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ORIGINAL RESEARCH PAPER

Quantifying nitrous oxide fluxes on multiple spatial scales in the Upper Midwest, USA

Xin Zhang · Xuhui Lee · Timothy J. Griffis · Arlyn E. Andrews · John M. Baker · Matt D. Erickson · Ning Hu · Wei Xiao

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Abstract This study seeks to quantify the roles of soybean and corn plants and the cropland ecosystem in the regional N_2O budget of the Upper Midwest, USA. The N_2O flux was measured at three scales (plant, the soil–plant ecosystem, and region) using newly designed steady-state flow-through plant chambers, a flux-gradient micrometeorological tower, and continuous tall-tower observatories. Results indicate that the following. (1) N_2O fluxes from unfertilized soybean (0.03 ± 0.05 nmol m^{-2} s^{-1}) and fertilized corn plants (-0.01 ± 0.04 nmol m^{-2} s^{-1}) were about one magnitude lower than N_2O emissions from the soil–plant ecosystem (0.26 nmol m^{-2} s^{-1} for soybean and 0.95 nmol m^{-2} s^{-1} for corn), confirming that cropland N_2O emissions were mainly from the soil. (2) Fertilization increased the corn plant flux for a short period (about 20 days), and late-season fertilization dramatically increased the soybean plant emissions. (3) The direct N_2O emission from cropland accounted for less than 20 % of the regional flux, suggesting a significant influence by other sources and indirect emissions, in the regional N_2O budget.

Keywords Nitrous oxide · Corn · Soybean · Agriculture · Land surface flux

Introduction

Nitrous oxide (N_2O), one of the three major greenhouse gases, has a global warming potential 298 times that of CO_2, and is an important substance contributing to stratospheric ozone depletion (Ravishankara et al. 2009). Atmospheric N_2O has been increasing steadily, from 270 ppb before the industrial revolution to 324.3 ppb in 2011 (Forster et al. 2007; Blunden and Arndt 2012), mainly due to anthropogenic emissions. Mitigation of N_2O emission requires a complete and accurate inventory of all N_2O sources and sinks. So far, its major sources and sinks have been identified, and global aggregation of land and ocean surface sources agrees with its atmospheric buildup and stratospheric sink (Reay et al. 2012; Syakila and Kroeze 2011). However, large uncertainties still exist at different spatial scales (plant, field, and region), especially for agricultural landscapes. For example, the IPCC (2006) methodology underestimates N_2O emissions at a corn field in Ontario, Canada by a factor of five (Del Grosso et al. 2008) and underestimates regional N_2O emissions in the USA and southern Canada by a factor of three (Kort et al. 2008; Miller et al. 2012). The IPCC N_2O emission calculation for cropland is based mainly on soil chamber observations, which have inherent difficulties in addressing

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X. Zhang · X. Lee
School of Forestry and Environmental Studies, Yale University, New Haven, CT, USA

T. J. Griffis · M. D. Erickson
Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN, USA

A. E. Andrews
Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, USA

J. M. Baker
Agricultural Research Service, US Department of Agriculture (USDA), St. Paul, MN, USA

N. Hu · W. Xiao
Yale-NUIST Center on Atmospheric Environment, Nanjing University of Information Science and Technology, Nanjing, Jiangsu, China

Present Address:
X. Zhang (✉)
Woodrow Wilson School of Public and International Affairs, Princeton University, Princeton, NJ, USA
e-mail: zhangxin.yale@gmail.com

the large spatial and temporal heterogeneity of emissions and measuring the N_2O flux from the aboveground section of plants.

One potential uncertainty in N_2O inventories for agricultural ecosystems is the significance of the N_2O flux from plants (Misselbrook et al. 2011). Some studies have suggested that plants should not be neglected as a source of N_2O (Chen et al. 1999; Pihlatie et al. 2005; Smart and Bloom 2001; Zou et al. 2005). For example, Chen et al. (1999) found that N_2O emissions from rye grass (*Lolium perenne* L.) can reach 1.16 nmol m^{-2} s^{-1} (unit ground area), while the emissions from their grass–soil ecosystem ranged from 0.33 to 5.50 nmol m^{-2} s^{-1}. Zou et al. (2005) suggested that N_2O emissions from wheat plants (*Triticum aestivum* L. cv. Veery 10) accounted for 25 % of the total ecosystem scale emissions for the whole growing season. In contrast, Lensi and Chalamet (1981) and Grundmann et al. (1993) observed that corn (*Zea mays* L.) can absorb N_2O at a rate of up to 15 μg N–N_2O plant^{-1} h^{-1} (1.19 nmol m^{-2} s^{-1}, unit ground area, assuming a typical plant density of 8 plants m^{-2}). Using the same method as Chen et al. (1999) and Zou et al. (2005), Müller (2003) found that some grass species can either emit or absorb N_2O during the photoperiod. At present, no consensus has been reached regarding the role of plants in the exchange of N_2O between the biosphere and the atmosphere.

The divergence in the observed plant N_2O flux can be partly attributed to differences in plant species and fertilization use. Measurement artifacts may also have affected these previous findings. Three major artifacts have been examined in the literature. (1) Choice of the carrier gas used in gas chromatography (GC) measurements: A positive relationship was found between the N_2O and CO_2 concentrations when nitrogen (N_2) was used as the carrier gas during a GC measurement (Zheng et al. 2008). This artifact would lead to artificial N_2O uptake when plants photosynthesize in clear chambers. (2) Discrepancies due to light conditions: Two pathways have been proposed to explain N_2O emission from plants, i.e., N_2O diffusion from roots and nitrate assimilation by the plants (Chang et al. 1998; Smart and Bloom 2001). Use of an opaque chamber or taking measurements in the dark will affect both of these potential pathways by reducing photosynthesis and transpiration (Müller 2003). (3) Uncertainties due to the use of controlled environments and indirect measurement methods: In the field, the N_2O flux is affected by many factors such as precipitation and soil conditions, which complicate the extrapolation of laboratory results to estimate the actual emissions in the field (Marinho et al. 2004). Among the few studies conducted under field conditions, the plant flux was determined by comparing the N_2O emissions from the soil–plant ecosystem before and after harvesting the plants (Chen et al. 1999; Müller 2003; Zou et al. 2005). This indirect method is based on the assumption that N_2O emission from the soil is not affected by harvesting.

