COMPUTATIONAL AND EXPERIMENTAL APPROACHES RELATED TO NITROUS OXIDE EMISSIONS AND ECONOMIC ANALYSIS OF PRIVATE AND SOCIAL RETURNS FROM MAIZE FERTILIZATION

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COMPUTATIONAL AND EXPERIMENTAL APPROACHES RELATED TO NITROUS OXIDE EMISSIONS AND ECONOMIC ANALYSIS OF PRIVATE AND SOCIAL RETURNS FROM MAIZE FERTILIZATION

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Continued research and development of computational methods are needed to effectively address both environmental and economic issues related to nitrogen (N) use for maize fertilization. This research consists of three major inter-related components. The first constitutes an experiment in Willsboro, New York to estimate the impact of management practices, especially tillage and timing of N application on nitrous oxide (N_2O) emissions for clay loam and loamy sand. The second component includes the use of N_2O emissions, and soil physical and chemical data collected from the Willsboro experiment to 1) calibrate the Precision Nitrogen Management (PNM) model, 2) determine the N_2:N_2O ratio from partial N budgets and incorporate it into the PNM model for N_2O losses estimations, and 3) evaluate different combinations of process representations of the PNM model. The final component involves an integration of the PNM model and economic analyses by 1) simulating long-term yield and environmental N losses for maize production on three textural soils, and 2) estimating private and social returns based on PNM-simulated data.

Nitrous oxide losses averaged four times higher on the clay loam than the loamy sand soil. Under no-tillage, full fertilizer application at planting resulted in 4.7 and 2.3 kg N ha^{-1} greater cumulative N_2O losses than starter-only fertilizer application on maize after grass and continuous maize plots, respectively. Nitrogen management critically affects the extent of N_2O losses, particularly for fine-textured soils under no-

tillage, and must be an important consideration in soil and crop management for greenhouse gas (GHG) reduction.

With the process complexities in the soil-plant-atmosphere system, modeling of N_2O losses was challenging, especially for short-term periods. The incorporation of the biological aspects of the denitrification process is important to capture the dynamics involved in the production of N_2O fluxes.

Timing of N application affected optimum N rates depending on soil type and weather conditions. The economic modeling effort provided a framework for computations of revenue that incorporates environmental impacts of N fertilizer management. A more sophisticated approach is necessary to 1) increase PNM model accuracy, and 2) refine the calculations on environmental losses and associated damage costs for practical farm application.

BIOGRAPHICAL SKETCH

Ivy Yin Sean Tan was born in Penang, Malaysia, and grew up in several states in the peninsula of Malaysia before she came to the United States in June 1998 to continue her undergraduate studies. She earned her B.S. degree in computer engineering with a minor in entrepreneurial studies, and M.S. degree with a major concentration in Geographic Information System (GIS) and minor in computer science, both from Iowa State University. In August 2003, she came to Cornell University to pursue her Ph.D. studies under the direction of Professor Harold van Es to address issues related to greenhouse gas impact on land management practices and computational approaches to nitrous oxide emissions from maize fertilization in New York. Her studies also included an economic component on analysis and estimations of private and social returns. She was the Gamma Sigma Delta Honor Society initiate in 2003, and the MacDonald/Musgrave Graduate Student Award recipient in 2006.

To my parents

and

my eldest brother

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SINGLE-EVENT NITROUS OXIDE LOSSES UNDER MAIZE PRODUCTION AS AFFECTED BY SOIL TYPE, TILLAGE, ROTATION, AND FERTILIZATION

INTRODUCTION

Increased greenhouse gas (GHG) concentrations in the atmosphere have generated considerable concern, and no-till practices and sod-based rotations are regarded as mitigation measures because they sequester C into the soil (Paustian et al., 1997; Duiker and Lal, 1999; McConkey et al., 2003). In the US and Europe, large-scale conversion from conventional tillage to no-till farming systems can potentially sequester 10 to 40 million Mg of C per year (approximately 350 kg C ha^{-1} y^{-1}) depending on the level of adoption (Smith et al., 1998; Sperow et al., 2003). The greatest potential in the US for increased C sequestration through no-tillage and improved rotations is in the moist temperate cropping areas of the Northeast and Midwest. These regions have approximately 75% of the cropland in the US, of which about 7% is currently under no-till with an additional 25% under reduced tillage systems (Sperow et al., 2003).

Increased C sequestration under no-tillage results from slower decomposition of organic C by soil microorganisms in the surface horizons (top 10-20 cm of the soil profile), especially on soils of high clay content (McConkey et al., 2003). Although no-tillage increases soil C sequestration, its long term potential may be limited once a new, higher C equilibrium level is reached and no further C sequestration occurs (Smith et al., 1998; West and Marland, 2002). Compared to the total annual GHG emissions, the potential contribution of increased C sequestration through conversion to no-tillage and improved rotations to mitigate GHG losses is relatively small. Smith et al. (1998) estimated the mitigation of GHG emissions through large scale (50-100%) implementation of no-tillage for crop production in the US and Europe to be approximately 1-3% of total fossil C emissions from these two regions. Moreover, there are limitations to the adoption of no-tillage due to field location, crop and soil type that make full implementation for all cropping systems and crop acreage unlikely (Smith et al., 1998; Sperow et al., 2003).

Nitrous oxide emissions from cropland

A recent study showed that agriculture contributes 20% to the annual global increase in GHG concentrations, 25% of which is N_2O emission during crop growth (Smith and Conen, 2004). Nitrous oxide is largely generated by denitrification, with some contribution from nitrification. Each molecule of N_2O has approximately 310 times more global warming impact than a molecule of CO_2. Denitrification is a microbial process that occurs primarily in the surface horizons under anaerobic conditions. Nitrate (NO_3) is reduced to N_2 by soil bacteria in the absence of oxygen and N_2O is generated as an intermediate volatile compound (Duxbury et al., 1982). Denitrification rates can be very high if, in addition to anaerobic soil conditions, there is also an abundant C-based energy source and high soil NO_3 levels (Shaffer and Ma, 2001). Other forms of N fertilizer (organic or inorganic) may also eventually lead to N_2O emissions since they can be rapidly transformed into NO_3 through processes such as urea hydrolysis and mineralization followed by nitrification.

Studies have reported higher denitrification rates and N_2O losses (Rice and Smith, 1982; Ball et al., 1999; Smith and Conen, 2004), and higher populations of denitrifiers (Aulakh et al., 1984) under no-tillage where higher soil organic C levels and lower porosity in the surface horizon can occur. Also, higher rates of N fertilizer may be used in no-tillage, especially during early stages of conversion from conventional tillage (Rice and Smith, 1982; Bacon and Freney, 1989), that can result in higher levels of NO_3 and increased likelihood of N_2O losses from denitrification. Potentially higher N_2O losses under no-till raise concerns because they could negate any benefits of C sequestration.

Timing of N application is critical for minimizing N losses under no-tillage systems. High N application rates during the early spring season (as opposed to starter plus a later sidedress application) may lead to greater potential N losses from denitrification on poorly drained soils and NO_3 leaching out of the root zone on well-drained soils (van Es et al., 2002). Significant water and N uptake by a maize crop usually does not occur until around eight weeks after seeding, creating a high risk for soil saturation and N losses. If high N rates are applied at planting the potential for N_2O losses is considerable, especially when major rainfall events occur in the spring.

N_2O emissions from agricultural systems are currently inadequately quantified, especially as they relate to the effects of various crop and soil management practices, and during the critical late-spring season under maize production. The objectives of this study were to quantify N_2O emissions on two different soil types following a simulated 50-mm precipitation event, and to determine the effects of management practices (rotation, tillage, and fertilization) on those emissions.

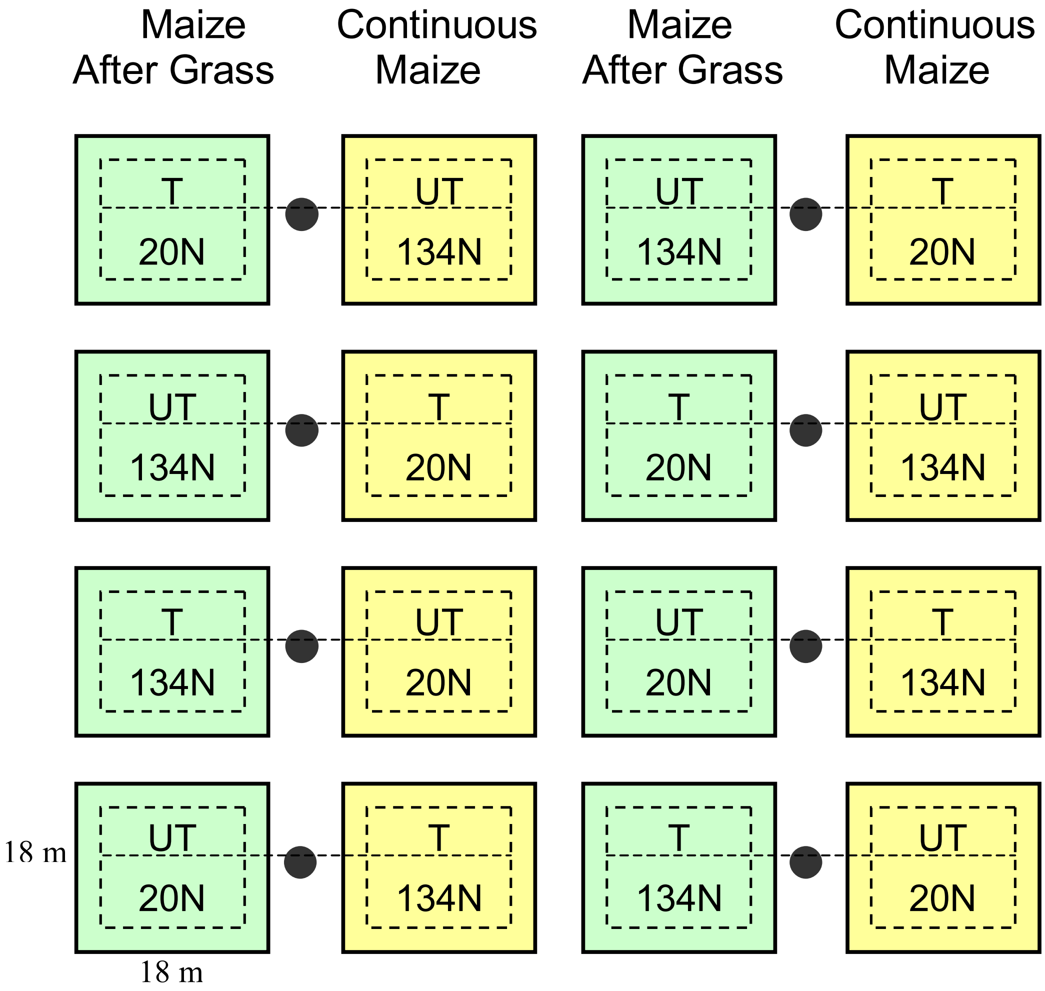
MATERIALS AND METHODS

Study sites

The experiment was carried out on two sites located at the Cornell University Experimental Farm in Willsboro, New York (44°22'N, 73°26'W) for one week starting on 21 June 2004. Each site represents a different soil type: a Muskellunge clay loam (fine, mixed, active, frigid Aeric Epiaqualf) derived from glacio-lacustrine material, and a Stafford loamy fine sand (mixed, mesic Typic Psammaquent) that has formed in glacial outwash sand and is underlain by glacio-lacustrine clay at depths ranging from 0.6 to 1.5 m.

On each site, 16 plots in a four-by-four pattern (Figure 1.1) were established in 1987 and 1992 for the clay loam and loamy fine sand sites, respectively. The plots are surrounded by 0.8 mm-thick impermeable PVC geomembrane to a depth of 1.8 m to make them hydrologically independent. On the clay loam, plots are 18 × 18 m and include perimeter drains that discharge to a central drain line (Figure 1.1). On the loamy fine sand, plots are 14 × 14 m and, because of their smaller size and higher soil hydraulic conductivity, include only a central drain line. All drains were installed at 0.9-m depth.

The clay loam soil has approximately 400 g kg^{-1} clay material in the 0- to 30-cm depth, but up to 800 g kg^{-1} in the subsoil (Sogbedji et al., 2001a). The loamy fine sand site shows sand contents greater than 800 g kg^{-1} in the top layers, but clay contents up to 700 g kg^{-1} in the bottom profile where the underlying glacio-lacustrine material resides. Previous research efforts have demonstrated that the plots function well for nutrient fate studies and allow for considerable precision in detecting subtle tracer and N fertilizer treatment effects (van Es et al., 1991; Sogbedji et al., 2000). The clay loam plots experience longer periods of saturation in the surface horizon than the loamy fine sand plots (van Es et al., 2005) and have higher N losses through denitrification (Sogbedji et al., 2001a; 2001b). The loamy fine sand plots have shown higher NO_3-N leaching losses (Sogbedji et al., 2000).



—— PVC liner
- - - - - - Drain line
● Manhole

UT	Untilled
T	Tilled
20N	20 kg N ha^{-1} at planting (additional 114 kg N ha^{-1} sidedress applied after the experiment)
134N	134 kg N ha^{-1} applied in two applications prior to the experiment

Note: Untilled under maize-after-grass had not been tilled for eight years while untilled under continuous maize had been plowed the year prior on both clay loam and loamy fine sand soils

Figure 1.1. Plot layout and experimental design on the clay loam site. The loamy fine sand site has an identical layout and experimental design, except that each plot is 14 × 14 m and only has a single central drain. Note: Untilled under maize-after-grass had not been tilled for eight years while untilled under continuous maize had been plowed the year prior on both clay loam and loamy fine sand soils.

Treatment application and irrigation

Identical experiments were conducted on both sites using a split-plot design, with cropping rotations of maize after orchardgrass (‘maize-after-grass’) and continuous maize (‘continuous maize’) as main plots; and a 2 × 2 factorial arrangement of tillage (‘untilled’, ‘tilled’) and N treatments (‘Full’, ‘Starter’) as split plots, all laid out in a spatially balanced allocation (van Es and van Es, 1993) with two replications (Figure 1.1). The maize-after-grass and continuous maize plots have been in these rotations for eight and twelve years respectively. On the clay loam site, all plots on continuous maize and tilled plots on maize-after-grass were moldboard-plowed in fall 2003, as is usual in this region. Tilled plots for both rotations on the clay loam were again disked in the spring. On the loamy fine sand site, all tilled plots were spring moldboard-tilled on 8 May 2004, as is common for this soil type. We use the terms “untilled” and “tilled” to refer to the loosening of the soil in the early growing season, as opposed to the terms “no-till” and “plow-till” which would signify a longer-term tillage system.

All plots were planted to maize on 14 May 2004 at a density of 70 000 plants ha^{-1} using a Buffalo planter (Fleisher Manufacturing, Lincoln, NE). Application of fertilizers and pesticides were made in accordance with Cornell Cooperative Extension guidelines (CCE, 2004). Two N fertilizer rates were applied to the plots at each site: ’Full’ treatment (134 kg N ha^{-1}) applied as 20 kg N ha^{-1} in a band as 6-24-24 with the planter on 14 May 2004, and an additional 114 kg N ha^{-1} as ammonium nitrate (AN, 34-0-0) broadcasted on 5 June 2004, and ‘Starter’ treatment that consisted of only a 20 kg N ha^{-1} application with the planter. Both the Full and Starter fertilizer treatments were applied prior to the start of the simulated rainfall experiment. There were no large natural rainfall events between planting (on 14 May 2004) and the start of the simulated rainfall experiment. Additional sidedress N was applied on 26 June 2004 at the V6 to V8 stage, after the experiment.

Soil saturation and denitrification were induced by applying a simulated 50-mm rainfall event using a sprinkler irrigation system. The 24-hour rainfall for a 2-year return period, which is the expected average frequency of a given precipitation event to occur once every two years within 24 hours, is approximately 63.5 mm in New York. Water was supplied from nearby Lake Champlain to the clay loam site, and a municipal water source was used for the loamy fine sand site. One sprinkler was assembled in the middle of each plot, providing irrigation at an average rate of 7.4 mm hr^{-1}. Irrigation was initiated on June 21 on the clay loam plots and June 22 on the loamy fine sand plots. Water application was monitored for each plot using rain gauges.

N_2O flux measurements

N_2O flux was measured using the vented static chamber method (Duxbury et al., 1982; McConnaughey and Duxbury, 1986) for a one-week period at both sites. During that time, flux measurements were made prior to (0 hour), and 10, 24, 47, 54, 68, 95 and 120 hours after the simulated rainfall application. Stationary one-piece PVC gas chamber bases each of 0.30 m diameter and 0.18 m height were inserted into the soil to a depth of 0.08 m using a Giddings hydraulic probe (Fort Collins, CO). Four gas chambers were installed in each plot, with pairs placed on the rows and interrows of the field for the entire study. Installation of gas chambers began on June 18 and was completed by June 20 on both sites. Vented lids were attached to the top of chambers prior to each flux measurement. At time zero and 45-minute intervals up to 90 minutes, chamber headspace was sampled with a 10-mL syringe and injected into a pre-evacuated glass serum vial, crimp-sealed with a gray butyl rubber stopper.

Lids were removed after the three samplings until the next flux measurements were made. Calibrated thermistors were installed in eight maize-after-grass and continuous maize plots at both sites to measure soil temperature at 5 cm and 15 cm depths outside the gas chambers, and on the soil surface in the gas chambers during the N_2O flux measurements. Temperature readings were made using a digital multimeter each time gas samples were obtained.

Nitrous oxide concentrations were determined using a gas chromatograph (Varian 3700 model, Varian, Inc., Palo Alto, CA) with a backflush system and equipped with an electron capture detector (ECD) and a Poropak QS column. Temperatures in the column and detector were adjusted to 80 and 360 ˚C respectively. A carrier gas of 5% methane and 95% argon was used and adjusted to approximately 414 kPa for it to flow through the columns. Nitrous oxide fluxes were calculated from the change in the concentration inside the chambers as follows:

$$\text{Flux} = [N_2O] \times \text{ChamberVolume} \times (28\ \mu g\ N / 22.4\ \mu L\ N_2O) \times 24\ h\ day^{-1} \\ \times (1 / \text{ChamberSurfaceArea}) \times 10^{8}\ cm^{2}\ ha^{-1}$$

where Flux is in kg N ha^{-1} day^{-1}; $[N_2O]$ in $\mu L\ L^{-1}\ h^{-1}$; obtained by fitting the peak height measurements (in mm) of each sample from the gas chromatograph to a set of N_2O standards that were measured each time the analyses were conducted; ChamberVolume is in cm^3; and ChamberSurfaceArea is in cm^2.

Soil physical and chemical analyses

Soil samples to a depth of 90 cm were collected from each plot at the beginning and end of the simulated rainfall experiment at both sites using a tractor-mounted Giddings hydraulic soil coring and sampling device (Sogbedji et al., 2001a).

A 1 m long × 5 cm diameter hollow steel soil tube was pushed into the soil to obtain the deep samples. Six composites of surface soil samples at 20 cm depth for each plot were collected at random and frozen until further analysis. Total N was determined from these samples using the dry combustion method adopted by the Cornell Nutrient Analysis Laboratories (Pella, 1990; Bremner, 1996; Nelson and Sommers, 1996). Soil organic matter was measured using the loss on ignition method (Storer, 1984). Tests for active C were performed on all surface soil samples from the clay loam and loamy fine sand sites using the $KMnO_4$ laboratory method (Weil et al., 2003). The tests were performed ten months after the experiment on air-dried samples. Frozen soil samples were also analyzed for NO_3-N in the Cornell Nutrient Analysis Laboratories within 24 hours of oven-drying at 105 ° C. Soil NO_3-N values are expressed as mass of NO_3 (mg) per mass of soil (kg).

Undisturbed soil core samples were collected in duplicate from inter-row locations in each plot at both sites prior to the experiment using 76-mm diameter, 60-mm high stainless steel rings. Samples were stored at 2 °C until further analysis. They were removed from storage and subsequently saturated by wetting from the bottom over a three-day period, and cores were allowed to drain to field capacity on a saturated cheese cloth (Karunatilake and van Es, 2002). The volume fraction of pores greater than 1.0 mm was determined as the difference in core weight between saturation and $\psi_m = 0.3$ kPa. Soil water retention at $\psi_m = 10$ kPa was determined using a custom-made sand table water retention apparatus, providing estimates of the volume fraction of pores greater than 0.03 mm. Bulk density and total porosity (assuming particle density of 2.65 Mg m^{-3}) were calculated for each core after determining oven-dry weight.

For evaluation of relative global warming impact, N_2O measurements were converted to CO_2 equivalents (CO_2e). CO_2e is the carbon dioxide (CO_2) equivalent unit used to compare the emissions from greenhouse gases based upon their global warming potential. CO_2e values for N_2O losses were obtained assuming a 310 molecular multiplication factor, and adjustment for the respective molecular weights of N_2O and CO_2.

Statistical analyses were performed using S-Plus software (Insightful, Seattle, WA), assuming that crop, tillage, and N application effects were fixed and site and block effects were random. Cumulative N_2O fluxes were analyzed using a one-way analysis of variance (ANOVA) for each site. Due to the large number of factors in this experiment and the limited degrees of freedom, main effects and interactions (except Tillage x NTreatment interaction with P-value = 0.122) were considered significant for P-values < 0.1.

RESULTS AND DISCUSSIONS

Soil properties

Soil physical data indicated that bulk density and total porosities were similar for the clay and loamy fine sand soils under maize-after-grass treatment, but that the loamy fine sand had significantly higher fractions of large pores across both crop rotations (Table 1.1). Statistical analyses for bulk density and soil porosity are shown in Table 1.1. The difference in the large-pore fraction presumably affected the soils' drainage rate and potential for leaching and denitrification. Based on a seasonal N budget analysis, Sogbedji et al. (2001c) surmised much larger seasonal denitrification losses from the clay loam plots. Untilled plots on clay under maize-after-grass showed higher density and lower volume fractions of rapidly draining pores (> 0.03 mm) than tilled plots, and the effects are especially significant compared to differences

Table 1.1. Bulk density and soil porosity (from 0-6 cm) taken prior to the experiment for clay loam and loamy sand soils under maize-after-grass and continuous maize rotations and the analysis of variance (ANOVA) table.

	Bulk Density ($Mg\ m^{-3}$)	**Total Porosity ($m^3\ m^{-3}$)**	**Pores > 1mm ($m^3\ m^{-3}$)**	**Pores > 0.03 mm ($m^3\ m^{-3}$)**
Muskellunge Clay Loam				
Maize-After-Grass				
Untilled [*]	1.25	0.50	0.03	0.16
Tilled	1.11	0.52	0.06	0.27
Mean	1.18	0.51	0.05	0.22
Continuous Maize				
Untilled [†]	1.18	0.55	0.03	0.28
Tilled	1.21	0.55	0.04	0.29
Mean	1.20	0.55	0.04	0.29
Stafford Loamy Sand				
Maize-After-Grass				
Untilled [*]	1.23	0.50	0.19	0.36
Tilled	1.21	0.51	0.19	0.41
Mean	1.22	0.51	0.19	0.39
Continuous Maize				
Untilled [†]	1.33	0.48	0.16	0.35
Tilled	1.21	0.48	0.17	0.37
Mean	1.27	0.48	0.17	0.36

[*] Untilled system that had not been tilled for eight years

[†] Untilled system that had been plowed in the previous year

	Bulk Density ($Mg\ m^{-3}$)		Total Porosity ($m^3\ m^{-3}$)		Pores > 1mm ($m^3\ m^{-3}$)		Pores > 0.03 mm ($m^3\ m^{-3}$)	
Main Effects	Degree of freedom	P Value	Degree of freedom	P Value	Degree of freedom	P Value	Degree of freedom	P Value
SoilType	1	0.19	1	0.09	1	0.00003	1	0.02
Rotation	1	0.42	1	0.68	1	0.06	1	0.50
Tillage	1	0.16	1	0.68	1	0.13	1	0.20

between untilled and tilled on sand under maize-after-grass. This may indicate a higher potential for extended saturation in the untilled plots, at least on the clay soil.

Active C and organic matter data also show effects of soil type and crop rotation (Table 1.2). The clay loam soil had higher organic matter levels than the loamy fine sand. Results showed higher active ($KMnO_4$-oxidizable) C on clay loam than loamy fine sand soils (Table 1.2). Higher active C was found in maize-after-grass than continuous maize on both soils. Higher soil C levels, especially when in reactive forms, can increase denitrification potential by providing an energy source for the microbial reduction of oxidized forms of nitrogen (Duxbury et al., 1982).

Soil NO_3-N levels at the onset of the simulated rainfall application mostly reflected the effects of the two different N fertilizer applications (Table 1.3), with mean values of 36.8 and 12.5 mg kg^{-1} for the Full and Starter fertilization treatments, respectively, averaged over cropping rotation and tillage treatment. The NO_3-N levels were very similar for the two soil types (36.8 and 36.2 mg kg^{-1} for Full, and 12.5 and 10.7 mg kg^{-1} for Starter on the clay loam and loamy fine sand sites, respectively). Also, the average soil NO_3-N levels were very similar for the maize-after-grass and continuous maize treatments (36.9 and 36.1 mg kg^{-1} for the Full fertilizer rate, and 13.3 and 9.9 mg kg^{-1} for the Starter, respectively), suggesting that accumulation of NO_3-N from mineralization of the plowed-down grass biomass was minimal during the first few weeks of the growing season. Similar results were reported by Sogbedji et al. (2000) for the same location. The similar pre-experimental soil NO_3-N levels for soil type, tillage, and rotation indicate that antecedent soil NO_3 levels were not confounding factors in the variable N_2O losses measured during the experiment, and that such variation may be ascribed to other factors, as discussed below.

Soil temperatures during the experiment were generally consistent among all the plots on each site and ranged from 6 to 20 ˚C for the 5 cm depth and 10 to 18 ˚C

Table 1.2. Active C and organic matter for clay loam and loamy sand soils under maize-after-grass and continuous maize rotations and the analysis of variance (ANOVA) table.

	Active C ($mg\ kg^{-1}$)	**Organic Matter ($mg\ kg^{-1} \times 10^4$)**
Muskellunge Clay Loam		
Maize-After-Grass	599.51	6.45
Continuous Maize	558.89	5.51
Stafford Loamy Fine Sand		
Maize-After-Grass	465.26	3.62
Continuous Maize	443.91	3.30

	Active C ($mg\ kg^{-1}$)		Organic Matter ($mg\ kg^{-1}$)	
Main Effects	Degree of freedom	P Value	Degree of freedom	P Value
SoilType	1	0.05	1	0.08
Rotation	1	0.19	1	0.29

Table 1.3. Soil nitrate-nitrogen (NO_3-N) content (from 0-20 cm) on clay loam and loamy fine sand soils before and after a 50-mm simulated rainfall event and analysis of variance (ANOVA) table for soil nitrate content loss.

Cropping Rotation	**Tilled**		**Untilled** [*]	
	Full	Starter	Full	Starter
	mg kg^{-1}			
	Clay loam			
Maize-After-Grass				
Before Experiment	34.87	15.97	29.01	10.09
After Experiment	25.81	14.23	24.27	6.32
Net Loss	9.06	1.74	4.74	3.77
Continuous Maize				
Before Experiment	36.94	10.83	46.44	13.13
After Experiment	26.74	9.79	21.82	8.91
Net Loss	10.20	1.04	24.62	4.22
	Loamy fine sand			
Maize-After-Grass				
Before Experiment	44.96	10.69	38.62	16.60
After Experiment	18.06	8.72	15.44	14.16
Net Loss	26.90	1.97	23.18	2.44
Continuous Maize				
Before Experiment	38.70	7.87	22.41	7.62
After Experiment	19.17	7.05	9.39	5.89
Net Loss	19.53	0.82	13.02	1.73

[*] Untilled plots under maize-after-grass had not been tilled for eight years while untilled plots under continuous maize had been plowed the year prior on both clay loam and loamy fine sand soils

		Degree of freedom	**P Value**
Main Effects	SoilType	1	0.27
	Tillage	1	0.81
	NTreatment	1	0.003
	Rotation	1	0.96
Interactions	SoilType x Tillage	1	0.37
	SoilType x NTreatment	1	0.18
	Tillage x NTreatment	1	0.80
	SoilType x Tillage x NTreatment	1	0.53

for the 15 cm depth (Figure 1.2). Diurnal fluctuations in soil temperature were minimal due to the cloudy and moist conditions during most of the experiment, especially the first 60 hours when most N_2O losses occurred.

N_2O losses

Differences in gaseous N_2O losses measured during this experiment reflect variations in soil type, rotation, tillage, and fertilization. The Full fertilizer treatment, where N fertilizer for the entire growing season is applied early in the season, presumably represents a management scenario that poses a greater potential for N losses, compared to the Starter treatment. The Starter treatment represents a management scenario with a reduced risk of N losses from large early season precipitation events since application of the majority of the fertilizer is delayed until the time of rapid crop N uptake. In this study, we quantified such risks by imposing a 50-mm simulated rain event in mid June. We should note that, in this study, the untilled plots in the maize-after-grass rotation reflected systems that had not been tilled for eight years. For the continuous maize treatment, however, the untilled plots had not been tilled for fourteen months at the loamy fine sand site and eight months at the clay loam site, and therefore do not represent the conditions that may be found under long-term no-tillage.

Nitrous oxide emission rates were very small (< 0.02 kg N ha^{-1} d^{-1} on both sites) at the onset of the experiment, increased slowly during the first 24 hours after irrigation started, and generally peaked around 48 hours for both soil types and all treatments (Figures 1.3 and 1.4). The initial increase in the N_2O emission rate likely represents the onset of anaerobic conditions and the transition from aerobic to anaerobic microbial respiration. We measured little or no N_2O losses after approximately 48 hours following irrigation. Similar patterns in N_2O flux observed in

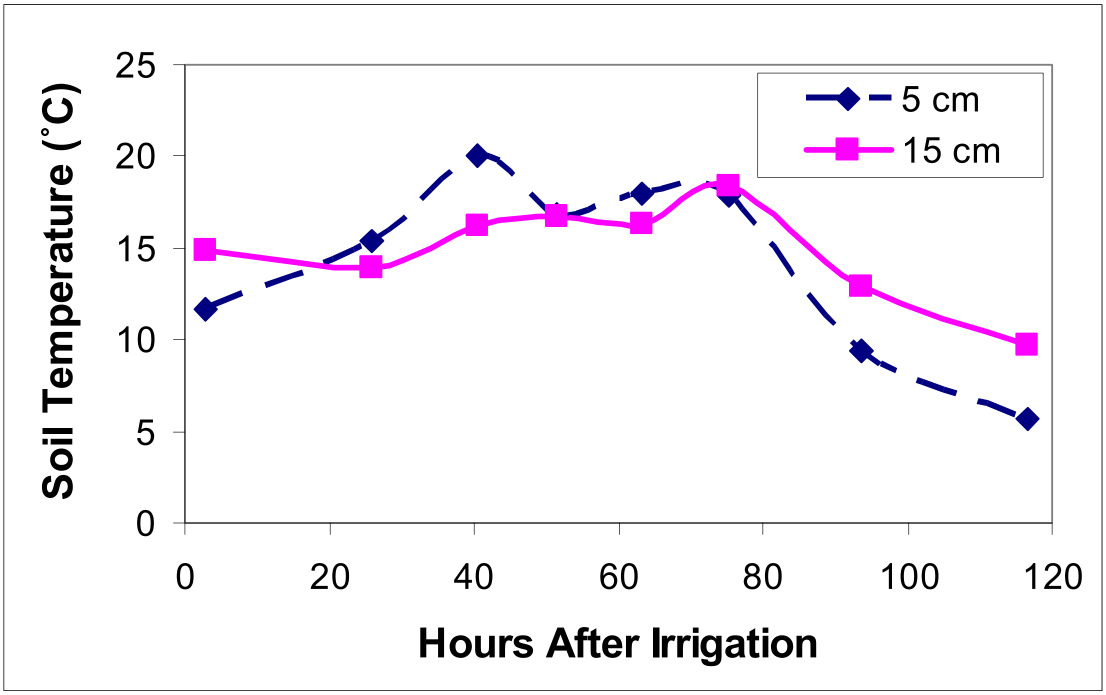


Figure 1.2. Average soil temperature (˚C) at 5 cm and 15 cm depths on clay loam site.

