Profile Analysis and Modeling of Reduced Tillage Effects on Soil Nitrous Oxide Flux

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Reduced tillage practices can increase moisture retention, reduce erosion, decrease fuel consumption, and increase soil C storage (Six et al., 2002). The latter two impacts have the potential to mitigate the GHG contribution of agricultural systems, although C storage under RT may be overestimated in some cases (Baker et al., 2007). The benefits of RT have been evaluated in economic terms as potential offsets to GHG emissions and are currently marketable via C-credit trading systems (Manley et al., 2005; CCX, 2007). One unintended consequence of RT may be to affect soil emissions of N₂O, which has a global warming potential 300 times greater than carbon dioxide (CO₂), potentially altering the net system GHG budget to a substantial degree (IPCC, 2001).

No till (NT) and other RT practices can alter several soil properties that are known to influence soil to atmosphere N₂O fluxes. Some of these effects, including increased water content and bulk density, would be expected to promote higher N₂O flux, while other changes, such as decreased soil temperature and N mineralization rates may promote lower N₂O emissions (Firestone and Davidson, 1989; Cox et al., 1990; Six et al., 2002). These contrasting effects make it difficult to predict the net impact of RT on N₂O emissions. In addition to these effects, RT can alter vertical distributions of microbial populations and potential enzyme activities that drive soil N₂O production. In light of these complications, it is not surprising that there has been disagreement in modeling efforts regarding tillage impacts on N₂O emissions. A model applied at the national scale predicted increased N₂O emissions across the U.S. with increasing adoption of RT (Mummey et al., 1998). The model-based inventory of Li et al. (1996) predicted the opposite effect, but a later version of the same model arrived at different conclusions (Li et al., 2005). A recent study compared model simulations to field N₂O data obtained under different tillage treatments with reasonable success (Del Grosso et al., 2006).
2008). But generally, there have been few attempts to account for tillage-induced changes in soil physical, chemical, and biochemical properties in models describing N\textsubscript{2}O flux. While N\textsubscript{2}O emissions have been measured in several tillage studies, results have been conflicting. Studies have shown increased (Goodroad et al., 1984), decreased (Kessavalou et al., 1998), or no change (Kaharabata et al., 2003) resulting from RT. A recent study found that the direction of the tillage effect differed depending on fertilizer practices (Venterea et al., 2005). There is no consensus regarding the magnitude, or even the direction, of tillage effects on N\textsubscript{2}O emissions that might inform policy with respect to C offsets.

The objective of the current study was to closely examine vertical distributions of key soil physical and biochemical factors that control N\textsubscript{2}O emissions in soil profiles from a long-term tillage study in Minnesota, USA. The profile data were then used as inputs to a process-based N\textsubscript{2}O emissions model as a means of investigating potential interactions among key driving variables that ultimately determine N\textsubscript{2}O fluxes.

### Materials and Methods

#### Research Site

Research plots were located at the University of Minnesota’s Research and Outreach Station in Rosemount, MN (44°45′N, 93°04′W) where annual 30-yr mean precipitation and temperature are 879 mm and 6.4°C, respectively. Soil was a loess-derived Waukegan silt loam containing 23% clay and 22% sand. Since 1991, tillage management treatments have been maintained in replicated 0.18-ha plots managed under a corn (Zea mays L.)-soybean (Glycine max L.) rotation. Treatments examined in the current study consisted of (i) CT, which employed fall moldboard plowing (to 18 cm) following corn, fall chisel plowing or disk-ripping (to 20 cm) following soybean, with spring pre-plant cultivation before both corn and soybean, and (ii) NT, which employed no fall tillage or spring cultivation (Venterea et al., 2005, 2006).

