Temperature sensitivity of N_2O emissions from fertilized agricultural soils: Mathematical modeling in ecosys

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Received 28 May 2008; revised 23 July 2008; accepted 10 September 2008; published 23 December 2008.

[1] N_2O emissions have been found to be highly sensitive to soil temperature (T_s) which may cause substantial rises in emissions with rises in T_s expected in most climate change scenarios. Mathematical models used to project changes in emissions during climate change should be able to simulate the physical and biological processes by which this sensitivity is determined. We show that the large rises in N_2O emissions with short-term rises in T_s ($Q_{10} > 5$) found in controlled temperature studies can be modeled from established Arrhenius functions for rates of microbial C and N oxidation ($Q_{10} \sim 2$) when combined with T_s effects on gaseous solubilities and diffusivities and with water effects on gaseous diffusivities, interphase gas transfer coefficients, and diffusion path lengths. Rises in N_2O emissions modeled with a long-term rise in T_s during a climate warming scenario were smaller than expected from short-term rises in T_s. Nonetheless, annual N_2O emissions rose by ~30% during three growing seasons in a cool humid maize-soybean rotation under a climate change scenario in which atmospheric CO_2 concentration C_a was raised by 50%, air temperature T_a by 3°C, and precipitation events by 5%. These model results indicate that climate warming may cause substantial rises in N_2O emissions from fertilized agricultural fields in cool, humid climates.

Citation: Grant, R. F., and E. Pattey (2008), Temperature sensitivity of N_2O emissions from fertilized agricultural soils: Mathematical modeling in ecosys, *Global Biogeochem. Cycles*, *22*, GB4019, doi:10.1029/2008GB003273.

1. Introduction

[2] The complexity of biological and physical controls on microbial processes that generate N_2O in soils has caused uncertainty in estimating N_2O emissions from agriculture as part of national greenhouse gas (GHG) inventories. This uncertainty is thought to be about ±70–80% of emissions calculated with the IPCC Tier 1 emission factor for direct effects of soil N amendments [*Lim et al.*, 1999]. Much of this uncertainty is attributed to variability in N_2O emissions caused by climate, soil and landscape properties that determine the length of time that soil water contents remain higher than a threshold value (~0.6 of WFPS) above which N_2O is generated. Thus N_2O emission factors have been found to rise with rainfall [*Lu et al.*, 2006], poor soil drainage [*de Klein et al.*, 2003] that may be caused by high clay content [*Bouwman et al.*, 2002a], and with lower topographic position [*Corre et al.*, 1999].

[3] Consequently more site-specific N_2O emission factors are needed for GHG inventories that account for variability caused by climate, soil and topography. This need has been addressed by deriving empirical relationships between emissions and site conditions in meta-analyses of N_2O flux measurements. *Bouwman et al.* [2002b] found that N_2O emissions from arable land would rise with N fertilizer rate, soil clay and organic C contents, poor drainage, and warm climate (subtropical versus temperate). *Lu et al.* [2006] found that emission from arable land increased significantly with annual precipitation (after accounting for N fertilizer rate), but was not significantly related to soil properties or air temperature (T_a). However, *Roelandt et al.* [2005] found a strong correlation between N_2O emissions and spring T_a for agricultural soils. *Flechard et al.* [2007] calculated that N_2O emission factors in grasslands would increase with WFPS, soil temperature (T_s) and cumulative precipitation. *Novoa and Tejeda* [2006] included temperature terms in empirical calculations of emission factors for N amendments.

[4] Some of the climatological conditions most closely related to N_2O emissions, such as T_s and precipitation, are likely to change during the next century as atmospheric CO_2 concentrations (C_a) rise. However, the impacts of these changes on the biological processes that drive N_2O emissions are not fully understood. In a meta-analysis of published research, *Barnard et al.* [2005] found that elevated C_a by itself had no significant effect on N_2O emissions, likely because elevated C_a decreased NO_3^- concentrations and thereby slowed denitrification. However, other researchers have found that elevated C_a may increase N_2O emissions by raising WFPS through reduced transpiration [*Arnone and Bohlen*, 1998; *Baggs et al.*, 2003], and by raising litterfall through increased primary productivity (NPP) if N is adequate [*Baggs et al.*, 2003; *Kettunen et al.*, 2006].

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0886-6236/08/2008GB003273

[5] Attempts to measure the direct effect of elevated T_a on N_2O emissions through soil warming studies have not given clear results. *Barnard et al.* [2005] found that soil warming did not have large direct effects on N_2O emissions in the field, although this finding appeared to be based on results from forest sites where emissions were constrained by low mineral N. Warming effects on N_2O emissions in agricultural fields may be offset by lower WFPS caused by accelerated soil drying [*Kamp et al.*, 1998]. Warming has raised emissions substantially in laboratory studies when WFPS was controlled [*Dobbie and Smith*, 2001; *Goodroad and Keeney*, 1984], and in short-term field studies when WFPS and mineral N were not limiting [*Clayton et al.*, 1997; *Phillips et al.*, 2007]. Under these conditions, activation energies and apparent Q_{10} values describing the temperature response of N_2O emissions [e.g., *Breuer and Butterbach-Bahl*, 2005; *Schindlbacher et al.*, 2004; *Smith et al.*, 1998] may become larger than those usually attributed to microbial activity, suggesting that nonbiological processes may be influencing this response. The strong interaction between WFPS and T_s causes a synergistic effect of rainfall and T_s on N_2O fluxes [*Jones et al.*, 2007], suggesting that rising precipitation and temperature expected under many climate change scenarios may have an unexpectedly large effect on N_2O emissions from fertilized ecosystems.

