Environmental Modelling & Software 72 (2015) 56–70

Contents lists available at ScienceDirect

Environmental Modelling & Software

journal homepage: www.elsevier.com/locate/envsoft

Evaluating four nitrous oxide emission algorithms in response to N rate on an irrigated corn field

Q.X. Fang [a, **], L. Ma [b, *], A.D. Halvorson [c], R.W. Malone [d], L.R. Ahuja [b], S.J. Del Grosso [c], J.L. Hatfield [d]

[a] *Qingdao Agricultural University, Qingdao, China*
[b] *USDA-ARS, 2150 Centre Ave. Bldg. D, Ste.200, USDA-ARS, Fort Collins, CO, USA*
[c] *USDA-ARS, 2150 Centre Ave. Bldg. D, Ste.100, Fort Collins, CO, USA*
[d] *USDA-ARS National Laboratory for Agriculture and the Environment, Ames, IA, USA*

ARTICLE INFO

Article history:
Received 15 October 2014
Received in revised form
15 June 2015
Accepted 16 June 2015
Available online xxx

Keywords:
RZWQM
Daycent
WNMM
NOE
FASSET
Greenhouse gas emission

ABSTRACT

In this study, the RZWQM2 (Root Zone Water Quality Model) was used to simulate the responses of N_2O emissions to different Nitrogen application rates on an irrigated corn field from 2003 to 2006, in eastern Colorado, USA. Four different algorithms from the literature were coupled with RZWQM2 and compared for simulating N_2O emissions during nitrification and denitrification processes. The RZWQM2 was first calibrated for corn yield, N uptake, soil water (0–10 cm) and soil Nitrate-N content (0–180 cm) and the simulated daily nitrification and denitrification rates were used to calculate N_2O emission using the algorithms from DAYCENT, NOE (Nitrous Oxide Emissions),WNMM (Water and Nitrogen Management Model), and FASSET models. The best N_2O emission was simulated when the fraction of N_2O release from nitrification was modified by water filled pore space (WFPS) as in the NOE model and the fraction N_2O release from denitrification was adopted from the DAYCENT model.

1. Introduction

Agricultural production systems are major source of nitrous oxide (N_2O) emissions (Mosier et al., 1998; Syakila and Kroeze, 2011), and contribute 10–12% of global greenhouse gas (GHG) emissions (Smith et al., 2007). The main drivers of N_2O emissions are agricultural soil amendments and management, such as mineral N fertilizers, manure, irrigation, tillage, crop residues, and N_2-fixing crops (Bøckman and Olfs, 1998). In the USA, agricultural soil management contributed about 75% of total N_2O emissions in 2012 (http://epa.gov/climatechange/ghgemissions/gases/n2o.html), and mitigating N_2O emissions can be accomplished through improved agricultural management practices, especially for N fertilizer, irrigation and tillage (Bøckman and Olfs, 1998; Halvorson et al., 2008, 2010, 2012).

N_2O emissions show high variability in space and time in a field due to the complex changes in soil temperature, water, nitrogen and carbon availability (Parton et al., 1996, 2001; Bouwman et al., 2002a,b), associated with the variability in soil, climate, cropping systems, and management practices (Liebig et al., 2005; Snyder et al., 2009; Halvorson et al., 2010). Therefore, correct assessment of N_2O emissions from an agricultural field requires high frequencies of spatial and temporal measurements of the driving variables which is impractical to do. A reasonable assessment requires field and laboratory measured data under typical controlled conditions, along with spatial and temporal model simulations across a wide range of environmental and soil conditions (Frolking et al., 1998; Li et al., 2005; Whittaker et al., 2013).

Many process-based simulation models have been developed for understanding agricultural ecosystem carbon and nitrogen biochemical cycle and the response of N_2O emissions to different agricultural managements (Chen et al., 2008; Pattey et al., 2007; Perlman et al., 2013; Necpálová et al., 2015; Qin et al., 2013). Most commonly used models are APSIM (McCown et al., 1996), DNDC (Li et al., 1992), DAYCENT (Parton et al., 1998; Del Grosso et al., 2000), Ecosys (Grant and Pattey, 1999), ExpertN (Engel and Priesack, 1993), FASSET (Olesen et al., 2002), NASA-Ames version of the CASA (Carnegie-Ames-Stanford approach) model (Potter et al., 1997), NOE (Henault et al., 2005), RZWQM (Ahuja et al., 2000) and WNMM

* Corresponding author.
** Corresponding author.
E-mail addresses: fangqx@igsnrr.ac.cn (Q.X. Fang), Liwang.Ma@ARS.USDA.GOV (L. Ma).

http://dx.doi.org/10.1016/j.envsoft.2015.06.005
1364-8152/Published by Elsevier Ltd.

(Li et al., 2007). The denitrification process in these models is calculated as a function of soil nitrate-N content, soil water content, soil temperature and soil pH (Heinen, 2006), except for DAYCENT where denitrification rate was a function of soil heterotrophic respiration rate, soil nitrate-N and water content (water filled pore space, WFPS), but not soil temperature which controls heterotrophic respiration indirectly. Similar relationships were also used to estimate nitrification in these models. Some models include soil nitrifier or denitrifier populations for estimating nitrification or denitrification (such as DNDC, ecosys, and RZWQM), whereas others do not directly consider microbial involvement (such as NOE, ExpertN, FASSET, and WNMM). In all these models, the denitrification and nitrification rates are estimated as a zero or first order kinetics function of nitrate substrates (Chen et al., 2008). N_2O emissions are assumed to occur during both nitrification and denitrification.

The algorithms for estimating N_2O emissions from nitrification and denitrification also differ among the models. For most models, N_2O emissions from nitrification is estimated as a proportion of nitrification amount (0.1%–2%), which is further regulated by soil water content (such as in NOE model) or temperature (DNDC) or both (such as FASSET and WNMM). While other models such as APSIM, DACENT, ExpertN and NASA-CASA use a fixed proportion of nitrification to estimate N_2O emissions (Frolking et al., 1998). Recently, Bessou et al. (2010) improved the NOE model for predicting N_2O emission from nitrification using an index of anoxia for N_2O emission, based on laboratory results (Khalil et al., 2004). For predicting N_2O emissions from denitrification, ratios of N_2 to N_2O and NO to N_2O are used in combination with the denitrification rate in the APSIM, DACYENT, and ExpertN models, which are further modified by soil nitrate-N content, soil respiration and WFPS. In DNDC, WNMM and NOE models, a simple fraction of denitrification, as a function of WFPS, oxygen availability or soil clay content, is used to estimate N_2O emission during denitrification process.

Studies have shown mixed model performance in simulating N_2O emissions under different climate and management conditions (Frolking et al., 1998; Li et al., 2005; Villa-Vialaneix et al., 2012; Vogeler et al., 2013). Comparisons of the different N_2O emission algorithms can improve our understanding of N_2O emissions. The various N_2O emission algorithms showed different responses to the environmental factors, such as soil temperature and moisture, and produced very different N_2O emissions predictions even under similar nitrogen cycle simulations (Frolking et al., 1998; Li et al., 2005). Recent DAYCENT model simulations of 6 cropland and 3 grassland sites in the United Kingdom showed that N_2O emissions were sensitive to soil pH and clay content, particularly when the initial values for these model inputs were low (Fitton et al., 2014). Regarding internal model parameters, Necpálová et al. (2015) found that N_2O emissions were sensitive to parameters controlling soil heat flux, the temperature effect on soil organic matter decomposition rates, and crop growth rates. Vogeler et al. (2013) compared APSIM and DNDC models and found that soil temperature had a larger effect on nitrification in APSIM model, while soil water content had more effect on nitrification in the DNDC model. In another study with measured N_2O data at five temperate agricultural sites from three countries, correct simulation of soil water content was essential for predicting N_2O emissions for the CENTURY, DNDC, ExpertN, and NASA-Ames version of CASA models (Frolking et al., 1998). They also found that the CENTURY and ExpertN models produced better simulations of surface soil water, soil nitrate-N, and N_2O emissions than the DNDC model. In the North China Plain, Li et al. (2005) compared the N_2O emission modules from WNMM, DAYCENT, and DNDC, where other processes (such as soil water and crop growth) except for nitrification and denitrification were simulated by WNMM model, and found better simulations of N_2O emissions by WNMM model than by DAYCENT and DNDC models at two sites in the region. These comparisons of N_2O emission simulations depended on both N_2O emission algorithms and the simulations of nitrification and denitrification by WNMM model. An inter-comparison among these different N_2O emissions algorithms from different models is only valid when simulations of all other variables, including soil water, nitrate, N uptake and crop yield, and soil nitrification and denitrification, are the same. Such inter-comparison can help assess and refine these N_2O emission algorithms, and improve our understanding of the response of N_2O emissions to different environmental factors. In addition, the above simulation studies only considered N_2O emissions in the top soils (0–20 cm), and assumed no or little contribution from the deeper soil, and did not consider the gas diffusion path to the surface soil, although there exist different N_2O emission models that conceive N_2O transport both in the liquid and gaseous phase of soil (Grant et al., 2006; Klier et al., 2011; Blagodatsky and Smith, 2012). Studies have shown that considering the N_2O emissions from deep soil layers and gas diffusions can improve the N_2O simulations (Xing et al., 2011; Chatskikh et al., 2005).

In this study, the main objective was to evaluate several algorithms for N_2O emissions during nitrification and denitrification using processes as simulated by RZWQM2, under different weather and management conditions. The different algorithms for N_2O emissions were inter-compared based on RZWQM2 simulated soil water, nitrogen dynamics, crop yield, N uptake, nitrification and denitrification rates. The N_2O emission simulations from the shallow soil layer (0–20 cm) and deep soil layer (0–60 cm) with gas diffusions were compared. The effects of soil water and soil nitrate-N on N_2O emissions were also evaluated. Different from previous model comparison studies, this study investigated different N_2O emission algorithms using the same nitrification and denitrification rates as simulated by RZWQM2.

2. Materials and methods

2.1. Nitrification and denitrification processes in RZWQM2

RZWQM2 (Root Zone Water Quality Model) is a comprehensive agricultural system model and has process-level simulations of soil water, soil temperature, plant growth, pesticide fate and soil C and N dynamics as influenced by various agricultural management practices (Ahuja et al., 2000). This model has been applied to assess the effect of various alternative agricultural managements on crop production and environmental quality across different climate and soil conditions (Ahuja et al., 2002; Fang et al., 2008, 2010; Ma et al., 2012).

The RZWQM2 model simulates the major processes in soil C/N dynamics, such as mineralization, immobilization, nitrification, denitrification and methane production. It has two surface residue pools, three humus pools and three microbial pools (Ma and Shaffer, 2001; Ahuja and Ma, 2002). Nitrification is a biological process under aerobic conditions, and the major factors controlling nitrification are soil NH_4–N concentration, soil water content, soil temperature, and soil pH (Malhi and McGill, 1982; Parton et al., 1996). Denitrification is a microbial process that occurs under anaerobic soil conditions, and the important controlling factors to this process are soil water content (or water-filled pore space, WFPS), soil NO_3–N, and available soil C (Firestone and Davidson, 1989; Weier et al., 1993). In the RZWQM2, a zero-order kinetics is used for nitrification rate (R_{nit}, Eq. (1)) and a first-order kinetics is used for dentification rate (R_{den}, Eq. (2)). The corresponding zero- and first-order rate coefficients are:

$$R_{nit} = F_{aer} \times \left(\frac{k_b T}{h_p}\right) \times A_{nit} \times \exp\left(-\frac{E_{an}}{R_g T}\right) \times \frac{[O_2]^{0.5}}{\left[H^{kh}\gamma_1^{kh}\right]} \times P_{aut} \quad (1)$$

$$R_{den} = F_{anaer} \times \left(\frac{k_b T}{h_p}\right) \times A_{den} \times \exp\left(-\frac{E_{den}}{R_g T}\right) \times \frac{C_s}{\left[H^{kh}\gamma_1^{kh}\right]} \times P_{ana} \quad (2)$$

$$F_{aer} = \begin{cases} 0.75 \times \mathrm{WFPS}, & \text{if WFPS} \le 0.2 \\ 0.253 + 2.03 \times \mathrm{WFPS}, & \text{if } 0.2 < WFPS < 0.59 \\ 41.1 \times \exp(-6.25 \times \mathrm{WFPS}), & \text{if WFPS} \ge 0.59 \end{cases} \quad (3)$$

$$F_{anaer} = \begin{cases} 0, & \text{if WFPS} < 0.60 \\ 0.000304 \times \exp(8.15 \times \mathrm{WFPS}), & \text{if WFPS} \ge 0.60 \end{cases} \quad (4)$$

$$WFPS = \frac{SW}{PO} \quad (5)$$

where F_{aer} and F_{anaer} are soil water effects (Ma et al., 2001; Linn and Doran, 1984); k_b is the Boltzman constant (1.383×10^{-23} J K^{-1}); T is soil temperature (K); h_p is the Planck constant (6.63×10^{-34} J s); R_g is the universal gas constant (1.99×10^{-3} kcal mol^{-1} K^{-1});E_{nit} and E_{den} are the apparent activation energy for nitrification and denitrification processes, respectively; A_{nit} and A_{den} are nitrification and denitrification rate coefficient (s day^{-1} $organism^{-1}$), and have calibrated values of 1.0×10^{-9} and 1.0×10^{-13} s day^{-1} $organism^{-1}$, respectively; $[O_2]$ is oxygen concentration in soil water with assumption that oxygen in soil air is not limited (Moles O_2 per liter pore water); H is hydrogen ion concentration (moles H per liter pore water); kh is hydrogen ion exponent for decay of organic matter microbes (organisms g^{-1}soil); γ_1 is the activity coefficient for monovalent ions ($1/\gamma_1^{kh} = 3.1573 \times 10^3$ if pH > 7.0 and = 1.0 if pH ≤ 7.0); C_s is weighted carbon in the soil (ug C g^{-1} soil); P_{aut} is the autotrophic biomass population (nitrifiers) (# organisms g^{-1} soil, minimum 500, default value 1000); P_{ana} is population of anaerobic microbes (# organisms g^{-1} soil, minimum 5000, default value 10000); SW is soil water content (cm^3 cm^{-3}); PO is soil porosity (cm^3 cm^{-3}); PO = 1-BD/2.65, where BD is soil bulk density (g cm^{-3}) and 2.65 is particle density (g cm^{-3}). The microbial populations are simulated based on the processes they are catalyzed, environmental condition, and soil carbon sources (Shaffer et al., 2000).