#### Potential Nitrous Oxide Production Rates

Soil samples were collected from between rows in three replicate plots under each treatment during the corn phase of the rotation in mid July 2006 and again in mid April 2007 before spring cultivation for soybean. Soils were collected from subplots that received 120 kg N ha\textsuperscript{-1} as urea which was surface-applied in mid June. Multiple samples (4-6) were collected from each plot using a manual corer (18-mm ID) to a depth of 30 cm. Each core was subdivided into 0 to 5, 5 to 10, 10 to 20, and 20 to 30 cm depth intervals. Samples from the same intervals within each plot were composited and stored at 4°C before measurements which were completed with 14 d of sampling. Production of N\textsubscript{2}O under aerobic conditions in the presence of NO\textsubscript{2}\textsuperscript{-} was determined in three replicate 10-g sieved (2 mm) subsamples using the methods of Venterea (2007). Samples in 160-mL glass serum bottles were amended with 0.5 mL of NaNO\textsubscript{3} solutions to generate NO\textsubscript{2}\textsuperscript{-} concentrations over the range of 0 to 50 mg N kg\textsuperscript{-1} soil. Bottles were sealed with caps lined with butyl-rubber septa, incubated at 25°C, and mixed manually at 30-min intervals. Gas samples were removed by syringe after 30, 60, and 90 min and transferred to 9-mL septum-capped glass vials which were analyzed by gas chromatography (GC) using electron capture detection (ECD) (Venterea et al., 2005). The ECD was calibrated using certified N\textsubscript{2}O gas standards (Scott Specialty Gases, Plumsteadville, PA). The N\textsubscript{2}O production rate (P, mg N kg\textsuperscript{-1} soil h\textsuperscript{-1}) was calculated from the slope of headspace N\textsubscript{2}O concentration versus time, headspace volume, dry soil mass, and accounting for equilibrium gas-liquid partitioning (Tiedje, 1994). Additional measurements performed across a range of soil water contents and O\textsubscript{2} headspace concentrations following amendment with either NO\textsubscript{2}\textsuperscript{-} or NO\textsubscript{3}\textsuperscript{-} indicated that >95% of the N\textsubscript{2}O produced under the above conditions was due to processes other than heterotrophic NO\textsubscript{3}\textsuperscript{-} reduction (i.e., denitrification) (Venterea, 2007). Potential N\textsubscript{2}O production under aerobic conditions was expressed as a rate coefficient K\textsubscript{p} (h\textsuperscript{-1}) obtained by linear regression of P versus NO\textsubscript{2}\textsuperscript{-} concentration (mg N kg\textsuperscript{-1} soil h\textsuperscript{-1}) using (Venterea, 2007):

\[
P = K_p [\text{NO}_2^-]
\]

Denitrifier enzyme activity (DEA) was determined in three replicate 10-g sieved subsamples using methods based on Tiedje (1994). Samples were added to microcosms consisting of 160-mL glass serum bottles amended with 10 mL of solution containing 1 mmol L\textsuperscript{-1} D-glucose and 7.1 mmol L\textsuperscript{-1} KNO\textsubscript{3} (100 mg N kg\textsuperscript{-1} soil). Initial headspace oxygen (O\textsubscript{2}) concentration was reduced to <0.1% using a vacuum/pressurization manifold equipped with a digital vacuum-pressure gauge (DPG-1000, Omega Engineering, Stamford, CT) (Venterea, 2007). Microcosms were amended with 12 mL of acetylene (C\textsubscript{2}H\textsubscript{2}) to inhibit N\textsubscript{2}O reduction. Bottles were incubated on a reciprocating shaker at 200 rpm and 25°C. Gas samples were collected for N\textsubscript{2}O analysis by GC at 30, 60, and 90 min. DEA was expressed as the N\textsubscript{2}O production rate (mg N kg\textsuperscript{-1} soil h\textsuperscript{-1}). Additional samples for DEA determination per above were collected from the 0 to 10 and 10 to 20 cm depth intervals in corn plots during June and August 2005.