[6] The complexity of interactions among WFPS, T_s and mineral N on N_2O emissions has caused regression models of these emissions to be of little predictive value [*Clayton et al.*, 1997]. Consequently, process models have found frequent use as an alternative to IPCC methodology in predicting N_2O emissions [e.g., *Del Grosso et al.*, 2005; *Li et al.*, 2001]. These models usually simulate N_2O emissions as substrate-driven, T_s-dependent functions of nitrification and denitrification rates, modified by texture-dependent functions of WFPS [e.g., *Li et al.*, 2005]. These WFPS functions are independent of T_s, so that an interaction between T_s and WFPS is not explicitly simulated. In some models additional empirical temperature functions are used to calculate the fraction of nitrification that generates N_2O and the fraction of denitrification product that is released as N_2O versus N_2 [e.g., *Chatskikh et al.*, 2005]. However, T_s has also been found strongly to affect the response of denitrification to WFPS in experimental studies, likely through the effect of T_s on demand versus supply of O_2 at microbial microsites [*Craswell*, 1978]. Therefore a model used to predict N_2O emission under warming climates needs to account for the strong interaction between T_s and WFPS on all the processes that generate N_2O.

[7] This interaction has been modeled through the combined effects of T_s and WFPS on the physical transfer versus microbial reduction of O_2, and thereby on microbial reduction of alternative electron acceptors [*Grant*, 1991; *Grant and Pattey*, 1999, 2003; *Grant et al.*, 1993a, 1993b; 2006] as part of the ecosys modeling program [*Grant*, 2001]. These combined effects are proposed to explain the large sensitivity of N_2O emissions to T_s found in experimental studies [e.g., *Dobbie and Smith*, 2001] while using realistic parameters for temperature sensitivity functions of microbial activity. The model is then used to assess the implications of this sensitivity for N_2O emissions from a fertilized agricultural field under a climate warming scenario.

2. Model Development: General Overview

[8] The hypotheses that govern N_2O transformations in ecosys are described by *Grant and Pattey* [2003] and *Grant et al.* [2006]. These hypotheses are further described in sections S1–S7 of Text S1, with particular reference to their temperature sensitivities.[1] The hypotheses that directly govern N_2O transformations and emissions are represented conceptually in Figure 1 with reference to sections S1–S7 in Text S1. All parameter values used in sections S1–S7 of Text S1 remain the same as those used in earlier simulations [*Grant and Pattey*, 1999, 2003; *Grant et al.*, 2006].

3. Model Experiments

3.1. Model Testing: Response of N_2O Emissions to Soil Warming

[9] Sensitivity of modeled N_2O emissions to T_s was tested with N_2O fluxes recorded by *Dobbie and Smith* [2001] from intact 0.07-m cores taken from an imperfectly drained gleysol under winter wheat, watered to 0.63 WFPS and incubated in a laboratory for two weeks at 5°C, 12°C and 18°C. To simulate site history prior to the experiment, ecosys was run for 10 years with the properties of the experimental soil (Table 1) under winter wheat and weather with mean annual temperature and precipitation similar to that at the experimental site. This part of the model run allowed soil microbial activity to equilibrate under conditions corresponding to those that existed at the experimental site before the soil cores were taken. Following the protocol of *Dobbie and Smith* [2001], the model run was then continued with just the upper 0.07 m of the soil profile (resolved into four layers with cumulative depths of 0.01, 0.03, 0.05, and 0.07 m) for 18 d under laboratory weather conditions (18°C, no radiation, no precipitation, 75% RH, low wind speed), and then for another 17 days at each of 5°C, 12°C and 18°C. After 3 d at these temperatures, the soil in each model run was fertilized and irrigated with the equivalent of 10 g N m^{-2} of NH_4NO_3 in 2.5 mm of water, irrigated to 0.63 WFPS (day 0), and irrigated again to 0.63 WFPS 7 days later (day 7). During the model run, all biological and physical processes were solved on time steps of 1 h and 2 min respectively. Hourly N_2O fluxes were compared with values recorded by *Dobbie and Smith* [2001] after each irrigation.

3.2. Model Predictions: Response of N_2O Emissions to Climate Change

[10] Ecosys was tested earlier against N_2O fluxes measured in 1998 and 2000 with a tunable diode laser (TDL) trace gas analyzer using a flux gradient technique following fertilizer application on a gleysol under a maize-soybean rotation at the Greenbelt Research Farm in Ottawa, ON, Canada (45°18′N, 75°44′W, mean annual temperature

[1] Auxiliary materials are available in the HTML. doi:10.1029/2008GB003273.

