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Quantification and simulation of nitrous oxide emissions from agroecosystems in the Boreal and Parkland regions of Alberta

by

Reynald L. Lemke ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Soil Science

Department of Renewable Resources
Edmonton, Alberta
Spring 1997

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Degree: **Doctor of Philosophy**

Year this Degree Granted: **1997**

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled *Quantification and simulation of nitrous oxide emissions from agroecosystems in the Boreal and Parkland regions of Alberta* submitted by *Reynald L. Lemke* in partial fulfillment of the requirements for the degree of *Doctor of Philosophy* in *Soil Science*.

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E. G. Beauchamp

Date: March 24/97

God will not inquire of thy birth, nor will He ask thy creed.

Alone He will ask:

"What hast thou done with the Land I loaned thee for a season?"

...Chinese proverb

This thesis is dedicated to my wife - Laura.

Her quiet sacrifice, endless patience, and unshakable faith gave me the courage to risk, and the strength to continue.

ABSTRACT

The concentration of atmospheric nitrous oxide (N_2O) is increasing rapidly. Nitrous oxide, a "greenhouse gas", contributes to global warming. It is also involved in the catalytic destruction of stratospheric ozone. Best estimates indicate that the increase is almost exclusively attributable to agricultural activities. These contributions need to be accurately quantified to reduce uncertainties in global N_2O budgets and facilitate the development of mitigation strategies. The objectives of this study were to: 1) quantify the seasonal and annual N_2O emissions from selected field plots in the Boreal and Parkland regions of Alberta; 2) identify the principle controls regulating N_2O emissions; 3) compare total N_2O emissions from plots under zero and conventional till managements; 4) evaluate the extent to which urea fertilizer, pea residue, manure and fallow promote N_2O emissions and; 5) test the ability of the DNDC model to simulate N_2O emissions under conditions prevailing in the Boreal and Parkland regions. Nitrous oxide emissions were measured from spring thaw to fall freeze-up at six sites over a three year period. Vented soil covers were placed on the soil surface for one hour. A gas sample was drawn from the headspace and transferred to pre-evacuated vacutainers. Gas samples were analyzed using a gas chromatograph equipped with a ^{63}Ni electron capture detector. Measurements of soil temperature, soil water content, mineral N and water-soluble organic C were taken periodically at some of the sites. Estimates of annual N_2O-N losses ranged from 0.5 to 4.0 kg N ha^{-1} . Up to 70% of this loss occurred during and just following spring thaw. There were significant differences in the magnitude of estimated annual N_2O-N losses among the sites. More than 90% of this variation could be explained by differences in soil clay content. When the spring thaw event was considered individually, variability was better explained by differences in the concentration of soil mineral N. Summer fallowing and additions of urea fertilizer and pea residue increased N_2O-N losses compared to control plots. Losses of N_2O-N were significantly

lower from zero compared to conventional till plots during spring thaw, but differences were not significant on an annual basis.

ACKNOWLEDGEMENTS

The successful completion of this project required the cooperation of many people. In particular, I wish to thank:

My parents and family, whose support was absolutely essential.

Dr. R.C. Izaurralde, supervisor, mentor, and friend, whose acceptance, patience, and insight never failed.

Dr. M. Nyborg, whose work inspired the project, and whose enthusiasm and dedication inspired me.

Dr. W.B. McGill and Dr. J.A. Robertson for their personal and professional interest, and invaluable advice and guidance.

Dr. P. Fedorak, Dr. R.F. Grant, Dr. Y. Feng, Dr. J. Leonard, and Dr. E.G. Beauchamp for their expert advice.

Mr. Z. Zhang, whose tireless hard work made the project possible.

C. Figueiredo, M. Molina, C. Nguyen, R. Pradhan, and J. Thurston for their technical support, and also their friendship.

The staff at Alberta Agriculture Food and Rural Development, B. Henriquez, J. Lecky, C. Strome, and most particularly E.D. Solberg.

Eco-Research Tri-Council, Agriculture and Agri-Food Canada Greenhouse Gas Initiative, and the Parkland Agricultural Research Initiative for financial support.

Friends and peers, who provided emotional support, professional advice, and levity when it was most required.

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CHAPTER 1

Introduction

1.1 THE PROBLEM

The atmospheric concentration of nitrous oxide (N_2O) is increasing at an accelerating rate (Crutzen and Ehalt, 1977; Duxbury et al., 1993). Gas samples extracted from ice cores in the Antarctic (Pearman et al., 1986) indicate a gradual increase since 1750, and a rapid increase since 1950 (Fig. 1-1). Nitrous oxide absorbs infrared radiation thereby contributing to the greenhouse effect. Models predict that the global mean annual temperature may increase by several degrees within the next century (Banin, 1986; Gullett and Skinner, 1992), if current loading rates of greenhouse gases such as N_2O remain unabated. The consequence of this temperature increase is the focus of much controversy, but the potential exists for significant ecological perturbations.

Nitrous oxide is photolytically oxidized to nitric oxide (NO) in the stratosphere. Nitric oxide in turn catalytically converts ozone (O_3) to molecular oxygen (O_2) (Crutzen and Ehalt, 1977). Thus the increasing concentration of N_2O presumably increases the rate of destruction of stratospheric O_3. The layer of O_3 in the stratosphere is extremely important, as it shields the earth's surface from biologically harmful ultraviolet radiation. Considering that N_2O is both a potent greenhouse gas and interacts deleteriously with stratospheric O_3, its increasing atmospheric concentration is of considerable concern.

Calculations based on our current understanding of global budgets do not accurately account for the observed atmospheric increase in N_2O concentrations (Duxbury et al., 1993). Best estimates suggest that the increase in atmospheric concentrations is almost exclusively attributable to agricultural activities. The bulk of these additions are due to increases in the amount of land under cultivation and to increases in nitrogen fertilizer inputs (OECD/IPCC, 1997). These facts do not bode well for the future. The amount of cultivated land in developing countries is expected to increase by 50%, while global nitrogen fertilizer inputs are expected to increase by 75% (Duxbury et al., 1993) by the year 2025.

Agroecosystems are managed systems, therefore the possibility exists for adopting management strategies that would reduce their contribution. The development of mitigation strategies is contingent upon a clear understanding of the factors controlling N_2O production and emission. Further, accurate quantification of current emissions is required before the efficacy of mitigation strategies can be evaluated.

1.2 LOCAL PERSPECTIVE

The contribution to atmospheric N_2O by agricultural soils in the Parkland and Boreal regions of Alberta (Fig 1-2) is largely unknown. Substantial over-winter losses have been identified from nitrogen mass balance studies (Heaney et al., 1992; Malhi and Nyborg, 1983). These losses were attributed to denitrification during spring thaw. High fluxes of N_2O measured in the field during spring thaw by Laidlaw (1993) support this conclusion. Laidlaw (1993) estimated cumulative losses during this period of up to 16 kg N_2O-N ha^{-1} on fertilized field plots, suggesting that these regions are important sources of atmospheric N_2O. No studies have quantified N_2O emissions from agricultural soils in the Boreal or Parkland regions on an annual basis.

A meaningful assessment of N_2O flux from a large area of land must account for the temporal and spatial variability within that area. Firstly, we must ask if the variability within the area is great enough to be of concern. In other words, is the error involved in multiplying some average flux value by the number of hectares in the area acceptable, or must the area be considered a population of smaller divisions all significantly different from one another? Assuming the latter, how do we identify these "individuals", what criteria do we use for stratification, and what scale of resolution would be required? Consideration of temporal variability is a critical issue when designing sampling schedules, and integrating flux measurements over time. Seasonal patterns in gaseous N loss have been described by various workers (Groffman and Tiedje, 1989; van Kessel et al., 1993). The regulating factors that function at the scale of investigation must be understood so that sampling units that reflect the spatial differences in those factors can be chosen, and temporal variability accommodated. A first step would be to identify the processes responsible for N_2O flux from agroecosystems in the Boreal and Parkland regions.

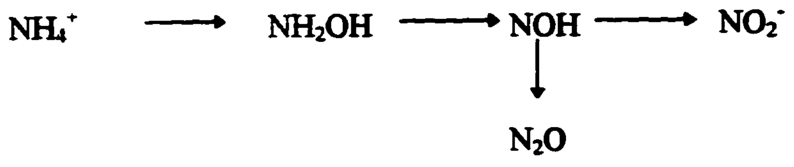
1.3 N_2O PRODUCING PROCESSES

Nitrous oxide is produced during natural processes in the soil ecosystem. It may be formed under: **a]** anaerobic conditions during the dissimilatory reduction of nitrate/nitrite to NH_4^+, or to N_2O/N_2 (hereafter referred to as denitrification), and **b]** under aerobic conditions during the oxidation of ammonium to nitrate (Blackmer et al., 1980). Chemodenitrification can also produce N_2O (Christianson and Cho, 1983).

Nitrous oxide can be produced in soils during dissimilatory reduction of NO_3^- to NH_4^+ by the actions of both bacteria and fungi growing fermentatively (Haynes and Sherlock, 1986). The proportion of NO_3^- released as N_2O is thought to be very small however, and the process appears only to be significant in environments that remain anaerobic for long periods of time. Dissimilatory reduction of NO_3^- to NH_4^+ would likely not be an important source of N_2O from agricultural soils in the regions we are considering.

Chemodenitrification describes a variety of chemical reactions involving NO_2^- and organic matter or exchangeable cations (Mosier et al., 1983). Reactions that produce N_2O require nitrous acid (HNO_2) as an intermediary. Nitrite is normally only present in trace amounts but can accumulate in highly alkaline conditions. Conversely, HNO_2 is formed from NO_2^- under acidic conditions. In agricultural soils these apparently mutually exclusive conditions could be met simultaneously during hydrolysis and subsequent nitrification of banded fertilizers such as urea or anhydrous ammonia. Excluding this situation, chemodenitrification is not expected to be a significant pathway of N_2O emission from agricultural soils.

The reaction sequence for the oxidation of NH_4^+ to NO_3^- (nitrification) has been conventionally represented as:



Nitrous oxide is thought to be generated by the chemical dismutation of HNO under reduced O_2 tensions. Poth and Focht (1986) have effectively argued that nitrifier denitrification may actually be the process giving rise to N_2O emissions by nitrifiers. They propose that NO_2^- serves as the terminal electron acceptor under conditions of O_2 stress, being reduced directly to N_2O. This decreases the competition for O_2 by removing the substrate for NO_2^- oxidizers, and disposes of the toxic product (NO_2^-). Thermodynamic calculations indicate that the overall reaction is energetically favorable (exothermic).

The list of microorganisms linked directly to nitrification in soil is rather short. Five NH_4^+ oxidizers have been isolated and identified, while a single NO_2^- oxidizer has been isolated and identified. Despite the limited roster of nitrifiers, nitrification occurs in virtually all soils where

NH_4^+ is present (Schmidt, 1982). Consequently, nitrification is assumed to be a major pathway of N_2O production in agricultural soils.

Denitrification is defined as the dissimilatory reduction of ionic nitrogen oxides to gaseous products by essentially aerobic bacteria when oxygen is limiting (Poth and Focht, 1986). The commonly accepted reductive pathway for denitrification (Aulakh et al., 1992) is as follows:

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

While most denitrifying bacteria possess all the reductase enzyme complexes necessary to reduce NO_3^- to N_2, some are NO_2^- dependent, while others yield N_2O as the terminal product. The capacity to use N oxides as electron acceptors in the absence of O_2 has been reported in approximately 20 genera of bacteria. The presence of denitrifiers in soils may be regarded as ubiquitous. Denitrification is a major pathway of N_2O production from soil. Denitrification and nitrification processes are assumed to be the principle sources of N_2O emissions from agroecosystems in the Boreal and Parkland regions of Alberta.

1.4 CONTROLLING FACTORS

Aeration, temperature, available carbon and nitrogen, moisture and pH are considered to be the most important factors controlling N_2O production in the field (Drury et al., 1992; Goodroad and Keeney, 1984; Skiba et al., 1993). While both denitrification and nitrification rates have been shown to be pH independent within the range typical for agricultural soils (6.0 - 7.0), N_2O reductase is quite sensitive to pH (Koskinen and Keeney, 1982). The proportion of N_2O produced during denitrification tends to increase with decreasing pH. Denitrification is often described mathematically as a first order reaction with respect to NO_3^- and soluble carbon concentration, and is frequently represented by a double Monod equation. Nitrification is also represented as a first order reaction with respect to available NH_4^+. Temperature strongly affects both processes. Measurable rates of denitrification and nitrification have been reported at temperatures as low as -4°C (Malhi and McGill, 1982; Malhi et al., 1990) in soils from the Parkland region. Nitrification reached optimum rates at temperatures near 20°C, but the rate of denitrification continues to increase up to 40°C.

Both processes are strongly affected by the aeration status of the soil. Nitrification is an aerobic process that is strongly inhibited when O_2 is limiting, conversely, denitrification is anaerobic and inhibited by available O_2. Soil water content is generally used as the "proxy" measure of aeration status. It directly affects the diffusion rates and storage of O_2 in the soil, and indirectly affects O_2 depletion by mediating respiration rates. Nitrification reaches optimum rates between 60% and 70% water-filled pore space (WFPS), dropping off rapidly thereafter (Fig. 1-3). Denitrification remains low at WFPS of less than 60% and increases rapidly as saturation is approached.

1.5 MANAGEMENT CONSIDERATIONS

Tillage practices alter temperature, moisture, and aeration regimes as well as mineralization rates. A comparison of soils under zero till and conventional till managements is one excellent example. Soils under zero till generally maintain higher moisture status, lower temperatures, and higher bulk density. Microbial biomass and soluble carbon are concentrated near the surface, and soil aggregates are larger but less aerobic (Aulakh et al., 1984; Linn and Doran, 1984). There is a significantly higher number of denitrifying bacteria (Doran, 1980). These observations suggest that denitrification is favored under zero till compared to conventional till, which could translate into higher N_2O emissions.

A shift towards reduced, minimal, or zero tillage has been occurring amongst producers in Alberta. While the value of these management practices regarding soil conservation has been closely attended to, the influence on N_2O emissions has not. A significant increase in the acreage of zero till might result in a significant increase in contributions to atmospheric N_2O.

Other agricultural practices have the potential to alter the magnitude of N_2O flux. Inputs of nitrogen fertilizers have been shown to increase N_2O emissions, particularly in early spring before plant competition is significant (Eichner, 1990). Increases in N_2O flux after the addition of organic soil amendments such as animal manure (Rolston et al., 1978; Laidlaw, 1993) and legume green manure (Aulakh et al., 1991) have been reported. These substrates indirectly stimulate nitrification by increasing available NH_4^+ via ammonification. The NO_3^- produced during nitrification may in turn increase denitrification rates. Further, organic soil amendments provide soluble carbon, a required substrate for denitrification, and enhance O_2 depletion by stimulating overall respiration rates. Summer fallowing increases mineralization of soil organic matter and has also been noted to increase the level of N_2O emissions (Aulakh et al., 1982; Laidlaw, 1993).

1.6 SIMULATION MODELING

The need for actual field data from the Boreal and Parkland regions in Alberta has already been articulated. It is not feasible to measure gas flux on a continuous basis, or to collect field data from all possible management-soil-climate combinations in a region. Concurrent measurements such as temperature and precipitation however, are often available on a continuous basis. A properly calibrated process-based simulation model could utilize such information to increase the accuracy of integration calculations. It could also facilitate the synthesis of the information gathered, and provide a concrete means of testing hypotheses regarding mitigation strategies.

Li et al. (1992) have developed and tested a process-oriented simulation model of carbon and nitrogen biogeochemistry in agricultural ecosystems. The DeNitrification-DeComposition model (DNDC) couples four interacting submodels. A thermal-hydraulic submodel calculates soil temperature and moisture profiles and soil water fluxes from air temperature and precipitation data and soil texture. A decomposition submodel calculates daily decomposition, nitrification, ammonia volatilization and soil microbial respiration. A plant growth sub-model calculates daily root respiration, as well as water and N utilization. The denitrification sub-model calculates hourly N_2O and N_2 production during periods when water-filled pore space is greater than 40%. The required inputs include pertinent management variables such as fertilizer N application, tillage operations, and crop selection. The model has performed well under a variety of soil-climate-management scenarios, but has not been tested for conditions that prevail in the Alberta Boreal or Parkland regions.

1.7 OBJECTIVES

The previous discussion has presented a number of important questions that need to be answered before meaningful estimates of N_2O flux from soils in the Boreal and Parkland regions of Alberta can be made. My aim is to attempt to answer some of those questions. Five main objectives have been identified as the purpose for this study. They are as follows: 1) to quantify the seasonal emissions of N_2O from selected field plots in the Boreal and Parkland regions of Alberta, 2) to identify the principal controls regulating N_2O emissions at the selected locations, 3) to verify that zero-till soil management induces greater N_2O emissions than conventional-till management under conditions prevailing in this region; 4) to evaluate the extent to which urea fertilizer, pea residue, manure, and fallow promote N_2O emissions; 5) to evaluate the ability of the DNDC model to simulate N_2O emission at the field plot scale in the Boreal and Parkland region.

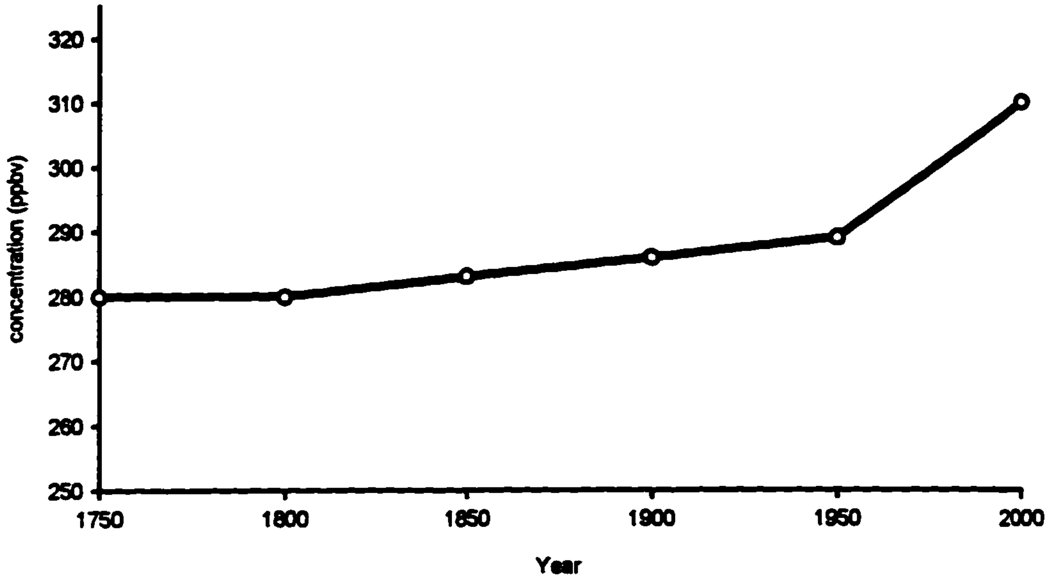


Figure 1-1. Changes in the concentration of atmospheric N_2O from 1750 to the present. Adapted from Duxbury et al. (1993).

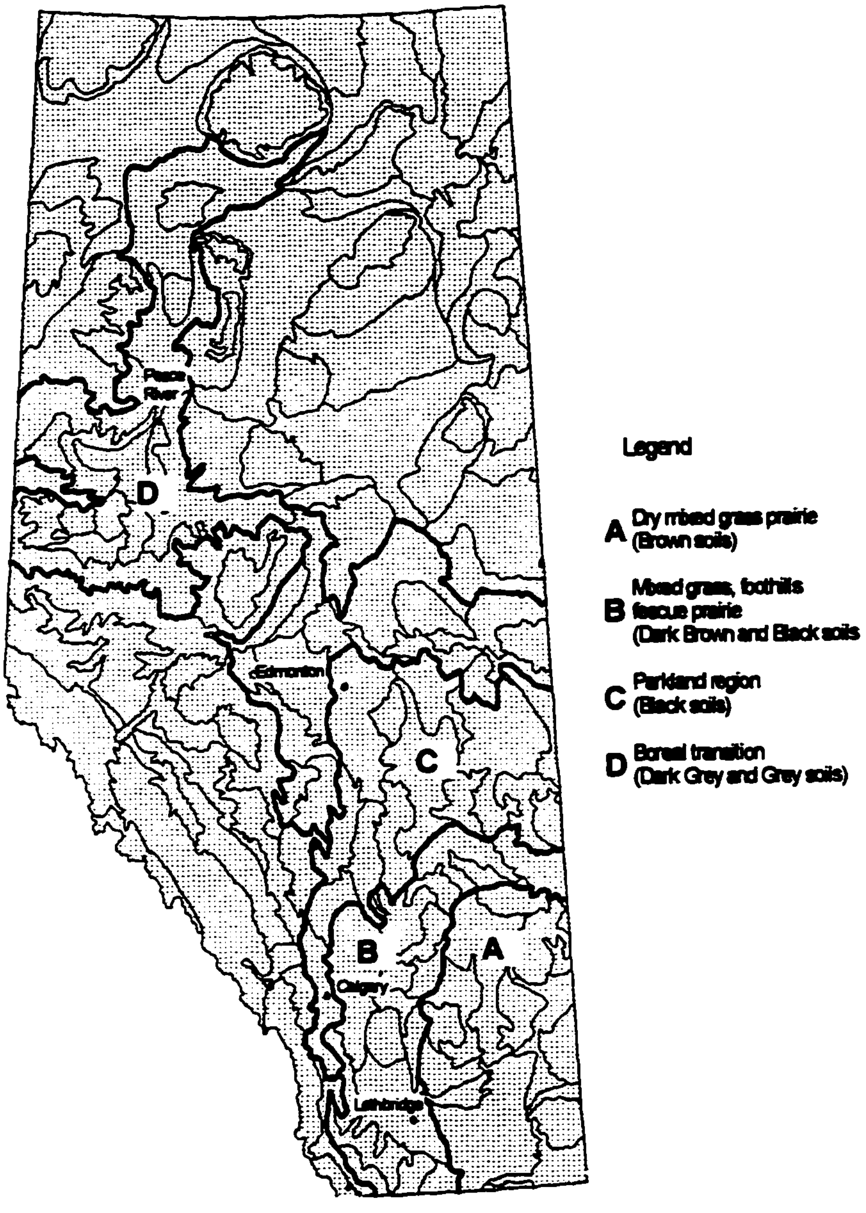


Figure 1-2. Map showing boundaries of the Parkland and Boreal regions in Alberta.

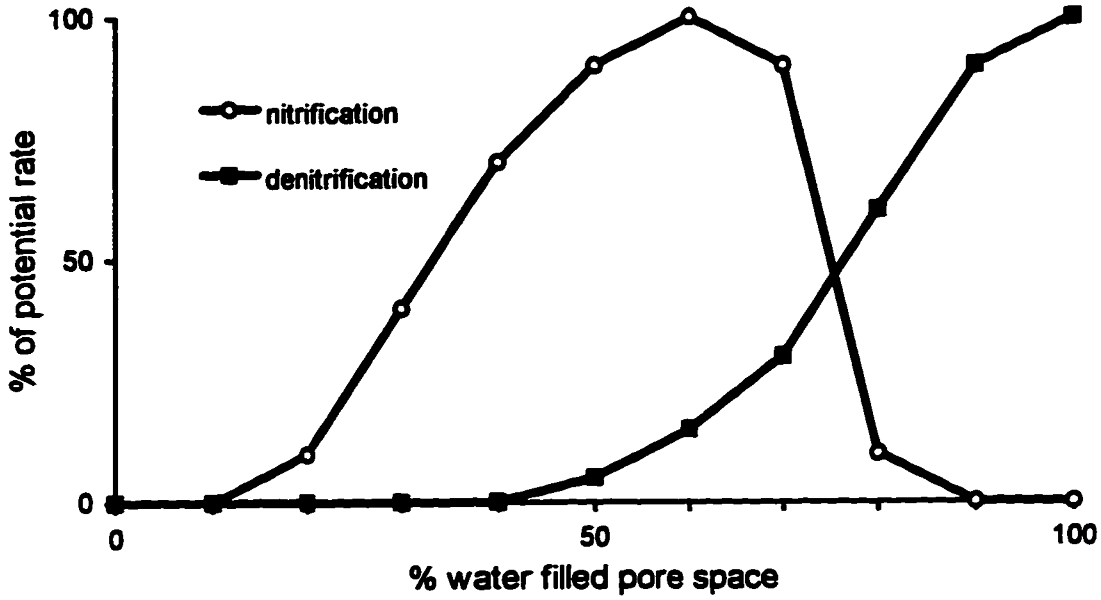


Figure 1-3. Model of relationship between potential nitrification and denitrification rates and water-filled pore space.

