Nitrogen Oxide and Methane Emissions under Varying Tillage and Fertilizer Management

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ABSTRACT

Comprehensive assessment of the total greenhouse gas (GHG) budget of reduced agriculture systems must consider emissions of nitrous oxide (N\textsubscript{2}O) and methane (CH\textsubscript{4}), each of which have higher global warming potentials than carbon dioxide (CO\textsubscript{2}). Tillage intensity may also impact nitric oxide (NO) emissions, which can have various environmental and agronomic impacts. In 2003 and 2004, we used chambers to measure N\textsubscript{2}O, CH\textsubscript{4}, and NO fluxes from plots that had been managed under differing tillage intensity since 1991. The effect of tillage on non-CO\textsubscript{2} GHG emissions varied, in both magnitude and direction, depending on fertilizer practices. Emissions of N\textsubscript{2}O following broadcast urea (BU) application were higher under no till (NT) and conservation tillage (CT) compared to conventional tillage (CT). In contrast, following anhydrous ammonia (AA) injection, N\textsubscript{2}O emissions were higher under CT and CT compared to NT. Emissions following surface urea ammonium nitrate (UAN) application did not vary with tillage. Total growing season non-CO\textsubscript{2} GHG emissions were equivalent to CO\textsubscript{2} emissions of 0.15 to 1.9 Mg CO\textsubscript{2} ha\textsuperscript{-1} yr\textsuperscript{-1} or 0.04 to 0.53 Mg soil-C ha\textsuperscript{-1} yr\textsuperscript{-1}. Emissions of N\textsubscript{2}O from AA-amended plots were two to four times greater than UAN- and BU-amended plots. Total NO + N\textsubscript{2}O losses in the UAN treatment were approximately 50% lower than AA and BU. This study demonstrates that N\textsubscript{2}O emissions can represent a substantial component of the total GHG budget of reduced tillage systems, and that interactions between fertilizer and tillage practices can be important in controlling non-CO\textsubscript{2} GHG emissions.

It has been widely stated that conversion from conventional to reduced tillage agriculture could have a favorable impact on atmospheric concentrations of greenhouse gases (GHGs) by promoting the storage of soil carbon (C) (Lal et al., 1998; West and Post, 2002). However, emissions of GHGs other than carbon dioxide (CO\textsubscript{2}), namely nitrous oxide (N\textsubscript{2}O) and methane (CH\textsubscript{4}), must also be considered (Six et al., 2004). Because N\textsubscript{2}O and CH\textsubscript{4} have global warming potentials (GWP) that are 297 and 23 times, respectively, greater than CO\textsubscript{2}, the total GHG budget of any ecosystem is more sensitive to changes in their emissions than to changes in soil CO\textsubscript{2} emissions (Intergovernmental Panel on Climate Change, 2001). While reduced tillage may result in the accumulation of C compared to conventional tillage, if the practice also results in increased N\textsubscript{2}O and/or CH\textsubscript{4} emissions, the benefits of increased soil C in relation to GHGs will be offset to an extent that depends on the magnitude of these emissions (Robertson et al., 2000).

Model projections suggest that the north central region of the United States contributes 25 to 33% of soil N\textsubscript{2}O emissions generated by agriculture within the entire United States (Li et al., 1996; Mummey et al., 1998). However, very limited information is available regarding the effects of tillage, or other management practices, on non-CO\textsubscript{2} GHGs within this region (Johnson et al., 2005). Goodroad et al. (1984) found increased growing season N\textsubscript{2}O fluxes from corn under reduced tillage in Wisconsin compared to plowed plots. Similarly, Robertson et al. (2000) found that N\textsubscript{2}O emissions under no till were slightly higher than a conventional system, and represented a small offset (approximately 3.6%) to soil C gains over 10 yr. Except for the accumulation of soil C that occurred under no till, N\textsubscript{2}O emissions represented the greatest single component of the GHG budget (Robertson et al., 2000). In contrast to these studies, Jacinthe and Dick (1997) and Kessavalou et al. (1998) reported higher N\textsubscript{2}O emissions under conventional tillage compared to no till plots in Ohio and Nebraska, respectively. More recently, Six et al. (2004) concluded that long-term tillage effects on total GHG emissions depend both on climatic regime and duration of the adoption period. There is little consensus within the central United States, or anywhere else, whether reduced tillage leads to increased or decreased N\textsubscript{2}O emissions and what the most important factors are in regulating the magnitude, or direction, of the effect.

There is also little information regarding tillage effects on emissions of nitric oxide (NO) gas. Soil NO emissions can significantly affect tropospheric ozone (O\textsubscript{3}) production, particularly in rural regions (National Research Council, 1992). Ozone is an important GHG, although estimation of its GWP is highly uncertain (Albritton et al., 1995). Perhaps more importantly, O\textsubscript{3} phytotoxicity results in more than $2 billion per year in crop damage in the United States (Delucchi et al., 1996).

Very few studies have examined long-term tillage effects simultaneously with the effects of fertilizer management, the latter of which can strongly influence both NO and N\textsubscript{2}O emissions (Amos et al., 2005; Mosier et al., 1998; Veldkamp and Keller, 1997). Emissions of NO can also represent substantial losses of fertilizer N in some cases (Veldkamp and Keller, 1997). The objective...
of the current study was to examine the impact of long-term tillage management, together with fertilizer practices, on N₂O, CH₄, and NO gas emissions within a corn (Zea mays L.)–soybean [Glycine max (L.) Merr.] rotation in southeastern Minnesota.

