

The effect of future climate perturbations on N₂O emissions from a fertilized humid grassland

Cheng-I Hsieh¹, Paul Leahy^{2,*}, Ger Kiely² and Changsheng Li³

¹Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei 10673, Taiwan; ²Department of Civil and Environmental Engineering, University College Cork, Cork, Ireland; ³Complex Systems Research Center, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824, USA; *Author for correspondence (e-mail: paul.leahy@ucc.ie)

Received 25 January 2005; accepted in revised form 2 May 2005

Key words: Climate change, DNDC model, Emission factor, Nitrogen fertilizer, Nitrous oxide

Abstract

N₂O emissions from a fertilized humid grassland near Cork, Ireland were continuously measured during 2003 using an eddy covariance system. For most of the year emissions were close to zero and 60% of the emissions occurred in eight major events of 2–20 days' duration. Two hundred and seven kg ha⁻¹ of synthetic N and 130 kg ha⁻¹ organic N were applied over the year and the total measured annual N₂O emission was 11.6 kg N ha⁻¹. The flux data were used to test the prediction of N₂O emissions by the DNDC (DeNitrification – DeComposition) model. The model predicted total emissions of 15.4 kg N ha⁻¹, 32 % more than the observed emissions. On this basis the model was further used to simulate (a) background (non-anthropogenic) N₂O emissions and (b) the effect on N₂O emissions of future climate perturbations based on the Hadley Center model output of the IS92a scenario for Ireland. DNDC predicts 1.7 kg N ha⁻¹ year⁻¹ of background N₂O emissions, accounting for 15% of the observed emissions. Climate shifts will increase total annual modeled N₂O emissions from 15.4 kg N ha⁻¹ to 22.4 kg N ha⁻¹ if current levels of N applications are maintained, or to 21.2 kg N ha⁻¹ if synthetic N applications are reduced to 170 kg N ha⁻¹ to comply with recent EU water quality legislation. Thus the projected increase in N₂O emissions due to climate change is far larger than the decrease expected from reduced fertilizer applications.

Introduction

Nitrous oxide (N₂O) is a potent greenhouse gas due to its high radiative forcing which is 296 times that of CO₂ over a 100-year time horizon (IPCC 2001) and its long atmospheric lifetime of approximately 120 years (Prather 1998). The concentration of N₂O in the atmosphere has risen from a pre-industrial level of about 270 ppb to its current level of 314 ppb and is estimated to be rising at a rate of 0.8 ppb per

annum (Prinn et al. 2000). N₂O is estimated to be responsible for 6% of the anthropogenic component of radiative forcing (IPCC 2001). Agricultural soils are a major source, responsible for an estimated 69% of anthropogenic N₂O emissions from Ireland in 2000 (UNFCCC 2004).

N₂O is emitted from soils as a result of the processes of denitrification and nitrification. Denitrification is a series of bacterially mediated reductions of nitrates (NO₃⁻) to: nitrites (NO₂⁻),

nitric oxide (NO), N₂O and ultimately molecular nitrogen (N₂). Denitrification in soils takes place under anaerobic conditions when the denitrifying bacteria use NO₃⁻ and NO₂⁻ instead of oxygen as electron acceptors. Moderately anaerobic conditions produce the highest emissions of N₂O as the denitrifying reactions do not fully proceed to complete the final step of reducing N₂O to N₂ (Smith et al. 2003). Denitrification is strongly dependent on temperature, especially within the range of 10–35 °C (Whitehead 1995, p. 186). Denitrification in acid soils produces a higher proportion of N₂O than in neutral or alkaline soils. Dobbie et al. (1999) identified denitrification as the dominant N₂O-producing process in fertilized Scottish grassland soils. Nitrification, the aerobic bacterial oxidation of ammonium (NH₄⁺) to NO, NO₂⁻ and eventually NO₃⁻, may produce N₂O as an intermediate product. Nitrification is also dependent on soil moisture content and soil temperature and is inhibited under dry soil conditions and with soil temperatures below 5 °C (Maag and Vinther 1996; Smith et al. 2003). Applications of synthetic and organic fertilizers to soil increase N₂O production by increasing the NH₄⁺ and NO₃⁻ concentrations.

