QUANTIFICATION OF GREENHOUSE GAS FLUXES FROM SOIL IN AGRICULTURAL FIELDS

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Quantification of Greenhouse Gas fluxes from Soil in Agricultural Fields

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SUMMARY

Field studies were conducted at Lincoln University of Missouri (USA) and Hokkaido University (Japan) to: (i) study the relationships between greenhouse gases emissions and soil properties, (ii) assess the influence of agricultural practices on greenhouse gas fluxes and soil properties and (iii) improve the quantification of greenhouse gases from soil in agricultural fields using geospatial technologies. Results showed that besides soil temperature (T), soil thermal properties such as thermal conductivity (K), resistivity (R) and diffusivity (D) and soil pore spaces indices such as the pore tortuosity factor (τ) and the relative gas diffusion coefficient (Ds/Do) are controlling factors for greenhouse gases emissions. Soil thermal properties correlated with greenhouse gases emissions when soil temperature could not. The study has found that predicted Ds/Do and τ correlate with greenhouse gas fluxes even when the air-filled porosity and the total porosity from which they are predicted did not. We have also showed that Ds/Do and τ can be predicted quickly from routine measurements of soil water and air and existing diffusivity models found in the literature. Agricultural practices do seriously impact greenhouse gases emissions as showed by the effect of mechanized tillage operations on soil physical properties and greenhouse gas fluxes in a corn and soybean fields. In fact, our results showed that tractor compaction increased soil resistance to penetration, water, bulk density and pore tortuosity while reducing air-filled porosity, total pore space and the soil gas diffusion coefficient. Changes in soil properties resulted in increased CO_2, NO and N_2O emissions. Finally, our results also confirmed that greenhouse gas fluxes vary tremendously in space and time. As estimates of greenhouse gas emissions are influenced by the data processing approach, differences between the different calculation approaches leads to uncertainty. Thus, techniques for developing better estimates

are needed. We have showed that Geographic Information Systems (GIS), Global Positioning System (GPS), computer mapping and geo-statistics are technologies that can be used to better understand systems containing large amounts of spatial and temporal variability. Our GIS-based approach for quantifying CO_2, CH_4 and N_2O fluxes from soil in agricultural fields showed that estimating (extrapolating) total greenhouse gas fluxes using the “standard” approach – multiplying the average flux value by the total field area – results in biased predictions of field total greenhouse gases emissions. In contrast, the GIS-based approach we developed produces an interpolated map portraying the spatial distribution of gas fluxes across the field from point measurements and later process the interpolated map produced to determine flux zones. Furthermore, processing, classification and modeling enables the computation of field total fluxes as the sum of fluxes in different zones, therefore taking into account the spatial variability of greenhouse gas fluxes.

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PART I. INTRODUCTION AND LITERATURE REVIEW

CHAP 1. Introduction

1.1. Atmospheric concentration of CO_2, CH_4 and N_2O

The atmospheric concentration of CO_2, CH_4 and N_2O is ever increasing (IPPC, 2001) and a good deal of research has been done to estimate emissions of these greenhouse gases from soils. Although numerous measurements have been made, emissions from soils still show variability based on a number of controlling factors (Robertson et al., 2000). In fact, differences in soil types, moisture, temperature, season, crop type, fertilization, and other agricultural practices all play a part in emissions from soils. Within a particular soil type, static and dynamic soil properties may affect greenhouse gas emissions, but the relationship between these soil properties and greenhouse gas emissions is still poorly understood. In addition, data available to estimate anthropogenic greenhouse gas emissions are generally of a lower quality (IPPC, 1996). This is the case for data on greenhouse gas emissions and removals from agricultural fields, which are often estimated with large ranges of uncertainty. One of the causes of this problem is the fact that estimates of greenhouse gas emissions from agricultural soils are often based on few point measurements. The mean value obtained from few sampled points is used to compute global budgets and models. There is therefore a need for approaches to improve the estimation of greenhouse gas emissions at field scale so that the models of emission response to climate change at a global scale can also be improved. Such approaches could also be used to improve methods to measure, monitor and predict changes in soil properties (Robert et al., 1991). Geographic Information Systems (GIS) and Global Positioning System (GPS), Computer mapping and Geostatistics are technologies that have been used to manage soil and nutrients (Robert et al., 1991; Mulla, 1991). GPS enables equipment operators to quickly obtain positioning information while a GIS is essentially a database for managing these geographic data. The goals of this work are (i) to improve our understanding on the relationship between static and dynamic soil variables and greenhouse gas fluxes from soil in various land use types and (ii) to improve methods to measure, monitor, quantify and predict greenhouse gas fluxes from soils. Specific objectives of this study were to: (i) study the relationships between greenhouse gases emissions and soil properties, (ii) assess the influence of agricultural practices on greenhouse gas fluxes and soil properties and (iii) improve the quantification of greenhouse gases from soil in agricultural fields using geospatial technologies.

1.2. Greenhouse gas fluxes from agricultural soils

1.2.1. Carbon dioxide (CO_2)

Soil represents about 80% of the carbon stocks in terrestrial ecosystems, ranging from 50% in tropical forests to 95% in tundra (IPCC 2001). The global impact of soil carbon loss due to agriculture is therefore considerable. Recent estimates suggest that 50-100 Gt C (CAST, 2004; Smith, 2004) have been lost from soils in the past few hundred years, although higher estimates range to 142 Gt C (Lal, 1999). Conversion of natural ecosystems to agriculture releases substantial CO_2 to the atmosphere. The release of CO_2 from cleared vegetation that is burned or left to decompose is one of the most well-documented and important sources of the atmospheric CO_2 increase. Historically, land clearing (biomass burning) has been a major contributor to atmospheric CO_2 loading; today it still accounts for about 25% (1.6 Gt C y^{-1}) of the total global CO_2 loading, which includes another 6.3 Gt C y^{-1} from fossil fuel use and cement production (IPCC 2001). Forests and savannahs newly cultivated usually lose a substantial fraction of their original carbon content in the decades following initial cultivation. This occurs for a number of reasons: reduced plant residue inputs, tillage-induced soil disturbance, erosion, and the creation of more favorable conditions for microbial decomposition (CAST, 2004). Generally soil carbon contents stabilize at 40-60% of original pre-cultivation values; the new equilibrium state is a function of climate, soil-mainly soil physical and chemical properties, and agronomic management factors such as tillage, crop types and cover, and residue management (Robertson and Paul, 2000). Soils can also gain carbon. The soil carbon balance is the net difference between carbon inputs from plant roots and aboveground litter (that remaining after harvest or fire), and carbon loss from microbial respiration and erosion. In agricultural systems, manure and compost can represent additional inputs. Because erosion repositions carbon in the landscape rather than converts it to CO_2, erosion is not in itself a source of greenhouse Gas Warming potential (GWP). Microbial respiration, on the other hand, is a major source of GWP – where respiration is slowed, as in no-till systems, carbon can accumulate at slow but significant rates to some new equilibrium (Paustian et al., 1997). Estimates of historic soil C loss provide a reference point for carbon sequestration potentials. Models suggest that 60-80% of the soil carbon lost as CO_2 could be regained under no-till conditions over a period of 50 years (IPCC, 1996); if this is the case, then as much as 60-85 Gt C could be regained by agricultural soils at a rate of about 1.1 to 1.7 Gt C y^{-1}. In soils of the United States Midwest, the median rate of annual carbon gain under no-till is 30 gC m^{-2} (Franzleubbers and Stuedemann, 2002), which is equivalent to a GWPof-110gCO_2-equivalents m^{-2} y^{-1}.

1.2.2. Nitrous oxide (N_2O)

Nitrous oxide is produced during nitrification and denitrification in agricultural soils. During nitrification ammonium is converted to nitrite (NO_2^-) and then to nitrate (NO_3^-) by aerobic autotrophic bacteria collectively known as nitrifiers; N_2O is a minor byproduct. Denitrification is a soil microbial process in which nitrate is converted to dinitrogen gas (N_2) by heterotrophic, facultatively anaerobic bacteria collectively known as denitrifiers; N_2O is a requisite intermediate that under some environmental conditions and for some denitrifier taxa is the end product (Cavigelli and Robertson, 2000). Nitrification occurs whenever soil ammonium is available and environmental conditions such as temperature and moisture are favorable for nitrifiers activity, which in many agronomic situations prevail most of the time (Robertson et al., 2000). Denitrification occurs whenever soil carbon and nitrate are available and oxygen is in short supply – denitrifiers can use nitrate rather than oxygen as a terminal electron acceptor if oxygen is unavailable (Robertson, 1993; Robertson and Grace, 2004). This occurs in wet soils when diffusion of oxygen to microsites is slowed by saturated conditions, and inside soil aggregates in even well-drained soils. In the center of aggregates oxygen demand is often greater than can be provided by diffusion through the aggregate from the surrounding soil atmosphere. Nitrous oxide can also be produced from livestock waste, though only when stored under relatively aerobic conditions such as in compost heaps. Under anaerobic conditions, as in waste lagoons, nitrification is inhibited by lack of oxygen and denitrification by the consequent lack of nitrate; further, any nitrate that is available tends to be denitrified all the way to N_2 rather than stop at N_2O (CAST, 2004) due to the low availability of electron acceptors. Of all the sources of GWP in agricultural systems, none are more poorly quantified than N_2O production. This is mainly because of the difficulty with which N_2O fluxes are measured. Unlike for CO_2 and CH_4, N_2O flux is not suited to micrometeorological measurement (Holland et al., 1997); rather fluxes must be measured using small chambers placed on the soil surface for 1-2 hour intervals. High temporal and spatial variability means that many chambers must be deployed simultaneously at weekly or more frequent intervals in a given cropping system; sampling and analysis costs are thus high. However, for the few cropping systems for which we have reliable N_2O fluxes, N_2O loss is frequently the major source of GWP. Robertson et al. (2000), for example, found for a 9-year measurement campaign in several annual and perennial cropping systems in Michigan that N_2O was the single greatest source of GWP in all four of their annual crop systems, ranging from 50 to 60 g CO_2-equivalents m^{-2} y^{-1}. IPPC methodology assumes that 1.25% of nitrogen inputs to most cropping systems is subsequently emitted as N_2O-N; if true, then for every 100 kg N ha^{-1} applied as fertilizer, about 1.25 kg N will be emitted as N_2O, for a GWP (over a 100-year time horizon) of 58 g CO_2-equivalents m^{-2} y^{-1}. Soil nitrogen availability appears to be the single best predictor of N_2O flux in most terrestrial ecosystems including agricultural fields. Any activity or process that acts to keep available soil nitrogen low should thus lead to smaller N_2O flux. Plant demand for nitrogen is therefore one of the most important determinants of N_2O flux, and more precise application of N-fertilizer — to maximize plant uptake of added N both spatially and temporally — may be one of the best means available for mitigating current N_2O fluxes from agriculture.

1.2.3. Methane (CH_4)

Methane is produced by anaerobic bacteria in soil, animal waste, and ruminant stomachs, and agricultural sources of methane are a significant fraction of the global methane budget. About 15% of the 598 Tg global CH_4 flux is from lowland rice systems, and another 15% is from enteric fermentation during livestock digestion (Hein et al., 1997; IPCC 2001). Because methanogenesis is a strictly anaerobic process, under normal conditions upland cropping systems are not a direct source of methane, and methane flux in paddy rice can be partly mitigated through water level and residue management and cultivar selection (Mosier et al., 1998a and b). Methane is also consumed, but by a different class of soil bacteria called methanotrophs, and methane consumption in soils is a small but significant part of the global methane budget, comparable in magnitude to the annual atmospheric increase in methane. In rice paddies and wetlands the total methane flux is the net difference between methanogenesis in submerged anaerobic horizons and methane consumption at or above the soil-water interface. In upland soils including field crops the net flux appears to be largely a function of methane consumption. Agricultural conversion tends to reduce natural rates of methane consumption in soils by a factor of 5-10 (Bronson and Mosier, 1993; Smith et al., 2000), and at our current state of knowledge there is no known way to restore consumption other than allowing natural revegetation. Consumption rates are not much affected by fertilization, organic management, or tillage. By reducing a natural source of mitigation, agriculture thus creates an indirect source of GWP. Robertson et al. (2000) found for a U.S. Midwest landscape that the GWP of methane oxidation in old-growth forest was -25 g CO_2-equivalents m^{-2} y^{-1}; for various cropping systems on the same soil type they found GWPs ranging from -4 to -6 g CO_2-equivalents m^{-2} y^{-1}. Similar changes have been documented for a variety of soil and climates (e.g. Smith et al., 2000), including tropical (Keller and Reiners, 1994).

1.3. Soil properties

1.3.1. Soil thermal properties

Soil heat is one of the most important factors controlling the intensity of biophysical, biochemical and microbiological processes taking place in soil (Ghidhyal and Triparti, 1987; Schilfgaarde, 1974; Brady, 1984). The rate of mineralization of organic matter (Hoyt and Hargrove, 1986; Bristow, 1988; Fortin and Pierce, 1991), the physical process of diffusion and viscous flow (Liu and Dane, 1993), the germination of seed (Xie et al., 1993), the growth and activity of roots in terms of water and nutrients absorption (Glinski and Lipiec, 1990) and respiration (Xie et al., 1993; Egley, 1986) are strongly dependent on the heat energy that a soil contains. The amount of heat absorbed by a soil is primarily determined by the quantity of effective radiation reaching the earth (Brady, 1984) while its movement in the profile is dependent on soil thermal properties. De Vries (1953) described heat movement as an apparent increase of thermal conductivity of soil which is the sum of normal conductivity and that due to vapor movement. Knowledge of thermal properties is therefore necessary to adequately predict the transport, flow and escape of greenhouse gases from soils. Unfortunately, research work on the relationship between soil heat and greenhouse gases emissions inexistent is restricted to soil temperature. Studies relating soil thermal diffusivity, conductivity and resistivity are almost inexistent. Furthermore, measurements of soil thermal properties are rarely done (Kluitenberg et al., 1993; Bristow et al., 1994).

1.3.2. Soil pore space indices

Greenhouse gases produced in soils move through the soil air-filled pore space before their emissions to the atmosphere. The probability for their consumption increases as impediments to their movement increase. The exchange of gas between the soil surface and the adjacent atmosphere can occur by means of two mechanisms: diffusion and advection. Diffusive gas transport depends primarily on the total volume and the tortuosity of continuous air-filled pore space. Advective gas transport is affected by gaseous permeability which, in turn, is dependent on total porosity, pore size distribution, and tortuosity of continuous air-filled pore space (Hillel, 1982). It is well documented that gaseous diffusion is the principal process involved in the exchange between the soil and the atmosphere (Taylor, 1949; Troeh et al., 1982). Gaseous diffusion and its variations with soil type and soil air-filled porosity typically control soil aeration (Buckingham, 1904; Taylor, 1949), fumigant emissions (Brown and Rolston, 1980), volatilization of volatile organic chemicals from industrially polluted soils (Petersen et al, 1996), and soil uptake and emissions of greenhouse gases such as methane (Kruse et al., 1996). Soil pore structural indices are therefore a key factor in determining greenhouse gas soil fluxes, because they are related to the redox potential in the soil, to soil moisture content (and hence microbial activity), the residence time in soil pores of greenhouse gases produced in the soil, and the ability for the atmosphere to supply methane to methanotrophs. Static and dynamic soil properties both affect the water, gases and solutes that pass through and over soils. Unfortunately, most of the studies investigating the relationship between soil properties and greehnouse gas fluxes have focussed on static soil variables influencing gas production rather than dynamic ones which control gases escape to the atmosphere. In the case of N_2O for example, Van Den Pol-Van Dusselaer (1998), Velthof et al. (1996) and Ambus and Christensen (1995) reported a poor relationship between emssions and static soil variables. In these studies, static soil variables were NO_3^- and NH_4^+ which have been cited among those operating at microbial level and influence N_2O production rather than its escape to the atmosphere (Firestone and Davidson, 1989). Kiese et al. (2003) could not relate N_2O fluxes to NO_3^- and NH_4^+. Linn and Doran (1984) found a significant relationship between the percentage of pore space filled with water (WFPS) and CO_2 and N_2O production. Davidson (1991), Firestone and Davidson (1989) suggested the Hole-in-the Pipe (HIP) conceptual model which relate the sum of $NO+N_2O$ emissions to NO_3^- and NH_4^+ (indices of availability of N), and the ratio $NO:N_2O$ to WFPS (water content). While these empirical relationships have worked in various conditions of studies (Davidson et al., 2000), in order to fully understand the effect of soil variables on greenhouses gases, it is important to consider also variables affecting the movement of gases in soils such as pore structural indices. In fact, only little work has focused on the relationship the soil gas diffusion and greenhouse gases emissions. Among the few investigators, Nkongolo et al. (2008) found a relationship between CO_2 and CH_4 emissions and pore structural indices in both a Japanese and Costa Rican forests. Born et al. (1990) and Dorr et al. (1993) stated that the most important factor controlling CH_4 fluxes (in non wetland soils) is gas transport resistance in soils. Kruse et al. (1996) reported a significant relation between methane emission and gas diffusion coefficient. Ball et al (1997) reported a relationship between N_2O fluxes and air permeability, the soil gas diffusion coefficient and tortuosity. Hu et al. (2001) found a significant relationship between the soil gas diffusion coefficient and CH_4 fluxes.

1.4. Experimental plan

1.4.1. Justification for integrating research work in USA and Japan

The results of field experiments conducted in both United States of America and Japan are analyzed and integrated in this thesis. The justifications for integrating these studies are : (i) to add confidence to our studies as replication helps provide assurance that the results are correct, (ii) to increase our understanding on whether the same parameters control gas fluxes in similar land use types in both countries and (iii) to investigate whether gas fluxes exhibit the same patterns in both countries. In fact, the development of a same approach to quantify greenhouse gas fluxes or the identification of same parameters controlling greenhouse gas fluxes in different environment or different countries is sought in building global models for controlling gases emissions. This thesis therefore provides data that can be used to improve, parameterize, and test existing global models of CO_2, N_2O and CH_4 fluxes and allow measurements to be extrapolated to different management scenarios and larger spatial scales.

1.4.2. Experimental sites in USA

1.4.2.1. George Washington Carver farm

This farm is located at 2 miles from the main campus of Lincoln University. Its coordinates are 38°31'45"N and 92°08'07"W. The soil type of the site is a Freedom Silt-Loam (Aquic Hapludalfs). In 2006, the total rainfall during the sampling period (June through November) was 310 mm and an average temperature of 27°C. The area has experienced a drought during the spring and summer months of 2006. The study area was 1.42 ha area dominated by Brome grass (Brumus inermis). Brome grass is a cool season grass that is very popular in the production of hay. The sampling chambers were arranged in a rectangular grid of 30 m by 35 m. The experiment was started in 2003 when twenty chambers were permanently inserted in the soil of this pasture at a first site. Soil air samples for determination of CO_2, CH_4 and N_2O concentrations were collected every two weeks a year later in 2004, 2005 and 2006 at this first site before the study was moved to second site in 2007 and where data are still being collected (2007, 2008 and 2009). The results discussed in this thesis focuses on site 1 and mainly on data collected in 2006 even though an account is also given for the 2004 and 2005 sampling periods.

1.4.2.2. Freeman farm

Freeman farm is located 15 miles west of the main campus of Lincoln University. The geographic coordinates of this site are 38°34′53″N and 92°08′07″W. The soil type is Waldron silty-clay (Aeric Fluvaquent). Corn and soybean are the crops planted at this farm. The tillage practiced on corn and soybean fields is chisel plowing and harrowing up to 15 cm soil depth at the beginning of the planting season (May). The corn experimental site consisted of 16 plots of equal size (91 m x 12 m) with a 12 m buffer strip between and within plots, so each plot stands separately, with 2 gas chambers per plot for a total of 32 gas sampling chamber. Bulk fertilizer application supplying NPK, consisting of Urea, DAP (Diammonium phosphate), and Potash was applied to the corn field in May, prior to planting. These fertilizer treatments (N1, N2, N3, and N4 represented 0, 60, 120, and 180 lb/acre of urea respectively) and supplied 26.32 (N1), 93.58 (N2), 160.84 (N3) and 228.10 (N4) kg N ha^{-1} from urea and DAP, while the DAP and Potash supplied 67.26 kg P_2O_5 ha^{-1} and 89.68 kg K_2O ha^{-1} respectively. An additional amount of nitrogen (N) is supplied from DAP, consequently, treatment N1 corresponds to 26.33 kg N ha^{-1}, but without any urea applied. The soybean field was adjacent to corn and was not fertilized.

1.4.3. Experimental sites in Japan

1. 4.3.1. Livestock farm, Faculty of Agriculture, Hokkaido University in Shizunai

The first experiment was conducted at the Livestock Farm, Faculty of Agriculture, Hokkaido University in Shizunai. Shizunai is located at 42°25.9'N and 14°25.9'E. The annual average temperature is 7°C, and the average temperature is 20°C in August and -5°C in February. Annual mean precipitation is 1,200 mm. Snow covers the land from late November to middle of March. The soil of this area is derived from Tarumae (B) volcanic ash, and is classified as Aquic Humic Udivitrand (USDA soil taxonomy). In situ measurements were conducted along a 2000 m transect extending from a forest, grassland, pasture and cornfield soils in August 2000. Mapple (Aceraceae rubrum) and oak (Fagaceae quercus) predominates in the forest. Forest floor was covered by Sasa nipponica Makino et Shibata. The grassland site was derived from a converted forest in 1965 (Hu et al., 2001). Phleum pratense L. and Trifolium pratense were the dominant grasses. Chemical fertilizers were applied annually in the middle of May. During the experimental year, N, 68, P, 58, K, 38 kg ha^{-1} fertilizers were applied. Cattle grazed 8 times from May to October during the observation. The cornfield had been used for growing corn for more than 30 years. Corn (Zea mays L.) is usually sowed in May and harvested in September. Fertilizers consisting of N, 120, P, 48; and K, 58 kg ha^{-1} are applied at sowing time, and farm manure (N, 64 kg ha^{-1}) incorporated into the soil during the previous year.

1. 4.3.2. Hokkaido University Experimental farm in Sapporo

The second study was conducted at Hokkaido University Experimental Farm in Sapporo, Hokkaido, Japan (43° 11’ N, 141° 30’ E), from early June to late December 2001. Sapporo, Japan's third largest city enjoys a mild climate with a year-round average temperature of 9.1°C. The average temperature was -3.5°C in January and 20.3°C in July 2001. The soil of the experimental site is classified as Typic Fluvaquents (Soil Taxonomy), Eutric Fluvisols (FAO). The physical and chemical properties of different horizons were reported by Hayashi and Hatano (1999). Soil texture consists of 25.4% sand, 47.0% silt and 27.6% clay. The saturated hydraulic conductivity is 2.99 x 10^{-5}cm s^{-1}. The carbon and nitrogen contents were 2.1% and 0.16 %, respectively. Field preparation began in April and in May, two plots of 30 m long by 20 m width were isolated in fields cropped to corn (Zea mays) and soybean (Glucine max). These fields were established maintained by the Crop Production Laboratory, Faculty of Agriculture, Hokkaido University. The corn field was fertilized with N, 130; P_2O_5, 180; K_2O, 100; and MgO, 40 kg ha^{-1} while soybean received N, 32; P_2O_5, 100; K_2O, 80; and MgO, 24 kg ha^{-1}. In June 2001, plots interrows in both soybean and corn fields were compacted by 1, 2, 3 and 4 cycles (1 cycle = 2 passes) with a 2.4 tons Fordson Major tractor (as during regular tillage operations). The ridges of crop rows were not compacted. Immediately after tractor compaction, soil penetration resistance (SPR) was measured to a depth of 100 cm and soil samples were taken in both interrows and ridges. A second measurement of SPR, sampling for soil properties and greenhouse gas fluxes was conducted three weeks later in August 2001.

1. 4.3.3. Farmer field in Mikassa, Hokkaido

The third study was conducted in a 140 by 140 m upland farmer field yearly cropped to onion (Allium cepa L.) in Mikassa, Hokkaido, Japan (43°14'N, 141°50'E). The annual average temperature in Mikassa is 7.2°C and the average annual rainfall is 1204 mm. The soil of the experimental site is classified as fine, mesic, mollic Fluvaquent. Soil texture consists of a silty or heavy clay from the Ap layer (0-28 cm) down to the C horizon (48-100+ cm). The groundwater table lays at 70-80 cm depth throughout the growing season (Hu et al., 2001). Surface drains were installed at 80-100 cm depth at 12 m intervals and were connected to the same effluent exit, draining about 0.95 ha (125 by 76 m) for monitoring nitrate leaching. Fertilizer nitrogen (322 kg N ha^{-1}) was applied at the end of April, shortly before transplanting. Onion was harvested during the second and third week of September. In June 1999, the field was sampled for N_2O emissions and soil physical and chemical properties, using a 100 by 100 m grid at 10 m spacing for a total of 100 sampling locations. A year later in September 2000, the same field was again sampled for N_2O and soil chemical and physical properties, using a 60 by 60 m grid at 10 m spacing for a total of 36 locations.

PART II. RELATIONSHIPS BETWEEN GREENHOUSE GASES EMISSIONS AND SOIL PROPERTIES IN AGRICULTURAL FIELDS

Chap. 2. Greenhouse gas fluxes and soil thermal properties in a pasture in central Missouri[1]

2.1 Abstract

Fluctuations of both greenhouse gases emissions and soil controlling factors occur at short spatial and temporal scales, however results are often reported for larger scales studies. We monitored CO_2, CH_4, and N_2O fluxes and soil thermal properties from 2004 to 2006 in a pasture at Lincoln University, and conducted a month-to-month assessment of trends in fluxes and soil thermal properties in 2006 data. Soil air samples for determination of CO_2, CH_4 and N_2O concentrations were collected from static and vented chambers. Air samples were analyzed within 2 hours with a gas chromatograph with an electron capture detector. Soil temperature (T), thermal conductivity (K), resistivity (R) and thermal diffusivity (D) were directly measured using a KD2 probe. Soil samples were also taken for measurements of soil chemical and physical properties. Results showed that, overall, the pasture acted as a sink in 2004, a source in 2005 and again a sink of CH_4 in 2006. CO_2 and CH_4 were highest, but N_2O as well as T, K and D were lowest in 2004. Only K was correlated with CO_2 in 2004 while T correlated with both N_2O ($r = 0.76$, $p = 0.0001$) and CO_2 ($r = 0.88$, $p = 0.0001$) in 2005. In 2006, all gas fluxes were significantly correlated with T, K, R when the data for the entire year was combined and averaged. However, an-in depth examination of 2006 data revealed the existence of month to month shifts, lack of correlation and differing spatial structures. For instance, T could not correlate with any of the gases in June, July and August, but only in September. These results call for further investigations to elucidate the

inconsistencies in the relationship between soil properties and gas fluxes across sampling periods. K and R offer a promise as potential controlling factors for greenhouse gas fluxes in this pasture.

Keywords: greenhouse gases, soil thermal properties, fluxes

2.2 Introduction

Soil and its use contribute greatly to the enhanced warming of the earth's surface and lower atmosphere as a result of increased emissions of greenhouse gases into the atmosphere by human activities such as agriculture (Dobbie and Smith, 2003). In soil, these greenhouse gases are mainly emitted through microbiological processes and their flux variations are regulated by processes that control microbial activities (Kang et al., 2003; Kang et al., 2000), such as soil temperature (Brito et al., 2009; Almagro et al., 2009), soil water content (Rover et al., 1999, Dobbie and Smith , 2003), depth to the water table (Huttunen et al., 2003), root activities (Raich and Tufekgcioglu, 2000), decomposition of organic matter (Epron et al., 2006; Xu and Qi, 2001), availability of substrate (Smith, 2000), soil N dynamics and C and N availabilities (Turner et al., 2008; Davidson et al., 2000; Mutegi et al., 2009; Le Mer and Roger, 2001; Raich and Tufekgcioglu, 2000; Saiz et al., 2006). Both greenhouse gas fluxes and their controlling factors also exhibit tremendous variability across ecosystems and this variability poses a serious problem in estimating N_2O, CH_4 and N_2O fluxes at larger scales (Nkongolo et al., 2009 (ab);

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Raich et al., 1990, Stoyan et al., 2000) and in assessing the relationship between soil properties and N_2O, CH_4 and N_2O fluxes (Nkongolo et al., 2008 (ab), Johnson et al., 2007 and Paro et al., 2007). Among soil properties, the relationship between soil temperature and greenhouse gas fluxes has received more attention. However, in many studies soil temperature has been correlated or not correlated with greenhouse gas fluxes (Smith et al., 2003). Other soil properties such as thermal properties have not received due attention. However, these properties control the movement of heat in the soil therefore affect directly the escape of greenhouse gases from these soils (Hopmans et al., 2002). Scientists have documented the importance of soil thermal properties as early as the 19th century (Forbes, 1849). Soil thermal properties influence the partitioning of energy at the ground surface and are related to soil temperature and the transfer of heat and water across the ground surface (Ochsner et al., 2001). Fluctuations of both greenhouse gas fluxes and soil controlling occur at short temporal and spatial scales, but results of studies are often reported for larger scales (several years). In fact, across shorter temporal and spatial scales, abrupt changes in greenhouse gases emissions may occur in response to a change in a soil controlling factor or any other event (Curtin et al., 2000; Duiker and Lal, 2000). The first objective of this study was to assess the fluctuations of CO_2, CH_4, and N_2O emissions and soil thermal properties in a pasture in central Missouri. A second objective was to investigate the relationship between soil thermal properties and greenhouse gas fluxes in this pasture.

2.3 Materials and methods

2.3.1 Study area

The experiment was conducted on a pasture at George Washington Carver farm at Lincoln University in Jefferson City, Missouri. The experiment was started in 2003 when twenty chambers were permanently inserted in the soil of pasture at a first site. Soil air samples for determination of CO_2, CH_4 and N_2O concentrations were collected every two weeks a year later in 2004, 2005 and 2006 at this first site before the study was moved to second site in 2007 and where data are still being collected (2007, 2008 and 2009). This study focuses on site 1 and mainly on data collected in 2006 even though an account is also given for 2004 and 2005 sampling period.

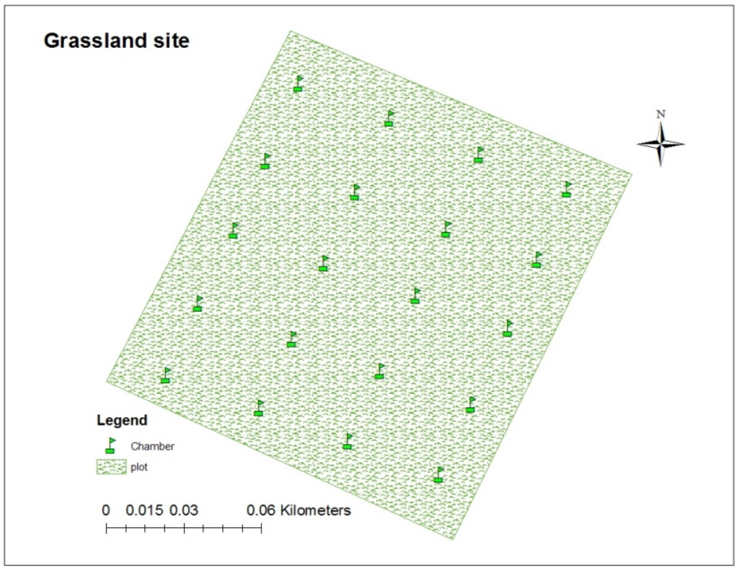

Figure 2.1. Experimental field

The geographical coordinates of the site are 38°31'45"N and 92°08'07"W. The soil type of this site is a Freedom Silt-Loam (Aquic Hapludalfs). The total rainfall from June through November was 310 mm with an average temperature of 27°C. This area has experienced a drought during the spring and summer months of 2006. The study area was 1.42 ha area dominated by Brome grass (Brumus inermis). Brome grass is a cool season grass that is very popular in the production of hay. The sampling chambers were arranged in a rectangular grid of 30 m by 35 m (Fig. 2.1) and air samples were collected from June to December.

2.3.2 Soil air sampling and gas measurement

Twenty cylindrical polyvinylchloride (PVC) chambers of 0.30 m long and 0.20 m in diameter were permanently inserted into the soil to a depth of 0.05 m since summer of 2003. The design of the sampling chamber is a modified version of Hutchinson and Mosier (Hutchinson and Mosier, 1981) and is illustrated in Figure 2.2.

