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Spatial and Temporal Patterns in Nitrous Oxide Flux from Agricultural Soil in Southern Ontario

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Spatial and temporal patterns in nitrous oxide flux from agricultural soil in southern Ontario

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THESIS

Submitted to the Department of Geography and Environmental Studies
in partial fulfillment of the requirements for the Master of Science degree.

Wilfrid Laurier University

Abstract

This research examines spatial and temporal variations in N_2O flux from agricultural clay loam in corn-wheat and corn-oat rotations in southern Ontario. Gas samples are collected by the chamber method following significant precipitation events, thaw events, fertilization events, and otherwise every two weeks over a two-year period. Crop type appears to influence the magnitude of N_2O emissions, whereas N_2O fluxes do not otherwise seem to vary by landscape position. The seasonal pattern of *in situ* N_2O flux at Strawberry Creek (SC) indicates that the highest N_2O emissions are occurring during the spring and growing season. Soil moisture and fertilization appear to be the prevailing flux drivers at these times. This pattern is common to most of the literature, although SC fluxes are up to two orders of magnitude lower than those from several studies in similar agricultural regions. Although field data appear to indicate that N_2O fluxes are insignificant during the winter, other researchers, in southern Quebec and in northern Europe, have found significant winter N_2O fluxes, especially during winter thaws. Soil temperature appears to be the predominant driver of N_2O flux during the winter and fall.

The SC field data is compared to that collected during an intensive non-growing season simulation, whereby intact soil mesocosms are exposed to winter and spring temperatures in a laboratory environment, and gas samples are collected daily. Increases and decreases in N_2O flux parallel fluctuations in soil temperature through 0°C during the winter simulation. N_2O fluxes quickly drop off following an initial spike in emissions as soil temperature increases during the spring simulation. The laboratory fluxes from the simulation exceed those from the field by up to two orders of magnitude. It may be that high N_2O fluxes exist during *in situ* winter thaws, but are undetected because of the timing of field sampling. It is also possible that the laboratory methodology created extreme and rapid soil temperature changes, which may not be representative of typical *in situ* conditions. Dramatic increases and decreases in soil temperature may cause a high level of physical, chemical and/or microbiological disturbance to the soil cores, which, in turn, may drive higher N_2O fluxes.

Strong SC correlations between N_2O flux and binned soil temperature data, by soil moisture category, may allow general predictions of N_2O flux based on readily available records, or estimates, of these two parameters. Derived N_2O flux estimates may be reliable predictors of N_2O emissions in northern temperate regions, from agricultural clay loams growing corn and grains. Predictive models would likely be improved by increasing the intensity of empirical measurements during winter and spring thaw conditions, and by incorporating antecedent soil temperature and soil moisture terms into the models.

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1 Introduction

Next to the halocarbons, nitrous oxide (N_2O) is the most powerful of the long-lived greenhouse gases. Its global warming potential is 298 times that of carbon dioxide (CO_2) per unit mass over 100 years (Forster *et al.* 2007). Between 1750 and 2005, N_2O contributed approximately 6% of the radiative forcing due to the long-lived greenhouse gases (Forster *et al.* 2007). Thus, with a tropospheric lifetime of 114 years, and an annual increase in annual atmospheric concentration of 0.26% (Forster *et al.* 2007), enhanced understanding of the dynamics of N_2O emissions is critical. Such understanding could not only improve the effectiveness of strategies to reduce N_2O emissions (Corre *et al.* 1996), but could also contribute to the understanding and modelling of global climate.

Agricultural practices, including fertilization, cultivation, and the burning of biomass, are the most significant sources of N_2O, representing 37% of total global emissions (Isermann 1994). Worldwide, agriculture produces 81% of total anthropogenic N_2O (Isermann 1994). Although agriculture is practiced over less than 4% of the surface area of Canada (Statistics Canada 2007), it is the greatest source of all (anthropogenic and natural) Canadian N_2O emissions (Rochette and McGinn 2008). Southern Ontario is one of Canada's most intensively farmed regions (Figure 1.1). Therefore, research into N_2O dynamics in this region is important to understand the role Canada plays in a global climate change context.

In temperate agricultural regions, both the denitrification of nitrate (NO_3^-), and the nitrification of ammonium (NH_4^+), can result in the production of N_2O. Some authors

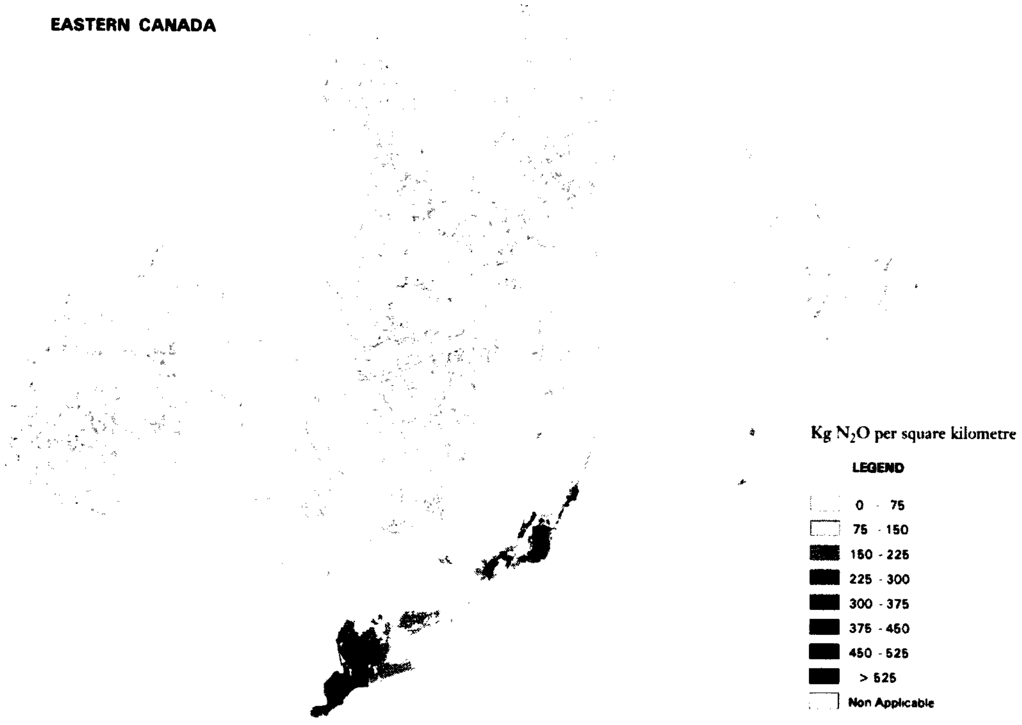


Figure 1.1. Direct agricultural N_2O emissions in eastern Canada, 1991 (Janzen *et al.* 1998).

find that denitrification is the predominant source of N_2O in agricultural soils (e.g. Williams *et al.* 1998). However, in an analysis of the relative contributions of denitrification and nitrification to N_2O production, Gödde and Conrad (2000) find that either can predominate in various agricultural soils, when held at constant temperature (25°C) and moisture content (60% water-filled pore space). The quantity of N_2O produced by nitrification, however, is generally small compared to that by denitrification (Spoelstra *pers. comm.*). Pihlatie *et al.* (2004) find that nitrification prevails in loamy sand, clay, and organic agricultural soils at 60% water-filled pore space (WFPS), and, unexpectedly, in agricultural loamy sand at 100% WFPS, while denitrification predominates in this soil at 80% WFPS.

N_2O production is generally understood to be directly proportional to soil temperature (Bouwman 1990), likely as a result of microbial stimulation. However, research reveals that winter and spring N_2O losses must be considered when assessing total N_2O emissions from agricultural soils in temperate climatic zones, as N_2O emissions during the non-growing season may be as significant as those of the growing season. Kaiser and Ruser (2000), amalgamating results from five field sites over several seasons in Germany, conclude that approximately 50% of annual N_2O emissions are released during the winter. During a 12-month field experiment in Germany, Rover *et al.* (1998) find that 70% of annual N_2O emissions occur from December to February. Flessa *et al.* (1995) find that 46% of N_2O emissions occur in December and January, during another year-long field experiment. A 2.5-year study in southern Quebec finds that non-growing season emissions can be up to two to four times greater than those of the growing season, including emissions through snow cover and during spring thaw (van Bochove *et al.* 2000).

Most non-growing season agricultural N_2O research to date has been conducted in Europe (e.g. Flessa *et al.* 1995, Kaiser *et al.* 1996, Kaiser *et al.* 1998, Rover *et al.* 1998, Ruser *et al.* 1998, Kaiser and Ruser 2000, Ruser *et al.* 2001, Flessa *et al.* 2002a, Flessa *et al.* 2002b, Cannavo *et al.* 2004, Dörsch *et al.* 2004, Koponen *et al.* 2004, Koponen *et al.* 2006, Mørkved *et al.* 2006, Ruser *et al.* 2006). Some North American non-growing season research has been undertaken, especially in semi-arid agricultural regions of Canada and the United States (e.g. Nyborg *et al.* 1997, Lemke *et al.* 1998, Phillips 2007, Dusenbury *et al.* 2008). Research on the non-growing season dynamics of N_2O emissions from agriculture in southern Ontario exists (e.g. Burton and Beauchamp 1994, Wagner-

Riddle *et al.* 1997, Wagner-Riddle *et al.* 2007, Wagner-Riddle *et al.* 2008), but is scant. In the temperate climate of southern Ontario, frequent mid-winter thaw cycles may augment the importance of non-growing season N_2O emissions. Thus, quantifying flux during these periods is essential to understanding overall N_2O contributions from this very important regional land use class.

The objective of this thesis research is to contribute to the understanding of growing and non-growing season N_2O dynamics in southern Ontario. Of specific interest is the timing, and soil moisture and soil temperature conditions, under which the highest magnitudes of N_2O flux occur. Both growing and non-growing season data are collected from three conventionally tilled and managed agricultural fields, sown to crops typical of this region. The non-growing season field work is coupled with a laboratory experiment, to more intensively examine the dynamics of winter and spring N_2O emissions.

2 Literature review of N_2O production and flux

2.1 Overview of the nitrogen cycle and N_2O production

Most transformations of nitrogen (N) (Figure 2.1) are driven by terrestrial microorganisms. When applied to agricultural soils, manure provides organic N, which is mineralized to ammonium (NH_4^+). Crop residues contribute to the agroecosystem via the same process. At this point, N loss to the atmosphere can occur as ammonia gas (NH_3) through the process of volatilization. Inorganic fertilizers yield NH_4^+, nitrate (NO_3^-), or both to the terrestrial N pool. NH_4^+ may be assimilated into growing crops or nitrified to

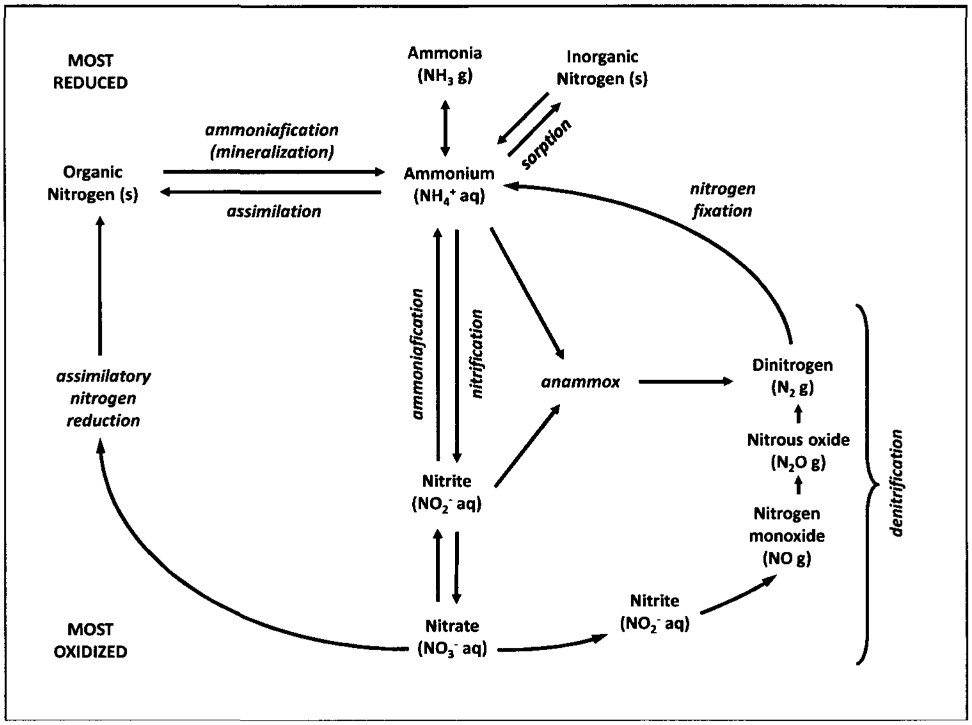


Figure 2.1. The nitrogen cycle. "Dissimilatory nitrogen reduction" includes both ammoniafication of NO_3^- or NO_2^-, and denitrification. Denitrification terminates in either N_2O or N_2 production, and eventual gaseous loss to the atmosphere. Content from Bohlke *et al.* (2006). aq = liquid, g = gas, s = solid, anammox = anaerobic ammonium oxidation (chemically coupled to NO_2^- reduction)

NO_3^-, which may also be assimilated into vegetation. Non-assimilated NO_3^- can be lost from agricultural soils via leaching or denitrification.

Denitrification is reported as the main source of N_2O in agricultural soils in Schlesinger (1991) and Knowles (1982, citing Denmead *et al.* 1979b, Matthias *et al.* 1980). This is the assumption made in much of the agricultural N_2O research. That is, depending on how far denitrification proceeds, in favourable conditions, NO_3^--N is lost from the system as N_2O or in the benign form of N as dinitrogen gas (N_2). N_2O is lost at higher proportions, with respect to N_2, when NO_3^- is abundant in the soil, because NO_3^- is preferred to N_2O as an electron receptor. Denitrification is driven by predominantly heterotrophic facultative anaerobes, able to utilize NO_3^-, instead of O_2, as an electron receptor during respiration. At high levels of O_2, denitrifiers cease NO_3^- reduction, and switch to aerobic metabolism (reviews by Bouwman 1990, Schlesinger 1991, Wrage *et al.* 2001).

Though not always acknowledged as a source of N_2O (e.g. Figure 2.1, Evangelou 1998), nitrification, in addition to denitrification, is another source of N_2O in aerobic soils (Figure 2.2, Schlesinger 1991). Nitrification occurs in aerobic environments, and is driven mainly by obligate autotrophic bacteria. N_2O can be formed during nitrification by chemodenitrification of hydroxylamine (NH_2OH) or nitrite (NO_2^-). N_2O may also be produced from the incomplete oxidation of NH_2OH during the nitrification process (Bouwman 1990, Wrage *et al.* 2001). In cold conditions, NO_2^-, and not NO_3^-, may be the terminal N species of nitrification. Bouwman (1990) cites research finding that *Nitrosomonas spp.*, which drive the oxidation of NH_4^+ to NO_2^-, are less sensitive to low

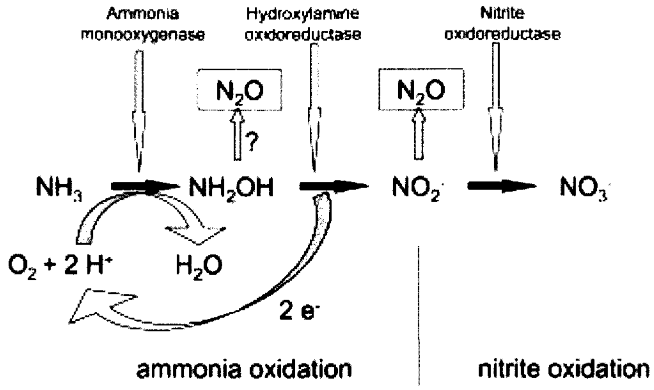


Figure 2.2. Potential sources of N_2O during nitrification. Illustration from Wrage *et al.* (2001).

temperatures than *Nitrobacter spp.*, which drive the oxidation of NO_2^- to NO_3^-. Denitrification processes may start, therefore, as seasons change, and soil warms and wets.

Nitrification may be the primary source of N_2O production in aerobic soils with low oxygen pressure (Bouwman 1990, citing Levine *et al.* 1984). Ruser *et al.* (2006) find that the primary source of N_2O, at WFPS < 60%, is nitrification, although the quantity of N_2O produced by this process is relatively low compared to denitrification. In aerobic soils, N_2O production may be correlated with the quantity of substrate available for nitrification, i.e. that applied as urea- or NH_4^+-based fertilizer, while not with added NO_3^- or glucose (Bouwman 1990, citing Bremner and Blackmer 1978, Breitenbeck *et al.* 1980, Seiler and Conrad 1981, Minami and Fukushi 1983).

Coupled nitrification-denitrification occurs at aerobic-anaerobic interfaces. Although these conditions are sub-optimal for both nitrifiers and denitrifiers, total N_2O

production is high (Wrage *et al.* 2001). Bouwman (1990) reports that simultaneous increases in soil NO_3^- and N_2O have been observed, suggesting evidence for this coupled process.

Wrage *et al.* (2001) and Bouwman (1990) report that in addition to the standard nitrification and denitrification pathways of N transformation (Figure 2.1), "nitrifier-denitrification" may occur (Figure 2.3). This appears to take place in the same low-oxygen conditions as coupled standard nitrification/denitrification. The difference is that the same bacteria drive both the oxidation and reduction reactions, and the end product of nitrification is NO_2^-, rather than NO_3^-. Microbiologists believe that the bacteria are autotrophic NH_3-oxidizers. However, there is not a consensus on whether nitrifier-denitrification is a significant source of N_2O. Some researchers report that this process may produce up to 30% of evolved N_2O (Webster and Hopkins 1996), while others find its contribution to N_2O production to be insignificant (Robertson and Tiedje 1987).

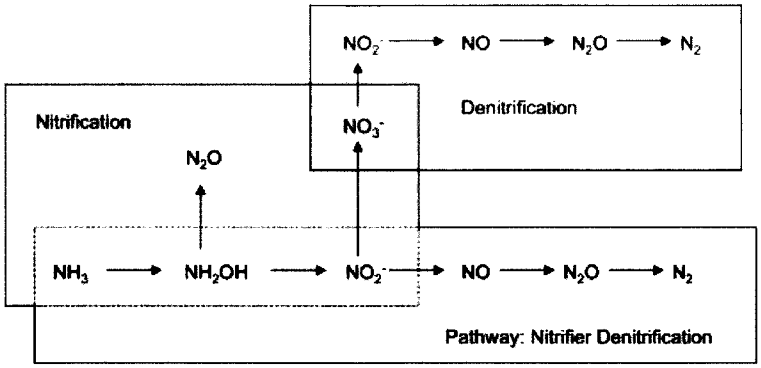


Figure 2.3. Nitrifier-denitrification. Illustration from Wrage *et al.* (2001).

Wrage *et al.* (2001) suggest a three-dimensional model for partitioning the possible modes of nitrification and denitrification, based on the relative O_2, N, and carbon (C) status of the soil (Figure 2.4). In this model, autotrophic nitrification occurs where soil O_2 and N content is relatively high, and C content relatively low. Conversely, heterotrophic denitrification occurs where soil O_2 and N content are limited, and C content relatively high. Both processes are coupled at moderate levels of O_2, N, and C, where conditions for each process are sub-optimal, as discussed above. Nitrifier-denitrification predominates where both O_2 and C are relatively limited, but N content is relatively high.

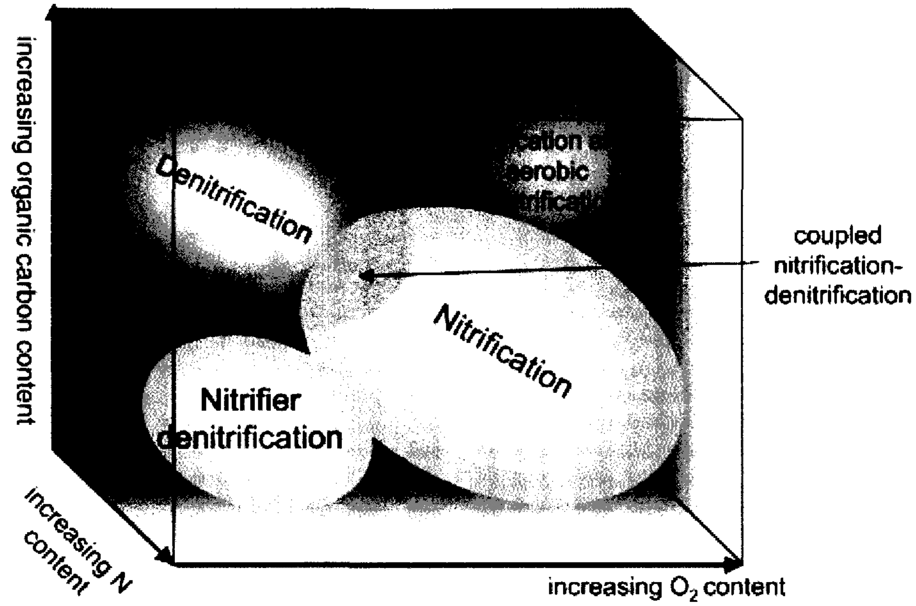


Figure 2.4. Hypothetical partitioning of modes of nitrification and denitrification. As heterotrophic nitrification and aerobic denitrification take place in N-poor, low-pH environments (Wrage *et al.* 2001), atypical of agricultural soils, this process is not discussed in the text. Illustration from Wrage *et al.* (2001).

2.2 Variables influencing N_2O production and flux

In the agroecosystem, N_2O can be produced from nitrification, denitrification, and potentially nitrifier-denitrification, as discussed above. N_2O flux is highly variable, as a result of this range in potential sources, each with their own specific controls. For example, acetylene (C_2H_2) inhibition and isotopic studies (Ryden and Lund 1980, cited by Knowles 1982), find that N_2O represents between 5% to 30% of the total N products of denitrification, and from 1% to 52% of applied fertilizer N. Peak N_2O fluxes are up to 7.5 kg N_2O-N ha^{-1} d^{-1} (1.2×10^3 mg N_2O m^{-2} d^{-1}) in these studies. Because soil pores are generally open under nitrifying conditions, more of the N_2O produced during nitrification may be lost to the atmosphere, than that produced from denitrification (Byrnes *et al.* 1990). Surface flux from nitrification is relatively constant, decreasing temporarily during rain events, while N_2O emissions due to denitrification are short-term and episodic (Byrnes *et al.* 1990).

Fourteen field studies reviewed by Knowles (1982) show a high variation in N_2O flux rates, with peak fluxes occurring two to seven days following fertilizer application, and shortly after irrigation or rainfall. The highest flux rates are associated with enhanced denitrification, due to the augmentation of soil moisture, soil temperature, organic C, and fertilizer. These variables, and their interactions over time, are discussed in detail below.

2.2.1 Soil moisture content

In general, nitrification is limited at low O_2 levels and high C:N ratios, which favour denitrification. Ruser *et al.* (2006) report maximum N_2O fluxes from soils at 90% WFPS. Bouwman (1990) reports a denitrification threshold of 65% field capacity (FC). It is possible for anaerobic microzones to serve as possible denitrification sites in otherwise aerobic soil (Knowles 1982, Bouwman 1990, Schlesinger 1991). There may be anaerobic intra-aggregate water-filled soil pores which support denitrification (Knowles 1982, citing Craswell and Martin 1974, Smith 1980).

Knowles (1982) reports that concentrations of soil water and O_2 can vary on a scale of micrometres. A water film as thin as 200 μm may provide a suitable denitrification zone (Knowles 1982, citing Greenwood 1961). Parkin (1987) speculates that denitrifying microsites may be as thin as 16 μm, as discussed below. Although precipitation increases the total anaerobic soil volume, denitrification levels may also be more dependent on the quantity and distribution of microbial respiratory activity, and the rate of gas diffusion in the soil (Knowles 1982). The rate of gas diffusion is influenced by the "geometry of the diffusion path" (Knowles 1982), which would be driven by soil texture and the level of soil compaction, in addition to soil moisture content.

Rochette *et al.* (2004) compare subsurface N_2O concentration and surface N_2O flux from arable sandy loam, clay loam, and clay soils. They find, that although there are differences in both concentration and flux from the three soil types, the differences are small and inconsistent. One might expect a clear difference in N_2O flux from the soil types, with finer textured soils retaining more soil water, and therefore increasing N_2O flux due to increased levels of denitrification. The authors speculate, however, that inconsistent patterns in flux, for the three soil types, reflect the complex effect of soil texture on the interaction between N_2O production, consumption, and diffusion (Rochette *et al.* 2004).

Cycles of wetting and drying promote denitrification (Bouwman 1990, citing Letey *et al.* 1981). Additionally, such cycles increase available C (Knowles 1982, citing Patrick and Wyatt 1964, Reddy and Patrick 1975, Galsworthy and Burford 1978, Patten *et al.* 1980). More N_2O is produced during wetting, and, if the soil is then quickly dried, the reduction of N_2O to N_2 is prevented (Bouwman 1990, citing Letey *et al.* 1981). Thus, mean N_2O flux is higher in irrigated soil (alternating dry and wet conditions), than during frequent rains of a winter, when soils are continuously wet (Bouwman 1990, citing Letey *et al.* 1981). When soil water content is relatively low, there may be a simultaneous production of N_2O and NO_3^- as soil moisture increases, indicating that nitrification is the dominant process in N_2O formation at this time (Bouwman 1990, citing Parton *et al.* 1988). It is possible that coupled nitrification-denitrification is also occurring in such conditions. When volumetric water content (VWC) is very high, in contrast, only N_2O concentration increases, indicating denitrification (Bouwman 1990, citing Parton *et al.* 1988).

Nitrogen oxide reductases are believed to be repressed by O_2. Knowles (1982) reports that dissimilatory nitrogen reduction is activated within 40 minutes to three hours after soil wetting or re-wetting (citing Payne *et al.* 1971, Payne 1973, Firestone and Tiedje 1979, Smith and Tiedje 1979). Gradual depletion of O_2, or a semi-anaerobic condition, allows the synthesis of dissimilatory nitrate reductase, and perhaps the reductases associated with the subsequent products of denitrification, which are shown in Figure 2.1 (Knowles 1982, citing Payne *et al.* 1971, Calder *et al.* 1980). A rapid shift in soil moisture status does not appear to support this synthesis (Knowles 1982, citing Payne *et al.* 1971, Zumft and Vega 1979).

Nitrite reductase is more strongly repressed by O_2 than nitrate reductase (Knowles 1982, citing Sacks and Barker 1949, Krul and Veeningen 1977, Meiberg *et al.* 1980), requiring a higher increase in soil moisture to be activated. The threshold level of anaerobiosis for N_2O reductase is unknown (Knowles 1982). At low levels of O_2, where denitrification occurs at a slower rate than in anoxic environments, the relative mole fraction of N_2O is higher than that of NO_2^- or N_2 (Knowles 1982, citing Focht 1974). The role of nitrogen monoxide (NO) in the denitrification process is uncertain (Knowles 1982).

Parsons *et al.* (1991) examine denitrifier enzyme activity (DEA) and denitrifier populations, with respect to N_2O production in soil. DEA measures the rate of synthesis of new denitrifying enzymes. Parsons *et al.* (1991) find that N_2O production is more highly correlated with soil moisture and soil respiration, than with DEA and population counts. Although DEA appears not to be important with respect to N_2O production, Parsons *et al.* (1991) postulate that the activation or de-activation of existing denitrifying enzymes, due to fluctuating O_2 levels, may play a role in N_2O production.

Higher N_2O flux may occur from aerated versus anoxic soil (Bouwman 1990, citing Levine *et al.* 1984). The reduction of N_2O may be slowed by competition from O_2 as an electron receptor (Bouwman 1990). Aerated conditions may also stimulate the production of N_2O from nitrification (Bouwman 1990). Bremner *et al.* (1981) find that the N sources urea, $(NH_2)_2CO$, and ammonium sulphate, $(NH_4)_2SO_4$, form significantly more N_2O at 60% WFPS, when compared to N_2O from the denitrification of potassium nitrate (KNO_3). Pihlatie *et al.* (2004) find that 78%, 44%, and 74% of N_2O emissions originate from nitrification, from an arable loamy sand, at 60%, 80%, and 100% WFPS, respectively. Nitrification or nitrifier-denitrification may be the dominant process, until soils become very wet or saturated (Bouwman 1990, citing Parton *et al.* 1988). In Christianson *et al.* (1979), Breitenbeck *et al.* (1980), and Conrad and Seiler (1980) (all cited by Knowles 1982), N_2O flux is predominantly attributed to the nitrifiable compounds NH_4^+, anhydrous NH_3, and $(NH_2)_2CO$, rather than to NO_3^-, implying that nitrification is the main source of N_2O (Knowles 1982, citing Bremner and Blackmer 1979). However, N_2O fertilizer loss in these conditions is low, at less than 0.1% of fertilizer N (Knowles 1982, citing Breitenbeck *et al.* 1980, Seiler and Conrad 1981).

Ruser *et al.* (2006) report on the influence of soil moisture and soil compaction on N_2O flux, from fine silt loam growing potatoes in controlled conditions. They consider differences in N_2O flux between potato ridge soil, uncompacted interrow soil, and compacted interrow soil, 15 days after fertilization. At constant moisture conditions ($\geq$ 70% WFPS), ridge soil has a higher N_2O flux than uncompacted interrow soil, which in turn has higher N_2O flux than compacted interrow soil. The higher ridge soil flux is attributed to the higher C content of the ridged topsoil. The opposite pattern, than that described above for high soil moisture conditions, is found at low moisture content, i.e. the compacted interrow soil has the highest levels of N_2O flux when all soils are maintained at the same moisture content. Doran *et al.* (1990, cited by Parkin 1993) find higher denitrification rates in compact versus less compact soil. During an earlier growing season field study, Ruser *et al.* (1998) find that WFPS in ridge soil is low (50%), while uncompacted and compacted interrow soils have significantly higher WFPS (68% and 85%, respectively), complicating the role of soil moisture and soil compaction in driving *in situ* N_2O flux. During average growing season conditions, with only compacted interrow soils having high WFPS, *in situ* fluxes may in fact be limited.

2.2.2 Soil temperature

Soil temperature influences the rate of denitrification, the rate of nitrification, and the terminal products of these processes (Bouwman 1990). Denitrification rates have been found to increase up to 60°C, or even 75°C (Bouwman 1990, citing Alexander 1977). The rate of denitrification increases exponentially ($Q_{10} = 2$) between 0°C and 25°C (Rochette *et al.* 2004, citing experimental work by Castaldi 2000). Dhont *et al.* (2004) report that N_2O flux is an order of magnitude higher at 15°C than at 5°C. The optimum denitrification rate occurs at temperatures ≥ 25°C, with the lowest rates of denitrification occurring at < 15°C (Bouwman 1990, citing Keeney *et al.* 1979). However, at these lower temperatures, relatively large mole fractions of N_2O are produced (Bouwman 1990, citing Keeney *et al.* 1979; Knowles 1982, citing Nömmik 1956). The same quantity of N_2O is produced at < 15°C than at 25°C even though the denitrification rate is low at these temperatures (Bouwman 1990, citing Keeney *et al.* 1979). Denitrification is measurable down to between 0°C and 5°C (Knowles 1982, citing Bremner and Shaw 1958, Bailey and Beauchamp 1973, Smid and Beauchamp 1976). For nitrification, the optimum rate occurs between 30°C and 35°C (Bouwman 1990, citing Alexander 1977). Nitrification is negligible at temperatures < 5°C and > 40°C (Bouwman 1990, citing Alexander 1977).

The greatest variations in N_2O flux in the literature are reported in soils at high temperatures with high rates of fertilization (Bouwman 1990). Significant losses of N_2O

may occur at sub-optimal temperatures when manures are applied to soil (Bouwman 1990:106, citing unpublished evidence).

2.2.3 Temporal variability of N_2O flux

Parsons *et al.* (1991) find highly variable N_2O production from soil, with the greatest production occurring during the spring. With respect to spring rates, the release of winter-produced N_2O, previously trapped by ice, is also possible (Bouwman 1990, citing Bremner *et al.* 1980, Goodroad and Keeney 1985). Parsons *et al.* (1991) find that denitrification in the summer and fall is low or below detection limits. They cannot correlate N_2O production with soil temperature, the relationship possibly confounded by changes in soil moisture, O_2 solubility, and C availability over different temperature ranges. Schmidt *et al.* (1988, cited by Bouwman 1990) find that high denitrification rates may occur during the late autumn, in addition to those during the early spring, evidence that high VWC due to precipitation and/or rising water tables, may drive significant production at low temperatures.

Soil temperature may create significant short-term temporal variations in N_2O flux. Several studies show a marked diurnal variation in N_2O flux (Bouwman 1990, citing Ryden *et al.* 1978, Denmead *et al.* 1979b, Keeney *et al.* 1979, Blackmer *et al.* 1982, Conrad *et al.* 1983, Minami 1987), with flux maxima coinciding with temperature highs in the early afternoon (Knowles 1982, citing Denmead *et al.* 1979a, b, Matthias *et al.* 1980).

2.2.4 Soil organic matter

Parsons *et al.* (1991) find that the rate of denitrification in pasture is strongly correlated with the level of soil respiration, and not with NO_3^- concentration. This suggests that soil C provides denitrifying microsites within the subsurface, and that denitrifiers may use NO_3^- below detection limits (Parsons *et al.* 1991).

"Hotspots" of denitrification, due to high variability of particulate organic matter, occur in a study by Parkin (1987) on undisturbed silt loam soil. Parkin (1987) measures the denitrification and CO_2 production rates from a 100-g soil sample, which contains a 0.08-g piece of decaying pigweed. By isolating the pigweed through successive divisions of the sample, Parkin (1987) finds that the pigweed contributes 85% of the total denitrification in the original 100 g of soil. Assuming that CO_2 production occurs over 100% of the pigweed surface, and using the diffusion coefficient of O_2 in water, Parkin (1987) determines that a water film, of only 160 µm thick, results in denitrification rates as high as those from bulked soil under ideal anaerobic conditions, with additions of glucose and NO_3^-. If CO_2 production occurs over only 10% of the pigweed, these denitrification rates could occur in water films as thin as 16 µm (Parkin 1987). Van Kessel *et al.* (1993) find that hotspots exhibit a distinct temporal pattern, tending to increase in number only in drier conditions, and thus generating N_2O flux outliers only when the overall rate of denitrification is low. Van Kessel *et al.* (1993) conclude, therefore, that hotspot activity is of limited importance when estimating seasonal rates of denitrification.

In a review of studies on biotic sources of N_2O, Umarov (1990) concludes that organic C is the main driver of denitrification, naming soil moisture and soil temperature as secondary drivers. Knowles (1982) speculates that freeze-thaw cycles break down organic matter, making C more available to denitrifying organisms. Rochette *et al.* (2004), however, point out that decomposition of crop residues may be slow in wet and cool soil, producing minimal quantities of substrate required for denitrification. Even where soil N is high, therefore, there may be a low denitrification rate and N_2O yield. Van Kessel *et al.* (1993) find that water-soluble organic carbon (WSOC) does not limit denitrification during the growing season in a pea (*Pisum sativum*) field.

2.2.5 Soil chemistry

The rate of denitrification is optimal between pH 7.0 and 8.0 (Knowles 1982, citing Wijler and Delwiche 1954, Nömmik 1956, van Cleempt and Patrick 1974, Delwiche and Bryan 1976, Müller *et al.* 1980). Many nitrifiers and denitrifiers are sensitive to low pH, but pH is rarely low enough to be limiting in arable soils in Ontario, as most soils range from pH 6.5 to 7 (Zwart 2006). Practices, such as fertilization and irrigation, may alter other aspects of soil chemistry, which are more relevant to N_2O production in an agricultural setting.

