# The impact of nitrogen placement and tillage on NO,  $N_2O$ ,  $CH_4$ and  $CO<sub>2</sub>$  fluxes from a clay loam soil

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#### Abstract

To evaluate the impact of N placement depth and no-till (NT) practice on the emissions of NO,  $N_2O$ , CH<sub>4</sub> and  $CO<sub>2</sub>$  from soils, we conducted two N placement experiments in a long-term tillage experiment site in northeastern Colorado in 2004. Trace gas flux measurements were made 2–3 times per week, in zero-N fertilizer plots that were cropped continuously to corn (Zea mays L.) under conventional-till (CT) and NT. Three N placement depths, replicated four times (5, 10 and 15 cm in Exp. 1 and 0, 5 and 10 cm in Exp. 2, respectively) were used. Liquid urea–ammonium nitrate (UAN, 224 kg  $\dot{N}$  ha<sup>-1</sup>) was injected to the desired depth in the CT- or NT-soils in each experiment. Mean flux rates of NO,  $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub> ranged from 3.9 to 5.2  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>, 60.5 to 92.4  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>, -0.8 to 0.5  $\mu$ g C m<sup>-2</sup> h<sup>-1</sup>, and 42.1 to 81.7 mg C m<sup>-2</sup> h<sup>-1</sup> in both experiments, respectively. Deep N placement (10 and 15 cm) resulted in lower NO and  $N_2O$  emissions compared with shallow N placement (0 and 5 cm) while CH<sub>4</sub> and CO<sub>2</sub> emissions were not affected by N placement in either experiment. Compared with N placement at 5 cm, for instance, averaged N<sub>2</sub>O emissions from N placement at 10 cm were reduced by more than 50% in both experiments. Generally, NT decreased NO emission and  $CH_4$  oxidation but increased N<sub>2</sub>O emissions compared with CT irrespective of N placement depths. Total net global warming potential (GWP) for N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> was reduced by deep N placement only in Exp. 1 but was increased by NT in both experiments. The study results suggest that deep N placement (e.g., 10 cm) will be an effective option for reducing N oxide emissions and GWP from both fertilized CT- and NT-soils.

## Introduction

Nitric oxide,  $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub> emissions from agricultural soils are important sources of anthropogenic trace gas emissions to the atmosphere (Mosier et al., 2004). These trace gases directly or indirectly contribute to the accelerated global warming and/or ozone depletion in the troposphere (IPCC, 2001). NO and  $N_2O$  are produced predominantly as by-products of two

microbial processes: nitrification and denitrification. Although both oxidative and reductive processes consume NO, the relative consumption by denitrification seems to be higher (Skiba et al., 1993). Therefore, nitrification typically is the main source of NO (Anderson and Levine, 1986). In contrast, denitrification is usually the main source of  $N_2O$  especially under condition of high soil water content (Azam et al., 2002). In the soil, CH4 is produced under anaerobic conditions by microbial decomposition of organic materials \* E-mail: liu310@cau.edu.cn whereas CO2 production results from oxidation



of soil organic materials by heterotrophic microorganims and the respiration of plant roots (Yamulki and Jarvis, 2002). However, soils can act as both a source and sink for atmospheric  $CH<sub>4</sub>$ .

Many studies have examined the contribution of soil to the atmospheric budgets balance of NO,  $N_2O$ ,  $CH_4$  and  $CO_2$ , but uncertainties remain because of the extreme variability of emissions in both space and time (Mosier et al., 2004). Variability of gas emission arises from soil–plant system heterogeneity and from the complex interactions which occur among the physical, chemical and biological variables controlling their generation and emission (Duxbury and McConnaughey, 1986; McTaggart et al., 1994). Banding/injection of N fertilizer and tillage, lead to mechanical soil disturbance and are thought to greatly alter gaseous fluxes in soils (Hansen et al., 1993; Kessavalou et al., 1998). So it becomes a concern on how to mitigate NO,  $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub> emissions from soils through proper N management and tillage practice (Maljanen et al., 2001; Shrestha et al., 2004). Therefore, best N management and tillage practices needed to be identified to minimize agricultural emissions of NO,  $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub>. Deep placement of fertilizer N, due to its higher N utilization efficiency by crops, is presumably one of those methods. On the other hand, conservation tillage or NT has been a common practice in North America (Vetsch and Randall, 2004). The use of NT has shown a number of agronomic benefits (Holland, 2004). Some of these benefits led to reductions in the emission of the greenhouse gas  $(GHG) CO<sub>2</sub>$  through less fuel and machinery used than in CT systems. NT also frequently increased the potential to store (sequester) more C in the soil organic matter. Large uncertainties of the NT impact on  $N_2O$ fluxes, however remain (Six et al., 2004). In a 5-yr tillage with N fertilization experiment, Liu et al. (2005a) found that  $N_2O$  fluxes peaked earlier but generally lasted a shorter period in NT (shallower N placement, 3–5 cm, due to surface residues) than in CT (deeper N placement, 5– 10 cm) after N fertilization. This finding suggests that N placement and tillage may affect the emission patterns of  $N_2O$  and  $NO_x$ . Limited evidence shows that NT is not likely to lead to an increase in  $N_2O$  emissions, provided that the N fertilizer