The purpose of this study is to model N₂O emissions at the ecosystem scale from a fertilized humid grassland near Cork, Ireland, and to estimate the effect of future climate perturbations on N₂O emissions. Since climate affects various soil biogeochemical processes through altering the soil temperature and moisture regimes, we expect changes in climate will affect N₂O emissions. To date, modeling of N₂O emissions has been limited by the lack of long-term, continuous, supporting observations, which are necessary for model validation. For this purpose, we used an eddy-covariance system to continuously measure N₂O emissions. Measured values of meteorological parameters and land management records were used as input variables to the DNDC (DeNitrification-DeComposition) soil nitrogen process model (Li et al. 1992a, b; Li 2000). Firstly, the N₂O emissions predicted by the model were compared with the measured N₂O emissions, and then the model was employed to estimate the background (non-fertilizer derived) N₂O emission as well as emissions under the IS92a climate change scenario, based on the standard Hadley Center model output.

Experiments and methods

Experiments

The measurement site is an intensively grazed and fertilized grassland of ~20 ha in Co. Cork in southern Ireland (Latitude: 52.14° N, Longitude: 8.66° W). The site has an average elevation of 180 m above sea level. The climate is temperate maritime. For 2003, the total rainfall was 121.0 cm and the January and July average daytime air temperatures were 5.5 and 14.3 °C, respectively.

The flux footprint was estimated based on a fetch to sensor height ratio of 100:1 combined with the probability density distribution of the wind direction (Scanlon and Kiely 2003). The footprint area is partitioned into small fields and paddocks to facilitate rotation of grazing cattle. Management practices are broadly similar across the whole footprint but the timing of fertilizer applications and grass cuttings varies from field to field. The dominant grass species is perennial ryegrass (*Lolium perenne*).

In 2003 the site received applications of 207 kg synthetic N ha⁻¹ (mainly as NH₄NO₃) and 130 kg organic N ha⁻¹ (as farmyard slurry). Applications were made to different paddocks at different times. For modeling purposes, all applications were area-weighted and averaged over the area of the entire site. The site was grazed by dairy and beef cattle at a density of 2.2 head ha⁻¹ between March and October. Cattle were kept indoors for the remainder of the year.

The eddy covariance flux measurement system consisted of a closed path tunable diode laser trace gas analyzer (TGA100, Campbell Scientific, USA) to measure N₂O concentrations and a 3-D sonic anemometer (CSAT-3, Campbell Scientific, USA) to measure wind speeds. Concentrations and wind speeds were logged at 10 Hz and flux values were calculated at 30-min intervals. The N₂O sensor intake was mounted 6 m above ground.

N₂O flux values were discarded when the mean of the vertical wind velocity was unsteady within a half-hour period. Further gaps in N₂O flux measurements were caused by instrument downtime. Gaps amounted to 21% of the total number of data points. A moving average of adjacent values was used to replace the missing measurements (Leahy et al. 2004).

Precipitation was measured using a tipping bucket rain gauge (ARG100, Environmental Measurements Ltd, UK). A net radiometer was used to measure the solar irradiance (CNR1, Kipp and Zonen, Netherlands). The initial soil moisture content was based on a measurement within a 25 m² area close to the flux tower using time domain reflectometry probes (CS615, Campbell Scientific, USA). The initial soil surface NH₄⁺ and NO₃⁻ concentrations were determined by an iterative modeling process. The model was repeatedly run using 2003 meteorological and management data. For each iteration, the final soil NH₄⁺ and NO₃⁻ concentrations from the previous model run were used as initial values until, after several iterations, the results converged. Soil bulk density, organic carbon content and pH were determined from samples taken from the top 10 cm of soil within the flux tower footprint. Soil texture and hydrological properties such as porosity and field capacity were found to be variable within the study area. The values listed in Table 1 were determined by optimization of model results and fall within the range of measured values.