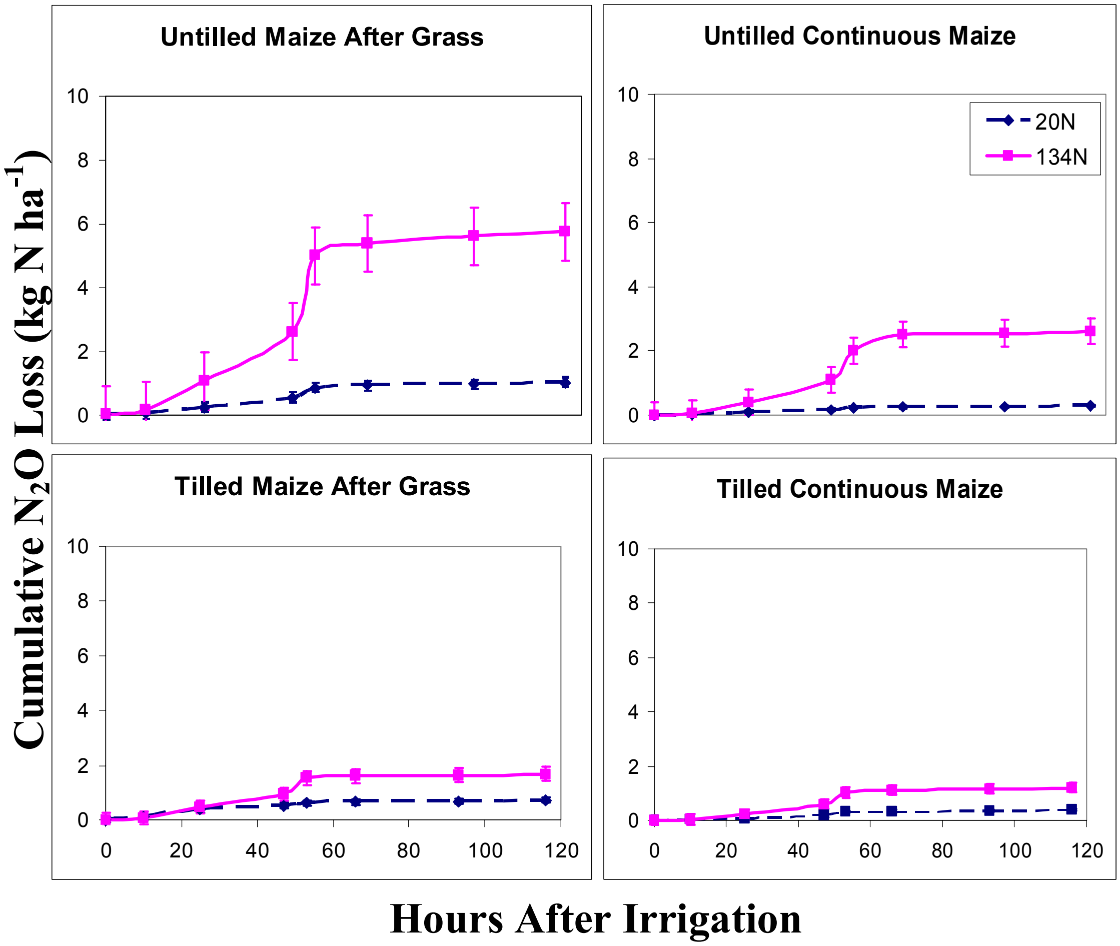


Figure 1.3. Cumulative nitrous oxide (N_2O) losses (kg N ha^{-1}) from the Muskellunge clay loam site following 50-mm simulated rainfall event. Error bars indicate standard errors. Note: Untilled under maize-after-grass had not been tilled for eight years while untilled under continuous maize had been plowed the year prior.

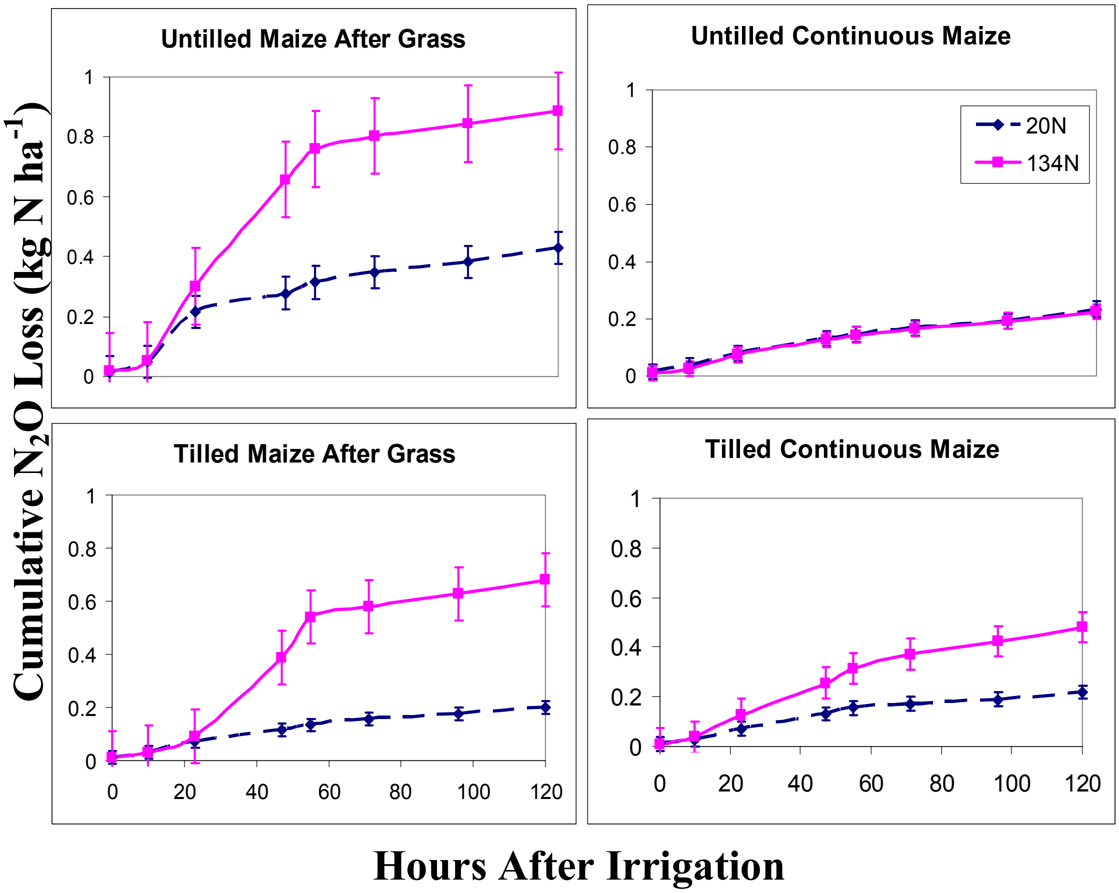


Figure 1.4. Cumulative N_2O losses (kg N ha^{-1}) from the Stafford loamy fine sand site after 50-mm simulated rainfall event. Error bars indicate standard errors. Note: Untilled under maize-after-grass had not been tilled for eight years while untilled under continuous maize had been plowed the year prior.

this experiment were found in other studies, due to the dynamics of denitrification enzymes that were induced sequentially following anaerobic conditions (Dendooven and Anderson, 1994; Dendooven et al., 1996; Cavigelli and Robertson, 2000).

Differences in cumulative N_2O losses after 50-mm simulated rainfall were significant ($P < 0.1$) for all main effects included in this experiment (Table 1.4). Soil type and N treatment had the greatest significance ($P < 0.01$), followed by tillage and rotation. Moreover, the SoilType x Tillage, SoilType x NTreatment, Tillage x NTreatment, and SoilType x Tillage x NTreatment interactions were also significant, indicating that soil and management factors influence N_2O emissions in complex ways.

On average, cumulative N_2O losses averaged over tillage and rotation treatments were four times higher for the clay loam than the loamy fine sand (1.72 and 0.42 kg N ha^{-1}, respectively; Table 1.4), presumably reflecting differences between soil types in pore size distributions and C and N contents (Tables 1.1 to 1.3). Higher N_2O losses from fine-textured compared to coarse-textured soils have also been observed by Sogbedji et al. (2000) and suggest that sound N management on fine-textured soils is critical for reducing N_2O losses. N treatment also had an important effect on N_2O losses, with three to six times higher cumulative N_2O losses from the Full (134 kg N ha^{-1}) treatment plots compared to the Starter (20 kg N ha^{-1}) treatment plots on the clay loam, and about double the losses on the loamy fine sand, respectively. This suggests that timing of N application is also critical: large N fertilizer additions early in the season, particularly on fine-textured soils, may result in greatly increased N_2O losses if considerable rainfall occurs in the spring. This risk may be reduced by use of slow-release fertilizer or nitrification inhibitors, but they were not considered in this study. Although measurements of N_2O fluxes following sidedressing were not studied in this experiment, the risk of significant losses is presumably lower than following Full fertilizer treatment due to higher corn water and

Table 1.4. Cumulative N_2O losses for clay loam and loamy sand sites following a 50-mm simulated rainfall and analysis of variance (ANOVA) table.

	Tilled		**Untilled** *		
Cropping Rotation	Full	Starter	Full	Starter	Mean
	kg N ha^{-1}				
			Clay Loam		
Maize-After-Grass	1.68	0.73	5.76	1.02	2.30
Continuous Maize	1.20	0.39	2.62	0.30	1.13
Mean	1.44	0.56	4.19	0.66	
Mean	1.00		2.43		1.72
			Loamy Sand		
Maize-After-Grass	0.68	0.20	0.89	0.43	0.55
Continuous Maize	0.48	0.22	0.23	0.23	0.29
Mean	0.58	0.21	0.56	0.33	
Mean	0.40		0.45		0.42

[*] Untilled plots under maize-after-grass had not been tilled for eight years while untilled plots under continuous maize had been plowed the year prior on both clay loam and loamy sand soils

		Degree of freedom	**P Value**
Main Effects	SoilType	1	0.01
	Tillage	1	0.08
	NTreatment	1	0.01
	Rotation	1	0.09
Interactions	SoilType x Tillage	1	0.10
	SoilType x NTreatment	1	0.03
	Tillage x NTreatment	1	0.12
	SoilType x Tillage x NTreatment	1	0.09

N uptake rates after sidedressing, thereby reducing the potential for anaerobic conditions and denitrification.

For both soil types, the cumulative N_2O losses were about twice as high for maize-after-grass compared to the continuous maize system. Since initial soil NO_3-N contents were generally similar for these treatments (Table 1.3), it may be inferred that the differential N_2O emissions are in part the result of variations in porosity and soil C levels (Table 1.1). The untilled plots also averaged higher N_2O losses than the tilled plots, presumably for the same reasons. Similar results were also observed in a study on a clay loam soil by Ball et al. (1999) who reported high N_2O emissions from untilled plots following heavy rainfalls.

Many interactions among the treatment effects contributed to the wide range of cumulative N_2O losses that we observed in this experiment. The lowest losses (0.20 to 0.43 kg N ha^{-1}) were associated with Starter fertilization on the loamy fine sand, with relatively little effect of tillage and rotation. The highest cumulative losses were measured from the Full fertilization, untilled, maize-after-grass plots on the clay loam (5.76 kg N ha^{-1}), which was nearly thirty times higher than the lowest measured cumulative N_2O emissions. It is postulated that the combination of a reduced fraction of large pores, higher active C, and relatively large quantities of soil NO_3 in this treatment combination all contributed to such high N_2O losses.

Soil NO_3 losses

Soil NO_3-N contents prior to and after the experiment indicate that large quantities of N inputs were susceptible to losses through leaching and denitrification following a 50-mm rainfall event (Table 1.3). N management was the most significant factor ($P = 0.003$) and the highest net NO_3-N losses (including unmeasured gains from mineralization during the six-day period) were observed with the Full fertilization treatment. Net losses of NO_3-N were low in the Starter fertilization treatment, remaining under 4.2 mg kg^{-1} (10.1 kg ha^{-1}). Net soil NO_3-N losses were generally greater for the loamy fine sand than the clay loam for the Full fertilization treatment, presumably because leaching is higher on the loamy fine sand than on the clay loam. This is the reverse of the fertilizer treatment effects on N_2O losses due to presumed higher denitrification rates on the clay loam. The net NO_3-N losses for the untilled, Full-fertilizer, maize-after-grass treatment on clay loam were only 4.74 mg kg^{-1} (11.8 kg ha^{-1}) yet this treatment showed the highest N_2O emissions. Further investigations of N budgets under different fertilizer and tillage regimes will be necessary to explore this discrepancy.

Greenhouse gas (GHG) effect

The highest N_2O emissions were measured for the untilled, maize-after-grass treatment; the one that would be expected to be most beneficial in terms of sequestration of atmospheric CO_2 into soil C. This poses the question whether the benefits of C sequestration may be offset by increased N_2O emissions (Johnson et al., 2005). Based on data from West and Marland (2002), it may be assumed that no-tillage soil experiences an average net C sequestration of 350 kg CO_2e ha^{-1} yr^{-1} compared to tilled soil. In our experiment, the short-term N_2O losses under early season Full N application in the untilled maize-after grass treatment resulted in as much as 2600 kg CO_2e ha^{-1} increase in GHG emissions. Therefore, the amount of global warming potential from short-term N_2O losses under early season Full N application from a 50-mm spring rainfall event alone eliminate any benefits of annual C sequestration, and are in fact several factors greater. In contrast, the largest net decrease in GHG emissions occurred in the untilled, Starter fertilization treatment. The short-term N_2O losses for this scenario in the maize-after-grass and continuous maize treatments were 450 kg CO_2e ha^{-1} and 100 kg CO_2e ha^{-1} respectively, following a single 50-mm rainfall event. These data suggest that real GHG reduction benefits from untilled and sod-based rotations are only attained when they are combined with well-timed and conservative N management. If full fertilizer rates are applied early in the season, combined GHG impact will likely be considerably higher for untilled compared to tilled soil under continuous maize, despite the presumed C sequestration.

CONCLUSIONS

In this experiment, we quantified the effects of various soil management practices on N_2O fluxes after a simulated rainfall event on loamy fine sand and clay loam soils. Results indicated that denitrification-related N_2O emissions are of much greater concern for fine-textured compared to coarse-textured soils, with losses for the clay loam soil about four times higher on average than for the loamy fine sand soil. Also, such emissions appear to be high in terms of GHG impact, indicating that crop production can be a significant contributor to the broader concern of GHG emissions. Rotation, tillage, and timing of N application all have strong effects on N_2O losses, and their significant interactions indicate that synergistic processes are involved. Higher N_2O emissions were associated with lower fractions of large pores and higher C availability, both of which have been correlated with increased denitrification rates. N management critically affects N_2O losses, particularly for fine textured untilled soils. Our data suggest that early fertilizer application at full rates may result in very high N_2O emissions when significant late-spring rainfall occurs. The increased N_2O losses measured for untilled soil raise concerns about the net GHG benefits of no-tillage systems. N management appears to be an important management tool in crop production for minimizing agricultural contributions to GHG emissions. Delayed N application is known to improve N use efficiency and production economics through reduced leaching and denitrification losses (Sogbedji et al., 2001c), and also has important GHG mitigation benefits.

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CHAPTER TWO:

MODELING OF N_2O LOSSES UNDER MAIZE PRODUCTION USING THE PNM MODEL

INTRODUCTION

Nitrous Oxide (N_2O)

Increasing use of nitrogen (N) fertilizer in agricultural fields is a growing concern for potential contamination of air and water quality. A study by Smith and Conen (2004) concluded that agriculture contributes 20% to the annual global increase in greenhouse gas (GHG) concentrations, of which 25% is nitrous oxide (N_2O) emission during crop growth. Most nitrous oxide is generated by denitrifying bacteria as a product of nitric oxide (NO) reduction under saturated anaerobic conditions, which is part of the denitrification pathway. N_2O is a potent greenhouse gas due to its high global warming potential or radiative and chemical effects. One molecule of N_2O has 310 times the GHG impact as a molecule of CO_2 over a 100-year period. Nitrous oxide emissions are closely connected with climate and environmental factors and interactions among these variables and emissions are important to providing a better understanding of the dynamics of these processes in the soil-plant-atmosphere system. Moreover, this can help improve fertilizer N use efficiency in agriculture while protecting environmental quality.

With that in mind, studies have been conducted to measure N_2O fluxes in agricultural fields as affected by soil types, land management practices, or N applications. Duxbury et al. (1982) concluded that agriculture caused N_2O emissions from soils to increase up to fourfold for mineral soil sites in New York and by as much as two orders of magnitude from the organic soil sites in Florida. The authors

(Duxbury et al., 1982) further stressed that it was difficult to estimate N_2O emission from agricultural lands on a global scale because the data are limited to a few agricultural systems and climate regions. Duxbury and McConnaughey (1986) found that, as expected, N_2O flux was highest following rainfall. Denitrification was responsible for at least 80% of the gaseous N loss in a maize field from the zero N and NO_3 treatments (Duxbury and McConnaughey, 1986). In a study to estimate N_2O emissions from agricultural fields over 28 months, Wagner-Riddle et al. (1997) observed seasonal patterns of fluxes, with the highest emissions during spring thaw in March and April when the average monthly temperature was approximately 5 °C. Results from a subsequent study found that management practices can play a role in mitigating emissions during spring thaw. Fallowing, manure application, and alfalfa incorporation in the fall contribute to high spring emissions, while the presence of plants (such as alfalfa and grass) can result in negligible emissions during thaw (Wagner-Riddle and Thurtell, 1998). Tillage practices also affect the release of N_2O. Ball et al. (1999) found high N_2O emissions mainly associated with heavy rainfalls after fertilization, particularly in no-till and in compacted soils. Similarly, Venterea et al. (2005) found that emissions of N_2O following urea application were higher under no-till and conservation tillage compared to conventional tillage. In another long-term study by Grandy et al. (2006), N_2O emissions were higher in no-till in two of ten years but there was no significant effect of tillage averaged across years. Observations from other studies concluded that no-till did not contribute to greater N_2O emissions than conventional tillage (Elmi et al., 2003; Parkin and Kaspar, 2006). Nitrogen fertilization is the controlling factor impacting N_2O emissions (Parkin and Kaspar, 2006) and N_2O fluxes can be reduced by using less N fertilizer without imposing a large effect on yield (McSwiney and Robertson, 2005). Studies associated with spatial variability of N_2O emissions and soil properties in agricultural fields demonstrated weak spatial dependency (Clemens et al., 1999) but Yanai et al. (2003) observed high N_2O fluxes at sites with relatively low elevation. A comparison of the N_2O emissions measured with a static chamber technique and the gas gradient method found that there were some differences in measurements with these two methods: the chamber method had greater flux rates than the gradient method in a wet summer, and the reverse was true in a dry summer (Maljanen et al., 2003). Other studies that focused on the denitrification process as affected by enzyme activities include those by Dendooven and Anderson (1994) and Dendooven et al. (1996). Field-based studies, however, are generally imprecise due to the volatility and variability of N_2O in the system. Given that in situ measurements are sparse, huge uncertainties are involved when fluxes are extrapolated from field to global scales. Currently, N_2O estimates by the Intergovernmental Panel of Climate Change (IPCC) are based on generalized extrapolations from the relationship between N_2O fluxes and N fertilizer application, without taking into account different soil types or management practices. Another approach that has been used to measure N_2O emissions is the inverse method which involves the use of chemical transport models, although large uncertainties are also involved when fluxes are estimated on a regional scale (Liu, 1996).

Field measurements of N_2O fluxes are oftentimes consuming and expensive. In addition, results are often affected by high sampling variability. These are some of the reasons that led researchers to exploring the use of process-based computer models to simulate N_2O emissions and the denitrification process (McConnaughey and Bouldin, 1985a; Hutson and Wagenet, 1992; Lin et al., 2000; Hutson, 2003; Kaharabata et al., 2003; Smith et al., 2004). Many physical, chemical, and biological processes are involved in the emissions and dynamic simulation models provide the platform to estimate simultaneous processes that are taking place in the system. A distinction between a process-based computer model and an extrapolation method is that the latter does not include interactions that occur in the soil profile such as transport of water and chemicals through each layer in the soil. Other N models that have been developed to simulate N dynamics and transformations in soils include those by Addiscott and Whitmore (1987); Johnsson et al. (1987); Bergstrom et al. (1991); Garrison et al. (1999); Wade et al. (2002); and Hutson (2003). Generally, these computer-based models differ in level of sophistication from simple to complex deterministic types. Models that are well calibrated and provide reliable estimations at field scale may be useful for providing estimates at regional and global scales.

It is noted that concerns are abound on the use of simulation models. One issue is that traditional scientific experiments may be replaced by speculative models (Philip, 1991). Although these doubts are justified, there are applications which can only be addressed by modeling efforts. It is then crucial to find a balance between the use of computer models and field studies, where models could be used to complement experimental efforts.

The goal of this study was to use the Precision Nitrogen Management (PNM) model (Melkonian, pers. comm.) to calibrate and evaluate N_2O losses at the field scale. Specific objectives were: 1) to determine the N_2:N_2O ratio from partial N budgets estimated from a field study and then incorporate it into the PNM model for estimations of N_2O losses; and 2) to evaluate different representations of processes in the PNM model with different combinations of water retention functions (Campbell, van Genuchten), denitrification rate constants (0.09 d^{-1}, 0.9 d^{-1}), and water flow processes (“tipping bucket”, “modified tipping bucket”) for a clay loam and a loamy sand soil using NO_3-N, N_2O, and volumetric water content data from a one-week field experiment.

PNM Model

The PNM model was developed to simulate N transport and transformations, and has been applied to provide precise sidedress N recommendations for maize (*Zea mays* L.) production. The model was developed by Jeff Melkonian, John Hutson, and Harold van Es and is based on two existing models: LEACHN (Dr. John Hutson, Flinders University, Adelaide, South Australia), which incorporates routines for simulation of soil N, water dynamics, N transformation and uptake (Hutson, 2003), and a maize N uptake/crop growth model (Dr. Tom Sinclair, USDA-ARS, University of Florida, Gainesville, FL, and others). The PNM model is deterministic process-based and aims to simulate the movement of water and solute through a soil profile with time. The current version of the PNM model is coded in Python, an object-oriented programming language, and consists of many modules or routines for handling various model parameter estimates. The program files of each routine end with a *.py* extension. When the model is initialized for each run, input parameters entered by users are processed and analyzed to generate output results. The input parameters needed by the model include soil physical and chemical properties, climate data, and crop and land management data as summarized in Table 2.1. The model has been extensively calibrated based on New York-based field experiments.

Input Data

Data on physical and chemical properties associated with each soil type of different textural classes are initialized and modified in the *soilInfo* module. Currently, ten different soil series common to the northeastern region of the United States are listed in *soilInfo*: Honeoye (fine-loamy, mixed, active, mesic Glossic Hapludalfs); Colonie (mixed, mesic Lamellic Udipsamments); Kingsbury (very-fine, mixed, active, mesic Aeric Endoaqualfs); Bernardston (coarse-loamy, mixed, active, mesic Oxyaquic

Table 2.1. Input data for the PNM model.

Input data
Soil physical properties
Bulk density
Saturated hydraulic conductivity
Water rentention curve or van Genuchten or Campbell parameter values
Soil chemical properties
Initial soil nitrate content
Organic carbon content
Climate data
Daily precipitation
Daily minimum and maximum temperature
Crop and land management
Planting date
Cropping history and rotation
N applications (organic or inorganic)

Dystrudepts); Windsor (mixed, mesic Typic Udipsamments); Rhinebeck (fine, illitic, mesic Aeric Endoaqualfs); Nunda (fine-loamy, mixed, active, mesic Glossaquic Hapludalfs); Kendaia (fine-loamy, mixed, active, nonacid, mesic Aeric Endoaquepts); Collamer (fine-silty, mixed, active, mesic Glossaquic Hapludalfs); and Bath (coarse-loamy, mixed, active, mesic Typic Fragiudepts). Each soil type has corresponding parameters to classify the depth of the soil profile; percentages of clay, silt, and organic matter; starting values for volumetric water content, water potential, soil temperature; bulk density (in kg dm^{-3}); pore interaction parameters used in Campbell's calculation and hydraulic conductivity; or van Genuchten's equations for water retentivity; and rate constants for N transformations from both organic and inorganic N sources. Input values for each parameter may be entered accordingly with reference to each soil layer through the profile, generally in increments of 50 mm. It should be noted that both Python and Fortran programming languages have different array indexing conventions. Array indexing in Python starts at 0 while Fortran starts at 1. Each index in the array represents a horizontal soil layer in the profile. In order to bridge the differences between the two indexing methods when the model was converted from Fortran to Python, all the values in index 0 in the current Python version of the program are not used. This distinction is important, especially in *soilInfo* where input data are listed in arrays, so that the input parameter values entered for each index accurately represents the corresponding parameter values for each soil layer in the profile.

Some of the input data such as bulk density were obtained from a field experiment by Sogbedji (2001a). Other values in *soilInfo* had also been well calibrated using field data from previous studies including a maize-N fertilizer experiment at Aurora, NY (Sogbedji et al., 2001c); a manure-maize experiment near Warsaw, NY (Cox and Cherney, 2002); an experiment on tillage and rotation effects on soil physical properties (Katsvairo et al., 2002); and studies in the Albany area (Thomas Kilcer, pers. comm.). The LEACHN component of the PNM model has been evaluated in several simulation studies. Sensitivity analyses of N transformations of the model was performed by Lotse et al. (1992), using LEACHN to predict soil NO_3 distribution, N leaching concentrations, and plant uptake in both manured and non-manured sites in Pennsylvania. Jemison et al. (1994) concluded that LEACHN performed well on NO_3-N leaching predictions when calibrated for each treatment and year, but performance was unsatisfactory without calibration. The model has also been evaluated for N transformations under different cropping history and soil types (Sogbedji et al., 2001b) and under manure fertilization (Sogbedji et al., 2006).

Weather data from the climate stations are initialized in the *climateInfo* routine, including maximum and minimum temperature, precipitation, and solar radiation. The *climateInfo* routine also includes information on climate stations in the state of New York which are referenced by station numbers as well as backup stations. In the event that data are unavailable from the original station, information will be gathered from the backup station. Ten official climate regions in New York State and additional climate stations from research sites in Aurora, Geneva, Willsboro, as well as in selected cities are also listed in *climateInfo*. When the PNM model runs are simulated on the Cornell Theory Center's cluster, users are only required to specify the climate station indicators from a selected location in *climateInfo*; this allows the model to automatically access the climate stations' database and generate data accordingly as input for the model. When the PNM model runs are generated from a local machine, users are required to enter all the climate data manually into *climateInfo*.

Crop and land management data are accessible through the *scenarioInfo* routine, which enables the model to simulate multiple combinations of scenarios. Input parameters that closely resemble the management practices from a field study can be entered by users in *scenarioInfo*, thus comparisons between field and PNM-simulated data can be evaluated. In *scenarioInfo*, information regarding cultivar; soil cultivation; N fertilizer type and rate for starter, additional, and sidedress applications; as well as cultivation and planting depths are included. The planting density default value is 28328 plants acre^{-1} which is approximately equivalent to 7.0 plants m^{-2}, typical for a maize crop. However, there is flexibility in the model that allows users to change the parameter values, if necessary. The routine also allows the options for manure and sod incorporations. Dates corresponding to chemical and manure applications, cultivation, and planting are specified by the users.

The PNM model was developed based on a one-dimensional soil profile concept to simulate water and chemical transport from the soil surface to the bottom layer of the profile. Generally, soil profiles consist of horizontal layers of variable thickness. Chemical, physical, and biological properties of the soils are often associated with the horizons, and depending on the soil types, may either vary gradually or abruptly across the horizons in the profile. In order to maintain uniformity on all soil types, the LEACHN component of the model was developed to divide the soil profile into segments of equal thickness, to reflect the horizons in soils. Segment thickness usually is less than horizon thickness and its values may be changed accordingly for different simulation objectives. For instance, simulations of field-scale processes with segment thicknesses ranging from 25 to 100 mm may be appropriate, while simulations of laboratory experiments may be based on horizons of a few millimeters. The default version of the model uses a segment thickness of 50 mm to simulate field-scale processes.

The boundary conditions of the soil profile are represented and maintained by boundary nodes that are located in the center of each segment. To further elaborate, a 500 mm soil profile divided into ten 50 mm segments has 12 nodes, one for each segment and two boundary nodes, with one being at the surface and one below the lowest depth. The higher the number of segments in a profile, the longer it takes to run the model, although it is encouraged to use at least 10 segments. Hypothetically, a thin surface layer is assumed to be present where organic and inorganic materials are added at the soil surface.

Aside from *soilInfo*, *climateInfo*, and *scenarioInfo* which are the primary input data files modified by users to fit the scenario runs, other routines in the model are responsible in initializing variable arrays and read parameter values from input files (*vars)*, and in physical processes and numerical calculations. These calculations include, but are not limited to, water retention data, chemical and water fluxes, and rate constant adjustments according to temperature and water content. Volumetric water content (θ), hydraulic conductivity (hc, mm day^{-1}), and soil water potential for both Campbell (1974) and van Genuchten functions are estimated in *utilities*. Table 2.2 is a summary of routines and the corresponding descriptions in the PNM model, presented generally in the order in which they are called by the program for each simulation run on a daily time step. Most of the routines in the model are called in *leachn*. The simulation output results generated by *leachn* in *_sum* file include rainfall; runoff; drainage; soil N losses; N inputs and transformations; root zone N; seed dry weight; total biomass; and mass balances (Table 2.3). Output results are on a daily time step from beginning to the end of the simulation dates. All output results are cumulative, except for root zone N.

In *fertn*, fertilizer and amendments are partitioned according to the properties into three different pools: precipitated, sorbed, and solution pools. Inorganic N fertilizer such as NH_4, NO_3, and urea are immediately partitioned and subjected to linear sorption. Organic N and P on the other hand, are added to the existing “sorbed”

Table 2.2. Outline of routines in PNM model. All routine files end with *.py* extension.

control_model	Initializes the program, calls *run_model( )*
run_model( )	Checks for scenario to run in the model
scenarioInfo	Input file that contains crop and land management data, called by *control_model*
climateInfo	Contains temperature and precipitation input data from climate stations
Leachn	Calls the following routines below, performs mass balancing, prints output results to *_btc* and *_sum* files
vars	Initializes variable arrays, reads input parameter values, initializes constant values
watdat	Reads water retention and hydraulic conductivity data for soil hydrological constants used from *utilities*, prints retention parameters used in simulation to *_out* file
utilities	Calculates volumetric water content (θ), hydraulic conductivity (hc, mm day^{-1}), and soil water potential based on either Campbell (1974) or van Genuchten function option
freundn	Partitions P into solution, sorbed, and precipitated phases using the Freundlich or Langmuir isotherms
cultn	Mixes N and P through specified depth of cultivation
runoff	Calculates runoff according to curve number (cn2) approach using equations by Williams (1991) since there is an equation that adjusts the cn2 according to slope
heat	Solves the heat flow equation
fertn	Partitions fertilizer and amendments according to properties
raten	Adjusts rate constants according to temperature and water content
soilInfo	Input file for physical and chemical properties of various soil types at each soil layer, called by *raten*
sinkn	Calculates gains and losses of C, N, and P through plants, microorganisms, and atmosphere
calfn	Calculates flux of chemical and water between adjacent layers, calculates extractable soil water (esw) and actual transpirable soil water (atsw) in unit mm
celln	Mixes leached N with solution in a hypothetical mixing cell below the profile to calculate water concentration moving into the profile from below
cadate	Calculates calendar day and month for the current day based on input of starting month and starting day

Table 2.3. Output data from *_sum* file for PNM model.