**MATERIALS AND METHODS**

**Site Description and Experimental Design**

The site (Fig. 1) is located at the University of Minnesota’s Research and Outreach Station in Rosemount, MN (44°45’ N, 93°04’ W). Soil at the site was a Waukegan silt loam (fine-silty over skeletal mixed, superactive, mesic Typic Hapludoll) containing 22% sand, 55% silt, and 23% clay. Annual 30-yr mean precipitation is 879 mm, and annual mean temperature is 6.4°C. Since 1991, plots planted in a corn–soybean rotation were maintained under the following tillage treatments: (i) conventional tillage (CT) employing fall moldboard plowing following corn, fall chisel plowing or disk ripping following soybean, with spring preplant cultivation before both corn and soybean; (ii) conservation tillage (CST) employing fall chisel plowing or disk ripping following corn, no fall plowing following soybean, with spring cultivation before soybean only; and (iii) no till (NT) employing no fall tillage or spring cultivation (Hansmeyer et al., 1997). Plots measured 27.4 m (36 corn rows) wide by 61 m long. In 2003 and 2004, we made measurements in nine plots planted in corn following soybean, that is, a different set of plots were studied each year (Fig. 1). Each set of nine plots was comprised of three replicate plots subjected to each tillage treatment. In 2003, 120 kg N ha⁻¹ as broadcast urea (BU) was applied to all plots when corn seedlings were approximately 20 cm high (23 June) in keeping with their daily mean values.

**Trace Gas Fluxes**

Static chambers were used to measure soil-to-atmosphere fluxes of N₂O and CH₄. Rectangular stainless steel (20 ga) chamber bases measuring 53 × 32 × 8.6 cm deep with a 1.9-cm-wide horizontal flange on the top end were inserted into the soil, so that the top was nearly flush with the soil surface. Bases remained in the soil for the entire season, except when removal and reinsertion were required by field operations. Vented stainless steel (20 ga) chamber tops (50 × 29 × 10.2 cm high) were designed with a 1.9-cm horizontal edge lined with ethylene propylene diene terpolymer (EPDM) rubber gasket material to aid sealing onto the base flange. During measurement, chamber tops were secured to bases with metal clamps, typically for 60 min. Outer surfaces of the chambers were covered with reflective insulating material (Reflectix, Markleville, IN). Using thermocouples, we observed deviations of <2°C between air and soil temperatures (at 1- and 5-cm depths) measured inside versus outside chambers over 1-h periods under clear conditions during mid-day early in the growing season (1 July). Chamber gas samples were collected at regular intervals of (typically) 0, 30, and 60 min by inserting the needle of a 12-mL polypropylene (Monoject) syringe through a septum in the chamber top and slowly withdrawing 9 to 12 mL. Samples were immediately transferred to 9-mL glass vials sealed with butyl rubber septa (Alltech, Deerfield, IL). We used either pre-evacuated vials, or un-evacuated vials containing “ambient” (lab) air. In the latter case, sample concentrations were adjusted for dilution with ambient air concentrations, as determined in four replicate ambient vials analyzed with each set of sample vials. We found excellent agreement (within 5%) in flux calculations between the two methods. Fluxes were generally measured between 1100 and 1400 h local time when soil temperatures were expected to be close to their daily mean values.

Gas samples were analyzed within 3 d of collection by gas chromatography (GC) using a headspace autosampler (Teledyne Tekmar, Mason, OH). The autosampler was modified by replacing the factory-supplied sample valve with a 14-port valve (Valco Instruments, Houston, TX), which permitted separate sample loops to be filled simultaneously from the same vial. Separate sample lines went to two different GCs (5890; Hewlett-Packard, Palo Alto, CA), one equipped with a flame ionization detector for CH₄ and the other equipped with an electron capture detector for NO. The system was calibrated using analytical grade standards (Scott Specialty Gases, Plumsteadville, PA). Gas fluxes were calculated from the rate of change in chamber concentration, chamber volume, and soil surface area using the formulation of Hutchinson and Mosier (1981). Chamber gas concentrations were converted from molar mixing ratio units (e.g., ppm) determined by GC analysis to mass per volume units (e.g., ng N m⁻²) assuming ideal gas relations using air temperatures during sampling.

Dynamic chamber methods were used to measure soil-to-atmosphere fluxes of NO. A chamber top of identical construction as above was also equipped with inlet and outlet ports, each connected to 10-cm-long perforated gas manifolds inside of the chamber. The ports were connected to a chemiluminescent NO analyzer (LMA 3D; Unisearch Associates, Concord, ON, Canada) via PTFE tubing encased within opaque plastic tubing. Using a vacuum pump inside the analyzer, chamber air was first passed through CrO₃-coated diatomaceous media (Unisearch) to convert NO to nitrogen dioxide (NO₂) before entering the analyzer which detects NO₂. The air stream was continuously recirculated through the chamber and analyzer at 0.06 m³ h⁻¹ (1 L min⁻¹) for 3 to 5 min. Air leaving the analyzer was passed through KMnO₄–coated po-
rous silica (Purafil, Doraville, GA) to ensure complete removal of NO\textsubscript{x}. Concentrations of NO were manually recorded every 30 s. Flux was calculated from the linear rate of change in concentration accounting for NO scrubbing (Venterea et al., 2003). The gas flow rate was low relative to chamber volume (approximately 16 L), so that scrubbing itself did not result in a net decrease in NO concentrations over time except when fluxes were $<2$ μg NO-N m\textsuperscript{-2} h\textsuperscript{-1}.

