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Impacts of Nitrogen Addition on Nitrous Oxide Emission: Model-Data Comparison

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Abstract.

The contributions of long-lived nitrous oxide (N_2O) to the global climate and environment have received increasing attention. Especially, atmospheric nitrogen (N) deposition has substantially increased in recent decades due to extensive use of fossil fuels in industry, which strongly stimulates the N_2O emissions of the terrestrial ecosystem. Several models have been developed to simulate N_2O emission, but there are still large differences in their N_2O emission simulations and responses to atmospheric deposition over global or regional scales. Using observations from N addition experiments in a subtropical forest, this study compared six widely-used N_2O models (i.e. DayCENT, DLEM, DNDC, DyN, NOE, and NGAS) to investigate their performances for reproducing N_2O emission, and especially the impacts of two types of N additions (i.e. ammonium and nitrate: NH_4^+ and NO_3^-, respectively) and two levels (low and high) on N_2O emission. In general, the six models reproduced the seasonal variations of N_2O emission, but failed to reproduce relatively larger N_2O emissions due to NH_4^+ compared to NO_3^- additions. Few models indicated larger N_2O emission under high N addition levels for both NH_4^+ and NO_3^-. Moreover, there were substantial model differences for simulating the ratios of N_2O emission from nitrification and denitrification processes due to disagreements in model structures and algorithms. This analysis highlights the need to improve representation of N_2O production and diffusion, and the control of soil water-filled pore space on these processes in order to simulate the impacts of N deposition on N_2O emission.

Keywords: Nitrous oxide; Model; Nitrogen deposition; Forest; Model-data comparison

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1 Introduction

Nitrous oxide (N_2O) is one of the most important greenhouse gases, and contributes 6.24 % to overall global radiative forcing as the third contributor after carbon dioxide and methane (Forster et al., 2007; WMO, 2011). N_2O plays an important role in depleting stratospheric ozone, which decreases harmful ultra-violet radiation reaching the earth. A doubling of the atmospheric N_2O concentration could decrease the ozone layer by 10 % (Crutzen and Ehhalt, 1977; Ravishankara et al., 2009). Since the industrial revolution, the atmospheric N_2O concentration has increased nearly 21 % from about 270 ppbv during the pre-industrial era to 325.9 ppbv in 2013, with an average increase rate of about 0.82 ppbv yr^{-1} during the last decade (WMO, 2014). Terrestrial ecosystems can act as either sources or sinks for atmospheric N_2O, depending on time and location (Potter et al., 1997; Ridgwell et al., 1999; Chapuis-Lardy et al., 2007; Xu et al., 2008). Globally, natural sources from terrestrial ecosystems contribute more than 50 % to the N_2O releases to the atmosphere (Denman et al., 2007). Quantifying N_2O fluxes in global terrestrial ecosystems, therefore, is an urgent task for predicting future climate change (Sheldon and Barnhart, 2009).

Several process–based N cycle models have been developed and widely used for quantifying the spatial–temporal variations in N_2O flux (Li et al., 1992; Engel and Prentice, 1993; Grant et al., 1993; Potter et al., 1996; Xu and Prentice, 2008; Zhuang et al., 2012). In general, these models usually integrate key biogeochemical processes, including nutrient mineralization, immobilization, nitrification, and denitrification. However, there exist substantial model disagreements in the estimated magnitude and spatial distribution of N_2O at regional and global scales (Figure 1). For example, Xu and Prentice (2008) used the DyN model to estimate global terrestrial ecosystem N_2O emission at 13.31 Tg N yr^{-1}, which is 3.94 times the estimate of 3.37 Tg N yr^{-1} arrived at by Zhuang et al. (2012) (Figure 1).