To comprehensively quantify the effects of alternative management practices on crop enhanced production and environmental impacts (such as N losses to environments), RZWQM2 must be modified for N_2O emissions from nitrification and denitrification. The existing N_2O emissions algorithms are very different and need to be evaluated with measured data (Shaffer et al., 2000). The algorithms for the N_2O emission modules are described below.

2.2. Algorithms for N_2O emissions during nitrification and denitrification processes

The N_2O was produced as intermediates and/or by-products due to incompletely pathways of nitrification and denitrification (Parton et al., 2001). A number of different approaches have been used to simulate N_2O emissions from agricultural soils (Grant and Pattey, 1999). The following N_2O emission algorithms are simplified process models, where N_2O emissions is estimated based on the nitrification and denitrification rates, as a function of soil water content, soil temperature, or soil nitrate-N levels.

2.2.1. N_2O emission algorithm in DAYCENT model

N_2O emission from nitrification ($N_2O_{\_nit}$) is estimated as

$$N_2O_{\_nit} = Fr_{N_2O\_Nit\_DAYCENT} \times R_{nit} \quad (6)$$

where $Fr_{N_2O\_Nit\_DAYCENT}$ is the fraction of nitrification for N_2O emissions, and a value of 0.02 was used as default in DAYCENT model (Parton et al., 2001; Del Grosso et al., 2001).

N_2O emission from denitrification ($N_2O_{\_den}$) is calculated as following (Del Grosso et al., 2000)

$$N_2O_{\_den} = Fr_{N_2O\_Den\_DAYCENT} \times R_{den} \quad (7)$$

$$Fr_{N_2O\_Den\_DAYCENT} = \frac{1}{1 + R_{NO\_N_2O} + R_{N_2\_N_2O}} \quad (8)$$

$$R_{NO\_N_2O} = 4 + \frac{9 \times \tan^{-1}(0.75 \times \pi \times (10 \times D - 1.86))}{\pi} \quad (9)$$

$$R_{N_2\_N_2O} = \max\left(0.16k1, k1 \times \exp\left(\frac{-0.8[NO3]}{[co2]}\right)\right) \times \max(0.1, 0.015 \times \mathrm{WFPS} \times 100 - 0.32) \quad (10)$$

$$k1 = \max(1.5, 38.4 - 350 \times D) \quad (11)$$

where $Fr_{N_2O\_Den\_DAYCENT}$ is the fraction of denitrification for N_2O emissions; $R_{NO\_N_2O}$ is the ratio of NO to N_2O; $R_{N_2\_N_2O}$ is the ratio of N_2 to N_2O; $[NO_3]$ is soil nitrate-N concentration; D is gas diffusivity in soil (Davidson and Trumbore, 1995); WFPS is water filled pore space.

2.2.2. The N_2O emission algorithm in NOE model

N_2O emissions during nitrification is estimated as

$$N_2O_{\_nit} = Fr_{N_2O\_Nit\_NOE} \times F_{SW\_Nit\_NOE} \times R_{nit} \quad (12)$$

$$F_{SW\_Nit\_NOE} = \frac{0.4 \times \mathrm{WFPS} - 1.04}{\mathrm{WFPS} - 1.04} \quad (13)$$

where $Fr_{N_2O\_Nit\_NOE}$ is the fraction of nitrification for N_2O emissions, and 0.0016 was used as the default value (Bessou et al., 2010); $F_{SW\_Nit\_NOE}$ is the soil water factor for the oxygen availability effect on N_2O emission during nitrification (Khalil et al., 2004).

N_2O emission from denitrification is calculated as following (Bessou et al., 2010)

$$N_2O_{\_den} = r_0 \times F_{N_2O\_Den\_NOE} \times R_{den} \quad (14)$$

$$F_{N_2O\_Den\_NOE} = F_O \times F_N \quad (15)$$

$$F_O = 1 - c_w \times \max(0, WFPS - 0.62) \quad (16)$$

$$F_N = \min(d_{N0}N, (c_N + d_N N), 1) \quad (17)$$

$$d_{N0} = \frac{c_N + d_N N_C}{N_C} \quad (18)$$

where r_0 is maximum ratio of N_2O emission to denitrification rate (default value is 0.63); $F_{N_2O\_DEN\_NOE}$ is the function of WFPS (F_O) and nitrate concentration (F_N) on N_2O emission during denitrification, including the five parameters (C_w = 2.05, C_N = 0.44, d_N = 0.0015, N_c = 3 mg l^{-1}, and N is soil nitrate-N concentration (mg N kg^{-1})) according to Bessou et al. (2010) and Khalil et al. (2005).

2.2.3. N_2O emission algorithm in WNMM

N_2O emissions from nitrification is estimated as

$$N_2O_{\_nit} = Fr_{N_2O\_Nit\_WNMM} \times F_{T\_Nit\_WNMM} \times F_{SW\_Nit\_WNMM} \times R_{nit} \tag{19}$$

$$F_{T\_Nit\_WNMM} = 0.9 \times \frac{t}{t + \exp(9.93 - 0.312t)} + 0.1 \tag{20}$$

$$F_{SW\_Nit\_WNMM} = \begin{cases} \dfrac{SW - WP}{SW25 - WP}, & \text{when } SW < SW25 \\ 1.0, & \text{when } SW25 \le SW \le FC \\ 1 - \dfrac{SW - FC}{PO - FC}, & \text{when } SW > FC \end{cases} \tag{21}$$

where $Fr_{N_2O\_Nit\_WNMM}$ is the fraction of nitrification for N_2O emission (default value is 0.002); $F_{T\_Nit\_WNMM}$ and $F_{SW\_Nit\_WNMM}$ are the functions of soil temperature (t, °C) and water content factors for N_2O emission by nitrification; SW is soil water content ($cm^3\ cm^{-3}$); WP is wilting point ($cm^3\ cm^{-3}$); $SW25 = WP + 0.25(FC - WP)$; FC is field capacity ($cm^3\ cm^{-3}$) (Li et al., 2007)

N_2O emissions from denitrification is estimated as

$$N_2O_{\_den} = \begin{cases} 0.05 \times R_{den}, & \text{when WFPS} \ge 1.0 \\ 0.5 \times R_{den} \times (1 - F_{SW\_den\_WNMM}), & \text{when WFPS} < 1 \end{cases} \tag{22}$$

$$F_{SW\_den\_WNMM} = \exp(-23.77 + 23.77 \times WFPS) \tag{23}$$

where $F_{SW\_den\_WNMM}$ is the soil water factor for N_2O emissions during denitrification.

2.2.4. N_2O emission algorithm in FASSET model

Potential N_2O production (N_2O_{Pot}) is first estimated as

$$N_2O_{Pot} = Fr_{Nit\_FASSET} \times F_{T\_Nit\_FASSET} \times F_{SW\_Nit\_FASSET} \times R_{nit} + R_{den} \tag{24}$$

$$F_{T\_Nit\_FASSET} = \min\left(1, \exp\left(-0.5 \times \left(\frac{t - 2 \times 17.1}{17.1}\right)^2\right)\right) \tag{25}$$

$$F_{SW\_Nit\_FASSET} = WFPS = \frac{SW}{PO} \tag{26}$$

where Fr_{Nit_FASSET} is the fraction of nitrification for N_2O emission (default value is 0.047); $F_{T\_Nit\_FASSET}$ and $F_{SW\_Nit\_FASSET}$ are soil temperature (t, °C) and water content factors for N_2O emissions during nitrification.

The actual N_2O emission estimation (N_2O_{Act}) is calculated as

$$N_2O_{Act} = N_2O_{Pot} \times F_{T\_N_2O\_FASSET} \times (1 - F_{sw\_N_2O\_FASSET}) \times F_{clay\_N_2O} \times F_{depth\_N_2O} \tag{27}$$

$$F_{T\_N_2O\_FASSET} = \frac{1}{(1 + \exp(-0.64 + 0.08 \times t))} \tag{28}$$

$$F_{SW.N_2O.FASSET} = \max\left\{0, \min\left(1, 0.0116 + \frac{1.36}{1 + \exp\left(-\frac{\frac{SW}{PO} - 0.815}{0.0896}\right)}\right)\right\} \tag{29}$$

$$F_{clay\_N_2O} = \max(0, \min(1,\ 1.26 \times \exp(-0.0116 \times Clay - 0.249))) \tag{30}$$

$$F_{depth\_N_2O} = \max\left(0, \min\left(1,\ 1.0008 - 0.0343 \times depth - 3.186 \times depth^2\right)\right) \tag{31}$$

where $F_{T\_N_2O\_FASSET}$ and $F_{sw\_N_2O\_FASSET}$ are the factors of soil temperature (t, °C) and soil water for N_2O emissions; $F_{clay\_N_2O}$, and $F_{depth\_N_2O}$ are the N_2O diffusion factors as affected by clay content (Clay) and soil depth (depth, m), respectively. The diffusion factor for N_2O emission decreased to 0 at soil depth of 60 cm based on the Eq. (31). Detailed information can be referred Chatskikh et al. (2005).

2.2.5. Comparisons of the above N_2O emission algorithms

Among the four models, different environmental factors, such as these involving soil water content and soil temperature, were used for calculating N_2O emissions. For example, the DAYCENT model used a simple fixed proportion (default value is 0.02) to estimate N_2O emission from nitrification, while the NOE, WNMM and FASSET models included the factors of soil temperature and soil water content for estimating N_2O emission from nitrification. For estimating N_2O emission from denitrification, the ratio of N_2/N_2O and NO/N_2O as influenced by soil water content was used in the DACYENT model, while the NOE, WNMM and FASSET models used the factors of soil temperature, soil water content and soil nitrate-N content to estimate N_2O emission from denitrification. In the FASSET model, the N_2O emissions from the deep soil depth (0–60 cm) and gas diffusions across the soil layers were considered (Eq. (30) and Eq. (31)), while the DAYCENT, NOE and WNMM models calculated N_2O emissions from the 0–20 cm soil layers only and did not consider the N_2O emission from deeper soil layers and gas diffusions across soil depths.

In addition, the responses of N_2O emissions to soil water content (WFPS) and soil temperature during nitrification and denitrification are also different among these models (Fig 1). For example, the N_2O emission during nitrification (Fig. 1A) decreased on both sides of the optimum soil water levels (Eq. (21) and Eq. (29)) in WNMM and FASSET model, but increased continuously with increased WFPS in the NOE model (Eq. (13)), whereas the DAYCENT model used a fixed parameter (fraction) for N_2O emission from nitrification (Eq. (6)). The N_2O emissions during denitrification generally decreased with increased WFPS in the NOE, FASSET, and WNMM models (Eq. (16), Eq. (23) and Eq. (29)), but showed a bell shape with an optimum level in DAYCENT model, where ratios of N_2/N_2O and NO/N_2O were used for estimating N_2O emission from denitrification (Eq. (10)). In the FASSET model, the N_2O emission during both nitrification and denitrification decreased with soil temperature (Eq. (28)), but increased with soil temperature in the WNMM model (Eq. (20)). The N_2O emissions were not directly affected by soil temperature in DAYCENT and NOE models.