#### Chemical and Physical Properties

Soluble organic C (SOC) was determined in samples collected from the 0- to 10-cm and 10- to 20-cm depths at monthly intervals over the course of the growing season, and in additional samples (above) collected in July and April. Sieved samples (8 g) were extracted with 32 mL of 10 mmol L\textsuperscript{-1} CaCl\textsubscript{2}. Extracts were passed through 0.4 μm polycarbonate filters and analyzed by UV-persulfate oxidation (Phoenix 8000, Tekmar-Dohrmann, Cincinnati, OH). Aerobically mineralizable C was determined in the July samples by incubating sieved 20-g subsamples from each depth at field moisture content and 25°C in 160-mL serum bottles for 7 d. Gas samples were collected at 2- to 3-d intervals for analysis of CO\textsubscript{2} concentrations by GC using thermal conductivity detection. Bottles were uncapped for 1-h periods immediately after each sampling event to maintain aerobic conditions and then sampled again immediately after re-sealing bottles. Cumulative mass of C per mass soil released over 7 d was calculated from increases in CO\textsubscript{2} concentration. Total C and N content of soils were determined in sieved and ball-milled subsamples collected in July by combustion (Model NA 1500 NC, Carlo Erba/Fisons,
Milan, Italy). Soil pH was determined in 5-g sieved July subsamples mixed with an equal mass of 1 mol L\(^{-1}\) KCl. Soil \(\text{NO}_x\) concentration data from multiple sampling events across the entire growing season for these plots were previously reported (Venterea et al., 2005). No differences by tillage were observed, although \(\text{NO}_x\) concentrations were higher in CT soils before spring fertilizer application (described below). Microbial and chemical property data were evaluated by analysis of variance (ANOVA) with tillage as the main treatment and depth as a sub-plot treatment using general linear model procedures in SAS (SAS, 2002). The appropriate least significant difference (LSD) was calculated manually for mean comparisons using significance criteria of \(P = 0.05\) (Gomez and Gomez, 1984). Soil water content and bulk density were determined by drying at 105°C for 24 h in samples collected for microbial enzyme analysis and from additional samples collected periodically. Soil temperature was measured using manual probes as well as thermocouples installed at 5- to 10-cm intervals over the 0- to 30-cm depth in three replicate plots under each treatment. Thermocouples were connected to continuous data loggers (Campbell Scientific, Logan Utah) and temperatures were recorded at 1-h intervals.

**Modeling**

**General Approach**

Measured vertical distributions of the above properties were used as inputs to steady-state diffusion-reaction models of the form (Venterea and Rolston, 2002a):

\[
\frac{d}{dz} \left( D_p \frac{d[N_2O]}{dz} \right) = \rho (P - S)
\]

where \(D_p\) is the soil-gas diffusion coefficient (m\(^3\) gas m\(^{-1}\) soil h\(^{-1}\)), \([N_2O]\) is the soil-gas \(N_2O\) concentration (mg N m\(^{-3}\) gas), \(\rho\) is bulk density (kg soil m\(^{-3}\) soil), and \(P\) and \(S\) are the gross \(N_2O\) production and consumption rates (mg N kg\(^{-1}\) soil h\(^{-1}\)), respectively, all of which may vary as a function of soil depth (\(z\), m soil). Values for \(D_p\) were determined from the diffusivity of \(N_2O\) in free air as a function of temperature, volumetric gas content, and total porosity using the empirical relationships of Rolston and Moldrup (2002), where gas content and porosity were calculated from bulk density and water content. Soil to atmosphere \(N_2O\) fluxes were calculated by solving Eq. [2] using finite difference methods with boundary conditions (i) \(z = 0, [N_2O] = 0.00035\) mg N m\(^{-3}\) gas and (ii) \(z = 0.3\) m, \(d[N_2O]/dz = 0\), to obtain soil-gas \(N_2O\) concentrations at 1 mm depth intervals and then applying Fick’s equation to the upper 1 mm. Two general cases were considered with respect to the origin of \(N_2O\) production: (i) nitrification-dominated conditions in the presence of soil \(NO_3^-\), and (ii) denitrification-dominated conditions in the presence of \(NO_3^-\).

**Nitrification-Dominated Nitrous Oxide Emissions**

The nitrification case assumed water content and bulk density profiles measured under relatively dry conditions (described below). The production of \(N_2O\) was described by Eq. [1], where \(K'_p\) values measured as a function of depth were used to supply the model with \(K'_p\) values at the base temperature (25°C). The temperature sensitivity of \(K'_p\) was described by the Arrhenius equation using activation energies of 56 and 60 kJ mol\(^{-1}\) for CT and NT, respectively (Venterea, 2007). No \(N_2O\) consumption was assumed (i.e., \(S = 0\)) based on measurements showing no \(N_2O\) reduction when these soils were incubated under headspace \(O_2 \geq 5\%\) (Venterea, 2007).