Model description

The DNDC model is a rain-event driven and process-oriented model for simulating emissions of trace gases (NO, N₂O, N₂, CH₄, and NH₃) from soils (Li et al. 1992a, b; Li 2000). The model has six submodels. Three of the submodels: (soil climate, crop growth and decomposition) are driven by environmental factors (e.g., temperature, precipitation, soil, vegetation). The soil climate submodel calculates vertical profiles of soil temperature, moisture and soil redox potential driven by meteorological data and soil properties. The crop growth submodel calculates crop growth and its influence on soil environmental factors such as soil moisture, dissolved organic carbon (DOC), and available nitrogen concentrations. The decomposition submodel then generates vertical concentration profiles of substrates (e.g., DOC, NH₄⁺, NO₃⁻).

The other three submodels (nitrification, denitrification, and fermentation) then predict emissions of trace gases using the modeled soil environmental factors. DNDC adopts biogeochemical and empirical equations (see Li 2000 for

summary) to simulate the carbon and nitrogen biogeochemical cycles including soil trace gas emissions. The site-specific input data for DNDC includes: (1) climate data, e.g., daily maximum and minimum air temperature, daily precipitation, and daily photosynthetically active radiation (PAR); (2) soil properties, e.g., texture, bulk density, pH, and soil organic carbon (SOC); (3) management activities, e.g., land use type, applications of fertilizers and slurry, tillage, irrigation, weeding and grazing. The input data used for the model validation are summarized in Table 1.

By integrating the soil environmental factors calculated from the soil climate, crop growth and decomposition submodels, the nitrification submodel predicts the production, consumption, and diffusion of NO and N₂O under aerobic condi-

Table 1. The DNDC model inputs of climate and soil properties for the Cork site.

Climate data	
Latitude (degree)	52.14° N
Yearly maximum of average daily temperature (°C)	25.5
Yearly minimum of average daily temperature (°C)	- 2.0
Yearly accumulated precipitation (cm)	121.0
Accumulated PAR (MJ/m ² /year)	1.44
N concentration in rainfall ^a (mg N/l)	0.56
Atmospheric CO ₂ concentrations ^b (ppm)	365 (2003) 700 (IS92a)
Soil Properties (0–10 cm depth)	
Vegetation type	Humid Grassland
Bulk density (g/cm ³)	1.3
Clay fraction	0.06
Soil pH	6.0
Initial organic C content at surface soil (kg C/kg)	0.05
Initial NO ₃ ⁻ concentration at soil surface (mg N/kg)	4.9
Initial NH ₄ ⁺ concentration at soil surface (mg N/kg)	4.9
Initial soil moisture (water-filled porosity) (%)	0.55
Initial soil temperature (°C)	2.0
Porosity (% volume)	70
WFPS at field capacity	55
WFPS at wilting point	26
Depth of water-retention layer (cm)	100
Slope (%)	2

^aMeasured at Cork Airport, 51.83° N, 8.48° W (Jordan 1997).

^b2003 concentration based on 1998 figure in IPCC (2001). IS92a concentration from Leggett et al. (1992).

tions. The denitrification submodels predict emissions of NO and N₂O under anaerobic conditions and the fermentation submodel predicts CH₄ emissions under anaerobic conditions. The final model outputs are daily emissions of NO, N₂O, N₂, CH₄, and NH₃. Our interest in this study is confined to N₂O emissions.

Climate projections – the IS92a scenario

Our climate projections are based on the standard Hadley Center model output of the IS92a scenario for Ireland in the period 2070–2100 (Legett et al. 1992). The scenario is based on a ‘business as usual’ emission rate and assuming a mid-range economic growth but no measures to reduce greenhouse gas emissions. The general circulation model used is HadCM3, which is a new generation of high-resolution coupled atmosphere-ocean general circulation model described by Gordon et al. (2000) and Pope et al. (2000). The model predicts a doubling of the atmospheric CO₂ concentration, increases of 2.0–2.5 °C in average daily temperature, an increase in winter rainfall and a decrease in summer rainfall compared to the period 1960–1990. The IS92a climate perturbations are summarized in Table 2. The DNDC input data for the IS92a scenario are generated by superimposing the perturbations in precipitation and temperature predicted by HadCM3 on the data measured at the site for the baseline year (Hsieh et al., 2005). N₂O flux measurements and fertilization application records are available for 2003, therefore this was chosen as the baseline year for the study.