2.3. Field experiments and measurements

The experiment was conducted in a clay loam soil (fine-loamy, mixed, superactive, mesic Aridic Haplustalfs) at the Agricultural Research Development and Education Center (ARDEC) (40°39′6″ N, 104°59′57″ W; 1555 m above sea level) near Fort Collins, CO. The annual precipitation was 23.06 cm, 22.89 cm, 29.64 cm and 11.68 cm for year 2003, 2004, 2005 and 2006. The field had been continuously cropped to corn using a conventional system (Halvorson et al., 2006). The corn was sprinkler-irrigated with a linear-move system as needed determined weekly by the feel

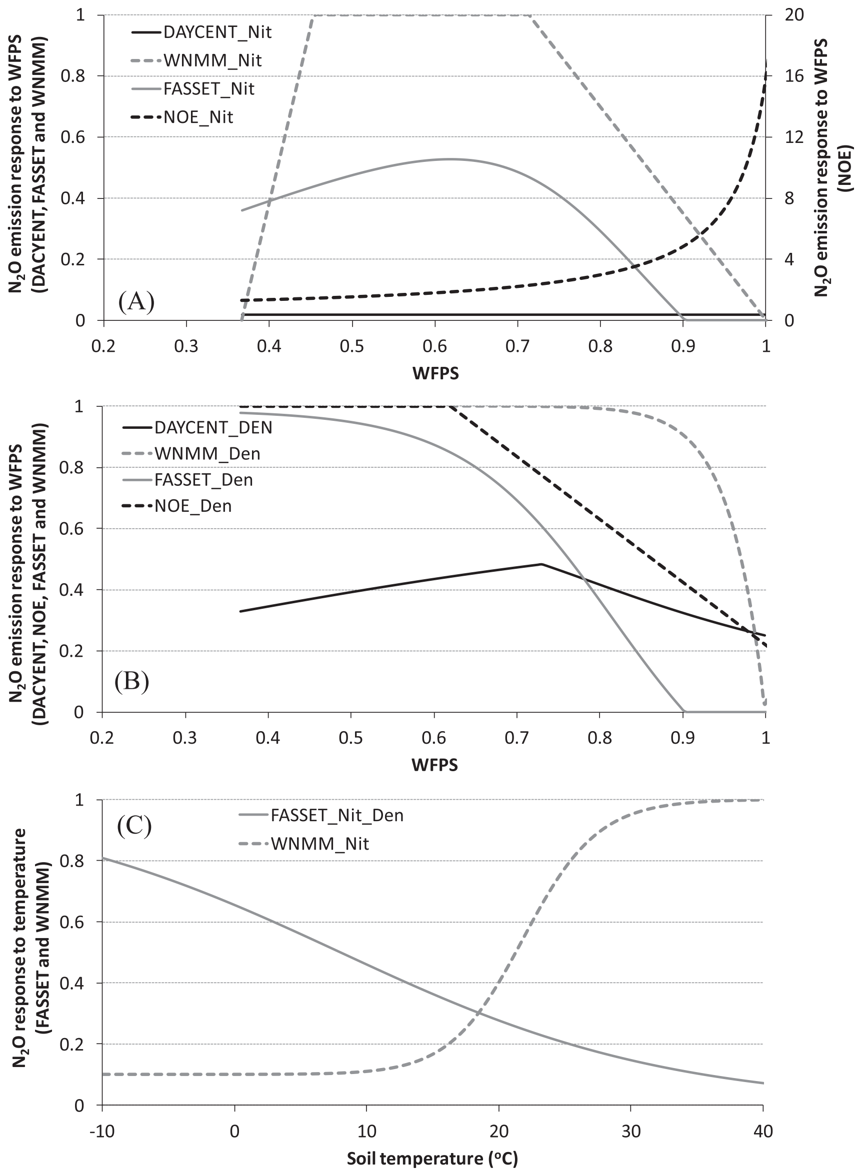

Fig. 1. The Effects of WFPS (water filled pore space) on N_2O emissions during nitrification (A: Eq. (6) for DAYCENT model; Eq. (13) for NOE model; Eq. (21) for WNMM model; Eqs. (26) and (29) for FASSET) and denitrification (B: Eq. (8) for DAYCENT model; Eq. (16) for NOE model; Eq. (23) for WNMM model; Eq. (29) for FASSET model), and the effect of soil temperature on N_2O emissions during nitrification and denitrification (C: Eq. (20) for WNMM model; Eq. (28) for FASSET model) in these algorithms from the four models (DAYCENT, NOE, WNMM and FASSET).

method (Klocke and Fischbach, 1998) during the growing season. Total irrigation amounts were 41.16 cm for 2003, 36.21 cm for 2004, 38.77 cm for 2005, and 40.28 cm for 2006.

Four N rates (0, 67, 134, and 202 kg N ha^{-1} referred to as N0, N67, N134, N202, respectively) were designed with three replicates under the conventional tillage (CT) system. The same rate of N was applied to the same plots each year with the exception of the N202 treatment. Due to only a minimal grain yield response to N fertilization at the 202 kg N ha^{-1} application rate in 2000, the fertilizer N rate for N202 treatment was reduced to 168 kg N ha^{-1} in 2001, increased to 202 kg N ha^{-1} in 2002, and then increased to 224 kg N ha^{-1} in 2003 and 2004 and 247 kg N ha^{-1} in 2005 and 2006. The N source was UAN (32-0-0), which was applied with a liquid fertilizer applicator that banded the N about 5 cm below the soil surface in bands spaced 33 cm apart (parallel to the corn row, but at varying distance from the corn row) the day before corn planting. Starter P and K fertilizer was applied directly with the seed at planting except in 2001. The detailed information on the experiment can be found in Halvorson et al. (2006).

Corn hybrid brands varied with year, but had similar genetic characters, e.g., DeKalb DkC44-46 RR/YGCB for 2003, Pioneer 38 PO4 LL for 2004, Pioneer 38 PO3 RR for 2005, Pioneer 38 P10 RR for 2006 (Jantalia and Halvorson, 2011) was planted with a 76 cm row spacing during end of April from 2000 to 2006. Planting rates were approximately 84,000 seeds ha^{-1} in 2000, 2003, 2004, 2005, and 2006; 91,000 seeds ha^{-1} in 2001; and 96,000 seeds ha^{-1} in 2002. Corn hybrid was changed from year to year to allow herbicide rotation and to replace older hybrids that were no longer available. Herbicides were applied for weed control, and the plots were essentially weed free during the study period.

Corn grain yields were generally determined in late October each year by hand-harvesting the ears from an 11.6 m^2 area of each plot. Aboveground corn biomass was determined in September each year by hand-harvesting 15 whole corn plants from a 1.5 m^2 or larger area from each plot. The plants were separated into grain, cobs, and stover for mass determination. Soil NO_3—N levels in the

0–180 cm profile were monitored from 2000 through 2006 using a continuous-flow analyzer (Lachat QuickChem FIA+8000 Series). The N content in grain and crop residue was analyzed using a Carlo Erba C/N analyzer (Haake Buchler Instruments, Inc., Saddle Brook, NJ) from 2000 through 2003 and an Elementar vario Macro C–N analyzer (Elementar Americas, Inc., Mt. Laurel, NJ) from 2004 through 2006. Detailed information on the experiment can be referred in Halvorson et al. (2006);

Measurement of the soil–atmosphere exchange of N_2O were made during corn growing season, following the same procedures reported by Mosier et al. (2006). Measurements were generally made one to three times per week during the growing seasons, midmorning of each sampling day. A vented, non-steady-state, closed chamber technique was used (Livingston and Hutchinson, 1995). The daily N_2O emissions were estimated between sampling days using a linear interpolation between adjacent sampling dates. The detailed information on the N_2O emission measurement and calculations can be found in Halvorson et al. (2008, 2010). Soil water content at 0–10 cm depth (soil dielectric constant ECH2O probes, Decagon Devices, Pullman, WA) and soil temperature at 5 cm depth (temperature probe HH21, digital thermometer from Omega Engineering, Stamford, CT) were monitored at most trace gas sampling events. The profile soil water in 0–180 cm depth was also measured before planting and after harvesting each year from 2000 to 2006.

2.4. RZWQM2 calibrations and N_2O emission algorithms comparisons

The RZWQM2 model was first calibrated for soil water content, soil temperature, soil nitrate-N, crop yield, above-ground biomass and crop N uptake using the measured data from the N202 treatment. Data from other treatments (N0, N67, and N134) were used for evaluation. After calibration and evaluations, the N_2O emissions were calculated from RZWQM2 simulated nitrification and denitrification rates based on the different N_2O emission algorithms for the four N treatments from 2003 to 2006.

Specifically, the four algorithms of N_2O emissions from DAYCENT, NOE, WNMM and FASSET were compared for their performance in simulating N_2O emissions based on other variables, such as soil water content, soil temperature, soil nitrate-N content and nitrification/denitrification rates as simulated by the calibrated RZWQM2.

First, the default parameter values for each algorithm (Table 1) were used to estimate N_2O emissions on each day. Secondly, we adjusted the default parameters in these algorithms based on measured daily or seasonal N_2O emissions from 2003 to 2006. Since the N_2O emissions from nitrification produced much more emissions than denitrification in the semiarid region (Mosier et al., 1996), the parameters related to N_2O emissions from nitrification were the main focus in this study (Table 1). Thirdly, we compared the simulated N_2O emissions from the top soil (0–20 cm) and from deep soil (0–60) using the N_2O diffusion equations from FASSET model (Eq. (31)). Finally, we evaluated the response curve of N_2O emissions to soil water content (WFPS) and soil temperature from the different models to further improve N_2O emission simulations.

2.5. Evaluation criteria

To evaluate the performance of RZWQM2 model in simulating daily soil water content, seasonal soil nitrate-N and crop yield and N uptake, the root mean square error (RMSE), coefficient of determination (r^2), mean difference (MD) and model efficiency (ME) were used with comparison graphs between measured and simulated data (Fang et al., 2014).

To compare the different N_2O algorithms, the RMSE and r^2 were used to evaluate the simulated daily or seasonal N_2O emissions. We also investigated the seasonal N_2O emissions and peak N_2O emission in response to 1) weather variations (seasonal variations from 2003 to 2006) and 2) N application rates (4 N treatments).

3. Results and discussion

3.1. RZWQM2 calibration and evaluations

Because the measured soil temperature at 5 cm depth and soil water contents in 0–10 cm depth were similar among the N treatments due to similar irrigation amounts and rainfall, we averaged these variables from the four treatments as shown in Fig. 2. Detailed statistic comparisons between all measured and simulated values for the calibration and validation datasets were presented in Table 2.

As showed in Fig. 2, the simulated average soil water content in the 0–10 cm depth followed similar trends with measured data averaged from the four treatments. The low standard deviations among these N treatments indicated that similar soil surface water contents were obtained among these treatments with similar irrigation amounts. However, obvious under-simulations of soil surface water content occurred in 2003, and slight over-simulations of surface soil water content were obtained in 2005. The measured abnormally high soil water contents (0.33–0.35 $cm^3\ cm^{-3}$, near the field water capacity) in the 0–10 cm depth during May–June in 2003 were mainly due to the precipitation of 4.3 cm during 23–24 April (N application and planting date) and 5.0 cm during 8–10 May (Halvorson et al., 2014). The RZWQM2 also under-simulated soil water content in the surface layer (0–15 cm) in an earlier study when soil was extremely wet following irrigation and rainfall in an irrigated corn field (Cameira et al., 1998). Although, the model did not capture the above measured soil water content data, it simulated similar whole profile soil water storage (0–180 cm) of 51.7 cm to measured value of 52.3 cm on 7 May in 2003, which suggested that the model simulated faster movement of soil water through the soil profile during the wet seasons.

During the calibration with N202 treatment from 2003 to 2006, the model slightly over-simulated soil water content by 0.001 $cm^3\ cm^{-3}$ (MD value), with RMSE and r^2 values of 0.04 $cm^3\ cm^{-3}$ and 0.14 (Table 2). The simulated profile soil water

Table 1
Calibrating the N_2O emission fractions from DAYCENT, NOE, WNMM and FASSET models based on RZWQM2 simulated nitrification and denitrification rates from the 0–20 cm depth or from the 0–60 cm depth with gas diffusions across soil and measured data for the four N treatments from 2003 to 2006.

Models	Fraction of nitrification for N_2O emissions				Fraction of denitrification for N_2O emissions			
	Default values	Range	Calibration for 0–20 cm	Calibration for 0–60 cm	Default values	Range	Calibration for 0–20 cm	Calibration for 0–60 cm
DAYCENT	0.02	0.001–0.02	0.008	0.0065	N/A	N/A	N/A	N/A
NOE	0.0016	0.001–0.1	0.005	0.006	0.63	0.25–1	0.63	0.7
WNMM	0.002	0.001–0.1	0.03	0.04	0.5	0.25–1	0.2	0.6
FASSET	0.047	0.001–0.1	0.05	0.05	N/A	N/A	N/A	N/A

N/A means not applicable.

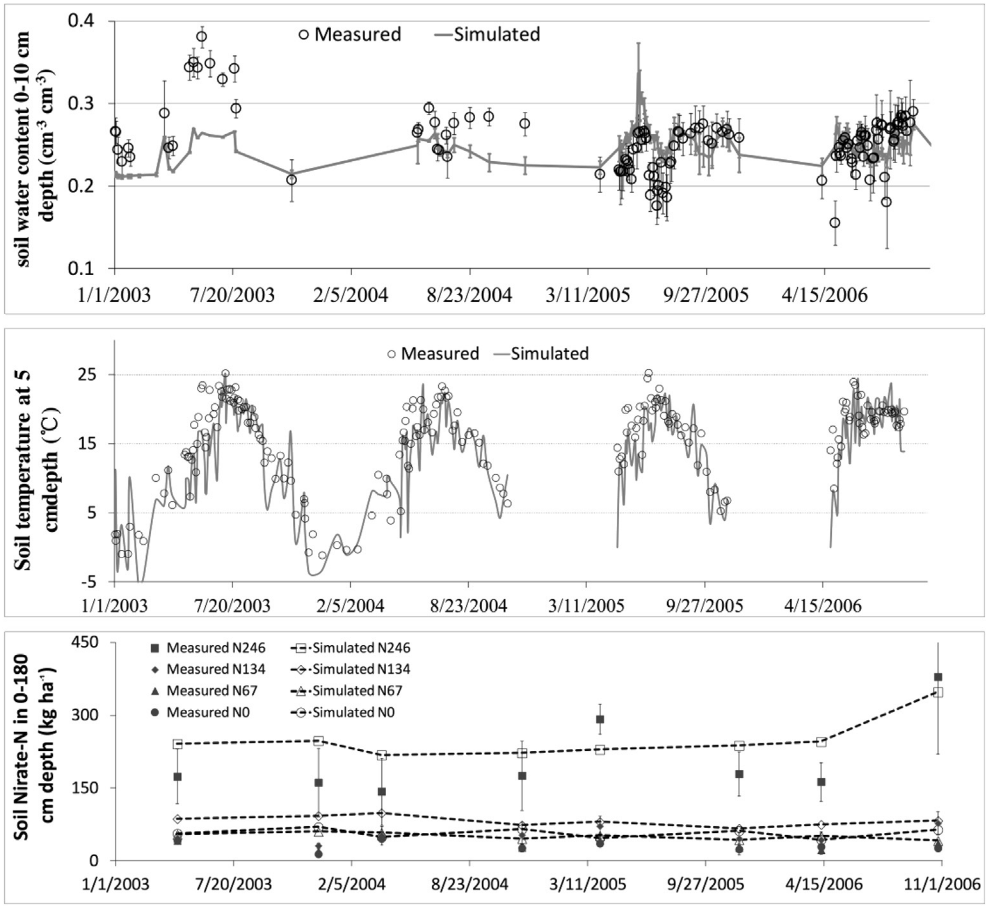

Fig. 2. Comparison between measured and simulated soil water content in the 0–10 cm depth, soil temperature at the 5 cm depth averaged from the four N treatments (N202, 168–246 kg N ha^{-1}; N134, 134 kg N ha^{-1}; N67, 67 kg N ha^{-1}; N0, 0 kg N ha^{-1}) and the soil nitrate-N content in the 0–180 cm depth for the four N treatments from 2003 to 2006.

