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ORIGINAL PAPER

The influence of plants on atmospheric methane in an agriculture-dominated landscape

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Abstract The primary objective of this study was to clarify the influence of crop plants on atmospheric methane (CH_4) in an agriculture-dominated landscape in the Upper Midwest of the United States. Measurements were carried out at two contrasting scales. At the plant scale, CH_4 fluxes from soybean and corn plants were measured with a laser-based plant chamber system. At the landscape scale, the land surface flux was estimated with a modified Bowen ratio technique using measurements made on a tall tower. The chamber data revealed a diurnal pattern for the plant CH_4 flux: it was positive (an emission rate of 0.4± 0.1 nmol m^{-2} s^{-1}, average of soybean and corn, in reference to the unit ground area) during the day, and negative (an uptake rate of −0.8±0.8 nmol m^{-2} s^{-1}) during the night. At the landscape scale, the flux was estimated to be 14.8 nmol m^{-2} s^{-1} at night and highly uncertain during the day, but the available references and the flux estimates from the equilibrium methods suggested that the CH_4 flux during the entire observation period was similar to the estimated nighttime flux. Thus, soybean and corn plants have a negligible role in the landscape-scale CH_4 budget.

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Introduction

Methane (CH_4) represents one of the primary greenhouse gases, and estimates of its terrestrial sinks and sources are subject to large uncertainties. To date, most studies have focused on CH_4 emissions from wetlands/peatlands, agricultural feed lots/lagoons, and municipal waste sites (Le Mer and Roger 2001; Mosher et al. 1999; Shurpali et al. 1993; Shurpali and Verma 1998). Recently, Keppler et al. (2006) suggested that the CH_4 flux of terrestrial vegetation may range from 62 to 236 Tg $year^{-1}$, accounting for 12 % to 45 % of global terrestrial emissions (Nisbet et al. 2009). The plant pathway of aerobic CH_4 generation suggested by Keppler et al. has led to a reevaluation of CH_4 sources and stimulated a new debate regarding the role of plants in greenhouse gas mitigation strategies (Butenhoff and Khalil 2007; Dueck and Van Der Werf 2008; Nisbet et al. 2009; Parsons et al. 2006). In this study, we examined the influence of agricultural crops (corn and soybean) on the plant-scale and landscape-scale CH_4 budget. Given the large spatial extent of corn and soybeans grown in the United States (US), their high net primary productivity, and the large nutrient inputs used to support these systems [US Department of Agriculture (USDA) 2009], we hypothesize that their influence on atmospheric CH_4 is important during the growing season and aim to better understand the underlying mechanisms.

At the plant scale, researchers have reported that CH_4 emissions are often below detection limits (Beerling et al. 2008; Dueck et al. 2007; Kirschbaum and Walcroft 2008), while others have demonstrated significant emissions for many plant species (Keppler et al. 2006, 2009; Vigano et al. 2008; Wang et al. 2008; Qaderi and Reid 2011). Even for

the same species, the findings are not consistent. For example, in previous studies, the CH_4 flux for corn (*Zea mays*) ranged from −0.43 nmol m^{-2} s^{-1} to 11 nmol m^{-2} s^{-1} (Table 1). The discrepancy among the published studies on plant-scale CH_4 flux can be attributed to mechanisms of CH_4 production in plants and experimental artifacts. Evidence suggests that abiotic stress may stimulate the production of CH_4 resulting from higher temperature, water stress, exposure to sodium azide, and other environment factors that increase the availability of reactive oxygen species in plants (Bruhn et al. 2009, 2012; Qaderi and Reid 2011; Wang et al. 2011; Wishkerman et al. 2011). The CH_4 production caused by abiotic stress can be significant. For example, CH_4 emission from six species of crop leaves increased by 20 % when the temperature was increased from 24 °C to 30 °C during the day, and from 20 °C to 26 °C at night (Qaderi and Reid 2011). As a result, different levels of abiotic stress, caused either by chamber artifacts or by different environmental conditions, can cause differences in the observed CH_4 flux.

There are four main types of chamber artifacts that can bias the observed CH_4 flux from plants. First, evidence indicates that the CH_4 flux is lower in the dark than if the plant is exposed to UV radiation (McLeod et al. 2008; Vigano et al. 2008, 2009), indicating that measurements made in artificial light environments may underestimate CH_4 emissions. Second, several experiments have involved detached plant tissues (Wang et al. 2008; Vigano et al. 2008), and their detected CH_4 emission may be caused by the physical damage associated with extracting tissue (Wang et al. 2009). Third, most plant chambers are characterized by increased temperature and humidity compared to ambient conditions (Keppler et al. 2006; Kirschbaum and Walcroft 2008; Nisbet et al. 2009), which can increase plant stress and bias the observed CH_4 flux from plants growing in field conditions. Finally, in some experiments, the plants are immersed in a CH_4-free gas or a gas with a low CH_4 concentration to improve the sensitivity of the CH_4 flux detection (Beerling et al. 2008; Keppler et al. 2006; Kirschbaum and Walcroft 2008; Vigano et al. 2008). This experimental design excludes the possibility of plant uptake and may lead to additional CH_4 flux through the adsorption/desorption processes and through diffusion via the plant tissue driven by an enhanced concentration gradient between the leaf and the soil.

Agricultural ecosystems are heavily managed and corn-soybean rotations require significant nutrient input (Karlen et al. 1995). However, the impact of nitrogen enrichment on plant flux has not been addressed in the literature, while soil nitrogen has been studied extensively as a regulatory factor involved in soil CH_4 flux. Nitrogen enrichment affects the production and consumption pathways of CH_4 by increasing the redox potential and competing against CH_4 to react with methane monooxygenase. For soils emitting CH_4, nitrogen enrichment can increase the net emission by up to 97 %, while for soils absorbing CH_4, nitrogen enrichment can suppress the uptake by 38 % (Liu and Greaver 2009). We hypothesize that nitrogen enrichment should increase CH_4 emission or suppress CH_4 uptake from plants.

To date, most CH_4 studies have been based on chamber techniques that have relatively poor temporal and spatial resolution. However, methane fluxes are known to be episodic (ebullition events can be triggered by changes in atmospheric pressure) and have been shown to vary significantly within similar field conditions (Hendriks et al. 2010; Kroon et al. 2007; Pattey et al. 2006; Smeets et al. 2009). The heterogeneity of CH_4 flux implies that upscaling plot-scale measurements (the bottom-up method) to estimate the regional CH_4 budget will carry large uncertainties.

