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Nonlinear nitrous oxide (N_2O) response to nitrogen fertilizer in on-farm corn crops of the US Midwest

J. P. HOBEN*, R. J. GEHL†, N. MILLAR‡, P. R. GRACE§ and G. P. ROBERTSON*‡

*Department of Crop and Soil Sciences, Michigan State University, East Lansing, MI 48824, USA, †Department of Soil Science, North Carolina State University, Mills River, NC 28759, USA, ‡W. K. Kellogg Biological Station, Michigan State University, Hickory Corners, MI 49060, USA, §Institute of Natural Resource Sciences, Queensland University of Technology, Brisbane, Australia

Abstract

Row-crop agriculture is a major source of nitrous oxide (N_2O) globally, and results from recent field experiments suggest that significant decreases in N_2O emissions may be possible by decreasing nitrogen (N) fertilizer inputs without affecting economic return from grain yield. We tested this hypothesis on five commercially farmed fields in Michigan, USA planted with corn in 2007 and 2008. Six rates of N fertilizer (0–225 kg N ha^{-1}) were broadcast and incorporated before planting, as per local practice. Across all sites and years, increases in N_2O flux were best described by a nonlinear, exponentially increasing response to increasing N rate. N_2O emission factors per unit of N applied ranged from 0.6% to 1.5% and increased with increasing N application across all sites and years, especially at N rates above those required for maximum crop yield. At the two N fertilizer rates above those recommended for maximum economic return (135 kg N ha^{-1}), average N_2O fluxes were 43% (18 g N_2O–N ha^{-1} day^{-1}) and 115% (26 g N_2O–N ha^{-1} day^{-1}) higher than were fluxes at the recommended rate, respectively. The maximum return to nitrogen rate of 154 kg N ha^{-1} yielded an average 8.3 Mg grain ha^{-1}. Our study shows the potential to lower agricultural N_2O fluxes within a range of N fertilization that does not affect economic return from grain yield.

Keywords: agriculture, corn, emission reduction, greenhouse gas, maize, N_2O, nitrogen fertilizer, nitrous oxide

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Introduction

Globally, the historic and projected trend of rising nitrous oxide (N_2O) emissions is mainly the result of increased fertilizer use and animal production (IPCC, 2007). From 1990 to 2005, global agricultural N_2O emissions increased 17% (USEPA, 2006). The Food and Agriculture Organization projects a 35–60% increase in current global agricultural N_2O emissions by 2030 (Bruinsma, 2003). Melillo *et al.* (2009) project even greater N_2O emissions with the development of a global cellulosic biofuels industry and its associated fertilizer needs.

Agriculture is responsible for about 80% (4–5 Tg N_2O–N) of contemporary annual global anthropic emissions (Prather *et al.*, 2001; Robertson, 2004). In the troposphere, N_2O has an average lifetime of 114 years, which contributes to a high global warming potential of 298 CO_2-equivalents (CO_2-Eq) for a 100-year time horizon (Forster *et al.*, 2007). N_2O also depletes stratospheric ozone (Ravishankara, *et al.*, 2009).

Correspondence: J. P. Hoben, tel. + 1 785 532 7897, fax + 1 785 532 7412, e-mail: jhoben@msu.edu

Crop type, tillage, residue management, soil water content, soil temperature, and fertilizer nitrogen (N) amount, source, timing, and placement can all influence N_2O flux from agricultural soils (CAST, 2004; Snyder *et al.*, 2007). Stehfest & Bouwman (2006), in an extensive review of published studies, concluded that soil N_2O flux is best predicted by N application rate, N source, crop type, soil pH, soil texture, climate, and soil organic matter (SOM). Among these factors, N application rate may be the most practical means for achieving decreased N_2O emissions without disrupting crop rotation or general agricultural practices so long as yield is not significantly attenuated. Early evidence for this potential includes, for example, Sehy *et al.* (2003), who in a study of corn following wheat found that decreasing fertilizer from 150 to 125 kg N ha^{-1} resulted in a 34% decrease in N_2O flux with no significant yield change.

Large amounts of N_2O loss have been reported in other studies of corn at N rates in excess of crop demand (McSwiney & Robertson, 2005; Ma *et al.*, 2010). Such rates are known to lead to large increases in nitrate (NO_3^-) leaching (Stanford, 1973; Chichester, 1977; Gehl *et al.*, 2005), and N_2O flux may respond similarly (McSwiney & Robertson, 2005): as increasing amounts of N are applied, yield eventually reaches a maximum at the agronomic optimum N rate (AONR), which is typically greater than the maximum economic return to N rate (MRTN) (Sawyer *et al*., 2006). Substantial N_2O flux could thus be avoided by using N recommendations that seek to more precisely match fertilizer use to crop N demand and economic return, a strategy that would also yield environmental co-benefits related to excess reactive N in the environment (Robertson & Vitousek, 2009). Outside of the United States, excessive N fertilization in China is a growing concern as demonstrated by the rise in the average annual N rate from $38\,kg\,N\,ha^{-1}$ in 1975 to $262\,kg\,N\,ha^{-1}$ in 2001 (Zhang *et al*., 1996; Li & Zhang, 1999; Zhu & Chen, 2002). Approaches to N recommendations that include an economic component may help incentivize reductions in N rate that aim to lower N_2O flux.

Response curves for N_2O flux as a function of N rate are not common but could help to better predict region- and site-specific N_2O emissions in response to N additions. For the few N_2O response experiments in which more than two levels of N were applied, N_2O flux in response to increasing N rates has been described by both linear and nonlinear functions. For example, Henault *et al*. (1998) found N_2O emissions increased linearly in response to three N fertilizer rates for canola at three locations in northeastern France, and Halvorson *et al*. (2008) found N_2O emissions increased linearly in response to three N fertilizer rates in irrigated corn in Colorado (from 0.6 to $5.9\,g\,N_2O\text{–}N\,ha^{-1}\,day^{-1}$; Halvorson *et al*., 2008).

Along a more finely resolved N gradient for nonirrigated corn in Michigan; however, McSwiney & Robertson (2005) reported a nonlinear exponentially increasing N_2O response to fertilizer N along a nine-point N gradient. In their study, N_2O fluxes more than doubled (20 vs. $>50\,g\,N_2O\text{–}N\,ha^{-1}\,day^{-1}$) at N rates $>100\,kg\,N\,ha^{-1}$, the N level at which yield was maximized at $6.8\,Mg\,ha^{-1}$. More recently, Ma *et al*. (2010) found results similar to those of McSwiney & Robertson (2005) for a four-level N gradient under corn in eastern Canada. On average in Ma *et al*. (2010), 150 compared with $90\,kg\,N\,ha^{-1}$ doubled N_2O emissions (16.3 vs. $37.1\,g\,N_2O\text{–}N\,ha^{-1}\,day^{-1}$, respectively) but only slightly increased corn grain yields (9.5 vs. $10.3\,Mg\,ha^{-1}$). Others have also found evidence of nonlinear N_2O emission responses (Bouwman *et al*., 2002a; Grant *et al*., 2006; Zebarth *et al*., 2008). In all cases where a nonlinear curve best describes the N_2O flux response to increasing amounts of N, small increases in applied N fertilizer result in proportionately higher N_2O fluxes at higher N application rates.

The proportion of N fertilizer converted to N_2O, the N_2O emission factor, is based on the N_2O emission response to fertilizer. Using results from a variety of fertilized vs. nonfertilized soils (Bouwman *et al*., 2002a; Novoa & Tejeda, 2006; Stehfest & Bouwman, 2006), the Intergovernmental Panel on Climate Change (IPCC) suggests a default linear emission factor of 1% for N additions from mineral fertilizers, organic amendments, and crop residue regardless of the rate of application (IPCC, 2006). If the N_2O–N response curve is instead nonlinear, then use of the IPCC (2006) methodology for national greenhouse gas (GHG) inventories will underestimate N_2O emissions. Conversely, N_2O mitigation resulting from the adoption of lower N rates will be likewise underestimated.

