

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

Rodney T. Venterea* and Adam J. Stenenas USDA-ARS

The impact of no-till (NT) and other reduced tillage (RT) practices on soil to atmosphere fluxes of nitrous oxide (N_2O) are difficult to predict, and there is limited information regarding strategies for minimizing fluxes from RT systems. We measured vertical distributions of key microbial, chemical, and physical properties in soils from a long-term tillage experiment and used these data as inputs to a process-based model that accounts for N_2O production, consumption, and gaseous diffusion. The results demonstrate how differences among tillage systems in the stratification of microbial enzyme activity, chemical reactivity, and other properties can control N_2O fluxes. Under nitrification-dominated conditions, simulated N_2O emissions in the presence of nitrite (NO_2^-) were 2 to 10 times higher in NT soil compared to soil under conventional tillage (CT). Under denitrification-dominated conditions in the presence of nitrate (NO_3^-), higher bulk density and water content under NT promoted higher denitrification rates than CT. These effects were partially offset by higher soluble organic carbon and/or temperature and lower N_2O reduction rates under CT. The NT/CT ratio of N_2O fluxes increased as NO_2^- or NO_3^- was placed closer to the surface. The highest NT/CT ratios of N_2O flux (>30:1) were predicted for near-surface NO_3^- placement, while NT/CT ratios < 1 were predicted for NO_3^- placement below 15 cm. These results suggest that N_2O fluxes from RT systems can be minimized by subsurface fertilizer placement and by using a chemical form of fertilizer that does not promote substantial NO_2^- accumulation.

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 N_2O , which has a global warming potential 300 times greater than carbon dioxide (CO_2), 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 N_2O fluxes. Some of these effects, including increased water content and bulk density, would be expected to promote higher N_2O flux, while other changes, such as decreased soil temperature and N mineralization rates may promote lower N_2O 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 N_2O emissions. In addition to these effects, RT can alter vertical distributions of microbial populations and potential enzyme activities that drive soil N_2O production (Linn and Doran, 1984; Groffman, 1985). The production of N_2O depends on the coexistence of microbial enzymes with other conditions, including anaerobiosis and sufficient levels of labile C and reduced inorganic N, each of which may also vary across the soil profile. Thus, the net result of changes in microbial enzyme vertical distributions on N_2O emissions are also difficult to predict. Quantitative models which explicitly account for spatial distributions of key driving variables are one means of evaluating the net impacts of these effects.

In light of these complications, it is not surprising that there has been disagreement in modeling efforts regarding tillage impacts on N_2O emissions. A model applied at the national scale predicted increased N_2O 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 N_2O data obtained under different tillage treatments with reasonable success (Del Grosso et al.,

Copyright © 2008 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Published in *J. Environ. Qual.* 37:1360–1367 (2008).
doi:10.2134/jeq2007.0283
Received 1 June 2007.

*Corresponding author (rod.venterea@ars.usda.gov).
© ASA, CSSA, SSSA
677 S. Segoe Rd., Madison, WI 53711 USA

USDA-ARS, Soil and Water Research Management Unit, 1991 Upper Buford Cir., 439 Borlaug Hall, St. Paul, MN 55108. Mention of product names is for the convenience of the reader and implies no endorsement on the part of the author or the USDA.

Abbreviations: CT, conventional tillage; DEA, denitrifier enzyme activity; GHG, greenhouse gas; NT, no till; RT, reduced tillage; SOC, soluble organic carbon; UAN, urea ammonium nitrate.

2008). But generally, there have been few attempts to account for tillage-induced changes in soil physical, chemical, and biochemical properties in models describing N₂O flux. While N₂O 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 N₂O 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 N₂O 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 N₂O emissions model as a means of investigating potential interactions among key driving variables that ultimately determine N₂O 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⁻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 N₂O under aerobic conditions in the presence of NO₂⁻ 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 NaNO₂ solutions to generate NO₂⁻ concentrations over the range of 0 to 50 mg N kg⁻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 N₂O gas standards (Scott Specialty Gases, Plumsteadville, PA). The N₂O production rate (P , mg N kg⁻¹ soil h⁻¹) was calculated from the slope of headspace N₂O 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 O₂ headspace concentrations following amendment with either NO₂⁻ or NO₃⁻ indicated that >95% of the N₂O produced under the above conditions was due to processes other than heterotrophic NO₃⁻ reduction (i.e., denitrification) (Venterea, 2007). Potential N₂O production under aerobic conditions was expressed as a rate coefficient K_p (h⁻¹) obtained by linear regression of P versus NO₂⁻ concentration (mg N kg⁻¹) using (Venterea, 2007):