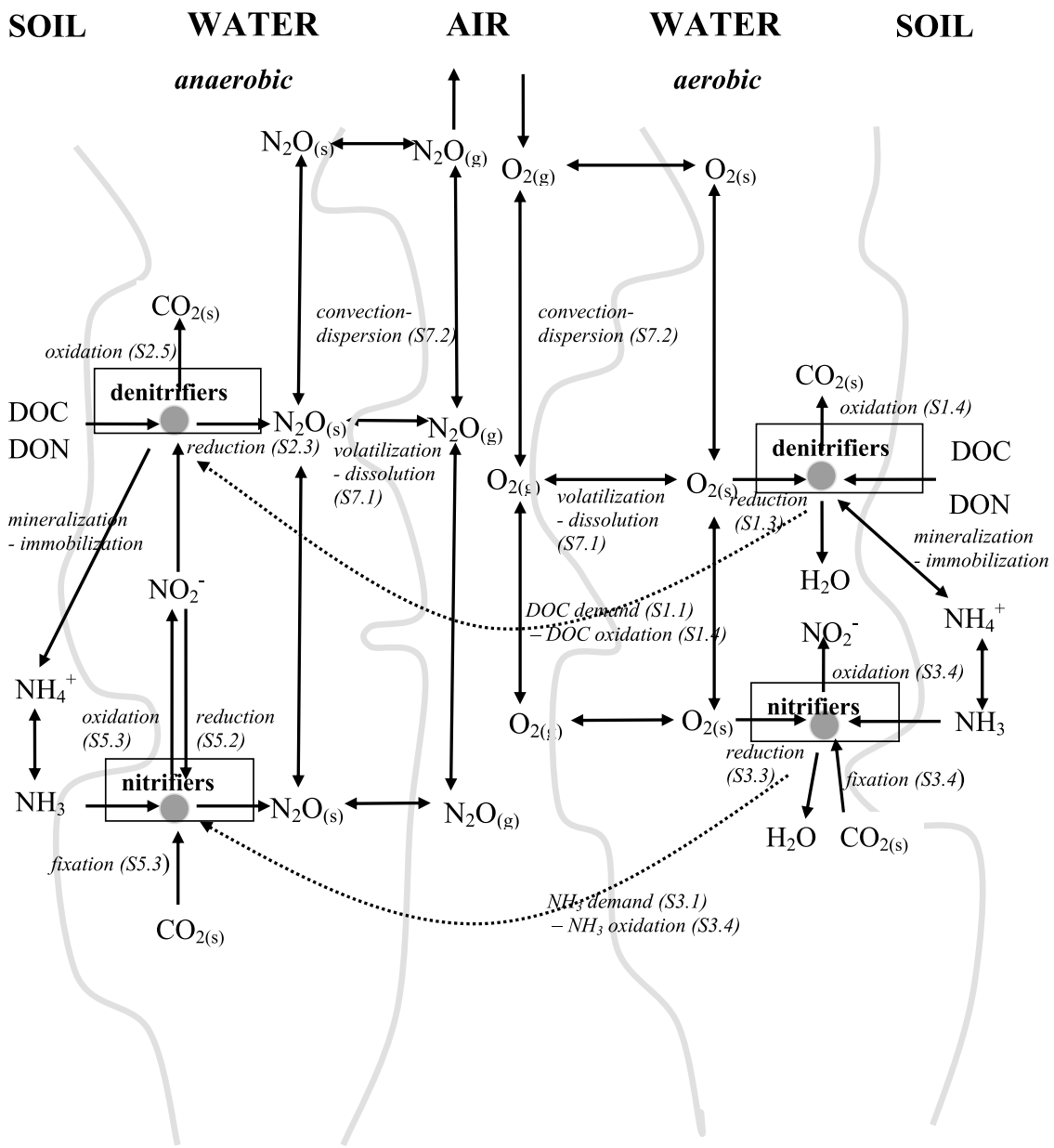

Figure 1. Diagram representing key hypotheses that govern N_2O transformations and emissions in ecosys. These hypotheses are described in the sections of Text S1 indicated by numbers in brackets.

6.0°C, mean annual precipitation 944 mm) [*Grant and Pattey*, 2003; *Grant et al.*, 2006]. Here we include an additional year of testing in 2002 in a nearby field belonging to the same Dalhousie soil series (45°17′N, 75°46′W). Additional details on the flux measuring system, field setup and flux processing is given by *Pattey et al.* [2006].

[11] Results from this testing were used as a reference for predictions of how N_2O emissions would change in years with different weather under a climate warming scenario. To simulate site history prior to prediction, ecosys was initialized with the physical properties of the soil at Ottawa [*Grant et al.*, 2006, Table 1a] and the biological properties of maize and soybean [*Grant et al.*, 2007]. The model was then run through ten cycles of a conventionally tilled and fertilized 2-year maize-soybean rotation under ambient C_a (370 μmol mol^{-1}) and repeated sequences of hourly surface boundary conditions for solar radiation, T_a, humidity, wind speed and precipitation recorded at the Greenbelt Farm during 1998 and 1999. The model run was then continued under hourly surface boundary conditions recorded from 1998 to 2002 with simulated tillage, fertilizing, planting and harvesting practices corresponding to those conducted at the field site (Table 2). A second model run was conducted under conditions identical to those of the first, except that C_a was raised by 50%, T_a by 3°C and precipitation events by 5%, thereby approximating the climate expected after 100 years of an Intergovernmental Panel on Climate Change Special Report on Emissions Scenarios Emission Scenario

Table 1. Properties of the Imperfectly Drained Gleysol Used to Test N_2O Response to Soil Warming in Ecosys[a]

Soil Property	Value
BD (Mg m^{-3})	0.98
θ_{FC} (m^3 m^{-3})[b]	0.34
θ_{WP} (m^3 m^{-3})[b]	0.16
K_{sat} (mm h^{-1})[b]	10
Sand (g kg^{-1})	500
Silt (g kg^{-1})	330
Clay (g kg^{-1})	170
pH	6.0
Organic C (g kg^{-1})	27
Organic N (g Mg^{-1})	2000

[a]From *Dobbie and Smith* [2001]. Here BD is the bulk density, θ_{FC} is the water content at −0.033 MPa, θ_{WP} is the water content at −1.50 MPa, and K_{sat} is the saturated hydraulic conductivity.
[b]Soil hydrological properties calculated from *Saxton et al.* [1986].

A2 (IPCC SRES A2) scenario [*Nakicenovic et al.*, 2000]. In addition, maize and soybean maturity requirements were raised by 2.5 phyllochron intervals [*Grant*, 1989] to offset the effect of warming on crop phenology. During both model runs, all biological and physical processes were solved on time steps of 1 h and 2 min respectively, with surface boundary conditions assumed constant during each hour. Surface N_2O fluxes modeled under the climate warming scenario were compared with those modeled and measured under current climate in 1998, 2000, and 2002.

4. Results

4.1. Model Testing: Response of N_2O Emissions to Soil Warming

[12] WFPS of the simulated soil cores reached set values of 0.63 after the first and second irrigations on days 0 and 7, and then declined with evaporation under the assumed RH of 75% to values consistent with those reported by *Dobbie and Smith* [2001] 7 days after each irrigation (Figure 2a). In the model, rises in WFPS with irrigation caused declines in gaseous diffusion coefficients (equation (S6)) and interphase gas transfer coefficients (equation (S4)), and rises in water film thicknesses (equation (S2)). These changes combined to cause sharp declines in $[O_{2s}]$ after irrigation (Figure 2b). These changes were reversed during subsequent soil drying, causing gradual rises in $[O_{2s}]$.