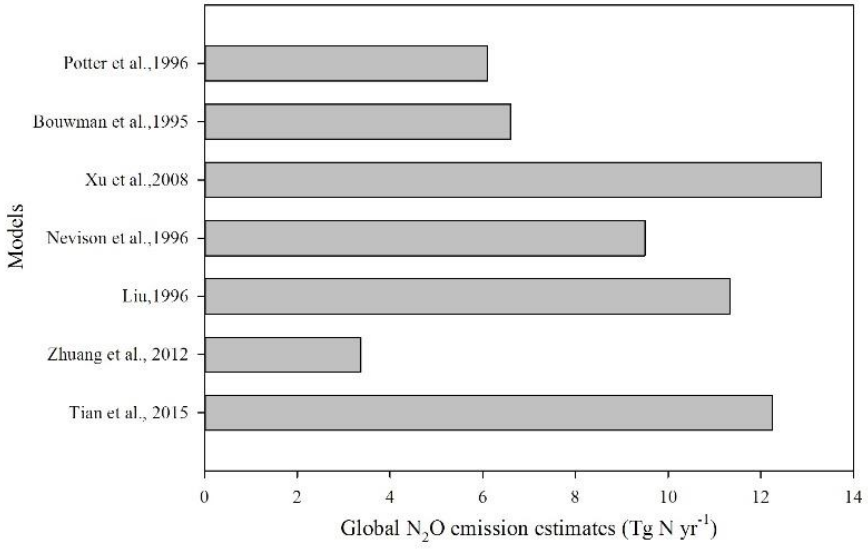

Figure 1. Comparison of global estimates of N_2O emission from the terrestrial ecosystem.

Each model is a combination of equations describing environmental regulations of N_2O emission. Individual model validations, however, are not sufficient to identify the sources of the wide range of model differences. A rigorous comparison must be conducted in a standardized framework with consistent validation datasets and driving variables. To generate more robust estimates of N_2O flux dynamics, it is necessary to compare estimates from a variety of N_2O models and compare them against consistent and extensive measurements that are available.

Atmospheric nitrogen (N) deposition, which is closely related to N_2O emission, has shown a strong increasing trend in recent decades due to the extensive use of fossil fuels in industry and transportation and the heavy application of fertilizers in agriculture (Galloway et al., 2004). It is estimated that global atmospheric N deposition has increased from 1 Tg N in the 1860s to 25–40 Tg N in the 2000s, and is projected to continuously increase to 210 Tg N by the year 2050 (Neff et al., 2002; Lamarque et al., 2005; Galloway et al., 2008; Lu et al., 2016). The forest ecosystem in eastern China was recognized as the region receiving the highest atmospheric N deposition in southeast China (Liu et al., 2013). The N deposition input into terrestrial ecosystems alters plant physiology and the soil microbial community (Litten et al., 2007; Treseder, 2008), thereby changing the soil biogenic N_2O flux (Butterbach–Bahl, 1997; Allen et al., 2004; Bange, 2006; Chen et al., 2015). Based on a meta–analysis of N addition experimental data worldwide, Liu and Greaver (2009) concluded that N addition could increase N_2O emission by up to 216 %. In general, chronic N deposition will increase ammonium (NH_4^+) and nitrate (NO_3^-) availability in terrestrial ecosystems, thereby affecting N_2O flux through changing the activity and composition of the microbial community (Smith et al., 2003; Bowden et al., 2004; Monteny et al., 2006). However, to our knowledge, few studies have evaluated model performance in simulating the impacts of N deposition on N_2O emission.

In this study, six widely–used N_2O models, i.e. DayCENT (the daily version of the CENTURY ecosystem model; Parton et al., 1996, 2001; Del Grosso et al., 2001), DNDC (the Denitrification–Decomposition model; Li et al., 2000), DLEM (Dynamic Land Ecosystem Model; Tian et al., 2010), DyN (the global Dynamic Nitrogen model; Xu and Prentice, 2008), NOE (the algorithm of Nitrous Oxide Emission; Henault et al., 2005), and NGAS (a hybrid of a process–oriented model and a nutrient cycling model; Parton et al., 1996), were chosen for examination of their performance under different levels of N deposition in a subtropical forest in southeast China. The study aims to (i) examine performance of the models in a forest ecosystem, particularly for seasonal variations of N_2O emission, (ii) investigate the ability of these models under different levels of N deposition as well as two N types, and (iii) identify the key issues in the application of these models and future model development so as to improve their simulation of N_2O emissions.