storage in the 0–180 cm depth was close to measured values with RMSE and r^2 values of 0.72 cm and 0.59 (Table 2). The soil temperature at 5 cm depth was under-simulated by 1.2 °C, with RMSE and r^2 values of 3.6 °C and 0.74 (Table 2). These results were comparable with previous simulation studies for RZWQM2 (Fang et al., 2010) and other models (Li et al., 2005). The under-simulations of soil temperature mainly occurred during early stages of corn growth from May to July (Fig. 2), which may be partly due to the air temperature used by RZWQM2 as soil surface boundary condition. Another reason is that RZWQM2 outputs daily

Table 2
Statistics (MD, mean difference; RMSE, root mean square error; ME, model efficiency; r^2, coefficient of determination) results for the RZWQM2 simulated soil water content, soil nitrate-N content, soil temperature at 5 cm depth, crop yield, biomass and N uptake from 2003 to 2006 during calibration (N202, 168–246 kg N ha^{-1}) and validation (N134, 134 kg N ha^{-1}; N67, 67 kg N ha^{-1} and N0, 0 kg N ha^{-1}).

Variables	Data number	Measured	Simulated	MD	RMSE	ME	r^2
Calibration (N202)							
Profile soil water (cm)	8	51.4	51.5	−0.05	0.72	0.56	0.59
Soil water at 0–10 cm (cm^{-3} cm^{-3})	182	0.26	0.26	0.001	0.04	0.09	0.14
Profile soil nitrate-N (kg ha^{-1})	8	208.6	230.3	21.7	65.3	0.29	0.42
Soil temperature at 5 cm depth (°C)	210	15	13.8	−1.2	3.6	0.64	0.74
Grain yield (kg ha^{-1})	4	9814	8830	−984	1017	−0.03	0.94
Biomass (kg ha^{-1})	4	15,828	15,891	63	1089	0.74	0.75
Grain N uptake (kg N ha^{-1})	4	129.7	153.8	24.1	21	−1.41	0.75
Plant N uptake (kg N ha^{-1})	4	191.3	206.6	15.3	26.2	−0.46	0.34
Validation (N134, N67 and N0)							
Profile soil water (cm)	24	52.5	52.2	−0.37	1.28	0.42	0.67
Soil water at 0–10 cm (cm^{-3} cm^{-3})	556	0.27	0.26	−0.005	0.03	0.06	0.38
Profile soil nitrate-N (kg ha^{-1})	24	39	62	23	28.3	−2.48	0.44
Soil temperature at 5 cm depth (°C)	630	16	14	−2	4.1	0.56	0.84
Grain yield (kg ha^{-1})	12	7663	6825	−838	1178	0.5	0.81
Biomass (kg ha^{-1})	12	13,003	12,668	−335	1304	0.67	0.82
Grain N uptake (kg N ha^{-1})	12	86.6	81.4	−5.2	20.9	0.46	0.67
Plant N uptake (kg N ha^{-1})	12	119.5	107.4	−12.1	23.53	0.63	0.76

soil temperature at midnight whereas measurements were taken during the daytimes. In a recent study, coupling SHAW with RZWQM2 produced more reasonable simulations of soil temperature and crop canopy temperature based on the soil surface energy balance (Fang et al., 2014).

The soil nitrate-N content was over-simulated by 21.7 kg N ha^{-1} (about 10%) for the calibration datasets, with RMSE and r^2 values of 65.3 kg N ha^{-1} (31.3%) and 0.42, respectively (Fig. 2 and Table 2). These simulations with relatively high errors were comparable with previous simulations of soil nitrate-N content in the region (Del Grosso et al., 2008) and in the North China Plain (Fang et al., 2008). Considering the high spatial variability of soil nitrate-N in the field as shown by high standard deviation of the measured data for the N202 treatment (Fig. 2), the above simulation results were acceptable. Crop yield was under-simulated by 984 kg ha^{-1} and above-ground biomass was simulated well with MD value of 63 kg ha^{-1}, and the corresponding RMSE values were 1017 kg ha^{-1} (10.4%) for crop yield and 1089 kg ha^{-1} (6.9%) for above-ground biomass. Grain N uptake and biomass N uptake were over-simulated by 24.1 kg N ha^{-1} and 15.3 kg N ha^{-1}, with RMSE values of 21.0 kg N ha^{-1} (16.2%) and 26.2 kg N ha^{-1} (13.7%), respectively. The above simulations were comparable with previous simulation in the region (Ma et al., 2012) and other areas, such as in North China Plain (Fang et al., 2008, 2010).

For model validation, simulated soil water content, grain yield and N uptake were comparable with those for calibration with similar RMSE values (Table 2). The model also under-simulated crop yield by 838 kg ha^{-1}, and the simulated above-ground biomass was close to measured data across the three N treatments (Fig. 3). On the other hand, the model over-simulated soil nitrate-N by 23.0 kg N ha^{-1} (59%) with RMSE and r^2 values of 28.3 kg N ha^{-1} and 0.44. In a previous simulation study in the North China Plain, the model under-simulated soil nitrate-N by about 50% at the low N treatments (Fang et al., 2008). However, both measured and simulated soil nitrate-N correctly responded to N treatments (Fig. 2). The measured and simulated average soil nitrate-N in the 0–180 cm depth from 2003 to 2006 were 208.6 and 230.3 kg N ha^{-1}, 52.8 and 75.5 kg N ha^{-1}, 33.7 and 50.0 kg N ha^{-1}, and 30.5 and 60.3 kg N ha^{-1} for the N202, N134, N67 and N0 treatments, respectively. The simulated final crop yield and above-ground biomass were close to measured values (Fig. 3), with respective ME values of 0.50 and 0.67 and respective r^2 of 0.81 and 0.82. The above results were similar to those obtained for the calibration dataset, with RMSE values of 1178 kg ha^{-1} (15.4%) and 1304 kg ha^{-1} (10.0%) for grain yield and biomass, respectively (Table 2). The relatively higher RMSE values for grain yield and biomass than previous simulation studies were partly due to the different corn cultivars used in these years while only one set of cultivar parameters was used in the model across the four years (Jantalia and Halvorson, 2011). The grain N uptake and biomass N uptake simulations were also close to measured data (Fig. 3), with r^2 values of 0.67 and 0.76, respectively. These simulations results were similar to previous studies (Fang et al., 2008, 2010; Ma et al., 2012).

3.2. Comparisons of the different N_2O emission algorithms based on the calibrated RZWQM2

When using the default parameter values for the algorithms from the four models (Table 1), the N_2O emissions were over-simulated by using the algorithms from DAYCENT model (more than 50%), and under-simulated by using the algorithms from the NOE, WNMM and FASSET models (70%–90%). The simulated errors were mainly associated with the simulated N_2O emissions from nitrification which is the main contributor to total N_2O emission in the semiarid region (Mosier et al., 1996). In another study, Del Grosso et al. (2008) also found that reducing the fraction of nitrification for N_2O from 2% to 1% improved model performance in simulating N_2O emissions in Colorado. According to the measured data, we specifically decreased the fraction of nitrification for N_2O in the algorithms from DAYCENT model ($Fr_{N_2O\_Nit\_DAYCENT}$ in Eq. (6)) and increased the fraction of nitrification for N_2O emissions in the algorithms from the NOE, WNMM, and FASSET models ($Fr_{N_2O\_Nit\_NOE}$ in Eq. (12); $Fr_{N_2O\_Nit\_WNMM}$ in Eq. (19); Fr_{Nit_FASSET} in

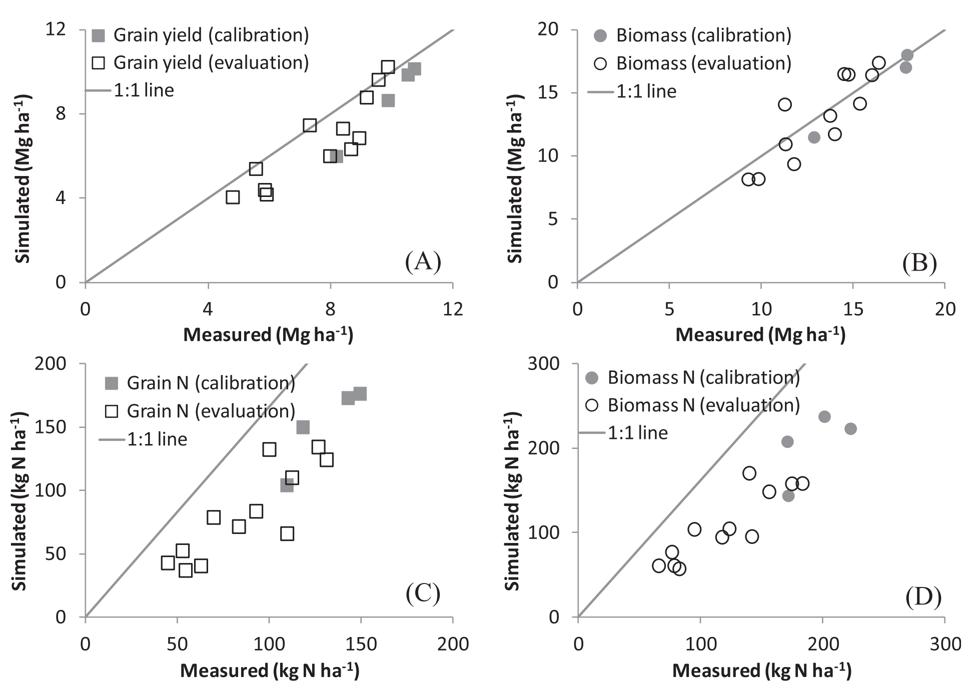

Fig. 3. Measured and simulated corn yield (A), above-ground biomass (B) and N uptake by grain (C) and biomass (D) for the four N treatments (N202, 168–246 kg N ha^{-1}; N134, 134 kg N ha^{-1}; N67, 67 kg N ha^{-1}; N0, 0 kg N ha^{-1}) from 2003 to 2006.

Table 3
Comparisons of measured and simulated daily N_2O emissions (N_2O_M and N_2O_S, g N ha^{-1} day^{-1}) from 2003 to 2006 by the different N_2O emission algorithms from DAYCENT, NOE, WNMM and FASSET models from the 0–20 cm soil depth or the 0–60 cm soil depth with diffusions across the soil layers (RMSE (root mean square error) and r^2 (coefficient of determination) were calculated for each N treatment across 2003 to 2006).

Treatment	N_2O_M	DAYCENT			NOE			WNMM			FASSET		
		N_2O_S	RMSE	r^2	N_2O_S	RMSE	r^2	N_2O_S	RMSE	R^2	N_2O_S	RMSE	r^2
0–20 cm													
N202	7.85	7.41	20.61	0.16	7.56	20.85	0.17	7.28	27.75	0.06	N/A	N/A	N/A
N134	4.75	4.45	14.24	0.11	4.48	14.28	0.11	4.00	18.50	0.04	N/A	N/A	N/A
N67	3.09	2.82	7.69	0.14	2.83	7.60	0.16	2.59	10.93	0.03	N/A	N/A	N/A
N0	1.03	0.99	1.88	0.04	0.99	1.88	0.05	0.9	1.95	0.04	N/A	N/A	N/A
Average	4.18	3.92	11.1	0.11	3.96	11.15	0.12	3.69	14.78	0.04	N/A	N/A	N/A
0–60 cm													
N202	7.85	7.17	15.45	0.19	7.53	15.3	0.20	7.78	23.4	0.07	7.86	15.25	0.18
N134	4.75	3.38	11.17	0.13	3.28	10.92	0.14	3.62	15.76	0.04	3.17	10.77	0.13
N67	3.09	2.07	6.04	0.16	2.00	5.84	0.18	2.28	9.26	0.04	1.87	5.83	0.16
N0	1.03	0.81	1.89	0.05	0.81	1.89	0.05	0.86	1.93	0.04	0.90	1.95	0.06
Average	4.18	3.35	8.64	0.13	3.40	8.49	0.14	3.64	12.59	0.05	3.45	8.45	0.13

N/A means not applicable because the algorithms from FASSET model calculate N_2O emissions from 0 to 60 cm depth with diffusions across depths based on Eq. (31).

Eq. (24)) as shown in Table 1. However, the fraction of denitrification for N_2O emissions was changed very little from its default value (Table 1), since the N_2O emissions from denitrification were small in the semiarid area. The simulated N_2O emissions from the 0–20 cm depth were compared with measured daily N_2O emissions (Table 3 and Fig. 4) and measured total seasonal N_2O emissions (Table 4).