The tall tower top-down method can help constrain these uncertainties at regional scales. Few studies have attempted to measure the landscape-scale CH_4 budget based on near-continuous monitoring of atmospheric mixing ratios. Using the Weather Research and Forecast (WRF) and the Stochastic Time-inverted Lagrangian Transport (STILT) model to interpret the CH_4 concentration measured at a tall tower, Zhao et al. (2009) found that the CH_4 emission was 37± 21 % higher than the bottom-up emission estimates. Another successful application of this approach was reported by Werner et al. (2003), who measured CH_4 gradients at a 447-m tall tower in Wisconsin, which is about 300 km from our Minnesota research site, in a landscape of wetland and upland forests. They found that the emission flux of the wetlands exceeded the uptake flux of the forests, resulting in a net regional CH_4 flux of 17±10 nmol m^{-2} s^{-1}.

Consequently, the objectives of this study were to:

(1) Use a new dynamic chamber design to reduce measurement artifacts to clarify the influence of crop plants on atmospheric CH_4.
(2) Explore whether nitrogen fertilization changes the magnitude or direction of CH_4 plant flux.
(3) Examine the regional CH_4 budget using a top-down approach involving CH_4 concentration and gradient measurements on a tall tower and examine the relative role of agricultural plants in the regional budget.

Materials and methods

Research site

The field experiment was conducted at the University of Minnesota Outreach, Research and Education Park. The research site is located 20 km south of Minneapolis. The plant flux measurement was made in a field of a soybean

Table 1 Summary of observed CH_4 flux from corn (*Zea mays*). For unit conversion, we assume a biomass value of 1,652 g m^{-2}. *DOY* Day of year

Reference	Light type	Light intensity (W m^{-2})	CH_4 background concentration (ppbv)	Intact/ detached	CH_4 flux (nmol m^{-2} s^{-1})
Beerling et al. 2008	Lamp	152	59	Intact	0.06±0.57
	Dark	0	59	Intact	0.14±1.15
Dueck et al. 2007	Lamp	65/130	2,100	Intact	0.80 ±1.03
Kirschbaum and Walcroft 2008	Lamp	1	0	Intact	−0.007±0.032
Nisbet et al. 2009	Lamp	39	1,984±6	Detached leaves	−0.43±0.49
	Lamp	39	2,021±5	Detached leaves	0.74±2.45
Keppler et al. 2006	Sunlight	–	0	Intact	11 (6–17)
	Dark	0	0	Intact	3 (1–6)
Vigano et al. 2008	UV lamp	49	Ambient or 0	Detached (fresh)	1.4
	UV lamp	49	Ambient or 0	Detached (dry)	0.7
This paper	Sunlight (with 10 % UV reduction)	Ambient	Ambient	Intact	0.11±0.06 (DOY 201–218)
	Dark	0	Ambient	Intact	−0.13±0.12 (DOY 201–218)

(*Glycine max*)-corn (*Zea mays*) rotation management that is characteristic of the Upper Midwest (Griffis et al. 2005). The soil is a Waukegan silt loam about 0.5–1.8 m thick, which is underlain by sand and gravel. This field was converted from a prairie to agriculture 130 years ago (Griffis et al. 2005). The land management techniques applied at this site are typical for the region. In the 2008 soybean phase, no fertilizer was applied, except in a small area that was reserved for the fertilizer treatment/experiment. In the 2009 corn phase, fertilizer in the form of anhydrous ammonia was applied at a rate of 112 kg N ha^{-1} on 15 April [day of year (DOY) 106] except for the zone reserved for non-fertilization treatment.

In the 2008 soybean phase, three soybean plants were selected from three random plots for flux measurements. In the middle of the growing season (10 July, DOY 192), three additional plots of 1 m radius were treated with fertilizer (24-8-16, NPK; Scotts Miracle-Gro, Marysville, OH) at a rate of 500 kg N ha^{-1}. The fertilizer intensity was the upper limit of the growing season total N application rate found in the literature. The flux measurement was carried out on one plant in the center of each fertilization plot. The chamber measurements started on DOY 160 and ended on DOY 225. The plant density was 30 plants m^{-2}.

In the 2009 corn phase, measurements were made on three corn plants in three random plots. To test the effect of fertilization, a buffer strip (8 m×30 m) was excluded from fertilization. Three unfertilized corn plants chosen from three random plots within the strip were also measured. The chamber measurement started on DOY 147 and ended on DOY 218. The plant density was 8.1 plants m^{-2}.

The tall tower (244 m) facility is located 3 km southeast of the soybean/corn field (Griffis et al. 2010). A footprint analysis using the STILT model (Lin et al. 2003) during the tall tower observation period (DOY 243–269, 2009) revealed that 66 % of the tower footprint was cropland.

Measurement with plant chambers

A steady-state flow-through chamber system was used to measure the plant CH_4 and CO_2 fluxes (Fig. 1). It consisted of plant chambers of varying sizes, a cooling apparatus, and gas analyzers. To accommodate plant growth, we used three chamber sizes: small (25 cm×25 cm×25 cm), medium (50 cm×50 cm×50 cm), and large (50 cm×50 cm×150 cm). Two fans positioned near the top of the chamber and pointed at downward-facing angles promoted mixing inside. The small and medium chambers were made of transparent plexiglass with minimum light attenuation [<8 % in the photosynthetically active radiation (PAR) waveband, and <10 % in the UV waveband]. The chamber was seated on a metal base frame 5 cm above the soil surface. Two plexiglass plates were placed on the base, allowing one plant stem to pass through a hole at the center. The chamber base was not sealed; instead, ambient air entered the chamber from the perimeter of the base, and the CH_4 and CO_2 concentrations in the air were sampled and measured continuously. The large chamber was used when the corn plants were taller than 1.5 m. It consisted of the medium chamber with the base removed and a skirt made of transparent polyethylene. The plexiglass chamber rested on

a metal frame whose height was adjustable from 1 m to 1.7 m. The polyethylene skirt was attached to the sides of the plexiglass chamber using strong bonding tape, and the bottom was tied loosely to the base of the plant allowing air to enter from the base of the plant.

A cooling system kept the chamber temperature consistent with ambient conditions by circulating chilled water through a heat exchanger inside the chamber. Control of the cooling was achieved by adjusting the water circulation rate. Temperature was monitored using thermocouples inside and outside the chamber. The difference between the chamber temperature and the ambient temperature was maintained to within ±3 °C.