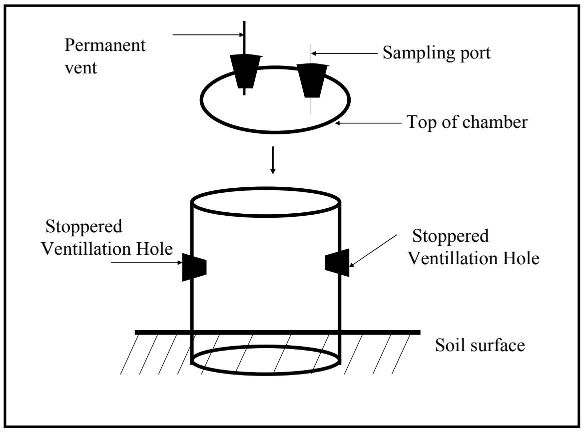

Figure 2.2. Soil air sampling chamber

The chambers were constructed with two ventilation holes on the sides. They had circular tops made from Plexiglas and containing two additional holes. One of the holes was covered by a stopper for the extraction of gases and while the other served for ventilation. Installation of these chambers permanently since 2003 kept soil undisturbed. In order to maintain an air tight seal, a groove was put on the bottom of the lid so that it would fit securely onto the sampling chamber. During sampling time the groove was filled with Dow-Corning high vacuum grease for sealing purpose. Soil air samples for gas analysis were collected as follows; (1) an air sample was collected at 2 m from the soil and above the chamber, (2) the two chamber ventilation holes were sealed off by rubber stoppers, (3) the greased (to seal the chamber) chamber tops were put on, (4) the chamber was allowed to fill up with air for thirty minutes and; (5) the air samples were collected with a 50 ml syringe and put in to a 200 ml Tedlar bag for storage. Analysis of CO_2, CH_4, and N_2O from soil air samples were conducted at Lincoln University's Dickinson Research Laboratory within two hours after samples collection. The concentration of each greenhouse gas was measured using a Gas Chromatograph with an electron capture detector. The data was then transferred into an Excel data sheet where the gas fluxes were calculated. A positive value represents gas emission from the soil, while a negative value represents gas uptake. Fluxes were calculated using the equation (Ginting et al., 2003):

$$F = \rho * \frac{V}{A} * \frac{\Delta C}{\Delta t} * (\frac{273}{T}) * \alpha$$

where, F is the gas production rate; ρ is the gas density (kg m^{-3}) under standard conditions; V (m^3) and A (m^2) are the volume and area of the chamber; ΔC/Δt is the ratio of change in the gas concentration inside the chamber (10^{-6} $m^3 m^{-3} h^{-1}$); T is the absolute temperature; and α is the transfer coefficient (12/44 for CO_2, 12/16 for CH_4 and 28/44 for N_2O).

2.3.3 Soil physical properties

Soil samples were taken at each chamber location using a soil sampling probe at 0.10 m depth. The soil fresh weights were measured and then the soil samples were put into an oven to be dried at 105°C for seventy two hours. After drying to constant weight, soil physical properties were calculated as follows; (1) Bulk density (ρ_b = Ms|Vt), where ρ_b (kg/m^3) is the bulk density, Ms (kg) is the mass of dry solids determined after drying the soil sample to constant weight at 105°C and Vt (m^3) is the total volume of soil; (2) Total pore space [TPS = Vw +Va/Vt = 1- (ρ_b /2.65 kg m^{-3})], where TPS (m^3 m^{-3}) is the total space of soil filled with fluid (air and water), ρ_b (kg/m^3) is the soil particle density; (3) Gravimetric water content (θ_g = Mt-Ms/Ms), where, θ_g (kg/kg^{-1}) is the gravimetric water content or mass of water present in each unit mass of dry soil; (4) Volumetric water content (θ_v = Mt-Ms/Vt) where θ_v (m^3 m^{-3})

is volumetric water content or the volume of water present in a unit volume of soil and (5) Air filled porosity (f_a = TPS-θ_v), where f_a (m^3 m^{-3}) is air filled porosity or the portion of the pore space filled with air. (7) Water-filled pore space (WFPS = (θ_v /TPS)*100).

2.3.4 Soil chemical properties

At each chamber location soil samples were taken at 0.1 m depth with a sampling probes for analyses of soil chemical properties. These samples were sent to the Soil and Testing Lab at the University of Missouri-Columbia for the chemical analysis (regular analysis). The properties studied were soil pH, organic matter (OM), phosphorus (P), calcium (Ca), magnesium (Mg), potassium (K), cation exchange capacity (CEC), sulfate (SO_4-^{2}), iron (Fe), electrical conductivity (EC), nitrate (NO_3^-), ammonium (NH_4^+), and total nitrogen (TN).

2.3.5 Soil thermal properties

The soil thermal properties were measured inside each chamber or on its neighborhood with a Decagon KD2 thermal properties meter at 0.06 m depth. The KD2 thermal meter uses three sensors to measure thermal diffusivity (D), thermal conductivity (K), thermal resistivity (R) as well and soil temperature. KD2 takes measurements at one second intervals during a ninety second measurement cycle by using the transient line heat source method. The soil thermal properties were measured during every sampling date.

2.3.6 Mapping and statistical analysis

Statistix 9.0 was used to calculate simple statistics, Pearson correlation matrix and to run a linear regression analysis for CO_2, N_2O, and CH_4 and the soil properties. GS+ 5.1 software was used to fit data to semivariogram models and produce maps portraying the spatial distribution of greenhouse gas fluxes across the pasture.

2.4 Results

2.4.1 Soil physical properties

The summary of simple statistics for soil physical properties measured in 2006 is showed in Table 2.1.

Table 2.1**.** Summary of simple statistics for soil physical properties in pasture in 2006

	f_a (m^3 m^{-3})	ρ_b (kg m^{-3})	D_s/D_o (m^2 s^{-1} m^{-2} s)	θ_g (kg kg^{-1})	θ_v (m^3 m^{-3})	τ (m m^{-1})	WFPS (%)	TPS (m^3 m^{-3})
Mean	0.26	1.23	0.07	0.22	0.27	3.89	51.16	0.53
SD	0.04	0.07	0.02	0.01	0.01	0.53	4.31	0.03
Variance	0.00	0.01	0.00	0.00	0.00	0.28	18.57	0.00
C.V.	13.76	5.80	28.32	4.39	4.30	13.58	8.42	5.03
Minimum	0.21	1.06	0.04	0.21	0.25	2.86	41.80	0.50
Median	0.26	1.24	0.07	0.22	0.27	3.84	50.99	0.53
Maximum	0.35	1.33	0.12	0.24	0.30	4.80	58.51	0.60
Skew	0.51	-0.78	0.96	0.24	0.50	0.27	0.03	0.78
Kurtosis	0.55	0.41	1.45	-0.84	0.01	-0.28	0.13	0.41

f_a = air-filled porosity, ρ_b = bulk density, D_s/D_o = relative gas diffusion coefficient, θ_g = gravimetric water content, θ_v = volumetric water content, τ = pore tortuosity factor, WFPS = water-filled pore space, TPS = total pore space.

Soil physical properties in 2004 and 2005 are not showed. At the time of sampling, the soil of this pasture had an average air filled porosity of 0.26 m^3 m^{-3}. The soil bulk density was 1.23 kg/m^3. Soil water was at an adequate level for plant growth as reflected by an average gravimetric water content of 0.22 kg/kg and a volumetric water content value of 0.27 m^3 m^{-3}. The pore tortuosity factor was 3.89 m m^{-1} while the relative gas diffusion coefficient was 0.07. Only 51.16% of the total pore space was filled with water. Overall, soil physical properties were in the range of normally reported data with very low variability (highest CV = 28.32). The distribution of these soil properties also approached normality as showed by means and medians which are equal.

2.4.2 Soil chemical properties and nutrients

The summary of simple statistics for soil chemical properties and nutrients measured in 2006 is showed in Table 2.2.

Table 2.2. Summary of simple statistics for soil chemical properties in pasture in 2006.

	pH	EC	NO_3^-	NH_4^+	P	K	Ca	Mg	SO_4^{-2}	OM
		(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})	(mg kg^{-1})	(g kg^{-1})
Mean	4.76	0.16	1.74	6.64	54.32	258.30	2610.70	340.83	3.55	17.00
SD	0.15	0.06	2.11	15.05	23.68	95.82	1356.90	276.19	0.77	2.88
C.V.	3.05	40.27	120.89	226.75	43.59	37.10	51.97	81.03	21.65	16.91
Min.	4.60	0.10	0.30	1.00	14.56	91.84	1403.40	110.88	1.70	12.00
Med.	4.75	0.15	1.00	2.53	48.72	286.72	1939.80	220.08	3.75	17.00
Max.	5.00	0.30	7.30	62.61	92.96	388.64	5637.00	991.20	4.60	23.00
Skew	0.28	0.59	2.13	3.52	-0.02	-0.18	1.21	1.43	-0.90	0.47
Kurt.	-1.26	-0.58	2.83	10.62	-0.85	-1.24	-0.04	0.61	0.22	0.04

CEC = cations exchange capacity, EC = electrical conductivity, OM = organic matter.

Soil chemical properties in 2004 and 2005 were omitted. The average pH of this pasture was 4.75, implying that the soil was acidic. The sum of N-indices (NO_3^-+ NH_4^+) was 8.34 mg kg^{-1} and an average organic matter (OM) of 17 mg kg^{-1}. The cation exchange capacity was 12.18 meq/100g. The pasture contained more Ca (2610.70 mg kg^{-1}) as compared to major nutrients such as K (258.30 mg kg^{-1}) or secondary nutrients such as Mg (340.83 mg kg^{-1}). The distribution of soil pH, Acidity, EC, SO_4^{-2}, Fe and OM approached normality as showed by their mean values closer or equal to their respective medians. Soil chemical properties and nutrients showed a range of variability with coefficient of variation (CV) ranging from 3.05 for soil pH to 226.75% for NH_4^+. Overall, indices of N-availability (NO_3^- and NH_4^+) showed the highest variability with highest CV. $NO_3^-$and NH_4^+ also had the highest skew and kurtosis values.

2.4.3 Soil thermal properties

The summary of simple statistics for soil temperature (T), thermal conductivity (K), resistivity (R), and diffusivity (D) measured in 2004, 2005 and 2006 are shown in Table 2.3.

Table 2. 3. Summary of simple statistics for soil thermal properties in 2004, 2005 and 2006

Simple Stat.	T (°C)			K (w/m/c)			D (mm^2/s)			R (m°c/w)		
	2004	2005	2006	2004	2005	2006	2004	2005	2006	2004	2005	2006
Mean	22.77	14.05	20.03	0.85	0.48	1.10	0.19	0.14	0.47	1.52	2.30	3.63
SD	3.80	11.42	6.01	0.29	0.14	0.5	0.05	0.03	0.58	1.38	0.77	1.59
CV	16.71	81.25	30.01	34.75	29.35	45.99	27.11	20.11	126.68	90.95	33.38	43.87
Min	17.80	2.30	7.40	0.14	0.27	0.15	0.09	0.10	0.2	0.74	1.32	0.65
Max	30.70	28.40	26.17	1.35	0.75	2.11	0.34	0.22	4.86	7.34	3.76	8.80
Skew	0.26	0.02	-0.88	-0.52	0.03	0.01	0.62	1.61	7.34	3.35	0.71	0.76
Kurt.	-1.27	-1.97	-0.80	0.15	-0.87	-0.96	1.00	2.93	53.03	10.44	-0.92	0.50

T= soil temperature, K= soil thermal conductivity, D= soil thermal diffusivity, R= soil thermal resistivity

The mean soil temperature was highest in 2006 as compared to 2004 and 2005. In addition, soil thermal K, R and D were highest in 2006 as compared to either 2004 or 2005. Coefficients of variation (CV) for soil thermal properties ranged from 16.71 to 126.68% with the lowest CV observed for soil temperature in 2004, and the highest for thermal diffusivity (D) in 2006. A month to month assessment of soil thermal properties in 2006 revealed that the mean of all four months was 20.03°C, with a minimum temperature of 7.40°C and a maximum of 26.16°C. Soil temperature increased by 5 units from June (20.55 °C) to July (25.52 °C), then decreased about one unit in August (23.78 °C) and finally decrease sharply about 14 units in September (10.42°C). The mean of soil thermal conductivity, resistivity, and diffusivity for all four months were 1.01wm^{-1} c^{-1}; 3.63 m°cw^{-1}; and 0.45 mm^2s^{-1}, respectively. Results showed that soil thermal properties had high monthly variability with coefficients of variation (CV) ranging from 24.36 to 137.89%. The decrease in soil temperature decreased from June to July seems to have an impact on soil thermal conductivity (K) and thermal resistivity (R) which decreased also during the same period. However, in opposition to June-July trend, the decrease in soil temperature (T) in August was accompanied by an increase in soil thermal conductivity (K), resistivity (R) and diffusivity (D). However this trend did not continue in September as showed in the analysis of the spatial distribution of soil thermal properties across the pasture.

2.4.4 Greenhouse gas fluxes

The summary of simple statistics for the greenhouse gas fluxes in 2004, 2005 and 2006 is showed in Table 2.4.

Table 2.4. Summary of simple statistics for greenhouse gas fluxes in 2004, 2005 and 2006

Simple Stat.	N_2O (μg N-N_2O /m^2/h)			CO_2 (mg C-CO_2 /m^2/h)			CH_4 (μg C-CH_4 /m^2/h)		
	2004	2005	2006	2004	2005	2006	2004	2005	2006
Mean	16.31	9.49	31.81	178.61	137.74	84.94	-32.16	16.74	-17.43
SD	21.58	11.90	37.22	77.49	107.27	60.21	14.32	34.36	62.29
CV	132.31	125.40	116.99	43.39	77.88	70.88	44.55	205.34	357.23
Min	-14.56	-10.34	-21.8	17.25	6.05	2.14	-59.26	-38.37	-133.14
Max	96.04	33.94	254.69	275.28	336.67	348.02	-1.79	119.61	93.22
Skew	1.87	0.09	3.41	-0.73	0.26	1.56	0.20	1.17	-0.52
Kurt	4.59	-0.72	16.32	-0.65	-1.28	3.56	-0.75	2.01	-0.92

N_2O= Nitrous Oxide, CO_2= Carbon Dioxide, CH_4= Methane

On average, there was more nitrous oxide emitted in 2006 (31.81 mg N-N_2O-N/m^2h) as compared to either 2004 (16.31 μg N-N_2O-N/m^2h) or 2005 (9.49 μg N-N_2O-N/m^2h). Carbon dioxide (CO_2) emissions decreased from 178.61 to 84.94 94 mg C-CO_2 /m^2h for 2004 to 2006, respectively. Methane (CH_4) fluxes shifted from uptake in 2004 (-32.16 μg CH_4-C /m^2h) to emissions in 2005 (16.74 μg CH_4-C /m^2h) and again to uptake in 2006 (-17.43 μg CH_4-C /m^2h). However, the minimum fluxes for both N_2O and CH_4 were all negative in 2004, 2005 and 2006, suggesting that there was uptake of these two gases in the soil. As for soil thermal properties, N_2O, CO_2, and CH_4 also showed strong variability across the pasture with coefficients of variation (CV) ranging from 43.39 to 357.23 % for CO_2 in 2004 and CH_4 in 2006, respectively. A month to month assessment of the data 2006 revealed that N_2O, CH_4 and CO_2 fluxes changed significantly from month to month as showed by the analysis of the spatial distribution of greenhouse gas fluxes across the pasture below.

2.4.5 Variogram models for soil thermal properties and greenhouse gas fluxes in 2006

Table 2.5 shows the summary of variogram models to which soil temperature (T), thermal conductivity (K), thermal resistivity (R) and thermal diffusivity (D) responded in June and July 2006. Data for August and September is discussed, but omitted for clarity reasons.

Table 2.5. Variogram model parameters for soil thermal properties in June and July 2006

	June				July		
Properties	T	K	R	D	T	K	R
Model	Spherical	Spherical	Spherical	Gaussian	Spherical	Spherical	Linear
Co	0.0001	0.0000	0.0001	0.0001	0.0000	0.0000	0.0066
Co + C	0.3000	0.0054	0.1600	0.0014	0.0177	0.0051	0.0566
Ao	0.0010	0.0000	0.0005	0.0022	0.0005	0.0005	0.0010
R2	0.9000	0.9700	0.9750	0.8670	0.8360	0.9740	0.9390
RSS	0.0090	0.0000	0.0006	0.0000	0.0001	0.0000	28.9000

Co= Nugget, Co + C= Sill, Ao= Range, R^2= Regression Coefficient, RSS= Residual Sum of Squares, T= soil temperature, K= Thermal conductivity, R= Thermal resistivity, and D= thermal diffusivity

GS^+ GeoStatistics for the Environmental Sciences software, version 5.0 was used to fit data to models. The criterion for model selection was maximum R^2, except in cases where another model was obviously more appropriate based on visual examination of the semivariogram. Neither an active lag distance nor a lag interval was set. Default values given by the program were used. Soil temperature (T) and soil thermal conductivity (K) data fitted to spherical variogram models in June and July and to linear models in August and September. Soil thermal resistivity (R) fitted to a spherical model in June and August and a linear model in July and September. Diffusivity (D) fitted to a Gaussian model in June, a linear model in August and an exponential variogram model in September. The ranges of spatial dependence for T and K increased when the data fitted to linear variogram models. However, no specific trend was observed for the range of spatial dependence for either R or D. Overall, the R^2 values for field measured soil T, K, R and D ranged from 0.80 to 0.99, suggesting the presence of moderate to highly developed spatial structure. Table 2.6 shows the summary of variogram models to which CO_2, CH_4 and N_2O responded for June and July 2006. Data for August and September is discussed but not shown.

Table 2.6. Variogram model parameters for greenhouse gases emissions in June and July 2006

Properties	June CO_2	CH_4	N_2O	July CO_2	CH_4	N_2O
Model	Linear	Spherical	Exponential	Linear	Spherical	Spherical
Co	10.0000	465.0000	0.0100	0.0100	0.3500	16.0000
Co + C	4116.0000	2397.0000	16.5400	30.9800	20.6700	394.8000
Ao	0.0010	0.0008	0.0001	0.0014	0.0005	0.0018
R2	0.9290	0.9840	0.5970	0.9920	0.6550	0.9840
RSS	1089.0000	11833.0000	108.0000	5.4400	123.0000	1244.0000

As for soil thermal properties, greenhouse gas fluxes responded to several variogram models. Except in August when the data responded to a spherical model, CO_2 was fitted to a linear variogram model in June, July and September. CH_4 fluxes responded solely to a spherical variogram in June, July, August and September. N_2O shifted from an exponential variogram in June, to a spherical model in July and finally a linear variogram model for August and September. The spatial structure was highly developed for CO_2 data as showed by R^2 values above 0.90 at each sampling period. The same trend was found for CH_4 throughout this experiment, except in July when the spatial structure was moderately developed (R^2 = 0.60). Similarly to its variogram models, the R^2 values for N_2O also shifted low to high and low to high in June to July and August to September, respectively.

2.4.6 Spatial distribution of soil thermal properties and greenhouse gas fluxes in 2006

Figures 2.3 to 2.6 show the spatial distribution of soil thermal properties across the pasture from June to September 2006. In June, soil temperature was high in the north central and low in central and southern region of the pasture. Soil thermal resistivity was high in the north and low in the central and southern region of the pasture and soil thermal conductivity was high in the central eastern region and lowest in the central northeastern region. These trends stayed generally the same through the month of July. However, in August, the trends changed. High soil temperature shifted to the southeast of the pasture. Similarly, high soil