**Denitrification-Dominated Nitrous Oxide Emissions**

The denitrification case assumed water content and bulk density profiles under relatively wet conditions (described below). Gross \(N_2O\) production (\(P\)) and consumption (\(S\)) were described by Michaelis-Menten formulations describing the dual dependence of denitrification rates on concentrations of \(N\) substrate and labile C (Bowman and Focht, 1974; Kremen et al., 2005):

\[
P = \varphi \left( \frac{V_{N2O}^{\text{NO}} [\text{NO}]_3}{K_{m}^{\text{NO}} + [\text{NO}]_3} \right) \left[ C \right] - \left[ C \right]
\]

\[
S = \varphi \left( \frac{V_{N2O}^{\text{NO}} H[\text{N}_2\text{O}]}{K_{m}^{\text{N}_2\text{O}} + H[\text{N}_2\text{O}]} \right) \left[ C \right] - \left[ C \right]
\]

In Eq. [3] and [4], denitrification occurs only in the anaerobic fraction (\(\varphi\)) of the soil volume, where \(\varphi\) varies from 0 to 1, and where concentrations of labile C (\([C]\), mg C m\(^{-3}\) H\(_2\)O) and the relevant N substrate (\([\text{NO}_3^-]\), mg N m\(^{-3}\) H\(_2\)O or \([\text{NO}_2^-]\), mg N m\(^{-3}\) gas), and the maximum production and consumption rates (\(V_{N2O}^{\text{NO}}\) and \(V_{N2O}^{\text{NO}}\), mg N kg\(^{-1}\) h\(^{-1}\)) may all vary with \(z\). The Henry’s Law coefficient for \(N_2O\) (\(H\), m\(^3\) gas m\(^{-3}\) H\(_2\)O) was calculated as a function of temperature (Sander, 1999) and was used to convert \(N_2O\) gas concentrations to a liquid phase basis assuming instantaneous equilibrium. Dinitrogen (\(N_2\)) flux was determined by simultaneously solving an equation analogous to Eq. [2] with \(P\) described by the right side of Eq. [4] and \(S = 0\).

Under conditions maintained in the DEA assays, i.e., \(\varphi = 1, [C] = K_{m}^{\text{C}}\) and \([\text{NO}_3^-] = K_{m}^{\text{NO}}\) Eq. [3] reduces to \(P = V_{N2O}^{\text{NO}}\). Thus, DEA data were used to represent the base temperature \(V_{N2O}^{\text{NO}}\) values in Eq. [3] as a function of depth in each tillage treatment. The base temperature \(V_{N2O}^{\text{NO}}\) values were estimated using a \(V_{N2O}^{\text{NO}} / V_{N2O}^{\text{NO}}\) ratio of 2.0 as used in other models (Leffelaar and Wessell, 1988; Riley and Matson, 2000; Li, 2000). Temperature sensitivities of \(V_{N2O}^{\text{NO}}\) and \(V_{N2O}^{\text{NO}}\) were modeled using a \(Q_10\) factor of 2.0. Values for \(K_{m}^{\text{NO}}\) and \(K_{m}^{\text{N}_2\text{O}}\) of 8.8 g \(\text{NO}_3^-\)-N m\(^{-3}\) H\(_2\)O (630 \(\mu\)mol L\(^{-1}\)) and 0.50 g \(\text{NO}_3^-\)-N m\(^{-3}\) H\(_2\)O (18 \(\mu\)mol L\(^{-1}\)) were taken from the model of Kremen et al. (2005). A value for \(K_{m}^{\text{C}}\) of 17 g C m\(^{-3}\) was taken from the value used by Li (2000) and Riley and Matson (2000). We found a very similar \(K_{m}^{\text{C}}\) value in these soils and no difference in \(K_{m}^{\text{C}}\) between CT and NT (Venterea, unpublished data, 2006). Measured values of SOC as a function of depth and tillage treatment were used as model inputs for [C].

Anaerobic fraction (\(\varphi\)) was calculated at each depth using the empirical model of Arah and Vinten (1995), where \(\varphi\) is a function of the matric potential, the soil \(O_2\) uptake.
rate \( (V_O) \), and the soil-gas \( O_2 \) concentration and diffusivity, as applied by Riley and Matson (2000) to successfully describe denitrification-driven \( N_2O \) emissions in fertilized soils. Soil-gas \( O_2 \) concentration profiles for use in calculating \( q \) were determined from analytical solution of the diffusion equation for \( O_2 \) assuming that \( V_O \) represented a zero-order uptake rate, with \( V_O = 0.3 \) mol \( O_2 \) m\(^{-3}\) h\(^{-1}\) (Venterea and Rolston, 2002a,b).