[13] Higher T_s raised demands for O_2 reduction (equation (S1)), lowered O_2 solubility (equation (S3)), and

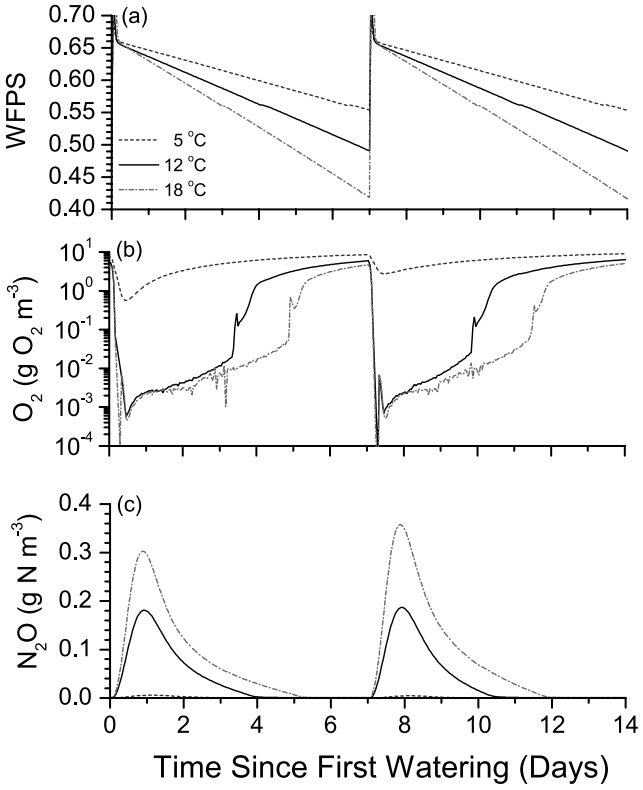

Figure 2. (a) Water-filled pore space (WFPS), (b) aqueous O_2 concentration, and (c) aqueous N_2O concentration in the 0–7 cm soil layer modeled during two 7 day watering cycles at 5, 12, and 18°C.

Table 2. Land Management Practiced at Ottawa During 1997–2002

Land Use	1997	1998	1999	2000	2001	2002
Crop	soybean	maize	soybean	maize	wheat	maize
Spring tillage						
First date		16 May	7 May	4 May	24 Apr.	17 May
First implement		cultivator	disc harrow	disc/ripper	disc/ripper	moldboard
Second date			17 and 20 May	17 May	25 April	21 May
Second implement			cultivator	disc harrow	cultivator	cultivator
Planting date	2 June	17 May	21 May	29 May	26 Apr.	22 May
First N fertilizer						
Date		16 May		29 May	26 Apr.	16 May
Amount		13.8 g urea-N m^{-2}		1.35 g NH_4^+–N m^{-2}	6.8g NH_4NO_3–N m^{-2}	13.8 g urea-N m^{-2}
Method		broadcast incorporated		banded	broadcast incorporated	broadcast incorporated
Second N fertilizer						
Date		17 May		5 Jul.		22 May
Amount		1.65 g urea-N m^{-2}		15.7 g NH_3–N m^{-2}		1.35 g $NH4^+$–N m^{-2}
Method		banded		injected		banded
Harvest date	21 Oct.	13 Oct.	7 Oct.	6 Nov.	22 Aug.	31 Oct.
Fall tillage						
Date		20 Nov.				
Implement		moldboard				

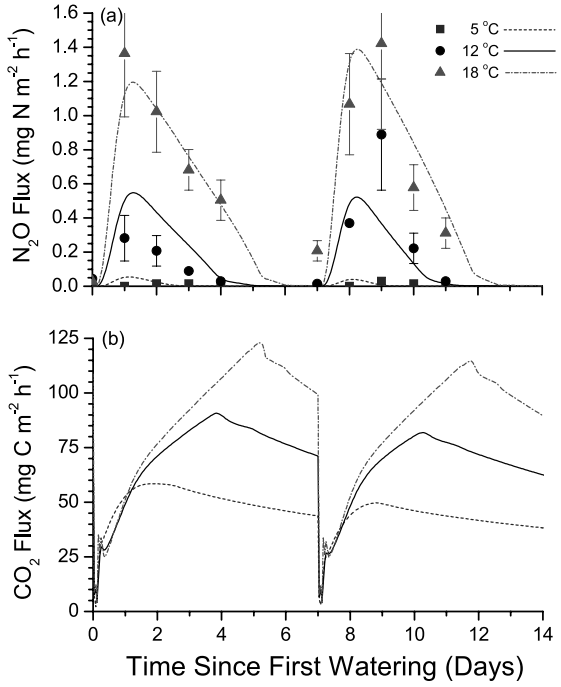

Figure 3. Fluxes of (a) N_2O and (b) CO_2 measured (symbols) and modeled (lines) during two 7 day watering cycles at 5, 12, and 18°C. Measured data from *Dobbie and Smith* [2001].

raised gaseous diffusivities (equation (S8)). These effects combined to cause larger and more persistent declines in $[O_{2s}]$ with higher T_s after irrigation (Figure 2b). These declines caused $[O_{2s}]$ to remain below the K_m used to calculate O_2 uptake by denitrifiers (section S1.3 in Text S1) and nitrifiers (section S3.3 Text S1) for 3 and 5 days at 12 and 18°C respectively, but to remain above these values at 5°C. Constraints imposed on O_2 reduction by low $[O_{2s}]$ caused reduction of NO_3^-, NO_2^-, and N_2O by denitrifiers (sections S2.2, S2.3, and S2.4 in Text S1), and reduction of NO_2^- by nitrifiers (section S5.2 in Text S1). Net production of N_2O by these reactions, combined with low gaseous diffusion and interphase gas transfer coefficients (equations (S6) and (S4)), raised aqueous N_2O concentrations ($[N_2O_s]$) while WFPS was high after irrigation at 12 and 18°C (Figure 2c). These rises were followed by declines in $[N_2O_s]$ caused by declining net N_2O production and rising N_2O volatilization with increasing $[O_{2s}]$ during soil drying.