Spatial and temporal variation in N transformation is enhanced by amendments of inorganic fertilizers, manure, and additions of plant residues to agricultural soil. These create localized zones of mineralization, nitrification, and denitrification (Knowles 1982, citing Burford 1976, Burford *et al.* 1976, Guenzi *et al.* 1978). Pulsed inputs of manure, inorganic fertilizer, and precipitation into agricultural soils cause periods of enhanced bacterial activity of short or long duration (Knowles 1982, citing Burford *et al.* 1976). For example, Bouwman (1990) reviews ten studies on cultivated unirrigated grain crops on mineral soils, which report flux ranges from 0.08 mg N_2O m^{-2} d^{-1} on unfertilized rye, to 3.4 mg N_2O m^{-2} d^{-1} on rye fertilized with NO_3^--N or NH_4NO_3-N. Annual emission rates range from 0.2 kg N ha^{-1} y^{-1} on the unfertilized rye, to 8.0 kg N ha^{-1} y^{-1} on the fertilized rye. The mass of N applied per unit area correlates with N_2O flux (Bouwman 1990). High soil concentrations of NO_3^- delay the reduction of N_2O to N_2 (Bouwman 1990, citing Fillery 1983). N_2O production may be higher in soil treated directly with NH_4^+-yielding fertilizer, than in soil treated with NO_3^--N (Bouwman 1990, citing Bolle *et al.* 1986). Bouwman (1990) reports the following N_2O losses by fertilizer type from Bolle *et al.* (1986): 0.04% of NO_3^- fertilizer, 0.15% to 0.19% of NH_3 and $(NH_2)_2CO$ fertilizers, and 5% of anhydrous NH_3 fertilizer. One study (Breitenbeck *et al.* 1980, cited by Bouwman 1990) finds that higher fertilizer application rates lower the fraction of fertilizer N lost as N_2O from the agricultural system. Van Kessel *et al.* (1993) find that denitrification in agricultural systems is only limited by soil N when the potential rates of denitrification are high, i.e. when both soil moisture and soil temperature are high. Rochette *et al.* (2004) find that flux is high when soil N_2O is high, but observe that the reverse is not always true. In one year of their two-year study, for example, April and early May N_2O fluxes increase while soil N_2O decreases.

Soil texture may play a role in the proportion of fertilizer N lost as N_2O. Byrnes *et al.* (1990) report N_2O flux from silt loam, silt clay loam, and clay loam (85% FC), with applications of two fertilizers at the rate of 50 kg N ha^{-1}. Emission rates are 1.8%, 0.1%, and 0.05% of urea-based fertilizer, respectively. Emissions are 1.5%, 0.2%, and 0% of

NH_3- based fertilizer (Byrnes *et al.* 1990). These results indicate that soil type may be more important than fertilizer type in constraining N_2O flux, at least from the nitrification of NH_4^+-yielding fertilizers.

Phosphate (PO_4^{-3}) and calcium carbonate ($CaCO_3$) may contribute to favourable conditions for N_2O formation (Bouwman 1990, citing Minami and Fukushi 1983). PO_4^{-3} may act as a microbial nutrient, and $CaCO_3$ would increase pH in acidic agricultural soils, thus favouring N_2O production by creating more favourable conditions for microbes (Spoelstra, *pers. comm.*). Although, in order to maintain crop health, farmers may need to add these compounds to their soils, slow release forms of PO_4^{-3} and $CaCO_3$ may minimize increases in N_2O emissions.

2.2.6 Spatial variability of N_2O flux

The spatial variability of N_2O flux is high. Folorunso and Rolston (1984, cited by Bouwman 1990) conclude that 350 samples are required to get a N_2O flux value within 10% of its true mean for a 90-m^2 plot, and 14 samples to get an accuracy of +/- 50%. Also, it is impossible to separate spatial from temporal variability. For example, the spatial and temporal heterogeneity of denitrification is enhanced by the evolving chemistry, mass, and location of plant roots in soil over a growing season. Roots exude sugars and C, and act as an O_2 sink in loose, unrestricted soils (Knowles 1982). Denitrifier populations may be one to two orders of magnitude greater in these zones (Parkin 1993). However, if nitrates are in relatively short supply, or inorganic N is strongly assimilated by plants, denitrification in the rhizosphere may be lower than in the greater pedosphere (Bouwman 1990, citing Haider *et al.* 1985).

The variables that drive N_2O production via microbial activity differ with the scale of investigation (Parkin 1993). Thus, at the microscale (4 mm^2), localized variations in NO_3^-, organic matter, anaerobiosis, and even pH, are relevant. At the plot scale, crop type, fertilization rate, and fertilization method are central. Crop type, in turn, influences the temporal variation in organic matter content, and the spatial distribution of the rhizosphere; the spatial pattern of soil moisture due to variations in throughfall, stemflow, and interception; and the solar impact due to differences in the morphology of the plant canopy. For example, due to plant physiology, corn leaves funnel up to 50% of total areal rainfall directly to the base of corn plants (Parkin 1993, citing Parkin and Codling 1990). Notable effects on soil moisture may be brief, however, because, at least in the case of corn, redirected water may rapidly be taken up by the crop. Fertilization also contributes to the heterogeneity of microbial activity at the plot scale via application method (Parkin 1993, citing Rice *et al.* 1988) and fertilizer type. Applications may be banded (interrow or intrarow) or broadcast, surface or subsurface, liquid or solid. The spatial distribution of solid organic amendments is especially patchy. The effects of pesticides on microbiota are heterogeneous at the plot scale as well (Parkin 1993, citing Parkin and Shelton 1992).

Other interconnected variables predominate to constrain N_2O flux at the larger landscape scale. Soil type integrates the plot-scale and microscale effects of soil texture, depth of topsoil, organic content, pH, and nutrient levels (Parkin 1993). Surface topography contributes to topsoil depth and soil moisture levels (Parkin 1993, van Kessel *et al.* 1993). Together, soil type and topography are appropriate summary variables for water distribution, which is the third main variable driving N_2O flux at the landscape scale (Parkin 1993). Parkin (1993) asserts that climate, land use pattern (with specific vegetation type), and physiography are appropriate summary variables for understanding N_2O flux at the regional scale.

2.2.7 Summary of N_2O flux drivers

There is no one N_2O flux driver, and researchers debate the relative importance of the variables which influence flux timing and magnitude. Umarov (1990) states that, in addition to a threshold soil moisture level, organic C content is the main constraint on denitrification. Nearly all bacteria are able to denitrify, and NO_3^-, soil temperature, and pH are flux drivers which are secondary to soil moisture and soil C (Umarov 1990). Other findings suggest that fertilizer concentration may be more important than soil C content (e.g. Bouwman 1990, citing Conrad *et al.* 1983). The predominance of one factor or one interaction may shift over time. Bouwman (1990) concludes that the variability of N_2O flux is a function of time-dependent interactions between soil temperature, microbial populations, organic C content, O_2 diffusion rate, soil moisture content, and occurrence and condition of root matter. It is therefore impossible to decouple spatial from temporal variability in the field.

2.3 Research Objectives

This research examines spatial and temporal variations in N_2O flux from an agricultural area in southern Ontario, and the linkage of these variations to landscape position, crop type, soil temperature, and soil moisture. The seasonal pattern, of *in situ* N_2O flux at Strawberry Creek (SC), is investigated to determine when the highest N_2O

emissions are occurring, and whether seasonal emissions reported in the literature are comparable, in terms of pattern and magnitude.

In addition to year-round field sampling, the non-growing season is examined in depth via a laboratory incubation, to better understand the sensitivity of winter and spring N_2O fluxes to soil temperature fluctuations at controlled soil moisture conditions. The pattern and magnitude of N_2O flux changes following a soil temperature increase or decrease are observed, with a focus on N_2O fluxes at soil temperatures near 0°C. Fluxes are tracked in the laboratory with daily measurements accompanied by continuous soil temperature and soil moisture logging.

Field and laboratory N_2O flux observations are compared. Correlations between N_2O flux, soil temperature, and soil moisture are examined to determine whether there might be a simple predictive model for *in situ* flux based on these two environmental parameters.

3 Spatial and temporal patterns in N_2O fluxes from agricultural soil in a temperate climate

Spatial variations of *in situ* N_2O flux at SC are compared by landscape position, that is, by field, and by crop type. Daily, seasonal, and monthly variations in N_2O flux are examined to determine flux patterns and to determine when the highest N_2O emissions are occurring. For the seasonal comparisons, the SC data is subdivided into spring (March and April), growing season (May through August), fall (September and October), and winter (November through February). The temporal patterns are compared to soil temperature and soil moisture conditions. The relative magnitude and absolute magnitude of SC N_2O fluxes are compared to those in the agricultural N_2O flux literature from similar climatic regions. When the literature uses parametric statistics to report N_2O flux data (see Table A 1), comparable parametric statistics for the SC dataset are calculated, as discussed in section 3.2.5. This may lead to skewed comparisons, as the SC data are non-parametric.

3.1 Site description

Nine field sites were located in the Strawberry Creek (SC) catchment in southern Ontario (Figure 3.1, Figure 3.2a). SC is an ephemeral first order stream in the Grand River watershed, approximately 15 km northeast of Waterloo, Ontario (43° 33' 28" N, 80° 23' 58" W), which flows through a gently rolling agricultural landscape of low widely-spaced glacial features including drumlins and eskers. The sites are situated at approximately 340 m above sea level, with relief ranging over 15 m. Surface geology at SC consists of a few metres of sand-silt till, over ≤ 3 m of clay till, over 3 – 7 m of stony

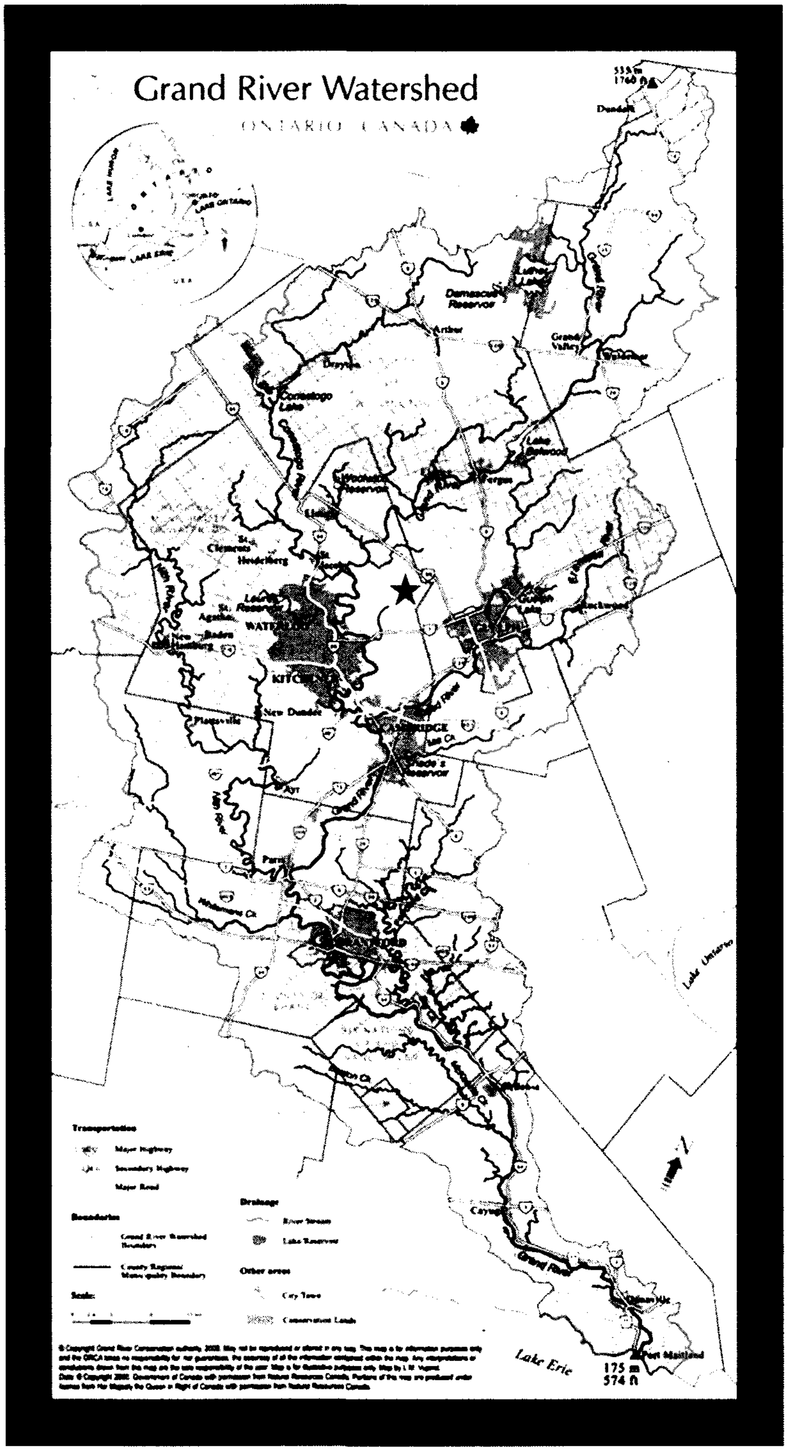
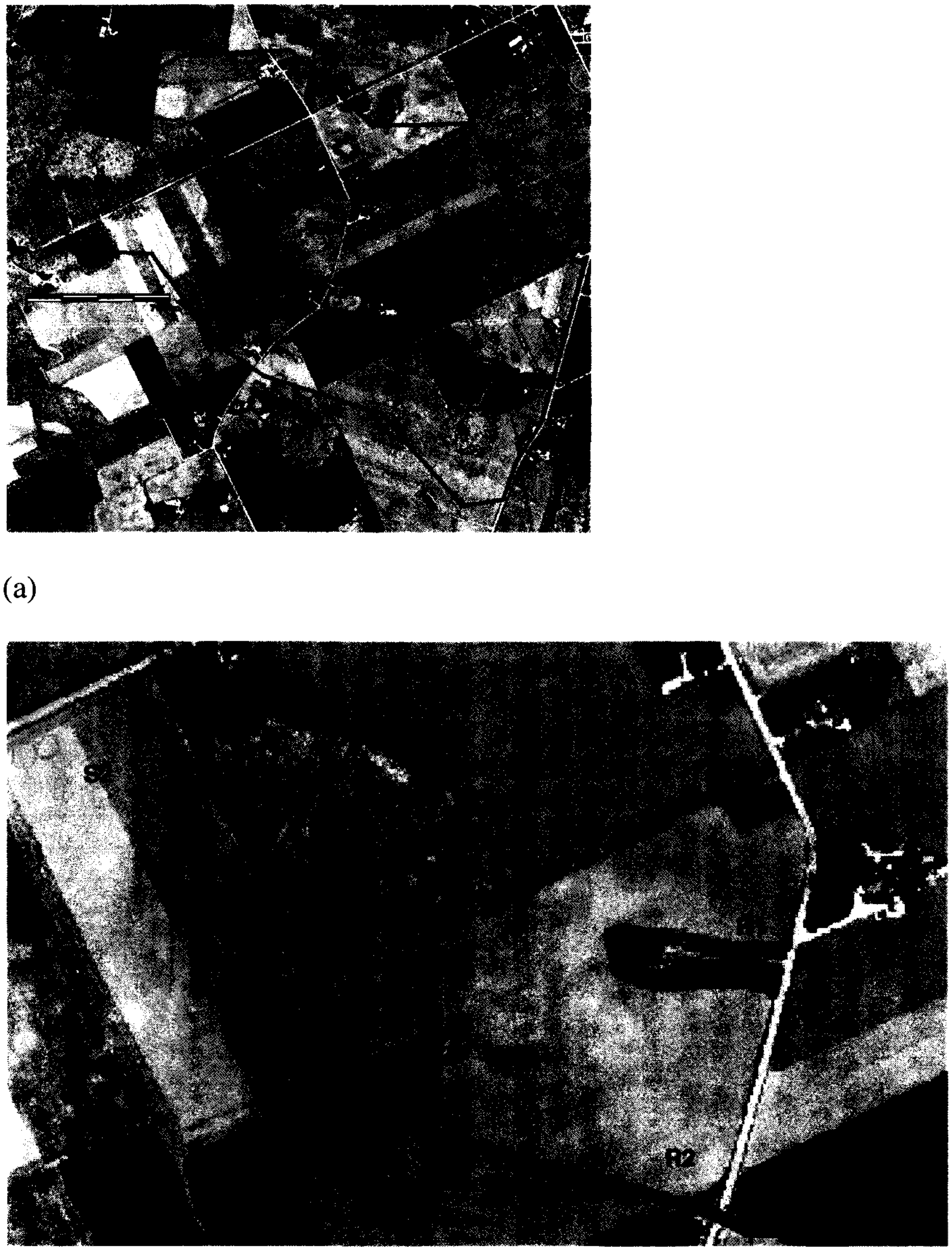


Figure 3.1. Location of SC (*) within the Grand River watershed. Inset shows the location of the Grand River within the Great Lakes basin of southern Ontario. Illustration from the Grand River Conservation Authority (http://www.grandriver.ca/index/document.cfm?Sec=12&Sub1=55&Sub2=24).



(b)

Figure 3.2. (a) SC with catchment boundary. Flow is southeast. (b) Nine SC field sites. Site S3 is near the creek origin which drains a forested wetland across the road to the north (upper left corner of photo).

till overlying bedrock (Vries and Dreimanis 1960, Karrow 1968, Karrow 1974, Karrow *et al.* 1993, cited by Harris 1999) The soil in this area is a clay loam (27% sand, 44% silt, 29% clay, Rashid, *unpublished data*). Mean annual air temperature (1971-2000) is 7°C, with monthly means ranging from -7°C (January) to 20°C (July). Mean total annual precipitation (1971-2000) is 910 mm, with mean monthly totals ranging from 50 mm (February) to 90 mm (July, Figure 3.3).

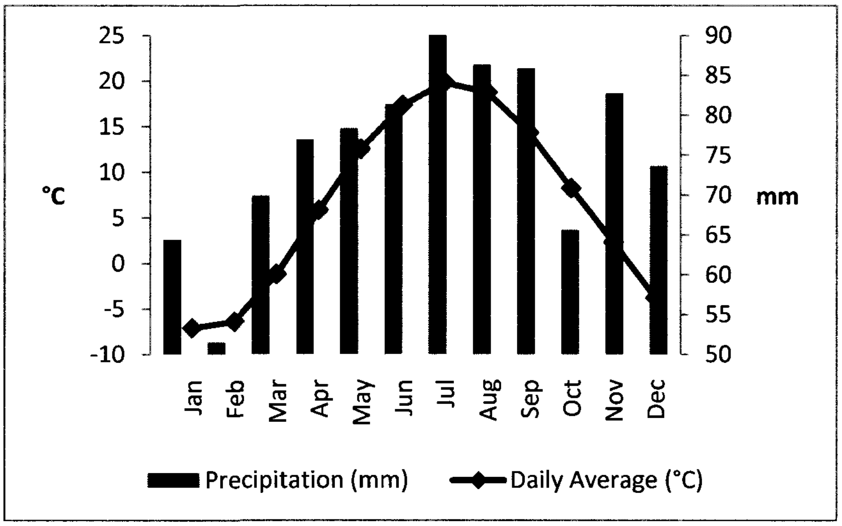


Figure 3.3. Climate normals 1971-2000, Waterloo-Wellington Station A (43°27'N, 80°23'W, elevation = 317 m, Environment Canada 2008). Mean daily average air temperature and total precipitation by month.

Three 16-m^2 field sites were located in each of three privately owned tile-drained agricultural fields, within a 1-km^2 area in the upper catchment (Figure 3.2b). The three fields were conventionally tilled and managed in terms of organic and inorganic fertilizers (Table 3.1, Table 3.2), and the sites were located within corn-oat and corn-wheat rotations (*Zea mays - Avena sativa, Zea mays - Triticum aestivum*), common crops in southern Ontario (Table 3.3).

Table 3.1. Crop rotations and organic fertilizer applied at SC, 2006 through 2008. *High straw content, N equivalent may be an overestimate. Note: S sites not established until spring 2007.

Season	Year	Field / Site	Manure Type	Succeeding Crop	Manure Date / Month	Nitrogen Equivalent (kg N ha^{-1})
spring	2006	R	solid layer hen	oats	May	11
fall	2006	R	solid layer hen	corn	Sept	32
spring	2006	T	solid layer hen	corn	May	11
fall	2006	T	none	oats	n/a	0
spring	2007	R	solid layer hen	corn	May	11
fall	2007	R	none	oats	n/a	0
spring	2007	S1	none	winter wheat / fallow	n/a	0
spring	2007	S2, S3	solid cattle*	corn	3-May	75
spring	2007	T	solid layer hen	oats	May	11
fall	2007	T	solid layer hen	corn	Sept	32
spring	2008	R	none	oats	n/a	0
fall	2008	R	solid layer hen	corn	Sept	32
spring	2008	S1	solid cattle*	corn	22-Apr	68
spring	2008	S2, S3	none	spring wheat	n/a	0
spring	2008	T	solid layer hen	corn	Apr	11
fall	2008	T	none	oats	n/a	0

Table 3.2. **Inorganic amendments at SC, 2006 through 2008. Note that all fertilizers are ammonium-based allowing for both nitrification as well as denitrification processes depending on soil redox conditions. Note: S sites not established until spring 2007.**

Year	Field / Site	Crop	Fertilization Date	Nitrogen Equivalent (kg N ha^{-1})	Fertilizer Chemistry
2006	R	oats	Apr	18	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2006	R	oats	June	75	$(NH_2)_2CO$ and NH_4NO_3
2006	T	corn	May	23	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2006	T	corn	June	101	$(NH_2)_2CO$ and NH_4NO_3
2007	R	corn	May	23	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2007	R	corn	June	101	$(NH_2)_2CO$ and NH_4NO_3
2007	S1	winter wheat / fallow	none	0	n/a
2007	S2, S3	corn	May	23	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2007	S2, S3	corn	June	101	$(NH_2)_2CO$ and NH_4NO_3
2007	T	oats	Apr	18	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2007	T	oats	June	75	$(NH_2)_2CO$ and NH_4NO_3
2008	R	oats	Apr	18	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2008	R	oats	June	75	$(NH_2)_2CO$ and NH_4NO_3
2008	S1	corn	13-May	186	$(NH_4)_3PO_4$
2008	S2, S3	spring wheat	Apr	23	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2008	S2, S3	spring wheat	June	101	$(NH_2)_2CO$ and NH_4NO_3
2008	T	corn	May	23	$(NH_4)_3PO_4$ and $(NH_2)_2CO$
2008	T	corn	June	101	$(NH_2)_2CO$ and NH_4NO_3

Table 3.3. Area in grain crops in Ontario in 2006 (McGee 2009). Highlighted crops indicate those studied at SC.

Rank by Area	Crop	Area (ha)
1	Hay	1,037,062
2	Soybeans	872,455
3	**Grain corn**	**638,538**
4	**Winter wheat**	**416,209**
5	**Silage corn**	**129,807**
6	Barley	89,447
7	**Spring wheat**	**82,112**
8	Mixed grain	70,194
9	Dry field beans	61,775
10	**Oats**	**53,399**
11	Fall rye	25,565
12	Tobacco	12,816
13	Canola	7,517

Three sites, designated R1, R2, and R3, were situated in field R (43° 33' 16" N, 80° 23' 38" W). Three sites, designated S1, S2, and S3, were situated in field S (43° 33' 23" N, 80° 24' 0" W). The last three sites, designated T1, T2, and T3, were situated in field T (43° 33' 24" N, 80° 23' 25" W). The nine sites were chosen to represent the full range of soil moisture conditions in each field. Sites 1 were selected to be drier than sites 2, which were selected to be drier than sites 3 (Figure 3.2b). This pattern was consistent for the sites of field R during all seasons, for field S during the spring and winter, and for field T during the spring, growing season, and winter (Figure 3.4).

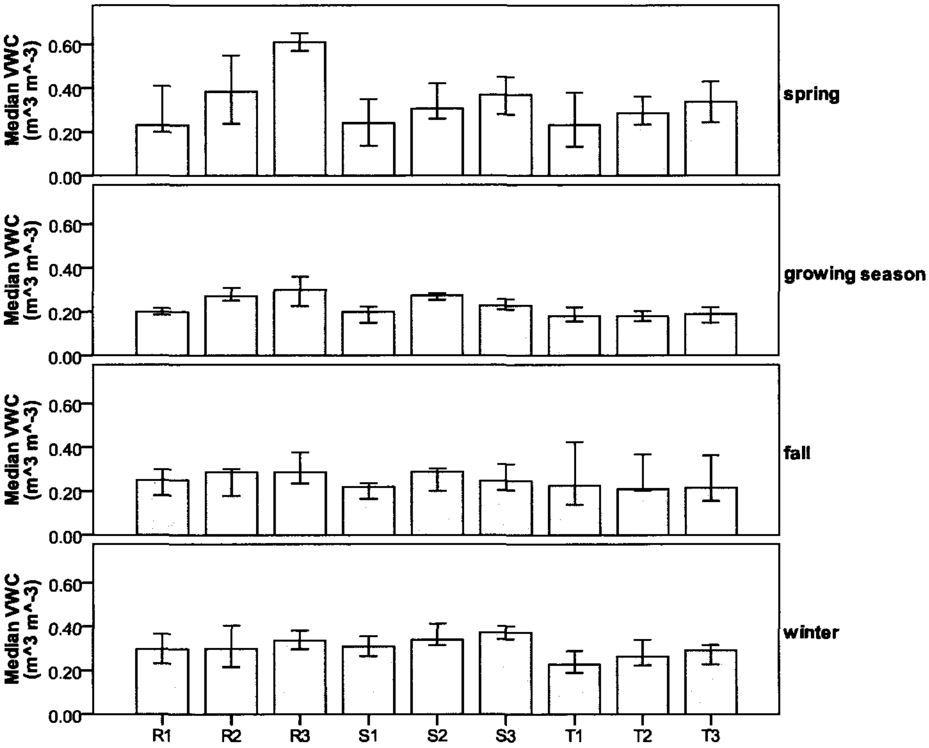


Figure 3.4. Relative moisture content by site at SC. All 2006 through 2008 data is illustrated.

3.2 Methods

3.2.1 Field methods

Soil gas flux samples were collected from August 2006 through October 2006, March 2007 through February 2008, and April 2008 through August 2008, with three replicates at each of the nine field sites. Sampling followed significant precipitation events, fertilization (in 2007 only), and otherwise every two to four weeks. During the winter (November 2007 through February 2008), samples were taken during thaw events, defined as ≥ 3 days at a daytime air temperature of ≥ 4°C. Otherwise, winter sampling occurred every two to four weeks. Sampling occurred three times between Jan 5/08 and Jan 13/08, during an extreme thaw event (Figure 3.5). Air temperature during this period reached a maximum of 14°C (Jan 7/08). During July 2008 and August 2008, sampling was carried out every two to four weeks only; there was no additional sampling following precipitation events.

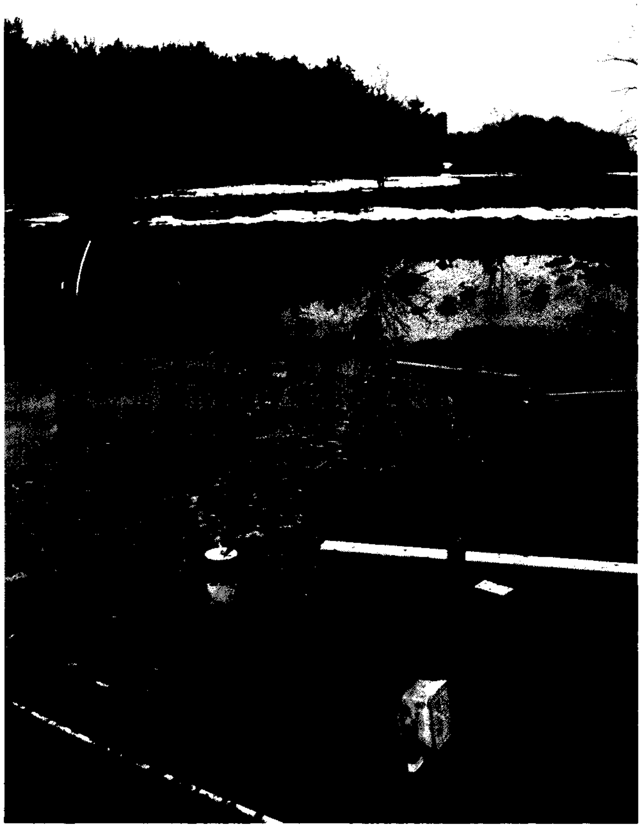


Figure 3.5. Mid-winter thaw conditions, early January 2008, SC, site R2.

Because of possible diurnal variations in N_2O flux (Bouwman 1990), sampling would have ideally taken place at the same time of day from each site. However, due to the time required for the installation of sampling chambers and for travelling between sites, the six R and T sites were sampled in the morning, and the three S sites were sampled in the afternoon.

Gas samples were collected using equipment and methodology developed by Petrone (*pers. comm.*). After each spring cultivation, three soil gas collars (Figure 3.6), constructed from 28 cm of polyvinyl chloride (PVC) pipe with an inside diameter (ID) of 10 cm, were inserted to a depth of 18 cm at each site. The collars remained in place until the following spring. Gas collection chambers were constructed of PVC pipe (10.7 cm

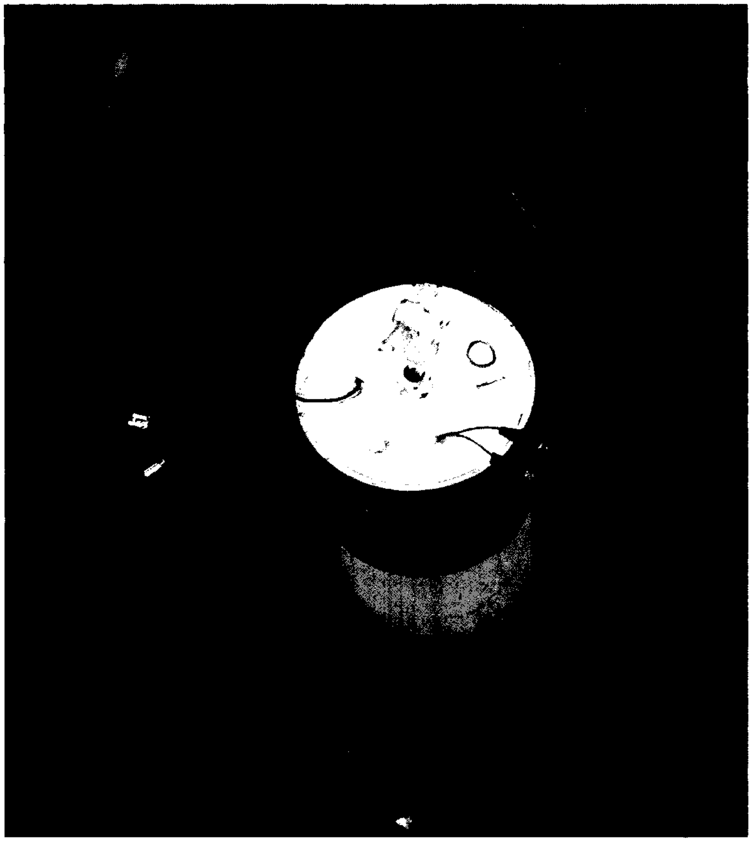


Figure 3.6. Soil gas chamber and collar used in the collection of N_2O gas flux data from the field at SC.

ID). Each chamber was 10 cm high, with a Plexiglas® top sealed on with silicone rubber sealant (Silicone I®, GE Inc.). A drilled opening in the Plexiglas® was fitted with an 11-mm Teflon® septum, held in place with a stainless steel and brass fitting enclosed with plumbing sealant (Amazing Goop®, Eclectic Products Inc.). Two small holes were drilled into the Plexiglas®, one to hold a thermocouple wire, another to hold a 40-mm fan (CFA 124010MS DC Brushless Fan, Circuit-Test Electronics). A 9-V battery was connected to this fan on the outside of the chamber at sampling time. These small openings were enclosed with plumbing sealant. The surface of the chamber was covered with aluminum tape to reflect solar radiation. Two 21G1½ needles (Becton Dickinson & Co.) were inserted into the chamber's septum. One was inserted and attached to a three-way valve. The other was inserted to maintain an equilibrium between the chamber air pressure and that of the atmosphere.

An ambient air sample was taken at the beginning of each sampling day. A 20-mL syringe (BD Luer-Lok™, Becton Dickinson & Co.) was attached to a three-way valve. A 23G1 needle was attached to the opposite end of the valve. The valve was closed to the needle and 20 mL of ambient air was drawn into the syringe. The valve was closed to the ambient air and the needle was purged using the ambient air in the syringe. The valve was closed to the needle once again and another 20 mL of ambient air was drawn into the syringe. The valve was closed to the ambient air. A 12-mL glass vial (Labco Exetainer®, Labco Ltd.), evacuated to 0.001 mbar, was inserted onto the needle. The syringe was then used to inject the 20 mL of ambient air into the vial.

The lower inside of each gas chamber was thinly coated with high vacuum silicone grease (Dow Corning Corp.). The chambers were positioned firmly over each soil collar, with the three-way valve closed to the chamber (Figure 3.6). After 1.5 to 2 hours, a 9-V battery was connected to the fan on each chamber. After 1 min, and with the fan running, the chamber air was sampled, using the same protocol outlined above to sample ambient air.

When there was over 5 cm of fresh snow on the ground, snow gas samples were collected using equipment and methodology developed by Spoelstra (pers. comm., Figure 3.7). Snow gas chambers were constructed were constructed from 27-cm diameter,

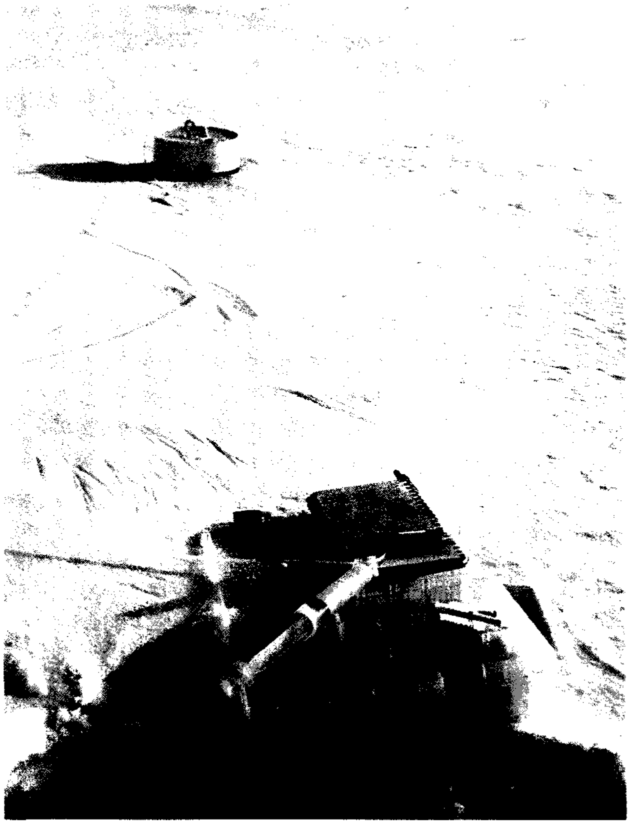


Figure 3.7. Snow gas chamber (background) and gas collection method illustrating 30-mL syringe and 12-mL Exetainer® (foreground), winter 2007-2008, SC.

