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RESEARCH ARTICLE

Estimates of N_2O Emissions and Mitigation Potential from a Spring Maize Field Based on DNDC Model

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Abstract

Agricultural production plays an important role in affecting atmospheric nitrous oxide (N_2O) concentrations. Field measurements were conducted in Dalian City, Liaoning Province in Northeast China from two consecutive years (2009 and 2010) to estimate N_2O emissions from a spring maize field, a main cropping system across the Chinese agricultural regions. The observed flux data in conjunction with the local climate, soil and management information were utilized to test a process-based model, DeNitrification-DeComposition (DNDC), for its applicability for the cropping system. The validated DNDC was then used for exploring strategies to reduce N_2O emissions from the target field. The results showed that the major N_2O pulse emissions occurred with duration of about 3-5 d after fertilizer application in both years 2009 and 2010, which on average accounted for about 60% of the total N_2O emissions each year. Rainfall and fertilizer application were the major factors influencing the N_2O emissions from spring maize field. The average N_2O fluxes from the CK (control plot, without fertilization) and FP (traditional chemical N fertilizer) treatments were 23.1 and 60.6 μg m^{-2} h^{-1} in 2009, respectively, and 21.5 and 64.3 μg m^{-2} h^{-1} in 2010, respectively. The emission factors (EFs) of the applied N fertilizer (270 kg N ha^{-1}) as N_2O-N were 0.62% in 2009 and 0.77% in 2010, respectively. The comparison of modeled daily N_2O emission fluxes against observations indicated that the DNDC model had a good performance even if without adjusting the internal parameters. The modeled results showed that management practices such as no-till, changing timing or rate of fertilizer application, increasing residue incorporation, and other technically applicable measures could effectively reduce N_2O emissions from the tested fields. Our study indicated that avoiding application of N fertilizers at heavy rainfall events or splitting the fertilizer into more applications would be the most feasible approaches to reduce N_2O emissions from spring maize production in Northeast China.

Key words: spring maize, N_2O, DNDC, mitigation measures, Northeast China

INTRODUCTION

Nitrous oxide (N_2O) has been recognized as one of the most important trace gases in the atmosphere that causes global warming and stratospheric ozone depletion. Atmospheric N_2O concentration at present is about 319 ppb, still increasing at a rate of approximately 0.26% per year (IPCC 2007). The main sources of atmospheric N_2O include fossil fuel combustion, biomass burning,

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arable land, animal excreta, soils under natural vegetation and oceans (Bouwman *et al*. 1995). Of global anthropogenic emissions in 2005, agriculture accounts for about 60% of N_2O (IPCC 2007). Nitrogen (N) fertilization is considered the primary source of N_2O emissions from agricultural soils (Mosier *et al.* 1998). China as a large agricultural country is now the largest consumer of synthetic N in the world, accounting for 30% of the world's total use (Huang *et al*. 2010). Therefore, quantifying agricultural N_2O emissions and seeking suitable mitigation measures have become an essential task in current scientific research. However, the task has proved to be uneasy due to the complex interactions among soil texture, soil water content, microbial activity, substrate concentration and soil N_2O production (Li *et al*. 1992).

Different approaches have been developed to predict N_2O emissions from agricultural soils. The IPCC default methodology, emission factors (i.e., EFs), is extensively used for calculating N_2O emissions from agricultural soils for their national inventories (IPCC 2006), which is deduced from a limited number of observations but represents an average value over all soil types, climate conditions and management practices. Therefore, there is a high degree of uncertainty associated with the emission factor method to evaluate regional or national N_2O emissions. While, direct measurement of greenhouse gas emissions through field observation is a normal method, but the method used for inventory purposes is impractical as it would require too many measurements to be made over large areas and for long periods of time. For these reasons the development of a more process-based approach is desirable. In fact, models offer the possibility to simulate the intricate processes in the soil and the change of N_2O emissions. Process-based models, such as CENTURY, CASA, EXPERT-N, DAYCENT and DNDC model, etc., are widely accepted and used to predict the impact of various agricultural management practices on N_2O emissions by simulating the two microbially mediated processes, nitrification and denitrification, the mainly processes in soil produced N_2O (Li *et al*. 2010). In comparison with these models, DNDC model is the most detailed in process description. It simulates N_2O emissions by tracking all the factors that impact nitrification and denitrification processes, such as microbial activity, redox potentials, active organic carbon, ammonium nitrate and nitrogen concentration, the dynamics of the microbial denitrifer population, etc. (Qiu *et al*. 2004; Wang *et al*. 2008; Gao *et al*. 2011; Li *et al*. 2011).