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CHAPTER 2

An alternate rapid analysis system for soil-emitted greenhouse gases[1]

2.1 INTRODUCTION

Increasing concentrations of atmospheric CO_2, CH_4, and N_2O have been documented (Banin, 1986; Duxbury, 1993). Since all three gases are radiatively active, concern exists about how increasing concentrations may influence the global heat balance. In addition, N_2O is involved in the destruction of stratospheric ozone (Crutzen, 1970). Efforts to understand the global cycle of these gases require an accurate quantification of their sources and sinks. These gases may be produced and/or consumed during natural soil-plant-microbial processes, therefore terrestrial ecosystems are considered important regulators of the global budget.

Use of soil covers is the trace gas measurement technique of choice for many process level field studies and other research requiring replicate measurements coincident in space or time (Hutchinson and Livingston, 1993). They are simple to use, inexpensive, and mobile. However, the spatial and temporal variability of these flux measurements has been found to be extreme (Folorunso and Rolston, 1984; Parkin, 1987). Furthermore, N_2O fluxes are episodic in nature, with intense flushes occurring after rainfall or irrigation (Mosier et al., 1986) and in temperate climate zones, during the spring snow melt (Christensen and Tiedje, 1990; Laidlaw et al., 1995). Large numbers of samples over short periods of time are required to quantify trace gas fluxes with a reasonable degree of accuracy. It is desirable to measure all three gases simultaneously so that complete budgets of greenhouse gas emissions can be constructed. Options for analyzing large numbers of samples with minimal expense and labor inputs are needed.

A method that allows for rapid analysis of all three gases from a single sample injection has recently been described by Sitaula et al. (1992). Their method utilizes wide bore capillary columns and has three detectors: a flame ionization detector (FID), thermal conductivity detector (TCD), and an electron capture detector (ECD). The column flow switches from the ECD, to the FID and TCD which are connected in series. Here an alternate system is described which utilizes packed columns and only two detectors. The use of only two detectors represents a considerable cost saving over larger systems designed to accommodate three or more detectors. As well, a

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[1] A version of this chapter has been submitted to the Soil Science Society of America Journal. (01/1997).

modest improvement in the variability of N_2O determinations in the ambient range was realized. The system is equipped with an automated stream selector allowing up to sixteen samples to be loaded at one time.

2.2 MATERIALS AND METHODS

Gas sampling and sample containers

Vented soil covers (Hutchinson and Mosier, 1981) were used for the collection of trace gases in my field studies. Gas samples were drawn from the headspace with a 30 mL syringe and transferred immediately into 22 mL Vacutainers (Becton-Dickinson, Rutherford, NJ) for transport to the lab. A total of 27 mL of sample was injected into the containers to ensure adequate volume for analysis. Prior to use, vacutainers were opened and aired for at least 24 h, then closed, re-evacuated, and the stopper was coated with a layer of silicone. Vacutainers only provide enough sample volume for a single injection, therefore I used 1 L Tedlar® (SKC, Eighty Four, PA) bags for the serial dilutions and variability tests described later in this paper to ensure that ample volume was available for repeated sampling of the same container.

Instrument Description

A gas chromatograph (GC) (Star 3400, Varian Canada, Mississauga, ON) was used for the determination of CH_4, CO_2 and N_2O. A schematic diagram of the plumbing configuration is shown in Fig. 2-1. The manual injection port on the GC is connected directly to an automated 16-port sample stream selector. Each port is plumbed directly to a 0.3 mm needle which is mounted on a manifold (not shown). Gas samples are loaded by inserting the needle through the septum or stopper of the sample container.

In the sample loading mode, the sample passes through a relay-operated on-off valve into two sample loops (L1 and L2) fitted in series; first via an eight port valve (V1) (Valco Instruments Co. Inc., Houston, TX) and second via a ten port valve (V2) (Valco Instruments Co. Inc., Houston, TX). The sample stream exits through a small personal monitoring diaphragm pump (SKC Inc., eighty Four, PA) which draws the sample from the containers at 5 mL min^{-1}. After one minute of sampling the valves switch to inject mode, and load the fixed sample volumes onto their respective columns. The relay then closes, and the stream selector rotates to the next port.

In the inject mode, vents at V1 ensure that the pressure in the lines remain near ambient. V1 remains in this position throughout the run. The sample from L1 is swept by N_2 carrier gas

(30 mL min^{-1}) through a 3.6 m porapak Q column (C1), then through the methanizer, and exits through the FID. The methanizer consists of a 2% coating of NiO on Chromosorb G, and is maintained at 350°C. A continuous supply of H_2 (20 mL min^{-1}) is provided for the reduction of CO_2 to CH_4 via a T connection at the methanizer inlet. The resulting chromatograph shows two distinct CH_4 peaks. The area under the first peak is proportional to the concentration of CH_4 originally in the sample, while the area under the second peak is proportional to the concentration of CO_2 originally in the sample.

The sample from L2, loads onto a 0.3 m porapak Q backflush column (C2), followed by a 1.5 m porapak QS analytical column (C3), and exits through the ECD. At 0.5 min. into the run, after the N_2O peak is on the analytical column, valve (V2) switches to the standby position. In this position C2 is flushed with 5% CH_4, balance Ar_2 carrier gas for the remaining 4.5 minutes of the run. The same carrier gas simultaneously flows at 30 mL min^{-1} through the analytical column and the ECD. The ECD is heated to 400°C, and its baseline is stabilized with a minute air bleed. The manual injector and columns are set at 100°C and 45°C, respectively.

Evaluation of the System

Linearity of the FID and ECD response was studied by preparing a serial dilution from standard gas. The system's ability to detect concentrations of CH_4, CO_2, and N_2O at sub-ambient levels was verified by extending the serial dilution to a point well below ambient concentration.

The variability of determinations for N_2O, CO_2, and CH_4 was documented by drawing a series of ten samples from the same sample container. Two standard gas mixtures were used, the first consisted of 10 $\mu L\ L^{-1}$ CH_4, , 495 $\mu L\ L^{-1}$ CO_2, and 5 $\mu L\ L^{-1}$ N_2O in N_2, the second consisted of 1500 $\mu L\ L^{-1}$ CO_2 in He. A series of six consecutive samplings of ambient lab air was used to study the variability of determinations for CH_4, CO_2, and N_2O at ambient concentrations.

The possibility of carry over from a sample of high concentration to a sample of low concentration was also investigated. Ambient lab air was sampled before and after a container filled with standard gas at high concentration (10 $\mu L\ L^{-1}$ CH_4; 7800 $\mu L\ L^{-1}$ CO_2; 5.0 $\mu L\ L^{-1}$ N_2O) was sampled. The sequence was repeated ten times. A paired t-test was used to determine if any significant enrichment could be detected in the ambient samples taken after the standard gas compared to those taken before.

2.3 RESULTS AND DISCUSSION

Analysis of serial dilutions indicated that the system could detect concentrations down to at least 0.75 μL L^{-1} for CH_4, 124 μL L^{-1} for CO_2, and 0.25 μL L^{-1} for N_2O. The detector response was linear over a wide range of values, as indicated by coefficients of determination (r^2) between serial dilutions and measured values of 0.998 for CH_4, 0.996 for CO_2, and 0.997 for N_2O. The ranges studied varied from 0.75 to 10.0 μL L^{-1} for CH_4, from 124 to 7800 μL L^{-1} for CO_2, and from 0.25 to 5.0 μL L^{-1} for N_2O.

Coefficients of variation between determinations of standard gas were 0.5% for CH_4, 0.8% for CO_2, and 0.8% for N_2O. Coefficients of variation between samples of ambient lab air were 1.0% for CH_4, 0.8% for CO_2, and 1.8% for N_2O. Methane and CO_2 compare favorably with results of Sitaula et al. (1992), but N_2O shows a modest improvement (Table 2-1). Systems utilizing ultrasonic detectors demonstrate similar variability for CO_2 and N_2O determinations, but considerably lower variability for CH_4 (Table 2-1). Ultrasonic detectors are also considerably more expensive compared to ECD/FID detectors. Based on this variability, minimum detectable concentration differences in the ambient range for this system would be 0.02 μL L^{-1} for CH_4, 3.0 μL L^{-1} for CO_2, and 0.006 μL L^{-1} for N_2O. In view of the variability encountered in field measurements of trace gases, this degree of resolution was considered acceptable. Replicate field measurements of N_2O, as an example, commonly exhibit CV's between 40% and 300% (Folorunso and Rolston, 1984; Mosier et al., 1986).

Five minute run times for each chromatograph preceded by a one minute sampling interval was found to give adequate time for the sample loops and columns to be flushed. Paired t-tests indicated that there were no significant differences between determinations of CH_4, CO_2, and N_2O in ambient lab air injected before and after a standard gas of high concentration. The total time required per sample was six minutes, thus ten samples can be run in an hour.

The system allows for a simultaneous analysis of CH_4, CO_2, and N_2O in a rapid manner with minimal labor requirements. Reliability and sensitivity are adequate for field studies employing static chamber systems. The configuration described here requires larger sample volumes than would be appropriate for applications such as soil atmosphere sampling. I noted that the methanizer degraded rapidly after samples taken during a manure composting study were run. I speculate that H_2S, which is known to deactivate the methanizer (Varian Canada, Mississauga, ON, pers. comm.), was present in these samples.

Table 2-1. Coefficient of variations reported for replicate determinations for systems designed to analyze CO_2, N_2O, and CH_4 from a single sample injection.

	This Study (ECD,FID)	Sitaula et al., (1992) (TCD,FID,ECD)	Blackmer and Bremner, (1977) (ultrasonic)	McCarty and Blicher-Mathiesen, (1996) (ultrasonic)
		%		
CO_2	0.8	0.6	1.6	0.9
N_2O	1.8	2.6	1.1	1.5
CH_4	1.0	0.7	0.2	na[†]

[†] not reported

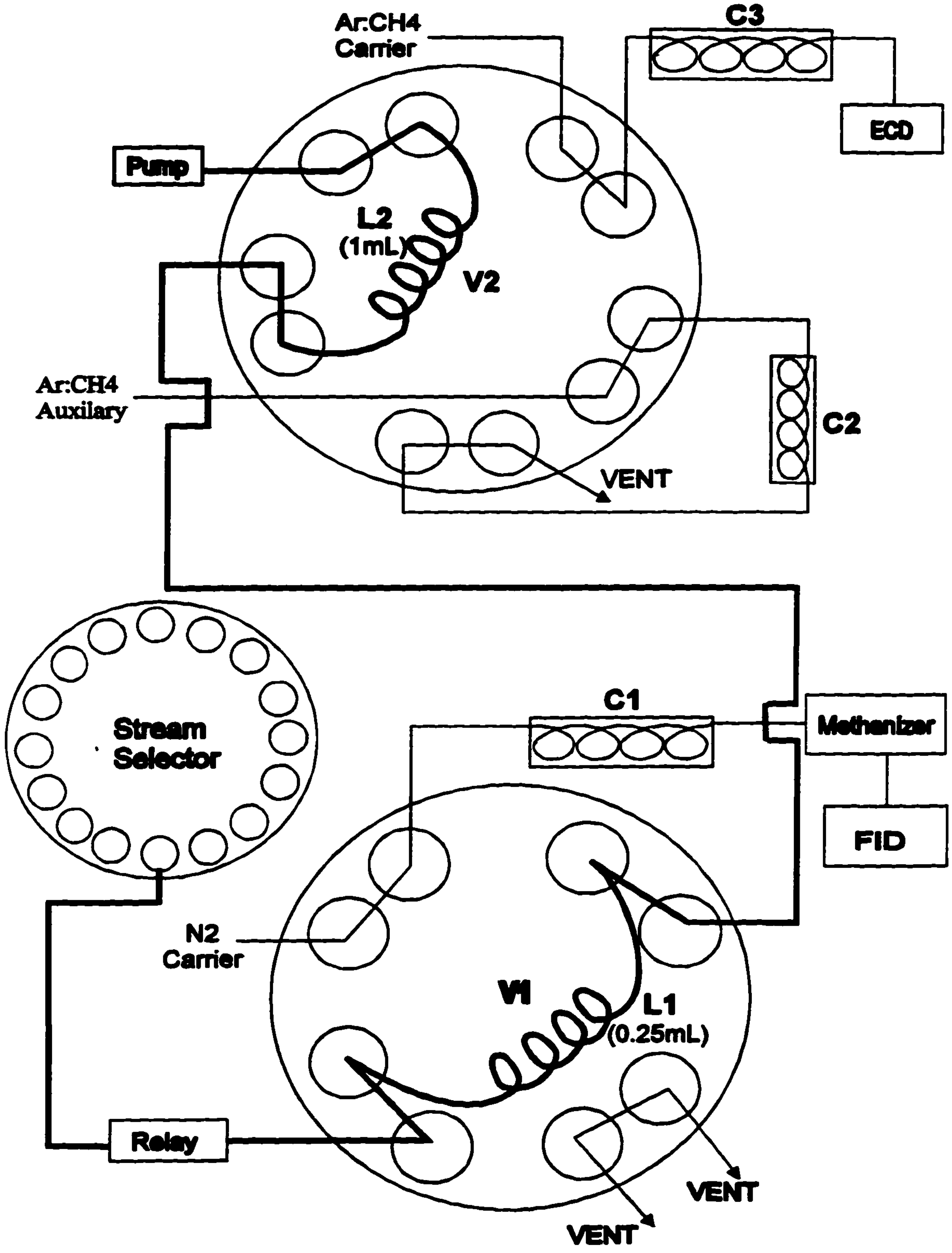

Figure 2-1. Schematic diagram of plumbing configuration used for simultaneous determination of CH_4, CO_2, and N_2O from a single injection. Darkened lines indicate the path of the sample stream when the system is positioned in sample loading mode.

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CHAPTER 3

Nitrous oxide emissions from agricultural soils of the Boreal and Parkland regions of Alberta[1]

3.1 INTRODUCTION

Canada, a signatory member of the United Nations Framework on Climate Change, is committed to stabilizing greenhouse gas emissions to 1990 levels by the year 2000. The first requirement for meeting this objective is an accurate accounting of the sources and sinks for these gases. Globally, agriculture is thought to be an important source, accounting for one-fifth of the annual increase in anthropogenic greenhouse gas emissions, with most of this due to methane and nitrous oxide (N_2O). Approximately 70% of all anthropogenic emissions of N_2O is attributed to agriculture (Cole et al., 1995). It is reasonable to expect that Canadian agriculture is an important source of atmospheric N_2O.

The contribution to atmospheric N_2O by agricultural soils in the Parkland and Boreal regions of Alberta is largely unknown. Substantial over-winter losses have been identified from nitrogen mass balance studies (Heaney et al., 1992; Malhi and Nyborg, 1983). The losses were attributed to denitrification during spring thaw. High fluxes of N_2O measured in the field during spring thaw from this region (Laidlaw, 1993) supports this conclusion. Laidlaw (1993) estimated cumulative losses during spring thaw period of up to 16 kg N_2O-N ha^{-1} on fertilized field plots. No studies have quantified N_2O emissions on an annual basis from agricultural soils in the Boreal or Parkland region of Alberta.

Fluxes of N_2O from soil vary widely over both time and space, making the estimation of losses over large geographical areas very difficult. The regulating factors that function at the scale of investigation must be understood, so that sampling units that reflect the spatial differences in those factors can be chosen. Available N and C, aeration, soil water content, temperature, and pH are considered to be the most important factors controlling N_2O production in soil (Drury et al., 1992; Fluhler et al., 1976; Goodroad and Keeney, 1984a; Skiba et al., 1993). Their interaction is complex, and attempts to relate these variables to the spatial variability of N_2O flux at the field scale have met with limited success (Burton and Beauchamp, 1985; Mosier et al., 1983). Groffman (1991) argued that increasing the scale of investigation in both time and space is useful for overcoming the variability problem, and by establishing quantitative

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[1] A version of this chapter has been submitted to the Soil Science Society of America Journal (9 / 96).

relationships with appropriate ecological variables, one could successfully develop flux estimates at the landscape or regional scale. Soil type and plant community type (production systems being surrogates for plant community type in cultivated areas) were proposed as appropriate controlling factors at the landscape scale. This conceptualization parallels Robertson's (1989) proximal and distal levels of regulation where climate, soil type, and plant community structure were considered the broadest integrators of N_2O production. Although soil and plant community type are not precisely defined, other closely related but quantifiable variables could be indexed to N_2O emission. Groffman and Tiedje (1989) found that soil texture and drainage, variables intimately related to soil and plant community type, could explain up to 86% of the spatial variability of annual N_2O emissions in a landscape level study of denitrification. Other workers (van Kessel et al., 1993; Parsons et al., 1991) have reported similar observations for N_2O emissions. Regulating factors that are appropriate and quantifiable need to be identified in order to develop large scale estimates of N_2O emissions from Canadian agricultural soils.

The availability of data must be considered when developing strategies for estimating N_2O-N loss over large spatial scales. Even ideal indicators of N_2O emission would be of limited value if their status were unknown or difficult to approximate. Resource limitations will probably require the use of existing data bases for information regarding soil properties, land use management and climate. It is important that scaling up methodologies can appropriately link the information in existing data bases.

Izaurralde et al. (1996) proposed that climate-soil-management combinations (CSMCs) aggregated to an ecodistrict level would be an appropriate scaling up technique for Canadian agriculture. An ecodistrict is characterized by distinctive landforms, relief, surficial geological material, soil, water bodies, vegetation, and land use (Ecological Stratification Working Group, 1995). The boundaries of ecodistricts represent a natural stratification of landscape or distal level regulators. Sampling units (CSMCs) can then be selected to capture the range of variability within the ecodistrict. Information pertaining to each element in the combination is readily available from existing data bases, although some modification is necessary to match spatial scales. The relative importance of each element in the CSMC on N_2O emission has not been quantified. It is not clear if each possible combination must be considered unique, or if some set of "typical combinations" would be representative. Comparisons of typical CSMCs between and within ecodistricts would provide a first step towards testing the validity of this strategy.

There are few alternative approaches to estimating N_2O flux over large spatial scales. The methodology currently proposed by the Intergovernmental Panel on Climate Change (IPCC) for estimating N_2O loss at a national level is based upon a linear extrapolation between N_2O emission and fertilizer N application. This approach does not reflect different crops, soils, or climates, all of which are thought to influence N_2O production. These factors have not been considered because of the limited data available to provide emission factors (OECD/IPCC, 1997). The applicability of the method for Canadian conditions has not been established. Clearly, data are required to test the IPCC methodology under Canadian conditions, and to provide insights into how the methodology might be refined to better account for spatial variability.

There were four objectives in this study. First, to estimate annual loss of N_2O from selected CSMCs in the Boreal and Parkland regions of Alberta; second, to assess the relative influence each element in the CSMC has on annual N_2O emission; third, to identify factors that regulate annual N_2O emission at the ecodistrict level. The final objective served to compare estimates of annual N_2O loss based on actual data to estimates calculated using current IPCC methodology.

3.2 MATERIALS AND METHODS

Description of Sites, Soils, and Ecodistricts

Sampling was conducted at six locations during 1993, 1994, and 1995. The selected sites ranged from a location near Rycroft (55° 43' N, 118° 41' W) in the Peace River district, to a location near Eckville (52° 23'N, 114° 22'W). The other four sites were all within a 110 km radius of Edmonton (53° 25' N, 113° 33' W). Some pertinent characteristics of the soils are listed in Table 3-1, and of the sites in Table 3-2. Detailed management histories for Breton and Ellerslie are described in Nyborg et al. (1995), for Cooking Lake and Josephburg in Larney et al. (1995), for Eckville in Malhi (1995), and for Rycroft in Arshad et al. (1995). All of the selected field plots were under conventional till management, and were continuously cropped except for Rycroft, which was left fallow in 1994. Crops and rates of fertilizer application are listed in Table 3-2. Fertilizer was broadcast and incorporated in late May or early June in all cases.

The six sites fall into five separate ecodistricts (Fig. 3-1), with two of the sites being located within the same ecodistrict. A soil and management thought to be typical was selected for each ecodistrict. Mixed grain, cattle, and dairy operations are usual, with barley, oilseeds and feeds/forage being common crops in all the ecodistricts considered.

Ecodistricts 727, 732 and 708 are located in the Parkland region of central Alberta. Soils in ecodistrict 727, encompassing Ellerslie and Josephburg, are predominantly Black Chernozems (Cryoborolls) complexed with Dark Gray Chernozems (Boralfic Borolls). The soil series at Ellerslie is Malmo, at Josephburg it is Angus Ridge, and together they occupy nearly 50% of the total area in ecodistrict 727 (W.W. Pettapiece, Alberta Land Resource Unit, Agriculture and Agri-Food Canada, Edmonton, AB pers. comm.). Ecodistrict 732 contains predominantly Gray Luvisols (Cryoboralfs) complexed with Dark Gray Chernozems, and includes the Cooking Lake site located on the soil series of the same name. Ecodistrict 708 contains predominantly Dark Gray Chernozems and Gray Luvisols complexed with Black Chernozems, and includes the Eckville site located on the Benalto soil series. The Cooking Lake series occupies nearly 50% of the area in ecodistrict 732, while the Benalto series occupies 22% of the area in ecodistrict 708.

Ecodistricts 593 and 692 are located in the Boreal region of north-west and central Alberta respectively. The Rycroft site, located on the Falher soil series, is included in ecodistrict 593, an area predominated by Solonetzic (Natric Boralfs) complexed with Dark Gray Chernozems and Gray Luvisols. The Breton site, located on the soil series of the same name, falls into ecodistrict 692, an area predominated by Gray Luvisols complexed with Organic (Histosols). The Falher series occupies 11% of ecodistrict 593, while the Breton series occupies 22% of ecodistrict 692 on an area basis.

Gas Sampling Schedules

Gas sampling schedules varied from site to site and from year to year. Periodic measurements for N_2O emissions were made during January, February and early March at the surface of the snow pack, at the soil surface with the snow pack removed, and during thawing temperatures when areas of soil were free of snow and the top few centimeters had thawed. No emissions were discerned until after the soil surface was free of snow and maximum daily soil surface temperatures approached or exceeded 0 °C for several days. The sites were closely monitored for N_2O emissions as soon as the snow pack began to melt, and continued until emissions of N_2O could no longer be detected. Discernible emissions were recorded during approximately 10 d in 1993, 12 d in 1994, and 21 d in 1995 (Table 3-3). During the 1993 and 1994 spring thaw, Ellerslie was sampled daily on consecutive days, while Breton, Cooking Lake, and Josephburg were sampled once daily on alternate days. All four sites were sampled on consecutive days during the 1995 spring thaw period. Measurements were made during early to mid-afternoon.

Gas sampling resumed immediately following fertilizer application in May, and continued until at least late September of each year. Measurements were taken twice monthly at Breton, Cooking Lake and Ellerslie during the summer of 1993, with the latter site sampled more intensely after significant rainfall events. No samples were taken during the summer of 1993 at Josephburg. Ellerslie and Cooking Lake were sampled with greater frequency during the summer of 1994, samples were taken at least once weekly in May, two or three times weekly through June and early July, and then with diminishing frequency through the balance of the summer. Breton and Josephburg were sampled twice monthly during the summer of 1994.

Eckville was sampled twice monthly during the summer of 1994, and twice weekly during the spring thaw of 1995. Rycroft was sampled twice weekly during the spring thaw of 1995. No other data from these two sites are reported here.

Sample Collection and Analysis

Vented soil covers (Hutchinson and Mosier, 1981) were inserted between crop rows for 1 h. Three or more replicates were taken at each sampling. Further discussion concerning the use of static chambers is provided in appendix A. Gas samples were drawn from the head space and transferred to vacutainers as described in chapter 2. Nitrous oxide flux was taken to be the change in concentration under the soil cover during the collection period, and was calculated by subtracting a time zero concentration from the final concentration, as described by Laidlaw (1993) and discussed further in appendix A. Time zero values were estimated in a fashion similar to Anthony et al. (1995). A series of ambient air samples was collected at each sampling time. The mean of these samples was used as the time zero concentration.

Analysis of N_2O was performed using a gas chromatograph equipped with a ^{63}Ni electron capture detector. A detailed description of the analysis system has been provided in chapter 2, with further discussion regarding sample container preparation and sample storage in appendix A.

Calculation of Seasonal and Annual Estimates

Spring thaw gas sampling was initiated as soon as the snow pack began to melt on the field plots, and continued until positive fluxes could no longer be confidently discerned. Samples were taken in mid-afternoon, and the flux from this sampling time was assumed to be constant for a 24 h period. The 24 h periods were then summed to give a cumulative estimate for the entire thaw event. This procedure was followed for each replicate at a site. The mean cumulative loss of N_2O and the standard error of the mean for each site was determined from the individual estimates.