Output data
Water (mm)
Rain
Runoff
Actual evaporation
Actual transpiration
Drainage
Soil N Losses (kg N ha^{-1})
Crop uptake of NH_4
Ammonia volatilized
NH_4 leached
Crop uptake of NO_3
Denitrified NO_3
N_2O loss
NO_3 leached
Average NO_3 concentration (mg L^{-1}) in water draining from profile over time
Soil N Inputs and Transformations (kg N ha^{-1})
Added urea-N fertilizer
Added NH_4-N fertilizer
Added NO_3-N fertilizer
Added sod-N fertilizer
Added manure-N fertilizer
NH_4-N from sod mineralization
NH_4-N from manure mineralization
NH_4-N from soil organic matter (SOM) mineralization
Net NH_4-N released
NO_3-N from nitrification of NH_4
Root Zone N from 0 - 30 cm (kg N ha^{-1})
NH_4-N
NO_3-N
Urea-N
Sod-N
SOM-N
Manure-N

Table 2.3. (continued)

Crop
Leaf N (kg N ha^{-1})
Stem N (kg N ha^{-1})
Leaf area index (m^2 m^{-2})
Seed dry weight (kg ha^{-1})
Above ground dry weight (kg ha^{-1})
N in grain (kg N ha^{-1})
Total N in above ground biomass (kg N ha^{-1})
Mass balances (kg N ha^{-1})
Urea-N
NH_4-N
NO_3-N
Sod-N
SOM-N
Manure-N
Sod-C
SOM-C
Manure-C
Others
Volumetric water content (m^3 m^{-3})
Water potential (kPa)
Temperature (°C)

pool of residue or manure N and P which do not dissolve. Added P fertilizer is assumed to be slowly soluble.

Rate Constants

The transformation rate constants for mineralization, nitrification, and denitrification respectively c_{mi}, c_{nit}, *and* c_{denit} can be adjusted for temperature and water content (Johnsson et al., 1987) in the *raten* routine of the model. A Q_{10}-type temperature response is assumed, with the Q_{10} value being the factor with which the rate constant changes over an interval of 10 °C. The temperature correction factor, C_T, at temperature T °C is defined as:

$$C_T = Q_{10}^{\ 0.1(T - T_{base})} \qquad [2.1]$$

where T_{base} is the base temperature for Q_{10} reactions.

The model uses default Q_{10} and T_{base} values of 2 and 20 respectively, both initialized in *vars*. The water content rate constants for denitrification increase with increasing water content but other rate constants decrease on either side of an optimum water content range between θ_{min} and θ_{max}.

The PNM model includes three major N transformation processes modeled in the *sinkn* routine:

1) mineralization rate associated with decomposition of the organic pool:

$$dN_i / dt = -c_{mi} N_i \qquad [2.2]$$

where N_i represents the concentration of humus, residue, or urea N, and c_{mi} are first-order rate constants;

2) nitrification, which converts NH_4 to NO_3 at a rate $c_{nit}N_{NH4}$ decreasing as a maximum NO_3^-/NH_4 concentration ratio r_{max} (Johnsson et al., 1987) is approached:

$$dNH_4 / dt = -c_{nit} \max(0, (N_{NH_4} - N_{NO_3} / r_{\max})); \qquad [2.3]$$

3) denitrification, which reduces NO_3 to gaseous N, follows Michaelis-Menten kinetics:

$$dN_{NO_3} / dt = -c_{denit} N_{NO_3} / (N_{NO_3} + C_{sat}) \qquad [2.4]$$

where c_{denit} is a potential rate and C_{sat} is a half-saturation constant. The denitrification process is temperature and moisture dependent. During cooler temperature, soil microbes are relatively inactive and subsequently c_{denit} remains low. As soil temperature increases in late spring, microbial activities increase, thus increasing c_{denit}. Similarly, c_{denit} decreases with decreasing water content below saturation, when anaerobiosis is minimal.

Water Flow

The water flow routine, *calfn*, in the model is based on the "tipping bucket" method whereby water is transferred downward to the layer below in the soil profile once the layer above exceeds its water-holding capacity. The assumption is that the model simulates free drainage. If water in the top soil layer is above field capacity, it flows down to the next layer in the soil profile; if it is not, then water in the soil layer gets filled up to field capacity, after which it flows downward to the next layer. This process continues for each soil layer until it reaches the bottom of the profile. This approach follows the method described in a review of modeling approaches by Addiscott and Wagenet (1985).

Each PNM model run involves many routines in the program to perform simulations on various processes in the soil-plant-atmosphere system, which adds to the level of complexity in the model. Rate constants, for example, can be calibrated in the model to better fit a specific geographical location or soil type. Given the variety of process functions that exists, how does one decide, say, whether the Campbell or the van Genuchten function gives better results in simulating N_2O losses in a field? Or, whether one water retention function only performs better than the other on a specific soil type? With the flexibility of the PNM model in which users are given the options to select the process functions and rate constant values for each simulation, there can be many interacting factors involved in determining the outcome of the results. Selecting the combination of functions and input values that gives the best fit between predicted and measured results is crucial. A model, after all, is only an abstract representation of the system, formulated based on certain theories and concepts, and calibration is still needed to improve its performance or accuracy.

Another water flow option is according to the mechanistic Richards equation which simultaneously uses the convection-dispersion equation (CDE) for solute transport. Although this method is not adapted into the PNM model, it can be found in the *watflo* and *soln* routines of the LEACHM model in Fortran programming language. Comparisons between the "tipping bucket" and Richards are discussed in Hutson (2003).

The PNM model uses the Campbell's equation to define the relationship between unsaturated conductivity and soil water content using water retention data. The Campbell's water retention equation is:

$$h = a(\theta / \theta_s)^{-b} \qquad [2.5]$$

where θ_s is volumetric water content at saturation and a and b are the alpha and beta slope constants, respectively.

The PNM model can also be adapted to use the van Genuchten water retentivity function, which is the following:

$$\theta = \theta_r + (\theta_s - \theta_r) * [1 + (h / h_g)^n]^{-m} \qquad [2.6]$$

where θ is the volumetric water content; θ_r is the residual water content (in most cases this is zero); θ_s is the volumetric water content at natural saturation which is chosen as the water content scale parameter; h is the soil water pressure head (matric potential);

h_g is the van Genuchten pressure head scale parameter; m and n are the two dimensionless water retention shape parameters defined by $m = 1 - 1/n$.

The “tipping bucket” approach used in the PNM model simulates water transport in soils and requires few input parameters, therefore, is computationally efficient. This method assumes that all water flow occurs through undefined pores and its simulation is limited to a fixed daily time step. If water reaches saturation, all the water is transferred to the layer below in the profile. This approach is a concern with denitrification, but less with leaching, since the immediate downward transfer of water does not truly simulate prolonged saturation in the soil, a condition which influences the denitrification process, as represented by C_{sat} in equation [2.4]. In order to address this issue, the “modified tipping bucket” approach was adapted to allow water to flow downward in the profile according to water levels in the soil at a rate constant factor.

N_2 to N_2O Ratio

Denitrification is a reduction process that converts nitrate (NO_3) to nitrous oxide (N_2O) and nitrogen gas (N_2). The presence of denitrifying bacteria under saturated anaerobic conditions provides the catalysts for N_2O emissions. The denitrification pathway is summarized as the following with four enzymes being sequentially induced (Cavigelli and Robertson, 2001):

$$NO_3^- \xrightarrow[Nar]{} NO_2^- \xrightarrow[Nir]{} NO \xrightarrow[Nor]{} N_2O\uparrow \xrightarrow[Nos]{} N_2\uparrow$$

The first three denitrification enzymes (nitrate reductase, Nar; nitrite reductase, Nir; and nitric oxide reductase, Nor) are critical in the accumulation of N_2O gas during denitrification. Nitrous oxide is further reduced to N_2 by nitrous oxide reductase, Nos, unless it volatilizes out of the soil system. In each of the biological reductions, N is used as an electron acceptor during microbial respiration. The primary environmental regulators that influence the enzymes' activity associated with N_2O flux include oxygen level, organic carbon substrate, pH (Tiedje, 1988; Firestone and Davidson, 1989), as well as NO_3^-, NO_2^- and possibly N_2O concentrations (Holtan-Hartwig et al., 2000) in soils. Cavigelli and Robertson (2000) found that Nar, Nir, and Nor (enzymes involved in N_2O production) respond differently from Nos (enzyme responsible for N_2O reduction to N_2) to oxygen and pH under different field management conditions. This suggests that enzyme communities may vary significantly for different fields and that population differences among denitrification enzymes may play an important factor in influencing N_2O fluxes in soil.

Due to high spatial and temporal variability, N_2O emissions are difficult to quantify even though considerable amounts of details on environmental properties are incorporated into N models (McConnaughey and Bouldin, 1985a; Johnsson et al., 1987; Li et al., 1992a; Li et al., 1992b; Parton et al., 1996). Since enzyme activity plays a major role in the production of N_2O emissions, incorporating the contributions of microbial processes to N_2O in soils would provide a better representation in the model.

Even though quantification of N_2O is important for risk assessment and regulatory purposes, Beauchamp (1997) concluded that the ratios of denitrification products are also important determinant parameters for estimating the change in the global N_2O budget, and should be examined. The N_2:N_2O ratios are highly variable. McConnaughey and Bouldin (1985b) reported ratios of N_2 to N_2O that ranged from 0.17 to 19.15 under various denitrification models. Vinther (2005) described the average N_2:N_2O ratio (as a function of clay content fitted with a Michaelis-Menten equation in the SimDen model) to be approximately four, a mean value which corresponds to ratios he found in other literature.

MATERIALS AND METHODS

Field Experiment

A field experiment was conducted on two experimental sites located at the Cornell University Research Farm in Willsboro, NY (44°22'N, 73°26'W) for a one week period (Tan et al., 2007). The objective of the experiment was to study the effects of soil type, tillage, rotation, and fertilization on short-term N_2O emissions from a single major (simulated) rainfall event under maize production (Tan et al., 2007). Each site represented a different soil type: a Muskellunge clay loam (fine, mixed, active, frigid Aeric Epiaqualf), and a Stafford loamy fine sand (mixed, mesic Typic Psammaquent). Both had similar treatments using a split-plot design, with crop rotations (maize after grass, continuous maize) as main plots, and a 2 × 2 factorial arrangement of tillage (untilled, tilled) and N fertilization (full, starter) as split plots, all laid out with two replications in a spatially balanced design (van Es and van Es, 1993), as described by Tan et al. (2007). The terms "untilled" and "tilled" were used to refer to the loosening of the soil in the early growing season, as opposed to the terms "no-till" and "plow-till" which are associated with longer-period tillage systems.

All plots were planted to maize at a density of 70 000 plants ha^{-1} and application of chemical amendments were made in accordance with Cornell Cooperative Extension guidelines (CCE, 2004). Nitrogen fertilizer rates were applied at each site according to the following treatments: full application (134 kg N ha^{-1}) involving 20 kg N ha^{-1} at planting and an additional 114 kg N ha^{-1} as ammonium nitrate (AN, 34-0-0) broadcasted three weeks later; and starter application which consisted of only a 20 kg N ha^{-1} application at planting.

A simulated 50-mm rainfall event using a sprinkler irrigation system was used to induce saturated and anaerobic conditions in the field on June 21, 2004 on the clay loam plots and June 22, 2004 on the loamy fine sand plots. Nitrous oxide fluxes were measured twice daily using the vented static chamber method (Duxbury et al., 1982; McConnaughey and Duxbury, 1986). In each plot, four gas chambers were installed on the rows and interrows of the field, with vented lids attached to the top of the chambers prior to each flux measurement. Chamber headspace was sampled with a 10 ml syringe and injected into pre-evacuated glass vials at time zero and 45-minute intervals up to 90 minutes. Lids were removed after three samplings and attached again to the chambers before the next flux measurements were made. Nitrous oxide concentrations were determined using a gas chromatograph (Tan et al., 2007).

On each plot, six composites of surface soil samples at 20 cm depth were collected at random prior to and after the experiment, and frozen until further analysis. Frozen soil samples were later analyzed in the Cornell Nutrient Analysis Laboratory for NO_3-N within 24 hours of oven-drying at 105 °C. Deep soil samples to a depth of 90 cm (two for each depth) were collected from each plot at the beginning and end of the experiment using a tractor-mounted Giddings hydraulic soil coring and sampling device (Sogbedji et al., 2001a). Soil organic matter was measured using the loss on ignition method (Storer, 1984).

Samples of undisturbed soil cores were collected in duplicate from inter-row locations in each plot at both sites prior to the experiment using 76-mm diameter and 60-mm high stainless steel rings, and were stored at 2 °C until further analysis. These samples were removed from storage and subsequently saturated by wetting from the bottom over a three-day period, and cores were allowed to drain to field capacity on a saturated cheese cloth (Karunatilake and van Es, 2002). The volume fraction of pores greater than 1.0 mm was determined as the difference in core weight between saturation and $\psi = 0.3$ kPa. Soil water retention at $\psi = 10$ kPa was determined using a custom-made sand table water retention apparatus, providing estimates of the volume fraction of pores greater than 0.03 mm. Bulk density and total porosity, assuming particle density of 2.65 Mg m^{-3}, were calculated for each core after determining oven-dry weight.

N_2 to N_2O Ratio

From the field experiment data, a partial N budget was calculated for both the 0 – 20 and 0 – 30 cm depth intervals, taking into account initial and final soil NO_3-N from before and after the experiment respectively, N_2O loss, the amount of NO_3-N transported to the lower soil profile, as well as NO_3-N leached into the drain line. The unaccounted value in the budget (difference between initial soil NO_3-N and sum of final soil NO_3-N, N_2O loss, NO_3-N gain and leached) was assumed to be N_2 that was volatilized. Partial N budgets were initially computed for each treatment but since results showed high and inconsistent N_2:N_2O variability among soil type, rotation, tillage, and fertilization treatments, all data were pooled and a single average ratio was determined. All the data were then pooled to yield a combined average for the budget, without taking into account the treatment effects.

The N_2:N_2O value from the partial N budget of pooled data was used to estimate N_2O loss based on denitrified NO_3 simulated by the PNM model. Based on the N_2:N_2O value obtained from the partial N budget and the assumption that denitrification is the sum of N_2O and N_2, N_2O is a constant fraction of the denitrification amount:

$$\mathrm{N}_2O = (1/(1 + N_2 : N_2O)) * Denitrification \qquad [2.7]$$

Some code was added into the PNM model to incorporate equation [2.7] and allow the model to simulate N_2O based on N_2:N_2O results from the N budget analyses. Model runs were performed to simulate N_2O based on each estimated N_2:N_2O value.

Process Representation

For each ratio, multiple runs were generated using different water retention parameters (Campbell; van Genuchten) and calibrated denitrification rate constants for clay loam (0.09 d^{-1}, 0.90 d^{-1}) to simulate cumulative N_2O losses based on daily measurements under scenarios similar to all treatments from the field experiment.

Simulations were performed as a 2 × 2 × 2 × 2 factorial for the following factors: soil types (clay loam; loamy sand); water retention equations (Campbell, van Genuchten); denitrification rate constants (0.09 and 0.9 d^{-1} on clay loam, 0.004 and 0.04 d^{-1} on loamy sand); and water flow options ("tipping bucket", "modified tipping bucket"). Table 2.4 summarizes the particle size distributions for the soil profiles of the clay loam and loamy sand, as used in the PNM model simulations. Percent organic carbon and bulk density are represented by the variables *oc* and *rho* respectively in *soilInfo* routine of the model. The values for both these parameters were differentiated by rotation and tillage from 0 – 20 cm for both soil types (Tables 2.5 and 2.6). Similar values were used for runs generated from each estimated N_2 to N_2O ratio.

The variable *modret* in the *soilInfo* routine determines the type of water retention function used in the model. A value of 0 is indicative of the Campbell equation, while a value of 6 is for the van Genuchten function. The variables *aaev* and *abcam* in *soilInfo* represents respectively the alpha parameter, which is the air entry water potential (kPa), and the beta slope parameter, in the Campbell water retention equation (Table 2.7). These alpha and beta slope parameters were obtained from Sogbedji (2001a) and were only differentiated by soil type. The parameter values for the van Genuchten equation were generated using RETC, a program that estimates water retention parameters. Volumetric moisture contents, θ, (m^3 m^{-3}) were fitted against tensions, ψ, in the retention function in RETC to obtain soil input parameters

Table 2.4. Particle size distribution parameter values for the clay loam and loamy fine sand as used in the model simulations.

Depth (cm)	Particle size (%)		
	Sand	Silt	Clay
Clay loam			
5	44.5	17.1	38.4
15	42.3	15.3	42.4
25	29.3	16.8	53.9
35	12.8	26.4	60.8
45	4.8	27.5	67.7
55	4.8	27.5	67.7
65	4.8	27.5	67.7
Loamy fine sand			
5	79.8	10.1	10.1
15	80.6	10.0	9.4
25	86.9	5.8	7.3
35	84.8	5.5	9.7
45	73.8	12.0	14.2
55	50.3	20.9	28.8
65	24.3	32.0	43.7

Table 2.5. Organic carbon levels for clay loam and loamy fine sand as used in the PNM model simulations.

Depth (cm)	Maize after Grass Untilled	Maize after Grass Tilled	Continuous Maize Untilled	Continuous Maize Tilled
	($g\ kg^{-1}$)			
Clay loam				
5	22.2	28.9	21.0	21.1
15	22.2	28.9	21.0	21.1
25	5.0	5.0	5.0	5.0
35	3.0	3.0	3.0	3.0
45	3.0	3.0	3.0	3.0
55	3.0	3.0	3.0	3.0
65	3.0	3.0	3.0	3.0
Loamy fine sand				
5	19.4	18.6	18.6	18.4
15	19.4	18.6	18.6	18.4
25	16.0	16.0	16.0	16.0
35	4.0	4.0	4.0	4.0
45	4.0	4.0	4.0	4.0
55	2.0	2.0	2.0	2.0
65	2.0	2.0	2.0	2.0

Table 2.6. Bulk density parameter values for clay loam and loamy fine sand as used in the PNM model simulations.

Depth	Maize after Grass		Continuous Maize	
(cm)	Untilled	Tilled	Untilled	Tilled
	(Mg m^{-3})			
Clay loam				
5	1.25	1.11	1.18	1.21
15	1.25	1.11	1.18	1.21
25	1.53	1.53	1.53	1.53
35	1.49	1.49	1.49	1.49
45	1.51	1.51	1.51	1.51
55	1.51	1.51	1.51	1.51
65	1.51	1.51	1.51	1.51
Loamy fine sand				
5	1.23	1.21	1.33	1.21
15	1.23	1.21	1.33	1.21
25	1.55	1.55	1.55	1.55
35	1.69	1.69	1.69	1.69
45	1.51	1.51	1.51	1.51
55	1.50	1.50	1.50	1.50
65	1.54	1.54	1.54	1.54

Table 2.7. Campbell equation parameter values for clay loam and loamy fine sand as used in the PNM model simulations.

Depth (cm)	Campbell equation retentivity parameters Alpha	 Beta
Clay loam		
5	- 0.26	7.40
15	- 0.30	12.00
25	- 4.89	12.00
35	- 4.89	12.00
45	- 4.89	12.00
55	- 4.89	12.00
65	- 4.89	12.00
Loamy fine sand		
5	- 0.52	3.87
15	- 0.95	4.38
25	- 0.60	4.61
35	- 0.26	5.00
45	- 0.01	8.20
55	- 0.16	7.72
65	- 1.10	8.10

alpha, n, and ResSat. These are read by the *utilities* routine and used for calculating volumetric water content, hydraulic conductivity, and water potential. The van Genuchten parameters for the top 5 cm were differentiated by soil type, rotation, and tillage. They were obtained by fitting θ values at 0.01; 0.3; 10; and 1500 kPa (Table 2.8) into RETC. Parameters below 5 cm were only differentiated by soil type, and obtained by fitting θ values from Sogbedji (2001a), at ψ of 1; 10; 40; 100; 300; and 1500 kPa (Table 2.9).

Rate constants for N processes on both soil types as used in the PNM model simulations were based on suggested values in the LEACHM manual (Hutson, 2003) and from previous studies (Sogbedji et al., 2001b), except for the denitrification rate constants which were calibrated (Table 2.10). Calibration involved iterative adjustments of the denitrification rate constant to optimize the fit between simulated and measured values of surface soil NO_3-N before and after the experiment. Multiple runs were performed for each combination of soil type, rotation, and tillage of the experimental treatments. Denitrification rate constant values were used ranging from 0.007 to 0.9 d^{-1} for clay loam and 0.004 to 0.04 d^{-1} for the loamy fine sand, but only the optimum two rate constants from each soil type are presented.

The water flow option in the model is based on Addiscott's "tipping bucket" algorithm whereby water is transferred downward to the layer below in the soil profile once the layer above exceeds its water-holding capacity (field capacity). Results from the original "tipping bucket" option were compared with the "modified tipping bucket" water flow option (*calfn* routine recoded by Melkonian and Hutson). In the modified version, water that is above saturation directly flows downward to the underlying soil layer, but water from saturation to field capacity drains downward based on a rate constant factor. This allows soil layers to remain at water contents above field capacity for extended periods, which is important when simulating

Table 2.8. Parameter values at 5 cm for clay loam and loamy fine sand as used in the model simulations.

Soil type	Maize after Grass		Continuous Maize	
	Untilled	Tilled	Untilled	Tilled
	van Genuchten equation parameter values			
Clay loam				
alpha	0.5781	4.1761	2.2742	2.2742
n	1.1395	1.1885	1.2575	1.2575
ResSat	0.0004	0.0743	0.1166	0.1166
Loamy fine sand				
alpha	0.9114	0.8968	1.5040	1.3703
n	1.2737	1.5115	1.2869	1.3761
ResSat	0.0014	0.0382	0.0197	0.0347
	Volumetric moisture content (m^3 m^{-3}) at tensions (kPa)			
Clay loam				
0.01 kPa	0.50	0.57	0.55	0.55
0.3 kPa	0.47	0.51	0.51	0.51
10 kPa	0.38	0.32	0.31	0.31
1500 kPa	0.19	0.17	0.17	0.17
Loamy fine sand				
0.01 kPa	0.50	0.51	0.48	0.48
0.3 kPa	0.48	0.49	0.45	0.45
10 kPa	0.27	0.19	0.23	0.20
1500 kPa	0.07	0.05	0.07	0.06

Table 2.9. Parameter values from 15 - 65 cm for clay loam and loamy fine sand as used in the model simulations.

Depth (cm)	van Genuchten equation parameter values			Water content (m^3 m^{-3}) at tensions (kPa)					
	alpha	n	ResSat	1	10	40	100	300	1500
Clay loam									
15	0.0363	1.5880	0.1981	0.40	0.36	0.34	0.28	0.24	0.22
25	0.0882	1.0932	0.0007	0.43	0.39	0.38	0.35	0.31	0.27
35	0.0309	1.2782	0.2355	0.45	0.43	0.41	0.39	0.34	0.31
45	0.1545	1.0567	0.0005	0.42	0.40	0.38	0.36	0.34	0.31
55	0.0379	1.0681	0.0004	0.45	0.43	0.42	0.41	0.37	0.34
65	0.0619	1.0094	0.0005	0.45	0.42	0.41	0.40	0.38	0.34
Loamy fine sand									
15	0.2771	1.3778	0.0312	0.38	0.25	0.22	0.10	0.09	0.08
25	0.2535	1.3381	0.0000	0.35	0.23	0.21	0.09	0.07	0.06
35	1.2764	1.2417	0.0009	0.28	0.17	0.15	0.09	0.07	0.06
45	0.7859	1.1537	0.0001	0.32	0.24	0.22	0.17	0.14	0.12
55	2.3184	1.1490	0.0002	0.35	0.25	0.23	0.18	0.14	0.13
65	1.3311	1.1274	0.0010	0.41	0.30	0.29	0.25	0.21	0.16

Table 2.10. Rate constants as used in the model simulations.

	Rate constants					
Soil type	Hydrolysis	Nitrification	Denitrification	Mineralization of plant residue (d^{-1})	Mineralization Of manure	Mineralization of native SOM
Clay loam	0.384	0.280	0.090	0.010	0.020	0.00015 (0 – 30 cm)
			0.900			0.00001 (below 30 cm)
Loamy fine sand	0.384	0.400	0.004	0.010	0.020	0.00015 (0 – 30 cm)
			0.040			0.00001 (below 30 cm)

denitrification and related processes. The “modified tipping bucket” approach provided denitrification estimates similar to those from the Richard’s equation approach, but is computationally more desirable (Melkonian, pers. comm.).

The PNM model simulations for each scenario began on March 1 to October 1, 2004, and were simulated on daily time steps. Temperature and precipitation data from the Willsboro station were used in the model runs. Starter and additional fertilizer applications were on May 14, 2005 and June 5, 2004 respectively, to resemble application dates from the field experiment. All plots were planted to maize on May 14, 2004 at a density of 70 000 plants ha^{-1}.

Simulated results of volumetric water content, NO_3-N, cumulative N_2O fluxes, and temperature for clay loam and loamy fine sand were compared with field measured data (Tan et al., 2007) using a 2 × 2 factorial combination of water retention functions (Campbell, van Genuchten) and water flow options (“tipping bucket”, “modified tipping bucket”) on two denitrification rate constants.

Model Performance Assessment

The accuracy of the model was evaluated using 1:1 scale plots, and RMSE and NRMSE estimates, similar to Garrison et al. (1999) and Sogbedji et al. (2001a). RMSE and NRMSE are defined as:

$$RMSE = \left[\sum_{i=1}^{n} (measured - predicted)^2 / n \right]^{0.5} \qquad [2.8]$$

$$NRMSE = (RMSE / measured\ grand\ mean) \qquad [2.9]$$

where *n* is the size of data set

The N_2:N_2O ratio that gave the model the best fit (lowest RMSE) between predicted and measured N_2O was selected as the parameter value for the model.

RESULTS

N_2 to N_2O Ratio

Tables 2.11 and 2.12 are the partial N budgets at 0 – 20 and 0 – 30 cm respectively for clay loam and loamy fine sand under different tillage, rotation, and N treatments. There were no differences between initial soil NO_3-N at 0 – 20 and 0 – 30 cm for clay loam under maize after grass but differences were observed under continuous maize. Initial soil NO_3-N varied between both depths for all treatments under loamy fine sand except under continuous maize, tilled, and starter N application. Final soil NO_3-N varied from 0 – 20 to 0 – 30 cm for all treatments except under continuous maize, untilled, and starter N fertilization for both soil types. The budgets for pooled data are shown in Table 2.13. Results from the budgets showed that the N_2:N_2O ratio was higher for the 0 – 20 cm analysis than the 0 – 30 cm (2.30 and 1.99, respectively Table 2.13). Substituting each ratio into equation [2.7] yields a multiplication factor of 0.30 and 0.33, respectively.

PNM Simulations

In general, the 1:1 scale plots showed a reasonable match between PNM-predicted and measured cumulative N_2O for each factorial of treatments (Figure 2.1) except for the case with the Campbell function and 0.9 d^{-1} denitrification rate constant. The trends of the plots were relatively similar for both N_2:N_2O ratios, which would be expected. Most of the cumulative N_2O losses were higher for simulated than measured values. All combinations of water retention parameters and denitrification rate constants (Campbell, 0.09 d^{-1}; Campbell, 0.90 d^{-1}; van Genuchten, 0.09 d^{-1}; van Genuchten, 0.90 d^{-1}) showed that only one data point was underestimated, except van Genuchten at rate constant of 0.09 d^{-1} where two data points were underestimated by

Table 2.11. Partial N budget for June 20 – June 24, 2004 at 0 – 20 cm. Means are based on two replications.

	Maize after Grass				**Continuous Maize**			
	Tilled		Untilled		Tilled		Untilled	
	Full	*Starter*	*Full*	*Starter*	*Full*	*Starter*	*Full*	*Starter*
	kg ha^{-1}							
	Muskellunge clay loam							
Initial soil NO_3-N	78.81	34.96	72.34	25.35	84.53	27.56	106.52	31.68
Final soil NO_3-N	41.99	24.26	45.83	21.58	51.41	15.05	59.61	14.85
N_2O loss	1.62	0.67	5.38	0.94	1.12	0.33	2.51	0.26
Gain* (20 – 90 cm)	28.87	9.21	26.04	8.61	25.28	18.23	10.75	12.69
Leached NO_3-N	0.88	0.27	0.66	0.09	0.87	0.24	0.67	0.22
Unaccounted	5.45	0.56	- 5.57	- 5.86	5.84	- 6.29	32.98	3.67
	Stafford loamy fine sand							
Initial soil NO_3-N	110.49	25.40	101.28	41.81	97.11	18.49	60.77	19.84
Final soil NO_3-N	29.89	17.24	43.04	37.97	43.51	20.90	28.46	22.78
N_2O loss	0.58	0.16	0.80	0.35	0.37	0.17	0.16	0.17
Gain* (20 – 90 cm)	46.14	32.27	56.21	-13.41	77.61	-11.92	28.45	6.89
Leached NO_3-N	0.13	0.09	0.14	0.09	0.39	0.28	0.13	0.13
Unaccounted	33.75	-24.36	1.09	16.81	-24.76	9.06	3.56	-10.12

* Gain (20 – 90 cm) = Final soil NO_3-N (20 – 90 cm) – Initial soil NO_3-N (20 – 90 cm)

Table 2.12. Partial N budget for June 20 – June 24, 2004 at 0 – 30 cm. Means are based on two replications.

	Maize after Grass				**Continuous Maize**			
	Tilled		Untilled		Tilled		Untilled	
	Full	*Starter*	*Full*	*Starter*	*Full*	*Starter*	*Full*	*Starter*
	kg ha^{-1}							
	Muskellunge clay loam							
Initial soil NO_3-N	78.81	34.96	72.34	25.35	95.65	32.70	117.86	31.68
Final soil NO_3-N	53.20	33.53	55.34	30.22	72.54	22.57	69.64	14.85
N_2O loss	1.62	0.67	5.38	0.94	1.12	0.33	2.51	0.26
Gain* (30 – 90 cm)	17.70	0.00	16.69	0.00	15.28	15.85	12.06	12.69
Leached NO_3-N	0.88	0.27	0.66	0.09	0.87	0.24	0.67	0.22
Unaccounted	5.41	0.49	- 5.73	- 5.90	5.84	- 6.29	32.98	3.66
	Stafford loamy fine sand							
Initial soil NO_3-N	121.94	33.55	101.28	49.53	108.87	18.49	64.45	23.54
Final soil NO_3-N	46.48	44.62	70.64	51.24	111.12	27.33	44.05	22.78
N_2O loss	0.58	0.16	0.80	0.35	0.37	0.17	0.16	0.17
Gain* (30 – 90 cm)	41.00	13.04	28.61	-18.96	26.07	-18.37	16.55	10.59
Leached NO_3-N	0.14	0.10	0.16	0.10	0.41	0.30	0.14	0.14
Unaccounted	33.74	-24.36	1.07	16.80	-29.10	9.06	3.55	-10.13

* Gain (30 – 90 cm) = Final soil NO_3-N (30 – 90 cm) – Initial soil NO_3-N (30 – 90 cm)

Table 2.13. Partial N budget and N_2:N_2O ratios of pooled averages for June 20 – June 24, 2004.