In addition, studies that use soil chambers also have inherent limitations in dealing with the high spatial and temporal heterogeneity of the soil N_2O flux (Denmead 2008; Fassbinder et al. 2013). High-frequency N_2O measurement techniques are becoming more readily available in recent years (Kroon et al. 2010b), allowing application of eddy covariance and flux-gradient approaches to estimate ecosystem-scale N_2O budgets (Wagner-Riddle et al. 1997; Phillips et al. 2007; Denmead et al. 2010; Desjardins et al. 2010; Kroon et al. 2010a; Molodovskaya et al. 2011). Some researchers have used the flux-gradient method to continuously measure N_2O flux with different cover crops and management methods and have determined the impact of manure application, fallow, and tillage on the timing and the amount of N_2O emission (Wagner-Riddle et al. 1997; Phillips et al. 2007). So far, few studies have made concurrent observations with these micrometeorological methods and soil and plant chambers. Denmead et al. (2010) reported good agreement between both methods when N_2O emissions were integrated over a 15-day period. However, they observed large disparities when daily averages were compared.

In this study, we measured the N_2O flux at three different spatial scales, including plant/soil, ecosystem, and region within the northern portion of the US Corn Belt. The specific objectives were: 1) to quantify the N_2O flux from soybean and corn plants growing in the field using a new chamber designed to limit measurement artifacts and explore whether nitrogen fertilizer enhances the plant N_2O flux; (2) to determine the N_2O budget at the ecosystem scale and regional scale; and (3) to evaluate the influence of the plant N_2O flux on ecosystem and regional scale budgets.

Materials and methods

Research site and overview of experimental strategy

This research was conducted at the University of Minnesota Outreach, Research, and Education Park, in Rosemount, MN, in parallel with the CH_4 research described in Zhang et al. (2013). In addition to the plant-chamber and tall-tower measurement of the N_2O flux, a flux-gradient system was installed in the middle of a soybean–corn rotation field to measure the N_2O flux of the soil–plant ecosystem. These measurement systems were used to assess N_2O fluxes at the plant, ecosystem, and regional scales. This strategy enabled us to evaluate the importance of the plants and the soil on the ecosystem and regional budgets of N_2O (Fig. 1).

The chamber (plant and soil) and flux-gradient measurements were conducted in a soybean (*Glycine max*)–corn (*Z. mays*) rotation field with a Waukegan silt loam soil about

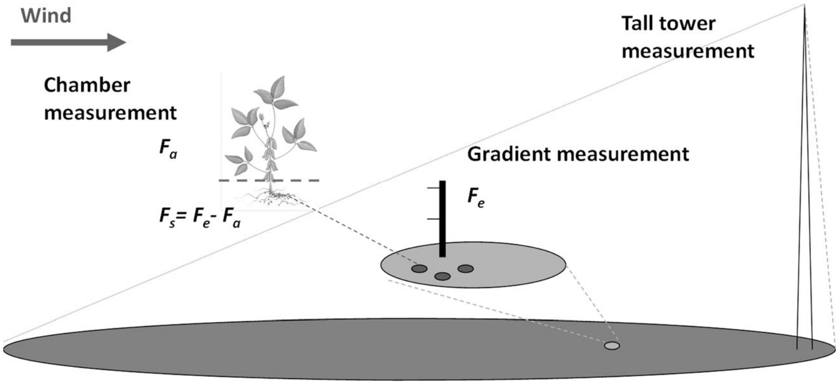


Fig. 1 Schematic diagram of the three-scale observation system: chamber measurement of plant-scale flux (F_a), flux-gradient measurement of soil–plant ecosystem scale flux (F_e), and tall-tower measurement of regional scale flux. F_s soil flux

0.5–1.8 m thick. The land management techniques are typical for the Upper Midwest region (Baker and Griffis 2005). Fertilizer was applied at the rate of 112 kg N ha^{-1} during the corn phase of the rotation (2009) before planting. To test the influence of fertilization on the plant N_2O flux, we reserved an unfertilized zone (8 m×30 m) during the corn season. During the soybean phase (2008), no fertilizer was applied except for three randomly selected plants, which were fertilized with a synthetic fertilizer (24-8-16, NPK; ScottsMiracle-Gro, Marysville, OH) at the rate equivalent to 500 kg N ha^{-1} in the middle of the growing season (July 10, 2008, DOY 192). This application rate was at the upper limit of the N fertilization rate for corn and soybean reported in the literature in order to maximize the N_2O signal. (Moreno et al. 1996; Schmidt et al. 2000).

Plant-scale chamber measurements

To measure the N_2O flux from the aboveground section of a plant, we designed a steady-state flow-through chamber system (Zhang et al. 2013). The chamber system includes seven basic components: (1) a chamber cover made of transparent Plexiglass; (2) a metal base frame installed above the soil surface for holding the chamber cover; (3) on the metal base, two Plexiglass plates that allow the plant stem to pass through the center of these plates; (4) one sampling tube around the base of the chamber and one inside the chamber, for sampling the inlet and outlet air streams of the chamber; (5) instruments for instantaneous concentration measurement; (6) an air cooling system; and (7) fans to circulate the chamber air. The chamber base was not sealed in order to allow ambient air to enter the chamber. The difference between the trace gas concentrations inside and outside the chamber was used to determine the trace gas flux from the aboveground section of plant combined with the airflow rate through the chamber. The details about the chamber design and plant flux calculation are described in Zhang et al. (2013).

The chamber system was designed to minimize any impact on the plant's living environment. We used a transparent material that allowed 92 % of the visible light and 90 % of the UV radiation to reach inside the chamber. The difference between the chamber temperature and the ambient temperature was maintained within±3 °C by a cooling system. The airflow through the chamber was kept high, between 30 and 60 l min^{-1}. The highest flow rates were used in the middle of the growing season to minimize CO_2 depletion inside the chamber. The CO_2 concentration difference between the chamber inlet and outlet was roughly 9 and 66 ppm during the day and 4 and 11 ppm at night for corn and soybean, respectively. The plant chamber did not appear to have a measurable effect on plant growth because leaf area index (LAI), dry weight, and plant height were not significantly different from those outside the measurement plots.

However, the chamber system is limited by its measurement capacity in that it can only measure one plant at a time. Consequently, for each growing season, three plants were randomly chosen as replicates in the fertilized and unfertilized zones, respectively, and were measured sequentially, one day for each plant.