Results and discussion

Figure 1 shows: (a) fertilizer and slurry nitrogen applications; (b) daily precipitation; (c) the daily temperature range; and (d) measured and DNDC-predicted daily emissions of N₂O for year 2003. Slurry applications were mostly made in spring (February and March) and autumn (September), whereas fertilizer applications were made throughout the growing season, from February to August. Seasonal variation in rainfall was low with the exception of a period from August to late October, which was notably drier, with a mean

daily rainfall of less than 1 cm. The N₂O emissions were small for most of the year and 60% of the total N₂O emission occurred in eight major events (numbered 1–8 in Figure 1d) of 2–20 days’ duration, confined to the spring and summer. Large emission events often follow nitrogen application and heavy rainfall (e.g., day 118), particularly if the rainfall occurs after a long dry period (e.g., days 88, 181, 239). The DNDC model simulations agree with observed N₂O emissions showing emission peaks broadly similar in magnitude and timing.

We also show the measured and modeled cumulative annual N₂O emissions (Figure 2 and Table 3). The measured cumulative annual N₂O emission was 11.6 kg N ha⁻¹. The model prediction of annual N₂O emission was 15.4 kg N ha⁻¹, 32 % higher than the measured value. Spatial variability of soil parameters within the flux tower footprint and the temporal variability of the footprint itself due to fluctuations in wind direction and speed may account for some of this discrepancy. It is also possible that even with gap filling, the measured emission may be less than the actual total if major emission events coincided with gaps in the measurement record. Short gaps in the measured data were coincident with the modeled flux pulses around days 125 and 160. In general, the results indicate that the DNDC model is able to capture most of the major N₂O emission events, although in some cases (e.g., day 156) the modeled emission events occur later than the observed events. The very large rainfall of day 103 (5.7 cm) produced a flux pulse in the model output but no pulse was observed by the EC system. A long pulse was measured by the EC system between days 205 and 215 but the model failed to capture this event, possibly due to the amount of available soil N being reduced by the previous pulse (day 198), which the model over-estimated. However, the overall reasonable agreement between observations and model predictions provides a basis for using the DNDC model to estimate background and predict future N₂O emissions under climate change scenarios.

The total nitrogen application from synthetic and organic fertilizers for the year was 337 kg N ha⁻¹. Given the measured N₂O emission of 11.6 kg N₂O–N ha⁻¹, the emission factor is 3.4%. The emission factor based on the modeled N₂O

