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## ON-FARM NITROUS OXIDE RESPONSE TO NITROGEN FERTILIZER IN CORN CROPPING SYSTEMS

presented by

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has been accepted towards fulfillment of the requirements for the

MASTER OF degree in SCIENCE

CROP AND SOIL SCIENCES

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## ON-FARM NITROUS OXIDE RESPONSE TO NITROGEN FERTILIZER IN CORN CROPPING SYSTEMS

John Patrick Hoben

## A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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#### ABSTRACT

## ON-FARM NITROUS OXIDE RESPONSE TO NITROGEN FERTILIZER IN CORN CROPPING SYSTEMS

By

## John Patrick Hoben

Previous studies have indicated that large reductions in  $N_2O$  emissions may be possible with relatively little impact on grain yield or economic return by better managing N fertilizer. To test this hypothesis in farm settings, experiments were conducted in Michigan at three farms and one experiment station, all planted to corn, in 2007 and in 2008. Six rates of nitrogen fertilizer (0-225 kg N ha<sup>-1</sup>) were broadcast and incorporated prior to planting. Across all sites and years, increases in N2O flux were best described by a nonlinear response to increasing N rate. Emission factors ranged from 1.4 to 3.4% and increased with increasing N application across all sites and years, especially at N rates above that required for maximum crop yield. Nitrous oxide flux increased by 43% (2.0 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>) and 115% (5.1 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>) for the 180 and 225 kg N ha<sup>-1</sup> rates, respectively, compared with the next lowest, 135 kg N ha<sup>-1</sup> rate, which was closer to the maximum return to N rate (MRTN). The MRTN (0.10 price ratio) of 154 kg N ha<sup>-1</sup> yielded 8.3 Mg ha<sup>-1</sup>. Application of N fertilizer at or slightly below the MRTN would have reduced total N<sub>2</sub>O flux by 79% on average. This study shows the potential to lower agricultural N<sub>2</sub>O fluxes within a range of N fertilization which does not greatly affect yield.

Copyright by JOHN PATRICK HOBEN 2009 ...to my parents, Ellen and Thomas Hoben, and my great grandfather, Homer Evans

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## ON-FARM NITROUS OXIDE RESPONSE TO NITROGEN FERTILIZER IN CORN CROPPING SYSTEMS

### INTRODUCTION

Atmospheric concentrations of nitrous oxide (N<sub>2</sub>O) have long been increasing, and agriculture is responsible for 4-5 Tg N<sub>2</sub>O-N (80%) of annual global anthropogenic emissions (Prather et al., 2001; Robertson, 2004). In the troposphere N<sub>2</sub>O has an average lifetime of 114 years, which contributes to a high global warming potential equal to 298  $CO_2$ -equivalents (CO<sub>2</sub>-eq) for a 100-year time horizon (Forster et al., 2007). The importance of N<sub>2</sub>O is further compounded by the ozone-depleting reaction products NO and NO<sub>2</sub> from N<sub>2</sub>O decay once N<sub>2</sub>O reaches the stratosphere (Crutzen, 1970; Forster et al., 2007; Johnston, 1971).

From 1990 to 2005, global agricultural N<sub>2</sub>O emissions increased 17% (USEPA, 2006). The Food and Agriculture Organization projects a 35-60% increase over current global agricultural N<sub>2</sub>O emissions by 2030 (Bruinsma, 2003). The increased agricultural emissions of the past 15 years and the projected future increases are mainly due to changes in fertilizer use and animal production (Bruinsma, 2003; USEPA, 2006). Melillo et al. (2009) project even greater fertilizer use with the development of a global cellulosic biofuels industry.

## The Source of Agricultural Soil N<sub>2</sub>O

The reduction of nitrate  $(NO_3)$  and nitrite  $(NO_2)$  to nitric oxide (NO), N<sub>2</sub>O, and dinitrogen (N<sub>2</sub>) by denitrifying bacteria in soils is a major source of atmospheric N<sub>2</sub>O emissions as is the oxidation of ammonia  $(NH_4^+)$  to NO<sub>3</sub> by nitrifying bacteria (Bremner, 1997; Firestone and Davidson, 1989; Robertson and Groffman, 2007). Production of N<sub>2</sub>O in soils occurs in many ecosystems, but agricultural soils are responsible for ~3 Tg N<sub>2</sub>O-N (50%) of global annual emissions (Prather et al., 2001; Robertson, 2004). In a long-term Michigan study, Robertson et al. (2000) found average daily fluxes in three different corn-soybean-wheat rotation systems and an alfalfa system (~3.5 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>) were three times greater than fluxes in an unmanaged successional system (~1.1 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>) and nearly six times greater than fluxes in a short-rotation poplar system (0.6 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>). Unlike natural ecosystems, unmanaged systems, or low input grasslands, the N<sub>2</sub>O flux from cropping systems is subject to a high level of management which can be directed to reduce emissions.

## Fertilizer N Effects on N<sub>2</sub>O

Crop type, tillage, residue management, soil moisture, soil temperature, and fertilizer N amount, source, timing, and placement can all influence  $N_2O$  emissions (CAST, 2004; Snyder et al., 2007). While the relationship between  $N_2O$  emission and

crop management is complex, fertilizer N generally increases N2O emissions. In an extensive review of published studies Stehfest and Bouwman (2006) found that N application rate, N source, soil pH, and crop type best predicted N<sub>2</sub>O emissions from agricultural fields. Other factors which were significant included soil texture, climate, and increased soil organic matter (SOM). Unlike the aforementioned factors, soil texture, climate, and increased SOM are more difficult to control or account for within a mitigation strategy. Among all the factors, N fertilizer may be the most straightforward factor to manage without disrupting crop rotation or general agricultural practices. Research suggests the ability of reduced N rates to translate into large reductions in N<sub>2</sub>O emissions. For example, in a study of corn following wheat, Sehy et al. (2003) found that reducing fertilizer from 150 to 125 kg N ha<sup>-1</sup> resulted in a 34% reduction in N<sub>2</sub>O flux; while yield did not differ significantly; cumulative N2O emissions increased with increasing N. Large amounts of N<sub>2</sub>O loss have also been reported in other studies on corn at N rates in excess of crop demand (Ma et al., 2009; McSwiney and Robertson, 2005). Nitrogen rates above crop demand are widely accepted to lead to large increases in NO<sub>3</sub> leaching (Chichester, 1977; Gehl et al., 2005; Stanford, 1973). A similar rapid increase in N<sub>2</sub>O flux may be occurring at N application rates above that needed to achieve maximum agronomic yield. Excess N application and N2O flux may be avoided by using N recommendations which seek to match crop N demand.