Refining the response of N_2O flux to crop N fertilizer rates is thus important for better defining both global fluxes and mitigation opportunities – decreasing excess N additions and soil N surpluses in cropping systems that receive N fertilizer may be the most effective and achievable GHG mitigation option for agriculture (CAST, 2004; Smith *et al*., 2007). Millar *et al*. (2010) proposed an N_2O mitigation protocol based on fertilizer N reduction. The rationale for their Tier 2 protocol was in part based on the nonlinear relationship documented in the present paper, which presents in full the original results.

The objectives of the present study are to determine the relationship between N fertilizer rate and N_2O emissions for corn grown on production fields in the US Midwest. To the best of our knowledge, this is the first on-farm study to report N_2O response to multiple fertilizer rates on production-scale fields managed commercially. On-farm studies are important for providing a more realistic range of spatial and farm operator variability than is available from plots located in experiment station settings, which are often chosen for their relatively homogeneous soils and greater control over labor and other agronomic variables (Robertson *et al*., 2007).

Specifically, we aim in this study to (i) determine the N_2O response to N rate in production settings and (ii) determine the relationship of N_2O flux to corn grain yield. We compare N_2O response to economically optimal N rates as determined by new N rate recommendation protocols for corn recently adopted in the US Midwest (Sawyer *et al*., 2006).

Materials and methods

Site description and agronomy

Five field experimental sites were established in Michigan in 2007 and 2008 at four on-farm locations and one at the W.K. Kellogg Biological Station (KBS). KBS (42.41N, 85.37W), Fairgrove (43.52N, 83.64W), and Reese (43.45N, 83.65W) were studied in both 2007 and 2008 whereas the Mason site

(42.47N, 84.51W) was used only in 2007 and the Stockbridge site (42.48N, 84.27W) was used only in 2008.

The Fairgrove and Reese soil is a Tappan-Londo loam (fine-loamy, mixed, active, calcareous, mesic Typic Endoaquolls, and Aeric Glossaqualfs). The Fairgrove and Reese sites typically receive 820 mm of precipitation annually and the mean annual temperature is 8.3 °C. Soil at the Mason site is a Marlette fine sandy loam (fine-loamy, mixed, semiactive, mesic Oxyaquic Glossudalfs). Soil at the Stockbridge site is a Colwood-Brookston loam (fine-loamy, mixed, active, mesic Typic Endoaquolls, and Typic Argiaquolls). The Mason and Stockbridge sites typically receive 800 mm of precipitation annually and the mean annual temperature is 8.3 °C. The soil at KBS is a Kalamazoo loam (fine-loamy, mixed, mesic Typic Hapludalfs). KBS typically receives 990 mm of precipitation per year with a mean temperature of 9.6 °C (Soil Survey Staff, 2010).

The studied crop was corn for both years at all sites, which were managed as a corn–soybean rotation with conventional tillage. Spring seedbed preparation at all locations included chisel plow followed by disking, then one or two passes (depending on the site) with an s-tine field cultivator and was not preceded by tillage the previous fall. On-farm sites were managed by the cooperating producers with the exception of N application and grain harvest on the portion of the fields to which different N rates were applied. The KBS site was a dairy-based production field managed for grain production without manure similar to the other sites, following general production practices common to the region. Typical tillage at the sites included fall chisel plowing and a spring seedbed preparation pass. Weed control included preemergence herbicides at all sites and postemergence herbicide applications when necessary. A wheat cover crop was established following soybeans at KBS and was killed with glyphosate approximately 2 weeks before planting corn.

A late season glyphosate application (24 July 2008) was made erroneously at Stockbridge to nontolerant corn late in the tassel vegetative growth stage. While the plots were harvested, no yield differences among the N fertilizer rates were observed and the average corn grain yield was minimal (3.5 Mg ha^{-1}).

Corn was planted at each site in either 76 or 71 cm row widths at a density of approximately 74 000 seeds ha^{-1}. The plots at KBS, Fairgrove, and Reese in 2008 were within 100 m of the 2007 locations (which had been subsequently planted to soybeans) but remained on the same soil series at each site. Plots at all sites were 4.6–5.8 m wide and 15.2 m long, and were arranged in a randomized complete block design (RCBD) with four replications of six nitrogen (N) treatments: 0, 45, 90, 135, 180, and 225 kg N ha^{-1}. Granular urea [$CO(NH_2)_2$, 46% N] was surface broadcast by hand and immediately incorporated before planting with a single pass using a spring tooth harrow. The sites were planted within 2 days of fertilizer application. Grain yield was determined by hand-harvesting 12 m of row from each of the center two rows of each plot. Grain was shelled with a spike cylinder sheller and then weighed, and yields were adjusted to 155 g kg^{-1} moisture content.

Precipitation data for each site were obtained using the Michigan Automated Weather Network (http://www.agweather.geo.msu.edu/mawn). Weather stations were located within 1 km at KBS, 12 km at Fairgrove, 16 km at Reese, 23 km at Mason, and 28 km at Stockbridge.

Soil sampling

Soil samples were collected at each site in each year, before fertilization. Fifteen 2.5 cm diameter cores (0–15 cm depth) were randomly collected and composited from each replication at each site for determination of soil chemical properties (Table 1). The composite samples were dried at 38 °C, ground to pass a 2 mm sieve, and analyzed for SOM, pH, and exchangeable base cations using procedures recommended for the North Central region (Ellis & Brown, 1998). To estimate the SOM fraction, the loss of weight on ignition (Storer, 1984) was converted to SOM using a conversion factor of 0.98. Soil pH was determined using a 1 : 1 soil : water slurry. Buffered soil pH, for use in the determination of exchangeable acidity, was determined using a mixture of one part soil, one part water, and two parts Shoemaker–McLean–Pratt (SMP) buffer. Mehlich III extractions were used for the determination of exchangeable P, K^+, Ca^{2+}, Mg^{2+}, and Na^+ using a TJA 61E inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Thermo Electron Corp., Waltham, MA, USA).

Additional soil samples were collected from each plot for inorganic N (NO_3^- and NH_4^+) analysis at gas sampling events. Fifteen 2.5 cm diameter cores (0–10 cm depth) were randomly collected and composited from each plot. The composite samples were dried at 38 °C, ground to pass a 2 mm sieve, and 10 g aliquots were extracted in 100 mL of 1 M KCl before analysis for NO_3^-–N and NH_4^+–N using flow injection analysis (QuikChem Methods, Lachat Instruments, Loveland, CO, USA).

N_2O measurements

N_2O fluxes were measured using the static chamber method as described by Holland *et al*. (1999). Chambers were white plastic cylinders (Letica, Rochester, MI, USA) 28 cm in diameter × 27 cm height. The bottom edge of each cylinder was slightly sharpened to ease soil insertion to a depth of 9.5 cm.

Table 1 Summary of soil chemical properties (0–15 cm depth) at the study locations

Site	SOM (g kg^{-1})	pH	Bray 1-P (mg kg^{-1})	Extractable K (mg kg^{-1})	CEC [cmol (+) kg^{-1}]
2007					
KBS	17	6.6	30	73	7
Mason	15	6.6	252	235	8
Fairgrove	27	6.5	30	180	17
Reese	25	7.6	65	163	19
2008					
KBS	21	6.8	11	69	6
Stockbridge	51	6.3	48	167	13
Fairgrove	29	7.6	25	225	15
Reese	23	7.5	40	168	11

SOM, soil organic matter; CEC, cation exchange capacity.