2 Materials and Methods

2.1 Study Site

This model–data comparison is based on field experiments conducted at a subtropical evergreen forest station, the Qianyanzhou Ecological Station (26 °44′39″ N, 115 °03′33″ E). The station is in Jiangxi Province of southern China, which is one of the important regions subject to atmospheric N deposition. The study plots were located in the slash pine plantation

established in 1958. Average tree height was about 15 m, with diameter at breast height of 16.1 cm, stand basal area of 35 m^2 ha^{-1}, and leaf area index of 4.5. Dominant understory and midstory species are *Woodwardia japonica* (L.f.) Sm., *Dicranopteris dichotoma* (Thunb.) Bernh., *Loropetalum chinense* (R.Br.) Olv., and *Quercus fabrei* Hance. The typical soil is weathered from red sandstone and mud stone. Soil texture is divided into 2.0–0.05 mm (17 %), 0.05–0.002 mm (68 %), and < 0.002 mm (15 %). Soil bulk density, organic carbon, total N content, and pH of the surface part (0–40 cm) were 1.57 g cm^{-3}, 7.2 g kg^{-1}, 0.55 g kg^{-1}, and 4.6, respectively. The study site has a humid monsoon climate with a mean air temperature of 17.9 ℃ and precipitation of 1469 mm per year. A large portion of the precipitation occurs in spring and early summer, but it is relatively dry in late summer and autumn with high air temperatures and low precipitation.

2.2. Field Experiments

The field experiments were conducted during April–December 2012. According to previously reported levels of atmospheric N deposition at the study area (Wang et al., 2011), two levels (low and high N of 0 and 120 kg N ha^{-1} yr^{-1}, respectively) of two different N fertilizers (NH_4Cl and $NaNO_3$) were applied to mimic two future scenarios of N deposition. At the same time, a control experiment was carried out for comparison. Each level of N treatment was conducted in a plot of 20 m × 20 m with a space of 10 m between any two plots. The N fertilizer solutions were sprayed on the plots once a month in 12 equal applications, and the control plots received only equivalent deionized water.

Flux data of N_2O were determined using a static opaque chamber and gas chromatography method (Fang et al., 2014), which were installed near an eddy covariance tower in the ecological station. Daily fluxes were collected from the measurements approximately every two weeks. The soil fluxes were calculated based on the rate of changes in their concentration within the chamber, estimated as the slope of the linear regression between concentration and time (Wang et al., 2011). Soil temperature at 5 and 10 cm depths were monitored at each chamber site, using portable temperature probes (JM624 digital thermometer, Living–Jinming Ltd., Tianjin, China). At the same time, soil samples were collected nearby the static chambers from a depth of 0–20 cm using an auger (2.5 cm in diameter). Volumetric soil moisture (m^3 m^{-3}) was measured using a moisture probe meter (TDR100, Spectrum Technologies Inc., PlainField, IL, USA). Soil pH was also measured using the potentiometry method. Soil water–filled pore space (WFPS) was calculated using the methods reported by Fang et al. (2014).

2.3. N_2O Models

Six N_2O models were selected in this model-data comparison: DayCENT (Parton et al., 1996, 2001; Del Grosso et al., 2001), DNDC (Li et al., 2000), DLEM (Tian et al., 2010), DyN (Xu and Prentice, 2008), NOE (Henault et al., 2005), and NGAS (Parton et al., 1996). All six investigated N_2O models are based on two major microbial processes: nitrification and denitrification, which are separately simulated from these two processes using the following equation:

$$F_{N_2O} = F_{nt} + F_{dn} \quad (1)$$

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where F_{N_2O} is the N_2O emission from soil to air (g N m^{-2} day^{-1}), and F_{nt} and F_{dn} are N_2O emissions from nitrification and denitrification processes, respectively. Detailed model algorithms can be found from the Supplemental Online Materials.

2.4. Simulation Protocol and Parameter Inversion

The field observations of soil temperature, soil moisture, pH, soil respiration, dissolved organic carbon, soil NH_4^+ content, and soil NO_3^- content were used to drive the six models. As one of the key drivers, WFPS was derived using the following equation (Fang et al., 2014):

$$WFPS = VWC/(1 - BD/2.65) \quad (2)$$

where *VWC* is soil volumetric moisture content (%), *BD* is soil bulk density (g cm^{-3}), and 2.65 is soil particle density (g cm^{-3}).