Inorganic Nitrogen Distributions

Two different sets of conditions were assumed with respect to the vertical distribution of soil \( NO_3^- \) and \( NO_2^- \). One set was used to represent conditions following fertilizer application during periods of peak soil N concentrations and high \( N_2O \) fluxes. Post-fertilizer soil \( NO_3^- \) measurements previously reported in these plots found no significant differences by tillage treatment across the growing season (Venterea et al., 2005). A Gaussian distribution given by

\[
NO_2^- or NO_3^- = M \exp \left( -0.5 \left( \frac{z - z_o}{1.5355} \right)^2 \right)
\]

was used to represent vertical profiles of \( NO_2^- \) and \( NO_3^- \) for the nitrification and denitrification cases, respectively, where \( M \) is the maximum concentration which occurs at depth \( z_o \) corresponding to the center of the “band” (shown in Fig. 1a). Simulations were conducted for inorganic N centered at differing depths over the range of \( z_o = 1 \) to 25 cm. For \( z_o \geq 5 \) cm, a value for \( M \) of 50 g N m\(^{-3}\) H\(_2\)O was assumed, which corresponds to approximately 5 kg N ha\(^{-1}\). For \( z_o < 5 \) cm, \( M \) was increased to compensate for truncation of the distribution to maintain a total of 5 kg N ha\(^{-1}\).

A second set of simulations, using the denitrification case only, was used to represent early-season conditions before fertilizer application when \( NO_3^- \) availability in CT soils were found to be greater than in NT soils \((P < 0.01)\), using data from Venterea et al. (2005). Weekly soil \( NO_3^- \) measurements during a 6-wk period (May to early June) found mean \( NO_3^- \) concentrations of 7.5 and 8.3 mg N kg\(^{-1}\) in CT at 0 to 10 and 10 to 20 cm, respectively, compared to 4.4 and 4.0 mg N kg\(^{-1}\) in NT. Therefore, simulations were performed assuming a fixed \( NO_3^- \) concentration of 4.2 mg N kg\(^{-1}\) for NT, while the \( NO_3^- \) concentration in CT was allowed to vary over 4.2 to 12.6 mg N kg\(^{-1}\) (representing a NT/CT ratio of 1:1 to 1:3).

Results and Discussion

Chemical and Physical Properties

Higher moisture content and bulk density, and lower temperature in surface soils under NT compared to CT have been reported in several previous studies (e.g., Cox et al., 1990) including studies at this site (Venterea et al., 2005, 2006). The main objective of reporting data here was to provide inputs for model simulations that were representative of conditions favoring either nitrification- or denitrification-driven \( N_2O \). The silt loam at this site is very well drained due to an underlying layer of outwash sands starting at 60 to 80 cm. Even following substantial rainfall, soil water-filled pore space (WFPS) rarely exceeds 80% and is generally in the range of 40 to 70% (Venterea et al., 2006). Therefore, for bulk density and moisture content, we used data collected under both moderately dry and moderately wet conditions, where WFPS at 10 cm was 45 to 55% and 60 to 70%, respectively (Fig. 1b,c). The selected profiles also reflect that differences in soil moisture between NT and CT are greatest during drier periods (Venterea et al., 2006). Differences in soil temperature between NT and CT are greatest in early spring, and by July differences generally disappear (Venterea et al., 2006). In the model simulations, we compare conditions using a temperature profile measured in April (Fig. 1d) to conditions where temperature is uniform (20°C) throughout both profiles.

Consistent with previous studies, soil C in NT soil was significantly higher than CT in the upper 0 to 5 cm (Fig. 1e) and soil pH in NT soil was lower than CT (Fig. 1f) (Dick, 1983; West and Post, 2002). Levels of SOC were higher in CT compared to
NT soils below 5 cm while contrasting patterns were observed at 0 to 5 cm in July and April (Fig. 1g). SOC at 0- to 10- and 10- to 20-cm depths throughout the growing season were consistent with the July profile data. Mean SOC concentrations at 0 to 10 and 10 to 20 cm under CT were 8.8 (1.1) and 9.7 (1.4) mg C kg\(^{-1}\), respectively, compared to 6.8 (0.46) and 6.7 (0.75) mg C kg\(^{-1}\) under NT. Mineralizable C levels were correlated with SOC (\(r^2 = 0.40, P = 0.001\)) and showed a similar vertical pattern to SOC although differences were not significant (Fig. 1f).

Tillage can promote residue decomposition (Six et al., 2002) and result in higher SOC under CT. However, higher soil moisture under NT may also promote greater mineralization rates (Venterea, 2007). Therefore, the contrasting results found on different sampling dates in surface soils is not surprising.