	0 – 20 cm	0 – 30 cm
	kg ha^{-1}	
Initial soil NO_3-N	58.56	63.19
Final soil NO_3-N	32.40	48.13
N_2O loss	0.97	0.97
Gain	22.62[*]	11.80[†]
Leached NO_3-N	0.33	0.34
Unaccounted	2.24	1.94
N_2:N_2O ratio	2.30	1.99

[*] Gain = Final soil NO_3-N (20 – 90 cm) – Initial soil NO_3-N (20 – 90 cm)

[†] Gain = Final soil NO_3-N (30 – 90 cm) – Initial soil NO_3-N (30 – 90 cm)

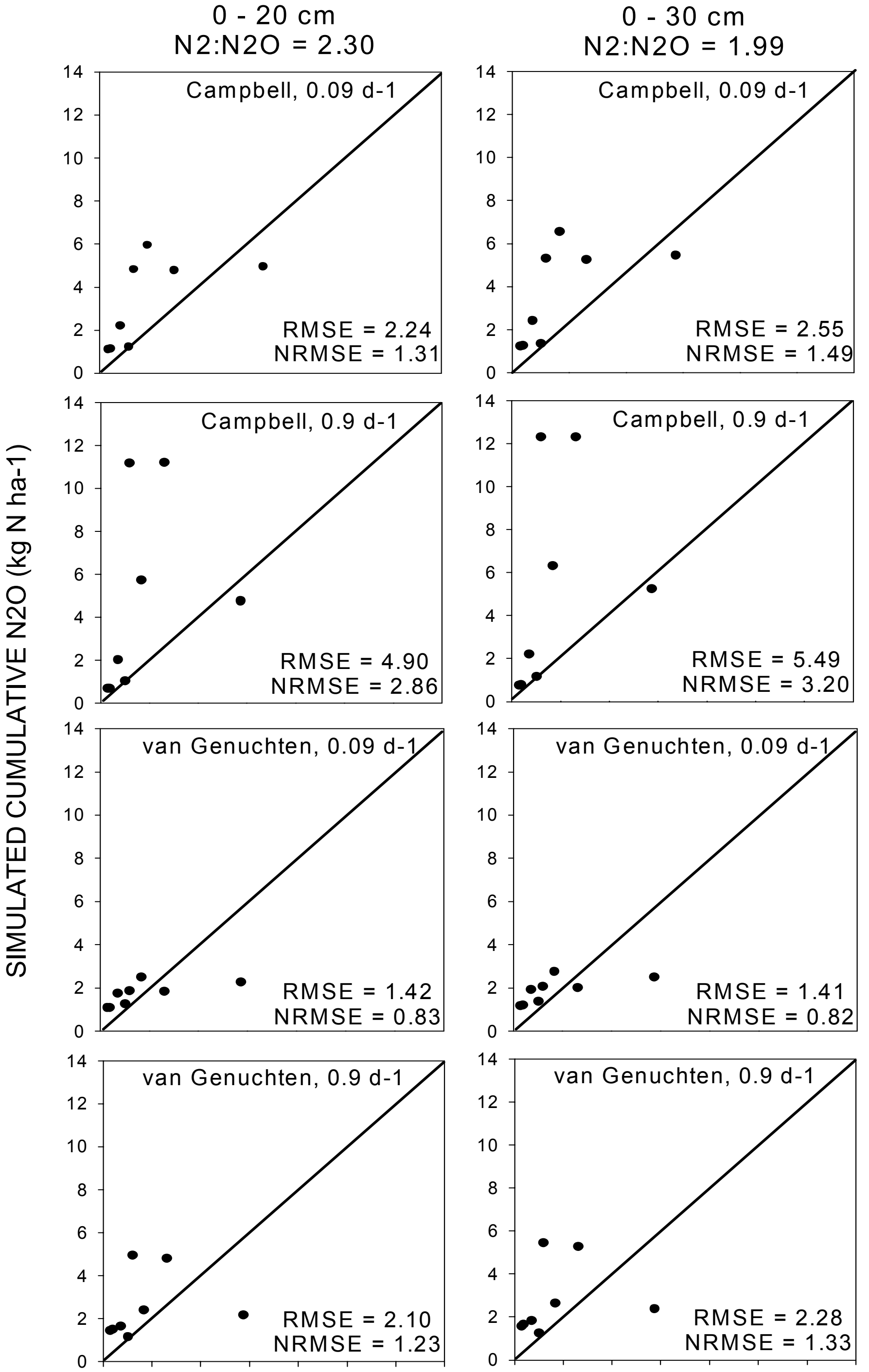

Figure 2.1. 1:1 scale plots of measured and simulated 5-day cumulative N_2O fluxes based on N_2:N_2O ratio from N budgets at 0 - 20 and 0 - 30 cm for clay loam using combination of Campbell vs. van Genuchten retentivity models, and denitrification rate constants of 0.09 and 0.9 d^{-1}.

the model. Data points were overestimated for all combinations of water retention parameters and denitrification rate constants. Serious overestimation of data points were observed for Campbell function and 0.9 d^{-1} denitrification rate constant under treatments with continuous maize, full fertilization for both untilled and tilled rotations. The simulations using van Genuchten parameters and the 0.09 d^{-1} denitrification rate constant also showed the best fit between simulated and measured N_2O. Data points of the 5-day cumulative N_2O losses averaged over all parameter combinations showed a general overestimation by the model (Figure 2.2). Each data point on the plots represents a factorial of treatments summarized in Table 2.14. Significant outliers were observed on both ratios with Campbell parameters at 0.90 d^{-1} rate constant. The model underestimated cumulative N_2O under maize after grass, untilled, and full N treatments on all parameters and ratios but had somewhat good predictions under maize after grass, untilled and starter N treatments. The model performed poorly on all cumulative N_2O predictions under continuous maize for both untilled and tilled with full N treatments.

For each combination of water retention parameters and denitrification rate constants, the RMSE and NRMSE values for predicted against measured cumulative N_2O loss were compared between the two N_2:N_2O ratios (Table 2.15). All combinations of parameters had lower RMSE and NRMSE values for the N_2:N_2O ratio of 2.30 than 1.99; this was an exception when the model was simulated using van Genuchten parameters and a denitrification rate constant of 0.09 d^{-1}, although the differences for both RMSE and NRMSE values were only a magnitude of 0.01. Among all parameters, the Campbell equation and denitrification rate constant of 0.90 d^{-1} resulted in the highest RMSE and NRMSE while the van Genuchten parameters and rate constant of 0.09 d^{-1} resulted in the best fit for the model, for both ratios. When the cumulative N_2O data were pooled from all combinations of parameters,

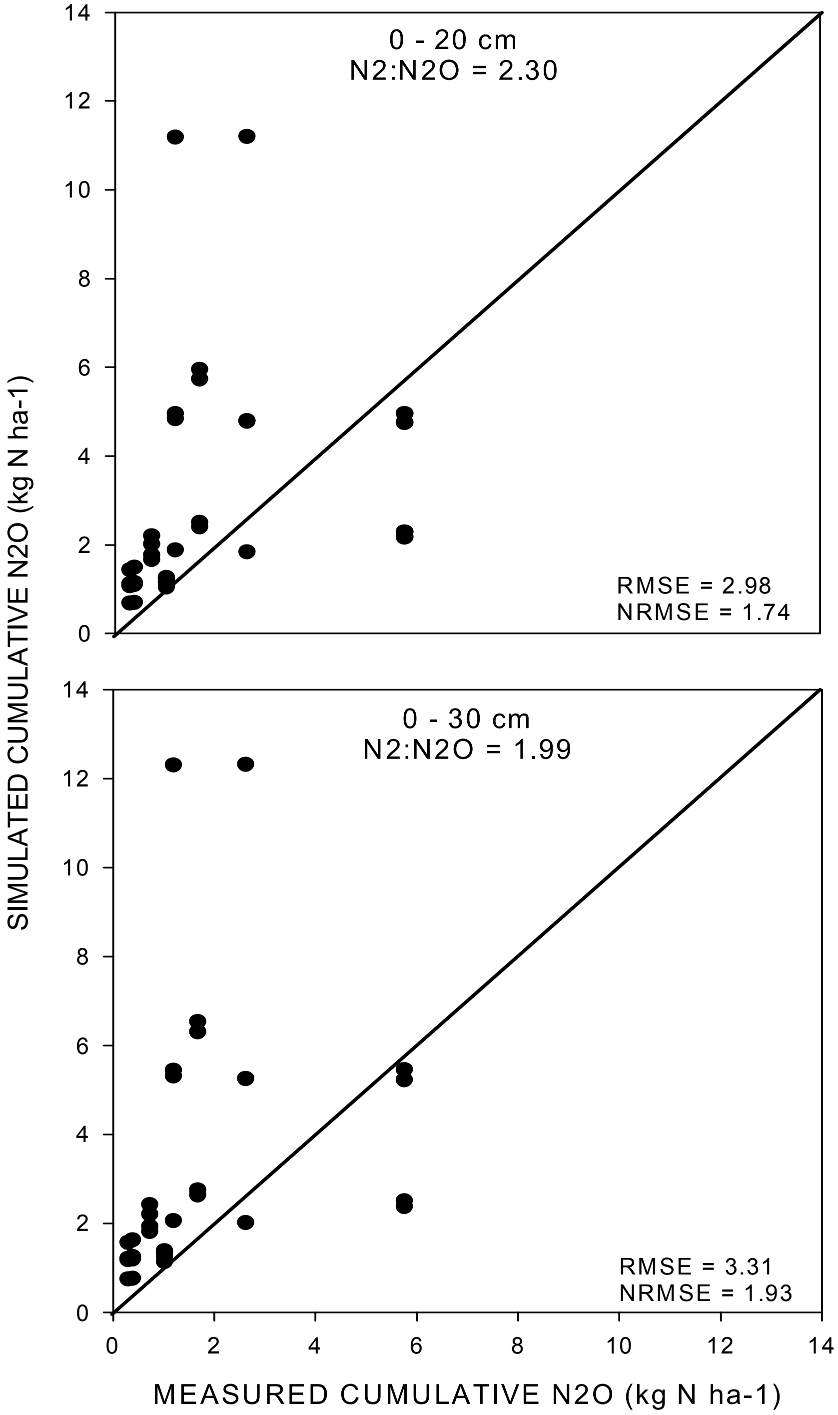

Figure 2.2. 1:1 scale plots of measured and simulated cumulative 5-day N_2O based on N_2:N_2O ratio from N budgets at 0 - 20 and 0 - 30 cm for clay loam, averaged for clay loam using combination of Campbell vs. van Genuchten retentivity models, and denitrification rate constants of 0.09 and 0.9 d^{-1}.

Table 2.14. Measured and simulated cumulative N_2O at clay loam site.

	Measured	Simulated			
		Campbell		van Genuchten	
		0.09 d^{-1}	0.90 d^{-1}	0.09 d^{-1}	0.90 d^{-1}
	kg ha^{-1}				
	0 - 20 cm N_2:N_2O = 2.30				
MAG, Untilled, Full	5.76	4.96	4.75	2.28	2.16
MAG, Untilled, Starter	1.02	1.22	1.04	1.26	1.14
MAG, Tilled, Full	1.68	5.95	5.73	2.50	2.40
MAG, Tilled, Starter	0.73	2.20	2.00	1.76	1.65
CM, Untilled, Full	2.62	4.78	11.20	1.83	4.78
CM, Untilled, Starter	0.30	1.10	0.68	1.07	1.43
CM, Tilled, Full	1.20	4.83	11.18	1.87	4.94
CM, Tilled, Starter	0.39	1.14	0.69	1.09	1.49
	0 - 30 cm N_2:N_2O = 1.99				
MAG, Untilled, Full	5.76	5.45	5.23	2.50	2.38
MAG, Untilled, Starter	1.02	1.34	1.14	1.38	1.25
MAG, Tilled, Full	1.68	6.54	6.31	2.75	2.64
MAG, Tilled, Starter	0.73	2.42	2.21	1.93	1.82
CM, Untilled, Full	2.62	5.26	12.32	2.02	5.26
CM, Untilled, Starter	0.30	1.22	0.75	1.18	1.57
CM, Tilled, Full	1.20	5.32	12.30	2.06	5.44
CM, Tilled, Starter	0.39	1.25	0.76	1.20	1.64

MAG indicates maize after grass, CM indicates continuous maize

Table 2.15. Statistical evaluation of PNM simulations for cumulative N_2O based on 0 – 20 and 0 – 30 cm N_2:N_2O for each combination of water retention and denitrification rate constant parameters at the clay loam site.

	0 – 20 cm N_2:N_2O = 2.30			0 – 30 cm N_2:N_2O = 1.99		
	n	RMSE	NRMSE	n	RMSE	NRMSE
		kg ha^{-1}			kg ha^{-1}	
Cumulative N_2O						
Parameters						
Campbell, 0.09 d^{-1}	8	2.24	1.31	8	2.55	1.49
Campbell, 0.90 d^{-1}	8	4.90	2.86	8	5.49	3.20
van Genuchten, 0.09 d^{-1}	8	1.42	0.83	8	1.41	0.82
van Genuchten, 0.90 d^{-1}	8	2.10	1.23	8	2.28	1.33
All parameters	32	2.98	1.74	32	3.31	1.93

RMSE and NRMSE results indicated that N_2:N_2O from 0 – 20 cm N budget analysis had better prediction on N_2O loss than for the ratio from 0 – 30 cm. The RMSE and NRMSE for N_2:N_2O ratios of 2.30 and 1.99 were 2.98 and 3.31, and 1.74 and 1.93 accordingly. This suggests, indirectly, that N_2O losses from denitrification events generally are derived from shallow soil depths.

Particle size distributions varied through soil profile depth and were more variable for the loamy fine sand than for the clay loam due to underlying clay layers (Table 2.4). Surface soil samples from the field experiment in Willsboro, NY, were analyzed for organic carbon content and bulk density, and used as input parameters in the PNM model simulations. Organic carbon content and bulk density on clay loam and loamy fine sand were differentiated by soil type, rotation and tillage for the top 15 cm (Tables 2.5 and 2.6). Below the 15 cm depth, organic carbon and bulk density values were based on those used by Sogbedji (2001a) and were differentiated only by soil type. Bulk density values on loamy fine sand were more variable compared to clay loam, especially for the lower depths of the profile from 45 – 65 cm.

Both alpha and beta parameters in Campbell's equation were more variable for the loamy fine sand than the clay loam (Table 2.7). However, this was not the case for van Genuchten equation parameters as the parameter values were about equally variable for both clay loam and loamy fine sand. The alpha parameter values in the van Genuchten equation were highest at 5 cm for clay loam but not for loamy fine sand (Tables 2.8 and 2.9). The values for the n parameter for both soil types were about the same. On average, ResSat values were higher for the clay loam than the loamy fine sand.

The rate constants for urea hydrolysis and mineralization were assumed to be the same for both clay loam and loamy fine sand. The nitrification rate constant as used for the clay loam (0.28 d^{-1}) was lower than for the loamy fine sand (0.40 d^{-1}), based on Sogbedji et al. (2001a). These values are higher than the 0.20 d^{-1} suggested by Hutson (2003), and similarly used by Johnsson et al. (1987) and Jansson and Anderson (1988). The proposed denitrification rate constant of 0.10 d^{-1} by Hutson (2003) is higher than the values ranging from 0.02 – 0.05 d^{-1} as used by Jemison (1994). The denitrification rate constants used in the PNM model simulations were higher for clay loam (0.09 and 0.9 d^{-1}) than for loamy fine sand (0.004 and 0.04 d^{-1}) (Table 2.10). Denitrification is a complex process which not only involves physical and chemical, but also biological factors. As results from the field experiments and modeling efforts have shown, there are many interacting factors that affect the denitrification process, which cannot necessarily be represented by a rate constant parameter value alone. Different water retention functions and water flow options will have some impact on the simulation results as well.

Volumetric Water Content

Volumetric water content measurements from the field experiment were higher for the clay loam than the loamy fine sand (Table 2.16). Results were differentiated by soil type, rotation, and tillage. Measurement results were highest at 24 hours after irrigation for all treatments except continuous maize -- untilled on the loamy fine sand.

Observations from the 1:1 scale plots showed that the Campbell equation and “tipping bucket” performed the best among all combinations of water retention equation and water flow options for the clay loam, with RMSE of 0.08 and NRMSE of 0.26 (Figure 2.3). The van Genuchten and “tipping bucket” approaches performed the worst, with RMSE and NRMSE of 0.14 and 0.47, respectively, and mostly underestimated the predictions for volumetric water content. When the “modified tipping bucket” method was used with Campbell function to simulate volumetric water content for clay loam, results indicated that all data points were overestimated by the

Table 2.16. Measured volumetric water content for June 20 – June 25, 2004 at 0 – 15 cm.

	Maize after Grass		**Continuous Maize**	
	Untilled	Tilled	Untilled	Tilled
Hours after Irrigation		**Muskellunge clay loam**		
0	0.002	0.201	0.168	0.168
24	0.373	0.359	0.325	0.359
48	0.334	0.341	0.279	0.307
72	0.330	0.348	0.279	0.314
96	0.341	0.352	0.283	0.315
120	0.326	0.348	0.275	0.291
		Stafford loamy fine sand		
0	0.136	0.152	0.105	0.055
24	0.283	0.238	0.242	0.234
48	0.234	0.177	0.254	0.197
72	0.234	0.189	0.242	0.197
96	0.242	0.197	0.234	0.177
120	0.218	0.173	0.218	0.197

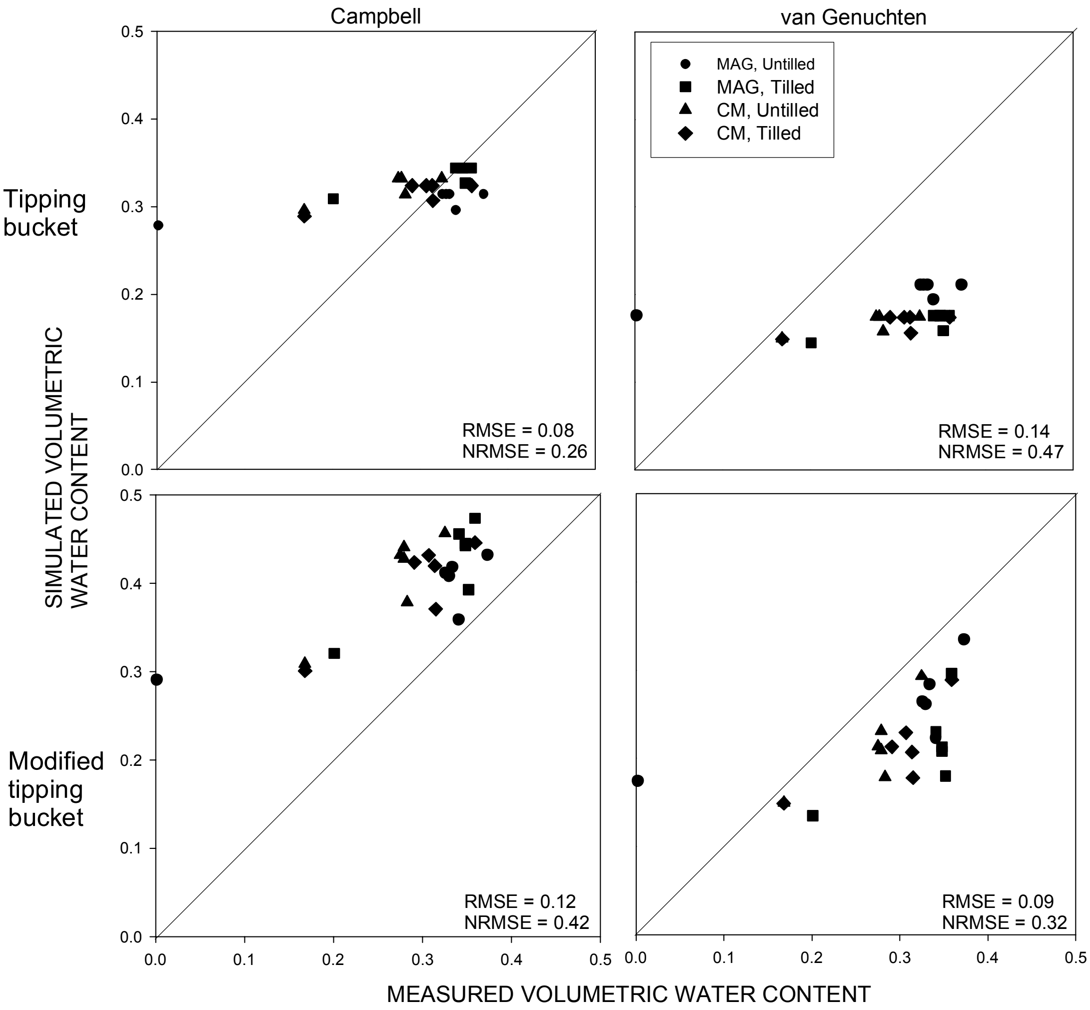

Figure 2.3. 1:1 scale plots of measured and simulated volumetric water content for clay loam.

model. Model-predicted data were mostly underfitted when the van Genuchten parameter values were used in the simulation runs. Comparing the 1:1 scale plots for loamy fine sand (Figure 2.4) with clay loam, the trends of data fitting were very similar. For instance, overestimations were observed for “modified tipping bucket” and Campbell approaches, although the RMSE and NRMSE values improved and were lower for loamy fine sand than for clay loam. Volumetric water contents were all underestimated for van Genuchten equation with either the “tipping bucket” or “modified tipping bucket” approach. “Modified tipping bucket” and van Genuchten gave the poorest predicted volumetric water content values for the loamy fine sand.

Profile Soil NO_3-N

Table 2.17 shows the results of measured and simulated initial and final profile NO_3-N at the clay loam site using the “tipping bucket” option. For each Campbell and van Genuchten water retention equations, the results were summarized by denitrification rate constants of 0.09 and 0.9 d^{-1}. Simulated results for van Genuchten were near identical for the two denitrification rate constants. Simulated results for Campbell on the other hand, showed more variability between the two denitrification rate constants. The van Genuchten equation simulated higher initial and final NO_3-N values than the Campbell equation for clay loam for all treatments.

The denitrification rate constants did not have any impact on simulated NO_3-N for the loamy fine sand (Table 2.18). Results for 0.004 and 0.04 d^{-1} for each water retention equation were identical (Table 2.18). Simulated initial NO_3-N using the van Genuchten equation were higher than for the Campbell equation for all the tilled treatments under both maize after grass and continuous maize rotations. The same treatments were found to have similar trends for simulated final NO_3-N, with the addition of treatments under untilled and full fertilization on both rotations.

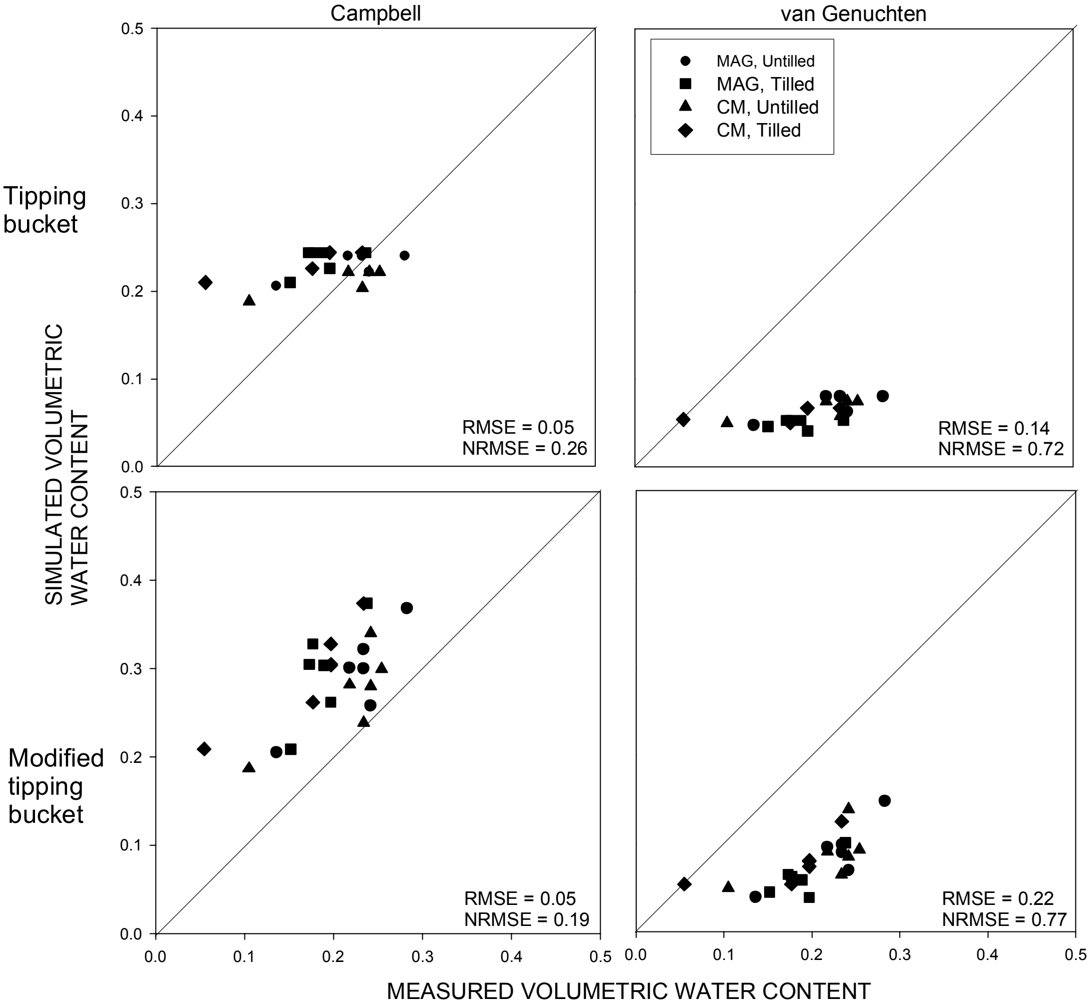

Figure 2.4. 1:1 scale plots of measured and simulated volumetric water content for loamy fine sand.

Table 2.17. Measured and simulated total profile soil NO_3-N at clay loam site using "tipping bucket" option.

	Measured	Simulated			
		Campbell		van Genuchten	
		0.09 d^{-1}	0.90 d^{-1}	0.09 d^{-1}	0.90 d^{-1}
	kg ha^{-1}				
	Initial (June 20)				
MAG, Untilled, Full	72.3	124.3	123.1	126.2	126.2
MAG, Untilled, Starter	25.4	25.4	24.2	26.8	26.8
MAG, Tilled, Full	78.8	143.5	142.2	151.6	151.6
MAG, Tilled, Starter	35.0	44.5	43.2	50.8	50.7
CM, Untilled, Full	117.9	122.4	110.8	132.3	132.2
CM, Untilled, Starter	31.7	23.5	14.6	31.5	31.5
CM, Tilled, Full	95.7	123.0	110.8	133.2	133.1
CM, Tilled, Starter	32.7	24.1	14.6	32.4	32.4
	Final (June 24)				
MAG, Untilled, Full	55.3	102.5	101.6	107.3	107.3
MAG, Untilled, Starter	30.2	18.7	17.8	21.1	21.1
MAG, Tilled, Full	53.2	119.9	118.9	143.9	143.9
MAG, Tilled, Starter	33.5	36.3	35.3	46.3	46.2
CM, Untilled, Full	69.6	100.5	88.5	125.2	125.1
CM, Untilled, Starter	14.9	17.0	9.4	27.2	27.1
CM, Tilled, Full	72.5	101.1	88.6	126.0	126.0
CM, Tilled, Starter	22.6	17.5	9.4	28.1	28.0
	Initial - Final				
MAG, Untilled, Full	17.0	21.8	21.5	18.9	18.9
MAG, Untilled, Starter	- 4.9	6.7	6.4	5.7	5.7
MAG, Tilled, Full	25.6	23.6	23.3	7.7	7.7
MAG, Tilled, Starter	1.4	8.2	7.9	4.5	4.5
CM, Untilled, Full	48.2	21.9	22.3	7.1	7.1
CM, Untilled, Starter	16.8	6.5	5.2	4.3	4.4
CM, Tilled, Full	23.1	21.9	22.2	7.2	7.1
CM, Tilled, Starter	10.1	6.6	5.2	4.3	4.4

MAG indicates maize after grass, CM indicates continuous maize

Table 2.18. Measured and simulated total profile soil NO_3-N at loamy fine sand site using "tipping bucket" option.

	Measured	Simulated			
		Campbell		van Genuchten	
		0.004 d^{-1}	0.04 d^{-1}	0.004 d^{-1}	0.04 d^{-1}
	kg ha^{-1}				
	Initial (June 20)				
MAG, Untilled, Full	101.3	116.0	116.0	111.6	111.6
MAG, Untilled, Starter	49.5	16.3	16.3	10.4	10.4
MAG, Tilled, Full	121.9	129.9	129.9	139.0	139.0
MAG, Tilled, Starter	33.6	30.1	30.1	38.0	38.0
CM, Untilled, Full	64.5	116.1	116.1	114.8	114.8
CM, Untilled, Starter	23.5	16.6	16.6	13.6	13.6
CM, Tilled, Full	108.9	115.0	115.0	116.8	116.8
CM, Tilled, Starter	18.5	15.3	15.3	15.6	15.6
	Final (June 24)				
MAG, Untilled, Full	70.6	83.4	83.4	99.1	99.1
MAG, Untilled, Starter	51.2	9.1	9.1	5.9	5.9
MAG, Tilled, Full	46.5	94.7	94.7	132.5	132.5
MAG, Tilled, Starter	44.6	20.1	20.1	33.3	33.3
CM, Untilled, Full	44.1	83.3	83.3	102.2	102.2
CM, Untilled, Starter	22.8	9.3	9.3	9.0	9.0
CM, Tilled, Full	111.1	82.7	82.7	106.3	106.3
CM, Tilled, Starter	27.3	8.2	8.2	11.1	11.1
	Initial - Final				
MAG, Untilled, Full	30.6	32.6	32.6	12.5	12.5
MAG, Untilled, Starter	- 1.7	7.2	7.2	4.5	4.5
MAG, Tilled, Full	75.5	35.2	35.2	6.5	6.5
MAG, Tilled, Starter	-11.1	10.0	10.0	4.7	4.7
CM, Untilled, Full	20.4	32.8	32.8	12.6	12.6
CM, Untilled, Starter	0.8	7.3	7.3	4.6	4.6
CM, Tilled, Full	- 2.3	32.3	32.3	10.5	10.5
CM, Tilled, Starter	- 8.8	7.1	7.1	4.5	4.5

MAG indicates maize after grass, CM indicates continuous maize

Using the “modified tipping bucket” water flow option, profile NO_3-N levels for clay loam were generally 15 to 25 kg ha^{-1} lower than for the original “tipping bucket” (Table 2.19). Simulated NO_3-N values between the two denitrification rate constants were more highly variable for Campbell than van Genuchten (Table 2.19). The van Genuchten function also simulated higher NO_3-N for all treatments than Campbell for the clay loam. This was the opposite for the loamy fine sand using the “modified tipping bucket” option, where the van Genuchten function generated lower initial and final NO_3-N for both denitrification rate constants under all treatments (Table 2.20).

The difference between initial and final soil NO_3-N were observed for all combinations of water retentivity functions and water flow options. The difference between simulated initial and final NO_3-N using the van Genuchten water retentivity function and “tipping bucket” approach were relatively close to the difference between measured initial and final values under maize after grass, untilled, full fertilization treatment for the clay loam soil (Table 2.17). The Campbell function and “tipping bucket” approach had a relatively similar difference between initial and final NO_3-N compared to the difference from the measured values for treatment under continuous maize, tilled, full fertilization on the clay loam soil (Table 2.17). The “modified tipping bucket” approach combined with the van Genuchten function showed a good match between measured and simulated difference between initial and final NO_3-N for full fertilization treatments under maize after grass, untilled and continuous maize, tilled on the clay loam soil (Table 2.19).