The nonlinear regression procedure (Proc NLIN) in the Statistical Analysis System (SAS, SAS Institute Inc., Cary, NC, USA) was applied to optimize the model parameters using observed N_2O emission for all five experiments. The calibrated parameter values were used to simulate N_2O emissions (Table S1).

Three metrics were used to evaluate the performance of these models:

(i) The coefficient of determination between observation and simulation (R^2).

(ii) Absolute predictive error (PE), quantifying the difference between simulated and observed values.

(iii) Relative predictive error (RPE), computed as:

$$RPE = (\bar{S} - \bar{O})/\bar{O} \times 100 \quad (3)$$

where $\bar{S}$ and $\bar{O}$ are mean simulated and mean observed values, respectively.

3 Results

All six models generally reproduced the seasonal variations of measured N_2O fluxes for the control and four N addition experiments. The measurements showed the largest N_2O emissions during April–July, and the lowest in winter (Figure 2). The simulated emissions showed some differences in estimates for various models. Although the simulated N_2O emissions from different models decreased from spring and summer to autumn and winter, indicating the seasonal pattern of emissions (Figure 1), there were some abrupt changes in model estimates. Most models captured the peak and trough of N_2O emission. Collectively, the six models explained 1 %–16 % of the variations in N_2O fluxes across all experiment plots (Table 1).

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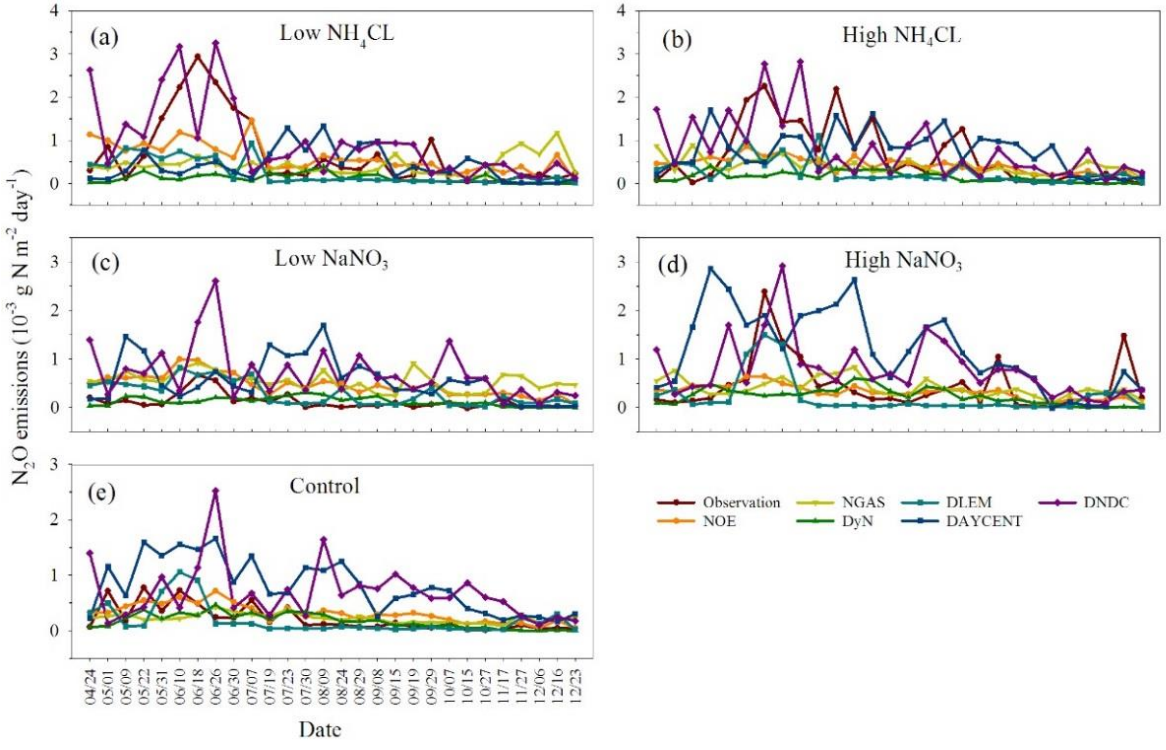

Figure 2. Comparisons of N_2O emission simulations and observations for five experiment treatments.