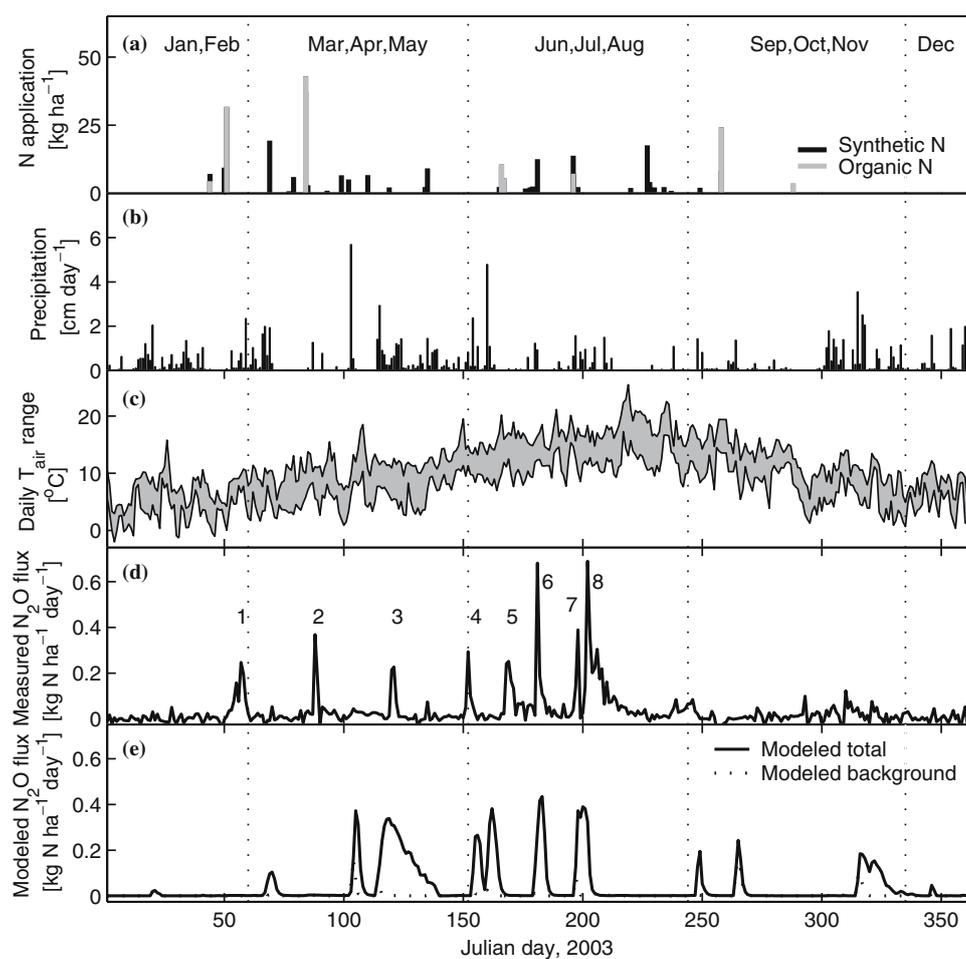


Figure 1. (a) Area-weighted applications of synthetic fertilizer and slurry to the footprint in kg N ha⁻¹ (b) Daily precipitation in cm day⁻¹ (c) Daily maximum and minimum temperatures in °C (d) Measured N₂O in kg N₂O-N ha⁻¹ day⁻¹ with major emission events labeled 1–9 (e) Modeled total N₂O emissions and modeled background emissions (calculated with zero N applications) in kg N₂O-N ha⁻¹ day⁻¹.

emission of 15.4 kg N₂O-N ha⁻¹ is 4.6%. Both the above emission factors are higher than the IPCC guideline value of $1.25 \pm 1.0\%$ (IPCC 2001) of applied N but within the range of 0.3–5.8% observed by Dobbie et al. (1999) for a set of grassland sites in the UK over several years.

Our calculated emission factors are uncorrected for background emissions. Under the same climate and soil conditions but with no nitrogen application, DNDC predicted an annual background emission of 1.7 kg N ha⁻¹ (Table 3). This indicates that background emission accounts for 11% of the total modeled N₂O emission (and accounts for 15% of the total measured N₂O emission). These figures are somewhat higher

than the global estimate for grasslands of 0.5 kg N ha⁻¹ presented by Bouwman et al. (1995). The modeled results indicate that the relatively higher background emission rate was related to the high SOC content (0.05 kg C/kg soil) in the test site. This result is consistent with worldwide observations on the SOC–N₂O correlation in soils (Li et al., in press). If we subtract the modeled background emission from the total observed emission, then the corrected anthropogenic emission factor is 3.0%. The modeled background daily N₂O emission is plotted in Figure 1. The majority of the background N₂O emission (68%) comes from just four events, each of less than a week in duration. Comparing the modeled background

Table 2. Baseline (2003) measured precipitation and temperature and perturbations under the IS92a scenario for southern Ireland.

Season:	2003 average precipitation (mm day ⁻¹)	IS92a change in precipitation (mm day ⁻¹)	2003 average daily air temperature (°C)	IS92a change in average daily air temperature (°C)
December–February (DJF)	3.35	+0.55	5.6	+2.5
March–May (MAM)	4.07	0	8.5	+2.0
June–August (JJA)	2.62	−0.66	14.2	+2.5
September–November (SON)	3.25	0	10.1	+2.5

emissions and the modeled emissions incorporating N applications (Figure 1), the results indicate that fertilizer and slurry applications are responsible for:

- (1) An enhancement of the four major emission events and
- (2) A further six significant N₂O emission events.