In 2003, chamber bases were installed in both inter-row and row locations (one in each location per plot for a total of 18 bases in nine plots). Bases in inter-row locations were centered between rows with long sides perpendicular to the row. Bases in row locations were placed parallel with and centered on the row. Flux measurements from inter-row locations began on 28 May and continued until 20 November. Flux measurements from row locations began on 28 May and were terminated on 3 July. Due to instrument problems, CH\textsubscript{4} fluxes were not obtained for the first five sampling events in 2003. Corn was harvested on 14 October, and fall tillage occurred on 3 November. Flux measurements from row locations were also made post-harvest through 4 November.

In 2004, flux measurements were made primarily from inter-row locations using one chamber in each of the 27 subplots. After 23 June 2004, additional measurements were made using nine chambers installed in row locations in the AA subplots only. Measurements of N\textsubscript{2}O and CH\textsubscript{4} fluxes began on 26 April (14 d before planting) and continued until 23 November. Corn was harvested on 10 November and fall tillage occurred on 17 November. Measurement of NO fluxes occurred during 5 May to 5 August.

**Ancillary Variables**

Soil temperature was measured during chamber deployment periods using soil temperature probes (Fisher, Hampton, NH) inserted to 1- and 5-cm depths within 1 m of each chamber. Air temperature was measured using a thermocouple placed in the shade of the corn canopy when present. Air temperature and daily precipitation data were also obtained from a weather station 1 km from the plots. Soil water content was determined in soils collected within 1 h of each flux measurement period using a steel core sampler (1.83-cm i.d.). Two or three cores from each plot were combined before drying for 12 to 24 h at 105°C. In 2003, samples were collected over the 0- to 10-cm depth. In 2004, samples were collected over the 0- to 10- and 10- to 20-cm depths. Bulk density was determined on 10 June, 15 July, and 17 Sept. 2004 by collecting three 7.6-cm-i.d. × 7.6-cm-long core samples from the inter-row region followed by drying at 105°C. Core samples from AA subplots were analyzed separately, while samples from UAN and BU subplots were pooled. Bulk density values interpolated between sampling dates were used to estimate water-filled pore space (WFPS) in the upper 0 to 10 cm in 2004.

Soil samples were collected periodically for inorganic N analysis. Three or four samples per subplot were collected from the inter-row region over 0 to 10 and 10 to 20 cm (2004 only) using the steel core sampler and transferred to plastic bags. In the AA subplots, samples were taken from the center 5 cm of the inter-row region. Within 48 h of collection, soils were homogenized manually, then extracted in 2 M KCl for 1 h at a soil to liquid ratio of 1:4. After settling for 24 h, extracts were filtered (no. 42; Whatman, Maidstone, UK) and stored (−20°C) until analysis. Filtrate samples were analyzed for ammonium (NH\textsubscript{4})-N and the sum of nitrite (NO\textsubscript{2})-N and nitrate (NO\textsubscript{3})-N using a flow-through injection analyzer (Lachat, Milwaukee, WI).

**Data Analysis and Statistics**

We estimated total integrated gas emissions from each plot or subplot during each growing season assuming that measured fluxes represented mean daily fluxes, and that mean daily fluxes changed linearly between measurements. Fluxes of N\textsubscript{2}O and CH\textsubscript{4} were converted to greenhouse gas units (CO\textsubscript{2} equivalents) using 100-yr horizon GWP\textsubscript{s} (297 and 23, respectively, for N\textsubscript{2}O and CH\textsubscript{4}) (Intergovernmental Panel on Climate Change, 2001). Integrated emission data from 2004 were evaluated by analysis of variance (ANOVA) appropriate to a split-plot design with tillage as the main effect and fertilizer type as the sub-plot effect. Flux data from 2004 were evaluated by ANOVA for split-plot design with multiple observations in time. Integrated emissions from BU plots in 2003 were evaluated by single-factor ANOVA, and flux data were evaluated by ANOVA with multiple observations in time. Means among different treatments were compared using least significant differences (LSD). Least significant difference values were calculated manually using error mean squares obtained by ANOVA or GLM procedures in SAS (SAS Institute, 2001) and critical r-values (Gomez and Gomez, 1984). Untransformed NO, N\textsubscript{2}O, and total GHG equivalents data were non-normally distributed (positively skewed). Preliminary ANOVA using untransformed data indicated that variances increased in proportion to treatment means and that residuals were not normally distributed. Logarithm (base 10) transformation rectified these issues and therefore the reported ANOVA and regression analyses were performed on log-transformed data (this was not required for CH\textsubscript{4} data). Tabulated and plotted data are shown in original units (untransformed) to aid interpretation. Regression analyses were conducted using Statgraphics (Statgraphics, 2001).

