mm</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>MWD(mm)</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>WAS</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Sand</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Clay</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Silt</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>SOM</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>pH</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Fe</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>TN</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DC</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>DN</td>
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<td>Yes</td>
</tr>
<tr>
<td>C/N</td>
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<td>Yes</td>
</tr>
<tr>
<td>$D_s/D_0(-10)$</td>
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<td>No</td>
</tr>
<tr>
<td>$D_s/D_0(-50)$</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$D_s/D_0(-100)$</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$D_s/D_0(-333)$</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$D_s/D_0(-1000)$</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$\theta_{a(-10)}$</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$\theta_{a(-50)}$</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>$\theta_{a(-100)}$</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>$\theta_{a(-333)}$</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>$\theta_{a(-1000)}$</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>$\theta_{c(-10)}$</td>
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<td>No</td>
</tr>
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<td>$\theta_{c(-50)}$</td>
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<td>Yes</td>
</tr>
<tr>
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<td>Yes</td>
</tr>
<tr>
<td>$\theta_{c(-1000)}$</td>
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<td>Yes</td>
</tr>
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</table>
Appendix 2: Comparing soil water retention measured under equilibrium and evaporation conditions

Soil water retention was measured at selected matric potentials using two methods. The water content at different water heads under equilibrium conditions was measured by weighing the soil core after it reached equilibrium with a particular pressure using a pressure plate apparatus when the soil cores were prepared for the gas diffusivity measurements in the lab. The other method was measuring the soil water content at different matric potentials using TDR under evaporation conditions when unsaturated hydraulic conductivity was measured using the evaporation method. The soil water content measured by the two methods using the same soil cores was compared to determine the differences of soil water retention under equilibrium and evaporation conditions measured by two different methods. Soil water retention measurements estimated at three soil matric potential values, -333, -100, and -50 cm under both evaporation and equilibrium conditions were compared.

The mean soil water retention estimated under evaporation conditions was significantly higher than under equilibrium conditions at all selected matric potentials in crop and grass systems (Figures A2.1-A2.3, Table A2.1). In the crop system, the soil water retention estimated under equilibrium conditions exhibited higher standard deviation, higher coefficient of variation, and higher variance than estimated under evaporation condition at all selected matric potentials (Table A2.1). In the grass system, likewise, the soil water retention determined under equilibrium conditions exhibited higher standard deviation, higher coefficient of variation, and
Figure A2.1. Soil water content at -50 cm matric potential measured under equilibrium conditions using pressure plate apparatus and under dynamic conditions using the evaporation method.
Figure A2.2. Soil water content at -100 cm matric potential measured under equilibrium conditions using pressure plate apparatus and under dynamic conditions using the evaporation method.
Figure A2.3. Soil water content at -333 cm matric potential measured under equilibrium conditions using pressure plate apparatus and under dynamic conditions using the evaporation method.
Table A2.1. Descriptive statistics of soil water retention at different matric potential and under evaporation and equilibrium conditions.

<table>
<thead>
<tr>
<th>ψ(cm)</th>
<th>-50</th>
<th>-100</th>
<th>-333</th>
<th>-50</th>
<th>-100</th>
<th>-333</th>
</tr>
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<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Evaporation</td>
<td></td>
<td></td>
<td>Equilibrium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Crop system</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.422</td>
<td>0.411</td>
<td>0.387</td>
<td>0.381</td>
<td>0.363</td>
<td>0.340</td>
</tr>
<tr>
<td>Min.†</td>
<td>0.399</td>
<td>0.382</td>
<td>0.354</td>
<td>0.297</td>
<td>0.278</td>
<td>0.258</td>
</tr>
<tr>
<td>Max.‡</td>
<td>0.479</td>
<td>0.469</td>
<td>0.441</td>
<td>0.415</td>
<td>0.403</td>
<td>0.387</td>
</tr>
<tr>
<td>SD</td>
<td>0.018</td>
<td>0.019</td>
<td>0.019</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>CV</td>
<td>0.043</td>
<td>0.045</td>
<td>0.050</td>
<td>0.066</td>
<td>0.068</td>
<td>0.073</td>
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<tr>
<td>Var.</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0004</td>
<td>0.0006</td>
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<td>0.0006</td>
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<td>Grass system</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.424</td>
<td>0.410</td>
<td>0.382</td>
<td>0.392</td>
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<td>0.347</td>
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<tr>
<td>Min.</td>
<td>0.396</td>
<td>0.382</td>
<td>0.358</td>
<td>0.369</td>
<td>0.311</td>
<td>0.285</td>
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<tr>
<td>Max.</td>
<td>0.490</td>
<td>0.477</td>
<td>0.448</td>
<td>0.412</td>
<td>0.438</td>
<td>0.406</td>
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<tr>
<td>SD</td>
<td>0.018</td>
<td>0.018</td>
<td>0.017</td>
<td>0.010</td>
<td>0.028</td>
<td>0.024</td>
</tr>
<tr>
<td>CV</td>
<td>0.044</td>
<td>0.045</td>
<td>0.045</td>
<td>0.027</td>
<td>0.076</td>
<td>0.069</td>
</tr>
<tr>
<td>Var.</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0001</td>
<td>0.0008</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