Contemporary N recommendations rely on yield response curves. Although the concept of an economical N rate based on the yield response curve to increasing N fertilizer has been previously described, recently there been wide scale adoption of the concept (Sawyer et al., 2006; Vanotti and Bundy, 1994; Vitosh et al., 1974). Several states within the U.S. Corn Belt have made efforts to build large data sets for use in state-specific N recommendations which include an economic component (Sawyer et al., 2006). The approach identifies the region of the yield response curve where the relationship of yield and N rate are optimized for different economic conditions as a function of fertilizer and corn grain price.

Conceptually, the calculated N rate (maximum return to N, MRTN) at a given fertilizer to corn grain price ratio is the point along the N rate gradient where an additional unit of N no longer pays for the produced increase in yield (Sawyer et al., 2006). Additional units of N greater than the MRTN are excessive and not economical. Excess N fertilizer application may be seen by some growers as a way to insure against reduced yield. However, the economic based MRTN approach provides a more empirical basis for determining maximum fertilization rates which are appropriate across soils of different yield potential.

Response curves for corn grain yield as a function of N rate have been described and their general features are known (Anderson and Nelson, 1975; Cerrato and Blackmer, 1990; Wallach and Loisel, 1994). As increasing amounts of N are applied, yield eventually reaches a plateau or maximum at the agronomic optimum N rate (AONR), which is typically greater than the MRTN.

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Response curves for N<sub>2</sub>O flux as a function of N rate are not as well established but could help to better predict region- and site-specific N2O emissions in response to N additions. Both linear and nonlinear response curves have been used to describe N2O flux in response to increasing N rates (Halvorson et al., 2008; Henault et al., 1998; Ma et al., 2009; McSwiney and Robertson, 2005). Henault et al. (1998) found N<sub>2</sub>O emissions increased linearly in response to N fertilizer for rapeseed at three locations in northeastern France. Nitrous oxide also rose linearly for increases in average daily flux from 0.6 to 5.9 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> in response to N fertilizer for irrigated corn in Colorado (Halvorson et al., 2008). In a similar study for non-irrigated corn in Michigan, McSwiney and Robertson (2005) reported a nonlinear N<sub>2</sub>O response to N where average daily flux ranged between 7.0 to 54.0 N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>. They found that N rates greater than a 100 kg N ha<sup>-1</sup> threshold, where grain yields were maximized, doubled N<sub>2</sub>O emissions. More recently, similar results were found by Ma et al. (2009), where on average 150 kg N ha<sup>-1</sup> compared with 90 kg N ha<sup>-1</sup> doubled N<sub>2</sub>O emissions (37.1 vs 16.3 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>, respectively) but only slightly increased corn grain yields. Others have also found evidence of nonlinear N<sub>2</sub>O emission responses (Bouwman et al., 2002a; Grant et al., 2006; Zebarth et al., 2008). In cases where a nonlinear curve best describes the N<sub>2</sub>O flux response to increasing amounts of N, small N fertilizer reductions would produce relatively large reductions in N<sub>2</sub>O emissions.

The proportion of N fertilizer converted to N<sub>2</sub>O, the N<sub>2</sub>O emission factor, is based on the N<sub>2</sub>O emission response to fertilizer. Using models based on a variety of soils (Bouwman et al., 2002a; Novoa and Tejeda, 2006; Stehfest and Bouwman, 2006), the Intergovernmental Panel on Climate Change (IPCC) assumes a default emission factor of 1% for N additions from mineral fertilizers, organic amendments, and crop residue regardless of the rate of application (IPCC, 2006). Some researchers have found that a single 1% emission factor can underestimate N<sub>2</sub>O emissions in some years in the Central USA (Adviento-Borbe et al., 2007; Bremner et al., 1981; Jarecki et al., 2008; McSwiney and Robertson, 2005; Parkin and Kaspar, 2006). Use of the IPCC (2006) methodology for establishing national greenhouse gas (GHG) inventories, would likely underestimate N<sub>2</sub>O emissions because it is based on a single emission factor for all soils without regard to N rate. Additionally, potential N2O mitigation resulting from the adoption of lower N rates could also be underestimated. The number of measurements (1008) from many references (204) represented by the 1% emission factor reflects the large body of research on the effect of fertilizer N on N2O flux (IPCC, 2006; Stehfest and Bouwman, 2006). However, the dataset employed in these models included studies lacking 0 kg N ha<sup>-1</sup> controls as well as studies with a limited number of measured N rates. Few studies to date have collected N<sub>2</sub>O flux measurements from more than two or three points along an N fertilizer gradient. Additional observations along the N fertilizer

gradient would be useful in determining if N<sub>2</sub>O emission factors need to account for N rate.

#### **Regional Context**

Substantial regional reductions in N2O emissions from cultivated soils will require N management practices that are applicable to large-scale production systems. Cropland comprises 54 Mha (46% of total area) in the north central USA (IL, IN, IA, MI, MN, MO, OH, and WI) of which about 21 Mha (39 % of total cropland area) is planted to corn in any given year (USDA, 2009a, 2009b; USDA, 2007). Soil N<sub>2</sub>O from this region has been estimated to contribute 34% of total soil N<sub>2</sub>O from cultivated soil within the USA (Mummey et al., 1998). Land in corn production is well suited as a target for potentially reducing agricultural N2O emissions given the large proportion of area devoted to corn production systems. Additionally, corn receives 43% of the total N fertilizer (12 Tg) applied in the USA (USDA, 2007). In this context, regional N rate studies for corn have the benefit of providing data for improved N rate recommendations and improved understanding of the relationship of N fertilizer management to N2O emissions. Reducing excess N additions and soil N surpluses may be the most effective and achievable GHG mitigation option within agriculture (Smith et al., 2007).