15-cm high plastic buckets. An 8-mm diameter eye bolt was fitted into the outer bottom centre of the bucket, and sealed in with a rubber washer. A 13-mm blood tube stopper was fitted into the outer bottom side of the bucket. Three metres of 3-mm ID rigid plastic tubing was inserted into the stopper, projecting ≤ 5 cm above the bottom of the bucket. A plastic barbed luer connector (Cole-Parmer Inc.) was inserted into the opposite end of the tubing and fitted with a three-way valve.

The snow gas chambers were inverted. Using a 3-m pole with a hook installed on the end, each chamber was lifted via the eye bolt and gently placed on an undisturbed area of the snowpack to a depth of 5 cm. Three chambers were placed near each field site, radiating out from the centre of each site at 0°, 120°, and 240°. The free end of the plastic tubing was secured above the ground at 2 m to 3 m from the snow gas chamber. The valves were closed to the tubing leading to the snow chambers. After 1.5 to 2 hours, a gas sample was extracted, using the same protocol as above to sample ambient air (Figure 3.7).

A time-domain reflectometer (TDR CS620 with CD620 display and two 20 cm CS620-20 rods, Campbell Scientific Inc., Logan, UT) was initially used during each sampling event to quantify soil moisture. The TDR rods were inserted into the ground, providing an average soil moisture value from 0 cm to 20 cm in depth. From March 2007 through June 2007, single soil moisture measurements were taken in the centre of each field site. Beginning in July 2007, a new TDR sensor was employed (PR2/6 with HH2 logger and PRC/d-HH2 cable, Delta-T Devices Ltd., Cambridge, UK), using three access tubes permanently installed at each site (ATL1, Delta-T Devices Ltd., Cambridge, UK).

This system allowed soil moisture data to be collected even when soils were relatively dry or snow-covered (Figure 3.8). The PR2/6 provided discrete soil moisture measurements at a depth of 10 cm. Three readings were taken at each access tube: at 0°, 120°, and 240°. These discrete 10-cm values were assumed to be comparable to the CS620 values, which represented the soil moisture average from 0 cm to 20 cm. When the PR2/6 was not functioning properly, the CS620 was used. When the CS620 was employed after June 2007, nine measurements were taken at each site, three at approximately 30 cm from each soil gas collar at 0°, 120°, and 240° from its centre. The collection of soil moisture data was occasionally prevented during the winter, due to the formation of an ice layer on or above the soil surface.

Figure 3.8. Winter 2007-2008 soil moisture and soil temperature measurements at SC in field S, illustrating PR2/6 TDR (left foreground) and multimeter connected to buried thermocouple wires (midground).

Soil temperatures were initially measured with a thermocouple thermometer inserted to a 5 cm depth at the centre of each site (EW-93756-06 and EW-90225-00, Cole-Parmer Inc., Vernon Hills, IL). Beginning in July 2007, permanent thermocouple wires were installed at three locations within each site (Figure 3.8).

3.2.2 Laboratory methods

Gas samples from the field were analyzed for N_2O within 7 days by the Department of Earth and Environmental Sciences, University of Waterloo, using a Varian CP3800 Gas Chromatograph (Varian Inc., Palo Alto, CA) and N_2O concentrations calibrated against gas standards included in each sample run. The detection limit for N_2O was approximately 3 nmol N_2O, and analytical accuracy was ± 10 ppbV N_2O.

3.2.3 N_2O flux calculation

N_2O fluxes were calculated for each sample using the following formula:

$$F_m = F_v \times \frac{V_h}{MV_g} \times \frac{1}{A_c} \times MM_{N_2O} \times 10^3 \qquad (3.1)$$

where:

F_m = molar flux, mg m^{-2} d^{-1}
F_v = volumetric flux, nL L^{-1} d^{-1}
V_h = volume of headspace, L
MV_g = molar volume of a gas corrected for chamber temperature and pressure, L mol^{-1}
= 22.414 × (273.16 + T) / 273.16 × 101.32 / P, where T units are K and P units are kPa
A_c = cross-sectional area of the chamber, m^2
MM_{N_2O} = molar mass of N_2O
= 44.0128 g mol^{-1}

3.2.4 Soil analysis

The soil organic matter content was determined through loss on ignition in a muffle furnace at 500°C for 1 hour. Total carbon (% TC) and total nitrogen (% TN) were determined by the Environmental Isotope Laboratory, Department of Earth and Environmental Sciences, University of Waterloo, with an Isochrom Continuous Flow Stable Isotope Mass Spectrometer (Micromass UK Ltd., Manchester), coupled to a Carlo Erba Elemental Analyzer (CHNS-O EA1108, Thermo Fisher Scientific, Milan). Detailed soil analysis methods can be found in Thuss (2010). Molar C:N ratios were calculated with the following formula:

$$C:N = \frac{TC}{TN} \times \frac{14}{12} \qquad (3.2)$$

3.2.5 Statistical methods

All statistical analysis was conducted using SPSS version 16.0 (SPSS Inc., Chicago, IL). Sets of N_2O flux data, subdivided by field, crop, season, month, and soil temperature categories, were tested for normality using the Kolmogorov-Smirnov and Shapiro-Wilk tests ($p \leq 0.05$). The same tests were applied to the climate data. These two tests assess the null hypothesis that data is normally distributed. In the majority of cases $p \leq 0.05$, therefore the null hypotheses were rejected.

Non-parametric statistics were used to summarize the non-normal N_2O flux and climatic data, as in van Kessel *et al.* (1993). Median values with 95% confidence intervals were calculated. Median fluxes are accurate to ± 0.04 mg N_2O m^{-2} d^{-1}, given the analytical accuracy noted in section 3.2.2. Statistical differences ($p \leq 0.05$) in N_2O flux among fields, crops, seasons, months, and soil temperature categories were determined via the non-parametric Mann-Whitney U test. This test was also used to determine whether there were significant climatic differences ($p \leq 0.05$) among seasons and months of different years at SC. When both $n_{group\ 1}$ and $n_{group\ 2} \leq 20$, the U statistic was reported, whereas, when both $n_{group\ 1}$ and $n_{group\ 2} > 20$, the z_U statistic was reported, as performed by the SPSS software. In contrast, parametric statistics were often reported in agricultural N_2O flux literature. Therefore, in order to compare the SC results to published studies, parametric SC results were calculated on an ad hoc basis, as reported in section 3.3.5.

3.3 Results and discussion

3.3.1 Soil physical and chemical properties

Bulk densities from the R and T sites at SC range from 1.69 to 2.14 g cm^{-3} (Table 3.4). Organic content ranges from 5.2% at R1 to 9.0% at T1 (Table 3.4) for the R and T fields, except for site R3. R3, uniquely situated at the edge of a forested wetland, which remains waterlogged during the non-growing season, has a high organic content of 14%. Organic content at all of the S sites is high, from 15% to 20%, even though, in contrast to R3, none of these sites is waterlogged. Total carbon (TC) content at the sites ranges from 2.0% (R1) to 4.0% (S2), except for R3, which has an anomalous C content of up to 10% (Table 3.4). Overall, soils show no obvious increase or decrease in either TC or TN between summer and fall. As with TC, TN at site R3 is high, at up to 0.72% (Table 3.4). Soils from the other sites range from 0.18% N (at R1 and T2) to 0.32% N (at S2 and T3). The C:N ratio for all nine sites ranges from 11.2 (at T3) to 18.6 (at T1). The C:N ratio at site R3 is 16.7.

Table 3.4. Soil properties at SC, including soil bulk density (BD) and organic content (OC) from the upper 0-25 cm of the soil profile, and TC, TN and C:N ratios from the upper 0-15 cm (Thuss, *unpublished data*). n^1 = sample size for BD and OC, n^2 = sample size for TN, TC, C:N. All data collected in 2006, except * (2007 collected). ** = collected in the fall of 2006. n/a = data not available.

Site	Season	n^1	Bulk Density (g cm^{-3})	Organic Content (%)	n^2	TC (%)	TN (%)	C:N
R1	summer	27	1.96	5.4	1	2.0 *	0.18 *	13 *
R1	fall	9	n/a	5.2	1	2.1 *	0.19 *	13 *
R2	summer	27	2.14	6	6	2.5	0.26	11
R2	fall	9	n/a	6.8	8	2.5	0.24	12
R2	summer	-	n/a	n/a	1	2.7 *	0.23 *	13 *
R2	fall	-	n/a	n/a	1	3.0 *	0.27 *	13 *
R3	summer	27	1.85	14.1	1	10.1 *	0.72 *	16 *
R3	fall	9	n/a	13.8	1	8.6 *	0.60 *	17 *
S1	summer	27	n/a	20.2	-	n/a	n/a	n/a
S2	summer	27	n/a	14.7	3	4.0 **	0.32 **	14 **
S3	summer	27	n/a	18.2	-	n/a	n/a	n/a
T1	summer	27	1.69	9	1	3.3 *	0.21 *	18 *
T1	fall	9	n/a	8.4	1	3.4 *	0.22 *	19 *
T2	summer	27	1.94	6.8	1	2.4 *	0.19 *	14 *
T2	fall	9	n/a	6.3	1	2.4 *	0.18 *	16 *
T3	summer	27	1.98	7.1	1	3.1 *	0.32 *	11 *
T3	fall	9	n/a	7	1	2.9 *	0.30 *	11 *

3.3.2 Climatic conditions

The N_2O flux dataset consists of SC samples from the period of August 2006 through August 2008, over which there are a wide range of climatic conditions (Figure 3.9). As sampling is precipitation- and thaw-event based, in addition to occurring at least biweekly, the data is thought to reflect a representative range of long-term *in situ* N_2O flux values.

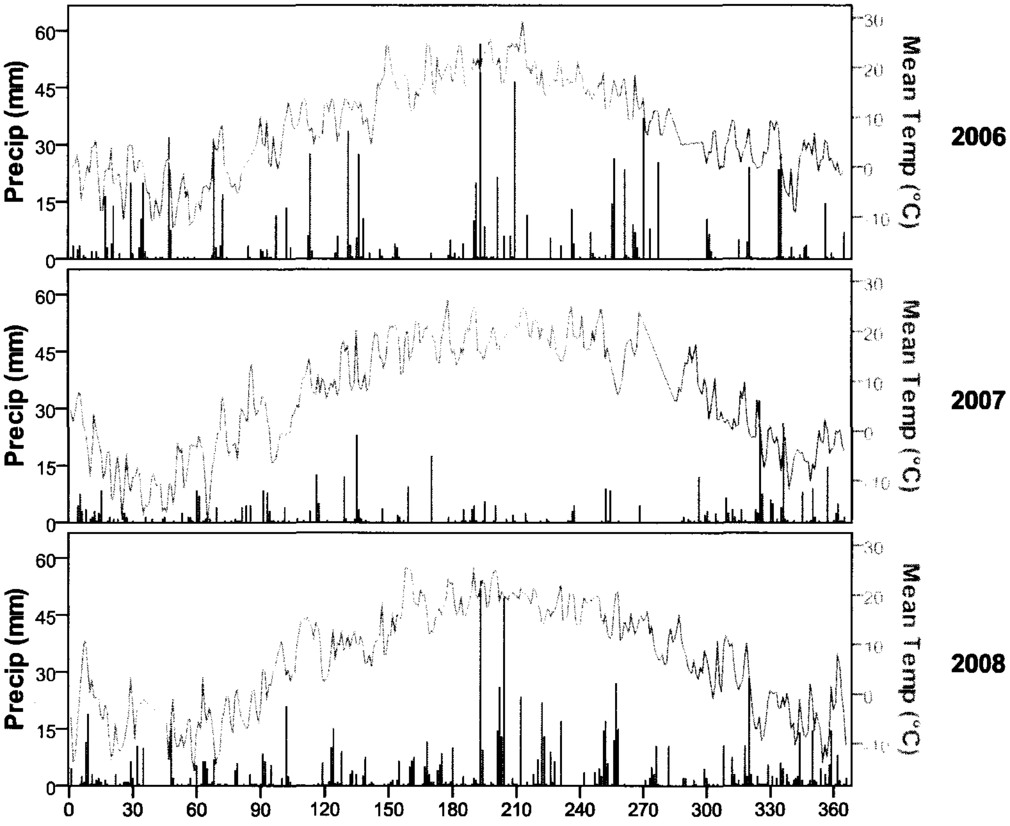


Figure 3.9. Regional daily air temperature (line) and total daily precipitation from 2006 through 2008 (bars), by Julian day. Data from Regional Waterloo International Airport meteorological station (43.46°N, 80.38°W) (Environment Canada 2009).

Air temperature during the fall of 2007 is higher than during the fall of 2006 (z_U = -3.9, $p < 0.001$). In terms of monthly differences, February and April 2008 are warmer than February and April 2007 (Table A 2; z_U = -2.3, p = 0.02; z_U = -2.1, p = 0.04, respectively). Conversely, March and May 2008 are cooler than March and May 2007 (Table A 2; z_U = -2.4, p = 0.02; z_U = -2.0, p = 0.04, respectively). Higher and lower N_2O fluxes may occur during these warmer and cooler inter-annual seasons and months, respectively. March 2007 has a notably large range of daily mean temperatures (-18°C through +14°C) as compared to March 2008 (-14°C through +5°C, Table A 2). N_2O fluxes sampled during March 2007, therefore, may be higher than those during average

March conditions, because the March 2007 temperature fluctuations would likely cause bursts of N_2O flux of greater magnitude and frequency. Such temperature fluctuations are known to cause higher fluxes (e.g. Hu *et al.* 2006, Henry 2007).

Precipitation during the growing season of 2008 is significantly higher than during the growing season of 2006 or 2007 ($z_U = -3.5, p < 0.001$; $z_U = -4.7, p < 0.001$, respectively). There are more rain events during August 2006 versus August 2007, February 2007 versus February 2008, and April 2007 versus April 2008. Conversely, there are fewer rain events during June 2007 versus June 2008 (Figure 3.9). There are three relatively extreme precipitation events in September 2006, November 2007, and July 2008 (37 mm, 32 mm, and 54 mm, respectively, Table A 3, Figure 3.9). These events may be reflected in high N_2O fluxes.

High air temperatures during the second week of January 2008 reflect an extreme winter thaw which occurred during this time. Precipitation levels were also very high during this thaw.

Soil moisture and soil temperature at SC follow expected seasonal patterns, with soil moisture highest during the spring, followed by winter, fall, and growing season (Figure 3.10a). Soil temperature is highest during the growing season followed by fall, spring, and winter (Figure 3.10a).

3.3.3 Spatial variation in N_2O flux at the landscape scale

Most differences in N_2O flux over the landscape, i.e. among fields, are not significantly different. However, certain significant seasonal differences in N_2O flux

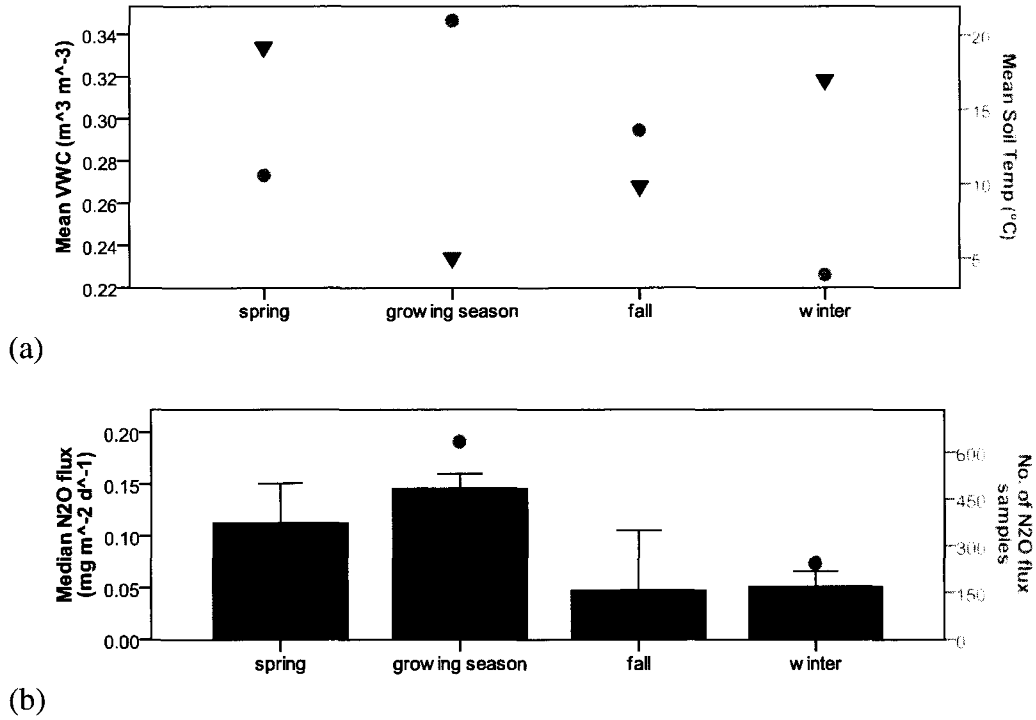


Figure 3.10. (a) Soil moisture content at 10 cm depth (inverted triangles) and soil temperature at 5 cm depth (dots) by season. (b) N_2O flux by season (bars) with sample size (dots). Error bars indicate the 95% confidence interval for median flux. Spring = March and April, growing season = May through August, fall = September and October, winter = November through February.

among fields do occur during the spring and winter. During the spring, field S has smaller N_2O fluxes than both field R ($U = 81, p = 0.03$, Figure 3.11a) and field T ($U = 55, p = 0.05$, Figure 3.11a). During the winter, field T has greater N_2O fluxes than both field R ($z_U = -2.7, p = 0.006$, Figure 3.11a) and field S ($z_U = -2.6, p = 0.009$, Figure 3.11a). This may be at least partly due to the fact that fields R and T are fall-manured in alternate years, with manure of a high nitrogen content (quantitative data not available). Field S belongs to a different property owner, and is consequently not fall-manured. Additionally, field S corn always has its residue removed from the field, whereas this is never the case for fields R and T.

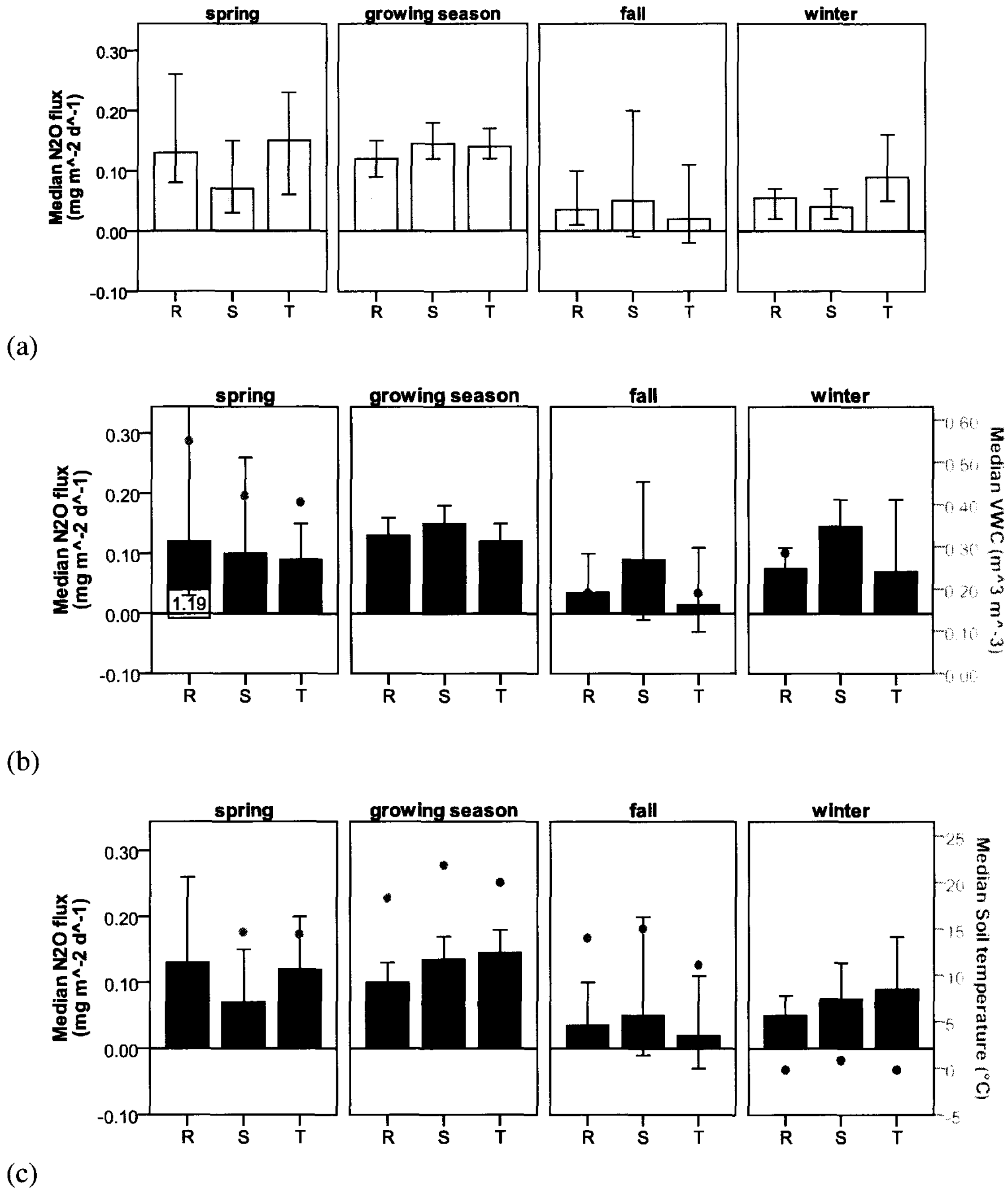


Figure 3.11. (a) Seasonal N_2O flux by field. (b) Seasonal N_2O flux (bars) and soil moisture content at 10 cm depth (dots) by field. (c) Seasonal N_2O flux (bars) and soil temperature at 5 cm depth (dots) by field. Error bars indicate the 95% confidence interval for median N_2O flux. R & T fields are in oat/corn rotations. S sites are in spring wheat/corn (2008) or winter wheat/corn (2007) rotations. *These plots illustrate data from sampling dates where all nine sites have (a) N_2O, (b) N_2O and VWC, and (c) N_2O and temperature records, to give a consistent base for comparing the three fields.* Flux values, therefore, do not represent all sampling dates from August 2006 through August 2008 at SC. Spring is represented by data from Apr 28/07 and Apr 18/08 only (a, b, c). Growing season is represented by data from (a) 15 dates, (b) 10 dates and (c) 12 dates. Fall is represented by data from 12 Sept 12/07 and Oct 24/07 only (a, b, c). Winter is represented by data from (a) 6 dates, (b) Nov 12/07 and Nov 25/07 only, and (c) 4 dates. The label in plot (b) indicates the upper confidence limit (off-scale).

Although the seasonal differences in N_2O flux over the landscape (Figure 3.11a) are generally not statistically significant ($p > 0.05$ by the Mann-Whitney U test), they do consistently mirror those of relative soil moisture content (Figure 3.11b). These flux patterns, however, do not reflect soil temperature, except during the fall (Figure 3.11c). No comparable landscape scale data in the literature are available for comparison with these SC inter-field results.

3.3.4 Influence of crop type on N_2O flux

At SC, there are several significant differences in N_2O fluxes among sites with different crops. These are likely due to a difference between organic/inorganic fertilizer application rates and timing. During the growing season and fall, the flux from sites with corn are higher than those with oats or winter wheat/fallow ($z_U = -5.4$, $p < 0.001$; $z_U = -4.9$, $p < 0.001$, respectively; Figure 3.12a, Figure 3.12b). This is likely the result of corn receiving greater amounts of fertilizer than oats, at rates and timing that may not maximize the efficiency of crop nutrient supply with respect to crop nutrient demand. (Sites planted in winter wheat in the fall are designated "winter wheat/fallow" during the following growing season because they are fallow after a mid-summer harvest. For SC data comparison, the "growing season" for winter wheat is the harvest year, and not the year of planting.)

There are two other significant differences in N_2O flux among crops during the growing season. Sites with spring wheat have a higher N_2O flux than oats, and oat sites,

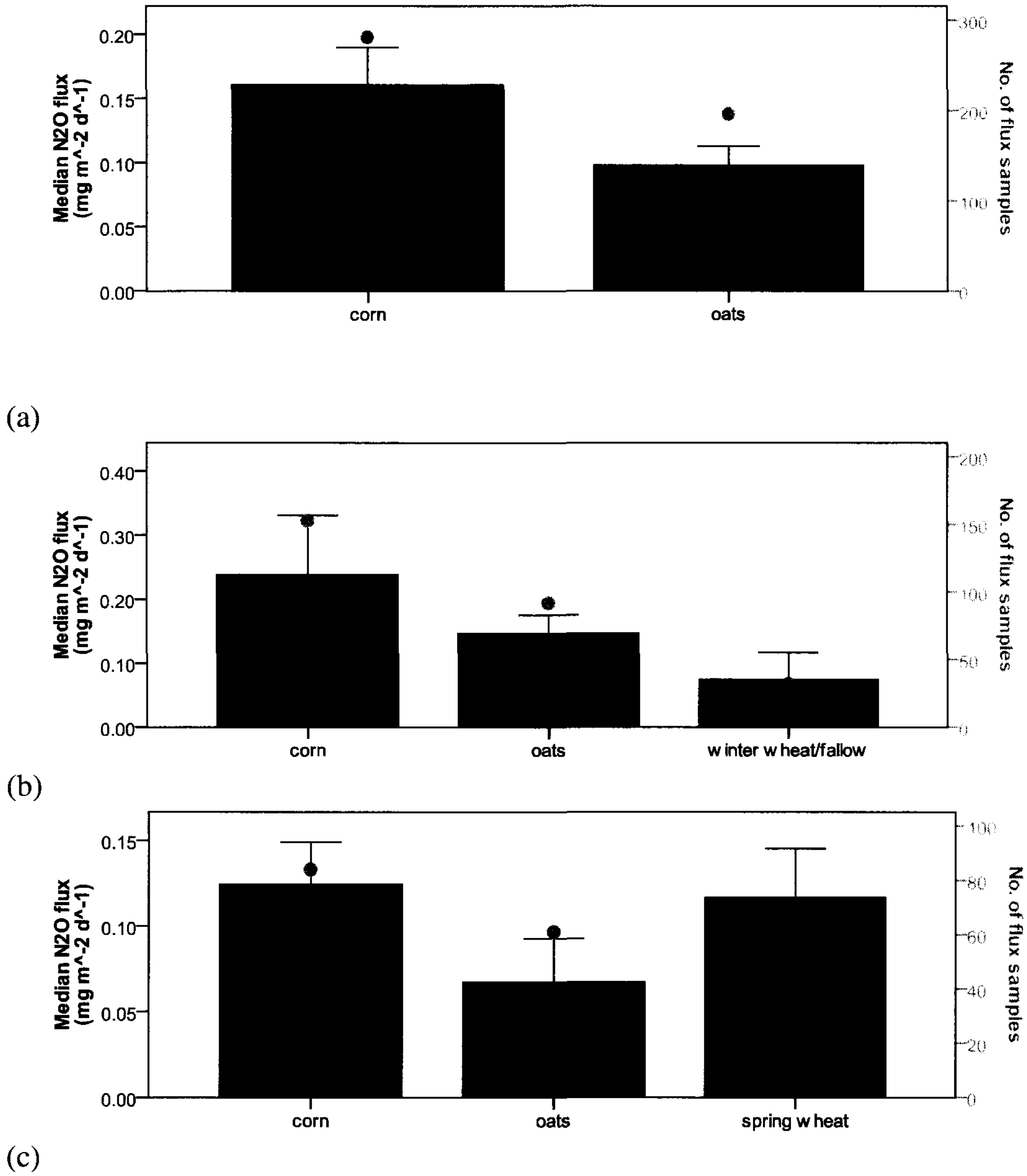


Figure 3.12. N_2O flux comparisons from different crops during the growing season and fall at SC. Bars illustrate N_2O flux and dots illustrate sample size. Error bars indicate the 95% confidence interval for median flux. *Each plot illustrates data from sample dates with records for all of the crops illustrated to give a consistent base for the comparisons.* Flux values, therefore, do not represent all growing season and fall sampling dates in the SC dataset. Sample sizes differ within each plot because there were 6 sites sown to corn each year, 3 sites sown to oats, 1 site in winter wheat (2007 only) and 2 sites in spring wheat (2008 only). (a) N_2O flux from corn versus oats, (b) N_2O flux from corn versus oats versus winter wheat (followed by fallow), (c) N_2O flux from corn versus oats versus spring wheat.

respectively, have a higher N_2O flux than winter wheat/fallow ($z_U = -2.1, p = 0.03$; $z_U = -3.4, p < 0.001$, respectively; Figure 3.12a, Figure 3.12b). Spring wheat was grown at SC in 2008 only. The fertilizer recommendation for spring wheat and oats is 90 kg N ha^{-1} and 35 kg N ha^{-1}, respectively (Reid 2008). Although both recommendation levels are exceeded at SC (Table 3.2), it is possible that more excess inorganic N was taken up by oats. Winter wheat/fallow sites receive neither organic nor inorganic fertilizer, which likely explains their low N_2O fluxes during the growing season and fall.

During the non-growing season of winter and spring, sites which grew oats, or were seeded to winter wheat during the previous season, have greater N_2O fluxes than the sites which grew corn during the previous season ($z_U = -2.9, p = 0.003$; $U = 52$, p 0.02, respectively). These N_2O fluxes are designated post-oats, winter wheat, and post-corn (Figure 3.13a, Figure 3.13c). It is possible that the N_2O flux differences, among SC fields which succeed different crops, may be explained by differences in soil N levels. At SC, the post-oat sites receive a fall manure application, whereas the post-corn sites do not. The winter wheat sites are cropped to peas in the fall prior to seeding, which would fix N_2 in the soil, providing a potential source for higher N_2O production during the non-growing season, as compared to the post-corn sites. The pea plants are ploughed into the soil, maximizing their contribution to soil N and C. Another possible contributing factor, to lower N_2O fluxes from post-corn sites, is soil temperature. Mean soil temperatures at 5 cm depth during the spring are 10°C, 12°C, and 14°C for post-corn, post-oat, and winter wheat sites, respectively. There are no significant differences in N_2O flux between either post-corn or post-oat sites and post-fallow sites (Figure 3.13b), i.e. those which are fallow during the previous growing season following a July harvest of winter wheat.

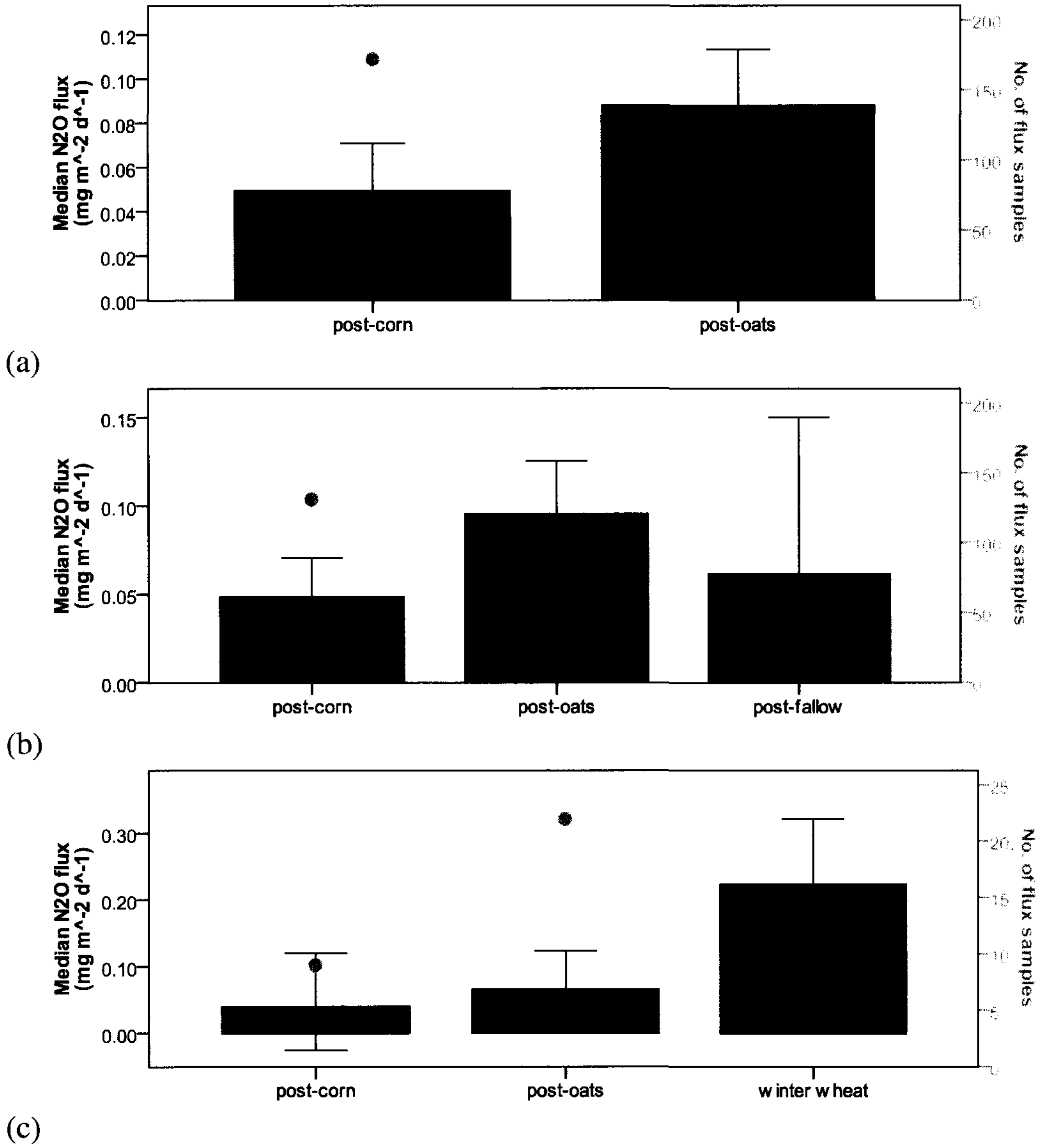


Figure 3.13. N_2O flux comparisons from different crops in the winter and spring at SC. Bars illustrate N_2O flux and dots illustrate sample size. Error bars indicate the 95% confidence interval for median flux. *Each plot illustrates data from sample dates with records for all of the crops illustrated to give a consistent base for the comparisons.* Flux values therefore do not represent all non-growing season sampling dates in the SC dataset. Sample sizes differ within each plot because there were 6 sites sown to corn each year, 3 sites sown to oats, 1 site in winter wheat (2007 only) and 2 sites in spring wheat (2008 only). (a) N_2O flux from post-corn versus post-oats, (b) N_2O flux from post-corn versus post-oats versus post-fallow, (c) N_2O flux from post-corn versus post-oats versus winter wheat.

As in the case of SC, Wagner-Riddle *et al.* (2007) report higher N_2O flux from corn versus winter wheat during the growing season. However, in contrast to SC results, Wagner-Riddle *et al.* (2007) find that crop type does not influence N_2O flux during the non-growing season. Spring wheat sites in Corre *et al.* (1996) have higher N_2O fluxes than those from oat sites monitored over the growing season, fall, and spring (Table A 1). These results conform to the significant ($p \leq 0.05$) growing season and fall pattern between spring wheat versus oat sites at SC during the growing season and fall.