During flux measurements chambers were closed with a snap lid fitted with a large rubber o-ring to create an air-tight seal around the circumference of the lid. A 1.6 cm diameter hole was drilled in each lid and fitted with a rubber septum to facilitate gas sampling. This design produced a 602 cm^2, 10 L chamber headspace. One chamber was installed in each plot 1–3 days before fertilization and removed only once for fertilization, the final cultivation pass, and planting. Within a day after planting, chambers were reinstalled in the exact location from which they were removed and were left in place for the remainder of the growing season. Chambers were placed between corn rows and did not include plants.

At the beginning of each flux, determination lids were secured onto each chamber and the first of four gas samples removed. Lids remained in place only during gas sampling periods of up to 1.5 h. Sampling occurred in the morning or late afternoon. Four gas samples were taken from each chamber at intervals of approximately 20 min. A 5 mL Exetainer vial (Labco Ltd., High Wycombe, UK) was flushed with 10 mL of mixed headspace atmosphere at the time each chamber was sampled for gas collection. An additional 10 mL headspace was then transferred to the flushed sample vial, which provided an overpressure to protect the sample from atmospheric contamination before analysis.

N_2O flux was measured before planting in all treatment plots, then following fertilization every other day for 15 days, and then weekly for a period of 30 days. After approximately 45 days, flux measurements were taken every 10–14 days and continued through grain harvest. In most cases, gas samples were analyzed within 36 h of collection.

Gas samples (0.5 mL) were analyzed for N_2O using gas chromatography (Hewlett Packard 5890 Series II, Rolling Meadows, IL, USA). N_2O was separated from air using a Porapak QS column (1.8 m, 80/100 mesh, held at 80 °C) and then detected using a ^{63}Ni electron capture detector at 350 °C. The limit of detection for N_2O by electron capture detection is near 200 ppb_v on our instrument which is calibrated to 270 ppb_v and capable of detecting changes of roughly $\pm$ 10 ppb_v. No samples from the field were found to be less than atmospheric N_2O levels at a particular site (>310 ppb_v). Linear regression of the N_2O concentration (ppb_v) against time for each of the four samples was used to calculate flux. The R^2-values were typically >0.90. Fluxes with R^2-values <0.45 were not included in the analysis and accounted for 2.7% of the data (109 of 4006 flux measurements). During periods of high flux (>4 g N_2O–N ha^{-1} day^{-1}), the accumulation of N_2O within the chamber headspace sometimes appeared to plateau, indicating the possibility of saturation and partial equilibration of the concentration gradient. In these cases, we used only the initial linear portion of the concentration curve to calculate N_2O flux.

Data analysis

Cumulative emissions (g N_2O–N ha^{-1}) for each plot were determined by interpolating daily fluxes (g N_2O–N ha^{-1} day^{-1}) between sample days over the course of the entire growing season (2 days before planting and up to the day of harvest). Average daily flux (g N_2O–N ha^{-1} day^{-1}) for each plot was calculated by dividing the cumulative emission for that plot by the sampling period. To normalize differences among sites for average daily flux, we used a relative scale whereby plot fluxes were scaled to the highest average daily flux for a plot at that site (plot of interest/highest flux plot).

At Stockbridge in 2008, 95% of the total flux measured accumulated during the 61-day period after planting [24 May 2008; day of year (DOY) 145]; although changes in emission patterns were not detected, average daily N_2O flux and subsequent results for Stockbridge were prepared using the cumulative N_2O emissions before 24 July 2008 to avoid the possibility of altered emissions due to the erroneous glyphosate application. Cumulative N_2O emissions for Stockbridge are shown for the entire growing season only to illustrate that the majority of emissions (95%) occurred before the glyphosate application.

Emission factors for the percent of emissions induced by fertilization were based on a conservative estimate for the annual flux. The observed data and the model results for the average daily flux were used to estimate total flux for the growing season (measurement period of approximately 153 days). For late (postharvest; October and November) fall and early (preplant; March and April) spring, the average daily flux across all sites for late September and early October was used to estimate a daily flux rate. For the winter months of December, January, and February, when soils were frozen, flux was assumed to be near zero.

A random coefficient model with either a linear or an exponential response curve was fitted to describe the average daily flux and the relative N_2O emission response to N rate. Specifically, the model with a linear response is

$$Y_{ijk} = (\beta_0 + b_{0jk}) + (\beta_1 + b_{1jk})N_i + e_{ijk}, \quad (1)$$

and for an exponential response

$$Y_{ijk} = \exp[(\beta_0 + b_{0jk}) + (\beta_1 + b_{1jk})N_i] + e_{ijk}, \quad (2)$$

where Y_{ijk} is the average calculated daily or relative N_2O from the four blocks at the ith N rate, jth site, and kth year, whereas β_0, β_1 are the overall mean intercept and slope, respectively. Terms b_0 and b_1 are random coefficients assumed to be multivariate normal distributed and e_{ijk} is the error term assumed to be normally distributed with different variances at different N rates to account for the apparent unequal variances across the different N rates. We also fitted linear [Eqn (1)] and exponential [Eqn (2)] response curves with equal variance across the different N rates for each site × year combination. All analyses were conducted using PROC NLMIXED (SAS 9.1.3, SAS® Institute Inc., Cary, NC, USA).

Model comparisons among linear and exponential response curves were made using Akaike's Information Criterion (AIC) and likelihood ratio-based R^2-values (Magee, 1990; Nagelkerke, 1991):

$$R^2 = 1 - \exp\left[-\frac{2}{n}\{l(\widehat{\beta}) - l(0)\}\right] = 1 - \left\{\frac{l(0)}{l(\widehat{\beta})}\right\}_{2/n}, \quad (3)$$

$$l(\widehat{\beta}) = \log L(\widehat{\beta}), \quad (4)$$

$$l(0) = \log L(0), \quad (5)$$

where $l(\widehat{\beta})$and $l(0)$ represent the log likelihood values for the full and the null (intercept only) model, respectively.

The results of the model [Eqns (1) and (2)] for the relative N_2O fluxes were used to derive a daily N_2O flux. First, the background ($0\,kg\,N\,ha^{-1}$) average daily N_2O flux ($g\,N_2O$–$N\,ha^{-1}\,day^{-1}$) at each site was averaged across the four replicates. For each site, the average daily N_2O flux at $0\,kg\,N\,ha^{-1}$ was multiplied by the ratio of the predicted relative daily flux at each of the six N rates to the predicted relative daily flux at $0\,kg\,N\,ha^{-1}$. Thus, the relative daily N_2O flux model was related to the background flux at each site to calculate the derived daily N_2O flux.

Yield response models were tested using treatment averages to assess the yield response to increasing N rate by PROC NLIN (SAS 9.1.3, SAS® Institute Inc.). Each of the 8 site-years was subjected to regression analysis to identify the best-fit curve from the quadratic, quadratic plateau, or linear plateau models (Wallach & Loisel, 1994). The corrected R^2-values were used for model selection in addition to visual inspection of each response curve type. The selected yield response equations were used to identify the point where yields no longer statistically increased with increasing amounts of N. In this way, the maximum yield and corresponding AONR was identified for each site and year. The yield response equations for each site and year were also used to generate an estimate for the maximum return to N rate (MRTN) across all sites and years at a N fertilizer to corn grain price ratio of 0.10 (Sawyer *et al*., 2006).

Data are archived on the KBS LTER data catalog (http://www.lter.kbs.msu.edu).

Results

Adequate precipitation preceded planting at all sites in 2007 (see Supporting Information, Table S1), but the lack of midsummer precipitation in June and July produced visual symptoms of drought stress at all sites. Drought stress was particularly an issue at KBS and Mason. Planting at KBS on 22 May 2007 was followed by a 50-day period with little or no rainfall. In 2008, precipitation was again limiting at KBS (May and August) and also at Stockbridge (April, May, and August), where visual symptoms of severe drought stress were observed (see Supporting Information, Figs S1 and S2).