Because of the relatively high flow rates through the plant chamber, the N_2O concentration difference between the inlet and outlet of the chamber was very small. We used a high-precision tunable diode laser analyzer (TDL, model TGA 100A, Campbell Scientific, Logan, UT) to measure the concentration difference. We conducted three blank chamber tests for each chamber type (small 25 cm×25 cm×25 cm, medium 50 cm×50 cm×50 cm, and large 50 cm×50 cm×150 cm) to determine the flux detection limit. Two sampling strategies were examined: (1) sampling the air from the chamber inlet and outlet sequentially (two-site switching) for 20 s each; and (2) sampling the air from the inlet, outlet, zero tank, and calibration tank sequentially (four-site switching) for 20 s each. The second sequence was only tested for the medium and large chamber during the corn season. The blank chamber tests were conducted by running the chamber system for 24 h without enclosing a plant. These results are summarized in Table 1. Even though incorporation of the zero and span calibration in every switching cycle would improve the accuracy of the concentration measurement, doing so reduced the number of concentration measurements by half, so that the

Table 1 The measurement noise of N_2O flux for each chamber type

Chamber	Calibration	N_2O (nmol m^{-2} s^{-1})
Small (soybean)	No	0.03
Medium (soybean)	No	0.04
Small (corn)	No	0.01
Medium (corn)	No	0.01
Medium (corn)	Yes	0.06
Large (corn)	Yes	0.09

Note: The difference between soybean and corn was caused by different plant density

measurement noise, as indicated by the standard deviation of the blank flux, was greater than those without calibration.

Ecosystem-scale flux-gradient measurements

The N_2O gradient was measured on a 10-m tower in the middle of the soybean–corn rotation field (G21 site) with an aerodynamic fetch greater than 180 m in all directions (Baker and Griffis 2005). We used a vacuum pump (RB0021, Busch, Virginia Beach, VA) to pull the air through two Synflex tubing lines (Synflex Type 1300, Aurora, OH) from two levels on the tower at the rate of 2.5 l min^{-1} to a second TDL analyzer (model TGA 100A, Campbell Scientific, Logan, UT) housed at the edge of the field. The sampling heights were 1.0 and 2.0 m above the ground in the 2008 soybean season. In the 2009 corn season, the initial measurement heights were 1.0 and 2.0 m and were raised gradually to 2.2 and 3.2 m by the end of the growing period to account for plant growth. The two inlet air streams were subsampled by a diaphragm pump (1023-101Q-SG608X, GAST Manufacturing, Warminster, PA) at the rate of 300 ml min^{-1} and was measured by the TDL analyzer sequentially, 30 s for each inlet. The laser temperature of the TDL was maintained at 120.8 K, and the sample cell pressure was kept at 3.0 kPa.

The ecosystem-scale flux (F_e) was determined as:

$$F_e = -K\frac{\partial c}{\partial z} \tag{1}$$

where $\partial c/\partial z$ is the vertical N_2O concentration gradient, and K is the eddy diffusivity (Kaimal and Finnigan 1994). The eddy diffusivity was calculated from:

$$K = \frac{ku_*(z-d)}{\phi_h} \tag{2}$$

where k is von Karman constant (k=0.41), u_* is friction velocity measured at the tower with an eddy covariance system consisting of a sonic anemometer (CSAT 3, Campbell Scientific, Logan, UT) and an open path CO_2/H_2O gas analyzer (LI-7500, LI-COR, Lincoln, NE) (Baker and Griffis 2005), z is the geometric mean of the two air intake heights z_1 and z_2 ($z=(z_1z_2)^{1/2}$), d is zero-plane displacement (equals 2/3 of the canopy height), and φ_h is the dimensionless stability correction given by:

$$\phi_h = \begin{cases} (1+16|(z-d)/L|)^{1/2}, & -2\le(z-d)/L\le 0 \\ (1+5(z-d)/L)\ , & 0\le(z-d)/L\le 1 \end{cases} \tag{3}$$

where L is the Monin–Obukhov length.

A zero-gradient test, conducted from DOY 118 to 128 in 2009, showed that no significant bias existed in the flux-gradient measurement. The test was carried out by co-locating the two sample inlets at the same height. The measured concentration difference between the two inlets was 0.0065±0.0319 ppb for the daily average, and the corresponding N_2O flux was −0.00±0.11 nmol m^{-2} s^{-1}. In other words, the flux-gradient measurement noise was 0.11 nmol m^{-2} s^{-1}.

Regional-scale tall-tower flux measurements

The N_2O mixing ratio was measured at the 3 m and 200 m heights above the ground during an intensive campaign period (DOY 243–269) in 2009. Air was drawn from intakes at these levels on a tall tower (Griffis et al. 2010; Zhang et al. 2014) into an instrument building at the base of the tower where its N_2O mixing ratio was measured with the first TDL analyzer, using a switching cycle of 20 s on each air intake, 20 s on a zero gas, and 20 s on a span gas. The regional flux was determined by the equilibrium boundary layer method that assumes that the land surface flux is in equilibrium with the gaseous exchange at the top of the boundary layer over relatively long averaging periods (i.e., weeks to months; Betts et al. 2004; Helliker et al. 2004). As a result, the land surface flux (F_{Eq}) can be estimated from the subsidence rate at the top of the boundary layer and the difference between the trace gas concentration within and above the boundary layer:

$$F_{Eq} = \rho W(c_+ - c_m) \tag{4}$$

In this equation, ρ and W are air density and the vertical velocity at the top of the boundary layer, c_+ and c_m are the trace gas mixing ratio above and within the boundary layer. The source footprint of the derived flux is on the order of 10^6 km^2 (Bakwin et al. 2004).

During the intensive campaign, the N_2O concentration within and above the boundary layer was determined by the N_2O mixing ratio measured at 200 m and the N_2O mixing ratio measured at NOAA background site NWR (Niwot Ridge) in Colorado, respectively (Dlugokencky et al. 2013). ρW was determined using H_2O as a tracer (Helliker et al. 2004); in other words, ρW was calculated as the land surface H_2O flux divided by the difference between the H_2O mixing ratios within and above the boundary layer. The land surface H_2O flux and H_2O mixing ratio within the boundary layer were measured at the tall tower. The water vapor mixing ratio above the boundary layer was determined by the water vapor mixing ratio at the 700 hPa level in the NCEP/NCAR Reanalysis-2 data (provided by the NOAA/OAR/ESRL PSD, Boulder, CO, USA, from http://www.esrl.noaa.gov/psd/). All the days with precipitation greater than 1 mm day^{-1} were excluded in the calculation (Helliker et al. 2004).