$$P = K_p[\text{NO}_2^-] \quad [1]$$

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⁻¹ D-glucose and 7.1 mmol L⁻¹ KNO₃ (100 mg N kg⁻¹ soil). Initial headspace oxygen (O₂) 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 (C₂H₂) to inhibit N₂O reduction. Bottles were incubated on a reciprocating shaker at 200 rpm and 25°C. Gas samples were collected for N₂O analysis by GC at 30, 60, and 90 min. DEA was expressed as the N₂O production rate (mg N kg⁻¹ soil h⁻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⁻¹ CaCl₂. 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 CO₂ 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 CO₂ 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 NO₃⁻ 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 NO₃⁻ 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):

$$-\frac{d}{dz}\left(D_p \frac{d[N_2O]}{dz}\right) = \rho[P - S] \quad [2]$$

where D_p is the soil-gas diffusion coefficient (m³ gas m⁻¹ soil h⁻¹), $[N_2O]$ is the soil-gas N₂O concentration (mg N m⁻³ gas), ρ is bulk density (kg soil m⁻³ soil), and P and S are the gross N₂O 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 N₂O 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 N₂O 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 N₂O 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 N₂O production: (i) nitrification-dominated conditions in the presence of soil NO₂⁻, and (ii) denitrification-dominated conditions in the presence of NO₃⁻.

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 N₂O 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 N₂O consumption was assumed (i.e., $S = 0$) based on measurements showing no N₂O reduction when these soils were incubated under headspace O₂ ≥ 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 N₂O 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):

$$P = \varphi \left(\frac{V_{\max}^{NO_3} [NO_3^-]}{K_m^{NO_3} + [NO_3^-]} \right) \left(\frac{[C]}{K_m^C + [C]} \right) \quad [3]$$

$$S = \varphi \left(\frac{V_{\max}^{N_2O} H[N_2O]}{K_m^{N_2O} + H[N_2O]} \right) \left(\frac{[C]}{K_m^C + [C]} \right) \quad [4]$$

In Eq. [3] and [4], denitrification occurs only in the anaerobic fraction (φ) of the soil volume, where φ varies from 0 to 1, and where concentrations of labile C ($[C]$, mg C m⁻³ H₂O) and the relevant N substrate ($[NO_3^-]$, mg N m⁻³ H₂O or $[N_2O]$, mg N m⁻³ gas), and the maximum production and consumption rates ($V_{\max}^{NO_3}$ and $V_{\max}^{N_2O}$, mg N kg⁻¹ h⁻¹) may all vary with z . The Henry's Law coefficient for N₂O (H , m³ gas m⁻³ H₂O) was calculated as a function of temperature (Sander, 1999) and was used to convert N₂O gas concentrations to a liquid phase basis assuming instantaneous equilibrium. Dinitrogen (N₂) 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., $\varphi = 1$, $[C] \gg K_m^C$, and $[NO_3^-] \gg K_m^{NO_3}$, Eq. [3] reduces to $P = V_{\max}^{NO_3}$. Thus, DEA data were used to represent the base temperature $V_{\max}^{NO_3}$ values in Eq. [3] as a function of depth in each tillage treatment. The base temperature $V_{\max}^{N_2O}$ values were estimated using a $V_{\max}^{NO_3} / V_{\max}^{N_2O}$ ratio of 2.0 as used in other models (Leffelaar and Wessel, 1988; Riley and Matson, 2000; Li, 2000). Temperature sensitivities of $V_{\max}^{NO_3}$ and $V_{\max}^{N_2O}$ were modeled using a Q_{10} factor of 2.0. Values for $K_m^{NO_3}$ and $K_m^{N_2O}$ of 8.8 g NO₃⁻-N m⁻³ H₂O (630 μmol L⁻¹) and 0.50 g N₂O-N m⁻³ H₂O (18 μmol L⁻¹) were taken from the model of Kremen et al. (2005). A value for K_m^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^C value in these soils and no difference in K_m^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 (φ) was calculated at each depth using the empirical model of Arah and Vinten (1995), where φ is a function of the matric potential, the soil O₂ uptake

rate (V_{O_2}), 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 ϕ were determined from analytical solution of the diffusion equation for O_2 assuming that V_{O_2} represented a zero-order uptake rate, with $V_{O_2} = 0.3 \text{ mol } O_2 \text{ m}^{-3} \text{ h}^{-1}$ (Venterea and Rolston, 2002a,b).