Most models did not fully indicate the stimulations of N additions to N_2O emission that were observed in field experiments. According to the observed N_2O fluxes, NO_3^- and NH_4^+ additions increased N_2O emission for four addition experiments, and high NO_3^- and NH_4^+ additions led to higher N_2O emission compared to low additions (Figure 3). Furthermore, larger increases of N_2O emission occurred for NH_4^+– compared to NO_3^-–addition experiments (Figure 3). However, NGAS, DyN, DayCENT, and DNDC models simulated larger NO_2 fluxes for low compared to high NH_4^+–addition treatments (Figure 3). NOE and NGAS did not correctly indicate the differences of N_2O fluxes between high and low NO_3^- treatments. In addition, the experiments also indicated higher simulations of N_2O emission for NH_4^+ compared with NO_3^- additions. However, only NOE and DLEM models reproduced larger impacts of NH_4^+ on N_2O emissions compared with low NH_4^+ level.

Table 1. Predictions of the six N_2O models for four N addition treatments

Model/N level		Low NH_4Cl	High NH_4Cl	Low $NaNO_3$	High $NaNO_3$	Control
Obs	Mean[#]	0.69^{b}	1.14^{a}	0.29^{c}	0.78^{ab}	0.18^{c}
NOE	Mean	0.62^{ab}	0.62^{b}	0.53^{b}	0.48^{b}	0.47^{a}
	R^2	0.55^{*}	0.35^{*}	0.61^{*}	0.40^{*}	0.33^{*}
	PE	–0.07	–0.51	0.24	–0.30	0.29
	RPE (%)	–11.16	–44.92	84.45	–38.43	163.51

NGAS	Mean	0.55^{b}	0.29^{d}	0.49^{b}	0.35^{d}	0.22^{bc}
	R^2	0.11	0.27*	0.50*	0.01	0.14*
	PE	–0.16	–0.85	0.19	–0.42	0.042
	RPE (%)	–22.33	–74.52	69.47	–54.73	24.33
DyN	Mean	0.49^{b}	0.41^{c}	0.48^{bc}	0.58^{b}	0.43^{ab}
	R^2	0.28*	0.23*	0.14*	0.15*	0.21*
	PE	–0.21	–0.73	0.19	–0.20	0.28
	RPE (%)	–29.65	–64.92	67.11	–26.02	139.70
DLEM	Mean	0.51^{b}	0.79^{ab}	0.42^{bc}	0.43^{b}	0.29^{b}
	R^2	0.38*	0.24*	0.58*	0.79*	0.57*
	PE	–0.19	–0.35	0.14	–0.39	0.11
	RPE (%)	–27.46	–30.87	47.86	–44.51	64.15
DayCENT	Mean	0.61^{ab}	0.52^{a}	0.62^{ab}	0.98^{a}	0.51^{a}
	R^2	0.13*	0.14*	0.01	0.23*	0.28*
	PE	–0.09	–0.62	0.33	0.20	0.34
	RPE (%)	–12.16	–54.51	115.36	24.92	188.84
DNDC	Mean	0.92^{a}	0.78^{ab}	0.78^{a}	0.98^{a}	0.59^{a}
	R^2	0.35*	0.13*	0.25*	0.31*	0.01
	PE	0.22	–0.36	0.49	0.19	0.41
	RPE (%)	30.85	–31.94	172.51	24.80	234.71

Note. Letters indicate significant differences among N_2O values for the same levels of N addition from different model simulations or observation. R^2 is the coefficient of determination between observation and simulation. PE is absolute predictive error. RPE is relative predictive error. # indicates the mean value of observed or simulated N_2O emissions (10^{-3} g N m^{-2} day^{-1}). * indicates the significance of $p < 0.05$.