The objectives of our study are to determine the relationship between N fertilizer rate and  $N_2O$  emissions for corn grown in Michigan on production fields. Specifically we aim to: (i) determine the  $N_2O$  response to N rate in production scale settings (on-farm) and (ii) determine the relationship of  $N_2O$  flux to corn grain yield.

#### **MATERIALS AND METHODS**

#### Site Description and Agronomy

Field experiments were established in Michigan in 2007 and 2008 at four on-farm locations and at the W.K. Kellogg Biological Station (KBS) in Kalamazoo County (N 42.41, W 85.37). The Mason site (N 42.47, W 84.51) was used only in 2007 and the Stockbridge site (N 42.48, W 84.27) was used only in 2008. Other sites including KBS, Fairgrove (N 43.52, W 83.64), and Reese (N 43.45, W 83.65) were used in both 2007 and 2008.

The soils at KBS are 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. The Fairgrove and Reese soils are a Tappan-Londo loam (fineloamy, mixed, active, calcareous, mesic Typic Endoaquolls and Aeric Glossaqualfs). The area near Fairgrove and Reese typically receives 820 mm of precipitation annually and the mean annual temperature is 8.3 °C. Soils at the Mason site are Marlette fine sandy loam (fine-loamy, mixed, semiactive, mesic Oxyaquic Glossudalfs). Soils at the Stockbridge site are a Colwood-Brookston loam (fine-loamy, mixed, active, mesic Typic Endoaquolls and Typic Argiaquolls). The area near Mason and Stockbridge typically receives 800 mm of precipitation annually and the mean annual temperature is 8.3 °C.

All sites were managed as a corn-soybean rotation with conventional tillage. Onfarm sites were managed by the cooperating producers as part of the entire field, with the exception of N application and grain harvest. The KBS site was part of an agricultural experiment station and was managed similarly as the other sites following general production practices common to the region. Typical tillage at the sites included fall

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chisel plowing and a spring seedbed preparation pass. Weed control included preemergence herbicides at all sites and post-emergence herbicide applications used when necessary. A wheat cover crop was established following soybeans at KBS and was killed with glyphosate approximately 2 weeks prior to planting corn.

Corn was planted at each site in either 76- or 71-cm row widths at a density of approximately 74,000 seeds ha<sup>-1</sup>. The plots at KBS, Fairgrove, and Reese in 2008 were within 100 m of the 2007 locations but remained in the same soil series at each site in both years. The geographic plot locations at these sites were moved slightly in 2008 to accommodate crop rotations. Plots at all sites were 4.6 to 5.8 m wide and 15.2 m long, and were arranged in a randomized complete block design (RCBD) with 4 replications of 6 nitrogen treatments: 0, 45, 90, 135, 180, and 225 kg N ha<sup>-1</sup>. Granular urea (CO(NH<sub>2</sub>)<sub>2</sub>, 46% N) was surface broadcast and immediately incorporated prior to planting. After fertilizer application, the sites were planted within 2 days. 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<sup>-1</sup> 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, prior to fertilization. Fifteen 2.5-cm diameter cores (0-15 cm) were randomly collected and composited from each

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replication at each site for determination of soil chemical properties. The composite samples were dried at 38° C, ground to pass a 2-mm sieve, and analyzed for soil organic matter (SOM), pH, and exchangeable base cations using procedures recommended for the North Central region (Ellis and 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 1 part soil, 1 part water, and 2 parts Shoemaker-McLean-Pratt (SMP) buffer. Mehlich III extractions were used for the determination of exchangeable P, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> using a TJA 61E inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Thermo Electron Corp., Waltham, MA).

Additional soil samples were collected from each plot for inorganic N (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) analysis at gas sampling events. Fifteen 2.5-cm diameter cores (0-10 cm) were randomly collected and composited from each plot. The composite samples were dried at  $38^{\circ}$  C, ground to pass a 2-mm sieve, and 10 g aliquots were extracted in 100 ml of 1 *M* KCl prior to analysis for NO<sub>3</sub>-N and NH<sub>4</sub>-N using flow injection analysis (QuikChem<sup>®</sup> Methods, Lachat Instruments, Milwaukee, WI).

#### Nitrous Oxide Measurements

Nitrous oxide fluxes were measured using the static chamber method as described by Holland et al. (1999). Chamber bases were installed in each plot prior to fertilization for measurement of background  $N_2O$  flux for 1-3 days, then were removed temporarily for fertilization, the final cultivation pass, and planting. Bases were immediately reinstalled after planting in the exact location from which they were removed and were left in place for the entire growing seasons.

Chambers were fashioned from food grade white plastic buckets (Letica, Rochester, MI). The bottom of each bucket was removed and the remaining plastic edge was slightly sharpened to ease soil insertion. Markings were placed on the chambers to guide accurate preparation and deployment. The chambers had an internal diameter of 27.7 cm and a height of 27 cm and were embedded to a depth of 9.5 cm. Lids for the chambers contained 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 equipped with a rubber septum to facilitate gas sampling. This design produced a 10 L chamber headspace when accounting for the tapered shape of the original bucket.

At the beginning of a flux determination, lids were secured onto each chamber and the first of four gas samples was taken. Lids remained in place only during gas sampling periods of up to 1.5 hrs. Four gas samples were taken from each chamber at an interval of approximately 20 minutes. The headspace atmosphere was mixed slightly by using the syringe before aliquots were taken. Sample vials (Labco Limited, 5ml Exetainer vials, High Wycombe, Buckinghamshire, United Kingdom) were prepared by flushing each with 10 mL of mixed headspace atmosphere at the time the chambers were sampled for gas collection. An additional 10 mL headspace was then transferred to the flushed sample vials which provided an overpressure to protect the sample from atmospheric contamination prior to analysis.