The application of N fertilizer increased soil inorganic N concentrations above the control plots ($0\,kg\,N\,ha^{-1}$) at all sites in all years and generally within 11 days of fertilizer application (Table 2). Increases in soil inorganic N were proportional to the amount of N applied. Soil inorganic N concentration tended to be higher in 2008 at all sites.

Daily flux

The effect of fertilizer N on daily N_2O flux could be detected at each location within a week of fertilizer application (see Supporting Information). Daily N_2O fluxes rapidly increased after fertilizer was applied and remained well above the prefertilizer background flux of $<4\,g\,N_2O\,ha^{-1}\,day^{-1}$ for up to 55 days. The largest increases in daily N_2O flux were proportional to N rate.

The duration of the increased rate of daily N_2O flux did not seem to be related to N rate. Sites with later planting dates and thereby later fertilizer application, tended to have a shorter period of increased flux (see Supporting Information, Figs S3 and S4). In 2007, the daily N_2O flux for the 135 and $225\,kg\,N\,ha^{-1}$ treatments remained greater than the control treatment for a period of 25–55 days. Increased daily N_2O flux continued for 25 and 42 days at the later planted sites KBS and Mason, respectively. At the earlier planted Fairgrove and Reese sites, the period of increased N_2O flux was 55 and 51 days, respectively. A similar trend for planting date and the duration of increased N_2O flux greater than background levels was seen in 2008. Daily N_2O fluxes for the 135 and $225\,kg\,N\,ha^{-1}$ treatments returned to rates similar to the control ($<4\,g\,N_2O\,ha^{-1}\,day^{-1}$) around DOY 170 on 19 June for all sites in 2007. In 2008, the

Table 2 Soil inorganic nitrogen (to 10 cm depth) in response to N rate approximately 11 days after fertilizer application

	2007*				2008†			
Fertilizer N rate ($kg\,ha^{-1}$)	KBS	Mason	Fairgrove	Reese	KBS	Stockbridge	Fairgrove	Reese
	Soil N ($NO_3^- + NH_4^+$) ($mg\,N\,kg^{-1}$)							
0	19.3 (1.2)	15.9 (0.9)	10.3 (0.4)	10.7 (0.7)	18.9 (6.3)	28.4 (1.4)	33.5 (6.1)	16.1 (1.1)
45	33.4 (1.1)	27.8 (1.4)	19.3 (1.0)	19.5 (0.9)	30.2 (2.6)	41.3 (2.3)	60.8 (5.6)	42.2 (2.9)
90	38.6 (2.0)	37.6 (1.8)	29.0 (1.9)	28.9 (1.6)	51.7 (4.5)	63.0 (4.5)	80.3 (7.2)	68.6 (4.4)
135	52.7 (3.4)	47.7 (2.2)	41.9 (2.5)	36.4 (1.6)	61.1 (7.7)	86.2 (6.3)	96.4 (7.4)	84.0 (8.4)
180	64.6 (3.4)	60.0 (2.9)	53.0 (3.4)	41.6 (2.6)	90.7 (7.0)	118.5 (9.6)	122.2 (10.4)	114.3 (6.4)
225	74.3 (3.2)	68.8 (3.4)	60.0 (3.1)	46.1 (1.9)	97.1 (9.4)	124.5 (15.2)	170.9 (14.0)	127.6 (7.7)

Values are means (± SE) for 3 or 4 (n = 12–16 plots) sampling events representing an approximately 30-day period.
*2007 sample dates: 30 May, 12, 26 June at KBS; 18, 21, 28 May, 12 June at Mason; 7, 15, 24, 29 May at Fairgrove and Reese.
†2008 sample dates: 23 May, 6, 11, 27 June at KBS; 4, 11, 20, 27 June at Stockbridge; 6, 19 May, 9 June at Fairgrove and Reese.

return to background rates of daily N_2O flux differed by site. In 2008 at KBS and Stockbridge, daily N_2O flux for the 135 and 225 kg N ha^{-1} treatments returned to rates similar to the control treatment (<4 g N_2O ha^{-1} day^{-1}) around DOY 200 (18 July). In 2008 at Fairgrove and Reese, the return to background daily flux rates was around DOY 170 (18 June) and DOY 203 (21 June), respectively.

Cumulative flux

The largest contributions to cumulative N_2O emissions occurred during 4–8 weeks after fertilizer application (Figs 1 and 2). After this period, the rate of increase in cumulative N_2O emissions slowed and approached a plateau near the middle of the growing season in both years. Mid-season cumulative N_2O emissions were similar in magnitude to end of season cumulative N_2O emissions. Using the 225 kg N ha^{-1} treatment as an example, between 61% and 95% of cumulative N_2O emissions occurred within 8 weeks of fertilizer application when daily flux was >4 g N_2O–N ha^{-1} day^{-1} (76% at 2007 KBS, 87% at 2007 Mason, 81% at 2007 Fairgrove, 85% at 2007 Reese, 92% at 2008 KBS, 95% at 2008 Stockbridge, 84% at 2008 Fairgrove, 61% at 2008 Reese). Similar trends in cumulative emissions were observed for the other N fertilizer treatments.

Average daily flux

Both linear and nonlinear increases in average daily N_2O fluxes were observed depending on the site and year (Figs 3 and 4). Curve fitting for the average daily flux vs. N rate was performed separately for each site year to describe the response at the individual site level. Average daily N_2O fluxes were well described at each site by either a linear or an exponential model ($R^2 = 0.67$–0.99).

An exponential response to N rate best described average daily N_2O flux in 2007 at KBS and Fairgrove and in 2008 at KBS and Stockbridge. The linear model provided the best fit for the Reese site in both 2007 and 2008 and at the Fairgrove site in 2008, although the relationship between average daily N_2O flux and N fertilizer rate at Reese in 2008 was not as strong as the other sites ($R^2 = 0.67$). Additionally, Reese in both years tended to produce comparably less N_2O than Fairgrove. At Mason in 2007, the exponential and linear models described the average daily N_2O response equally well ($R^2 = 0.75$) and a distinct curve type could not be assigned. This result may be due to the unexpected order of flux values where the 45 and 180 kg N ha^{-1} treatments were greater than the 90 and 225 kg N ha^{-1} treatments, respectively. In 2008, unexpected small flux was observed at KBS (180 kg N ha^{-1} treatment) and Reese (225 kg N ha^{-1} treatment). The abnormally large and small fluxes are difficult to account for given that