**Potential Nitrous Oxide Production Rates**

Over the entire sampled depth (0–30 cm) and accounting for bulk density differences, vertically integrated DEA was similar under CT and NT in July 2006 (7.1 and 6.8 kg N ha\(^{-1}\) d\(^{-1}\)) and April 2007 (9.7 and 10.4 kg N ha\(^{-1}\) d\(^{-1}\)). However, significant tillage-by-depth interaction effects were evident, with consistent patterns displayed on both dates (Fig. 2a). In CT soil, DEA was relatively uniform in the upper 0 to 20 cm and decreased at 20 to 30 cm. This pattern is consistent with vertical mixing resulting from tillage, which is typically done to a depth of 18 to 20 cm at this site. A lack of mixing was evident under NT soil, where DEA in the upper 0 to 5 cm was two to five times greater than CT and decreased with depth. At the 5- to 10- and 10- to 20-cm depths, DEA in NT soil was generally lower than in CT, but converged with CT at 20 to 30 cm. DEA in samples collected in June and August 2005 from the 0- to 10-cm and 10- to 20-cm depths were consistent with the above results. Mean DEA in CT and NT soil were 0.07 and 0.1 mg N kg\(^{-1}\) h\(^{-1}\) at 0 to 10 cm, respectively, and 0.06 and 0.03 mg N kg\(^{-1}\) h\(^{-1}\) at 10 to 20 cm. Using coarser spatial resolution than the current study, Linn and Doran (1984) and Groffman (1985) found the same pattern of higher potential denitrifier activity under NT compared to CT above the tillage zone and the reverse pattern or no differences below the tillage zone. The DEA assay measures activities of a large group of denitrifying microbes that depend on organic compounds for carbon and energy and thus would be expected to be stimulated by organic matter incorporation (Tiedje, 1994). The vertical distribution of soil C in CT soil displayed the same pattern of uniformity in the upper 0 to 20 cm and relatively lower amounts at 20 to 30 cm (Fig. 1e). DEA across both tillage treatments was positively correlated with soil total C (\(r^2 = 0.49, P < 0.001\)).

Across the entire 30-cm profile, potential aerobic N\(_2\)O production in the presence of 50 mg NO\(_2\)\(^{-}\) N kg\(^{-1}\) was higher in NT soil (2.3 and 3.4 kg N ha\(^{-1}\) d\(^{-1}\) in July and April, respectively) than CT (0.77 and 1.2 kg N ha\(^{-1}\) d\(^{-1}\)) (\(P < 0.05\)). Significant tillage by depth interaction effects were also evident in the \(K_p\) results (Fig. 2b), with consistent values observed on both dates. In contrast to DEA, \(K_p\) in the CT treatment was uniform across the sampled depth, while \(K_p\) in NT soil decreased with depth but remained greater than CT at all depths except at 20 to 30 cm where they converged.

The \(K_p\) assay measures a combination of abiotic and microbial processes (Stevenson et al., 1970; Venterea, 2007). Microbial N\(_2\)O production under these conditions may be largely dominated by autotrophic nitrifying bacteria, some of which are capable of reducing NO\(_2\)\(^{-}\) to N\(_2\)O via so-called “nitrifier denitrification” (Poth and Focht, 1985). Higher \(K_p\) values under NT (Fig. 2b) were likely due to several factors. Both the higher soil C at 0 to 5 cm (Fig. 1e) and generally lower pH (Fig. 1f) above 20 cm in NT soil would promote the abiotic component of aerobic N\(_2\)O production, which is driven by nitrosation reactions involving NO\(_2\)\(^{-}\) and soil organic matter (Stevenson et al., 1970). The generally higher prevailing soil moisture contents in near-surface soils under NT could also support greater proliferation of nitrifying organisms responsible for the biotic component, i.e., nitrifier denitrification (Doran, 1980; Groffman, 1985).

**Modeling**

**Nitrification-Dominated Nitrous Oxide Emissions**

Using water content and bulk density profiles obtained under “dry” conditions, model simulations of anaerobic status supported the assumption that these conditions were fully aerobic (\(\phi < 1\%\)), assuming an \(O_2\) uptake rate of 0.3 mol \(O_2\) m\(^{-2}\) soil h\(^{-1}\). Model simulations of nitrification-derived N\(_2\)O emissions using \(K_p\) data obtained from the July sampling varied from <0.05 to 0.6 kg N ha\(^{-1}\) d\(^{-1}\) depending on \(z_d\), soil treatment, and soil temperature (Fig. 3a). The NT/CT ratio of N\(_2\)O fluxes ranged from 0.8 to 7.6 and increased as \(z_d\) decreased, reflecting the \(K_p\) distributions (Fig. 3b). Using soil temperature profiles obtained in spring resulted in a 25% decrease in the NT/CT ratio. The NT/CT ratio was less than 1 only for spring soil temperature conditions and when the NO\(_2\)\(^{-}\) distribution was centered below 20 cm.