**RESULTS**

**Nitrous Oxide and Methane**

Nitrous oxide and CH\textsubscript{4} flux data collected in 2003 and 2004 are shown in Fig. 2, 3, and 4. In 2003, tillage had a significant effect on mean N\textsubscript{2}O flux ($p = 0.048$) and total N\textsubscript{2}O emissions ($p = 0.028$). Integrated emissions from the CsT and NT plots were both significantly higher than CT (Fig. 5a), although the difference in mean fluxes between the NT and CT plots was not significant in 2003 (Table 1). The effect of tillage on N\textsubscript{2}O emissions varied with fertilizer treatment. In 2004, this was reflected in a significant tillage-by-fertilizer interaction effect on mean flux ($p = 0.026$) and integrated emissions ($p = 0.038$). In BU-treated subplots in 2004, mean N\textsubscript{2}O flux and integrated emissions were higher under NT compared to CT, but did not vary significantly between CsT and CT (Table 1, Fig. 5a). In contrast to the BU treatment, N\textsubscript{2}O fluxes in subplots fertilized with AA tended to be lower under NT compared with CsT and CT (Fig. 3c). Mean inter-row N\textsubscript{2}O fluxes and integrated emissions across all measurements in the AA treatment were significantly lower under NT than CsT and CT (Table 1, Fig. 5a). There was no consistent trend with tillage in the urea ammonium nitrate (UAN) subplots (Fig. 3d), resulting in similar mean fluxes (Table 1) and total emissions (Fig. 5a) across tillage treatments. The main effect of tillage across fertilizer treatments was not significant in 2004 ($p > 0.45$). Fertilizer type did have a significant main effect ($p < 0.0001$).
Across all tillage treatments, mean N$_2$O fluxes and integrated emissions from AA plots exceeded those from UAN and BU plots by more than a factor of two (Table 1, Fig. 5a).

In all experiments, N$_2$O fluxes began to increase within 1 to 3 wk following fertilizer application, reached a peak within the next 1 to 2 wk, and then gradually declined (Fig. 2c, 3c, 3d, 3e). The temporal pattern in N$_2$O flux tended to correspond with the accumulation of NO$_3^-$ in the upper 10 to 20 cm (Fig. 2c, 3c, 3d, 3e, Tables 2 and 3). Across sampling dates where both N$_2$O emissions and soil inorganic N levels were measured, N$_2$O flux (log-transformed) was positively correlated with soil NO$_3^-$ in the upper 0 to 20 cm ($p < 0.001$, $r^2 = 0.16$). Concentrations of NH$_4^+$ and NO$_3^-$ were higher in AA subplots compared to the UAN and BU subplots across all measurements and sampling depths in 2004 ($p < 0.004$, Table 3). The only significant difference in inorganic N concentrations due to tillage was within the AA subplots at the 10- to 20-cm depth, where the mean NH$_4^+$ concentration was lower under CT (35 ± 11 mg N kg$^{-1}$) compared to both CsT (73 ± 16 mg N kg$^{-1}$) and NT (81 ± 17 mg N kg$^{-1}$) ($p = 0.031$).

Daily N$_2$O flux was positively correlated with soil temperature (5-cm depth, $p < 0.001$, $r^2 = 0.19$). In the AA and UAN treatments, N$_2$O flux was positively correlated with soil water content at 10 to 20 cm ($r^2 = 0.05$ and 0.06, respectively, $p < 0.001$), while there was no correlation with soil water content or WFPS at 0 to 10 cm. The reverse pattern was found in the BU treatments across both seasons, where there was a correlation of N$_2$O flux with both soil water content and WFPS at 0 to 10 cm ($r^2 = 0.05$, $p < 0.001$) but no correlation at 10 to 20 cm. Multiple regression models incorporating soil moisture and temperature parameters accounted for 51, 33, and 22% of the total variance in N$_2$O flux in the AA, UAN, and BU (2003–2004) treatments, respectively ($p < 0.001$). Across all measurements in 2004, soil water content at both depths was significantly higher under CsT compared to NT and CT, although the differences were small ($\leq$0.01 g H$_2$O g$^{-1}$). In 2003, there were no significant differences in soil water content. Mean WFPS in 2004 tended to be higher under NT (57 and 64% in the AA and UAN/BU subplots, respectively) compared to CT (57 and 61%) and CsT (55 and 62%). Across all measurements in both years, mean soil temperature (at 5 cm) was higher ($p < 0.05$) under CT (16.9°C) compared to NT and CsT (each 16.7°C).

Fig. 2. Environmental variables and gas fluxes during 2003 (mean ± standard error, $n = 3$). (a) Precipitation (cumulative during previous 10 d) and soil water content (0–10 cm), (b) air and soil (5-cm depth) temperatures, (c) N$_2$O fluxes, and (d) CH$_4$ fluxes under conventional (CT), conservation (CsT), and no tillage (NT). Values in parentheses in (c) are mean soil NO$_3^-$ concentrations (mg N kg$^{-1}$) over 0 to 10 cm across tillage treatments. Solid urea fertilizer was broadcast on 23 June.
Following 26 mm of rain that occurred on 20 Aug. 2003, resulting in a dramatic increase in soil water content, fluxes measured the following day were higher than fluxes measured on 15 August (Fig. 2). The magnitude of fluxes on this date were small (<10%) compared to peak fluxes of approximately 300 μg N m⁻² h⁻¹ apparently induced by fertilizer application. In 2004, following rainfall events of 21, 64, and 95 mm occurring on 16 August, 5 September, and 14–15 September, respectively, N₂O fluxes measured 1 to 5 d later displayed...
no significant increase above apparent baseline levels (Fig. 3). We also saw no response in N₂O fluxes measured 20 and 90 h after the addition of 50 mm of simulated rainfall on 4 Sept. 2004 to separate inter-row chamber bases (data not shown). Fluxes of N₂O in CT and CsT plots on the day following fall tillage in 2003 were eight- and fivefold higher, respectively, compared to measurements made 5 d earlier. Further increases were observed in CsT plots 4 d following tillage, although these increases may have also been related to soil temperature dynamics (Fig. 2b, 2c). Similarly, on the day following fall tillage in 2004, N₂O fluxes in CT and CsT plots displayed four- to fivefold increases compared to measurements made 2 to 3 h before tillage. In all cases, fluxes measured within a few days after tillage were small in relation to fluxes measured 3 to 5 wk after fertilizer application.