Because crop type does influence N_2O flux year-round at SC, this may indicate that N_2O production at SC is N-limited, as suggested by Dusenbury *et al.* (2008). Lemke *et al.* (1998) find that, statistically, NO_3^--N, NH_4^+-N, and water-soluble organic carbon (WSOC) explain 95% of spring flux variability, but, most importantly, the authors believe that high WFPS is the trigger for flux spikes. Higher WFPS provides higher denitrification potential. Lemke *et al.* (1998) hypothesize that most N_2O flux occurs after WFPS reaches a threshold value, and, only once initiated, is its magnitude governed by N and/or C levels. Rochette *et al.* (2004) determine that N_2O flux highs closely follow rain events, but, in their study, N_2O flux is not limited by soil N. Using DEA analysis, van Bochove *et al.* (2000) also find that N_2O flux appears not to be N- or C-limited, at least from January through April.

3.3.5 Temporal variation in N_2O flux

Daily N_2O flux with soil temperature data and soil moisture data is illustrated in Figure 3.14 and Figure 3.15. In general, the highest fluxes occur during the growing season. However, growing season fluxes are muted in 2008, possibly due to lower levels of microbial activity from May through mid-June, due to lower temperatures than 2007 (Figure 3.9). It is also possible that peak N_2O fluxes, following starter and four-leaf

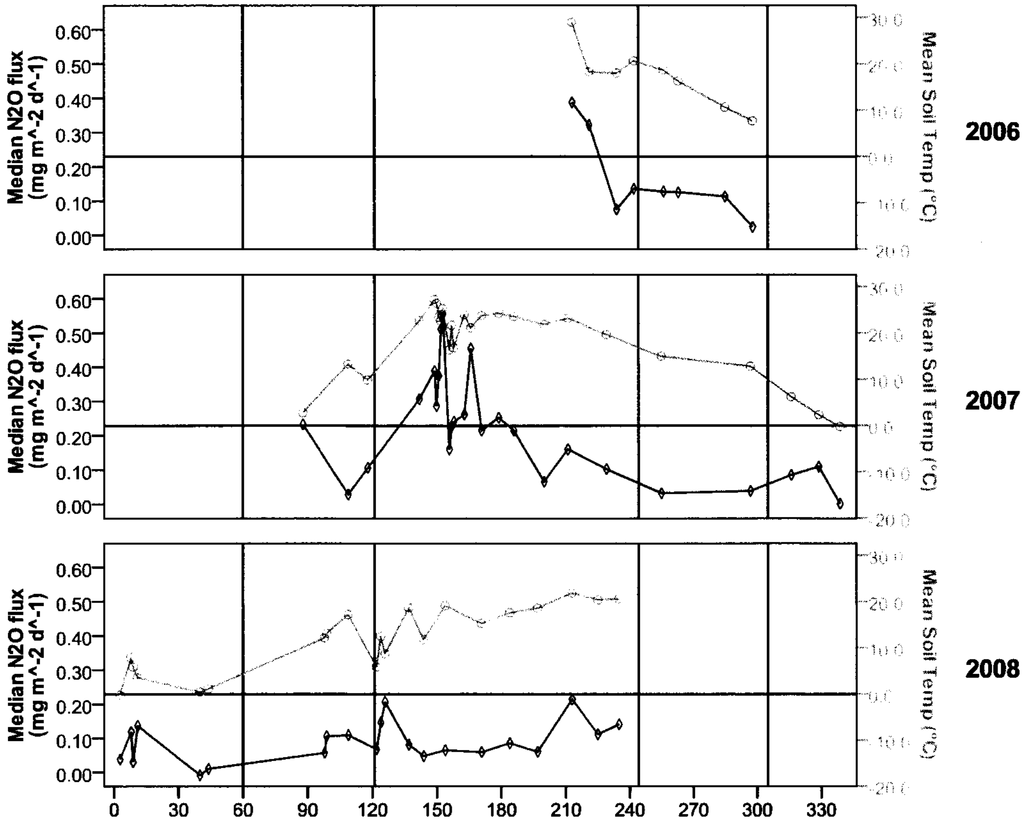


Figure 3.14. N_2O flux (diamonds) and soil temperature at 5 cm depth (circles) by Julian day (JD) and year, all SC data. Vertical reference lines divide seasons as follows: JD 60-120 = spring, JD 121-243 = growing season, JD 244-304 = fall and JD 305-059 = winter. Note that straight line interpolations are plotted to show N_2O flux and soil temperature trends only and may not reflect true inter-sample values.

fertilizer applications during these months, are missed in 2008, because sampling during 2008 does not intensify following fertilization events, in contrast to the protocol followed in 2007. Daily median fluxes in late 2006 peak at 0.4 mg N_2O m^{-2} d^{-1} at the beginning of August when soil temperature, precipitation, and soil moisture are high (Figure 3.14, Figure 3.9, Figure 3.15). The 2006 N_2O flux data may not be reliably compared to that of 2007 and 2008, because they only represent that from corn sites. The 2007 and 2008 data are from all nine SC sites and represent all crops in this study, that is corn, oats, winter

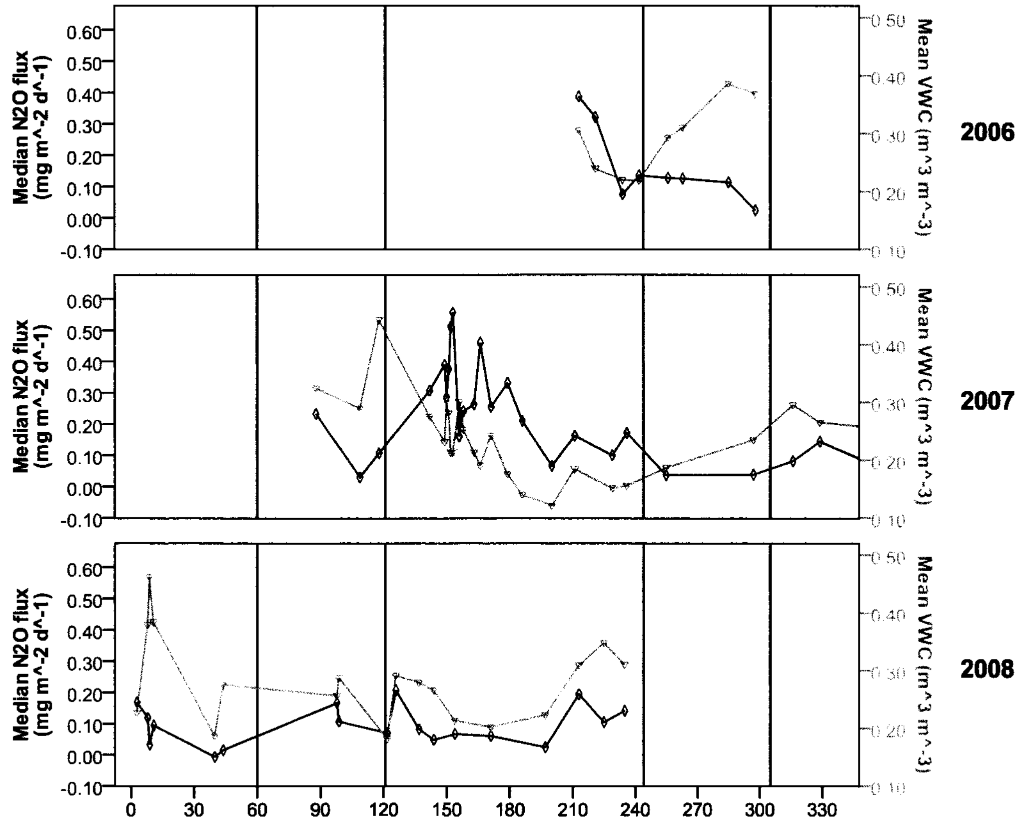


Figure 3.15. N_2O flux (diamonds) and soil moisture content at 10 cm depth (inverted triangles) by Julian day (JD) and year, all SC data. Vertical reference lines divide seasons as follows: JD 60-120 = spring, JD 121-243 = growing season, JD 244-304 = fall and JD 305-059 = winter. Note that straight line interpolations are plotted to show N_2O flux and soil moisture trends only and may not reflect true inter-sample values.

wheat, and spring wheat. In 2007, relatively high daily spring fluxes occur at the end of March (median of approximately 0.25 mg N_2O m^{-2} d^{-1}), corresponding with high spring soil temperature (Figure 3.14) and soil moisture content (Figure 3.15). The 2007 daily growing season fluxes are especially high (up to a median of 0.5 mg N_2O m^{-2} d^{-1}) during the first two weeks of June, when sampling occurred for several successive days following starter fertilization at the end of May. Although also possibly soil temperature driven (Figure 3.14), these high fluxes do not appear to correspond with high soil moisture content (Figure 3.15). During the non-growing season, relatively high daily peak fluxes of up to 0.15 mg N_2O m^{-2} d^{-1} occur during the second week of January 2008, during an extreme thaw event, when soil temperature at 5 cm depth reaches approximately 10°C (Figure 3.14). The peak fluxes of the growing season of 2008 occur at the beginning of May, and at the end of July. The May flux peak of 0.23 mg N_2O m^{-2} d^{-1} corresponds with sampling which occurs following starter fertilization (at least for oats), high precipitation levels, and high soil moisture content (Figure 3.9, Figure 3.15). The late July peak, at the same flux magnitude, corresponds with high precipitation and high soil moisture content (Figure 3.9, Figure 3.15).

Overall, daily N_2O fluxes reflect the following patterns: spring N_2O fluxes follow the pattern of soil moisture in 2007 and soil temperature in 2008, growing season N_2O fluxes follow the pattern of soil temperature in July and August, fall N_2O fluxes follow the pattern of soil temperature, and winter N_2O fluxes follow the pattern of soil temperature during January and February (Figure 3.14, Figure 3.15). On an annual basis, therefore, it would appear that soil temperature is a more important driver of N_2O flux from agricultural land in southern Ontario than soil moisture content.

As with the daily median N_2O fluxes discussed above, all of the seasonal median N_2O flux values at SC are low. The median N_2O flux at SC from all sites is the same in the spring, when soil moisture is highest, and in the growing season, when soil temperature is highest, at 0.1 mg N_2O m^{-2} d^{-1}. Winter and fall median fluxes are also equivalent at 0.05 mg N_2O m^{-2} d^{-1} (Figure 3.10b, Table A 4). Median spring N_2O flux is greater than both median fall N_2O flux ($z_U = -3.5, p < 0.001$) and median winter N_2O flux ($z_U = -5.1, p < 0.001$). Median growing season N_2O flux is also greater than both median fall N_2O flux ($z_U = -6.6, p < 0.001$) and median winter N_2O flux ($z_U = -11.4, p < 0.001$). When analytical error (± 0.04 mg N_2O m^{-2} d^{-1}) is taken into account, however, the differences between seasonal SC N_2O fluxes may not be statistically significant (see section 3.2.5).

Wagner-Riddle *et al.* (2007) measure N_2O fluxes by a micrometeorological method. Their research also takes place in southern Ontario, from crops and soil which are equivalent to those at SC. Wagner-Riddle *et al.* (2007) subdivide their continuous N_2O flux data into two, rather than four, seasonal categories: a "growing season" of May through October, and a "non-growing season" of November through April. The SC data, by the categories of Wagner-Riddle *et al.* (2007), have a "growing season" median flux of 0.2 mg N_2O m^{-2} d^{-1}, from both corn and winter wheat sites (Table A 1). In Wagner-Riddle *et al.* (2007), median growing season N_2O flux from corn is up to eight times greater (Table A 1). For winter wheat, in contrast, the median growing season flux in Wagner-Riddle *et al.* (2007) is comparable to that at SC (Table A 1). It is possible that flux values from corn sites in Wagner-Riddle *et al.* (2007) may be more accurate, as their methods may capture a more representative flux range than those at SC. SC fluxes were measured as seldom as bi-weekly, and therefore the dataset may exclude sudden flux spikes following precipitation (especially precipitation events after a fertilization), and/or thaw events. In contrast, growing season winter wheat receives no fertilization in either study, which may explain the comparable fluxes at SC and in Wagner-Riddle *et al.* (2007).

Wagner-Riddle *et al.* (2007) find that non-growing season N_2O fluxes can be significant. For example, non-growing season N_2O fluxes, from fields with corn residue, can be as high as those from the corn crop itself during the growing season (Table A 1). In Wagner-Riddle *et al.* (2007), non-growing season fluxes for winter wheat are small and equivalent to those of the growing season (Table A 1). These N_2O fluxes, too, are comparable to SC non-growing season winter wheat fluxes (Table A 1). N_2O flux records, over four non-growing seasons, indicate that these fluxes make up between 38% to 88% of annual emissions, from fields in a soy/corn/wheat rotation under conventional management practices (Wagner-Riddle *et al.* 2007). At least for corn sites, the pattern, of growing season flux > non-growing season flux, does appear to be the same in both studies (Table A 1), although non-growing season post-corn median N_2O flux in Wagner-Riddle *et al.* (2007), from sites under similar treatment as the SC R & T fields, is higher than the growing season median flux for corn sites at SC (Table A 1).

Only one winter season, that of 2007/2008, is monitored for N_2O flux at SC. Median November, December, and January N_2O fluxes range from 0.04 to 0.09 mg m^{-2} d^{-1}, similar to those of the fall of both 2006 and 2007 (0.03 to 0.13 mg m^{-2} d^{-1}, Figure 3.16, Table A 5). In contrast, February has a very low median N_2O flux at 0.01 mg m^{-2} d^{-1} (Figure 3.16, Table A 5, Figure 3.17). Neither December nor February experienced thaw conditions during the winter of 2007/2008, as defined in the SC methodology as ≥ 3 days at ≥ 4°C. Additionally, given that 2007/2008 was a snowy winter, there are only snow flux samples for those two months. The snow gas samples in February are considerably smaller than those on Dec 17/07 and Jan 3/08 (Figure 3.17). There are no appreciable differences in soil moisture between these periods, while soil temperature appears to be

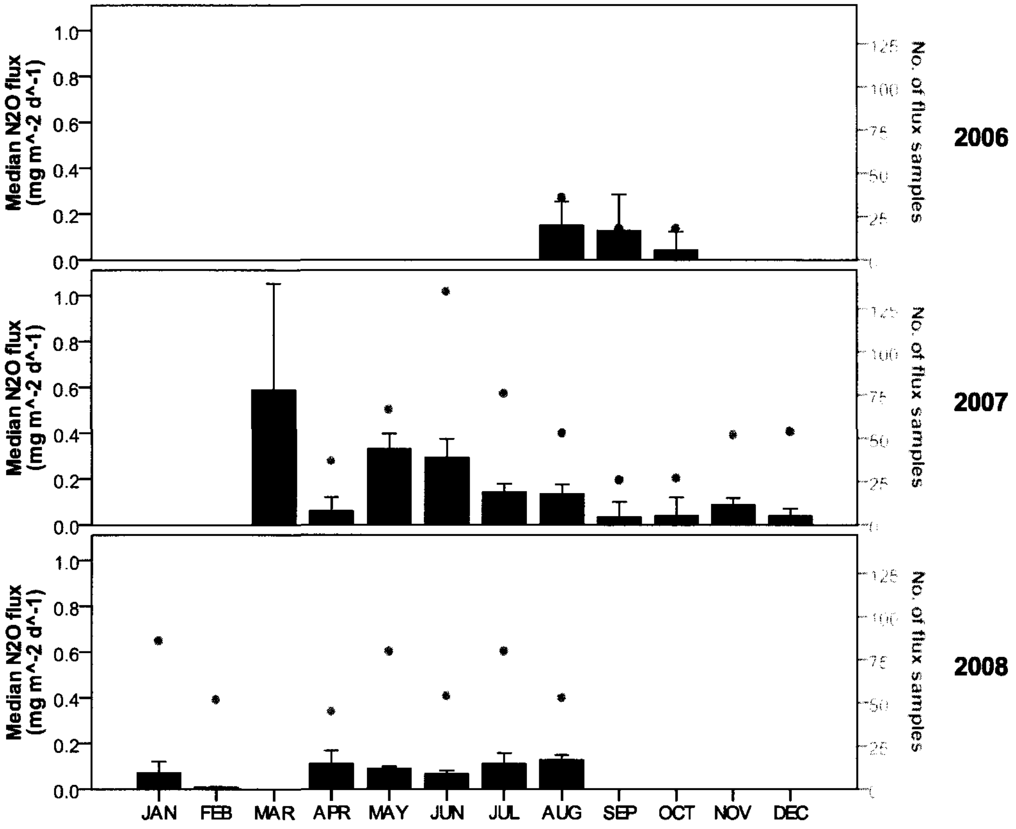


Figure 3.16. N_2O flux (bars) and sample size (dots) for months monitored during the SC field study. Error bars indicate the 95% confidence interval for median N_2O flux. The large confidence interval for median N_2O flux during March 2007 reflects a wide range of replicate flux values, which reaches a maximum flux of 26.09 mg N_2O m^{-2} d^{-1} on Mar 22/07.

higher in February, as compared with the earlier sampling dates, when fluxes would be expected to be lower. N_2O diffusion from the soil to the snow surface may be limited in February due to the possibility of increased snow depth, higher snow density, and the possible existence of ice lenses.

Goodroad and Keeney (1984) report a January mean N_2O flux from silt loam soil in Wisconsin, which is an order of magnitude higher than that from all SC sites in January (Table A 1). However, the comparison may be skewed because Goodroad and Keeney (1984) sample on only one date, whereas there are four SC January sampling

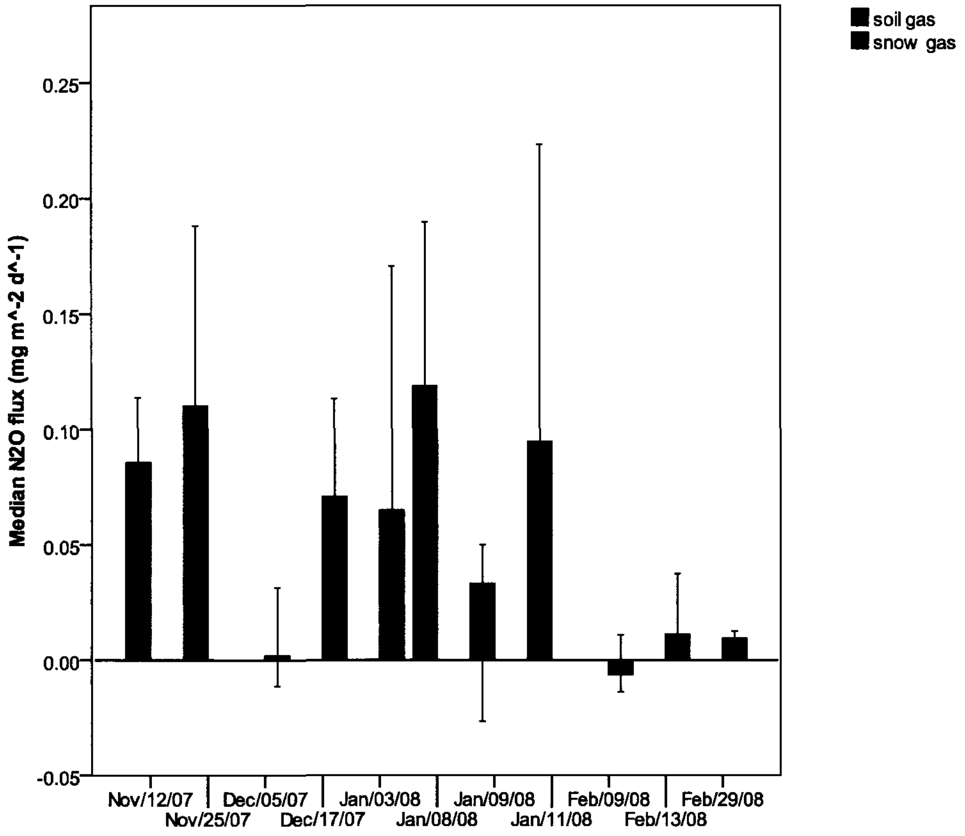


Figure 3.17. N_2O flux during the winter of 2007/2008. Error bars indicate the 95% confidence interval for median N_2O flux. Measured N_2O flux from snow was significantly lower than that from soil $z_U = -5.500, p < 0.001$).

dates. The crop grown during the growing season preceding the Goodroad and Keeney (1984) study is unreported.

Lemke *et al.* (1998) report daily geometric mean N_2O flux from agricultural soils in Alberta. They find no "appreciable" emissions in winter (Table A 1), similar to those at SC. In contrast, Lemke et al. (1998) find that flux, during the main spring snowmelt alone, contributed 16% to 60% of annual N_2O emissions. Spring fluxes in Lemke et al. (1998) are up to 50 times greater than at SC (Table A 1).

Van Bochove *et al.* (2000) find that winter and spring fluxes, from southern Quebec barley fields over three years, are equivalent or higher than those of the growing season. Van Bochove *et al.* (2000) incorporate snow depth, snow porosity, snow resistance to diffusion, and N_2O concentrations within the snowpack, into their calculations for N_2O flux, as opposed to sampling solely at the surface as for SC. In van Bochove *et al.* (2000), mean fluxes, from three winters, range over an order of magnitude (Table A 1). These are notably five to 70 times higher than the mean winter flux at SC (Table A 1). Perhaps the snow fluxes measured at SC would be higher if the more complex method of van Bochove *et al.* (2000) is used. Conversely, the higher total fluxes from van Bochove *et al.* (2000) versus SC might be explained by climatic differences. Soil temperatures remained almost consistently ≥ 0°C in Quebec, due to the insulating effect of a continuous snow cover, potentially generating higher total amounts of N_2O than those in the more temperate southern Ontario climate, which is prone to generally lower soil temperatures (Wagner-Riddle *et al.* 2007, Petrone and Macrae, *unpublished data*), due to a lack of continuous snow cover.

Van Bochove *et al.* (2000) attribute annual differences in winter fluxes as at least partly due to differences in the duration and thickness of snow cover. They ascribe their lowest mean winter flux measurement to lower soil moisture, late snowfall, and early snowmelt. They attribute the highest mean winter flux, during year three of their study, to high soil moisture, more grain residue, a tripled fertilization rate (70 kg N ha^{-1} versus 24 kg N ha^{-1} in years one and two), and higher soil temperatures, due to a thick snow cover. SC fields (grain in rotation with corn) have amendment levels which total approximately 100 kg N ha^{-1} y^{-1} (Table 3.2), representing 40% higher levels than the highest fertilization rate in van Bochove *et al.* (2000). Curiously, van Bochove *et al.* (2000) find that, although mean December to January N_2O fluxes are high (7.6 mg N_2O m^{-2} d^{-1}) during the early winter of the year three of their study, the mean flux in April, during the main snowmelt period of the same year, is three times smaller (Table A 1). The authors do not provide an hypothesis to explain why this would be the case. At SC during the winter of 2007/2008, mean flux is 0.1 mg N_2O m^{-2} d^{-1}, while mean spring flux is three times higher in 2007, and seven times higher than this value in 2008 (Table A 1). Although van Bochove *et al.* (2000) measure N_2O fluxes daily during the two weeks following snowmelt during the first two years of their study, they do not report these data, so it is not possible to observe exactly when their fluxes dropped off to a negligible level (defined by the authors as mean flux ≤ 0.17 mg N_2O m^{-2} d^{-1}).

In van Bochove *et al.* (2001), spring N_2O fluxes are reported from a clay loam soil treated with pig slurry in the fall. The authors speculate that, due to the existence of a basal ice layer in this later study, and high, short-lived N_2O fluxes during melt, N_2O accumulates in the subsurface and is quickly released when basal ice degrades. Winter 1998/1999 soil temperatures, reported by van Bochove *et al.* (2001), are unseasonally cold due to a lack of continuous snow cover, and remain frozen to 15 cm through the winter, unlike the three winters of 1994/5, 1995/6, and 1996/7 (van Bochove *et al.* 2000). In contrast to van Bochove *et al.* (2001), Wagner-Riddle *et al.* (2008) determine, through isotopic methods, that spring N_2O is mainly newly produced, and not physically released from sub-surface storage. The maximum mean flux reported by van Bochove *et al.* (2001) is 19 mg N_2O m^{-2} d^{-1} on Apr 19, an order of magnitude higher than spring flux in van Bochove *et al.* (2000), quickly dropping to a "negligible" mean flux of 0.8 mg N_2O

m^{-2} d^{-1}, two days after full snow ablation/melt. The maximum mean spring flux from all sites at SC, which occurs on Mar 22/07, is five times smaller, and falls to "negligible" levels, as defined by van Bochove *et al.* (2001), by Mar 29/07 (Table A 1). In 2008, no SC measurements were taken during March, so a second main melt period at SC is not available for further quantitative or qualitative comparison.

Burton and Beauchamp (1994) find spring flux maxima that are similar to van Bochove *et al.* (2001), an order of magnitude greater than those at SC (Table A 1). The fluxes reported by Burton and Beauchamp (1994) originate from arable loamy sand in southern Ontario, with a 50% higher fertilization rate (150 kg N ha^{-1}) than that at SC (100 kg N ha^{-1}). Dörsch *et al.* (2004) study January to April N_2O fluxes from German agricultural sites fertilized, ploughed, and ridged in the previous fall, in preparation for growing potatoes during the following growing season. The authors report a maximum daily mean flux during an extended thaw in mid-February, which is four times the maximum daily mean flux that occurs during the non-growing season at SC (Table A 1) on Mar 22/07, as noted above. The higher non-growing season N_2O fluxes in Dörsch *et al.* (2004) may largely result from their fall fertilizer and manure applications, along with their augmentation of soil organic matter by ploughing in unharvested mustard (*Brassica alba*) in the fall.

Figure 3.16 illustrates median N_2O flux at SC, by year and month. There are no March 2008 samples with which to compare the median March 2007 N_2O flux of 0.6 mg m^{-2} d^{-1}, the highest of all recorded months. The wide range of sub-zero and above-zero air temperatures, during March 2007, may contribute to both the relatively high SC flux magnitude, and the high spatial and temporal variability in N_2O flux, during this time (Figure A 1), through disruption of soil macropores and organic matter, and consequent increase of labile C and N. In April 2008, the N_2O flux is higher than April 2007 (0.1 versus 0.06 mg N_2O m^{-2} d^{-1}, Table A 5). This may be attributable to the higher air temperatures of April 2008, as noted above in section 3.3.2, taking prevalence as the major flux driver at his time.

Goodroad and Keeney (1984) report March N_2O fluxes from manured silt loam soils in Wisconsin, which are comparable to those at SC. There is an order of magnitude difference between mean N_2O flux on the two March dates of their study (Table A 1). Mean daily N_2O flux in March 2007 at SC also ranges through an order of magnitude (Table A 1), with a monthly mean of 2.4 mg N_2O m^{-2} d^{-1}.

In addition to the importance of the spring snowmelt period, Lemke et al. (1998) report high N_2O fluxes from mid-June to late July, with summer peaks following fertilization and precipitation events, a pattern also found in many other studies (e.g. van Kessel *et al.* 1993). In van Kessel *et al.* (1993), daily median N_2O fluxes, measured sporadically from May to October, reach a maximum on Jun 4 (Table A 1), while the daily maximum median N_2O flux for the equivalent time period, at SC in 2007, is 30 times lower (Table A 1), even though this is a post-fertilization SC flux. Lemke *et al.* (1998), who report geometric means rather than medians, find maximum daily geometric mean fluxes that are 30 times higher than the maximum daily geometric mean flux at SC (Table A 1). In the first year reported in Lemke *et al.* (1998), the daily geometric mean N_2O flux, during a segment of a wet growing season (WFPS > 60%), ranges over 6 mg

m^{-2} d^{-1}, with a maximum single replicate N_2O flux of 38 mg m^{-2} d^{-1} (Table A 1). For growing season spring wheat sites at SC, daily geometric mean fluxes range over 0.3 mg N_2O m^{-2} d^{-1} (Table A 1). At SC, WFPS exceeds 60% only once during the growing season, on Aug 12/08, when geometric mean N_2O flux is up to two orders of magnitude lower than that of Lemke *et al.* (1998), at 0.1 mg m^{-2} d^{-1}.

During a two-year study in New York state, Duxbury *et al.* (1982) calculate a very high maximum mean daily cornfield flux of 57 mg N_2O m^{-2} d^{-1} from silt loam. This high flux occurs in early July. Mosier and Hutchinson (1981) report an equally high growing season daily maximum mean flux from irrigated corn in Northern Colorado. These fluxes contrast with a SC daily mean growing season flux high which occurs in May, at two orders of magnitude lower than these earlier studies. Growing season flux maxima reported by Wagner-Riddle *et al.* (2007) are also lower than those of Mosier and Hutchinson (1981) and Duxbury *et al.* (1982). Compared to contemporary agricultural practices, those of the early 1980s may have resulted in a lower efficiency of fertilizer uptake in crops. Also, fertilization rates are higher in these two studies, at 130 kg N ha^{-1} (Duxbury *et al.* 1982), and at 200 kg N ha^{-1} (Mosier and Hutchinson 1981, double the SC rate of application).

For the early growing season months, median fluxes at SC are approximately four times higher in 2007 as compared to 2008, at 0.33 versus 0.09 mg N_2O m^{-2} d^{-1} for May, and at 0.29 versus 0.07 mg N_2O m^{-2} d^{-1} for June (Figure 3.16, Table A 5). This may partly result from May and June 2007 data, which includes some samples that immediately follow fertilization events, as mentioned above. However, as each 2007 sample from these two months is consistently higher than those from 2008 (Figure A 2), the higher air temperatures of May 2007 may also play a role.

Later in the growing season, median N_2O flux at SC is virtually equivalent in 2007 and 2008, at approximately 0.1 mg m^{-2} d^{-1} for both July and August at all sites (Figure 3.16, Table A 5), apparently not reflecting any difference due to, for example, the large storm events of July 2008 and/or the generally high levels of precipitation of the growing season of 2008. The August 2006 N_2O flux is similar to that of August 2007 and August 2008 (Figure 3.16, Table A 5). Typical mean, as opposed to median, daily spring and growing season fluxes, reported by Rochette *et al.* (2004) from sites growing corn, are up to 3.6 mg N_2O m^{-2} d^{-1}. These increase at times of elevated WFPS, and peak during July 2001 and June 2002 (Table A 1, Rochette *et al.* 2004). The highest maximum daily mean growing season N_2O flux reported by Rochette *et al.* (2004) reaches two orders of magnitude higher than that at SC, which occurs in May (Table A 1). Maxima in Rochette *et al.* (2004) are comparable to those in Duxbury *et al.* (1982) and Mosier and Hutchinson (1981), as discussed above. However, Corre *et al.* (1996) reports maximum daily median growing season N_2O fluxes for wheat and oat sites, which are up to two orders of magnitude lower than the maximum daily mean fluxes in Mosier and Hutchinson (1981), Duxbury *et al.* (1982), and Rochette *et al.* (2004). The maximum daily median growing season flux at SC for oat sites is similar to Corre *et al.* (1996), while the equivalent statistic for SC wheat sites is lower (Table A 1).

The median N_2O flux at SC in September is four times higher in 2006 (0.13 mg m^{-2} d^{-1}) than 2007 (0.03 mg m^{-2} d^{-1}, Figure 3.16, Table A 5), potentially reflecting the higher temperatures of the fall of 2006. October, however, had equivalent N_2O fluxes in 2006 and 2007 (0.04 mg m^{-2} d^{-1}). Negligible fall N_2O fluxes are also reported elsewhere (e.g. Duxbury *et al.* 1982, van Kessel *et al.* 1993, Burton and Beauchamp 1994, Lemke *et al.* 1998, Dusenbury *et al.* 2008).

Temporal patterns in N_2O flux at SC generally follow those reported in the literature with high fluxes in the spring and summer, corresponding to soil temperature increases, soil moisture increases, and applications of inorganic and organic fertilizer. Low N_2O fluxes tend to occur in the fall and winter at SC, with only minor increases in flux corresponding to the one (greater than two-day) winter thaw which occurs in January 2008 (Figure 3.17). This finding conflicts with some winter literature (e.g. van Bochove *et al.* 2000, Ruser *et al.* 2006, Table A 1), but corresponds with other studies (e.g. Lemke *et al.* 1998, Wagner-Riddle *et al.* 2007). The magnitude of N_2O flux during all months at SC is low. The highest recorded daily mean flux at SC occurs in March. Daily mean maxima in the literature can reach up to two orders of magnitude higher than those at SC (e.g. Rochette *et al.* 2004). The generally low N_2O fluxes at SC, as compared with some in the literature, may reflect real *in situ* N_2O flux magnitudes. Alternatively, they may be partially attributable to SC flux spikes which may have been missed following fertilization, precipitation, and thaws at SC. Discrepancies, between SC N_2O fluxes and some of those reported in the literature, may also be due to differences in sampling methodology. There is significant variation in fluxes among replicates at SC, which may additionally contribute to these differences. At SC, there are differences of up to three orders of magnitude in N_2O flux between replicates measured in the spring.

3.3.6 Modelling N_2O flux using soil temperature and soil moisture data

As discussed above, some of the temporal differences in N_2O flux appear to be correlated with climate, and, specifically, its influence on soil temperature and/or soil moisture. When the SC N_2O flux dataset is divided into soil moisture classes, N_2O fluxes generally increase as soil temperature increases (Figure 3.18). Median N_2O flux generally

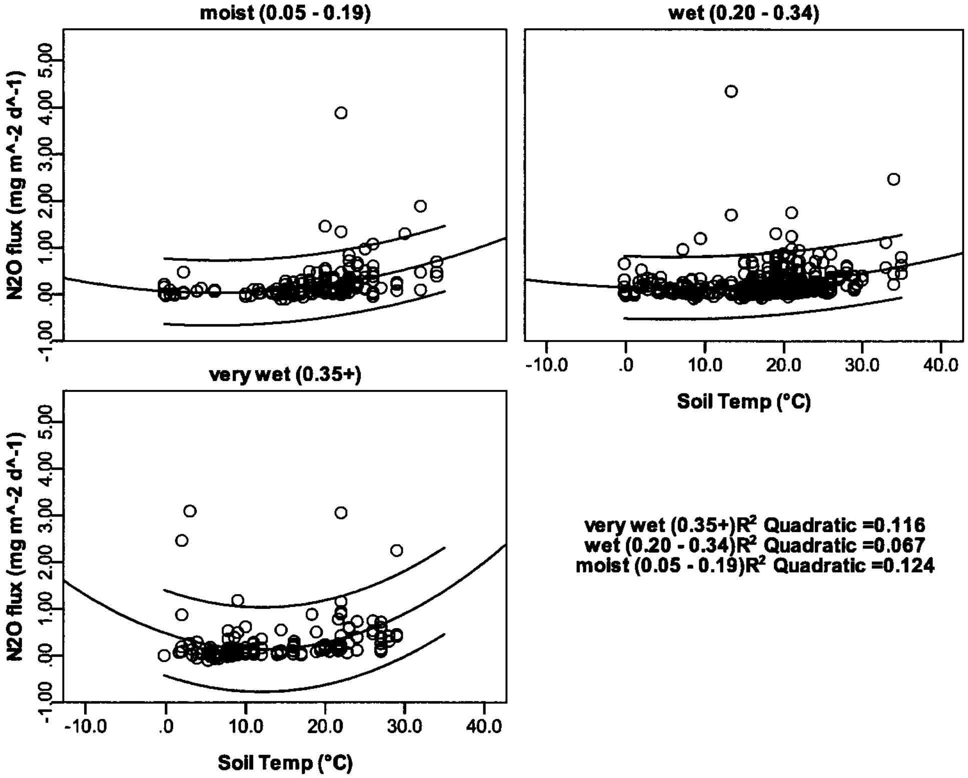


Figure 3.18. Soil temperature at 5 cm depth versus N_2O flux by soil moisture categories (VWC in $m^3\ m^{-3}$ at 10 cm depth) at SC with regression lines for moist ($y = 0.69 - 0.011\,t + 0.001\,t^2$, $F = 14.1, p_F < 0.001, n = 202, r = 0.35, p_{\rho=0} < 0.01$), wet ($y = 0.155 - 0.006\,t + 0.001\,t^2, F = 14.1, p_F < 0.001, n = 397, r = 0.26, p_{\rho=0} < 0.01$) and very wet ($y = 0.485 - 0.058\,t + 0.002\,t^2, F = 9.4, p_F < 0.001, n = 147, r = 0.34, p_{\rho=0} < 0.01$) soils. 95% confidence intervals bound the regression lines.

increases from lows at ≤ 0°C through highs at 30°C, with the ranges by moisture class as follows: 0 to 0.3 mg m^{-2} d^{-1} (moist soils), 0.05 to 0.3 mg m^{-2} d^{-1} (wet soils), and from 0.01 to 0.4 mg m^{-2} d^{-1} (very wet soils) (Table A 8). Moist soils are defined as 0.05 to 0.19 m^3 m^{-3} VWC, wet soils as 0.20 to 0.34 m^3 m^{-3} VWC, and very wet soils as ≥ 0.35 m^3 m^{-3} VWC. Between 0°C and 15°C, however, there are anomalies in this pattern of increasing flux with increasing soil temperature, especially in the very wet cores (Figure 3.18).