As shown in Fig. 4, all the N_2O emission algorithms captured most of the measured N_2O emission peaks during May–June after N applications, and the low N_2O emission levels during July–September from 2003 to 2006, except for at the end of May and early June in 2003 where measured N_2O emission peaks were not simulated mainly due to the obvious under-simulated soil surface water content. The measured high N_2O emission peaks during the end of May in 2003 was mainly related to the denitrification with high soil water content (WFPS > 65%) from the high snowfall event in March of 2003 (Del Grosso et al., 2008; Mositer et al., 2006) and high precipitation during April–June (Halvorson et al., 2014). On the other hand, a few simulated N_2O emission peaks after N application were not observed, such as during early May in 2004, middle June in 2005 and end May in 2006 (Fig. 4), and high simulated peaks in June 2006 were not recorded in the measured data (Fig. 4). Similarly, high simulated N_2O emission peaks by DAYCENT model than measured data were also reported by Del Grosso et al. (2008). Failure to measure some of the simulated N_2O emission peaks was possible partly due to missing measurements following irrigation/rainfall by the chamber method as reported from Parkin (2008), when N_2O emission peaks may occur due to the sharply increased soil water content from rainfall and soil nitrate-N content after N application which affects the dissolved nutrients and microbial activity (Weitz et al., 2001). For the N0 treatment, some measured small N_2O emission peaks (such as at the end of July in 2004 or early June in 2006) were not captured by the model, but these measured small peaks may be questionable, possible due to the disturbance by field wildlife. The above results suggested that the most important factors influencing N_2O emissions were soil water content (precipitation plus irrigation) and soil N level (N application). Frolking et al. (1998) compared the CENTURY model, DNDC, ExpertN and NASA-ames version of the CASA model using measured data from different experimental sites and also found that accurate simulation of soil water content was essential for simulating N_2O emissions.

Across the four years, the simulated average daily N_2O emission from the four algorithms were comparable with measured data for the four N treatments, with RMSE values between 8.45 and 14.78 g N ha^{-1} d^{-1} (Table 3). Similar simulation results were obtained for seasonal total N_2O emissions with RMSE values between 623.5 g ha^{-1} and 872.9 g ha^{-1} (Table 4). The standard deviations for

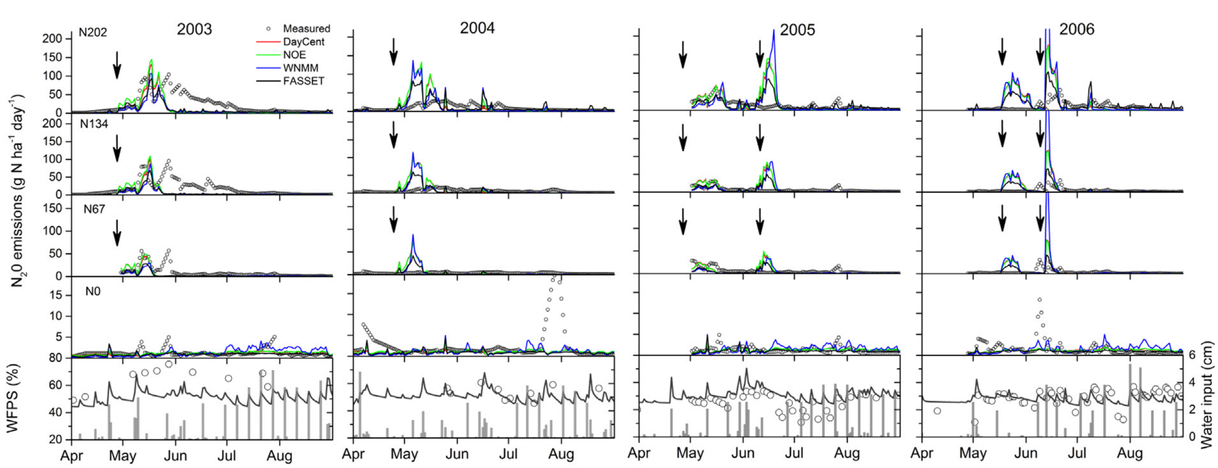

Fig. 4. Measured and simulated daily N_2O emissions (0–20 cm depth) from 2003 to 2006 using the different algorithms (DayCent model, NOE model, WNMM model and FASSET model (0–60 cm)) based on the RZWQM2 simulated soil water filled pore space (WFPS), soil temperature and nitrate-N and the soil nitrification and denitrification for the four N treatments (circles are measured and lines are simulated; bars are water inputs (rainfall plus irrigation) and arrows indicate N fertilizer applications).

Table 4
Comparisons of measured and simulated seasonal N_2O emissions (g N ha^{-1}) using the different N_2O emission algorithms from DAYCENT, NOE, WNMM and FASSET models from the 0–20 cm depth or the 0–60 cm depth with diffusions across the soil for the four N treatments from 2003 to 2006 (RMSE (root mean square error) and r^2 (coefficient of determination) were calculated for all the four N treatments across 2003 to 2006).

Emission depth	Statistics	Measured N_2O emission	Calculated N_2O emission			
			DAYCENT	NOE	WNMM	FASSET
0–20 cm	Average (2003)	1784.2	879.1	920.9	610.5	N/A
	Average (2004)	822.2	975.9	991.8	822.6	N/A
	Average (2005)	817.7	958.9	985	861.3	N/A
	Average (2006)	600.1	990.4	956.6	1330.6	N/A
	Average (N0)	248.8	229.3	231.8	221.4	N/A
	Average (N67)	686.0	624.3	624.9	574.2	N/A
	Average (N134)	1153.4	1101.9	1111.4	1001.6	N/A
	Average (N202)	1935.9	1848.8	1886.2	1827.7	N/A
	RMSE		649	623.5	872.9	N/A
	r^2		0.43	0.47	0.15	N/A
0–60 cm	Average (2003)	1784.1	751.9	775.3	632.8	721.5
	Average (2004)	822.2	825.2	847.9	793.8	835.9
	Average (2005)	817.7	836.7	857.3	882.1	805.5
	Average (2006)	600.1	849.9	835.8	1265.6	830.8
	Average (N0)	248.8	187.7	188.7	212.4	173.9
	Average (N67)	686	457.2	443.4	507.1	424.2
	Average (N134)	1153.3	835.3	811.2	906.6	781.5
	Average (N202)	1935.9	1783.4	1873	1948.1	1814.1
	RMSE		678.6	673	852.1	694.7
	r^2		0.42	0.43	0.19	0.41

N/A means not applicable because the algorithms from FASSAT model calculate N_2O emissions from 0 to 60 cm depth with diffusions across depths based on Eq. (31).

the measured data from 2003 to 2006 were 1.48, 3.06, 7.39 and 6.96 g N ha^{-1} d^{-1} for the four N treatments, respectively, which were comparable with the RMSE values for simulated data from N0 and N67 treatments, but lower than the RMSE values for simulated data from N134 and N202 treatments (Table 3). All the four algorithms under-simulated daily or seasonal N_2O emissions in 2003 as discussed above. While in other three years, all the algorithms over-simulated N_2O emissions compared to the measured data (Tables 3 and 4), possibly due to missing measured N_2O emission peaks using chamber method in the field experiments (Parkin, 2008; Smemo et al., 2011). Wang et al. (2013) found that the chamber method measured N_2O emissions were general lower by 17–20% than the measured N_2O emissions using eddy covariance method in a cotton field in Shanxi, China. The slightly over-simulated soil nitrate-N as shown in Fig. 2 can also contribute to the over-simulated N_2O emissions from nitrification. If the year of 2003 was removed from the statistics, the RMSE values for the simulated seasonal N_2O emissions were between 343.9 g N ha^{-1} and 537.1 g N ha^{-1} from 2004 to 2006.

Comparing the four algorithms, better simulations of daily N_2O emission were obtained by the algorithm from FASSET that considered the gas diffusions across soil depth (Table 3 and Fig. 4), whereas the algorithms from NOE model produced better simulations of seasonal N_2O emissions, with lower RMSE and higher r^2 values (Table 4). The algorithms in WNMM produced relatively worse simulations of both daily and seasonal N_2O emissions with highest RMSE and lowest r^2 values (Tables 3 and 4). The algorithms from FASSET under-simulated N_2O emissions for the N134, N67 and N0 treatments by about 30%, but produced very similar N_2O emissions for the N202 treatment across the four years (Table 4). The algorithms from DAYCENT and NOE models simulated N_2O emissions better in response to the N application rates, with lower RMSE and higher r^2 values (Tables 3 and 4). However, all the algorithms simulated the measured increase in N_2O emissions with increased N application rates (Tables 3 and 4).

All algorithms under-simulated the seasonal N_2O emissions in 2003 mainly due to the under-simulated soil water content at the end of May and in early June in 2003, while high measured N_2O emission peaks was mainly from denitrification with high soil water content during this period (May–June) as discussed above. The measured lowest seasonal N_2O emissions in 2006 compared to other seasons were only simulated by the algorithms from NOE model (Table 4), and this result was associated with WFPS effects on N_2O emissions (Eq. (13)). Other algorithms from DAYCENT, WNMM and FASSET resulted in the highest N_2O emissions in 2006 than in other years, which was different from the seasonal variations in measured N_2O emissions (Table 4). The algorithms from NOE model resulted in better simulations of both daily and seasonal N_2O emissions across the four years, with lower RMSE and high r^2 values (Tables 3 and 4). The inclusion of WFPS effect (Eq. (13)) on N_2O emissions during nitrification improved the N_2O emissions simulations, which were also demonstrated by a previous simulation study using NOE model in France (Bessou et al., 2010) and the laboratory or field experimental results (Bollmann and Conrad, 1998; Khalil et al., 2004; Mørkved et al., 2006). Del Grosso et al. (2008) also discussed the fraction of nitrification for N_2O emissions in DAYCENT model can be derived based on oxygen availability (WFPS) if the above fraction values did not work well.

Comparing the N_2O emission simulations from the 0–20 cm depth (Fig. 4) and the 0–60 cm depth (considering the N_2O diffusions to soil depth using Eq. (31)) (Fig. 5), very similar simulation results were obtained from 2003 to 2006. Daily N_2O emission simulation was improved with lower RMSE and higher r^2 values, while the seasonal N_2O emission simulation became slightly worse with higher RMSE values (mainly due to the under-simulation in 2003), when considering the 0–60 cm depth and N_2O diffusions in soil (Tables 3 and 4), especially for the algorithms from DAYCENT and NOE models. But lower N_2O emission peaks were sometimes simulated when considering N_2O emissions from the 0–60 cm depth than from the 0–20 cm depth, such as in early June of 2005 and 2006. The high N_2O emission peaks following N application events were mainly attributed to nitrification in the surface layer (0–20 cm depth) at the location as reported from Linn and Doran (1984) and Halvorson et al. (2011). The low N_2O emission peaks, such as in early June in 2003, at end of July in 2005, and in middle July in 2006, mainly associated with soil denitrification in the deeper soil layers with higher soil water contents (soil nitrification in the surface soil was low due to low soil water content during

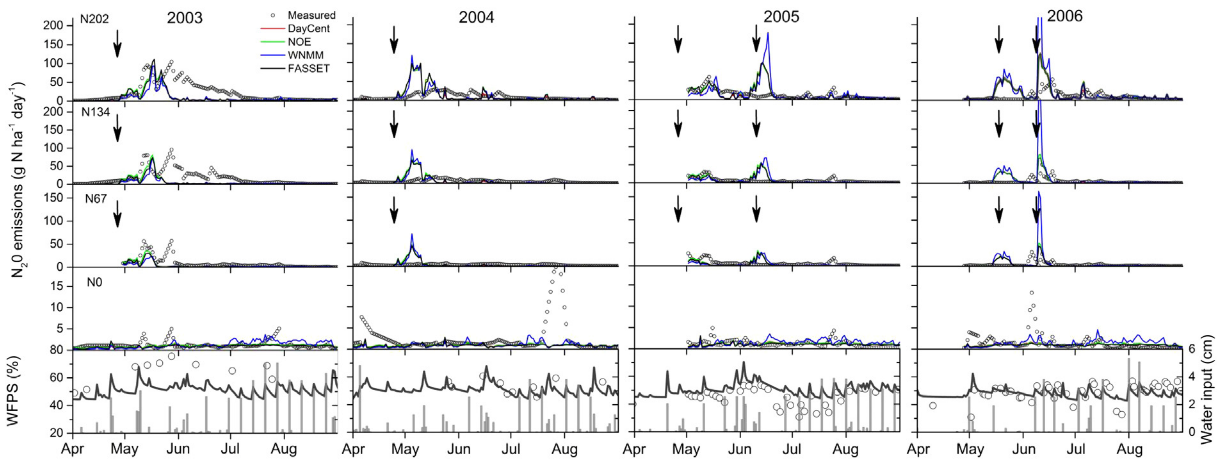

Fig. 5. Measured and simulated daily N_2O emissions (0–60 cm depth) from 2003 to 2006 for the different algorithms (DayCent, NOE, WNMM and FASSET) based on the RZWQM2 simulated soil water filled pore space (WFPS), soil temperature and nitrate-N and the soil nitrification and denitrification for the four N treatments (circles are measured and lines are simulated; bars are water inputs (rainfall plus irrigation) and arrows indicate N fertilizer applications).

these periods), were better simulated by considering the 0–60 cm depth than considering the 0–20 cm depth only (Fig. 4 versus Fig. 5). The contributions of N_2O emissions from the deeper soil depth can be also potentially used to simulate the N application placement effect on N_2O emissions as observed from field experiments (Hultgreen and Leduc, 2003; Halvorson and Del Grosso, 2012, 2013; Engel et al., 2010).