Table 3. Spring Temperature and Precipitation Recorded at Ottawa During 1998, 2000, and 2002 Versus 30-Year Normal

	1998	2000	2002	30-Year Normal
		Temperature (°C)		
April	8.5	5.0	6.4	5.7
May	17.5	13.2	10.9	13.4
June	19.2	16.9	17.3	18.3
		Precipitation (mm)		
April	55	109	85	72
May	33	123	92	79
June	119	131	225	85

[14] Rises and falls in $[N_2O_s]$ drove rises and falls in N_2O emissions after irrigation that were consistent with those measured by *Dobbie and Smith* [2001] (Figure 3a). Their measured emissions rose by a factor of 16 with warming from 5 to 12°C (apparent Q_{10} of 50), and by a factor of almost 4 with warming from 12 to 18°C (apparent Q_{10} of 9). Total N_2O emissions modeled over 14 d rose from 3 mg N m^{-2} at 5°C to 52 mg N m^{-2} at 12°C and 175 mg N m^{-2} at 18°C. This sharp response of emissions to higher T_s was achieved in spite of more rapid soil drying by using an independently parameterized temperature function with a Q_{10} of ~2 over the temperature range of the experiment (equation (S1)). This smaller Q_{10} was indicated by the relatively smaller rises in CO_2 emissions with T_s (Figure 3b) which were driven by the oxidation reactions (sections S1.4, S2.5, S3.4, and S5.3) by which N_2O production was generated.

4.2. Model Predictions: Response of N_2O Emissions to Climate Change

[15] Weather during spring 1998 was drier than normal (Table 3), causing low WFPS at the time of fertilizer application. Frequent rainfall during early to mid-June 1998 (Figure 4a) caused soil wetting after DOY 160 (Figure 4b), followed by soil warming after DOY 170

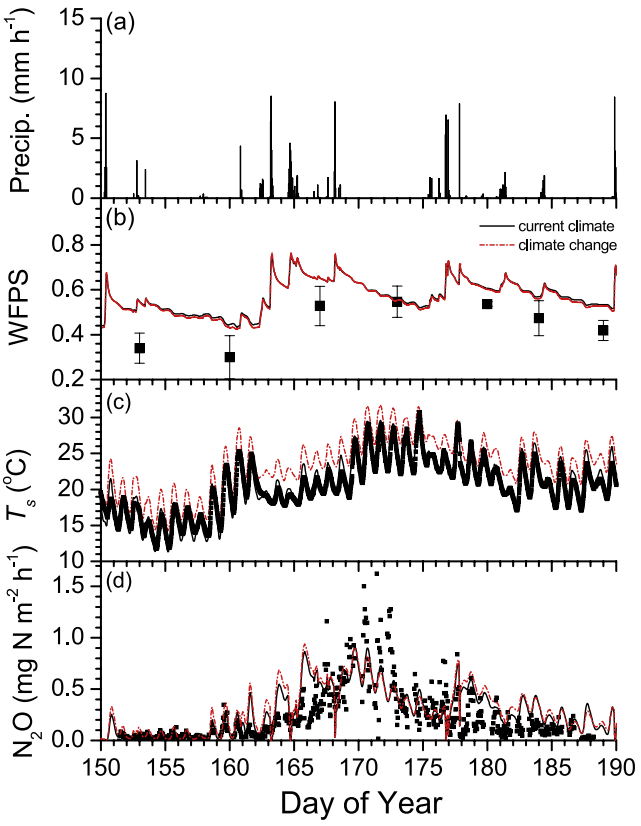

Figure 4. (a) Precipitation, (b) soil water-filled pore space WFPS (0.1 m), (c) soil temperatures T_s (0.1 m), and (d) N_2O fluxes measured (symbols) and modeled (lines) at Ottawa, Ontario, during 1998 under current climate and climate change (see text). Measured N_2O flux from *Grant and Pattey* [2003].

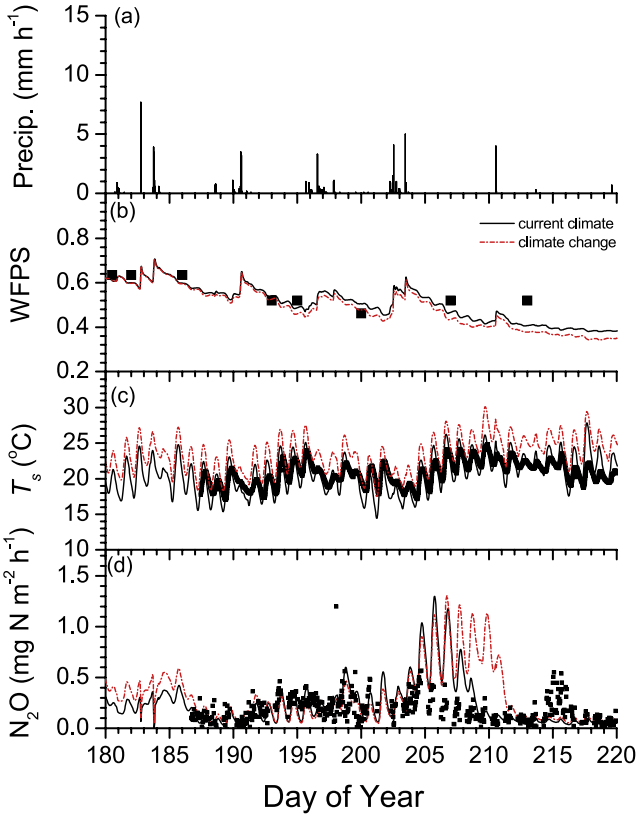

Figure 5. (a) Precipitation, (b) soil water-filled pore space WFPS (0.1 m), (c) soil temperatures T_s (0.1 m), and (d) N_2O fluxes measured (symbols) and modeled (lines) at Ottawa, Ontario, during 2000 under current climate and climate change (see text). Measured N_2O fluxes from *Grant et al.* [2006].