Marked diurnal fluctuations in N_2O fluxes during the growing season have been reported. Ryden et al. (1978) and Denmead et al. (1979) reported peak fluxes in the early afternoon. Blackmer et al. (1982) however, found that the time of maximum and minimum daily flux was not consistent, and concluded that there was no clear cut method to account for diurnal changes. They calculated mean 24 h flux rates from hourly measurements with coefficients of variation ranging from 12% to 66%. Further discussion regarding diurnal patterns during spring thaw is given in chapter 4.

Daily flux through the growing season was calculated in the same fashion. Unsampled days were estimated using the mean of the sampled days before and after. If measurements were made on August 1 and 15, the period from August 2 to 14 was assumed to be the average of the flux on August 1 and that on August 15.

Calculation Using IPCC Methodology

Estimates based upon the IPCC methodology (OECD/IPCC, 1997) were calculated using the following linear equation:

$$\text{Total } N_2O\text{DIRECT} = [(\text{FSN} + \text{FAW} + \text{FBN} + \text{FCR}) * \text{EF1}] + \text{FOS} * \text{EF2}$$

The following terms are not applicable to this study:

FAW = animal waste N used as fertilizer (kg N y^{-1})

FBN = N fixed by N-fixing crops (kg N y^{-1})

FOS = area of cultivated organic soils

EF2 = emission factor for organic soil mineralization due to cultivation

After these terms are dropped the equation reduces to:

$$N_2O \text{ DIRECT} = [(\text{FSN} + \text{FCR}) * \text{EF1}]$$

where:

N_2O DIRECT = direct N_2O emissions from agricultural soil (kg N y^{-1})

FSN = NFERT * (1- FRACGASF)

FCR = 2* [CROPO * FRACNCRO] * (1-FRACR)

EF1 = emissions factor for direct soil emissions (kg N_2O-N [kg N input]$^{-1}$)

and:

NFERT = synthetic fertilizer applied (kg N ha^{-1} yr^{-1})]

FRACGASF = fraction of synthetic fertilizer N applied to soils that volatilizes as NH_3 or NOx [kg N (kg N applied)$^{-1}$]

CROPO = crop production (kg dry biomass ha^{-1} yr^{-1})

FRANCRO = fraction of N in crop [kg N (kg of dry biomass)$^{-1}$]

FRACR = fraction of the crop removed during harvest

Actual values from the respective sites were input for NFERT, CROPO, and FRACR. Values for FRACNCRO and FRACGASF were taken from those suggested in the IPCC methodology report. A range of values is provided for EF1, therefore the mid-point was selected.

3.3 RESULTS AND DISCUSSION

Overview of Spatial Variability

Box plots were prepared using data collected during the summer of 1994 (Fig. 3-2), and the spring of 1995 (Fig. 3-3) from three sites chosen to capture the range of flux values observed in our study. Box plots offer an overview of the relative "activity" of N_2O emission for a particular site and season, and allow visual comparisons of medians, interquartile ranges, and overall range of fluxes. The summer 1994 data set consisted of 20 sampling points from 6 days spread through the summer at Breton, while Ellerslie and Cooking Lake were sampled on 25 separate days totaling approximately 100 sampling points per site. The spring 1995 data set consists of approximately 50 data points spread over a three week period at each of the sites. Variability between replicates was high, with coefficients of variation ranging between 50% and 300% for specific sampling times, but was consistent with the results of other studies (Parkin, 1987; Folorunso and Rolston, 1984).

Annual and Seasonal Estimates

Estimated losses of N_2O-N varied from year to year and from site to site, ranging from a low of 0.4 kg ha^{-1} at Breton in the 1993/1994 season, to a high of 2.6 kg ha^{-1} at Eckville in the

1994/1995 season (Table 3-3). Losses of N_2O-N during the spring thaw ranged from 0.05 kg ha^{-1} at Breton in 1994, to 1.8 kg ha^{-1} at Ellerslie in 1995, representing as much as 70% of the total annual estimated loss, and confirming that spring thaw is extremely important to the annual budget of N_2O emission in the Parkland and Boreal region. Values recorded in this study were an order of magnitude lower than those reported by Laidlaw (1993), but very similar to those reported at other locations (van Kessel et al., 1993; Goodroad and Keeney, 1984b). Note that measurements in Laidlaw (1993) were taken on plots amended with NO_3^- either just prior to freeze up in the fall, or to the snow melt in spring. Total losses of N_2O-N during the growing season ranged from 0.3 kg ha^{-1} yr^{-1} at Breton to 1.6 kg ha^{-1} yr^{-1} at Eckville, and were very similar to other published data (Eichner, 1990; Aulakh et al., 1984; van Kessel et al., 1993).

Influence of Individual Elements within a CSMC

The magnitude of the estimated loss at specific sites varied from year to year, but trends between the sites remained consistent. The influence of climatic variability on annual estimated N_2O loss appeared to be masked by soil type or management factors. Precipitation and temperature regimes at Ellerslie and Cooking Lake are similar, yet absolute differences in N_2O loss between the two sites ranged from 25% to 100%. Eckville receives similar precipitation but lower growing degree days than Ellerslie, Josephburg, or Cooking Lake; and similar growing degree days but lower annual precipitation than Breton. Based upon climatic conditions, Eckville could be expected to have lower N_2O emission than the other four sites, but in fact it had the highest estimated total N_2O loss. I concluded that the influence of climate, as indicated by mean annual precipitation and growing degree days, can be considered uniform throughout an ecodistrict.

The study sites were selected to keep management as uniform as possible, however, fertilizer N rates did range from 0 to 100 kg ha^{-1}. Fertilizer application is considered a major determinant of N_2O emission (Mosier et al., 1983; Eichner, 1990) and I looked for possible relationships between fertilizer rate and total estimated N_2O loss. Eckville received the lowest rate of N application but recorded the highest estimated loss of N_2O. Ellerslie had the next highest estimated loss of N_2O, yet received the same rate of N as Breton, and lower rates than Josephburg or Cooking Lake. Rycroft, which received no fertilizer, had higher losses than Breton in spring of 1995, however measurements at Rycroft were taken on fallow plots making the comparison tenuous. While nitrogen fertilizer application does increase annual N_2O emissions (see chapter 5), the influence of differing fertilizer rates in this study appeared to be masked by other site-specific factors.

The comparisons of CSMCs made in this study were based upon a limited number of sites and must be viewed with caution. The results do suggest that inherent soil properties (soil type) had a stronger influence on the magnitude of annual N_2O-N loss than did the other two elements in the selected CSMCs. This observation could be extremely important to the logistics of the scaling up procedure. If each element in the CSMC functions at the same scale of resolution and is of equal importance, then the number of possible combinations increases rapidly. If there were 2 managements, 2 soils, and 2 contrasting climates in an ecodistrict, the number of combinations to be sampled would be 8 (2 x 2 x 2). If, even one of the elements (climate) could be held constant, then the number of combinations would drop substantially (from 8 to 4 in this example).

Regulating Factors

Soil appeared to be the element having the strongest influence, prompting me to try to identify soil characteristics that could quantify and/or predict those differences. I investigated possible correlations between the mean overall annual estimated loss of N_2O-N, based upon a one year estimate for Josephburg and Eckville, and the mean of two years for Breton, Ellerslie, and Cooking Lake, and each of the soil properties listed in Table 3-1. Ninety-two percent of the variability in annual N_2O-N loss from the five sites could be explained by differences in clay content (Table 3-5), a finding consistent with that of Groffman and Tiedje (1989).

The strength of the relationship between soil properties and total N_2O flux appears to be dependent upon season. Total N_2O-N lost during spring thaw, based upon a single spring season for Rycroft and Eckville, and an average of three springs for Breton, Ellerslie, Cooking Lake and Josephburg, was not significantly correlated with clay content. The uniformly saturated conditions experienced during snow melt might explain the weak relationship. Only the surface layer of the soil profile is thawed by the time the snow pack has melted, drainage is impeded by the underlying frozen layers, and the soil surface layer becomes uniformly saturated. Anoxic conditions are governed more by the depth of snow pack and the speed that the soil profile thaws, than by inherent soil properties such as texture.

Analysis of the relationship between clay content and spring N_2O-N loss caused me some concern. When Rycroft was excluded from the spring correlation, the coefficient of correlation between percent clay and cumulative spring N_2O -N loss rose from 0.20 to 0.75. One possibility is that contrasting management conditions at Rycroft were confounding the comparison. However, correlations using total N_2O-N loss from individual springs also indicated a weak relationship between clay content and N_2O-N loss, leading me to accept the 0.20 coefficient as representative.

Malhi and Nyborg (1986) postulated that mineralization processes continue at low levels during the winter months, providing available carbon and nitrate to power the denitrification process during spring thaw. This would be consistent with the strong relationship observed between yield (an indicator of available crop residue), and the magnitude of N_2O-N loss during the following spring thaw. It would also imply that initial levels of mineral N and/or available carbon prior to spring thaw would be good indicators of the magnitude of N_2O flux. This implication will be explored further in chapters 4 and 5.

Yield and clay content correlated strongly to N_2O emission during the summer season. These results are consistent with the assumption that N_2O production during the growing season arises from both nitrification and denitrification (Skiba et al., 1993). In general, conditions that favor crop growth also favor microbial activity. Enhanced mineralization provides NH_4^+ for nitrification, and carbon for denitrification, while enhanced respiration increases O_2 consumption. Strong crop growth not only increases O_2 consumption, but also provides available carbon from root through-put for denitrification and mineralization, and coupling high O_2 demand with high clay content favors the development of anaerobic microsites. Thus, conditions favoring high crop yields could simultaneously stimulate nitrification and denitrification.

Intra vs. Inter Ecodistrict Comparison

Since ecodistrict boundaries are based upon ecoclimatic, physiographic and general soil characteristics, I expected CSMCs within the same ecodistrict to be more similar to each other than to CSMCs in other ecodistricts, and predicted N_2O emissions would parallel these similarities. However, in 1994 (the only year both inter and intra ecodistrict comparisons could be made) there was a greater difference between the two sites in the same ecodistrict, Josephburg and Ellerslie; than there was between Ellerslie and Eckville, or Josephburg and Cooking Lake - pairs of sites in different ecodistricts. This is not surprising, since the variability between annual estimates from the sites in this study appeared to be governed by a single dominating factor - clay content. A factor which is not necessarily stratified by ecodistrict boundaries.

IPCC Methodology

The estimates calculated using the IPCC methodology (Table 3-4) were quite similar to those calculated using actual field data. The trend between sites apparent in the estimate from measured values was reasonably well reflected in the IPCC calculation. The inclusion of a crop residue factor in the calculation appears to have partly captured the site specific conditions. The methodology tended to under estimate N_2O losses from the finer textured soils, and over estimate losses from the coarser textured soils. Predictions for medium textured soils (20-35% clay) were similar to estimates based on field measurements, however populations of soils are not evenly distributed in terms of texture within an ecodistrict. As an example, in Ecodistrict 727 about 30% of the soils, on an area basis, have greater than 35% clay, with 10% of the soils having 20% clay or less. The IPCC methodology would likely underestimate total loss in this ecodistrict, and errors may become even greater in ecodistricts that have greater relative proportions of finer or coarser textured soils. In actual practice, the calculation would be made using long term yield data and fertilizer rates estimated from census data or fertilizer sales information, further reducing the sensitivity to site specific conditions and possibly increasing the level of error. The lack of sensitivity to varying soil conditions needs to be addressed.

3.4 CONCLUSIONS

Estimated annual losses of N_2O-N ranged from 0.4 to 2.6 kg ha^{-1} from selected sites in the Boreal and Parkland regions of Alberta. Soil type very strongly influenced the magnitude of annual N_2O emission, masking the influences of management or climate variations. Up to 92% of the large scale spatial variability in the annual estimates of N_2O-N loss could be explained by differences in clay content, suggesting that soil type be an important criteria for stratification. Estimates calculated using the current recommended IPCC methodology were close to estimates based upon actual field measurements for medium textured soils, but diverged markedly for finer or coarser textured soils, indicating that refinements to account for differences in soil type are necessary.

Table 3-1. Soil properties of six sites selected for N_2O flux measurements.

Site	Soil	Organic C	Bulk Density	Clay Content	pH
		(%)	(Mg m^{-3})	(%)	
Breton	Gray Luvisol	1.5	1.30	12	6.4
Cooking Lake	Gray Luvisol	3.4	1.25	22	6.5
Eckville	Gray Luvisol	2.6	1.20	40	5.9
Ellerslie	Black Chernozem	5.5	1.01	39	6.0
Josephburg	Black Chernozem	4.0	1.17	30	6.6
Rycroft	Solodized Solonetz	4.0	1.24	52	5.4

Table 3-2. Site characteristics and treatments of the six sites selected for N_2O flux measurements.

Site	Precipitation	Growing degree days	Drainage class	Crop	Fertilizer rate
	(mm)	(d)			(kg N ha^{-1})
Breton	550	1090	imperfectly	wheat	56
Cooking Lake	450	1230	imperfectly	wheat	100
Eckville	450	1090	imperfectly	barley	25
Ellerslie	450	1230	well	wheat	56
Josephburg	450	1230	well	wheat	100
Rycroft	419	1296	poorly	fallow	0

Table 3-3. First and final dates of discernible N_2O emissions recorded during the spring thaw period.

	1993	1994	1995
Ellerslie	March 23 - April 1	March 28 - April 8	March 19 - April 13
Breton	March 25 - April 1	March 25 - April 5	March 16 - March 30
Cooking Lake	March 24 - April 2	March 30 - April 11	March 19 - April 15
Josephburg	March 24 - April 2	March 25 - April 8	March 18 - April 6

Table 3-4. Estimated loss of N_2O-N based on actual field measurements and calculated using the IPCC methodology.

	Summer		Spring			Annual[†]		Calculated (IPCC)	
Site	**1993**	**1994**	**1993**	**1994**	**1995**	**1994**	**1995**	**1994**	**1995**
	(kg ha^{-1} y^{-1})								
Breton	**0.3** (0.16)[‡]	**0.7** (0.27)	**0.15** (0.07)	**0.05** (0.02)	**0.2** (0.19)	**0.4**	**0.9**	**1.1**	**1.3**
Cooking Lake	**0.6** (0.12)	**0.7** (0.11)	**0.84** (0.13)	**0.3** (0.41)	**1.3** (0.39)	**0.9**	**2.0**	**2.1**	**1.7**
Ellerslie	**1.5** (0.77)	**0.7** (0.07)	**0.54** (0.34)	**0.2** (0.26)	**1.8** (0.91)	**1.7**	**2.5**	**1.3**	**1.7**
Josephburg	n/a	**0.6** (0.15)	**0.12** (0.04)	**0.6** (0.06)	**1.4** (0.48)	n/a	**2.0**	**2.0**	**1.5**
Eckville	n/a	**1.6** (0.10)	n/a	n/a	**1.0** (0.47)	n/a	**2.6**	n/a	**1.6**
Rycroft	n/a	n/a	n/a	n/a	**0.5** (0.04)	n/a	n/a	n/a	n/a

[†] Conditions during spring thaw are directly related to the previous growing season, therefore annual values are combined estimates from summer plus the following spring.

[‡] The value in brackets is the standard error of the mean.

Table 3-5. Coefficients of determination (r^2) between estimated spring, summer and annual N_2O-N loss and selected parameters.

Means	**Sample Size**	**Organic C**	**Clay Content**	**Bulk Density**	**pH**	**Grain yield**
Spring[†]	6	0.25	0.20	0.31	0.01	0.62*
Summer[‡]	5	0.03	0.68*	0.20	0.83*	0.95*
Annual[‡]	5	0.17	0.92**	0.29	0.43	0.35

*,** Significant at 0.05 and 0.01 levels respectively.

[†] Spring estimates are based upon the mean of 3 years except for Rycroft and Eckville where only one estimate is available.

[‡] Summer and annual estimates are based upon mean of two years except for Eckville and Josephburg where only one value was available, Rycroft was not included in the summer or annual estimates since no summer season data was available.

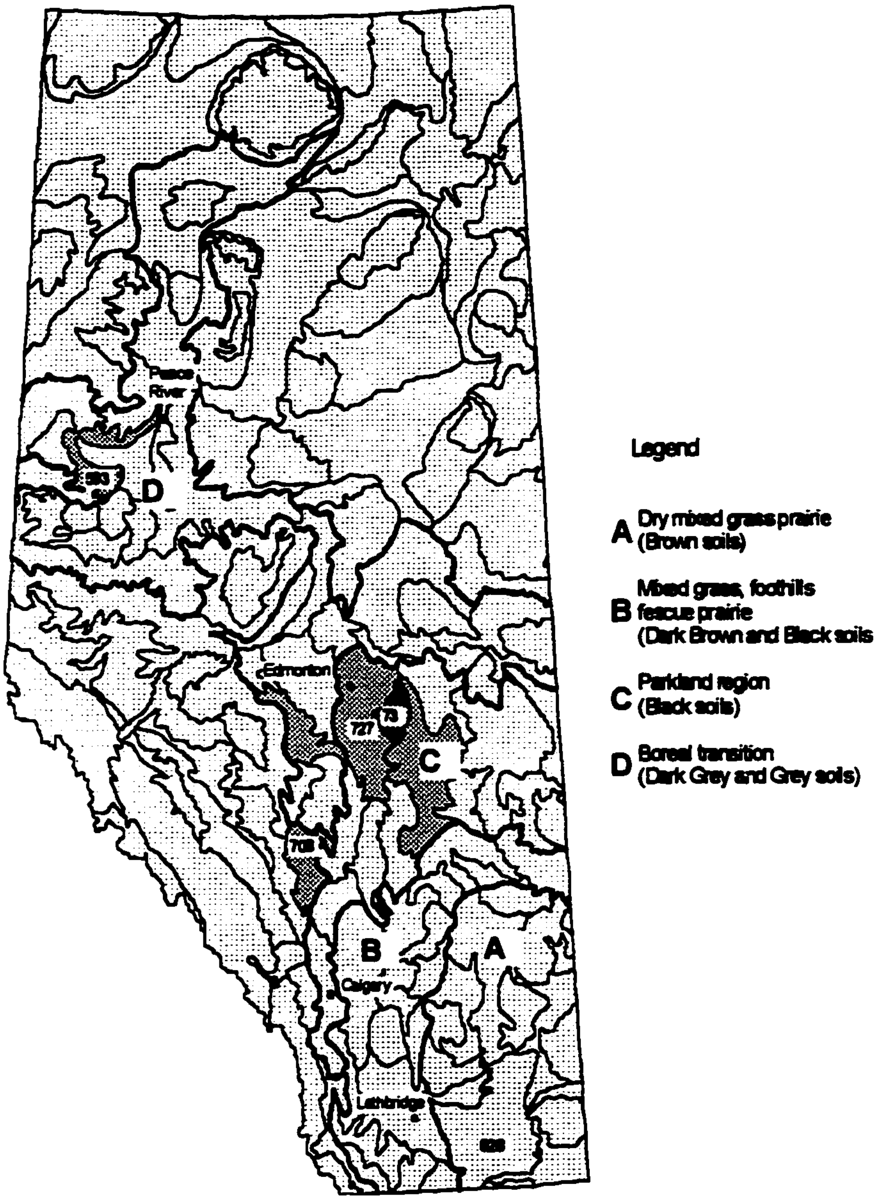

Figure 3-1. Map showing the ecodistricts of Alberta. Ecodistricts considered in this study are indicated by darker shade.

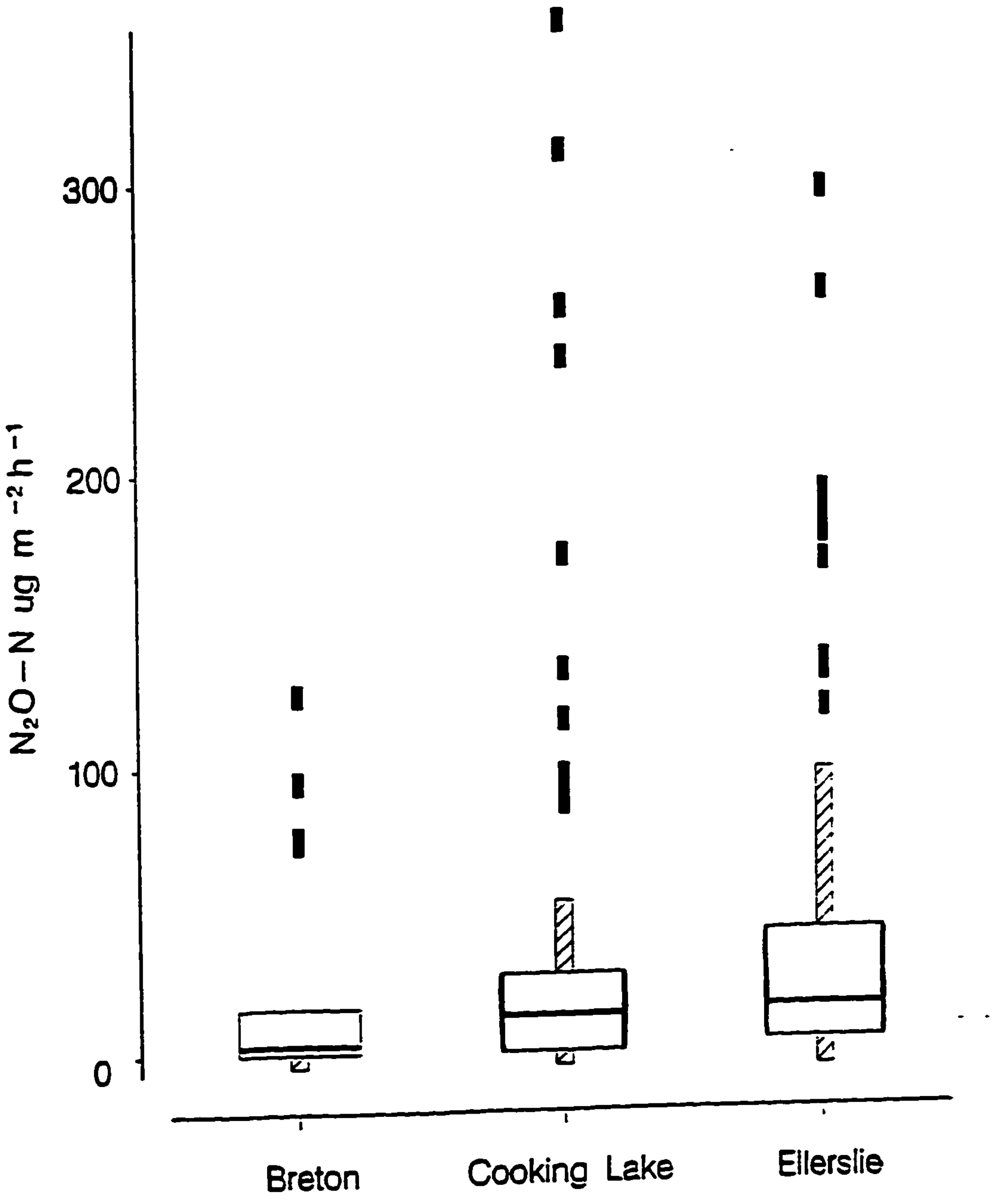

Figure 3-2. Box plot indicating the range of fluxes measured at three sites during the summer of 1994. The dark horizontal lines within the box indicate the median, while the box is the interquartile range. The hatched area includes values up to 1.5 times the interquartile range, while values beyond this are indicated in black.