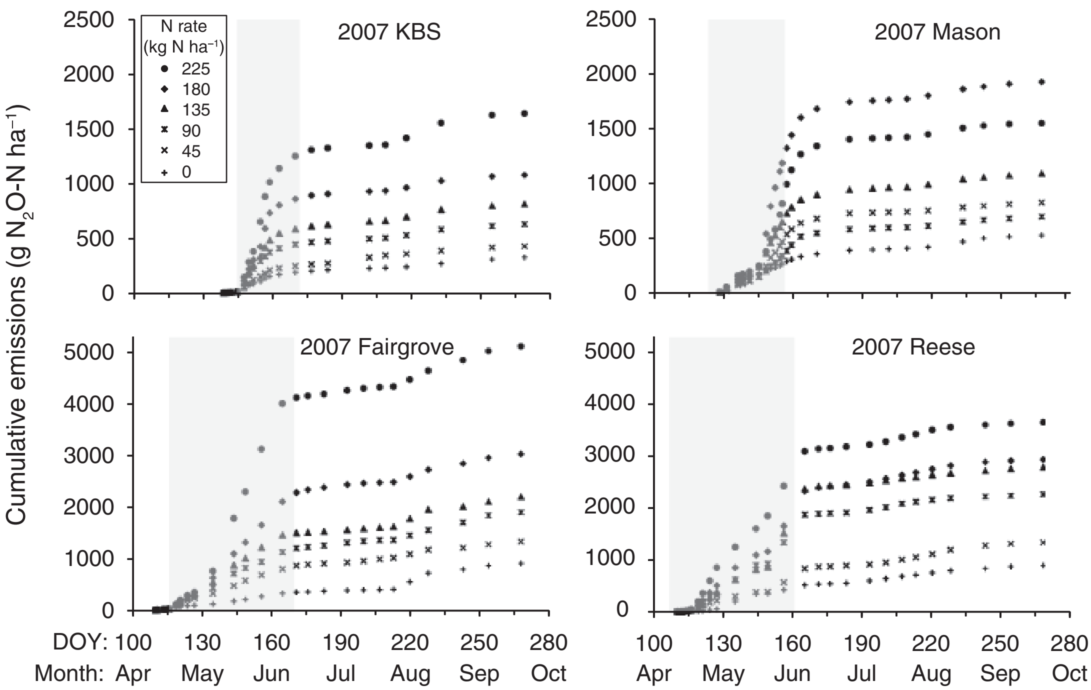

Fig. 1 Cumulative N_2O emissions during the 2007 growing season. The shaded portion of the graph represents the 25–55-day period where daily flux for the N treatments was greater than the control treatment ($\geq$ 4 g N_2O ha^{-1} day^{-1}).

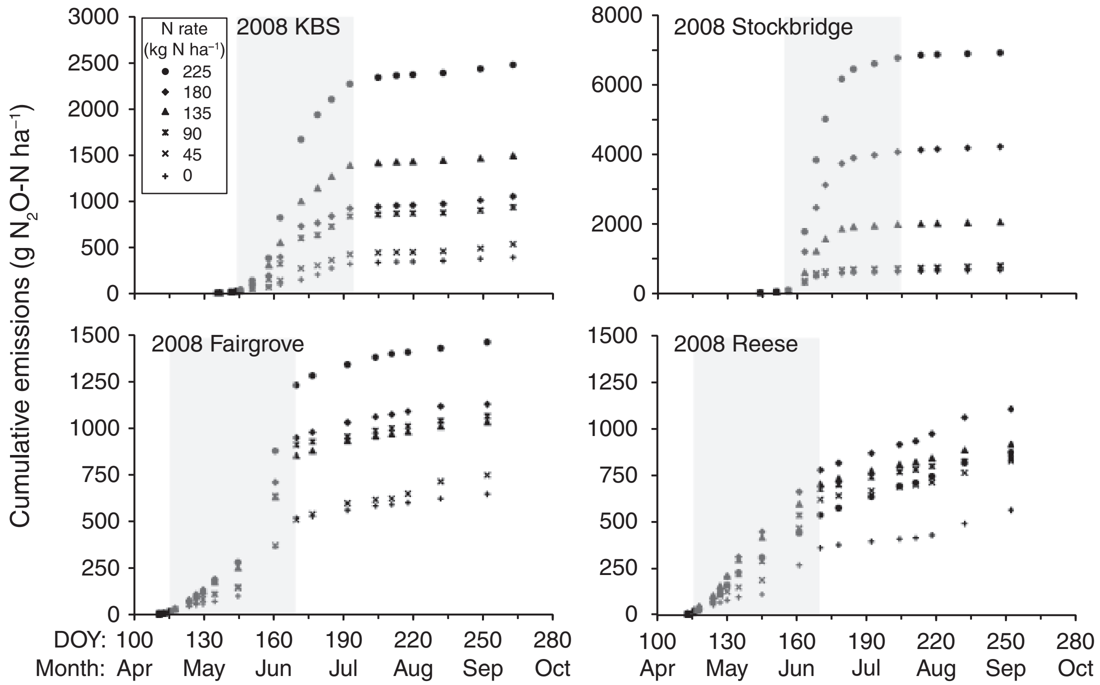

Fig. 2 Cumulative N_2O emissions during the 2008 growing season. The shaded portion of the graph represents the 47–54-day period where daily flux for the N treatments was greater than the control treatment ($\geq 4\,g\,N_2O\,ha^{-1}\,day^{-1}$).

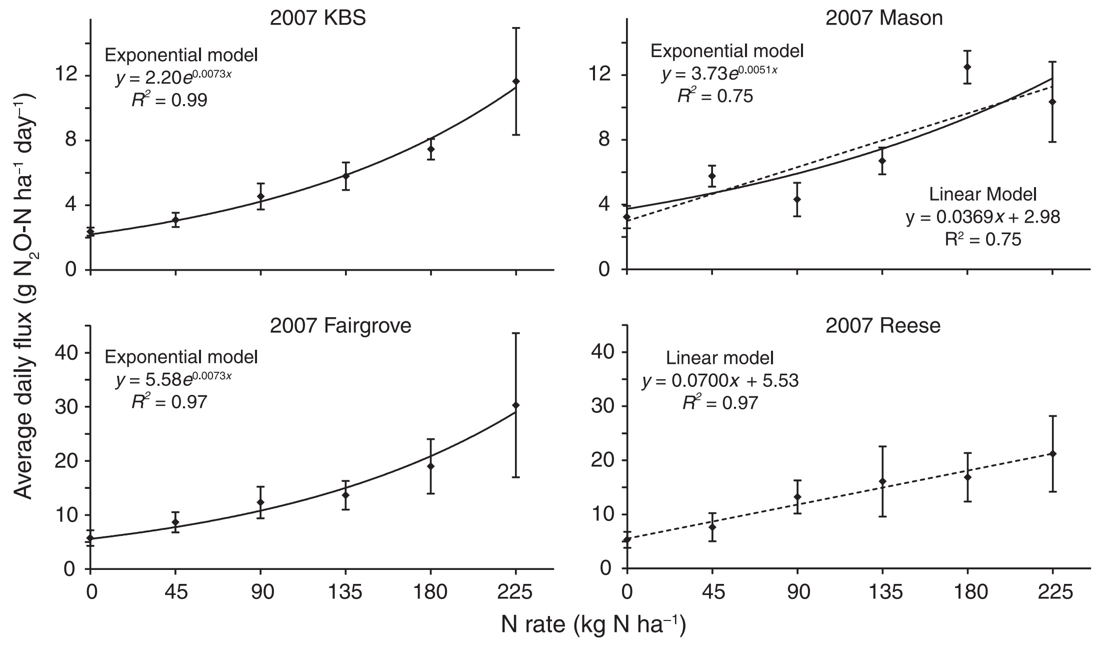

Fig. 3 Average daily N_2O flux during the 2007 growing season. Results from regression analysis [Eqns (1) and (2)] are shown for the best fit model using the treatment averages from each site. Error bars represent standard error of the treatment averages.

they were not accompanied by similar observations for soil inorganic N (Table 2) or corn grain yield (Table 3).