(Figure 4c). In the climate change scenario, the effect on WFPS of the 3°C rise in T_a through more rapid evaporation was mostly offset by the effect on WFPS of the 5% rise in precipitation through greater water inputs, and by that of the 50% rise in C_a through slower transpiration [*Grant et al.*, 2001, 2004]. Consequently WFPS was only slightly lowered by climate change (Figure 4b). The effect on T_s of higher T_a through larger soil heat fluxes was partially offset by that of larger crop LAI and surface residue through lower soil net radiation, so that T_s at 0.10 m was raised by only 1–3°C (Figure 4c).

[16] Addition of urea on DOY 135 (Table 2) was followed in the model by hydrolysis to NH_4^+ and then nitrification to NO_2^- (section S.3 in Text S1) and NO_3^- (section S.4 in Text S1). Under current climate, nitrification occurred in comparatively dry soil (WFPS < 0.6) before DOY 160, during which modeled and measured N_2O emissions remained small (Figure 4d). Nitrification continued during soil wetting (WFPS > 0.6) after DOY 160 and warming (T_s > 25°C) after DOY 170 which caused modeled and measured N_2O fluxes to rise (section S5.2 in Text S1). Diurnal variation in T_s (Figure 4c) caused large diurnal variation in both modeled and measured N_2O emissions during nitrification. Cooling soil, slowing nitrification and accelerating plant N uptake (section S6.5 in Text S1) after DOY 175 caused modeled and measured N_2O fluxes to decline, even while rainfall kept WFPS high (Figure 4b). Higher T_s modeled under climate change raised N_2O emissions modeled during this period only slightly (Figure 4d). Total N_2O emissions modeled from DOY 147 to DOY 188 (27 May to 6 July) 1998 were 269 mg N m^{-2} under current climate and 300 mg N m^{-2} under climate change, versus 218 mg N m^{-2} calculated from aggregating N_2O fluxes measured during the same period under current climate [*Grant and Pattey*, 2003].

[17] The spring of 2000 was cooler and wetter than that of 1998 (Table 3). The soil remained moist (WFPS > 0.6) and temperate ($T_s \sim 20$°C) during most of July 2000 (Figures 5b and 5c). As in 1998, climate change lowered WFPS slightly but raised T_s by 2–3°C. Soil conditions allowed rapid nitrification under both climate scenarios after NH_3 application on DOY 186 (Table 2). Soil wetting on DOY 191 and 203 (Figure 5b), followed by several days of soil warming, caused modeled and measured N_2O emissions to rise until DOY 206 (Figure 5d), but soil drying and slowing nitrification reduced emissions thereafter. As in 1998, diurnal variation in T_s (Figure 5c) drove large diurnal variation in N_2O emissions as long as nitrification continued. N_2O emission events modeled under climate change coincided with those under current climate, but fluxes rose sharply with soil warming from DOY 207 to 211 (Figure 5d). Total N_2O emissions modeled from DOY 187 to 241 (6 July to 29 August) 2000 were 209 mg N m^{-2} under current climate and 264 mg N m^{-2} under climate change, versus 170 mg N m^{-2} calculated from aggregating N_2O fluxes measured during the same period under current climate [*Grant et al.*, 2006].

[18] Rainfall during June 2002 was almost 3 times normal (Table 3) with several large rainfall events (Figure 6a) which caused WFPS to remain above 0.6 until early July (Figure 6b). Wet soils caused several N_2O emission events in the model (Figure 6d), prolonged by soil warming from DOY 178 to 185 (Figure 6c). N_2O emissions were measured consistently during most of June and early July, although values were often smaller than those modeled. Warmer soil modeled under climate change (Figure 6c) accelerated nitrification and raised N_2O emissions (Figure 6d). Total N_2O emissions modeled from DOY 147 to 238 (27 May to 26 August) 2002 were 536 mg N m^{-2} under current climate and 683 mg N m^{-2} under climate change, versus 370 mg N m^{-2} calculated from aggregating N_2O fluxes measured during the same period under current climate.

[19] Longer-term model results indicated that yearly averaged N_2O emissions from the maize phase of the maize-soybean rotation at Ottawa rose 30% from 476 mg N m^{-2} a^{-1} (where a is years) after 20 years under current climate (1997–2002) to 628 mg N m^{-2} a^{-1} after 20 years under climate change, assuming no change in land use practices (Table 4).

4.3. Uncertainty in Modeled and Measured N_2O Fluxes

[20] Regressions of measured on modeled hourly averaged fluxes gave highly significant correlation coefficients in all 3 years of comparison (R^2 = 0.2–0.4, P < 0.0001). These coefficients were similar to those from stepwise

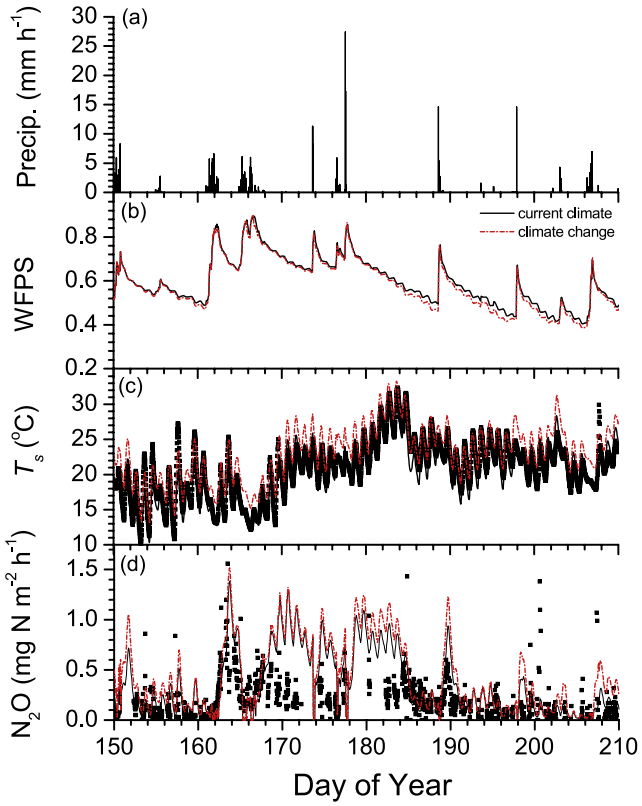

Figure 6. (a) Precipitation, (b) soil water-filled pore space WFPS (0.1 m), (c) soil temperatures T_s (0.1 m), and (d) N_2O fluxes measured (symbols) and modeled (lines) at 0.1 m at Ottawa, Ontario, during 2002 under current climate and climate change (see text).