The chamber system could accommodate only one plant at a time. Therefore, we were limited to measuring one plant per day. The system was rotated sequentially among the replicated plots. One complete rotation took 6–7 days. The cooling system permitted continuous measurement throughout the daytime and nighttime without overheating in full sunlight. This arrangement was a compromise between capturing temporal variations at the diurnal and seasonal time scales and spatial variations among the replicates.

Two analyzers were used to measure the CO_2, N_2O, and CH_4 mixing ratios of the inlet and outlet air streams of the chamber. The base flow rate of the outlet was maintained at 35 L min^{-1}, 47 L min^{-1}, and 51 L min^{-1} for the small, medium, and large chambers, respectively. The flow rate was set relatively high to reduce the impact of the strong CO_2 depletion inside the chamber during the daytime. The inlet air was sampled with a tube with evenly distributed holes attached to the outside perimeter of the bottom of the chamber. Air entered from the unsealed bottom of the chamber as described and was pumped out (outlet air) at the base flow rates by a tube placed vertically inside the chamber (Fig. 1). This tube had small sampling holes distributed evenly from the bottom to the top to avoid the artifact of the concentration gradient inside the chamber. All sampling tubes were made of high-density polyethylene material. Two subsamples were drawn from the inlet and outlet tubes for the CH_4/N_2O and CO_2/H_2O measurements, at flow rates of 180 mL min^{-1} and 1.0 L min^{-1}, respectively. A tunable diode laser analyzer (TDL, model TGA 100A, Campbell Scientific, Logan, UT) was used to measure the CH_4 and N_2O mixing ratios. The laser temperature was optimized and maintained at 90.80 K in 2008 and 91.30 K in 2009, while the temperature of the detectors was maintained at 135.5 K using liquid nitrogen. The sample cell pressure was maintained at 36 mb. The TDL was plumbed to a four-port manifold that used a switching sequence in the order of inlet, outlet, calibration zero, and calibration span, with 20 s spent on each port and the first 10 s after each switching omitted from the analysis. The CO_2 and H_2O mixing ratios were measured using an infrared gas analyzer (IRGA; LI-6262, LI-COR, Lincoln, NE). This analyzer was switched between the inlet and outlet air flows every 1 min, with the first 30 s after each switching excluded from the computation of the average concentrations. The analyzers were housed in an air-conditioned hut to minimize the impact of temperature fluctuations on the measurements. The CH_4 span calibration standard had a mixing ratio of 2.2 ppmv (accuracy ±5 %). The IRGA was calibrated manually with a standard CO_2 gas (391.03±0.03 ppmv) and a dew point generator (model LI-610, LI-COR) at the beginning of each field season.

The difference in mixing ratios between the chamber inlet and outlet was used to determine the plant flux as,

$$F_a = (C_o - C_i)\frac{P_a QD}{RT} \tag{1}$$

where F_a is the flux expressed on the ground area basis (μmol m^{-2} s^{-1}), C_o and C_i are the gas mixing ratios of the outlet and inlet samples, respectively, P_a is the ambient air pressure, Q is the air flow rate through the chamber, D is the plant density (plants m^{-2}), R is the ideal gas constant, and T is the temperature. This calculation was performed at half-hour intervals for three gases (CO_2, CH_4, and N_2O). The analysis of the N_2O data will be reported later.

Tall tower gradient measurement

From 30 August to 25 September 2009 (DOY 243–269), the TDL and IRGA analyzers were deployed at the tall tower to explore the behaviors of the CH_4 and CO_2 mixing ratios in the atmospheric boundary layer. Air was drawn from the 200 m and 3 m height at a flow rate of 1.3 L min^{-1} and 0.9 L min^{-1}, respectively, through two tubes (ID 0.96 cm) to the analyzers housed in a temperature-controlled building at the base of the tower (Griffis et al. 2010). A portion of the flow (180 ml min^{-1} for TDL and 0.6 L min^{-1} for IRGA) was subsampled by the analyzers. The TDL air sampling sequence included 200 m, 3 m, calibration zero, and calibration span. Each sample lasted for 30 s. The data following the first 15 s of valve switching were excluded to avoid using residual air from the previous sample when calculating the mean concentrations. The IRGA was used to analyze the 200 m and 3 m concentrations sequentially with a sample interval of 1 min.

We calculated the landscape-scale CH_4 flux using the modified Bowen ratio method (MBR) (Meyers et al. 1996; Werner et al. 2003). This method is based on the assumption that the scalar quantities are transferred indiscriminately by turbulent eddies in the atmospheric boundary layer. Under this assumption, the CH_4 flux is given by