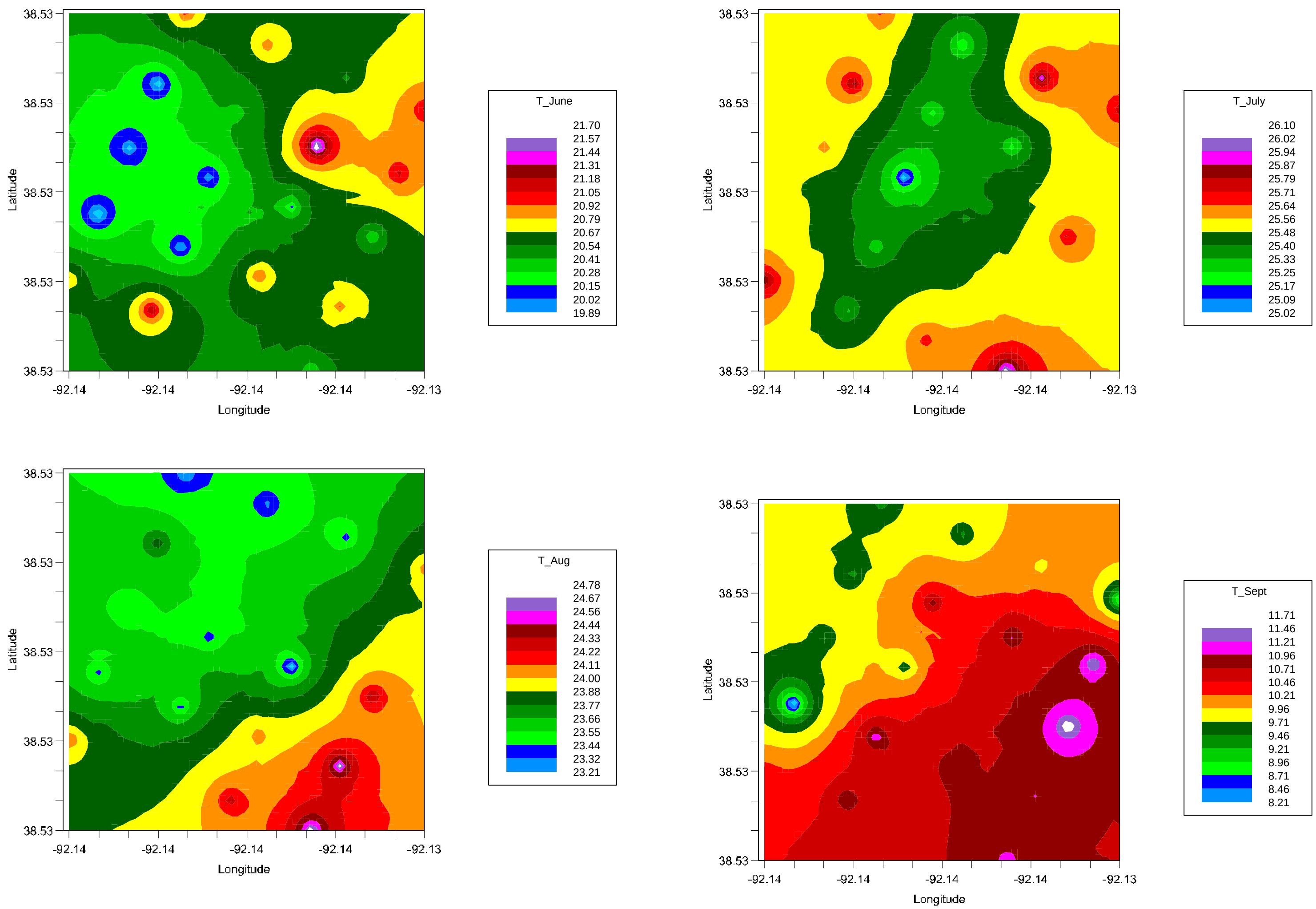

Figure 2.3. Soil temperature (T) in a pasture from June to September 2006

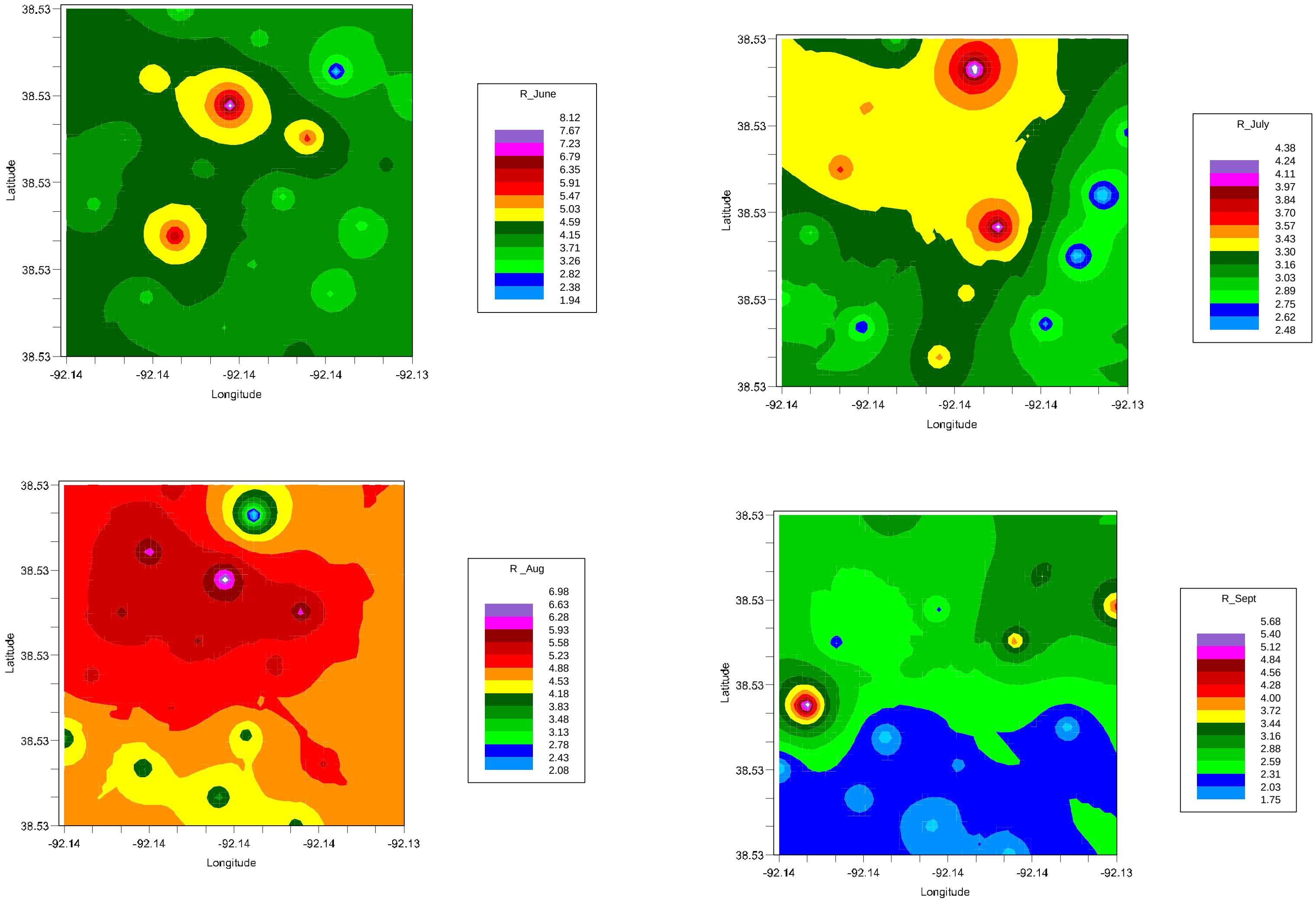

Figure 2.4. Soil thermal resistivity (R) from June to September 2006

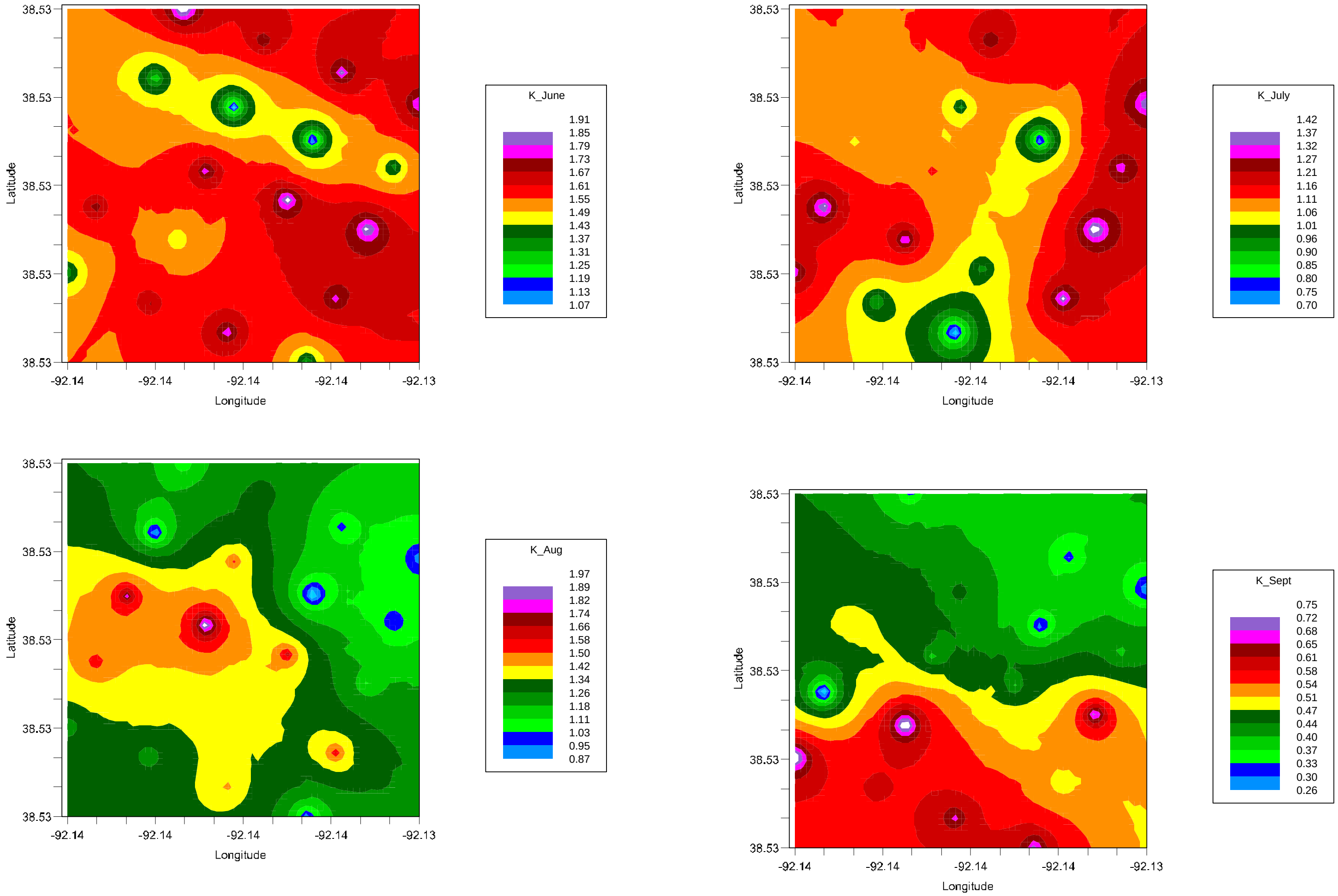

Figure 2.5. Soil thermal conductivity (K) from June to September 2006

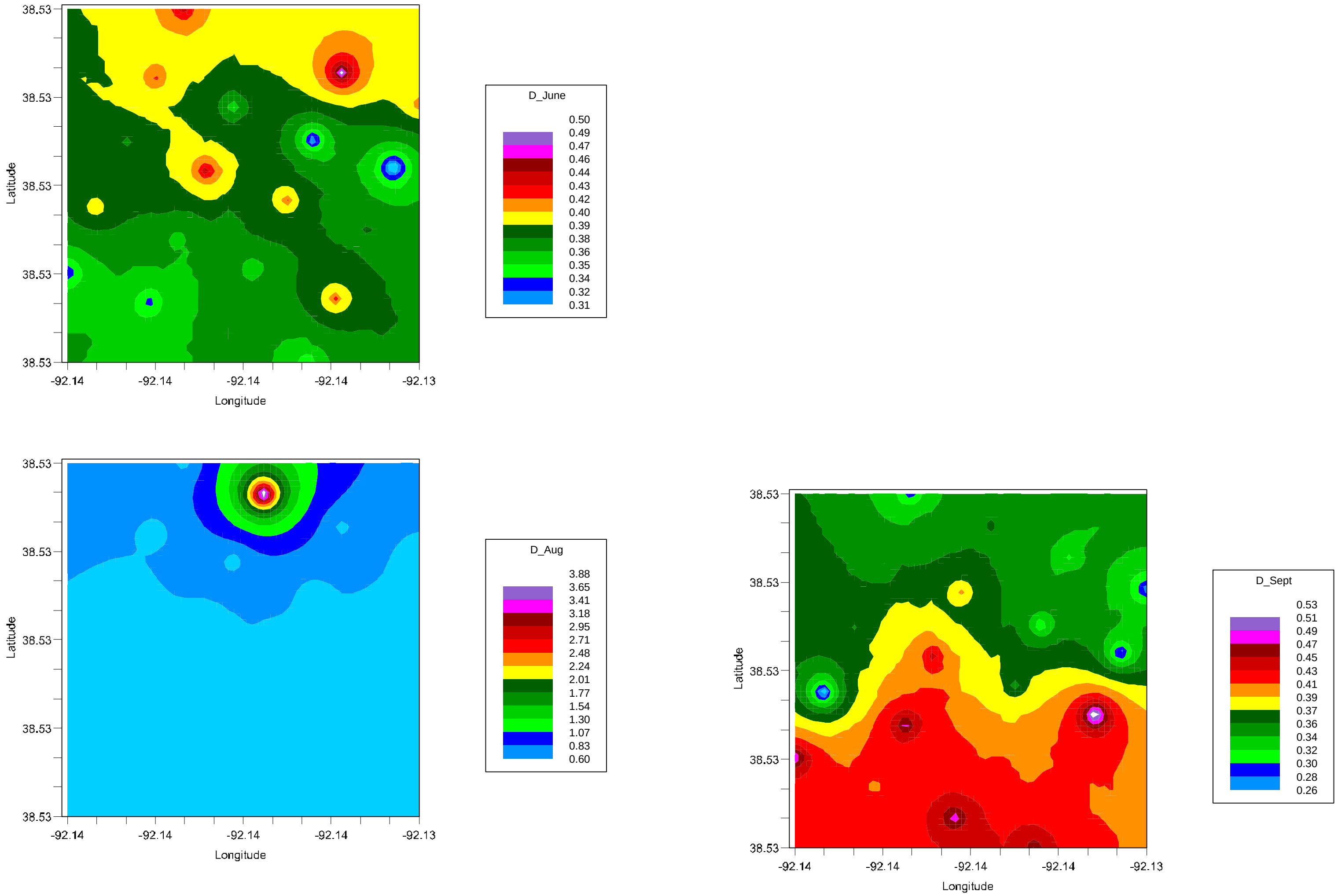

Figure 2.6. Soil thermal diffusivity (D) from June to September 2006

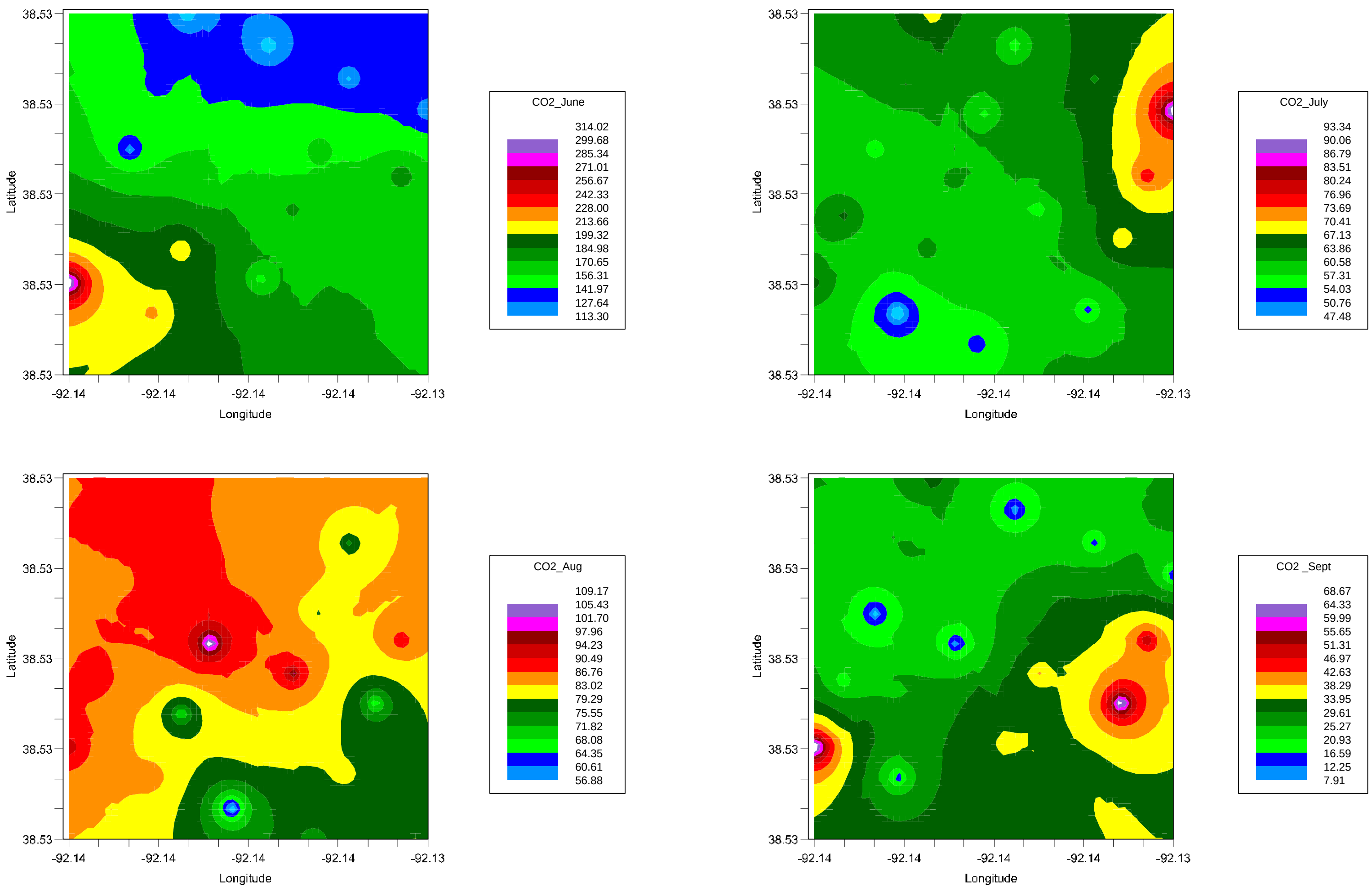

Figure 2.7. Carbon dioxide (CO_2) emissions from soil in a pasture from June to September 2006

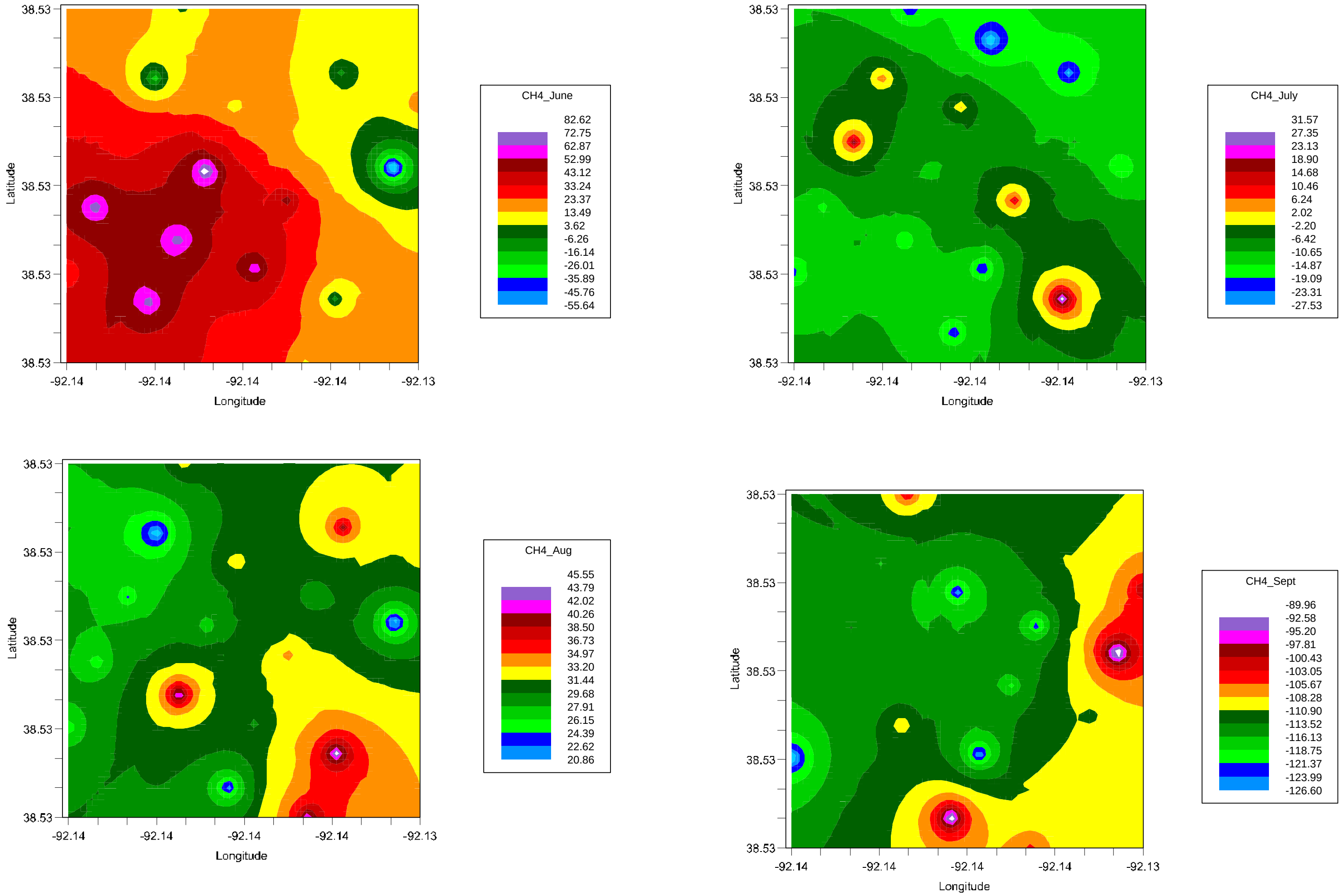

Figure 2.8. Methane (CH_4) emissions from soil in a pasture from June to September 2006

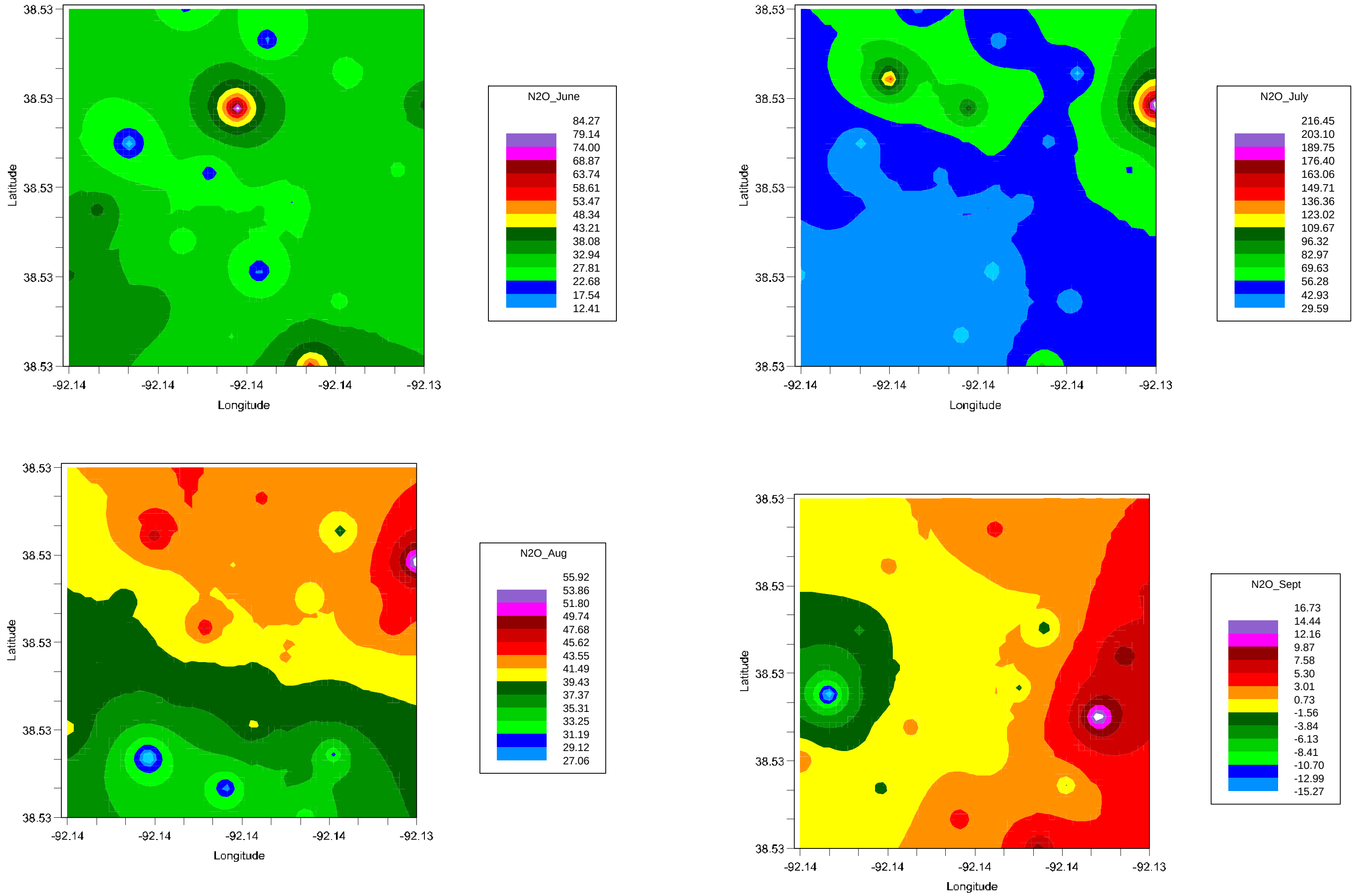

Figure 2.9. Nitrous oxide (N_2O) emissions from soil in a pasture from June to September 2006

thermal resistivity was found in the central region while high values of soil thermal conductivity shifted slightly to the south but for the most part stayed the same. For September the soil temperature and soil resistivity were very similar to the spatial distribution in August. Figures 2.7 to 2.9 show the spatial distribution of greenhouse gas fluxes across the pasture from June through September 2006. Maps portrayed three zones of distribution for greenhouse gas fluxes. In June, CO_2 emissions were low in the north and high in the southwest region of the pasture. This spatial pattern shifted to high in the east and low in the south during the month of July. In August the CO_2 fluxes shifted from the east to the north. However, in September, CO_2 showed high emissions in the north, low emissions in the south just as it did in June. CH_4 uptake was higher in the east and southwest region of the pasture and low in the north and east region for the month of June. This shifted to high in the central region and low in the north and south region. In August and September emissions changed to high emissions in the southeast and the low emission stayed relatively the same. N_2O was high in the central region of the pasture and low in the south in June. The trend shifted to high in the northeast in July. This trend stayed through out August. The high emissions in the north shifted to the east during the month of September. These shifts in emissions pattern over the months makes it difficult to predict with accuracy the distribution of gas fluxes. Shifts in greenhouse gases seem to agree with shifts in soil thermal properties.

2.4.7 Correlation between greenhouse gas fluxes and soil thermal properties in 2006

The monthly linear correlation matrices between greenhouse gas fluxes and soil thermal properties from June to September 2006 are showed in Table 2.7 (a, b, c and d). In June (Table 27.a), only three significant correlations were found: CO_2 emissions was negatively correlated with soil thermal diffusivity (D) was negatively while N_2O positively correlated with soil thermal conductivity (K) and negatively correlated with soil thermal resistivity (R).

In July (Table 27.b), only one significant correlation was found between CO_2 and soil thermal conductivity (K). In addition, CO_2 and N_2O significantly correlated among themselves ($p = 0.0037$; $r = 0.62$). In August (Table 27.c), there was no correlation between greenhouse gas fluxes and soil thermal properties, but CO_2 and N_2O significantly correlated among themselves again ($p = 0.035$; $r = 0.47$).

Table 2.7. Correlation matrices (r values) between greenhouse gas fluxes and soil thermal properties in a pasture,

(a) June 2006

	CO_2	CH_4	N_2O	T	K	R
CH_4	0.14^{ns}					
N_2O	0.22^{ns}	-0.10ns				
T	0.06ns	-0.29ns	-0.03ns			
K	-0.28ns	0.34ns	-0.48*	-0.13ns		
R	0.24ns	-0.07ns	0.55*	-0.07ns	-0.83****	
D	-0.52*	0.18ns	-0.28ns	-0.43ns	0.68***	-0.53*

(b) July 2006

	CO_2	CH_4	N_2O	T	K
CH_4	-0.26ns				
N_2O	0.62**	0.15ns			
T	0.34ns	0.02ns	0.27ns		
K	0.52*	0.03ns	0.21ns	0.15ns	
R	-0.42ns	-0.01ns	-0.17ns	-0.25ns	-0.38ns

(c) August 2006

	CO_2	CH_4	N_2O	T	K	R
CH_4	-0.26ns					
N_2O	0.47*	-0.23ns				
T	-0.42ns	0.06ns	-0.29ns			
K	0.31ns	0.02ns	-0.14ns	-0.31ns		
R	0.21ns	0.01ns	0.19ns	-0.22ns	0.14ns	
D	0.02ns	0.01ns	0.09ns	-0.24ns	0.04ns	-0.68**

(d)September 2006

	CO_2	CH_4	N_2O	T	K	R
CH_4	-0.09ns					
N_2O	0.49*	0.38ns				
T	0.56*	0.01ns	0.52*			
K	0.49*	-0.02ns	0.49*	0.62**		
R	-0.36ns	0.01ns	-0.59**	-0.68***	-0.88***	
D	0.38ns	-0.13ns	0.49*	0.57**	0.89***	-0.82***

ns = no significant, *, **, ***, **** = significantly different at 0.5, 0.01, 0.001 and 0.0001 probability levels

In September (Table 2.7d), several significant correlations were found between gas fluxes and soil thermal properties: CO_2 was positively correlated with soil temperature (T) and soil thermal conductivity (K). N_2O positively correlated with soil temperature (T) and soil thermal conductivity (K), thermal diffusivity (D) and negatively correlated with soil thermal resistivity (R). In addition, CO_2 and N_2O significantly correlated among themselves ($p = 0.01$; $r = 0.49$).

All greenhouse gas fluxes and soil thermal properties (except thermal diffusivity, D) significantly correlated when the data was averaged for the entire sampling period as discussed below. In addition, CO_2, CH_4 and N_2O also correlated among themselves. Correlation coefficient also increased and ranged from 0.25 to 0.89 for the relationship between gas fluxes and soil thermal properties and from 0.52 to 0.69 for greenhouse gas fluxes among themselves. Finally, only positive correlations were observed when data was pulled together and averaged. The correlation matrix between soil thermal properties and gas fluxes for the entire year for 2006 is showed in Table 2.8. Data for 2005 and 2004 are discussed but not showed.

Table 2.8. Correlation matrix (r values) between greenhouse gas fluxes and soil thermal properties from June to September 2006 (combined data)

	CO_2	CH_4	N_2O	T	K	R
CH_4	0.61****					
N_2O	0.52****	0.69****				
T	0.54****	0.89****	0.78****			
K	0.62****	0.76****	0.47****	0.71****		
R	0.29*	0.45***	0.54****	0.47****	0.13ns	
D	-0.03ns	0.10ns	0.12ns	0.12ns	0.09ns	-0.29*

Fitted regression lines for the relationships between greenhouse gases emissions and soil thermal properties (T, K and R) in 2006 are showed in Figures 2.10, 2.11 and 2.12 for CO_2, CH_4 and N_2O, respectively. In 2006, the highest significant correlation between gas fluxes themselves was that between CH_4 uptake and N_2O emissions ($r = 0.69$, $p = 0.0001$) and the highest correlation between gas fluxes and soil thermal properties was between CO_2 and T. In 2005, CO_2 and N_2O also significantly correlated ($p = 0.75$; $r = 0.0001$) while N_2O correlated with soil temperature ($p = 0.0001$, $r = 0.75$).

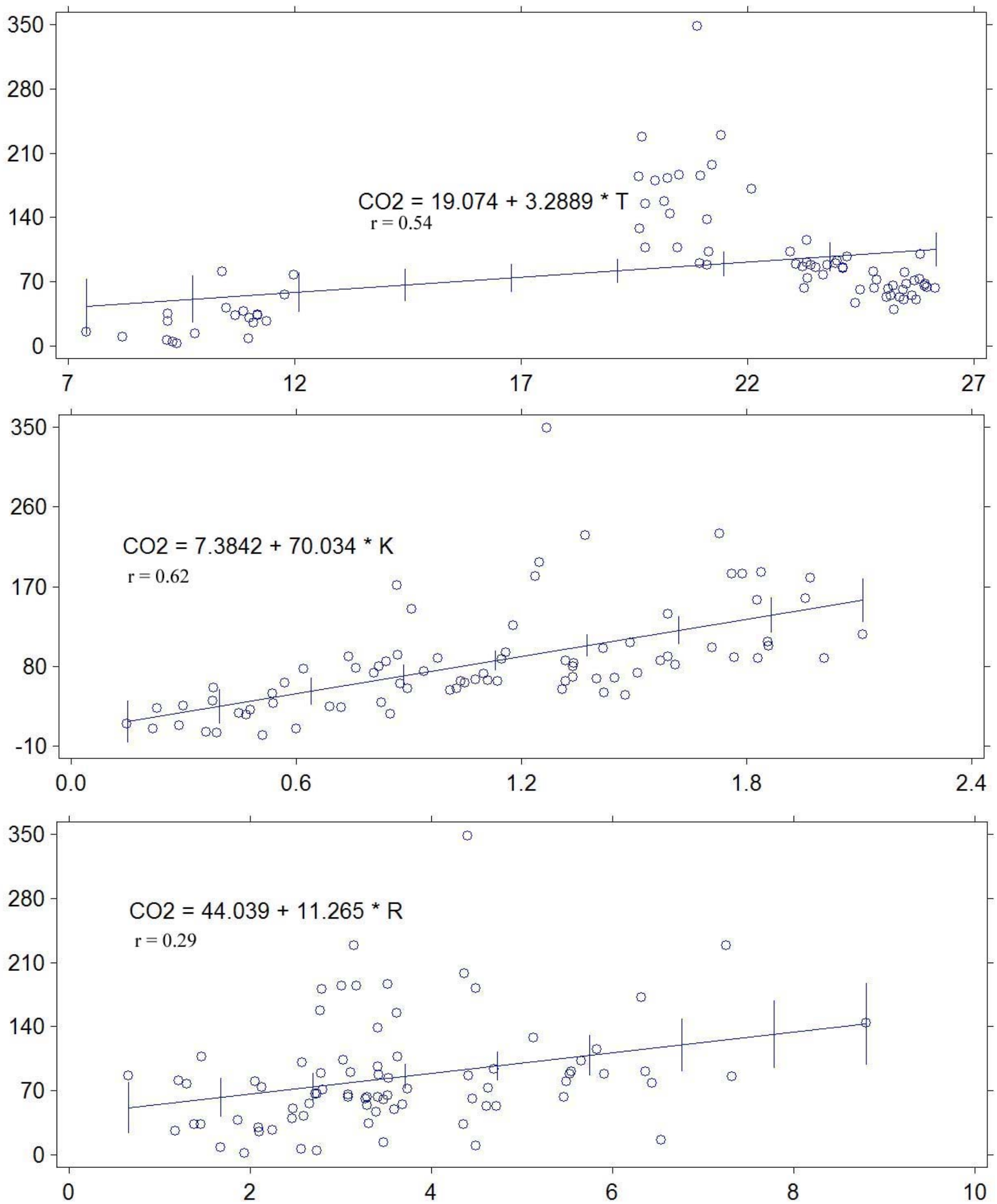

Figure 2.10. Fitted linear regression lines between CO_2 emissions (Y axis) and soil temperature (T), thermal conductivity (K) and thermal resistivity (R)

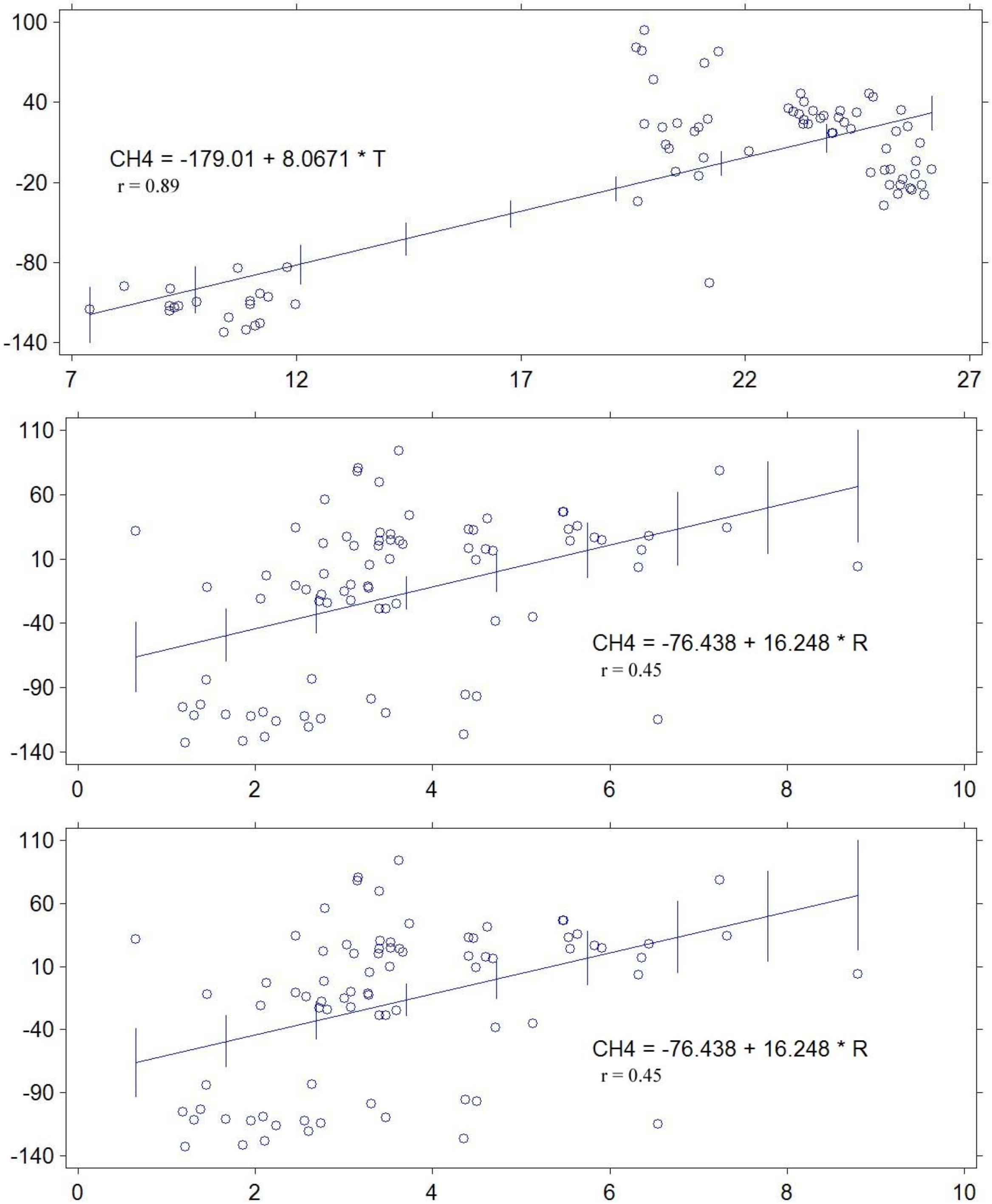

Figure 2.11. Fitted linear regression lines between CH_4 fluxes (Y axis) and soil temperature (T), thermal conductivity (K) and thermal resistivity (R)

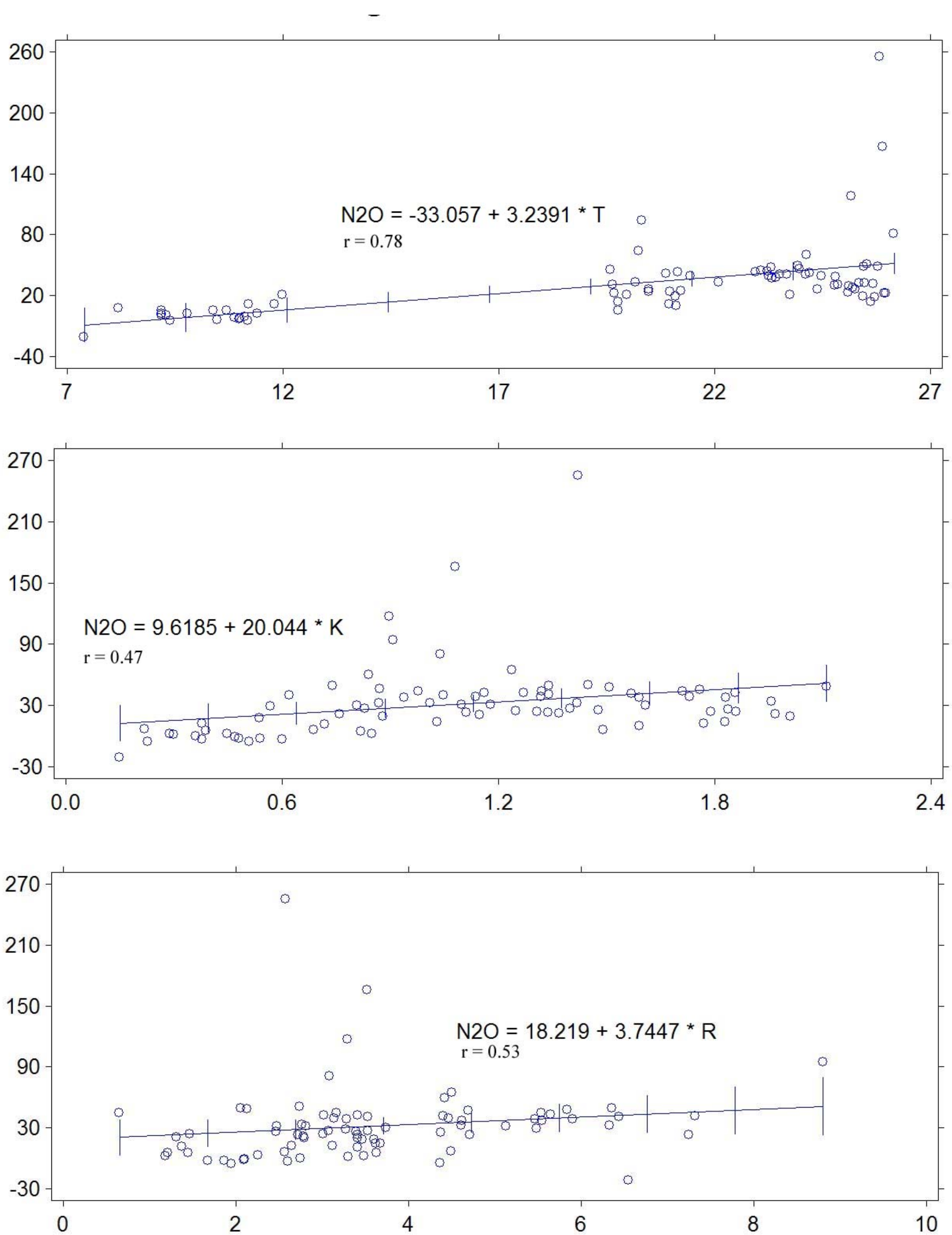

Figure 2.12. Fitted linear regression lines between N_2O fluxes (Y axis) and soil temperature (T), thermal conductivity (K) and thermal resistivity (R)

2.5 Discussion

2.5.1 Soil physical and chemical properties

Soil physical properties had very low variability. Similar results were also obtained by Johnson et al (2007) who previously conducted a study in the same pasture. The air-filled porosity and water content were at adequate level. In fact, it has been suggested that a minimum air content above 0.10 m^3/m^3 was sufficient to stimulate plant growth and microbial activities in soil (Verdonck and Demeyer, 2004). Soil organic matter in this pasture was also at adequate level. In fact, Buyanovski and Wagner (1985) reported that for Missouri soils, the mean annual mineralization of soil organic matter is about 2%, which is consistent with the results of this study.