To estimate the annual N_2O flux from the landscape around the tall tower, we assume the seasonal pattern of N_2O mixing ratio at our tall tower was the same as that at the West Branch tower (WBI) in Iowa (Andrews et al. 2013a) and extrapolated our September N_2O concentration measurement to the whole year for 2009. The WBI tower was 358 km southeast of our tall tower, and the N_2O mixing ratio was measured by NOAA at a height of 379 m (Andrews et al. 2013b). This assumption was made for the following reasons: (1) the WBI tower is also located in the Upper Midwest USA and surrounded by an agriculture-dominated landscape. According to the US Department of Agriculture (USDA) Crop Data Layer in 2009, cropland and pasture accounted for 39 and 16 % of the land within the 600-km radius around the WBI tower, and for 40 and 22 % around our tower, respectively. (2) A tall-tower network in the same region suggested a coherent seasonal pattern of CO_2 mixing ratios, which is strongly influenced by corn crops in the tower footprint (Miles et al. 2012). Similarly, N_2O emissions in the Central USA also share similar spatial and temporal pattern as corn production (Miller et al. 2012). (3) The seasonal pattern of N_2O mixing ratio observed at the WBI site in 2009 was similar to the pattern observed at our tall-tower site in 2010 and 2011 (Griffis et al. 2013). Both observations suggested two emission peaks, one in March and one in June, corresponding to the two emission episodes during spring warming and after fertilization. The above boundary layer concentration and the subsidence rate were determined with the same method as the intensive campaign.

As a comparison to the annual N_2O flux at our tall-tower site, we also derived the N_2O flux at the WBI site with the equilibrium boundary layer method using the subsidence rate from the NCEP/NCAR Reanalysis-2 data (Helliker et al. 2004; Zhang et al. 2014).

Supporting measurements

In the literature, some plant N_2O flux values are reported on the basis of leaf area and dry weight. To enable comparison with published results, we measured LAI and dry weight of the aboveground biomass every week. Five plants were sampled from the fertilized and unfertilized plots, and their dry weight and leaf area were measured.

Standard micrometeorological and eddy flux variables were measured at half-hourly intervals at the G21 site and at an adjacent field with an opposite soybean–corn rotation schedule. These measurements included environmental parameters such as soil moisture and air temperature (Bavin et al. 2009).

Results

Soybean plant flux

Through the 2008 observation period (DOY 160–225), the unfertilized soybean plants emitted N_2O at the rate of 0.03 ±0.05 nmol m^{-2} s^{-1}. Figure 2a summarizes the daily mean flux. Considering all of the observations, 69 % had a positive flux, and among these, 80 % were higher than

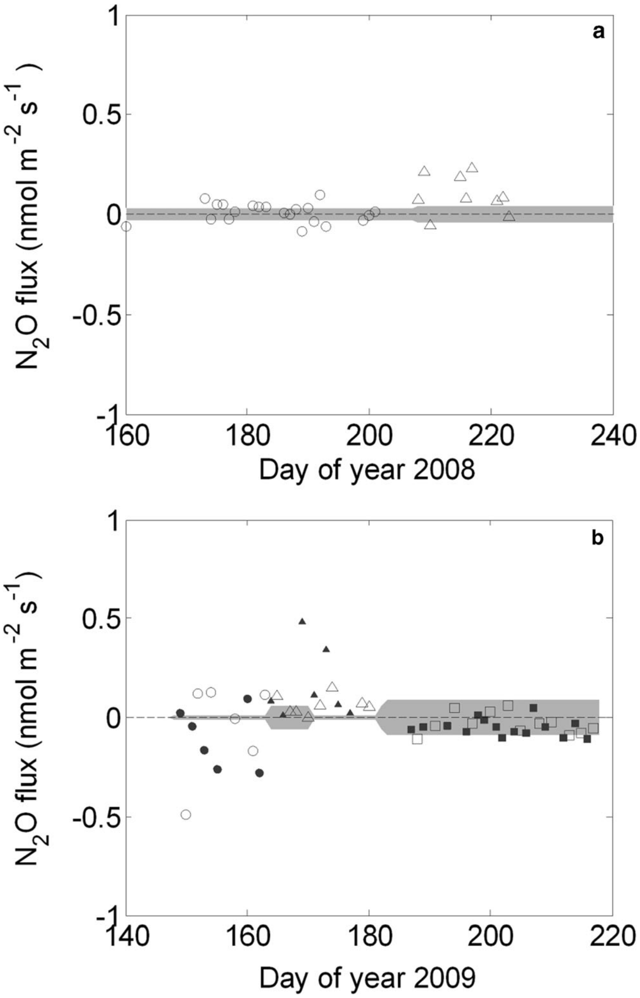


Fig. 2 Daily plant N_2O flux in the soybean (**a**) and corn (**b**) field: *filled symbols* fluxes from fertilized plants; open symbols fluxes from unfertilized plants, *circles*, *triangles*, *squares* fluxes measured using a small chamber, a medium chamber, and a large chamber, respectively, *grey area* detection limit of each type of chamber measurement. Only unfertilized soybean plant fluxes were displayed in panel a, because the fertilized soybean fluxes were one to two orders of magnitude higher

the detection limit of the chamber system. Continuous emission of N_2O was observed in the later growing season (DOY 205–225), and the highest emission was 0.23 nmol m^{-2} s^{-1} or about five times higher than the detection limit. A negative daily flux was observed on nine days, but the magnitude was small. About half of the negative daily flux values were smaller than the detection limit. The midnight (22:00–4:00) N_2O flux was mostly positive throughout the growing season (mean value 0.06±0.06 nmol m^{-2} s^{-1}), and the midday (10:00–16:00) flux had a larger variation from −0.21 to 0.41 nmol m^{-2} s^{-1} (mean value 0.02±0.07 nmol m^{-2} s^{-1}).

Corn plant flux

Both N_2O emission and uptake were observed during the corn-growing season (Fig. 2b). From DOY 163 to 180 all the sampled plants in both the fertilized and unfertilized treatments had a positive flux. The mean N_2O emission from the fertilized plants was 0.16±0.18 nmol m^{-2} s^{-1} and was higher than that of the unfertilized plants (0.06±0.05 nmol m^{-2} s^{-1}). Some large negative daily flux values were observed before DOY 163. The largest uptake rate was −0.49 nmol m^{-2} s^{-1} on DOY 147. This observation was not likely caused by a measurement bias because: (1) the TDL diagnostics indicated a high quality of the N_2O concentration measurement; (2) calibration was made for every 2-min measurement cycle; (3) these negative flux values were 50 times larger in magnitude than the detection limit; and (4) it happened when the background N_2O concentration change was steady with time, eliminating the possibility that the negative flux was caused by a time lag between the inlet and outlet air samples of the plant chamber.