Although, the simulations for seasonal N_2O emissions were slightly worse using the algorithms from DAYCENT and NOE models with higher RMSE values when considering the 0–60 cm soil depth (Table 4), the algorithms from NOE and DAYCENT still produced better simulations of both daily and seasonal N_2O emissions from the 0–60 cm depth across the four years than the algorithms from WNMM and FASSET models. Better response of N_2O emissions to the seasonal weather variations were also obtained using the algorithms from NOE model (Tables 3 and 4). The above comparisons of simulated N_2O emissions showed that the algorithms from DAYCENT and NOE were better than those from WNMM and FASSET in simulating daily N_2O emissions in the semiarid region. However, in another simulation study, Li et al. (2005) compared the N_2O emission modules from WNMM, DAYCENT and DNDC models for simulating N_2O emissions in the North China Plain, and found WNMM N_2O emission module produced better simulations than other modules of DNDC and DAYCENT. More inter-comparisons of the different N_2O emissions modules are needed with measured data from various climate and soil conditions, which should be helpful to understand the N_2O emissions processes and their controlling factors.

We found that accounting for the WFPS effects on N_2O emissions (Eq. (13)) in the algorithms from DAYCENT, FASSET or WNMM model improved the daily N_2O emissions and the response of N_2O emission to seasonal weather variations, which was first used to improve the NOE performance in simulating N_2O emissions in response to fertilizer N addition by Bessou et al. (2010). The simulation results using the algorithm in DAYCENT after taking into account of WFPS effects on N_2O emissions as in NOE model (multiplying Eq. (13) to the right hand side of Eq. (6)) were similar to the results using the algorithms from DAYCENT and NOE models during the simulation period (especially during N application periods, Fig. 6), because the numerical value from Eq. (13) was close to 1 when the WFPS values were between 0.4 and 0.6 (Fig. 6; Fig. 1A). However, some small N_2O emission peaks during the middle or late growing season were better simulated compared to the original algorithms, such as in June in 2003 for N202, at end of July and early

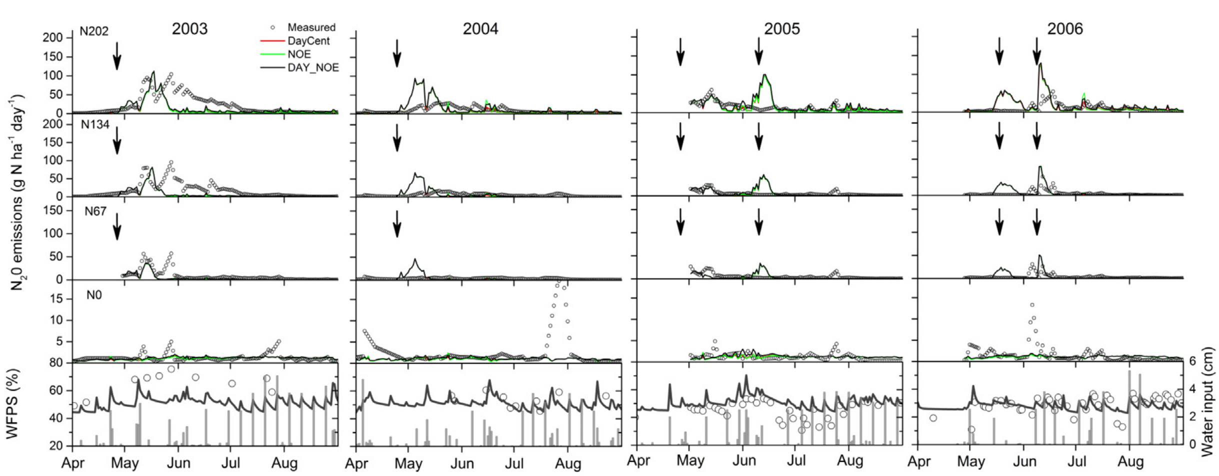

Fig. 6. Measured and simulated daily N_2O emissions (0–60 cm depth) from 2003 to 2006 for the coupled algorithms from DayCent model and the water filled pore space (WFPS) effects on N_2O emissions (Eq. (13)) from NOE model (DAY_NOE) based on the RZWQM2 simulated WFPS, soil temperature and nitrate-N and the soil nitrification and denitrification for the four N treatments (circles are measured and lines are simulated; bars are water inputs (rainfall plus irrigation) and arrows indicate N fertilizer applications).

August in 2005 for N202, in early June in 2005 for N0 and in July–August in 2006 for N202 (Fig. 6). The new algorithms resulted in higher r^2 values for daily N_2O emission, and lower RMSE values for seasonal N_2O emissions (Table 5).

3.3. Crop yield, N_2O emissions, and N budgets in responses to N rates

The seasonal N_2O emissions responded differently to N application rate in 2003 and in 2004–2006 (Fig. 7A). In 2003, a linear relationship between measured N_2O emissions and N rate was found, while in 2004–2006, a quadratic relationship explained higher ($r^2 = 0.91$) variations in N_2O emissions associated with N rate than a linear relationship ($r^2 = 0.88$). Similar results were obtained from the simulated data from 2003 to 2006 ($r^2 = 1$ for quadratic relationship versus $r^2 = 0.93$ for linear relationship, Fig. 7B). The relationships between N_2O emissions and N rate were shown experimentally in the literature as nonlinear, such as in US Corn Belt (McSwiney and Robertson, 2005; Hoben et al., 2011) and in the North China Plain (Cui et al., 2013, 2014b), or as linear, such as in Northern Colorado corn field (Mosier et al., 2006; Halvorson et al., 2008, 2014). The different relationships between N_2O emissions and N rates may be related to the weather variations across seasons (such as 2003 versus 2004–2006 in the current study) and the excessive N application rates to crop N requirement, such as in North China Plain where exponential increase of N_2O emissions was mainly related to the high soil N surplus caused by over-applied high N rate up to about 400–500 kg N ha^{-1} per crop (Cui et al., 2013, 2014a,b). The relationship between crop yield and N rate generally showed a spherical-plateau (Fig. 7C, D) in this study, which was consistent with the above studies from different regions, but with different minimum N rates for the maximum crop yield among these studies. Similar relationships between seasonal N_2O emissions and grain yield were found for both measured and simulated data (Fig. 7E, F), suggesting a great potential in reducing N_2O emissions without compromising grain yield. The minimum seasonal N_2O emissions for highest corn yield was about 1.5 kg N ha^{-1} for both measured and simulated data, which was close to the values of 1.0–2.0 kg N ha^{-1} for maximum corn yield in southwest Michigan, US (McSwiney and Robertson, 2005) and North China Plain (Cui et al., 2013). These values, however, were much lower than the minimum seasonal N_2O emission values of 3.5–3.9 N kg ha^{-1} for the highest wheat yield in the North China Plain (Cui et al., 2014a), probably due to the high N application rates (about 420 kg N ha^{-1}) and long growth duration of wheat in the region. For the current study, the corresponding N application rate to the minimum N_2O emissions was about 150 kg N ha^{-1}, achieving more than 95% of the maximum grain yield.

The soil N surplus (N application rate minus crop N uptake) was negative for the N application rates of 0, 67 and 134 kg N ha^{-1}, and positive for the highest N application rate (N202) suggesting an over application of fertilizer N (Table 6). In the North China Plain, higher N application rates of more than 200 kg N ha^{-1} per crop also resulted in positive soil N surplus (Fang et al., 2006; Cui et al., 2013). The N recovery efficiency for applied N fertilizer (NRE, the ratio of the difference in crop N uptake between N treatments and none N treatment to the applied N rates) was higher for N134 treatment than for N202 treatment for both measured and simulated data (Table 6). Across the four N treatments, the NRE values were between 0.49 and 0.65 for measured data and between 0.51 and 0.71 for simulated data, which was generally higher than the NRE values of 0.20–0.40 for the major cereal production systems, mainly due to the poor match between N apply and crop N demand during growth season (Ladha et al., 2005; Cui et al., 2010). The high NRE values in this study were mainly associated with high corn yield (N uptake), and lower N leaching and soil N surplus under the N application rates (Table 6).

The emission factor (EF, a ratio of the difference in N_2O emissions between N treatment and none N treatment to the applied N rate) ranged from 0.65 % to 0.72 % for measured data and from 0.43% to 0.95% for the simulated data, and both measured and simulated data showed an increase in EF with N application rates (Table 6). The EF values were lower than the 1% value suggested by IPCC method (IPCC, 2006a), and similar results for measured and simulated EF below 1% were also reported for a cotton-wheat rotation system in Australia using DAYCENT model (Scheer et al., 2014). The above result indicates that the IPCC method is the worst scenario to calculate soil potential N_2O emissions from applied N, in spite of high uncertainty (−70%–200%, IPCC, 2006b). More accurate method, such as N surplus approach, may be better for estimating N_2O emissions as influenced by N application rate (Van Groenigen et al., 2010; Grassini and Cassman, 2012). The process-based models like RZWQM2 can be more reliable for estimating N_2O emission in response to N application rate at field scale, even the model tended to under-simulated EF at the low N application rate and over-simulated EF at the high N application rate. Both measured and simulated GHG (greenhouse gas) intensity (kg N_2O Mg $yield^{-1}$) data showed an increase with N application rates, and ranged from 0.04 kg N_2O Mg gain $yield^{-1}$ to 0.23 kg N_2O Mg gain $yield^{-1}$, which were comparable with the experimental measurements in the corn fields in North China Plain(Cui et al., 2013) and in Nebraska (Grassini and Cassman, 2012), but higher than the GHG intensity for wheat cropping system in the North China Plain mainly due to the limited denitrification from low soil carbon and soil moisture levels (Cui et al., 2014a). Therefore, the most reasonable N rate for irrigated corn in the Central Great Plains of the U. S. is about 150 kg N ha^{-1}, which produced high crop yield and N recovery, and lower N_2O emissions (EF and GHG intensity values).

Table 5
Statistic results (RMSE, root mean square error; r^2, coefficient of determination) for the simulated daily (g N ha^{-1} day^{-1}) or seasonal N_2O emissions (g N ha^{-1}) from the 0–60 cm soil depth for the four N treatments from 2003 to 2006 using the algorithms from DAYCENT coupled with the water filled pore space (WFPS) effects on N_2O emission (Eq. (13)) from NOE model[a].

Treatment	Measured N_2O emission	Daily N_2O emission			Seasonal N_2O emission			
		Simulated	RMSE	r^2	Measured	Simulated	RMSE	r^2
N202	7.85	8.96	16.14	0.21	1935.9	2230.4	N/A[b]	N/A
N134	4.75	3.84	11.27	0.14	1153.4	952.7	N/A	N/A
N67	3.09	2.3	6	0.18	686	508.8	N/A	N/A
N0	1.03	0.94	1.87	0.06	248.8	219.8	N/A	N/A
Average	4.12	4.01	8.82	0.15	1006	977.9	666.1	0.45

[a] RMSE and r^2 for daily N_2O emission were calculated for each N treatment from 2003 to 2006, which was consistent with the RMSE and r^2 calculations in Table 3; RMSE and r^2 for seasonal N_2O emission were calculated for all the 4 N treatments from 2003 to 2006, which was consistent with the RMSE and r^2 calculations in Table 4.
[b] N/A means not applicable.

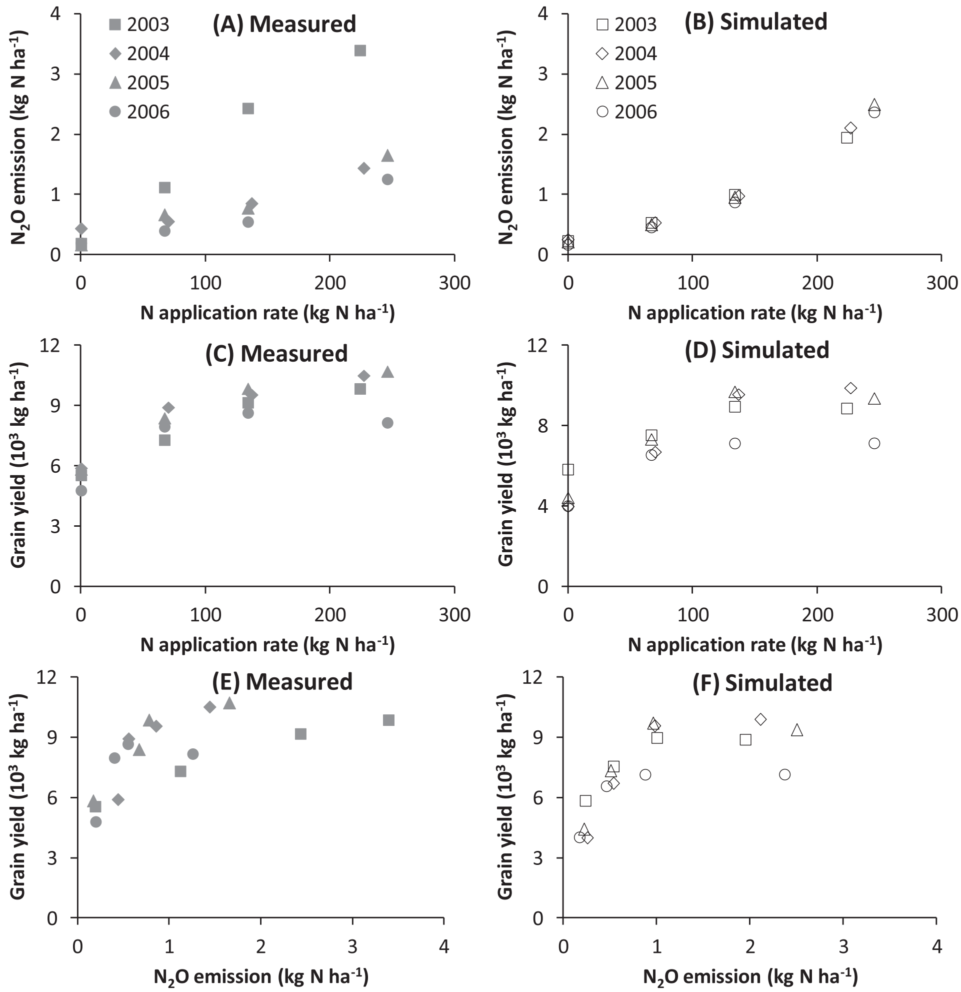

Fig. 7. Relationship between seasonal N_2O emissions, crop yield to N rate or between N_2O emissions and crop yield for the four N treatments from 2003 to 2006.