Significant variations in weather were observed between the 2003 and 2004 growing seasons. In 2004, precipitation during March through October (724 mm) was similar to the 30-yr mean value (738 mm), while precipitation during the same period in 2003 (514 mm) was

![Graph showing total integrated emissions of N₂O and CH₄](image)

**Fig. 5.** Total integrated emissions of (a) N₂O, and (b) CH₄, expressed as mass flux (left-hand axes) and CO₂ equivalents (right-hand axes), and (c) total non-CO₂ greenhouse gas (GHG) emissions (i.e., N₂O + CH₄) expressed as CO₂ equivalents from anhydrous ammonia (AA), urea ammonium nitrate (UAN), and broadcast urea (BU) treated plots under conventional (CT), conservation (CsT), and no tillage (NT) (mean ± standard error, n = 3). For each parameter and within each year, bars with the same letter designation are not significantly different (p > 0.05).

Table 1. Mean fluxes (±standard error, n = 3) of nitrous oxide (N₂O), methane (CH₄), and nitric oxide (NO) from inter-row locations in plots treated with anhydrous ammonia (AA), urea ammonium nitrate (UAN), or broadcast urea (BU) and maintained under conventional (CT), conservation (CsT), or no tillage (NT).†

<table>
<thead>
<tr>
<th>Fertilizer</th>
<th>N₂O‡</th>
<th>CH₄</th>
<th>NO‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CT (µg N m⁻² h⁻¹)</td>
<td>CsT (µg C m⁻² h⁻¹)</td>
<td>NT (µg N m⁻² h⁻¹)</td>
</tr>
<tr>
<td>AA</td>
<td>120 (29) e</td>
<td>130 (23) e</td>
<td>67 (10) d</td>
</tr>
<tr>
<td>UAN</td>
<td>27 (4.6) b</td>
<td>28 (5.1) b</td>
<td>29 (4.0) c</td>
</tr>
<tr>
<td>BU</td>
<td>16 (1.9) ab</td>
<td>16 (1.8) a</td>
<td>25 (3.9) c</td>
</tr>
<tr>
<td>2003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BU</td>
<td>10 (1.7) a</td>
<td>23 (4.5) b</td>
<td>20 (5.1) ab</td>
</tr>
</tbody>
</table>

† For each variable (N₂O, CH₄, and NO) and within each year, means having the same letter designation are not significantly different based on least significant difference (LSD) comparisons (p > 0.05).

‡ For N₂O and NO, analysis of variance and LSD comparisons were performed using logarithm-transformed data. Untransformed data are presented for ease of interpretation.
Table 3. Mean inorganic N concentrations (± standard error, n = 9) in the 0- to 20-cm depth across all tillage treatments in plots amended with anhydrous ammonia (AA), urea ammonium nitrate (UAN), and broadcast urea (BU) in 2004.

<table>
<thead>
<tr>
<th>Date</th>
<th>NH₃~N</th>
<th>NO₃~N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AA</td>
<td>UAN</td>
</tr>
<tr>
<td>5 May</td>
<td>91 (16)</td>
<td>23 (6.7)</td>
</tr>
<tr>
<td>14 May</td>
<td>75 (15)</td>
<td>66 (1.8)</td>
</tr>
<tr>
<td>25 May</td>
<td>78 (13)</td>
<td>69 (1.2)</td>
</tr>
<tr>
<td>8 June</td>
<td>81 (22)</td>
<td>12 (9.5)</td>
</tr>
<tr>
<td>17 June</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1 July</td>
<td>23 (11)</td>
<td>0.99 (0.35)</td>
</tr>
<tr>
<td>20 July</td>
<td>25 (11)</td>
<td>0.13 (0.13)</td>
</tr>
<tr>
<td>18 August</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>28 September</td>
<td>2.6 (1.1)</td>
<td>0.63 (0.24)</td>
</tr>
<tr>
<td>18 November</td>
<td>7.4 (1)</td>
<td>2.7 (0.81)</td>
</tr>
</tbody>
</table>

Table 2. Mean concentrations (± standard error, n = 9) of ammonium (NH₄⁺) and nitrate (NO₃⁻) in the 0- to 10-cm depth across all tillage treatments in plots amended with broadcast urea in 2003.

<table>
<thead>
<tr>
<th>Date</th>
<th>NH₄⁺</th>
<th>NO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AA</td>
<td>UAN</td>
</tr>
<tr>
<td>18 June</td>
<td>55 (5.9)</td>
<td>7.5 (1.0)</td>
</tr>
<tr>
<td>24 June</td>
<td>33 (3.2)</td>
<td>49 (11)</td>
</tr>
<tr>
<td>3 July</td>
<td>34 (4.0)</td>
<td>27 (7.7)</td>
</tr>
<tr>
<td>11 July</td>
<td>41 (3.5)</td>
<td>6.0 (0.84)</td>
</tr>
<tr>
<td>31 July</td>
<td>28 (6.8)</td>
<td>1.6 (0.52)</td>
</tr>
<tr>
<td>5 August</td>
<td>19 (4.1)</td>
<td>1.6 (0.31)</td>
</tr>
<tr>
<td>15 August</td>
<td>27 (5.5)</td>
<td>2.9 (1.3)</td>
</tr>
<tr>
<td>27 August</td>
<td>21 (7.5)</td>
<td>3.0 (1.0)</td>
</tr>
<tr>
<td>16 September</td>
<td>10 (1.9)</td>
<td>0.72 (0.07)</td>
</tr>
<tr>
<td>17 October</td>
<td>14 (2.1)</td>
<td>0.92 (0.2)</td>
</tr>
<tr>
<td>21 November</td>
<td>18 (4.0)</td>
<td>0.69 (0.06)</td>
</tr>
</tbody>
</table>

40% lower (Fig. 2a, 3a). Mean daily temperature during June through August was 19.0°C in 2004 compared to 20.6°C in 2003 (Fig. 2b, 3b). These factors resulted in higher mean soil water content (0–10 cm) during 2004 (0.23 ± 0.001 g H₂O g⁻¹) compared to 2003 (0.20 ± 0.002) (p < 0.001). Despite wetter soil conditions in 2004, neither mean N₂O fluxes nor integrated emissions in BU-amended plots compared over equivalent seasonal periods (28 May–23 November) differed significantly between years (p > 0.05).