multiple regressions of daily N_2O fluxes fitted to site data for T_a, T_s, and *WFPS* in other studies [e.g., *Kanerva et al.*, 2007; *Reth et al.*, 2005], indicating that ecosys had predictive power comparable to that of fitted statistical models while using generally applicable parameters. Much of the variation in measured fluxes not explained by the model might be attributed to measurement uncertainty, estimated to be 25% of daytime and 60% of nighttime N_2O hourly flux measurements using tunable diode lasers with the flux gradient technique [*Laville et al.*, 1999; *Phillips et al.*, 2007]. Much of this uncertainty might be attributed to spatial variability in N_2O fluxes, which may be 30 to 200% at a meter scale, caused by short-term changes in fetch areas arising from changes in wind speeds and directions during measurement [*Laville et al.*, 1999]. However, the extent to which these measurement uncertainties apply to the site at Ottawa is not known. This uncertainty, expressed in terms of the measured fluxes, was comparable to differences in modeled versus measured fluxes, expressed as root mean squares for differences (RMSD) from regressions of measured on modeled values. These RMSDs were 0.20, 0.10, and 0.20 mg N m^{-2} h^{-1} in 1998 (n = 741), 2000 (n = 374), and 2002 (n = 792) respectively, or about one-third of average fluxes measured during emission events (Figures 4–6). Further constraint in model testing will require that uncertainty in the measured values be reduced.

[21] Some uncertainty in modeled fluxes was attributed to uncertainty in model inputs and parameters. Soil bulk density (BD) is an input to which the model was found to be sensitive because BD determines air-filled porosity and hence soil gas fluxes. Raising or lowering BD by 5% from its measured value of 1.28 Mg m^{-3} raised or lowered average annual N_2O emissions in the model by 23 or 17% respectively (Table 4). Such changes are consistent with experimental observations of soil compaction effects on N_2O emissions [*Ruser et al.*, 1998]. This sensitivity indicates the importance of accurately measuring or estimating key soil properties that determine soil air- and water-filled porosities such as BD, field capacity and wilting point when using models to estimate N_2O emissions. Small spatial variation in these properties likely contribute to the large spatial variation in N_2O fluxes typically measured in the field. N_2O emissions have also been found to rise with SOC [*Bouwman et al.*, 2002a], but model values remained insensitive to increases or decreases of 5% of measured values (Table 4), considered to be the likely precision of SOC measurements. This was because O_2 demand in the model was driven mostly by autotrophic and heterotrophic respiration of current root reserves and litterfall, rather than by total SOC.

[22] The construction cost of denitrifier biomass (sections S1.4 and S2.5 in Text S1) is a key model parameter affecting N_2O emissions because it determines denitrifier biomass growth and hence denitrifier activity, but has not been derived independently of the model. The value of 25 kJ g^{-1} C used in the model for obligate aerobes was derived from the known energy yield of C oxidation and O_2 reduction to give a maximum short-term growth yield of 0.6 (discounting maintenance respiration), consistent with ex-

Table 4. Annual N_2O emissions modeled during 1998, 2000, and 2002[a]

	1998	2000	2002
	Climate[b]		
Current climate	471	383	573
Climate change	576	563	745
	Inputs[c]		
BD +5%	580	524	659
BD −5%	375	266	543
SOC-N +10%	474	391	574
SOC-N −10%	467	382	569
	Parameters[d]		
CCD +10%	432	350	510
CCD −10%	592	468	797
CNN +10%	562	443	677
CNN −10%	383	323	523

[a]All values given in mg N m^{-2} a^{-1}.
[b]Modeled under current climate and climate change (IPCC SRES A2; see text [*Nakicenovic et al.*, 2000]).
[c]Modeled under current climate with soil bulk density (BD) or soil organic carbon-nitrogen (SOC-N) raised or lowered from measured value by 5% and 10%, respectively.
[d]Modeled with construction costs of denitrifier biomass (CCD) or ratio of CO_2 fixation versus NH_3 oxidation by nitrifiers (CNN) raised or lowered from model value by 10%.

perimental observations [e.g., *Shields et al.*, 1973]. This value was raised by 15% to 28.75 kJ g^{-1} C for facultative anaerobes to give the slightly lower aerobic growth yields of denitrifiers observed by *Koike and Hattori* [1975]. Raising or lowering the denitrifier construction cost by 10% lowered or raised annual N_2O emissions in the model by 10% or 30%, respectively (Table 4). The lower denitrifier construction cost is likely unrealistic because there would then be little advantage to obligate aerobes under aerobic conditions. The higher cost could be realistic, although it would give denitrifier aerobic growth yields slightly lower than those measured. The CO_2 uptake yield from NH_3 oxidation by autotrophic nitrifiers (sections S3.5 and S5.3 in Text S1) is another key model parameter because it determines nitrifier growth and hence activity. The yield used in the model was taken from *Belser* [1984], who derived a standard error of nearly 10% of the measured value. Raising or lowering the yield by 10% in the model raised or lowered average annual N_2O emissions by 18% and 14% respectively.

[23] The model is thus sensitive to variation in some inputs and parameters which may be smaller than the precision with which they can be measured. These sensitivities cause uncertainty of perhaps 20% in modeled N_2O fluxes, which is comparable to that in the measured values, and limit the precision with which N_2O fluxes can be estimated for site-specific conditions. However, once determined, the model parameters are unlikely to change with land use and climate, and so the model may provide robust estimates of changes in N_2O emissions under hypothesized environmental changes.