is banded, as is the common practice with farmers using NT systems (Liu et al., 2005a). The objectives of this study were to identify (1) the impact of depth of N fertilizer placement on NO,  $N_2O$ ,  $CH_4$  and  $CO_2$  emissions from CT and NT soils and (2) the potential of decreasing  $NO<sub>x</sub>$ and  $N_2O$  emissions by deep N placement and tillage strategy.

## Materials and methods

## N placement experiments

The N placement experiments were located within two zero-N plots of the CT and NT treatments in a long-term experiment which was initiated in 1999 at the Agricultural Research, Development, and Education Center (ARDEC) northeastern Colorado  $(40^{\circ}39' \text{ N}; 104^{\circ}59' \text{ W})$ , USA. The region has a semi-arid temperate climate with typical mean temperature of 10.6  $\degree$ C and low rainfall of 382 mm  $yr^{-1}$  (the average of 1900–2003). The soil is classified as fine-loamy, mixed, superactive, mesic Aridic Haplustalfs. The detailed information of the field experiment was introduced by Halvorson et al. (2005). Briefly, the CT continuous corn rotation used mechanical tillage (stalk shredder, disk, moldboard plow, mulcher, land leveler, etc.) for seed bed preparation. The NT continuous corn rotation, initiated in 1999, however, left the residues on the soil surface after corn harvest without mechanical tillage. Corn seeds were sown in late April each year. The two N placement experiments were placed at the center of two corn rows within unfertilized CT and NT plots designated as CT-N0 and NT-N0, by inserting a set of 20.4 cm diameter polyvinyl chloride (PVC) 10 cm long cylinders, to establish microplots, 8 cm into the soil. The microplot cylinders also served as gas sampling anchors. Anchors were set between two corn rows so that the measurements could be done with little effect on corn plants in the plots. Liquid urea–ammonium nitrate (UAN, 32% N) was injected at three locations (to simulate banding) using 5, 10 or 15 cm long syringe needles to provide the equivalent of 224 kg N  $ha^{-1}$  within each microplot. There were three depths of N placement in both CT-N0 and NT-N0 plots with four replications of each treatment. The depths of N placement were 5, 10, and 15 cm in Experiment (Exp.) 1. When Exp. 1 ended, anchors were removed and set to nearby positions within the same plots to initiate Exp. 2. Because the  $NO<sub>x</sub>$ and  $N<sub>2</sub>O$  fluxes observed from the microplots in which fertilizer was injected 10 or 15 cm into the soil were not detectably different, fertilizer was on or 5, and 10 cm below the soil surface in Exp. 2. Experiment 1 was initiated on May 12, and ended on June 9, 2004 while Exp. 2 started on June 15 and ended on July 14, 2004.

## Gas sampling and measurements

Fluxes of NO, N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> (began in May 2004 and ended in July 2004) were measured two to three times per week, midmorning of each sampling day. Ten-centimeter-high vented round PVC chambers (inner diameter 20.4 cm) were installed on permanently fixed microplot cylinders that served as flux chamber anchors. The chambers were sealed to the anchors using a 5-cm wide rubber band that was cut from a truck tire intertube. Gas samples from the chamber headspace were collected by syringe (size: 35 ml with scale) at 0, 15 and 30 min after installation. Twenty-five milliliter of each sample in syringe was injected into 12 ml evacuated tubes (to insure over pressure of sample in the tubes) that were sealed with butyl rubber septa and transported to the laboratory for analysis by gas chromatography (GC) within 24 h. The GC used was a fully automated instrument Varian 3800 (Varian Inc., Walnut Creek, CA, USA) equipped with thermoconductivity, flame ionization and electron capture detectors to quantify  $CO<sub>2</sub>$ , CH<sub>4</sub> and N<sub>2</sub>O, respectively. The fluxes of the three gases were calculated from the change in concentration in the chamber headspace with time (Liu et al., 2005a).