During the later growing season (DOY 181–218), the plant N_2O flux was very small and mostly negative. Only four (out of 27) daily flux values were greater than the detection limit and all four of them were negative. The mean N_2O flux from the fertilized and unfertilized plants for this period was −0.05±0.03 nmol m^{-2} s^{-1} (fertilized plants) and −0.03±0.04 nmol m^{-2} s^{-1} (unfertilized plants), indicating that the corn plants were a small N_2O sink during the late growing season. Over the whole growing season, the mean N_2O flux from the fertilized corn plants was −0.01±0.04 nmol m^{-2} s^{-1}, and the flux from unfertilized corn plants was −0.01±0.06 nmol m^{-2} s^{-1}.

Ecosystem-scale N_2O flux

During the soybean-growing season (2008), 72 % of the N_2O daily flux values were above the noise level and were mostly positive (Fig. 3). The average N_2O flux for the soybean ecosystem was 0.22 nmol m^{-2} s^{-1}.

In the corn season (2009), the observations can be divided into three distinct periods (Fig. 3). (1) From the beginning of the year to the first strong rain event after fertilization (DOY 1–116), the N_2O flux was generally small, and on average was −0.06±0.25 nmol m^{-2} s^{-1}. The average N_2O flux in this period was not significantly different from zero. (2) From DOY 117 to 201, the N_2O flux was larger, with an average of 1.32 nmol m^{-2} s^{-1} and with the daily values reaching a maximum of 5.48 nmol m^{-2} s^{-1}. The first large episodic emission was observed on DOY 138. (3) From the peak canopy development to the reproductive stage (DOY 202–220), the ecosystem-scale N_2O flux was highly variable and uptake was observed on several days. During this time period, the average N_2O flux was −0.30 nmol m^{-2} s^{-1}, and the daily uptake flux reached the most negative value of −2.62 nmol m^{-2} s^{-1}.

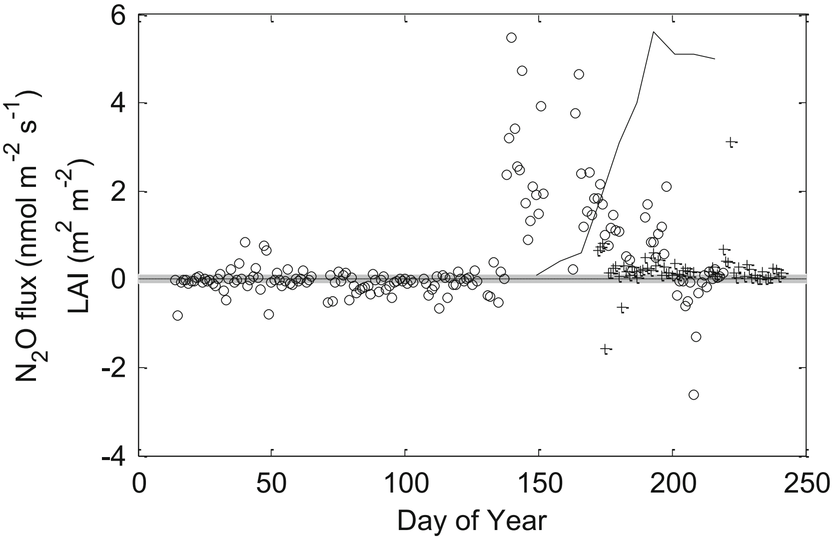
Impact of fertilization

Fertilization led to a greater N_2O emission from the fertilized corn plants than the unfertilized corn plants during the early growing season. From DOY 163 to 180, the fertilized corn plants emitted N_2O at the rate of 0.16 nmol m^{-2} s^{-1}, accounting for 9 % of the corn ecosystem emission, while unfertilized corn plants emitted only 0.06 nmol m^{-2} s^{-1}. However, the plant emissions in the fertilized plot were only sustained for about 20 days during the period when the soil N_2O flux was very strong and was compensated by the uptake in the later growing season. Averaged over the whole experiment, there was no significant difference between the fertilized and unfertilized corn plants.

During the soybean phase of the soybean-corn cropping system, fertilizer is not usually applied at sowing since it is ineffective in yield enhancement (Beard and Hoover 1971; Bharati et al. 1986; Gutierrez-Boem et al. 2004; Mendes et al. 2003). Fertilizer application during the reproductive stage has been proposed, but with mixed results on productivity. Few studies have examined N_2O emissions from fertilized soybean systems (Freeborn et al. 2001; Salvagiotti et al. 2008; Wesley et al. 1998). Our investigation on the soybean plant response to late season fertilization suggests that fertilization increased the soybean plant N_2O flux from 0.03±0.05 nmol m^{-2} s^{-1} (unfertilized soybean flux) to 2.01±2.54 nmol m^{-2} s^{-1}. The fertilized soybean showed positive flux during the nighttime, with an average midnight mean of 3.08±3.39 nmol m^{-2} s^{-1}, and slightly negative flux during the daytime, with an average midday mean of −0.34±0.25 nmol m^{-2} s^{-1}).

In addition to fertilization, soil moisture and plant activities, such as photosynthesis and respiration, may also affect the plant N_2O flux (Grundmann et al. 1993; Turpin et al. 1997; Grant and Pattey 2003; Denmead et al. 2010; Desjardins et al. 2010). We examined the relationship of the plant N_2O flux with the soil moisture and plant CO_2 flux for daytime and

Fig. 3 Daily median N_2O flux from soybean ecosystem (*cross*) and corn ecosystem (*circle*). *Grey area* measurement noise, *solid line* LAI of corn



nighttime conditions by using Pearson Correlation (Kitzler et al. 2006). The results indicate that (1) the corn plant N_2O flux was positively correlated with soil moisture ($r=0.36$, $p<0.005$, $n=53$) and the plant CO_2 flux ($r=0.35$, $p<0.005$, $n=55$) during nighttime, and (2) the soybean plant N_2O flux was only positively correlated to plant CO_2 flux ($r=0.50$, $p<0.005$, $n=53$) during nighttime. The correlation between the N_2O flux and the other variables were slightly stronger for fertilized plants compared to the unfertilized plants.