Nitrous oxide flux was measured within 2 days of fertilization, then every other day for 14 days following fertilization, and then every 10-14 days until fluxes

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diminished. In most cases, gas samples were analyzed within 36 hours of collection. Gas Samples (0.5 mL) were analyzed for N<sub>2</sub>O using gas chromatography (Hewlett Packard 5890 Series II, Rolling Meadows, IL, USA). Nitrous oxide was separated using a Porapak QS column (1.8 m, 80/100 mesh, held at 80°C) and then detected using a  $^{63}$ Ni electron capture (350°C). Linear regression of the N<sub>2</sub>O concentration (ppb) against time for each of the four samples was used to calculate flux. During periods of increased flux (>4 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup>), the accumulation of N<sub>2</sub>O within the chamber headspace sometimes appeared to plateau, indicating the possibility of saturation and partial equilibration of the concentration gradient. In such cases, the removal of the last sample collected from the flux calculation often provided a linear increase in N<sub>2</sub>O for the remaining three measurements. Rarely, when saturation was apparent for more than a single sample, a flux calculation was not made for the corresponding plot and sampling day.

#### Data Analysis

Cumulative emissions (g N<sub>2</sub>O ha<sup>-1</sup>) were determined by linearly interpolating daily flux (g N<sub>2</sub>O ha<sup>-1</sup> day<sup>-1</sup>) for each plot between days over the course of the entire growing season. Average daily flux (g N<sub>2</sub>O ha<sup>-1</sup> day<sup>-1</sup>) for each plot was then calculated by dividing the cumulative emissions by the sampling period for each site. To reduce the magnitude of difference between sites for the average daily flux measurement, a relative scale was used. Each plot within a site was scaled to the highest average daily flux plot (plot of interest  $\div$  highest flux plot). 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:

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

and similarly for an exponential response:

$$Y_{ijk} = \exp \left[ (\beta_0 + b_{0jk}) + (\beta_1 + b_{1jk}) * N_i \right] + e_{ijk}$$

where  $Y_{ijk}$  is the average calculated daily or relative nitrous oxide from the four blocks at the *i*<sup>th</sup> N rate, *j*<sup>th</sup> site, and *k*<sup>th</sup> year, while  $\beta_0$ ,  $\beta_1$  are the overall mean intercept and slope, respectively, for either the linear or exponential response curve. Terms  $b_0$  and  $b_1$  are random coefficients and are assumed to be multivariate normal distributed,  $e_{ijk}$  is the error term and is 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 and exponential response curves with equal variance across the different N rates for each site × year combination. All N<sub>2</sub>O analyses were conducted using PROC NLMIXED (SAS 9.1.3, SAS<sup>®</sup> 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):

$$R^{2} = 1 - \exp\left[-\frac{2}{n}\left\{l(\hat{\beta}) - l(0)\right\}\right] = 1 - \left\{l(0)/l(\hat{\beta})\right\}^{2/n}$$

$$l(\hat{\beta}) = \log L(\hat{\beta})$$

$$l(0) = \log L(0)$$

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

The results of the model for the relative  $N_2O$  fluxes were used to derive an annual  $N_2O$  flux. First, the background (0 kg N ha<sup>-1</sup>) average daily  $N_2O$  flux (g  $N_2O$ -N ha<sup>-1</sup> day<sup>-1</sup>) at each site was averaged across the four replicates. For each site, the average background  $N_2O$  flux was multiplied by the ratio of the predicted relative flux at each of the 6 N rates to the relative flux at 0 kg N ha<sup>-1</sup>. Thus, the relative  $N_2O$  flux model was related to the background flux at each site to calculate the derived  $N_2O$  flux. Daily  $N_2O$  flux was converted to an annual flux by multiplying by 365 days for the observed and the derived annual 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<sup>®</sup> Institute Inc., Cary, NC, USA). 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 and 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 agronomic

optimum N rate (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).

Economic returns were determined using the average yield response across N responsive sites and the N<sub>2</sub>O flux from the observed model. Fixed costs included N fertilizer ( $0.18 \text{ kg}^{-1}$ ) and grain drying and transportation ( $19.67 \text{ Mg}^{-1}$ ). The GWP of 298 CO<sub>2</sub>-eq for N<sub>2</sub>O at the 100 year time horizon was used to convert N<sub>2</sub>O emissions to CO<sub>2</sub>-eq emissions (Forster et al., 2007). The high range of the MRTN (172 kg N ha<sup>-1</sup>) was used for the CO<sub>2</sub>-eq emissions baseline. Nitrogen rates below the baseline produce less CO<sub>2</sub>-eq emissions leading to a carbon offset. Nitrogen rates above the baseline produce excess CO<sub>2</sub>-eq emissions and were treated as a fixed cost. The net return to fixed costs (NRF) was determined at different prices per tonne CO<sub>2</sub>-eq: a= \$0.00; b= \$5.00; c= \$22.35; d= \$44.70.

#### RESULTS

#### **Precipitation**

Adequate precipitation preceded planting at all sites in 2007 (Figure 1). The lack of midsummer precipitation in 2007 produced visual symptoms of drought stress at all sites. Drought stress was particularly an issue at KBS and Mason. Planting at KBS in 2007 was slightly late (22 May) for the region and was followed by a 50 day period of very dry conditions. In 2008, midsummer precipitation was again limiting at KBS and also at Stockbridge, where visual symptoms of severe drought stress were observed (Figure 2).

#### Soil Nitrogen

The application of N fertilizer increased soil inorganic nitrogen concentrations at all sites in all years and generally within 11 days (Table 3). Increases in soil inorganic nitrogen were proportional to the amount of N applied. Soil inorganic nitrogen concentration tended to be higher in 2008 at all sites.

## Daily N<sub>2</sub>O Flux

The relationship of daily N<sub>2</sub>O flux (log transformed) to inorganic soil N for all sites is shown in Figure 3. The 0 kg N ha<sup>-1</sup> treatment tended to have the least amounts of inorganic soil N and lowest daily N<sub>2</sub>O flux in both years. The 135 and 225 kg N ha<sup>-1</sup> treatments tended to have greater amounts of inorganic soil N. However, not all data correspond to a proportionally greater flux. In 2007, the difference between the 135 and 225 kg N ha<sup>-1</sup> treatments is not clear. In 2008, the 225 kg N ha<sup>-1</sup> treatment shows slightly greater daily flux with increasing inorganic soil N compared with the 135 kg N ha<sup>-1</sup> treatment. The relationship of daily N<sub>2</sub>O flux to inorganic soil N is somewhat poor. Fertilizer N application clearly increased inorganic soil N amounts. Increased amounts of

inorganic soil N, however, did not always produce increases daily flux. Figure 3 shows a range of daily flux is likely to occur in response to N application.