$$F_2 = F_1 \frac{\partial c_2/\partial z}{\partial c_1/\partial z} \tag{2}$$

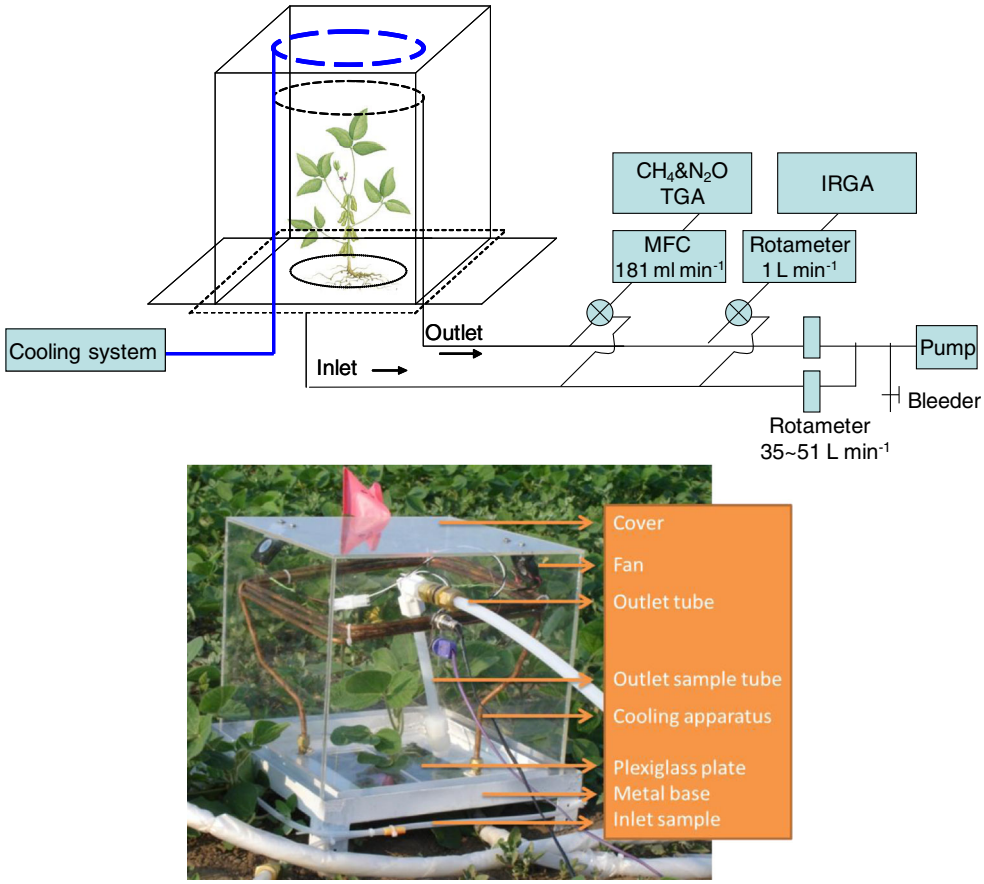

Fig. 1 Schematic diagram and photograph of the plant chamber system

where F_2 is the CH_4 flux, F_1 is the CO_2 flux, $\partial c_2/\partial z$ is the CH_4 gradient, and $\partial c_1/\partial z$ is the CO_2 gradient. The CO_2 flux was measured using the eddy covariance at 100 m at the tall tower (Griffis et al. 2010).

Supporting measurements

At the chamber measurement site, standard micrometeorological and eddy flux variables were measured at half-hour intervals, including variables relevant to this study such as CO_2 flux, soil moisture, air temperature, solar radiation, and precipitation. The same set of measurements was made simultaneously in an adjacent field with a soybean-corn rotation schedule opposite that of the main field. Details of these measurements can be found in Baker and Griffis (2005) and Bavin et al. (2009).

Results

Leaf area index and biomass

In the literature, plant CH_4 flux is often expressed based on unit dry biomass weight and unit leaf area. To facilitate comparison with the published results, we measured the leaf area index (LAI) and the plant biomass. During the experimental period, we randomly sampled five plants in the fertilized zone and the unfertilized zone every week, measured the leaf area, dried the plant samples in an oven (temperature maintained at 60 °C) for 1 week, and then measured the dry weight.

The unfertilized soybean plants had a maximum LAI of 3.3 m^2 m^{-2} on DOY 224 (11 August) and a dry weight of 14 gdw (grams dry weight) $plant^{-1}$ on DOY 231 (18 August). The LAI and the dry weight for the fertilized soybean plants, measured at the end of the experiment on DOY 242, were 1.7 m^2 m^{-2} and 22.6 gdw $plant^{-1}$, respectively. The maximum LAI of the unfertilized and fertilized corn plants during the 2009 season was 3.5 m^2 m^{-2} and 5.6 m^2 m^{-2}, respectively, and the maximum dry weight was 181 gdw $plant^{-1}$ and 231 gdw $plant^{-1}$, respectively. The unfertilized soybean plants grew to a maximum height of 0.40±0.01 m while the fertilized ones reached 0.53±0.13 m at the end of the experiment. The maximum height of the unfertilized and fertilized corn plants was 1.84±0.30 m and 2.23±0.04 m, respectively.

Zero gradient test and chamber blank tests

To quantify the precision of the CH_4 concentration measurements and to determine the detection limits of the chamber

system, we conducted a zero gradient test and three blank tests on each chamber.

The zero gradient test was carried out by co-locating two sample inlets at the same height (about 1 m above ground) to assess the difference between the two inlets resulting from potential sample artifacts. The results from this test indicate that the measurement precision for the half-hourly averaged CO_2 and CH_4 concentration was 0.15 ppmv and 1.25 ppbv (the standard deviation σ of the zero-gradient test result), respectively. The concentration difference between the two inlets was 0.04 ppmv and −0.05 ppbv and therefore not significantly different from 0 (Student's *t*-test at the 5 % significance level for both gases).

Three blank tests were carried out on each chamber, with each test lasting 24 h, by placing the chamber in the field without including any plants. The half-hour averaged concentration difference resulting from the blank test was not significantly different from 0 (Fig. 2), indicating that there was no significant bias in the chamber flux measurement. The chamber flux detection limit was defined as three times the blank standard deviation for each chamber size. The blank test flux was calculated with Eq. 1 by assuming a plant density of 30 plants m^{-2} and 8.1 plants m^{-2} for soybean and corn, respectively. As a result, the detection limit of CH_4 flux for the small and medium chambers was 0.40 nmol m^{-2} s^{-1} and 0.21 nmol m^{-2} s^{-1} for soybean and 0.11 nmol m^{-2} s^{-1} and 0.06 nmol m^{-2} s^{-1} for corn, respectively. The different detection limits between corn and soybean were due to the different plant densities. The large chamber was used only for corn plants, and the CH_4 flux detection limit was 0.83 nmol m^{-2} s^{-1}. The small and the medium chambers had better precision than the large chamber.

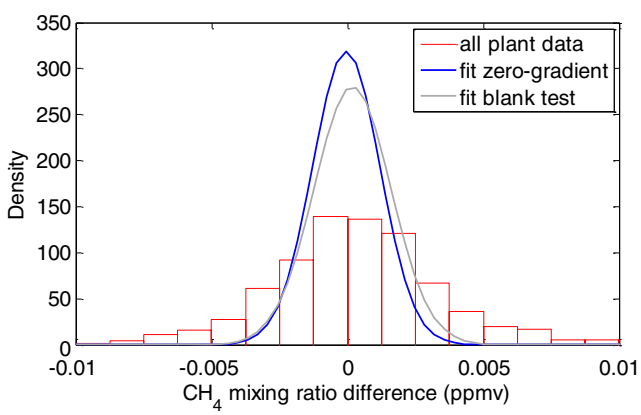

Fig. 2 Distribution of the half-hour averaged CH_4 mixing ratio difference between two sample points during a 24-h chamber measurement period taken in 2009. The *blue* and *grey* lines are the normal distribution curves of the zero-gradient test and the blank test, respectively. The *red bars* are the mixing ratio difference measured when the plant was enclosed in the chamber

Even though reducing the flow rate of the sampling system can improve the detection limit, reducing the flow will result in large CO_2 depletion inside the chamber during the daytime. Note that if we applied the flow rate that was used at the beginning of the growing season (35 L min^{-1}) to the middle of the growing season, the CO_2 concentration inside the chamber would be more than 100 ppmv lower than the ambient value because of the plants' strong photosynthetic activity. Consequently, we adjusted the flow rate to reduce the artifact of CO_2 depletion. As a result, 35 % of the measured CH_4 concentration difference, when plants were present in the chamber, was between −1.25 ppbv and 1.25 ppbv (±1σ of the zero gradient test), suggesting that the plant flux was too small to be resolved with this method (Fig. 2). However, 65 % of the flux data was detected with relatively high confidence, and the mean CH_4 flux of the three duplicates throughout the corn season was 0.085± 0.056 nmol m^{-2} s^{-1}, i.e., significantly higher than 0 (with a 5 % significance level).