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-126
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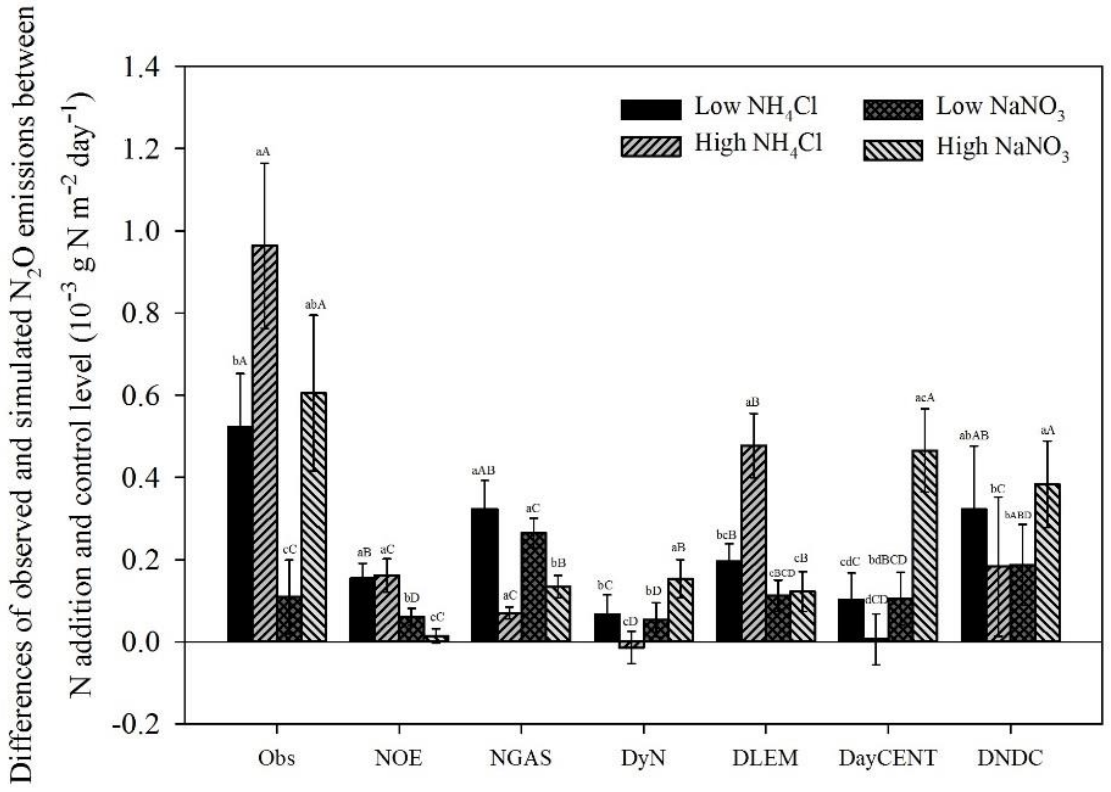

Figure 3. Comparisons of N_2O emission differences between N addition and control treatments from observation and model simulations. Lower–case letters indicate significant differences among the values for different N addition level for an individual model or observation. Capital letters indicate the significant difference among the values for the same levels of N addition from different model simulations or observation.

Because N_2O emissions are generally from two different microbial processes, i.e. nitrification and denitrification, the proportions of N_2O emissions due to both processes were calculated to quantify their contributions to total emissions. All six models showed consistently negative correlations between the ratios of N_2O emission from nitrification and WFPS (Figure 4a). The six models showed that nitrification contributed more than half of N_2O emissions; however, there were large differences in the ratios of N_2O fluxes generated by nitrification and denitrification among the models (Figure 4b). On average, the DayCENT model simulated the lowest ratio (about 55.4 %) of N_2O emissions generated by nitrification, and the largest ratio (about 89.5 %) was for the DyN model (Figure 4b).