A treatment effect of increased daily N<sub>2</sub>O flux could be detected at each location within a week of fertilizer application (Figures 4 and 5). Daily N<sub>2</sub>O fluxes rapidly increased after fertilizer application and remained well above the pre-fertilizer background flux of less than 4 g N<sub>2</sub>O ha<sup>-1</sup> day<sup>-1</sup> for up to 55 days. The largest increases in daily N<sub>2</sub>O 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. In 2007, the daily  $N_2O$  flux for the 135 and 225 kg N ha<sup>-1</sup> treatments remained greater than the control treatment for a period of 25-55 days. In 2007 at KBS and Mason, increased daily  $N_2O$  flux continued for 25 and 42 days, respectively. In 2007 at Fairgrove and Reese, increased daily flux continued for 55 and 51 days, respectively.

Daily N<sub>2</sub>O fluxes for the 135 and 225 kg N ha<sup>-1</sup> treatments returned to rates similar to the control (<4 g N<sub>2</sub>O ha<sup>-1</sup> day<sup>-1</sup>) around day of year (DOY) 170 on 19 June for all sites in 2007. In 2008, the return to background rates of daily N<sub>2</sub>O flux differed by site. In 2008 at KBS and Stockbridge, daily N<sub>2</sub>O flux for the 135 and 225 kg N ha<sup>-1</sup> treatments returned to rates similar to the control treatment (<4 g N<sub>2</sub>O ha<sup>-1</sup> day<sup>-1</sup>) around DOY 193 (11 July) and DOY 203 (21 July), respectively. 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. The period of increased flux lasted 47 days at the relatively late-planted sites KBS and Stockbridge in 2008. At the sites planted earlier in 2008, Fairgrove and Reese, the period of increased flux lasted 54 days.

#### **Cumulative Emissions**

The largest contribution to cumulative N<sub>2</sub>O emissions occurred during 4 to 8 weeks after fertilizer application (Figures 6 and 7). After this period, the rate of increase in cumulative N<sub>2</sub>O emissions slowed and approached a plateau near the middle of the growing season in both years. Mid-season cumulative N<sub>2</sub>O emissions were similar in magnitude to end of season cumulative N<sub>2</sub>O emissions. Using the 225 kg N ha<sup>-1</sup> treatment as an example, between 61% and 95% of cumulative N<sub>2</sub>O emissions occurred within 8 weeks of fertilizer application when daily flux was greater than 4 g N<sub>2</sub>O-N ha<sup>-1</sup> day<sup>-1</sup> (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 N<sub>2</sub>O Flux Models

Both linear and nonlinear increases in average daily  $N_2O$  fluxes were observed depending on the site and year (Figure 8 and 9). Curve fitting for the average daily flux was performed separately for each site year to describe the response at the individual site level. Average daily N<sub>2</sub>O fluxes were well described at each site by either a linear or an exponential model ( $R^2 = 0.67$  to 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. Erroneously, a late season glyphosate application (24 July 2008) was made at Stockbridge to non-tolerant corn. 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 prior to 24 July 2008 to control for the possibility of altered emissions. Yield, however, was negatively affected.

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<sub>2</sub>O 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<sub>2</sub>O. At Mason in 2007, the exponential and linear models described the average daily N<sub>2</sub>O response equally well ( $R^2$ = 0.75) and a distinct curve type could not be assigned.

Variation in average daily  $N_2O$  flux was greatest at the 180 and 225 kg N ha<sup>-1</sup> fertilizer rates (Figure 10A). Relative  $N_2O$  flux, scaled to the highest average daily flux plot within a site (Figure 10B), tended to equalize this variation. For both observed and relative fluxes, the exponential model best described the relationship between  $N_2O$  flux

and N fertilizer across all sites (Figure 11). For the average daily N<sub>2</sub>O flux, the  $R^2$  for the linear model was 0.41 compared with 0.79 for the exponential model. For the relative N<sub>2</sub>O 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<sub>2</sub>O flux, the relative flux improved confidence in the prediction of N<sub>2</sub>O flux at N rates greater than 135 kg N ha<sup>-1</sup> (Figure 11).

The relative N<sub>2</sub>O flux model predictions for the 6 tested N fertilizer rates (0-225 kg N ha<sup>-1</sup>) were used to back-calculate a derived annual flux (kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>). The derived annual flux ranged from 1.6 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup> ( $\pm$ 0.3 SE) for the 0 kg N ha<sup>-1</sup> treatment, to 6.9 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup> ( $\pm$ 1.1 SE) for the 225 kg N ha<sup>-1</sup> treatment (Figure 12A). Compared with the observed values, the derived annual flux provided a more conservative estimate of N<sub>2</sub>O losses as N fertilizer rate increased, and resulted in lower standard error.

The difference between the derived fluxes and the IPCC estimated fluxes is insignificant at N rates up to 90 kg N ha<sup>-1</sup>, but at higher N rates the difference is as great as 50% (Figure 12A). Figure 12B shows this difference more clearly, wherein emission factor estimates of fertilizer-induced emissions increased with increasing N rates for both the observed and the derived fluxes. Derived emission factors ranged from 1.2% to 2.4%; while observed emission factors ranged from 1.4% to 3.4%. Similar to the annual flux, the standard error for the observed emission factor increased with increasing N rate.

The 1% IPCC emission factor significantly underestimated the observed and the derived emission factors, especially at the 180 and 225 kg N ha<sup>-1</sup> treatments.

Yield

Across all sites corn grain yields in 2007 averaged 6.0 Mg ha<sup>-1</sup> with a range of 3.5 to 8.6 Mg ha<sup>-1</sup>, and in 2008 (not including Stockbridge) yields averaged 8.0 Mg ha<sup>-1</sup> with a range from 3.1 to 14.0 Mg ha<sup>-1</sup> (Table 2). With the exception of KBS in 2007, yield significantly (P > 0.1) responded to N fertilizer. At KBS in 2007, late planting date and drought stress contributed to limited yield. For N responsive sites, model estimates were made for the maximum yield and corresponding AONR. Maximum yields occurred at 138 kg N ha<sup>-1</sup> or less in 2007. With one exception in 2008, maximum yield was achieved at 175 kg N ha<sup>-1</sup> or less. The exception was Reese in 2008, where the AONR of 238 kg N ha<sup>-1</sup> was greater than the highest N rate tested in the fertilizer gradient.