Plant CO_2 flux

To evaluate the validity of the chamber approach, the plant CO_2 flux measured with the chamber approach was compared with the plant flux estimated from the eddy covariance and soil chamber data. Here, we assume that the plant flux can be estimated as the difference between the net ecosystem CO_2 exchange (NEE) and soil respiration. In 2009, the NEE was measured in the middle of the G21 cornfield by an eddy covariance system (EC), and soil respiration was measured using three soil chambers located within the same field. The CO_2 flux measured from the plant chamber and that derived from the NEE showed that (1) the flux measured with the plant chambers captured the diurnal pattern of plant activity (Fig. 3); (2) the flux measured with the plant chamber was linearly correlated with that estimated by the EC and soil flux ($P<0.01$), and the fitted line was close to the 1:1 line (Fig. 4).

Plant CH_4 flux

Figure 5 shows the plant flux observed during the midday (10:00–16:00 LST) and midnight (22:00–04:00 LST) periods over the two growing seasons. The flux exhibited some diurnal variations, with slightly positive values during the day and negative values during the night. Throughout the soybean growing season, 91 % of the midday average flux values were positive, with a maximum emission rate of 1.31 nmol m^{-2} s^{-1}. The flux did not simply increase as biomass accumulated. In comparison, 86 % of the midnight flux values were negative, and the uptake signal appeared stronger later in the growing season with a maximum uptake rate of −4.38 nmol m^{-2} s^{-1}. During the corn season, 90 % of

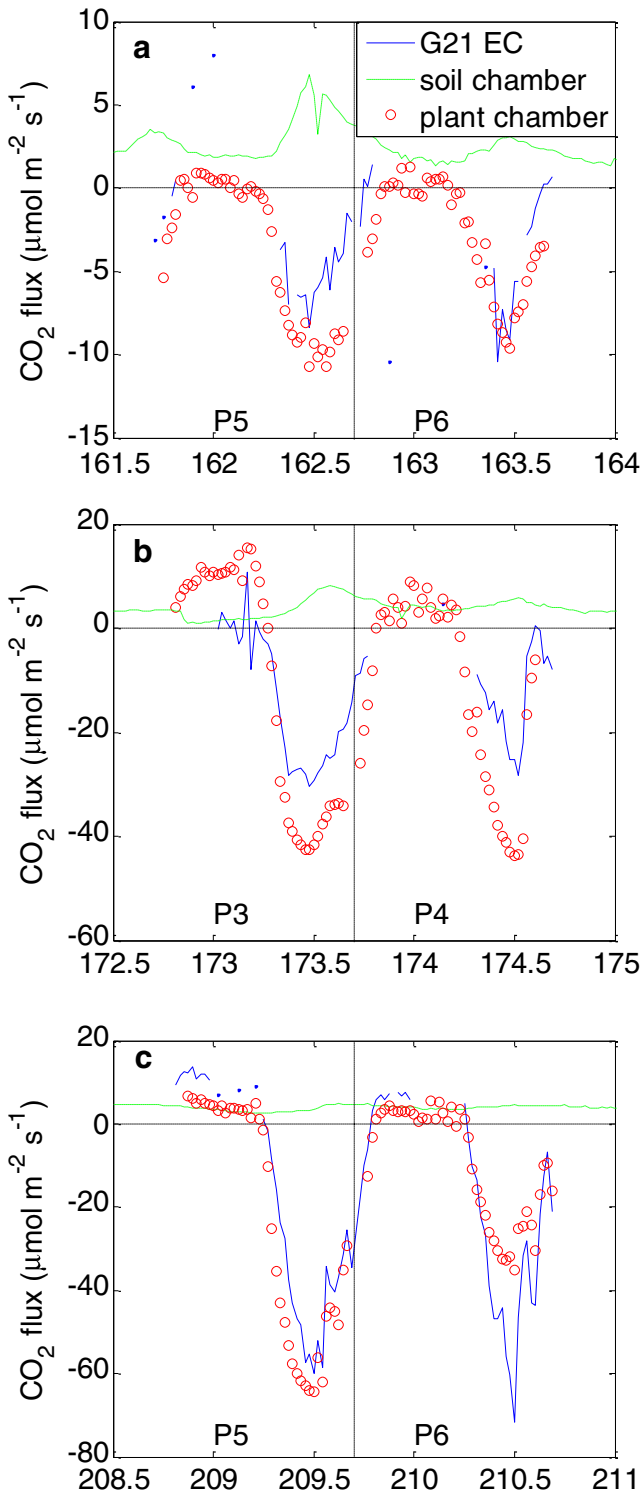

Fig. 3 Half-hour averaged CO_2 flux measured with the eddy covariance system in the cornfields (*blue lines*), soil chambers (*green dashed lines*), plant chambers (*red circles*). **a** Small chamber, **b** medium chamber, **c** large chamber. P3–P6 means sampled corn plant 3–6. P3 and P5 were fertilized, while P4 and P6 were not fertilized. The measurement period was chosen according to the availability of the chamber measurement data and the G21 eddy covariance measurement data