Figure 2.5 shows the 1:1 scale plots of simulated against measured NO_3-N for clay loam. Regardless of the denitrification rate constants, the “tipping bucket” option for Campbell equation, with RMSE and NRMSE of 31.37 and 0.60 respectively, generally performed better than the van Genuchten which had RMSE and NRMSE

Table 2.19. Measured and simulated total profile soil NO_3-N at clay loam site using "modified tipping bucket" option.

	Measured	Simulated			
		Campbell		van Genuchten	
		0.09 d^{-1}	0.90 d^{-1}	0.09 d^{-1}	0.90 d^{-1}
	kg ha^{-1}				
		Initial (June 20)			
MAG, Untilled, Full	72.3	106.4	106.0	113.2	113.2
MAG, Untilled, Starter	25.4	15.8	15.3	17.7	17.7
MAG, Tilled, Full	78.8	121.1	120.6	131.6	131.6
MAG, Tilled, Starter	35.0	29.9	29.3	35.6	35.6
CM, Untilled, Full	117.9	105.7	58.1	111.5	111.3
CM, Untilled, Starter	31.7	14.8	4.7	16.7	16.5
CM, Tilled, Full	95.7	105.9	57.7	111.7	111.4
CM, Tilled, Starter	32.7	15.1	4.8	17.1	16.8
		Final (June 24)			
MAG, Untilled, Full	55.3	81.6	81.4	88.8	88.7
MAG, Untilled, Starter	30.2	10.0	9.7	10.8	10.8
MAG, Tilled, Full	53.2	95.3	95.0	106.5	106.5
MAG, Tilled, Starter	33.5	22.4	22.1	25.4	25.4
CM, Untilled, Full	69.6	81.4	21.2	90.9	88.9
CM, Untilled, Starter	14.9	9.2	2.0	10.4	9.9
CM, Tilled, Full	72.5	81.4	20.9	91.4	88.8
CM, Tilled, Starter	22.6	9.4	2.0	10.8	10.1
		Initial - Final			
MAG, Untilled, Full	17.0	24.8	24.6	24.4	24.5
MAG, Untilled, Starter	- 4.9	5.8	5.6	6.9	6.9
MAG, Tilled, Full	25.6	25.8	25.6	25.1	25.1
MAG, Tilled, Starter	1.4	7.5	7.2	10.2	10.2
CM, Untilled, Full	48.2	24.3	36.9	20.6	22.4
CM, Untilled, Starter	16.8	5.6	2.7	6.3	6.6
CM, Tilled, Full	23.1	24.5	36.8	20.3	22.6
CM, Tilled, Starter	10.1	5.7	2.8	6.3	6.7

MAG indicates maize after grass, CM indicates continuous maize

Table 2.20. Measured and simulated total profile soil NO_3-N at loamy fine sand site using "modified tipping bucket" option.

	Measured	Simulated			
		Campbell		van Genuchten	
		0.004 d^{-1}	0.04 d^{-1}	0.004 d^{-1}	0.04 d^{-1}
	kg ha^{-1}				
	Initial (June 20)				
MAG, Untilled, Full	101.3	112.6	112.6	102.4	102.4
MAG, Untilled, Starter	49.5	15.0	15.0	7.4	7.4
MAG, Tilled, Full	121.9	125.8	125.8	112.0	112.0
MAG, Tilled, Starter	33.6	27.8	27.8	18.1	18.1
CM, Untilled, Full	64.5	112.4	111.8	101.3	101.3
CM, Untilled, Starter	23.5	15.0	14.6	7.6	7.6
CM, Tilled, Full	108.9	111.9	111.3	101.3	101.3
CM, Tilled, Starter	18.5	14.2	13.9	6.9	6.9
	Final (June 24)				
MAG, Untilled, Full	70.6	85.9	85.9	67.1	67.1
MAG, Untilled, Starter	51.2	8.4	8.4	2.2	2.2
MAG, Tilled, Full	46.5	96.9	96.9	78.5	78.5
MAG, Tilled, Starter	44.6	18.8	18.8	10.2	10.2
CM, Untilled, Full	44.1	84.6	83.2	66.7	66.7
CM, Untilled, Starter	22.8	8.3	8.0	2.6	2.6
CM, Tilled, Full	111.1	85.6	84.1	68.3	68.3
CM, Tilled, Starter	27.3	7.8	7.5	2.3	2.3
	Initial - Final				
MAG, Untilled, Full	30.6	26.7	26.7	35.3	35.3
MAG, Untilled, Starter	- 1.7	6.6	6.6	5.2	5.2
MAG, Tilled, Full	75.5	28.9	28.9	33.5	33.5
MAG, Tilled, Starter	-11.1	9.0	9.0	7.9	7.9
CM, Untilled, Full	20.4	27.8	28.6	34.6	34.6
CM, Untilled, Starter	0.8	6.7	6.6	5.0	5.0
CM, Tilled, Full	- 2.3	26.3	27.2	33.0	33.0
CM, Tilled, Starter	- 8.8	6.4	6.4	4.6	4.6

MAG indicates maize after grass, CM indicates continuous maize

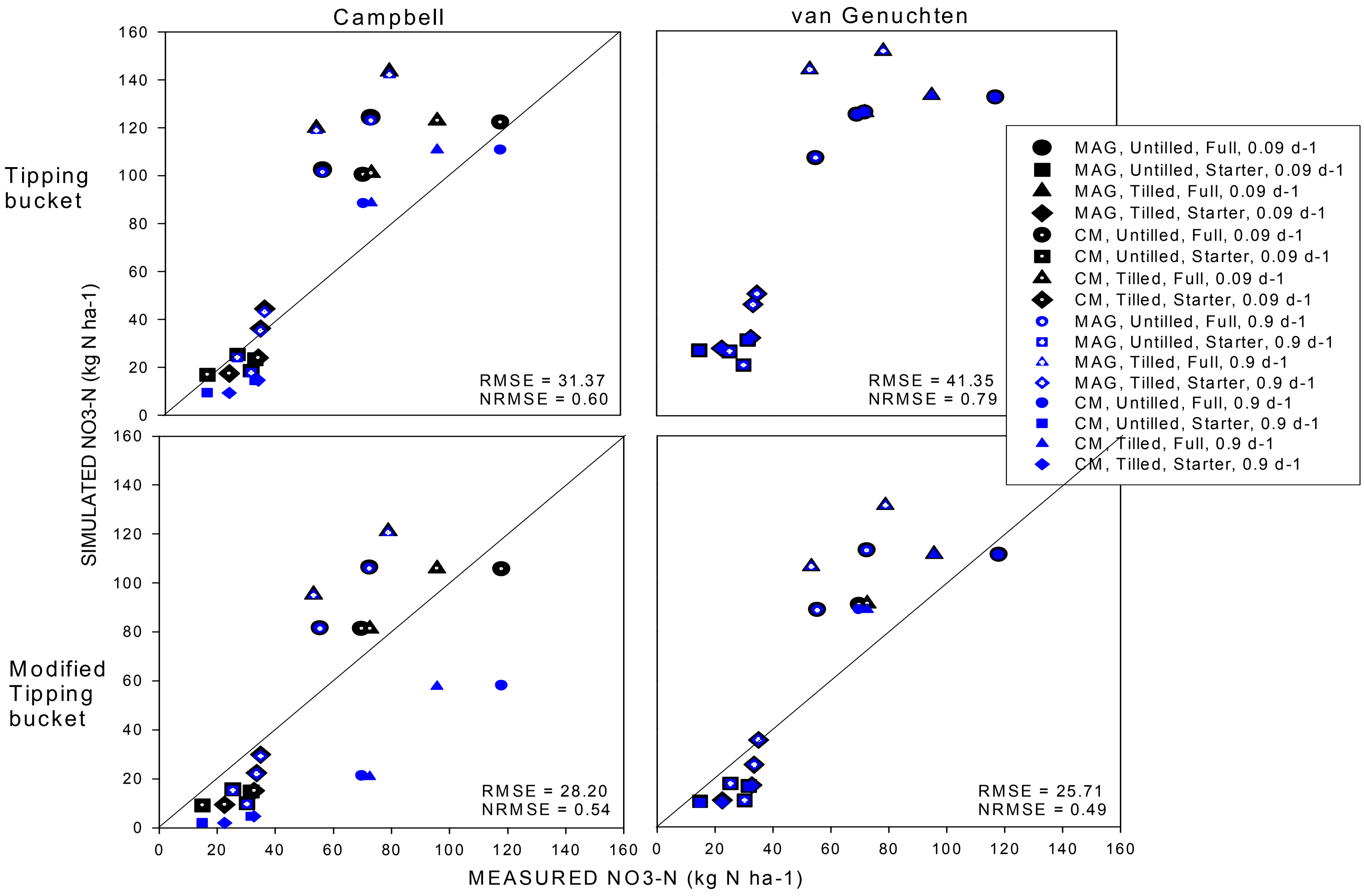

Figure 2.5. 1:1 scaleplot of measured and simulated profile total NO_3-N for clay loam.

values of 41.35 and 0.79 respectively. The reverse was true when the “modified tipping bucket” option was used to simulate the PNM model runs. Better predicted results were observed for the van Genuchten than Campbell equation. This was because the 0.9 d^{-1} rate constant and Campbell equation did not perform as well with the “modified tipping bucket” option. Overall, the “modified tipping bucket” performed better than the “tipping bucket” approach, with lower NRMSE values (Figure 2.5).

The “modified tipping bucket” water flow option did not show much improvement on RMSE values for the loamy fine sand, especially when combined with the Campbell equation in the simulations. Figure 2.6 showed that the NRMSE values of 0.46 for both water flow options using the Campbell function were the same. Slight improvements from the “modified tipping bucket” were observed when model runs were performed using the van Genuchten function.

Scale plots for both clay loam and loamy fine sand indicated that underestimations of the predicted results were more likely for treatments with starter fertilization and that overestimations were more common among treatments with full fertilization. Better predictions were found for starter fertilization than full fertilization treatments. The PNM model also performed better in predicting results for the loamy fine sand than the clay loam.

The measured soil NO_3-N values were quite variable and could likely be due to sampling error since the number of samples per treatment that were measured was minimal.

N_2O Losses

Nitrous oxide losses for each treatment were measured daily up to 120 hours after irrigation (Table 2.21). Cumulative N_2O losses were on average lower on the

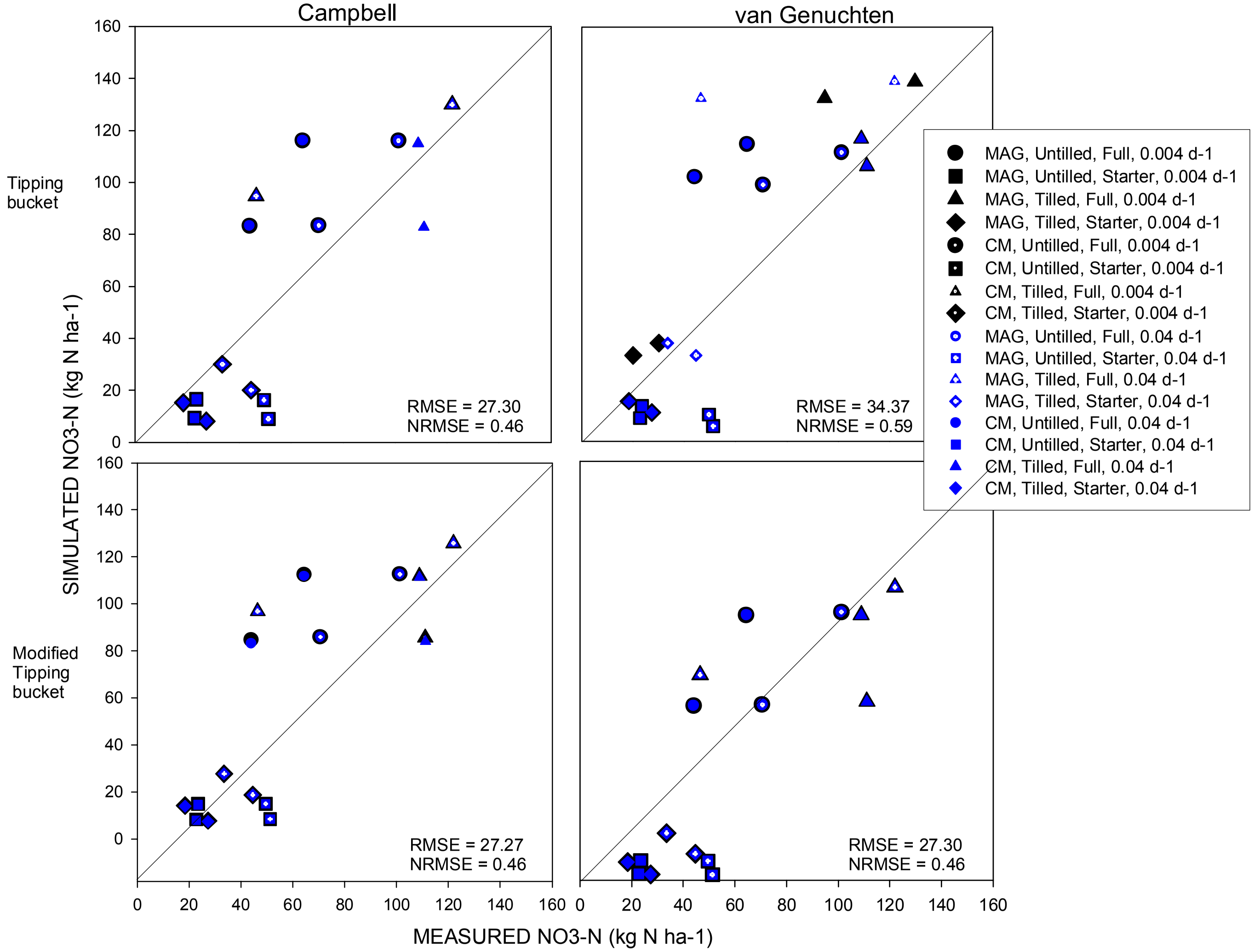

Figure 2.6. 1:1 scaleplot of measured and simulated profile total NO_3-N for loamy fine sand.

Table 2.21. Measured cumulative N_2O losses for June 20 - June 25, 2004 on clay loam and loamy fine sand.

	Maize after Grass				**Continuous Maize**			
	Untilled		Tilled		Untilled		Tilled	
	Full	*Starter*	*Full*	*Starter*	*Full*	*Starter*	*Full*	*Starter*
	kg N ha^{-1}							
Hours after Irrigation	**Muskellunge clay loam**							
0	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.01
24	1.08	0.25	0.48	0.39	0.41	0.12	0.22	0.09
48	2.62	0.55	0.95	0.52	1.10	0.18	0.60	0.19
72	5.38	0.94	1.62	0.67	2.51	0.26	1.12	0.33
96	5.61	0.98	1.65	0.69	2.57	0.28	1.17	0.35
120	5.76	1.02	1.68	0.73	2.62	0.30	1.20	0.39
Means by tillage	2.02		0.78		0.86		0.47	
Means by rotation	1.40				0.67			
Means by soil type	1.04							
	Stafford loamy fine sand							
0	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01
24	0.30	0.22	0.09	0.07	0.08	0.07	0.13	0.07
48	0.66	0.28	0.39	0.12	0.13	0.13	0.26	0.13
72	0.80	0.35	0.58	0.16	0.17	0.16	0.37	0.17
96	0.84	0.38	0.63	0.17	0.19	0.19	0.42	0.19
120	0.89	0.43	0.68	0.20	0.23	0.23	0.48	0.22
Means by tillage	0.43		0.26		0.13		0.21	
Means by rotation	0.35				0.17			
Means by soil type	0.26							

loamy fine sand than the clay loam as discussed by Tan et al. (2007). Nitrous oxide emissions were highest on the second day after precipitation for all treatments. In general, treatments under the maize after grass rotation had higher average N_2O losses than the continuous maize for both clay loam and loamy fine sand soils. The maize after grass, untilled, full fertilization treatment under clay loam had the highest cumulative N_2O losses of 5.76 kg N ha^{-1}. For both soil types, the untilled treatments for both fertilization applications under maize after grass generated higher N_2O losses than the tilled plots. For continuous maize, this trend was not found in any of the treatments. Full fertilization at planting under untilled on previous grass resulted in large N_2O emissions for the clay loam, with a cumulative N_2O loss of 4.74 kg N ha^{-1} greater than late fertilization. Similar soil type and N and tillage treatments on previous corn, however, had a relatively smaller emission, with a cumulative N_2O loss of 2.33 kg N ha^{-1} greater than late fertilization. Small N_2O emissions were observed on plots under tilled treatments for the clay loam. Full fertilization under tilled on previous grass emitted 0.96 kg N ha^{-1} greater cumulative N_2O loss than starter-only fertilization, while full fertilization under tilled on previous corn resulted in 0.81 kg N ha^{-1} greater cumulative N_2O loss than starter-only fertilization.

Predicted results from the PNM model are only presented for the clay loam since N_2O losses for the loamy fine sand were relatively insignificant. Discussions on N_2O results from this point onward are for the clay loam, unless otherwise indicated. Simulated cumulative N_2O results using the “tipping bucket” approach with Campbell and van Genuchten functions are presented in Tables 2.22 and 2.23 respectively, each summarizing PNM-model-predicted results for two denitrification rate constants. Predictions using Campbell function were almost identical between the two rate constants for all treatments, except for treatments under continuous maize and full fertilization. This was not the case for results generated using the van Genuchten

Table 2.22. Simulated cumulative N_2O losses for Campbell equation and denitrification rate constants of 0.09 and 0.9 d-1 with "tipping bucket" option for June 20 – June 25, 2004 on clay loam.

	Maize after Grass				**Continuous Maize**			
	Untilled		Tilled		Untilled		Tilled	
	Full	*Starter*	*Full*	*Starter*	*Full*	*Starter*	*Full*	*Starter*
	kg N ha^{-1}							
Hours after Irrigation	**0.09 d^{-1}**							
0	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.1
24	0.3	0.3	0.4	0.4	0.4	0.2	0.3	0.3
48	0.6	0.4	0.8	0.6	0.6	0.4	0.6	0.4
72	0.9	0.6	1.2	0.9	0.9	0.5	0.9	0.5
96	1.2	0.7	1.6	1.1	1.2	0.6	1.2	0.7
120	1.5	0.9	2.0	1.3	1.5	0.8	1.4	0.8
	0.9 d^{-1}							
0	0.2	0.2	0.2	0.1	0.2	0.1	0.2	0.1
24	0.3	0.3	0.4	0.3	0.3	0.2	0.3	0.2
48	0.6	0.4	0.8	0.5	1.4	0.4	1.3	0.4
72	0.9	0.5	1.1	0.7	2.2	0.6	2.2	0.5
96	1.1	0.6	1.5	0.9	3.0	0.7	3.0	0.7
120	1.4	0.8	1.8	1.1	3.6	0.8	3.6	0.8

Table 2.23. Simulated cumulative N_2O losses for van Genuchten equation and denitrification rate constants of 0.09 and 0.9 d-1 with “tipping bucket” option for June 20 – June 25, 2004 on clay loam.

	Maize after Grass				**Continuous Maize**			
	Untilled		Tilled		Untilled		Tilled	
	Full	*Starter*	*Full*	*Starter*	*Full*	*Starter*	*Full*	*Starter*
	kg N ha^{-1}							
Hours after Irrigation	**0.09 d^{-1}**							
0	0.0	0.1	0.0	0.0	0.1	0.1	0.0	0.0
24	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0
48	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
72	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1
96	0.2	0.3	0.2	0.2	0.2	0.2	0.1	0.1
120	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2
	0.9 d^{-1}							
0	0.1	0.1	0.0	0.0	0.1	0.1	0.1	0.1
24	0.1	0.1	0.0	0.0	0.2	0.2	0.2	0.2
48	0.2	0.1	0.1	0.1	0.3	0.3	0.2	0.2
72	0.2	0.2	0.1	0.1	0.4	0.4	0.4	0.3
96	0.3	0.2	0.2	0.2	0.5	0.5	0.5	0.4
120	0.3	0.2	0.2	0.2	0.6	0.6	0.6	0.5

parameters, where changes in the denitrification rate constants did not have much effect on predicted N_2O. Moreover, the Campbell parameters performed better than van Genuchten in differentiating treatment effects on N_2O losses. Higher variability was observed among different treatments in Campbell than van Genuchten function. Campbell parameters generally also predicted higher average N_2O losses than van Genuchten.

Tables 2.24 and 2.25 show simulated cumulative N_2O losses using the "modified tipping bucket" for Campbell and van Genuchten equations, respectively. The "modified tipping bucket" approach simulated higher cumulative N_2O losses than the original "tipping bucket" method. Compared to the "tipping bucket" option, differences of simulated results between the two denitrification rate constants of 0.09 and 0.9 d^{-1} were greater for both Campbell and van Genuchten parameters in "modified tipping bucket", especially under continuous maize treatments.

The 1:1 scale plots showed that the PNM model generally did not perform well in predicting cumulative N_2O losses using the "tipping bucket" method for any combination of water retention function and denitrification rate constants, and any of the treatments (Figures 2.7 to 2.10). Differences in performance between Campbell and van Genuchten parameters were observed for each denitrification rate constant. When simulations were run using the Campbell parameters and rate constant of 0.09 d^{-1}, the model overestimated the predicted values for all treatments except for maize after grass, untilled, both full and starter fertilizer applications; and continuous maize, untilled, and full fertilization. When the rate constant was changed to 0.9 d^{-1} with all other parameters remained unchanged, predictions for treatments under maize after grass, tilled, full fertilizer application; and continuous maize, untilled, and full fertilization improved and were relatively closer to the corresponding measured N_2O values. However, increasing the rate constant to 0.9 d^{-1} adversely affected the

Table 2.24. Simulated cumulative N_2O losses for Campbell equation and denitrification rate constants of 0.09 and 0.9 d-1 with "modified tipping bucket" option for June 20 – June 25, 2004 on clay loam.

	Maize after Grass				**Continuous Maize**			
	Untilled		Tilled		Untilled		Tilled	
	Full	*Starter*	*Full*	*Starter*	*Full*	*Starter*	*Full*	*Starter*
	kg N ha^{-1}							
Hours after Irrigation					**0.09 d^{-1}**			
0	0.25	0.18	0.34	0.27	0.24	0.16	0.24	0.17
24	0.48	0.34	0.64	0.51	0.45	0.32	0.45	0.32
48	1.90	0.59	2.30	0.98	1.84	0.54	1.85	0.56
72	3.03	0.82	3.64	1.42	2.93	0.75	2.96	0.77
96	4.12	1.03	4.92	1.83	3.98	0.94	4.02	0.96
120	4.96	1.22	5.95	2.20	4.78	1.11	4.83	1.14
					0.9 d^{-1}			
0	0.22	0.15	0.30	0.23	0.17	0.09	0.17	0.09
24	0.41	0.28	0.57	0.44	0.30	0.16	0.31	0.16
48	1.79	0.50	2.19	0.88	5.51	0.36	5.49	0.37
72	2.89	0.69	3.49	1.28	8.23	0.51	8.21	0.52
96	3.95	0.88	4.74	1.66	10.21	0.60	10.19	0.62
120	4.75	1.04	5.73	2.01	11.20	0.68	11.18	0.69

Table 2.25. Simulated cumulative N_2O losses for van Genuchten equation and denitrification rate constants of 0.09 and 0.9 d^{-1} with "modified tipping bucket" option for June 20 – June 25, 2004 on clay loam.

	Maize after Grass				**Continuous Maize**			
	Untilled		Tilled		Untilled		Tilled	
	Full	*Starter*	*Full*	*Starter*	*Full*	*Starter*	*Full*	*Starter*
	kg N ha^{-1}							
Hours after Irrigation								
				0.09 d^{-1}				
0	0.16	0.15	0.19	0.17	0.15	0.13	0.15	0.13
24	0.31	0.28	0.35	0.33	0.28	0.24	0.28	0.25
48	0.79	0.53	0.77	0.66	0.58	0.45	0.59	0.46
72	1.27	0.78	1.30	1.02	0.97	0.66	0.99	0.67
96	1.77	1.02	1.87	1.38	1.38	0.87	1.41	0.88
120	2.28	1.26	2.50	1.76	1.83	1.07	1.87	1.09
				0.9 d^{-1}				
0	0.14	0.12	0.17	0.15	0.08	0.06	0.08	0.06
24	0.27	0.23	0.32	0.29	0.15	0.11	0.15	0.11
48	0.73	0.47	0.72	0.60	0.88	0.43	0.93	0.45
72	1.19	0.70	1.22	0.94	2.21	0.80	2.34	0.84
96	1.66	0.92	1.78	1.29	3.53	1.13	3.71	1.18
120	2.16	1.14	2.40	1.65	4.78	1.43	4.94	1.49

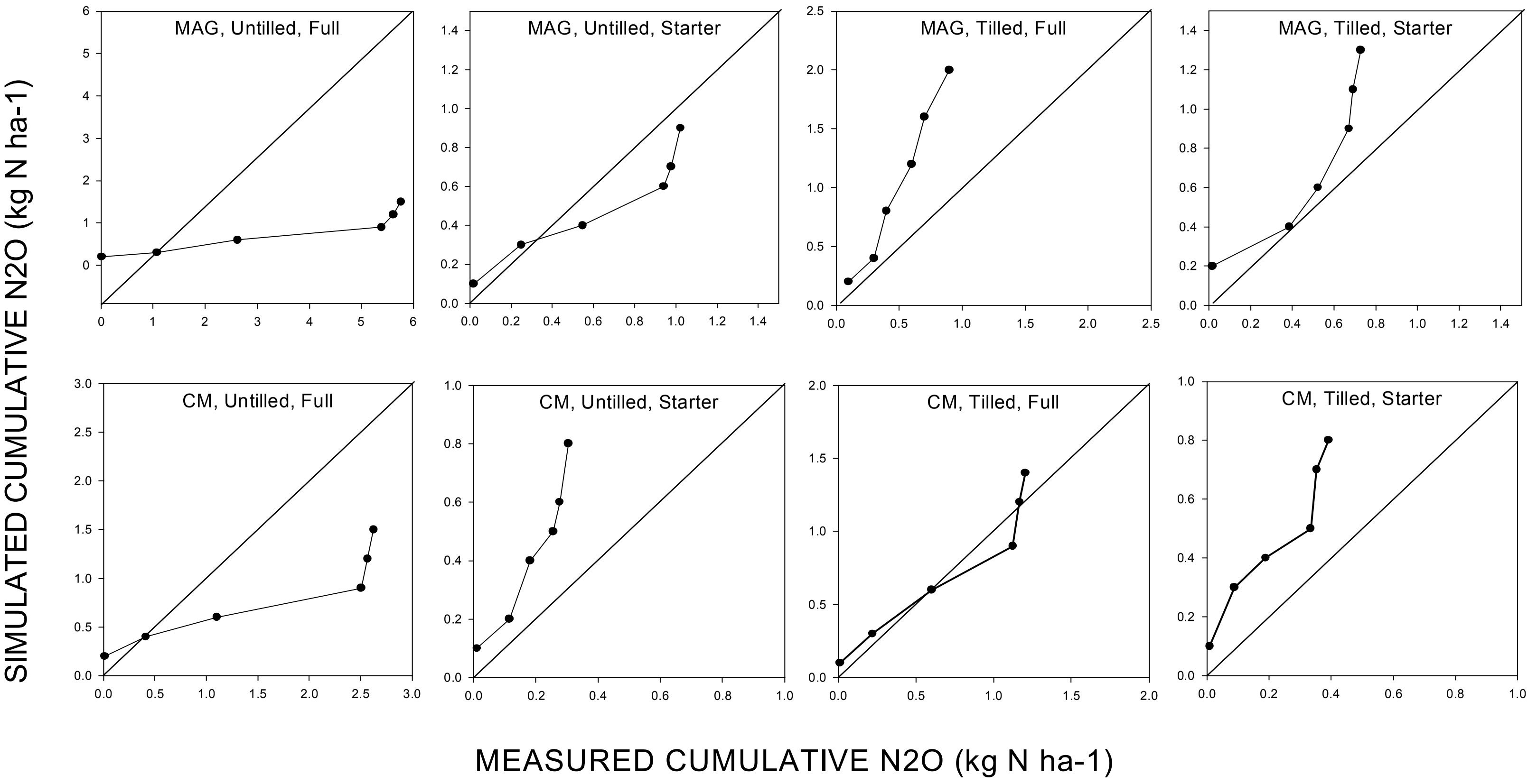

Figure 2.7. Measured and simulated cumulative N_2O losses for "tipping bucket" with Campbell equation and denitrification rate constants of 0.09 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

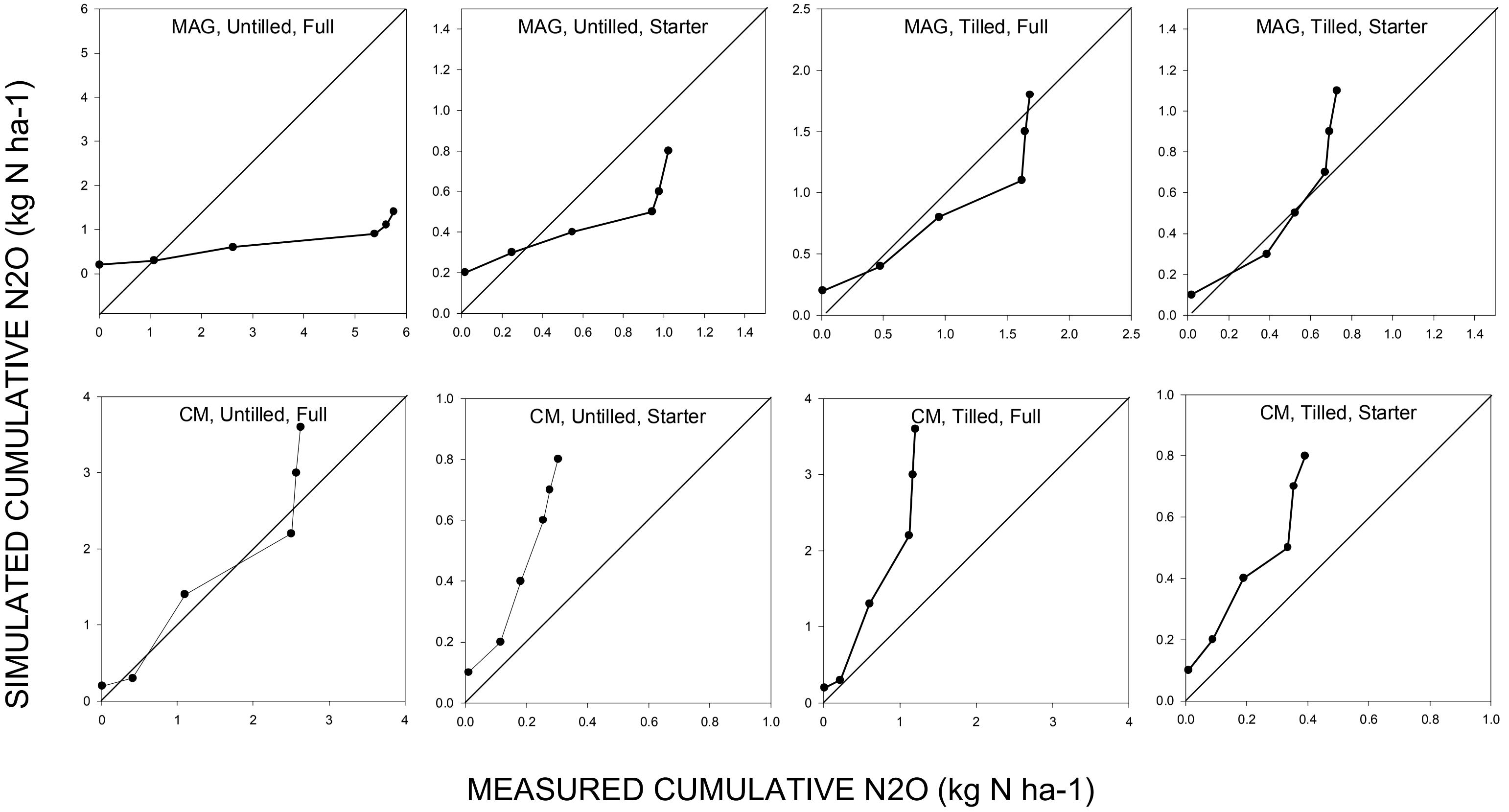

Figure 2.8. Measured and simulated cumulative N_2O losses for "tipping bucket" with Campbell equation and denitrification rate constants of 0.9 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