Table 6
Measured and simulated crop N uptake (Nup_M or Nup_S, kg N ha^{-1}), N leaching (NL_S, kg N ha^{-1}), N surplus (N_sur, kg N ha^{-1}), N_2O emission (N_2O_M or N_2O_S, kg N ha^{-1}), N recovery (Nre_M or Nre_S), emission factor (EF_M or EF_S), greenhouse gas intensity (GHG_M or GHG_S, kg N N_2O Mg grain $yield^{-1}$) for the four N treatments (N0, N67, N134 and N202) from 2003 to 2006.

N rate	N_sur	Nup_M	Nup_S	Nre_M	Nre_S	NL_S	N_2O_M	N_2O_S	EF_M	EF_S	GHG_M	GHG_S
N0	-32.1^{a}	75.7^{d}	64.1^{d}	–	–	0.36^{bc}	0.249^{c}	0.220^{d}	–	–	0.05^{b}	0.04^{d}
N67	-15.7^{a}	119.4^{c}	98.4^{c}	0.65^{a}	0.51^{b}	0.32^{c}	0.686^{b}	0.509^{c}	0.65^{a}	0.43^{c}	0.10^{b}	0.06^{c}
N134	-18.8^{a}	163.4^{b}	159.6^{b}	0.65^{a}	0.71^{a}	0.45^{b}	1.153^{b}	0.953^{b}	0.68^{ab}	0.55^{b}	0.13^{b}	0.10^{b}
N202	$+24.0^{b}$	191.3^{a}	206.6^{a}	0.49^{ab}	0.61^{ab}	0.84^{a}	1.936^{a}	2.230^{a}	0.72^{a}	0.85^{a}	0.22^{a}	0.23^{a}

Note: The different letters among the four N treatments mean significant difference ($P < 0.05$).

4. Conclusions

The simulation results in the study showed that the different algorithms from DAYCENT, NOE, WNMM, and FASSET simulated most of the measured N_2O emission peaks during the experimental period, suggesting that these algorithms along with RZWQM2 simulated soil water, soil temperature, soil nitrate-N content and nitrification and denitrification were reasonable for N_2O emissions. The algorithms from DAYCENT and NOE models produced better response of daily and seasonal N_2O emissions to N application rate and to weather variations than the algorithms form WNMM and FASSET models. The simulated daily N_2O emissions from the 0–60 cm depth considering gas diffusions across soil depth produced better simulations than that from the surface soil layer (0–20 cm depth), and can be more applicable in simulating N_2O emissions from deep soil layer in response to the irrigation or N fertilizer application methods (such as deep N application and irrigation). Including the effect of WFPS on N_2O emissions during nitrification improved the N_2O emission simulations for all the algorithms from the four models, which was consistent with the laboratory experimental results (Khalil et al., 2004, 2005). Based on this study, we concluded that the best algorithms to be used in RZWQM2 were the WFPS effects on the N_2O emission fraction of nitrification from the NOE model and the ratios of NO/N_2O and N_2/N_2O for denitrification from the DAYCENT model. However, since denitrification played a minor role in this study, further test of N_2O

emissions from the denitrification was warranted.

Both measured and simulated seasonal N_2O emissions showed a quadratic relationship with grain yield, suggesting a great potential in reducing N_2O emissions without reducing grain yield. The minimum seasonal N_2O emissions for the highest corn yield were about 1.5 kg N ha^{-1} for both measured and simulated data. The most reasonable N rate for irrigated corn in the region is about 150 kg N ha^{-1}, which produced high crop yield and N recovery, and lower N_2O emissions. The measured and simulated EF values in this study and other studies were lower than the 1% as suggested in the IPCC method (IPCC, 2006a), indicating that the IPCC method may be the upper limit for estimating potential N_2O emissions from N applications. The process-based model can be more reliable for estimating N_2O emissions in response to N application rate and weather variations at field scale, and be used to assess agricultural management practices effects on N_2O emissions and the related mitigating strategy for climate change.

References

Ahuja, L.R., Ma, L., 2002. Parameterization of agricultural system models: current approaches and future needs. In: Ahuja, L.R., Ma, L., Howell, T.A. (Eds.), Agricultural System Models in Field Research and Technology Transfer. CRC Press, Boca Raton, FL, pp. 273–316.

Ahuja, L.R., Rojas, K.W., Hanson, J.D., Shaffer, M.J., Ma, L., 2000. The Root Zone WaterQuality Model. Water Resources Publications, Highlands Ranch, CO.

Ahuja, L.R., Ma, L., Howell, T.A. (Eds.), 2002. Agricultural System Models in Field Research and Technology Transfer. CRC Press.

Bessou, C., Mary, B., Léonard, J., Roussel, M., Gréhan, E., Gabrielle, B., 2010. Modelling soil compaction impacts on nitrous oxide emissions in arable fields. Eur. J. Soil Sci. 61, 348–363.

Blagodatsky, S., Smith, P., 2012. Soil physics meets soil biology: towards better mechanistic prediction of greenhouse gas emissions from soil. Soil Biol. Biochem. 47, 78–92.

Bøckman, O.C., Olfs, H.W., 1998. Fertilizers, agronomy and N_2O. Nutr. Cycl. Agroecosystems 52, 165–170.

Bollmann, A., Conrad, R., 1998. Influence of O_2 availability on NO and N_2O release by nitrification and denitrification. Glob. Change Biol. 4, 387–396.

Bouwman, A.F., Boumans, L.J.M., Batjes, N.H., 2002a. Emissions of N_2O and NO from fertilized fields: summary of available measurement data. Glob. Biogeochem. Cy 16, 1058–1070.

Bouwman, A.F., Boumans, L.J.M., Batjes, N.H., 2002b. Modeling global annual N_2O and NO emissions from fertilized fields. Glob. Biogeochem. Cy 16, 1080–1107.

Cameira, M.R., Sousa, P.L., Farahani, H.J., Ahuja, L.R., Pereira, L.S., 1998. Evaluation of the RZWQM for the simulation of water and nitrate movement in level-basin, fertigated maize. J. Agric. Eng. Res. 69 (4), 331–341.

Chatskikh, D., Olesen, J., Berntsen, J., Regina, K., Yamulki, S., 2005. Simulation of effects of soils, climate and management on N_2O emission from grasslands. Biogeochemistry 76, 395–419.

Chen, D., Li, Y., Grace, P., Mosier, A.R., 2008. N_2O emissions from agricultural lands: a synthesis of simulation approaches. Plant Soil 309, 169–189.

Cui, Z., Chen, X., Zhang, F., 2010. Current nitrogen management status and measures to improve the intensive wheat–maize system in China. Ambio 39, 376–384.

Cui, Z., Yue, S., Wang, G., Zhang, F., Chen, X., 2013. In-season root-zone N management for mitigating greenhouse gas emission and reactive N losses in intensive wheat production. Environ. Sci. Technol. 47, 6015–6022.

Cui, Z.L., Wu, L., Ye, Y.L., Ma, W.Q., Chen, X.P., Zhang, F.S., 2014a. Trade-offs between high yields and greenhouse gas emissions in irrigation wheat cropland in China. Biogeosciences 11, 2287–2294.

Cui, Z., Wang, G., Yue, S., Wu, L., Zhang, W., Zhang, F., Chen, X., 2014b. Closing the N-use efficiency gap to achieve food and environmental security. Environ. Sci. Technol. 48, 5780–5787.

Davidson, E.A., Trumbore, S.E., 1995. Gas diffusivity and production of CO_2 in deep soils of the eastern Amazon. Tellus B 47, 550–565.

Del Grosso, S.J., Parton, W.J., Mosier, A.R., Ojima, D.S., Kulmala, A.E., Phongpan, S., 2000. General model for N_2O and N_2 gas emissions from soils due to denitrification. Glob. Biogeochem. Cy 14, 1045–1060.

Del Grosso, S.J., Parton, W.J., Mosier, A.R., Hartman, M.D., Brenner, J., Ojima, D.S., Schimel, D.S., 2001. Simulated interaction of carbon dynamics and nitrogen trace gas fluxes using the DAYCENT model. In: Schaffer, M., Ma, L., Hansen, S. (Eds.), Modeling Carbon and Nitrogen Dynamics for Soil Management. CRC Press, Boca Raton, FL, pp. 303–332.

Del Grosso, S.J., Halvorson, A.D., Parton, W.J., 2008. Testing DAYCENT model simulations of corn yields and nitrous oxide emissions in irrigated tillage systems in Colorado. J. Environ. Qual. 37, 1383–1389.

Engel, T., Priesack, E., 1993. Expert-N, a building block system of nitrogen models as resource for advice, research, water management and policy. In: Eijsackers, H.J.P., Hamers, T. (Eds.), Integrated Soil and Sediment Research: a Basis for Proper Protection. Kluwer Academic Publishers, Dodrecht, The Netherlands, pp. 503–507.

Engel, R., Liang, D.L., Wallander, R., Bembenek, A., 2010. Influence of urea fertilizer placement on nitrous oxide production from a silt loam soil. J. Environ. Qual. 39, 115–125.

Fang, Q., Yu, Q., Wang, E., Chen, Y., Zhang, G., Wang, J., Li, L., 2006. Soil nitrate accumulation, leaching and crop nitrogen use as influenced by fertilization and irrigation in an intensive wheat–maize double cropping system in the North China Plain. Plant Soil 284, 335–350.

Fang, Q., Ma, L., Yu, Q., Malone, R.W., Saseendran, S.A., Ahuja, L.R., 2008. Modeling nitrogen and water management effects in a wheat–maize double-cropping-system. J. Environ. Qual. 37, 2232–2242.

Fang, Q., Ma, L., Yu, Q., Ahuja, L.R., Malone, R.W., Hoogenboom, G., 2010. Irrigationstrategies to improve the water use efficiency of wheat–maize double cropping systems in China. Agric. Water Manag. 97, 1165–1174.

Fang, Q.X., Ma, L., Flerchinger, G.N., Qi, Z., Ahuja, L.R., Xing, H.T., Yu, Q., 2014. Modeling evapotranspiration and energy balance in a wheat–maize cropping system using the revised RZ-SHAW model. Agric. For. Meteorol. 194, 218–229.

Firestone, M.K., Davidson, E.A., 1989. Microbiological basis of NO and N_2O production and consumption in soil. In: Andreae, M.O., Schimel, D.S. (Eds.), Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere. John Wiley and Sons Ltd., Chichester, UK, pp. 7–21.

Fitton, N., Datta, A., Hastings, A., Kuhnert, M., Topp, C.F.E., Cloy, J.M., Rees, R.M., Cardenas, L.M., Williams, J.R., Smith, K., Chadwick, D., Smith, P., 2014. The challenge of modelling nitrogen management at the field scale: simulation and sensitivity analysis of N_2O fluxes across nine experimental sites using DailyDayCent. Env. Res. Let. 9, 095003. http://dx.doi.org/10.1088/1748-9326/9/9/095003.

Frolking, S.E., Mosier, A.R., Ojima, D.S., Li, C., Parton, W.J., Potter, C.S., Smith, K.A., 1998. Comparison of N_2O emissions from soils at three temperate agricultural sites: simulations of year-round measurements by four models. Nutr. Cycl. Agroecosystems 52, 77–105.

Grant, R.F., Pattey, E., 1999. Mathematical modelling of nitrous oxide emissions from an agricultural field during spring thaw. Glob. Biogeochem. Cy 13, 679–694.

Grant, R.F., Pattey, E., Goddard, T.W., Kryzanowski, L.M., Puurveen, H., 2006. Modeling the effects of fertilizer application rate on nitrous oxide emissions. Soil Sci. Soc. Am. J. 70, 235–248.

Grassini, P., Cassman, K.G., 2012. High-yield maize with large net energy yield and small global warming intensity. Proc. Natl. Acad. Sci. U. S. A. 109, 1074–1079.

Halvorson, A.D., Del Grosso, S.J., 2012. Nitrogen source and placement effects on soil nitrous oxide emissions from no-till corn. J. Environ. Qual. 41, 1349–1360.

Halvorson, A.D., Del Grosso, S.J., 2013. Nitrogen placement and source effects on nitrous oxide emissions and yields of irrigated corn. J. Environ. Qual. 42, 312–322.

Halvorson, A.D., Mosier, A.R., Reule, C.A., Bausch, W.C., 2006. Nitrogen and tillage effects on irrigated continuous corn yields. Agron. J. 98, 63–71.

Halvorson, A.D., Del Grosso, S.J., Reule, C.A., 2008. Nitrogen, tillage, and crop rotation effects on nitrous oxide emissions from irrigated cropping systems. J. Environ. Qual. 37, 1337–1344.