As discussed above, van Bochove *et al.* (2000) report significant N_2O fluxes from snow-covered arable sandy loam during three winter seasons. The authors observe that microbes are quite active at cold temperatures, with winter DEA at up to 50% of growing season DEA. The incidence of some near-0°C flux spikes at SC (Figure 3.18) suggest that there is a temperature threshold to such microbial activity. There may be a more rapid biotic response to thaw conditions in wetter soils (Figure 3.18).

The SC dataset consists of over 1000 samples, taken during a range of spatial and temporal (climatic) conditions, and it therefore represents a comprehensive range of N_2O flux values from arable clay loam, over a range of soil temperatures and moisture conditions, representative of those found across southern Ontario. The dataset may also be representative of N_2O fluxes from other clay loams overlying tills in similar climatic regions across southern Canada, the upper Midwest and New England states of the U.S., the U.K., northern continental Europe, and Scandinavia. The quantitative relationships among soil temperature, soil moisture content, and N_2O flux are investigated to attempt to predict flux based on these parameters, in addition to shedding light on the mechanics of the processes that generate N_2O. The raw data illustrate that there is much variability in N_2O flux for any given soil temperature or moisture level. This may be because a given temperature can occur over a range of moisture conditions, and vice versa. However, when the N_2O flux data are grouped according to soil moisture conditions, there is still substantial variability even within small ranges of soil temperatures (Figure 3.18). There is a moderate correlation between the N_2O flux and soil temperature in moist, wet, and very wet soils (Figure 3.18). Log-transforming the N_2O flux only marginally improves the correlations for all moisture groups (Figure 3.19),

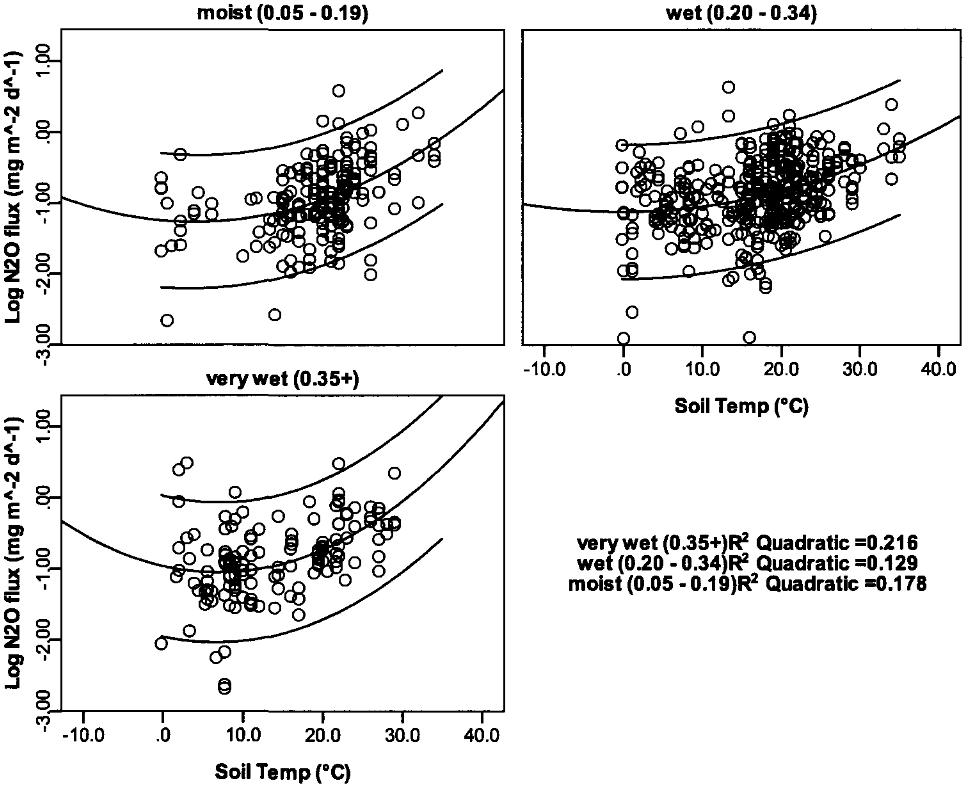


Figure 3.19. Soil temperature at 5 cm depth versus log N_2O flux by soil moisture categories (VWC in m^3 m^{-3} at 10 cm depth) at SC with regression lines for moist ($y = -1.246 - 0.010\,t + 0.001\,t^2$, $F = 19.7$, $p_F < 0.001$, $n = 185$, $r = 0.42$, $p_{\rho=0} < 0.01$), wet ($y = -1.124 + 0.0003\,t + 0.001\,t^2$, $F = 27.6$, $p_F < 0.001$, $n = 377$, $r = 0.36$, $p_{\rho=0} < 0.01$) and very wet ($y = -0.962 - 0.026\,t + 0.002\,t^2$, $F = 18.5$, $p_F < 0.001$, $n = 137$, $r = 0.47$, $p_{\rho=0} < 0.01$) soils. 95% confidence intervals bound the regression lines.

which demonstrates the effect of the other factors which influence N_2O flux. In a review, Bouwman (1990) summarizes that soil temperature and soil moisture are only two of several interconnected and time-dependent factors influencing N_2O emission rates. Other important factors include microbial populations, redox conditions, and the availability of N and organic C. Anaerobic microsites, e.g. water-filled pores or intra-aggregate zones, may play a significant role in the production of N_2O (Bouwman 1990, Parkin 1993), and therefore flux magnitude. Duxbury *et al.* (1982) find that, although high N_2O fluxes always occur at high soil moisture levels, the reverse is not always the case, that is a wet soil does not always produce high N_2O fluxes. Therefore, antecedent soil moisture and soil temperature conditions are likely additional critical factors influencing the magnitude of N_2O flux rates.

Nevertheless, strong quadratic relationships between summarized N_2O flux and soil temperature SC data are found when soil temperature is binned and plotted against median N_2O flux. (Because of an unequal distribution of data over soil temperatures in the SC dataset, bin divisions are delineated based on equal percentiles of flux data.) N_2O flux in all soil moisture conditions (VWC = 0.05 - 0.43 m^3 m^{-3}) is well correlated with soil temperature (r^2 = 0.52, Figure 3.20), as is the flux from very wet soil (r^2 = 0.49, Figure 3.21). The correlation, between the two variables, is even stronger when moist and wet soils are examined individually (r^2 = 0.79, r^2 = 0.78, respectively, Figure 3.21). This demonstrates that soil temperature is a key driver of N_2O flux at SC, and can be used to predict median flux values when general soil moisture levels are known.

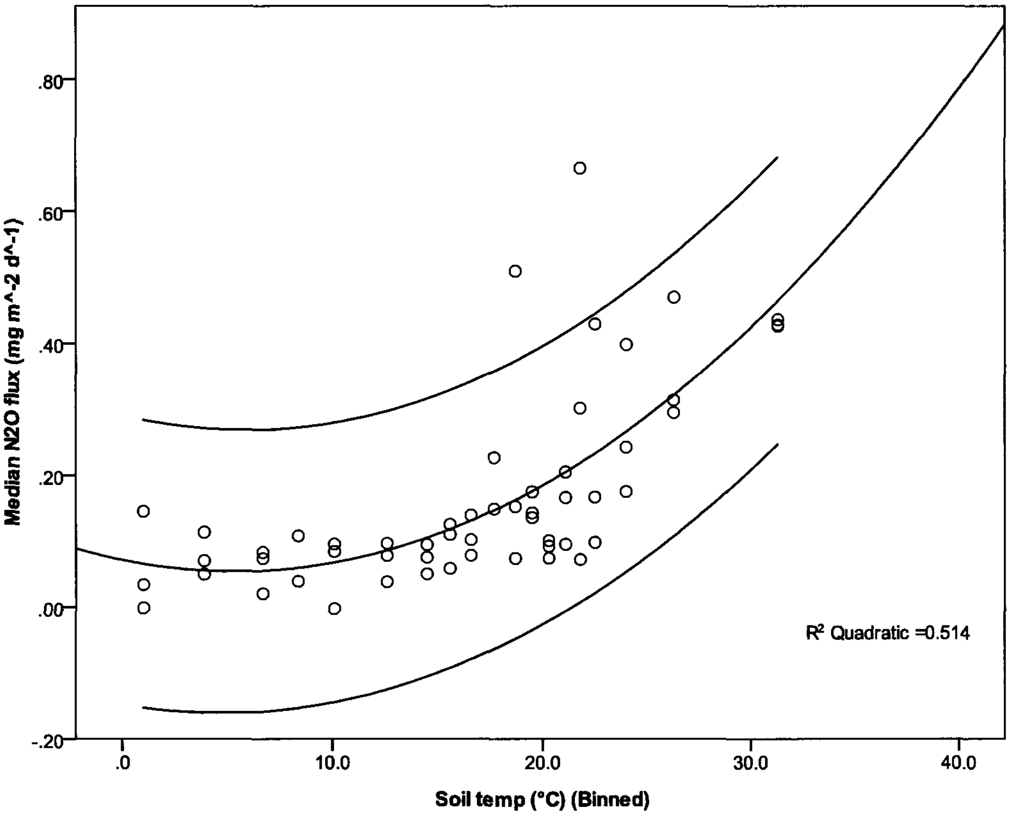


Figure 3.20. Binned soil temperature (mean value per bin) at 5 cm depth versus median N_2O flux at SC for moist through very wet soil moisture categories (0.05 to 0.43 m^3 m^{-3}, 10 cm depth). The regression line ($y = 0.072 - 0.007\,t + 0.001\,t^2$, $F = 27.5$, $p_F < 0.001$, $n = 55$, $r = 0.72$, $p_{\rho=0} < 0.01$) is bounded by its 95% confidence interval.

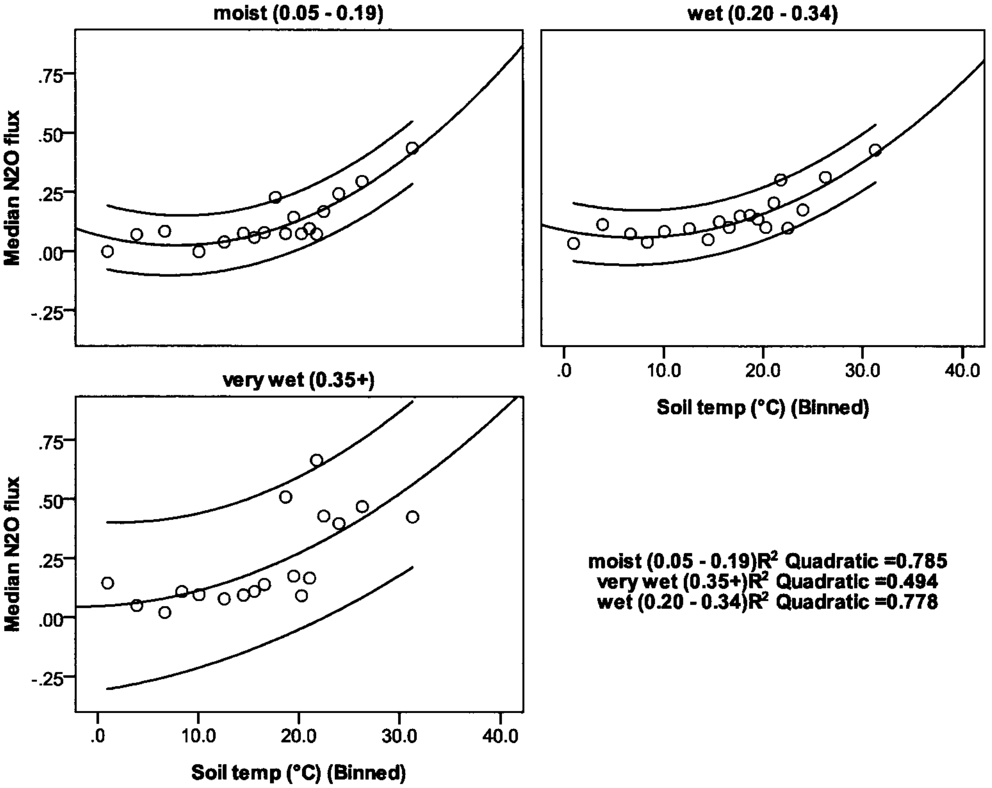


Figure 3.21. Binned soil temperature (mean value per bin) at 5 cm depth versus median N_2O flux (mg m^{-2} d^{-1}) at SC with regression lines for moist ($y = 0.068 - 0.011\,t + 0.001\,t^2$, $F = 27.4$, $p_F < 0.001$, $n = 18$, $r = 0.89$, $p_{\rho=0} < 0.01$), wet ($y = 0.090 - 0.009\,t + 0.001\,t^2$, $F = 28.1$, $p_F < 0.001$, $n = 19$, $r = 0.88$, $p_{\rho=0} < 0.01$) and very wet ($y = 0.047 + 0.002\,t + 0.0005\,t^2$, F = 7.3, $p_F = 0.006$, $n = 18$, $r = 0.70$, $p_{\rho=0} < 0.01$) soils. 95% confidence intervals bound the regression lines.

4 Importance of freeze-thaw cycles on N_2O fluxes from soil

The sensitivity of winter and spring N_2O fluxes to soil temperature change, by exposing soil mesocosms to winter and spring air temperature fluctuations while holding soil moisture constant, is examined below. The rapidity with which N_2O fluxes change in response to soil temperature fluctuations through 0°C is examined. Through daily N_2O flux sampling during multiple freeze-thaw cycles, N_2O emissions are quantified and compared.

4.1 Experimental methods

The Strawberry Creek freeze-thaw (SCFT) experiment was designed to expose SC soils to the air temperatures of a typical southern Ontario winter, from the surface downward. Soil moisture was held constant to reduce the complexity of the experiment, and to isolate the effect of soil temperature on N_2O flux. Additionally, space restrictions prohibited the incorporation of soil moisture variation into the experiment, in terms of total liquid and solid water content. (Due to soil temperature change through 0°C, the proportion of liquid water to ice did vary.)

The freezer used to simulate freezing temperatures during the experiment could only accommodate cores from one site. Nine intact soil cores were collected from the SC catchment in early November 2007, close to the R2 field site (Figure 3.2b). R2 soils were representative of soil properties found in the majority of the field sites (Table 4.1, Table 3.4). PVC tubes (30 cm high, 10 mm thick, and 16.5 cm ID), were inserted to a depth of 20 cm into the R2 soils. There was thus 10 cm of headspace above each soil core. Each

Table 4.1. Soil properties in the SCFT experiment. *Estimate based on soil data from SC soils at site R2, collected and analyzed in 2006 (Thuss, *unpublished data*).

Replicate	Bulk Density ($g\ cm^{-3}$)	Organic Content (%)	% C*	% N*	C:N*
D1	1.08	8	2.5	0.25	12
D2	1.07	12	2.5	0.25	12
D3	1.26	8	2.5	0.25	12
M1	1.09	9	2.5	0.25	12
M2	1.20	12	2.5	0.25	12
M3	1.16	12	2.5	0.25	12
W1	1.04	8	2.5	0.25	12
W2	1.03	9	2.5	0.25	12
W3	1.08	10	2.5	0.25	12
mean of 9 cores	1.11	10	2.5	0.25	12

PVC tube had a 5-mm x 5-mm groove along the top of the rim. The soil cores were secured into the PVC tubes from the bottom with Plexiglas® and duct tape. Three cores were designated dry (D1, D2, D3), three medium (M1, M2, M3), and three wet (W1, W2, W3). The three dry cores were oven-dried at 100°C for 24 hours. The remaining six cores were covered with perforated plastic caps. All nine cores were then stored at 4°C until the beginning of the SCFT experiment.

At the end of January 2008, fresh snow was collected from parkland in Kitchener, Ontario (43° 25' 6" N, 80° 28' 21" W). The three wet cores were saturated to field capacity with meltwater from this snow. Each of these cores was opened from the bottom, placed on a fine sieve, and the meltwater slowly added until it dripped through the sieve. The wet cores were then placed in 8 cm of meltwater for 24 hours, and then allowed to drain freely for an additional 24 hours. The Plexiglas® bottoms for all nine cores were sealed the following day with polyurethane construction adhesive (LePage PL Premium®, Henkel Canada Corp.). The medium and wet cores were covered with the perforated caps, and all nine cores were returned to storage at 4°C.

The experiment was delayed until April 2008. By that point the medium and wet cores had dried out significantly due to the low humidity of the refrigerator. Prior to the initiation of the experiment on Apr 15, the medium cores were watered with 9 mm of snowmelt. The wet cores were watered with 14 mm of snowmelt. M1 was still quite dry; an additional 7 mm was added to this core. M1 was redesignated W4 because its moisture content, after this addition of meltwater, was closer to the three wet cores than to M2 or M3 (Figure 4.1).

Thermocouple wires were inserted into each core, at 5 cm and at 15 cm, to measure soil temperature. Additionally, 20-cm TDRs (EC-20, Decagon Devices Inc., Pullman, WA) were installed in each core. The soil cores were insulated, from the bottom to 10 cm from the top (level with the soil surface), with flexible foil insulation. During the experiment, the cores were stored on 2.5-cm rigid foam to insulate the bottom (Figure 4.2). The temperature data was logged at 15-min intervals (CR10X logger, Campbell Scientific Inc., Logan, UT), and moisture data was logged at the same interval using an Onset™ weather station logger (H21-001, Onset Inc., Bourne, MA).

The experiment used temperature manipulations to simulate a series of winter thaws, followed by a more prolonged and extreme deep freeze / spring thaw. For the winter thaws, air temperature oscillations, representative of average conditions during winter freeze-thaw cycles in southern Ontario (Petrone and Macrae, *unpublished data*),

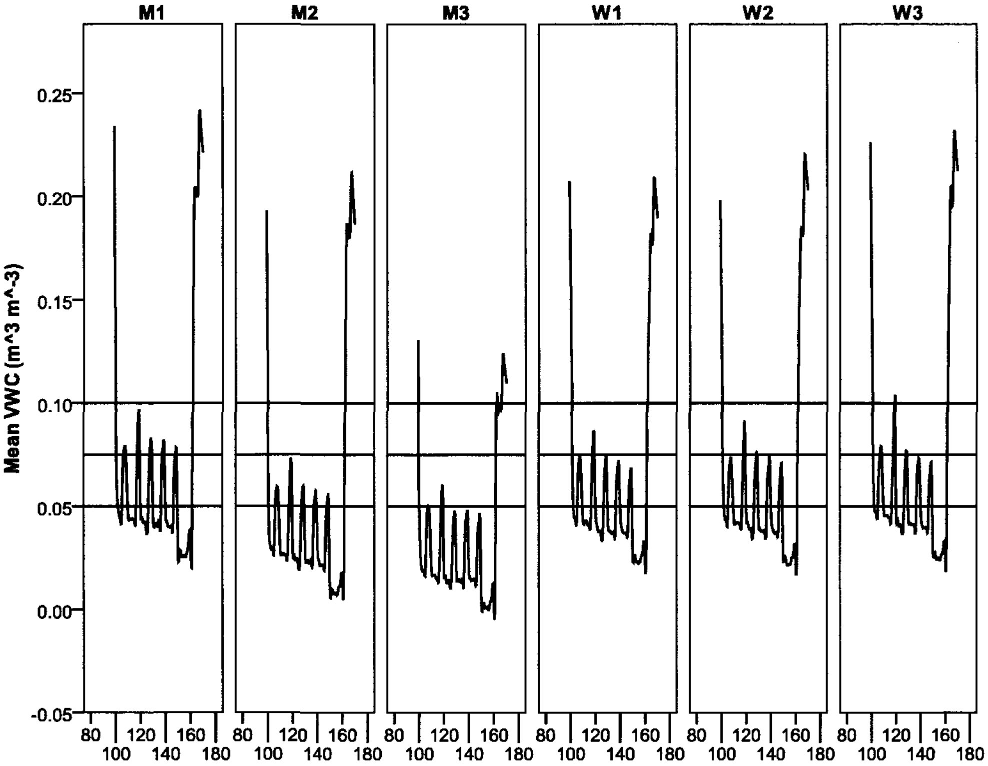


Figure 4.1. Liquid soil moisture content as sensed by the TDR for the 6 moist and wet cores during the SCFT experiment by Julian day. M1 was redesignated W4.

were applied to the soil cores to simulate five 10-day freeze-thaw cycles. Air temperature, for the first 7 days of each cycle, was maintained at approximately -5°C. The soil cores were then moved to the refrigerator (4°C) for 3 days, for approximately 8 hours each day, simulating average winter day-length at 43°N latitude. During these simulated thaws, the cores were returned to the freezer overnight (-5°C) for 16 hours, simulating average overnight sub-zero temperatures during a thaw period in southern Ontario. At the end of the winter thaw simulations, the cores were subjected to a "deep freeze" followed by a simulated spring thaw, during which they were held in the freezer at -10°C for 5 days followed by -5°C for 5 days. The cores were then moved to

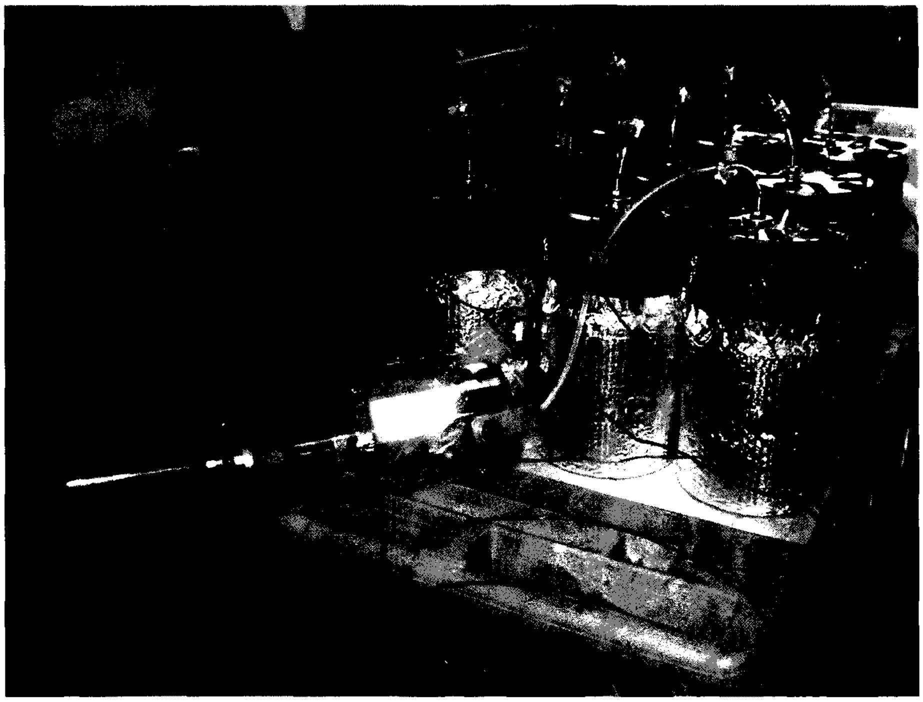


Figure 4.2. Insulated soil cores with sealed Plexiglas® lids and sampling procedure into Teflon® bags.

the refrigerator at 4°C for 5 days, to simulate early spring conditions, and then monitored at room temperature (≈ 20°C) for 4 days, to simulate late spring conditions as best as possible.

Before the beginning of the experiment, Plexiglas® lids were constructed, in order to collect N_2O samples from the headspace of the soil cores. These were 16.5 cm in diameter, with a 5-mm x 5-mm circular piece of flexible foam glued 5 mm from the edge of each lid along its bottom, aligned to fit the groove on the top of the rim of the PVC cores (Figure 4.3, Figure 4.2). Two holes were drilled into each lid, one 10 mm in diameter, and the other 3 mm in diameter. The large hole was fitted with a 10-mm ID barbed brass fitting, with the 15-mm barb on the top of each lid. An 8-cm piece of 4-mm ID flexible tubing was secured to the barb. A three-way valve was sealed onto the free

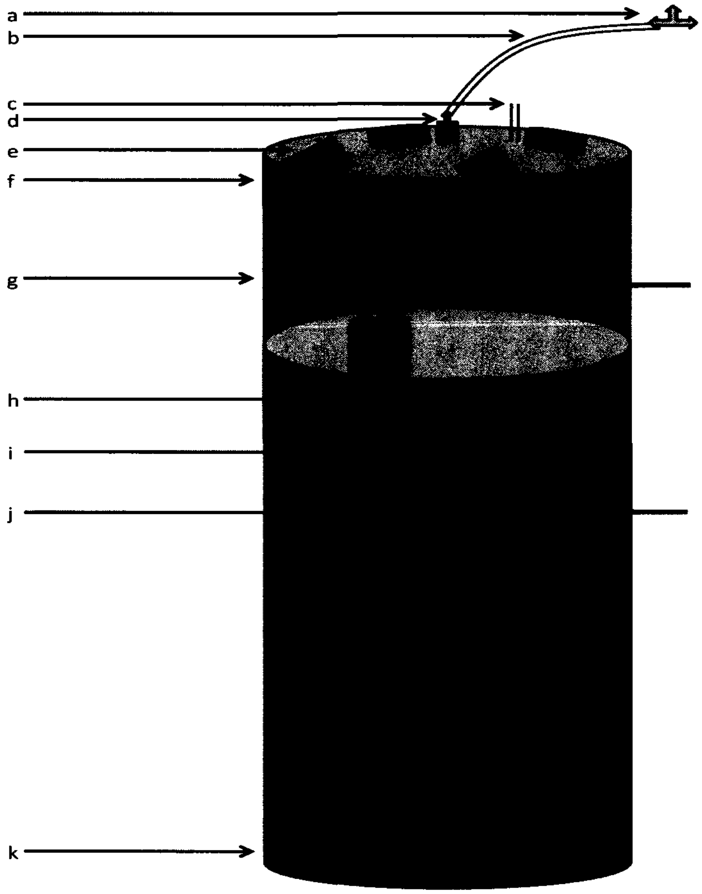


Figure 4.3. Soil core design. (a) Three-way sampling valve, (b) sampling tube, (c) vent tube, (d) barbed brass fitting, (e) Velcro®, (f) Plexiglas® chamber lid, (g) PVC tube, (h) soil core, (i) TDR, (j) thermocouple wire, (k) Plexiglas® bottom.

end of this tubing with plumbing sealant (Amazing Goop®, Eclectic Products, Inc.). Ten cm of 2-mm ID rigid plastic tubing was sealed into the small hole, with 8 cm protruding from the bottom of each lid, to equalize the pressure between the chamber air and ambient air, similar to methods employed by Hutchinson and Mosier (1981). This tubing was coiled and taped to the bottom of each lid, to prevent clogging from soil. Four 3-cm pieces of hook-type Velcro® were glued near the edge of the top of each lid, at equal distances apart. Each PVC core was fitted with corresponding hook-type Velcro® around the top sides of its circumference. This allowed each lid to be sealed onto the core when sampling: the foam underlying each lid was tightly held into the groove of the PVC core with four free pieces of 6 cm of loop-type Velcro®.

Soil cores were sampled once a day during the 7-day freeze portion of the simulated freeze-thaw cycles. During the 3-day thaw portions, they were sampled in the morning, prior to being moved from -5°C to 4°C, and then again in the evening, prior to being moved from 4°C to -5°C. During the 19-day deep freeze / spring thaw experiment, the cores were sampled approximately once a day.

Prior to sampling, the perforated plastic caps were removed from the medium and wet cores. The lids were secured onto the nine cores, with the three-way valves closed to the sampling tube. After 2 hours, a 0.7-L ambient air sample was drawn into a Teflon® bag (232-945A, SKC Gulf Coast, Houston, TX), using a manual vacuum apparatus (231-945, SKC Gulf Coast, Houston, TX, Figure 4.2). The Teflon® bags used during the SCFT experiment were purged with N_2 gas prior to sampling. Collection of an ambient air sample was followed by extraction of gas samples from each enclosed soil core, using the same bags and apparatus. Gas samples were analyzed for N_2O within 48 hours at the Department of Geography and Environmental Studies, Wilfrid Laurier University, using a Fourier transform infrared gas analyser (Gasmet DX-4015, Helsinki, FI), with a detection limit of approximately 30 ppbV N_2O and analytical accuracy of ± 20 ppbV N_2O.

All statistical analysis was conducted using SPSS version 16.0 (SPSS Inc., Chicago, IL). Sets of N_2O flux data, subdivided by thaw period, spring period, soil moisture and soil temperature categories, were tested for normality using the

Kolmogorov-Smirnov and Shapiro-Wilk tests ($p \leq 0.05$). These two tests assess the null hypothesis that data is normally distributed. In all cases $p \leq 0.05$, therefore the null hypotheses were rejected.

In order to summarize the non-normal N_2O flux data, non-parametric statistics were employed as in van Kessel *et al.* (1993). Median values with 95% confidence intervals were calculated. Median values are accurate to ± 0.045 mg N_2O m^{-2} d^{-1}, given the analytical accuracy discussed above. Statistical differences ($p \leq 0.05$) in N_2O flux, among thaw and spring periods, soil moisture categories, and soil temperature categories, were determined via the non-parametric Mann-Whitney U test. When both $n_{group\ 1}$ and $n_{group\ 2} \leq 20$, the U statistic is reported, whereas, when both $n_{group\ 1}$ and $n_{group\ 2} > 20$, the z_U statistic is reported, as performed by the SPSS software. In order to compare the results of the experiment to parametric data (when reported) in the literature, parametric SCFT results were calculated on an ad hoc basis.

4.2 Results and discussion

4.2.1 Overall pattern of N_2O flux

As detailed in the previous section of this chapter, nine soil cores from SC were exposed to simulated winter and spring temperature regimes (three dry cores, two moist cores, and four wet cores). The winter simulation consisted of five freeze-thaw cycles of 10 days duration. These were followed by a deep freeze period (-10°C for five days), freeze period (-5°C for five days), a simulated early spring (4°C for five days), and a simulated late spring (20°C for four days). Median N_2O flux for the dry, moist, and wet core replicates over the entire experiment is illustrated in Figure 4.4. N_2O flux remains

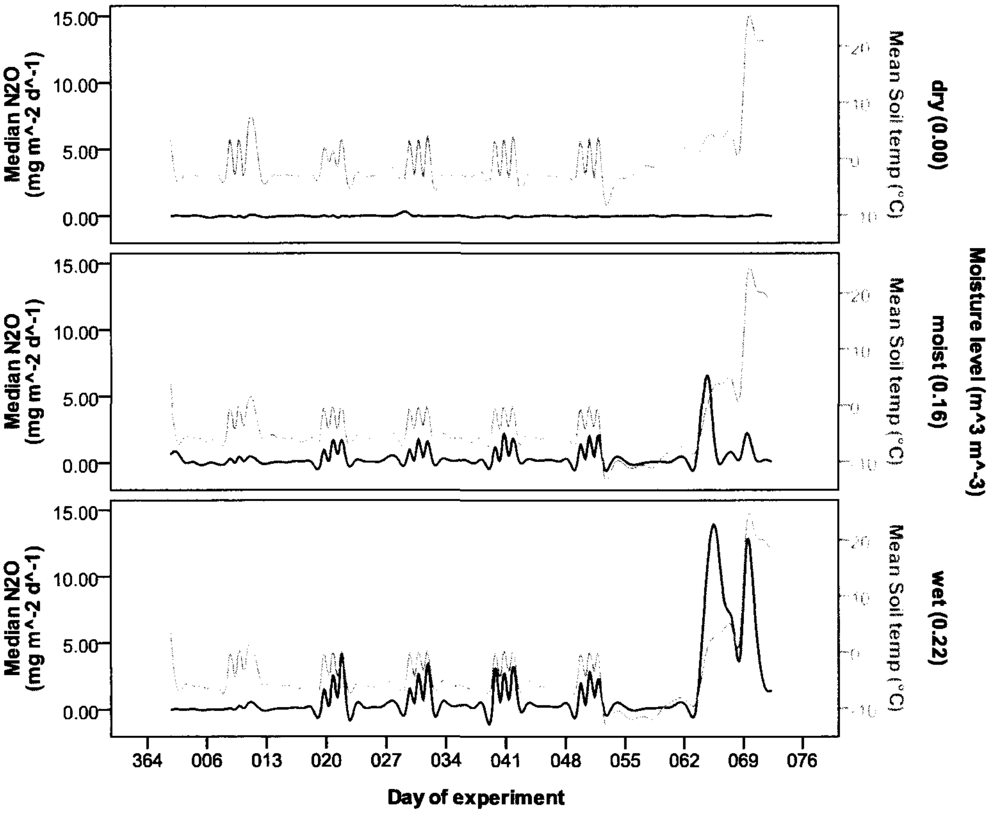


Figure 4.4. Median N_2O flux (dark blue) and mean soil temperature (light green) throughout the SCFT experiment for dry (*n* = 3), moist (*n* = 2), and wet (*n* = 4) replicates.

negligible in the dry cores throughout the incubation. These cores, with a VWC of 0 m^3 m^{-3} (oven-dried), are included in the simulation for comparison purposes only. No soils would be this dry during the non-growing season in southern Ontario. Therefore the following discussion pertains to the moist and wet cores only.