Tall-tower N_2O concentrations and the regional flux

During the intensive campaign period (DOY 243–269 in 2009), N_2O concentrations at the 3- and 200-m heights were consistently higher than N_2O concentration observed at the NOAA NWR background site (Fig. 4b), indicating that the landscape around the tall tower was a source of N_2O. The averaged N_2O concentration at 200 m was 324.8 ppb, 2.1 ppb higher than that at the NWR background site. According to the equilibrium boundary layer method, the regional N_2O flux during the observation period was 0.19 ± 0.04 nmol m^{-2} s^{-1}. Assuming the same seasonal pattern of N_2O mixing ratio as observed at the WBI tower, we computed a mean annual regional N_2O flux of 0.49 nmol m^{-2} s^{-1}in 2009 for our tall-tower site.

The diurnal variation of the N_2O concentration at the 3-m level and the nighttime N_2O gradient also indicate that the landscape around the tall tower was a source of N_2O. N_2O concentration at the 3-m height shows a weak diurnal pattern. According to the diurnal composite of N_2O concentration at this height (Fig. 4b), the concentration was slightly higher at night than during the day. The hourly mean N_2O concentration increased with time after sunset and reached a peak (332.2±25.1 ppb) around 01:00; after sunrise, it dropped steadily to 322.9±4.5 ppb at 16:00. This diurnal pattern was similar to that observed for CO_2 (Fig. 4a), indicating that N_2O

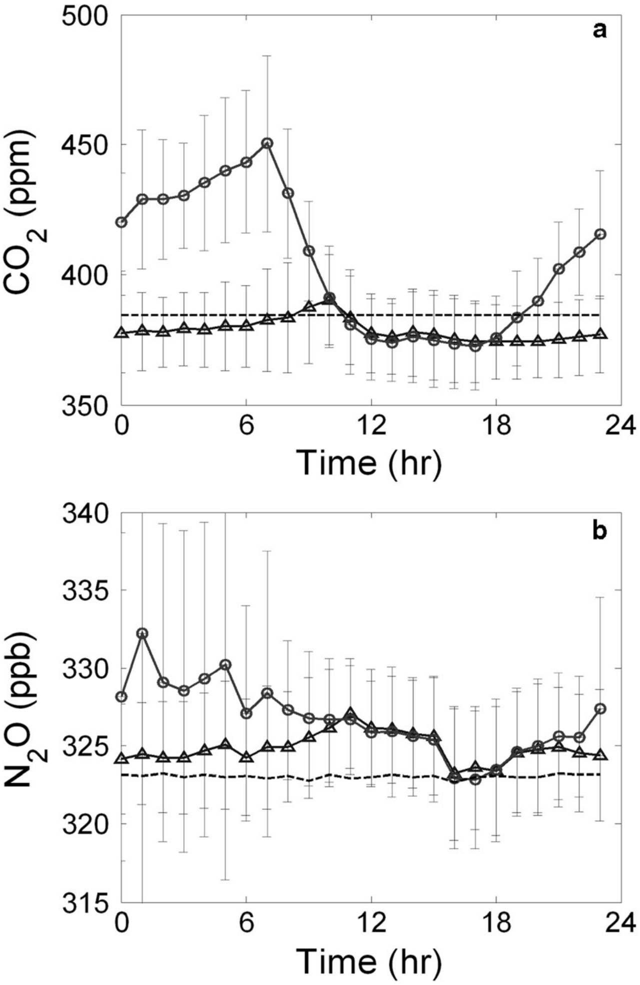


Fig. 4 Diurnal composite of CO_2 (**a**) and N_2O (**b**) concentration at the heights of 3 and 200 m above the ground during DOY 243–269 in 2009. *Triangles* and *circles* are the hourly mean values of the concentration at 3 and 200 m, respectively

emitted from the land surface accumulated near the ground at night—similar to the accumulation of respired CO_2.

The N_2O gradient between 3 and 200 m was mostly negative at night and close to zero during the day. During the observation period, 23 out of 25 midnight N_2O gradients (22:00–4:00) were negative; similarly, all 25 midnight CO_2 gradients were negative, indicating the land surface was a source of N_2O and CO_2 at night.

Discussion

Plant flux and soil–plant ecosystem flux

The N_2O flux of the soybean and corn plants was relatively small compared to the ecosystem (soil–plant) flux (Table 2). During the soybean-growing season, the average N_2O flux of the soybean plants only accounted for 12 % of the ecosystem emission. During the corn year, the average N_2O flux of the fertilized corn plants was more than one order of magnitude lower than the N_2O flux at the ecosystem scale, and the average plant flux was slightly negative (−0.01±0.04 nmol m^{-2} s^{-1}).

The comparison between the ecosystem N_2O flux and soil N_2O flux also indicated a negligible role of the plants on the ecosystem scale N_2O budget. We compared the ecosystem N_2O flux obtained from the flux-gradient measurement in 2008 and 2009 and soil N_2O flux measured with soil chamber in 2010 in the same soybean and corn field (Fassbinder et al. 2013). (Unfortunately we did not have simultaneous measurements using both approaches.) The comparison shows that (1) the corn ecosystem flux in May and June was about five times higher than the soil flux, but it is within the N_2O spatial variation range observed by Fassbinder et al. (2013), and (2) the corn ecosystem flux in July and August and the soybean ecosystem flux for the entire growing season was not significantly different from the soil flux.

Origin of the plant N_2O flux

Two mechanisms have been proposed for the plant N_2O flux. In one mechanism, plants are passive conduits that mediate the N_2O exchange between the soil and the atmosphere (Chang et al. 1998). In the second mechanism, plants generate N_2O during nitrate assimilation in leaves (Smart and Bloom 2001).