Nitric oxide emissions were measured on each anchor, 30–60 min after N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> flux measurements had been made, using a dynamic chamber technique in conjunction with a commercial  $NO-NO<sub>2</sub>-NO<sub>x</sub>$  analyzer (model 42C; Thermo Environmental Instruments, Franklin, MA, USA). The size of dynamic chamber used in the study is 20.4 cm (inner diameter) by 15 cm (height). In this method, NO-,  $NO<sub>2</sub>$ -, and  $O<sub>3</sub>$ -free air with a flow rate of about  $1.8$  L min<sup>-1</sup> was generated with a pump attached to activated charcoal and Purifil filters and was introduced to each chamber via an entry port. A portion of the outlet air stream from each chamber was sampled consecutively via a quarter-inch outer-diameter polytetrafluoroethylene (PTFE) tube (covered with a PTFE film 'Tygaflor' on the inside walls) for NO analysis. NO fluxes were calculated from the differences in respective concentrations at the inlet and outlet air, the flow rate of air through the chamber, and the surface area covered by the chamber. Total emissions of NO,  $N_2O$ , CH<sub>4</sub> and  $CO<sub>2</sub>$  during each experiment were calculated from the averaged daily-based fluxes multiplied by the time interval between measurements. Using the same methods, background flux rates of NO,  $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub> from the unfertilized CT and NT plots were measured for the same time period (Liu et al., 2005a).

## Other measurements

Soil water content (0–15 cm) and soil (5 cm) and air temperature were measured in CT-N0 and NT-N0 plots at each trace gas-sampling event by a soil dielectric constant probe (Decagon Devices, Inc., Pullman, WA, USA) and a hand-held digital thermometer (Omega Engineering, Stamford, CT, USA), respectively. Mean bulk densities  $(B_d)$  were 1.38 and 1.44 g cm<sup>-3</sup> for CT and NT soils, respectively. Soil water content  $(v/v)$ was then expressed as water filled pore space (WFPS) values according to bulk density [WFPS  $(\%)$  = Soil water content  $\times 1/(1-B_d/2.65)$   $\times$ 100%]. Soil samples (0–30 cm) were collected at the beginning and end of each N placement experiment and were analyzed for ammonium N and nitrate N using a continuous flow analyzer (Lachat QickChem FIA+8000 Series, Hach Company, Loveland, CO, USA) after the extraction by 1 mol  $L^{-1}$  KCl solution. The date and amount of precipitation and irrigation were recorded during the study period.

# Statistical analysis

Determination of differences in NO,  $N_2O$ ,  $CH_4$ and  $CO<sub>2</sub>$  emissions in both experiments by N

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placement and tillage as well as soil mineral N affected by N placement and tillage was determined statistically (ANOVA and GLM regressions) using a MINITAB statistical software (release 13 for windows, Minitab Inc., USA). Significant differences are expressed at  $P \leq 0.05$ , unless otherwise stated.

## Results

#### Temperature and water conditions

Daily air temperature, precipitation and irrigation are illustrated in Figure 1(a–d). Average air temperature was about 2.6  $\degree$ C higher in Exp. 2 than in Exp. 1 although air temperature showed much more variation in Exp. 1 (Figure 1a) compared with that in Exp. 2 (Figure 1b). Soil temperature in CT (average  $17.3 \text{ }^{\circ}\text{C}$ ) was generally higher than in NT (average  $16.0 \degree C$ ) in Exp. 1 (Figure 1a,  $P = 0.193$ ) but no differences between CT (average  $19.8 \text{ °C}$ ) and NT (average 19.4 °C) were observed in Exp. 2 (Figure 1b,  $P = 0.659$ . Rainfall and irrigation amounts in Exp. 2 (165 mm) were greater than those in Exp. 1 (97 mm). Water filled pore space (WFPS) was 10–25% higher in NT than that in CT in both experiments (Figure 1c,d,  $P \le 0.001$  for Exp. 1 and Exp. 2). So the soil conditions in Exp. 2 may have favored denitrification loss especially under NT condition compared with Exp. 1.

### $NO$  and  $N<sub>2</sub>O$  emissions

The fluxes of NO and  $N_2O$  in both experiments are illustrated in Figure 2 (a–d). In Exp. 1, NO fluxes remained at very low level  $(-1.3-$ 4.7  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>) within the first several days (13–17 May) after N fertilization, peaked on 18– 20 May (10.9–42.1  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>), then dropped to background level quickly since 21 May, after that a unique peak flux of NO was observed only in CT 5 cm on 1 June (Figure 2a). The average NO fluxes of were 5.9 and 2.0  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> for CT and NT irrespective of the depths of N placement, which were slightly higher than the background NO fluxes of 4.6 (CT) and 1.1 (NT)  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> from the same non-fertilized plots during the same time period (calculated from Liu et al., 2005a). The corresponding  $N_2O$  fluxes were much higher, with mean fluxes of  $26.7 \mu$ g N m<sup>-2</sup> h<sup>-1</sup> for CT and 94.2  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> for NT across N placement (Figure 2c), compared with the mean  $N_2O$  fluxes of 5.0 (CT) and 2.9 (NT)  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> from the same non-fertilized plots



Figure 1. Maximum/minimum air temperature and daily mean soil temperature (a,b), and rainfall/irrigation and soil water filled pore space (c,d) in Exp. 1 (left) and Exp. 2 (right) during the study periods.