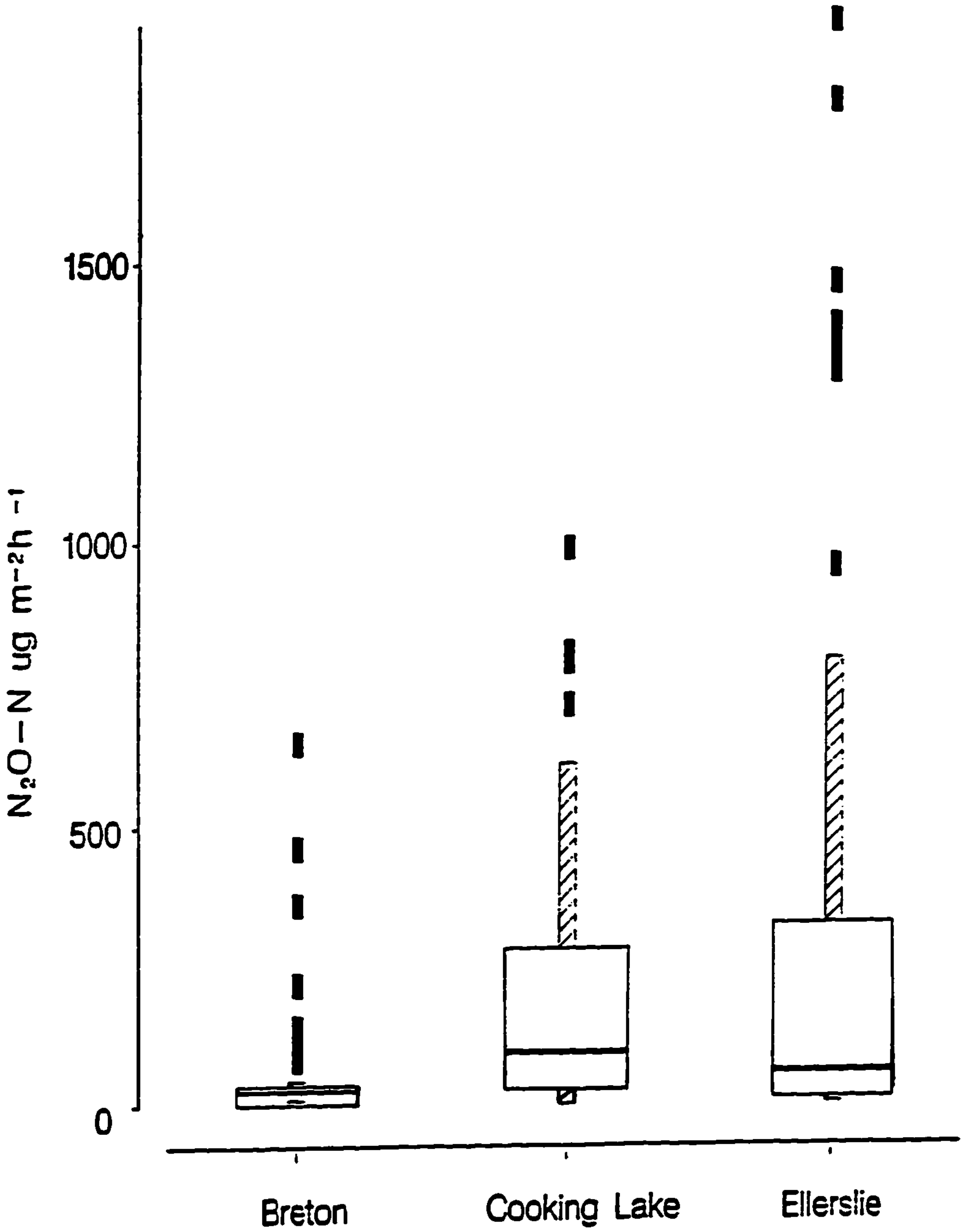

Figure 3-3. Box plot indicating the range of fluxes measured at three sites during the spring of 1995. The dark horizontal lines within the box indicate the median, while the box is the interquartile range. The hatched area includes values up to 1.5 times the interquartile range, while values beyond this are indicated in black.

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CHAPTER 4

Seasonal patterns of N_2O emissions from agricultural soils of the Boreal and Parkland regions of Alberta[1]

4.1 Introduction

An increased concentration of atmospheric nitrous oxide (N_2O) has been documented (Banin, 1986; Duxbury et al., 1993), and concern over how this may influence the earth's temperature balance and ozone layer (Crutzen and Ehalt, 1977; Shine et al., 1990) has triggered a major effort to quantify the sources and sinks of atmospheric N_2O. Globally, agricultural soils have been identified as important sources of anthropogenic N_2O emission (Cole et al., 1995), but estimates are still speculative. Documentation of N_2O-N losses from many agroecosystems is scarce. This, together with the high degree of spatial (Folorunso and Rolston, 1984) and temporal (Christensen, 1983; van Kessel et al., 1993) variability in field measured N_2O emissions presents a major challenge to the accurate quantification of N_2O-N loss from agricultural soils.

Consideration of temporal variability is a critical issue when designing sampling schedules, integrating flux measurements over time, or developing predictive models. Seasonal patterns in gaseous N loss have been described by various workers; these patterns have differed according to ecosystem and/or geographic location. 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 the summer. Conversely, at an agricultural site in Saskatchewan, van Kessel et al. (1993) found highest emissions of N_2O during early spring and summer, with fluxes declining to negligible levels into the late growing season and fall. Laidlaw (1993), reported high fluxes of N_2O during spring thaw, but negligible fluxes during the following growing season at an agricultural site in Alberta.

Despite the divergence in seasonal patterns of gaseous N loss from different sites, there appears to be a commonality in the factors controlling temporal variability on a seasonal scale. Groffman and Tiedje (1989) concluded that soil water content strongly governed the timing of gaseous N loss, although NO_3^- and possibly C may have been limiting at times. The pattern of precipitation and the activity of the forest trees resulted in the distinct seasonal pattern observed. Similarly, van Kessel et al. (1993) concluded that an adequate supply of soil water was the triggering event for N_2O emission, with other soil factors being of secondary importance. I

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[1] A version of this chapter has been submitted to the Soil Science Society of America Journal (01/1997).

therefore speculated that water filled pore space (WFPS) and the availability of mineral N and WSOC could also explain the seasonal distribution of N_2O emissions from agricultural soils in the Boreal and Parkland regions of Alberta.

Intense emissions of N_2O during spring thaw from soils in the Boreal and Parkland regions of Alberta have been reported (Laidlaw, 1993; Chapter 3). Loss of N_2O-N during this event is a substantial component of the annual N_2O flux budget for the region. The surface of soils in these regions generally becomes uniformly saturated as the snow pack melts. Since WFPS is more uniform during this event, then factors such as the concentration of pre-thaw soil mineral N and/or water soluble organic carbon (WSOC) may account for much of the variability in cumulative N_2O-N loss during spring thaw. Laidlaw, (1993) observed much more intense fluxes of N_2O from soils amended with NO_3^- at freeze up in the preceding fall than from soils receiving no NO_3^-. This suggests that soil concentrations of mineral N and WSOC at fall freeze-up may be indicators of cumulative N_2O-N loss during the following spring.

The objectives of this study were: 1) to characterize seasonal flux patterns of N_2O emissions from selected field plots in the Parkland and Boreal regions of Alberta; 2) to test the hypothesis that temporal variability in WFPS, and the availability of mineral N and WSOC can explain the temporal variability of N_2O emissions during the summer season, and; 3) to test the hypothesis that soil concentrations of mineral N and WSOC at fall freeze-up can explain the variability of cumulative N_2O-N loss measured during the following spring thaw.

4.2 MATERIALS AND METHODS

Gas sampling was conducted during the spring of 1993, 1994, and 1995, and the summer of 1993 and 1994, on four existing experimental sites, Breton, Ellerslie, Cooking Lake, and Josephburg. All four sites are within a 110 km radius of Edmonton, Alberta. Soils at Cooking Lake and Breton are Gray Luvisol (Typic Cryoboralfs), while soils at Ellerslie and Josephburg are Black Chernozems (Typic Cryoborolls). Field plots established in 1978 under zero and conventional till were selected as the main treatments at Ellerslie and Breton (Table 4-1). The CT plots are cultivated in autumn and spring to a depth of 10 cm with a rotovator. The plots are seeded with a hoe drill, this being the only soil disturbance on the ZT treatment. Two levels of simulated erosion, 0 (non-eroded) and 20 cm of top soil removed, were selected as the main treatments at Cooking Lake and Josephburg. Detailed site and treatment descriptions for Cooking

Lake and Josephburg are given in Larney et al. (1995), and of Breton and Ellerslie in Nyborg et al. (1995).

In 1992 the main treatments at each site were split and six subplots created. Two subplots were utilized for a crop-fallow rotation with both phases of the rotation present each year. Weeds were controlled with chemicals on the ZT treatment, and by tillage (hand rotovator) on the CT treatment during the fallow phase. Field peas (*Pisum sativum L.*) were grown on a third plot. The residue was removed after harvest (fall 1992) and an equal amount returned to the plots at seeding time in 1993. Fertilizer was applied to the fourth plot, while the other two were left as control (no additions). Sheep manure (40 Mg ha^{-1} dry basis) was added to one of these controls at seeding time in 1993. Fertilizer N was applied as urea at rates of 56 kg ha^{-1} at Ellerslie and Breton, and 100 kg N ha^{-1} at Cooking Lake. Fertilizer was surface applied just prior to seeding, and was immediately incorporated with a hand rotovator to a depth of 10 cm on the CT treatments. All plots were seeded to continuous spring wheat (Triticum aestivum L.).

The sites were monitored for N_2O emissions as soon as the snow pack began to melt, usually mid-March, and continued until emissions of N_2O were negligible. During the 1993 and 1994 spring thaw, Ellerslie was sampled daily on consecutive days. Samples were collected at 2:00 PM on all days and all treatments, with additional samples at 11:00 AM, and 5:00 PM on most of days. On selected treatments, an 8:00 AM and 8:00 PM time was also included. Breton, Cooking Lake, and Josephburg were sampled once daily in the early afternoon on alternate days. All four sites were sampled in the early afternoon on consecutive days during the 1995 spring thaw period.

Gas sampling resumed after tillage and fertilizer application in May, and continued until at least late September of each year. Measurements were taken twice monthly at Breton, Cooking Lake and Ellerslie during the summer of 1993, the latter site being sampled more intensively after significant rainfall events. No samples were taken during the summer of 1993 at Josephburg. Ellerslie and Cooking Lake were sampled with increased frequency during the summer of 1994. Samples were taken at least once weekly in May, two or three times weekly through June and early July, and then with diminishing frequency through the balance of the summer. Breton and Josephburg were sampled twice monthly during the summer of 1994.

A detailed description of gas sampling methodology and flux calculations is given in appendix A, and of the analysis methodology in chapter 2. Briefly, gas samples were taken using a vented soil cover. Each gas sample was analyzed simultaneously for N_2O and CO_2 using a gas chromatograph equipped with a ^{63}Ni electron capture detector for N_2O, and a methanizer and flame ionization detector for CO_2. Flux was calculated from the change in headspace concentration during the sampling period.

Soil bulk density to a depth of 10 cm was determined with a MC-1 moisture/density gauge (Campbell Pacific Nuclear Corp., Pacheco, CA), and soil water content to the same depth was established by gravimetric determination of weight loss when soil samples were dried at 105°C for 24 h. Water-filled pore space (WFPS) in the top 10 cm of soil was calculated assuming a particle density of 2.65 Mg m^{-3}. Thermistors (model 107, Campbell Scientific, Logan, Utah), buried at 2 and 4 cm depths and connected to a data logger (model CR-10, Campbell Scientific, Logan, Utah) recorded mean hourly soil temperatures (Ellerslie site only).

Soils were sampled for mineral N and WSOC to a depth of 10 cm at Ellerslie on June 2, July 6, August 11, September 15 and October 19 during 1993. In 1994, samples were taken at Ellerslie and Cooking Lake on consecutive days from June 26 to 29, August 2 to 5, and September 20 to 23. Soil mineral N was extracted by shaking the sample in a 2 M KCl solution (extractant:soil ratio of 5:1w/w) for 1 h, and then filtering with a 47 mm dia. Whatman ashless filter paper. The filtrate was analyzed with a Technicon Autoanalyzer II (Technicon Industrial Systems, Tarrytown, NY). Water-soluble organic carbon was extracted by shaking 10 g of soil in 20 ml of deionized water for 1 h , and centrifuging at 10,000 x g at 4°C for 30 min. The supernatant was filtered through a 47 mm dia. 0.2 µm Metricel membrane filter, and analyzed for TOC, using an Astro 2001 series 2 soluble carbon analyzer (Astro Inter. Corp., League City, TX).

4.3 RESULTS AND DISCUSSION

Overview

Ellerslie received 343 mm of precipitation in 1993 and 366 mm in 1994, both values being considerably below the long term mean of 450 mm. Breton received 402 mm in 1993 and 489 mm in 1994, both values also lower than the long term mean of 550 mm. Meteorological stations were not installed at Josephburg or Cooking Lake, although their proximity to Ellerslie suggests that climatic conditions would be very similar to that site. Differences in the distribution of precipitation at Ellerslie during the growing season in 1993 and 1994 were notable. Less than average precipitation during May and early June of 1993 was followed by high rainfall beginning on Day 173 (Fig. 4-1). Precipitation during 1994 was more evenly distributed, although rainfall in July was unusually low. Air temperatures were very close to long term means during the growing season of 1993 and the early part of 1994, but were cooler than average from mid-July to end of August in 1994.

The temporal distribution of N_2O fluxes from a fertilized conventional till (CT) treatment at Ellerslie is representative of the seasonal patterns observed at all sites in this study (Fig. 4-1). A brief but intense period of activity occurred at and just following the spring snow melt; from Day 82 to Day 92 in 1993, and from Day 88 to Day 98 in 1994. A second period of activity occurred during the early to mid-growing season; from approximately Day 170 to 190 in 1993 and Day 160 to 190 in 1994. Emissions measured at other points during the summer were very low. The great majority of N_2O-N loss in both years occurred during the spring thaw event, and a five or six week period between early to mid-June and mid-July.

The seasonal pattern of N_2O emissions just described was consistent across treatments, although the magnitude of the fluxes measured on different treatments varied considerably. The distribution of N_2O emissions during the summer of 1993 from 5 subtreatments on a ZT main treatment at Ellerslie (Fig. 4-2) provides a representative example. Emissions from all subtreatments were low until Day 173, increased considerably between Day 170 and 186, and then trailed off to negligible levels. The fallow treatment was an exception, having elevated emissions on Day 223.

A similar temporal distribution of N_2O fluxes was observed on a fertilized CT treatment at Breton (Fig. 4-3) and Cooking Lake (not shown) during 1993, and Cooking Lake (Fig. 4-1), and Josephburg (Fig. 4-3) in 1994. Emissions measured at Breton and Cooking Lake in 1993 were much less intense than those measured at Ellerslie. The similarity in the temporal distribution of N_2O emissions at all locations investigated during 1993 and 1994 suggests that seasonal patterns in the Boreal and Parkland regions are relatively stable from year to year and site to site. Temporal patterns observed were consistent with those reported by van Kessel et al. (1993) and Cates et al. (1987).

Controlling Factors -Summer Season

Van Kessel et al. (1993) concluded that precipitation was the dominant factor triggering N_2O emission events. The distribution of N_2O emissions observed at Ellerslie during the summer of 1993 clearly supports this conclusion. Soil concentrations of NO_3^-, NH_4^+, and WSOC, measured shortly after urea fertilization (June 2), ranged as high as 62 mg kg^{-1} of NO_3^--N , 33 mg kg^{-1} of NH_4^+-N , and > 200 mg kg^{-1} of WSOC (Table 4-2). Emissions of N_2O-N from all but two treatments remained low, with an interquartile range lying between 0 and 10 µg m^{-2} h^{-1}. A fertilized CT treatment and a pea residue on ZT treatment were the two exceptions, having interquartile ranges between 10 and 25 µg m^{-2} h^{-1}. Minimal precipitation was received during this time period with WFPS at 50% or less, and respiration (as indicated by CO_2 flux) remained very low. The combination of low WFPS and minimal O_2 consumption probably maintained the soil volume in a well aerated state and may explain the low N_2O emissions. A precipitation event beginning on June 22 increased soil WFPS to > 60% and triggered a flush of N_2O emissions that continued until at least July 5. Fluxes as high as 1000 µg m^{-2} h^{-1} were recorded during this two week period, with the interquartile range of flux from all treatments lying between 10 and 80 µg m^{-2} h^{-1}. Water filled pore space remained high (> 60%) through the balance of the growing season (Table 4-2), but N_2O emissions trailed off by the end of July, with most (75%) of the recorded emissions being less than 8 µg m^{-2} h^{-1}. The concentration of WSOC was > 200 mg kg^{-1} at all points in the season, levels well in excess of the value of 114 mg kg^{-1} found to limit denitrification in this soil (Monreal and McGill, 1983). Conversely, soil concentrations of NO_3^- dropped to 5 mg kg^{-1} or less by early August. The enzymatic affinity of denitrifying bacteria for NO_3^- is reported to be high, which would allow bacteria to utilize NO_3^- at concentrations much lower than this (Parsons et al., 1991), however diffusion to microsites at such low concentrations could have been a constraint.

In a laboratory study using soil from Ellerslie, Malhi et al. (1990) found that NO_3^- loss (assumed to be primarily via denitrification) was well represented by a Michaelis-Menten model. Using this simple model and the soil NO_3^--N values measured in this study, I calculated the predicted rate of denitrification on August 11 relative to the predicted rate of denitrification on July 5. I adjusted for soil temperature differences based upon the results of Malhi et al. (1990), assumed that WSOC was not limiting, and that N_2O emission was proportional to denitrification. The ratio of 0.13 calculated from predicted denitrification rates agrees well with the ratio of 0.10 calculated from the mean of measured N_2O emission rates. This is consistent with the hypothesis that low NO_3^- concentrations might explain the low N_2O emissions recorded during the latter part of the growing season, despite high WFPS and favorable WSOC availability.

More evenly distributed precipitation during the summer of 1994 resulted in more evenly distributed N_2O emissions (Fig. 4-1). Fluxes of N_2O from both Cooking Lake and Ellerslie during early summer of 1994 were almost identical to fluxes from Ellerslie during the same period in 1993. The interquartile range of fluxes from the control and fallow treatments lay between 0 and 10 $\mu g\ m^{-2}\ h^{-1}$. The interquartile range on fertilized treatments increased to between 4 and 25 $\mu g\ m^{-2}\ h^{-1}$ after urea application. Intermittent but more intense emissions began during the second week of June, and continued until the second week of July, with peak emissions at Ellerslie reaching > 300 $\mu g\ m^{-2}\ h^{-1}$ and having an interquartile range between 6 and 45 $\mu g\ m^{-2}\ h^{-1}$. Emissions at Cooking Lake reached peaks of 1700 $\mu g\ m^{-2}\ h^{-1}$, with an interquartile range lying between 5 and 85 $\mu g\ m^{-2}\ h^{-1}$. Emissions trailed off to levels comparable to early summer (May and early June) at both sites by the end of July, even though on August 5, median soil concentrations of NO_3^--N and WSOC appeared not to be limiting at either Ellerslie or the non-eroded treatment at Cooking Lake (Table 4-3). Water filled pore space had dropped below 50 %, which may explain the low emissions of N_2O. The 20 cm simulated erosion treatment at Cooking Lake had much lower soil concentrations of NO_3^- and WSOC compared to the non-eroded and either or both may have become limiting during this time.

I attempted to quantify the factors controlling temporal variability of N_2O emissions on a seasonal scale using a step-wise multiple regression model (SAS Institute, 1987) with N_2O-N flux as the dependent variable. Four sampling times were selected; early growing season (late-June / early-July), late growing season (mid-August), and post harvest (late-September). A late fall (mid-October) sampling time was included in 1993. Median values, being more resistant to the influence of skewedness and more robust to departures of normality (Pennock et al., 1992), were used as the measure of central tendency. In 1993 the median value for each treatment was calculated from four replications. Soil factors and N_2O fluxes had been measured on several consecutive days for each point in the season during 1994, and the median was determined after pooling the data from each set of consecutive days.

The relationship between median N_2O-N flux and median soil NO_3^--N concentration at Ellerslie was similar and highly significant in both years (Table 4-4). A multiple regression model was able to explain 64 % of the temporal variability in 1993 by including the medians of soil NO_3^--N, NH_4^+-N, and WSOC concentrations, and 70 % of the temporal variability in 1994 by utilizing NO_3^--N and NH_4^+-N (Table 4-5). When CO_2-C was included in the latter model the

R^2 value increased to 85% for 1993, but the improvement was not statistically significant in 1994. Since N_2O emissions from the 20 cm simulated erosion treatment at Cooking Lake were essentially zero throughout July, August and September, only the non-eroded treatment was used for analysis of temporal controls. Nitrate-N alone accounted for 80% of the temporal variability in N_2O-N emission in 1994. No other factor improved the regression coefficient significantly. These results are consistent with those of Parsons et al. (1991), who found that seasonal variations of mean NO_3^-, CO_2, moisture, and temperature could explain 74% and 91% of the temporal variability in N_2O emissions from two soils at a site in Kentucky.

Spring Thaw Event

No N_2O emissions were recorded during the winter months in this study. Measurements were taken at the surface of the snow pack, at the soil surface with the snow pack removed, and during thawing temperatures when areas of soil were free of snow and the top few centimeters had thawed. Sustained N_2O emissions were only discerned after the soil surface was free of snow, and maximum daily soil surface temperatures approached or exceeded 0 °C for several days. This event generally occurs between March 15 and April 15. Temporal and spatial variability of N_2O emissions during this spring thaw event is extreme. Air temperatures frequently fall below zero at night, and can reach day time highs of 20 °C or warmer. Soil temperatures are less extreme, but the top few centimeters alternate between freezing and daily maximums of up to 10 °C. Assuming that N_2O emissions arise from current biological activity, then temperature fluctuations would be expected to strongly affect emission rates. The fact that emissions have not been recorded prior to thawing, and that during the spring thaw event emissions are generally absent or negligible on days when soil temperatures do not exceed zero, implies that microbial production of N_2O is strongly curtailed at zero or sub-zero soil temperatures.

I used the model developed by Malhi et al. (1990) to see if it is reasonable to invoke denitrification as an explanation for the N_2O emissions recorded during this time. Fall soil nitrate concentrations were used as proxy measures for initial soil nitrate concentrations at spring thaw, denitrification was assumed to be the major source of N_2O emissions, and the mole fraction of N_2O (N_2O / [N_2O + N_2]) was set at 0.1. Surface soil temperatures vary between 0°C and 10°C, and this range of temperature was used for the calculations. Predicted fluxes ranged from 192 to 929 μg N_2O-N m^{-2} h^{-1}, while 90% of actual measured fluxes lay between 0 and 700 μg N_2O-N m^{-}

^{2} h^{-1}. Peak fluxes of >6000 μg N_2O-N m^{-2} were measured in the field. Considerably greater mole fractions would be expected however, under the conditions prevailing during spring thaw (Cates et al., 1987), and/or localized sites of high NO_3^- concentration. Assuming a mole fraction of 0.5, a localized NO_3^--N concentration of 50 mg kg^{-1}, and a soil temperature of 10°C, fluxes predicted by the model surpassed 6000 μg N_2O-N m^{-2} h^{-1}, confirming that the range of N_2O flux measured during spring thaw could be explained by denitrification.

I also attempted to identify diurnal trends in N_2O fluxes by taking measurements at three hour intervals from early morning to late evening. Emissions were invariably absent or minimal at the early morning measurement (8 AM), however there appeared to be no regular trend in the timing of daily peak emissions, and no statistically significant correlation between hourly soil (2 or 4 cm depth) or air temperature and N_2O-N flux could be discovered. Recognizing that considerable time may elapse between production of N_2O within the profile and emission from the surface, I looked for phase relationships between the diurnal trends of soil temperatures and N_2O emissions. Improvements in the strength of the correlation between soil temperature (2 cm depth) and N_2O flux were achieved by assuming a lag between maximum N_2O flux and maximum soil temperature. The required lag times were inconsistent however, ranging from 2 to 20 hours, and correlations after adjusting for lag time remained weak.

Blackmer et al. (1982) suggested that changes in the solubility of N_2O could be a significant factor affecting the diurnal variability of N_2O emissions during the growing season. I made simple calculations, using soil properties and temperature measurements pertinent to the Ellerslie site, to estimate the influence that changes in N_2O solubility may have had during the spring thaw period. Since diurnal temperature fluctuations at 4 cm were minimal during the period of N_2O emission, solubility changes due to temperature would be negligible below 5 cm. Thus, only the 0 to 5 cm depth was considered. I assumed that the top 5 cm of soil was at or near saturation, that bulk density was 1.0 Mg m^{-3} and that the maximum daily temperature reached within this layer would be 10° C. I used the gravimetric solubility coefficient for N_2O in water of 0.0593 mol kg^{-1} atm^{-1} at freezing point and 0.0402 mol kg^{-1} atm^{-1} at 10° C reported by Weis and Price (1980). The net release of N_2O over this range of temperature would depend upon the partial pressure of N_2O in the gas phase at the liquid-air interface. No information concerning the concentration of N_2O in the soil atmosphere for this study was available, but if the soil had been perfectly saturated and underlain by an impermeable frozen layer, then the liquid-air interface would have been in equilibrium with ambient air. If the partial pressure of N_2O in ambient air is used and the net release spread over a six hour period, the average N_2O-N flux due to the change in solubility would be less than 1 μg m^{-2} h^{-1}. This value represents less than 2 % of the magnitude of typical fluxes recorded during spring thaw. Burton and Beauchamp (1994) reported mean soil atmosphere N_2O concentrations of < 2 μL L^{-1} to a depth of 10 cm during spring thaw at a site in Manitoba. Using this value as an example, the flux of N_2O-N due to solubility changes would be < 4 μg m^{-2} h^{-1}. Conversely, Cates and Keeney (1987) measured N_2O concentrations of up to 1900 μL L^{-1} in the soil atmosphere to a depth of 10 cm. Since temperature fluctuations were minimal even at 4 cm, soil atmosphere concentrations of N_2O within the top few centimeters of soil would have to be very high before this process would emerge as an important component of diurnal variability during the spring thaw event.