To study the effect of future climate perturbations on N₂O emission, we consider the following scenario: a future climate projection based on the Hadley Center IS92a scenario for Ireland with current fertilization practices maintained. Based on this condition, the DNDC model predicts an annual N₂O emission of 22.4 kg N ha⁻¹ (Table 3). Also, under the same conditions, the DNDC model predicts a background N₂O emission of 2.2 kg N ha⁻¹. This result suggests that the future climate shifts based on the IS92a scenario would increase the total N₂O emission by

45% and background N₂O emissions by 30%. The wetter winters predicted under the IS92a scenario will promote anaerobic soil conditions, increasing the rate of denitrification and lead to greater emissions of N₂O to the atmosphere, provided it is able to diffuse out of the soil before becoming reduced to N₂ (Smith et al. 2003). The higher year-round temperatures will promote microbial activity, increasing the rates of both nitrification and denitrification (Whitehead 1995). Figure 3 shows the seasonal effects of the climate perturbations on modeled emissions, with the highest increases occurring in the March–May and September–November seasons. There is almost no change in emissions for the dry June–August season, where denitrification is likely to be limited by the low soil moisture (Maag and Vinther 1996). The increase in emissions during the September–November season may be due to more anaerobic soil conditions (favorable to

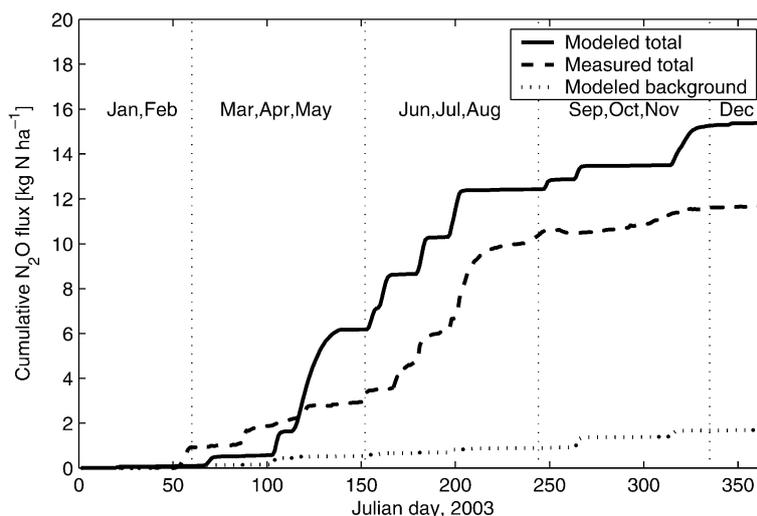


Figure 2. Cumulative total modeled, total observed and modeled background N₂O emissions for 2003 in kg N₂O–N ha⁻¹.

Table 3. Summary of N applications, measured N₂O emissions for 2003 and modeled N₂O emissions for all scenarios.

Scenario	Organic N application (kg ha ⁻¹)	Synthetic N application (kg ha ⁻¹)	N ₂ O emission (kg ha ⁻¹)	% of baseline emission	Emission factor ^a %
2003 measured	130	207	11.6	75	3.4
2003 modeled (baseline)	130	207	15.4	100	4.6
2003 reduced N applications ^b	130	170	14.5	94	4.3
IS92a current N applications	130	207	22.4	145	6.7
IS92a reduced N applications ^b	130	170	21.2	138	6.3
2003 background	0	0	1.7	11	–
IS92a background	0	0	2.2	14	–

^aEmission factors include background emission.

^bSynthetic fertilizer applications reduced in accordance with EU Nitrates Directive (CEC 1991).

denitrification) caused by increased rainfall as well as the higher temperatures. The emissions remain almost unchanged from December to February. Lack of available soil N, rather than environmental conditions, is the probable controlling factor during this season. It should be noted that other factors that may influence future N₂O emissions are not considered in this study. For example, seasonal grazing patterns will be affected by the grass growing season becoming longer, but growth during the summer may be limited due to drought (Holden and Brereton 2002).