†minimum
‡maximum
higher variance than under evaporation conditions at -333 and -100 cm matric potentials but lower standard deviation, lower coefficient of variation, and lower variance than under evaporation conditions at -50 cm water head. The differences between water retention measured under the two conditions may be because two different methods were used rather than due to the conditions under which it was measured (evaporation or equilibrium).

It can be concluded that soil water retention differed under evaporation conditions compared to equilibrium conditions with a higher mean observed under evaporation conditions at all selected matric potentials in both land uses. The spatial variation of water retention under evaporation conditions was different than that for water retention estimated under equilibrium conditions with higher variations under equilibrium condition at all selected matric potential in the crop system and at -333 and -100 cm in the grass system.
Appendix 3: Estimating oxygen mass balance and oxygen consumption in a soil core

The gas diffusion process in a soil core is driven by a concentration gradient between the two ends of the soil core. This assumption was tested by quantifying the oxygen mass balance between the two ends of the soil core in the lab. Oxygen was used as a trace gas for estimating soil gas diffusivity. However, it was possible that oxygen might be consumed by soil microorganisms in the soil core during the measurement period. To quantify the mass balance and to determine whether or not the microbial activity might have affected the computed diffusion coefficient during the experiment period, a preliminary experiment was conducted in the lab using four gas diffusion chambers described in Chapter 2 and two soil cores.

Two soil cores taken from 4 to 10 cm depth were used for this experiment and each one was attached between two chambers (Figure A3.1). Soil core 1 was used to quantify oxygen mass balance and core 2 was used to estimate the oxygen consumption. Before the soil cores were used, they were saturated and placed in a pressure plate apparatus at -50 cm matric potential until they reached an equilibrium condition. One of the first two chambers (chamber 1) that were used for the mass balance estimation was flushed with helium to reduce the oxygen concentration and the other (Chamber II) was not flushed and kept at atmospheric oxygen concentration by turning off the two valves. The two valves in each of the other chambers (Chambers III and IV) used for the oxygen consumption experiment were turned off so there was no loss or gain of oxygen to or from the atmosphere. The oxygen concentration was measured inside each chamber at the same time every day for 11 days using a gas chromatograph and by following the same
Figure A3.1. Photos show two soil cores, each attached to two gas diffusion chambers.
procedure described in Chapter 2. In the first three days of the experiment, just one gas sample from each chamber was taken every day. After 3 days, an average of three samples taken from each chamber each day was used for the data analysis to minimize the measurement error.

The first experiment using chambers 1 and 2 was conducted to estimate the mass balance for oxygen between the two chambers. This experiment was performed by establishing a concentration gradient between the two chambers (the ends of a soil core) and letting the gas diffuse through the soil core. The first soil core had a bulk density of 1.19 g cm$^{-3}$ and air-filled porosity of 0.07 m$^3$ m$^{-3}$. The oxygen mass increased from 54 to 216 mg after 11 days with a rate of 14.7 mg d$^{-1}$ in the flushed chamber. The oxygen mass decreased in chamber 2 (air-filled chamber) with time from 553 to 215 mg after 11 days with a rate of 30.7 mg d$^{-1}$. This result indicated that oxygen diffused from the higher concentration chamber (air-filled chamber) to the lower concentration chamber (helium-filled chamber). The decreased rate of the oxygen mass increase in the helium-filled chamber was double the increase rate of the oxygen mass in the air-filled chamber. This difference might be because of the oxygen consumption occurred due to the microbial activities in the soil and/or oxygen dissolution into the soil solution. Figure A3.2 shows that the two chambers reached equilibrium after 6 days. Therefore, the effective oxygen mass increase and decrease rates in the helium-filled and air-filled chambers were 28.6 and 52.3 mg d$^{-1}$, respectively. The effective increase or decrease rate indicated the change rate during the
Figure A3.2. Oxygen mass as a function of time measured in two gas diffusion chambers attached to a soil core and field with, high and low, oxygen concentrations.
period before the chambers reached equilibrium (the sixth day). There was a slight
decrease (0.4%) of soil moisture in the soil core after the 11 days.