2.5.2 Soil thermal properties and greenhouse gas fluxes

Soil thermal properties had very high monthly variability with coefficients of variation (CV) ranging from 24.36 to 137.89%. These results agree with those of Paro et al. (2008) who reported that CO_2 was linearly correlated with soil thermal conductivity (K), thermal resistivity (R), soil temperature (T) and and thermal diffusicity (D) whereas N_2O linearly correlated with R and T. Johnson et al. (2007) also found that CO_2 linearly correlated with K and T, CH_4 correlated with K and R while N_2O correlated with R. Similarly to soil thermal properties, N_2O, CO_2, and CH_4 also showed strong variability across the pasture with high coefficients of variation. In fact, the spatial variability of greenhouse gases emissions such as CO_2 flux has been characterized in several studies (Davidson et al., 2002; Rayment and Jarvis, 2000; Rochette et al., 1991), and coefficients of variation in the range of 25 to 500 % have been reported. The fluxes changed significantly from month to month and year to year as did soil temperature. Changes in greenhouse gas fluxes, for example CO_2 emissions, have been reported to follow seasonal temperature trends (Anderson, 1973; Buyanovsky et al., 1985; Franzluebbers et al., 2002; Rochette et al., 1991; Raich and Tufekcioglu, 2000;). It was found that the pasture released more CO_2 during the months that received more rainfall. Similar trends were reported in Hatano and Lipiec (2004). Negative fluxes of N_2O were observed in 2004, 2005 and 2006. This behavior is unusual as in most studies, soils have been reported a source of N_2O (Ball et al., 2000, Matson et al., 1990). However, several studies where soils have acted occasionally as sinks have also been reported. Using a micrometeorological method, Maggiotto and Wagner-Riddle (2001) measured N_2O, NO and NO_x fluxes from ryegrass field fertilized with three different mineral fertilizers. They found that NO_2 fluxes were always negative (–6 ng N m^{-2} s^{-1}), but decreased to –2 ng N $m^{-2}s^{-1}$ when snow was present on the soil surface. They suggested that the form of inorganic N applied has an effect on NO+ N_2O emissions but not on NO_2 fluxes. Glatzel and Stahr (2001) examined the effect of fertilization on the exchange of N_2O and CH_4 in the soil–plant system of meadow agroecosystems in southern Germany. Using closed chamber method, they we regularly determined the gas fluxes and associated environmental parameters. They found that N_2O fluxes at the unfertilized and fertilized plots were small, generally between 50 and –20 ug N m^{-2} h^{-1}. They identified some incidents of N_2O uptake. They concluded that apparently, rapid N mineralization and uptake in the densely rooted topsoil prevents N losses and the inhibition of CH_4 oxidation.

2.5.3 Correlations between greenhouse gas fluxes and soil thermal properties

CO_2 consistently correlated with N_2O during two of the three years of this study and during three of four months in 2006 investigation. Although N_2O and CO_2 emissions are different processes in soil, these significant correlations confirm that some common factors controlled N_2O and CO_2 emissions in this pasture. In fact, both N_2O and CO_2 were significantly correlated with soil temperature (T) and soil thermal conductivity (K) in years and months when these two gases correlated. The correlation between gases has also been reported by Konda et al. (2005), Xiu-jun et al., (2001) and Xiu-jun et al., (2000). Soil temperature (T) could not be correlated with any of the gases in 2004, but correlated with two in 2005 and with all gases in 2006. A month to month examination of the 2006 data revealed that during three months successively (June, July and August) out of the four months study, soil temperature (T) could not act as a controlling factors for CO_2, CH_4 and N_2O fluxes. However, sporadic correlations between soil K, R or D were found when soil temperature could not act as controlling factor for with gas fluxes. Several authors have suggested that consistent correlations between soil controlling factors and greenhouse gases have mainly been observed in controlled environments (Hatano and Lipiec, 2004; Pilegaard et al., 2006; Schindlbacher et al., 2004) with conflicting results in field environments (Janssens et al., 2001). In a study assessing the spatial variability of soil properties and gases emissions in southern Ohio (USA), Jacinthe and Lal (2006) found stronger and statistically significant relationships between gas emissions and soil properties in July 2003. However, in May 2004, this trend changed and they observed only few statistically significant relationships. Paro et al (2007) studied the spatial variability of soil thermal properties and CO_2, CH_4 and N_2O emissions in central Missouri. They reported a significant correlation between soil temperature and CO_2 and N_2O emissions, but no correlation with CH_4. However, Johnson et al. (2007) conducted a similar study in a pasture in central Missouri, but could not relate CO_2 and N_2O to soil temperature. In opposite, only CH_4 was related to soil temperature. Jones et al. (2007) studied the influence of organic and mineral N fertilizer on N_2O emissions from a temperate grassland in Scotland. They investigated the influence of environmental conditions on N_2O emissions by a series of single and multiple regression analysis but could not find a relationship between soil moisture and N_2O.

2.6 Conclusion

We monitored CO_2, CH_4, and N_2O fluxes and soil thermal properties from 2004 to 2006 in a pasture at Lincoln University of Missouri and conducted a month-to-month assessment of trends in fluxes and soil thermal properties in 2006 data. Our results showed that the pasture acted as a sink in 2004, a source in 2005 and again a sink of CH_4 in 2006. CO_2, CH_4, and N_2O and soil thermal properties shifted from month to month and year to year, exhibiting various trends. CO_2, CH_4, and N_2O correlated among themselves with a consistent correlation between N_2O and CO_2. Soil temperature (T) and thermal properties (K, R, D) acted as controlling factors for CO_2, CH_4, and N_2O, but not consistently. Studies in various ecosystems and conditions are therefore still needed to increase our understanding of greenhouse gases fluctuations and potential soil controlling factors.

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Chap. 3. Diffusivity models and greenhouse gas fluxes from a forest, pasture, grassland and corn field in northern Hokkaido[2]

3.1 Abstract

Information on the most influential factors determining gas flux from soils is needed in predictive models for greenhouse gases emissions. An intensive soil and air sampling was conducted along a 2000 m transect extending from a forest, pasture, grassland and a corn field in Shizunai, Hokkaido (Japan), measured CO_2, CH_4, N_2O and NO fluxes and calculated soil bulk density (ρ_b), air-filled porosity (f_a) and total porosity (Φ). Using diffusivity models based on either f_a alone or on a combination of f_a and Φ, two pore space indices were predicted: the relative gas diffusion coefficient (D_s/D_o) and the pore tortuosity factor (τ). Finally, the relationship between D_s/D_o and τ and CO_2, CH_4, N_2O and NO fluxes was studied. Results showed that the grassland had the highest ρ_b while f_a and Φ were highest in the forest. CO_2, CH_4, N_2O and NO fluxes were highest in the grassland while N_2O dominated in the cornfield. On average, D_s/D_o was higher for models based on f_a alone as compared to those based on a combination of f_a and Φ. An opposite trend was observed for τ. Few correlations existed between f_a, Φ, ρ_b and gas fluxes, however, D_s/D_o and τ significantly correlated with CO_2, and CH_4 and N_2O even when gas fluxes could not correlated with either f_a or Φ. Furthermore, coefficients of correlation between D_s/D_o and τ and gas fluxes were higher than those betweenf_a or $\Phi$and fluxes and ranged from 0.20 to 0.80. Inclusion of D_s/D_o and τ in predictive models may improve our understanding of the dynamics of greenhouse gas fluxes from soils. D_s/D_o and τ can be easily and quickly obtained from routine soil air and water measurement and existing diffusivity models.

Key Words: Gas diffusion coefficient, greenhouse gas fluxes, pore space indices

3.2 Introduction

Greenhouse gases produced in soils move through the air-filled pore space before their emission to the atmosphere. The probability for their consumption increases as impediments to their movement increase. The exchange of gas between the soil surface and the adjacent atmosphere can occur by means of two mechanisms: diffusion and advection. Diffusive gas transport depends primarily on the total volume and the tortuosity of continuous air-filled pore space. Advective gas transport is affected by gaseous permeability which, in turn, is dependent on total porosity, pore size distribution, and tortuosity of continuous air-filled pore space (Hillel, 2004). It is well documented that gaseous diffusion is the principal process involved in the exchange between the soil and the atmosphere (Taylor, 1949; Troeh et al.,1982). Gaseous diffusion and its variations with soil type and soil air-filled porosity typically control soil aeration (Buckingham, 1904; Taylor, 1949), fumigant emissions (Brown and Rolston, 1980), volatilization of volatile organic chemicals from industrially polluted soils (Petersen et al., 1996) and soil uptake and emissions of greenhouse gases (Kosugi et al., 2007; Smith et al., 2000). However, in comparison to other soil parameters such soil temperature and moisture (Almagro et al., 2009; Smith et al., 2000; Cook and Orchard, 2008; Dilustro et al., 2006; Zhou et al., 2006; Davidson et al., 2000), indices of N availability (NO_3^- and NH_4^+) (Turner et al., 2008; Davidson et al., 2000; Mutegi et al., 2009; Xiu-jun et al., 2001; Carno and Ineson, 1999; Mühlher and Hiscock, 1997; Vermoesen et al., 1996 and Whalen, 2000), only few authors have focused on soil gas diffusion coefficient and the pore tortuosity factor as potential controlling factors for greenhouse gases emissions

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Among these few studies, Kruse et al. (1996) reported a significant relation between methane emission and gas diffusion coefficient. Ball et al. (1997) reported a relationship between N_2O fluxes and air permeability, the soil gas diffusion coefficient and the tortuosity factor. Hu et al. (2001) found a significant relationship between the soil gas diffusion coefficient and CH_4 fluxes. Nkongolo et al. (2008) found similar relationships in an onion, corn and soybean fields in Japan. Measurements of the gas diffusion coefficient, and subsequent calculation of the pore tortuosity factor are tedious, expensive and time consuming. This fact may have contributed to fewer studies on the relationship between the soil gas diffusion coefficient and other soil processes. However, the gas diffusion coefficient and the pore torotuosity factor can be predicted from easily measurable soil properties such as air-filled porosity using either Penman (1940), Buckingham (1904), Marshal (1957) or Moldrup et al., (2000) models. Models predicting the gas diffusion coefficient and the pore tortuosity factor as a function of both air-filled porosity and total porosity (Jin and Jury, 1996; Millington, 1959; Moldrup, 1997; Sallam et al., 1984, Moldrup, 2005) are also available. Finally, predictive models using a few or several points of the moisture release curve alone (Moldrup et al., 1996 and Moldrup et al., 2000) or in combination with the saturated hydraulic conductivity (Allaire et al., 1996; Nkongolo and Caron, 1999; Nkongolo et al., 2000; Caron and Nkongolo, 2004) have been suggested for mineral as well as organic soils but all these models are not usually tested. The first objective of this study was to predict pore space indices from routine measurements of soil air and water contents and existing diffusivity models. A second objective was to assess the relationships between these pore space indices and greenhouse gases emissions.

3.3 Materials and methods

3.3.1 Experimental setup

The experiment was conducted at the Livestock Farm, Faculty of Agriculture, Hokkaido University in Shizunai. Shizunai is located at 42°25.9'N and 14°25.9'E. The annual average temperature is 7°C, and the average temperature is 20°C in August and -5°C in February. Annual mean precipitation is 1,200mm. Snow covers the land from late November to middle of March. The soil of this area is derived from Tarumae (B) volcanic ash, and is classified as Aquic Humic Udivitrand (USDA soil taxonomy). In situ measurements were conducted along a 2000m transect extending from a forest, grassland, pasture and cornfield soils in August 2000 (Fig. 1). Mapple (*Aceraceae rubrum*) and oak (*Fagaceae quercus*) predominates in the forest. Forest floor was covered by *Sasa nipponica* Makino et Shibata. The grassland and pasture sites were derived from a converted forest in 1965 (Hu et al., 2001). *Phleum pratense* L. and *Trifolium pratense* were the dominant grasses. The pasture is used for cattle grazing while the grassland is cut for hay. Chemical fertilizers are applied annually in the middle of May. During the experimental year, N, 68, P, 58, K, 38 kg ha^{-1} fertilizers were used. Cattle grazed 8 times from May to October during the observation. The cornfield had been used for growing corn for more than 30 years. Corn (*Zea mays* L.) was sowed on May 15 and harvested on September 28, 2000. Fertilizers consisting of N, 120, P, 48; and K, 58 kg ha^{-1} were applied at sowing time, and farm manure (N, 64 kg ha^{-1}) was applied during the previous year.

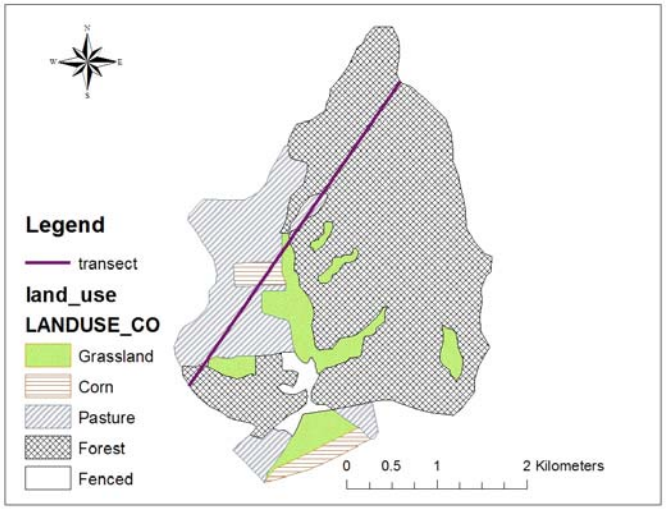

Figure 3.1. Sampling transect in Shizunai, northern Hokkaido (Japan)

3.3.2 Soil sampling and physical properties measurements

Soil samples were collected with a 5 cm diameter and a 5 cm height cylinder and brought to the laboratory for analysis. Soil fresh weights were measured then soil samples were oven dried at 105^{o}C for 72 hours until constant weight. Soil bulk density (ρ_b), total porosity (Φ), volumetric (θ_v) and gravimetric (θ_g) water contents, air-filled porosity (f_a) and water filled pore space (WFPS) were later calculated as described in Nkongolo et al. (2007 a and b).

3.3.3 Soil air sampling for CO_2, CH_4, NO and N_2O fluxes measurements

CO_2, CH_4, NO and N_2O emissions from the soil surface were measured using a closed-chamber technique (Rolston, 1986). The chambers were circular with steel frames. The top of each chamber had a gas sampling tube and a bag to control air pressure inside the chamber. The height and diameter of the chamber were 0.35 m and 0.30 m respectively. At each sampling time, 6 chambers were installed into the soil and kept for 20 minutes, and then samples of the enclosed atmosphere were withdrawn by a 50 ml syringe and transferred into a 1L Tedlar ® Bag. The air temperature inside the chamber was recorded using a digital thermometer. Ambient air between 0 and 2 m from the soil surface was collected and its mean concentration was used as a background concentration for calculation of gas fluxes. These operations were repeated successively as we moved along the 2000 m transect. Few hours after air and samples collection, a gas chromatography with electron capture detector was used for N_2O and CH_4 analyses. NO flux was analyzed by chemo-iluminescence with a nitrogen oxide analyzer (Kimoto, Model 265 P) and an infra-red analyzer was used for CO_2. Fluxes were calculated according to Ginting et al. (2003):

$$F = \rho * (V / A) * (\Delta C / \Delta T) * (273 / T)) * \alpha \qquad [21]$$

Where, F is the gas production rate; ρ is the gas density (mg m^{-3}) under standard conditions; V (m^3) and A (m^2) are the volume and bottom area of the chamber; ΔC/Δt is the ratio of change in the gas concentration inside the chamber (10^{-6} m^3 m^{-3} h^{-1}); T is the absolute temperature; and α is the transfer coefficient (12/44 for CO_2, 12/16 for CH_4, 14/30 for NO and 28/44 for N_2O). A positive value indicates gas emission from the soil, while a negative value indicates gas uptake. The detectable limits were 0.1 mg C m^{-2} h^{-1} for CO_2, 0.01 μg C m^{-2} h^{-1} for CH_4 and 0.1 μg N m^{-2} h^{-1} for NO and N_2O. Soil temperature was measured at 5 cm and 10 cm from the top soil layer, using a digital thermometer.

3.3.4 Measurements of the gas diffusion coefficient

The experimental procedure followed was the same as that described in Caron and Nkongolo (2004). It consisted in measuring the concentration of N_2 diffusing through the substrate cores in a gas diffusion chamber. The gas diffusion apparatus, constructed in plexiglass, was based on the design suggested by Rolston (1986) and adapted by Xu et al. (1992). Two rubber O-rings, one at the top of the base plate in a slot around the opening and the other immediately underneath the soil core, were used for sealing purposes. A tank of compressed gas containing a mixture of 80% Ar and 20% N_2 was used to fill the diffusion chamber and to establish the initial gas concentration of the diffusion experiment. A gas chromatograph was used to analyze the concentration of N_2 in the diffusion chamber. The room temperature during the experiment varied from 21 to 23°C with a mean value of 22°C. A 5-mL gas sample was taken with a 6-mL syringe at 0, 3, 10, 20, 30, 40, 50, 60, 75, and 90 min after the start of the experiment. The gas sample was injected directly into the gas chromatograph. Then, from N_2 concentration in the chamber C, a plot of $\ln[(C - C_s/(C_0 - C_s)]$ vs. time was drawn, where C_s is the gas concentration in the atmosphere and C_0 the initial concentration within the chamber. A linear regression was run from those data points within the linear part of the plot. As the slope of this line corresponded to $-D_s\alpha^2/\theta_a$, the value of D_s was calculated from the value of α found in Table 46-1 from Rolston (1986) and the θ_a obtained on the cores.

3.3.5 Prediction of the gas diffusion coefficient and the pore tortuosity factor

The relative gas diffusion coefficient (D_s/D_o) and the pore tortuosity factor (τ) were predicted using diffusivity models found in the literature as described below.

Theoretical background

The general equation for the diffusion of one gas into a reference gas is given by Fick's first law and is stated in Crank (1956). In soils, this equation will overestimate the flux of gas because the gas must diffuse over a greater distance to get from one point to another and also because the cross- sectional area available for flow is reduced by solid and liquid barriers. Consequently, gas diffusion in the soil is calculated by modifying the diffusion flux in the air by a gas tortuosity factor producing the flux equation (Jury et al., 1996):

$$q_x = -D_o \xi (\partial C / \partial x) = -D_s (\partial C / \partial x) \quad [1]$$

where $D_s = \xi . D_o$ is the soil gas diffusion coefficient and $\xi = \gamma . f_a$, where f_a is the air-filled porosity, γ is the pore effectiveness, and $\gamma = 1/\tau$ with τ being the pore tortuosity factor. The effective diffusivity of a gas through the soil, D_s, can therefore be related to its diffusivity in the air, D_o , where the pore space within the medium is air-filled, by the relation (Reible and Shair, 1982; King and Smith, 1987):

$$\mathbf{D_s} = (\gamma . f_a).D_o = (fa / \tau).D_o \quad [2]$$

Several models found in the literature predict D_s/D_o as either a function of air-filled porosity (f_a) alone :

$$Ds / Do = 0.66\, f_a \quad \text{(Penman, 1940)} \quad [3]$$

$$Ds / Do = fa^{1.5} \quad \text{(Marshall, 1957)} \quad [4]$$

$$Ds / Do = fa^2 \quad \text{(Buckingham, 1904)} \quad [5]$$

$$Ds_{100} / Do = 2\, f_{a_{100}}^3 + 0.04\, f_{a_{100}} \quad \text{(Moldrup et al., 2000)} \quad [6]$$

or as a quotient of air-filled porosity over total porosity (Φ):

$$Ds / Do = fa^{3.1} / \Phi^2 \quad \text{(Sallam et al., 1984)} \quad [7]$$

$$Ds / Do = fa^{3.33} / \Phi^2 \quad \text{(Millington, 1959)} \quad [8]$$

$$Ds / Do = fa^2 / \Phi^{2/3} \quad \text{(Jin and Jury, 1996)} \qquad [9]$$

$$\frac{D_s}{D_o} = 0.66\, f_a \left[fa / \Phi \right]^{(12 - \mathrm{m})/3} \quad \text{(Moldrup et al.,1997)} \qquad [10]$$

By comparing equations [3 -10] to [2], the pore tortuosity factor can be predicted as a function of either air-filled porosity alone:

$$\tau = 1/0.66 \quad \text{(Penman, 1940)} \qquad [11]$$

$$\tau = 1/ fa^{0.5} \quad \text{(Marshall, 1957)} \qquad [12]$$

$$\tau = 1/ fa \quad \text{(Buckingham, 1904)} \qquad [13]$$

$$\tau = 1/\left[2\, fa_{100}\right]^2 + 0.04 \quad \text{(Moldrup et al., 2000)} \qquad [14]$$

or as a quotient of total porosity (Φ) over air-filled porosity:

$$\tau = \Phi^2 / fa^{2.1} \quad \text{(Sallam et al., 1984]} \qquad [15]$$

$$\tau = \Phi^2 / fa^{2.33} \quad \text{(Millington, 1959)} \qquad [16]$$

$$\tau = \Phi^{2/3} / fa \quad \text{(Jin and Jury, 1996)} \qquad [17]$$

$$\tau = \Phi^{\frac{12 - m}{3}} / 0.66\, fa^{(12 - m)/3} \quad \text{(Moldrup et al., 1997)} \qquad [18]$$

To compare gas diffusivity models, the root mean square error (RMSE) of prediction was used for best overall fit compared with chamber measured data:

$$\text{RMSE} = \sqrt{1/n \sum_{i=1}^{n} \mathrm{d}_\mathrm{i}^2} \qquad [19]$$

where di is the difference between the model predicted and the chamber measured value of Ds/Do and n is the number of measurements. The bias was used to evaluate model overestimation (positive bias) or underestimation (negative bias) of chamber measured Ds/Do (Moldrup et al., 2003):

$$\text{bias} = 1/n\sum_{i=1}^{n}\mathrm{d}_i \qquad [20]$$

3.4 Results and discussion

3.4.1 Soil physical properties

The forest site had the highest air-filled porosity and total porosity, but the lowest bulk density and water filled pore space which was highest in the corn field. Chamber measured gas diffusion coefficient was also highest in the forest (Table 4.3) while volumetric water content was nearly constant over sites. Overall, coefficients of variation were lower total porosity (4.64 to 21.10%), followed by bulk density (10.23 to 40.83%), but higher for other soil physical properties (11.08 to 72%). Except for water filled pore space in the forest, grassland and pasture, all median values were close to their means, implying that the distribution for these properties approached normality. Overall, soil physical properties were in the range of normally reported data.

Table 3.1. Summary of simple statistics for soil physical properties measured along a transect extending from a forest, pasture, grassland and corn field in Shizunai, northern Hokkaido (Japan).

Soil Physical Properties	Simple statistics				
	Mean	SD	CV	Median	Skew
Forest (n = 54)					
f_a (m^3 m^{-3})	0.22	0.09	40.60	0.21	0.31
ρ_b (kg m^{-3})	0.57	0.23	40.83	0.51	0.88
θ_v (m^3 m^{-3})	0.52	0.10	19.09	0.51	0.39
Φ (m^3 m^{-3})	0.73	0.13	18.35	0.73	-0.79
WFPS (%)	71.23	22.17	37.98	65.41	-0.67
Pasture (n= 27)					
f_a (m^3 m^{-3})	0.12	0.07	58.15	0.09	1.36
ρ_b (kg m^{-3})	0.80	0.25	31.70	0.81	-0.29
θ_v (m^3 m^{-3})	0.56	0.15	27.50	0.54	-0.06
Φ (m^3 m^{-3})	0.67	0.14	21.10	0.66	0.07
WFPS (%)	83.58	31.72	50.02	78.32	-0.79
Grassland (n = 11)					
f_a (m^3 m^{-3})	0.10	0.05	54.61	0.09	1.24
ρ_b (kg m^{-3})	0.89	0.19	21.59	0.89	-0.36
θ_v (m^3 m^{-3})	0.55	0.10	17.42	0.54	0.53
Φ (m^3 m^{-3})	0.66	0.10	14.81	0.63	-0.26
WFPS (%)	83.33	37.89	72.39	80.62	-0.20
Cornfield (n = 8)					
f_a (m^3 m^{-3})	0.14	0.06	46.27	0.11	1.22
ρ_b (kg m^{-3})	0.76	0.08	10.23	0.76	0.24
θ_v (m^3 m^{-3})	0.56	0.07	12.29	0.57	-0.19
Φ (m^3 m^{-3})	0.69	0.03	4.64	0.69	0.54
WFPS (%)	81.16	8.91	11.08	83.83	-1.14
All (n = 101)					
f_a (m^3 m^{-3})	0.14	0.08	59.21	0.11	1.03
ρ_b (kg m^{-3})	0.75	0.26	34.20	0.75	-0.08
θ_v (m^3 m^{-3})	0.54	0.13	23.63	0.53	0.12
Φ (m^3 m^{-3})	0.69	0.13	19.20	0.69	-0.15
WFPS (%)	78.26	29.59	47.95	74.60	-0.74

SD = standard deviation, CV = coefficient of variation, Skew = skewness coefficient. f_a = air filled porosity, ρ_b = soil bulk density; θ_v = volumetric water content, Φ= total porosity, WFPS = water filled pore space

3.4.2 Greenhouse gas fluxes

CH_4 fluxes over the 2000 m transect showed a net source in the pasture whereas the forest, grassland and corn field portions constituted sinks (Table 3.2). In addition, CH_4 uptake in the grassland and corn field was less than in the forest. It has been reported that CH_4 uptake in aerobic soils, as in the case of this study, depends on several environmental parameters (Boeckx and Van Cleemput, 1998; Ullah et al., 2008). In general, two main factors are responsible for the differences in CH_4 uptake capacity between soil ecosystems: (1) soil disturbance caused by cultivation of soils, and (2) fertilization with NH_4^+ containing fertilizers. Mosier et al. (1991) suggested that methane oxidation occurs in certain soil units or niches. Disturbance of the original soil structure by cultivation may reduce the probability of biological, chemical and physical parameters that define these ecological niches for methanotrophs (Hutsh, 1998). In this study, the grassland site was derived from a converted forest in 1965 while the corn field (converted from the same forest) has been used for growing corn for more than 30 years. As our results suggested, other studies also found that conversion of forests or native grasslands to agricultural fields reduces the CH_4 uptake rate (Johnson et al., 2007). These reductions can be as high as 60% (Dobbie et al., 1996) as found in this study. In addition, it has been reported that nitrogen fertilizer reduces CH_4 uptake (Li and Kelliher, 2007; Price et al., 2004**)**. In this study, nitrogen fertilizers were applied to the corn field (120 kg N ha^{-1}) and grassland (68 kg ha^{-1}). However, it has also been reported that N application caused no change to soil CH_4 oxidation rates in a number of field studies (Yamulki et al., 1999; Kammann et al., 2001) while it decreased or increased rates in other studies (Kruger and Frenzel, 2003; Reay and Nedwell, 2004). The grassland emitted more CO_2 (218.04 mg C-CO_2 $m^{-2}h^{-1}$) than the forest, pasture and corn field which had similar level of CO_2 emissions with forest (128.21 mg C-CO_2 $m^{-2}h^{-1}$). Similar results were observed by

Shrestha et al. (2009) who monitored greenhouse gas fluxes from post-reclamation land uses (forest, hay, and pasture) and found that the CO_2, CH_4, and N_2O

Table 3.2. Summary of simple statistics for methane (CH_4), carbon dioxide (CO_2), nitric oxide (NO) and nitrous oxide (N_2O) fluxes measured along a 2 km transect in Shizunai: forest, pasture grassland and corn field.

Greenhouse Gas Type	Simple statistics				
	Mean	SD	CV	Median	Skew
Forest (n = 54)					
CH_4 (µg C-CH_4 m^{-2} h^{-1})	-50.00	60.0	108.76	-60.0	1.55
CO_2 (mg C-CO_2 m^{-2} h^{-1})	128.21	44.05	34.35	124.35	0.56
NO (µg N-NO m^{-2} h^{-1})	5.87	12.48	212.74	1.95	2.84
N_2O (µg N-N_2O m^{-2} h^{-1})	2.03	0.37	18.62	2.20	-0.65
Pasture (n = 27)					
CH_4 (µg C-CH_4 m^{-2} h^{-1})	420.00	1090	261.29	-50.0	2.98
CO_2 (mg C-CO_2 m^{-2} h^{-1})	142.94	51.34	35.92	150.15	-0.38
NO (µg N-NO m^{-2} h^{-1})	3.83	4.68	122.36	2.60	2.35
N_2O (µg N-N_2O m^{-2} h^{-1})	63.43	155.00	244.39	23.00	5.45
Grassland (n = 11)					
CH_4 (µg C-CH_4 m^{-2} h^{-1})	-20.00	0.00	0.00	-20.0	-0.22
CO_2 (mg C-CO_2 m^{-2} h^{-1})	218.04	37.41	17.16	152.30	-0.33
NO (µg N-NO m^{-2} h^{-1})	8.80	11.89	135.10	3.80	1.034
N_2O (µg N-N_2O m^{-2} h^{-1})	34.11	33.56	98.38	30.60	1.11
Corn field (n = 8)					
CH_4 (µg C-CH_4 m^{-2} h^{-1})	-20.00	10.0	34.64	-20.0	0.71
CO_2 (mg C-CO_2 m^{-2} h^{-1})	124.86	26.91	21.55	129.60	-0.14
NO (µg N-NO m^{-2} h^{-1})	5.68	7.72	135.90	0.90	1.04
N_2O (µg N-N_2O m^{-2} h^{-1})	253.28	262.80	103.76	126.05	0.92
All (n = 101)					
CH_4 (µg C-CH_4 m^{-2} h^{-1})	190.00	820	420.90	-20.0	4.38
CO_2 (mg C-CO_2 m^{-2} h^{-1})	146.17	53.29	36.46	145.80	0.07
NO (µg N-NO m^{-2} h^{-1})	4.86	7.85	161.63	2.20	3.29
N_2O (µg N-N_2O m^{-2} h^{-1})	81.94	172.44	210.44	26.00	3.87

CH_4= methane, CO_2 = carbone dioxide, NO = nitric oxide, N_2O = nitrous oxide. SD = standard deviation, CV = coefficient of variation, Skew = skewness coefficient

fluxes were consistently high in the pasture and hay as compared to the forest. Nitric oxide (NO) fluxes were also higher in the grassland while N_2O fluxes dominated in corn field where nitrogen fertilizer (120 kg N ha^{-1}) was applied. These results are consistent with those of previous researchers. In fact, agronomic use of chemical fertilizers has been correlated with high rates of N_2O emissions (Eichmer, 1990; Veldkamp and Keller, 1997; Veldkamp et al., 1998; Williams et al., 1992; Hao et al., 2001). The forest had 17, 31 and 125 times less N_2O fluxes as compared to grassland, pasture and corn field, respectively. There was a strong variability in fluxes as showed by high coefficients of variation (C.V.). CH_4 and N_2O had CV values of over 200% in the pasture while NO varied mostly in the forest. CO_2 had moderate CV not exceeding 40%. The distribution of CO_2 along the transect approached normality in the forest, pasture and corn field as showed by medians close to their respective means and lower skew values.

3.4.3 Relative gas diffusion coefficient

The relative gas diffusion coefficient (D_s/D_o) showed different trends depending on whether it was predicted from models based either on air-filled porosity alone or on a combination of air-filled and total porosity (Table 3.3). For models based on air-filled porosity alone, three specific trends were observed: (i) in the forest, the mean D_s/D_o value from chamber measurement (0.0118 m s m^{-1} s^{-1}) was higher to that predicted from Buckingham (0.054), Marshall (0.106) and Moldrup (0.038) models; (ii) in the grassland, the mean D_s/D_o value from chamber measurement was lower to that predicted from models and (iii) for the pasture and corn field: the mean D_s/D_o value from chamber measurement was higher for Buckingham and Moldrup models, but lower to that predicted from Marshall model. These trends were also confirmed by biases values which showed that in the forest, D_s/D_o was underestimated by Buckingham (-0.0071), Marshall (-0.0608) and Moldrup (-0.0071) models.

Table 3.3. Summary of simple statistics for chamber-measured and predicted relative gas diffusion coefficient (D_s/D_o, m^2s^{-1} m^{-2} s) in a forest, pasture, grassland and cornfield in Shizunai.