5. Discussion

[24] The large sensitivity of N_2O emissions to short-term changes in T_s measured by *Dobbie and Smith* [2001] (Figure 2a) was modeled from the combined effects of WFPS on water film thickness (equation (S2)), interphase gas transfer coefficients (equation (S4)), and gaseous diffusion coefficients (equation (S6)), together with the combined effects of T_s on O_2 reduction (equation (S1)), O_2 solubility (equation (S3)), and O_2 diffusivity (equation (S8)). These effects allowed the apparent Q_{10} of 8–50 for N_2O emissions measured by *Dobbie and Smith* [2001] to be modeled from realistic parameters in the Arrhenius temperature function used for all microbial processes in the model, including those from which N_2O was generated and consumed (equation (S1)).

[25] This large sensitivity of N_2O emissions to T_s is consistent with other findings under controlled laboratory conditions. *Goodroad and Keeney* [1984] found that N_2O emissions increased rapidly with T_s ($Q_{10} > 4$) at higher WFPS ($\theta_w = 0.3$ m^3 m^{-3}), but less rapidly ($Q_{10} < 4$) at lower WFPS ($\theta_w = 0.1$ or 0.2 m^3 m^{-3}). The model algorithms cause sensitivity of N_2O emissions to WFPS to rise with T_s [*Grant*, 1991]. Such rises were found experimentally by *Craswell* [1978] who observed that denitrification rates rose with WFPS 4–6 times more rapidly at 30°C than at 20°C, and did not rise at all with WFPS at 10°C.

[26] The sensitivity of N_2O emissions to T_s in the field is more difficult to evaluate because of confounding effects of WFPS. Field measurements at hourly to daily timescales, during which change in WFPS would be small, have given Q_{10} values of 6–12 from a cut grassland [*Smith et al.*, 1998] and 3.7 from a maize-soybean rotation [*Parkin and Kaspar*, 2006]. These responses to short-term warming suggest that an increase in T_a of 3°C under long-term climate change might raise N_2O emissions by 50–100%. However, N_2O emissions modeled after 20 years under higher T_s often rose much less (Figures 4d, 5d, and 6d and Table 4), even though higher C_a increased net primary productivity (NPP) and hence litterfall [*Grant et al.*, 2004]. More litterfall in the model drove more rapid DOC oxidation (section S1.1 in Text S1) and hence greater demand for O_2 reduction (section S1.2 in Text S1) without a concomitant rise in O_2 supply (section S1.3 in Text S1), raising demands for NO_3^- and NO_2^- reduction (sections S2.1 and S2.2 in Text S1) and hence contributing to increases in N_2O production (section S2.3 in Text S1). Such increases in N_2O emission with C_a have been found experimentally under high N by *Baggs et al.* [2003] and *Kettunen et al.* [2006]. Elevated C_a also raised N_2O emissions by slowing transpiration [*Grant et al.*, 2004] and thereby raising WFPS [*Arnone and Bohlen*, 1998; *Baggs et al.*, 2003], but in this study the effect on WFPS of elevated C_a was offset by that of elevated T_a (Figures 4b, 5b, and 6b).

[27] The comparatively smaller rises in N_2O emissions modeled under long-term climate change versus short-term warming were attributed in the model to gradual declines in SOC and microbial biomasses, including nitrifiers and denitrifiers, from those modeled under current climate. These declines were caused by more rapid SOC turnover and microbial respiration with long-term soil warming. Thus while soil warming raised specific microbial respiration (equation (S1)), it raised total microbial respiration progressively less as the model run continued. Higher T_s has been found to reduce microbial biomass in soil warming experiments [e.g., *Arnold et al.*, 1999], which may partly explain the declining response over time of soil respiration to higher T_s found in long-term soil warming experiments [*Rustad et al.*, 2001].

[28] However soil warming experiments are of limited utility in evaluating the response of N_2O emissions to long-term rises in T_s because the response is offset by concurrent soil drying [*Kamp et al.*, 1998]. Alternatively, meta-analyses of field experiments under a range of climates have been used to infer rises in annual N_2O emissions with longer-term soil warming which are comparable to those modeled here. *Roelandt et al.* [2005] calculated a partial regression coefficient for annual N_2O flux on mean annual T_a of 75 mg N m^{-2} a^{-1} $°C^{-1}$ (cf. Table 4). Similarly *Bouwman et al.* [2002b] estimated that annual N_2O emissions from fertilized fields in tropical climates would be 2.3 times greater than those in temperate climates where mean annual T_a is about 10°C lower, all other factors affecting emissions being equal. This increase in emissions corresponds to one of 28% for a rise in mean annual T_a of 3°C (cf. Table 4). Similar rises in N_2O emissions with climate change have been predicted by other models [e.g., *Hsieh et al.*, 2005]. Collectively these results indicate that N_2O emissions from fertilized agricultural fields could rise by approximately

30% after 100 years under the IPCC SRES A2 climate scenario [*Nakicenovic et al.*, 2000].

6. Conclusions

[29] Model results suggest that climate change may cause substantial rises in annual N_2O emissions from fertilized agricultural fields during the next century. These rises will be smaller than those inferred from short-term warming experiments, but may nonetheless be as much as 30%. The rises modeled here are subject to two key conditions: (1) the decline in WFPS caused by elevated T_a will be largely offset by the rise in WFPS caused by elevated C_a and precipitation (Figure 4b, 5b, and 6b) and (2) NPP and litterfall will rise with T_a, C_a and precipitation to drive more rapid oxidation in soils than would be driven by a rise in T_s alone. Both these conditions seem likely to exist in cool, humid climates, suggesting that future N_2O emissions from fertilized agricultural fields in such climates may become substantially higher in the future unless land use practices are changed.

[30] **Acknowledgments.** The research at Ottawa was conducted with the support of CCFIA and Agriculture and Agri-Food Canada's PERD program. We gratefully acknowledge the assistance of Dave Dow for the tower-based N_2O flux measurements. Ecosys was run on computer facilities provided through the Westgrid computing network.

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