We cannot be certain why emissions were greater at some sites compared with others. Differences in emissions among sites are largely due to different soil types, SOM content and composition, and microclimate at a given site. At Stockbridge, both flux and soil inorganic N tended to be comparatively large for all treatments. The site had nearly twice the SOM as the other sites. Planting occurred late (24 May 2008; DOY 145) during

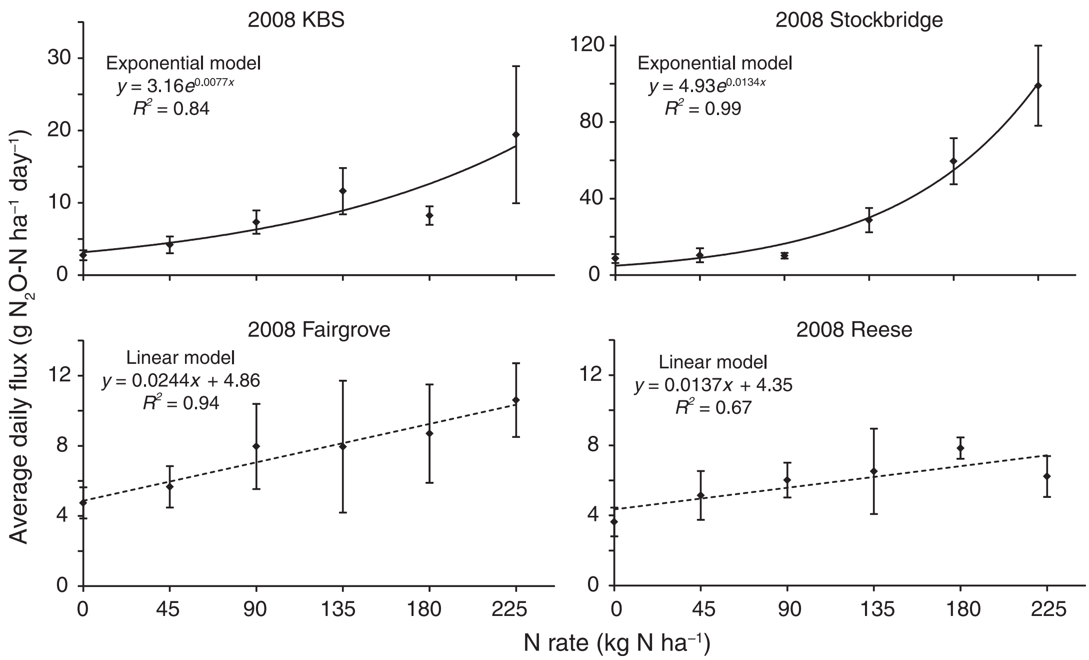

Fig. 4 Average daily N_2O flux during the 2008 growing season. Results from regression analysis [Eqns (1) and (2)] are shown for the best-fit model using the treatment averages from each site. Error bars represent standard error of the treatment averages.

Table 3 Corn grain yield as a function of N rate and the results from regression analysis of yield response to N for each site

	2007 (Mg ha^{-1})				2008 (Mg ha^{-1})		
Fertilizer N rate (kg ha^{-1})	KBS	Mason	Fairgrove	Reese	KBS	Fairgrove	Reese
0	3.7	5.7	5.3	3.5	3.1	5.9	4.1
45	4.0	6.0	7.0	5.7	3.9	8.9	7.9
90	3.6	6.9	7.4	6.5	4.5	10.9	10.2
135	3.7	6.7	8.4	7.8	3.4	11.7	11.9
180	3.6	7.1	7.3	8.6	3.6	12.1	12.1
225	3.7	6.6	8.3	8.4	3.1	12.5	13.9
Curve type*	NS†	QP	QP	LP	Q	QP	QP
R^2	NS	0.79	0.86	0.98	0.61	0.99	0.98
Max. yield‡	NS	6.8	8.0	8.5	4.0	12.2	13.5
AONR	NS	139	138	152	104	155	238

*Curve type selected among quadratic plateau (QP), linear plateau (LP), or quadratic (Q) models (Wallach & Loisel, 1994).
†Not significant (no yield response to N fertilizer due to drought).
‡Maximum yield at each location determined by either a quadratic, quadratic plateau, or linear plateau model fit of the data.
AONR, agronomic optimum N rate (kg N ha^{-1}).

abnormally dry weather (See Supporting Information). Warmer soil temperatures for the late planting into 5.1% organic matter soil likely contributed mineralization and an increase in an already large soil inorganic N pool. Dry conditions produced visual symptoms of drought, stunted plants, and thus likely reduced plant N demand. The series of events and site conditions at Stockbridge help to explain the large flux measured by identifying contributions to the soil N pool potentially available for microbial nitrification and denitrification.

Variation in average daily N_2O flux was greatest at the 180 and 225 kg N ha^{-1} fertilizer rates (Fig. 5a). Relative N_2O flux, scaled to the highest average daily flux plot within a site (Fig. 5b), tended to decrease the amount of variation across sites for a given fertilizer level. For both observed and relative fluxes, the exponential model best described the relationship between N_2O flux and N fertilizer across all sites (Fig. 6). For the average daily N_2O flux, the R^2 for the linear model was 0.41 compared with 0.79 for the exponential model. For the relative N_2O

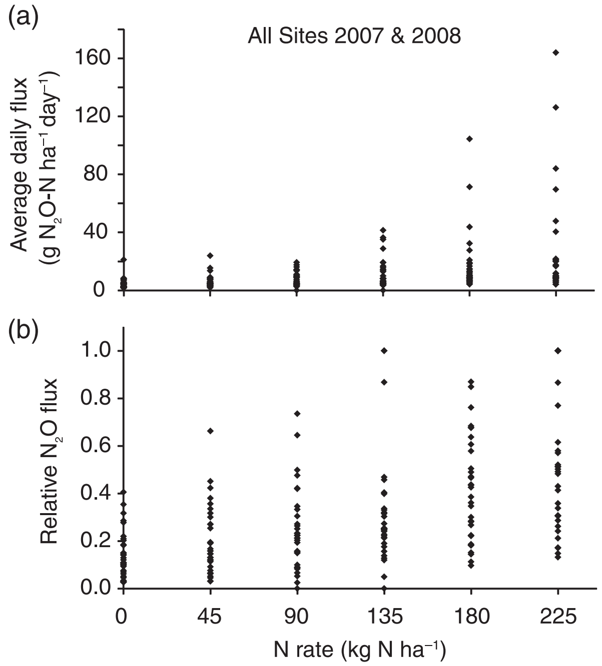

Fig. 5 Nitrous oxide flux across the sampling period for 8 site years representing five locations in 2007 and 2008. Each data point represents a single plot at a given N level. (a) Average daily N_2O flux was calculated by dividing the cumulative N_2O flux by the number of days in the sampling period. (b) Relative flux was calculated by dividing the average daily N_2O flux data for the plot of interest by the highest average daily flux for each site.

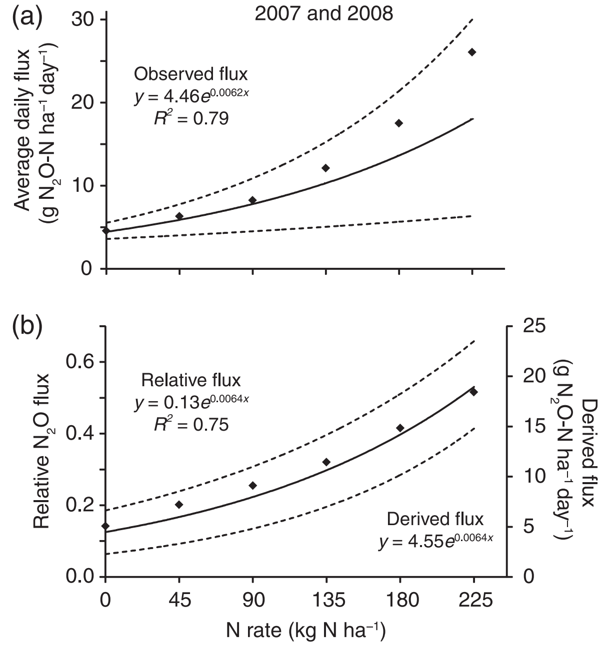

Fig. 6 Results from regression analysis using site averages for each N rate. (a) The model curve for the average daily flux is shown with the observed averages. (b) The relative flux model was used to calculate the derived flux using model predictions and the observed flux for $0\,kg\,N\,ha^{-1}$ at each site to back-calculate a scaled value ($kg\,N_2O$–$N\,ha^{-1}\,yr^{-1}$). The 95% confidence intervals are shown only for the observed and relative flux model predictions [Eqn (2)].

flux, the R^2 for the linear model was 0.74 compared with 0.75 for the exponential model. Compared with the exponential model for the daily N_2O flux, the relative flux improved confidence in the prediction of N_2O flux at N rates $>135\,kg\,N\,ha^{-1}$ (Fig. 6).