		Chamber measured	Models based on air-filled porosity			Models based on air-filled porosity and total pore space		
Simple Statistics		Chamber (Eperim.)	Marsh. (1959)	Buck. (1904)	Mold. (2000)	Sall. (1984)	Jin (1996)	Mill. (1959)
Forest	Mean	0.118	0.106	0.054	0.038	0.022	0.064	0.016
	SD	0.108	0.061	0.040	0.036	0.020	0.044	0.016
	Min	0.001	0.016	0.004	0.003	0.001	0.007	0.000
	Med	0.096	0.093	0.042	0.026	0.016	0.051	0.011
	Max	0.412	0.262	0.168	0.154	0.093	0.191	0.076
	Skew	1.250	0.906	1.310	1.802	1.841	1.217	2.001
Grassland	Mean	0.005	0.035	0.011	0.006	0.003	0.016	0.002
	SD	0.007	0.029	0.015	0.009	0.005	0.016	0.003
	Min	0.001	0.010	0.000	0.000	0.000	0.002	0.000
	Med	0.003	0.030	0.010	0.000	0.002	0.012	0.001
	Max	0.022	0.110	0.050	0.030	0.017	0.062	0.012
	Skew	2.299	1.650	1.655	1.570	2.063	1.804	2.115
Pasture	Mean	0.035	0.044	0.018	0.012	0.008	0.024	0.006
	SD	0.056	0.040	0.022	0.017	0.026	0.033	0.020
	Min	0.002	0.007	0.001	0.002	0.000	0.002	0.000
	Med	0.016	0.029	0.009	0.005	0.001	0.012	0.001
	Max	0.290	0.221	0.134	0.113	0.188	0.217	0.149
	Skew	3.129	2.298	2.996	3.829	4.905	3.645	4.972
Corn Field	Mean	0.031	0.053	0.022	0.014	0.014	0.007	0.005
	SD	0.039	0.036	0.020	0.014	0.014	0.010	0.008
	Min	0.003	0.025	0.007	0.005	0.005	0.001	0.001
	Med	0.018	0.036	0.016	0.009	0.009	0.003	0.002
	Max	0.121	0.137	0.070	0.048	0.048	0.033	0.024
	Skew	1.796	1.590	1.673	1.792	1.792	1.769	1.792

Marsh= Marshall, Buck = Buckingham, Mold = Moldrup et al, Sall = Sallam et al, Jin = Jin and Jury and Mill = Millington models. SD = standard deviation, CV = coefficient of variation, Skew = skewness coefficient

Similarly, D_s/D_o was overestimated in the grassland as showed by biases values of 0.0500, 0.0500 and 0.0548 for Marshall, Buckingham and Moldrup models, respectively. In the pasture (bias = 0.0141) and cornfield (bias =0.0218), D_s/D_o was overestimated by Marshall only, but underestimated by Buckingham and Moldrup models. The Marshall model gave the lowest RMSE (0.0583) when all that data was combined (n = 101), but when the data is examined in each land use type, it was found that the lowest RMSE were obtained with the

Marshall (0.0794), Moldrup (0.0041), Buckingham (0.00500) and Buckingham (0.00200) in the forest, grassland, pasture and cornfield, respectively. For models based on a combination of air-filled porosity and total porosity, the mean D_s/D_o value from chamber measurement was lowest to that predicted by models in all land use type, except for Jin & Jury model in the grassland. Similarly, all models based on a combination of air-filled porosity and total porosity underestimated D_s/D_o (negative bias), except Jin & Jury model in grassland which overestimated D_s/D_o (positive bias). The lowest RMSE was obtained with Jin & Jury for all land use type, except in the grassland where both Sallam and Millington models gave the lowest RMSE. Significant correlations were observed between chamber measured D_s/D_o and D_s/D_o obtained from models. Coefficient of correlation were higher and ranged from 0.69 to 0.71 for models based on air-filled porosity alone while they were lower and ranged from 0.45 to 0.67 for models based on a combination of air-filled porosity and total pore space. The corresponding graphs for these relationships are showed in Figure 3.2 for models based on air-filled porosity alone (Buckingham, Marshall and Moldrup models). However, among these models, the correlation with chamber measured D_s/D_o were highest for D_s/D_o predicted by Marshall ($p = 0.00001$, $r = 0.71$) and Buckingham ($p = 0.00001$, $r = 0.709$) models. The relationship between chamber measured and predicted D_s/D_o values from models based on air-filled porosity alone is showed in Figure 3.2.

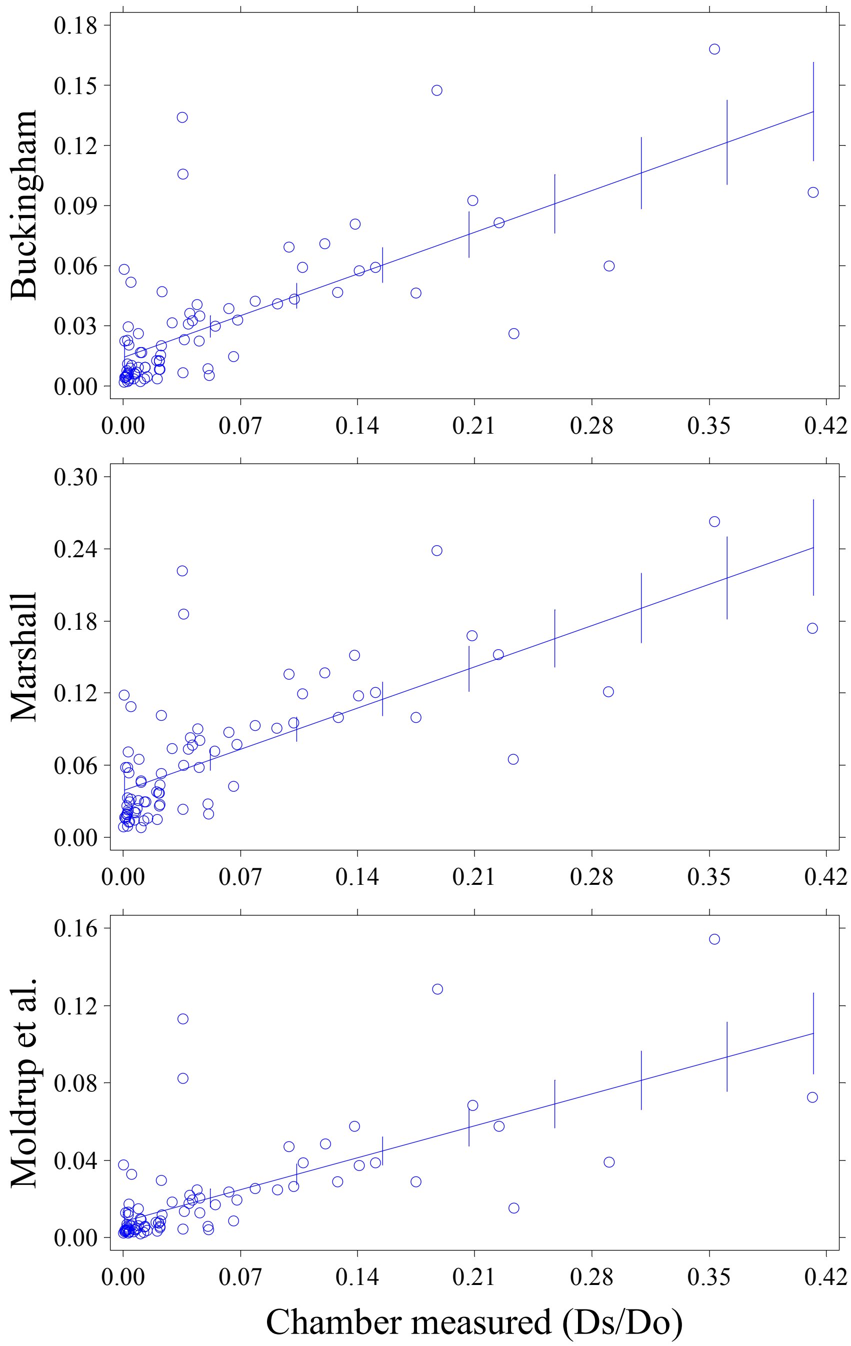

Figure 3.2. Relationship between chamber measured and predicted D_s/D_o values from models based on air-filled porosity alone (all transect data combined)

3.4.4 Pore tortuosity factor

As for the gas diffusion coefficient, the magnitude of the pore tortuosity factor (τ) depended on whether it was predicted from models based on air-filled porosity alone and on a combination of air-filled porosity and total porosity (Table 3.4)

Table 3.4. Summary of simple statistics for the pore tortuosity factor (τ, m m^{-1}) in a forest, pasture, grassland and corn field in Shizunai.

		(τ) calculated from models based on Air-filled porosity alone			(τ) calculated from models based on Air-filled porosity and Total porosity		
		Mars. (1959)	Buck. (1904)	Mold. (2000)	Sall. (1984)	Jin (1996)	Mill. (1959)
Forest	Mean	2.32	5.70	22.31	35.69	4.43	9.54
	SD	0.57	3.09	22.07	40.30	1.99	10.93
	Min	0.57	2.44	4.39	5.39	1.99	1.48
	Med	2.19	4.80	14.52	20.82	3.80	5.84
	Max	3.99	15.90	93.65	167.26	9.68	50.47
	Skew	0.29	1.83	1.92	1.99	1.38	2.35
Grassland	Mean	3.46	12.61	120.09	234.24	9.53	36.48
	SD	0.80	5.69	158.21	338.37	4.88	25.82
	Min	0.80	4.40	13.25	18.63	3.69	4.74
	Med	3.36	11.30	86.47	158.83	7.62	28.30
	Max	5.08	25.86	600.31	1268.43	22.38	100.17
	Skew	-0.64	0.89	2.18	2.21	1.47	1.24
Pasture	Mean	3.28	11.43	96.25	181.51	8.63	31.72
	SD	0.84	5.72	106.76	218.23	4.36	25.14
	Min	0.84	2.73	1.95	2.45	1.69	1.85
	Med	3.26	10.60	69.60	123.01	8.28	25.26
	Max	5.31	28.24	467.79	1008.64	21.15	110.91
	Skew	-0.11	0.87	2.00	2.15	0.88	1.23
Corn Field	Mean	2.88	8.53	48.32	81.86	6.66	18.19
	SD	0.50	2.75	28.28	51.12	2.17	9.52
	Min	0.50	2.75	8.06	10.94	2.17	3.51
	Med	2.79	7.81	37.04	59.42	6.17	14.36
	Max	3.40	11.55	93.62	163.73	9.41	29.43
	Skew	-1.42	-0.41	0.34	0.37	-0.34	0.02

SD = standard deviation, Min = minimum, Max = maximum, Med = median, Skew = skewness. Marsh= Marshall, Buck = Buckingham, Mold = Moldrup et al, Sall = Sallam et al, Jin = Jin and Jury and Mill = Millington models

Models based on air-filled porosity alone gave τ values ranging from 2.32 to 120.09 m m^{-1}. For these models, Marshall gave the lowest pore tortuosity values, ranging from 2.32 to 3.46 m m^{-1}. Pore tortuosity factor (τ) values from models based on a combination of air-filled porosity and total porosity where a twice as much those from models based on air-filled porosity alone and ranged from 4.43 to 234.24 m m^{-1}. Jin & Jury model gave moderate tortuosity values between 4.43 and 9.53 m m^{-1}. For land use types, the forest had the lowest pore tortuosity values (2.32 to 35.69), followed by cornfield (2.88 to 81.86), pasture (3.28 to 181.51) and finally grassland (3.46 to 234.24 m m^{-1}).

3.4.5 Correlation between greenhouse gas fluxes and pore structural indices

Overall, CO_2 and CH_4 were the two greenhouse gases which mostly correlated with pore space indices in the forest (Table 3.5). In addition, there were more significant correlations in the forest, followed by the grassland, cornfield and few in the pasture. In the forest, both CO_2 and CH_4 were significantly correlated with chamber measured and models predicted Ds/Do. CO_2 was positively, but CH_4 negatively correlated with Ds/Do, regardless of the method of measurement. Ds/Do based on a air-filled porosity alone explained 29 to 31% of the variability in CO_2 emissions in the forest while Ds/Do from models based on both air-filled porosity and total pore space explained 33 to 35% of the variability in forest CO_2 emissions. Similarly to Ds/Do, both CO_2 and CH_4 also significantly correlated with the pore tortuosity factor (τ). CO_2 was negatively correlated, but CH_4 positively with τ, regardless of the approach of calculation used. Overall, τ explained 15 to 25% of variability in CO_2 emissions while it explained 41 to 59% of CH_4 uptake in the forest. CO_2 and CH_4 were correlated with model predicted Ds/Do in the corn field and pasture ($p = 0.10$). The pore tortuosity factor (τ) also correlated with CO_2.

Table 3.5. Linear regression analysis (Y =Yo + aX) between pore space indices (D_s/D_o and τ) and greenhouse gas fluxes (CO_2 and CH_4) in Shizunai forest

	X	Yo	a	F	P	r	R^2
Linear regressions between CO_2 emissions and pore space indices	D_sD_o_Marsh	83.80	499.82	10.90	0.0030	0.56	0.31
	D_sD_o _Buck.	93.74	699.21	10.52	0.0035	0.55	0.31
	D_sD_o _Mold.	100.74	807.92	9.57	0.0050	0.53	0.29
	D_sD_o _Sall.	96.42	1684.41	12.65	0.0016	0.59	0.35
	D_sD_o _Jin	87.99	681.19	12.00	0.0020	0.58	0.33
	D_sD_o _Mill.	98.39	2158.33	12.74	0.0016	0.59	0.35
	Chamber	-0.054	0.0013	11.66	0.0026	0.59	0.35
	τ_Marsh	217.45	-38.01	7.85	0.0099	-0.50	0.25
	τ_Buck.	165.60	-6.41	6.37	0.018	-0.46	0.21
	τ_Mold.	143.59	-1.56	4.52	0.0439	-0.40	0.16
	τ_Sall.	145.14	-0.75	4.17	0.0524	-0.45	0.15
	τ_Jin	172.74	-9.85	6.14	0.0207	-0.45	0.20
	τ_Mill.	143.16	-0.41	4.08	0.0546	-0.38	0.15
	f_a	64.19	308.14	10.88	0.0030	0.56	0.31
	X	Yo	a	F	P	r	R^2
Linear regressions between CH_4 fluxes and pore space indices	D_sD_o_Marsh	0.004	-0.520	9.77	0.0049	-0.56	0.307
	D_sD_o _Buck.	-0.013	-0.690	7.20	0.0136	-0.50	0.25
	D_sD_o _Mold.	-0.026	-0.649	4.76	0.0400	-0.42	0.18
	D_sD_o _Sall.	-0.030	-0.977	3.36	0.0802	-0.36	0.14
	D_sD_o _Jin	-0.011	-0.628	6.91	0.0154	-0.49	0.24
	D_sD_o _Mill.	-0.032	-1.198	3.31	0.0824	-0.36	0.13
	τ_Marsh	-0.224	0.076	28.72	0.00001	0.75	0.57
	τ_Buck.	-0.129	0.014	31.43	0.00001	0.77	0.59
	τ_Mold.	-0.087	0.004	31.09	0.00001	0.77	0.59
	τ_Sall.	-0.085	0.002	12.79	0.00170	0.61	0.37
	τ_Jin	-0.130	0.018	15.53	0.00070	0.64	0.42
	τ_Mill.	-0.082	0.001	15.03	0.00080	0.64	0.41
	f_a	0.039	-0.414	13.43	0.0173	-0.67	0.38
	ρ_b	-0.140	0.154	12.67	0.0090	0.62	0.37
	Φ	0.143	-0.26	12.53	0.0039	-0.60	0.36

D_s/D_o= relative gas diffusion coefficient, τ = pore tortuosity factor. Marsh= Marshall, Buck = Buckingham, Mold = Moldrup et al, Sall = Sallam et al, Jin = Jin and Jury and Mill = Millington models

grassland (p = 0.10) and corn field. In the corn field, τ calculated from all models based on air-filled porosity alone significantly correlated with CO_2 in the cornfield (p = 0.05, r = -

0.76). Our results agree with those previously reported by Kruse et al. (1996); Ball et al. (1997), Hu et al. (2001) and Nkongolo et al. (2008) that pore structural indices control greenhouse gas fluxes from soils. In the forest, air-filled porosity (f_a) significantly correlated with CO_2 (p = 0.003, r = 0.56) and CH_4 (p = 0.017, = -0.62) while total porosity (Φ) could correlated only with CH_4 (p = 0.0039, r = -0.60). However, correlation between pore space indices and greenhouse gas fluxes were stronger than those between either air-filled porosity or total porosity and gas fluxes. For example, Table 3.5 shows that the pore tortuosity factor (τ) predicted from air-filled porosity (f_a) alone using Marshall, Buckingham and Moldrup models explained 57, 59 and 59% (r^2 values) of the variability in CH_4 uptake in the forest. However, f_a or Φ could explain only 36 or 38% of this variability, respectively.

3.5 Conclusion

Identification of parameters controlling soil fluxes are needed for predictive greenhouse gas fluxes models. While several soil properties have been studied, discrepancies in their potential to act as controlling factors across ecosystems still exist and call for more research. Soil pore space indices such as the gas diffusion coefficient and the pore tortuosity factor have been recognized as potential soil controlling factors for greenhouse gases such as methane. However, measurement of soil gas diffusion is tedious and time consuming. This study has showed that the soil gas diffusion coefficient can be estimated quickly from routine measurements of soil water and air and existing diffusivity models. The study has found that predicted pore structural indices: the relative gas diffusion coefficient and the pore tortuosity factor relate to greenhouse gas fluxes even when the air-filled porosity and the total porosity from which they are calculated do not relate to gas fluxes. Buckingham and Moldrup models were particularly significant in this study. Inclusion of these pore structural indices in predictive models may certainly improve our understanding of greenhouse gas fluxes dynamics.

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PART III. **INFLUENCE OF AGRICULTURAL PRACTICES ON GREENHOUSE GAS FLUXES AND SOIL PROPERTIES**

Chap 4. Effect of mechanized tillage operations on soil physical properties and greenhouse gas fluxes in two agricultural fields[3]

4.1 Abstract

Soil management practices may affect greenhouse gases emissions and exacerbate global warming. We studied the short-term effect of mechanized tillage operations on soil properties and CO_2, CH_4, NO and N_2O fluxes in a corn and soybean fields. The study was conducted from June to December 2001 at Hokkaido University in Sapporo (Japan). The soil of the experimental site is classified as Eutric Fluvisols (FAO). Two plots of 20 m long by 30 m width each were isolated in fields planted to corn (Zea mays) and soybean (Glucine max). Plot interrows were compacted by 1, 2, 3 and 4 cycles a tractor. Soil and air samples were collected for measuring CO_2, CH_4, NO and N_2O fluxes and other soil properties. Results showed that soil volumetric water content (θ_v), bulk density (ρ_b), the pore tortuosity factor (τ) and soil penetration resistance (SPR) increased while air-filled porosity (f_a), total pore space (TPS) and the soil gas diffusion coefficient (D_s/D_o) decreased linearly with increasing tractor cycle in both corn ($p < 0.0001$) and soybean ($p < 0.01$) fields. In corn field, CO_2 ($p < 0.0011$), NO ($p < 0.0257$) and N_2O ($p < 0.0116$) fluxes increased quadratically with increasing tractor cycle. In soybean field, CO_2 and CH_4 fluxes increased while N_2O and NO fluxes decreased linearly with increasing tractor cycle. CO_2 ($r=0.45$, $p<0.003$) and N_2O ($r= 0.45$, $p<0.003$) fluxes were significantly correlated with soil penetration resistance in corn and soybean field, respectively. Increasing tractor cycle deteriorated soil physical properties and increased greenhouse gas fluxes. More studies are needed to determine if these effects are permanent or only temporary on both soil and gas fluxes.

Key Words: Gas fluxes, soil properties, tillage operations

4.2 Introduction

Global atmospheric concentrations of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) have increased markedly as a result of human activities since 1750 and now far exceed pre-industrial values determined from ice cores spanning many thousands of years. The increase in carbon dioxide concentration is due primarily to fossil fuel use and land-use change, while methane and nitrous oxide increases are primarily caused by agriculture (IPCC, 2007). Agricultural practices such as tillage have been shown to change emissions of N_2O and the consumption of patterns of CH_4 in agricultural soils (Teepe et al., 2004). Tractor traffic during tillage operations is one of the practices that influence the exchange of CO_2, CH_4, NO and N_2O between the soil and the atmosphere as during such traffic, depending on the moisture level, soil compaction increases (Meek, 1994; Rollerson, 1990). In fact, compaction packs the primary soil particles (sand, silt, clay) and soil aggregates closer together and dramatically alter the balance between solids, air-filled and water-filled pore space (Albrook, 1986; Bruand and Cousin, 1995). By increasing the portion of water-filled pores, compaction makes the soil prone to denitrification and therefore increases N_2O losses (Ball et al., 2000; Douglas and Crawford 1993). There are numerous studies on the effects of soil compaction on soil properties (Greene and Stuart, 1985; Rollerson, 1990 and Meek, 1994). However, less work has been reported on the effect of tractor compaction on gas fluxes. Among these few studies, Flessa et al. (2002) quantified N_2O and CH_4 fluxes for ridges, uncompacted interrows and tractor-compacted interrows from potato (Solanum tuberosum) fields. They found that N_2O emissions were highest

[3]This chapter is based on a paper published in the Research Journal of Environmental Sciences—Authors: Nkongolo et al (2008), doi: 10.3923/rjes.2008.68.80

for the tractor compacted soil. However, the major fraction of the total CH_4 uptake (+86%) occurred on the ridges. Ruser et al. (1998) observed that the gaseous fluxes of N_2O and CH_4 fluxes from potato field were strongly affected by ridge-till practices; this produced areas with increased (ridges) and strongly reduced (tractor-compacted interrows) soil porosity. Hansen et al. (1993) compared tractor-compacted and uncompacted soils. They found that N_2O emissions (approximately 35%) increased due to soil compaction. Tractor "trips" during farming operations affect soil properties which lead to greenhouse emissions. Unfortunately the magnitude of these emissions is not still well quantified as many of these studies are conducted either at the beginning, middle or end of the growing season. However, in order to accurately predict the total emissions from agricultural systems, contribution at each stage of farming operations should be known. The objective of this study was therefore to assess the short-term (at early stage of field operations) effect of tractor induced compaction on soil properties and gas fluxes in a corn and a soybean fields of northern Hokkaido.

4.3 Materials and methods

4.3.1 Experimental site

This study was conducted at Hokkaido University Experimental Farm in Sapporo, Hokkaido, Japan (43^o 11' N, 141^o 30' E), from early June to late December 2001. Sapporo, Japan's third largest city enjoys a mild climate with a year-round average temperature of 9.1°C. The average temperature was -3.5°C in January and 20.3°C in July 2001. The soil of the experimental site is classified as Typic Fluvaquents (Soil Taxonomy), Eutric Fluvisols (FAO). The physical and chemical properties of different horizons were reported by Hayashi and Hatano (1999). Soil texture consists of 25.4% sand, 47.0% silt and 27.6% clay. The saturated hydraulic conductivity is 2.99 x 10^{-5}cm s^{-1}. The carbon and nitrogen contents were

2.1% and 0.16 %, respectively. Field preparation began in April and in May, two plots of 30 m long by 20 m width were isolated in fields cropped to corn (Zea mays) and soybean (Glucine max). These fields were established maintained by the Crop Production Laboratory, Faculty of Agriculture, Hokkaido University. The corn field was fertilized with N, 130; P_2O_5, 180; K_2O, 100; and MgO, 40 kg ha^{-1} while soybean received N, 32; P_2O_5, 100; K_2O, 80; and MgO, 24 kg ha^{-1}. In June 2001, plots interrows in both soybean and corn fields were compacted by 1, 2, 3 and 4 cycles (1 cycle = 2 passes) with a 2.4 tons Fordson Major tractor (as during regular tillage operations) as showed in Figure 4.1. The ridges of crop rows were not compacted. Immediately after tractor compaction, soil penetration resistance (SPR) was measured to a depth of 100 cm and soil samples were taken in both interrows and ridges. A second measurement of SPR, sampling for soil properties and greenhouse gas fluxes was conducted three weeks later in August 2001.

4.3.2. Measurement of soil chemical properties

Soil samples were taken at each sampling locations immediately after measurements of greenhouse gases emissions, for analyses of chemical properties. Soil samples were collected to a depth of 5cm from the soil surface with a 5.1 cm height and 5 cm diameter aluminum cylinder. The properties studied were soil pH (H_2O and KCl), electrical conductivity (EC), nitrite (NO_2^-),

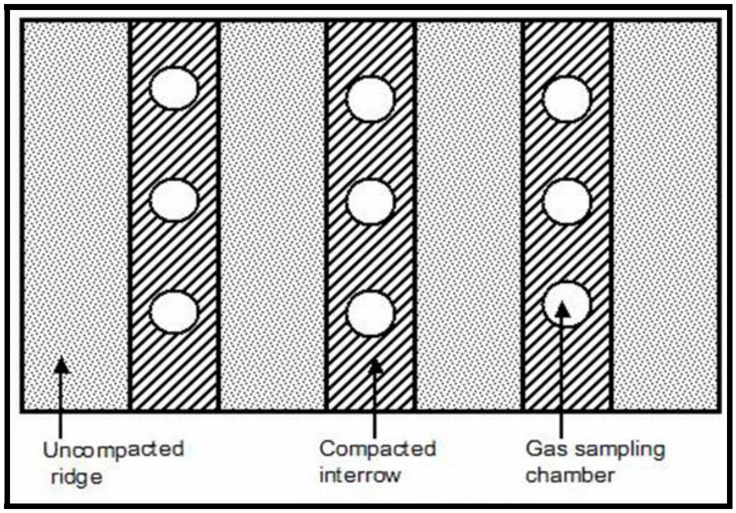

Figure 4.1. Experimental site, showing gas sampling chamber, compacted-non compacted interrows and ridges

nitrate (NO_3^-) and ammonium (NH_4^+). For analyses of NO_2^- and NO_3^-, 10g of field moist soil sample was extracted by 50 ml of deionized water (1:5 = soil : water) and concentrations of the above anions were determined by ion exchange chromatography. This extract was also used to measure pH (H_2O) and EC. For NH_4^+ determination, 7 g of field moist sample was extracted using 70 ml of 2M KCl. pH (KCl) was measured using this extract and soil NH_4^+ was determined by colorimetry with indophenol-blue.

4.3.3 Measurements of soil physical properties

For soil physical properties, soil cores (3 replicates for each of the 5 tractor cycles) were taken in each of corn and soybean fields to a depth of 5cm from the soil surface with a 5 cm diameter and a 5.1 cm height cylinder (volume = 100 cm^3). Cores fresh weights were first measured then their bottom covered with a filter paper. The filter paper was strongly held with rubbed elastic. Cores without their top covers were thereafter transferred onto a tension table. The top of the tension table was covered with a plastic paper to prevent evaporation. Cores were saturated for comparison purpose between calculated total pore space (TPS) to that determined as core volumetric water content at saturation. However, in this report only

TPS values calculated were used. After 72 hours of saturation, cores fresh weights were again measured. They were then transferred into an oven to be dried at 105^{o}C for 72 hours. Soil bulk density (ρ_b), total pore space (TPS), volumetric water content (θ_v), air-filled porosity (f_a), relative gas diffusion coefficient (D_s/D_o) and the pore tortuosity factor (τ) were later calculated as follows:

Bulk density (ρ_b)

$$\rho_b = Ms/Vt \qquad [1]$$

where, ρ_b (kg m^{-3}) is the soil bulk density, Ms (kg) is the mass of dry solids determined after drying the soil sample to constant weight at 105^{o}C and Vt (m^3) is the total volume of soil, and thus Vt is the volume of cylinder.

$$Vt = Va + Vw + Vs \qquad [2]$$

Where, V_s (m^3) is the volume of soil solids, Vw (m^3) is the volume of water and V_a (m^3) is the volume of the air fractions successively.

Total pore space (TPS)

$$TPS = (Vw+Va)/Vt \qquad [3]$$

Where, TPS (m^3 m^{-3}) is the total pore space or the total space of soil filled with fluid (air + water).

Gravimetric water content (θ_g): $\theta_g = (Mt-Ms)/Ms$ [4]

where, θ_g (kg soil water kg^{-1} soil) is the gravimetric water content or mass of water present in each unit mass of the dry soil, Mt (kg) is the weight of the moist soil sample as taken from the field.

Volumetric water content (θ_v): $\theta v = [(Mt-Ms).\rho w]/Vt$ [5]

where, θ_v (m^3 soil water m^{-3} soil) is volumetric water content or the volume of water present in a unit volume of the sample. ρ_w is the density of water taken as equals to 1000 kg m^{-3}.

Air-filled porosity (f_a): f_a=TPS-θv [6]

where f_a (m^3 soil air m^{-3} soil) is air-filled porosity or the portion of the pore space filled with air (air space).

Relative gas diffusivity (D_s/D_o)

Relative gas diffusivity was calculated using Buckingham (1904) equation:

$$Ds/Do =(f_a)^2 \qquad [7]$$

where, D_s/D_o(m^2 s^{-1}. m^{-2} s) is the relative gas diffusion coefficient, Ds is the gas diffusion coefficient in the soil (m^3 soil air m^{-1} soil s^{-1}), D_o is the gas diffusion coefficient in free air (m^2 air s^{-1}).

Pore tortuosity (τ)

The pore tortuosity factor was calculated by comparing Reible and Shair (1982).

$$\tau = 1/f_a \qquad [8]$$

where, τ (m m^{-1}) is the pore tortuosity factor.

Water filled pore space (WFPS)

$$WFPS = (\theta v/TPS) \times 100 \qquad [9]$$

where, WFPS (%) is the percentage of the total pore space filled with water.

4.3.4 Gas sampling for CO_2, CH_4, NO and N_2O flux measurements

CO_2, CH_4, NO and N_2O emissions from tractor-compacted interrows and non-compacted ridges were measured using a closed-chamber technique. This technique has also been used by Tokuda and Hayatsu (2000) and Tokuda and Hayatsu (2004). The chambers were circular with steel frames. The top of each chamber had a gas sampling tube and a bag to control air pressure inside the chamber. The height and diameter of the chamber were 0.35m and 0.30m, respectively. At each sampling time, 3 chambers (each chamber corresponding to a replicate) spaced 10 m were installed in the soil in the interrow or ridge and kept for 20 minutes, and then samples of the enclosed atmosphere were withdrawn by a 50 ml syringe and transferred into a 1L Tedlar ® Bag with non-sorbant walls. A total of 30 samples (3 replicates x 5 tractor cycles x 2 fields) were taken in both corn and soybean fields. The air temperature inside the chambers was recorded using a digital thermometer. Ambient air between 0 and 2 m from the soil surface was collected and its mean concentration was used as a background concentration for calculation of gas fluxes. Immediately after sampling, a gas chromatography with an electron capture detector and FID used for N_2O and and CH_4 analyses, respectively. NO flux was analyzed by chemo-iluminescence with a nitrogen oxide analyzer (Kimoto, Model 265 P) and an infra-red analyzer was used for CO_2. Fluxes were calculated using the equation:

$$F = \rho * \frac{V}{A} * \frac{\Delta C}{\Delta t} * (\frac{273}{T}) * \alpha \qquad [10]$$

Where, F is the gas production rate; ρ is the gas density (mg m^{-3}) under standard conditions; V (m^3) and A (m^2) are the volume and bottom area of the chamber; $\Delta C/\Delta t$ is the ratio of change in the gas concentration inside the chamber; T is the absolute temperature; and α is the transfer coefficient (12/44 for CO_2, 12/16 for CH_4, 14/30 for NO and 28/44 for N_2O). A positive value indicates gas emission from the soil, while a negative value indicates gas uptake. The detectable limits were 0.1 mg C m^{-2} h^{-1} for CO_2, 0.01μg C m^{-2} h^{-1} for CH_4 and 0.1 μg N m^{-2} h^{-1} for NO and N_2O. Soil temperature was measured at 5 cm and 10 cm from the top soil layer, using a digital thermometer. Statistix 8.0 statistical package was used to calculate summary of simple statistics, analysis of variance, polynomial contrasts, correlation matrix and linear regression.

4.4 Results

4.4.1 Effect of tractor cycle on soil chemical properties

Soil chemical properties as affected by tractor load and cycle are showed in Tables 4.1 and 4.2 for corn and soybean, respectively. At 5% probability level, tractor load and cycle did not affect any of the soil chemical properties studied. In magnitude, values of chemical properties observed in ridges were similar to those found in tractor-compacted interrows, except for NO_3^- which tended to increase with tractor cycles (for corn field mainly).

4.4.2 Effect of tractor cycle on soil physical properties

Tables 4.3 and 4.4 summarize the effect of tractor load and cycle on soil physical properties. The non compacted ridge had a very low bulk density, high aeration and high total pore space. Crop residues returned to the soil and sampling shortly after tillage can explain these values. All soil physical properties studied were significantly affected by tractor cycle. Volumetric water content (θ_v), bulk density (ρ_b) and pore tortuosity (τ) increased, whereas air-filled porosity (f_a), total pore space (TPS) and the gas diffusion coefficient (D_s/D_o) decreased linearly with increasing tractor cycle. In comparison to all compacted interrows, average ridge values for θ_v, ρ_b and τ were lower while those for f_a, TPS and D_s/D_o were higher. In addition, in magnitude, values of θ_v, ρ_b, τ, f_a, TPS and D_s/D_o were similar in both corn and soybean fields. However, for tractor-compacted interrows, average values of θ_v, ρ_b and τ were higher in corn while those for f_a, TPS and D_s/D_o were higher in soybean field. Tables 4.5 and 4.6 show the effect of tractor load and number of cycle on soil resistance to penetration in July 2001 for corn and soybean, respectively. Tractor cycle linearly increased soil resistance to penetration for both sampling dates and in both fields, but the effect was prevalent only in the top 20 cm of the soil profile. Below this depth, the relationship was no longer prevalent. In addition, in magnitude, values of soil resistance to penetration measured immediately after compaction treatments were as twice as high in comparison to those measured three weeks later. Finally, in comparison to tractor-compacted interrows, SPR values measured on the ridges were lower.