Inorganic Nitrogen Distributions

Two different sets of conditions were assumed with respect to the vertical distribution of soil NO_2^- and NO_3^- . 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

$$NO_2^- \text{ or } NO_3^- = M \exp \left[-0.5 \left(\frac{z - z_0}{1.5355} \right)^2 \right] \quad [5]$$

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_0 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 $z_0 = 1$ to 25 cm. For $z_0 \geq 5$ cm, a value for M of $50 \text{ g N m}^{-3} \text{ H}_2\text{O}$ was assumed, which corresponds to approximately 5 kg N ha^{-1} . For $z_0 < 5$ 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 $12.6 \text{ mg N kg}^{-1}$ (representing a NT/CT ratio of 1:1 to 1:3).

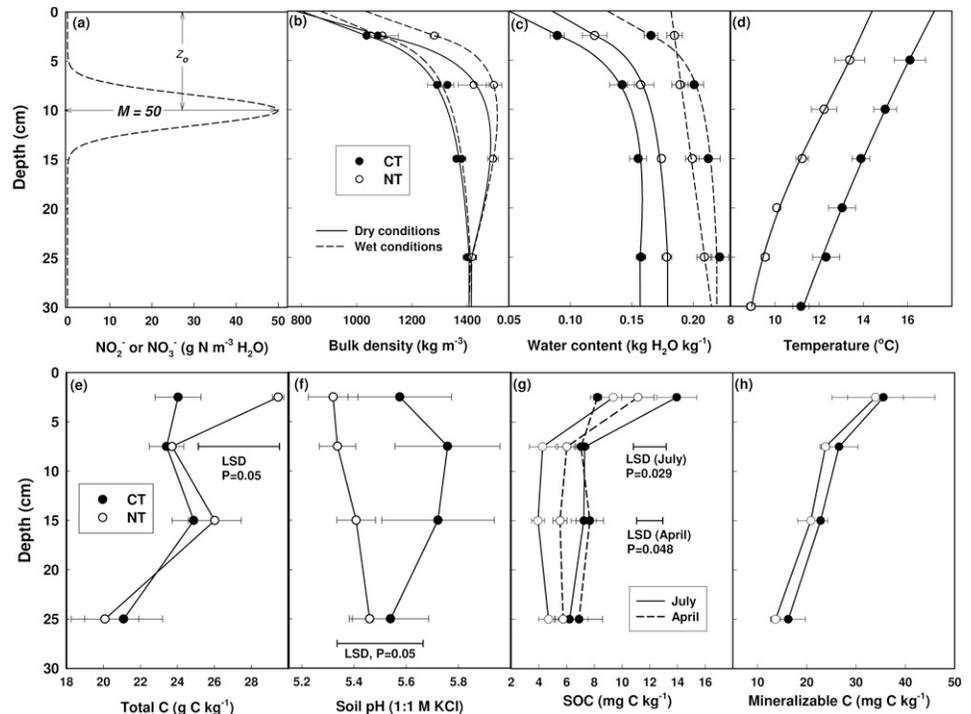


Fig. 1. Vertical profiles of (a) nitrite (NO_2^-) or nitrate (NO_3^-) concentration, (b) bulk density, (c) water content, (d) temperature, (e) total C, (f) pH, (g) soluble organic C (SOC), and (h) 7-d mineralizable C. Symbols in (b-h) are means (with standard error bars) from three plot replicates under conventional tillage (CT) and no till (NT). LSD = least significant difference. In (a), M is the maximum concentration occurring at depth z_0 corresponding to the center of the “band” per Eq. [5].

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

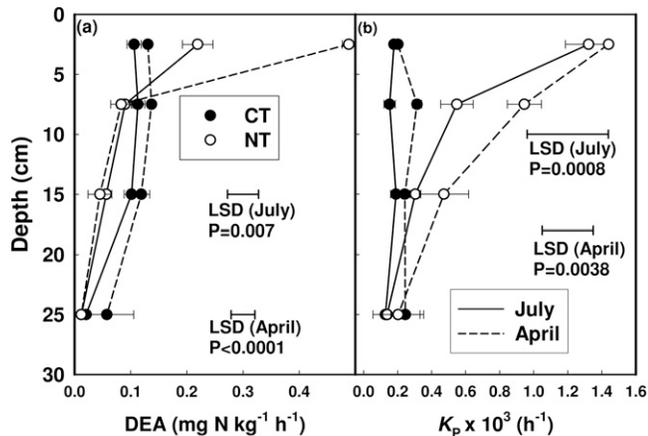


Fig. 2. Vertical profiles of (a) denitrifier enzyme activity (DEA) and (b) potential N₂O production under aerobic conditions expressed as a rate coefficient (K_p , Eq. [1]), in samples collected from conventional tillage (CT) and no till (NT) treatments in July (solid lines) and April (dashed lines). Symbols are means of three plot replicates with standard error bars. LSD = least significant difference.