Emissions of CH₄ were negative on the majority of sampling dates (Fig. 2d, 4) indicating net CH₄ uptake (consumption). In 2004, there was a significant tillage-by-fertilizer interaction effect on both mean CH₄ flux (p = 0.018) and integrated emissions (p = 0.011). Methane uptake tended to increase in the order CT < CxT < NT in the UAN and BU treatments, while the reverse pattern (NT < CT < CxT) was observed in the AA treatment (Table 1, Fig. 5b). There were no significant main effects of tillage in 2003 or 2004 or fertilizer in 2004 (p > 0.25). There was a highly significant difference in mean uptake rates between growing seasons (p < 0.001). In the drier year (2003), mean uptake in the BU treatment across all tillage treatments was nearly three times higher (9.0 ± 1.4 μg CH₄-C m⁻² h⁻¹) than in 2004 (3.2 ± 0.3 μg CH₄-C m⁻² h⁻¹). Total uptake compared over equivalent seasonal periods in the BU treatments was 35 ± 7.6 mg CH₄-C m⁻² in 2003 compared to 13 ± 2.5 mg CH₄-C m⁻² in 2004 (p < 0.003). There were no apparent short-term effects of tillage on CH₄ fluxes. A cluster of positive CH₄ fluxes occurred within days following tillage in 2003, although this also occurred in the NT treatment (Fig. 2d). There were no significant correlations between CH₄ flux and soil properties or N₂O flux.

Differences in calculated total non-CO₂ GHG emissions followed the same or similar trends as N₂O emissions due to the predominant contribution of N₂O to total CO₂ equivalents (Fig. 5c). Tillage had a significant effect on non-CO₂ GHGs in BU-amended plots in 2003 (p = 0.023), while a significant tillage-by-fertilizer interaction (p = 0.036) and a highly significant fertilizer effect (p < 0.0001) were found in 2004. In the AA treatment, mean non-CO₂ GHGs emissions represented CO₂ emissions of 0.15 to 1.9 Mg CO₂ ha⁻¹ yr⁻¹, corresponding to 0.04 to 0.53 Mg soil-C ha⁻¹ yr⁻¹. In the BU treatment in 2004, the NT plots displayed mean total non-CO₂ GHG emissions that were 0.05 Mg soil-C ha⁻¹ yr⁻¹ greater than CT. Conversely, in the AA-fertilizer treatment, NT plots emitted 0.16 and 0.23 Mg soil-C ha⁻¹ yr⁻¹ less than CT and CxT, respectively.

Nitric Oxide and Total Nitrogen Oxides

Similar to N₂O, peak NO fluxes occurred within a few days to 4 wk following fertilizer application, with the greatest lag period between fertilizer application and peak fluxes occurring in the AA treatment (Fig. 6). The tillage-by-fertilizer interaction effect on NO emissions was significant at p = 0.067 and p = 0.093 for mean flux and integrated emissions, respectively. The only significant difference in NO emissions with tillage occurred in the AA treatment where, in contrast to N₂O, mean and integrated NO fluxes were higher under NT than CT (p < 0.05, Table 1, Fig. 7). Also in contrast to N₂O, NO fluxes and integrated emissions in the BU treatment under CT were greater than in the AA and UAN treatments (p < 0.05). The contrasting patterns in NO and N₂O emissions between fertilizer treatments resulted in similar total NO + N₂O emissions in the AA and BU treatments, which were both significantly greater than in the UAN treatment (p = 0.036, Fig. 7). Total NO + N₂O emissions did not differ by tillage within any of the fertilizer treatments (Fig. 7). The ratio of NO to N₂O flux was negatively correlated (p < 0.001) with soil water content at 0 to 10 cm (r² = 0.05) and 10 to 20 cm (r² = 0.12), but was not correlated with WFPS (0–10 cm).
locations to exceed those from the inter-row locations during the period before fertilizer application ($p = 0.12$) and during the four sampling dates after harvest ($p = 0.08$). On the five sampling dates following fertilizer application, when $N_2O$ fluxes were highest, this trend was least evident ($p = 0.56$).