Figure 2. Effect of N placement and tillage on the fluxes of NO (a,b) and N<sub>2</sub>O (c,d) from soils in Exp. 1 (left) and Exp. 2 (right) during the study periods. Bars denote standard error of means (SEM). Arrows denote fertilization.

(calculated from Liu et al., 2005a). N<sub>2</sub>O fluxes, in contrast to those of NO, increased steadily and peaked several times after N fertilization during the study period (12 May to 9 June). The highest N<sub>2</sub>O flux (about 380  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>) was observed in NT 5 cm on May 26 and 27, which corresponded to a rainfall (8.1 mm) with a moderate irrigation (30.7 mm). Compared with CT, NT generally led to lower NO fluxes but greater  $N_2O$ fluxes at all placement depths in Exp. 1.

In Exp. 2, mean NO fluxes were 5.3 and 5.1  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> for CT and NT (Figure 2b) compared with the mean fluxes of 7.6 and 2.5  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> for CT and NT non-fertilized plots (calculated from Liu et al., 2005a), respectively. The small NO fluxes observed were relatively constant in both NT and CT except where fertilizer was applied to the soil surface. This was likely due to the 40 mm of rain that fell during the week after applying the fertilizer (Figure 1d) which moved the surface application into the soil. In contrast,  $N_2O$  fluxes increased quickly and peaked about 1 week after N application then dropped dramatically to the background level (Figure 2d). The peak fluxes of  $N_2O$  always followed rainfall and irrigation events while those of NO were reversed in the two experiments (Figures 1 and 2). Deep N placement (10 and 15 cm) reduced both NO and  $N<sub>2</sub>O$  fluxes compared with shallow N placement (5 cm in Exp. 1 and 0 and/or 5 cm in Exp. 2) under both CT and NT conditions. NT usually caused lower NO fluxes but much greater  $N_2O$  fluxes than CT at the same depth of N placement in both experiments.

Total cumulative  $N_2O$  fluxes were significantly greater in NT than in CT while the situation was reversed for total cumulative NO fluxes in Exp. 1 (Table 1). Total cumulative emissions of NO and  $N<sub>2</sub>O$  were significantly higher in the shallow placement (5 cm) than from the deeper placement. However, the NO and  $N<sub>2</sub>O$  emissions were not significantly different between the 10 and 15 cm N placements. Total cumulative emissions of  $N_2O$  (100–300 g N ha<sup>-1</sup> for CT and 350–1020 g N ha<sup>-1</sup> for NT) were much higher than those of NO (30–60 g N ha<sup>-1</sup> for CT and 5–20 g N ha<sup>-1</sup> for NT). In Exp. 2, the cumulative emissions of both N gases followed the same trends as those in Exp. 1 (Table 2). But  $N_2O$ emissions from CT  $(230-726 \text{ g N} \text{ ha}^{-1})$  were greater than those in Exp. 1 (125–385 g N ha<sup>-1</sup>), probably due to higher WFPS in Exp. 2 (Figure 2c, d). Surface N application (0 cm) and

Table 1. Total emissions of NO, N<sub>2</sub>O, CH<sub>4</sub> (g N or C ha<sup>-1</sup>) and  $CO_2$  (kg C ha<sup>-1</sup>) from soils as affected by N placement and tillage in Exp. 1

Treatment	CТ 5 cm	CТ $10 \text{ cm}$	CТ $15 \text{ cm}$ 5 cm	NT	NT $10 \text{ cm}$	NT $15 \text{ cm}$
NO N <sub>2</sub> O	61.9 385	21.3 174	34.9 125	21.5 1005	5.9 405	13.5 316
CH <sub>4</sub>	$-1.4$	7.0	3.8	3.7	2.0	4.3
CO <sub>2</sub> Statistical analysis	250	168	211	349	354	365
	Tillage $(T)$		Placement (P)		Interaction $(T \times P)$	
NO.	***		$* *$		NS	
N <sub>2</sub> O	***		***		***	
CH <sub>4</sub>	NS		NS		<b>NS</b>	
CO <sub>2</sub>	***		<b>NS</b>		<b>NS</b>	

NS, \*\* and \*\*\* represent not significant, significant at 0.01 and 0.001 levels, respectively.

shallow N placement (5 cm) resulted in significantly smaller emissions of  $N_2O$  compared with deep N placement (10 cm, Table 2). The only significant interaction between N placement and tillage occurred for  $N_2O$  emission in Exp. 1 (Table 1).