Soil atmosphere studies have indicated a build up of N_2O within the soil profile (Burton and Beauchamp, 1994; Cates and Keeney, 1987) during the winter months. It is hypothesized that N_2O is emitted during over-winter N transformations, and is trapped below the overlying frozen soil. This N_2O is released as the soil thaws in spring, contributing to surface measured fluxes. The physical release of N_2O would coincide with the thawing of the soil, could be impeded if the soil surface re-freezes, but would not be strongly influenced by more subtle temperature fluctuations. This would confound attempts to relate diurnal temperature changes to N_2O-N fluxes, and would be consistent with qualitative observations made at spring thaw event during this study.

Fluxes of N_2O that are one or more orders of magnitude greater than typical values (hot spots) are often encountered during the spring thaw event. The importance of these outliers to the total cumulative loss during a particular event is unclear since their frequency and temporal stability is unknown. A hot spot was identified during routine sampling at Ellerslie on the afternoon of April 2, 1994. That particular location, and several others of varying activity were then sampled hourly from early evening until early morning, and again the following day, to investigate temporal stability and to allow a closer study of the relationship between soil temperature and N_2O-N flux. A flux of 1693 μg N_2O-N m^{-2} h^{-1} was recorded at 5 PM (Fig. 4-4) on a ZT treatment. The flux had dropped to 1017 μg N_2O-N m^{-2} h^{-1} by 9 PM, and continued to drop until the final sample taken at 5 AM, when it reached a low of 88 μg N_2O-N m^{-2} h^{-1}. At 2 PM the following afternoon the flux at the same location was 328 μg N_2O-N m^{-2} h^{-1}. Air temperature at 5 PM was 11 °C, reached a minimum of 2 °C by 5 AM, and then had returned to 7 °C by 2 PM the following day (April 3). Soil temperature (2 cm depth) on this plot only fluctuated 0.1 degrees however, remaining just at the freezing point throughout the 24 h period. In contrast, flux from a sampling location on a nearby CT treatment was 210 μg N_2O-N m^{-2} h^{-1} at 5 PM, dropped to 153 μg N_2O-N m^{-2} h^{-1} by 9 PM and then increased steadily until 5 AM when it reached 389 μg N_2O-N m^{-2} h^{-1}. Soil temperature at 2 cm depth on this treatment was 8 °C at 5 PM, had fallen to 0 °C by 2 AM, and then reached 7 °C by 2 PM the following day. Eight sampling locations were measured concurrently during this 27 h period. Four of the locations maintained a generally steady flux from late afternoon until the 5 AM sampling time. Flux from two of the locations showed a distinct decline by the early morning sampling time, while flux at the other two locations increased from early evening until early morning. Flux patterns did not appear to be related to treatment.

Two points arise from these observations. Firstly, although flux from the hot spot diminished rapidly from the peak measurement, activity remained high at all sampling times during the 27 h period. The cumulative loss of N_2O-N during this 27 h period represents approximately 30% of the total estimated N_2O-N loss from that treatment over the 10 d spring event. Secondly, fluxes measured at 8 AM at this site were generally negligible, and I had expected emissions to decrease or even stop during the night or early morning. On this occasion at least, emissions not only continued up to the 5 AM sampling time, but in some cases increased substantially from day time levels. If the soil surface freezes prior to 8 AM, the lack of flux often observed at this time may be due to a temporary physical blocking of N_2O release, which may be released when the surface re-thaws later in the day. This may explain "spikes" of N_2O occasionally measured at the 11 AM sampling time. The observations from this 27 h sampling period appear to stand against expected changes in biological activity and the influence of solubility changes due to temperature fluctuations, or may simply attest to the complexity of the factors controlling transport times of N_2O through the soil profile.

Cumulative losses during the spring thaw of 1994 were considerably less than during the corresponding period of 1995. The period of intense N_2O emission during spring of 1994 was relatively brief, while emissions during spring 1995 were of greater intensity and were sustained over a longer period of time. Undoubtedly, the length of time that soils remain at or near saturation strongly governs cumulative N_2O-N loss over the spring event, however during the spring of 1994 emissions from many of the plots trailed off to negligible levels while the soil surface still appeared to be at or near saturation. I noted that soil mineral N concentrations were very low in the fall of 1993, and were relatively high in the fall of 1994, and speculated that the cumulative N_2O-N loss during the spring thaw may be related to fall mineral N levels. Laidlaw (1993) reported N_2O fluxes that were an order of magnitude greater from plots amended with N fertilizer just prior to freeze-up compared to non-amended plots. It would seem logical that increased mineral N levels in the fall might increase the availability of N during the following spring thaw, and may also increase the extent of over-winter N transformations. In either or both cases the end result could be increased emissions of N_2O-N during the spring thaw event.

I tested the hypothesis that fall soil concentrations of mineral N and WSOC may be indicators of cumulative N_2O-N loss during the following spring by comparing soil concentrations of mineral N and WSOC taken at Ellerslie in 1993 (September 15), and at Ellerslie and Cooking Lake in 1994 (September 20), to the estimated total N_2O-N loss in the following spring. The procedure used for estimating cumulative spring N_2O-N loss has been described in chapter 3. The data were combined into a single data set and a step-wise multiple regression model (SAS Institute, 1987) was used to quantify the relationships. I found that mean levels of mineral N in September explained 82% of the variability in mean cumulative N_2O-N loss during spring thaw (Table 4-6). Inclusion of WSOC in the regression model expanded the explanatory power to 94%.

4.4 CONCLUSIONS

The seasonal pattern of N_2O emissions was distinct and consistent in both years and at all sites investigated in this study. A brief but intense period of activity occurred during and just following snow melt in the spring. Calculations using a soil-specific model indicate that denitrification alone could account for the range of N_2O fluxes recorded during this event. Qualitative observations however, suggested that N_2O emissions were a combination of physical release and current biological activity. Fluxes were low during May and early June, and from late July onwards, ranging from 0 to 10 μg N_2O-N m^{-2} h^{-1}. A second period of high N_2O-N loss occurred between mid-June and mid-July when soil water status was high and mineralization processes and/or anthropogenic activities combined with minimal crop uptake induced an accumulation of mineral N. The availability of mineral N, particularly NO_3^-, explained between and 60 and 80% of the temporal variability observed in N_2O emissions at the seasonal scale. Fall soil concentrations of mineral N were able to explain > 80% of the variability in estimated cumulative N_2O-N emissions during the following spring thaw event.

Table 4-1. Treatments and subtreatments at the four locations sampled for N_2O during 1993 and 1994.

Ellerslie - Breton		Cooking Lake - Josephburg	
main treatments	subtreatments‡	main treatments	subtreatments
conventional till	urea fertilizer (56 Mg N ha^{-1})	non-eroded	urea fertilizer (100 Mg N ha^{-1})
	fallow		fallow
zero till	pea residue† (5 Mg ha^{-1})	20 cm simulated erosion	pea residue† (5 Mg ha^{-1})
	sheep manure† (40 Mg ha^{-1})		sheep manure† (40 Mg ha^{-1})
	control		control

† Urea fertilizer was applied to these plots in 1994.

‡ Each main treatment was subdivided into five subtreatments

Table 4-2. Median values of soil mineral N, water soluble organic carbon (WSOC), and water-filled pore space (WFPS) from 2 subtreatments of a conventional till treatment at Ellerslie during the summer of 1993.

	NO_3^--N		NH_4^+-N		WSOC		WFPS	
	fertilizer	control	fertilizer	control	fertilizer	control	fertilizer	control
	mg kg^{-1}						%	
June 2	62	18	33	4	208	230	45	44
July 5	13	4	9	4	216	345	62	63
Aug. 11	2	1	6	3	302	237	63	70
Sept. 15	4	2	9	6	256	273	61	66
Oct. 19	4	3	3	3	216	204	42	49

Table 4-3. Median values of soil mineral N, water soluble organic carbon (WSOC), and water-filled pore space (WFPS) from a fertilized conventional till subtreatment at Ellerslie and Cooking Lake during the summer of 1994.

	Ellerslie				Cooking Lake			
	NO_3^--N	NH_4^+-N	WSOC	WFPS	NO_3^--N	NH_4^+-N	WSOC	WFPS
	mg kg^{-1}			%	mg kg^{-1}			%
June 26-29†	63	6	186	60	53	4	139	54
Aug. 2-5	24	7	158	47	14	6	130	34
Sept. 20-23	16	8	130	58	13	5	81	53

† represents the median of measurements taken on consecutive days

Table 4-4. Coefficients of determination (r^2) between selected soil variables, CO_2-C flux, and N_2O-N flux.

	Ellerslie 1993 (n=40)	Ellerslie 1994 (n=18)	Cooking Lake 1994 (n=9)
WFPS	0.04	0.31*	0.07
WSOC	0.01	0.14	0.30
NO_3^--N	0.55***	0.59***	0.80***
NH_4^+-N	0.57***	0.04	0.16
CO_2-C	0.47***	0.29*	0.72**

***,**,* Significant at $p < 0.001$, 0.01, and 0.05 levels respectively.

Table 4-5. Coefficients of determination (R^2) between N_2O-N flux and soil concentrations of NO_3^--N, NH_4^+-N, and water-soluble organic carbon (WSOC).

Ellerslie 1993 (n=40)		Ellerslie 1994 (n=18)		Cooking Lake 1994 (n=9)	
NO_3^-	0.55***	NO_3^-	0.59***	NO_3^-	0.80***
WSOC	0.59*†	NH_4^+	0.70*†		
NH_4^+	0.64*				

***,* Significant at $p < 0.001$, and 0.05 levels respectively.

† step-wise regression model includes this variable and preceding variable(s).

Table 4-6. Coefficients of determination (R^2) between estimated cumulative spring N_2O-N flux and mean fall soil concentrations of NO_3^--N, NH_4^+-N, and water-soluble organic carbon (WSOC) at Ellerslie in 1993 and 1994, and Cooking Lake in 1994.

	All Data Points (n=62)	Mean of Replicates (n=18)
NO_3^-	0.24**	0.47**
NH_4^+	0.42**†	0.82**
WSOC	ns‡	0.94**

** Significant at 0.01 level of probability

† step-wise regression model includes this variable and preceding variable(s)

‡ not significant

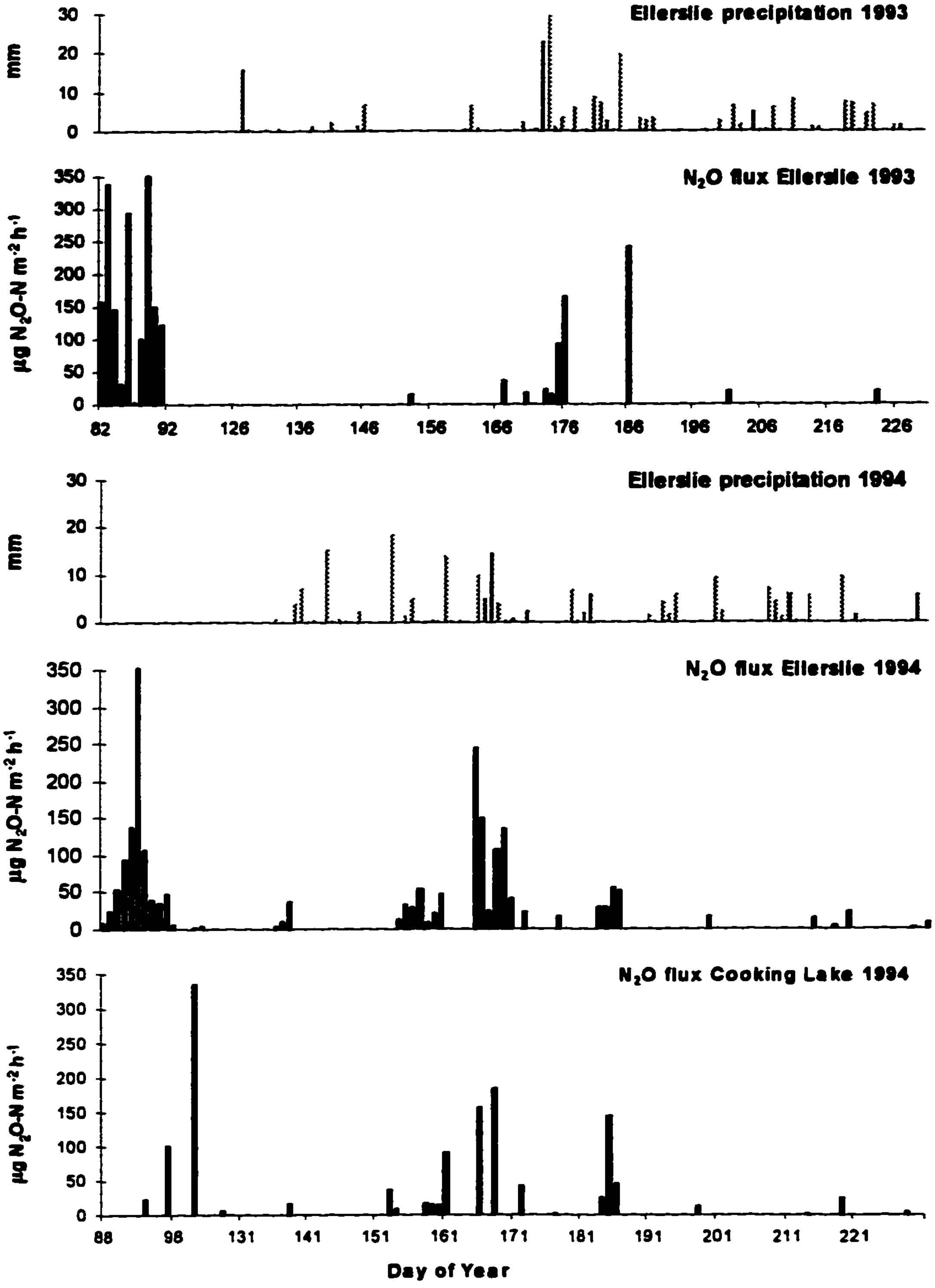

Figure 4-1. Distribution of precipitation and mean N2O fluxes measured at early afternoon from fertilized CT treatment at Ellerslie in 1993, and Ellerslie and Cooking Lake in 1994. In 1993, measurements were taken on 7 dates in June and then bi-weekly thereafter. In 1994, measurements were taken 2 or 3 times weekly through May, June, and early July, and with diminishing frequency thereafter.

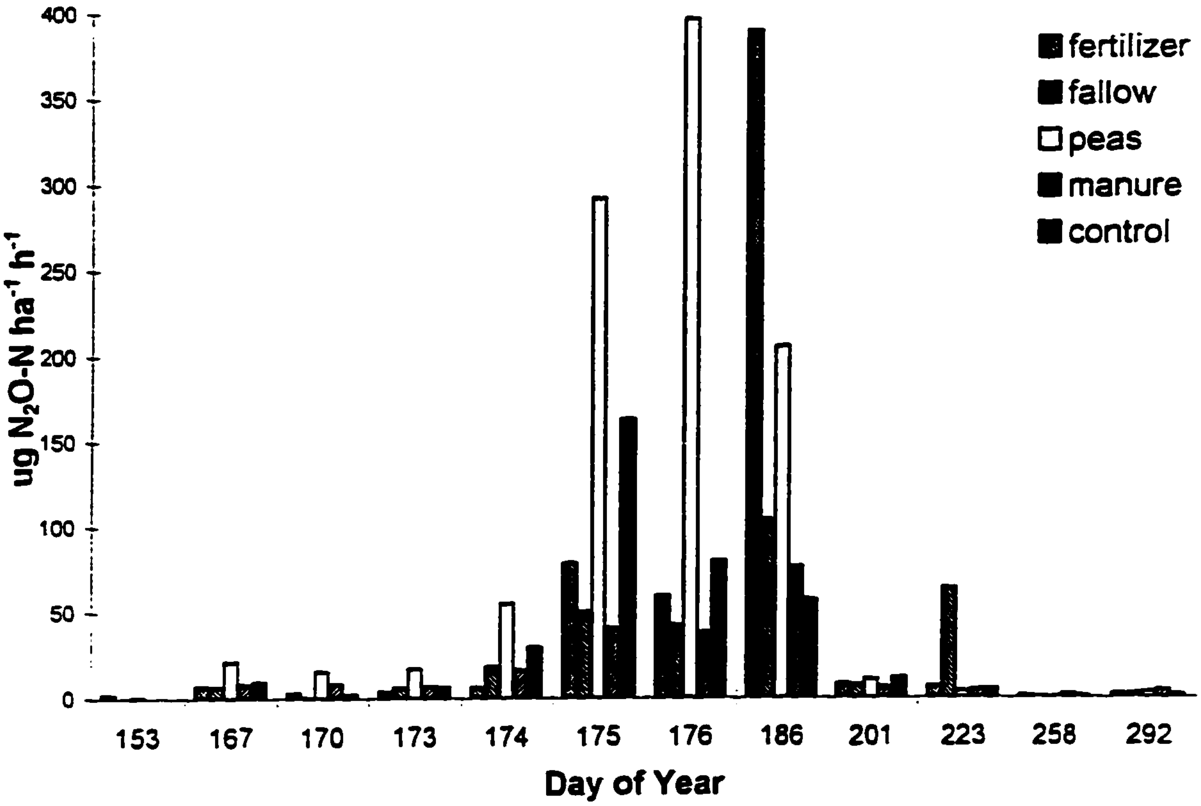

Figure 4-2. Mean N2O-N flux measured on 12 dates from 5 subtreatments of a zero till main treatment at Ellerslie during 1993. Measurements were taken in early afternoon.

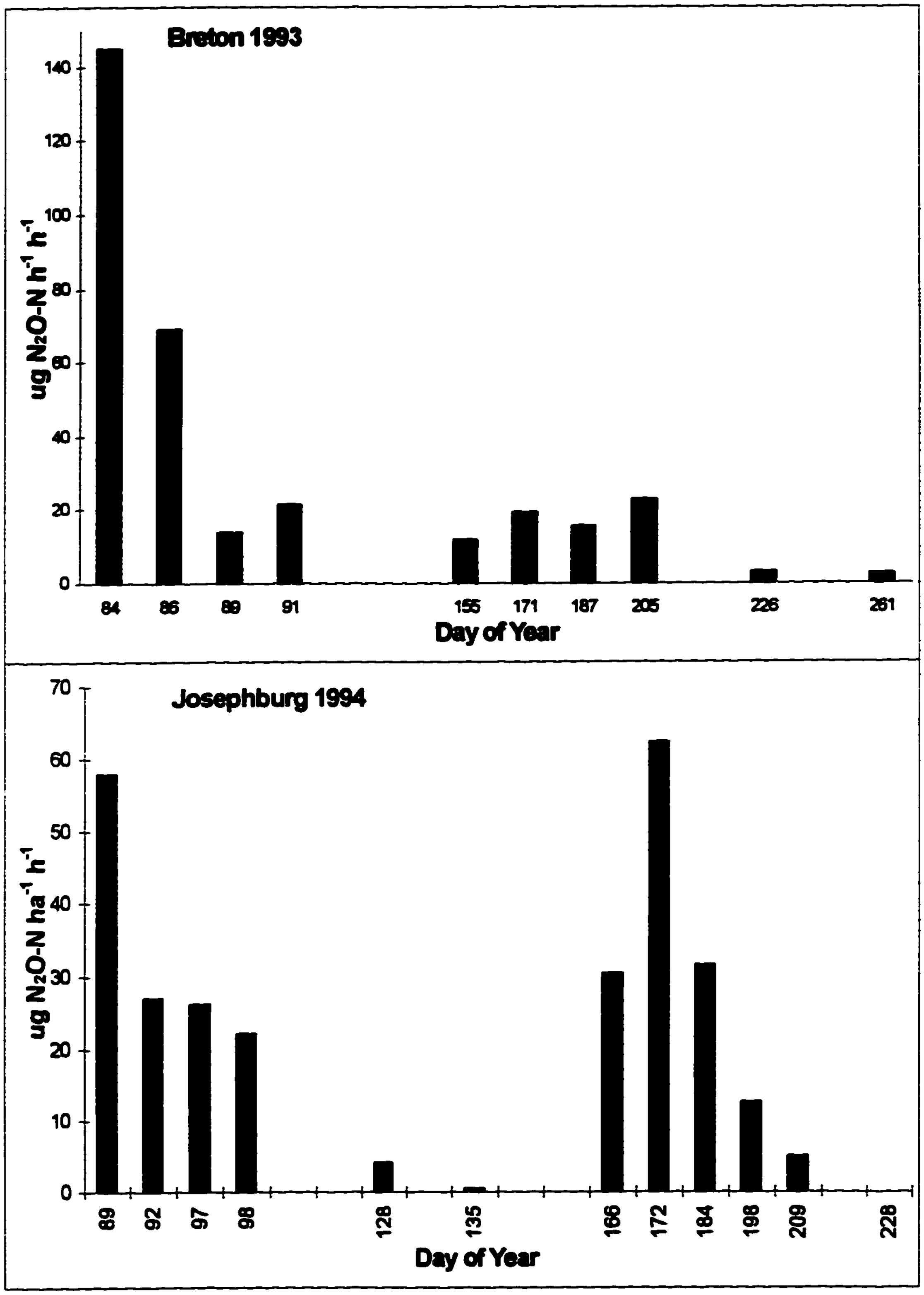

Figure 4-3. Mean N2O-N flux measured at early afternoon from a fertilized-conventional till treatment on selected days in 1993 at Breton, and 1994 at Josephburg.

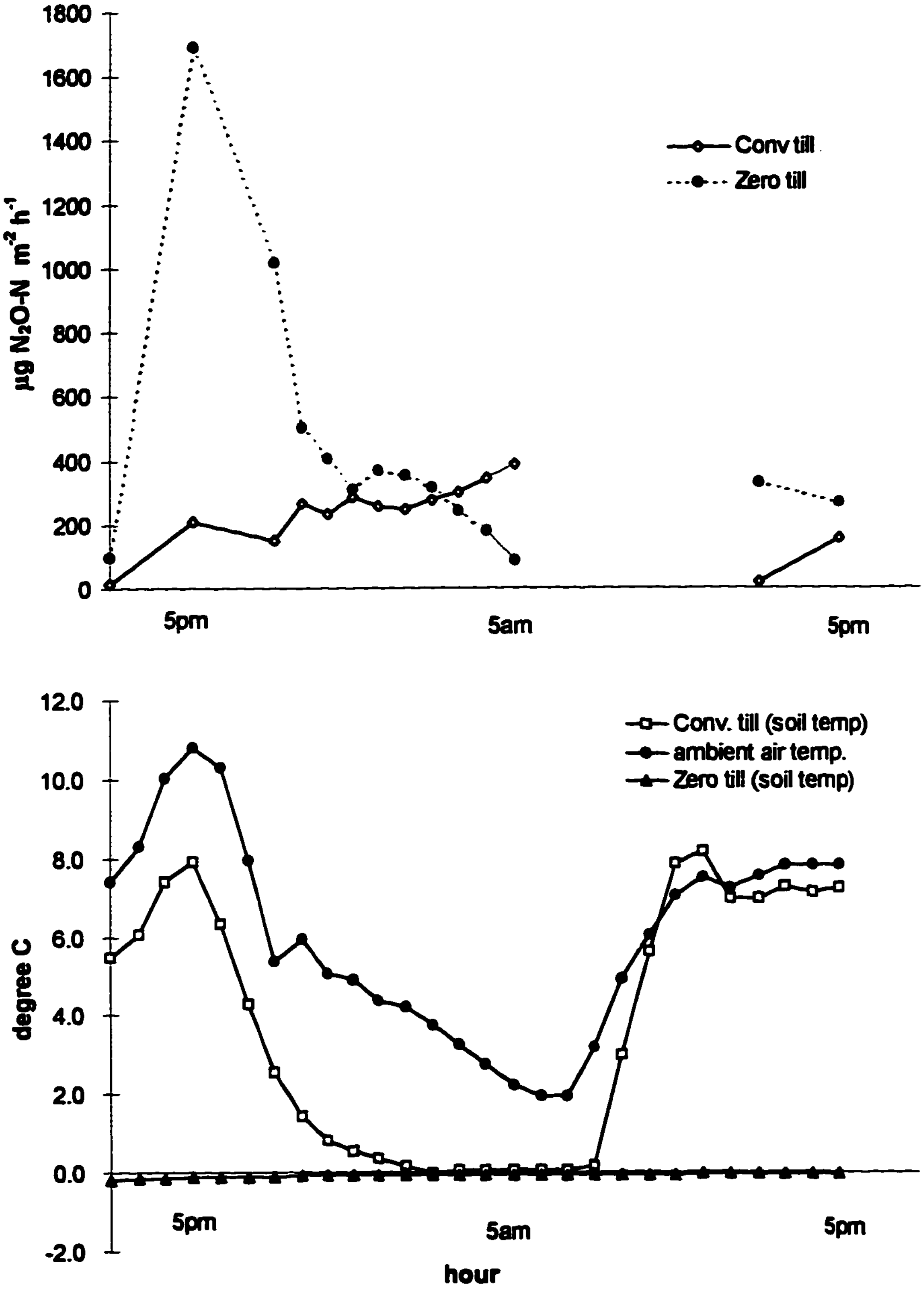

Figure 4-4. N2O flux measured on two plots at Ellerslie over a 27 h period from 2 PM on April 2 to 5 PM on April 3, and hourly air and soil temperature (2 cm) during the same time period.