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-126
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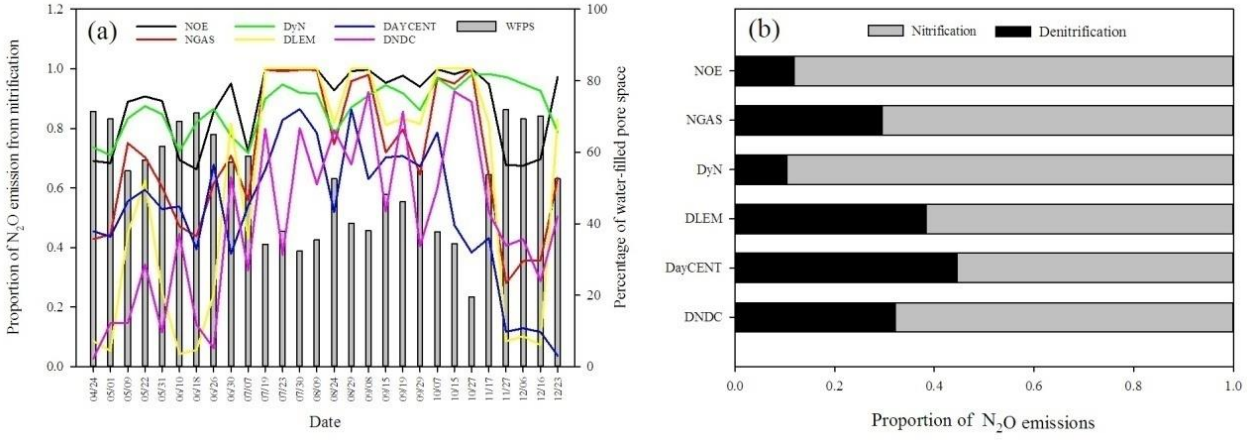

Figure 4. Proportions of N_2O emissions for different models. (a) Seasonal proportion of N_2O emission from nitrification and seasonal water–filled pore space (WFPS). (B) Averaged proportion of emissions from nitrification and denitrification.

4 Discussion

4.1. Model Performance

Compared with ecosystem carbon dioxide emissions, few studies have evaluated model performance for simulating N_2O emissions due to the relative scarcity of N cycle measurements (Henault et al., 2012). Notably, N depositions from the atmosphere have been documented to increase with industry processes (Galloway et al., 2004), which are believed to have significant impacts on soil N_2O emissions due to their impacts on microbial processes. Therefore, the sixth IPCC report, which will be conducted in the next five years, requires Earth System Models integrate N cycle (IPCC, 2017). Therefore, process–based N_2O models have been widely developed and applied in recent years (Li et al., 1992; Engel and Priesack, 1993; Parton et al., 1996; Potter et al., 1997; Del Grosso et al., 2001; Henault et al., 2005; Xu and Prentice, 2008; Tian et al., 2010). These models are now being used not only for the prediction of N_2O emissions from different ecosystems, but estimation of N_2O inventories on national, regional, and global scales, and for assessing climate change impacts and mitigation strategies (Del Grosso et al., 2006, 2009; EPA, 2006). However, it should be noted that these model predictions may not be reliable when applied to a new environment, and their performance should be first tested with different data streams from real world experiments.

Our comparison showed the general performance of six investigated models in reproducing seasonal variations and magnitudes of N_2O emissions (Figure 2). This conclusion was supported by several recent model evaluations, which revealed unstable performance of N_2O models (Senapati et al., 2016). For example, different studies with the DayCent model have found a range of correlations from weak to strong across different agroecosystems (Henault et al., 2012). Parton et al. (2001) found correlations between daily measured vs. simulated N_2O emissions, with range 0–0.44, from a variety of five

different grassland sites in the USA. Other ecosystem models also face similar difficulties in simulation of daily N_2O emissions, for example DNDC (Yeluripati et al., 2015) and CoupModel (He et al., 2016).

The comparison revealed the complexity in modeling the impacts of N addition on N_2O emission. The field observations in the current study indicated larger N_2O emissions for NH_4^+ compared with NO_3^- additions at two addition levels (Figure 3). However, these impacts were not reproduced by all of the six models except for the DELM and NOE models. Previous study showed that the impacts of NH_4^+ addition on N_2O emissions are, to some extent, larger compared with NO_3^- addition (Wang et al., 2016). This is probably due to two primary reasons. One is that under favorable temperature and moisture, nitrification dominates N_2O emission compared with denitrification if soil is acidic and rich in NH_4^+. The addition of NH_4^+ can significantly increase the substrates for ammonia–oxidizers and the abundance of ammonia–oxidizing archaea, which give rise to increases in soil autotrophic nitrification rate (Gao et al., 2016a; 2016b). The other reason is that additions of NH_4^+ fertilizers can have larger impacts on the acidification of soil compared with the additions of NO_3^-, which is closely related to the accumulation of H^+ in soil solution and the leaching of NO_3^- from soil (Tian and Niu, 2015). Soil acidification decreases availability of NH_4^+, which is favorable to the growth of soil nitrifiers, i.e. ammonia–oxidizing archaea, but unfavorable to soil denitrifiers (Isobe et al., 2012).