Data comparing NO\(_2\)\(^{-}\) levels in NT and CT soil are not available. Assuming similar soil NO\(_2\)\(^{-}\) concentrations under NT and CT, the above results indicate that under drier conditions, higher N\(_2\)O fluxes are expected from NT soil. This effect will be more pronounced when NO\(_2\)\(^{-}\) is located closer to the surface,
even when CT surface soils are more than 2°C warmer than NT soil. Most soils produce some NO₂⁻ following fertilizer application. Morrill and Dawson (1967) showed that 72 of 92 soils accumulated NO₃⁻ in perfusion experiments. Anhydrous ammonia and urea, which together account for 80% of worldwide N fertilizer use (IFA, 2006), can generate NO₂⁻ levels exceeding 50 mg N kg⁻¹ (Chapman and Liebeng, 1952; Chalk et al., 1975). Lower NO₃⁻ levels are expected with NH₄⁺ or NO₂⁻ salts or urea-ammonium-nitrate (UAN). Except under highly alkaline conditions, these forms would not be expected to generate as much free ammonia (NH₃) as anhydrous ammonia or urea. Free NH₃ is believed to promote NO₂⁻ accumulation via its toxicity to NO₃⁻ oxidizing bacteria (Van Cleemput and Samatar, 1996).

Denitrification-Dominated Nitrous Oxide Emissions

Due to higher water content and bulk density in NT soil, the simulated N₂O soil-gas diffusivity (Dₚ) was two to three times higher in the upper 10 cm of CT soil compared to NT (Fig. 4a). This difference in Dₚ resulted in substantially lower simulated O₂ soil-gas concentrations and higher anaerobic fractions (φ) in NT soil (Fig. 4b). Using these φ profiles and the SOC profiles measured in July, the denitrified N₂O production rates (P) as a function of depth were calculated assuming varying depths of the NO₂⁻ distribution (z) (Fig. 4c,d). One set of calculations assumed that Vₚₜₐₓ values were constant with depth, using mass-weighted values of DEA measured across the entire 0-30-cm depth in July. These values were similar in CT and NT (0.075 and 0.073 mg N kg⁻¹ h⁻¹, respectively). With this assumption, P was predicted to be consistently higher in NT soil across all values of z (Fig. 4c), indicating that the higher φ in NT soil predominated over the higher SOC in CT soil. A second set of calculations was made that also accounted for vertical variation in Vₚₜₐₓ using DEA measured at each depth interval in July. This case resulted in higher P values in NT relative to CT for z < 7.5 cm, but more similar P values for NT and CT when z ≥ 15 cm (Fig. 4d). These calculations demonstrate the importance of vertical variation in Vₚₜₐₓ in controlling N₂O emissions. They also reveal that rates expected under field conditions where φ, SOC, and NO₂⁻ all limit denitrification were small in relation to DEA measured under non-limiting laboratory conditions. For example, the maximum calculated rates in CT and NT for z = 15 cm were 11 and 43% of DEA measured in samples from the 10-20 cm depth (Fig. 4d, 2a).

Using P profiles in Fig. 4d and also accounting for gaseous diffusion and reduction of N₂O in the profile, simulated denitrification-derived N₂O fluxes varied greatly depending on z (Fig. 5a). For z < 10 cm, the NT/CT ratio was even higher than the nitrification case, approaching 40 for z = 5 cm (Fig. 5b). However, when NO₂⁻ was deeper in the profile (z > 15 cm), simulated N₂O flux was higher from CT than NT. Thus, the model calculates that for NO₂⁻ located below 15 cm, the higher SOC and DEA in CT soil at these depths counteracted the lower anaerobic fractions, resulting in higher net N₂O emissions than in NT. Another factor contributing to this result was that a greater fraction (~25%) of the N₂O produced in NT soil was reduced to N₂ before reaching