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CHAPTER 5

N_2O emissions from soils under zero and conventional till managements in the Boreal and Parkland Regions of Alberta

5.1 INTRODUCTION

A shift towards reduced till management systems has been occurring in the agricultural sector. Reducing the risk of soil erosion by wind and water is the primary motivation for this shift. More recently, concern over the increasing levels of atmospheric greenhouse gases, particularly CO_2, has prompted researchers to seek avenues for mitigation. Reduced till systems have garnered attention for their carbon sequestering potential.

Early indications suggest that reduced tillage systems can increase soil carbon content in low organic matter soils (Nyborg et al., 1995). This "benefit" must be balanced against the complete budget of soil-emitted greenhouse gases. Higher losses of N_2O from soils under zero till as compared to conventional till managements have been reported (Aulakh et al, 1984; Linn and Doran, 1984). Most investigations have only considered the growing season, however intense losses of N_2O-N have been reported during spring snow melt (Laidlaw, 1993) and chapter 3 of this work. No studies are available on the influence of tillage on N_2O-N loss from agricultural soils on an annual basis in the Boreal or Parkland regions of Alberta.

Nitrogen fertilizers (McKenney et al., 1980; Eichner, 1990), organic amendments such as manure or legume residue (Laidlaw, 1993; Aulakh et al., 1991), and fallow (Aulak et al., 1982), have all been reported to promote the emission of N_2O-N from agricultural soils. We may assume that one common feature among these "treatments" facilitating N_2O production is an increase in available N, and for this discussion I will refer to them as "N-source" treatments. Limited information is available regarding the relative influence that each of these treatments may have on N_2O emissions.

In chapter 4, I speculated that cumulative N_2O-N loss during spring thaw is strongly governed by the availability of mineral N, which in turn is determined to a great extent by conditions during the previous growing season. Strong correlations between cumulative N_2O-N loss during spring thaw and soil mineral N concentrations in the previous fall supported this hypothesis. Management practices such as fall plow down of crops with a low C:N ratio would likely increase the availability of mineral N during the following spring thaw, and thereby increase N_2O emissions.

The objectives for this study were fourfold. First, to compare the annual emissions of N_2O-N from zero and conventional till systems on two contrasting soil types. Second, to assess the influence of five different "N-sources" on seasonal N_2O-N loss from soils at three locations. Third, to investigate possible interactions between tillage regime and N-sources. Lastly, to compare N_2O flux during spring thaw from field plots expected to be low in mineral N (wheat stubble) with field plots expected to be high in mineral N.

5.2 MATERIALS AND METHODS

Nitrous oxide emissions measured from field plots at three locations, Ellerslie, Breton, and Cooking Lake, were included in this study. The pertinent field data was extracted from previously collected data sets. The sites, treatments, sampling methodology, and sampling schedules were described in chapters 3 and 4. In brief, measurements from the two main treatments, zero till (ZT) and conventional till (CT) were included at Ellerlsie and Breton, and a CT treatment was selected at Cooking Lake. Each of the main treatments were split into six subplots, urea fertilizer, pea residue, sheep manure, fallow and check (no amendment). It should be noted that manure and field pea amendments were added only once. These plots were fertilized with urea at a N rate equivalent to the original fertilizer subtreatment during the 1994 and 1995 growing season. It was assumed that no residual effect from the legume or manure would be apparent by the 1995 spring thaw and growing season, therefore only the fertilized, fallow, and control plots were monitored for N_2O emissions in that year. A summary of the subtreatments by year is provided in Table 5-1.

Nitrous oxide emissions were also measured on an adjacent long-term study at Breton during the spring thaw period of 1995 and 1996. This study, on what is referred to as the "Classical Plots", was established in 1930 to compare the long term productivity of a wheat/fallow rotation (WF) and a five year rotation consisting of spring wheat, oats, barley underseeded to alfalfa/brome, followed by two years of the hay mixture (WOBHH). Gas measurements were taken on the second hay phase of the WOBHH, and on the wheat stubble of the WF rotation. The hay mixture was plowed in the fall to prepare for the following wheat crop. Two subtreatments, nil (no additions) and amended with cattle manure, were selected from each main treatment. Cattle manure was added at a rate calculated to supply 175 kg N ha^{-1} per rotation cycle on the WOBHH rotation, and 91 kg N ha^{-1} on the WF rotation. Half of the manure addition was added at the end of the oats crop, the other half was added after the second hay crop on the WOBHH rotation. Manure was added once every 5 years to both phases of the

WF rotation. The manure application on both rotations was made on May 10 in 1995, and May 21 in 1996. Juma et al. (1995) reported notable differences in total soil C and N between the treatments on the "Classical Plots" (Table 5-2). The concentrations of total soil C and N in the CT-fertilizer treatment, as reported by Nyborg et al. (1995) in the original study site Breton are included for comparative purposes.

Gas measurements on the "Classical Plots" were taken in the early afternoon on consecutive days during 1995 and alternate days in 1996. Fluxes of N_2O began on March 16 and continued until April 1 in 1995. In 1996, emissions of N_2O began on April 7 and continued until April 18 in 1996.

Frozen soil cores to a depth of 10 cm were taken prior to the 1995 spring thaw from both the original study site and the Classical Plots at Breton. The snow pack was removed from the soil sampling area, and then carefully replaced. The frozen cores were allowed to thaw overnight, then soil mineral N and WSOC were extracted and analyzed as described in chapter 4.

Daily data sets from the Classical Plots were analyzed using t-tests. Daily data sets from the other locations were analyzed as a split plot design using a General Linear Model (SAS Institute, 1987). The original data sets frequently failed the Shapiro-Wilk test of normality (SAS Institute, 1987). After a $\log_{10}$ transformation was applied, 175 of the original 189 daily data sets passed the Shapiro-Wilk test of normality. Final statistical analyses were performed on the transformed data. Estimates of cumulative N_2O-N losses were calculated as described in chapter 3. All but one of the 24 derived data sets (cumulative losses) passed the Shapiro-Wilk test, therefore statistical analyses were performed without data transformation.

5.3 RESULTS

Comparison of N-sources

The Ellerslie site was sampled on six dates in June, twice in July, and once in each of August, September and October during the summer of 1993. A significant interaction between tillage and N source occurred during the early part of the growing season. Ranking the magnitude of N_2O flux from highest to lowest (Tables 5-3 and 5-5) clearly shows the overall trends between sub-treatments at the three sites. N_2O emissions increased markedly from CT, but much less so on ZT, after fertilizer application. The reverse was true for the pea residue amendment.

The fluxes from the CT fertilizer treatment were significantly higher than; (a) all other CT subtreatments on June 16, 19 and 22; (b) than the CT-control, fallow, and manure on June 23 and; (c) CT-fallow, manure and control on July 5, and CT-peas, manure and control on August 11 (Table 5-4). Conversely, N_2O flux from the ZT-fertilizer treatment was not significantly different from other ZT subtreatments except on July 5 when it was significantly higher than ZT-control and manure. Pea residue amended to ZT strongly increased N_2O emissions. Flux from this subtreatment was significantly higher than flux from all other ZT subtreatments throughout June, and higher than the ZT-control and manure on July 5. The influence of pea residue on CT was less strong. Flux from this subtreatment was significantly higher than flux from all other CT-treatments on June 23; and higher than CT-control, fallow and manure on July 5.

Seasonal N_2O-N losses were estimated for each sampling location (replication) as described in chapter 3. In this way several estimates for the same subtreatment were developed, and the new data sets were analyzed as a split-plot design using a General Linear Model (SAS Institute, 1987). The daily trends discussed before were also apparent in the cumulative estimates of N_2O-N loss during the summer of 1993 at Ellerslie. Total N_2O-N losses from CT were ranked in the order of CT-fertilizer > CT-pea residue > CT-manure > CT-fallow > CT-control (Table 5-7), the difference between CT-fertilizer and CT-fallow and CT-control being statistically significant. The ranking order for cumulative N_2O-N losses from the ZT treatment were ZT-pea residue > ZT-fertilizer > ZT-fallow > ZT-control > ZT-manure. Estimated losses from the ZT-pea residue and ZT-fertilizer were significantly greater than the ZT-control and manure, but were not significantly different from each other.

The response of the main treatments to the N-source subtreatments at Breton was consistent with observations made at Ellerslie. N_2O flux from CT-fertilizer was significantly greater than all other CT subtreatments on June 4 and June 20; than CT-manure and control on July 6; and CT-peas, manure and control on July 24 (Table 5-6). CT-fallow was higher than CT-peas, manure and control on July 24 and all other CT treatments on August 14. Flux from CT-peas was significantly higher than CT-fallow, manure and control on June 4; than CT-fallow and control on June 24; and than CT-manure and control on July 6 and 24. Flux from the ZT-pea residue subtreatment was significantly higher than all other ZT subtreatments on June 4 and July 6. Flux from ZT-fallow was significantly higher than ZT-peas and control on July 24; and all other ZT subtreatments on August 11.

Cumulative seasonal estimates for CT were ranked in the order of CT-fertilizer > CT-fallow > CT-pea residue > CT-manure > CT-control (Table 5-8). The CT-fertilizer, CT-fallow, and CT-pea residue were significantly greater than CT-control and CT-manure. Meanwhile, ZT subtreatments were ranked in the order of ZT-pea residue > ZT-fallow > ZT-manure > ZT-fertilizer > ZT-control. The ZT-pea residue was significantly greater than ZT-fertilizer and ZT-control.

Flux from the CT fertilizer subtreatment at Cooking Lake, was significantly higher than flux from all other subtreatments except CT-peas on June 3 and July 7. Flux from CT-peas was significantly higher than CT-fallow and control on June 3 and CT fallow, manure and control on July 21. Estimates of cumulative losses are ranked in the order of fertilizer > pea residue > manure > control > fallow (Table 5-9). Cumulative N_2O-N losses from the fertilizer and pea residue treatments were significantly greater than from the other subtreatments, with the fertilizer treatment also being significantly greater than the pea residue treatment.

Trends between the fertilizer, fallow, and control subtreatments during the summer of 1994 and 1995 were clear and generally consistent with results from 1993. There were no significant differences between subtreatments at any site prior to fertilization. Between seeding (June 3) and mid-July at Ellerslie, fluxes were higher on CT-fertilizer compared to CT-fallow and CT-control on 7 of 9 sampling dates (2 days significant $p < 0.10$) in 1994, and 6 of 7 sampling dates (4 dates significant $p < 0.10$) in 1995. Breton was only sampled once during this time period in 1994, and three times in 1995. On all 4 sampling dates, N_2O emissions from CT-fertilizer was significantly greater than either CT-fallow or CT-control. Trends on the ZT treatments were almost identical to CT at Ellerslie, however the differences noted at Breton were not significant.

Ranking of estimated cumulative losses for Ellerslie in 1994 was as follows; CT-fertilizer > CT-control > CT-fallow (Table 5-7). Losses of N_2O-N from CT-fallow and CT-control were not significantly different from each other, however the CT-fertilizer treatment was significantly higher than both. The ZT subtreatments were ranked as follows: ZT-fertilizer > ZT-fallow > ZT-control. Loss of N_2O-N from ZT-fertilizer was significantly different from ZT-control. In 1995 the rankings were: CT-fertilizer > CT-fallow > CT-control and ZT-fertilizer > ZT-fallow > ZT-control. Losses of N_2O-N from CT-fertilizer and CT-fallow were significantly different from CT-control but not from each other. Losses of N_2O-N from ZT-fertilizer and ZT-fallow were significantly different from ZT-control but not from each other.

Cooking Lake was sampled 9 times during this same time period (early June to mid-July) in 1994, on 7 dates the fertilizer treatment had the highest flux, however the difference was only significant on 2 occasions. In general the control tended to be lowest, followed by fallow and then fertilizer but the differences were rarely statistically significant. The daily trends were born out in the estimates of cumulative losses for the season. The fertilizer treatment had the greatest losses followed by fallow and then control (Table 5-9), but the differences were not statistically significant. No measurements were made at Cooking Lake during the summer of 1995.

Comparison of Zero and Conventional Till

Pairwise comparisons (e.g., ZT-fertilizer vs. CT-fertilizer) revealed that the trend noted in 1993 for CT-fertilizer to be greater than ZT-fertilizer was consistent in 1994 (Fig. 5-2) and 1995 (not shown). No consistent trend was apparent for the fallow and control subtreatments in 1993 (Fig. 5-1) or 1995, but in 1994 (Fig. 5-2) both subtreatments showed higher fluxes on the CT compared to ZT treatment.

The Ellerslie site was sampled on 11 days spaced over the summer of 1993. On eight of those occasions the overall flux from all subtreatments on CT was greater than from ZT, the difference being significant at $p < 0.10$ on two occasions. When this comparison was made on cumulative estimates, the N_2O-N loss from ZT was greater than CT but the difference was not significant. At Breton, 4 out of 6 sampling days had higher overall fluxes from CT with only one date being significant. However, when the comparison is made on estimates of cumulative losses, ZT plots emitted significantly more N_2O ($p < 0.10$) than CT plots. In 1994 and 1995, the majority of sampling dates showed higher overall fluxes from the CT treatments, although the differences were rarely significant. Sampling was not intense enough to justify developing estimates of cumulative losses from ZT subtreatments at Breton in either 1994 or 1995.

Comparisons at Ellerslie in 1995 were similar to Breton, with 7 out of 11 sampling days having higher overall fluxes from the CT treatment, none of the differences being significant. In 1994, 26 out of 30 sampling dates had higher overall fluxes from the CT treatment, with 17 of those instances being significant ($p < 0.10$). Estimated cumulative N_2O-N losses from CT were virtually equal to ZT in 1995, but were significantly ($p < 0.05$) higher than ZT in 1994.

Spring Thaw Event

The 1993 spring thaw at Ellerslie lasted about ten days. Mean flux was greatest from CT on 7 out of 10 days. The difference between CT and ZT was significant ($p < 0.1$) on three sampling times, with CT being higher two of the three times. These trends were repeated almost identically in the spring of 1994. Positive fluxes were recorded on ten days, the mean flux on seven of those days was greatest from CT plots, with 4 of the occasions being statistically significant. Positive fluxes were recorded for 20 days during the spring of 1995, on 17 of those days the mean flux was greatest from CT, 9 of these occasions being significant ($p < 0.1$)

Estimated losses of cumulative N_2O-N from ZT and CT during spring thaw 1993 at both sites showed CT to be greater than ZT but the difference was not significant. Estimates of cumulative N_2O-N from ZT and CT during spring thaw 1994 were virtually equal. When the same comparison was made for the 1995 spring thaw, CT was found to be significantly greater than ZT ($p < 0.10$).

The Breton site was sampled on alternate days during the spring of 1993 and 1994 and on consecutive days during 1995. Samples were taken on a total of four days in 1993, the mean flux was highest on CT for all four days, with the difference on two of the days being significant. In 1994 the site was sampled on six days. Mean flux was highest from CT on 3 days, two of those days being significant ($p < 0.1$), however two other days showed significantly higher flux from ZT. In 1995 a total of 15 days were sampled, mean flux was highest on CT for all but one of those days, with three days being significant.

Soil concentrations of NO_3^- and NH_4^+ in frozen soil cores taken prior to spring thaw, were significantly higher in the WBOHH rotation than in the WF rotation or the CT-fertilized treatment from the original study at Breton, included here for comparative purposes (Table 5-10). No significant difference was noted for WSOC. Emissions from the WF and WF+manure treatments were very similar to fluxes from the original study at Breton. Intense fluxes were measured on the WOBHH rotation in 1995 and 1996. The WOBHH rotation had significantly greater fluxes on 14 of the 15 sampling dates in 1995, and 5 out of 7 sampling dates in 1996. Estimated cumulative N_2O-N losses were significantly higher from the WOBHH treatments compared to WF treatments (Table 5-11).

5.4 DISCUSSION

In general, all N source treatments tended to increase N_2O emissions during the growing season as compared to the control subtreatment. However, cumulative estimates of N_2O-N loss from the manure subtreatment was either equal to or only marginally higher than the control. The fertilizer subtreatment increased N_2O-N emissions consistently during the growing season, however the differences were less noticeable when annual estimates, which included spring thaw values, were compared. With the exception of the fallow subtreatment, no significant differences between N sources were apparent during spring thaw. The estimated annual N_2O-N loss from fertilizer subtreatment minus the estimated N_2O-N loss from the control subtreatment was assumed to represent the N loss due to fertilizer application. At Ellerslie this value was 2% of applied N for both CT and ZT in 1993/1994, but was only 0.2% for CT and 0.7% for ZT in 1994/1995. The values for Breton were 1% on CT in both years, but 0% on the ZT in 1993/1994. No estimate is available for ZT in the 1994/1995 year. The values calculated for Cooking Lake were 0% and 0.1% in the respective years. These results are consistent with values reported in the literature (Eichner, 1990).

Comparisons of N_2O-N emissions by tillage regime in this study indicate either no difference or losses of N_2O-N to be greater from CT compared to ZT. The one exception was at the Breton site in 1993 where cumulative losses of N_2O-N during the summer were significantly higher from the ZT treatment. The strong response of ZT-pea residue subtreatment was the determining factor. When the same analysis was run excluding the pea residue subtreatments, there was no significant difference in the cumulative estimates. Losses of N_2O-N from CT were consistently greater than ZT during the spring thaw period, which represents a major portion of annual N_2O-N loss for the regions under study. These results contrast results from studies at other locations (Aulakh et al., 1984; Burford et al., 1981; Linn and Doran, 1984).

Cumulative N_2O-N losses during the 1995 and 1996 spring thaw from the WF rotation were comparable to losses previously reported for the Breton site in this study, but losses of N_2O-N from the WOBHH rotation were significantly greater and not dissimilar to losses at Ellerslie and Cooking Lake (Table 5-11). The notably higher mineral N concentrations in the WOBHH treatment (Table 5-10) support the hypothesis that available N is a primary factor controlling N_2O-N emissions during the spring thaw event in the Boreal and Parkland region of Alberta.

5.5 CONCLUSIONS

Fertilizer, fallow, and pea residue all increased N_2O-N losses on an annual basis when compared to control. Manure did not increase losses of N_2O-N at the rates of application used in this study. Losses of fertilizer N as N_2O ranged from 0 to 2%. Higher soil concentrations of mineral N were observed in fall plow down of second year hay stubble in a WOBHH rotation. Significantly higher losses of N_2O-N occurred on this treatment during the following spring thaw when compared to wheat stubble on a WF rotation. This tends to support the hypothesis that available N is a primary control on N_2O emission during spring thaw.

A statistically significant interaction between tillage regime and N source occurred, with losses of N_2O-N being more strongly increased by pea residue amendment on ZT than on CT during the summer season. Conversely, urea fertilizer increased N_2O-N losses from CT more strongly than from ZT. Excluding the pea residue amendment, annual losses of N_2O-N from CT were either equal to or greater than ZT, particularly during the spring thaw event.

Table 5-1. Treatments monitored for N_2O emissions from spring 1993 to summer 1995 at Ellerslie, Breton, and Cooking Lake.

	Spring 1993	Summer 1993	Spring 1994	Summer 1994	Spring 1995	Summer 1995
Conv. Till	urea	urea	urea	urea	urea	urea
	fallow	fallow	fallow	fallow	fallow	fallow
	-	pea residue	pea residue	urea	-	-
	-	manure	manure	urea	-	-
	-	control	control	control	control	control
Zero Till[†]	urea	urea	urea	urea	urea	urea
	fallow	fallow	fallow	fallow	fallow	fallow
	-	pea residue	pea residue	urea	-	-
	-	manure	manure	urea	-	-
	-	control	control	control	control	control

[†] No zero till treatment present at the Cooking Lake site.

Table 5-2. Soil C and N concentrations in the surface 15 cm of a CT-fertilizer treatment at Breton, and selected treatments from the "Classical Plots" also at Breton.

Treatment	Total Organic C	Total N
	g kg^{-1}	g kg^{-1}
CT-fertilizer	16.26	1.40
WF	7.50	0.64
WF+manure	8.20	0.82
WOBHH	10.3	0.95
WOBHH+manure	21.10	1.78

Table 5-3. Within treatment ranking (1 = highest) of N_2O-N fluxes from subtreatments on selected dates at Ellerslie during the summer in 1993.

	June 16	June 19	June 22	June 23	June 24	June 25	July 5	July 20	August 11
Conv. Till									
fertilizer	1	1	1	2	2	1	2	2	1
fallow	3	3	3	4	5	5	3	1	2
peas	4	5	4	1	1	3	1	5	3
manure	5	4	2	3	4	2	4	4	4
control	2	2	5	5	3	4	5	3	5
Zero Till									
fertilizer	5	3	5	5	3	3	1	2	2
fallow	3	5	4	4	5	4	3	3	1
peas	1	1	1	1	1	1	2	1	5
manure	4	2	2	2	4	5	4	5	4
control	2	4	3	3	2	2	5	4	3

Table 5-4. Geometric means of N_2O-N flux measured at early afternoon for selected dates at Ellerslie during the summer in 1993.

	June 16	June 19	June 22	June 23	June 24	June 25	July 5	July 20	Aug 11
	$\mu g\ N\ m^{-2}\ h^{-1}$								
Conv. Till									
fertilizer	31 a[†]	13 a	17 a	9 b	36 ab	162 a	191 a	12 a	19 a
fallow	13 b	4 b	7 bc	3 d	15 b	43 c	65 bc	12 a	8 ab
peas	11 b	2 b	5 bc	23 a	63 a	132 ab	195 a	6 a	5 b
manure	9 b	3 b	10 ab	6 c	25 b	138 a	45 c	10 a	4 b
control	14 b	4 b	3 c	2 d	34 ab	74 bc	26 d	10 a	4 b
Zero Till									
fertilizer	6 b	3 b	4 b	2 c	47 bc	44 b	191 a	6 a	6 b
fallow	7 b	0 c	4 b	7 b	14 d	31 b	100 ab	5 a	30 a
peas	20 a	14 a	16 a	62 a	148 a	245 a	138 ab	9 a	3 b
manure	6 b	5 b	6 b	16 b	19 cd	22 b	65 bc	4 a	4 b
control	9 b	2 bc	5 b	9 b	81 ab	49 b	36 c	5 a	4 b

[†] Values in columns within treatments followed by the same letter are not significantly different ($P < 0.1$).

Table 5-5. Within treatment ranking (1 = highest) of N_2O-N fluxes from subtreatments on selected dates at Breton and Cooking Lake during the summer in 1993.

	Breton					Cooking Lake				
	June 4	June 20	July 6	July 24	Aug 14	June 3	June 19	July 7	July 21	Aug 13
Conv. Till										
fertilizer	2	1	2	2	4	1	1	2	1	4
fallow	3	4	3	1	1	5	5	4	5	2
peas	1	3	1	5	3	2	2	1	2	3
manure	4	2	4	3	5	3	3	3	3	5
control	5	5	5	4	2	4	4	5	4	1
Zero Till										
fertilizer	5	3	2	2	4	-[†]	-	-	-	-
fallow	2	5	3	3	1	-	-	-	-	-
peas	1	1	1	5	5	-	-	-	-	-
manure	3	2	4	1	2	-	-	-	-	-
control	4	4	5	4	3	-	-	-	-	-

[†] Not applicable at this site

Table 5-6. Geometric means of N_2O-N flux measured at early afternoon for selected dates at Breton and Cooking Lake during the summer in 1993.

	Breton					Cooking Lake				
	June 4	June 20	July 6	July 24	Aug 14	June 3	June 19	July 7	July 21	Aug 13
	$\mu g\ N\ m^{-2}\ h^{-1}$									
Conv. Till										
fertilizer	8 a[†]	19 a	4 ab	19 a	2 b	19 a	8 a	25 a	28 a	0 a
fallow	1 b	6 c	2 bc	20 a	14 a	2 b	2 a	4 b	10 b	2 a
peas	9 a	8 bc	8 a	5 c	3 b	15 a	6 a	28 a	19 ab	2 a
manure	1 b	10 b	1 c	6 b	2 b	7 b	6 a	5 b	15 ab	0 a
control	1 b	6 c	0 c	6 b	3 b	4 b	5 a	4 b	15 ab	3 a
Zero Till										
fertilizer	4 b	7 ab	2 b	12 ab	1 a	-[‡]	-	-	-	-
fallow	6 b	6 b	1 b	10 bc	1 a	-	-	-	-	-
peas	24 a	10 a	16 a	3 c	1 a	-	-	-	-	-
manure	6 b	7 ab	1 b	25 a	4 a	-	-	-	-	-
control	5 b	7 ab	1 b	5 c	3 a	-	-	-	-	-

[†] Values in columns followed by the same letter are not significantly different ($P < 0.1$).