The second soil core had a bulk density of 1.35 g cm$^{-3}$ and air-filled porosity of 0.02 m$^3$
m$^{-3}$. There was not much difference of oxygen mass in air filled chambers used to
quantify oxygen consumption except for the second and third days (Figure A3.3), and
that might be a measurement error because just one measurement was taken from each
chamber on these days. The oxygen mass decreased in both chambers with rates of 10.7
and 6.4 mg d$^{-1}$ respectively. The decrease of oxygen mass in both chambers was 1.2 and
2.0% relative to the initial oxygen mass in the chambers. The decrease of oxygen mass in
both chambers was most likely due to oxygen consumption because of microbial
activity in the soil. This result indicates that the oxygen consumption rate in this soil was
low and it can be negligible if the laboratory gas diffusion measurements using the
chambers were performed within a few hours.
Figure A3.3. Oxygen mass as a function of time in two gas diffusion chambers attached to a soil core and had similar gas concentration.
Appendix 4: Spatial associations between soil properties in crop and grass systems

This appendix contains figures showing the spatial distribution and the cross-semivariograms for different soil physical variables in crop and grass systems. The cross-semivariogram analysis was used to quantify the spatial associations of soil physical properties and characteristics with other soil measurements.
Spatial associations between soil bulk density and selected soil measurements

Figure A4.1. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for bulk density with sand and clay contents in crop (b) and grass (c) systems.
Figure A4.2. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between bulk density and soil organic matter in crop (b) and grass (c) systems.
Figure A4.3. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for bulk density with total nitrogen (TN) and dissolved nitrogen (DN) in crop (b) and grass (c) systems.
Spatial relations between relative gas diffusivity and selected soil measurements

Figure A4.4. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between $D_s/D_{0(-10)}$ and bulk density in crop (b) and grass (c) systems.
Figure A4.5. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for $D_s/D_0(-10)$ with sand in crop (b) and grass (c) systems.
Figure A4.6. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between $D_s/D_{0(-10)}$ and silt content in crop (b) and grass (c) systems.
Figure A4.7. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between $D_s/D_{0(100)}$ and bulk density in crop (b) and grass (c) systems.
Figure A4.8. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between $D_s/D_{0(-1000)}$ and sand contents in crop (b) and grass (c) systems.
Figure A4.9. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between $D_s/D_{0(1000)}$ and silt content in crop (b) and grass (c) systems.
Spatial relations between air-filled porosity and selected soil measurements

Figure A4.10. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between air-filled porosity at -1000 cm matric potential and bulk density in crop (b) and grass (c) systems.
Figure A4.11. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between air-filled porosity at -1000 cm matric potential and sand contents in crop (b) and grass (c) systems.
Figure A4.12. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between air-filled porosity at -1000 cm matric potential and silt contents in crop (b) and grass (c) systems.
Spatial relations between the pore-continuity index and selected soil measurements

Figure A4.13. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between pore-continuity index at -10 cm matric potential and bulk density in crop (b) and grass (c) systems.
Figure A4.14. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between pore-continuity index at -10 cm matric potential and sand contents in crop (b) and grass (c) systems.
Figure A4.15. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms between pore-continuity index at -10 cm matric potential and silt contents in crop (b) and grass (c) systems.
Appendix 5: Temporal patterns of soil temperature and soil water content in crop and grass systems

This appendix contains figures showing the spatial distribution and the semivariograms for soil temperature at 5 cm depth and average soil water content at 0-30 cm depth in crop and grass systems.
Figure A5.1. Temporal distribution (a) and experimental (dots) and fitted (line) spherical semivariograms for soil temperature in crop (b) and grass (c) systems.
Figure A5.2. Temporal distribution (a) and experimental (dots) and fitted (line) spherical semivariograms for average soil water content at the upper 30 cm depth in crop (b) and grass (c) systems.
Appendix 6: Temporal associations for CO₂ flux with soil temperature and soil water content in crop and grass systems