In China, maize is the second most important cereal crop in China (FAO 2010), and the area sown to maize has increased from 19.6 million ha in 1978 to 31.2 million ha in 2010. Spring maize is mainly grown in Liaoning, Jilin, Heilongjiang, Gansu, Shanxi, and Shaanxi provinces and Ningxia Hui and Inner Mongolia Autonomous Regions (Fig. 1). The sowing area of spring maize is almost 36% of the total maize area, and the yield accounts for 40% of the total maize yield (National Statistics Bureau of the People's Republic of China 2011). Maize requires more fertilizer N than other crops (IFA 2009), but the N use efficiency for maize worldwide is only 30% because much of the applied N is lost to the environment (Huang *et al*. 2010). Maize may be an important source of N_2O (Zhang *et al*. 2012). Therefore, a great number of studies have been conducted on N_2O flux measurements from maize cropping system (Sun *et al*. 2008; Wang and Hu 2011), but only very few studies with limited sites have conducted N_2O flux measurements in spring maize system, which mainly focus on N_2O emissions from irrigated and N fertilized spring maize cropping system in North China Plain (Liu *et al*. 2008; Zhou *et al*. 2011). It still lacks of studies in the no-irrigation regions of the northwest and northeast China, especially applying the process-based biogeochemical model to predict the N_2O emission from spring maize system is seldom reported. In addition, the large differences of fertilizer-induced N_2O emission factors due to the large temporal-spatial variations of N_2O fluxes from the agricultural field indicate that more field measurements are still needed. The objectives of this study are: (1) to identify the seasonal variation and main environmental drivers of N_2O emissions under the traditional management practices from a spring maize field in northeast China; (2) to test the DNDC model for the simulation of N_2O emissions using the observed data; (3) to assess the total seasonal amount of N_2O emissions and EFs by integrating field and model methods; and (4) to devise feasible strategies to reduce N_2O emissions.

RESULTS

Measured N_2O fluxes

Fig. 2 shows episodic emissions of N_2O and precipitation pattern for the experimental field during the two consecutive maize growing years. N_2O emissions showed similar seasonal variations in 2009 and 2010. The average N_2O fluxes from FP and CK treatments were 60.6 and 23.1 µg m^{-2} h^{-1} in 2009, and 64.3 and 21.5 µg m^{-2} h^{-1} in 2010, respectively (Table 1). High peaks of N_2O fluxes from the fertilization plots induced by the fertilizer application only observed during short durations in both years. The maximum N_2O fluxes after the fertilizer application on June 10 in 2009 were lower than those in 2010 (Fig. 2). The observed N_2O emission peak was 379.8 µg m^{-2} h^{-1} with standard errors 109.4 µg m^{-2} h^{-1} in 2009, and 406.9 µg m^{-2} h^{-1} with standard errors 60.4 µg m^{-2} h^{-1} in 2010, for the whole spring maize season. The repeated measurements during the two maize seasons revealed that the spatial variations could usually be higher than 30%. The difference in precipitation between the two years might be responsible for the yearly variation of N_2O emissions from the fertilizer plot. The precipitation in 2009 (545 mm) was 30% lower than that in 2010 (780 mm). The significant positive correlation between N_2O fluxes and soil water-filled pore space (WFPS) for the FP ($P<0.05$) and CK ($P<0.01$) treatments in both years revealed that soil moisture played important roles for N_2O emissions from these plots. By using the interpolation approach, the cumulative emissions of N_2O for the FP treatment were calculated to be 2.56 and 2.71 kg N ha^{-1} for 2009 and 2010, respectively, while those from the CK treatment were 0.88 and 0.64 kg N ha^{-1}, respectively. During the 2 years, N_2O emission from the fertilized plot was significantly greater than that from the unfertilized plot ($P<0.01$, Table 1). In addition, the emission factors (EFs) were 0.62% in 2009 and 0.77% in 2010, respectively.

Fig. 1 Area where spring maize is grown in China and location of the experiment site at Dalian.

Table 1 Comparison of N_2O fluxes (means±standard error) and fertilizer-induced N_2O-N emission factors (EFs) in different plots

Year	Treatment	Total N (kg N ha^{-1})	Mean N_2O fluxes (µg N m^{-2} h^{-1})	Cumulative N_2O emissions (kg N ha^{-1})	EF (%)
2009	CK	-	23.14±4.65	0.88	-
	FP	270	60.64±13.25	2.56	0.62
2010	CK	-	21.53±5.69	0.64	-
	FP	270	64.32±12.94	2.71	0.77