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 et al., 2006). 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, respectively) 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 deni-

trifier 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 N₂O production in the presence of 50 mg NO₂⁻-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 N₂O production under these conditions may be largely dominated by autotrophic nitrifying bacteria, some of which are capable of reducing NO₂⁻ to N₂O 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 N₂O production, which is driven by nitrosation reactions involving NO₂⁻ 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 O₂ uptake rate of 0.3 mol O₂ m⁻³ soil h⁻¹. Model simulations of nitrification-derived N₂O 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_0 , tillage treatment, and soil temperature (Fig. 3a). The NT/CT ratio of N₂O fluxes ranged from 0.8 to 7.6 and increased as z_0 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 NO₂⁻ distribution was centered below 20 cm.

Data comparing NO₂⁻ levels in NT and CT soil are not available. Assuming similar soil NO₂⁻ concentrations under NT and CT, the above results indicate that under drier conditions, higher N₂O fluxes are expected from NT soil. This effect will be more pronounced when NO₂⁻ is located closer to the surface,

even when CT surface soils are more than 2°C warmer than NT soil. Most soils produce some NO_2^- following fertilizer application. Morrill and Dawson (1967) found that 72 of 92 soils accumulated NO_2^- in perfusion experiments. Anhydrous ammonia and urea, which together account for 80% of worldwide N fertilizer use (IFA, 2006), can generate NO_2^- levels exceeding 50 mg N kg^{-1} (Chapman and Liebeg, 1952; Chalk et al., 1975). Lower NO_2^- levels are expected with NH_4^+ or NO_3^- salts or urea-ammonium-nitrate (UAN). Except under highly alkaline conditions, these forms would not be expected to generate as much free ammonia (NH_3) as anhydrous ammonia or urea. Free NH_3 is believed to promote NO_2^- accumulation via its toxicity to NO_2^- 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 N_2O soil-gas diffusivity (D_p) was two to three times higher in the upper 10 cm of CT soil compared to NT (Fig. 4a). This difference in D_p resulted in substantially lower simulated O_2 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 N_2O production rates (P) as a function of depth were calculated assuming varying depths of the NO_3^- distribution (z_0) (Fig. 4c,d). One set of calculations assumed that $V_{\text{max}}^{\text{NO}_3}$ values were constant with depth, using mass-weighted values of DEA measured across the entire 0- to 30-cm depth in July. These values were similar in CT and NT (0.075 and $0.073 \text{ mg N kg}^{-1} \text{ h}^{-1}$, respectively). With this assumption, P was predicted to be consistently higher in NT soil across all values of z_0 (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 $V_{\text{max}}^{\text{NO}_3}$ using DEA measured at each depth interval in July. This case resulted in higher P values in NT relative to CT for $z_0 \leq 7.5 \text{ cm}$, but more similar P values for NT and CT when $z_0 \geq 15 \text{ cm}$ (Fig. 4d). These calculations demonstrate the importance of vertical variation in $V_{\text{max}}^{\text{NO}_3}$ in controlling

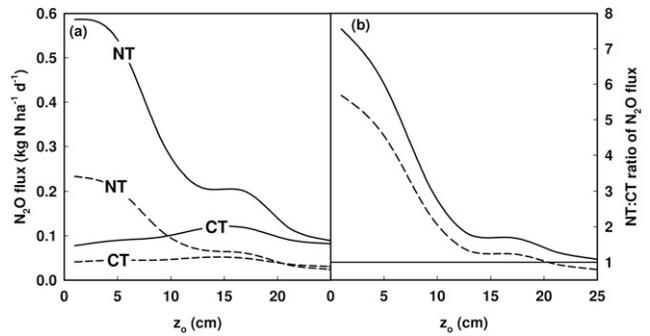


Fig. 3. Simulated (a) nitrification-driven N_2O flux and (b) ratio of nitrified N_2O flux in no till (NT) to conventional tillage (CT) treatments as a function of depth of NO_3^- distribution (z_0) assuming (solid lines) uniform soil temperature profiles (20°C) and (dashed lines) spring soil temperature profile (Fig. 1d). Simulations used K_d data obtained in July 2006 (Fig. 2b) and assumed $M = 50 \text{ g N m}^{-3}$ (Fig. 1a). Horizontal line in (b) corresponds to NT/CT ratio = 1.