This appendix contains figures showing the temporal distribution and the temporal cross-semivariograms for CO₂ flux with soil temperature and average soil water content in crop and grass systems. The cross-semivariogram analysis was used to quantify the temporal associations of soil respiration with soil temperature and soil moisture.
Figure A6.1. Temporal distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms (b) for CO$_2$ flux with soil temperature in the crop system.
Figure A6.2. Temporal distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms (b) for CO$_2$ flux with soil temperature in the grass system.
Figure A6.3. Temporal distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms (b) for CO$_2$ flux with average soil moisture at 0-30 cm depth in the crop system.
Figure A6.4. Temporal distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms (b) for CO$_2$ flux with average soil moisture at 0-30 cm depth in the grass system.
Appendix 7: Spatial patterns of soil temperature, soil water content, and soil pH in crop and grass systems

This appendix contains figures showing the spatial distribution and the semivariograms for soil temperature, average soil water content, and soil pH in crop and grass systems.
Figure A7.1. Spatial distribution (a) and experimental (dots) and fitted (line) spherical semivariograms of soil temperature measured at different dates in crop (b) and grass (c) systems.
Figure A7.2. Spatial distribution (a) and experimental (dots) and fitted (line) spherical semivariograms of average soil moisture at 0-30 cm depth in crop (b) and grass (c) systems.
Figure A7.3. Spatial distribution (a) and experimental (dots) and fitted (line) spherical semivariograms for soil pH in crop (b) and grass (c) systems.
Appendix 8: Spatial association for CO$_2$ flux with soil water content in crop and grass systems

This appendix contains figures showing the spatial distribution and the cross-semivariograms for CO$_2$ flux with soil moisture in crop and grass systems. The cross-semivariogram analysis was used to quantify the spatial associations of soil respiration with soil moisture.
Figure A8.1. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for CO$_2$ flux with average soil moisture at 0-30 cm depth measured at different dates in crop (b) and grass (c) systems.
Appendix 9: Spatial associations for CO$_2$ flux with selected soil biochemical and physical properties in crop and grass systems

This appendix contains figures showing the spatial distribution and the cross-semivariograms for CO$_2$ flux with different soil biochemical and physical factors in crop and grass systems. The cross-semivariogram analysis was used to quantify the spatial associations of soil respiration and characteristics with other soil measurements.
Figure A9.1. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for soil organic matter with CO₂ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.2. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for total nitrogen with CO$_2$ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.3. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for soil pH with CO$_2$ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.4. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for sand content with CO$_2$ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.5. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for silt content with CO$_2$ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.6. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for bulk density with CO₂ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.7. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for $D_s/D_{0(-10)}$ with CO$_2$ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.8. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for $D_s/D_0(-1000)$ with CO$_2$ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.9. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for air-filled porosity at -1000 cm water head with CO₂ flux measured on four selected dates in crop (b) and grass (c) systems.
Figure A9.10. Spatial distribution (a) and experimental (dots) and fitted (line) spherical cross-semivariograms for the pore-continuity index at -10 cm water head with CO$_2$ flux measured on four selected dates in crop (b) and grass (c) systems.
Appendix 10: Temporal semivariograms of soil temperature and soil water content in crop and grass systems

This appendix contains figures showing the temporal semivariograms for soil temperature and average soil water content at selected locations in crop and grass systems.
Figure A10.1. Temporal semivariograms of soil temperature measured at different locations in crop and grass systems.
Figure A10.2. Temporal semivariograms of average soil water content measured at different locations in crop and grass systems.
Appendix 11: Temporal associations for N$_2$O fluxes with soil temperature, soil water content, and soil respiration in crop and grass systems