Table 2 Midnight, midday, and daily N_2O flux (nmol m^{-2} s^{-1}) from plants and soil–plant ecosystems during the chamber measurement period in the growing season

	Midnight	Midday	Daily
Fertilized corn	−0.07	−0.00	−0.01
Corn ecosystem	1.30	0.89	0.95
Unfertilized soybean	0.06	0.02	0.03
Soybean ecosystem	0.20	0.52	0.26

Several lines of evidence from our observations suggest that corn plants mediated soil–atmosphere exchange of N_2O. First, the daily N_2O flux of the fertilized corn plants was positively correlated with the daily N_2O flux of the corn ecosystem ($r=0.47$, $p<0.05$, $n=20$; Fig. 5), as well as the soil flux. Here, the soil flux was the difference between the ecosystem and the plant flux. Second, the plant N_2O emissions were significant in the middle of the growing season (DOY 163–180) when the ecosystem-scale emissions reached a maximum. Third, the plant flux was positively correlated with soil water content. High soil water content is known to be a critical driver of N_2O production in soil (Grant and Pattey 2003; Denmead et al. 2010; Desjardins et al. 2010). Therefore, higher soil water content may lead to higher plant N_2O emission if the plants mediate the N_2O produced in the soil.

During the observation period, we observed 5 days that had a negative corn plant N_2O flux while the corn ecosystem N_2O flux was positive, suggesting an uptake mechanism by the corn plant. This observation is consistent with the N_2O uptake reported by Lensi and Chalamet (1981), Grundmann et al. (1993), Chen et al. (1997), and Müller (2003). Corn plants may absorb N_2O via two pathways. (1) Corn leaves can metabolize N_2O into plant tissues. Grundmann et al. (1993) found that corn leaves exposed to $^{15}N_2O$ have higher ^{15}N than control plants. (2) N_2O may be stored within plants. Bidirectional exchange between the atmosphere and plants has been observed for many trace gases (Fowler et al. 2009). For example, SO_2 and NH_3 could be dissolved in the water film of the mesophyll cells and stored by plant (van Hove et al. 1989). Even though the solubility of N_2O is smaller than SO_2 and NH_3, studies have shown that the dissolution and release

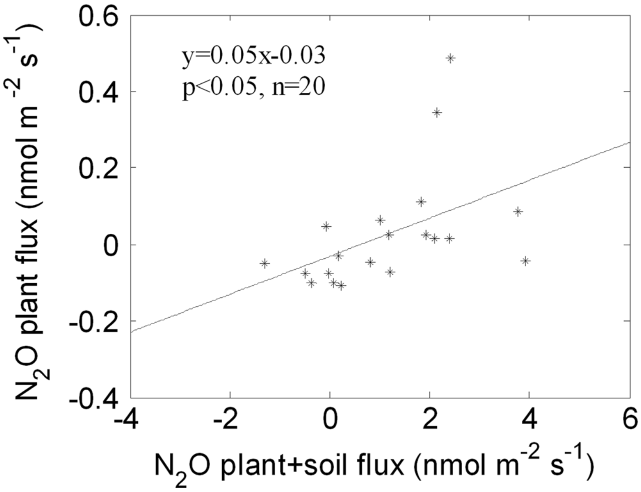


Fig. 5 Significant correlation (Pearson correlation) between the N_2O flux from fertilized corn plant and the corn–soil ecosystem flux

of N_2O by soil water or leaf water can affect the N_2O flux from plants or soil (Pihlatie et al. 2005; Chapuis-Lardy et al. 2007).

It is difficult to distinguish whether the observed soybean flux was transported from soil or produced by the soybean plant. It is possible that the soybean plants were producers of N_2O. There is some evidence that the production rate was higher at night than during the day, in opposite to the diurnal pattern of the soybean ecosystem flux. In addition, the nighttime N_2O flux of the soybean plants was positively correlated with the plant CO_2 flux, similar to the finding by Zou et al. (2005). The correlation between the plant N_2O emission and plant respiration indicates that the N_2O may be produced by the plant during the inorganic nitrogen assimilation process which relies on ATP, reductant, and carbon skeletons provided by respiration (Turpin et al. 1997).

Ecosystem flux and emission factors

The corn–soil ecosystem flux was found to be continuously negative for about 10 days (DOY 202–211) during the transition period from peak canopy development to reproductive stage. Considering the small plant flux measured during the period, the negative ecosystem flux was mainly contributed by soil and was within the range of reported N_2O uptake by soil (−5 to 0 nmol m^{-2} s^{-1}; Chapuis-Lardy et al. 2007). Soil uptake during the late corn-growing season was also observed by Mahmood et al. (1998). The uptake was observed after a sharp drop of NO_3^- level (from about 19 to 8 mg N kg^{-1} in 7 days) and following irrigation events. Similarly, during the canopy development and the early reproductive period, the NO_3^- level in our corn field dropped from about 137 mg N kg^{-1} (measured on DOY154) to 41 mg N kg^{-1} (measured on DOY225), and the N_2O uptake by the corn–soil ecosystem occurred on and after the strong rain event on DOY 202 (the precipitation rate was 23.5 mm day^{-1}). According to previous studies, lower NO_3^- reduces N_2O production and encourages N_2O reductase (NOR) activity which is responsible for N_2O reduction during denitrification (Schmidt et al. 2004). The rain or irrigation events may encourage N_2O consumption in several ways: (1) the water infiltration may trap or temporarily store N_2O and leach out more dissolved N_2O (Clough et al. 2005); (2) higher water-filled pore space tends to slow down N_2O diffusion to the soil surface and create more anoxic conditions that encourage N_2O consumption activities by nitrifiers and NOR (Chapuis-Lardy et al. 2007). Further study is needed to quantify the impact of NO_3^- level and rain/irrigation events on N_2O emissions from soil.

The mean annual N_2O flux from the G21 corn field was estimated to be 0.26–0.30 nmol m^{-2} s^{-1} (or 2.29–2.65 kg N_2O–N ha^{-1}) in 2009, according to the flux-gradient measurement from January to August and an assumption that the corn ecosystem flux was 0–0.11 nmol m^{-2} s^{-1} from September to December. Considering the nitrogen input from synthetic fertilizer (112 kg N ha^{-1}), crop residue (72 kg N ha^{-1}, IPCC 2006), and the loss of soil organic matters (20 kg N ha^{-1}, range of 0 to 40 kg N ha^{-1}, reported by Baker and Griffis 2005), the direct emission factor at the G21 corn field in 2009 was 1.1–1.3 %. This emission factor was slightly higher than the default IPCC emission factor (1 %) and within the range (1.1±0.5 %) summarized in a review by Liebig et al. (2005) on all types of crop ecosystems without manure treatment in northwestern USA.