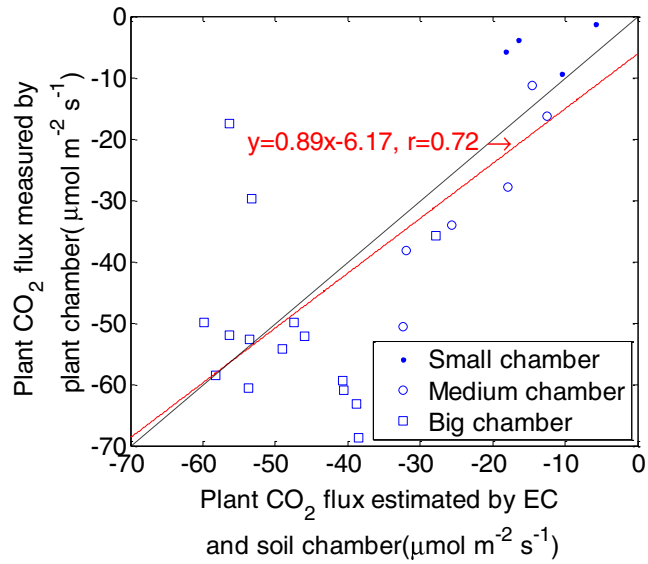

Fig. 4 Comparison of the midday (10:00–16:00) averaged CO_2 flux estimated with the eddy covariance (EC)-soil and measured with the plant chamber

the midday averages were positive, 76 % of the midnight averages were negative, and the daytime fluxes peaked at the time when the biomass growth rate was the greatest. The maximum emission rate and the uptake rate for corn were 2.21 nmol m^{-2} s^{-1} and −2.55 nmol m^{-2} s^{-1}, respectively.

The flux values shown in Fig. 5 are much lower than the values reported by Keppler et al. (2006), who estimated that intact plants emit CH_4 at a rate of 370 ng CH_4 gdw^{-1} h^{-1}, with a range of variations of 200–600 ng CH_4 gdw^{-1} h^{-1} under sunlight and 120 ng CH_4 gdw^{-1} h^{-1} (range 30–210 ng CH_4 gdw^{-1} h^{-1}) in the dark. Keppler et al. (2006), measured CH_4 emissions from intact plant (including the roots) while the method in our study isolated the CH_4 flux of the aboveground section of the plant. However, Keppler et al.'s emission rate is determined by the amount of CH_4 emitted per unit of dry weight per hour, and they did not distinguish a separate emission rate for leaves and roots. As a result, we multiplied Keppler et al.'s emission rates with the dry weight for the aboveground section of plant measured throughout the growing season and the plant density to obtain the flux in units of nmol m^{-2} s^{-1}, and compared the results with our observations (Fig. 5). In the comparison, the daytime and nighttime flux from Keppler et al. was determined by the emission rate observed with and without sunlight, and the same method was used in Keppler et al. (2006) to estimate the annual CH_4 production. Our results were below the lower limit of Keppler et al.'s estimate except at the beginning of the growing season when the plants were very small. Furthermore, for nighttime periods, Keppler et al.'s values were positive while our observed flux

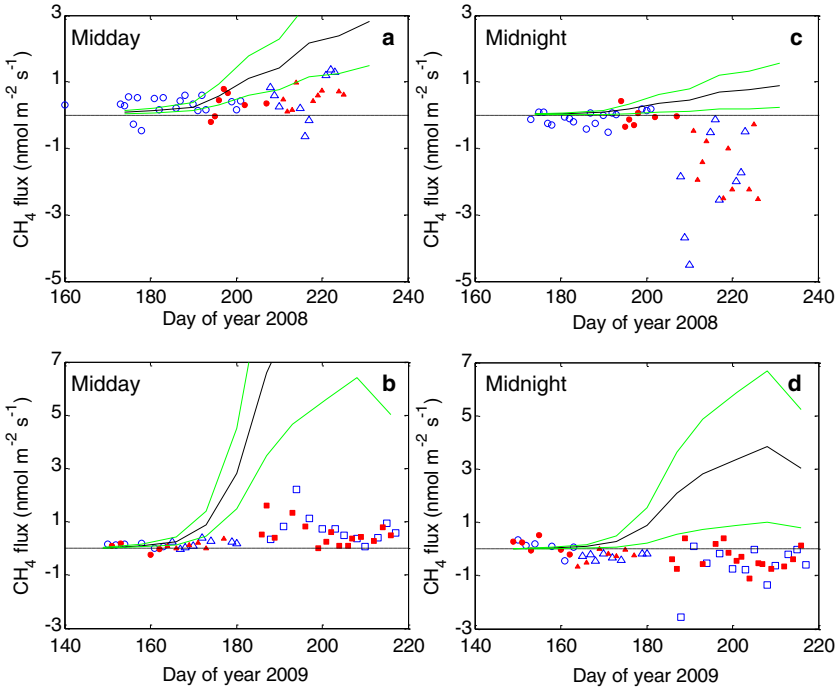

Fig. 5 Midday (10:00–16:00 LST) and midnight (22:00–04:00 LST) plant fluxes in the soybean fields (**a**, **c**) and the cornfields (**b**, **d**) throughout the growing season: *red filled symbols* fertilized plant flux; *blue open symbols* unfertilized plant flux; *circles*, *triangles*, *squares* fluxes measured with the small chamber, the medium chamber, and the large chamber; *black lines* CH_4 flux suggested by Keppler et al. (2006); *green lines* boundary of Keppler et al.'s estimates

was mostly negative. The fact that Keppler et al.'s emission rate was determined mainly using small plants in their early growth stage, suggests that their observation may not be representative of the CH_4 flux from various phenological stages of growth.

The daily mean (24-h average) flux was small for both crops (Fig. 6). During the soybean season, the daily flux ranged from −0.70 nmol m^{-2} s^{-1} to 0.47 nmol m^{-2} s^{-1} and was mostly positive during the first half (DOY 160–202) and negative during the second half of the growing season (DOY 207–225). During the corn season, the daily flux was slightly positive at the beginning, negative from DOY 160 to 175, and mostly positive over the last 42 days of the measurement period. Relatively large emissions (up to 1.08 nmol m^{-2} s^{-1}) were observed near the end of the measurement period in 2009. These daily values were much lower than those reported by Keppler et al. (2006).