This appendix contains figures showing the temporal distribution and the temporal cross-semivariograms for N$_2$O flux with soil temperature, average soil water content, and CO$_2$ flux in crop and grass systems. The cross-semivariogram analysis was used to quantify the temporal associations of N$_2$O flux with soil temperature, soil moisture, and soil respiration.
Figure A11.1. Temporal distribution and cross-semivariograms for N₂O flux with soil temperature and at three locations in the crop system.
Figure A11.2. Temporal distribution and cross-semivariograms for N$_2$O flux with soil temperature and at three locations in the grass system.
Figure A11.3. Temporal distribution and cross-semivariograms for N₂O flux with average soil water content at 0-30 cm depth at three locations in the crop system.
Figure A11.4. Temporal distribution and temporal cross-semivariograms for N\textsubscript{2}O flux with average soil water content at 0-30 cm depth at three locations in the grass system.
Figure A11.5. Temporal distribution and temporal cross-semivariograms for N$_2$O flux with CO$_2$ flux at three locations in the crop system.
Figure A11.6. Temporal distribution and temporal cross-semivariograms for N$_2$O flux with CO$_2$ flux at three locations in the grass system.
Appendix 12: Spatial Associations for N$_2$O fluxes with soil temperature and soil water content in crop and grass systems

This appendix contains figures showing the spatial distribution and the spatial cross-semivariograms for N$_2$O flux with soil temperature and average soil water content in crop and grass systems. The cross-semivariogram analysis was used to quantify the spatial associations of N$_2$O flux with soil temperature and soil moisture.
Figure A12.1. Spatial distribution (a) and spatial semivariograms for soil temperature and average water content measured on 21 June 2010 in crop (b) and grass (c) systems.
Figure A12.2. Spatial distribution (a) and spatial cross-semivariograms for N₂O flux with soil temperature at 5 cm depth in crop (b) and grass (c) systems.
Figure A12.3. Spatial distribution (a) and spatial cross-semivariograms for N\textsubscript{2}O flux with average soil water content at 0-30 cm depth in crop (b) and grass (c) systems.
Appendix 13: Spatial Associations for N$_2$O fluxes with selected soil biochemical properties in crop and grass systems

This appendix contains figures showing the spatial distribution and the spatial cross-semivariograms for N$_2$O flux with different soil biochemical measurements in crop and grass systems. The cross-semivariogram analysis was used to quantify the spatial associations of N$_2$O flux with the selected biochemical factors.
Figure A13.1. Spatial distribution (a) and spatial cross-semivariograms for N$_2$O flux with soil organic matter in crop (b) and grass (c) systems.
Figure A13.2. Spatial distribution (a) and spatial cross-semivariograms for N\textsubscript{2}O flux with total nitrogen in crop (b) and grass (c) systems.
Figure A13.3. Spatial distribution (a) and spatial cross-semivariograms for N\textsubscript{2}O flux with soil pH in crop (b) and grass (c) systems.
Figure A13.4. Spatial distribution (a) and spatial cross-semivariograms for N$_2$O flux with CO$_2$ flux in crop (b) and grass (c) systems.
Appendix 14: Spatial association between N₂O flux and physical factors in crop and grass systems

This appendix contains figures showing the spatial distribution and the spatial cross-semivariograms for N₂O flux with soil physical factors in crop and grass systems. The cross-semivariogram analysis was used to quantify the spatial associations of N₂O flux with the selected soil physical factors.
Figure A14.1. Spatial distribution (a) and spatial cross-semivariograms for N₂O flux with sand contents in crop (b) and grass (c) systems.
Figure A14.2. Spatial distribution (a) and spatial cross-semivariograms for N₂O flux with silt contents in crop (b) and grass (c) systems.
Figure A14.3. Spatial distribution (a) and spatial cross-semivariograms for N₂O flux with bulk density in crop (b) and grass (c) systems.
Figure A14.4. Spatial distribution (a) and spatial cross-semivariograms for N$_2$O flux with relative gas diffusivity at -10 cm matric potential in crop (b) and grass (c) systems.
Figure A14.5. Spatial distribution (a) and spatial cross-semivariograms for N$_2$O flux with relative gas diffusivity at -1000 cm matric potential in crop (b) and grass (c) systems.
Figure A14.6. Spatial distribution (a) and spatial cross-semivariograms for N\textsubscript{2}O flux with air-filled porosity at -1000 cm matric potential in crop (b) and grass (c) systems.
Figure A14.7. Spatial distribution (a) and spatial cross-semivariograms for N₂O flux with pore-continuity index at -10 cm matric potential in crop (b) and grass (c) systems.
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Conference Papers


Published Abstracts


Kreba, S., O. Wendroth, and M. Coyne. 2012. Soil gas diffusivity and air-filled porosity and their spatial patterns in crop and grass systems. ASA-CSSA-SSSA Conference. Cincinnati, OH.


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