For N responsive sites, the maximum return to N (MRTN) rate (Sawyer et al., 2006) was 154 kg N ha<sup>-1</sup>, which corresponds to an average yield of 8.3 Mg ha<sup>-1</sup>. Using the  $\pm$  \$1 of the MRTN approach, the average MRTN range is 135-172 kg N ha<sup>-1</sup> yielding 8.2-8.4 Mg ha<sup>-1</sup>.

The economic benefit of a carbon offset is greatest within the MRTN range of 135-172 kg N ha<sup>-1</sup> (Table 4). At the emissions baseline (172 kg N ha<sup>-1</sup>), NRF was equal across all carbon prices per tonne CO<sub>2</sub>-eq (0.00-44.70). The MRTN (154 kg N ha<sup>-1</sup>)

provided the greatest economic return with higher CO<sub>2</sub>-eq prices being the most profitable.

#### DISCUSSION

Nitrous oxide responded significantly (P < 0.05) to increasing N rate at all sites in 2007 and 2008 as indicated by the model for observed flux. We observed both linear and nonlinear N<sub>2</sub>O responses to N depending on the site and year. Across all site-years, a nonlinear response curve best described increases in N<sub>2</sub>O with increasing N rate.

Authors of previous N rate field studies describe the N<sub>2</sub>O response to N rate as either linear or nonlinear (Halvorson et al., 2008; Henault et al., 1998; Ma et al., 2009; McSwiney and Robertson, 2005). However, for most studies where a linear response was described only 2-3 fertilizer N rates were examined (Bouwman, 1996; Stehfest and Bouwman, 2006). At an irrigated site in Colorado, for example, Mosier et al. (2006) and Halvorson et al. (2008) examined a 3-point fertilizer gradient (0, 134, and 202 or 224 kg N ha<sup>-1</sup>) under conventional-till and no-till continuous corn. They found linear increases in N<sub>2</sub>O in response to N rate. Fertilizer gradients with fewer than 5 rates limit the power over which nonlinear responses can be detected. McSwiney and Robertson (2005) showed nonlinearity for a 9-point fertilizer gradient (0, 34, 67, 101, 134, 168, 202, 246, and 291 kg N ha<sup>-1</sup>) in a rainfed continuous corn system in Michigan over a 3-year period. Others have described nonlinear N<sub>2</sub>O flux (Bouwman et al., 2002a; Grant et al., 2006; Ma et al., 2009) or found evidence for large increases in N<sub>2</sub>O flux at N rates above the

crop demand (Bouwman et al., 2002b; Chantigny et al., 1998; Sehy et al., 2003; Zebarth et al., 2008).

Using a nearby field at the same site (KBS), our results were in agreement with those of McSwiney and Robertson (2005) and provided further support for the nonlinear N<sub>2</sub>O response to N. The analysis of McSwiney and Robertson (2005) did not include formal regression and comparison of a linear to a nonlinear response. In our study and regression analysis, Kellogg Biological Station (KBS) was best described by a nonlinear N<sub>2</sub>O response curve in both 2007 and 2008. Linear N<sub>2</sub>O responses were observed at Reese in both years and at Fairgrove in 2008. Cumulative emissions and the rate of increase in average daily flux with increasing N rate tended to be low at Reese and Fairgrove in 2008. Conversely, cumulative emissions and the rate of increase in average daily flux with increasing N rate tended to be the greatest at Stockbridge, which was best described by a nonlinear N<sub>2</sub>O response curve ( $R^2 = 0.99$ ). The later planting date (24) May 2008; DOY 145), warmer soil temperatures, and double the amount of SOM (~22 g kg<sup>-1</sup>) at Stockbridge may have played a role in the trend of greater cumulative emissions. Ideally, Stockbridge and Mason would have been studied in both years to provide more evidence of the typical  $N_2O$  response curve at these sites. Despite the overall result of a nonlinear trend, N<sub>2</sub>O flux did not respond nonlinearly at all sites in all years.

Previous results at KBS and our work support that at KBS the N<sub>2</sub>O response to N rate is nonlinear. Conversely, our results suggest that N<sub>2</sub>O at Reese increases linearly to N. Concluding Reese would respond linearly in future years is contradicted by the observation of nonlinear flux observed for the same soil series at the nearby Fairgrove site in 2007.

### Nonlinear overall response

The overall trend for annual N<sub>2</sub>O flux increased nonlinearly with increasing N. Compared with the 90 kg N ha<sup>-1</sup> treatment (3.0 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>), the observed annual flux for the 135, 180, and 225 kg N ha<sup>-1</sup> treatments increased by 47%, 110%, and 213%, respectively. The nonlinear trend was further supported by the improved fit of the nonlinear model for the observed annual flux and the relative flux. Increased variance in N<sub>2</sub>O flux at the high N rates resulted in poor confidence for model predictions at the highest N rates. Scaling the observed flux to the highest flux plot within each site reduced the variance and improved model confidence. The overall trends for all nonlinear models were similar to the observed fluxes, with the largest increases in N<sub>2</sub>O flux occurring at N rates of 135 kg N ha<sup>-1</sup> and greater. The different measures of annual flux were similar in magnitude and standard error up to 90 kg N ha<sup>-1</sup>. Above this N rate, the annual flux measures differed in magnitude. The model for observed flux provided the most conservative estimate (1.6-6.6 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>).

Nitrous oxide measurements are often conducted at a single site that is studied more intensively than the sites in our study. One goal of our study was to evaluate multiple sites and describe the overall trends in N<sub>2</sub>O emissions. Intensive monitoring of environmental conditions and soil status along with sub-daily N<sub>2</sub>O measurements are helpful for providing data to test process-based  $N_2O$  emission models. With regards to predicting  $N_2O$  emissions, many process-based models lack empirical confirmation for multiple sites. However, such modeling efforts help to identify important physical and biological mechanisms responsible for  $N_2O$  emission.