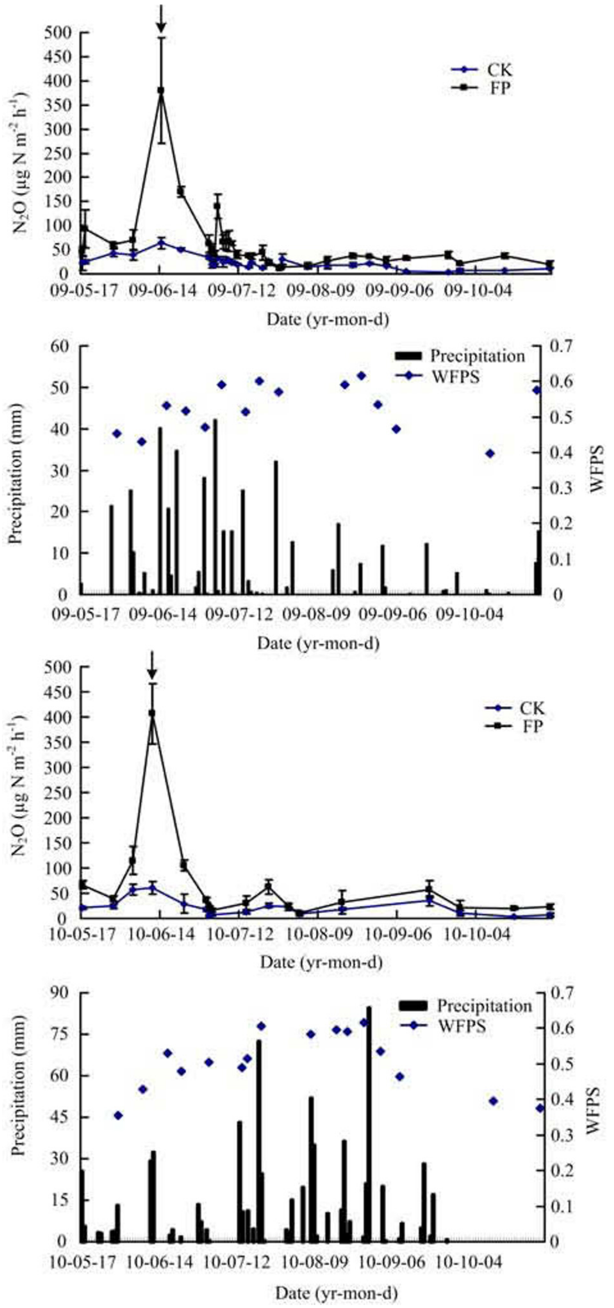

Fig. 2 The seasonal variation of climate and N_2O emissions during the spring maize season. Arrows: fertilizer time.

Model validation

DNDC quantifies N_2O fluxes by simulating both nitrification and denitrification rates at daily and hourly time steps, respectively. Therefore, the measured daily N_2O fluxes were utilized to test DNDC for its applicability for the spring maize system. Two fertilizer application rates, full fertilization with 270 kg N ha^{-1} applied annually (FP) and no fertilizer used (CK) in 2009 and 2010, were simulated. The simulated data indicated that the modeled background emissions of N_2O were mostly from denitrification, and the episodic peak fluxes were dominated by nitrification. The model well predicted the magnitudes and patterns of the observed N_2O emissions for both FP and CK treatments during two maize growth seasons (Fig. 3). Especially, the model captured the timing and magnitude of high peaks of N_2O emissions measured at the FP field, which were induced by the N-fertilizer applications or precipitation in both years. The results showed the applicability of DNDC for the tested cropping system. However, DNDC underestimated N_2O emissions for the maize maturing period especially in the last month of observation period in 2009. The discrepancy could be related to underestimation of the soil residual N by the end of the season. The overall correlation between observed and simulated daily N_2O fluxes was acceptable for FP and CK (R^2=0.87 and 0.51 in 2009, and 0.74 and 0.49 in 2010, respectively). The simulated cu-

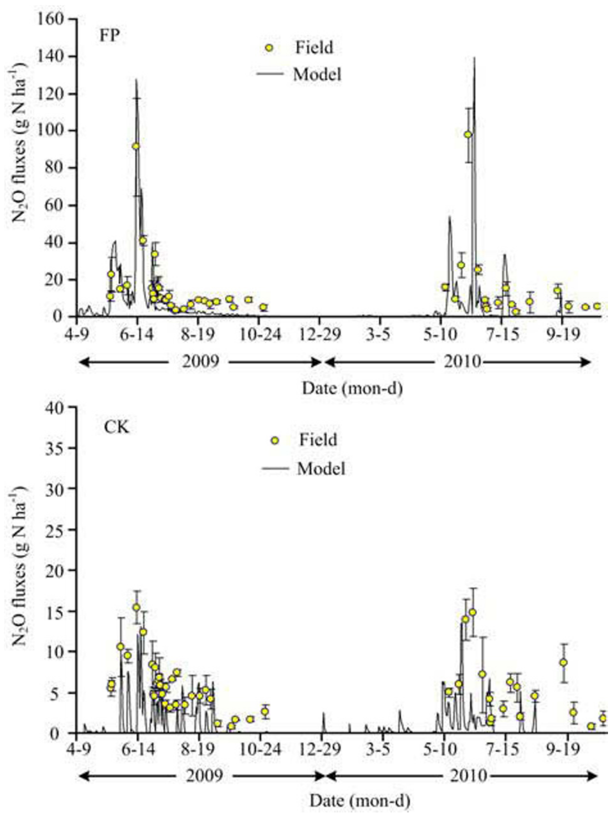

Fig. 3 The comparison of observed and simulated seasonal variation of N_2O emissions.

mulative emissions of N_2O during the maize growing season were 1.57 and 0.33 kg N ha^{-1} yr^{-1} for the fertilized plot and the unfertilized plot in 2009, respectively, and 1.81 and 0.26 kg N ha^{-1} yr^{-1} for the two treatments in 2010, respectively. The absolute differences between the observed and modeled N_2O fluxes for the CK and FP treatments were 0.55 and 1 kg N ha^{-1} yr^{-1} in 2009, respectively, and 0.4 and 0.9 kg N ha^{-1} yr^{-1} in 2010, respectively. The discrepancy on the N_2O emissions could be related to the interpolation approach converting the observed daily N_2O fluxes to an annual total. Overall, considered the inherently complex processes involved in the N_2O production/consumption in the field and the high spatial variations, the modeled results were encouraging though discrepancies existed in some cases.