N_2O emissions. They also reveal that rates expected under field conditions where ϕ , SOC, and NO_3^- 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 $z_0 = 15 \text{ cm}$ were 11 and 43% of DEA measured in samples from the 10- to 20-cm depth (Fig. 4d, 2a).

Using P profiles in Fig. 4d and also accounting for gaseous diffusion and reduction of N_2O in the profile, simulated denitrification-derived N_2O fluxes varied greatly depending on z_0 (Fig. 5a). For $z_0 < 10 \text{ cm}$, the NT/CT ratio was even higher than the nitrification case, approaching 40 for $z_0 = 5 \text{ cm}$ (Fig. 5b). However, when NO_3^- was deeper in the profile ($z_0 > 15 \text{ cm}$), simulated N_2O flux was higher from CT than NT. Thus, the model calculates that for NO_3^- located below 15 cm, the higher SOC and DEA in CT soil at these depths counteracted the lower anaerobic fractions, resulting in higher net N_2O emissions than in NT. Another factor contributing to this result was that a greater fraction ($\sim 25\%$) of the N_2O produced in NT soil was reduced to N_2 before reaching

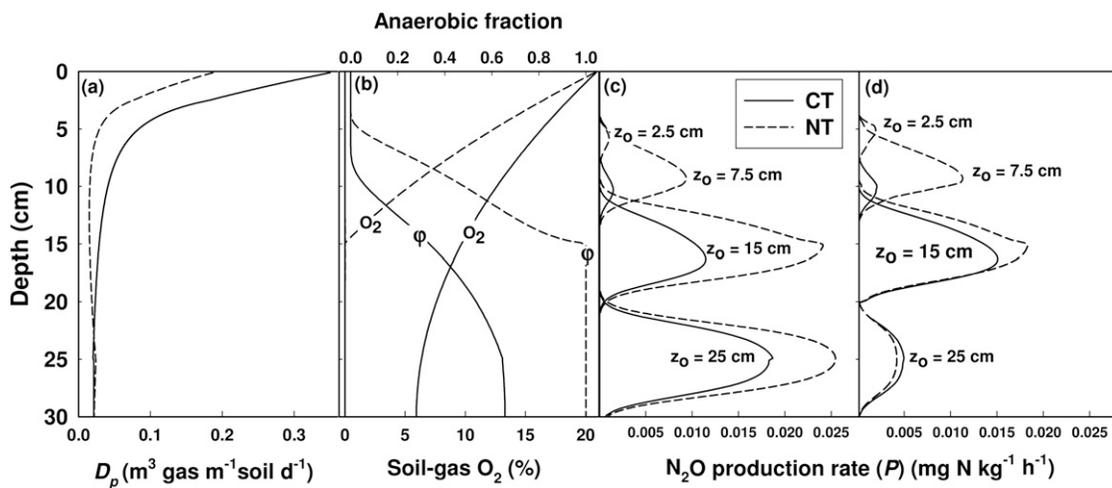


Fig. 4. Simulated vertical profiles under no till (NT, dashed lines) and conventional tillage (CT, solid lines) of (a) N_2O soil-gas diffusivity (D_p), (b) soil-gas oxygen (O_2) concentrations and anaerobic fractions (ϕ), and (c and d) denitrified N_2O production rates (P) calculated using Eq. [3] with varying depths of NO_3^- distribution (z_0). In (c), a constant maximum production rate ($V_{\text{max}}^{\text{NO}_3}$) was assumed for each tillage treatment across depths (see text for more details). In (d), P was calculated with $V_{\text{max}}^{\text{NO}_3}$ varying with depth based on measured DEA data (Fig. 2a). In (c) and (d), lines showing P for CT at $z_0 = 2.5 \text{ cm}$ cannot be distinguished from the vertical axes.