Overall, the wet cores exhibit higher median flux than moist cores (Figure 4.4). The effect of the first winter thaw on all six cores is notable (Figure 4.5). During this

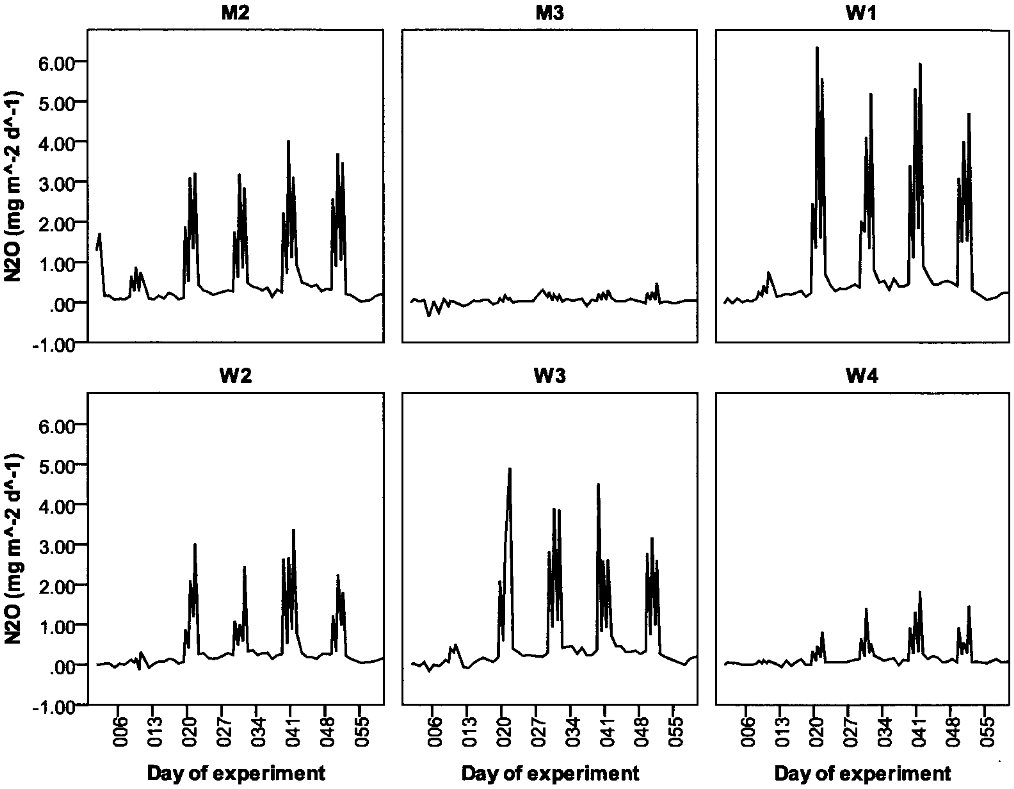


Figure 4.5. Fluctuations in N_2O flux during the five simulated winter freeze-thaw cycles for the moist (M, *n* = 2), and wet (W, *n* = 4) replicates.

simulated thaw, there are only small fluctuations in N_2O flux corresponding to soil temperature changes. This is the only consistent pattern across all cores. For the remaining four winter thaws, five out of the six moist and wet cores exhibit large, immediate, and parallel fluctuations in N_2O flux in response to soil temperature change. However, there is no common pattern in relative flux magnitude among these thaws. For example, in replicate W1, thaw 2 flux > thaw 4 flux > thaw 3 flux > thaw 5 flux, while in replicate W4, thaw 4 flux > thaw 5 flux > thaw 3 flux > thaw 2 flux. There is a common intra-thaw pattern across replicates, however, in that no flux maximum occurs on day 1 of the 3-day thaws (with one exception out of 30) (see replicate W3, thaw 5, in Figure 4.5).

Both moist and wet soils have very high N_2O flux spikes during the early spring simulation (4°C), while N_2O flux falls in these soils during the late spring simulation (20°C). The maximum moist core N_2O flux, during the late spring, is comparable to the moist core flux maxima during the winter thaws. The maximum wet core N_2O flux, during the late spring, falls from that of the early spring, but still remains higher than the wet core winter thaw maxima (Figure 4.4).

4.2.2 N_2O flux during the simulated warm periods

Figure 4.6 illustrates N_2O flux during each of the simulated thaw and spring periods. Again, the dry core flux is negligible and is excluded from this discussion. Although the difference in moisture levels is small (initial VWC of 0.22 m^3 m^{-3} versus 0.16 m^3 m^{-3}, respectively), the wet cores have a significantly higher N_2O flux than the moist cores during the winter thaw periods ($z_U = -2.4$, $p = 0.02$) and spring periods ($U = 82$, $p < 0.001$). This suggests that there may be a threshold number of anoxic microsites, which is surpassed in the wet cores (but not in the moist cores), triggering a non-linear intensification of wet core heterotrophic activity, and therefore an overall greater denitrification rate, driving more N_2O production and N_2O flux.

The moist and wet cores exhibit distinctly different patterns in relative N_2O fluxes among thaw and spring periods. For the moist cores, the N_2O fluxes are highest during winter thaw 2 to winter thaw 5, followed by early spring, winter thaw 1, and finally late

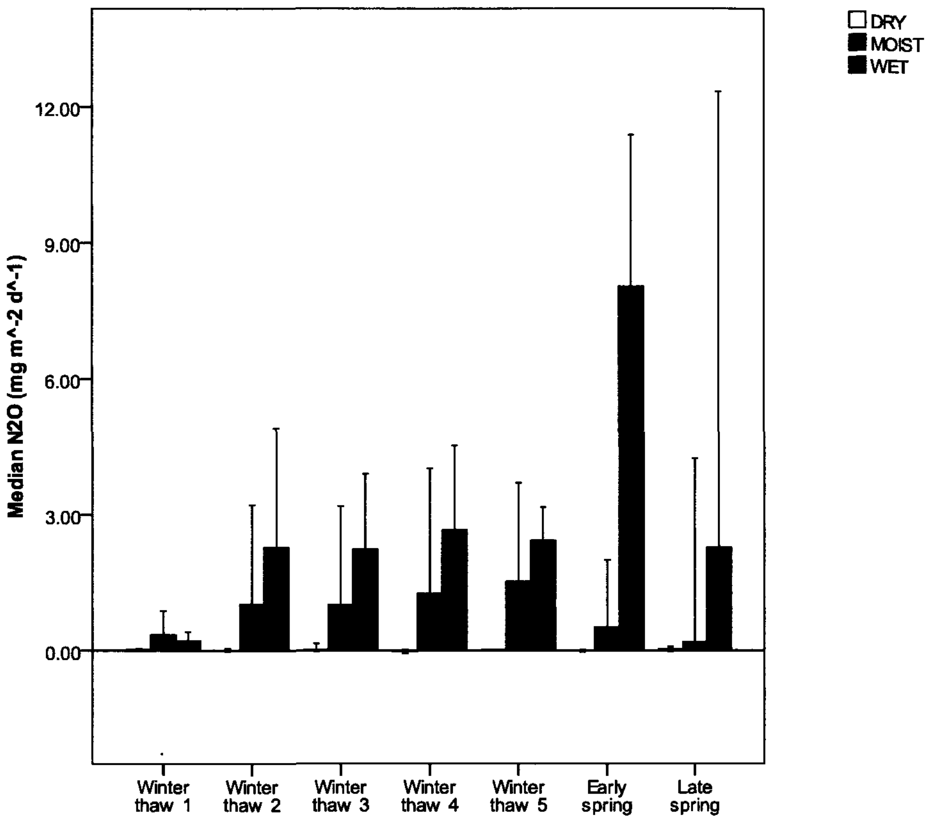


Figure 4.6. Median N_2O flux during the simulated winter thaws (air temperature = 4°C for 8 of 24 hours), early spring (air temperature = 4°C for 5 days), and late spring (air temperature = 20°C for 4 days), by soil moisture category. Dry (*n* = 3), moist (*n* = 2), wet (*n* = 4). Error bars illustrate the 95% confidence interval for median N_2O flux.

spring (1.0 – 1.5, 0.5, 0.4, and 0.2 mg N_2O m^{-2} d^{-1}). For the wet cores, in contrast, maximum N_2O flux by period occurs during the early spring, followed by winter thaws 2 to 5 / late spring (late spring flux was within the range of these winter thaws), and winter thaw 1 (8.0, 2.2 to 2.7, and 0.2 mg N_2O m^{-2} d^{-1}, respectively, Figure 4.6, Table B 1). The only statistically significant differences in N_2O fluxes among thaw or spring periods occur in the wet cores, where all thaw and spring periods have significantly higher N_2O fluxes than that of winter thaw 1 ($0 \leq U \leq 11, p < 0.001$). Additionally, the early spring

N_2O flux, in the wet cores, is significantly higher than the N_2O fluxes during all five winter thaw periods ($11 \leq U \leq 67, p \leq 0.04$).

Daily moist core (*n* = 2) and wet core (*n* = 4) N_2O fluxes, on the other hand, exhibit a similar pattern in relative magnitude. The maximum daily N_2O flux, in the moist cores, is highest during the early spring, followed by late spring and winter thaws 2 to 5 (6.6 and 1.7 to 2.2 mg N_2O m^{-2} d^{-1}, respectively, Table B 2). The N_2O flux is lowest during winter thaw 1 (0.5 mg m^{-2} d^{-1}, Table B 2). In the wet cores, the maximum daily N_2O flux is highest during the early spring as well, closely followed by the maximum daily N_2O flux of the late spring, and then followed by winter thaws 2 to 5, and lastly winter thaw 1 (13.6, 12.1, 2.7 to 4.0, and 0.4 mg N_2O m^{-2} d^{-1}, respectively, Table B 3).

Daily replicate fluxes provide an additional means for comparison. Throughout the SCFT experiment, maximum daily replicate fluxes exhibit a different pattern in relative magnitude than those of the thaw period fluxes, however, for the moist cores, maximum daily replicate fluxes exhibit the same pattern in relative magnitude as the daily (median) N_2O fluxes (Table B 1, Table B 2). Moist core winter thaw maximum daily replicate fluxes, notably, reach magnitudes as high as the maximum late spring daily replicate N_2O flux. Overall, the moist core maximum daily replicate fluxes are highest during the early spring, followed by late spring and winter thaws 2 to 5, and lastly winter thaw 1 (12.7, 4.3/4.0, and 0.9 mg N_2O m^{-2} d^{-1}, respectively, Table B 1). Wet core maximum daily replicate fluxes follow a different pattern in relative magnitude than that of the moist cores. The wet cores have the highest daily replicate N_2O flux during the late spring, followed by early spring, winter thaws 2 to 5, and winter thaw 1 (35, 15, 6.4, and

0.8 mg N_2O m^{-2} d^{-1}, respectively; Table B 1). This wet core pattern is different than that of the wet core daily (median) fluxes, as well as the wet core pattern in the relative magnitude of N_2O fluxes among thaw and spring periods, overall.

4.2.3 Comparison of simulated thaw results to the literature

There are few published papers on N_2O flux from freeze-thaw incubations on intact arable soils, but those that are available are compared with the SCFT experiment below. Because soils used in the literature are wetter than those in the SCFT experiment, SCFT wet core summary statistics are used for these comparisons. The mean initial WFPS in the SCFT wet cores is 38%, and is used below to highlight quantitative moisture differences between the SCFT soils and those in the literature. Mean initial WFPS in the wet cores is calculated using the following formula from Cannavo *et al.* (2004):

$$\boldsymbol{WFPS} = \left(\frac{\boldsymbol{VWC}}{\left(1-\frac{\boldsymbol{BD}}{\boldsymbol{PD}}\right)}\right) \qquad \textbf{(4.1)}$$

where:

mean initial VWC = 22% for wet cores (n = 4)
BD = average bulk density of soil cores = 1.11 g cm^{-3}
PD = particle density (assumed) = 2.65 g cm^{-3}

N.B.: Because arable surface soils are assumed to have only 3-5% organic matter content, and therefore an approximate PD of 2.65 g cm^{-3} (Brady 1990), SCFT soils, with an average organic matter content of 10%, may have particle densities as low as 2.45 g cm^{-3}, which could increase actual WFPS to 40% (in the wet cores).

Although the results from the SCFT experiment suggest that the first freeze-thaw cycle has relatively little impact on N_2O flux (section 4.2.1), Koponen *et al.* (2006) report a different pattern from a freeze-thaw simulation on wet (85% WFPS) loamy sand previously growing barley. Their soil is exposed to four freeze-thaw cycles of -17°C to 4°C. Mean fluxes ($n = 6$) are 3.6, 17, 5.9, and 0.3 mg N_2O m^{-2} d^{-1}, respectively (Koponen *et al.* 2006). Relative flux magnitudes are therefore thaw 2 flux > thaw 3 flux > thaw 1 flux > thaw 4 flux. Koponen *et al.* (2006) conclude that there is a clear pattern of declining N_2O flux *after a second thaw.*

SCFT mean wet core flux is 0.3, 2.7, 2.4, 3.1, and 2.4 mg N_2O m^{-2} d^{-1} for thaws one to five, respectively. Relative flux magnitudes show no distinct pattern, except that all thaws are greater than thaw 1, as discussed in section 4.2.1 for individual replicates. SCFT mean fluxes are comparable to those from thaws 1, 3, and 4 in Koponen *et al.* (2006), even though the clay loam soil of the SCFT experiment has a much lower average moisture level (38% WFPS). The similar mean flux values may be due to an otherwise higher soil N (0.25%, Table 4.1) in the SCFT soils as opposed to the soil N (0.16%) in Koponen *et al.* (2006). There may also be more anoxic microsites in the SCFT clay loam than would otherwise be in a loamy sand at the equivalent WFPS, increasing the SCFT denitrification rate as compared to Koponen *et al.* (2006). Additionally, and unexpectedly, Koponen *et al.* (2006), citing Pihlatie *et al.* (2004), provide evidence that nitrification is as important as denitrification for N_2O production in loamy sand at this high WFPS (85%). This may indicate that high levels of moisture are not necessary for significant N_2O flux to occur.

In contrast to the study discussed above (Koponen *et al.* 2006), Koponen *et al.* (2004) report a maximum mean flux of only 0.1 mg N_2O m^{-2} d^{-1} at 2°C when loam, at 42% WFPS and previously growing barley, is thawed from -2°C to 4°C. This compares to a maximum mean flux of 0.4 mg N_2O m^{-2} d^{-1} at 0.1°C during the first winter thaw simulation of the SCFT experiment for the wet cores. Here, as noted above, SCFT WFPS is only 38%. In contrast, Koponen *et al.* (2004) find a large maximum mean flux of 83 mg N_2O m^{-2} d^{-1} at 0°C when the same loam is wetted to 90% WFPS and warmed from a lower temperature (-8°C to 10°C). (Note that the soil temperature of maximum flux is reported from Figure 6b in Koponen *et al.* (2004), and not from Table 2 of Koponen *et al.*(2004), which appears to contradict Figure 6b.) The flux maximum from the wet cores of the SCFT experiment, through a similar temperature increase (simulated deep freeze through early spring), is smaller at 10.6 mg N_2O m^{-2} d^{-1} at 2.7°C. However, this represents a surprisingly small difference compared to the findings in Koponen *et al.* (2004) given that, again, SCFT WFPS is only 38%.

Overall, flux magnitudes during the SCFT experiment are similar to those under somewhat similar incubations reported in the available literature (Koponen *et al.* 2004, Koponen *et al.* 2006). However, it would be premature to assume that this would be the case with other work. The only discussion of relative patterns on the effect of successive freeze-thaw cycles on N_2O fluxes (Koponen *et al.* 2006) conflicts with those of the SCFT experiment. More study on the effect repeat freeze-thaw cycles on N_2O fluxes from arable soil is needed. Multiple cycles are likely an important consideration in the assessment of N_2O fluxes during northern temperate winters. The frequency, amplitude, and duration of cycles will likely change as climate change evolves through time.

4.2.4 Analysis of N_2O flux at cold soil temperatures

This section examines median N_2O flux by 2.5°C soil temperature bins using freeze as well as winter thaw and early spring data (Figure 4.7, Table B 4). There are

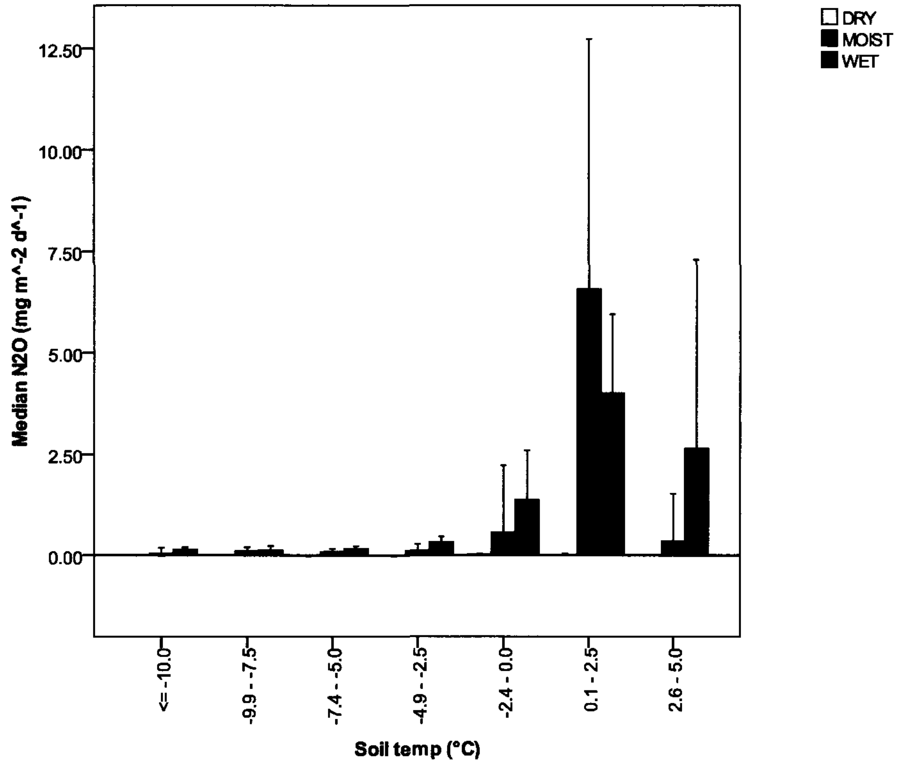


Figure 4.7. Median N_2O flux, by 2.5°C soil temperature categories, for all of the simulated winter through to early spring soil temperatures. Error bars illustrate the 95% confidence interval for median N_2O flux.

distinct increases in N_2O flux in both the moist and wet cores from -2.4°C to 2.5°C with a consequent drop in N_2O flux between 2.6°C and 5°C. Although the confidence interval is large, the moist cores exhibit a maximum median N_2O flux between 0.1°C and 2.5°C (6.6 mg m^{-2} d^{-1}). The wet core maximum median N_2O flux occurs between 0.1°C and 2.5°C as well (4.0 mg m^{-2} d^{-1}, Figure 4.7, Table B 4). The high magnitude of the confidence intervals for median N_2O flux between 0.1°C to 5°C is primarily driven by the large range of N_2O fluxes in the moist core 0.1°C to 2.5°C soil temperature bin (0.4 to 13 mg m^{-2} d^{-1}) and in the wet core 0.1°C to 2.5°C, and 2.6°C to 5°C bins (0.2 to 15, and 0 to 11 mg m^{-2} d^{-1}, respectively).

When differences in N_2O flux from the three -2.4°C to 5°C bins are examined statistically, the moist core changes in median N_2O flux over this range are not significant (Mann-Whitney U test, $p > 0.05$). In the wet soils, the median N_2O flux between 0.1°C and 2.5°C is significantly higher than that of -2.4°C to 0°C ($z_U = -3.6, p < 0.001$), but not than that of 2.6°C to 5°C. Had it been possible to accommodate a greater number of replicates in the SCFT experiment, it is possible that both the moist and wet core N_2O fluxes would have statistically significant median cold temperature peaks at 0.1°C to 2.5°C with respect to the higher 2.6°C to 5°C bin as well as the lower -2.4°C to 0°C bin.

When the -4.9°C to -2.5°C category is included in these comparisons, all three of the -2.4°C through 5°C wet core bins exhibit significantly higher median N_2O fluxes than that associated with the -4.9°C to -2.5°C wet core bin ($z_U = -4.8, p < 0.001$; $z_U = -6.3, p < 0.001$; $U = 334, p = 0.04$, respectively, for the -2.4°C to 0°C, 0.1°C to 2.5°C, and 2.6°C to 5°C bins). These results conform to the general expectation that N_2O flux increases as soil temperature increases, as discussed in section 2.2.2. However, in the moist cores, only the median N_2O flux from the -2.4°C to 0°C bin is significantly higher than median N_2O flux from the -4.9°C to -2.5°C bin ($z_U = -3.1, p = 0.002$). That is, the median flux from -4.9°C to -2.5°C is not statistically lower than that from the 0.1°C to 2.5°C or 2.6°C to 5°C soil temperature bins. This emphasizes that it is important not to ignore the substantial confidence intervals shown in Figure 4.7, as it may be, generally, that there is no appreciable difference between median fluxes from -4.9°C to -2.5°C and those from 0.1°C to 5°C. Such findings emphasize the need for additional replicates to make stronger conclusions about the temperature effect on N_2O flux at cold temperatures. It is important to note, also, that fluxes between the soil temperatures of 0.1°C to 5°C are extremely variable. Their magnitude is likely dependent on antecedent conditions as evident in the moist and wet cores during the simulated early spring and late spring of the SCFT experiment (Figure 4.4, day 63 through day 73). Fluxes may be very high when soil temperatures are increasing through 0°C but lower at comparable temperatures that are trending downward. Continuous sampling as soils freeze and thaw through 0°C, via automated methods, would improve the understanding of when the largest N_2O fluxes are occurring, and would provide critical data for models. The interpolation of fluxes, between values attained by periodic sampling at these temperatures, likely results in inaccurate N_2O flux estimates.

4.2.5 Correlating N_2O flux with soil moisture and soil temperature

The dataset from the SCFT experiment consists of approximately 500 moist and wet N_2O flux samples from soil cores ranging in temperatures from -15°C through 20°C. Soil moisture categories for the soil cores are based on those used for categorizing the SC field data in section 3.3.6, i.e. dry (< 0.05 m^3 m^{-3}), moist (0.05 – 0.19 m^3 m^{-3}), wet (0.20 – 0.34 m^3 m^{-3}), and very wet (≥ 0.35 m^3 m^{-3}) VWC. As no moisture was added during the SCFT experiment, moisture classifications are based on initial soil core VWC. Neither dry cores nor very wet cores are represented in the SCFT temperature-flux regression analysis. Since the dry cores exhibited no appreciable N_2O flux as discussed above (section 4.2.1, Figure 4.4), these cores are excluded, and with respect to the very wet moisture category, none of the SCFT cores fit this description.

Most of the sampling was undertaken over the -5°C to 4°C air temperature range, as this was the focus of the SCFT experiment. The dataset should therefore represent a comprehensive range of N_2O flux values from agricultural clay loams within a typical range of winter soil temperatures for southern Ontario. If the N_2O data is transformed (Figure 4.8), there is a moderate temperature-flux correlation for the moist cores (r^2 = 0.21), and for the wet cores (r^2 = 0.47). It is notable that the quadratic line of best fit for the SCFT experiment's data over its whole temperature range indicates a positive quadratic relationship, where the slope of the line of best fit decreases, from

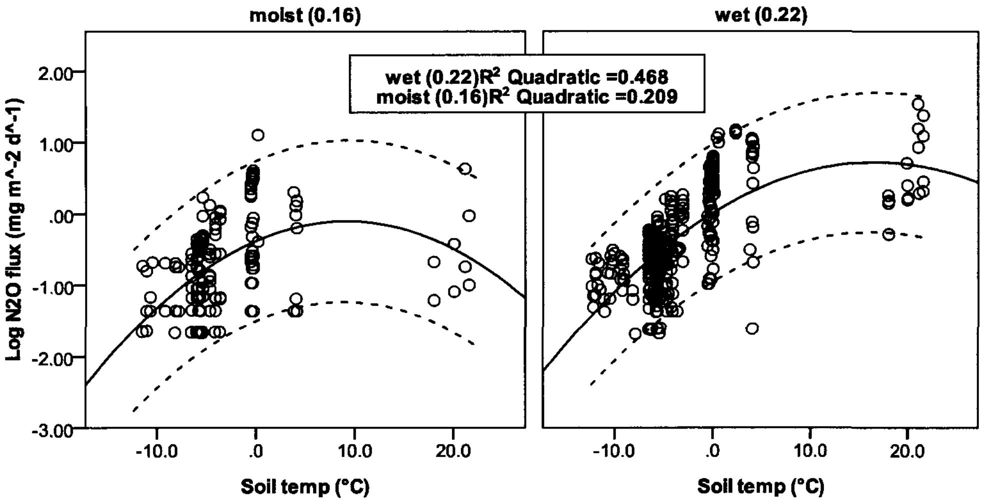


Figure 4.8. Soil temperature at 5 cm depth versus log N_2O flux by soil moisture category (VWC in m^3 m^{-3} at 10 cm depth) during the SCFT experiment, with regression lines for moist ($y = 0.061\,t - 0.003\,t^2 - 0.381$, $F = 19.3$, $p_F < 0.001$, $n = 149$, $r = 0.46$, $p_{\rho=0} < 0.01$), and wet ($y = 0.085\,t - 0.003\,t^2 + 0.007$, $F = 132$, $p_F < 0.001$, $n = 302$, $r = 0.69$, $p_{\rho=0} < 0.01$) soils. 95% confidence intervals bound the regression lines.

-12°C to approximately 10°C for the moist cores, and from -15°C to approximately 15°C for the wet cores, at which point the relationship becomes negative.

The SCFT N_2O flux data is next examined within the -15°C to 5°C temperature range, as the data gap between 5°C and 20°C (Figure 4.8) may hinder the dependability of the correlation between the two variables. Excluding this data from the late spring simulation does not appreciably strengthen the temperature - N_2O flux relationship, although it changes its configuration (Figure 4.9). The quadratic line of best fit between soil temperature and N_2O flux remains positive through this soil temperature range and exhibits an increasing slope for the wet cores (Figure 4.9). The increasing slope may be more realistic as it follows the trend discussed in section 3.3.6, and illustrated in Figure 3.19, for the field dataset, which is larger and continuous over the 5°C to 20°C soil

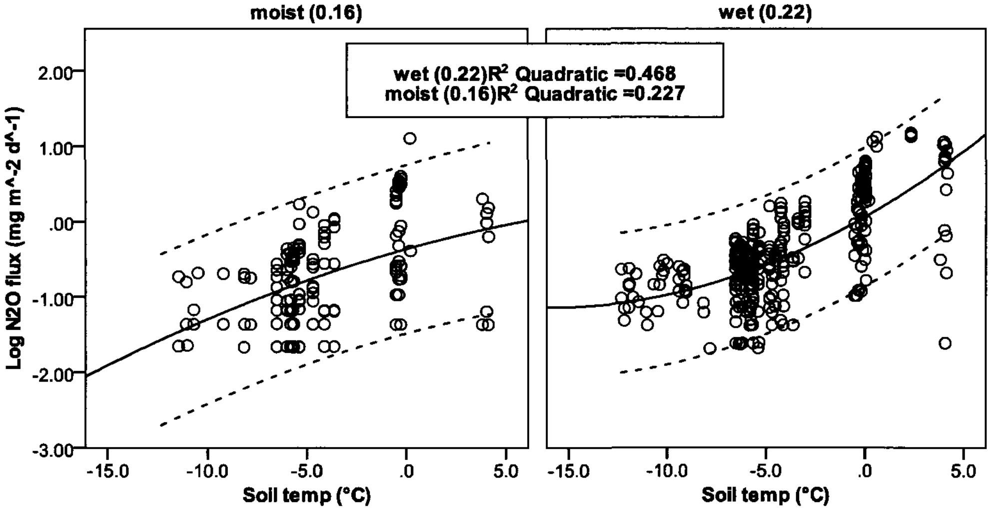


Figure 4.9. Soil temperature (≤ 5°C) at 5 cm depth versus log N_2O flux by soil moisture category (VWC in m^3 m^{-3} at 10 cm depth) during the SCFT experiment, with regression lines for moist ($y = 0.074\,t - 0.002\,t^2 – 0.363$, $F = 20.3$, $p_F < 0.001$, $n = 141$, $r = 0.48$, $p_{\rho=0} < 0.01$), and wet ($y = 0.150\,t + 0.005\,t^2 + 0.059$, $F = 124$, $p_F < 0.001$, $n = 286$, $r = 0.68$, $p_{\rho=0} < 0.01$) soils. 95% confidence intervals bound the regression lines.

temperature range. The moderate relationship between soil temperature and flux suggest that other factors are important drivers of N_2O flux in these soils. These likely include changes in soil structure, microbial activity, labile C, and labile N, which may be related to changes in soil temperature through 0°C.

Unfortunately, it is beyond the scope of the present work to monitor any but the temperature and moisture parameters. The data are therefore summarized, by examining median N_2O flux by soil temperature bins (Figure 4.10). Because the N_2O flux data is unevenly distributed over the soil temperature sampling range of the SCFT experiment, soil temperature bin divisions are based on equal percentiles of flux data. A single soil temperature is assigned to each bin based on the mean soil temperature within each bin. By binning the data, the correlation between soil temperature and N_2O flux is stronger,

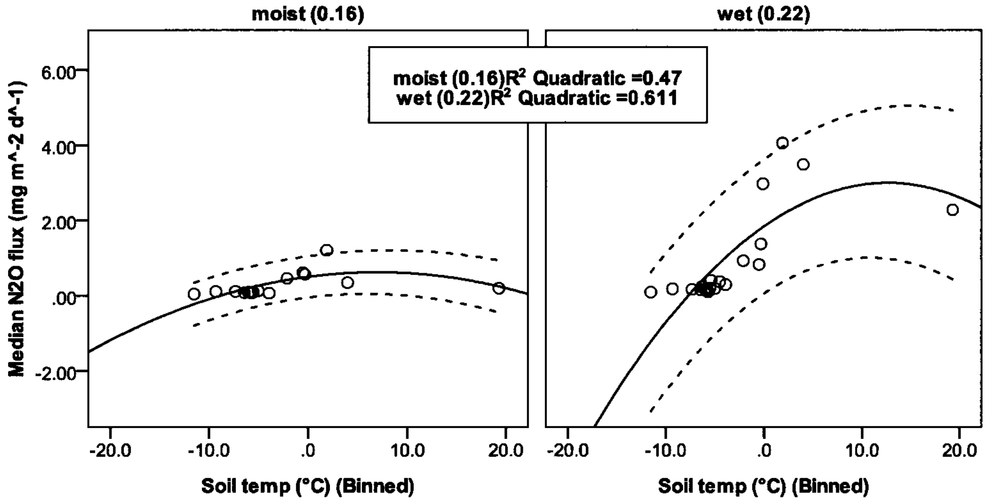


Figure 4.10. Binned soil temperature (mean value per bin) at 5 cm depth versus median N_2O flux (mg m^{-2} d^{-1}) during the SCFT experiment, with regression lines for moist ($y = 0.035\,t - 0.002\,t^2 + 0.499$, $F = 5.8, p_F = 0.02, n = 16, r = 0.69, p_{\rho=0} < 0.01$), and wet ($y = 0.183\,t - 0.007\,t^2 + 1.837, F = 13.4, p_F < 0.001, n = 20, r = 0.78, p_{\rho=0} < 0.01$) soils. 95% confidence intervals bound the regression lines.

though remains moderate, for the moist cores ($r^2 = 0.47$), and becomes high for the wet cores ($r^2 = 0.61$), with quadratic lines of best fit in this case (Figure 4.10). Again, however, the positive line of best fit between soil temperature and N_2O flux decreases in slope as soil temperatures increase, and thus conflicts with the line of best fit for the larger SC dataset, which increases in slope as soil temperature increases (Figure 3.21). If only SCFT N_2O flux data ≤ 5°C is used for the regression analysis with binned soil temperature values, the temperature-flux relationships are further improved. Linear relationships between binned soil temperature and flux replace quadratic ones (Figure 4.11). The correlation between soil temperature and N_2O flux becomes more highly

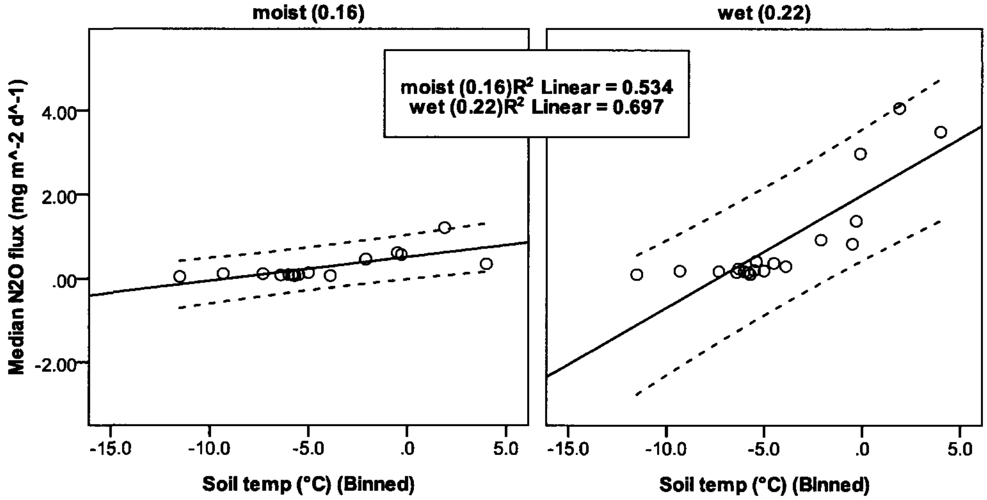


Figure 4.11. Binned soil temperature (≤ 5°C) (mean value per bin) at 5 cm depth versus median N_2O flux (mg m^{-2} d^{-1}) during the SCFT experiment, with regression lines for moist ($y = 0.057\,t + 0.512$, $F = 14.9$, $p_F = 0.002$, $n = 15$, $r = 0.73$, $p_{\rho=0} < 0.01$), and wet ($y = 0.269\,t + 1.991$, $F = 39.1$, $p_F < 0.001$, $n = 19$, $r = 0.84$, $p_{\rho=0} < 0.01$) soils. 95% confidence intervals bound the regression lines.

correlated ($r^2_{moist\ cores} = 0.53$, $r^2_{wet\ cores} = 0.70$, Figure 4.11). When all N_2O flux data is used from VWC categories spanning 0.05 through 0.34 m^3 m^{-3}, however, the model is weaker ($r^2 = 0.45$, $y = 1.309 + 0.168\,t$, $F = 26.0$, $p < 0.001$, $n = 34$, $r = 0.67$, $p_{\rho=0} < 0.01$).

The regression equations presented here make it possible to predict median N_2O fluxes from SC soil cores based on average soil temperatures, but these are most appropriate for wet soils with VWCs between 0.20 and 0.34 $m^3\ m^{-3}$, and temperatures $\leq$ 5°C. The model for moist soils may be weaker than that for the wet soils because of its smaller number of data points (Figure 4.8). (There were two moist cores versus four wet cores in the experiment.) Overall, greater sample sizes would likely improve predictive models for N_2O flux from incubated soil based on binned soil temperature and soil moisture values.

5 Summary

5.1 *Spatio-temporal patterns of N_2O flux at Strawberry Creek*

There is no consistent pattern in N_2O flux among fields at SC, which suggests that the flux data collected over the study period is representative of fluxes over the landscape, and perhaps even regionally from arable soils throughout southern Ontario. There are significant differences among N_2O fluxes from different crops, during both the growing and non-growing seasons. During the growing season, corn sites have the highest N_2O fluxes. Both corn sites and spring wheat sites have significantly greater N_2O fluxes than oat sites, and oat sites have significantly greater N_2O fluxes than winter wheat sites. During the non-growing season, both sites previously growing oats, and those fall-planted to winter wheat, have significantly greater N_2O fluxes than those previously growing corn. These differences among sites growing different crops suggest that the N-status of the soil at SC may be an important flux driver.