Mitigation measures

The DNDC model is a useful tool for interpreting how the varied management practices affected N_2O emissions. In this study, DNDC was run with each of alternative management practices to produce an annual flux of N_2O for the tested site, and hence the sensitivity of the main factors could be determined by comparison the simulated annual N_2O fluxes (Fig. 4). According to the simulated results, among the tested farming management practices, fertilizer application rate showed almost linear effect on N_2O emissions. Increase in fertilizer application rate from 90 to 330 kg N ha^{-1} increased N_2O emission rate from 0.49 to 2.9 kg N ha^{-1} yr^{-1}, with nearly an increase of 5 times. In the tests, conventional tillage with a tilling depth 20 cm elevated N_2O emissions. The simulated results indicated that the soil disturbance with tillage increased the soil aeration and decomposition rate that led to more substrates (e.g., DOC, ammonium, nitrate and etc.) released into the soil to stimulate nitrification and denitrification. Splitting the annual fertilizer into three or more applications showed significant effect on N_2O emissions by reducing 25% of N_2O emissions. This result was consistent with observations reported by Xu *et al*. (2000). Adding organic material to the soil, e.g., manure amendment of 100 kg N ha^{-1} yr^{-1}, can significantly increase N_2O emissions by 30%, which would in a large degree offset the carbon benefit by manure input. Manure amendment increased SOC content that provided more substrates to stimulate N_2O emissions through nitrification and denitrification in the soil. However, tests showed that elevating the rate of crop residue incorporation from 0 to 100% resulted in 23% less N_2O emitted.

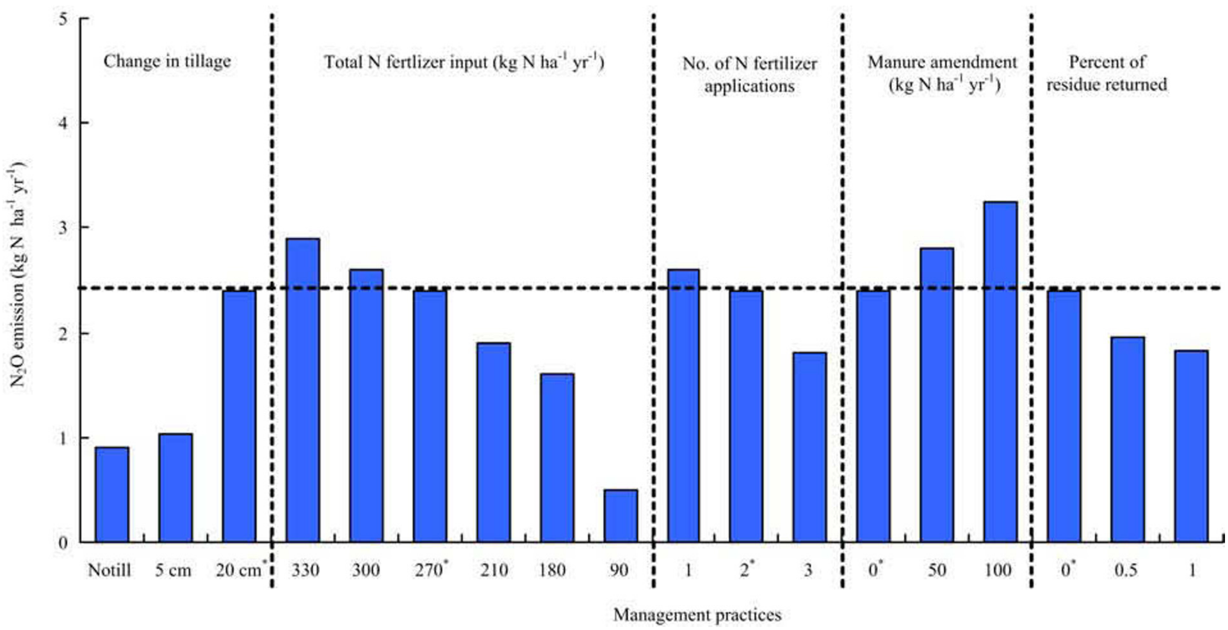

Fig. 4 Test of N_2O emissions to alternative management practices including tillage, fertilizer application, number of fertilizer application, manure amendment, and percent of residue returned. The alternative management practices, with asterisks, are baseline conditions. Notill, 5 cm, and 20 cm stand for no-tillage, tilling 5 cm and tilling 20 cm, respectively. 330, 300, 270, 210, 180, 90 stand for the amount of total N fertilizer input, respectively.

It was likely that the addition of organic carbon would result in insufficient oxygen supply and reduce the activity of autotrophic nitrification bacteria, and impact N_2O emissions. Some studies also revealed that decayed crop straw may produce chemical compounds which can significantly reduce N_2O emissions from the soil (Zhou and Huang 2002).