In addition to changes in climate, the pattern of synthetic fertilizer usage is likely to be reduced due to environmental protection legislation such as the EU Water Quality Directive (CEC 1991), which is currently being implemented across Europe. The primary aim of this legislation is to reduce pollution of surface water with NO₃⁻ and other

nitrogenous contaminants. However, this regulation will also affect N₂O emissions by limiting the application of synthetic fertilizer to 170 kg N ha⁻¹, thereby reducing the availability of soil N. For the study site, reducing fertilizer N applications from the current level of 207 to 170 kg ha⁻¹ corresponds to an overall reduction of 11% in N applications. Under current climate conditions, DNDC predicts that this will lead to a reduction of 6% in N₂O emissions.

We also modeled a scenario with IS92a future climate projection and reduced nitrogen applications (from 207 to 170 kg synthetic N ha⁻¹). Based on these conditions, the DNDC model predicts an annual N₂O emission of 21.2 kg N ha⁻¹ (Table 3). This implies that a 10% reduction in overall nitrogen applications under the future IS92a climate projection will only reduce annual N₂O emission by 6% relative to the no-reductions IS92a scenario.

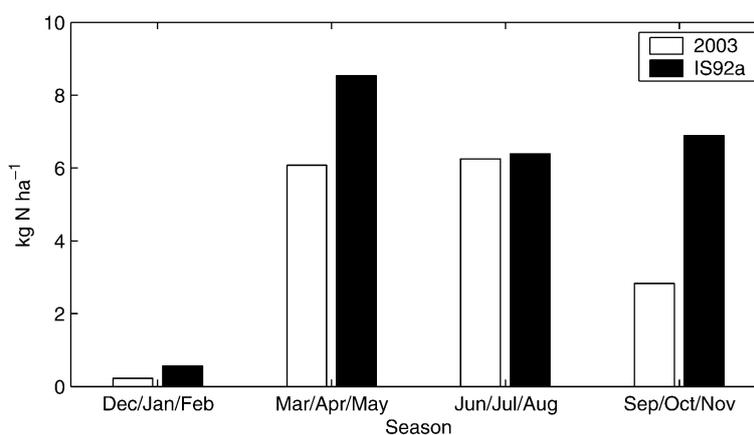


Figure 3. Seasonal totals of modeled baseline (2003) and modeled IS92a N₂O emissions in kg N₂O-N ha⁻¹.

Conclusions

Our measurements and model predictions have demonstrated the following:

- (1) The measured annual N₂O emission was 11.6 kg N ha⁻¹ and the emission factor for this humid grassland site is 3.4%, uncorrected for background emission.
- (2) The DNDC model predicts an annual N₂O emission of 1.7 kg N ha⁻¹ with no N applications. This indicates that background emission accounts for 15% of the observed N₂O emission.
- (3) If we subtract the modeled background N₂O emission from the observed emission, the corrected anthropogenic emission factor is 3.0% of applied synthetic and organic N.
- (4) The DNDC model predicts that in a scenario with future climate shifts based on the IS92a scenario and current N application levels maintained, annual N₂O emission will increase by 45%.
- (5) In the IS92a scenario, background N₂O emission is predicted to increase by 30%.
- (6) Reducing current N applications by 11% to comply with the EU Water Quality Directive is predicted to decrease N₂O emissions by only 6%.
- (7) The predicted increase in N₂O emissions due to future climate change will far outweigh (by a factor of ~6) the reduction in emissions expected from reduced synthetic fertilizer applications in order to comply with the EU Water Quality directive.

Acknowledgements

Hsieh acknowledges support from the National Science Council, Taiwan and the Irish EPA. Leahy and Kiely acknowledge support from the ERTDI program managed by the Irish EPA and funded by the Irish Government under the National Development Plan, 2000–2006 (CELTICFLUX, 2001-CC-C2-M1). Changsheng Li's study was supported by the NASA Terrestrial Ecology Program through project NAG5-12838.