The relative N_2O flux model predictions for the six tested N fertilizer rates (0–225 $kg\,N\,ha^{-1}$) were used to back-calculate a derived daily flux ($kg\,N_2O$–$N\,ha^{-1}\,yr^{-1}$). The derived daily flux ranged from $4.6\,g\,N_2O$–$N\,ha^{-1}\,day^{-1}$ (± 0.7 SE) for the $0\,kg\,N\,ha^{-1}$ treatment, to $19.3\,g\,N_2O$–$N\,ha^{-1}\,day^{-1}$ (± 3.1 SE) for the $225\,kg\,N\,ha^{-1}$ treatment (Fig. 6b). Compared with the observed values, the derived daily flux provides a more conservative estimate of N_2O losses as N fertilizer rate increased, and resulted in lower SE.

The difference between the derived fluxes and the IPCC estimated fluxes is insignificant at N rates up to $90\,kg\,N\,ha^{-1}$, but at higher N rates the difference is $>50\%$ (Fig. 7). Similar to the study-wide daily flux, emission factors increased with increasing N rate. Under our study conditions, the 1% IPCC emission factor underestimated the observed and the modeled emission factors at the 180 and $225\,kg\,N\,ha^{-1}$ treatments.

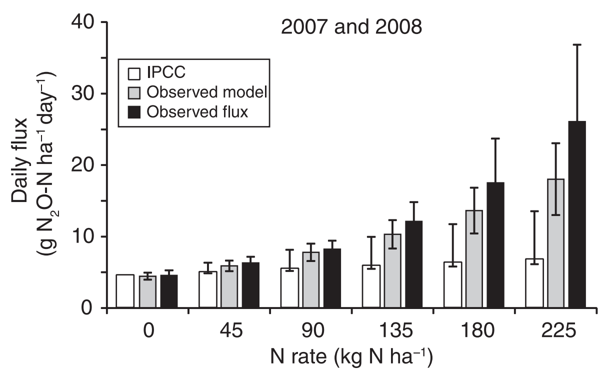

Fig. 7 Comparison of daily flux measures. The error bars for the IPCC data represent the uncertainty range (0.3–3%). The error bars for the observed model represent the standard error of the model [Eqn (2)]. The error bars for the observed flux data represent the standard error of the site averages.

Yield

Across all sites, corn grain yields in 2007 averaged $6.0\,Mg\,ha^{-1}$ with a range of 3.5–$8.6\,Mg\,ha^{-1}$, and in 2008 (not including Stockbridge) yields averaged $8.0\,Mg\,ha^{-1}$ with a range from 3.1 to $13.9\,Mg\,ha^{-1}$ (Table

3). With the exception of KBS in 2007, yield significantly ($P > 0.1$) responded to N fertilizer. At KBS in 2007, late planting date (DOY 142; 22 May) and drought stress contributed to limited yield. For N responsive sites ($P > 0.1$), model estimates were made for the maximum yield and corresponding AONR using either a quadratic plateau or linear plateau model. Maximum yields occurred at 152 kg N ha^{-1} or less in 2007. With one exception in 2008, maximum yield was achieved at 155 kg N ha^{-1} or less. The exception was Reese in 2008, where the AONR of 238 kg N ha^{-1} was greater than the highest N rate tested in the fertilizer gradient.

For N responsive sites, the maximum return to N (MRTN) rate was 154 kg N ha^{-1}, which corresponds to an average yield of 8.3 Mg ha^{-1}. Using the ± $1 range of the MRTN approach (Sawyer *et al*., 2006), the average MRTN range was 135–172 kg N ha^{-1} yielding 8.2–8.4 Mg ha^{-1}.

Discussion

High rates of N fertilization led to increasing rates of N_2O loss without economic gains in yield. We observed both linear and nonlinear N_2O responses to fertilizer N depending on the site and year (Figs 3 and 4), but across all site-years, a nonlinear response curve best described increases in N_2O with increasing N rate (Fig. 6).

Authors of previous N rate field studies describe the N_2O response to N rate as either linear or nonlinear (Henault *et al*., 1998; McSwiney & Robertson, 2005; Halvorson *et al*., 2008; Ma *et al*., 2010). However, for most studies where a linear response was described, only two to three fertilizer N rates were examined (Bouwman, 1996; Stehfest & Bouwman, 2006). The ability to compare curve types is nil with two points and very limited with three. McSwiney & Robertson (2005) showed nonlinearity for a nine-point fertilizer gradient (0, 34, 67, 101, 134, 168, 202, 246, and 291 kg N ha^{-1}) in Michigan over a 3-year period for continuous corn. Others have also described nonlinear N_2O flux (Bouwman *et al*., 2002a; Grant *et al*., 2006; Ma *et al*., 2010) or found evidence for large increases in N_2O flux at N rates above that required for maximum yields (Chantigny *et al*., 1998; Bouwman *et al*., 2002b; Sehy *et al*., 2003; Zebarth *et al*., 2008).

Our results are in agreement with those of McSwiney & Robertson (2005) for KBS, although they did not include formal regression and comparison of a linear to a nonlinear response. In our study and regression analysis, KBS results were best described by a nonlinear N_2O response curve in both 2007 and 2008. Most other sites also had a nonlinear response, but on the other hand, linear N_2O responses were observed at Reese in both years and at Fairgrove in 2008. The magnitude of N_2O flux may play a role in the shape of the response curve: among all sites Reese had the lowest cumulative fluxes in both years, and at Fairgrove a linear response was observed only in 2008 when cumulative fluxes were substantially lower than in 2007. Moreover, we observed a strikingly nonlinear response in our site with the highest cumulative N_2O flux (Stockbridge; Fig. 4). Thus a nonlinear response may not be present when flux is relatively low or may simply not be detectable.

Overall, N_2O increased exponentially with increasing N (Fig. 6). In aggregate, compared with the 90 kg N ha^{-1} treatment (8 g N_2O–N ha^{-1} day^{-1}), the observed N_2O flux for the 135, 180, and 225 kg N ha^{-1} treatments increased by 47%, 113%, and 217%, respectively (Fig. 7). A GHG mitigation protocol proposed by Millar *et al*. (2010) utilized the same dataset we now present in full. However, the authors summarized the data using raw averages rather than using full regression analysis which we employ herein.

This overall nonlinear trend is further supported by the improved fit of the nonlinear model for both the observed and relative models (Fig. 6). Increased variance in N_2O flux at high N rates resulted in poor confidence for model predictions of observed fluxes at the highest N rates. Scaling observed fluxes to the highest flux within each site decreased model variance and improved model confidence. The overall model for relative fluxes is similar to that for absolute fluxes, with the largest increases in N_2O flux occurring at N rates of 135 kg N ha^{-1} and greater.

Optimal N fertilizer rates

At sites where yield responded to N, maximum corn yield (8.3 Mg ha^{-1}) on average was achieved at an AONR of 167 kg N ha^{-1}. The largest increases in N_2O flux occurred above 135 kg N ha^{-1} for all sites. This N rate is less than the AONR but within the range for the MRTN rate (135–173 kg N ha^{-1}), which factors in the additional cost of fertilizer and its diminishing economic return as yields approach AONR: at some rate less than AONR the cost of added N cannot be justified by the sale of additional yield.