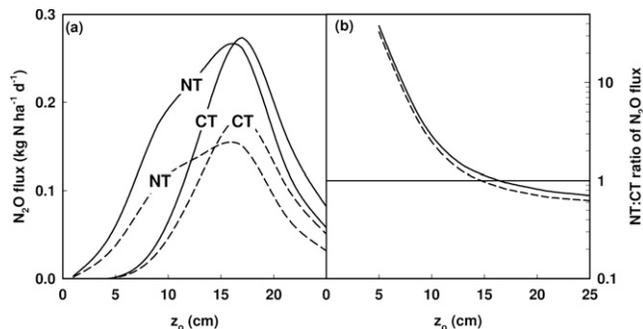


Fig. 5. Simulated (a) denitrification-driven N_2O flux and (b) ratio of denitrified N_2O flux in no till (NT) to conventional tillage (CT) treatments as a function of depth of NO_3^- distribution (z_0) assuming (solid lines) uniform soil temperature profiles (20°C) and (dashed lines) spring soil temperature profile (Fig. 1d). Simulations used SOC and DEA data obtained in July 2006 (Fig. 1g and 2a) assuming $M = 50\ g\ N\ m^{-3}$ (Fig. 1a). In (b), vertical axis is log-scale, horizontal lines correspond to NT/CT ratio = 1, and NT/CT ratios at $z_0 < 5$ cm are not shown because simulated N_2O fluxes in CT approached 0.

the soil surface than in CT soil (~15%) for $z_0 > 18$ cm.

With the assumption of NO_3^- uniformly distributed in the soil profile as indicated by pre-fertilizer field measurements, similar N_2O fluxes were predicted under NT and CT. For NT/CT ratios of soil NO_3^- concentration ranging from 1:1 to 1:3, simulated NT/CT ratios of N_2O flux ranged from 0.7 to 0.6 for $V_{O_2} = 0.3\ mol\ O_2\ m^{-3}\ h^{-1}$ and 0.96 to 1.2 for fully anaerobic conditions ($\phi = 1$ throughout the profile) (results not shown). The simulations therefore suggest that differences in N_2O fluxes by tillage will be more pronounced during the growing season (i.e., after spring fertilizer application). The overall trends are also consistent with results of Venterea et al. (2005) who found that growing season N_2O emissions (i) were higher from CT than NT following injection of anhydrous ammonia, (ii) were higher from NT following surface-applied urea, and (iii) did not differ by tillage following liquid UAN application.

The current steady-state model simplifies reality by not considering temporal dynamics. However, even the most detailed dy-

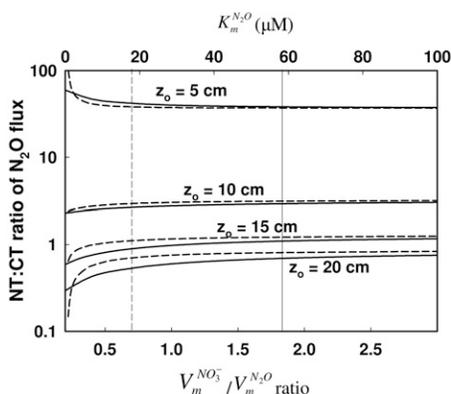


Fig. 6. Simulated ratio of denitrified N_2O flux in no till (NT) to conventional tillage (CT) treatment as functions of (solid lines, lower axis) the ratio of maximum nitrate and nitrous oxide reduction rates ($V_m^{NO_3^-}/V_m^{N_2O}$) and (dashed lines, upper axis) nitrous oxide half-saturation concentration ($K_m^{N_2O}$) at varying depths of NO_3^- distribution (z_0) as applied to conditions simulated in Fig. 5. Vertical lines indicate parameter values used in other simulations.

amic models (e.g., Riley and Matson, 2000; Li, 2000; Grant et al., 2006) do not 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_2O 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., $K_m^{NO_3^-}$, $V_m^{N_2O}$, and $K_m^{N_2O}$.

We did attempt to measure the parameters describing N_2O reduction kinetics ($V_m^{N_2O}$ 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 N_2O 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 $V_m^{NO_3^-}/V_m^{N_2O}$ ratio of 2.0 used here based on Leffelaar and Wessel (1988) and Riley and Matson (2000) compares 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_2O flux as a function of z_0 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_2O flux. Improved methods for determining N_2O reduction kinetics, perhaps utilizing ^{15}N -labeled N_2O (Clough et al., 2006), would improve N_2O 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 anaerobiosis 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_2O 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_2O 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_2O 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_2^- 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_2^- -driven N_2O fluxes (Venterea, 2007).

Acknowledgments

The authors acknowledge the assistance of S. Claussen, M. Dolan, Z. Jorgensen, and R. Schaubach and two anonymous reviewers for their helpful input.