[‡] Not applicable at this site.

Table 5-7. Estimates of seasonal and annual cumulative N_2O-N loss from various treatments at Ellerslie.

	Spring 1993	Summer 1993	Spring 1994	Total[†]	Summer 1994	Spring 1995	Total[†]	Summer 1995
	kg N ha^{-1}							
Conv. Till								
fertilizer	0.5 a[‡]	1.5 a	0.1 a	1.7 a	0.7 a	1.8 a	2.5 a	0.5 a
fallow	0.6 a	0.6 b	0.1 a	0.7 b	0.2 b	2.6 a	2.8 a	0.4 a
peas	-	1.0 ab	0.1 a	1.2 ab	-	-	-	-
manure	-	0.6 ab	0.1 a	0.8 ab	-	-	-	-
control	-	0.5 b	0.1 a	0.6 b	0.4 b	2.0 a	2.4 a	0.1 b
Zero Till								
fertilizer	0.3 a	1.4 a	0.2 a	1.7 a	0.4 a	0.4 a	0.8 ab	0.5 a
fallow	0.4 a	0.9 ab	0.1 b	1.1 ab	0.3 a	0.7 a	1.1 a	0.4 a
peas	-	1.5 a	0.1 b	1.6 a	-	-	-	-
manure	-	0.5 b	0.1 b	0.6 b	-	-	-	-
control	-	0.5 b	0.1 b	0.6 b	0.1 b	0.3 a	0.4 b	0.2 b

[†] Total of spring and previous summer's estimates.

[‡] Values in columns followed by the same letter are not significantly different ($P < 0.1$).

Table 5-8. Estimates of seasonal and annual cumulative N_2O-N loss from various treatments at Breton.

	Spring 1993	Summer 1993	Spring 1994	Total[†]	Summer 1994	Spring 1995	Total[†]
				kg N ha^{-1}			
Conv. Till							
fertilizer	0.1 b[‡]	0.3 a	0.0 b	0.4 a	0.7 a	0.2 a	0.9 a
fallow	0.4 a	0.3 a	0.1 b	0.3 a	0.2 b	0.2 a	0.4 b
peas	-	0.3 a	0.1 a	0.4 a	-	-	-
manure	-	0.1 b	0.1 a	0.2 b	-	-	-
control	-	0.1 b	0.0 b	0.1 b	0.0 b	0.3 a	0.4 ab
Zero Till							
fertilizer	0.1 a	0.2 b	0.0 a	0.2 b	-	0.2 a	-
fallow	0.1 a	0.3 ab	0.0 a	0.3 ab	-	0.2 a	-
peas	-	0.4 a	0.1 a	0.5 a	-	-	-
manure	-	0.3 ab	0.1 a	0.3 ab	-	-	-
control	-	0.1 b	0.0 a	0.2 b	-	0.1 a	-

[†] Total of spring and previous summer's estimates.

[‡] Values in columns followed by the same letter are not significantly different ($P < 0.1$).

Table 5-9. Estimates of seasonal and annual cumulative N_2O-N loss from various treatments at Cooking Lake.

	Spring 1993	Summer 1993	Spring 1994	Total[†]	Summer 1994	Spring 1995	Total[†]
				kg N ha^{-1}			
Conv. till							
fertilizer	0.8 b[‡]	0.6 a	0.3 ab	0.9 a	0.7 b	1.3 b	2.0 a
fallow	3.6 a	0.1 c	0.3 ab	0.4 b	0.5 b	3.5 a	4.0 b
peas	-	0.5 b	0.3 ab	0.8 ab	-	-	-
manure	-	0.2 c	0.1 b	0.3 b	-	-	-
control	-	0.2 c	0.7 a	0.9 ab	0.5 b	1.4 b	1.9 a

[†] Total of spring and previous summer's estimates.

[‡] Values in columns followed by the same letter are not significantly different ($P < 0.1$).

Table 5-10. Concentrations of NO_3^-, NH_4^+, and WSOC in samples of frozen soil taken prior to the 1995 spring thaw from CT-fertilizer treatment at Breton, and selected treatments on the "Classical Plots" also at Breton.

	NO_3^--N	NH_4^+-N	WSOC
		mg kg^{-1}	
CT-fertilizer	4 b[†]	3 a	60 a
WF	1 b	3 a	13 a
WF + manure	5 b	5 a	24 a
WOBHH + manure	25 a	11 a	35 a

[†] Values in columns followed by the same letter are not significantly different ($P < 0.1$).

Table 5-11. Estimated loss of N_2O-N from selected treatments on Classical Plots at Breton.

	Spring 1995	Spring 1996
	kg N ha^{-1}	
WF	0.0 b[†]	0.0 b
WF + manure	0.0 b	0.0 b
WOBHH	na[‡]	1.2 a
WOBHH + manure	1.5 a	1.6 a

[†] Values in columns followed by the same letter are not significantly different ($P < 0.1$).

[‡] no measurements taken in this year.

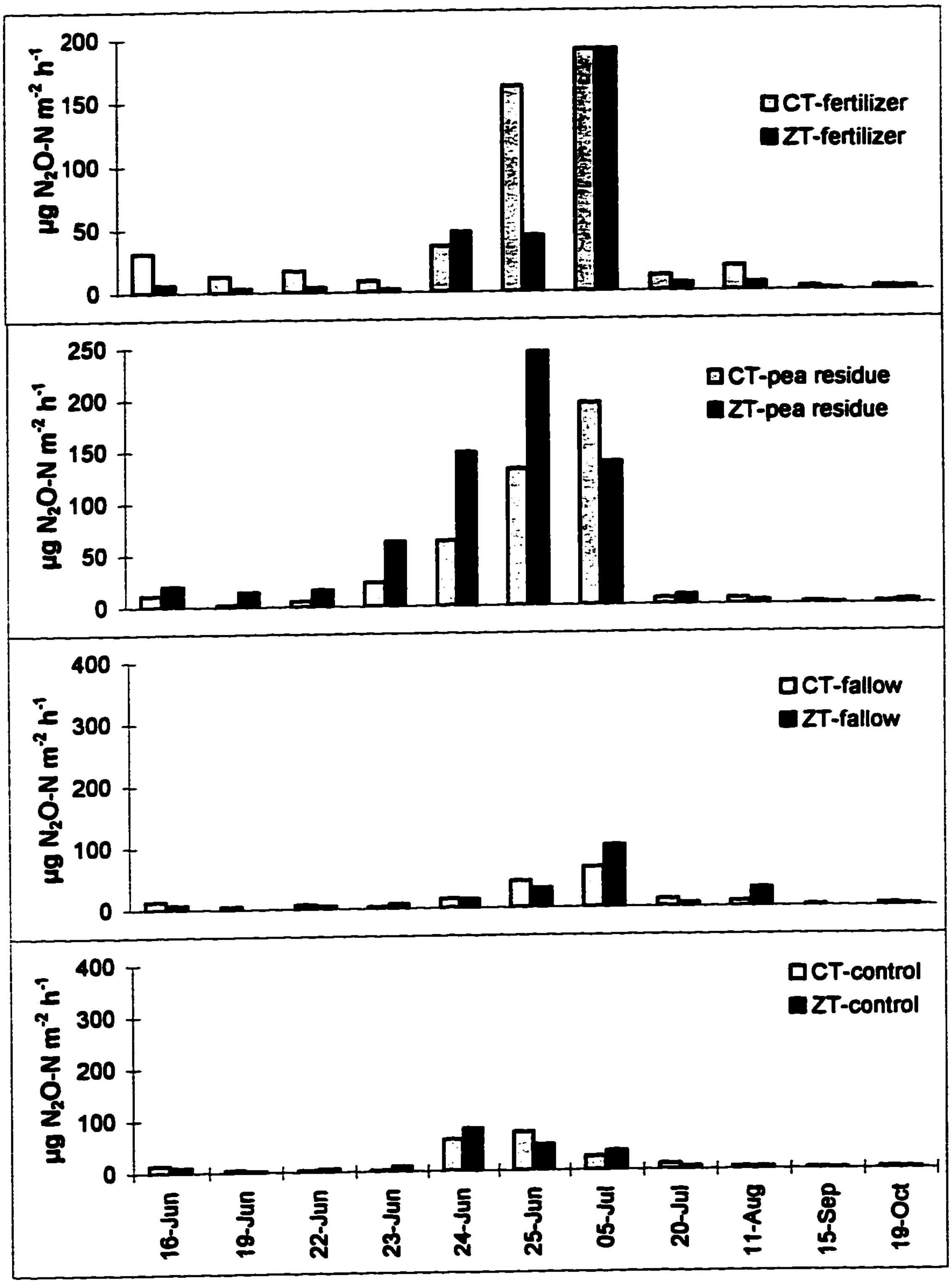

Figure 5-1. Geometric mean N_2O-N flux measured at early afternoon from selected treatments at Ellerslie during the summer of 1993.

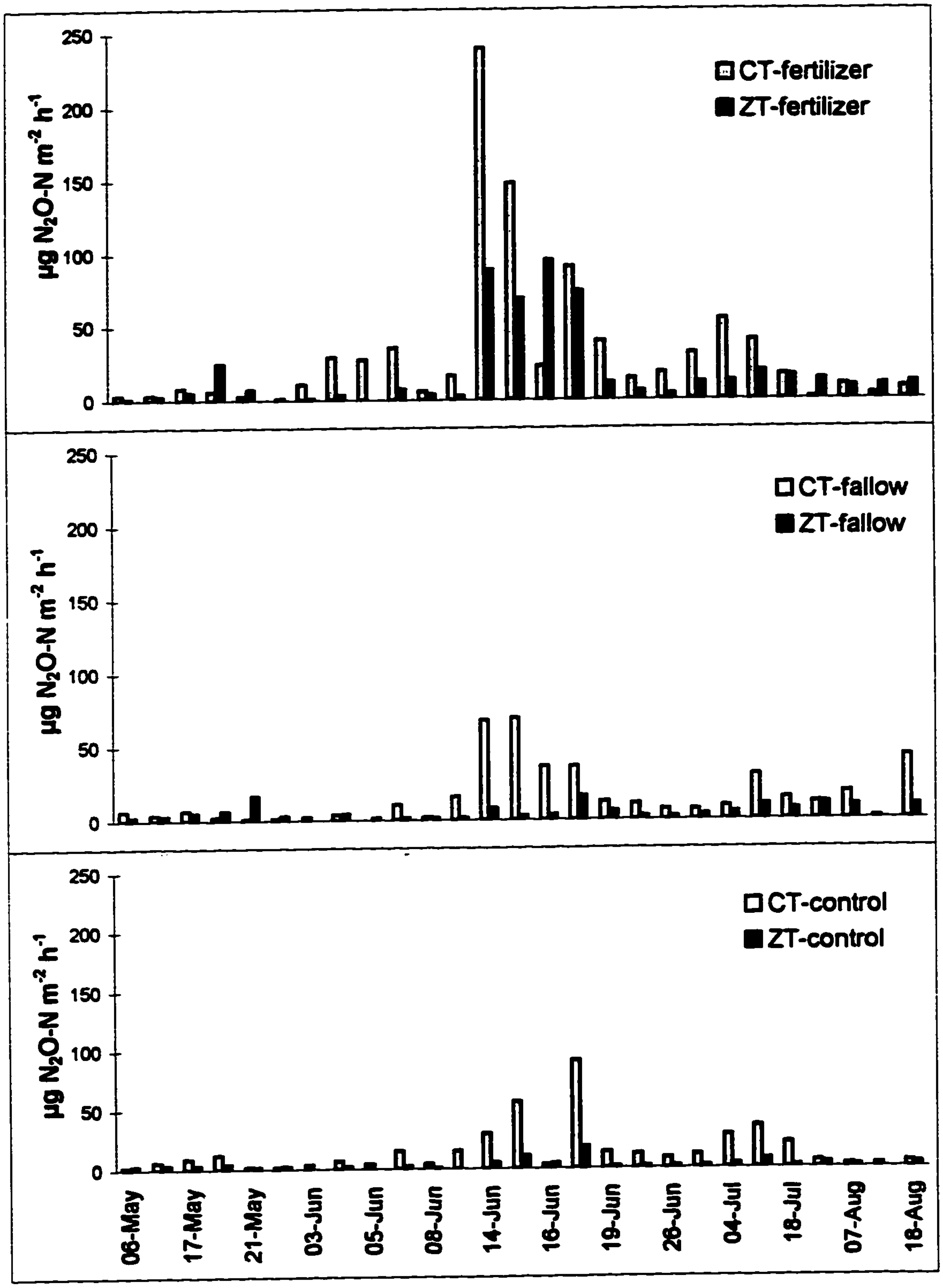

Figure 5-2. Mean N2O-N flux measured at early afternoon from selected treatments at Ellerslie during the summer of 1994.

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CHAPTER 6

A test of DNDC's ability to simulate N_2O fluxes from Boreal and Parkland agroecosystems

6.1 INTRODUCTION

The contribution of atmospheric nitrous oxide (N_2O) from agricultural soils needs to be accurately quantified to reduce uncertainties in global N_2O budgets, and to facilitate the development of mitigation strategies. The occurrence and rate of N_2O emission from agricultural soil is governed by a complex interaction of factors, most importantly soil water content, temperature, and the availability of carbon and nitrogen. The episodic nature of N_2O emissions measured in the field reflects the transient status of the principle controlling variables. Practical considerations generally limit field studies to periodic measurements, therefore the reliability of estimated seasonal or annual N_2O-N loss developed from such data is unclear.

A simulation model could facilitate temporal integrations, and be a useful predictive tool for investigating the influence of changing management and/or climate scenarios. Recent field investigations have provided insight into the controls operating on N_2O emissions from soils in the Boreal and Parkland regions. In chapter 4, I found that soil water content and mineral N cycling could explain up to 80% of temporal variability in soil-emitted N_2O from field plots. The respective rates of N_2O emissions were strongly influenced by the addition of nitrogen fertilizer and to a lesser extent by the tillage regime. These findings were consistent with similar studies (van Kessel, 1993; Aulakh et al., 1984) conducted in western Canada.

Li et al. (1992a) have developed and tested a process-oriented simulation model of carbon and nitrogen biogeochemistry in agricultural ecosystems. The hypothesis underpinning the DeNitrification-DeComposition model (DNDC) appears consistent with the insights gained from field studies in the regions under consideration. DNDC couples four interacting submodels. A thermal-hydraulic submodel calculates soil temperature and moisture profiles and soil water fluxes from air temperature and precipitation data and soil texture. A decomposition submodel calculates daily decomposition, nitrification, ammonia volatilization and soil microbial respiration. A plant growth sub-model calculates daily root respiration, as well as water and N utilization. The denitrification sub-model calculates hourly N_2O and N_2 production during periods when water-filled pore space is greater than 40%. The required inputs include pertinent management variables such as fertilizer N application, tillage operations, and crop selection. The model has performed well under a variety of soil-climate-management scenarios (Li et al., 1992b; Li et al., 1994), but has not been tested for conditions that prevail in the Alberta Boreal or Parkland regions.

There were two objectives for this study. Firstly, to test the DNDC simulation model's ability to capture seasonal N_2O emission patterns. Secondly, to compare the annual N_2O-N losses calculated by the model to annual N_2O-N losses estimated from field measurements.

6.2 MATERIALS AND METHODS

Computer simulations using the DNDC model (version 5.8) were run for three sites, Breton, Ellerslie and Cooking Lake, all within a 110 km radius of Edmonton, Alberta (53° 23'N, 114° 22'W). Two treatments, urea added and control (no N added), were chosen at each site. The urea treatment at Ellerslie and Breton received 56 kg N ha^{-1} y^{-1}, while Cooking Lake received 100 kg N ha^{-1} y^{-1}. All treatments were managed as conventional till under continuous spring wheat. Seeding, harvesting, and tillage dates are provided in Table 6-1. Plots were tilled with a rotovator to a depth of 10 cm, therefore a chisel cultivator tillage option was selected as the closest substitute provided by the DNDC model.

Simulations were run on urea treatments at each site in 1993 and 1994, and on the control treatments for 1994 only. Default values (background NH_3, optimum crop yield, SOC partitioning) were selected in all cases. To facilitate comparisons, initial values that were considered realistic for the study were selected and kept uniform for all simulations. Initial soil temperature was set at -5°C, soil moisture (WFPS) was set at 55%, while NO_3^- and NH_4^+ concentrations were each initialized at 5 mg N kg^{-1}.

Site-specific soil properties required as inputs are provided in Table 6-2. Ellerslie and Breton sites are equipped with meteorological stations allowing weather files (mean daily precipitation and air temperature) to be prepared for input. Similar data were not available for the Cooking Lake site, but in view of its proximity (20 km) to Ellerslie, the same weather files were employed.

Field values of N_2O emissions, soil concentrations of mineral N, WSOC, and soil temperature were extracted from previously collected data sets. Gas sampling and analysis procedures are described in appendix A. Gas sampling schedules, methodology for estimating seasonal and annual N_2O-N loss, mineral N and WSOC analysis, and soil temperature determinations were described in chapters 3 and 4.

6.3 RESULTS AND DISCUSSION

The temporal distribution of N_2O flux predicted by DNDC was similar in both years and at both sites (Fig. 6-1) Low but continuous emissions were predicted from Day 1 to Day 80 with higher spikes closely mimicking soil temperature fluctuations (Fig. 6-2). Simulated mean daily soil temperatures hovered near 0°C while air temperatures remained sub-zero, but quickly peaked into the thawing range as air temperatures surpassed 0°C. Measured mean daily soil temperatures however, did not surpass 0°C at any point in this same time period. Similarly, no N_2O fluxes were measured in the field prior to approximately Day 80, the point at which soil temperatures surpassed 0°C. This disparity between measured and modeled soil temperatures might explain the differences in temporal distributions of measured and modeled N_2O flux during this time.

Notably, simulated daily N_2O-N loss integrated from Day 1 to Day 120 (Jan 1 - April 30) fell within one unit of standard error of the field-based estimate for N_2O-N loss during spring thaw at Ellerslie in 1993 and 1994, and at Cooking Lake in 1994 (Table 6-3). It has been hypothesized that over-winter N transformations within the soil profile generates N_2O (Malhi and Nyborg, 1986; Burton and Beauchamp, 1994) which is trapped below the overlying frozen soil. This N_2O is then released as the soil surface thaws during the following spring. The intense surface emissions measured during spring thaw would be a reflection of both current production, and the magnitude of over-winter production. The model also predicts over-winter N_2O production, but indicates that this N_2O is immediately emitted from the soil surface rather than being trapped until the soil thaws in spring.

The most intense fluxes predicted by DNDC appeared to be triggered by cultivation and fertilizer application events occurring around Day 130 in both 1993 and 1994. Fluxes of similar intensity were measured in the field, but not until Day 170 in 1993 and Day 160 in 1994. In both cases field fluxes were strongly associated with precipitation events. DNDC predicted similar losses of N_2O-N each year at any given site. In the summer of 1993, cumulative N_2O-N loss predicted by DNDC at Ellerslie fell within one unit of standard error of the field-based estimate. Simulated losses were higher than field-based estimates by a factor of 4 at Breton, and a factor of 2.5 at Cooking Lake. For the summer of 1994, simulated and field-based estimates at Breton were very similar (within unit of standard error). Simulated losses were higher than field-based estimates by a factor of 3 at Ellerslie, and a factor of 2.5 for Cooking Lake (Table 6-3).

Estimates based upon field measurements indicate N_2O-N losses at Cooking Lake and Ellerslie were similar, and greater than those at Breton. As well, field measurements indicate losses of N_2O-N during the summer were lower on control compared to urea treatments. Both of these trends were captured by the DNDC model.

The temporal trends observed in measured soil mineral N concentrations at Ellerslie in 1993 were captured by the model (Table 6-4). Magnitudes cannot be compared directly as field measured values are based upon a depth of 10 cm compared to a depth of 15 cm for the model. In 1994, a notable divergence can be observed between the temporal pattern of field measured and simulated NO_3^- concentrations. Field values remained high through to the end of September at both Ellerslie and Cooking Lake, while DNDC predicted very low values (Table 6-4). As well, differences can be observed between modeled dissolved organic C (DOC) and measured water soluble organic C (WSOC). While the magnitudes of DOC and WSOC cannot be compared, the seasonal trends should be related. DNDC predicted DOC levels during September of 1994 that were similar to those in June, while field measured WSOC values show a considerable decline at both Ellerslie and Cooking Lake.

Field measurements indicated that emissions of N_2O from October to December were negligible, however DNDC predicted 0.3 kg ha^{-1} of N_2O-N loss at Ellerslie in 1993 and 1994, and at Cooking Lake in 1994 during this time period. Some of this discrepancy may be explained by the notably warmer soil temperatures simulated by DNDC. While field-measured mean daily soil temperatures dropped to -5 °C by the end of December, simulated soil temperatures remained at or above 0 °C.

6.4 CONCLUSIONS

Marked differences between the temporal distribution of field measured and modeled N_2O flux were noted during January to April and October to December. Warmer simulated soil temperatures may have accounted for some of the discrepancy in both instances. Higher levels of available C predicted by the model during the fall period may have also been a contributing factor. While the temporal distribution of simulated and measured N_2O flux differed during January to April, the cumulative N_2O-N loss simulated for this period agreed well with estimates based upon field measurements. The magnitude of field measured and simulated fluxes during the summer were comparable, although field measured values occurred somewhat later in the season than those predicted by DNDC. Overall, DNDC predicted higher annual estimates of N_2O-N loss compared to estimates based upon field measurements, however model estimates frequently fell within one unit of the standard error calculated for field based estimates.

Table 6-1. Management data required as input for DNDC simulation runs.

	Ellerslie		Cooking Lake		Breton	
Dates	1993	1994	1993	1994	1993	1994
Seeding	May 24	June 3	May 22	June 6	May 19	June 3
Harvesting	Sept 24	Sept 16	Sept 23	Sept 15	Sept 25	Sept 19
First tillage	May 14	May 6	May 10	May 10	May 13	May 5
Second tillage	Oct 12	Oct 11	Oct 5	Oct 12	Oct 13	Oct 20
Fertilizer application	May 13	May 5	May 9	May 9	May 12	May 4

Table 6-2. Soil parameters required as input for the DNDC model.

	Ellerslie	Cooking Lake	Breton
Clay content (g kg^{-1})	390	220	120
pH	6.0	6.4	6.4
Bulk density (Mg m^{-3})	1.0	1.2	1.3
Soil organic C (g kg^{-1})	55	34	15

Table 6-3. Seasonal and annual losses of N_2O-N estimated from field measurements and calculated by DNDC.

	Spring		Summer		Total	
Site	Field	Model	Field	Model	Field	Model
	kg N ha^{-1}					
			1993 - fertilized treatments			
Breton	0.2 (0.1)[†]	0.4	0.3 (0.2)	1.2	0.4	1.6
Cooking Lake	0.8 (0.1)	0.4	0.6 (0.1)	1.5	1.4	2.0
Ellerslie	0.5 (0.3)	0.5	1.5 (0.8)	1.8	2.0	2.3
			1994 - fertilizer treatments			
Breton	0.1 (0.0)	0.2	0.7 (0.3)	1.0	0.8	1.2
Cooking Lake	0.3 (0.4)	0.4	0.7 (0.1)	1.7	1.0	2.1
Ellerslie	0.2 (0.3)	0.4	0.7 (0.1)	1.9	0.8	2.3
			1994 - control treatments			
Breton	0.0 (0.0)	0.2	0.1 (0.0)	0.8	0.1	1.0
Cooking Lake	0.7 (1.2)	0.4	0.5 (0.0)	1.2	1.2	1.6
Ellerslie	0.1 (0.0)	0.4	0.4 (0.1)	1.5	0.5	1.9

[†] Value in brackets is the standard error of the mean (n = 3).

Table 6-4. Measured and modeled soil parameters from selected dates.