Although the soybean ecosystem N_2O flux was not measured directly in 2009, the flux-gradient measurement of the soybean ecosystem flux in 2008 and the soil chamber measurement in 2010 (Fassbinder et al. 2013) suggested no/or weak seasonality of the N_2O flux from the soybean ecosystem and a relatively small interannual variation. We used the soil chamber flux as a surrogate for the ecosystem flux because the N_2O emission from unfertilized soybean plants was relatively small, about 10 % of the soil flux. Soil N_2O flux was measured from April to October in 2010, and the average monthly flux was 0.14±0.02 nmol m^{-2} s^{-1}, with very small month-to-month variation. The ecosystem N_2O flux was measured from June to August in 2008, and the average monthly flux was similar (0.20±0.09 nmol m^{-2} s^{-1}). Therefore, assuming that the soybean ecosystem flux in 2009 was similar to 2010 flux, the annual N_2O emission from soybean ecosystem was 1.08± 0.11 kg N_2O–N ha^{-1}, within the flux range reported by Gregorich et al. (2008) for Eastern Canada (1.73±1.32 kg N_2O–N ha^{-1}). Our observations and the Gregorich et al.'s review indicate that N_2O emissions from unfertilized soybean systems are about 1 % of the nitrogen fixed by soybean plants (84 kg N ha^{-1} $year^{-1}$ for soybean plants in the Upper Midwest USA according to Russelle and Birr 2004).

Regional flux and the role of cropland

The regional N_2O flux derived from the equilibrium boundary layer method during the 2009 intensive campaign period (0.19 ±0.04 nmol m^{-2} s^{-1}) was about 30 % less than the reported

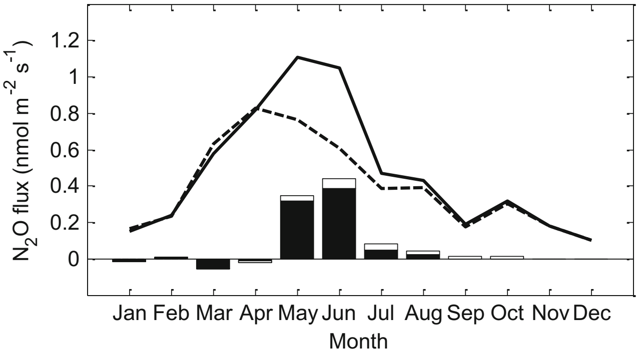


Fig. 6 N_2O fluxes from corn and soybean ecosystems and the region around the tall tower. *Solid line* regional N_2O flux in 2009, *dashed line* the difference between regional flux and cropland flux, *black bar* N_2O flux from the corn ecosystem in tall-tower footprint in 2009, *white bar* N_2O flux from soybean ecosystem in tall-tower footprint in 2009

N_2O flux for September 2010 (0.28 nmol m^{-2} s^{-1}) using the same method (Griffis et al. 2013). The difference may attribute to the uncertainty of the equilibrium boundary layer method and/or the much drier conditions observed in September 2009. The accumulated precipitation for September 2009 was 92 mm (28 % less) compared to 128 mm in 2010.

The annual tall-tower regional N_2O flux for 2009 was 0.49 nmol m^{-2} $s^{-1}$and was comparable to the N_2O flux observed using the same methodology for 2010–2011 (0.35± 0.05 nmol m^{-2} s^{-1}) at the same tower (Griffis et al. 2013). It was also comparable to the N_2O flux derived using the same methods at the WBI tower in 2009 (0.32 nmol m^{-2} s^{-1}). The difference between our tall tower and WBI tower could be attributed to the uncertainties in the equilibrium boundary layer method, the different source strengths in the respective footprints, and climate. The small spread of the three regional estimates indicates that the equilibrium boundary layer method can provide a reasonable regional N_2O flux (the footprint on the scale of 10^6 km^2) based on concentration measurement on the tall tower.

The seasonal cycle of the regional flux from the landscape surrounding our tall tower was similar to the N_2O flux measured in the G21 corn field located in the tall-tower footprint. Both the regional flux and corn ecosystem peaked during the month of May and June (Fig. 6), indicating that the higher regional N_2O emission in these 2 months was mainly caused by emissions from corn fields. However, the annual N_2O emission from the G21 corn field was 0.26–0.30 nmol m^{-2} s^{-1}, which only accounts for 12–14 % of the regional flux after weighted by the fractional land area for corn field.

N_2O emission from soybean ecosystem plays a minor role in both the seasonality and the annual average of the regional flux. N_2O flux from soybean ecosystem showed no/or weak seasonality in contrast to the seasonal trend of the regional flux. Weighting the annual soybean ecosystem flux (1.08± 0.11 kg N_2O–N ha^{-1}) with the fraction of soybean in the tall-tower footprint showed that the soybean ecosystem accounted for about 4 % of the regional flux.

Overall, the soybean and corn plots accounted for about 40 % of the land surface around our tall tower. However, the direct N_2O emissions from those plots accounted for less than 20 % of the regional flux. The other major N_2O sources include natural ecosystems, manure, and indirect cropland emissions through nitrogen leaching and runoff. According to reported N_2O flux densities for natural vegetation, open water, manure, urban areas, corn and soybean fields, and the fraction of each land cover type within the tall-tower footprint, the aggregated N_2O flux only accounts for about 34 % of the regional flux (Griffis et al. 2013), indicating a large underestimation of current sources or the possibility of undefined sources. Recent studies have suggested than indirect N_2O emissions associated with agricultural drainage channels have been severely underestimated by emission inventories (Outram and Hiscock 2012). Further, emission estimates for natural sources remain scarce and uncertain (Groffman et al. 2009; Zhuang et al. 2012; Saikawa et al. 2013). A systematic approach, therefore, is needed to quantify the N_2O emissions from natural ecosystems and the indirect N_2O emissions from croplands in order to reduce the uncertainties in the regional budget.

Conclusions

During the growing season, unfertilized soybean plants emitted N_2O at the average rate of 0.03 nmol m^{-2} s^{-1}, about 10 % of the N_2O emission from soybean ecosystem, while corn plants were a negligible sink of N_2O during the growing season. The N_2O flux of the fertilized corn plants was positively correlated with the corn ecosystem flux. The nighttime N_2O flux of the soybean plants was correlated with the plant CO_2 flux. The impact of fertilization on the corn plant flux was not significant, but the late-season fertilization increased the soybean plant flux by nearly two orders of magnitude.

The direct N_2O emissions from cropland only accounted for less than 20 % of the regional flux from the landscape around the tall tower. However, the regional N_2O flux shared the same seasonal pattern as the corn ecosystem flux.

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