In the discussion above, we did not distinguish fertilized and unfertilized plots. Figure 7 shows the fertilization effects on the daily, midday, and midnight CH_4 and CO_2 fluxes throughout the growing season. For each flux, we paired the data with and without fertilization treatment, and used a Student's *t*-test to examine the significance of the fertilization effect. The result shows that fertilization did not affect CH_4 fluxes in any of the three periods ($P>0.05$). Fertilization increased the midday corn uptake of CO_2 ($P<0.05$), and the daily corn CO_2 flux increased significantly as well ($P<0.05$). However, the nighttime CO_2 emission from corn was not significantly affected. The fertilization effect on the daily and midday soybean CO_2 fluxes was not as

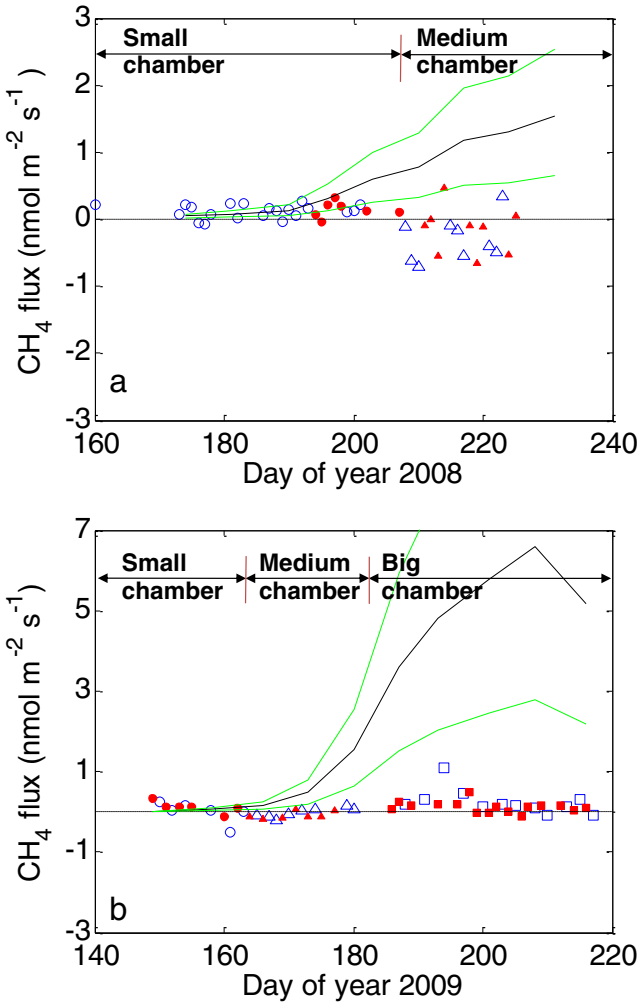

Fig. 6 As in Fig. 5 except for the daily average plant CH_4 flux in soybean fields (**a**) and cornfields (**b**)

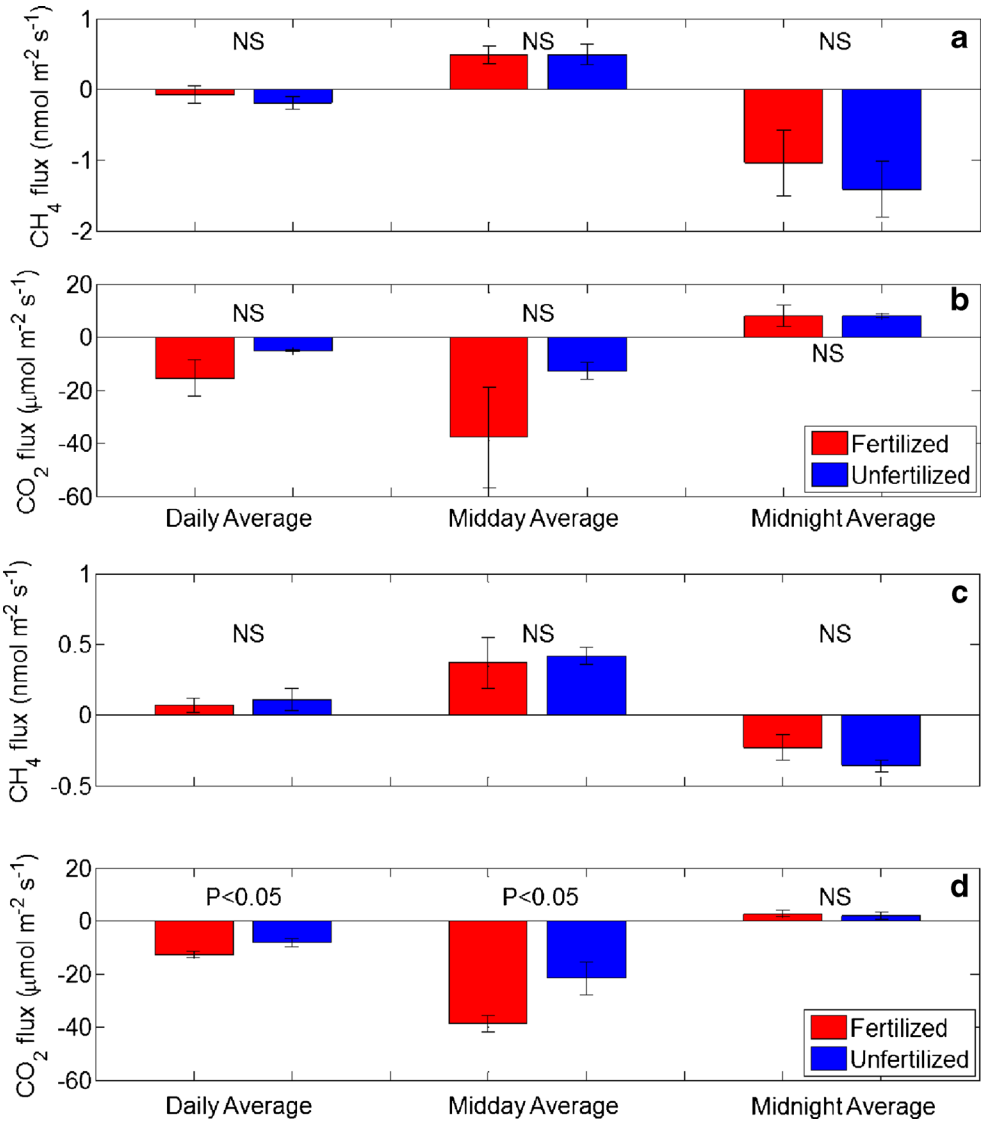

Fig. 7 Daily, midday (10:00–16:00 LST), and midnight (22:00–04:00 LST) fluxes averaged over the soybean (**a**, **b**) and (**c**, **b**) corn growing seasons. *Error bars* Standard deviations of the three replicate plants. *NS* Difference between fertilized and unfertilized plant fluxes insignificant ($P>0.05$)

significant as for corn ($P=0.06$ and 0.09, respectively), and the midnight flux was not significantly affected by fertilization.