DISCUSSION

Environmental variables

It is well known that the production of N_2O is governed by many factors, such as soil temperature, available organic carbon and soil water content as well as soil NH_4^+ and NO_3^- content, which control the growth and metabolism of microorganisms (Sun *et al*. 2010). Even within a same tested site total N_2O emissions showed large annual variability. N_2O emissions from the control and conventional cultivated spring maize field in 2009 reported by Liu *et al*. (2011) were 0.21 and 1.19 kg N ha^{-1}, respectively, which were 0.18 and 1.17 kg N ha^{-1}, respectively by Zhou *et al*. (2011) in the same field in 2010. The climate factors such as rainfall and temperature could be the main cause inducing the deviation. Soil temperature is one of the key environmental factors which drives N_2O emission due to its effect on the activity of microorganisms. In our study N_2O emission in spring maize field was significantly correlated with N fertilizer application rates. The relationship between N_2O fluxes and fertilizer application observed in the study was in agreement with other observations in the spring maize fields of China (Liu *et al*. 2011). In addition, our field measurements indicated that fertilizer application was not the only factor determining N_2O fluxes. For example, a peak of N_2O flux was measured following an event of heavy rainy over 40 mm, which ranged between 114.2 and 165.5 μg m^{-2} h^{-1} in the fertilizer plot on July 4, 2009. It was likely that the soil nitrate accumulation and high soil moisture inherently created a suitable environment for nitrification reactions that drove the higher N_2O flux. However, variation of the soil temperature did not affect N_2O emissions very much, which was not in agreement with the results of Wang *et al*. (2008, 2010). We found that, in comparison with soil temperature, the rainfall had greater effects in promoting N_2O emission, especially just after topdressing with urea. An experiment conducted in dry farmland of Northeast China by Huang *et al*. (1999) indicated that in the dry climate and low soil moisture content, N_2O production mainly come from the process of nitrification. After heavy rainfall, the soil water content was high and it was mainly governed by the denitrification process. The role of rainfall in promoting N_2O emissions in some extent could overcome the effects of temperature (Xu *et al*. 2002; Beare *et al*. 2009). Zhou *et al*. (2011) also found that there was a significant correlation between N_2O emission and soil water content during the spring maize growth period. The factors such as fertilizer and precipitation had the greatest effects on N_2O emissions for the tested spring maize site.

Uncertainties of the N_2O emission estimates

The estimates of the cumulative N_2O emission from the cultivated spring maize field could have high uncertainties due to the method of interpolation, especially for N_2O that is characterized with episodic emissions. Most previous studies measured N_2O emission using the closed static chamber method with low frequency of sampling (e.g., once a week or month) in a long period or high frequency of measurement in a short period (e.g., 6 mon). Therefore, annual emission rates of N_2O were estimated by interpolating the measured datasets with monthly or weekly intervals, which may led to the overestimation of total N_2O emissions. A test by Ju *et al*. (2011) showed that a sampling frequency of 3 or 6 d led to 112-228% or 112-236% overestimation of total N_2O emissions. In this study, N_2O emission was only governed by the factors fertilizer and precipitation, and hence the N_2O peak emissions were found in 1-5 d after fertilizer application and rainfall events (Fig. 2). The emission rates of N_2O were obviously overestimated by filling the missing days with observed peak N_2O fluxes. Fig. 5 showed the comparison of modeled and observed cumulative N_2O emission rates in 2009. Once the rainfall or fertilizer event happened, the observed cumulative N_2O emission calculated by the interpolation method increased sharply and greatly exceeded the simulations along with the time prolonged. Over the entire investigation period, the

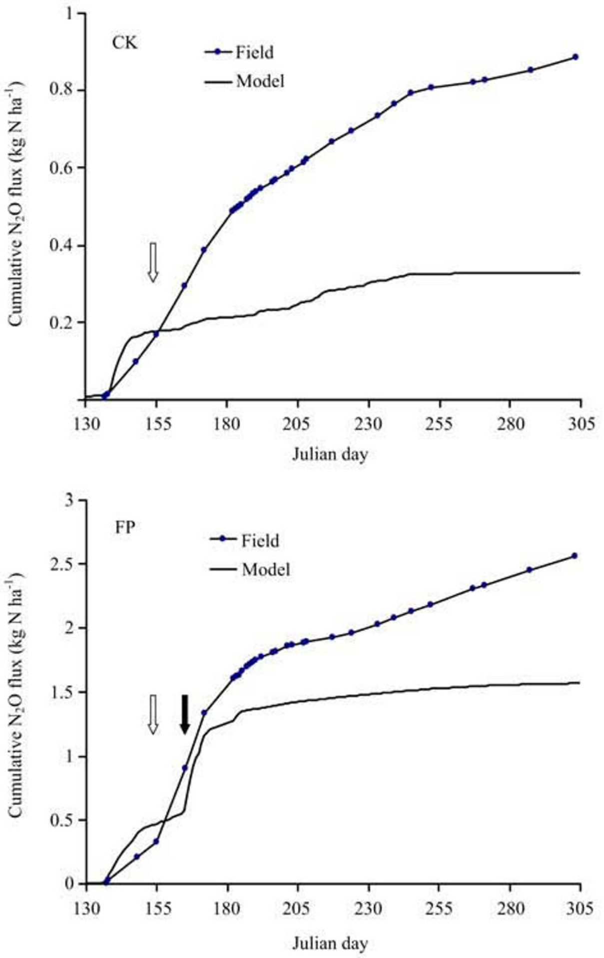

Fig. 5 Comparison of model and field cumulative N_2O emission flux. Unfilled arrow, rainfall; filled arrow, fertilization.

cumulative N_2O emissions calculated from manual measurements were 62% higher than those from DNDC model in the fertilizer plots and 38% higher in the non-fertilizer plots. From the results of present and previous studies, we realized that an overestimation or underestimation of seasonally accumulative N_2O emissions from upland soils cannot be avoided by static chambers (Yao *et al*. 2009; Ju *et al*. 2011). The underestimation was due to missing a number of transient high-flux events stimulated by environmental or management factors. However, the comparisons of simulated daily N_2O emissions based on daily time steps showed that the DNDC model also underestimated the N_2O emissions in our experiment. Fortunately, the manual measurements with static chamber system have been recently improved, for example, with a well-designed sampling strategy, i.e., daily flux measurements following fertilization, tillage or rainfall events and then at intervals of three measurements per week, the seasonal dynamic of N_2O fluxes can be captured well (Yao *et al*. 2009). Therefore, further field measurements and model simulations were still needed.