# $CH<sub>4</sub>$  and  $CO<sub>2</sub>$  emissions

The dynamics of  $CH_4$  and  $CO_2$  fluxes as affected by N placement and tillage in both experiments are shown in Figure 3(a–d). In Exp. 1, N appli-

Table 2. Total emissions of NO, N<sub>2</sub>O, CH<sub>4</sub> (g N or C ha<sup>-1</sup>) and  $CO_2$  (kg C ha<sup>-1</sup>) from soils as affected by N placement and tillage in Exp. 2

Treatment	CТ $0 \text{ cm}$	CТ 5 cm	<b>CT</b> $10 \text{ cm}$	NT $0 \text{ cm}$	NT 5 cm	NT $10 \text{ cm}$			
NO.	51.5	33.1	21.7	74.0	14.0	15.9			
N <sub>2</sub> O	438	726	230	897	939	531			
CH <sub>4</sub>	$-5.9$	$-8.6$	$-12.2$	0.2	$-1.8$	$-2.0$			
CO <sub>2</sub>	516	476	510	622	584	592			
Statistical analysis									
	Tillage $(T)$		Placement (P)		Interaction				
					$(T \times P)$				
N <sub>O</sub>	<b>NS</b>		***		<b>NS</b>				
N <sub>2</sub> O	**		$* *$		<b>NS</b>				
CH <sub>4</sub>	*		NS		NS				
CO2	$*$		<b>NS</b>		<b>NS</b>				

NS, \*, \*\* and \*\*\* reresent not significant, significant at 0.05, 0.01 and 0.001 levels, respectively.

cation caused a quick  $CH<sub>4</sub>$  flux (a net result of methane production and oxidation, up to 8.5  $\mu$ g C m<sup>-2</sup> h<sup>-1</sup>) from CT and NT soils then CH4 production and oxidation were in equilibrium and no net  $CH<sub>4</sub>$  fluxes occurred. No significant effects of N placement and tillage on  $CH<sub>4</sub>$ fluxes were found in the Exp. 1 (Figure 3a). Carbon dioxide fluxes followed emission patterns that were similar to  $N_2O$ . NT led to several higher emission peaks of  $CO<sub>2</sub>$  compared with CT but N placement did not affect  $CO<sub>2</sub>$  fluxes from either CT or NT soils (Figure 3c). In Exp. 2, CH4 uptake (negative emission) was observed in most cases (Figure 3b) while  $CO<sub>2</sub>$  fluxes tended to increase, coinciding with the increase in soil temperature during the study period (Figures 3d and 1b).

Total cumulative fluxes of  $CH<sub>4</sub>$  and  $CO<sub>2</sub>$ were illustrated in Tables 1 and 2. In contrast to N oxides, N placement did not affect either  $CO<sub>2</sub>$  or  $CH<sub>4</sub>$  flux in either experiment. Higher cumulative  $CO<sub>2</sub>$  emissions were observed in NT plot than in CT plot in Exp. 1 (Table 1) and Exp. 2 (Table 2). Methane consumption was small but generally lower in NT than in CT during the study periods (Tables 1 and 2). The interactions between N placement and tillage for  $CH<sub>4</sub>$  and  $CO<sub>2</sub>$  were not significant in the two experiments.

## Global warming potential (GWP)

GWP (kg CO<sub>2</sub>-equivalents ha<sup>-1</sup>) for (N<sub>2</sub>O, CH<sub>4</sub> and  $CO<sub>2</sub>$ ) were estimated using values of 296, 23 and 1, respectively for a 100-year time frame on a per molecule basis (IPCC, 2001) for the gas in each experiment period (~4 weeks) in Figure 4. In Exp. 1, deep N placement (10 and 15 cm depths) significantly reduced the total GWP compared with shallow N placement (5 cm depth). In contrast, NT led to greater total GWP for  $N_2O$ ,  $CH<sub>4</sub>$  and  $CO<sub>2</sub>$  than CT. In Exp. 2, similar effect of tillage on the GWP was observed although the GWP for all the three gases was much greater in Exp. 2 than in Exp. 1 (Figure 4). However, N placement did not show obvious effect on the GWP in Exp. 2. The three greenhouse gases contributed to 73–95% (CO<sub>2</sub>), 5–27% (N<sub>2</sub>O) and  $-0.02-0.03\%$  (CH<sub>4</sub>) of the total GWP, respectively.



Figure 3. Effect of N placement and tillage on the fluxes of CH<sub>4</sub> (a,b) and CO<sub>2</sub> (c,d) from soils in Exp.1 (left) and Exp.2 (right) during the study periods. Bars denote standard error of means (SEM). Arrows denote fertilization.