Both linear and nonlinear process-based models have been proposed. For a barley site, the DeNitrification DeComposition (DNDC) model predicted linear increases but underestimated N<sub>2</sub>O flux by 24% for fertilized plots (70-160 kg N ha<sup>-1</sup>) and was poorly correlated with the control plots (Abdalla et al., 2009). A process-based model proposed by Schmid et al. (2001) for two grassland sites predicted linear increases in N<sub>2</sub>O for N rates up to 200 kg N ha<sup>-1</sup> above which the response was nonlinear. In a similar model simulation that included factors for corn N uptake, N<sub>2</sub>O flux increased nonlinearly, with the largest increases at N rates above the crop N demand (Grant et al., 2006). Nonlinear increases in N<sub>2</sub>O flux at N rates above the crop demand has also been proposed for a multiple regression model fitted to the large number (846) of independent field measurements from many sites (Bouwman et al., 2002a, 2002b). Our results are in agreement and support the occurrence of increased N<sub>2</sub>O flux at excessive N rates.

Nitrogen rates in excess of crop demand results in large increases in  $NO_3^$ leaching and may similarly result in large increases in N<sub>2</sub>O flux (Chichester, 1977; Gehl et al., 2005; Stanford, 1973). At sites where yield responded to N, maximum corn yield (8.3 Mg ha<sup>-1</sup>) on average was achieved at an AONR of 167 kg N ha<sup>-1</sup>. For Reese, in 2008 maximum yield may not have been achieved at the highest N rate tested. The resulting estimate for the AONR (238 kg N ha<sup>-1</sup>) was much higher than those for the other sites.

The largest increases in N<sub>2</sub>O flux occurred above 135 kg N ha<sup>-1</sup> for all sites. The N rate is slightly less than the AONR but within the range for the MRTN (135-173 kg N ha<sup>-1</sup>). Reducing N rates to 135 kg N ha<sup>-1</sup>, compared with 180 and 225 kg N ha<sup>-1</sup> would have resulted in a reduction of N<sub>2</sub>O ranging from 32% (1.2 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>) to 75% (2.8 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>) for the observed flux model and 44% (2.0 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>) to 115% (5.1 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup>) for the observed average flux. In addition to large increases in N<sub>2</sub>O, the high N rates marginally increased yield. The 180 and 225 kg N ha<sup>-1</sup> rates compared to the 135 kg N<sup>-1</sup> rate yielded 2% (8.2 Mg ha<sup>-1</sup>) and 6% more (8.5 Mg ha<sup>-1</sup>), respectively. The small increases in yield did not cover the expense of fertilizer rates greater than the MRTN of 154 kg N ha<sup>-1</sup>. For N rates greater than the MRTN, there is a loss of potential profit at the cost of environmental risk.

### **Emission Factors**

Nitrous oxide emission factors increased with increasing N rate and were within the ranges previously reported for similar studies. Ranges for our emission factors were 1.4-3.4% for the observed flux averages and 1.2-2.2% for the model of the observed flux averages. Compared with the range of 0-7% reported in a survey of agricultural soils, the emission factors in our study were on the lower end of the range (Bouwman, 1996). The emission factors from our study were also less than the 2-7% range reported by McSwiney and Robertson (2005) for continuous corn receiving 0-291 kg N ha<sup>-1</sup>. Studies were included in the survey by Bouwman (1996) where N rates were well above those in our study. The smaller maximum N rate of 225 kg N ha<sup>-1</sup> in our study may explain the observation of lower emission factors. Sites which tended to have low N<sub>2</sub>O flux and responded linearly to N would also reduce the magnitude of the emission factors.

The IPCC (2006) default emission factor (1%) greatly underestimated all measures of annual flux and emission factors (Figure 12). Intended as a method for calculating national budgets for N<sub>2</sub>O on a continental scale, emission factors provide an accessible cross-site reference to quantify fertilizer induced emissions (Bouwman, 1996; Eichner, 1990). Emission factors account for very few environmental or management factors and more complex methods for generating N<sub>2</sub>O budgets at the landscape scale have been proposed (Bouwman et al., 2002b). However, management specific emission factors may be appropriate at a county, state or regional scale depending on the available data. Confirmation of our results in systems other than corn and further investigation of site-specific N<sub>2</sub>O response curves will aid the creation of a regional based emission factor.

## **Conclusions**

Our results suggest a nonlinear  $N_2O$  response to N rate that may be typical for corn-soybean rotations in the US Midwest. Using the IPCC default 1% emission factor

greatly underestimated N<sub>2</sub>O emissions (IPCC, 2006). Linear and nonlinear increases in N<sub>2</sub>O were observed depending on the study locations and year, but nonlinear response models best represented the overall N2O response to N fertilizer across all site-years. A nonlinear trend in observed N<sub>2</sub>O flux was also suggested by the 43% and 114% increases at 180 and 225 kg N ha<sup>-1</sup>, respectively, over the 135 kg N ha<sup>-1</sup> (4.4 kg N<sub>2</sub>O-N ha<sup>-1</sup>) treatment. The 180 and 225 kg N ha<sup>-1</sup> rates were greater than both the AONR (167 kg N  $ha^{-1}$ ) or the MRTN (154 kg N  $ha^{-1}$ ) required to achieve maximum corn grain yield (8.3) Mg ha<sup>-1</sup>). Little increase in yield could be expected at N rates greater than 135 kg N ha<sup>-1</sup> <sup>1</sup>, however, large increases in  $N_2O$  resulted at N rates above the crop demand. The relationship of yield to N<sub>2</sub>O suggests that with increasing N rate, yield reaches a plateau just as the N<sub>2</sub>O response sharply increases. Applying N fertilizer slightly below the yield plateau can generate profitable and environmentally significant carbon offsets. Economic return was greatest at the MRTN and most profitable when N rate reductions were credited with carbon offsets (CO<sub>2</sub>-eq). A reduction in N fertilizer below the MRTN range would require higher CO<sub>2</sub>-eq prices to compensate for a possible corn yield penalty.