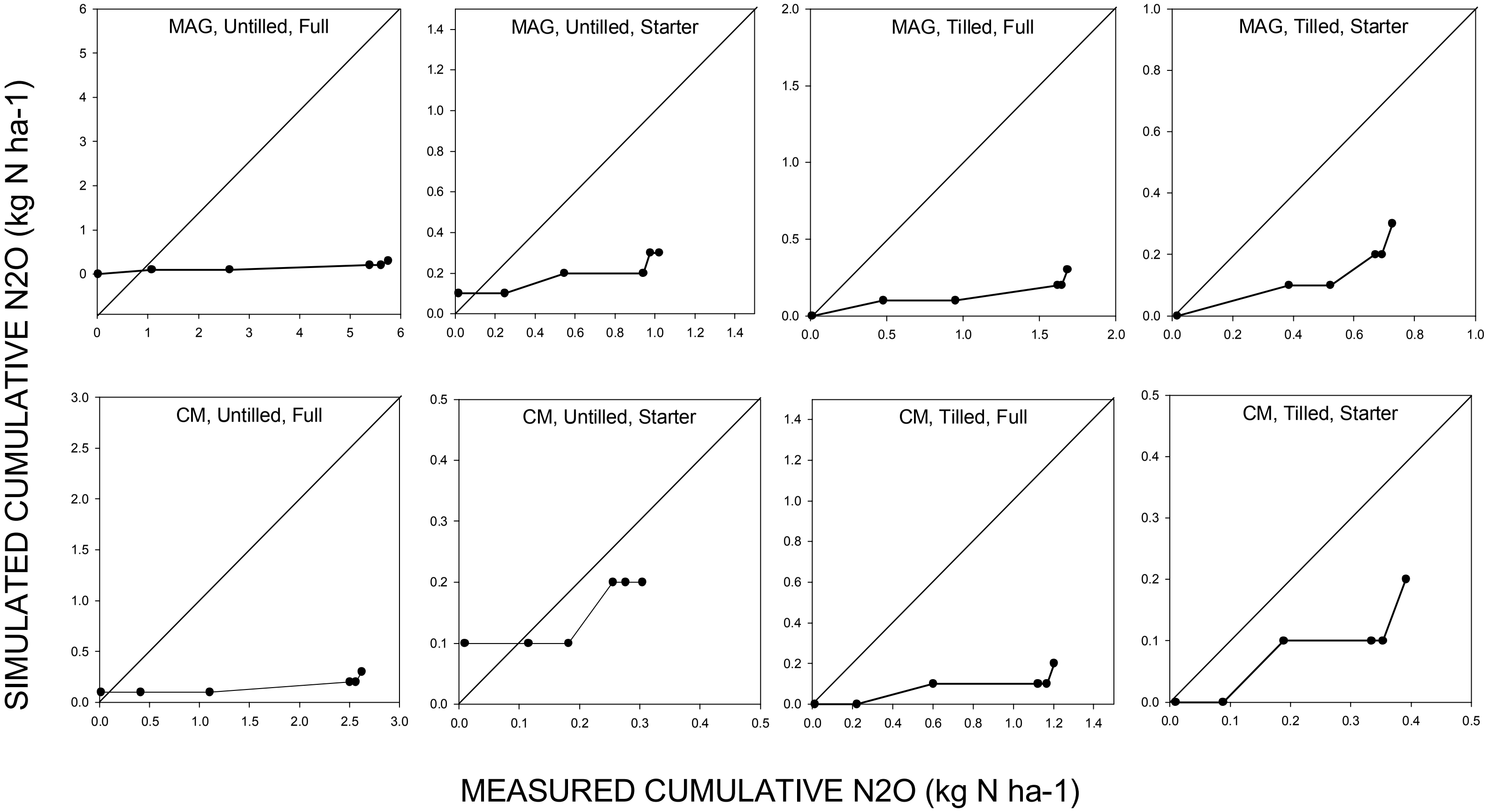

Figure 2.9. Measured and simulated cumulative N_2O losses for "tipping bucket" with van Genuchten equation and denitrification rate constants of 0.09 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

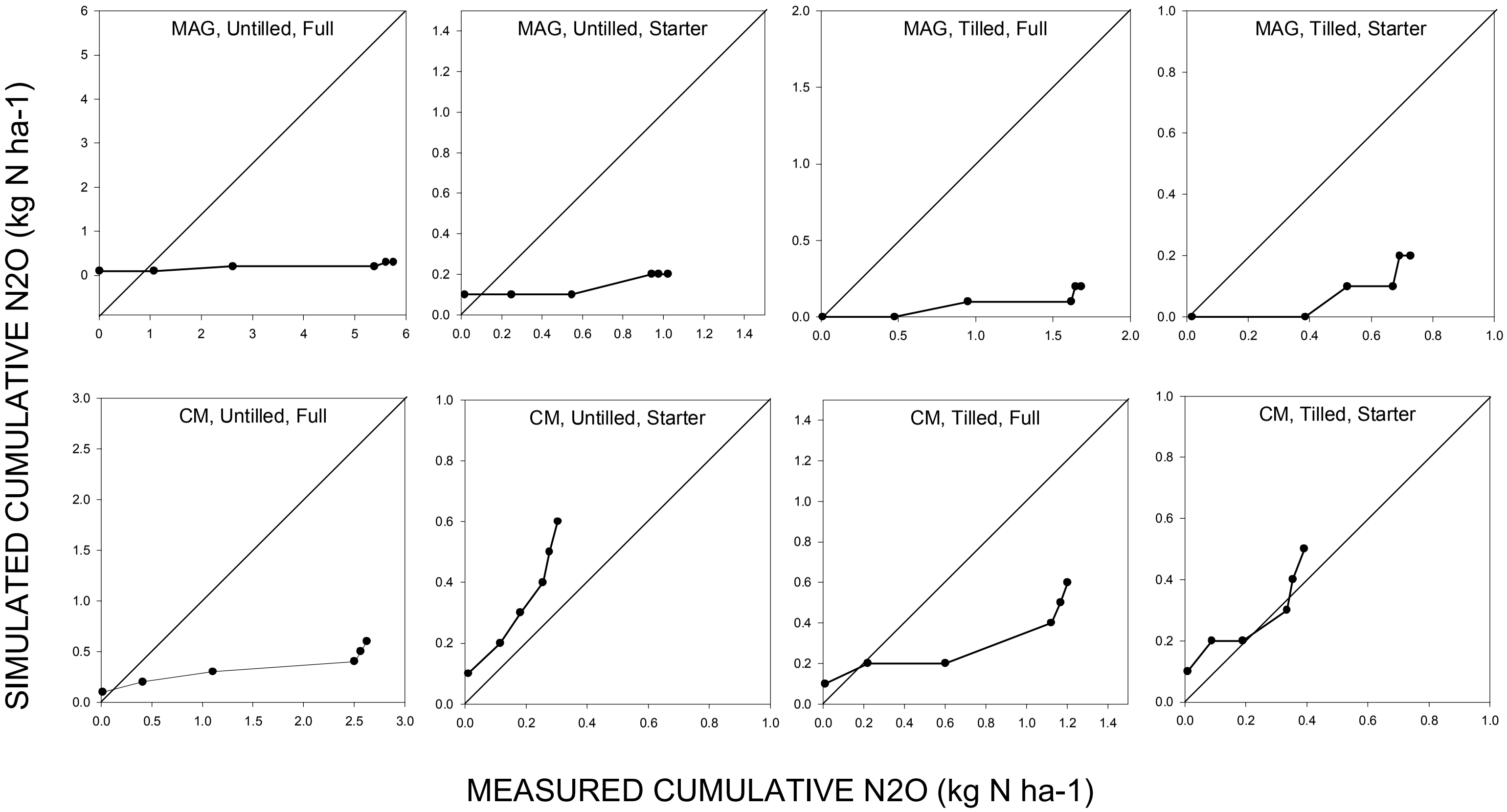

Figure 2.10. Measured and simulated cumulative N_2O losses for "tipping bucket" with van Genuchten equation and denitrification rate constants of 0.9 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

predicted results for continuous maize, tilled, and full fertilization, leading to overestimation of N_2O losses. Results for maize after grass, untilled, full continuous maize, untilled, starter; and continuous maize, tilled, starter fertilizations remained about the same when the rate constant was increased from 0.09 to 0.9 d^{-1}.

From the plots in Figures 2.7 to 2.10, it was found that the Campbell equations on average predicted better cumulative N_2O losses than the van Genuchten functions. Using a rate constant of 0.09 d^{-1}, the van Genuchten approach underestimated the N_2O losses for all treatments. Adjusting the denitrification rate constant to 0.9 d^{-1} improved these predictions for treatments under continuous maize, tilled, and overestimated N_2O values for continous maize, untilled, and starter application treatment.

Observations were also made for each combination of water retention function and rate constant using the “modified tipping bucket” method (Figures 2.11 to 2.14). The model overestimated N_2O losses for all treatments that were generated using the Campbell parameters and 0.09 d^{-1} denitrification rate constant, except for maize after grass, untilled, for both fertilization applications. This trend was also similarly observed when the rate constant value was increased to 0.9 d^{-1}. Simulated values generated with the van Genuchten equation were much higher when the “modified tipping bucket” water flow option was used. This was the case when the van Genuchten parameters were used with the “modified tipping bucket” method for both denitrification rate constants. Overestimations of data were observed, especially for rate constant of 0.9 d^{-1} under the continuous maize treatments.

For all treatments that were simulated with any combinations of water retention functions and rate constants, the PNM model simulations indicated consistent N_2O loss rates for the 120-hour period. However, field measurements showed strong tapering off 72 hours after irrigation for all treatments.

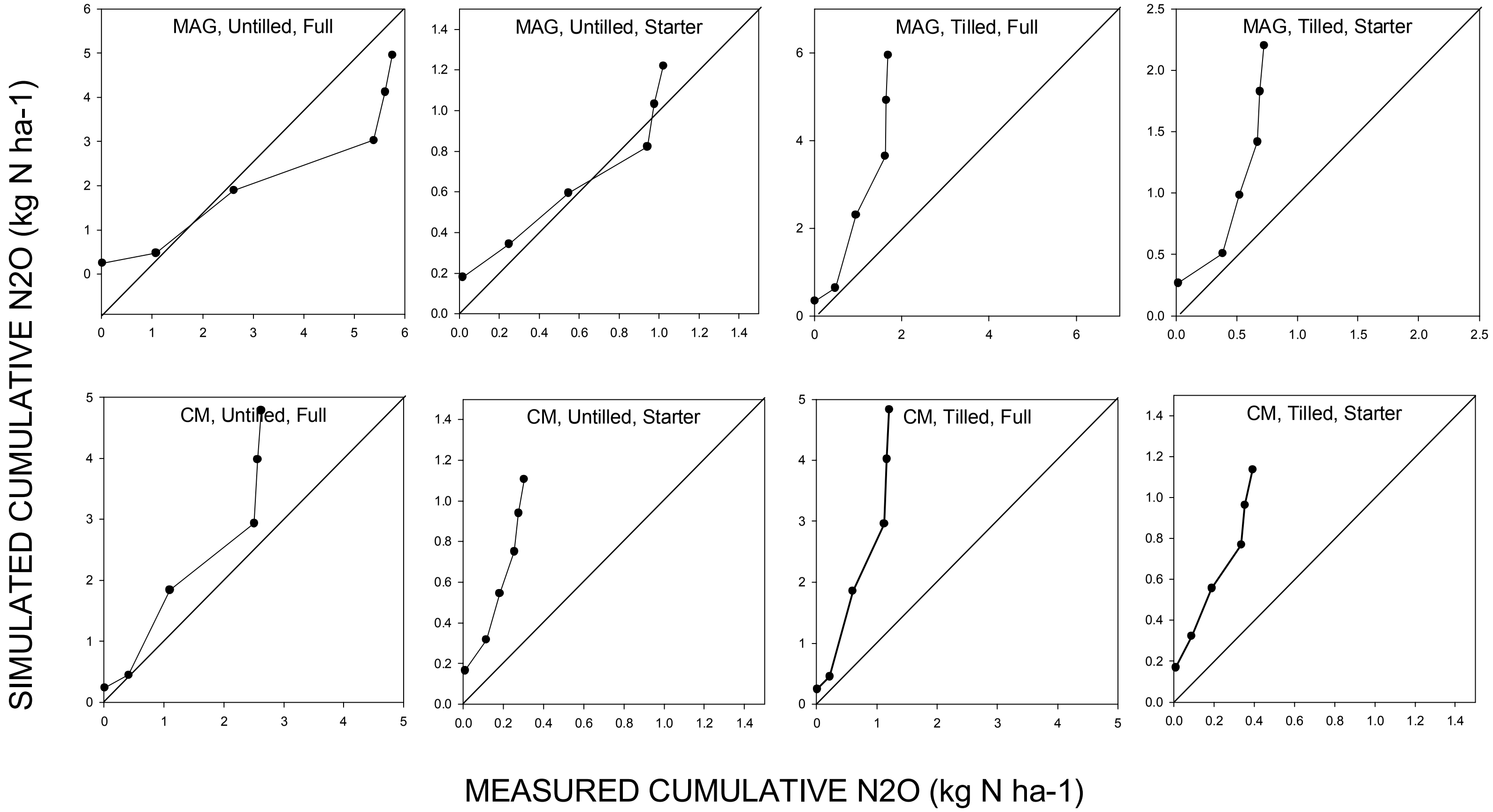

Figure 2.11. Measured and simulated cumulative N_2O losses for "modified tipping bucket" with Campbell equation and denitrification rate constants of 0.09 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

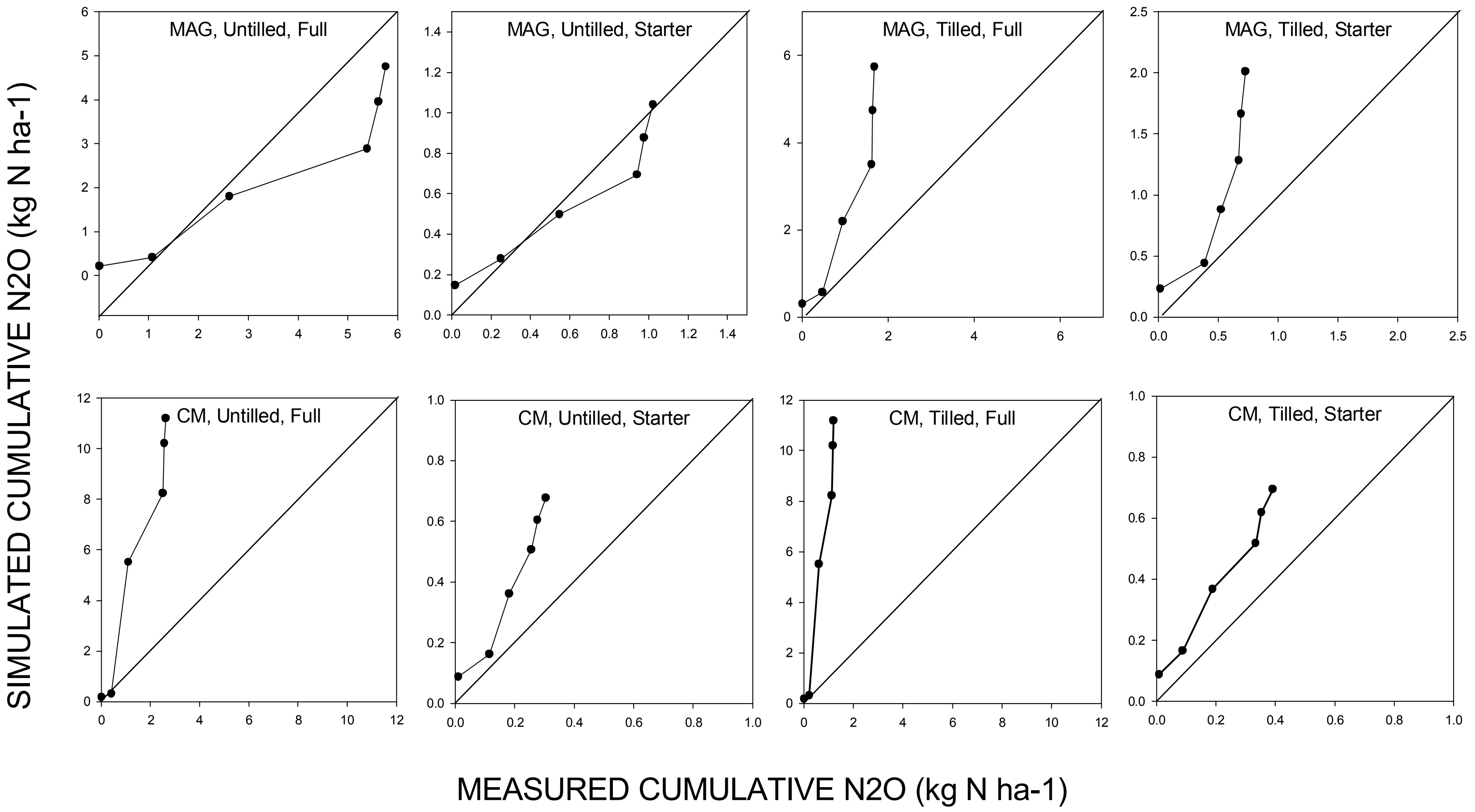

Figure 2.12. Measured and simulated cumulative N_2O losses for "modified tipping bucket" with Campbell equation and denitrification rate constants of 0.9 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

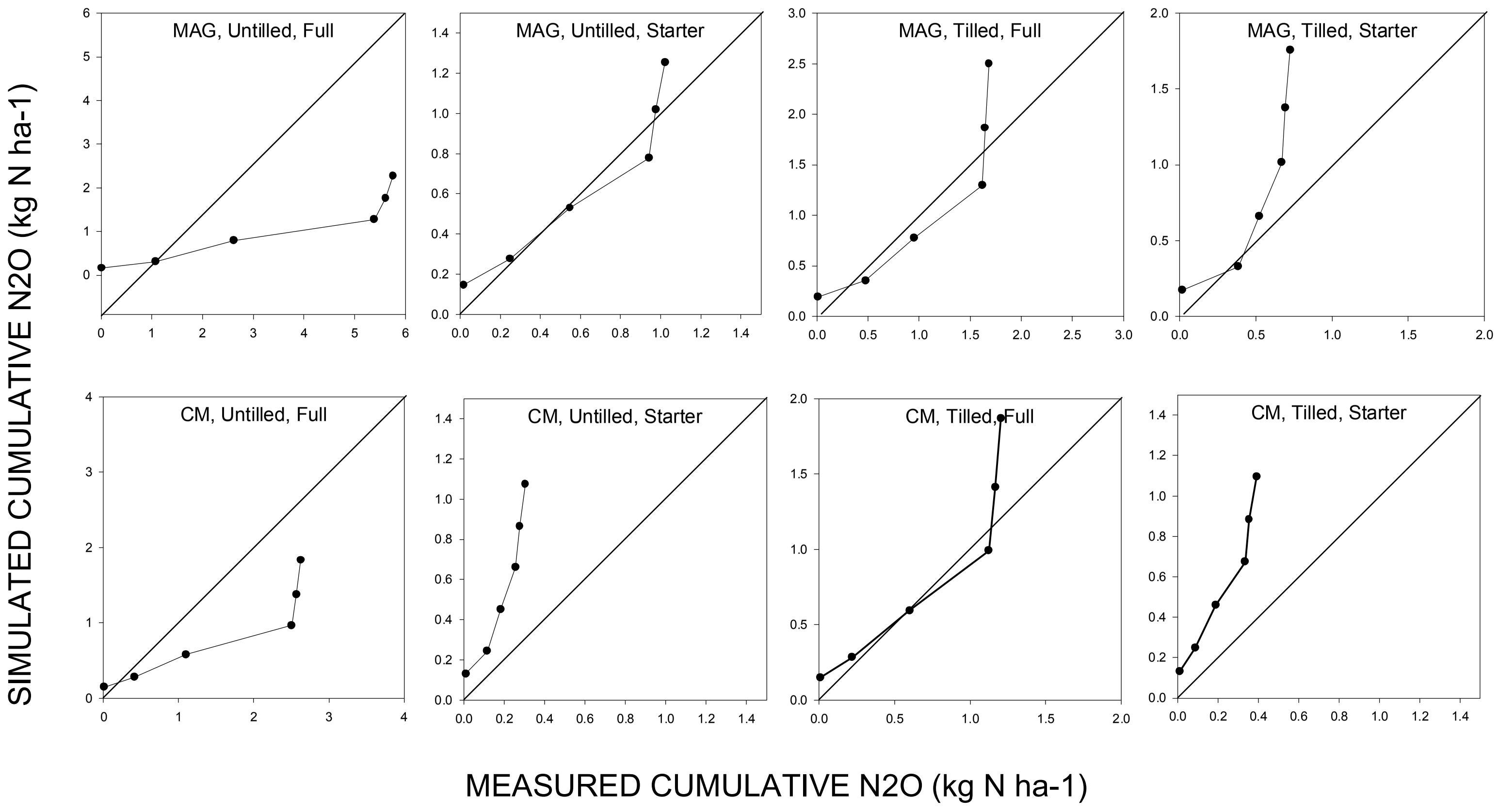

Figure 2.13. Measured and simulated cumulative N_2O losses for "modified tipping bucket" with van Genuchten equation and denitrification rate constants of 0.09 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

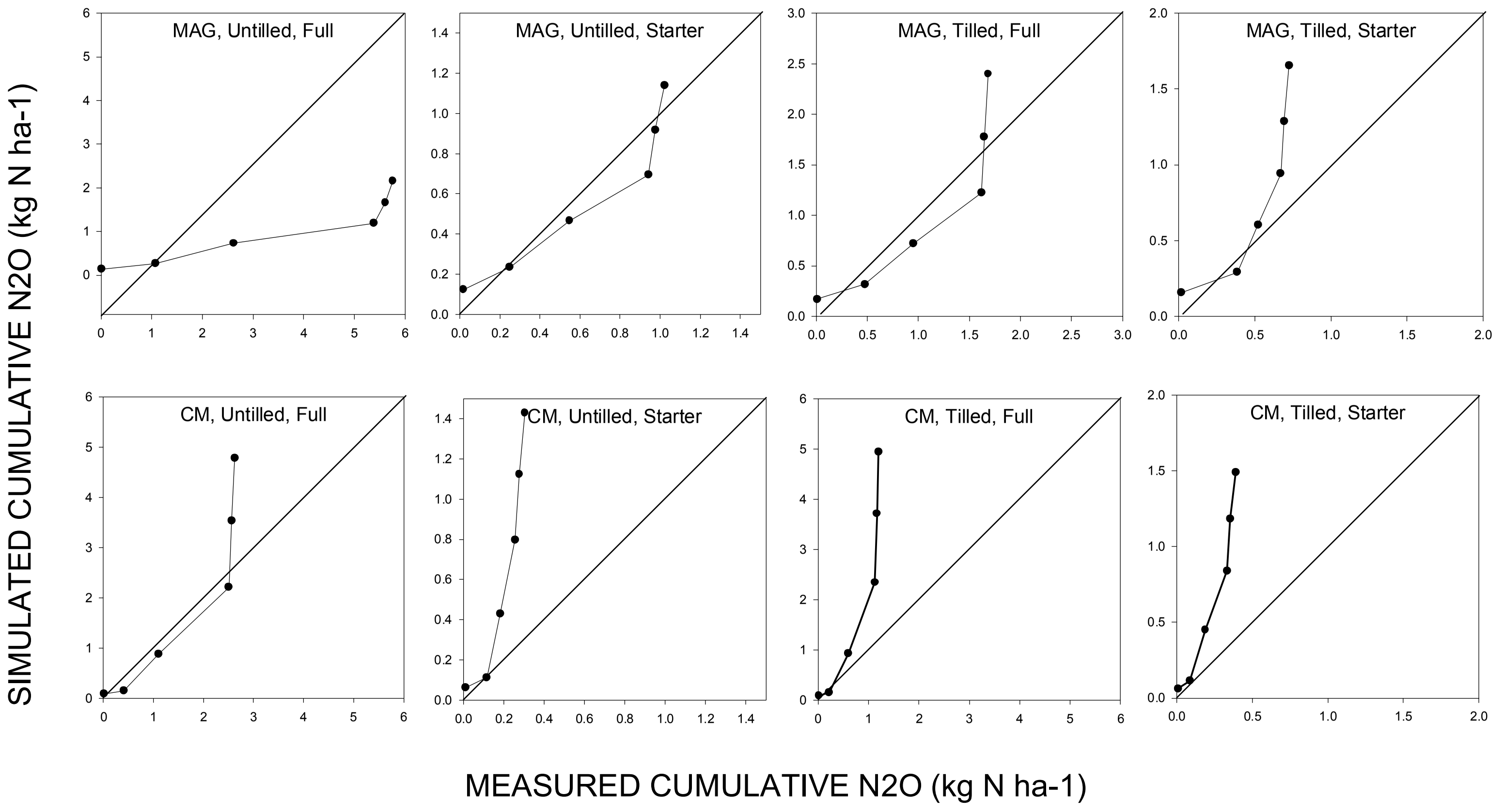

Figure 2.14. Measured and simulated cumulative N_2O losses for "modified tipping bucket" with van Genuchten equation and denitrification rate constants of 0.9 d^{-1} on clay loam. Each internodal length on each curve represents 24 hours.

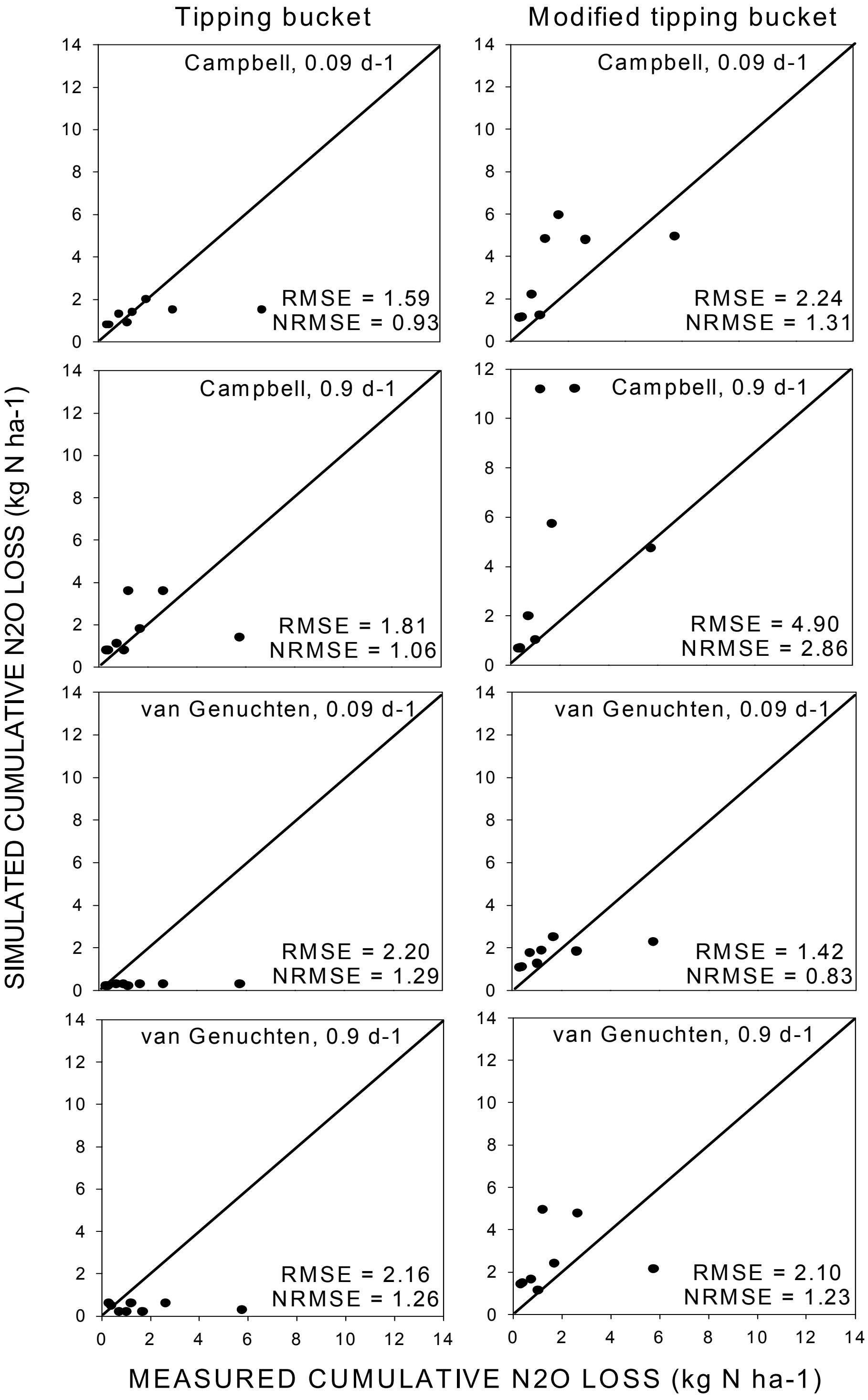

Figure 2.15. 1:1 scale plots of measured and simulated 120-hour cumulative N_2O losses using the "tipping bucket" and "modified tipping bucket" methods with different water retention parameters and denitrification rate constants for the clay loam soil.

Figure 2.15 compares the 1:1 scale plots of simulated against measured 120-hour cumulative N_2O losses at the end of the experiment for each combination of water flow option ("tipping bucket" and "modified tipping bucket"), water retention equation (Campbell and van Genuchten), and denitrification rate constants of 0.09 and 0.9 d^{-1} on clay loam. The Campbell parameters were found to predict better results than van Genuchten with the "tipping bucket" method, but the reverse held for the "modified tipping bucket" method for both rate constants. This was because overestimation of some of the results was observed with "modified tipping bucket" option. For all combinations of parameters, the 0.09 d^{-1} rate constant performed better than 0.9 d^{-1}.

When all the data were grouped and only differentiated by the water flow options, the original "tipping bucket" method (NRMSE = 1.14) performed better in predicting N_2O than the "modified tipping bucket" (NRMSE = 1.74) (Figure 2.16). Some outliers were found in the "modified tipping bucket" method, which were associated with treatments under continuous maize, full fertilization for both tilled and untilled rotations.

CONCLUSIONS

Results from partial N budgets showed that the N_2:N_2O ratio was higher for 0 – 20 cm than 0 – 30 cm. The PNM model predicted better cumulative N_2O results based on an N_2:N_2O ratio from 0 – 20 cm (RMSE = 2.98 and NRMSE = 1.74) than 0 – 30 cm (RMSE = 3.31 and NRMSE = 1.93). This suggests that the majority of the denitrification losses occur from shallow depths.