4.4.3 Effect of tractor cycle on greenhouse gas fluxes

The effect of tractor load and number of cycle on greenhouse gas fluxes is showed in Tables 4.7 and 4.8 for corn and soybean fields, respectively. Except for CH_4which failed to respond, all greenhouse gas fluxes were significantly affected by tractor load and cycle. In addition, except for N_2O fluxes which increased linearly in the soybean field, all gas fluxes increased quadratically with increasing tractor cycle. In soybean field, CO_2 and N_2O fluxes measured in the ridges were lower than those obtained in tractor-compacted interrows. However, NO and CH_4 fluxes were higher in the ridges than tractor-compacted interrows. There was no specific trend for the relationship between ridges and compacted interrows fluxes in the corn field, but after computing the average values for all tractor-compacted interrows and comparing them with ridge values, the same trend as in the soybean field was found. Among ridges, CO_2 and N_2O fluxes were higher in the corn as compared to soybean while NO fluxes dominated in soybean. A close examination of the means also reveal that in both fields, the highest CO_2

and N_2O fluxes were obtained after 2 and 4 cycles of interrows compaction, respectively. The highest fluxes for NO were obtained after 2 cycles in corn, but in the ridge for soybean. In cornfield, CH_4 was consumed in both ridges and tractor-compacted interrows. However, in soybean field, CH_4 was emitted in non-compacted ridges and consumed in tractor-compacted interrows. Finally, uptake of N_2O (negative fluxes) was observed in non-compacted ridge of soybean field, indicating that denitrification was enhanced as a result of soil compaction.

4.4.4 Correlation between soil physical properties and greenhouse gas fluxes

Figure 4.2 shows the relationship between CO_2 fluxes and soil penetration resistance (SPR) measured at 2.5 cm depth in the cornfield. CO_2 fluxes were also significantly correlated with SPR measured at 5 cm ($r = 0.58$, $p = 0.029$) and 10 cm ($r = 0.58$, $p = 0.044$) depth. CH_4 fluxes were only correlated with SPR measured at 15 cm depth ($r = 0.62$, $p = 0.014$). Figure 4.3 shows the relationship between N_2O fluxes and SPR measured at 2.5 cm depth for the soybean field. N_2O fluxes were also significantly correlated with SPR measured at 15 cm ($r = 0.64$, $p = 0.011$) and 20 cm ($r = 0.52$, $p = 0.045$) depth. CO_2 was only correlated with SPR measured at 20 cm ($r = 0.59$, $p = 0.021$). In addition, among the gasses, NO was positively correlated with f_a ($r = 0.68$, $p = 0.005$), D_s/D_o ($r = 0.71$, $p = 0.003$) and TPS ($r = 0.70$, $p = 0.004$) and negatively correlated with ρ_b ($r = -0.69$, $p = 0.0044$), θ_v ($r = 0.67$, $p = 0.006$), WFPS ($r = -0.67$, $p = 0.0067$) and with pore tortuosity in Figure 4.4. Other gases also correlated with other soil physical properties, but these correlations were most significant with NO.

Table 4.1. Soil chemical properties in a cornfield as affected by mechanical tillage operations in June 2001

Tractor cycle	$pH(H_2O)$	pH(KCl)	EC (mS)	NO_2^- (mg N/kg soil)	NO_3^- (mg N/kg soil)	NH_4^+ (mg N/kg soil)
Ridge (non compacted)	6.24	4.71	5.29	0.07	11.13	0.90
1 Cycle compacted interrows	6.15	4.51	4.79	0.09	9.34	0.96
2 Cycles compacted interrows	5.82	4.38	6.11	0.04	10.38	0.96
3 Cycles compacted interrows	6.03	4.59	5.16	0.07	12.67	1.36
4 Cycles compacted interrows	6.12	4.69	5.11	0.10	9.78	1.09
ANALYSIS OF VARIANCE						
Replications	ns	ns	ns	ns	ns	ns
Cycle (C)	ns	ns	ns	ns	ns	ns

ns = non significantly different at LSD = 0.05

Table 4.2. Soil chemical properties in a soybean field as affected by by mechanical tillage operations in June 2001

Tractor cycle	$PH(H_2O)$	pH Kcl)	EC (mS)	NO_2^- (mg N/kg soil)	NO_3^- (mg N/kg soil)	NH_4^+ (mg N/kg soil)
Ridge (non compacted)	5.91	4.47	5.30	0.23	4.93	1.13
1 Cycle compacted interrows	6.13	4.98	5.84	0.08	10.46	1.27
2 Cycles compacted interrows	5.72	4.64	8.81	0.05	17.87	0.86
3 Cycles compacted interrows	5.84	4.67	5.54	0.05	8.44	1.09
4 Cycles compacted interrows	5.94	4.46	5.25	0.04	6.13	0.82
ANALYSIS OF VARIANCE						
Replications	ns	ns	ns	ns	ns	ns
Cycle (C)	ns	ns	ns	ns	ns	ns

Table 4.3. Soil physical properties in a cornfield as affected by by mechanical tillage operations in June 2001

Tractor cycle	θ_v $m^3\ m^{-3}$	ρ_b $kg\ m^{-3}$	f_a $m^3\ m^{-3}$	TPS $m^3\ m^{-3}$	D_s/D_o $(m^2\ s^{-1} m^{-2} s$	τ $m\ m^{-1}$
Ridge (non compacted)	0.23	0.53	0.57	0.80	0.34	1.77
1 Cycle compacted interrows	0.32	0.74	0.40	0.72	0.16	2.60
2 Cycles compacted interrows	0.38	0.89	0.28	0.66	0.08	3.61
3 Cycles compacted interrows	0.39	0.95	0.25	0.64	0.06	4.08
4 Cycles compacted interrows	0.44	1.06	0.17	0.60	0.03	6.50
ANALYSIS OF VARIANCE						
Replications	ns	ns	ns	ns	ns	ns
Cycle	****	****	****	****	****	***
Cycle linear	****	****	****	****	****	****
Cycle quadratic	*	ns	*	ns	**	ns

Table 4.4. Soil physical properties in a soybean field as affected by mechanized tillage operations in June 2001

Tractor cycle	θ_v $(m^3\ cm^{-3})$	ρ_b $kg\ m^{-3}$	f_a $m^3\ m^{-3}$	TPS $m^3\ m^{-3}$	D_s/D_o $m^2\ s^{-1} m^{-2} s$	τ $m\ m^{-1}$
Ridge (non compacted)	0.23	0.52	0.57	0.80	0.34	1.79
1 Cycle compacted interrows	0.29	0.73	0.43	0.73	0.19	2.34
2 Cycles compacted interrows	0.32	0.81	0.37	0.69	0.14	2.74
3 Cycles compacted interrows	0.33	0.86	0.35	0.68	0.13	2.90
4 Cycles compacted interrows	0.38	0.98	0.26	0.63	0.07	4.30
ANALYSIS OF VARIANCE						
Replications	ns	ns	ns	ns	ns	ns
Cycle	*	**	*	**	*	*
Cycle linear	**	***	**	***	**	**
Cycle quadratic	ns	ns	ns	ns	ns	ns

[a, b, c, d] = significantly different at 5, 1, 0.1 and 0.01 %, respectively

Table 4.5. Soil resistance to penetration in a corn field as affected by mechanized tillage operations in July 2001

	Depth					
Tractor cycle	2.5 cm	5 cm	7.5 cm	10 cm	15 cm	20 cm
Ridge (non compacted)	0.13	0.20	0.23	0.25	0.43	0.97
1 Cycle compacted interrows	0.57	0.65	0.73	0.75	1.10	1.60
2 Cycles compacted interrows	0.61	0.72	0.74	0.76	1.03	1.13
3 Cycles compacted interrows	0.76	0.81	0.80	0.85	0.94	1.08
4 Cycles compacted interrows	0.77	0.84	0.89	0.92	0.88	1.27
ANALYSIS OF VARIANCE						
Replications	ns	ns	ns	*	**	**
Cycle (C)	****	****	****	****	****	**
Cycle linear	***	****	***	****	***	ns
Cycle quadratic	*	***	***	***	****	ns

Table 4.6. Soil resistance to penetration (kg cm^{-2}) in a soybean field as affected by mechanized tillage operations in July 2001

	Depth					
Tractor cycle	2.5 cm	5 cm	7.5 cm	10 cm	15 cm	20 cm
Ridge (non compacted)	0.11	0.11	0.16	0.22	0.68	1.25
1 Cycle compacted interrows	0.58	0.66	0.70	0.64	0.60	1.27
2 Cycles compacted interrows	0.98	1.03	0.94	0.93	1.02	0.94
3 Cycles compacted interrows	0.90	1.01	1.02	0.98	1.27	1.52
4 Cycles compacted interrows	0.99	1.03	1.02	0.93	1.19	1.38
ANALYSIS OF VARIANCE						
Replications	ns	**	*	**	*	**
Cycle (C)	****	****	****	****	****	*
Cycle linear	****	****	****	****	****	ns
Cycle quadratic	***	****	****	****	ns	ns

Table 4.7. Greenhouse gas fluxes in a cornfield as affected by mechanized tillage operations in August 2001

Tractor cycle	CO_2 (mg CO_2-C m^{-2} h^{-1})	CH_4 (µg CH_4-C m^{-2} h^{-1})	NO (µg NO-N m^{-2} h^{-1})	N_2O (µg N_2O -N m^{-2} h^{-1})
Ridge (non compacted)	66.55	-15.18	3.79	77.43
1 Cycle compacted interrows	65.54	-27.05	2.17	68.85
2 Cycles compacted interrows	85.47	-13.32	9.09	47.96
3 Cycles compacted interrows	71.25	-27.27	1.05	77.61
4 Cycles compacted interrows	69.28	-15.47	1.94	92.48
LSD (0.05)	*6.35*	-	*3.18*	*26.07*
ANALYSIS OF VARIANCE				
Replications	ns	ns	ns	ns
Cycle (C)	***	ns	**	*
Cycle linear	ns	ns	ns	ns
Cycle quadratic	***	ns	*	**

Table 4.8. Greenhouse gas fluxes in a soybean field as affected by mechanized tillage operations in August 2001

Tractor cycle	CO_2 (mg CO_2-C m^{-2} h^{-1})	CH_4 (µg CH_4-C m^{-2} h^{-1})	NO (µg NO-N m^{-2} h^{-1})	N_2O (µg N_2O -N m^{-2} h^{-1})
Ridge (non compacted)	45.28	7.31	8.02	-16.35
1 Cycle compacted interrows	62.98	-12.14	0.10	18.55
2 Cycles compacted interrows	83.97	-5.62	1.06	60.75
3 Cycles compacted interrows	73.97	-17.89	3.55	39.01
4 Cycles compacted interrows	57.92	-8.36	2.52	73.25
ANALYSIS OF VARIANCE				
Replications	ns	ns	ns	ns
Cycle	*	ns	*	**
Cycle linear	ns	ns	ns	***
Cycle quadratic	**	ns	**	ns

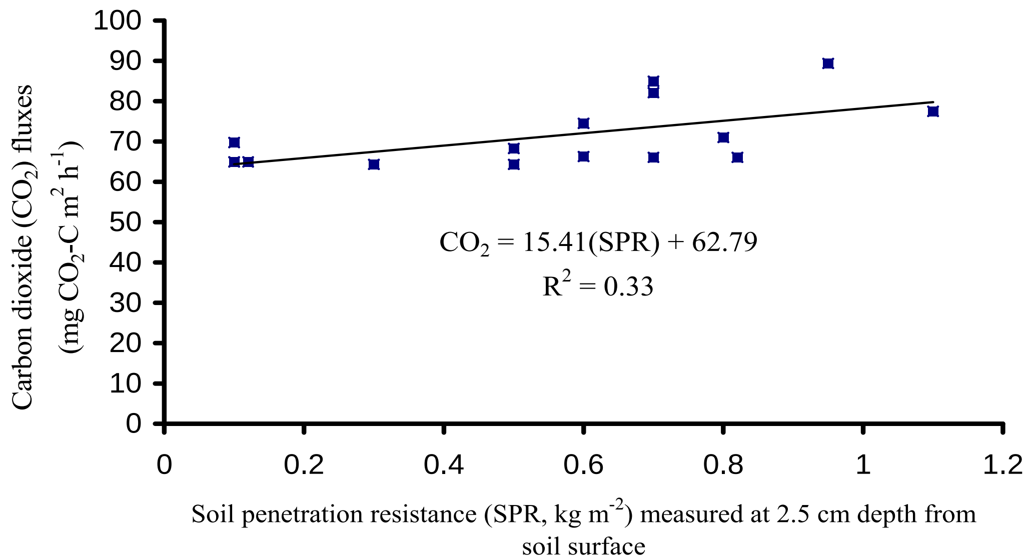

Figure 4. 2. Relationship between Carbon dioxide (CO_2) fluxes and soil penetration resistance in a cornfield

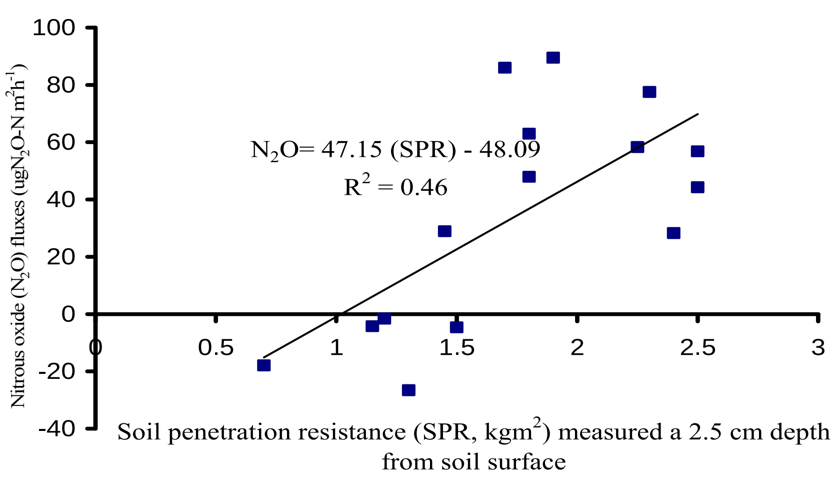

Figure 4.3. Relationship between Nitrous oxide (N_2O) fluxes and soil penetration resistance in soybean field

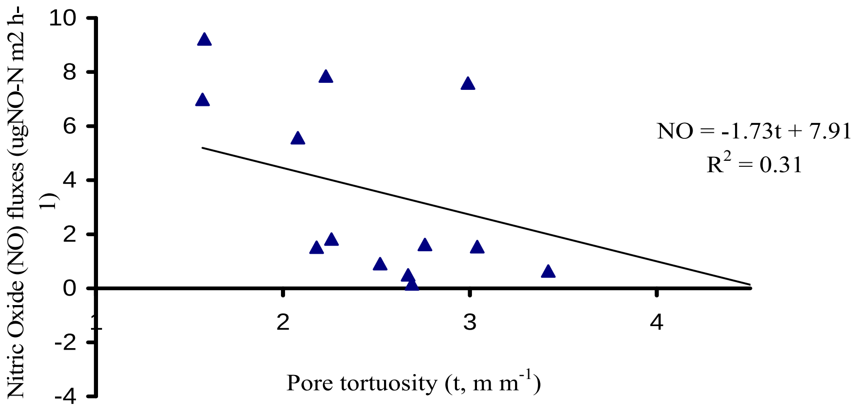

Fig. 4.4 Relationship between Nitrous oxide (NO) fluxes and the pore tortuosity factor in soybean field

4.5 Discussion

The average values for bulk density, volumetric water content and pore tortuosity were higher in tractor-compacted interrows as compared to rigdes. These results agree with those reported by Canqui et al (2004) who found that wheel traffic reduced K_{sat} by three times and increased bulk density by 6%. Our results are however opposed to those reported by Ginting and Eghball (2005) who found that wheel traffic had no significant effect on a specific soil physical property [(bulk density, soil moisture, and water filled porosity (WFP)] and N_2O fluxes.

The lack of difference in bulk density for example in Ginting and Eghball (2005) study could be due to their depth of soil bulk density measurements (20 cm) as compared to our depth of sampling (5 cm). In fact, it has been suggested that small depth increments might detect bulk density differences that would be obscured in a large depth increment samples (Unger, 1991). Logsdon and Cambardella (2000) indicated that changes in no-till bulk density at the 0- to 12-cm depth was partially due to biopores from surface-feeding earthworms (Lumbricus terrestris L.) that were observed in the no-till field but not in the disk field. The air-filled porosity, total pore space and the gas diffusion coefficient were higher in ridges as compared to tractor-compacted interrows.

These results agree with those of Ruser et al. (1998) who reported that ridge-till practice produced areas with increased (ridges) and strongly reduced (interrow soil compacted by tractor traffic) soil porosity. The air-filled porosity and soil gas diffusion coefficient were lowest and soil penetration resistance of 0-10 cm depth highest in the 4 cycles tractor-compacted interrows. This treatment also corresponded to the highest N_2O fluxes in both corn and soybean fields. These results agree with those of Klemedtsson et al. (1988) who suggested that the highest N_2O production should occur in the presence of low concentrations of O_2, at the transition between aerobic and anaerobic conditions. Flessa et al. (2002) and Ruser et al. (1998) also found that soil compaction was an important factor for increased N_2O emissions from ridge-tilled potato fields. Teepe et al (2004) reported that high N_2O emissions which occurred after compaction were restricted to short periods at the sandy loam and silty clay loam sites whereas emissions at the silt site remained high throughout the entire growing season. Hansen et al. (1993) compared tractor-compacted and uncompacted soils and found increased N_2O emissions (approximately 35%) due to soil compaction. However, emission rates reported by these authors are considerably higher as compared to flux rates measured in the present study. The higher N_2O fluxes in these studies can be explained by the much stronger soil compaction (e.g., a bulk density of 1.56 g cm^{-3} for tractor-compacted soil) and greater WFPS (mean of 85% for tractor-compacted soil) in Ruser et al. (1998) for example. In our study, the highest bulk density observed for the 4 cycles tractor-compacted interrows was less than unity and the corresponding WFPS below 65%. In non-compacted ridges, even though the averages air-filled porosity and gas diffusion coefficient were highest, denitirification could still happen, perhaps at a lower level in comparison to compacted soil. In fact, Rolston (1981) reported that in aerobic soils, anaerobiosis can still occur at microsites where consumption of oxygen exceeds the oxygen-supply via diffusion. In addition, uptake of N_2O (negative fluxes) was observed in the ridges of soybean. This behavior is unusual as in most studies, soils have been reported a source of N_2O (Ball et al., 2000, Matson et al., 1990). However, several studies where soils have acted occasionally as sinks have also been reported. Donoso et al. (1993) found that in contrast with a significant emission in the rainy season, the soil of a scrub-grass savannah of Venezuela acted as a sink for N_2O in the dry season. Cicerone et al. (1978) found a significant sink activity in wet grass-covered soil of Michigan. Blackmer and Bremner (1976) found that cultivated soils of Iowa acted as sinks for atmospheric N_2O at certain times during spring. Ryder (1981) reported that the soil acts as both a source and sink for atmospheric N_2O depending on soil condition and the amount of nitrogenous fertilizer applied, the sink activity was observed in conditions conducive to microbial reduction of N_2O (i.e. very low nitrate in the soil). Matson and Vitousek (1987) suggested that even though the overall average fluxes measured in La Selva, Costa Rica were positive, under certain conditions uptake of N_2O occurred in this tropical soil. The mechanism by which soil acts as a sink for N_2O is not known. It has been suggested that the net flux of N_2O to the atmosphere results from its production by nitrifying and or denitrifying bacteria. N_2O consumption is therefore likely due to the reduction of N_2O to N_2 (Donoso et al., 1993). It has also been reported that N_2O production was somewhat higher and N_2O uptake somewhat lower in the more disturbed communities and that N_2-fixing cyanobacteria could both produce and consume N_2O (http://gane.ceh.ac.uk/award3.shtml). In this study, N_2O uptake was observed in soybean field. Soybean is a N_2-fixing legume in symbiosis with bacteria living in its roots. Even though we did not investigate the nature of bacterial flora in our soil, it may be also thought that soybean, through its bacterial symbiosis, contributed to this phenomenon. Another explanation may be a temporal N deficit in the soil. In fact, the soybean crop received a starter dose of N of 32 kg N. This amount might have been taken up by the soybean plants during early growth when the root nodules were not established and the rhizobium bacteria where not actively fixing N_2. During such periods with low nitrate availability, the soil may consume atmospheric N_2O. All soil physical properties studied were significantly correlated with either CO_2, CH_4, N_2O or NO with correlation coefficients ranging from 0.30 to 0.70. Correlation between soil physical properties and gas fluxes have also been reported by Ball et al (1997) who found significant relationships between N_2O fluxes and air permeability, the soil gas diffusion coefficient and tortuosity. Hu et al. (2001) also reported a significant relationship between the soil gas diffusion coefficient and CH_4 fluxes.

4.6 Summary

Tractor compaction increased soil resistance to penetration, water, bulk density and pore tortuosity while reducing air-filled porosity, total pore space and the soil gas diffusion coefficient. Changes in soil physical properties resulted in increased CO_2, NO and N_2O emissions. This work helped identify rarely measured soil physical properties such as D_s/D_o and τ which significantly influence soil gas exchange. More studies are needed to determine if these effects are permanent or only temporary on both soil and gas fluxes.

4.7 Acknowledgements

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4.8 References

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PART IV: QUANTIFICATION OF GREENHOUSE GASES FROM SOIL IN AGRICULTURAL FIELDS

CHAP 5. Nitrous oxide (N_2O) emissions from a Japanese lowland soil cropped to onion: I. Spatial and temporal variability of fluxes[4]

5.1 Abstract

Field studies were conducted to assess the spatial and temporal variability of nitrous oxide (N_2O) emissions in an agricultural field cropped to onion in Mikassa, northern Hokkaido (Japan). N_2O emissions measurements were conducted in 100 m by 100 m and 60 m by 60 m grids in 1999 and 2000, respectively with samples taken at 10 m spacing. Air samples for N_2O determinations were collected using the closed-chamber technique. The chambers were circular with steel frames. The top of each chamber had a gas sampling tube and a bag to control air pressure inside. The height and diameter of the chamber were 0.35 m and 0.30 m, respectively. Air samples were stored in vial bottles for analysis with a gas chromatograph with electron capture detector within 24 h after sampling. GS+ 3.0 geostatistical software and statistix 8.0 were used for data analysis. Results showed that N_2O emissions were highest in 1999 as compared to 2000. N_2O emissions were fitted to a linear variogram in 1999 and responded to a spherical variogram model in 2000. Positive first degree surface trends were also found for N_2O emissions data in both years. However, the removal of these trends did not change variogram models, but significantly improved them by increasing the R^2 and Q values. N_2O emissions systematically varied with small zones of uptake (negative flux) across the field, suggesting the presence of hot spots.

Keywords: Nitrous oxide emissions, spatial variability, lowland soil

5.2 Introduction

The tropospheric concentration of nitrous oxide (N_2O), a potent greenhouse gas also involved in the catalytic degradation of stratospheric ozone (Cicerone, 1987), has increased since the beginning of the Industrial Era, with a rate of 0.8 ppb per year during the 1990s (Dambreville et al., 2008). Nitrous oxide (N_2O) is a trace gas that has received considerable attention because of its importance in atmospheric chemistry and its influence in controlling the global heat budget (IPCC, 2007). In fact, enrichment of the air with N_2O (and chlorofluorocarbons) threatens depletion of the ozone (O_3) layer in the stratosphere, thus allowing passage of more UV-B ultraviolet radiation and enhancing the incidence of skin cancer (Cicerone, 1987). Anthropegenic activities such as agriculture have been named among the major causes for the increase of this pollutant (Bouwman, 1996; Mosier et al., 1998, Duxubury, 1994). That is why it is important to quantify the importance of these activities on the soil-atmosphere exchange of trace gases in order to understand their changing atmospheric concentrations and to provide research-based information to local, regional, national and international policy makers. Unfortunately, the high degree of spatial variability of N_2O (as well as other greenhouse gases) emissions and soil-controlling soil properties present a major challenge to accurately quantifying fluxes (Ball et al., 1997). In fact, N_2O fluxes across geographic regions vary in response to major and repetitive differences in the soil environment (Matson et al., 1989; Robertson, 1993; Parkin, 1993). For example, at a micro-to-plot scale, N_2O fluxes are controlled by the availability of soil water, labile C, and inorganic N. These factors are, in turn influenced by soil type and plant community type at the landscape scale. The distributions of soil types and plant communities are interrelated, and their variation in a region is again largely controlled by geomorphology, land use, and climate.

[4]This chapter is based on a paper published in the International Journal of Agricultural Research—Authors: Nkongolo et al (2009), doi**:** 10.3923/ijar.2009.17.28

Therefore, quantification of N_2O flux rates from different sites, ecosystems, crops, climate and agricultural practices is necessary to improve the accuracy of N_2O emissions inventories (Eichmer, 1990). The objective of this study was to assess the spatial and temporal variability of N_2O emissions in a field cropped to onion.

5.3 Materials and methods

5.3.1 Study area

Air and soil samples for determination of N_2O emissions and soil properties, respectively, were collected in Mikassa, Hokkaido province (Fig. 5.1), but all analyses were done in the Laboratory of Soil Science at Hokkaido University in Sapporo. Sapporo is Japan's third largest city in area and is located on the western plains of Hokkaido, the northernmost island of Japan. Its geographical locations are 43°11'N, 141°30'E. Sapporo enjoys a mild climate with a year-round average temperature of 9.1°C. The average temperature in January was -3.7°C, and in July, 20.3°C in 2000. More than sixty percent of surface area of Sapporo (primarily in the southwest) is mountainous, creating a concentration of urban activity focused around the Toyohira River, which runs through the city.

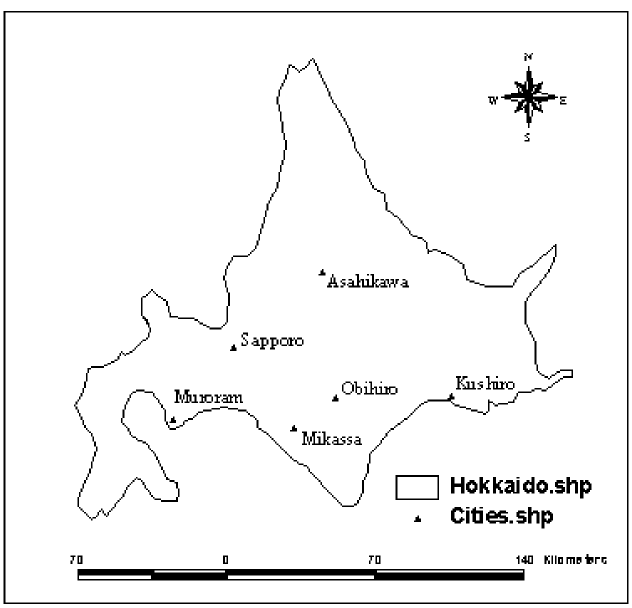

Figure 5.1. Hokkaido, Japan

5.3.2 Experimental field

The study was conducted in a 140-m by 140-m upland field yearly cropped to onion (Allium cepa L.) in Mikassa, Hokkaido, Japan (43°14'N, 141°50'E). The experimental field is showed in Figure 5.2.

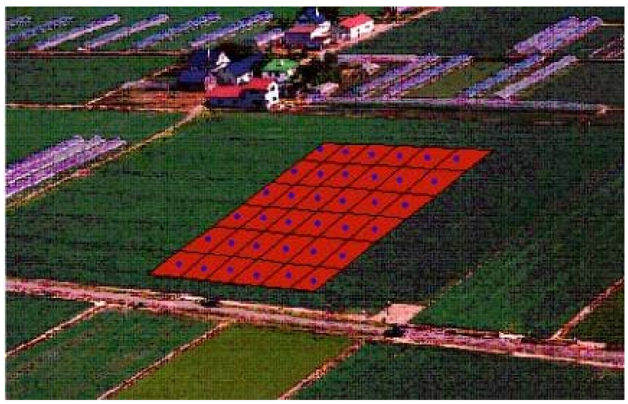

Figure 5.2. Experimental fField in Mikassa, Hokkaido (Japan)

The annual average temperature in Mikassa is 7.2°C and the average annual rainfall is 1204 mm. The soil of the experimental site is classified as fine, mesic, mollic Fluvaquent. The physical and chemical properties of different horizons were reported elsewhere (Hu et al., 2001). Soil texture consists of a silty or heavy clay from the Ap layer (0-28 cm) down to the C horizon (48-100+ cm). The groundwater table lays at 70-80 cm depth throughout the growing season. Surface drains were installed at 80-100 cm depth at 12-m intervals and were connected to the same effluent exit, draining about 0.95 ha (125 m by 76 m) for monitoring nitrate leaching. Fertilizer nitrogen (322 kg N/ha) was applied at the end of April, shortly before transplanting. Onion was harvested during the second and third week of September. In June 1999, the field was sampled for N_2O emissions and soil physical and chemical properties, using a 100-m by 100-m grid at 10-m spacing for a total of 100 sampling locations. A year later in September 2000, the same field was again sampled for N_2O and soil chemical and physical properties, using a 60-m by 60-m grid at 10-m spacing for a total of 36 locations. Data collected in both 1999 and 2000 are analyzed in this paper.

5.3.3 Measurements of N_2O emissions

N_2O emissions from the soil surface, which may have been produced in the root zone or in deeper horizons, were measured using a closed-chamber technique. The chambers were circular with steel frames. The top of each chamber had a gas sampling tube and a bag to control air pressure inside the chamber. The height and diameter of the chamber were 0.35 m and 0.30 m, respectively. At each sampling time, 6 chambers were installed into the soil and kept for 20 minutes, and then samples of the enclosed atmosphere were withdrawn by a 50 ml syringue and transferred into a 1L Tedlar ® Bag. Sampling was done in one day. The air temperature inside the chamber was recorded using a digital thermometer. Ambient air between 0 and 2 m from the soil surface was collected and its mean concentration was used as a background concentration for calculation of gas fluxes. A gas chromatography with electron capture detector (Shimadzu, model 14 C) was used for N_2O analysis. N_2O fluxes were calculated using the equation:

$$F = \rho * \frac{V}{A} * \frac{\Delta C}{\Delta t} * (\frac{273}{T}) * \alpha \qquad [1]$$

Where, F is the gas production rate (μg N_2O-N m^{-2} h^{-1}); ρ is the gas density (mg m^{-3}) under standard conditions; V (m^3) and A (m^2) are the volume and bottom area of the chamber; ΔC/Δt is the ratio of change in the gas concentration inside the chamber (10^{-6} m^3 m^{-3} h^{-1}); T is the absolute temperature; and α is the transfer coefficient (28/44 for N_2O). A positive value indicates gas emission from the soil, while a negative value indicates gas uptake. The detectable limit was 0.1 ug N m^{-2} h^{-1}. Soil temperature was measured at 5 cm and 10 cm from the top soil layer, using a digital thermometer.