References

Bouwman A.F., van der Hoek K.W. and Olivier J.G.J. 1995. Uncertainties in the global source distribution of nitrous

- oxide. *J. Geophys. Res.* 100(D2): 2785–2800. doi: 10.1029/94JD02946.
- CEC 1991. Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources. Council Directive. Council of the European Communities, Brussels, Belgium.
- Dobbie K.E., McTaggart I.P. and Smith K.A. 1999. Nitrous oxide emissions from intensive agricultural systems: variations between crops and seasons, key driving variables, and mean emission factors. *J. Geophys. Res.* 104(D21): 26891–26899. doi:10.1029/1999JD900378.
- Gordon C., Cooper C., Senior C.A., Banks H.T., Gregory J.M., Johns T.C., Mitchell J.F.B. and Wood R.A. 2000. Simulation of SST, sea ice extents and ocean heat transports in a version of the Hadley Centre coupled model without flux adjustments. *Clim. Dynam.* 16: 147–168.
- Holden N.M. and Brereton A.J. 2002. An assessment of the potential impact of climate change on grass yield in Ireland over the next 100 years. *Irish J. Ag. Food Res.* 41: 213–226.
- Hsieh C.-I., Kiely G., Birkby A. and Katul G. 2005. Photosynthetic responses of a humid grassland ecosystem to future climate perturbations. *Adv. Wat. Res.* doi: 10.1016/j.advwatres.2005.02.007 (in press).
- IPCC 2001. Climate change 2001: The scientific basis. Report. Cambridge University Press, New York, NY, USA.
- Jordan C. 1997. Mapping of Rainfall Chemistry In Ireland 1972–1994. *Biol. Env.: Proc. Royal Irish Acad.* 97B(1): 53–73.
- Leahy P., Kiely G. and Scanlon T.M. 2004. Managed grasslands: a greenhouse gas sink or source? *Geophys. Res. Lett.* 31(L20507). doi:10.1029/2004GL021161. vol. 31, art. L20507.
- Leggett J., Pepper W.J. and Swart R.J. 1992. Emissions scenarios for the IPCC: an update. In: Houghton J.T., Callander B.A. and Varney S.K. (ed), *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*. Cambridge University Press, Cambridge, UK, pp. 69–95.
- Li C.S. 2000. Modeling trace gas emissions from agricultural ecosystems. *Nutr. Cycl. Agroecosyst.* 58: 259–276.
- Li C.S., Frolking S. and Frolking T.A. 1992a. A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. *J. Geophys. Res.* 97: 9759–9776.
- Li C.S., Frolking S. and Frolking T.A. 1992b. A model of nitrous oxide evolution from soil driven by rainfall events: 2. Model applications. *J. Geophys. Res.* 97: 9777–9783.
- Maag M. and Vinther F.P. 1996. Nitrous oxide emission by nitrification and denitrification in different soil types and at different soil moisture contents and temperatures. *Appl. Soil Ecol.* 4: 5–14.
- Pope V.D., Gallani M.L., Rowntree P.R. and Stratton R.A. 2000. The impact of new physical parameterizations in the Hadley Centre climate model – HadAM3. *Clim. Dynam.* 16: 123–146.
- Prather M.J. 1998. Time scales in atmospheric chemistry: coupled perturbations to N₂O, NO_y, and O₃. *Science* 279: 1339–1341.
- Prinn R.G., Weiss R.F., Fraser P.J., Simmonds P.G., Cunnold D.M., Alyea F.N., O'Doherty S., Salameh P., Miller B.R., Huang J., Wang R.H.J., Hartley D.E., Harth C., Steele L.P., Sturrock G., Midgley P.M. and McCulloch A. 2000. A history of chemically and radiatively important gases in air

- deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.* 105(D14): 17751–17792. doi: 10.1029/2000JD900141.
- Scanlon T. and Kiely G. 2003. Ecosystem-scale measurements of nitrous oxide fluxes for an intensely grazed, fertilized grassland. *Geophys. Res. Lett.* 30(16): 1852–1856. doi: 10.1029/2003GL017454.
- Smith K.A., Ball T., Conen F., Dobbie K.E., Massheder J. and Rey A. 2003. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur. J. Soil Sci.* 54: 779–791. doi:10.1046/j.1365-2389.2003-00567.x.
- UNFCCC. 2004. UNFCCC Greenhouse Gases Inventory Data Base, United Nations Framework Convention on Climate Change. Web Page. <http://ghg.unfccc.int/>.
- Whitehead D.C. 1995. *Grassland Nitrogen*. 1st edn. CAB International, Wallingford, Oxon, UK.