Figure 4. Estimated global warming potential (GWP, kg CO<sub>2</sub>-equivalents ha<sup>-1</sup>) of three greenhouse gases (N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub>) emitted from soils as affected by N placement and tillage in both experiments. Column pairs labeled with different uppercase letter for N placement across tillage are significantly different. Columns labeled by different lowercase letters for tillage within each N placement depth are significantly different.

## Mineral N in 0–30 cm soil layers

Soil mineral N as  $NH_4$ -N and  $NO_3$ -N in 0–30 cm layers at the end of both experiments is shown in Figure 5. In Exp. 1, most  $NH_4$ -N was transformed to  $NO<sub>3</sub>-N$  in the soil with CT across N placement,

while NH4-N in the soil with NT still remained as high as 30–40 kg N  $ha^{-1}$  and NH<sub>4</sub>-N mainly concentrated on the specific layer where fertilizer N was injected (e.g.,  $NH_4$ -N in NT 10 cm treatment mainly distributed in 7.5–15 cm layer, Figure 5a), indicating slower rates of nitrification in NT soils



Figure 5. Effect of N placement depth on the distribution of NH<sub>4</sub>-N (a,b) and NO<sub>3</sub>-N (c,d) in CT and NT soil profiles (0–7.5, 7.5– 15 and 15–30 cm) at the end of Exp. 1 (left) and Exp. 2 (right). Fertilizer nitrogen rate of 224 kg N ha<sup>-1</sup> was injected to 5, 10, 15 cm depths in Exp.1 and 0, 5, 10 cm depths in Exp. 2, respectively.

than in CT soils. Opposite to  $NH_4-N$ , we observed more  $NO_3-N$  in soils with CT than in NT soils. The distribution of  $NH_4-N$  and  $NO_3-N$  in soil profile suggests that the fluxes of N oxides originate mainly from the depth at which N fertilizer was applied. Total mineral N in soils ranged from 177 to 198 kg N  $ha^{-1}$  for NT and from 196 to 220 kg N ha<sup>-1</sup> for CT (Figure 5c) while the initial  $NH_4$ -N plus  $NO_3$ -N were only 39 and 31 kg N  $ha^{-1}$  for CT and NT plots. In Exp. 2, the distribution pattern of mineral N in soil profile was similar to that in Exp. 1.  $NH_4-N$  in each soil layer was very small (less than 6 kg N  $ha^{-1}$ ) across tillage and N placement with the exception of the surface N application in CT, while  $NO<sub>3</sub>-N$  in soils was the major part of mineral N in 0–30 cm layers (Figure 5b,d). Accordingly, the initial  $NH_4-N$  plus  $NO_3-N$  were only 20 and 18 kg N ha<sup>-1</sup> for CT and NT plots at the beginning of Exp. 2. Compared with Exp. 1, however, total mineral N in soils with either CT or NT was much lower in Exp. 2 except for the CT 0 cm treatment. That suggests fertilizer N, particularly  $NO<sub>3</sub>-N$ , leached out of 0–30 cm soil profile because of higher WFPS in the second experiment. Plant N uptake was likely greater in the second experiment as well.

#### **Discussion**

## Nitrogen oxides

The present study shows that both N placement and tillage had a significant effect on fluxes of NO (Exp. 1) and  $N<sub>2</sub>O$  (Exps. 1 and 2) from soils. The negative relationship between the depth of N placement and NO and/or  $N_2O$  emission showed that deep N placement could be an effective option to reduce the emissions of two trace N gases from arable soils. While the total cumulative flux of NO was decreased by NT,  $N_2O$  fluxes in contrast were increased by NT. In an earlier study, Hilton et al. (1994) found that deep placement of N (as a 28% N solution of UAN) in NT reduced  $N_2O$  emissions to levels similar to soil incorporation of N fertilizer in CT, and much less than  $N_2O$  emissions from NT with surface application and incorporation of N. These results indicate that factors controlling emissions of these gases are different.

A complicated relationship between N placement and NO and  $N_2O$  emissions was observed from the results in Exp. 1 and Exp. 2. For example, no further decline in NO emission occurred