The above data were considered in deciding how to estimate total integrated emissions. For $\text{CH}_4$, and for $N_2O$ treated with UAN and BU, we assumed that inter-row chamber fluxes were representative of the entire surface area because no significant differences in row versus inter-row fluxes were observed for $\text{CH}_4$, or for $N_2O$ during the peak $N_2O$ flux periods. Part of the reason for higher inter-row $N_2O$ fluxes in the AA treatment was likely the nonuniformity of the line-injection application method compared to more uniformly applied UAN and BU. Studies have shown that inorganic N levels following AA injection tend to decrease sharply within 10 cm of the injection line even several weeks after application (McIntosh and Frederick, 1958). We therefore assumed during the period following AA application and before UAN application (5 May–23 June) that $N_2O$ and NO fluxes from the nonmeasured row region in the AA treatment (covering an area located 25–37 cm from the injection line) were equal to fluxes in the inter-row region of the unfertilized UAN subplot within the same plot. Following UAN application, we installed additional chamber bases in the row region of the AA subplots and measured fluxes from these locations until late July (this required removal of some plants). Integrated $N_2O$ (Fig. 5a) and NO (Fig. 7) emissions were calculated by weighting the inter-row and row fluxes according to their proportion of the total area (0.67 and 0.33, respectively). It should be noted that even if we assumed that fluxes from the row region in the AA subplots were zero for the entire season, the resulting integrated $N_2O$ emissions in the AA treatment ($300 \pm 39 \text{ mg N m}^{-2}$) were still two to four times greater and statistically higher than in the UAN and BU treatments.

**DISCUSSION**

These findings demonstrate that net $N_2O + \text{CH}_4$ emissions can substantially affect the potential benefits of reduced tillage with respect to the total ecosystem GHG budget, depending on fertilizer practices. We observed that non-$\text{CO}_2$ GHG emissions (i) decreased under NT when AA was applied, (ii) increased under reduced tillage when BU was applied, and (iii) did not vary with tillage when UAN was applied. Under NT in the AA treatment, reductions in $N_2O + \text{CH}_4$ emissions were equivalent to reductions in $\text{CO}_2$ emissions of 0.59 to 0.84 Mg $\text{CO}_2$ ha$^{-1}$ yr$^{-1}$, corresponding to soil C increases of 0.16 to 0.23 Mg soil-C ha$^{-1}$ yr$^{-1}$. Conversely, in the BU treatment, non-$\text{CO}_2$ GHG emissions under NT exceeded emissions under CT by an amount equivalent to soil C losses of approximately 0.05 Mg soil-C ha$^{-1}$ yr$^{-1}$ in a recent survey, soil C storage rates under reduced tillage were found to average $0.40 \pm 0.61$ Mg soil-C ha$^{-1}$ yr$^{-1}$ in 44 treatment pairs (Johnson et al., 2005). Differences in non-
CO₂ GHG emissions due to tillage treatment in the current study are therefore substantial (12–58%) when compared to potential rates of soil C sequestration. The results also indicate that shifting away from AA fertilizer can result in reduced emissions equivalent to 0.1 to 0.4 Mg soil-C ha⁻¹ yr⁻¹.

Studies have shown that vertical distributions of aerobic and anaerobic microbial populations and potential denitrifying activity tend to vary in plowed versus untilled soil profiles. Using agricultural soils from three sites in the midwestern United States, Linn and Doran (1984a) found that facultative anaerobe populations and potential denitrification rates were higher in the upper 7.5 cm under NT compared to CT. Conversely, over the 15- to 30-cm depth, plowed soils contained more facultative anaerobes and tended to have higher potential denitrification rates. Similarly, Groffman (1985) observed higher denitrification activity under NT compared to CT in the top 5 cm of a Georgia agricultural soil and the reverse pattern at greater depth. The patterns in field N₂O emissions observed in the current study are consistent with these previous findings. Injection of AA fertilizer below the most active denitrifying zone in the NT treatment may have first of all resulted in less denitrifying activity compared to CT in the 10- to 20-cm zone. Higher WFPS under NT in the overlying 0- to 10-cm zone may have further reduced net N₂O emissions by enhancing reducing conditions, thereby promoting the reduction of N₂O to nitrogen (N₂) during transport toward the soil surface (Linn and Doran, 1984b). Conversely, surface-applied urea would be expected to stimulate more denitrifying activity in the upper soil layers, thereby favoring more denitrification under NT compared to CT. The inorganic N data support the above explanation. During the period of highest N₂O emission in 2004 (11 May–1 August), 62% of the soil inorganic N measured in the upper 20 cm in BU plots was found in the upper 10 cm, compared to 38% in the AA treatment. The patterns of correlation between N₂O flux and soil water content and WFPS (see Results, above) also support the idea that the primary zones of N₂O production varied in the AA (10–20 cm) and BU (0–10 cm) treatments, consistent with the above discussion.

The low degree of correlation (r² < 0.07) between N₂O flux and moisture parameters was likely due to the well-drained nature of the site soil. The loess-derived silt loam is underlain starting at the 60- to 100-cm depth by outwash sands, facilitating drainage. Previous studies in fertilized systems have shown that the highest N₂O fluxes occurred when WFPS was 70 to 90% (e.g., Dobbie et al., 1999). Values of WFPS above 70% (approximately 0.25 g H₂O g⁻¹) were attained in this study, but were not maintained for extensive periods (Fig. 2a, 3a). The temporal dynamics of N₂O (and NO) emissions exhibited a near-Gaussian response to fertilizer applications, and did not appear to be driven by rainfall events that occurred before, during, or after the apparent fertilizer-induced response (Fig. 2, 3, 6). This was also supported by the lack of response to simulated rainfall. The data therefore suggest that growing season N₂O production at this site was limited more by NO₃⁻ levels and/or other factors than by anaerobic status. We also observed no significant correlation between NO flux and WFPS, as might be expected (e.g., Davidson, 1993). There was a weak negative correlation (r² ≤ 0.12) between NO flux and soil water content. As pointed out by Ludwig et al. (2001), it is the interaction of multiple factors including water content, temperature, N availability, and N processes that ultimately controls net NO flux. Atmospheric NO concentrations can also impact NO emissions because increasing atmospheric NO favors soil NO uptake (Conrad, 1994). However, when soil production processes are highly dynamic, as expected following N application, it is difficult to assess the importance of aboveground NO levels on soil NO emissions. The “NO compensation point,” defined as the atmospheric NO concentration at which soil NO consumption completely balances NO production, has been found to vary over nearly three orders of magnitude, and this variation is likely due to wide variation in soil production rates (Ludwig et al., 2001).