Simulated results for profile volumetric water content, NO_3-N, and N_2O losses, generally did not show a good fit with measured data. Performance of the model was

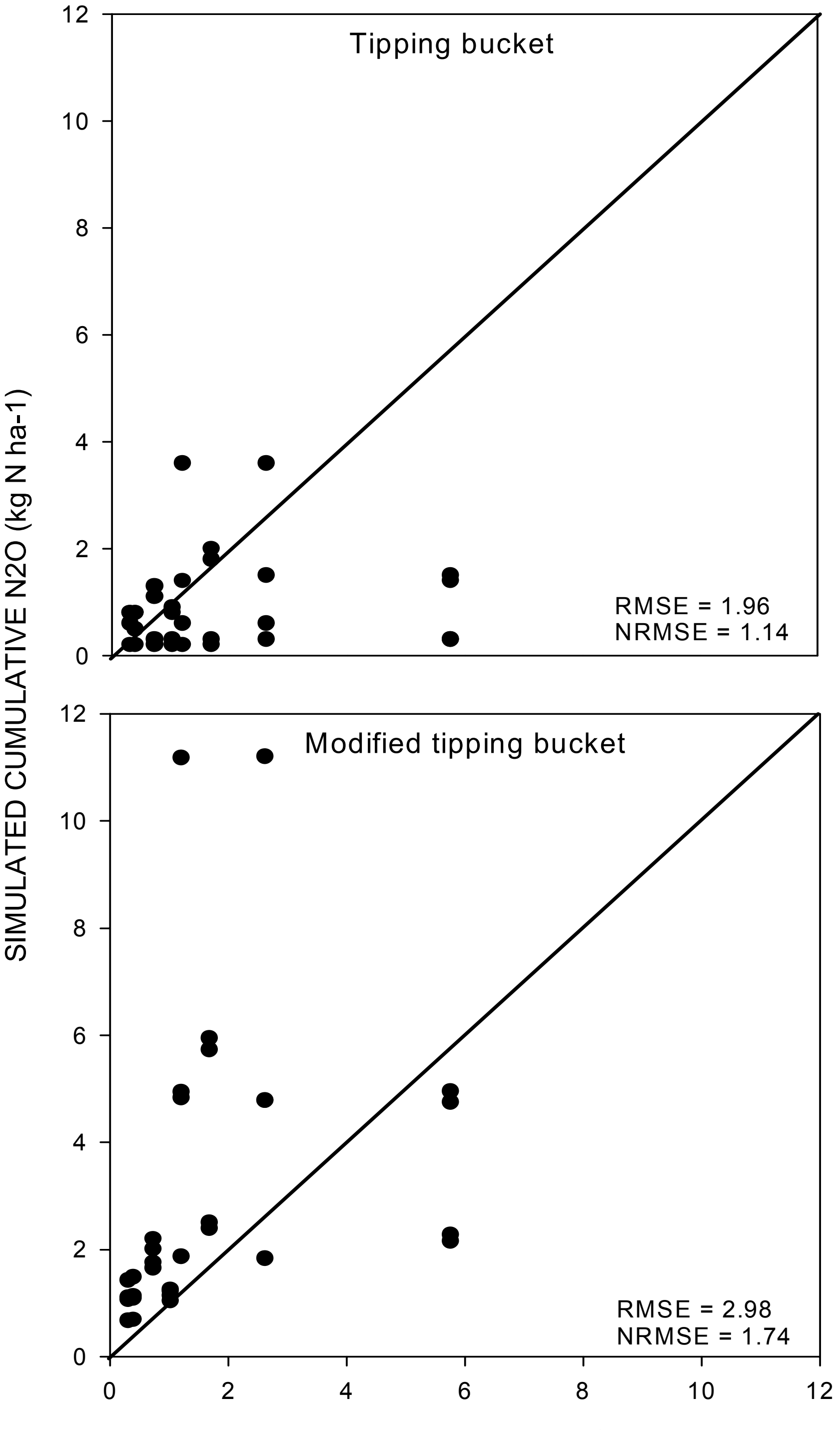

Figure 2.16. 1:1 scale plots of measured and simulated cumulative 120-hour N_2O losses using the "tipping bucket" and "modified tipping bucket" approaches for the clay loam.

inconsistent when different combinations of water retention functions, denitrification rate constants, and water flow options were used. Moreover, the effects of cropping rotation, tillage, and fertilization were not well captured by the model.

The "modified tipping bucket" method generated better results than the "tipping bucket" approach when used with van Genuchten parameter values but not with the Campbell equation in predicting volumetric water content on clay loam. The opposite was the case for the loamy fine sand. By switching from the "tipping bucket" to the "modified tipping bucket" method, predictions on NO_3-N improved, especially on clay loam, with either the Campbell or van Genuchten functions.

Results of simulated cumulative N_2O losses were very inconsistent throughout all treatments. The "modified tipping bucket" approach generated better results than the "tipping bucket" method when used with van Genuchten parameter values but not with the Campbell equation. However, when the model performance was evaluated based on the water flow option alone, "tipping bucket" had lower prediction error than "modified tipping bucket".

Modeling of N transformations, especially processes associated with N_2O emissions, is complex as a result of the above considerations. There are many underlying interacting factors that affect the denitrification process and hence, the emissions of N_2O. Moreover, there is an added challenge associated with simulations of process for the short term, 5 days in this case, as opposed to long-term since very detailed input parameter values are necessary in order for the results to be more accurate. The "tipping bucket" approach in the PNM model is generally more suited to simulate the leaching process rather than denitrification. With denitrification, good prediction of saturated and near saturated conditions are important. Due to high inconsistencies of the results, further research is needed in improving the performance of the PNM model. It appears that the incorporation of the biological aspects of the denitrification process is important to effectively capture the dynamics that affect the production of N_2O fluxes.

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CHAPTER THREE:
SIMULATION OF NET REVENUE FROM N FERTILIZER APPLICATION TO MAIZE USING THE PNM MODEL

INTRODUCTION

Farmers generally prefer to apply all the nitrogen (N) fertilizer needs for maize (*Zea mays L.*) in early spring and in one full application, to reduce extra labor cost incurred with a sidedress application in late spring. Moreover, high amounts of N are usually applied early in the season, often exceeding the required level that is needed, to insure against low yields from N deficiencies. Sheriff (2005) confirmed the reason farmers over-apply fertilizer is based on an agronomic perspective to obtain a given yield target. However, other studies have shown that delaying N fertilizer by applying a sidedress application could significantly reduce the amount of N losses through leaching and denitrification. High applications of N during early spring often lead to environmental losses before N is taken up by the crop. This study aims to evaluate the economic benefits of delaying N fertilization with sidedress application. A budgeting approach that computes both private and social returns is detailed. The level and timing of N applications may optimize private net revenue, but may not optimize net social return when social cost (environmental impact) is taken into account.

Nitrogen and N Loss via Leaching and Denitrification

Nitrogen is an essential component for plant growth, and N fertilizer use in agricultural systems has been a growing concern due to its negative effects on the environment. Water resources and the atmosphere are vulnerable to potential damaging effects from N losses from agricultural fields. Groundwater contamination and the eutrophication of streams, rivers, and lakes are some of the potential problems that may result. Estimates indicate that half of the nitrogen surplus in the Gulf of Mexico comes from N fertilizer from farms in the Mississippi River basin (Goolsby et al., 1999). A significant increase in N entering the aquatic system has been observed over the years in the United States (Howarth et al., 2002). The increase of nutrients to an aquatic system may cause algal blooms and decrease the number of species, creating a condition known as eutrophication (Carpenter et al., 1998).

Additionally, there are serious concerns regarding the effects of N fertilizer as a greenhouse gas (GHG). Smith and Conen (2004) estimated that agriculture contributes about 20% to the annual global increase in GHG concentrations, 25% of which is nitrous oxide (N_2O) emissions that occur during crop growth. Nitrous oxide is largely generated by denitrification, with some contribution from nitrification, and has a global warming equivalent of approximately 310 times that of CO_2.

The seasonal effect on N losses under maize production is crucial. Leaching and denitrification risks are high during major spring rainfall events, especially when high levels of N are applied at planting in the early spring. Typically, substantial N uptake and high evapotranspiration rates by a maize plant do not occur until around two months after planting, which implies that conditions for excessive soil water and environmental N losses are likely when high rainfall amounts occur during the spring (Sogbedji et al., 2001c). This risk decreases once the crop has entered its rapid growth phase when soil N is readily depleted and the potential for excessive soil wetness greatly diminishes. This poses a great potential risk for N losses if high rates of N fertilizer are applied at planting, especially under wet spring conditions. According to Addiscott (1988), a rainfall event in spring is likely to remove approximately 15% of N fertilizer from the soil to groundwater. Applying high N rates during the early spring instead of using sidedress (late spring) application has been shown to lead to greater potential N losses from leaching on well-drained soils and denitrification on poorly drained soils (van Es et al., 2002).

Previous Research on Economic and Environmental Modeling

Various studies have examined the economics of N fertilizer management related to environmental quality and farm profitability (Hoag and Hornsby, 1992; Taylor et al., 1992; Williams et al., 1992; Carriker, 1995; Teague et al., 1995; Chowdhury and Lacewell, 1996; Sun et al., 1996; Lambert and Lowenberg-DeBoer, 2003; Lu et al., 2003; Valentin et al., 2004). Some studies have analyzed the economic feasibility of mitigating pollution from a policy perspective (Mapp et al., 1994; Thomas and Boisvert, 1995; Randhir and Lee, 1997; Hendy et al., 2006; Pendell et al., 2006). Policy makers have developed several tools including incentives, taxes, and restrictions to address the issue (Ribaudo et al., 1999). In recent years, an increasing number of studies have attempted to evaluate the feasibilities of such tools and regulations. One common component in all of the cited studies is the incorporation of both economic and environmental effects into the analyses. Generally, these studies evaluate the relationship between farm production, revenue, and effects of N fertilizer on either groundwater quality or GHG emissions from denitrification. None of these studies analyze both damage costs from leaching and GHG emissions, other than von Blottnitz (2004), who concluded that the socially optimal fertilizer application rate is approximately 5% below the private optimum for farmers.

Some studies were conducted at the farm-level using data from field experiments (Teague et al., 1995; Lambert and Lowenberg-DeBoer, 2003; Liu et al., 2006; Pendell et al., 2006) while others including Mapp et al. (1994); Lu et al. (2003); and Hendy et al. (2006) integrated biophysical dynamic simulation and economic models to assess tradeoffs among different treatments and revenue of the production system. An advantage of this method is the ability to simulate long-term data on yield and nutrient losses which otherwise would have been very costly to obtain through experimental studies. However, not all dynamic models perform well on every geographical location and conditions, and calibration of the model to fit the study site may be needed in order for the model to produce reliable results.

Theory of Externalities

Excessive N levels in soil are damaging to the environment and human health. Water and air are often open access resources, with no barriers for any users. The quality of these resources can be reduced by one user (the farmer or land manager operating the production system) which results in lower environmental qualities for all other users ("society"). Therefore, decreased water and air quality (negative externalities) imposed by one user on society can lead to market failure when the effects of external costs are not taken into account by decision makers (Hardaker, 1997).

A negative externality associated with farming would result if inputs or farming activities imposed costs on others that were not reflected in the direct input prices and operating costs that a farmer pays. Pigou (1932) was one of the first economists to discuss a situation where there would be a divergence between marginal social and private net products. He recommended regulations and taxes on activities that produced negative externalities. In contrast, Coase's (1960) approach did not focus on public involvement but argued that in a system where property rights are well defined and transaction costs are small, externalities will be internalized through negotiations and tort law.

A negative externality due to excessive or inappropriately timed N fertilizer in the field produces harmful effects on drinking water, the ecosystem, and atmosphere when fertilizer leached into water sources or denitrified. Given that there are great concerns for environmental damages due to N losses, fertilizer decisions should not be based on profits alone, but also must reflect the environmental costs involved to achieve a balance between the marginal private benefit and marginal social cost.

The objectives of this study were to: 1) simulate long-term yield and environmental N losses associated with leaching and denitrification from 1970 to 2004 for maize production on three different textural soil types (loamy fine sand; loam; and silty clay) using the Precision Nitrogen Management (PNM) model, and 2) estimate private and social returns based on simulated data and a budgeting approach for low and high late spring precipitation years.

MATERIALS AND METHODS

Data

The PNM model was developed by Jeff Melkonian, John Hutson, and Harold van Es and is based on two existing models: LEACHN (Dr. John Hutson, Flinders University, Adelaide, South Australia), which incorporates routines for simulation of soil N, water dynamics, N transformation and uptake (Hutson, 2003), and a maize N uptake/crop growth model (Dr. Tom Sinclair, USDA-ARS, University of Florida, Gainesville, FL, and others). The PNM model was developed based on a one-dimensional soil profile concept to simulate transport and transformation of N and provide precise sidedress N recommendations for maize production. The model is deterministic and process-based, and simulates the movement of water and solute in soils through soil profile depth and time. The PNM model estimates, among other outputs, N levels in soils, environmental N losses, and yield on a daily time step based on physical and chemical properties, weather, and land management practices. The model had been evaluated in several simulation studies including those by Lotse et al. (1992), Jemison et al. (1994), and more recently by Sogbedji et al. (2001b; 2006) for N transformations under different cropping history, fertilization, and soil types.

In this study, the PNM model was used to simulate yield, N levels, and environmental losses associated with leaching and denitrification over a 35-year period (1970 – 2004) for a cash grain system producing maize on three soil types: a Colonie loamy fine sand (mixed, mesic Lamellic Udipsamments); a Honeoye loam (fine-loamy, mixed, active, mesic Glossic Hapludalfs); and a Kingsbury silty clay (very-fine, mixed, active, mesic Aeric Endoaqualfs). Some assumptions on N application dates, rates, and incorporation depths were made for the simulations. The following N treatments were observed: full at planting (which included starter plus additional fertilization on May 11); starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29; each consisting of nine additional or sidedress N rates (0; 75; 100; 125; 150; 175; 200; 225; 250 kg N ha^{-1}). Starter fertilizer of monoammonium phosphate (MAP) at 20 kg N ha^{-1} was applied for all treatments at a depth of 50 mm on May 10 of each year to coincide with the planting date. Full fertilization included starter and additional fertilizer, which was a 32% solution N (urea ammonium nitrate) applied on May 11 of each year at a depth of 100 mm. Sidedress application consisting of 32% solution N for each scenario was applied on the respective dates indicated above at a depth of 100 mm. Other assumptions were that the planting density was at 8 plant m^{-2} and no other N sources were applied. Soils were assumed to be cultivated to a depth of 200 mm on May 1 of each year.

Real historical climate data which included temperature and precipitation on daily time steps from a weather station in Syracuse, New York, were used as input for the model. Simulations were generated using the computing resources at Cornell University's Theory Center in collaboration with the Northeast Region Climate Center. The PNM model has been used in other experiments and calibrated to fit the weather conditions in the Northeastern region of the United States (Sogbedji et al., 2001a).

Farm Budgeting

A farm budgeting approach, similarly adopted by Hoag and Hornsby (1992); Carriker (1995); Sun et al. (1996); and Pendell et al. (2006), was used to compute the net revenue of each treatment. New York State average annual maize grain prices from the USDA National Agricultural Statistics Service (NASS) from 1970 to 2004 were used, which averaged \$0.10 kg^{-1}. Simulated yield and average price were used to calculate net revenue to each land management treatment by subtracting variable costs. Operating costs, which include fuel, power, equipment repairs and maintenance, labor, and depreciation were obtained from Lazarus and Selley (2005). Prices for seed and N fertilizer were based on actual values paid in an experimental study conducted in Willsboro, New York in 2004. Table 3.1 summarizes the input and operating costs for calculating net returns.

Private Net Revenue

The private net revenue or private return only accounts for the revenue and costs associated with grain production and does not consider externality costs associated with N losses. Private net revenues were calculated in each of 35 years based on yields estimated by PNM model simulations multiplied by an average maize grain price, and subtracting input and operation costs:

Table 3.1. Costs for Calculating Returns on Per Hectare Basis

	Fertilization	
	Full	Starter and Sidedress
Costs		
Fertilizer[†], $/kg	0.34	0.34
Seed[‡], $/ha	115.65	115.65
Fuel, power, equipment repairs and maintenance, labor, and depreciation, $/ha	24.16	39.13
Drying and Storage	39.52	39.52
Harvest	83.13	83.13

[†] Cost per pound of 6-24-24

[‡] At approximately 89000 seeds per hectare

$$\pi^{P}_{ij} = P \times Y_{ij} - (C_0 + CN \times S_0) - (C_1 + CN \times S_1) \times B - OC \qquad [3.1]$$

where π^{P}_{ij} (in units of \$ ha^{-1}) is the private net return to land management for N rate observation i for treatment j; i is observation for additional or sidedress N fertilizer rate, i = 1 to 9; j is N fertilizer treatment, j = 1 to 4; P is the 35-year average corn price from 1970 to 2004 (\$ kg^{-1}); Y_{ij} (in units of kg ha^{-1}) is the 35-year average simulated yield from 1970 to 2004 for N rate i for treatment j; C_0 and C_1 are operational costs for starter and additional fertilizer application (\$ ha^{-1}), respectively; CN is the cost of N fertilizer (\$ kg^{-1}); S_0 is the amount of N starter and additional N (kg N ha^{-1}) on May 11; S_1 is the N sidedress rate (kg N ha^{-1}); B equals 0 for no sidedress application, and 1 if any sidedress is applied; and OC refers to other costs such as input price for seed and cost of drying and storage.

Higher maize prices and lower operational and other costs will result in higher private net revenue and vice versa.

Externality and Social Cost from N

External costs (also known as damage costs) of N fertilizer are more complex to estimate than private costs. Even though estimates for private costs are generally based on average financial costs of a production system that may vary from year to year, such costs are more straightforward and can be introduced into a farm budget. Data on operating and input costs for corn production can be obtained from several published sources, including the USDA National Agricultural Statistics Service (NASS); Hallman and Lowenberg-DeBoer (1999); Heartland Ag-Business Group (2001); Kansas State University (2002); University of Illinois Extension (2004); Beaton et al. (2005); and Lazarus and Selley (2005). On the other hand, the actual costs of externalities are difficult to quantify (Carriker, 1995). According to Hoag and

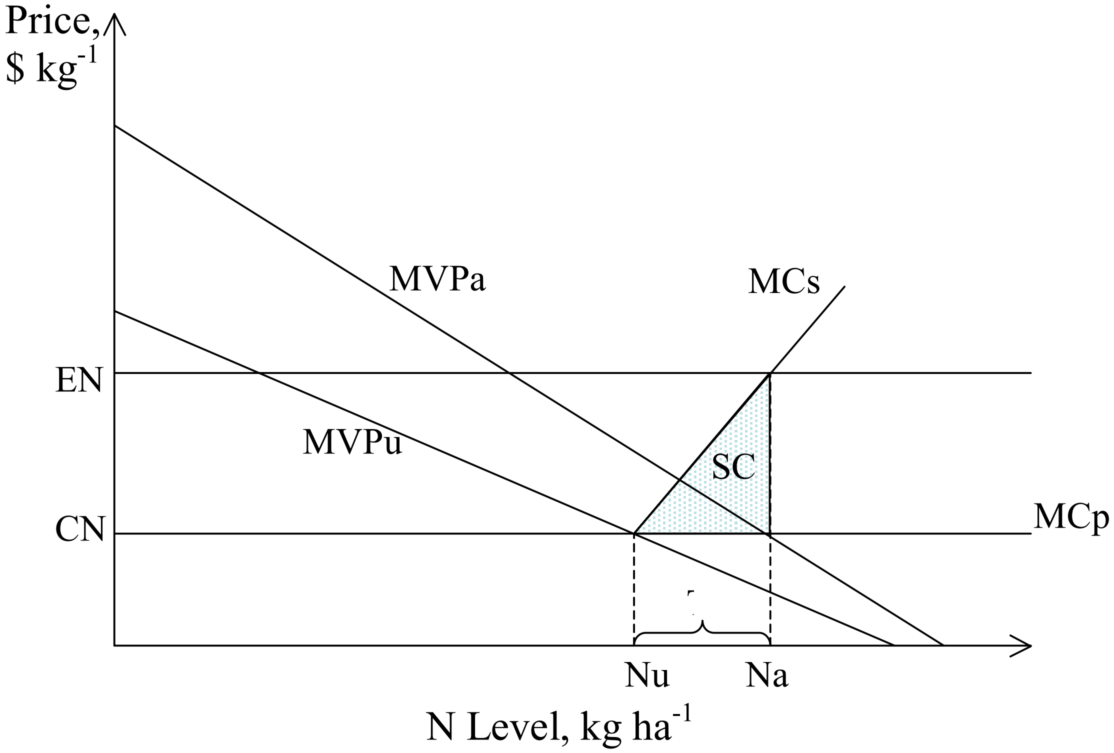
Hornsby (1992), one approach of assigning monetary value to external effects is on a relative scale, where the external cost is calculated on a relative scale in proportion to the cost of N fertilizer.

To illustrate, the graph in Figure 3.1 is a representation of the model. Ideally, the farmer wants all N fertilizer applied in the field, Na, fully taken up by the maize crop, Nu, i.e., Na = Nu. Following this assumption, the marginal value product for the level of N applied, MVPa, equals the marginal value product for the level of N used by the crop. However, due to the dynamics of N in the field, Na ≠ Nu, and some studies suggest that an average of 20% (EWG, 1996) or even higher (Baird, 1990) of applied N fertilizer may not be used by the crop. Therefore, when Na exceeds Nu, MVPa and MVPu diverge. The N surplus from the field accounted as total environmental loss is indicated by T. The external cost of N fertilizer, EN, is shown as in Figure 3.1 and will be calculated according to equation [3.2] below. The marginal social cost of N fertilizer use is greater than the private marginal cost (the cost to the farmer, MCp, which also equals CN) when Na exceeds Nu. CN represents the per unit cost paid by the farmer for N fertilizer applied, Na. The farmer operates the production system at Na, the level where MVPa equals MCp. However, the socially optimal level is where MVPu equals MCs, i.e., at Nu. This results in environmental N losses of T and social cost, SC, represented by the shaded region (Figure 3.1).

Approximating Social Cost

Simulated N losses through leaching and denitrification were viewed as a social cost in these analyses. To quantify the social cost a parameter EN, which represents the external cost of N, is defined as follows:

$$EN = [(S_0 + S_1) / (S_0 + S_1 - T^*)] \times CN \qquad [3.2]$$



Social Cost, SC, is represented by the shaded triangular area, = ½ * (EN – CN) * T

Figure 3.1. Private and social marginal costs (MCp and MCs) and marginal value products of applied and used N level input (MVPa and MVPu).

where S_1 is N sidedress rate (kg N ha^{-1}); T^* is adjusted total simulated N loss through leaching and denitrification (kg N ha^{-1}), $T^* = T_x - T_{20}$ where T_x is unadjusted total simulated N loss through leaching and denitrification (kg N ha^{-1}) for N fertilizer rate x; x is observation for additional or sidedress N fertilizer rate, x = 95; 120; 145; 170; 195; 220; 245; 270 kg N ha^{-1}; T_{20} is simulated N losses from treatment under 20 kg N ha^{-1} application that was used as baseline to adjust for T^*; and CN is cost of N fertilizer (\$ kg^{-1}).

One assumption is that $S_0 + S_1 > T \geq 0$, holding farmers responsible only for amount of N that they applied.

Social cost, SC (\$ ha^{-1}), is then defined as the following:

$$SC = \tfrac{1}{2} \times (EN - CN) \times T \qquad [3.3]$$

This approach follows the method used by Carriker (1995) to estimate social costs from N lost in maize production in Kansas. The social return on farming subtracts SC from π^P_{ij} yielding:

$$\pi^S_{ij} = P * Y_{ij} - (C_0 + FC_0 * S_0) - (C_1 + FC_1 * S_1) * B - OC - SC \qquad [3.4]$$

equivalent to:

$$\pi^S_{ij} = \pi^P_{ij} - SC \qquad [3.5]$$

where π^P_{ij} is defined in [3.1] above and SC defined in [3.3].

Therefore, in the presence of a negative externality, private return is greater than social return.

RESULTS

The private return is most sensitive to maize price, and any slight change in this price significantly affected the return, compared to input, operating, and other costs. Maize grain prices have varied over the years, with the highest price in 1995 at \$0.15 kg^{-1} and lowest in 1970 at \$0.06 kg^{-1}.

The 35 yearly yield and total N losses were pooled by the corresponding yearly precipitation and were divided into two categories of low and high precipitation for analyses. Precipitation in the month of June was chosen based on work by Sogbedji et al. (2001c), and ranged from 22 (in 1995) to 315 mm in 1972 over the 35 years, with a median of 83. Observation in the month of June was critical with nitrification and denitrification rates being higher, as opposed to July when potential environmental N losses are less likely. The low precipitation category consisted of the first 50th percentile of the distribution while the high precipitation category consisted of the remaining years with relatively higher rainfall.

Data were also pooled by both June precipitation and temperature in several ways: May; May and June; and April 15 to June 15 temperature, and were divided into four categories of low precipitation and low temperature; low precipitation and high temperature; high precipitation and low temperature; and high precipitation and high temperature, but temperature did not show much impact on total N losses for all soil types.

Yield Averages

Figure 3.2 illustrates the average maize response to N at various fertilization levels. The average yields were higher for low June precipitation years than high June precipitation years at 20 kg N ha^{-1} of N fertilizer, presumably due to losses of mineralized soil organic N, but when greater levels of N fertilizer were applied, average yield were lower on low precipitation years than high precipitation years. Yield differences between the Colonie loamy fine sand and the Kingsbury silty clay were relatively small, especially during years with low June rainfall. Yield averages among starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 were almost identical with minimal differences for Honeoye, Colonie, and Kingsbury. The Honeoye loam showed little difference in yield average between full and starter plus sidedress fertilization. However, both Colonie loamy fine sand and Kingsbury silty clay had greater average yield differences between full and starter plus sidedress N applications than the Honeoye loam. The average yield differences between full and starter plus sidedress N fertilization in Colonie and Kingsbury were especially greater at N levels from 95 to 120 kg N ha^{-1}. Even though yield was slightly higher (at 120 kg N ha^{-1}) under full fertilization than starter plus sidedress on Honeoye when June precipitation was low, the reverse was true when precipitation was high. Similar yield trend was found for the Colonie loamy fine sand. Full fertilization on the Kingsbury silty clay, on the other hand, resulted in lower yields than starter plus sidedress applications regardless of precipitation amount.

Yield distributions at 120 kg N ha^{-1} rate over the 35-year period were variable for all three soil types (Figure 3.3). Greater simulated yield differences between full fertilization at planting and starter plus sidedress applications were found in the Kingsbury silty clay.

Average Total N Losses

Among the three soil types, Kingsbury, a silty clay, was found to have the highest total N losses[1] with the majority contributed by the denitrification process (Figure 3.4; Tables 3.2 and 3.3) for both low and high June precipitation years. Colonie, a loamy fine sand soil, had the lowest total N losses with most of it from leaching. However, the difference in average total N losses between Colonie and Honeoye were minimal.

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[1] This is an approximation and relatively small environmental losses were observed.

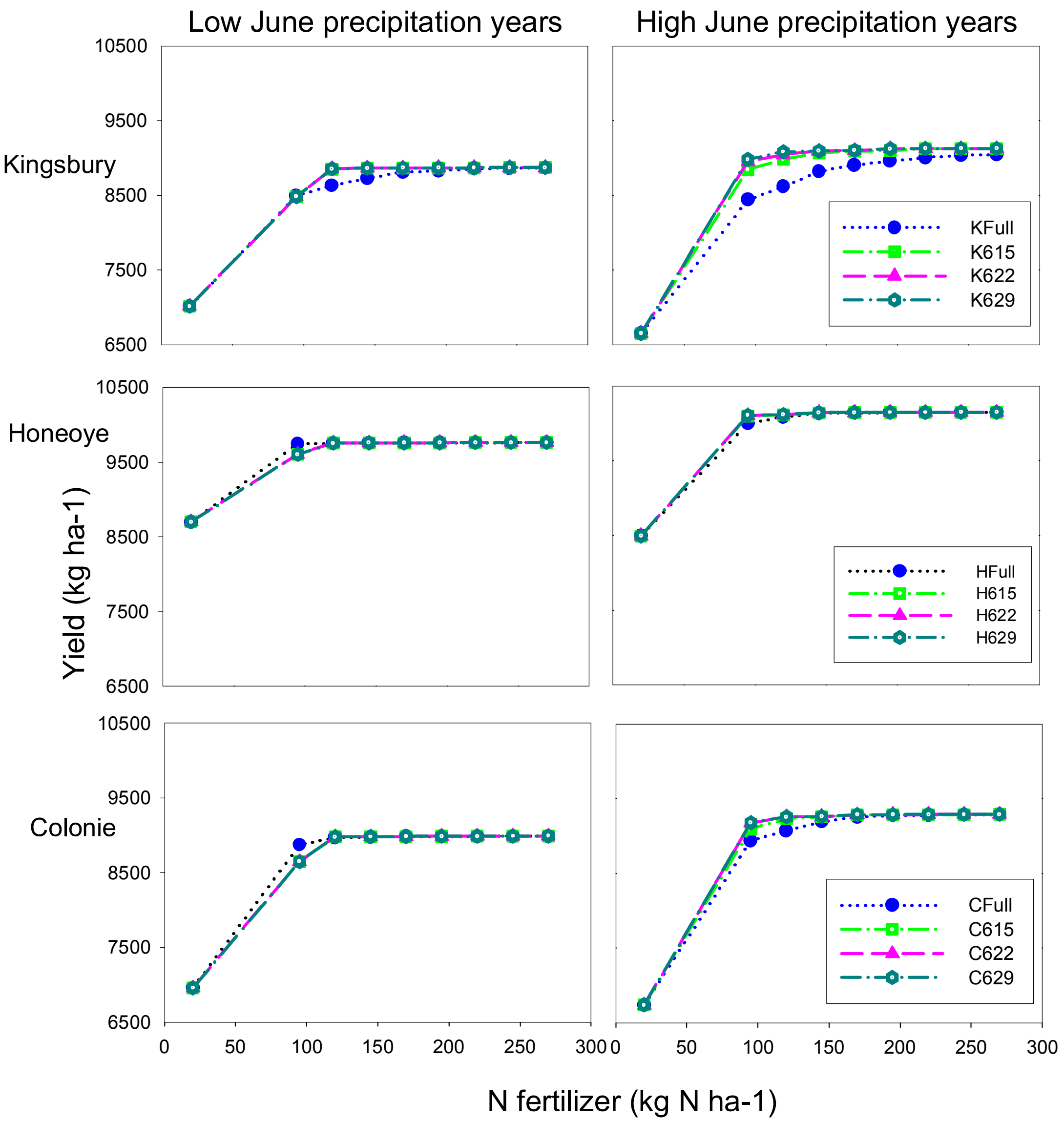

Figure 3.2. Average corn yield response to N for low and high June precipitation years on Kingsbury, Colonie, and Honeoye for full; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29. Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Honeoye (HFull; H615; H622; H629); and Colonie (CFull; C615; C622; C629).