When determining AONR, residual inorganic profile N is not commonly included or specifically credited in the determination of corn N recommendations in most humid regions of the United States. Warm temperatures and rainfall in these regions complicate the use of such preplant tests for predictions of crop response due to rapid N movement and transformations including mineralization, immobilization, leaching, and denitrification. Several reports have documented the inherent difficulties in using preplant soil tests for predicting N availability for a crop (Keeney, 1982; Olson & Kurtz, 1982; Fox *et al*., 1989; Bock & Kelley, 1992; Grove, 1992).

Although data presented in Table 2 show slight differences among sites in the inorganic N concentrations in the surface 0–10 cm for the control treatments early in the season, these samples represent only a small fraction of the corn root zone and are not representative of the entire rooting profile.

Consequently, available and potentially mineralizable N in the root zone will affect crop response to applied fertilizer, but due to interannual variability the actual contribution of preseason inorganic N is often not specifically accounted for when developing N recommendations in humid regions. As yet, there are no proven reliable or regionally accepted methods for predicting N availability during the crop growing season. Rather, multiple site and year data are commonly pooled to determine the expected response over time. Thus, the AONR as defined in our manuscript reflects the inflection point where yield no longer responds to increasing N fertilizer rate at a given site in the years of our study. Under similar crop management at a site, the AONR will reflect a reasonable estimate of the N requirement in future years. The AONRs reflect actual response data for each site-year and provide a solid comparison for the yield response relationships to N_2O flux. Decreasing N rates to 135 kg N ha^{-1}, compared with 180 and 225 kg N ha^{-1}, would have resulted in N_2O decreases ranging from 44% (2.0 kg N_2O–N ha^{-1} yr^{-1}) to 115% (5.1 kg N_2O–N ha^{-1} yr^{-1}) for the observed average flux. For the more conservative statistical model of all fluxes, the decreases would have ranged from 32% (1.2 kg N_2O–N ha^{-1} yr^{-1}) to 75% (2.8 kg N_2O–N ha^{-1} yr^{-1}).

Large increases in N fertilizer application above the MRTN rate only marginally increased yield and were not justified by the expense of added N. Compared with the 135 kg N ha^{-1} rate, corn grain yield increases of 2% (8.2 Mg ha^{-1}) and 6% (8.5 Mg ha^{-1}) were achieved by the 180 and 225 kg N ha^{-1} rates, respectively. The MRTN is designed to provide the most economical corn N recommendation using large pools of response trial data that have been grouped according to criteria that indicate differing N response for regions of similar management, climate, and soils (Sawyer *et al*., 2006). Our application of the MRTN approach was to describe an overall economic N rate for the site-years where yield significantly ($P > 0.1$) responded to N. The small increases in yield require fertilizer rates greater than the MRTN (154 kg N ha^{-1}) and represent direct loss of profit to the grower in addition to the externalized indirect expense of environmental harm to society.

N_2O emission factors

N_2O emission factors increased with increasing N rate and were within the ranges previously reported for similar studies. Our emission factors ranged from 0.6% to 1.5% for the observed flux averages. Compared with the range of 0–7% reported in a survey of agricultural soils receiving roughly 0–300 kg N ha^{-1} (Bouwman, 1996), the emission factors in our study were on the lower end of the range. The emission factors from our study were also less than the 2–7% range reported by McSwiney & Robertson (2005) for continuous corn receiving 0–291 kg N ha^{-1}. However, our calculated annual emission factor estimations are conservative. Although we did not determine N_2O fluxes during winter and early spring (December–April), our assumption of zero fluxes of N_2O from frozen soils and during soil freeze–thaw cycles during this period likely underestimates emissions. In conventionally tilled corn (150 kg N ha^{-1}), Van Bochove *et al*. (2000) measured N_2O fluxes from a Quebec silty loam during winter that were comparable to, or exceeded, N losses during the growing season (~ 0.5–3.1 g N_2O–N ha^{-1} day^{-1} from December to March). In a silt loam in Ontario, Wagner-Riddle & Thurtell (1998) measured total N_2O emissions over five freeze–thaw cycles between January and April of 1.3 and 1.7 kg N_2O–N ha^{-1} from spring- and fall-ploughed corn crops, respectively, receiving 100 kg N ha^{-1}. Wagner-Riddle *et al*. (2008) found that the source of the N_2O 'burst' at spring thaw is predominantly from 'newly' produced N_2O in the surface layer, and not the release of N_2O trapped in the unfrozen soil beneath the frozen layers. Accounting for winter and early spring emissions could increase our estimate of annual N_2O emissions and emission factors.

The fertilizer N rates used in our study are comparatively lower than many of the studies summarized by Bouwman (1996) but more importantly, within the range commonly required for optimum corn grain production and recommended for the US Midwest (Vitosh *et al*., 1995; Sawyer *et al*., 2006)

The IPCC (2006) default emission factor (1%) underestimated emission factors for the observed flux but not for the more conservative modeled flux (Fig. 6). Intended as a method for calculating national budgets for N_2O on a continental scale, emission factors provide an accessible cross-site reference to quantify fertilizer induced emissions (Eichner, 1990; Bouwman, 1996). Emission factors account for very few environmental or management factors; however, and more complex methods for generating N_2O budgets at the landscape scale have been proposed (e.g. Bouwman *et al*., 2002b). Our finding that the rate of N_2O loss accelerates as a function of added N fertilizer rate should also be considered for other intensively fertilized systems outside of the US Midwest.

Conclusions

Our results suggest a nonlinear exponentially increasing N_2O response to N rate that may be typical for corn–soybean rotations in the US Midwest. Using the IPCC default 1% emission factor (IPCC, 2006) for our on-farm systems underestimated N_2O emissions for N rates above the MRTN. Linear and nonlinear increases in N_2O were observed depending on the study locations and year, but nonlinear exponential response models best represented the overall N_2O response to N fertilizer across all site-years. A nonlinear trend in observed N_2O flux was also suggested by the 44% and 115% increases in N_2O flux at 180 and 225 kg fertilizer–N ha^{-1}, respectively, over the 135 kg fertilizer–N ha^{-1} (12 g N_2O–N ha^{-1} day^{-1}) treatment. These higher N rates were greater than both the AONR (167 kg N ha^{-1}) and the MRTN rate (154 kg N ha^{-1}) required to achieve maximum and economically optimum corn grain yield (8.3 Mg ha^{-1}), respectively. Little increase in yield could be expected at N rates >135 kg fertilizer–N ha^{-1}, although large increases in N_2O resulted at N rates above this rate. The relationship of yield to N_2O suggests that with increasing N rate, yield reaches a plateau just as the N_2O response sharply increases. Providing farmers an incentive to apply N at MRTN rates (e.g. Millar *et al*., 2010) could provide a powerful opportunity for mitigating N_2O emissions from agricultural soils, with co-benefits likely to include lower leached N loss as well.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Daily and cumulative precipitation from 10 April to 7 October 7, 2007. Arrows denote the fertilizer and planting date: KBS on May 22; Mason on May 8; and Fairgrove and Reese on April 22.

Figure S2. Daily and cumulative precipitation from 9 April 9 to 6 October 6 2008. Arrows denote the fertilizer and planting date: KBS on May 16; Stockbridge on May 24; and Fairgrove and Reese on April 22.

Figure S3. Daily N_2O flux during the 2007 growing season. Data collection began prior to fertilizer application (0–225 kg N ha^{-1}) and continued until harvest.

Figure S4. Daily N_2O flux during the 2008 growing season. Data collection began prior to fertilizer application (0–225 kg N ha^{-1}) and continued until harvest.

Figure S5. Corn grain yield response to N fertilizer for the N responsive site-years. The results from regression analysis are given by the best fit equations selected among quadratic plateau (QP), linear plateau (LP), or quadratic (Q) models (Wallach & Loisel, 1994).

Table S1. Monthly precipitation, planting and harvest date for each site-year.