**Fig. 4.** Simulated vertical profiles under no till (NT, dashed lines) and conventional tillage (CT, solid lines) of (a) N₂O soil-gas diffusivity (Dₚ), (b) soil-gas oxygen (O₂) concentrations and anaerobic fractions (φ), and (c and d) denitrified N₂O production rates (P) calculated using Eq. [3] with varying depths of NO₂⁻ distribution (z). In (c), a constant maximum production rate (Vₚₜₐₓ) was assumed for each tillage treatment across depths (see text for more details). In (d), P was calculated with Vₚₜₐₓ varying with depth based on measured DEA data (Fig. 2a). In (c) and (d), lines showing P for CT at zₚ = 2.5 cm cannot be distinguished from the vertical axes.
The simulations therefore suggest that differences in N$_2$O fluxes under NT following liquid UAN application.

However, even the most detailed dynamic models account for vertical variations in microbial enzyme and chemical reaction potential as done here. An advantage of steady-state models is that they allow for closer examination of a more limited number of factors and assumptions compared to dynamic models. While dynamic models account for additional processes such as water transport, mineralization, nitrification, plant uptake, and others, this requires additional assumptions and introduces significantly more uncertainty in the simulated N$_2$O emissions. The models of Li (2000) and Grant et al. (2006) each employ more than 16 parameter values obtained from literature that are not confirmed for the conditions being simulated. The current application used only three parameter values that were not directly measured, i.e., $K_{m}^{NO_3}$, $V_{max}^{NO_3}$, and $K_{m}^{N_2O}$.

We did attempt to measure the parameters describing N$_2$O reduction kinetics ($V_{max}^{N_2O}$ and $K_{m}^{N_2O}$) using methods based on Holtan-Hartwig et al. (2000). However, we do not report data due to methodological issues which make calculation of the parameters highly uncertain. These issues include (i) pre-incubation and leaching of the soils to reduce ambient NO$_3^-$ levels, (ii) extended incubation leading to possible biomass growth, and (iii) dynamic NO$_3^-$ concentrations during the incubation. Reported literature values for $K_{m}^{N_2O}$ range from 0.1 to 100 $\mu$mol L$^{-1}$ (Holtan-Hartwig et al., 2000) compared to 18 $\mu$mol L$^{-1}$ used here. The $V_{max}^{NO_3}/V_{max}^{N_2O}$ ratio of 2.0 used here based on Leffelaar and Wessel (1988) and Riley and Matson (2000) compared to values in the range of 0.2 to 2.0 measured by Holtan-Hartwig et al. (2000). A sensitivity analysis of these parameters in the current model indicates that the overall trends in NT/CT ratios of N$_2$O flux as a function of $z_o$ are not greatly affected by parameter variations, except for values near the low end of the range (Fig. 6). However, a key question here is whether these parameters vary by tillage treatment, which could substantially alter the NT/CT ratios of N$_2$O flux. Improved methods for determining N$_2$O reduction kinetics, perhaps utilizing $^{15}$N-labeled N$_2$O (Clough et al., 2006), would improve N$_2$O emissions models that employ these formulations. It should also be noted that the current model also does not account for other tillage-induced properties that may be important. For example, $O_2$ uptake rates may vary with depth and tillage treatment, and the interiors of soil aggregates close to the surface may undergo anaerobic conditions that is not simulated here (Kremen et al., 2005).

**Conclusions**

Subsurface application of N fertilizer in RT systems appears to have the greatest potential for minimizing N$_2$O emissions relative to CT. This practice would minimize contact between N substrates and the most active zone of enzyme activity while also promoting greater reduction to N$_2$ as N$_2$O diffuses through surface soils. Over the long term, subsurface N application is not likely to alter microbial enzyme profiles since these are driven largely by organic C, water content, and soil pH distributions, although this issue should be examined experimentally. The potential for higher N$_2$O fluxes under drier, nitrification-dominated conditions in RT soil found here also needs to be considered. Fertilizer forms such as anhydrous ammonia and urea which
promote NO\textsubscript{2}\textsuperscript{−} accumulation should be avoided, especially in acid soils. Slow-release fertilizers injected below the surface may be the best overall solution (see Halvorson et al., 2008). Another consideration would be pH management to achieve near-neutral conditions, since both acidic and alkaline soil conditions may promote NO\textsubscript{2}−-driven N\textsubscript{2}O fluxes (Venterea, 2007).

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**References**