Seasonally, median spring and growing season N_2O fluxes at SC are small (0.1 mg m^{-2} d^{-1}), though higher than those during the fall and winter (0.05 mg m^{-2} d^{-1}). These seasonal fluxes are negligible according to levels suggested in the literature (e.g. van Bochove *et al.* 2000, van Bochove *et al.* 2001, Lemke *et al.* 1998). SC flux values are smaller, though similar, to those of Wagner-Riddle *et al.* (2007), from a similar agroecosystem sampled via micrometeorological methods. While the seasonal flux pattern at SC is common to much of the literature, fluxes reported elsewhere are up to two orders of magnitude higher than those at SC. It is possible that this is an issue related to sampling methods or timing. Alternatively, southern Ontario may not be a significant source of Canadian agricultural N_2O emissions. Small winter N_2O fluxes at SC are particularly notable, as they contradict some reports of high winter fluxes from temperate North American agricultural sites (e.g. Goodroad and Keeney 1984, van Bochove *et al.* 2000).

Daily median fluxes at SC are highest during the growing season, with large fluctuations in N_2O fluxes between sampling dates during May and June, when N_2O flux spikes likely reflect short-lived fertilizer-driven increases in N_2O production. N_2O flux spikes also occur during the winter thaw and two spring seasons encompassed by the SC study. Overall, changes in daily fluxes appear to reflect changes in soil temperatures, and, secondarily, changes in soil moisture content. Regression analysis indicates that it is possible to predict N_2O flux at SC based on soil temperature alone, especially when soils are moist to wet (0.2 to 0.4 m^3 m^{-3} VWC).

5.2 Evaluation of field methods

There is a considerable range of non-flow-through non-steady-state chamber techniques to measure N_2O flux from soil (Rochette and Eriksen-Hamel 2008). In a review of approximately 360 studies from 1978 to 2007, Rochette and Eriksen-Hamel (2008) find that 60% of absolute N_2O flux values are unreliable because of inadequate methods and reporting. Fifty per cent of the recent studies (2005-2007) that Rochette and Eriksen-Hamel (2008) review report unreliable absolute flux values. Using recommendations from Hutchinson and Livingston (1993), Livingston and Hutchinson (1995), Holland *et al.* (1999), Davidson *et al.* (2002), Hutchinson and Livingston (2002), Smith and Conen (2004), Rochette and Hutchinson (2005), and Rochette and Bertrand

(2007), Rochette and Eriksen-Hamel (2008) establish a quantitative method to evaluate chamber methodologies for calculating N_2O flux. This evaluation grades methodologies by chamber type, chamber height, chamber depth, chamber area/perimeter ratio, chamber insulation, chamber vent, timing of gas collection, and collection vial type. Additional considerations include having an experimental control and confirming linearity of N_2O accumulation, if that is the basis of flux calculations (as in equation 3.1). In terms of N_2O field gas sampling and flux calculation methods, the SC methods receive a 64% grade by this protocol (Rochette and Eriksen-Hamel 2008, Table A 10).

Because there is a multitude of methods used to calculate N_2O flux (Henry 2007, Rochette and Eriksen-Hamel 2008), qualitative comparisons with respect to SC flux will be more dependable than quantitative comparisons. Some of the discrepancies, among SC N_2O fluxes and those in the literature (see section 3.3.5, Table A 1), may be due to inaccurate absolute SC N_2O flux values. The empirical model developed in section 3.3.6 may be more valid for predicting flux patterns rather than absolute fluxes.

For snow flux, van Bochove *et al.* (2000) use a concentration gradient method, measuring N_2O within the snowpack at 20-cm intervals. Although Groffman *et al.* (2006) and Maljanen *et al.* (2003) use snow chambers for the determination of surface N_2O fluxes, van Bochove *et al.* (2000) assert that this method is inadequate. Snow chambers, such as those used at SC, can both underestimate (Mast *et al.* 1998) and overestimate (Winston *et al.* 1995) gas fluxes. Possible sources of snow chamber error and variability include temporary entrapment of gas by snow structures (Mast *et al.* 1998), dilution of snow gas concentrations by wind penetration (Mast *et al.* 1998), and channelling of soil gas fluxes to the snow surface via melt channels and tree wells (Winston *et al.* 1995). Limited resources, however, prevent the use of a snow gas profiler for N_2O flux determination at SC. Therefore, the comparison of SC N_2O snow fluxes and SC N_2O soil fluxes, as discussed in section 3.3.5, may not be as reliable as the comparisons among SC N_2O soil fluxes alone.

5.3 Patterns in N_2O flux during simulated winter and spring conditions

The SCFT experiment is a detailed investigation into the patterns of N_2O emissions from soil mesocosms during simulated winter and spring thaws, in response to soil temperature manipulations. The first winter thaw triggers only negligible N_2O flux from the soil cores, otherwise there is no distinct pattern in the N_2O flux among replicates, as winter thaws increase in frequency through a total of five thaws. Although Koponen *et al.* (2006) report N_2O fluxes from successive freeze-thaw simulations which are comparable in magnitude to those of the SCFT experiment, the authors find that fluxes consistently decline after a second thaw.

SCFT N_2O fluxes measured in the laboratory during the simulated winter thaws and spring periods are high, and N_2O flux increases parallel soil temperature increases. Furthermore, there is no time delay in flux response to soil temperature change. During the winter thaw simulations, median daily fluxes reach 2.1 mg N_2O m^{-2} d^{-1} in moist soil, and 4.0 mg N_2O m^{-2} d^{-1} in wet soil, with spikes recurring on each day of the simulated thaws. During the early spring simulation, moist and wet soil N_2O fluxes reach daily medians of 6.6 and 14 mg m^{-2} d^{-1}, respectively. While the median daily late spring N_2O flux does not exceed that which occurs during the winter thaws in the moist soils, the late spring wet soil N_2O flux spike is again extremely high, at 12 mg m^{-2} d^{-1}. In contrast to the winter thaw simulations, the fluxes during each of the simulated spring periods spike only once. Therefore, the experiment indicates that successive winter thaws, at least those simulated *ex situ*, may produce cumulative N_2O fluxes which are as significant, if not more significant, than those generated cumulatively during spring periods.

5.4 Evaluation of experimental methods

In a review of 28 studies involving freeze-thaw simulations, Henry (2007) concludes that a wide-range of findings may be due to experimental artefacts, resulting from a lack of scientific consensus on appropriate freeze-thaw methodologies to mimic natural systems. As with most of the freeze-thaw experiments reviewed by Henry (2007), snow, rain, snowmelt, and icemelt are not simulated in the SCFT experiment. An incorporation of these could change the physics, chemistry, and biology of soil cores, and could increase or decrease N_2O fluxes. Henry (2007) notes that heterotrophs, for example, are typically more active under a consistent snow cover at ≈ 0°C. Saturation of soil is common in lower sections of farm fields in southern Ontario over prolonged periods in the winter (November through March), as another example.

Physical disruption of aggregates may be reduced in the SCFT experiment, relative to typical SC *in situ* conditions, due to rapid freezing and thawing because of sudden air temperature change (Henry 2007). This may cause underestimates of typical N_2O fluxes during freeze-thaw conditions. However, the opposite might be the case, as discussed below.

Half of the studies reviewed by Henry (2007) do not report the soil collection date, although he points out that soil microbial communities change over the year. N_2O fluxes from freeze-thaw experiments could, therefore, be unrepresentative if soils are not collected in the fall (Henry 2007). Although fall-collected, SCFT soils are stored for five months prior to the beginning of the winter and spring simulation. This time lapse between soil collection and soil incubation may change the response of the soil mesocosms to the winter and spring experiment, and therefore change the magnitude and/or pattern of N_2O fluxes, due to possible changes in soil O_2, redox conditions, microbial populations and microbial activity.

In terms of SCFT soil temperature manipulations, the experiment may not accurately simulate *in situ* SC conditions (see Figure 4.4 for soil temperature fluctuations). The freezer temperature is low, and the insulation may be insufficient to moderate the effect of air temperature on soil temperature fluctuations from the sides and bottom of the soil cores. Highly muted diurnal soil temperature fluctuations are reported during winter thaws in southern Ontario (Henry 2007, Petrone and Macrae, *unpublished data*). Even when soils are not covered by snow, soil as shallow as 5 cm may not freeze, despite air temperatures being well below freezing during cold conditions. However, English (*pers. comm.*) reports *in situ* observations of frozen SC soils well below 5 cm depth, more than once in the last 12 years at SC. During the SCFT experiment, soil temperatures frequently reach -5°C at 5 cm depth during the freeze simulations, and never exceed 0°C during the thaw simulations (Figure 4.4).

Hu *et al.* (2006) conclude that freeze-thaw experiments using soil cores insulated with filled-in soil better simulate natural conditions, and that uninsulated 25-cm soil cores, which are exposed to freezing and thawing temperatures from all sides, have higher fluxes. Cores insulated with soil have low fluxes, and those with a simulated water table at 25 cm depth, in addition to insulation by soil, have moderate fluxes. Hu *et al.* (2006) and Henry (2007) speculate that higher uninsulated core fluxes may be due to a greater duration and intensity of freezing. The mechanisms by which freezing intensity and duration increase N_2O flux might be explained by increased microbial activity during the thaw period, due to increased labile C from freezing lysis and disruption of soil aggregates; N_2O production in a saturated near-surface caused by a sub-surface ice barrier as frozen soil thaws; and/or the accumulation, and thus concentration, of ice-trapped N_2O, followed by its release (Hu *et al.* 2006, citing several research papers). High N_2O fluxes from uninsulated versus soil-insulated cores may therefore represent both previously and newly produced N_2O (Hu *et al.* 2006). Hu *et al.* (2006) find that N_2O flux is more highly correlated with the intensity and the duration of freezing than with soil moisture content, which, in and of itself, would likely increase the production of N_2O due to increased levels of denitrification.

In addition to appropriate insulation of soil cores, Hu *et al.* (2006) recommend continuous N_2O flux and soil profile measurements to better characterize freeze-thaw dynamics. Henry (2007) notes that freeze-thaw experiments need to incorporate controls into their design, including soil core replicates maintained at a constant average thaw temperature. Also, researchers should compare fluxes from different freeze-thaw cycle lengths and frequencies, in order to characterize emissions from a complete range of possible winter conditions (Henry 2007).

In terms of gas sampling and flux calculation methods, the SCFT experiment receives a 49% grade by the protocol established by Rochette and Eriksen-Hamel (2008, Table B 5), which is lower than the grade for the SC field sampling and flux calculation methods as discussed above in section 5.2. Improvements could be made, therefore, in this aspect of the experimental design as well.

5.5 Comparison of field and laboratory results

If the field sampling methods and frequency accurately characterize N_2O fluxes at SC, overall annual, seasonal and monthly emissions are low. Only one thaw longer than three days occurs during the winter studied at SC (2007-2008), an extreme thaw event over a period of six days when daily air temperatures reach a maximum of 13.6°C on Jan 7/08. During this thaw, daily median N_2O fluxes from three sample dates reach a maximum of only 0.1 mg m^{-2} d^{-1} from very wet soil (38% VWC). During the laboratory simulation, daily winter thaw flux medians are up to 40 times higher at 4.0 mg N_2O m^{-2} d^{-1} from wet soil cores, with an initial mean VWC of only 22%. While individual replicate fluxes reach a maximum of only 0.5 mg N_2O m^{-2} d^{-1} during the *in situ* winter thaw, the maximum individual replicate flux in the laboratory is an order of magnitude higher (6.4 mg N_2O m^{-2} d^{-1} during winter thaw 2 in the wet cores, Table B 3).

For spring thaws, *in situ* March and April N_2O fluxes reach a maximum daily median of 0.9 mg N_2O m^{-2} d^{-1}, while individual replicate fluxes reach a maximum of 26 mg N_2O m^{-2} d^{-1} during these months. Although this maximum *in situ* replicate flux from the spring is comparable to that of the SCFT experiment (35 mg N_2O m^{-2} d^{-1}, Table B 3), *median* daily early spring N_2O flux from the laboratory simulation reaches 14 mg N_2O m^{-2} d^{-1} (Table B 3), an order of magnitude higher than the *median* daily *in situ* N_2O flux.

Median N_2O fluxes from moist and wet laboratory soil in the 0°C to 2.5°C soil temperature category are two orders of magnitude higher than that from comparable field soil temperatures and moisture contents. In the 2.5°C to 5.0°C soil temperature category, median N_2O fluxes from moist and wet laboratory soil are one order of magnitude higher than that from comparable field soil temperatures and soil moisture contents. Moist and wet SCFT laboratory soils exceed median SC *in situ* N_2O fluxes by far, even in very wet field soils although this moisture category is not represented in the SCFT experiment.

The laboratory simulation reveals N_2O fluxes that are much greater than those observed *in situ*. The gas collection methods employed in the laboratory and field are similar. It is possible that *in situ* winter flux spikes are higher, but not captured by the current sampling protocol. However, the laboratory simulation suggests that these pulses occur over at least three days during thaws, at least when soil temperatures decrease below 0°C at night. Field thaw sampling occurs within this time frame.

In the field, there were three 2-day winter thaws in addition to the Jan 6-11/08 thaw. These occurred from Dec 22-23/07, Jan 29-30/08, and Feb 17-18/08. Because these thaws did not fit the SC field sampling protocol, i.e. they were not greater than two days in duration, no N_2O flux data was collected during these periods. However, because the SCFT simulation reveals that N_2O fluxes respond immediately to soil temperature change

(Figure 4.4), it may be that high N_2O fluxes occur during these periods, fluxes which may be closer in magnitude to those attained during the SCFT winter thaw simulations.

It is also possible that the differences between *in situ* and laboratory fluxes are due to insufficient soil core insulation, which allows the cores to freeze to soil temperatures much lower than those typically found in southern Ontario agricultural soils during the winter. *In situ* soils generally remain warmer than 0°C at 5 cm depth during a typical winter. In contrast, soil temperatures at this depth in the SCFT soil cores never exceed 0°C, varying between -5°C and 0°C during the winter thaws. The higher laboratory fluxes may in fact result from physical, chemical, and/or microbiological disturbance, caused by warming soils through sub-zero (°C) temperatures. Hu *et al.* (2006) report that the use of extruded polystyrene (Styrofoam™) coolers, filled with soil to insulate soil cores, provides flux results that are more representative of those that occur during natural freeze-thaw conditions. In addition to better simulating a gradual freezing process from above, which leads to realistic soil temperatures at depth, such a regime triggers a natural movement of soil moisture upwards towards the freezing front (Hu *et al.* 2006). It would also slow the freezing process which would create less physical disturbance, and possibly lower N_2O fluxes. Hu *et al.* (2006) suggest that a simulated water table, at a representative depth, helps to simulate an even more natural soil moisture regime. In Hu *et al.* (2006), N_2O fluxes are approximately seven times higher in uninsulated versus soil-insulated cores. N_2O fluxes are approximately three times higher in uninsulated versus soil-insulated cores with a simulated water table.

Zero to 5°C soil temperatures are not attained in the laboratory until the spring thaw simulation, which occurs after the soils are cooled to -10°C. Therefore, the reason for high laboratory versus low field fluxes, in the 0°C to 5°C range, may again be the enhancement of physical, chemical, and/or microbiological disturbance, which creates large N_2O flux pulses near 0°C in laboratory soils.

The laboratory model is likely inapplicable to the natural SC system due to the nature of the data on which it is based. Unrepresentative 5 cm soil temperatures, which remain below 0°C, appear to skew the N_2O fluxes upward. At this point, predictive modeling for *in situ* N_2O fluxes at SC should therefore be based on field data alone. Freeze-thaw simulations for SC soils, if improved, may better reveal realistic N_2O flux patterns during the winter and spring, and guide refinements of *in situ* sampling methods. However, Haag and Matschonat (2001) warn, that regardless of its complexity, the most that any experiment can do is to provide a set of "capacities" of how the ecosystem *may* behave. In this conservative view, experimentation cannot give researchers the ability to predict ecosystem behaviour.

5.6 Recommendations

Ideally this research will be continued, with refined gas collection methods, based on those developed for the laboratory incubation. Adding more years and events to the field dataset would provide better modeling capabilities. Continuous soil temperature and soil moisture logging could provide the capacity to quantify antecedent conditions and factor these into the flux model. The incorporation of N-input and N-consumption levels, based on crop type, would help refine the model as well. If found significant by comparative study on its effect on N_2O flux, a soil texture term would also likely improve the N_2O flux model, in terms of its applicability at a regional scale.

More sophisticated snow flux methods, such as those in van Bochove *et al.* (2000), could be used to better characterize the dynamics of N_2O emissions through snow. Year-round fluxes could be monitored by a continuous flow-through method with a portable analyzer such as the Fourier transform infrared gas analyzer (Gasmet DX-4015, Helsinki, FI).

For event-based field data, ideally, sampling would begin on the first day of each thaw and precipitation event, and on the day prior to each inorganic and organic fertilizer application. Sampling would be repeated for several days following each thaw, precipitation event, and fertilizer application. Bulk density, organic content, soil N, and soil C could be measured on a monthly basis from each site. Additional soil samples for these parameters could be obtained following the first significant precipitation event after fertilization. Microbial analyses could also be performed on a regular basis, along with isotope studies to determine the relative contribution of denitrification and nitrification to N_2O production during different seasons.

Van Kessel *et al.* (1993), Pennock *et al.* (1994), and Corre *et al.* (1996) use $p \leq 0.20$ to compare differences in N_2O flux between landscape elements. It may be that using a higher p-level, than that employed for the SC and SCFT comparisons, would lead to different conclusions regarding spatial and/or temporal differences in N_2O flux. At $p \leq 0.05$, field and laboratory spatial differences are largely insignificant, except in the case of crop influences on N_2O flux.

Laboratory work should be repeated using the same air temperatures, but using soil as an insulator, along with a simulated water table, as recommended by Hu *et al.* (2006). A greater and more representative range of VWCs could be simulated, in addition to realistic snowmelt and icemelt scenarios. As Henry (2007) suggests, freeze-thaw cycles of different lengths could be incorporated into the simulation, along with appropriate controls. Experimental designs should include soil core replicates maintained at a constant average thaw air temperature (Henry 2007), and designs could additionally incorporate different freeze-thaw cycle lengths and frequencies, in order to characterize emissions from a complete range of possible winter conditions (Henry 2007). The simulation of possible climate change scenarios could broaden freeze-thaw experiments even more.

Future research on the effect of various alternative agricultural practices on N_2O flux might help lower N_2O emissions in the future. Some work on the influence of conventional farming versus "best management practices", i.e. no tillage and reduced fertilization, indicates that BMP reduces N_2O emissions from agriculture (e.g. Wagner-Riddle *et al.* 2007). Malhi *et al.* (2006) find that no-till and retention of crop residues reduces N_2O flux. However, the effect of no-till alone may depend on the method of fertilizer application (Venterea *et al.* 2005). In a review of the no-till literature, Six *et al.* (2004) conclude that no-till increases the global warming potential (GWP) of agricultural soils in the short term, and only decreases GWP in humid climates after 10 years. Although government agencies strongly encourage farmers to adopt BMP (e.g. Ontario Ministry of Agriculture 2008), further examination of the potential of different BMP scenarios to reduce N_2O emissions in temperate zones is an important area of study.

Agroforestry may likewise have the potential to decrease N_2O flux from agriculture. However research in temperate regions is scant and not yet conclusive (e.g. Evers 2009).

Along with scientific investigation into the possible role of BMP and agroforestry in reducing N_2O emissions, there is a lack of research into the potential of organic methods to reduce agricultural emissions of N_2O. The contribution of organic agriculture to the Canadian economy is growing at the substantial rate of 20% (Conference Board of Canada 2009), but little research exists on the relative contribution of organic versus conventional agriculture to N_2O emissions. It is undeniable that eliminating the demand for inorganic nitrogen fertilizers would decrease CO_2 emissions, due to a decrease in energy consumption from the energy-intensive manufacture of inorganic fertilizer (Makhijani *et al.* 1992). In a review, Fortune *et al.* (2001) find that the results of comparative studies between N_2O emissions from agricultural soils under organic versus conventional management are inconclusive, while other publications conclude that organic soil management practices reduce N_2O emissions (e.g. El-Hage Scialabba and Hattam 2002, Küstermann and Hülsbergen 2008). Organic agricultural practices are more diverse than those in conventional agriculture. Aspects of this diversity include a greater variety of crops, more complex crop rotation schemes, and a greater variety of farming standards imposed by multiple public and private sector certifying bodies at the provincial, national and international level. Although widespread adoption of organic methods may significantly reduce agricultural emissions of N_2O, research on a full range of organic practices could determine this conclusively, and is therefore a worthwhile topic for future biogeoclimatic investigation.

5.7 Conclusions

IPCC models may overestimate N_2O emissions from agricultural land in Canada (e.g. Khakbazan *et al.* 2004). Much of the flux literature from arable soils reports parametric statistics for N_2O. If data are not in fact normal, but right-skewed, as the SC data are, such parametric results may contribute to overestimates of N_2O emissions. Hutchinson *et al.* (2007) determine that revised IPCC estimates are effective, but are limited to historical versus predictive modeling. These estimates assume that there is a simple linear relationship between N input and N_2O emission (Hutchinson *et al.* 2007). For example, they do not account for the influence of climatic factors, such as those which drive thaws, or management practices beyond total N input (Hutchinson *et al.* 2007). The uncertainty in IPCC estimates for Canadian N_2O emissions is 40% (Hutchinson *et al.* 2007).

Although there are many observational studies on *in situ* N_2O fluxes from arable soil, many do not follow fluxes year-round. Some important work, however, is both year-round and multi-year (e.g. Wagner-Riddle *et al.* 2007), while some analyzes flux dynamics in consecutive winter-spring seasons (e.g. van Bochove *et al.* 2000). The SCFT laboratory simulation contributes to a dearth of N_2O flux studies in a controlled environment on intact agricultural soils, as most freeze-thaw simulations on N_2O in agricultural soils focus on N_2O production (e.g. Goodroad and Keeney 1984, Chantigny *et al.* 2002, Yanai *et al.* 2007). There are no other known N_2O flux studies which combine field and laboratory research on arable soils to date.

The findings here illustrate that there are few landscape-scale differences in N_2O flux over time, from arable clay loam in two southern Ontario fields under similar management regimes, although significant crop-based spatial differences do occur. This research supports conclusive spring and summer trends in the *in situ* N_2O flux literature over the last three decades, that is, spring and summer are significant periods of N_2O emissions from agricultural soils in temperate northern regions, even when soil temperatures are low, as during the spring. During the growing season, soil temperature would appear to be less significant in driving N_2O flux, when precipitation and fertilization events prevail. Field results during the winter are less conclusive, in both the literature and at SC. The SC sites undergo only one significant thaw period during the winter of study, that is, there is only one SC thaw event when daily air temperature maxima equal or exceed 4°C for more than two days. Although this thaw is long and extreme, and causes soil moisture to reach near-saturation levels, N_2O fluxes are not exceptionally high. On the other hand, daily fluxes in the laboratory experiment, which intensively examines flux dynamics and magnitudes during a series of simulated winter thaws, exceed those in the field by an order of magnitude.

Laboratory results show that winter N_2O fluxes increase in response to soil temperature increases, and that fluctuations in N_2O emissions parallel fluctuations in winter soil temperature. These N_2O flux spikes and fluctuations exhibit virtually no time delay in response to soil temperature change, and fluxes quickly drop following the onset of the early spring thaw and late spring simulations (Figure 4.4). The quantification of *in situ* winter thaw N_2O fluxes during a more typical winter, when more winter thaws of this length (Petrone and Macrae, *unpublished data*) occur, may reveal that winter thaw fluxes are closer to those quantified in the lab. Alternatively, a laboratory experiment, which more closely mimics *in situ* soil temperatures, may result in lower *ex situ* N_2O fluxes. Field results from a typical winter, with multiple thaws, would likely be more closely aligned with those from a laboratory simulation, especially when both field and laboratory methods incorporate the methodological improvements discussed in sections 5.2 and 5.4.

Overall, *in situ* N_2O flux observations at SC indicate that fluxes from arable soils in southern Ontario may be low, relative to those of other temperate agricultural regions, although they likely vary during both the growing and non-growing seasons based on crop type. The work presented here also broadens the understanding of agricultural N_2O flux dynamics during the non-growing season in southern Ontario, and indicates that their significance, in terms of annual N_2O emissions from arable soils, may be high. While additional research, combining refined field and laboratory work as outlined above, could supplement this knowledge, and likely reconcile field and laboratory results, the importance of soil temperature and soil moisture as drivers of N_2O flux is evident, and can be used in the refinement of N_2O emission models for agricultural land.

Appendices

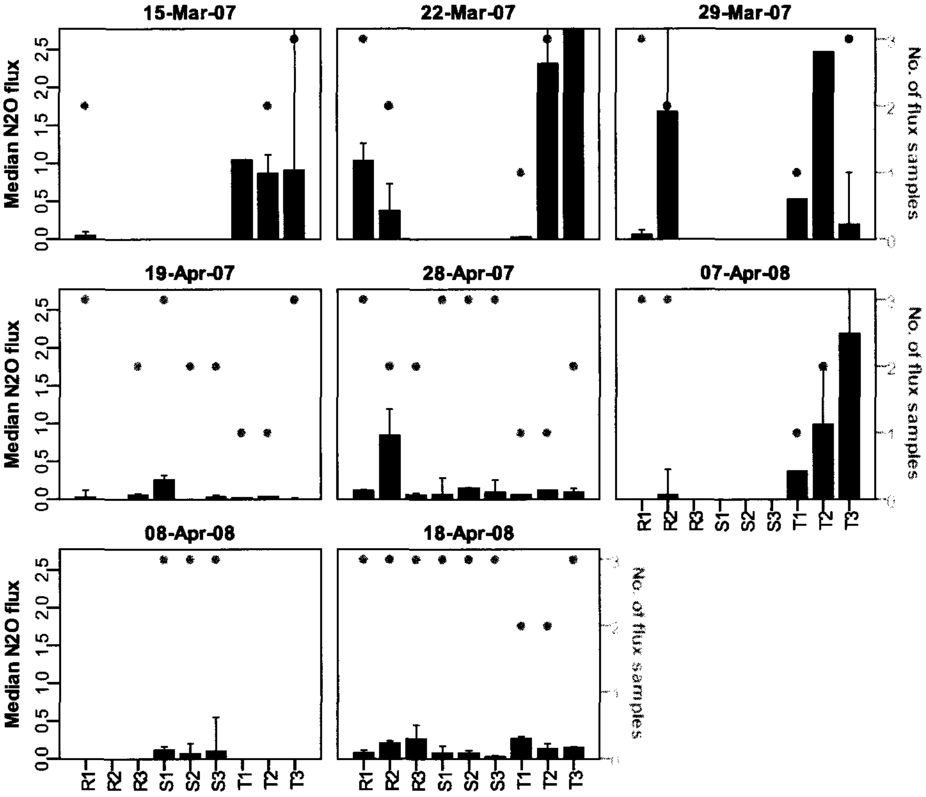


Figure A 1. N_2O flux (mg m^{-2} d^{-1}) (bars) and sample size (dots) by site for all March and April sampling dates. Error bars indicate the 95% confidence interval for median N_2O flux. Error bars are infinite where $n \leq 2$, and therefore not illustrated. For N_2O fluxes > 2.50 mg m^{-2} d^{-1}, see Table A 6.

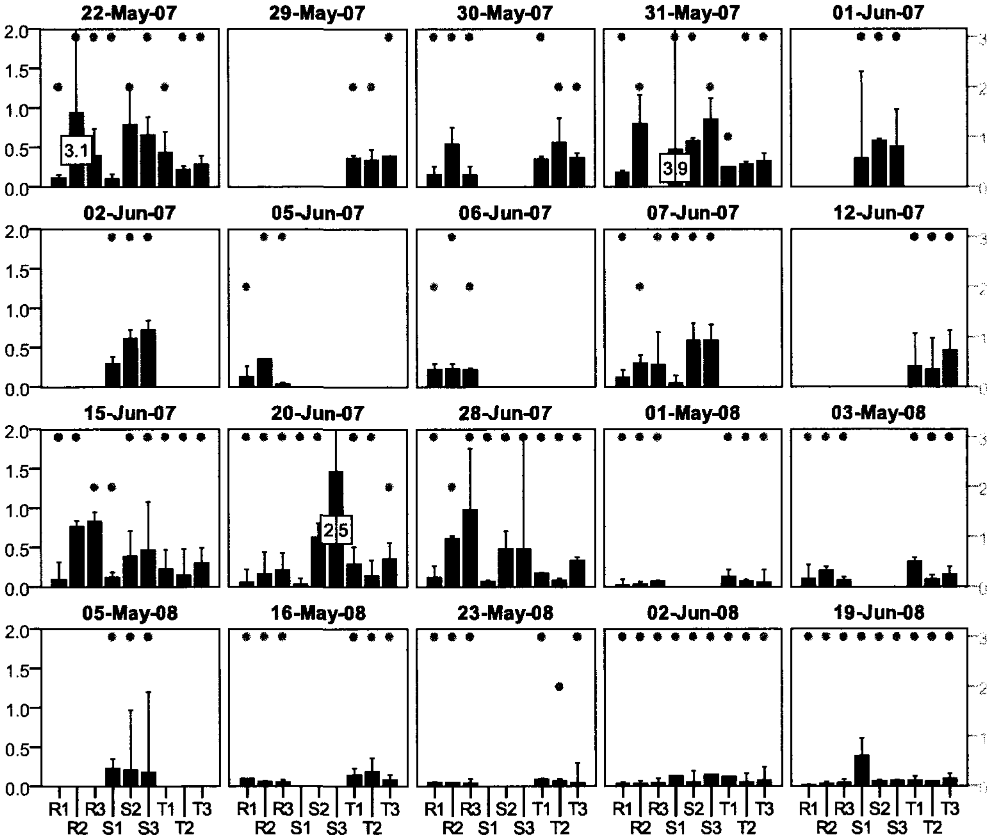


Figure A 2. Median N_2O flux (mg m^{-2} d^{-1}, left y-axis, bars) and sample size (right y-axis, dots) by site for all May and June sampling dates. Error bars indicate the 95% confidence interval (CI) for median N_2O flux. Numbers indicate the upper CI when it lies off-scale. Note that error bars are infinite where n ≤ 2, and therefore not illustrated.

Table A 1. Agricultural N_2O fluxes from the literature in northern temperate climates with equivalent SC statistics. Parametric SC statistics are calculated where necessary for comparisons. n/a = data not available.

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux ($mg\ m^{-2}\ d^{-1}$)	equivalent SC statistic	SC N_2O flux ($mg\ m^{-2}\ d^{-1}$)	SC notes
Burton and Beauchamp (1994)	Delhi, Ontario	non-growing season 1988-89	loamy sand	corn residue	—	maximum mean daily spring flux	25	maximum mean daily spring flux, post-corn	6.9 (Mar 22/07)	—
Burton and Beauchamp (1994)	Delhi, Ontario	non-growing season 1989-90	loamy sand	corn residue	—	maximum mean daily spring flux	28	maximum mean daily spring flux, post-corn	6.9 (Mar 22/07)	—
Corre *et al.* (1996)	Saskatchewan	Jun 1994 through May 1995	clay loam	wheat	anhydrous NH_3 & urea	maximum median daily flux	2.4 (mid-Jun 1994 and mid-Apr 1995)	maximum median daily flux, wheat	0.5 (Jul 31)	NH_4^+ &/or urea
Corre *et al.* (1996)	Saskatchewan	Jun 1994 through May 1995	sandy loam	oats	anhydrous NH_3 & urea	maximum median daily flux	0.5 (mid-Apr 1995)	maximum median daily flux, oats	0.4 (May 29)	NH_4^+ &/or urea

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux (mg m^{-2} d^{-1})	equivalent SC statistic	SC N_2O flux (mg m^{-2} d^{-1})	SC notes
Dörsch *et al.* (2004)	Germany	non-growing season	loamy sand	previously winter wheat	fall tilled & ridged with NH_4^+ & residue	maximum flux (single replicate)	28	maximum flux (all crops), maximum flux (post-winter wheat)	26 (Mar 22/07), 0.3 (Jan 8/08)	no manure or fertilizer, peas after winter wheat
								note: no March post-winter wheat samples were available from SC		
Dörsch *et al.* (2004)	Germany	non-growing season	loamy sand	previously winter wheat	fall tilled & ridged with NH_4^+ & residue	maximum mean daily flux	16	maximum mean daily flux (all crops), maximum mean daily flux (post-winter wheat)	4.3 (Mar 22/07), 0.3 (Jan 8/08)	no manure or fertilizer, peas after winter wheat
								note: no March post-winter wheat samples were available from SC		
Duxbury *et al.* (1982, Nature)	New York State	May 1979 through April 1981	silt loam	corn	NH_4^+ &/or urea	maximum daily mean flux	44 - 57	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux (mg m^{-2} d^{-1})	equivalent SC statistic	SC N_2O flux (mg m^{-2} d^{-1})	SC notes
Goodroad and Keeney (1984)	Wisconsin	non-growing season	silt loam	previous crop n/a	manure	mean flux Jan 20	1.0	mean Jan flux, all crops (range of daily means), all crops	0.1 (0.07 – 0.17)	usually fall manure following oats in R & T fields
Goodroad and Keeney (1984)	Wisconsin	non-growing season	silt loam	previous crop n/a	manure	mean flux Mar 5	6.3	mean Mar flux (range of daily means), all crops	2.4 (0.8 - 4.3)	usually fall manure following oats in R & T fields
Goodroad and Keeney (1984)	Wisconsin	non-growing season	silt loam	previous crop n/a	manure	mean flux Mar 24	0.7	mean Mar flux (range of daily means), all crops	2.4 (0.8 - 4.3)	usually fall manure following oats in R & T fields
Lemke *et al.* (1998)	Alberta	winter	n/a	n/a	—	daily geometric means	< 0.4	daily geometric means, winter, all crops	≤ 0.1	—
Lemke *et al.* (1998)	Alberta	spring	n/a	n/a	—	maximum daily geometric means	13.2	maximum daily geometric means, spring, all crops	0.7	—

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux (mg m^{-2} d^{-1})	equivalent SC statistic	SC N_2O flux (mg m^{-2} d^{-1})	SC notes
Lemke *et al.* (1998)	Alberta	growing season 1993	n/a	spring wheat	urea	range of daily geometric means	1.3 - 7.3	range of daily geometric means, spring wheat	0.04 - 0.3	NH4+ &/or urea
Lemke *et al.* (1998)	Alberta	growing season 1993	n/a	spring wheat	urea	maximum daily geometric mean	7.3	maximum daily geometric mean, spring wheat	0.4 (Jun 2/07); 0.2 (Jul 31/08)	NH4+ &/or urea
Lemke *et al.* (1998)	Alberta	growing season 1993	n/a	spring wheat	urea	maximum replicate flux	38	maximum replicate flux, spring wheat	1.2	NH4+ &/or urea
Lemke *et al.* (1998)	Alberta	growing season 1994	n/a	spring wheat	urea	maximum daily geometric mean	13	maximum daily geometric mean, spring wheat	0.4 (Jun 2/07); 0.2 (Jul 31/08)	NH4+ &/or urea

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux (mg m^{-2} d^{-1})	equivalent SC statistic	SC N_2O flux (mg m^{-2} d^{-1})	SC notes
Mosier and Hutchinson (1981)	Northern Colorado	growing season	clay loam	irrigated corn	NH_3-N	maximum daily mean flux (Jul 22, 2d after 1st irrigation)	55	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea
Rochette *et al.* (2004)	S.W. Quebec	April through August 2001	clay	corn	anhydrous NH_3	maximum daily mean flux (July 2001)	56	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea
Rochette *et al.* (2004)	S.W. Quebec	April through August 2001	clay loam	corn	anhydrous NH_3	maximum daily mean flux (July 2001)	88	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea
Rochette *et al.* (2004)	S.W. Quebec	April through August 2001	sandy loam	corn	anhydrous NH_3	maximum daily mean flux (July 2001)	84	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux (mg m^{-2} d^{-1})	equivalent SC statistic	SC N_2O flux (mg m^{-2} d^{-1})	SC notes
Rochette *et al.* (2004)	S.W. Quebec	April through August 2002	clay	corn	anhydrous NH_3	maximum daily mean flux (June 2002)	32	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea
Rochette *et al.* (2004)	S.W. Quebec	April through August 2002	clay loam	corn	anhydrous NH_3	maximum daily mean flux (June 2002)	16	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea
Rochette *et al.* (2004)	S.W. Quebec	April through August 2002	sandy loam	corn	anhydrous NH_3	maximum daily mean flux (June 2002)	6.0	maximum daily mean flux, corn (May 22)	0.8	NH_4^+ &/or urea
van Bochove *et al.* (2000)	S.W. Quebec	winter 1	sandy loam	previously barley	—	mean flux	0.5	mean winter (Nov through Feb), post-oats	0.1	note: only post-oat sites receive a fall manure at SC
van Bochove *et al.* (2000)	S.W. Quebec	winter 2	sandy loam	previously barley	—	mean flux	3.5	mean winter (Nov through Feb), post-oats	0.1	—

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux (mg m^{-2} d^{-1})	equivalent SC statistic	SC N_2O flux (mg m^{-2} d^{-1})	SC notes
van Bochove *et al.* (2000)	S.W. Quebec	winter 3	sandy loam	previously barley & corn	—	mean flux	7.6	mean winter (Nov through Feb), post-oats & post-corn	0.1	—
van Bochove *et al.* (2000)	S.W. Quebec	April following winter 3	sandy loam	previously barley & corn	—	mean flux	2.3	mean Mar & Apr flux 2007, mean Apr flux 2008 (no Mar 2008 data available)	0.3, 0.7	—
van Bochove *et al.* (2001)	S.W. Quebec	spring	clay loam	n/a	fall pig manure	maximum daily mean flux	19 (Apr 19)	maximum daily mean (all crops), maximum daily mean (post-oats)	4.3 (Mar 22/07), 1.3 (Apr 7/08)	—
van Kessel *et al.* (1993)	Saskatchewan	growing season	n/a	pea	NH_4^+	maximum daily median (Jun 4)	16	maximum daily GS median, all crops (Jun 2)	0.6	all SC crops
Wagner-Riddle *et al.* (2007)	Elora, Ontario	2 growing seasons	silt loam	corn	urea	median GS flux, corn	0.9 / 1.5	median GS flux, corn (all corn sites)	0.2	NH_4^+ &/or urea

Reference	Location	Season	Soil texture	Crop / Residue	Manure / Fertilizer	Statistic	N_2O flux ($mg\ m^{-2}\ d^{-1}$)	equivalent SC statistic	SC N_2O flux ($mg\ m^{-2}\ d^{-1}$)	SC notes
Wagner-Riddle *et al.* (2007)	Elora, Ontario	growing season	silt loam	winter wheat	urea (previous year)	median GS flux, winter wheat	0.3	median GS flux, winter wheat (site S1)	0.2	NH_4^+ &/or urea (previous year)
Wagner-Riddle *et al.* (2007)	Elora, Ontario	non-growing season	silt loam	chopped corn	—	median NGS flux, corn residue	0.7 / 0.4	median NGS flux, corn residue (R&T fields)	0.06	—
Wagner-Riddle *et al.* (2007)	Elora, Ontario	non-growing season	silt loam	winter wheat	—	median NGS flux, winter wheat	0.3	median SPRING flux, winter wheat (site S1)	0.2	note: no winter SC winter wheat data available

Table A 2. Regional mean daily air temperature statistics from 2006 through 2008. Data from Regional Waterloo International Airport meteorological station (43.46°N, 80.38°W) (Environment Canada 2009).