N_2O emission factors

The current study indicated that fertilizer induced N_2O emissions accounted for 0.62% in 2009 and 0.77% in 2010, respectively, of the fertilizer N applied in the conventional treatment. The IPCC (2006) advocated the use of EFs (1% of applied N) to estimate the amount of N_2O directly emitted from fertilizer applications for inventory purposes. Our result was considerably less than the factor IPCC (2007) recommended. Therefore, the N_2O emissions could be overestimated for the spring maize fields of north China if using the IPCC factor. A research by Liu *et al*. (2011) also found a low EF (0.55% of applied fertilizer 180 kg N ha^{-1}) from a spring maize field in Northeast China which was lower than that produced in this study. At a range of N fertilizer application rate from 180 to 360 kg N ha^{-1} for the tested site, significant correlation was also found between the total amounts of the N fertilizer application and the cumulative N_2O emissions (R^2=0.985, P<0.01, n=7), which indicated that the relatively low fertilizer input might effectively reduce the fertilizer loss in form of N_2O (Fig. 6-A). To certify the above conclusion, taking 2009 as an example, N_2O flux was further modeled by DNDC through changing fertilizer rates. The model results indicated that the relationship between EFs and fertilizer application rates had significant correlations (Fig. 6-B, P<0.05) for the tested sites, implying that the less fertilizer input, the lower emission factor. This conclusion was also in agreement with the results reported by Hu *et al*. (2011) who found that the EFs were 1.15, 0.94 and 0.91%, respectively, from a maize field with fertilizer rates of 300, 250 and 185 kg N ha^{-1}.

Mitigation of N_2O emissions

According to the simulation with DNDC in this study, management practices such as no-tillage, change in timing and rate of fertilizer application, increasing the rate of residue returned, etc., can effectively mitigate N_2O emission rates. The field observation and model simulation both showed that the fertilizer-induced N_2O emissions were episodic and the highest emissions occurred during the 5-d period just after application of fertilizer N, accounted for 60% of total seasonal emissions. The results implied that reducing fertilizer application rates was feasible for N_2O mitigation in the tested sites while maintaining the food productivity. We also found that the time interval between fertilization and rainfall induced different patterns of N_2O emission, indicating the fertilizer should not be applied during periods of heavy rainfall. A result also showed that N_2O emissions would be increased by 50% if rainfall followed immediately after fertilization (Parkin and Kaspar 2006), the inorganic N (e.g., ammonium and nitrate) due to the fertilization in the soil profile stimulated both nitrifiers and denitrifiers during the rainfall events and that more N_2O would be emitted in upland soils (Li 2007). These results suggested that management options to reduce N_2O emissions should focus on optimizing the timing, amount and method of N fertilization. More mitigation measures such as increasing nitrification inhibitor or applying controlled-release fertilizer were needed to be assessed in future modeling studies to search the best management practices (Ding *et al*. 2007). However, optimized management practices should be developed to cope with the conflict among greenhouse gas mitigation, crop production and C sequestration. Since the alternative management practices (e.g., reducing fertilizer rate) were employed N_2O emission rates decreased, however, crop yields or soil organic carbon (SOC) would decline for these practices, since the soil degradation has started threatening the sustainability of Chinese agriculture. Fig. 7 showed that the effect of SOC change on the N_2O emissions by DNDC model. The management practices increased SOC content would significantly stimulate N_2O emissions (R^2=0.95, P<0.01), indicating that the effects on CO_2 and N_2O could offset each other regarding the global warming mitigation (Qiu *et al*. 2009). From the view of global warming, it is crucial to assess the comprehensive impacts of mitigation strategies on not only N_2O but also CO_2 and CH_4.

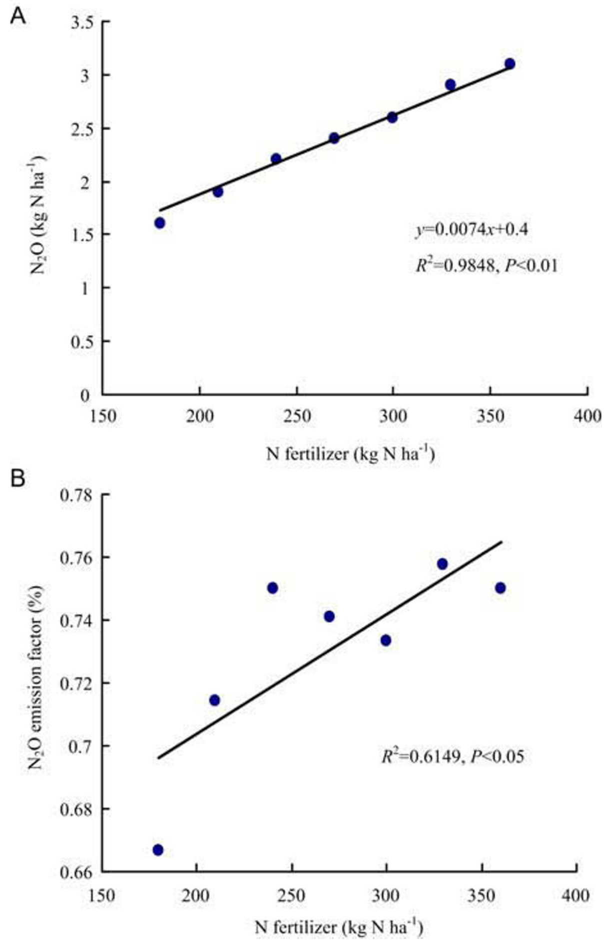

Fig. 6 The relationship between the N fertilizer application rate and seasonal emissions (A), as well emission factors (B).