	NO_3^--N		NH_4^+-N		WFPS[†]		WSOC[‡]	DOC[§]
	field[¶]	model	field[¶]	model	field[¶]	model	field[¶]	model
	——— mg N kg^{-1} ———				m^3 m^{-3}		mg C kg^{-1}	kg C ha^{-1}
				1993 - Ellerslie				
June 2	62	35	33	7	45	47	208	4.9
July 5	13	27	9	2	62	57	216	5.3
Aug. 11	2	9	6	1	63	56	302	4.2
Sept. 15	4	1	9	1	61	54	256	3.2
Oct. 19	4	7	3	3	42	42	216	4.1
				1994 - Ellerslie				
June 26-29	63	33	6	2	60	46	186	3.9
Aug. 2-5	24	7	7	1	47	55	158	2.5
Sept. 20-23	16	1	8	1	58	45	130	3.4
				1994 - Cooking Lake				
June 26-29	53	13	4	4	54	54	139	4.1
Aug. 2-5	14	2	6	1	34	52	130	2.7
Sept. 20-23	13	1	5	2	53	52	81	3.8

[†] WFPS = Water Filled Pore Space

[‡] WSOC = Water Soluble Organic Carbon

[§] DOC = Dissolved Organic Carbon

[¶] median values

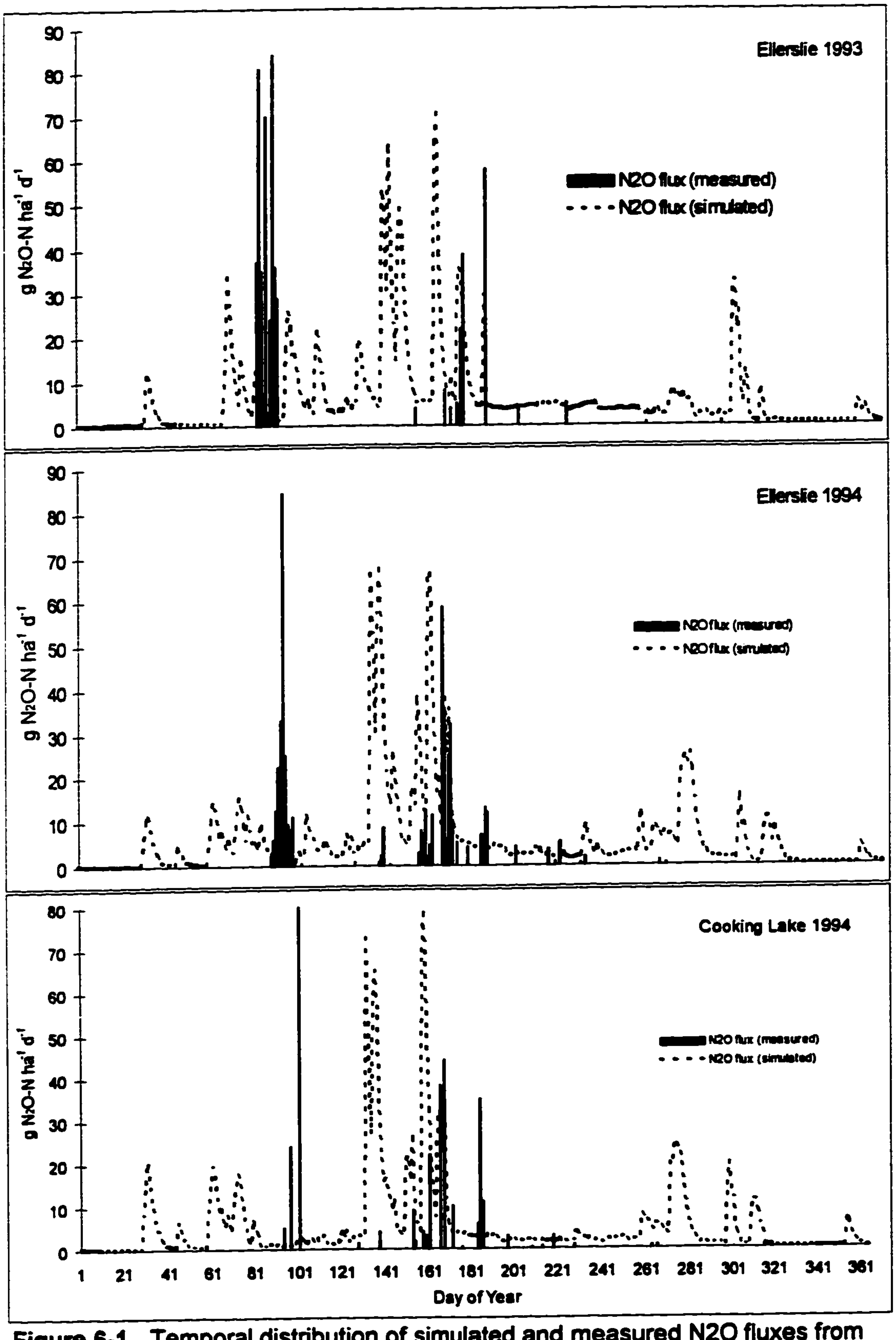

Figure 6-1. Temporal distribution of simulated and measured N2O fluxes from fertilized field plots at Ellerslie in 1993, and Ellerslie and Cooking Lake in 1994.

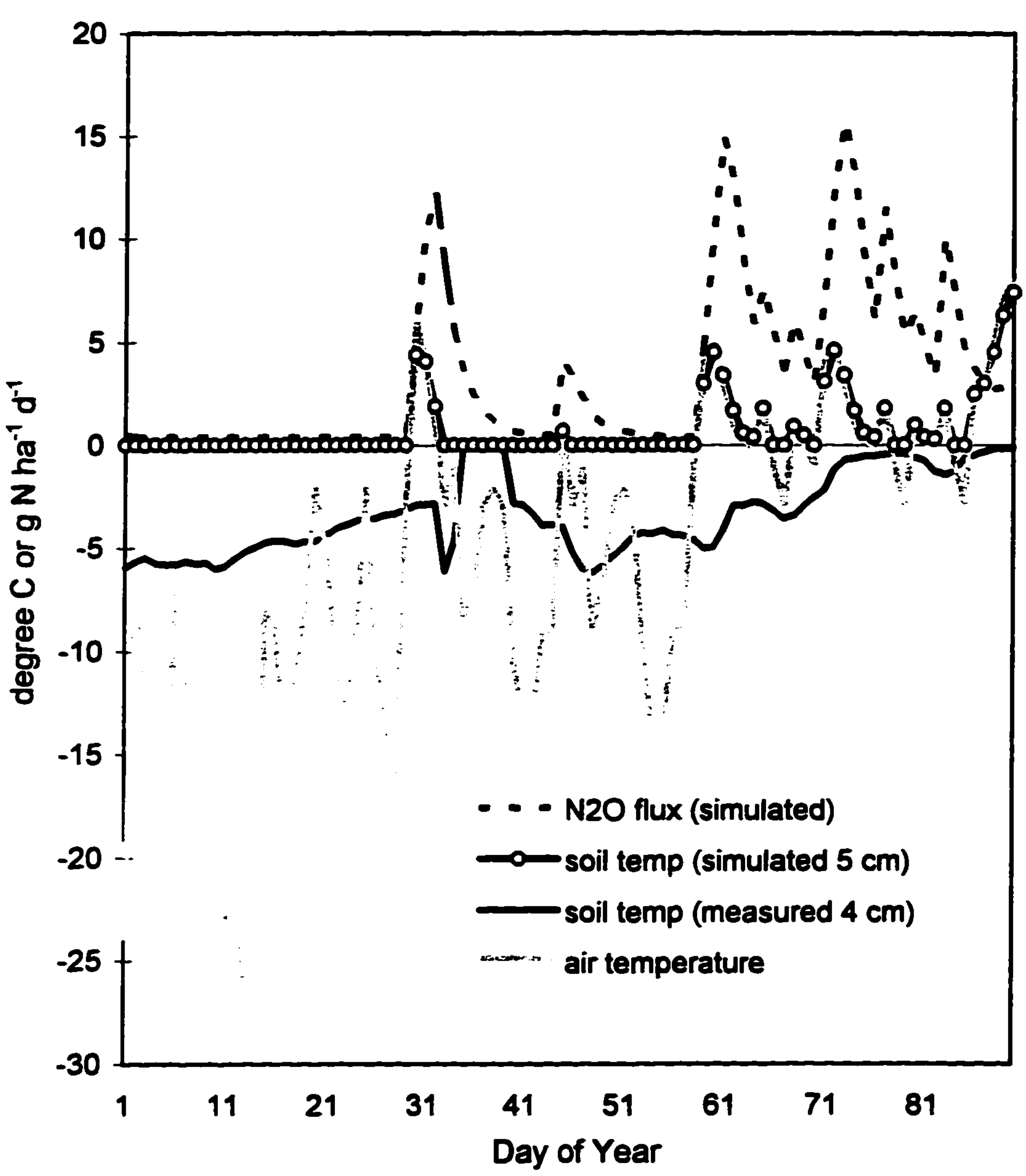

Figure 6-2. Comparison of simulated and measured mean daily soil temperatures, measured air temperature, and simulated N_2O flux from January 1 to March 31 at Ellerslie in 1994.

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CHAPTER 7

Synthesis

7.1 IN PERSPECTIVE

There were five objectives stated for this study. In the next few paragraphs I will recap these objectives, and summarize the major findings pertinent to each. I will then offer some thoughts on future directions.

The first objective was to quantify seasonal emissions of N_2O from selected field plots in the Boreal and Parkland regions of Alberta. The estimates of annual N_2O-N losses from agroecosystems reported here, are the first to be based upon extensive field sampling throughout both the spring and summer seasons in these regions. I estimated annual N_2O-N losses of between 0.1 and 2.4 kg ha^{-1} from control plots in this study. This range is consistent with the base line value of 1.0 kg N_2O-N ha^{-1} suggested for agricultural soils (Cole et al., 1995). The loss of N_2O-N from control plots during the spring thaw period ranged from 0.1 to 2.0 kg ha^{-1}, representing as much as 70% of the total annual N_2O-N loss.

The second objective was to identify the principal controls regulating N_2O emissions at the selected locations. Temperature and water-filled pore space (WFPS) correlated positively but weakly with median daily N_2O emissions. When viewed on an annual basis, however, N_2O fluxes were absent or minimal while soils remained frozen or WFPS remained below approximately 50%. I interpret these values as minimum thresholds that must be surpassed before substantial N_2O emissions occur. Laboratory studies using soil from the Ellerslie site have shown measurable but very slow denitrification and nitrification at temperatures as low as -4°C, with rapid increases in the rate of both at temperatures exceeding 4°C (Malhi and McGill, 1983; Malhi et al., 1990). Rates of denitrification are reported to be negligible below 65% or 70% WFPS (Aulakh and Rennie, 1985; Doran et al., 1990). However, substantial denitrification has been reported at lower water contents due to rapid O_2 depletion in metabolically active soil microsites (Aulakh and Rennie, 1987; Aulakh et al., 1991). Meanwhile, nitrification is generally considered to be maximal at approximately 60% WFPS (Linn and Doran, 1983). Assuming that N_2O measured in this study is a result of both denitrification and nitrification, the 50% WFPS threshold could represent the point beyond which a significant number of anaerobic microsites develop, and nitrification is approaching maximal rates.

There were large differences in magnitudes of annual N_2O-N loss among the sites included in this study. These differences correlated strongly with clay content. This would be logical, assuming annual precipitation and temperature among the sites were comparable, the incidence and duration of WFPS above the lower threshold would be largely determined by differences in soil texture and water flow. Clay content had a stronger influence on the magnitude of N_2O-N loss than did the variability in climatic or management factors included in the study. If annual N_2O-N loss can be indexed to clay content, then this relationship could be an important ingredient for scaling-up techniques.

I also found a strong correlation between fall concentrations of mineral N and cumulative N_2O-N loss during the following spring thaw. This relationship has not been reported previously, although its existence was implied by, and is completely consistent with the over-winter losses of fall applied nitrogen reported for the Boreal and Parkland regions (Heaney et al., 1992; Malhi and Nyborg, 1983). Clay content was not strongly correlated to cumulative N_2O -N loss when the spring thaw event was considered individually. This might be explained by the nature of conditions during spring thaw. As the snow pack melts, WFPS becomes relatively uniform across sites (near saturation) regardless of textural class, and available soil mineral N (particularly NO_3^-) and WSOC emerge as the most important soil factors controlling the variability of cumulative N_2O-N loss during spring thaw.

The third objective was to verify that zero-till soil management induces greater N_2O emissions than conventional-till management under conditions prevailing in the Boreal and Parkland regions. The results from this study do not support the assumption that N_2O-N losses are greater from ZT compared to CT management. Indeed, N_2O-N losses from CT treatments were either equal to or greater than ZT treatments. This trend was particularly clear during the spring thaw event. Based upon the strong correlation between fall mineral N status and cumulative N_2O-N loss during spring thaw discussed earlier, I speculated that differences in mineral N availability might also explain the lower fluxes of N_2O from ZT compared to CT treatments observed during the spring thaw period. Inspection of mineral N concentrations in soil samples taken just prior to spring thaw at Ellerslie in 1995 lends support to this hypothesis (Table 7-1). Soil NO_3^- concentrations in the ZT treatments was significantly lower than CT treatments.

The fourth objective was to evaluate the extent to which urea fertilizer, pea residue, manure, and fallow promote N_2O emissions. Urea fertilizer, fallow, and pea residue all increased

N_2O-N losses on an annual basis when compared to control. Although manure did increase losses of N_2O-N compared to the control, the differences were never significant. A statistically significant interaction between tillage regime and N source occurred, with losses of N_2O-N being more strongly increased by the pea residue amendment on ZT than on CT during the summer season. Conversely, urea fertilizer increased N_2O-N losses from CT more strongly than from ZT.

The last objective was an evaluation of the DNDC model's ability to simulate N_2O emission at the field plot scale in the Boreal and Parkland region. There was considerable divergence between the temporal distributions of N_2O fluxes predicted by the model, and those measured in the field. Field measurements indicated that no N_2O emission events occur during the winter months in the study region. The model, however, predicted several emission events during January, February and early March. As well, field-measured N_2O fluxes during the spring thaw event were higher than simulated emissions by a factor of 2 or 3. Overall, DNDC predicted higher annual estimates of N_2O-N loss compared to estimates based upon field measurements, however model estimates frequently fell within one unit of the standard error calculated for field based estimates. Improvements in the model's ability to correctly represent regional soil temperature regimes would likely translate into a more accurate representation of the timing and magnitude of N_2O emissions in the study region.

7.2 THE FUTURE

- Scaling up methodologies remain a weak link in attempts to quantify N_2O emissions from agroecosystems. Conventional statistical procedures are severely challenged by the tremendous variability inherent in field measurements of N_2O flux, limiting our confidence in comparative studies, and extrapolations over space and time.
- Relationships between sampling technologies using different scales of investigation need to be clarified.
- Tighter matching of N application to crop N uptake is one suggested avenue to reduce N_2O losses. This will require better understanding of N cycling in the cropping systems, and overlaps such areas as site specific management and precision farming. It will also require a better understanding of the processes involved in the production of N_2O. Pursuit of this knowledge is hampered by our inability to partition N_2O arising from nitrification, denitrification, and/or other sources. It is also hampered by our inability to determine the

factors affecting the mole fraction of N_2O in denitrification products, and N_2O/NO_3^- production ratios during nitrification.

- Zero and conservation till managements require further evaluation in terms of their carbon sequestration capability and total greenhouse gas budget.
- Strategies for legume residue management need to be developed. Decisions such as the timing of plow down appear to be critical in terms of N_2O emissions.

Table 7-1. Concentrations of mineral N and water-soluble organic C in frozen soil cores taken prior to 1995 spring thaw at Ellerslie.

Treatment	NO_3^--N	NH_4^+-N	WSOC
	mg N kg^{-1}		mg C kg^{-1}
Zero till - fertilizer[†]	8 b[‡]	7 a	131 a
Zero till - control	3 c	5 a	141 a
Conventional till - fertilizer[†]	12 a	7 a	117 a
Conventional till - control	11 a	7 a	143 a

[†] Plots received urea fertilizer during seeding operations in the previous growing season.

[‡] Values in columns followed by the same letter are not significantly different ($P < 0.1$).

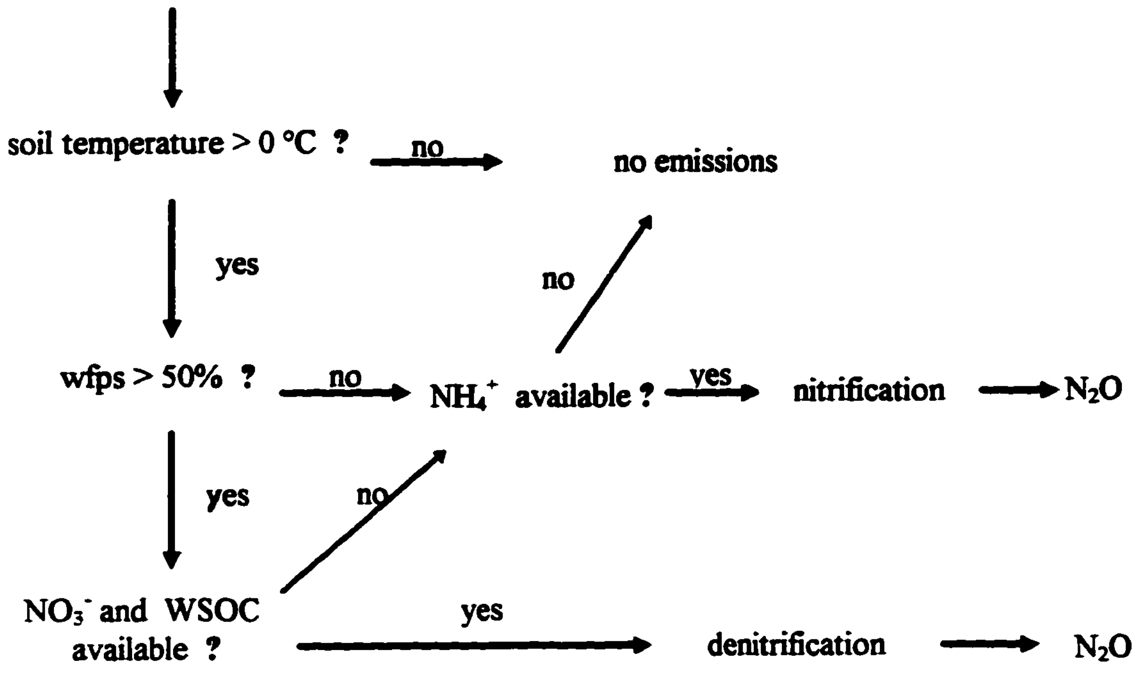

Figure 7-1. Diagram indicating minimal soil conditions required to initiate N_2O emissions in the Boreal and Parkland regions of Alberta.

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APPENDIX A

A.1 SAMPLING PROTOCOL

Vented soil covers built to the specifications described by Hutchinson and Mosier (1981) were selected for sample collection in this study. Soil covers are considered the appropriate measurement technique for process level studies of N_2O emissions (Denmead, and Raupach, 1993; Hutchinson and Livingston, 1993; Ryden et al., 1978). They are simple to use, inexpensive, and mobile. Cost and mobility were of particular importance for the current study. A large number of sites, each having up to ten treatments and requiring replication, necessitated a large inventory of sample collectors. In addition, due to the episodic nature of N_2O emission as many sites as manpower would allow were measured simultaneously, each site requiring a complete "set" of sample collectors. Sample collection was undertaken by numerous field technicians, therefore the simplicity of the technique was also an important consideration.

The soil covers were inserted 3 cm into the soil surface in an inter-row position. The timing of their placement was staggered to ensure that all covers were on the soil for an equal period of time. A gas sample was drawn from the headspace after a 60 min. using a disposable 30 ml syringe. The syringe was filled to maximum capacity (ca. 32 mL) and injected into a 22 mL vacutainer, creating a positive pressure. Time zero concentrations were approximated by an average of ambient air samples taken 15 cm from the soil surface at time of placement.

Vacutainers were prepared by first opening the containers and allowing the stopper and tube to equilibrate with ambient air for at least 24 h. Approximately 1 g of silica gel (desiccant) was added to the tubes before replacing the stopper. The containers were then evacuated to at least 0.1 kPa, and a layer of silicone was applied to the surface of the stopper. After the sample was injected into the vacutainer in the field, another layer of silicone was applied to the top surface of the stopper. Degassing of N_2O from the stopper material has been noted, however evacuation prior to use reduces degassing to negligible levels (Brooks et al., 1993). Laidlaw et al. (1993) found no detectable loss of N_2O from samples of known concentration stored in vacutainers prepared as described above after 28 d.

A.2 FLUX CALCULATION

The N_2O concentration increase in the headspace was assumed to be linear and was calculated in the following fashion:

$$\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1} = [\Delta C\ (ppmv)\ N_2O\ h^{-1} \times 10^{-6}] \times [44\ g\ N_2O\ mol^{-1}] \times [22.4\ L\ mol^{-1}]^{-1} \times [28\ g\ N\ mol^{-1}] \times [44\ g\ N_2O\ mol^{-1}]^{-1} \times [1.2\ L] \times [114.9\ cm^2]^{-1} \times [10^4\ cm^2\ m^{-2}]$$

It is assumed that the soil-atmosphere N_2O exchange is driven primarily by diffusion (Hutchinson and Mosier, 1981). As such, a cover placed over the soil surface would disrupt the established concentration gradient as soon as N_2O begins to accumulate within the headspace. If the concentration gradient remained undisturbed we would expect the shape of the N_2O accumulation curve to be linear (Fig A-1). However, as the concentration gradient decreases, the rate of N_2O efflux would similarly decrease. The actual N_2O accumulation curve would be non-linear (Fig A-1). The instantaneous flux estimated from a sample drawn at some point in time (t_1) after cover placement would underestimate the true flux by a factor proportional to the deviation between the two curves at that point.

Hutchinson and Mosier (1981) proposed a calculation to adjust for this non-linearity. Application of the calculation requires a time zero concentration (C_0) and 2 further samples to be drawn from the soil cover at equally spaced time periods (C_1 and C_2). The calculation is only valid when $(C_1 - C_0) / (C_2 - C_1) > 1$. In actual practice, this assumption only holds for a subset of all cases. In a subsequent study, Anthony et al. (1995) found that out of 2224 soil cover deployments, only 1172 met the requirement. While the assumption of linearity for flux calculations may result in a downward bias of up to 34% (Anthony et al., 1995), the systematic exclusion of nearly 50% of the samples taken may also introduce considerable bias. Secondly, an additional sample for each cover deployment would double the number of samples to be handled - a critical consideration for my study. I elected to base flux calculations upon a single sample drawn from the headspace after a 1 h deployment.

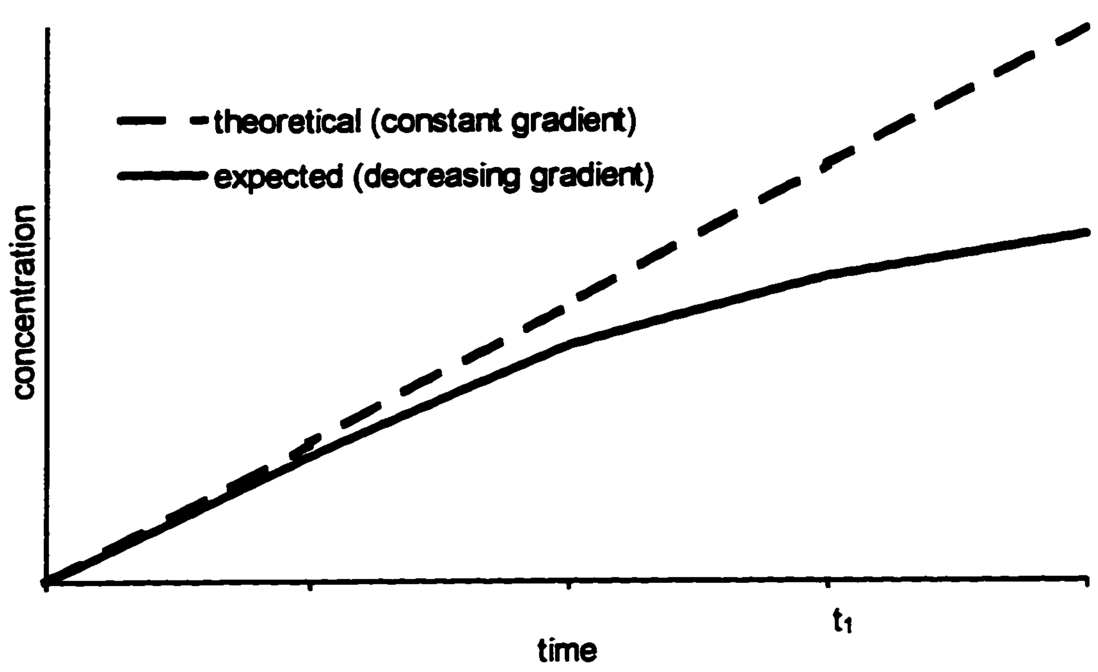

Figure A-1. Graph representing the shape of the accumulation curve in a soil-cover headspace with a constant concentration gradient, and a continuously decreasing concentration gradient.

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