## **TABLES AND FIGURES**

Site	SOM†	pН	Bray 1-P	Extractable K	CEC‡
	g kg <sup>-1</sup>		m	g kg <sup>-1</sup>	cmol(+) kg <sup>-1</sup>
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

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

† Soil organic matter

‡ Cation exchange capacity

	2007					2008	
	KBS	Mason	Fairgrove	Reese	KBS	Fairgrove	Reese
N Rate			_			_	
kg ha <sup>-1</sup>				Mg ha <sup>-1</sup>			
0	3.7	5.4	5.3	3.5	3.1	5.2	4.1
45	4.0	5.8	7.0	5.7	3.9	8.9	7.9
90	3.6	6.5	7.4	6.5	4.5	10.9	10.2
135	3.7	6.7	8.0	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	12.6	14.0
Max. Yield†	NS‡	6.8	8.0	8.3	4.0	11.5	12.6
AONR§	NS	137	138	129	104	175	238

Table 2. Corn grain yield as a function of N rate and the results from regression analysis of yield response to N for each site.

<sup>†</sup> Maximum yield at each location determined by either a quadratic, quadratic plateau, or linear plateau model fit of the data

<sup>‡</sup> Not significant (no yield response to N fertilizer due to drought)

Agronomic optimum N rate (kg N ha<sup>-1</sup>)

		2007				2008		
	KBS	Mason	Fairgrove	Reese	KBS	Stockbridge	Fairgrove	Reese
N Rate				Soil N (NO3	$- + NH_4^+)$			
kg ha <sup>-1</sup>				mg N	kg <sup>-1</sup>			
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)
†0- to 10-c	m dept							

Table 3. Soil inorganic nitrogen in response to N rate approximately 11 days after fertilizer application. Values are means  $(\pm SE)$  for 3 or 4 (n= 12-16 plots) sampling events representing an approximately 30 day period.

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Table 4. Economic return and value of CO<sub>2</sub>-equivalent (CO<sub>2</sub>-eq) offsets relative to a baseline of 172 kg N ha<sup>-1</sup>. The shaded portion represents values within the maximum return to N range (0.10 price ratio). Fixed costs included N fertilizer ( $$0.18 \text{ kg}^{-1}$ ) and grain drying and transportation ( $$19.67 \text{ Mg}^{-1}$ ).

N Rate	NRF-a†	NRF-b	NRF-c	NRF-d
kg ha <sup>-1</sup>		\$	ha <sup>-1</sup>	
0	634	639	655	675
45	864	868	881	898
90	1020	1023	1033	1045
135	1103	1104	1109	1116
154	1116	1117	1119	1122
172	1110	1110	1110	1110
180	1109	1108‡	1107	1105
225	1100	1097	1088	1075

† Net return to fixed costs under different prices per tonne  $CO_2$ -eq: a= \$0.00; b= \$5.00; c= \$22.35; d= \$44.70

‡ Emissions at N rates above the baseline were treated as a fixed cost



Figure 1. 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 2. 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 3. Daily N<sub>2</sub>O flux during the growing season as a function of soil inorganic N in the upper 4 cm of the soil. For clarity, only the 0, 135 and 225 kg N ha<sup>-1</sup> treatments are shown in Figure 4 and 5. The other treatments exhibit the tendency of the treatments shown.



application (0- 225 kg N ha<sup>-1</sup>) Figure 4 and 5. The other treatments exhibit the tendency of those shown. Figure 4. Daily  $N_2O$  flux during the 2007 growing season for 4 corn sites in Michigan. Data collection began prior to fertilizer ) and continued until harvest. For clarity, only the 0, 135 and 225 kg N ha<sup>-1</sup> treatments are shown in



application (0- 225 kg N ha<sup>-1</sup>) Figure 4 and 5. The other treatments exhibit the tendency of those shown. Figure 5. Daily N<sub>2</sub>O flux during the 2008 growing season for 4 corn sites in Michigan. Data collection began prior to fertilizer ) and continued until harvest. For clarity, only the 0, 135 and 225 kg N ha<sup>-1</sup> treatments are shown in













shown for the best fit model using the treatment averages from each site. Error bars represent standard error of the treatment averages









Figure 10. Nitrous oxide flux across the sampling period for 8 site years representing 5 locations in 2007 and 2008. Each data point represents the value of 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 plot for each site.



Figure 11. Results from regression analysis using site averages for each N rate. (A) The observed average daily flux was modeled and rescaled to yearly flux for comparison. (B) The 95% confidence intervals are shown only for the observed and relative flux model predictions. The relative flux model was used to calculate the derived flux using model predictions and the background flux at each site to back-calculate a scaled value (kg  $N_2O-N$  ha<sup>-1</sup> yr<sup>-1</sup>). Regression for both the relative and derived daily flux was performed on 48 data points representing site averages at each N level.



Figure 12. Comparison of annual flux (A) and emission factors (B) for the yearly loss of  $N_2O$ . Annual flux for the IPCC estimate was calculated using the control for the observed site averages and the 1% emission factor. 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 predictions. The error bars for the derived model and observed flux data represent the standard error of the standard error err



Figure 13. Annual N<sub>2</sub>O flux as compared to grain yield at the maximum return to N rate (MRTN) of 153 kg N ha<sup>-1</sup>. The arrow denotes the range of \$2.47 ha<sup>-1</sup> above and below the MRTN (135 to 172 kg N ha<sup>-1</sup>) corresponding to 8.2 to 8.4 Mg grain ha<sup>-1</sup>. Yield averages were calculated using the optimized yield response curve for each site at the corresponding N level. The MRTN was calculated at a fertilizer N to corn grain price ratio of 0.10. Yield was not significantly affected by N rate at KBS 2007 and Stockbridge 2008 (see text) and therefore these sites were not included in the yield analysis. Error bars represent the standard error of the observed model predictions.



Figure 14. Net return to fixed costs (NRF) under different prices per tonne CO<sub>2</sub>equivalent: NRF-a= 0.00; NRF-b= 5.00; NRF-c= 22.35; NRF-d= 44.70. The high range of the maximum return to N rate (172 kg N ha<sup>-1</sup>) was used as an emissions baseline. Nitrogen rates below the baseline generate a carbon offset.

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