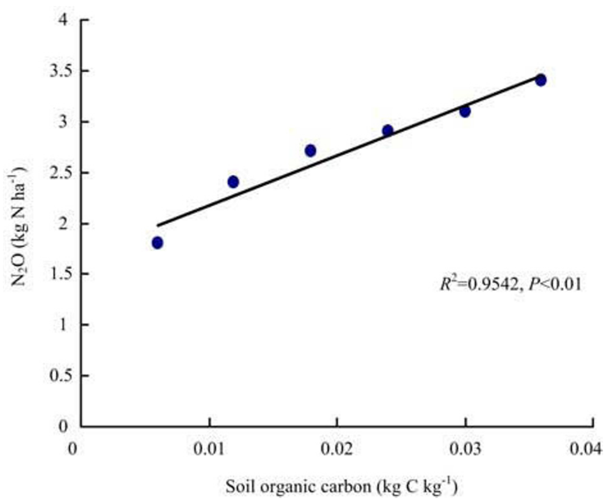

Fig. 7 The effect of soil organic carbon change on the N_2O emissions.

CONCLUSION

Nitrous oxide emissions were measured at a field site planted with spring maize in Northeast China in 2009 and 2010. The observed N_2O fluxes showed significant yearly variation between different fertilizer management practices. The rainfall and fertilization were identified as the major environmental factors controlling N_2O emissions from the tested soil. The N_2O emission factors (0.62 and 0.77% for 2009 and 2010) derived from the present study were lower than that recommended by IPCC (2006). In order to more precisely study N_2O emissions, quantitative tools are required to predict impacts of various environmental or management factors on N_2O emissions from interest ecosystems. Process-based models such as DNDC could play a key role in N_2O emission inventory and mitigation. In the study, we tested the applicability of DNDC for the spring maize ecosystem against observations with promising results. The mode well captured the pattern and magnitude of N_2O fluxes measured at the experimental site. The validated DNDC was then utilized to assess alternative management practices such as no-tillage, change in timing and rate of fertilizer application, increasing the rate of residue returned, and other feasible alternatives. The results indicated there are ways to effectively mitigate N_2O emissions from agricultural lands. We suggest that no N fertilizers be applied during periods of heavy rainfalls or split the fertilizer into more applications to reduce N_2O emissions from spring maize in Northeast China. Our study also indicated that comprehensive assessment should be conducted to include not only N_2O but also crop yield, C sequestration and other environmental services; and using models will turn this kind of complex tasks to be feasible.

MATERIALS AND METHODS

Experimental site description

The study site was at Yangjia Town, Dalian City in Northeast China (39.5°N, 121.75°E). Field experiments were conducted during the maize growing periods from May to September in two years of 2009 and 2010. The site is 19 m above the mean sea level with a typical temperate monsoon climate (warm and wet conditions in summer and cold in winter, yearly mean temperature 8.3-10.3°C, annual precipitation 650 mm). About 80% of the precipitation occurs during the period from June to September. No irrigation was applied in this area. The soil of this experimental site can be classified as brown soil, with bulk density 1.38 g cm^{-3}, pH 7.6, soil organic matter content 12.3 g kg^{-1}, available N 45.19 mg kg^{-1}, available P 54.62 mg kg^{-1}, and 72.18 mg available K kg^{-1} for the top 20 cm soil profile. Spring maize (Dongdan 80) was sown by hand in the tested site soils at intervals of 80 cm in lines and 20 cm in rows on May 14 and harvested on September 27 by hand. The soil was tilled 20 cm depth once on May 12. After harvest, none of the aboveground maize residue was left in the field. Two treatments, with and without fertilizer application (i.e., FP and CK), were implemented during the experimental period to test the impacts of fertilization on N_2O fluxes from the agroecosystem. Each of the treatments with 3 replicates was applied at a plot of 4 m×8 m. For the treatment with fertilization, 270 kg urea-N per ha was applied annually, including 180 kg N ha^{-1} applied as basal fertilizer on May 25 (20 cm deep placement) and 90 kg N ha^{-1} as additional fertilizer on June 10 (hole application near plants). The fertilizer application rates and timing were determined based on the typical practices of the local farmers.