References

- Arah, J.R.M., and A.J.A. Vinten. 1995. Simplified models of anoxia and denitrification in aggregated and simple structure soils. *Eur. J. Soil Sci.* 46:507–517.
- Baker, J.M., T.E. Ochsner, R.T. Venterea, and T.J. Griffis. 2007. Tillage and soil carbon sequestration- What do we really know? *Agric. Ecosyst. Environ.* 118:1–5.
- Bowman, R.A., and D.D. Focht. 1974. The influence of glucose and nitrate concentrations upon denitrification rates in sandy soil. *Soil Biol. Biochem.* 6:297–301.
- CCX. 2007. Chicago climate exchange. Agricultural soil carbon offsets via conservation tillage. Available at <http://www.chicagoclimatex.com/> (verified 11 Feb. 2008).
- Chalk, P., D. Keeney, and L. Walsh. 1975. Crop recovery and nitrification of fall and spring applied anhydrous ammonia. *Agron. J.* 67:33–41.
- Chapman, H., and G. Liebeg. 1952. Field and laboratory studies of nitrite accumulation in soils. *Soil Sci. Soc. Am. Proc.* 16:276–282.
- Clough, T., F. Kelliher, Y. Wang, and R. Sherlock. 2006. Diffusion of ^{15}N -labelled N_2O into soil columns: A promising method to examine the fate of N_2O in subsoils. *Soil Biol. Biochem.* 38:1462–1468.
- Cox, W.J., R.W. Zobel, H.M. van Es, and D.J. Otis. 1990. Tillage effects on some soil physical and corn physiological characteristics. *Agron. J.* 82:806–812.
- Del Grosso, S.J., A.D. Halvorson, and W.J. Parton. 2008. Testing DAYCENT model simulations of corn yields and nitrous oxide emissions in irrigated tillage systems in Colorado. *J. Environ. Qual.* 37:1383–1389.
- Dick, W. 1983. Organic carbon, nitrogen, and phosphorous concentrations and pH in soil profiles as affected by tillage intensity. *Soil Sci. Soc. Am. J.* 47:102–107.
- Doran, J.W. 1980. Microbial changes associated with residue management with reduced tillage. *Soil Sci. Soc. Am. J.* 44:518–524.
- Firestone, M., and E. Davidson. 1989. Microbiological basis of NO and N_2O production and consumption in soil. p. 7–21. *In* M. Andreae and D. Schimel (ed.) Exchange of trace gases between terrestrial ecosystems and the atmosphere. John Wiley, UK.
- Gomez, K.A., and A.A. Gomez. 1984. Statistical procedures for agricultural research. 2nd ed. John Wiley & Sons, New York.
- Goodroad, L., D. Keeney, and L. Peterson. 1984. Nitrous oxide emissions from agricultural soils in Wisconsin. *Soil Sci. Soc. Am. J.* 13:557–561.
- Grant, R., E. Pattey, T. Goddard, L. Kryzanowski, and H. Puurveen. 2006. Modeling the effects of fertilizer application rate on nitrous oxide emissions. *Soil Sci. Soc. Am. J.* 70:235–248.
- Groffman, P.M. 1985. Nitrification and denitrification in conventional and no-tillage soils. *Soil Sci. Soc. Am. J.* 49:329–334.
- Halvorson, A., S. Del Grosso, and C. Reule. 2008. Nitrogen, tillage, and crop rotation effects on nitrous oxide emissions from irrigated cropping systems. *J. Environ. Qual.* 37:1337–1344.
- Holtan-Hartwig, L., P. Dorsch, and L.R. Bakken. 2000. Comparison of denitrifying communities in organic soils: Kinetics of NO_3^- and N_2O reduction. *Soil Biol. Biochem.* 32:833–843.
- IFA. 2006. International Fertilizer Industry Association, Paris. Available at <http://www.fertilizer.org/ifa/statistics.asp> (verified 11 Feb. 2008).
- IPCC. 2001. Climate Change, 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the International Panel on Climate Change. *In* J. Houghton et al. (ed.) Cambridge Univ. Press, New York.
- Kaharabata, S.K., C.F. Drury, E. Priesak, R.L. Desjardins, D.J. McKenney, C.S. Tan, and D. Reynolds. 2003. Comparing measured and Expert-N predicted N_2O emissions from conventional and no till corn treatments. *Nutr. Cycling Agroecosyst.* 66:107–118.
- Kessavalou, A., A.R. Mosier, J.W. Doran, R.A. Drijber, D.J. Lyon, and O. Heinemeyer. 1998. Fluxes of carbon dioxide, nitrous oxide, and methane in grass sod and winter wheat-fallow tillage management. *J. Environ. Qual.* 27:1094–1104.