There was a trend toward higher NO emissions in the BU compared to AA and UAN treatments (Fig. 7). With more N cycling (nitrification and denitrification) and NO production presumed to be occurring closer to the soil–atmosphere interface (0–10 cm zone) following surface BU application, there would be less opportunity for highly reactive NO to be transformed to other N species before its release to the atmosphere (Venterea and Rolston, 2002). While there may have been comparable rates of NO production occurring in the 10- to 20-cm zone in the AA treatment, transformation of NO to N₂O (and other N species) during its transport to the surface would be favored by greater residence times.

Our estimates of total N₂O integrated emissions in the UAN and BU treatments (approximately 130 and 80–120 mg N m⁻², respectively, across tillage treatments) are consistent with the 1997 Intergovernmental Panel on Climate Change (IPCC) estimates for N₂O emissions (Mosier et al., 1998). The IPCC estimate assumes that 10% of the applied N is lost as NH₃ and NO, and that 0.25 to 2.25% of the remaining N is emitted as N₂O. In the current case (120 kg N ha⁻¹ applied), the estimates range from 27 to 240 mg N m⁻². Emissions from the AA treatment under CT and CsT were approximately three times greater than the mid-range of the IPCC estimate and about 1.5 times greater than the upper limit, while emissions under AA/NT were close to the upper limit. Peak N₂O emissions in the range of 1 to 4 mg N m⁻² h⁻¹ have also been observed following AA application to corn and other crops (Bremner et al., 1981; Eichner, 1990; Thornton et al., 1996; Venterea and Rolston, 2000). Emissions of N₂O induced by AA application have, in general, tended to be higher than other synthetic N fertilizers (Bouwman et al., 2002). Venterea and Rolston (2000, 2002) attributed at least some of the elevated emissions under AA to the accumulation of NO₃⁻ and its subsequent involvement in biotic and abiotic reactions. While not measured here, the tendency for NO₃⁻ to accumulate following AA application has been known for decades (Chalk et al., 1975) and has been attributed to the greater sensitivity...
of NO\textsubscript{2}--oxidizing bacteria to free NH\textsubscript{3} toxicity than NH\textsubscript{3}--oxidizing bacteria (Van Cleemput and Samater, 1996).

Data reported here represent more than 2000 individual chamber measurements of each GHG flux and 400 measurements of NO flux, with an average frequency of two measurement dates per week. Integrated emissions in previous studies have been made utilizing measurements with equal or lesser sampling frequency (e.g., Goodroad et al., 1984; Jacinthe and Dick, 1997; Palma et al., 1997). Uncertainties regarding total emissions estimates remain as an inherent limitation of chamber-based flux methods. Measurement of fluxes in the row region comprising a fast-growing crop are particularly problematic given the constraints imposed by chamber height, since method sensitivity to baseline fluxes decreases in proportion to chamber height unless deployment time is increased proportionately. Our trials during 2003 indicated that attempting to force corn plants inside of the 10-cm-high chambers for row measurements caused plant damage within a few weeks of seedling emergence. While the focus of this study was growing season response to fertilizer inputs, a possible additional source of N\textsubscript{2}O emissions is that occurring during thaw-freeze cycles (e.g., Nyborg et al., 1997). In the autumn of both years, we made several measurements while soils were relatively wet and near 0°C in the upper few centimeters, and found no evidence for “bursts” of N\textsubscript{2}O flux greater than 10 to 20 μg N m\textsuperscript{-2} h\textsuperscript{-1}. The period of December through late April, however, was not encompassed by this study, and it is possible that significant fluxes could have been occurring during this time.

The higher CH\textsubscript{4} uptake rates observed here under reduced tillage in the UAN- and BU-fertilized subplots are consistent with previous studies (Cochran et al., 1997; Hütsch, 1998; Kessavalou et al., 1998; Robertson et al., 2000). This effect has been attributed to more stable and porous soil structure under reduced tillage that facilitate CH\textsubscript{4} diffusion into oxidizing zones (Ball et al., 1997), and to negative effects of tillage on methanotrophic activity (Hütsch, 1998, 2001). To our knowledge, the reverse pattern observed here under AA fertilization has not been previously reported. This effect may have been related to competitive inhibition of methanotrophic enzyme systems due to substrate similarity between CH\textsubscript{4} and NH\textsubscript{3}+ (or NH\textsubscript{3}) and possibly to noncompetitive inhibition from NO\textsubscript{2}, which has been found to accumulate after AA application (Hütsch, 2001). The high soil pH and NH\textsubscript{3}/NH\textsubscript{3}+ concentrations that follow AA application can also alter the ratio of different classes of microbial populations (Eno and Blue, 1954) and release significant amounts of dissolved organic C (Clay et al., 1995). These impacts may have altered the activities of methanogenic and methanotrophic microbes. The greater CH\textsubscript{4} uptake observed in the drier year (2003) was likely due to enhanced diffusion of atmospheric CH\textsubscript{4} into soil under drier conditions (Ball et al., 1997). The current findings suggest that CH\textsubscript{4} uptake can, under some circumstances, make a nontrivial contribution to the total net balance of GHGs in well-drained agricultural soils. In the BU/CT treat-