Measurements of N_2O emissions

Gas samples were collected with static chamber method basically same as described by other researchers (Debnath *et al*. 1996; Pathak 2002). Each of the chambers consisted of two parts, the chamber cylinder (50 cm×50 cm×60 cm) made of steel and the base collar with 5 cm internal diameter fixed in the ground. The collar was inserted at 10 cm depth in the soil and filled with water to make the system air-tight. A ventilator was installed inside the chamber to ensure the internal air mixing. A diaphragm pump was used to transport the gas samples at a flow rate of 50 mL min^{-1} to the gas bags made of aluminum (100 mL for each) (Dalian Guangming Special Gas Chemical Research Institute, China) for analysis. Each sampling lasted for 30 min. During each sampling within the closed chamber, a total of 6 samples were taken at an interval of 6 min. Gas fluxes were calculated based on the slope of the gas concentrations in the five samples taken at 0, 6, 12, 18, 24, and 30 min after the chamber closure. Each sampling was performed between 9:00 a.m. and 12:00 a.m. at local time. The field measurement was conducted once or twice per month during the non crop growth period from November to May, and once or twice per week during the period from May to October. Since we expected pronounced flux variations following fertilization events the frequency was increased to three times per week. Daily average N_2O fluxes and their standard errors were calculated based on the original data measured in the field.

Gas samples were analyzed for N_2O using GC HP-7890A (HP Company, USA) in the lab within 3-5 d after sampling. N_2O concentrations in the gas samples were determined by GC using a ^{63}Ni electron capture detector (ECD). The N_2O concentration of each sample was quantified against the concentration of the calibration gas. Further methodology details are given in Li *et al*. (1997, 2010). The N_2O emissions fluxes (F) were calculated with the equation as follows (Li *et al*. 2010):

$$F=60\times10^{-2}[273/(273+T)](P/760)\times\rho\times H\times(dc/dt)$$

Where F is the N_2O emissions flux (μg N_2O m^{-2} h^{-1}), ρ (g L^{-1}) represents N_2O density at 0°C and 760 mm Hg, T (°C) is the mean value of air temperature inside the chamber measured during the closure, H (cm) is the height of chamber headspace, t (min) is time for sampling, dc/dt (10^{-9} min^{-1}) is the increase of the N_2O concentration per minute in the closed chamber, P (mm Hg) is the air pressure of experimental site. The altitude of the experimental site for this study is very close to that of sea surface, so $P/760=1$. The measured results were processed with the statistical analysis tools provided by Microsoft Excel software package.

Daily ambient air temperature and precipitation data were collected from the local meteorological station in the experimental site. The air temperature and pressure within the chambers were also recorded during each of gas samplings. Soil moisture at approximately 5 cm depth inside the chamber was measured with the oven drying method. Soil properties, i.e., soil texture, pH, bulk density, and SOC content, measured in the field or collected from existing databases were utilized either as input information or as ground truth for the model tests.

The DNDC model

The denitrification-decomposition or DNDC model was originally developed from University of New Hampshire of the USA for predicting carbon sequestration and trace gas emissions from upland agricultural lands. It had already been used and expanded by many research groups covering a range of countries and crop systems, such as Institute of Agricultural Resources and Planning, Chinese Academy of Agricultural Sciences, China (Li *et al*. 2009, 2011). The core of DNDC was built up by integrating a group of biochemical and geochemical reactions commonly occurring in agroecosystems, which govern carbon (C) and nitrogen (N) transport and transformation in the plant-soil-climate systems, including CO_2, N_2O, and CH_4 emissions, SOC (soil organic carbon) dynamics, and so on. DNDC is recognized as one of the most successful biogeochemical models, which is suitable for a wide range of agroecosystems across climatic zones (Li *et al*. 1994; Smith *et al*. 1997; Qiu *et al*. 2009b). The DNDC model consists of six sub-models for simulating soil climate, plant growth, decomposition, nitrification, denitrification and fermentation, respectively. The soil climate submodel calculates soil temperature and moisture profiles based on soil physical properties, daily weather and plant water use. The plant growth submodel tracks crop growth and partitioning of the biomass into grain, stalk and roots according to crop types, air temperature, soil moisture, and management practices (i.e., fertilizer application, irrigation, tillage, harvest, grazing, etc.). The decomposition submodel simulates production and decomposition of soil organic matter driven by the soil microbial respiration. The nitrification submodel calculates growth of nitrifiers and oxidation of ammonium to nitrate. The denitrification submodel operates at an hourly time step to simulate denitrification and the production of nitric oxide, nitrous oxide, and dinitrogen. The fermentation submodel simulates methane production and oxidation under anaerobic conditions. The six sub-models interact to enable DNDC to simulate a relatively complete suite of biochemical and geochemical processes occurring under both aerobic and anaerobic conditions. More information about the concepts or mathematics of the model can be found in former publications (Li *et al*. 1992, 1994, 2002, 2004). The DNDC model is available *via* the internet (http://www.dndc.sr.unh.edu).

Validation of the model

Although each simulating process embedded in DNDC is well-founded, it still needs to test whether the model can interpret and extrapolate the field observations under different climate, soil and management conditions and the more validations the better. During the past two decades, the DNDC model has been independently tested and applied for soil C and N studies in 20 countries including China with promising results. The validation is to compare the goodness of fit between the field observations and the model simulations of N_2O emissions driven by actual input data. The input data supporting for the model runs include daily climatic data (i.e., temperature and rainfall), soil property (i.e., soil density, texture, initial SOC and pH), land use (i.e., crop type and rotation system), and management practices (i.e., tillage, fertilizer, irrigation, crop residue returned rates and grass cutting). In this study, we tested DNDC against the observations gained at the experimental site in Dalian.

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