- Kremen, A., J. Bear, U. Shavit, and A. Shaviv. 2005. Model demonstrating the potential for coupled nitrification-denitrification in soil aggregates. *Environ. Sci. Technol.* 39:4180–4188.
- Leffelaar, P.A., and W.W. Wessel. 1988. Denitrification in a homogeneous closed system: Experiment and simulation. *Soil Sci.* 146:335–349.
- Li, C.S. 2000. Modeling trace gas emissions from agricultural ecosystems. *Nutr. Cycling Agroecosyst.* 58:259–276.
- Li, C., V. Narayanan, and R. Hariss. 1996. Model estimates of nitrous oxide emissions from agricultural lands in the United States. *Global Biogeochem. Cycles* 10:297–306.
- Li, C., S. Frolking, and K. Butterbach-Bahl. 2005. Carbon sequestration in arable soils is likely to increase nitrous oxide emissions, offsetting reductions in climate radiative forcing. *Clim. Change* 72:321–338.
- Linn, D., and J. Doran. 1984. Aerobic and anaerobic microbial populations in no-till and plowed soils. *Soil Sci. Soc. Am. J.* 48:794–799.
- Manley, J., G.C. Van Kooten, K. Moeltner, and D.W. Johnson. 2005. Creating carbon offsets in agriculture through no-till cultivation: A meta-analysis of costs and carbon benefits. *Clim. Change* 68:41–65.
- Morrill, L., and J. Dawson. 1967. Patterns observed for the oxidation of ammonium to nitrate by soil organisms. *Soil Sci. Soc. Am. Proc.* 31:757–760.
- Mummey, D., J. Smith, and G. Bluhm. 1998. Assessment of alternative soil management practices on N_2O emissions from US agriculture. *Agric. Ecosyst. Environ.* 70:79–87.
- Poth, M., and D. Focht. 1985. ^{15}N kinetic analysis of N_2O production by *Nitrosomonas europaea*: An examination of nitrifier denitrification. *Appl. Environ. Microbiol.* 49:1134–1141.
- Riley, W., and P. Matson. 2000. NLOSS: A mechanistic model of denitrified N_2O and N_2 evolution from soil. *Soil Sci.* 165:237–249.
- Rolston, D., and P. Moldrup. 2002. Gas diffusivity. p. 1113–1139. *In* G.C. Topp and J.H. Dane (ed.) Methods of soil analysis, Part 1, Physical methods, 3rd ed. SSSA, Madison, WI.
- SAS. 2002. SAS Institute System for Windows, Release 9.1. SAS Inst., Cary, NC.
- Sander, R. 1999. Compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry (Version 3). Available at <http://www.henrys-law.org> (verified 11 Feb. 2008).
- Six, J., C. Feller, K. Denef, S.M. Ogle, J.C. de Moraes Sa, and A. Albrecht. 2002. Soil organic matter, biota, and aggregation in temperate and tropical soils: Effects of no-tillage. *Agronomie* 22:755–775.
- Stevenson, F., R. Harrison, R. Wetselaar, and R. Leeper. 1970. Nitrosation of soil organic matter: III. Nature of gases produced by reaction of nitrite with lignins, humic substances and phenolic constituents under neutral and slightly acidic conditions. *Soil Sci. Soc. Am. J.* 34:430–435.
- Tiedje, J. 1994. Denitrifiers. p. 245–267. *In* R.W. Weaver et al. (ed.) Methods of soil analysis, Part 2: Microbiological and biochemical properties. SSSA, Madison, WI.
- Van Cleemput, O., and A. Samatar. 1996. Nitrite in soils: Accumulation and role in the formation of gaseous N compounds. *Fert. Res.* 45:81–89.
- Venterea, R. 2007. Nitrite-driven nitrous oxide production under aerobic soil conditions: Kinetics and biochemical controls. *Glob. Change Biol.* 13:1798–1809.
- Venterea, R., J. Baker, M. Dolan, and K. Spokas. 2006. Carbon and nitrogen storage are greater under biennial tillage in a Minnesota corn-soybean rotation. *Soil Sci. Soc. Am. J.* 70:1752–1762.
- Venterea, R., M. Burger, and K. Spokas. 2005. Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *J. Environ. Qual.* 34:1467–1477.
- Venterea, R., and D. Rolston. 2002a. Nitrogen oxide trace gas transport and transformation: II. Model simulations compared with data. *Soil Sci.* 167:49–61.
- Venterea, R., and D. Rolston. 2002b. Nitrogen oxide trace gas transport and transformation: I. Evaluation of data from intact soil cores. *Soil Sci.* 167:35–48.
- West, T., and W. Post. 2002. Soil organic carbon sequestration rates by tillage and crop rotation: A global data analysis. *Soil Sci. Soc. Am. J.* 66:1930–1946.