4.2. Structure Differences among N_2O Models

The performance of these N_2O models strongly depends on model algorithms, and also on the major pathways of N_2O emissions and their responses to environmental conditions. This is because the processes of N_2O emissions are extremely competitive and are controlled by many drivers, e.g. soil temperature, moisture, soil redox potential, and the availability of substrates for microbes (Schmidt et al., 2000). In the present study, the models did not adequately capture the environmental regulation of N_2O emission. Nitrification and denitrification are two major processes of N_2O production. Numerous experiments have shown that nitrification and denitrification can occur simultaneously because of the coexistence of aerobic and anaerobic zones in soils (Henault et al., 2012; Hu et al., 2015); however, the availability of soil oxygen–determined by soil water content and other soil properties – strongly regulates the proportion of nitrification and denitrification (Li et al., 1992). Numerous studies have investigated the relationship between soil moisture and the contributions of nitrification and denitrification processes. In N fertilizer–amended soil, N_2O emission has been found to be highly correlated with WFPS, with the highest emission at around 70 % WFPS, which was attributed to a combination of nitrification (35 %–53 %) and denitrification (only 2 %–9 %) (Huang et al., 2014). In sandy loam soils, when moisture status was sub–optimal for denitrification (50 % and 70 % WFPS), nitrification was the significant contributor (around 29 %) to N_2O emissions (Kool et al., 2011); however, in wetter soils (–0.1 kPa) nitrification contributed less than 3 % (Webster and Hopkins, 1996). Well et al. (2008) attributed 88 % of total N_2O emission to nitrification at 45 %WFPS. This suggests that favorable conditions for N_2O production from nitrification occur within the range of 30 %–70 %, whereas denitrification dominates N_2O production in wet soils with WFPS>80 % (Braker and Conrad, 2011; Huang et al., 2014). The values of WFPS in the current study were within the range of 30 %–70 %, which was favorable to the occurrence of nitrification in all of these models.

In general, all six N_2O models use soil water content to control the balance of two processes. NOE uses a simplified scheme to separate the nitrification and denitrification processes. Nitrification only occurs if WFPS < 80 %, whereas denitrification only occurs if WFPS > 62 %; within the range of 62 %–80 %, the two processes may occur simultaneously (Henault et al., 2005). For DLEM, denitrification and nitrification are simulated as a one–step process. Due to the effect of soil moisture, denitrification only occurs when soil moisture exceeds field capacity (Tian et al., 2010). For DyN and DNDC, aerobic and anaerobic microsites are assumed to simultaneously exist in most soils. Nitrification occurs in aerobic microsites, but denitrification is mainly in anaerobic microsites. The key factor affecting the ratio between aerobic and anaerobic microsites is soil redox potential, which controls the ratio between nitrification and denitrification (Li et al., 1992; Xu and Prentice, 2008). For NGAS and DayCENT, no specific threshold is applied for the occurrences of the two processes and they are assumed to occur simultaneously (Parton et al., 1996, 2001; Del Grosso et al., 2001). Thus, the differences in the algorithms of the six models are believed to be the key reasons for the differences in the model estimates of N_2O emission.

5 Conclusions

We examined the performance of six N_2O models for indicating the impacts of different levels of N addition on N_2O emission. Results indicated that the investigated models can represent the general seasonal variations of N_2O emissions under both N addition and non–N addition levels. However, additions of NH_4^+ rather than NO_3^- could have more significant effects on N_2O emissions from soils, which were not represented by most of the models. In addition, most of the models failed to reproduce larger N_2O emissions at high level of nitrate additions compared with ammonia additions. Moreover, the analysis suggested that the disagreements in model structure and algorithms resulted in substantial differences in N_2O emission and mediating processes (i.e. nitrification and denitrification).

Competing interests. The authors declare that they have no conflict of interest.

Data availability. The data can be obtained upon request to the authors.

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