5.3.4 Geostatistical and statistical analyses

5.4.3.1 Data detrending

Basic assumptions of regionalized variable studies are often overlooked or rarely verified by many researchers. This may introduce artifacts and confound the interpretation of results. Therefore it is important to conduct a thorough data analysis before and during geostatistical analysis to filter out site-specific potential problems (producing trends) related to the unknown regionalized variable (i.e. soil gas flux under investigation). We used the median polishing technique to clean (polish) our field data to satisfy the basic assumptions for the estimation of a semivariogram, that is, for second-order stationarity or the weaker intrinsic hypothesis. Second-order stationarity implies that the mathematical expectation $E[Z(x)]=\mu$ exists and does not depend upon the position x and that for each pair of regionalized variables [Z(x), Z(x+h)], the covariance exists and depends only upon the separation vector h. On the other hand, the weaker intrinsic hypothesis implies that the mathematical expectation $E[Z(x)]=\mu$ exists, and for all vectors h the increment [Z(x+h)-Z(x)] has a finite variance that does not depend on x (Journel and Huijbregts, 1978). The methodology consisted in first determining whether there was a statistically significant linear or polynomial trend surface to the data. The procedure consisted in solving either a linear or a second order trend surface equation. Using Mathcad 4.0 software, the linear trend surface equation was developed and solved as follows:

$$Y = b_0 + b_1 X_1 + b_2 X_2 \qquad [2]$$

Where Y, the field measured gas flux or soil property is regarded as a linear function of some constant value (b_o) related to the means of observation, plus an east-west (b_1) coordinate component and a north-south (b_2) component. Since this equation contains three unknowns, three normal equations were needed to find its solution

$$\begin{aligned}
\sum Y &= b_0 n + b_1 \sum X_1 + b_2 \sum X_2 \\
\sum X_1 Y &= b_0 \sum X_1 + b_1 \sum X_1^2 + b_2 \sum X_1 X_2 \\
\sum X_2 Y &= b_0 \sum X_2 + b_1 \sum X_1 X_2 + b_2 \sum X_2^2
\end{aligned} \qquad [3]$$

Solving this series of simultaneous equations with Mathcad software gave the coefficients of the best linear trend surface.

$$\begin{bmatrix} n & \sum X_1 & \sum X_2 \\ \sum X_1 & \sum X_1^2 & \sum X_1 X_2 \\ \sum X_2 & \sum X_1 X_2 & \sum X_2^2 \end{bmatrix} . \begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} \sum Y \\ \sum X_1 Y \\ \sum X_2 Y \end{bmatrix} \qquad [4]$$

For the second-degree trend surface, the following equation was used:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_1^2 + b_4 X_2^2 + b_5 X_1 X_2 \qquad [5]$$

The equation contains terms that are the squares of the two geographic coordinates (X_1 for X and X_2 for Y) and a cross product term X_1X_2. Because its contains six unknowns, six normal equations were developed. The solution of these equations gave the coefficients of the best fit:

$$\begin{bmatrix} n & \sum X_1 & \sum X_2 & \sum X_1^2 & \sum X_2^2 & \sum X_1 X_2 \\ \sum X_1 & \sum X_1^2 & \sum X_1 X_2 & \sum X_1^3 & \sum X_2^2 X_1 & \sum X_1^2 X_2 \\ \sum X_2 & \sum X_2 X_1 & \sum X_2^2 & \sum X_1^2 X_2 & \sum X_2^3 & \sum X_2^2 X_1 \\ \sum X_1^2 & \sum X_1^3 & \sum X_1^2 X_2 & \sum X_1^2 & \sum X_1^2 X_2^2 & \sum X_1^3 X_2 \\ \sum X_2^2 & \sum X_2^2 X_1 & \sum X_2^3 & \sum X_2^2 X_1^2 & \sum X_2^2 & \sum X_2^3 X_1 \\ \sum X_1 X_2 & \sum X_1^2 X_2 & \sum X_1 X_2^2 & \sum X_1^3 X_2 & \sum X_2^3 X_1 & \sum X_1^2 X_2^2 \end{bmatrix} \cdot \begin{bmatrix} b_0 \\ b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \end{bmatrix} = \begin{bmatrix} \sum Y \\ \sum X_1 Y \\ \sum X_2 Y \\ \sum X_1^2 Y \\ \sum X_2^2 Y \\ \sum X_1 X_2 Y \end{bmatrix}$$

[6]

When significant trend was found, the field data matrix was detrended as follows:

$$D_{ij} - T_{ij} = R_{ij} \qquad [7]$$

Where, D_{ij} is the original data matrix for points ij, T_{ij} is the trend surface at points ij, and R_{ij} is the matrix of residuals, i is the column and j the corresponding row. The subsequent geostatistical analysis was performed on the residual matrix. The map developed by kriging using the results of the geostatistical analysis of the residual matrix was then added to the trend surface to determine the final maps of gas fluxes and soil properties. The examination of the trend surface determined whether universal (with trend surface) or ordinary (no trend surface) kriging was to be performed.

5.4.3.2 Variograms fitting

Isotropic (direction independent) semivariance of data was calculated using GS^+ geostatistical software (Gamma Design Software, 1993). Semivariance is defined in the following equation:

$$\gamma(h) = \frac{1}{\left[2m(h)\right]} \sum_{i=1}^{m(h)} \left[Z_{(xi)} - Z_{(xi+h)} \right]^2 \qquad [8]$$

where, γ is the semivariance for m data pairs separated by a distance of h, known as a lag, and Z is the value at positions xi and xi+h.

5.3.4.3 Statistical analysis.

Statistix 8.0 was used for computing summaries of simple of statistics and well as histograms.

5.4. Results and discussion

5.4.1. Summary of simple statistics for nitrous oxide emissions

Histograms for N_2O emissions and their transformation into logarithmic scale are showed in Figures 5.3 (a and b) and 5.4 (a and b) for 1999 and 2000, respectively.

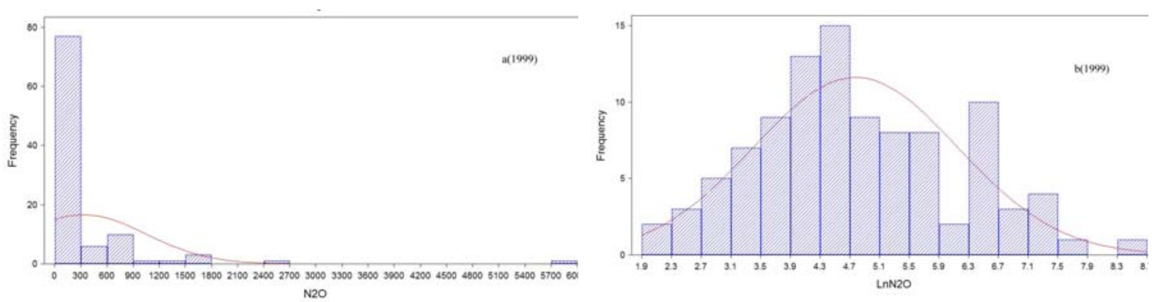

Figure 5.3. Histograms of N_2O emissions in 1999: (a) original data, (b) log-transformed data

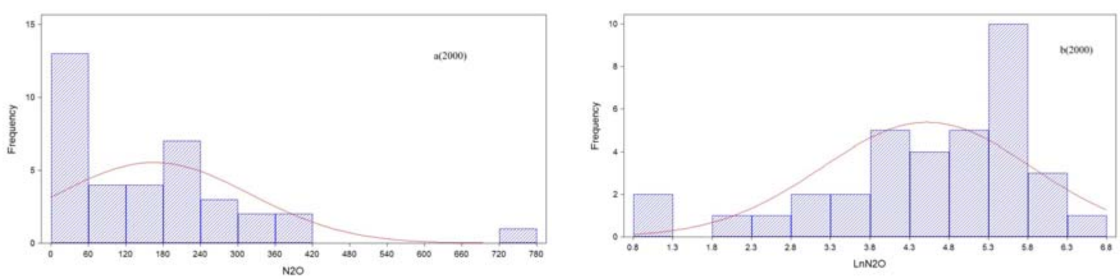

Figure 5.4. Histograms of N_2O emissions in 2000:(a) original data, (b) log-transformed data

Descriptive statistics for nitrous oxide emissions in Mikassa in June 1999 and September 2000 are given in Table 5.1.

Table 5.1. Summary of simple statistics for nitrous oxide (N_2O) emissions in Mikassa

	1999		2000	
Simple statistics	N_2O ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)	Ln (N_2O) ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)	N_2O ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)	Ln (N_2O) ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)
Mean	313.41	4.72	165.26	4.52
SD	704.72	1.38	155.24	1.34
CV	224.86	29.39	93.94	29.55
Median	94.35	4.55	148.47	4.99
Skew	5.85	0.29	1.78	0.99

Overall, N_2O emissions in June 1999 were highest as compared to values obtained in September 2000. The mean value of N_2O emissions in June 1999 was almost two times higher as compared to that measured in September 2000. However, both means become statistically different when data are transformed into logarithmic scale. The difference in N_2O emissions between these two years of studies can be explained by several factors such as the month of sampling within each year: June 1999 versus September 2000; the number of samples collected each year: 100 samples in 1999 versus 36 samples in 2000 and by soil properties such as soil temperature. With particular attention to soil temperature, during field sampling in June 1999, the average soil temperatures at 5 and 10 cm depth from the soil surface (our sampling depth) were 30.99 and 28.04^{o}C, respectively (data not shown). However, in September 2000, the soil temperature at these two depths dropped to 17.53 and 15.91, respectively. These results agree with those of Hu et al. (2001) who also reported an increase in N_2O emissions as a result of increasing soil temperature. In fact, soil temperature has been reported as one of the factors influencing the seasonal variability of nitrous oxide emissions. Weiss and Price (1980) suggested that N_2O solubility generally increases as the solution temperature decreases, this implies that during fall and winter, the N_2O emitted from soil could be lower than the actual N_2O produced in the soil because part of the N_2O stayed in the soil solution (Davidson and Swank, 1986; Burton and Beauchamp, 1994). As for the means, coefficients of variation (CV) were also highest in 1999 as compared to 2000, confirming that N_2O emissions exhibited considerable spatial and temporal variability. In fact, temporal patterns in gaseous N losses have been described by various workers. These patterns have differed according to ecosystem and geographic location (Lemke et al., 1998). In a denitrification study at a forest site in Michigan, Groffman and Tiedje (1989) found that gaseous N fluxes were highest in early spring and late fall with negligible values recorded during summer. Van Kessel et al. (1993) found highest emissions of N_2O during early spring and summer with fluxes declining to negligible levels in the late growing season and fall. Nyborg et al. (1997) reported high fluxes of N_2O during spring thaw, but negligible flux during the following growing season at an agricultural site in Alberta.

5.4.2 Trends surface trends analysis for nitrous oxide emissions

Table 5.2. First degree surface trend analysis for N_2O emissions in Mikassa (Japan)

	1999		2000	
Analysis variable	N_2O ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)	Ln (N_2O) ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)	N_2O ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)	Ln (N_2O) ($\mu g\ N_2O\text{-}Nm^{-2}\ h^{-1}$)
r	0.43	-	0.44	-
F value*	10.99	-	3.97	-

*Critical F value = 2.56

There was a significant first degree trend analysis for N_2O emissions measured in both years. However, the trend was more prevalent in 1999 in comparison to 2000 as showed by the higher probability value of 10.99 observed in 2000 data analysis. Log-transformed data did not, however, show any significant trend.

5.4.3 Variogram models fitting for nitrous oxide emissions

Isotropic semivariogram parameters for field measured N_2O emissions and their detrended residuals are shown in Table 5.3 for both 1999 and 2000, respectively. Figures 5 (a and b) and 6 (a and b) show semivariogram models fitted to data in both years.

Table 5.3. Isotropic semivariogram parameters for N_2O and their de-trended residuals

	1999		2000	
	N_2O	Residuals	N_2O	Residuals
Par.	(μg N_2O-N m^{-2} h^{-1})	(μg N_2O-Nm^{-2} h^{-1})	(μg N_2O-Nm^{-2} h^{-1})	(μg N_2O-Nm^{-2} h^{-1})
Model	LIN	LIN	SPH	SPH
Nugget	516.00	100.00	1.00	1.00
Sill	1442.95	115390.51	1665	2873
Range	61.32	61.32	16.48	24.97
Q	0.64	0.99	0.99	1.00
R^2	0.68	0.94	0.45	0.90

LIN = linear, SPH = spherical

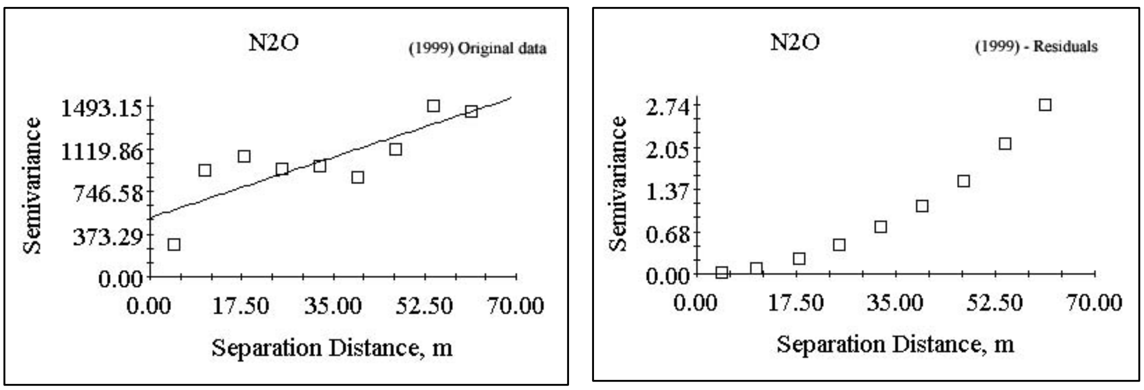

Figure 5.5. Variogram of N_2O emissions in 1999: (a) Original data, (b) De-trended Residuals.

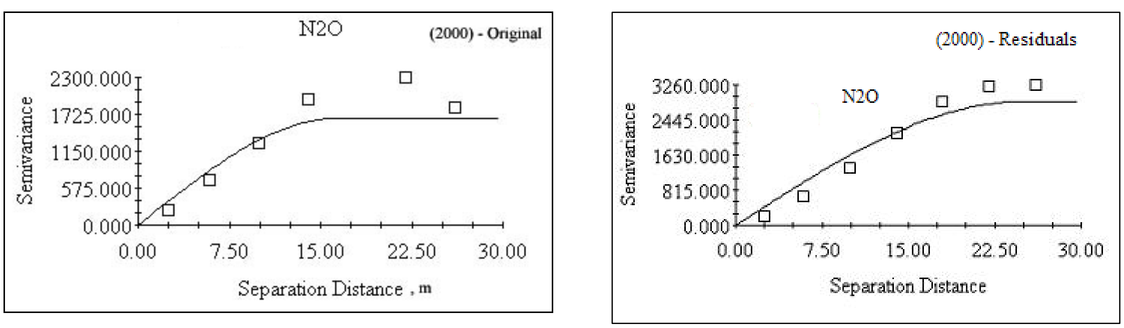

Figure 5.6. Variogram of N_2O emissions in 2000: (a) Original data, (b) De-trended residuals

The criterion for model selection was maximum R^2, except in cases where another model was obviously more appropriate based on visual examination of the semivariogram. Neither an active lag distance nor a lag interval was set. Default values given by the program were used.

A linear variogram was fitted to data in 1999 and a spherical model was more appropriate for N_2O emissions data in 2000. This applies to both field measured data and detrended residuals. With isotropic models of field data, the ranges or limits of spatial dependency were 61.32 and 16.48 m for 1999 and 2000, respectively. Detrended residuals for 1999 had the same limit of spatial dependency as field measured data. However, this situation changed in 2000 when the limit of spatial dependency for detrended residuals exceeded that of field measured data. In both cases, the limit of spatial dependency was lower than the sampling distance, which is usually accepted. The sill values for field measured N_2O were lowest as compared to those obtained with detrended data. The Q value for field measured N_2O fluxes in 1999 was 0.68 and it approached unity (0.99) in 2000, suggesting a highly developed spatial structure for N_2O fluxes in 2000 and a moderate development of spatial structure in 1999. Detrended residual Q values were also very high, showing highly developed spatial structure for both years. In opposite to the Q values trend the R^2 for field measured N_2O fluxes were higher in 1999 and lower in 2000. However, when data were detrended the R^2 became high for both year, suggesting that removing the trend was useful in the analysis of this data. Figure 5.5 shows the semivariograms of N_2O fluxes in 1999 and 2000 for both original field data and detrended residuals.

A linear variogram model was fitted to N_2O fluxes in 2000 (Fig. 5.5, a and b) with an active lag distance of 100 m. As the figure clearly shows, multiple spatial scales seemed to be present in this isotropic variogam with evidence of a trend. After detrending the data, the isotropic variogram exhibited a linear trend with the same range, but with higher Q and R^2 and an improved fit. For the 2000 (Fig. 5.6, a and b) data, a spherical trend was fitted to the data with an active lag of 60 m. After detrending the data, a better fit was obtained with not only increased Q and R^2, but the range of spatial dependence also increased.

5.4.4 Mapping nitrous oxide emissions across the field

Maps of N_2O emissions distribution in an onion field in Mikassa in 1999 and 2000 with first degree trend surface and contoured residuals are shown in Figures 5.7 and 5.8 (a, b and c). Estimation of N_2O emissions at unsampled locations was made using the geostatistical technique of kriging. A default grid spacing was used for interpolation purposes. After estimation of N_2O emissions, isarithmic maps were produced with different contour levels. Maps showed that there is a systematic variability with spatial patterns of N_2O emissions in the onion field. These patterns also differ for each year. In fact, Figure 5.7a shows that in 1999, field measured N_2O emissions were nearly homogenous across the onion field with spots of higher values in the western part of the onion field. A small zone of N_2O uptake (negative flux) was also observed in the southwestern part of the onion field. However, maps produced after detrending the data (Fig. 5.7c) showed a different picture: several zones of N_2O emissions spots with spots of higher values in northwest but also southern parts of the onion field. However, the small zone of uptake has moved in northwestern part of the onion field. Maps of N_2O emissions in 2000 showed more variability. For field collected data, a large zone of higher N_2O emissions was observed in northwestern, moved to the middle and extended to east and southern parts of the onion field. Two spots of N_2O uptake were also found in the western part of the onion field. Detrending data did not change much of the variability of N_2O emissions across the onion field in 2000. In fact, a large zone of higher N_2O emissions is still observed in northern, middle and southern parts of the onion field. However, only one spot of uptake is found and concentrated in northwestern part of the onion field (Fig.5.8a).

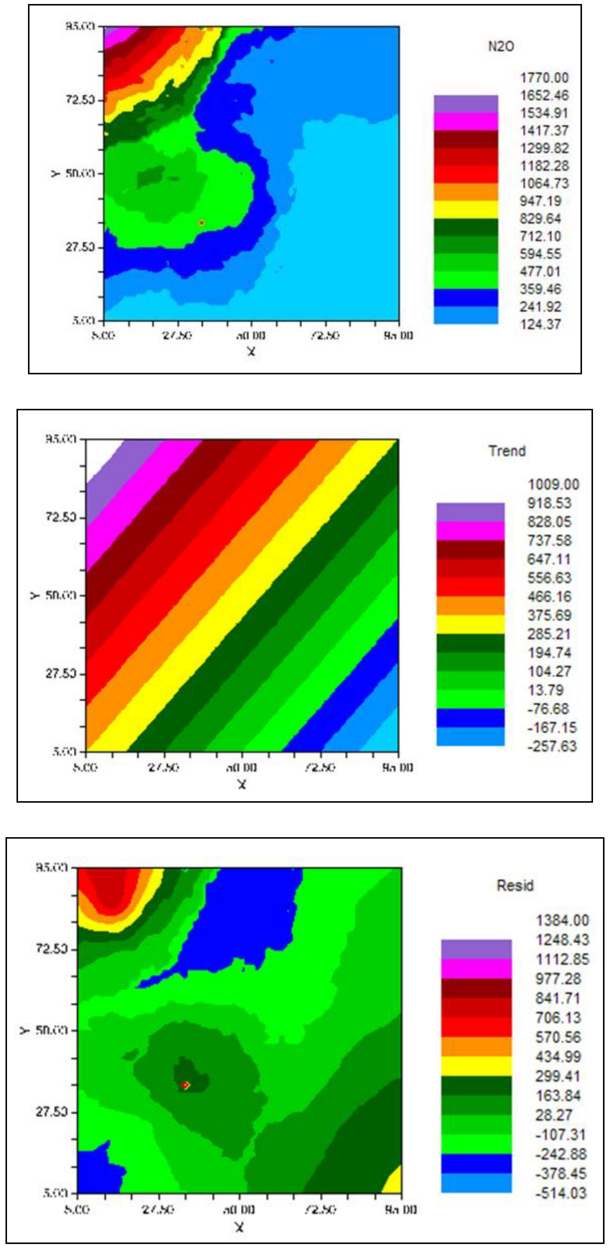

Figure 5.7. N_2O emissions in Mikassa in 1999: a) Contour maps, b) First degree trend surface and c) Contoured residuals from first degree trend.

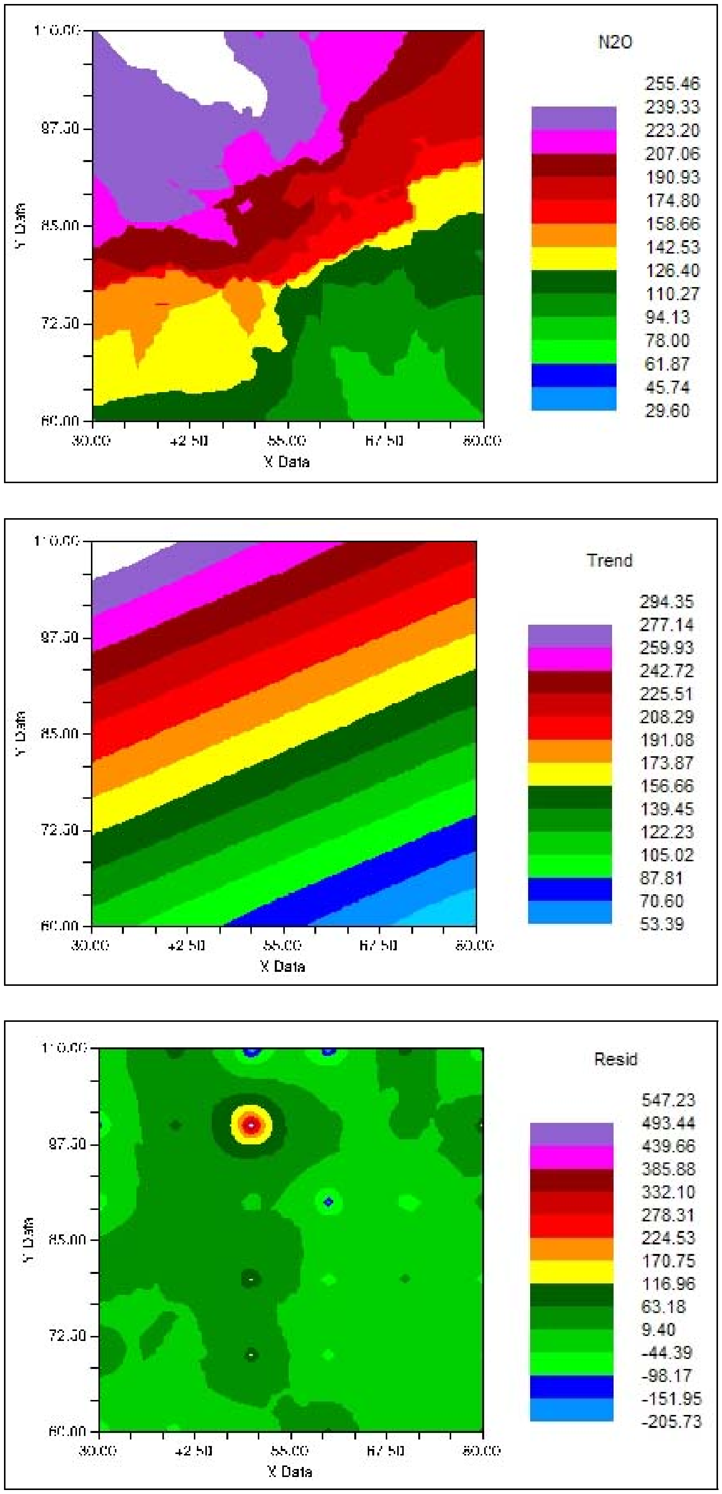

Figure 5.8. N_2O emissions in Mikassa in 2000: a) Contour maps, b) First degree trend surface. c) Contoured residuals from first degree trend.

5.5 Conclusion

This study was conducted to assess the spatial variability of N_2O fluxes in a field cropped to onion. Results obtained showed that N_2O emissions were highest in 1999 as compared to 2000. They were fitted to a linear variogram in 1999 while they responded to a spherical variogram model in 2000. Positive first degree surface trends were also found in N_2O emissions data in both years and the removal of these trends did not change variogram models, but significantly improved them by increasing the R^2 and Q values. N_2O emissions systematically varied with small zones of uptake (negative flux) across the field. This study is another confirmation of the tremendous spatial and temporal variability of N_2O emissions. Variability of N_2O emissions in space may be influenced by site-specific potential problems (producing trends) related to the unknown regionalized variable (i.e. soil property under investigation). Therefore, removal of a potential trend was used in this study to improve variogram fitting. However, the results showed that in many cases, the variogram fitted to data after trend removal had poor spatial structure and low R^2. In some cases however, both the spatial structure and R^2 improved. N_2O emissions systematically varied with small zones of uptake (negative flux) across the field, suggesting the presence of hot spots.

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Chap. 6. Improved quantification of CO_2, CH_4, and N_2O fluxes from soil in agricultural fields in central Missouri[5].

6.1 Abstract

As it is the case for soil chemical and physical properties, greenhouse gas fluxes also exhibit tremendous variability across fields. However, because of the cost of collecting numerous samples, measurements of fluxes across agricultural fields are often limited to few points. The average value of point measurements is later used to calculate the total flux for the sampled area This approach may result in an over or underestimation of the total flux. The objective of this study was to assess if geographic information systems (GIS) could improve the estimation of N_2O, CH_4 and CO_2 total field fluxes from soil in agricultural fields in central Missouri. We sampled for N_2O, CH_4 and CO_2 fluxes in a pasture, fitted variogram models to fluxes data, predicted fluxes at un-sampled locations by kriging or inverse distance weighing, produced fluxes maps and classified them according to fluxes distribution zones. Thereafter, we calculated a total flux (TF) by multiplying field minimum and maximum flux value for each gas by the total area sampled. Then, we also computed a GIS-based improved total field flux (ITFF) as the sum of "TF" for each flux distribution zone for each gas at each sampling period. Results showed that "TF" method over-estimated (up to 800%) the total minimum and maximum flux for N_2O, CH_4 and CO_2 as compared to "ITFF". Our approach provides in an improved quantification of greenhouse flux. The approach can be extended to other soil and environmental parameters.

Keywords: Greenhouse gases, geographic information systems, fluxes

6.2 Introduction

Globally, soil-atmosphere exchange of greenhouse gases is thought to contribute roughly 30, and 70% to the annual emissions of CH_4 and N_2O, respectively (Mosier, 1998). Agriculture contributes substantially to this budget (Boeckx and Cleemput, 2001). Unfortunately, the data available to estimate anthropogenic greenhouse gas emissions resulting from agricultural and land use activities are generally of a lower quality. This is the case for data on greenhouse gas emissions and removals from agricultural soils, which are often estimated with large ranges of uncertainty (IPCC, 2001). One of the causes of this problem is that estimates of greenhouse gas emissions from agricultural soils are often based on point measurements. Average values obtained from few sampled points are used to compute global budgets and models (Potter et al., 1996). There is therefore a need for approaches for more precise estimation of greenhouse gas emissions at field scale so that the models of emission response to climate change at a global scale can be improved (IPCC, 2001). In this study, we attempted to improve the estimation of N_2O, CH_4 and CO_2 emissions from a pasture using geographic information systems (GIS). GIS, often integrated with geostatistics, remote sensing (RS), cartography, global positioning systems (GPS) and other techniques, has become an indispensable tools in the assessment of the study of soil chemical, physical and biological properties. Rogowski (1995) and Rogowski (1996) quantified soil variability to estimate position and spatial distribution of soil properties using GIS. Kenan (1998) used geographic information management systems (GIM) for managing soil nitrogen. Shih-Hsien (1997) studied nitrate dynamics of small agricultural streams in western corn belt plains ecoregions and used GIS. Olivier and Webseter (1990) used kiriging as a method of interpolation for geographic information system.

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D'Itiri et al. (1985) investigated spatial and temporal changes in nitrate concentration of groundwater in Michigan using GIS. Halliday and Wolfe (1990) used GIS to assess the groundwater pollution potential of nitrogen fertilizers applied to a cropped area in Texas. Wylie et al. (1994) used GIS to predict spatial distribution of nitrogen leaching in Northern Colorado. Mulla (1991) gave three steps to analyze detailed soil test P and K maps using techniques available in GIS. The first step in the GIS process was to specify a set of two test cutoff levels for both P and K. The second step was to compute the percent area on the fertility maps within each of the possible categories. These fertility categories represent all possible combinations of P and K soil test fertility cutoff combinations such as low P and low K, low P and moderate K, and low P and high K. The third step was to aggregate fertility categories together into a management zone that differs in fertilizer requirements. Each management zone ideally represents portions of the field that are relatively uniform in soil fertility status. This will enable fertilizer recommendation to be made for each zone. Verhagen (1997) generated fertilizer maps using simulation and identified three pattern types. Research concluded that since fertilizer pattern in the field was not changing, a temporal change overruled the spatial variation. Therefore, a single dose application of fertilizer cannot be adjusted according to expected production level. In addition, split applications of fertilizer should be a prerequisite for specific nitrogen management. Kristensen and Olesen (1997) analyzed aerial photography to map soil moisture content in the root zone by kriging, co-kriging and inverse distance algorithms. Their observations indicated that even when they included soil texture, there was no improvement in prediction accuracy among the algorithms employed. Anderson and Yang (1996) conducted a study on site-specific farm management. They used ArcView to visualize and query spatial data and to generate statistics for each management zone, and to create charts. These researchers concluded that the integration of aerial photography, GPS and GIS provided an effective way to collect, process and analyze information. In our approach, GPS, GIS, Computer Cartography and simulation of aerial photo were all used. The approach consisted in sampling several points for greenhouse gases and soil properties across the field as usually done, interpolating emissions and soil properties at un-sampled points using variography and kriging, mapping the entire field, classifying map zones and calculating their averages and finally displaying the classified maps. After classification, each zone's area was multiplied by the corresponding average flux value. The total flux for the field was calculated by the summation of all zone areas multiplied by their corresponding average fluxes. The objective of this study was to investigate how using geospatial technologies improve our estimation of emissions and soil properties.

6.3 Materials and methods

6.3.1 Study area

The study was conducted simultaneously in corn and soybean fields, forest and a pasture at Lincoln University’s Freeman, Busby and Carver farms, respectively. However, only results for the pasture site are reported here. The experimental field is showed in Figure 6.1. The geographical coordinates of the experimental field were 38^{o}31’45” N and 92^{o}08’07” W. The study area was a 1.42 ha area dominated by brome grass (Bromus tectorum L). Brome grass is a cool season, perennial and smooth bladed grass. It is drought resistant and prefers well drained soils of silt/clay basis. It is used for early pastures and haying. It is best suited at 6.0-7.5 pH with some degree of salinity tolerance. The soil type of this site was an Elk Silt-Loam (Ultic hapludalts). In 2007, this area received an annual precipitation of 990 mm.

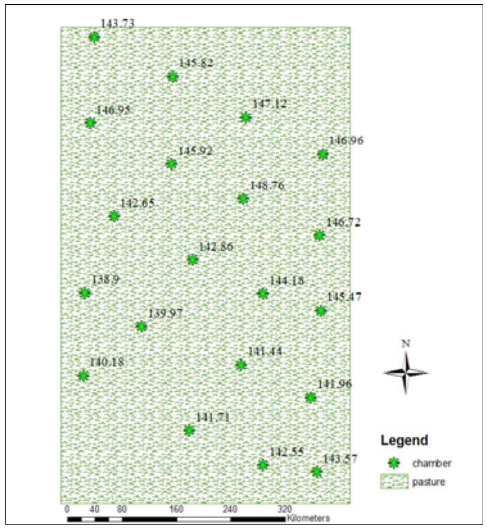

Figure 6.1. Experimental field

The total rainfall from May through December was 310 mm with an average temperature of 27°C. This area has experienced a drought during the spring and summer months of 2006 (Johnson et al., 2007).

6.3.2 Air sampling and gas measurements

Twenty cylindrical polyvinylchloride (PVC) chambers of 0.30 m long and 0.20 m in diameter were permanently inserted into the soil to a depth of 0.03 m since summer 2003. The design of the sampling chamber is a modified version of Hutchinson and Mosier (1981) and Robertson (1989) and is shown in Johnson et al., 2007. The chambers were constructed with two ventilation holes on the sides. They had circular tops made from Plexiglas and containing two additional holes. One of the holes was covered by a stopper for the extraction of gases and while the other served for ventilation. Installation of these chambers since 2003 kept soil undisturbed. In order to maintain an air tight seal, a groove was put on the bottom of the lid so that it would fit securely onto the sampling chamber. During sampling time the groove was filled with Dow-Corning high vacuum grease. Soil air samples for gas analysis were collected as follows; (1) the two chamber ventilation holes were sealed off by rubber stoppers, (2) the greased (to seal the chamber) chamber tops were put on, (3) the chamber was allowed to fill up with air for thirty minutes and; (4) the air samples were collected with a 50 ml syringe and put in to a 200 ml Tedlar bag for storage. Analysis of CO_2, CH_4, and N_2O from soil air samples was conducted at Lincoln University's Dickinson Research Laboratory within two hours after samples collection. The concentration of each greenhouse gas was measured using a Gas Chromatograph with an electron capture detector. The data was then transferred into an Excel data sheet and fluxes were calculated according to Ginting et al., 2003 and Hu et al., 2001:

$$F = \rho * \frac{V}{A} * \frac{\Delta C}{\Delta t} * (\frac{273}{T}) * \alpha$$

where, F is the gas production rate; ρ is the gas density (mg m^{-3}) under standard conditions; V (m^3) and A (m^2) are the volume and bottom area of the chamber; $\Delta C/\Delta t$ is the ratio of change in the gas concentration inside the chamber (10^{-6} m^3 m^{-3} h^{-1}); T is the absolute temperature; and α is the transfer coefficient (12/44 for CO_2, 12/16 for CH_4 and 28/44 for N_2O). A positive value indicates gas emission from the soil, while a negative value indicates gas uptake. The detectable limits were 0.1 mg C m^{-2} h^{-1} for CO_2, 0.01 μg C m^{-2} h^{-1} for CH_4 and 0.1 μg N m^{-2} h^{-1} for N_2O. Soil temperature was measured at 0.06 m from the top soil layer, using a KD2 Theta probe.