when the depth of N application was increased from 10 to 15 cm in Exp. 1 (Table 1). Surface N application decreased  $N_2O$  emission from both CT and NT soils compared with shallow N placement (5 cm depth) in Exp. 2 (Table 2). The movement of fertilizer a few days after application because of a 40 mm rain may have confounded the observations, however. In Alberta of Canada, Drury et al. (2004) also found shallow N placement (2 cm depth) decreased  $N_2O$  emissions from the soil by 25% compared to deep N placement (10 cm depth). Their results were similar to our findings from the Exp. 2. Surface soil is more likely to be aerobic compared to subsoil following rainfall. Dry soil conditions usually enhance NO emissions but decrease N<sub>2</sub>O emissions when fertilizer N was applied at or near surface soil according to the hole-in-the-pipe model (Firestone and Davidson, 1989). In the conceptual model, the amount of N that 'leaks' out of the pipe as NO and  $N_2O$  is determined by several soil properties, but most commonly and most strongly by soil water content. In dry soils, NO is the dominant gas that leaks out of the pipe while in wetter soils  $N_2O$  is the most important end product (Davidson and Verchot, 2000). Davidson (1991) observed that the largest NO emissions could be expected at WFPS values of  $30-60\%$  and the highest N<sub>2</sub>O emissions at 50–80% WFPS. In the present study, we also observed similar linear relationships of WFPS and N oxide emissions in the two experiments: higher WFPS due to rainfall and irrigation enhanced N<sub>2</sub>O emissions (Exp. 1:  $R^2 = 0.2719$  for CT and 0.0405 for NT; Exp. 2:  $R^2 = 0.3927$  for CT and 0.4037 for NT) but reduced NO emissions (Exp. 1:  $R^2 = 0.2329$  for CT and 0.2688 for NT; Exp. 2:  $R^2 = 0.7901$  for CT and 0.5982 for NT) compared with lower WFPS (Figure 2). This relationship was also found in soils under CT and NT in this study. Generally, NO emissions from NT-soil (with higher WFPS) were lower than from CT-soil (with lower WFPS) but N2O emissions were reversed (Figure 2, Tables 1 and 2). Moreover, the location of ammonia oxidizing and denitrifying bacteria with soil depth may affect  $NO$  and  $N<sub>2</sub>O$  emissions. It was reasonable that ammonia oxidizing bacteria mainly concentrate on the upper soil layer (e.g.,  $0-7.5$  cm depth) while deeper soil layer (e.g., 7.5–15 cm depth) may be the most likely location

of denitrifying bacteria if considering both soil organic carbon distribution and change of soil aerobic condition with depth (Mosier, 2005, pers. commun.). So deep N placement usually led to slower nitrification rates and delayed denitrification. As a consequence, deep N placement resulted in lower  $N_2O$  and NO emissions compared with shallow N placement in this study. In addition, we suspect that greater  $NH<sub>3</sub>$  volatilization induced by surface N application (soil pH value of 7.7 will favor such volatilization loss) may explain less  $N<sub>2</sub>O$  emission compared with deeper N placement in Exp. 2.

Mineral N content in soils is another important factor that controls the emissions of both  $NO$  and  $N<sub>2</sub>O$  from nitrification and denitrification (Liu et al., 2004). The mineral N contents in 0–30 cm soil layers at the beginning (to see result section) and the end of each experiment (Figure 4) suggests that fertilizer N utilization and loss from Exp. 1 were much less than from Exp. 2. The sum of NO and  $N_2O$  emissions also reflected more N oxide losses in Exp. 2 compared with Exp. 1 (with the exception of treatment NT 5 cm, calculated from Tables 1 and 2). In fact, more  $N_2$  loss as well as  $NO_3-N$  leaching might have occurred due to greater WFPS in Exp. 2 especially under NT. Additionally, many corn roots were found below the anchors (10 cm soil depth) in Exp. 2, indicating that N uptake by corn may have happened during the study period of the Exp. 2 (June to July, 2004). Liu et al. (2005b) observed that N uptake by corn was as high as 60 kg N ha<sup>-1</sup> within a 4 week of rapid corn growth. Thus the greater N loss and N uptake by corn could explain why residual mineral N in Exp. 2 was much less than that in Exp. 1.

The effect of NT on trace N gas emissions has become a concern given its increased adoption since the 1980s (Campbell et al., 2001; Six et al., 2004). The present study showed that NT led to lower NO emissions but greater  $N_2O$  emissions in both experiments (from May to July). Similar results in the 2004 corn growing season were observed in a long-term tillage experiment with different N rates at the same site (Liu et al., 2005a). Greater  $N_2O$  emissions from NT soil in this short-period study were probably related to: (i) higher WFPS in NT compared to CT; (ii) corn residues on the surface of NT soil providing soluble organic C that enhances denitrification; and (iii) less N uptake by corn due to delayed corn growth by NT. However, Lemke et al. (1999) found that combined estimates (spring plus summer) of  $N_2O$  loss under zero tillage were equal to or lower than those under intensive tillage although emissions of  $N_2O$  during summer were sometimes slightly higher in zero tillage than those under intensive tillage. They conclude that zero tillage management systems have potential for reducing agricultural greenhouse gas emissions in the Alberta Parkland region, Canada. Their results agreed well with Liu et al. (2005a) and Mosier et al. (2005) when several years' results of  $N_2O$  and NO emissions were summarized together. Therefore, we should keep in mind that the influence of NT on N oxide emissions largely depends on specific crop, soil and weather conditions.