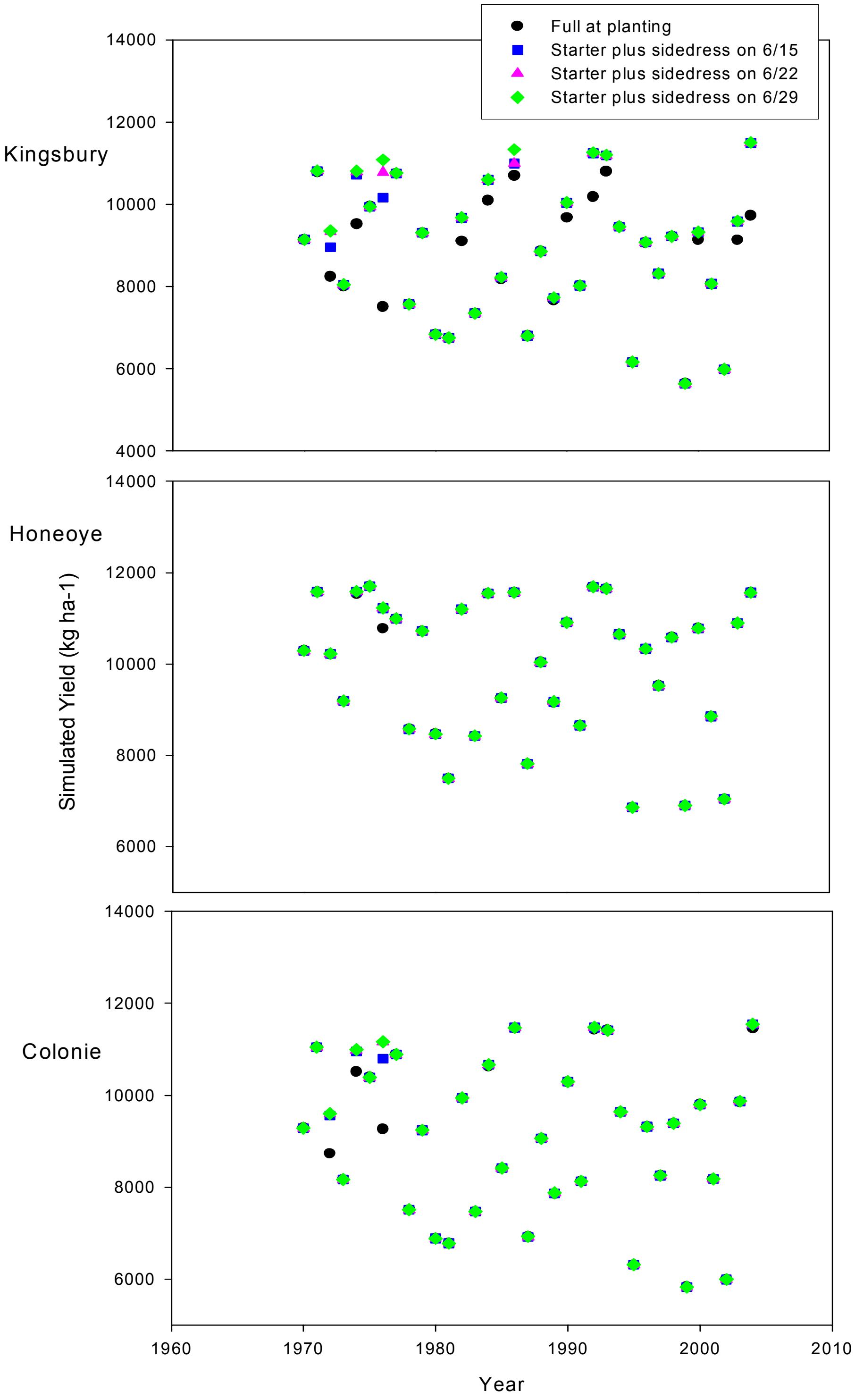

Figure 3.3. Simulated yield distribution from 1970 – 2004 for Kingsbury, Honeoye, and Colonie.

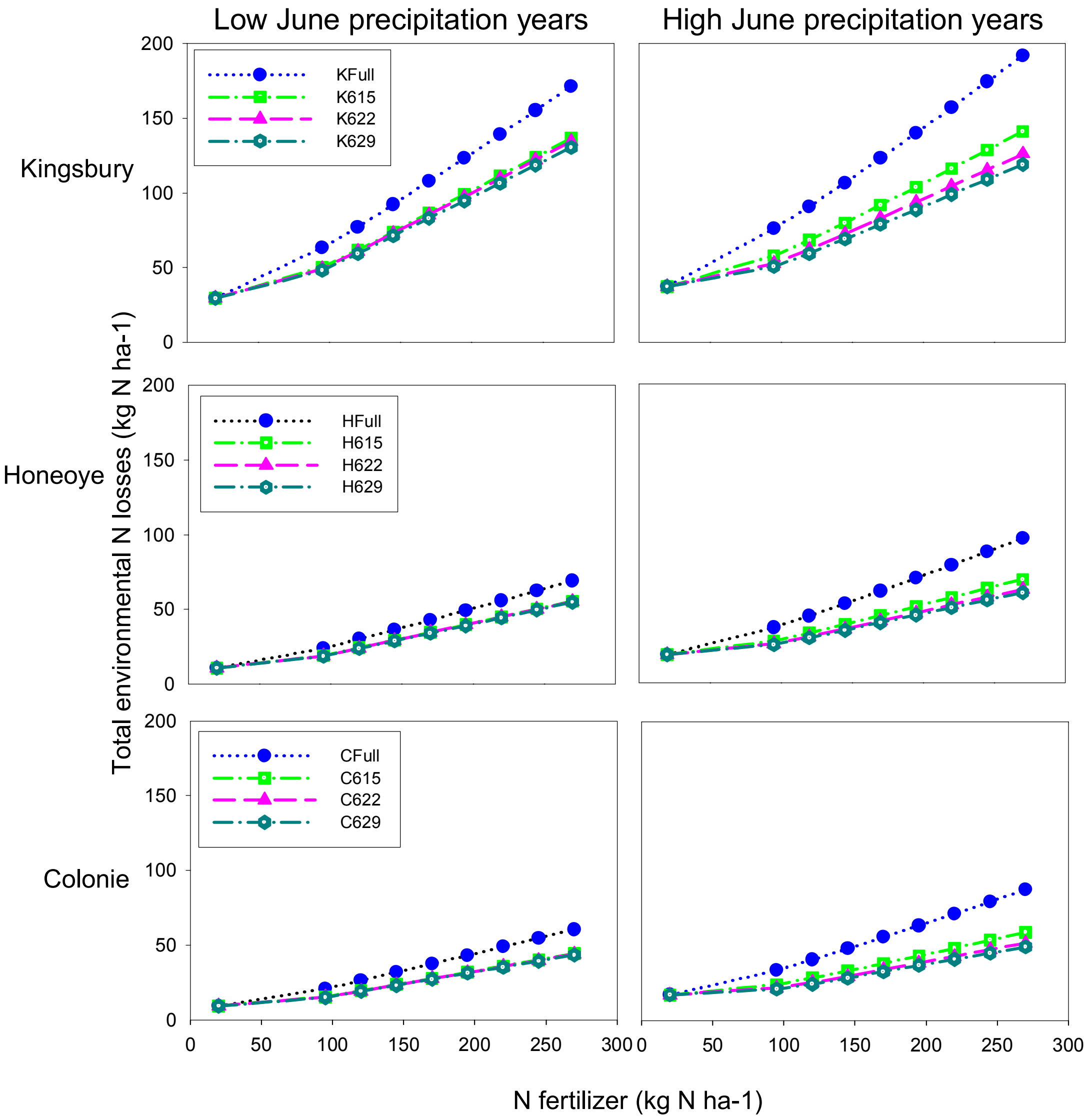

Figure 3.4. Average total N losses for low and high June precipitation years on Kingsbury, Colonie, and Honeoye for full; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29. Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Honeoye (HFull; H615; H622; H629); and Colonie (CFull; C615; C622; C629).

Table 3.2. N Losses for Low June Precipitation Years

Net Returns	N Fertilizer Level Applied, kg N ha^{-1}	N Treatment[†]											
		Kingsbury				**Honeoye**				**Colonie**			
		KFull	K615	K622	K629	HFull	H615	H622	H629	CFull	C615	C622	C629
		Average N Losses (kg N ha^{-1})											
Leaching	20	6.6	6.6	6.6	6.6	6.6	6.6	6.6	6.6	9.0	9.0	9.0	9.0
	95	11.9	9.0	9.0	9.0	13.4	11.1	11.1	11.1	19.9	14.6	14.5	14.2
	120	13.9	10.5	10.5	10.5	16.6	14.0	13.9	14.1	25.1	18.6	18.5	18.3
	145	16.1	12.2	12.2	12.2	19.8	16.9	16.9	16.9	30.4	22.5	22.4	22.2
	170	18.5	13.6	13.8	13.9	23.1	19.7	19.8	19.8	35.8	26.5	26.3	25.9
	195	20.6	15.2	15.4	15.4	26.4	22.4	22.5	22.5	41.2	30.3	30.2	29.8
	220	22.8	17.0	17.0	17.1	29.6	25.2	25.4	25.4	46.7	34.3	34.1	33.8
	245	25.2	18.3	18.5	18.6	32.9	28.0	28.2	28.2	52.3	38.3	38.1	37.7
	270	24.9	19.9	20.3	20.0	36.2	30.8	31.1	31.1	57.7	42.4	41.9	41.5
Denitrification	20	23.0	23.0	23.0	23.0	4.4	4.4	4.4	4.4	0.5	0.5	0.5	0.5
	95	51.6	41.3	40.3	39.2	10.5	7.9	7.8	7.6	0.9	0.7	0.8	0.8
	120	63.2	51.5	50.5	49.0	13.6	10.4	10.1	9.8	1.2	1.0	0.9	0.8
	145	76.2	61.8	60.7	59.2	16.5	12.5	12.2	11.9	1.6	1.2	1.0	0.9
	170	89.3	72.9	71.5	69.2	19.8	15.0	14.7	14.3	1.8	1.3	1.4	1.3
	195	102.6	83.8	82.1	79.4	22.8	17.4	17.2	16.6	2.0	1.6	1.4	1.5
	220	116.4	94.7	92.7	89.5	26.2	19.9	19.5	19.1	2.2	1.7	1.6	1.5
	245	129.9	105.6	103.7	100.1	29.6	22.3	21.8	21.5	2.4	1.9	1.8	1.6
	270	146.5	116.8	114.3	110.5	33.1	24.8	24.3	23.8	2.7	2.0	2.1	1.9

[†] Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Colonie (CFull; C615; C622; C629); and Honeoye (HFull; H615; H622; H629).

Table 3.3. N Losses for High June Precipitation Years

	N Fertilizer	N Treatment[†]											
Net	Level Applied,	**Kingsbury**				**Honeoye**				**Colonie**			
Returns	kg N ha^{-1}	KFull	K615	K622	K629	HFull	H615	H622	H629	CFull	C615	C622	C629
		Average N Losses (kg N ha^{-1})											
Leaching	20	11.9	11.9	11.9	11.9	14.0	14.0	14.0	14.0	16.9	16.9	16.9	16.9
	95	20.8	16.1	14.4	14.0	24.9	19.7	18.2	17.8	32.8	23.6	21.3	20.6
	120	24.1	18.2	16.1	15.6	29.6	22.8	21.2	20.8	39.8	27.8	24.7	23.9
	145	27.6	20.3	17.9	17.3	34.4	26.3	24.4	23.9	47.1	32.3	28.6	27.6
	170	31.2	22.8	19.9	19.4	39.6	30.1	27.7	27.2	54.6	37.1	33.0	31.7
	195	34.6	25.2	22.0	21.1	44.7	33.9	31.0	30.3	61.9	42.1	37.2	35.7
	220	38.1	27.6	23.9	22.9	50.1	37.5	34.1	33.3	69.7	47.2	41.4	39.7
	245	41.4	30.1	25.8	24.7	55.2	41.3	37.4	36.4	77.7	52.3	45.8	43.6
	270	45.2	32.4	27.9	26.7	60.2	44.9	40.7	39.6	85.6	57.3	50.0	47.6
Denitrification	20	25.4	25.4	25.4	25.4	4.9	4.9	4.9	4.9	0.4	0.4	0.4	0.4
	95	55.4	42.0	38.6	36.8	12.1	8.4	8.1	7.7	0.9	0.7	0.8	0.7
	120	66.9	50.2	46.1	43.9	15.1	10.5	9.7	9.3	1.1	0.9	0.9	0.7
	145	79.2	59.7	54.4	51.8	18.5	12.7	11.7	11.2	1.2	1.1	1.1	1.0
	170	92.2	69.2	63.2	59.7	21.8	14.8	13.7	13.2	1.4	1.2	1.2	1.2
	195	105.4	78.7	71.8	67.6	25.4	17.1	15.7	15.0	1.6	1.4	1.5	1.4
	220	119.1	88.7	80.7	76.1	28.8	19.7	18.0	17.0	1.9	1.4	1.6	1.5
	245	133.1	98.7	89.6	84.3	32.7	22.1	19.9	18.9	1.9	1.8	1.7	1.8
	270	146.8	108.8	98.2	92.3	36.3	24.3	21.9	20.7	2.2	1.9	2.1	1.9

[†] Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Colonie (CFull; C615; C622; C629); and Honeoye (HFull; H615; H622; H629).

At 20 kg N ha^{-1} of N fertilizer applied during low June precipitation years, average total N losses for the Colonie loamy fine sand was 9 kg N ha^{-1} while the Honeoye loam's was 11 kg N ha^{-1}; the same amount of N fertilizer applied during high June precipitation years resulted in average total N losses of 17 and 19 kg N ha^{-1} respectively (Figure 3.4). Kingsbury, being the most susceptible to N losses, had 20 kg N ha^{-1} of in both dry and wet years. When 270 kg N ha^{-1} of N fertilizer was applied all at once under full fertilization during years with low June precipitation, Colonie and Honeoye each lost 60 and 69 kg N ha^{-1} of average total N respectively. The average total N loss difference between Colonie and Honeoye were similar in wet years too; with Honeoye, having an average total N loss of 97 kg N ha^{-1}, 9 kg N ha^{-1} greater total N than Colonie. As the amount of N increased, so did the average total losses. The average total losses for Kingsbury in both dry and wet years under full fertilization at 270 kg N ha^{-1} were greater than the average total losses for both Colonie and Honeoye combined (Figure 3.4).

Simulation data showed that there was an apparent difference in average N losses between full and starter plus sidedress on June 15 fertilization treatments, especially during the wet years and on Kingsbury soil. This should encourage farmers to not apply all the N needs during the early season but to split the amount applied and using sidedress applications. Moreover, yield data had shown relatively close results between full and starter plus sidedress on June 15 N application treatment, and therefore, delaying the N application did not affect yield returns.

Observations were made on average N losses among the treatments with different sidedress application dates. The differences, especially in Kingsbury, in average total environmental N losses among starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 were minimal during the low June precipitation years (Figure 3.4). In the wetter years, however, the differences in average N losses among the three N treatments with different sidedressing dates were greater. Delaying sidedress to the latest possible date is beneficial in preventing N fertilizer being lost to the environment, as the starter plus sidedress on June 29 scenario had the lowest average N losses for all soil types. Using sidedress applications and delaying N fertilization as late as possible is more crucial and useful for years with high rainfall event.

Impact on Returns

The average private and social returns were positive for all N treatments on all three soil types (Tables 3.4 and 3.5). Honeoye (loam) generated the highest private and social returns, followed by Colonie (loamy fine sand), and Kingsbury (silty clay) respectively. This occurred primarily because Honeoye had the highest average yield during both dry and wet years compared to the other soils. Since private costs (Table 3.1) were assumed to be the same for all soil types, all operating costs incurred in the grain production system were not the main factors that contributed to the differences in returns among the soils, and returns were therefore largely reflected by crop response to N.

The external cost of N was calculated based on a ratio of total amount of N fertilizer applied to the amount of N lost (Equation [3.2]). This results in a significantly higher damage cost the greater the N fertilizer amount is applied, especially during early in the season when almost all of the N applied is susceptible to leaching and denitrification (Table 3.6).

Applying more than 120 kg N ha^{-1} of N fertilizer did not increase revenue, but instead had an adverse impact on the environment (with greater average N losses), increased the cost of production, and lowered both private and social cost net return.

Table 3.4. Private and Social Returns per Hectare for Low June Precipitation Years

Net Returns	N Fertilizer Level Applied, kg N ha^{-1}	N Treatment†											
		Kingsbury				**Honeoye**				**Colonie**			
		KFull	K615	K622	K629	HFull	H615	H622	H629	CFull	C615	C622	C629
		Average Net Returns ($ ha^{-1})											
Private (π^P)	95	571.3	554.8	555.1	555.3	699.2	669.8	669.8	669.8	609.7	572.1	572.2	572.3
	120	576.9	584.5	584.6	584.8	691.5	676.7	676.7	676.7	611.0	597.3	597.3	597.3
	145	578.0	577.1	577.2	577.2	683.2	668.4	668.4	668.5	603.7	589.1	589.2	589.2
	170	578.4	568.8	568.8	568.9	674.9	660.1	660.1	660.1	595.5	580.8	580.9	580.9
	195	571.2	560.5	560.5	560.6	666.5	651.7	651.7	651.8	587.2	572.5	572.5	572.6
	220	566.1	552.1	552.2	552.2	658.1	643.4	643.4	643.4	578.8	564.2	564.2	564.2
	245	558.0	543.7	543.8	543.8	649.7	635.0	635.0	635.0	570.4	555.8	555.9	555.9
	270	549.7	535.3	535.4	535.4	641.3	626.6	626.6	626.6	562.0	547.5	547.5	547.5
Social (π^S)	95	567.7	553.5	553.8	554.2	698.7	669.5	669.6	669.6	609.3	572.0	572.0	572.1
	120	570.9	581.9	582.2	584.6	690.6	676.2	676.3	676.3	610.3	597.0	597.0	597.1
	145	568.9	572.9	573.2	577.0	681.9	667.7	667.8	667.8	602.7	588.6	588.7	588.7
	170	565.6	562.7	563.1	568.7	673.1	659.1	659.1	659.2	594.1	580.1	580.2	580.2
	195	554.6	552.4	552.9	560.4	664.2	650.4	650.5	650.5	585.3	571.6	571.7	571.7
	220	545.1	541.8	542.6	552.1	655.2	641.7	641.8	641.9	576.5	563.0	563.1	563.2
	245	532.2	531.3	531.9	543.7	646.2	633.1	633.1	633.2	567.7	554.4	554.5	554.6
	270	518.8	520.4	521.3	535.3	637.2	624.3	624.3	624.4	558.8	545.9	545.9	546.0

† Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Colonie (CFull; C615; C622; C629); and Honeoye (HFull; H615; H622; H629).

Table 3.5. Private and Social Returns per Hectare for High June Precipitation Years

Net Returns	N Fertilizer Level Applied, kg N ha^{-1}	N Treatment[†]											
		Kingsbury				**Honeoye**				**Colonie**			
		KFull	K615	K622	K629	HFull	H615	H622	H629	CFull	C615	C622	C629
		Average Net Returns ($ ha^{-1})											
Private (π^P)	95	565.8	592.1	603.4	606.0	724.8	720.5	721.0	721.1	616.9	618.0	626.1	626.4
	120	575.3	597.7	604.1	608.0	725.4	713.4	713.5	713.6	622.0	623.3	625.8	625.9
	145	587.8	597.6	600.5	600.8	721.7	707.5	707.7	707.7	625.9	617.8	617.9	618.0
	170	587.8	591.9	592.7	592.8	713.9	699.3	699.4	699.5	623.5	611.7	611.8	611.9
	195	584.7	584.1	586.6	586.7	705.6	691.0	691.2	691.2	617.2	603.4	603.5	603.6
	220	581.1	578.1	578.2	578.3	697.3	682.7	682.8	682.8	609.3	595.0	595.1	595.2
	245	575.5	569.7	569.8	569.9	688.9	674.3	674.4	674.4	601.1	586.6	586.7	586.8
	270	567.7	561.2	561.4	561.4	680.6	665.9	665.9	665.9	592.7	578.2	578.3	578.4
Social (π^S)	95	560.7	591.0	602.8	605.6	723.8	720.2	720.8	721.0	616.0	617.9	626.0	626.4
	120	567.3	595.6	602.9	607.0	723.7	712.9	713.2	713.2	620.5	622.9	625.5	625.7
	145	576.0	594.2	598.3	599.0	719.2	706.7	707.0	707.1	623.7	617.1	617.5	617.6
	170	571.6	586.8	589.3	590.1	710.5	698.1	698.5	698.6	620.5	610.7	611.1	611.3
	195	563.8	577.3	582.0	582.9	701.1	689.3	689.9	690.1	613.3	602.0	602.6	602.7
	220	554.7	569.3	572.2	573.3	691.6	680.5	681.2	681.4	604.4	593.3	593.9	594.1
	245	543.3	558.7	562.2	563.7	681.9	671.5	672.4	672.6	595.1	584.4	585.2	585.4
	270	529.2	547.9	552.2	553.9	672.3	662.6	663.6	663.8	585.6	575.5	576.5	576.7

[†] Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Colonie (CFull; C615; C622; C629); and Honeoye (HFull; H615; H622; H629).

Table 3.6. Social Costs (SC) per Hectare

		N Treatment†											
		Kingsbury				**Honeoye**				**Colonie**			
Net Returns	N Fertilizer Level Applied, kg N ha^{-1}	KFull	K615	K622	K629	HFull	H615	H622	H629	CFull	C615	C622	C629
						Average Social Costs (\$ ha^{-1})							
Low June	95	3.8	0.0	1.3	1.2	0.5	0.2	0.2	0.2	1.6	0.8	0.8	0.7
Precipitation	120	6.3	2.6	2.4	2.2	0.9	0.4	0.4	0.4	2.0	1.0	1.0	1.0
Years	145	9.5	4.2	3.9	3.7	1.3	0.7	0.7	0.7	2.4	1.3	1.2	1.2
	170	13.3	6.1	5.7	5.2	1.8	1.0	1.0	0.9	2.9	1.5	1.5	1.4
	195	17.3	8.1	7.6	6.9	2.3	1.3	1.3	1.2	3.3	1.8	1.7	1.7
	220	21.9	10.3	9.6	8.8	2.9	1.6	1.6	1.5	3.8	2.0	2.0	1.9
	245	26.9	12.5	11.8	10.7	3.5	1.9	1.9	1.8	4.3	2.3	2.2	2.1
	270	32.2	14.9	14.0	12.7	4.2	2.3	2.2	2.2	4.8	2.6	2.5	2.4
High June	95	5.1	1.1	0.6	0.4	1.0	0.2	0.2	0.1	7.2	2.5	1.7	1.5
Precipitation	120	8.0	2.1	1.3	1.0	1.6	0.5	0.3	0.3	7.2	2.5	1.7	1.5
Years	145	11.8	3.4	2.2	1.8	2.5	0.8	0.6	0.6	7.7	2.8	1.9	1.8
	170	16.2	5.0	3.4	2.7	3.4	1.2	0.9	0.8	8.6	3.2	2.3	2.1
	195	20.9	6.7	4.6	3.7	4.5	1.7	1.2	1.1	9.5	3.7	2.6	2.4
	220	26.3	8.8	6.1	4.9	5.7	2.2	1.6	1.4	10.6	4.2	3.0	2.7
	245	32.2	11.0	7.6	6.2	7.0	2.8	2.0	1.8	11.9	4.8	3.3	3.0
	270	38.5	13.3	9.2	7.5	8.2	3.3	2.3	2.1	13.3	5.3	3.7	3.3

† Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Colonie (CFull; C615; C622; C629); and Honeoye (HFull; H615; H622; H629).

The private return from farm production showed that economic benefits were generally on a downward sloping trend when more than 120 kg N ha^{-1} of N fertilizer was applied due to higher costs for N fertilizer (Tables 3.4 and 3.5).

Full fertilization resulted in higher average private returns than starter plus sidedress applications during dry years for all soil types, except for the Kingsbury silty clay at 120 kg N ha^{-1} where all the starter plus sidedress applications had better private returns than full fertilization. Although the average social returns during dry years were higher in full fertilization than starter plus sidedress applications for the Honeoye loam and Colonie loamy fine sand, it was the reverse for the Kingsbury silty clay, which had higher social returns under starter plus sidedress applications than full fertilization at N fertilizer rates greater than 120 kg N ha^{-1}.

During wet years, average private and social returns were higher under full fertilization than starter plus sidedress applications for Honeoye on all N rates, and Colonie on N rate at 145 kg N ha^{-1} and greater. Kingsbury (silty clay) resulted in the highest private benefits during wet years among all the soil types; starter plus sidedress applications generated better private returns than full fertilization at 170 kg N ha^{-1} and below. Due to higher leaching and denitrification potential during wet conditions, especially on finer textured soils like the Kingsbury silty clay, the benefit was even greater to use starter plus sidedress applications than full fertilization; as results had confirmed that the average social returns under starter plus sidedress applications were higher than full fertilization, and the differences in social returns between full and starter plus sidedress fertilizations were larger for high than low June precipitation years, regardless of the N levels of fertilizer applied (Tables 3.4 and 3.5).

When external cost on N fertilizer was increased to 3 × EN, social costs more than doubled, especially for high June precipitation years, under full fertilization than starter plus sidedress applications for all three soil types (Table 3.7). For 3 × EN

Table 3.7. Social Costs (SC) per Hectare for 3 x EN.

	N Fertilizer Level Applied, kg N ha^{-1}	N Treatment[†]											
		Kingsbury				**Honeoye**				**Colonie**			
		KFull	K615	K622	K629	HFull	H615	H622	H629	CFull	C615	C622	C629
		Average Social Costs ($ ha^{-1})											
Low June Precipitation Years	95	23.1	0.0	10.5	9.8	5.9	3.4	3.3	3.2	5.1	2.5	2.4	2.3
	120	35.3	18.8	17.9	16.8	9.2	5.9	5.7	5.6	7.8	4.4	4.3	4.1
	145	50.3	27.6	26.6	25.2	12.5	8.4	8.3	8.1	10.8	6.3	6.1	6.0
	170	67.1	37.6	36.1	33.9	16.3	11.1	10.9	10.7	13.9	8.4	8.2	8.0
	195	84.4	47.9	45.8	43.0	20.1	13.7	13.6	13.2	17.0	10.4	10.2	10.0
	220	103.8	58.8	55.9	52.5	24.1	16.4	16.3	16.0	20.3	12.5	12.3	12.0
	245	124.3	69.5	66.9	62.4	28.1	19.2	19.0	18.7	23.6	14.7	14.4	14.0
	270	146.0	81.1	77.8	72.5	32.3	21.9	21.8	21.5	27.0	16.8	16.5	16.1
High June Precipitation Years	95	28.4	10.4	7.1	5.9	9.1	3.9	3.0	2.6	8.3	2.9	1.9	1.5
	120	42.3	16.8	12.2	10.5	13.7	6.4	5.1	4.8	12.5	5.0	3.5	3.0
	145	59.0	24.6	18.5	16.1	19.0	9.3	7.7	7.2	17.1	7.3	5.4	4.9
	170	77.9	33.6	25.6	22.3	24.7	12.5	10.4	9.8	22.3	10.0	7.7	7.0
	195	97.5	42.9	33.1	28.7	31.0	16.0	13.2	12.3	27.4	12.8	10.0	9.2
	220	119.8	53.2	41.0	35.8	37.4	19.6	16.1	15.0	33.1	15.9	12.3	11.3
	245	143.3	64.1	49.3	43.0	44.4	23.4	19.0	17.7	39.1	19.1	14.8	13.6
	270	168.1	75.3	57.7	50.4	51.1	26.9	21.8	20.4	45.4	22.2	17.3	15.9

[†] Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Colonie (CFull; C615; C622; C629); and Honeoye (HFull; H615; H622; H629).

estimates on all three soil types, social returns were the highest at 95 kg N ha^{-1} under full fertilization at planting and 120 kg N ha^{-1} under starter plus sidedress applications during low June precipitation years (Table 3.8). During high June precipitation years, the optimal N rate was 95 kg N ha^{-1} for the Kingsbury silty clay, Honeoye loam, and Colonie loamy fine sand under all N treatments except for Colonie's full fertilization at planting and starter plus sidedress on June 15 treatments which were socially optimal at 120 kg N ha^{-1} (Table 3.8).

Differences in private returns between full and starter plus sidedress applications for both dry and wet years were not only due to the additional operating costs incurred for sidedress applications, but also, in some scenarios, yield differences which had an impact on the gross revenue from the sales of maize. In summary, sidedress has only a small effect on private and social net return except for the Kingsbury silty clay, especially during high June precipitation years, in which obvious differences were observed between full and starter plus sidedress fertilizations.

CONCLUSIONS

This study examined the private and social returns for a maize production system using 35-year data simulated using the PNM model. Average yield, N losses, and net returns were observed for full vs. starter-only N application for Kingsbury (silty clay), Honeoye (loamy sand), and Colonie (loamy fine sand) soils under different N levels. Results indicate that the Honeoye soil generated the highest private and social returns, followed by Colonie, and Kingsbury. Kingsbury had the highest average N losses, which were primarily contributed by the denitrification process, while Colonie had the lowest average losses, mostly from leaching. Temperature had little impact on total N losses on all three soil types compared to June precipitation.

Table 3.8. Social Returns per Hectare for 3 x EN.

	N Fertilizer Level Applied, kg N ha^{-1}	N Treatment[†]											
		Kingsbury				**Honeoye**				**Colonie**			
		KFull	K615	K622	K629	HFull	H615	H622	H629	CFull	C615	C622	C629
		Average Net Returns ($ ha^{-1})											
Low June Precipitation Years	95	548.7	543.7	544.6	545.5	693.3	666.4	666.4	666.5	604.6	569.6	569.7	570.0
	120	542.6	565.7	566.7	568.0	682.3	670.8	671.0	671.1	603.2	593.0	593.1	593.2
	145	529.2	549.5	550.6	552.0	670.7	660.1	660.2	660.4	592.9	582.8	583.0	583.2
	170	513.4	531.2	532.7	535.0	658.6	649.0	649.2	649.5	581.6	572.5	572.6	572.8
	195	489.5	512.6	514.7	517.6	646.5	638.0	638.2	638.5	570.2	562.1	562.3	562.5
	220	465.8	493.3	496.2	499.7	634.1	626.9	627.1	627.4	558.5	551.7	551.9	552.3
	245	438.0	474.2	476.8	481.4	621.6	615.8	616.0	616.3	546.8	541.2	541.5	541.9
	270	409.0	454.2	457.6	462.9	609.0	604.6	604.8	605.1	535.0	530.7	531.0	531.4
High June Precipitation Years	95	537.4	581.7	596.3	600.1	715.7	716.6	718.0	718.5	608.6	615.1	624.2	624.9
	120	533.0	580.9	591.9	597.4	711.7	707.0	708.4	708.8	609.5	618.3	622.3	622.8
	145	528.9	573.0	582.0	584.6	702.7	698.2	700.0	700.5	608.7	610.5	612.5	613.0
	170	509.9	558.2	567.0	570.5	689.2	686.8	689.0	689.7	601.2	601.7	604.1	604.8
	195	487.2	541.2	553.5	558.0	674.7	675.0	678.0	678.9	589.7	590.5	593.5	594.4
	220	461.3	524.9	537.2	542.5	659.8	663.1	666.7	667.9	576.2	579.2	582.8	583.9
	245	432.2	505.6	520.5	526.9	644.5	650.9	655.4	656.7	562.0	567.6	571.9	573.2
	270	399.6	485.9	503.7	511.0	629.4	639.0	644.1	645.5	547.3	555.9	561.0	562.5

[†] Full fertilization; starter plus sidedress on June 15; starter plus sidedress on June 22; and starter plus sidedress on June 29 for Kingsbury (KFull; K615; K622; K629); Colonie (CFull; C615; C622; C629); and Honeoye (HFull; H615; H622; H629).

The difference in private and social returns between full vs. starter plus sidedress fertilization was minimal for Colonie and Honeoye during low June precipitation years, with full fertilization having higher net returns than starter-only fertilization due to the cost savings from the second field operation. However, under high June rainfall accumulation on soils with high clay content, average social return under full fertilization proved to be lower than starter plus sidedress application. For all soil types, applying more than 120 kg N ha^{-1} of N fertilizer did not increase yield and revenue, instead, N > 120 kg ha^{-1} negatively affected the environment and private net revenue. Evidently, findings from this study encourage farmers to: 1) use sidedress applications and delay fertilization to as late as possible during the season, and 2) limit the amount of N fertilizer applied in the field, especially on clay soils under wet conditions.

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