Case Summaries

		Mean Temp (°C)			
Month	Year	N	Median	Minimum	Maximum
1	2006	31	-1.00	-11	6
	2007	31	-4.30	-18	8
	2008	31	-4.30	-14	11
	Total	93	-2.80	-18	11
2	2006	28	-5.40	-12	2
	2007	28	-10.60	-17	-2
	2008	26	-6.70	-16	0
	Total	82	-8.15	-17	2
3	2006	31	-.80	-9	10
	2007	31	-.70	-18	14
	2008	31	-4.70	-14	5
	Total	93	-2.40	-18	14
4	2006	30	7.40	0	14
	2007	30	5.20	-6	15
	2008	30	7.45	-1	16
	Total	90	6.75	-6	16
5	2006	31	12.60	4	25
	2007	31	11.70	6	21
	2008	31	10.20	5	19
	Total	93	11.30	4	25
6	2006	30	17.50	11	25
	2007	30	18.40	11	27
	2008	30	17.90	12	26
	Total	90	17.95	11	27
7	2006	31	21.90	16	26
	2007	31	19.40	13	25
	2008	31	19.90	16	25

	Total	93	20.00	13	26
8	2006	31	17.70	14	30
	2007	31	18.90	14	26
	2008	31	18.00	14	22
	Total	93	18.50	14	30
9	2006	30	14.25	6	19
	2007	29	16.50	7	25
	2008	30	15.05	11	21
	Total	89	15.00	6	25
10	2006	31	6.50	1	17
	2007	31	11.10	2	23
	2008	31	7.10	0	16
	Total	93	8.20	0	23
11	2006	30	3.35	0	10
	2007	30	1.05	-8	10
	2008	30	.70	-9	12
	Total	90	1.95	-9	12
12	2006	31	1.30	-9	7
	2007	31	-4.20	-12	3
	2008	31	-5.50	-14	8
	Total	93	-2.50	-14	8
Total	2006	365	7.60	-12	30
	2007	364	8.25	-18	27
	2008	363	8.10	-16	26
	Total	1092	8.10	-18	30

Table A 3. Regional total daily precipitation statistics from 2006 through 2008. Data from Regional Waterloo International Airport meteorological station (43.46°N, 80.38°W) (Environment Canada 2009).

Case Summaries

Total Precip (mm)

Month	Year	Median	Minimum	Maximum	Sum
1	2006	.500	.0	20.0	76.5
	2007	.500	.0	8.5	44.0
	2008	1.000	.0	19.0	64.5
	Total	.500	.0	20.0	185.0
2	2006	.250	.0	32.0	79.0
	2007	.000	.0	2.5	11.5
	2008	.250	.0	17.5	49.5
	Total	.000	.0	32.0	140.0
3	2006	.000	.0	31.0	63.0
	2007	.000	.0	8.5	38.5
	2008	.500	.0	8.5	52.5
	Total	.000	.0	31.0	154.0
4	2006	.000	.0	27.5	69.5
	2007	.000	.0	12.5	48.0
	2008	.000	.0	21.0	46.0
	Total	.000	.0	27.5	163.5
5	2006	.000	.0	33.5	93.5
	2007	.000	.0	23.0	46.0
	2008	.500	.0	15.0	62.5
	Total	.000	.0	33.5	202.0
6	2006	.000	.0	5.0	17.5
	2007	.000	.0	17.5	33.0
	2008	1.000	.0	11.5	81.5
	Total	.000	.0	17.5	132.0
7	2006	.500	.0	56.5	182.5
	2007	.000	.0	5.5	28.0
	2008	.500	.0	54.0	203.5

	Total	.500	.0	56.5	414.0
8	2006	.000	.0	13.0	38.0
	2007	.000	.0	4.5	13.5
	2008	.000	.0	22.0	84.5
	Total	.000	.0	22.0	136.0
9	2006	.500	.0	37.0	141.0
	2007	.000	.0	9.0	23.5
	2008	.500	.0	27.0	112.0
	Total	.000	.0	37.0	276.5
10	2006	.000	.0	25.5	45.0
	2007	.500	.0	12.0	24.5
	2008	.000	.0	10.5	38.5
	Total	.000	.0	25.5	108.0
11	2006	.000	.0	24.0	58.0
	2007	.250	.0	32.0	76.5
	2008	.500	.0	28.5	89.0
	Total	.000	.0	32.0	223.5
12	2006	.000	.0	27.5	64.0
	2007	.500	.0	26.0	77.0
	2008	1.500	.0	14.5	89.5
	Total	.500	.0	27.5	230.5
Total	2006	.000	.0	56.5	927.5
	2007	.000	.0	32.0	464.0
	2008	.500	.0	54.0	973.5
	Total	.000	.0	56.5	2365.0

Table A 4. Median, minimum and maximum N_2O flux by season for all data collected during the SC field study.

Case Summaries

N_2O flux (mg m^-2 d^-1)

Season	N	Median	Minimum	Maximum
spring	112	.1126	-.10	26.09
growing season	634	.1461	-.07	3.88
fall	89	.0479	-.10	.70
winter	244	.0511	-.09	.66
Total	1079	.1111	-.10	26.09

Table A 5. Median, minimum and maximum N_2O flux by month and year for all data collected during the SC field study.

Case Summaries

N_2O flux (mg m^-2 d^-1)

month	Year	N	Median	Minimum	Maximum
1	2008	86	.0702	-.09	.66
2	2008	52	.0078	-.02	.10
3	2007	30	.5883	.00	26.09
4	2007	37	.0589	-.04	1.19
	2008	45	.1101	-.10	4.35
5	2007	67	.3312	.00	3.88
	2008	80	.0894	.02	1.20
6	2007	135	.2936	.00	2.48
	2008	54	.0655	.01	.62
7	2007	76	.1420	-.04	1.30
	2008	80	.1094	-.07	3.01
8	2006	36	.1494	.05	2.25
	2007	53	.1338	-.02	1.34
	2008	53	.1272	.03	.89
9	2006	18	.1266	.01	.69
	2007	26	.0323	-.10	.70
10	2006	18	.0408	-.01	.62
	2007	27	.0387	-.08	.22
11	2007	52	.0859	.01	.48
12	2007	54	.0380	-.04	.52

Table A 6. N_2O flux statistics for individual sites on all March and April sampling dates of the SC field study.

Case Summaries

N_2O flux (mg m^-2 d^-1)

Date	Site	N	Median	Minimum	Maximum
2007-03-15T00:00:00.000	R1	2	.0480	.00	.10
	T1	1	1.0529	1.05	1.05
	T2	2	.8686	.62	1.12
	T3	3	.9118	.10	9.39
	Total	8	.7663	.00	9.39
2007-03-22T00:00:00.000	R1	3	1.0381	.56	1.27
	R2	2	.3783	.02	.74
	T1	1	.0312	.03	.03
	T2	3	2.3185	.07	14.04
	T3	3	5.8117	.09	26.09
	Total	12	.8868	.02	26.09
2007-03-29T00:00:00.000	R1	3	.0635	.06	.13
	R2	2	1.6849	.27	3.10
	T1	1	.5287	.53	.53
	T2	1	2.4691	2.47	2.47
	T3	3	.1963	.09	.88
	Total	10	.2332	.06	3.10
2007-04-19T00:00:00.000	R1	3	.0319	-.04	.12
	R3	2	.0534	.03	.08
	S1	3	.2587	.19	.32
	S2	2	-.0217	-.02	-.02
	S3	2	.0349	.02	.05
	T1	1	.0222	.02	.02
	T2	1	.0401	.04	.04
	T3	3	-.0253	-.03	.02
	Total	17	.0284	-.04	.32
2007-04-28T00:00:00.000	R1	3	.1179	.05	.12

	R2	2	.8431	.50	1.19
	R3	2	.0542	.03	.08
	S1	3	.0621	.04	.29
	S2	3	.1504	.03	.15
	S3	3	.0959	.03	.26
	T1	1	.0589	.06	.06
	T2	1	.1209	.12	.12
	T3	2	.0972	.05	.15
	Total	20	.1069	.03	1.19
2008-04-07T00:00:00.000	R1	3	-.0738	-.10	-.07
	R2	3	.0587	-.08	.39
	T1	1	.3712	.37	.37
	T2	2	.9921	.27	1.71
	T3	2	2.1915	.03	4.35
	Total	11	.0587	-.10	4.35
2008-04-08T00:00:00.000	S1	3	.1168	.02	.16
	S2	3	.0732	.06	.20
	S3	3	.1070	.05	.55
	Total	9	.1070	.02	.55
2008-04-18T00:00:00.000	R1	3	.0796	.04	.12
	R2	3	.2058	.14	.24
	R3	3	.2598	.19	.45
	S1	3	.0791	.03	.17
	S2	3	.0772	.04	.11
	S3	3	.0283	.03	.05
	T1	2	.2657	.23	.30
	T2	2	.1360	.07	.20
	T3	3	.1526	.10	.16
	Total	25	.1151	.03	.45
Total	R1	20	.0716	-.10	1.27
	R2	12	.2534	-.08	3.10

	R3	7	.0804	.03	.45
	S1	12	.1399	.02	.32
	S2	11	.0732	-.02	.20
	S3	11	.0459	.02	.55
	T1	8	.2657	.02	1.05
	T2	12	.4478	.04	14.04
	T3	19	.1450	-.03	26.09
	Total	112	.1126	-.10	26.09

Table A 7. N_2O flux by replicate illustrating extremely high variation in values between replicates on Mar 22/07, with the highest variation at site T3.

Case Summaries[a]

			N_2O flux (mg m^-2 d^-1)
Replicate	R1N1	1	1.27
	R1N2	1	.56
	R1N3	1	1.04
	R2N1	1	.74
	R2N2	1	.02
	T1N2	1	.03
	T2N1	1	2.32
	T2N2	1	.07
	T2N3	1	14.04
	T3N1	1	26.09
	T3N2	1	5.81
	T3N3	1	.09

a. Limited to first 100 cases.

Table A 8. Median, minimum and maximum N_2O flux by 5°C soil temperature bin from SC, August 2006 through August 2008.

Case Summaries

N_2O flux (mg m^-2 d^-1)

Moisture level	Soil temperature (C) at 5 cm depth (Binned)	N	Median	Minimum	Maximum
dry (< 0.05 m3 m-3)	15.1 - 20.0	4	.2873	.09	.42
	Total	4	.2873	.09	.42
moist (0.05 - 0.19 m3 m-3)	<= 0.0	10	-.0052	-.02	.23
	0.1 - 5.0	11	.0552	.00	.48
	5.1 - 10.0	4	.0434	-.03	.10
	10.1 - 15.0	26	.0571	-.10	.29
	15.1 - 20.0	63	.1147	-.05	1.46
	20.1 - 25.0	67	.1433	.00	3.88
	25.1 - 30.0	15	.2639	-.04	1.30
	30.1+	6	.4798	.10	1.89
	Total	202	.1117	-.10	3.88
wet (0.20 - 0.34 m3 m-3)	<= 0.0	12	.0509	-.02	.66
	0.1 - 5.0	30	.0906	-.01	.53
	5.1 - 10.0	51	.0770	-.08	1.20
	10.1 - 15.0	43	.0732	-.07	4.35
	15.1 - 20.0	127	.1293	-.07	1.31
	20.1 - 25.0	93	.1745	-.04	1.76
	25.1 - 30.0	33	.3175	.03	.87
	30.1+	8	.6086	.22	2.48
	Total	397	.1363	-.08	4.35
very wet (0.35+ m3 m-3)	<= 0.0	1	.0088	.01	.01
	0.1 - 5.0	13	.1380	-.05	3.10
	5.1 - 10.0	56	.0710	-.09	1.19
	10.1 - 15.0	18	.0891	.03	.55

	15.1 - 20.0	24	.1754	.02	.89
	20.1 - 25.0	21	.3984	.07	3.06
	25.1 - 30.0	14	.4415	.09	2.25
	Total	147	.1253	-.09	3.10
Total	<= 0.0	23	.0112	-.02	.66
	0.1 - 5.0	54	.0773	-.05	3.10
	5.1 - 10.0	111	.0747	-.09	1.20
	10.1 - 15.0	87	.0661	-.10	4.35
	15.1 - 20.0	218	.1353	-.07	1.46
	20.1 - 25.0	181	.1675	-.04	3.88
	25.1 - 30.0	62	.3358	-.04	2.25
	30.1+	14	.5342	.10	2.48
	Total	750	.1235	-.10	4.35

Table A 9. Median, minimum and maximum N_2O flux by 2.5°C soil temperature bin from SC, August 2006 through August 2008.

Case Summaries

N_2O flux (mg m^-2 d^-1)

Moisture level	Soil temperature (C) at 5 cm depth (Binned)	N	Median	Minimum	Maximum
dry (< 0.05 m3 m-3)	15.1 - 17.5	2	.2308	.09	.37
	17.6 - 20.0	2	.3087	.20	.42
	Total	4	.2873	.09	.42
moist (0.05 - 0.19 m3 m-3)	<= 0.0	10	-.0052	-.02	.23
	0.1 - 2.5	8	.0329	.00	.48
	2.6 - 5.0	3	.0780	.07	.14
	5.1 - 7.5	2	.0836	.07	.10
	7.6 - 10.0	2	-.0078	-.03	.02
	10.1 - 12.5	5	.0387	-.02	.12
	12.6 - 15.0	21	.0576	-.10	.29
	15.1 - 17.5	23	.0657	-.05	.31
	17.6 - 20.0	40	.1435	.01	1.46
	20.1 - 22.5	40	.0911	.00	3.88
	22.6 - 25.0	27	.2228	.05	.98
	25.1 - 27.5	11	.2952	-.04	1.08
	27.6 - 30.0	4	.2408	.08	1.30
	30.1 - 32.5	3	.4774	.10	1.89
	32.6+	3	.4821	.39	.70
	Total	202	.1117	-.10	3.88
wet (0.20 - 0.34 m3 m-3)	<= 0.0	12	.0509	-.02	.66
	0.1 - 2.5	15	.0447	-.01	.53
	2.6 - 5.0	15	.1257	.04	.37
	5.1 - 7.5	17	.0918	.02	.97
	7.6 - 10.0	34	.0662	-.08	1.20

	10.1 - 12.5	13	.1057	-.04	.30
	12.6 - 15.0	30	.0696	-.07	4.35
	15.1 - 17.5	54	.1002	-.07	.70
	17.6 - 20.0	73	.1490	.01	1.31
	20.1 - 22.5	61	.1807	-.04	1.76
	22.6 - 25.0	32	.1634	.06	.87
	25.1 - 27.5	19	.3142	.03	.87
	27.6 - 30.0	14	.3526	.10	.62
	32.6+	8	.6086	.22	2.48
	Total	397	.1363	-.08	4.35
very wet (0.35+ m3 m-3)	<= 0.0	1	.0088	.01	.01
	0.1 - 2.5	5	.1963	.08	2.47
	2.6 - 5.0	8	.1003	-.05	3.10
	5.1 - 7.5	17	.0316	-.09	.18
	7.6 - 10.0	39	.1133	-.01	1.19
	10.1 - 12.5	12	.1232	.03	.36
	12.6 - 15.0	6	.0804	.03	.55
	15.1 - 17.5	9	.1104	.02	.31
	17.6 - 20.0	15	.1843	.09	.89
	20.1 - 22.5	14	.3461	.09	3.06
	22.6 - 25.0	7	.3984	.07	.74
	25.1 - 27.5	9	.4697	.09	.75
	27.6 - 30.0	5	.4264	.31	2.25
	Total	147	.1253	-.09	3.10
Total	<= 0.0	23	.0112	-.02	.66
	0.1 - 2.5	28	.0619	-.01	2.47
	2.6 - 5.0	26	.1179	-.05	3.10
	5.1 - 7.5	36	.0582	-.09	.97
	7.6 - 10.0	75	.0819	-.08	1.20
	10.1 - 12.5	30	.1008	-.04	.36
	12.6 - 15.0	57	.0629	-.10	4.35

	15.1 - 17.5	88	.0897	-.07	.70
	17.6 - 20.0	130	.1491	.01	1.46
	20.1 - 22.5	115	.1424	-.04	3.88
	22.6 - 25.0	66	.1865	.05	.98
	25.1 - 27.5	39	.3232	-.04	1.08
	27.6 - 30.0	23	.3877	.08	2.25
	30.1 - 32.5	3	.4774	.10	1.89
	32.6+	11	.5862	.22	2.48
	Total	750	.1235	-.10	4.35

Table A 10. Scoring template (Rochette and Eriksen-Hamel 2008) for non-flow-through, non-steady-state chamber design and deployment with evaluation of SC methods.

	Chamber characteristics		Unit	Very poor (0)	Poor (1)	Good (2)	Very good (3)	SCFT Score	Perfect Score	SCFT/Perfect Score (%)
				Binary and Non-numerical Characteristics						
1	Type of chamber				push-in		base and chamber	3	3	100
2	Insulation				no		yes	3	3	100
3	Vent				no		yes	3	3	100
4	Pressurized sample (fixed-volume container only)				no		yes	3	3	100
5	Quality control sample			no			yes	3	3	100
6	Time zero sample taken				no		yes	1	3	33
7	Non-linear model considered			no			yes	0	3	0
8	Zero slope tested				no	yes		1	2	50
9	Temperature corrections				no		yes	3	3	100
10	Type of sample vial			plastic syringe	glass syringe	all other vials	exetainers, vacutainers, Al tubes, gas chromatography in the field, photoacoustic	3	3	100
				Numerical Characteristics						
11	Height of chamber		cm h^{-1}	<10	10 to <20	20 to <40	≥40	1	3	33
12	Chamber base insertion		cm h^{-1}	<5	5 to <8	8 to <12	≥12	3	3	100
13	Area:perimeter ratio		cm	<2.5	2.6 to <6.25	6.26 to <10	≥10	0	3	0
14	Duration of deployment		min	>60	>40 to 60	>20 to 40	≤20	0	3	0
15	Number of samples		no.	1	2	3	>3	0	3	0
16	Duration of sample storage	Plastic syringe	d	>2	1 to 2	<1		3	3	100
		Glass syringe	d	>4	>2 to 4	1 to 2	<1			
		Other	d	>90	>45 to 90	>15 to 45	≤15			
				Total Score				30	47	64

Table B 1. Median, minimum and maximum N_2O flux by soil moisture category during the 5 simulated winter thaws and simulated spring period of the SCFT experiment.

Case Summaries

N_2O (mg/m^2/day)

Moisture Level	Thaw cycle	N	Median	Minimum	Maximum
DRY		172	.0000	-.23	.33
	Early spring	15	.0000	-.05	.07
	Late spring	12	.0406	-.04	.10
	Winter thaw 1	9	.0231	-.02	.05
	Winter thaw 2	9	.0000	-.02	.13
	Winter thaw 3	9	.0219	-.02	.20
	Winter thaw 4	9	-.0218	-.07	.05
	Winter thaw 5	9	.0223	-.02	.04
	Total	244	.0000	-.23	.33
MOIST		116	.0888	-.35	1.71
	Early spring	10	.5204	.00	12.73
	Late spring	8	.1964	.06	4.25
	Winter thaw 1	6	.3492	.00	.88
	Winter thaw 2	6	1.0282	.11	3.22
	Winter thaw 3	6	1.0055	.17	3.19
	Winter thaw 4	6	1.2616	.21	4.03
	Winter thaw 5	6	1.5309	.24	3.70
	Total	164	.1590	-.35	12.73
WET		231	.1909	-.15	1.84
	Early spring	20	8.0337	.21	14.97
	Late spring	16	2.2805	.52	34.78
	Winter thaw 1	12	.2111	.10	.76
	Winter thaw 2	12	2.2798	.35	6.36
	Winter thaw 3	12	2.2361	.54	5.20
	Winter thaw 4	12	2.6636	.93	5.95
	Winter thaw 5	12	2.4354	.56	4.72
	Total	327	.2824	-.15	34.78
Total		519	.0664	-.35	1.84
	Early spring	45	.6317	-.05	14.97
	Late spring	36	.4477	-.04	34.78
	Winter thaw 1	27	.1045	-.02	.88
	Winter thaw 2	27	.4780	-.02	6.36
	Winter thaw 3	27	.6647	-.02	5.20
	Winter thaw 4	27	1.3297	-.07	5.95
	Winter thaw 5	27	.9264	-.02	4.72
	Total	735	.0884	-.35	34.78

Table B 2. Moist core N_2O flux and soil temperature at 5 cm depth by Julian day during the SCFT experiment. Maximum daily medians for each thaw cycle are highlighted.

Thaw cycle	Julian Day	N_2O flux (mg m^-2 d^-1)					Soil temp (°C)				
		N	Mean	Minimum	Maximum	Median	N	Mean	Minimum	Maximum	Median
Winter 1	106	2	0.3	0.0	0.7	0.3	2	-0.5	-0.5	-0.5	-0.5
Winter 1	**107**	**2**	**0.5**	**0.0**	**0.9**	**0.5**	**2**	**-0.3**	**-0.3**	**-0.3**	**-0.3**
Winter 1	108	2	0.4	0.0	0.7	0.4	2	-0.4	-0.4	-0.4	-0.4
Winter 2	117	2	1.0	0.1	1.9	1.0	2	-0.5	-0.5	-0.5	-0.5
Winter 2	118	2	1.6	0.2	3.1	1.6	2	-0.3	-0.3	-0.3	-0.3
Winter 2	**119**	**2**	**1.7**	**0.1**	**3.2**	**1.7**	**2**	**-0.4**	**-0.4**	**-0.4**	**-0.4**
Winter 3	127	2	1.0	0.3	1.8	1.0	2	-0.5	-0.5	-0.5	-0.5
Winter 3	**128**	**2**	**1.7**	**0.2**	**3.2**	**1.7**	**2**	**-0.3**	**-0.3**	**-0.3**	**-0.3**
Winter 3	129	2	1.5	0.2	2.8	1.5	2	-0.4	-0.4	-0.4	-0.4
Winter 4	137	2	1.2	0.2	2.2	1.2	2	-0.5	-0.5	-0.5	-0.5
Winter 4	**138**	**2**	**2.1**	**0.3**	**4.0**	**2.1**	**2**	**-0.3**	**-0.3**	**-0.3**	**-0.3**
Winter 4	139	2	1.7	0.3	3.1	1.7	2	-0.4	-0.4	-0.4	-0.4
Winter 5	147	2	1.4	0.2	2.6	1.4	2	-0.5	-0.5	-0.5	-0.5
Winter 5	**148**	**2**	**2.0**	**0.3**	**3.7**	**2.0**	**2**	**-0.3**	**-0.3**	**-0.3**	**-0.3**
Winter 5	**149**	**2**	**2.0**	**0.5**	**3.5**	**2.0**	**2**	**-0.4**	**-0.4**	**-0.4**	**-0.4**

Thaw cycle	Julian Day	N_2O flux (mg m^-2 d^-1)					Soil temp (°C)				
		N	Mean	Minimum	Maximum	Median	N	Mean	Minimum	Maximum	Median
Early spring	162	2	6.6	0.4	12.7	6.6	2	0.2	0.2	0.2	0.2
Early spring	163	2	1.0	0.0	2.0	1.0	2	3.8	3.8	3.8	3.8
Early spring	164	2	0.3	0.0	0.6	0.3	2	4.1	4.1	4.1	4.1
Early spring	165	2	0.8	0.0	1.5	0.8	2	4.1	4.1	4.1	4.1
Early spring	166	2	0.5	0.1	1.0	0.5	2	4.0	4.0	4.0	4.0
Late spring	167	2	2.2	0.2	4.2	2.2	2	21.2	21.2	21.2	21.2
Late spring	168	2	0.5	0.1	0.9	0.5	2	21.6	21.6	21.6	21.6
Late spring	169	2	0.2	0.1	0.4	0.2	2	20.1	20.1	20.1	20.1
Late spring	170	2	0.1	0.1	0.2	0.1	2	18.0	18.0	18.0	18.0

Table B 3. Wet core N_2O flux and soil temperature at 5 cm depth by Julian day during the SCFT experiment. Maximum daily medians for each thaw cycle are highlighted.

Thaw cycle	Julian Day	N_2O flux (mg m^-2 d^-1)					Soil temp (°C)				
		N	Mean	Minimum	Maximum	Median	N	Mean	Minimum	Maximum	Median
Winter 1	106	4	0.2	0.1	0.3	0.1	4	-0.3	-0.5	-0.2	-0.2
Winter 1	107	4	0.3	0.1	0.4	0.3	4	-0.1	-0.3	0.1	0.0
Winter 1	**108**	**4**	**0.4**	**0.1**	**0.8**	**0.4**	**4**	**-0.1**	**-0.4**	**0.0**	**-0.1**
Winter 2	117	4	1.4	0.4	2.5	1.5	4	-0.3	-0.5	-0.2	-0.2
Winter 2	118	4	3.0	0.5	6.4	2.5	4	-0.1	-0.3	0.1	0.0
Winter 2	**119**	**4**	**3.6**	**0.8**	**5.6**	**4.0**	**4**	**-0.1**	**-0.4**	**0.0**	**-0.1**
Winter 3	127	4	1.7	0.7	2.8	1.6	4	-0.3	-0.5	-0.2	-0.2
Winter 3	128	4	2.6	1.0	4.1	2.7	4	-0.1	-0.3	0.1	0.0
Winter 3	**129**	**4**	**3.0**	**0.5**	**5.2**	**3.2**	**4**	**-0.1**	**-0.4**	**0.0**	**-0.1**
Winter 4	**137**	**4**	**2.9**	**0.9**	**4.5**	**3.0**	**4**	**-0.3**	**-0.5**	**-0.2**	**-0.2**
Winter 4	138	4	3.0	1.3	5.3	2.6	4	-0.1	-0.3	0.1	0.0
Winter 4	**139**	**4**	**3.4**	**1.8**	**6.0**	**3.0**	**4**	**-0.1**	**-0.4**	**0.0**	**-0.1**
Winter 5	147	4	2.0	0.9	3.1	2.0	4	-0.3	-0.5	-0.2	-0.2
Winter 5	**148**	**4**	**2.5**	**0.6**	**4.0**	**2.7**	**4**	**-0.1**	**-0.3**	**0.1**	**0.0**
Winter 5	149	4	2.7	1.5	4.7	2.2	4	-0.1	-0.4	0.0	-0.1

Thaw cycle	Julian Day	N	Mean	Minimum	Maximum	Median	N	Mean	Minimum	Maximum	Median
		N_2O flux (mg m^-2 d^-1)					Soil temp (°C)				
Early spring	162	4	9.1	1.9	13.2	10.7	4	0.5	0.2	0.6	0.5
Early spring	**163**	**4**	**10.6**	**0.3**	**15.0**	**13.6**	**4**	**2.7**	**2.4**	**3.8**	**2.4**
Early spring	164	4	7.0	0.2	11.4	8.3	4	4.1	4.0	4.1	4.0
Early spring	165	4	6.1	0.6	10.6	6.6	4	4.1	4.1	4.2	4.1
Early spring	166	4	4.4	0.8	7.3	4.7	4	4.1	4.0	4.1	4.1
Late spring	**167**	**4**	**15.2**	**1.9**	**34.8**	**12.1**	**4**	**21.1**	**21.1**	**21.2**	**21.1**
Late spring	168	4	10.3	2.1	23.9	7.6	4	21.6	21.6	21.6	21.6
Late spring	169	4	2.7	1.6	5.1	2.1	4	20.0	19.9	20.1	20.0
Late spring	170	4	1.3	0.5	1.8	1.5	4	18.0	18.0	18.1	18.0

Table B 4. Median, minimum and maximum N_2O flux by soil temperature and soil moisture categories during the 5 simulated winter thaws and simulated spring period of the SCFT experiment.

Moisture Level	Soil temperature (C) at 5cm depth	N	Median	Minimum	Maximum
DRY	-7.4 - -5.0	5	.0000	-.02	.00
	-4.9 - -2.5	131	.0000	-.23	.16
	-2.4 - 0.0	26	.0222	-.07	.33
	0.1 - 2.5	6	.0111	.00	.05
	2.6 - 5.0	64	.0000	-.07	.20
	17.6 - 20.0	3	.0000	-.02	.00
	20.1+	9	.0823	-.04	.10
	Total	244	.0000	-.23	.33
MOIST	<= -10.0	10	.0437	-.02	.21
	-9.9 - -7.5	8	.1117	.02	.20
	-7.4 - -5.0	66	.0889	-.35	1.71
	-4.9 - -2.5	30	.1230	-.09	1.33
	-2.4 - 0.0	30	.5676	.00	4.03
	0.1 - 2.5	2	6.5708	.41	12.73
	2.6 - 5.0	10	.3481	.00	2.01
	17.6 - 20.0	2	.1364	.06	.21
	20.1+	6	.2797	.08	4.25
	Total	164	.1590	-.35	12.73
WET	<= -10.0	22	.1424	.00	.31
	-9.9 - -7.5	14	.1326	.02	.28
	-7.4 - -5.0	132	.1703	-.15	.91
	-4.9 - -2.5	59	.3259	-.12	1.84
	-2.4 - 0.0	40	1.3722	.10	4.91
	0.1 - 2.5	27	4.0057	.17	14.97
	2.6 - 5.0	17	2.6400	-.02	11.38
	17.6 - 20.0	7	1.5627	.52	5.12
	20.1+	9	8.5553	1.67	34.78
	Total	327	.2824	-.15	34.78
Total	<= -10.0	32	.0982	-.02	.31
	-9.9 - -7.5	22	.1326	.02	.28
	-7.4 - -5.0	203	.1460	-.35	1.71
	-4.9 - -2.5	220	.0229	-.23	1.84
	-2.4 - 0.0	96	.4472	-.07	4.91
	0.1 - 2.5	35	2.6788	.00	14.97
	2.6 - 5.0	91	.0220	-.07	11.38
	17.6 - 20.0	12	.9605	-.02	5.12
	20.1+	24	.2797	-.04	34.78
	Total	735	.0884	-.35	34.78

Table B 5. Scoring template (Rochette and Eriksen-Hamel 2008) for non-flow-through, non-steady-state chamber design and deployment with evaluation of SCFT methods.

	Chamber characteristics		Unit	Very poor (0)	Poor (1)	Good (2)	Very good (3)	SCFT Score	Perfect Score	SCFT/Perfect Score (%)
				Binary and Non-numerical Characteristics						
1	Type of chamber				push-in		base and chamber	3	3	100
2	Insulation				no		yes	1	3	33
3	Vent				no		yes	3	3	100
4	Pressurized sample (fixed-volume container only)				no		yes	1	3	33
5	Quality control sample			no			yes	0	3	0
6	Time zero sample taken				no		yes	1	3	33
7	Non-linear model considered			no			yes	0	3	0
8	Zero slope tested				no	yes		1	2	50
9	Temperature corrections				no		yes	3	3	100
10	Type of sample vial			plastic syringe	glass syringe	all other vials	exetainers, vacutainers, Al tubes, gas chromatography in the field, photoacoustic	2	3	67
				Numerical Characteristics						
11	Height of chamber		$cm\ h^{-1}$	<10	10 to <20	20 to <40	≥40	1	3	33
12	Chamber base insertion		$cm\ h^{-1}$	<5	5 to <8	8 to <12	≥12	3	3	100
13	Area:perimeter ratio		cm	<2.5	2.6 to <6.25	6.26 to <10	≥10	1	3	33
14	Duration of deployment		min	>60	>40 to 60	>20 to 40	≤20	0	3	0
15	Number of samples		no.	1	2	3	>3	0	3	0
16	Duration of sample storage	Plastic syringe	d	>2	1 to 2	<1		3	3	100
		Glass syringe	d	>4	>2 to 4	1 to 2	<1			
		Other	d	>90	>45 to 90	>15 to 45	≤15			
				Total Score				23	47	49

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