# $CH<sub>4</sub>$  and  $CO<sub>2</sub>$

In the current study,  $CH<sub>4</sub>$  emissions were negligible (near zero) or negative but  $CO<sub>2</sub>$  emissions were much greater (up to  $622 \text{ kg C ha}^{-1}$ ). N placement did not affect either CH4 uptake (negative emission) or  $CO<sub>2</sub>$  emissions in the two experiments. NT tended to reduce  $CH<sub>4</sub>$  uptake compared with CT presumably due to higher WFPS and greater bulk density in NT soil, as also shown in other studies (Yamulki and Jarvis, 2002). In contrast, NT increased  $CO<sub>2</sub>$  fluxes by 40–110% (Exp. 1) or 16–23% (Exp. 2) compared to CT where  $CO<sub>2</sub>$  emissions prior to initiation of this study was greater than in NT system due to tillage and residue decomposition. This could be explained by the higher microbiological activity induced by crop residues on the soil surface and relatively higher WFPS under NT (Lupwayi et al., 1999). Similar results were reported by Linn and Doran (1984) with 3.4 times greater  $CO<sub>2</sub>$  production from non-tillage soils over 24 h than from plowed soils. They indicated 90% was accounted for by a difference in WFPS regardless of the application of N fertilizer. However, Kessavalou et al. (1998) indicated a significantly higher  $CO<sub>2</sub>$  flux from a plowed than a NT system. Sanhueza et al. (1994) showed insignificant differences in  $CO<sub>2</sub>$  emissions between control (unplowed soil) and plowed soil with or without fertilization. The above inconsistent results suggest that the tillage effects on  $CO<sub>2</sub>$  flux will

depend on other factors (e.g., water content, temperature) involved in  $CO<sub>2</sub>$  production. What should be stressed is that  $CO<sub>2</sub>$  emission from NT is similar or slightly lower than that from CT if entire crop growing and fallow seasons are considered (Mosier et al., 2005).

## Total GWP

The overall balance between the net exchange of  $CO<sub>2</sub>$ , CH<sub>4</sub> and N<sub>2</sub>O constitutes the net GWP of a cropping system. No-till management has been promoted as a practice that offsets the GWP from emissions of  $N_2O$  and CH<sub>4</sub> in crop production because of its ability to sequester carbon in the soil (Cole et al., 1997). In our study, total GWP for  $N_2O + CH_4 + CO_2$  was increased by NT mainly due to the increase in both  $N_2O$  and  $CO<sub>2</sub>$  emissions when the change in soil organic carbon was neglected. Nitrogen placement, however, did not show consistent effects on the total GWP in Exp. 1 and Exp. 2. Deep N placement reduced total GWP substantially in Exp. 1 but such effect diminished in Exp. 2. It was mainly because the increase in  $CO<sub>2</sub>$  emissions induced by higher soil temperature more than offset the decrease in  $N_2O$  emissions (CH<sub>4</sub> emissions were negligible) in Exp. 2. Six et al. (2004) summarized all available data of soil-derived GHG emission comparisons between CT and NT systems for humid and dry temperate climates. They found that newly converted NT systems increase GWP relative to CT practices, in both humid and dry climate regimes, and longer-term adoption of NT ( $>10$  years) only significantly reduces GWP in humid climates. Mean cumulative GWP over a 20-year period is reduced under continuous NT in dry areas, but with a high degree of uncertainty (Six et al., 2004). Our results provide evidence on the potential of NT in increasing GWP in a semi-dry climate regime. In the same site near Fort Collins of Colorado, Mosier et al. (2005) found that  $N_2O$  and  $CO_2$  emissions in NT plots, with the adoption of no till, tended to be from lower to higher than in CT plots at N rate ranged from 0 to 224 kg N ha<sup>-1</sup> over a 3-year period. Therefore, the overall effects of NT and deep N placement on total GWP and/or GHG emissions mainly depend on the cropping history and specific soil as well as climate conditions.

#### **Conclusions**

In the present study, we evaluated the effect of fertilizer N placement and tillage on trace gas emissions in a cornfield. Deep N placement (e.g., 10 cm) significantly reduced both NO (Exp. 1) and  $N_2O$  (Exps.1 and 2) emissions without obvious influence on  $CH_4$  oxidation and  $CO_2$  evolution compared to shallow N placement (e.g.,  $\leq$  5 cm). NT generally decreased NO emission and CH<sub>4</sub> oxidation but increased  $N_2O$  emissions compared with CT irrespective of N placement depths. Total GWP for  $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub> was reduced by deep N placement only in Exp. 1 but was increased by NT in both experiments, suggesting that NT management has potential for increasing agricultural GHG emissions or GWP especially under moist soil condition. The study reveals that fertilizer N placement and tillage practices should be considered carefully when attempting to mitigate NO,  $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub> emissions from agricultural soils.

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