Halvorson, A.D., Del Grosso, S.J., Alluvione, F., 2010. Tillage and inorganic nitrogen source effects on nitrous oxide emissions from irrigated cropping systems. Soil Sci. Soc. Am. J. 74, 436–445.

Halvorson, A.D., Del Grosso, S.J., Jantalia, C.P., 2011. Nitrogen source effects on soil nitrous oxide emissions from strip-till corn. J. Environ. Qual. 40, 1775–1786.

Halvorson, A.D., Snyder, C.S., Blaylock, A.D., Del Grosso, S.J., 2014. Enhanced-efficiency nitrogen fertilizers: potential role in nitrous oxide emission mitigation. Agron. J. 106, 715–722.

Heinen, M., 2006. Simplified denitrification models: overview and properties. Geoderma 133, 444–463.

Hénault, C., Bizouard, F., Laville, P., Gabrielle, B., Nicoullaud, B., Germon, J.C., Cellier, P., 2005. Predicting in situ soil N_2O emission using NOE algorithm and soil database. Glob. Change Biol. 11, 115–127.

Hoben, J.P., Gehl, R.J., Millar, N., Grace, P.R., Robertson, G.P., 2011. Nonlinear nitrous oxide (N_2O) response to nitrogen fertilizer in on-farm corn crops of the US Midwest. Glob. Change Biol. 17, 1140–1152.

Hultgreen, G., Leduc, P., 2003. The Effect of Nitrogen Fertilizer Placement, Formulation, Timing, and Rate on Greenhouse Gas Emissions and Agronomic Performance. Saskatchewan Department of Agriculture and Food. Final Report Project No. 5300G, ADF#19990028. Regina, Saskatchewan, Canada.

IPCC, 2006a. IPCC guidelines for national greenhouse gas inventories. In: Eggleston, H.S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (Eds.), Prepared by the National Greenhouse Gas Inventories Programme. IGES, Japan.

IPCC, 2006b. Intergovernmental Panel on Climate Change Guidelines for National Greenhouse Gas Inventories. In: Agriculture, Forestry and Other Land Use; N_2O Emissions from Managed Soils, and CO2 Emissions from Lime and Urea Application, vol. 4 (Chapter 11).

Jantalia, C.P., Halvorson, A.D., 2011. Nitrogen fertilizer effects on irrigated conventional tillage corn yields and soil carbon and nitrogen pools. Agron. J. 103, 871–878.

Khalil, K., Mary, B., Renault, P., 2004. Nitrous oxide production by nitrification and denitrification in soil aggregates as affected by O_2 concentration. Soil Biol. Biochem. 36, 687–699.

Khalil, K., Renault, P., Guérin, N., Mary, B., 2005. Modelling denitrification including the dynamics of denitrifiers and their progressing ability to reduce nitrous oxide: comparison with batch experiments. Eur. J. Soil Sci. 56, 491–504.

Klier, C., Gayler, S., Haberbosch, C., Ruser, R., Stenger, R., Flessa, H., Priesack, E., 2011.

Modeling nitrous oxide emissions from potato-cropped soil. Vadose Zone J. 10, 184–194.
Klocke, N.L., Fischbach, P.E., 1998. Estimating Soil Moisture by Appearance and Feel. Publication G84-690-A. Nebraska Cooperative Extension Service.
Ladha, J.K., Pathak, H., Krupnik, T.J., Six, J., van Kessel, C., 2005. Efficiency of fertilizer nitrogen in cereal production: retrospects and prospects. Adv. Agron. 87, 85–156.
Li, C., Frolking, S., Frolking, T.A., 1992. A model of nitrous oxide evolution from soil driven by rainfall events: I. Model structure and sensitivity. J. Geophys. Res. 97, 9759–9776.
Li, Y., Chen, D.L., Zhang, Y.M., Ding, H., 2005. Comparison of three modeling approaches for simulating denitrification and nitrous oxide emissions from loam-textured arable soils. Glob. Biogeochem. Cy 19, 1–15.
Li, Y., Chen, D.L., White, R.E., Zhang, J.B., Li, B.G., Zhang, Y.M., Huang, Y.F., Edis, R., 2007. A spatially referenced water and nitrogen management model (WNMM) for (irrigated) intensive cropping systems in the North China Plain. Ecol. Model 203, 395–423.
Liebig, M.A., Morgan, J.A., Reeder, J.D., Ellert, B.H., Gollany, H.T., Schuman, G.E., 2005. Greenhouse gas contributions and mitigation potential of agricultural practices in northwestern USA and western Canada. Soil Till. Res. 83, 25–52.
Linn, D.M., Doran, J.W., 1984. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. Soil Sci. Soc. Am. J. 48, 1267–1272.
Livingston, G.P., Hutchinson, G.L., 1995. Enclosure-based measurement of trace gas exchange: applications and sources of error. In: Matson, P.A., Harriss, R.C. (Eds.), Biogenic Trace Gases: Measuring Emissions from Soil and Water, Methods in Ecology. Blackwell Science/Cambridge Univ. Press, Cambridge, UK, pp. 14–51.
Ma, L., Shaffer, M.J., 2001. Review of carbon and nitrogen processes in nine U.S. soil nitrogen dynamics models. In: Shaffer, M.J., et al. (Eds.), Modeling Carbon and Nitrogen Dynamics for Soil Management. CRC Press, Boca Raton, FL, pp. 55–102.
Ma, L., Shaffer, M.J., Ahuja, L.R., 2001. Application of RZWQM for soil nitrogen management. In: Shaffer, M.J., Ma, L., Hansen, S. (Eds.), Modeling Carbon and Nitrogen Dynamics for Soil Management. Lewis Publ., Boca Raton, FL, pp. 265–301.
Ma, L., Trout, T.J., Ahuja, L.R., Bausch, W.C., Saseendran, S.A., Malone, R.W., Nielsen, D.C., 2012. Calibrating RZWQM2 model for maize responses to deficit irrigation. Agric. Water Manag. 103, 140–149.
Malhi, S.S., McGill, W.B., 1982. Nitrification in three Alberta soils: effect of temperature, moisture and substrate concentration. Soil Biol. Biochem. 14, 393–399.
McCown, R.L., Hammer, G.L., Hargreaves, J.N.G., Holzworth, D.P., Freebairn, D.M., 1996. APSIM: a novel software system for model development, model testing, and simulation in agricultural systems research. Agric. Syst. 50, 255–271.
McSwiney, C.P., Robertson, G.P., 2005. Nonlinear response of N_2O flux to incremental fertilizer addition in a continuous maize (Zea mays L.) cropping system. Glob. Change Biol. 11, 1712–1719.
Mørkved, P.T., Dörsch, P., Henriksen, T.M., Bakken, L.R., 2006. N_2O emissions and product ratios of nitrification and denitrification as affected by freezing and thawing. Soil Biol. Biochem. 38 (12), 3411–3420.
Mosier, A.R., Parton, W.J., Valentine, D.W., Ojima, D.S., Schimel, D.S., Delgado, J.A., 1996. CH_4 and N_2O fluxes in the Colorado shortgrass steppe: 1. impact of landscape and nitrogen addition. Glob. Biogeochem. Cy 10, 387–399.
Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., Van Cleemput, O., 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. Nutr. Cycl. Agroecosystems 52 (2–3), 225–248.
Mosier, A.R., Halvorson, A.D., Reule, C.A., Liu, X.J., 2006. Net global warming potential and greenhouse gas intensity in irrigated cropping systems in Northeastern Colorado. J. Environ. Qual. 35, 1584–1598.
Necpálová, M., Anex, R.P., Fienen, M.N., Del Grosso, S.J., Castellano, M.J., Sawyer, J.E., Barker, D.W., 2015. Understanding the DayCent model: calibration, sensitivity, and identifiability through inverse modeling. Environ. Model. Softw. 66, 110–130.
Olesen, J.E., Petersen, B.M., Berntsen, J., Hansen, S., Jamieson, P.D., Thomsen, A.G., 2002. Comparison of methods for simulating effects of nitrogen on green area index and dry matter growth in winter wheat. Field Crops Res. 74, 131–149.
Parkin, T.B., 2008. Effect of sampling frequency on estimates of cumulative nitrous oxide emissions. J. Environ. Qual. 37, 1390–1395.
Parton, W.J., Mosier, A.R., Ojima, D.S., Valentine, D.W., Schimel, D.S., Weier, K., Kulmala, A.E., 1996. Generalized model for N_2 and N_2O production from nitrification and denitrification. Glob. Biogeochem. Cy 10, 401–412.
Parton, W.J., Hartman, M., Ojima, D.S., Schimel, D.W., 1998. DAYCENT and its land surface submodel: description and testing. Glob. Planet Change 19, 35–48.
Parton, W.J., Holland, E.A., Del Grosso, S.J., Hartman, M.D., Martin, R.E., Mosier, A.R., Ojima, D.S., Schimel, D.S., 2001. Generalized model for NO_x and N_2O emissions from soils. J. Geophys. Res. 106, 17403–17420.
Pattey, E., Edwards, G.C., Desjardins, R.L., Pennock, D.J., Smith, W., Grant, B., MacPherson, J.I., 2007. Tools for quantifying N_2O emissions from agroecosystems. Agric. For. Meteorol. 142, 103–119.
Perlman, J., Hijmans, R.J., Horwath, W.R., 2013. Modelling agricultural nitrous oxide emissions for large regions. Environ. Model. Softw. 48, 183–192.
Potter, C.S., Riley, R.H., Klooster, S.A., 1997. Simulation modeling of nitrogen trace gas emissions along an age gradient of tropical forest soils. Ecol. Model 97, 179–196.
Qin, X., Wang, H., Li, Y., Li, Y., McConkey, B., Lemke, R., Li, C., Brandt, K., Gao, Q., Wan, Y., Liu, S., Liu, Y., Xu, C., 2013. A long-term sensitivity analysis of the denitrification and decomposition model. Environ. Model. Softw. 43, 26–36.
Scheer, C., Del Grosso, S.J., Parton, W.J., Rowlings, D.W., Grace, P.R., 2014. Modeling nitrous oxide emissions from irrigated agriculture: testing DayCent with high-frequency measurements. Ecol. Appl. 24, 528–538.
Shaffer, M.J., Rojas, K.W., DeCoursey, D.G., Hebson, C.S., 2000. Nutrient chemistry processes— OMNI. In: Ahuja, L.R., Rojas, K.W., Hanson, J.D., Shaffer, M.J., Ma, L. (Eds.), The Root Zone Water Quality Model. Water Resources Publications LLC, Highlands Ranch, CO, pp. 119–144.
Smemo, K.A., Ostrom, N.E., Opdyke, M.R., Ostrom, P.H., Bohm, S., Robertson, G.P., 2011. Improving process-based estimates of N_2O emissions from soil using temporally extensive chamber techniques and stable isotopes. Nutr. Cycl. Agroecosystems 91, 145–154.
Smith, P., Martino, D., Cai, Z.C., Gwary, D., Janzen, H., Kumar, P., McCarlg, B., Ogleh, S., O'Marai, F., Ricej, C., Scholesk, B., Sirotenkol, O., Howdenm, M., McAllistere, T., Pann, G., Romanenkovo, V., Schneiderp, U., Towprayoonq, S., 2007. Policy and technological constraints to implementation of greenhouse gas mitigation options in agriculture. Agric. Ecosyst. Environ. 118, 6–28.
Snyder, C.S., Bruulsema, T.W., Jensen, T.L., Fixen, P.E., 2009. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. Agric. Ecosyst. Environ. 133, 247–266.
Syakila, A., Kroeze, C., 2011. The global nitrous oxide budget revisited. Greenh. Gas Meas. Manag. 1, 17–26.
Van Groenigen, J.W., Velthof, G.L., Oenema, O., Van Groenigen, K.J., Van Kessel, C., 2010. Towards an agronomic assessment of N_2O emissions: a case study for arable crops. Eur. J. Soil Sci. 61, 903–913.
Villa-Vialaneix, N., Follador, M., Ratto, M., Leip, A., 2012. A comparison of eight metamodeling techniques for the simulation of N_2O fluxes and N leaching from corn crops. Environ. Model. Softw. 34, 51–66.
Vogeler, I., Giltrap, D., Cichota, R., 2013. Comparison of APSIM and DNDC simulations of nitrogen transformations and N_2 O emissions. Sci. Total Environ. 465, 147–155.
Wang, K., Zheng, X., Pihlatie, M., Vesala, T., Liu, C., Haapanala, S., Liu, H., 2013. Comparison between static chamber and tunable diode laser-based eddy covariance techniques for measuring nitrous oxide fluxes from a cotton field. Agric. For. Meteorol. 171, 9–19.
Weier, K.L., Doran, J.W., Power, J.F., Walters, D.T., 1993. Denitrification and the denitrogen nitrous-oxide ratio as affects by soil–water, available carbon, and nitrate. Soil Sci. Soc. Am. J. 57, 66–72.
Weitz, A.M., Linder, E., Frolking, S., Crill, P.M., Keller, M., 2001. N_2O emissions from humid tropical agricultural soils: effects of soil moisture, texture and nitrogen availability. Soil Biol. Biochem. 33, 1077–1093.
Whittaker, C., McManus, M.C., Smith, P., 2013. A comparison of carbon accounting tools for arable crops in the United Kingdom. Environ. Model. Softw. 46, 228–239.
Xing, H.T., Wang, E.L., Smith, C.J., Rolston, D., Yu, Q., 2011. Modelling nitrous oxide and carbon dioxide emission from soil in an incubation experiment. Geoderma 167–168, 328–339.