6.3.3 GIS and statistical analysis

Statistix 8.0 was used to calculate summary of simple statistics for CO_2, N_2O, and CH_4 and the soil properties. ArcGIS 9.2 and its Spatial Analyst Extension were used to produce interpolated maps using the Inverse Distance Weighing method (ID). GS+ 5.1 software was used to produce model semivariogram. The model semivariogram uses a mathematical equation to describe the spatial variability defined by the experimental semivariogram. Isotropic (direction independent) semivariance of data was calculated using GS^+ geostatistical software (Gamma Design Software, 2007). Semivariance is defined in the following equation:

$$\gamma(h) = \frac{1}{\left[2m(h)\right]} \sum_{i=1}^{m(h)} \left[Z_{(xi)} - Z_{(xi+h)} \right]^2 \qquad [2]$$

where, γ is the semivariance for m data pairs separated by a distance of h, known as a lag, and Z is the value at positions xi and xi+h. The schematic process from data collection to classification is showed below (Fig. 6.2).

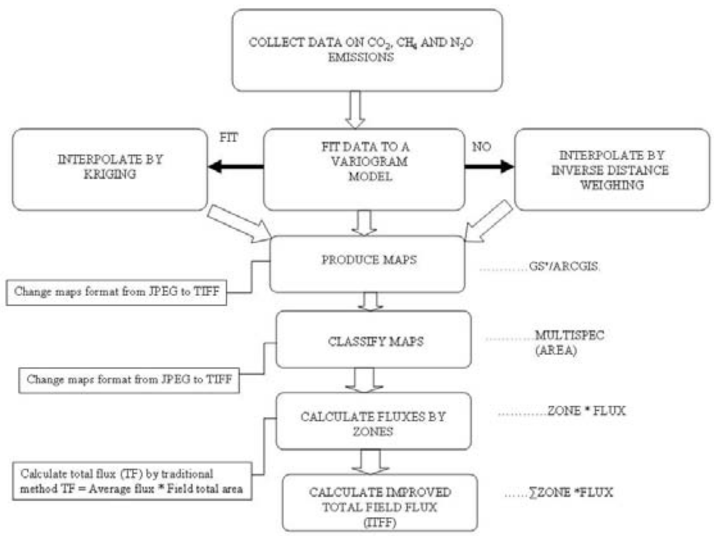

Figure 6.2. A GIS-based approach for calculating an improved total field flux (ITFF)

6.4 Results and discussion

6.4.1 Fluctuations of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O)

Summaries of simple statistics for CO_2 and CH_4, and N_2O emissions are presented in Tables 6.1 and 6.2, respectively.

Table 6.1. Summary of simple statistics for carbon dioxide (CO_2, mg C-CO_2 m^2h^{-1}) and methane (CH_4, ug C-CH_4 m^2h^{-1}) measured in a pasture at Lincoln University Carver arm from June to December 2007

	Jun.		Jul.		Aug.		Sept.		Oct.		Nov.		Dec.	
	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
Mean	116	-88.1	148.1	43.9	127.4	-15.9	89.7	45.8	99.4	12.7	96.5	-88.9	45.3	52.9
SD	35.0	92.3	29.3	71.8	28.4	33.8	24.4	69.2	38.6	36.1	27.6	50.9	20.5	82.9
C.V.	30.2	104.8	19.8	163.7	22.3	212.8	27.2	151.3	38.9	284.1	28.6	57.2	45.2	156.8
Min.	62.5	-197.8	81.5	-64.5	63.7	-63.8	40.3	-25.5	36.6	-37.7	14.9	-173.5	9.8	-60.6
Med.	109	-108.9	147.5	46.3	131.7	-26.9	86.1	29.1	105.7	9.2	102.7	-105.7	52.6	18.9
Max.	176	199.7	204.2	193.9	180.7	78.3	144.3	255.3	162.7	93.4	140.8	11.3	75.3	277.0
Skew	0.3	1.6	-0.15	0.1	-0.3	1.2	0.6	1.9	-0.2	0.9	-1.1	0.5	-0.5	1.0
Kurt.	-1.3	2.7	-0.06	-0.8	0.0	1.4	0.5	2.9	-1.2	0.2	1.9	-0.8	-0.9	0.7

Table 6.2. Summary of simple statistics for nitrous oxide (N_2O, ug N-N_2O m^2h^{-1}) measured in a pasture at Lincoln University Carver farm from June to December 2007

	Jun.	Jul.	Aug.	Sept.	Oct.	Nov.	Dec.
Mean	24.05	29.18	33.02	14.04	16.89	10.46	10.55
SD	33.34	31.47	21.30	8.02	11.20	15.34	6.64
C.V.	138.62	107.84	64.50	57.11	66.32	146.60	63.01
Minimum	-20.86	-6.26	5.49	-1.67	-14.89	-9.83	-1.89
Median	16.21	18.11	31.33	13.42	16.27	6.97	11.51
Maximum	104.25	112.50	89.24	29.33	32.46	63.01	21.94
Skew	0.62	1.46	0.93	0.09	-0.84	2.09	-0.15
Kurtosis	-0.21	1.34	0.52	-0.21	1.35	5.02	-0.80

Table 6.1 shows that CO_2 emissions were higher from June to August, but decreased from September to December. Lower CO_2 emissions in September to December were associated with higher variability as shown by a CV of 45% in December. Methane (CH_4) fluxes fluctuated from uptake (negative fluxes) in June, August and November to emissions in the remaining months. While there was no specific trend for uptake, CH_4 emissions followed an opposite trend to that observed for CO_2 as they increased from July to December. In fact, the highest CH_4 emissions were observed in December. As for CO_2, higher values of N_2O emissions were observed from June to August and lower values from September to December (Table 6.2). The trend observed for CO_2 and N_2O emissions was similar to that of soil thermal diffusivity and soil temperature (data not shown). In fact, these two soil properties also drastically decreased in December**.** Variability in greenhouse gas fluxes has been

reported by researchers. Ambus and Christensen (1995) measured fluxes of N_2O and CH_4 along a topogradient in a spruce forest (Picea abies L.), beech forest (Fagus silvatica L.), riparian grassland, coastal grassland, abandoned farmland, upland arable soil, and drained arable soil in Denmark. They found that spatial CVs in CH_4 fluxes ranged between 166 and 1787%.

6.4.2 Variogram models for carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O)

Isotropic variogram models for CH_4, CO_2 and N_2O are shown in Figure 6.3 for June and November sampling periods only.

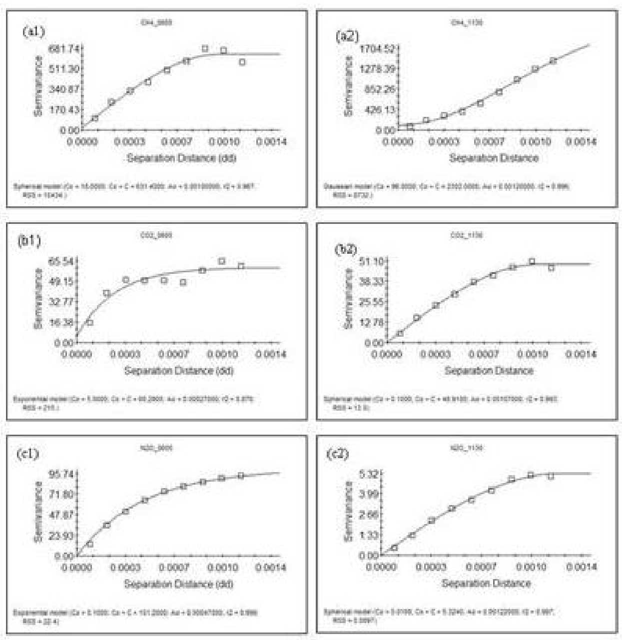

Figure 6.3. Isotropic variograms of CH_4, CO_2 and N_2O for June and November sampling

Data from August to October is discussed but not shown for clarity reasons. A variogram describes the relationship between the variance of the difference between measurements and the distance of the corresponding sampling points from each other. Variogram parameters usually examined are: 1) the sill (Co+C) which describes where the variogram develops a flat region, i.e. where the variance no longer increases; 2) the range (A0) or the distance between locations beyond which observations appear independent; 3) the nugget variance (Co) which represents variation not spatially dependent over the range examined and 4) the regression coefficient (R^2) which provides an indication of how well the model fits the variogram data. When the data respond to a model, the information from the variogram model is used to estimate values at unsampled locations through a technique known as kriging. Interpolating values at unsampled locations enables the production of maps portraying the entire spatial distribution of the property being investigated. In this study, methane (CH_4) flux responded to a spherical variogram model in June and July, linear model in August and October, and finally to a Gaussian variogram model in November. All these models fitted CH_4 data as shown by regression coefficients ranging from 0.94 to 0.99. The ranges of spatial variability were also the same for the spherical variogram models in June and July (0.001 dd) and the linear models of August and October (0.002 dd) as shown in Figure 6.3 (for June and November only). We also calculated the proportion of spatial structure or C/(Co+C) which provides a measure of the proportion of sample variance (Co+C) that is explained by spatially structured variance (C). Calculated C/(Co+C) values ranged from 0.95 to 0.99 indicating a strong spatial structure. Carbon dioxide (CO_2) emissions fitted to exponential variograms in June and November (Fig. 6.3), Gaussian model in July, and spherical models in August and November. Regression coefficients ranged from 0.76 to 0.99, indicating moderate (June and August) to strong (July, October and November) fit as can be visually noted in Figure 6.3. This is also confirmed by calculated values of C/(Co+C) which were 0.99 for July, October and November, but 0.92 in June and 0.95 in August; therefore, indicating moderately developed spatial structures. Except for June, the range of spatial variability (0.001dd) was the same for all other sampling periods. As for Carbon dioxide (CO_2), nitrous oxide (N_2O) emissions fitted to exponential data in June and October, but spherical variograms in July, August and November (Figure 7.3). Regression coefficients ranged from 0.61 to 0.99 with the lowest fit in August and October. As previously discussed for CH_4 and CO_2, weaker spatial structure were exhibited in these two months with low R^2. Overall, none of CH_4, CO_2 or N_2O fitted to the same variogram model throughout this study (month to month). Variograms models varied from linear, exponential, spherical to Gaussian. However, for (A0) which was about 0.001 dd with only 3 exceptions. This is an indication that the sampling distance used was appropriate.

6.4.3 Mapping methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) distribution

Maps portraying the spatial distribution of methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O) fluxes are shown in Figure 6.4 for June and November only. Maps for July to October are omitted but discussed. Classified maps are shown in Figure 6.5. CH_4 fluctuated from uptake or consumption (negative fluxes) to emissions throughout the experiment. In June, CH_4 was essentially consumed across the pasture with only two pockets of emissions in the northwest and southeast corners of the pasture plot. However, in July, an opposite trend was observed with about 70% of the pasture plot emitting methane. The largest zone of uptake was shifted to the west of the plot. This trend was similar to that observed in August but the uptake zone here was shifted in the middle of the plot. In October, there was no emission, but only CH_4 uptake. Finally, in November (Fig. 6.4), the pasture plot emitted more CH_4 than it kept into the soil.

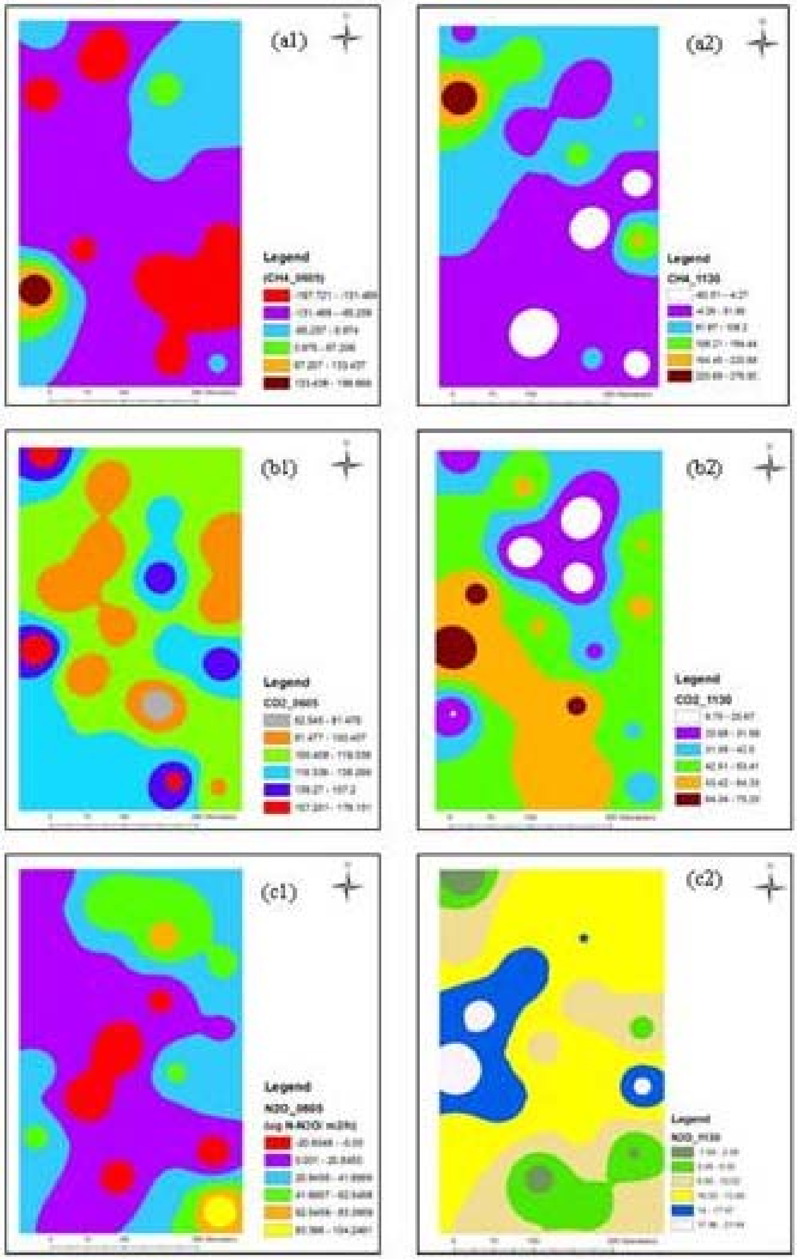

Figure 6.4. Interpolated maps of CH_4 (a1 and a2) CO_2 (b1 and b2) and N_2O (c1 and c2)

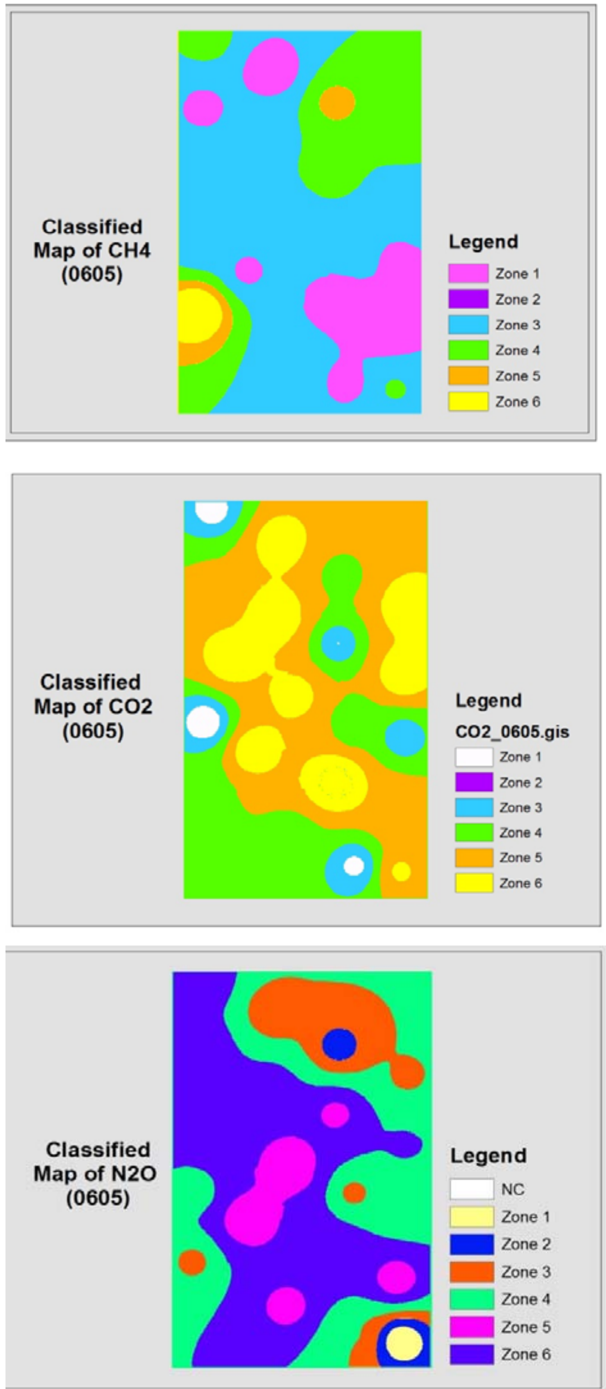

Figure 6.5. Classified maps of CH_4 (a), CO_2 (b) and N_2O (c)

results are in agreement with those reported by other authors. In fact, Liebig et al. (2008) quantified the effects of tannin affected cattle urine, normal cattle urine, and NH_4NO_3 in solution on greenhouse gas flux in mixed-grass prairie in the northern great plains. They found that methane uptake was prevalent throughout the study, as soil conditions were predominantly warm and dry. Van den Pol-van Dasselaar et al. (1995) studied the effects of soil moisture content and temperature on methane uptake by grasslands on sandy soils. They found that atmospheric CH_4 uptake was highest at high soil temperatures and intermediate soil moisture contents. At soil moisture contents higher than 50% w/w), CH_4 uptake was greatly reduced, probably due to the slow down of diffusive CH_4 and O_2 transport in the soil, which may have resulted in reduced CH_4 oxidation and possibly some CH_4 production. Ambus and Christensen (1995) reported that uptake, as well as emission of CH_4 reached maximum rates when soils dried up, presumably because CH_4 diffusion became unconstrained in a spruce forest (Picea abies L.), beech forest (Fagus silvatica L.), riparian grassland, coastal grassland, abandoned farmland, upland arable soil, and drained arable soil in Denmark. Mosier et al (1997) studied CH_4 and N_2O fluxes in the Colorado shortgrass steppe. They found that conversion of grassland to croplands typically decreased the soil consumption of atmospheric CH_4 and increased the emission of N_2O. Jonesa et al (2005) studied greenhouse from a managed grassland. They reported that CH_4 emissions were only significantly increased for a short period following applications of cattle slurry. Cumulative total N_2O flux from manure treatments was 25 times larger than that from mineral fertilizers. Finally, soil respiration from plots receiving manure was up to 1.6 times larger than CO_2 release from control plots and up to 1.7 times larger compared to inorganic treatments. Verchota et al (2008) evaluated the effect of leguminous fallows on methane (CH_4), carbon dioxide (CO_2), N oxides (N_2O and NO) fluxes. They observed significantly higher CH_4 uptake during the dry season relative to wet season, indicating the importance of soil water content and gas transport on CH_4 fluxes. Mosier and Delgado (1997) monitored methane and nitrous oxide fluxes in grasslands in western Porto Rico. They reported that CH_4 uptake rates averaged 5.8 g CH_4-C m^{-2} h^{-1} with no significant differences across sites. These uptake rates were generally 10-fold lower than those reported for tropical forests. Fertilizer addition had a small negative affect on CH_4 uptake in the Vertisol, tended to enhance CH_4 uptake in the Ultisol and significantly decreased CH_4 uptake in the Oxisol. These background emission rates were typically higher than those in temperate grasslands. Mosier et al. (1991) studied methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands. They found that nitrogen fertilization and cultivation both decreased CH_4 uptake and increased N_2O production, thereby contributing to the increasing atmospheric concentrations of these gases. Carbon dioxide (CO_2) emissions (Fig. 6.4) varied greatly across the pasture with pockets high and low emissions. In June, CO_2 emissions varied essentially from 62 to 119 mg CO_2-C with pockets of higher emissions (158 mg CO_2-C m^2 h^{-1}) distributed in the southern, middle and northern corner of the pasture. In July, two zones of CO_2 emissions were observed: high emissions in the north and low emissions in the southern portion of the pasture. Although CO_2 emissions continued to fluctuate from the remaining sampling period, emissions magnitude dropped tremendously. In fact, in June and July, the minimum emissions were 62.55 and 81.55 mg, respectively while the maximum were 176.13 and 204.15 mg CO_2-C m^2h^{-1}, respectively. However, from August to November, the minimum emissions dropped from 15 to nearly 10 mg CO_2-C m^2 h^{-1} while the maximum emissions also dropped to from 140 to 76 mg C-$CO_2m^2h^{-1}$). This sharp drop in emissions did not, however, affect their spatial distribution across the pasture. Two zones were still observed in August with higher emissions in the north and lower in the south and a few pockets of higher values. Our results agree with those reported by Johnson et al. (2007) who conducted a similar investigation on an adjacent site to this study. They found that the pasture released more CO_2 during the months that received more rainfall. The pasture soil acted as a source for carbon dioxide, a sink for methane, and a source for nitrous oxide. These results are also in agreement with those reported by Nkongolo and Schmidt (2005, 2006) for work conducted on the same pasture. In other ecosystems, similar trend was reported in Hatano and Lipiec (2004). Gregorich et al. (2006) studied emission of CO_2, CH_4 and N_2O from lakeshore soils in an Antarctic dry valley. They reported that simultaneous emission of all three gases from the same site indicated that aerobic and anaerobic processes occurred in different layers or different parts of each soil profile. Furthermore, they found that the pattern of concentration with depth in the soil profile was not consistent across sites. Emission of N_2O was low and highly variable while that of CO_2 was high and was strongly related to soil temperature. Nitrous oxide (N_2O) showed a similar behavior to methane (CH_4) with emissions and uptake (negative fluxes). In June 2007 (Fig. 6.4), two main zones of emissions extending north to south of the pasture were observed with three pockets of negative fluxes (uptake). In July, there was only emission while pockets of uptake continued to manifest during the remaining sampling period. Our results agree with several other studies where soils have been reported to act occasionally as sinks for N_2O. In a study assessing the effect of mechanized tillage operations on soil physical properties and greenhouse gas fluxes in two agricultural fields in Hokkaido (Japan), Nkongolo et al. (2008) found negative fluxes of N_2O in a corn and soybean field. Donoso et al. (1993) found that in contrast with a significant emission in the rainy season, the soil of a scrub-grass savannah of Venezuela acted as a sink for N_2O in the dry season. Cicerone et al. (1978) found a significant sink activity in wet grass-covered soil of Michigan. Blackmer and Bremner (1976) found that cultivated soils of Iowa acted as sinks for atmospheric N_2O at certain times during spring. Ryder (1981) reported that the soil acts as both a source and sink for atmospheric N_2O depending on soil condition and the amount of nitrogenous fertilizer applied, the sink activity was observed in conditions conducive to microbial reduction of N_2O (i.e. very low nitrate in the soil). Matson and Vitousek (1987) suggested that even though the overall average fluxes measured in La Selva, Costa Rica were positive, under certain conditions uptake of N_2O occurred in these tropical soils. The mechanism by which soil acts as a sink for N_2O is not known. It has been suggested that the net flux of N_2O to the atmosphere results from its production by nitrifying and or denitrifying bacteria. N_2O consumption is therefore likely due to the reduction of N_2O to N_2 (Donoso et al., 1993). It has also been reported that N_2O production was somewhat higher and N_2O uptake somewhat lower in the more disturbed communities and that N_2-fixing cyanobacteria could both produce and consume N_2O. Finally, Chapuis-Lardy et al. (2007) have provided an extensive review of soils as a sink of N_2O. They further suggested that a contribution of various processes could explain the wide range of conditions found to allow N_2O consumption, ranging from low to high temperatures, wet to dry soils, and fertilized to unfertilized plots. Generally, conditions interfering with N_2O diffusion in the soil seem to enhance N_2O consumption. However, the factors regulating N_2O consumption are not yet well understood and merit further study

6.4.4 Total flux for carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O)

Tables 6.3 to 6.5 present the summary of simple statistics and the analysis of variance (paired comparison) for the total flux of CO_2, CH_4 and N_2O. For each gas and each sampling period, a total flux for the field was calculated for the lower end or total minimum field flux (min) and the higher end or total maximum field flux (max). Two methods of calculation were used: a traditional approach (TF) which consisted in multiplying the minimum and maximum field flux values by the total area of the field, and a GIS-based improved approach (ITFF) which was described in Fig.6.2.

Table 6. 3. Summary of simple statistics and Paired test for CH_4 fluxes in a 12800 m^2 pasture field calculated by method 1 (TF) and Method 2 (ITFF)

Simple statistics	CH_4 (ug C-CH_4 m^2 h^{-1})			
	TF		ITFF	
	Min	Max	Min	Max
Mean	-1138.40	2027.60	-327.49	189.82
SD	869.63	1265.90	783.18	788.66
C.V.	76.39	62.44	239.15	415.48
Min	-2531.20	144.65	-1500.80	-938.94
Median	-816.38	2482.10	14.68	294.36
Max	-326.91	3545.10	368.41	1042.3
Skew	-0.83	-0.24	-0.69	-0.30
Kurtosis	-1.03	-1.34	-1.24	-1.43
Paired T Test for Method 1 (TF) vs Method 2 (ITFF)				
Parameters	Min flux (TF vs ITFF)		Max flux (TF vs ITFF)	
Mean	810.96		-1,837.70	
St Dev	98.72		327.18	
Mean H0	810.96		-1,837.70	
Lower 95% CI	569.39		-2,638.30	
Upper 95% CI	1,052.50		-1,037.20	
T	8.21		-5.62	
DF	6		6	
P	0.0002		0.0014	

Table 6. 4. Summary of simple statistics and Paired test for CO_2 fluxes in a 12800 m^2 pasture field calculated by method 1 (TF) and Method 2 (ITFF)

Simple statistics	CO_2 (mg C-CO_2 m^2 h^{-1})			
	TF		ITFF	
	Min	Max	Min	Max
Mean	565.72	1982.4	1194.90	1430.80
SD	339.81	529.37	407.34	441.93
C.V.	60.07	26.70	34.09	30.89
Min	124.80	963.20	508.19	647.78
Median	516.10	2082.8	1127.90	1396.50
Max	1043.7	2613.3	1767.90	2029.30
Skew	-0.01	-0.92	-0.27	-0.47
Kurtosis	-1.30	0.11	-0.56	-0.34
Paired T Test for Method 1 (TF) vs Method 2 (ITFF)				
Parameters	Min flux (TF vs ITFF)		Max flux (TF vs ITFF)	
Mean	629.18		551.55	
St Dev	60.09		47.42	
Mean H0	629.18		551.55	
Lower 95% CI	482.15		435.52	
Upper 95% CI	776.21		667.59	
T	10.47		11.63	
DF	6		6	
P	0.00001		0.00001	

Table 6.5. Summary of simple statistics and Paired test for N_2O fluxes in a 12800 m^2 pasture field calculated by method 1 (TF) and Method 2 (ITFF)

Simple statistics	N_2O (ug N-$N_2O m^2$ h^{-1})			
	TF		ITFF	
	Min	Max	Min	Max
Mean	340.93	847.09	184.42	-115.04
SD	128.13	460.58	86.06	114.72
C.V.	37.58	54.37	46.66	99.72
Min	213.12	375.42	60.61	-267.01
Median	268.91	806.53	168.54	-125.82
Max	508.56	1440.0	331.25	70.27
Skew	0.30	0.15	0.44	0.34
Kurtosis	-1.67	-1.68	-0.42	-0.92
Paired T Test for Method 1 (TF) vs Method 2 (ITFF)				
Parameters	Min flux (TF vs ITFF)		Max flux (TF vs ITFF)	
Mean	-156.51		962.12	
St Dev	29.21		176.35	
Mean H0	-156.51		962.12	
Lower 95% CI	-227.98		530.60	
Upper 95% CI	-85.03		1393.60	
T	-5.36		5.46	
DF	6		6	
P	0.0017		0.0016	

This approach took into account the spatial variability of gas fluxes across the field. It calculated a "TF" for each classified "flux distribution zone" of the field and computed an "ITFF" as the sum of individual "TF". Tables 6.3 to 6.6 show that the two methods were significantly different in their outputs of the minimum and maximum total flux field for CO_2, CH_4 and N_2O in this 12,800 m^2 pasture. The null hypothesis examined was that the mean of the differences was zero for both methods of calculation. The small p-values of 0.0002 and 0.0014 for CH_4 (Table 6.3); 0.00001 and 0.00001 for CO_2 (Table 6.4) and 0.0017 and 0.0016 for N_2O (Table 6.5) suggest that the means of the differences were not zero, i.e., the two different methods of total minimum (min) and total maximum (max) flux calculation produced different values. In closely examining the total flux for CH_4 (Table 6.3), it shows that CH_4 calculated with the traditional approach (TF) was 3.4 (min) and 10 (max) times higher as compared to ITFF method. This resulted in a higher value (more than 300%) of the field total minimum CH_4 uptake and maximum CH_4 emission. Table 6.4 also shows that the total maximum CO_2 emissions was more closer for both methods of calculation as CO_2 max under TF as only 1.34 times higher as compared to the calculation with the GIS-based "ITFF" approach. However, a reverse situation was observed for CO_2 min since the calculated value under " ITFF" was 2 times that with the traditional "TF" approach. Finally, as for methane (CH_4), nitrous oxide (N_2O) total flux for the pasture calculated by the traditional approach were 85 and 800% higher for the minimum and maximum values, respectively.

6.5 Summary

An attempt was made to improve the calculation of total gas flux using a GIS-based approach which took into account the spatial variability of gas fluxes across the sampled area. The traditional approach is to consider the field as homogenous and compute total flux by multiplying the average field flux by the field total area. Results indicate that there is an over-estimation of total flux by the traditional approach. The GIS-based approach offers a promising tool which needs to be investigated further.

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Chap. 7 Summary and conclusion

The objectives of this study were to investigate the relationships between greenhouse gases emissions and soil properties, assess the influence of agricultural practices on greenhouse gas fluxes and soil properties and to improve the quantification of greenhouse gases from soil in agricultural fields using geospatial technologies. Results showed that soil temperature is not the only factor controlling greenhouse gas fluxes from soil, but also soil thermal thermal properties and pore spaces indices. Greenhouse gas fluxes correlate with soil thermal properties even when there is no correlation with soil temperature. Similarly, soil pore space indices correlate with greenhouse gas fluxes even when the soil properties from which they are predicted do not correlated with gas fluxes. We showed that soil pore space indices can be predicted quickly from routine measurements of soil water and air and existing diffusivity models. Inclusion of these pore structural indices in predictive models may certainly improve our understanding of greenhouse gas fluxes dynamics. Our study also confirmed that agricultural practices can negatively affect soil properties which in turn results in increasing greenhouse gases emissions. Finally, our results confirmed that greenhouse gas fluxes are still subjected to tremendous variability in space and time, thus in the quantification of greenhouse gas fluxes, techniques taking into account this variability are needed. We have shown that geographic information systems (GIS), global positioning system (GPS), computer mapping and geostatistics are technologies that can be used to better understand systems containing large amounts of spatial and temporal variability. Our GIS-based approach for quantifying CO_2, CH_4 and N_2O fluxes from soil in agricultural fields, pasture and forest showed that estimating (extrapolating) total greenhouse gas fluxes using the "standard" approach – multiplying the average flux value by the total field area – results in biased predictions of field total greenhouse gases emissions. In contrast, the GIS-based approach we developed produces an interpolated map portraying the spatial distribution of gas fluxes across the field from point measurements and later process the interpolated map produced like a “satellite image”. Furthermore, processing, classification and modeling enables the computation of field total fluxes as the sum of fluxes in different zones, therefore taking into account the spatial variability of greenhouse gas fluxes. This approach is a promising tool that can also used for improving the quantification of other environmental parameters.

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