Table 2 summarizes the linear correlation between plant CH_4 fluxes and environmental variables, including incident solar radiation, air temperature, soil water content at 10 cm depth, and soil temperature at 10 cm. These variables were considered in previous studies on plant CH_4 emission and uptake (Keppler et al. 2006; Nisbet et al. 2009). These results show that the midday flux of corn and soybean was positively correlated with solar radiation, with P-values of 0.004 and 0.08, respectively. The correlation with other environmental variables was not consistent for soybean and corn. The midday corn CH_4 flux was moderately correlated with air temperature, soil water content, and soil temperature, but the soybean CH_4 flux was not. Regarding the midnight measurement, corn CH_4 flux was negatively correlated only with air temperature, while soybean CH_4 flux was weakly correlated only with soil moisture.

The correlation between the CH_4 and CO_2 fluxes was also tested to examine the potential relations between CH_4 flux and the process of photosynthesis and respiration. The analysis shows that CH_4 plant flux was negatively correlated with CO_2 flux throughout the day for corn and soybean, and that fertilization did not affect this correlation.

Tall tower CH_4 observation

The CH_4 concentration at 3 m and 200 m at the tall tower site exhibited diurnal variations, which suggests that this agriculture-dominated landscape released CH_4 at night, but the direction of the daytime flux was not clear (Fig. 8). After 19:00 LST, with the formation of the stable nighttime boundary layer, CH_4 accumulated near the ground surface,

Table 2 Linear correlation of plant CH_4 flux with environmental variables and CO_2 flux

	n	Solar radiation	Air temperature	Soil moisture	Soil temperature	CO_2 flux
Corn						
Midday flux	52	0.37****	0.25**	−0.36***	0.27**	−0.35***
Midnight flux	56	N/A	−0.30**	0.09	0.05	−0.15*
Soybean						
Midday flux	46	0.21*	0.04	−0.07	0.08	−0.21*
Midnight flux	45	N/A	0.00	0.24*	−0.08	−0.72****

* ($0.05<P<0.1$), ** ($0.01<P\leq0.05$), *** ($0.001<P\leq0.01$), **** ($P\leq0.001$), ns ($P>0.1$)

and the 3 m concentration peaked around 07:00 LST. The peak value varied from day to day, and the average at 07:00 LST was 2.232±0.291 ppmv. After sunrise, turbulent motion in the surface layer diluted the CH_4-rich air near ground with air from higher altitudes and increased the CH_4 concentration at 200 m above the ground. The concentration at both heights decreased until 16:00 LST, when the concentration at both heights was approximately 1.996 ppmv. These diurnal trends suggest that the surface was a source at night. However, these trends cannot indicate land surface uptake during the daytime because the depletion could also be attributed to the entrainment at the top of the convective boundary layer.

The CH_4 and CO_2 concentration gradients at night also suggest nighttime release of CH_4 by the landscape. The CH_4 concentration gradient in the 3 to 200 m air layer was consistently negative (concentration at 200 m<concentration at 3 m) at night (−0.62±0.60 ppbv m^{-1}), similar to the CO_2 gradient (−0.23±0.09 ppmv m^{-1}). During the observation period, the midnight (22:00–04:00 LST) average CH_4 gradient (G_{CH4}) was positively correlated to the midnight CO_2 gradient (G_{CO2}) (Fig. 9a). The relation between the two gradients was $G_{CH4}=3.8\times10^{-3}\ G_{CO2}+2.6\times10^{-4}$ (linear correlation $r=0.54$, number of observations $n=25$). Due to the strong daytime mixing in the boundary layer, the CH_4 and CO_2 gradients during midday (10:00–16:00) were very small: the CH_4 gradient was $-6.2\times10^{-3}\pm3.0\times10^{-2}$ ppbv m^{-1} (not significantly different from 0 according to a Student's *t*-test with a significance level of 5 %), and the CO_2 gradient was $9.12\times10^{-3}\pm9.97\times10^{-3}$ ppmv m^{-1}.

The CH_4 fluxes calculated with the MBR method also indicated a nighttime emission, similar to the pattern observed from the concentration gradient. During the observation period, the CH_4 flux at night was 14.8±10.3 nmol m^{-2} s^{-1}. Unfortunately, the CH_4 fluxes from the MBR method during the daytime were not reliable due to the small CH_4 and CO_2 gradients.

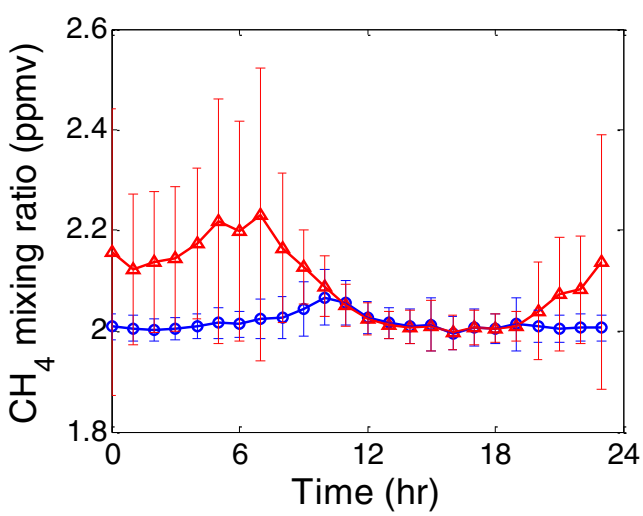

Fig. 8 Diurnal composite of the CH_4 mixing ratio at 3 m and 200 m above the ground during DOY 243–269, 2009. *Red triangles* and *blue circles* are the hourly mean values of the mixing ratio at 3 m and 200 m, respectively. *Error bars* Standard deviation of 30-min observations

Discussion

Plant-scale CH_4 exchange

Comparison with published results

Corn is one of the most studied plant species regarding CH_4 source/sink behavior. Table 1 presents a comprehensive summary of all known results. Our results are presented for the period between DOY 201 and 218 when LAI exceeded 5.1 m^2 m^{-2} and the plant biomass density exceeded 202 gdw $plant^{-1}$. To facilitate the comparison, we multiplied the published values in units of ng CH_4 gdw^{-1} h^{-1} by the mean dry biomass density over this period (1,652 gdw m^{-2}) to obtain flux values in units of nmol m^{-2} s^{-1}. During this period, the midday flux was 0.11±0.06 nmol m^{-2} s^{-1}. Beerling et al. (2008), Dueck and van der Werf (2008), Kirschbaum and Walcroft (2008), and Nisbet et al. (2009) all showed that the flux of the intact shoot and detached

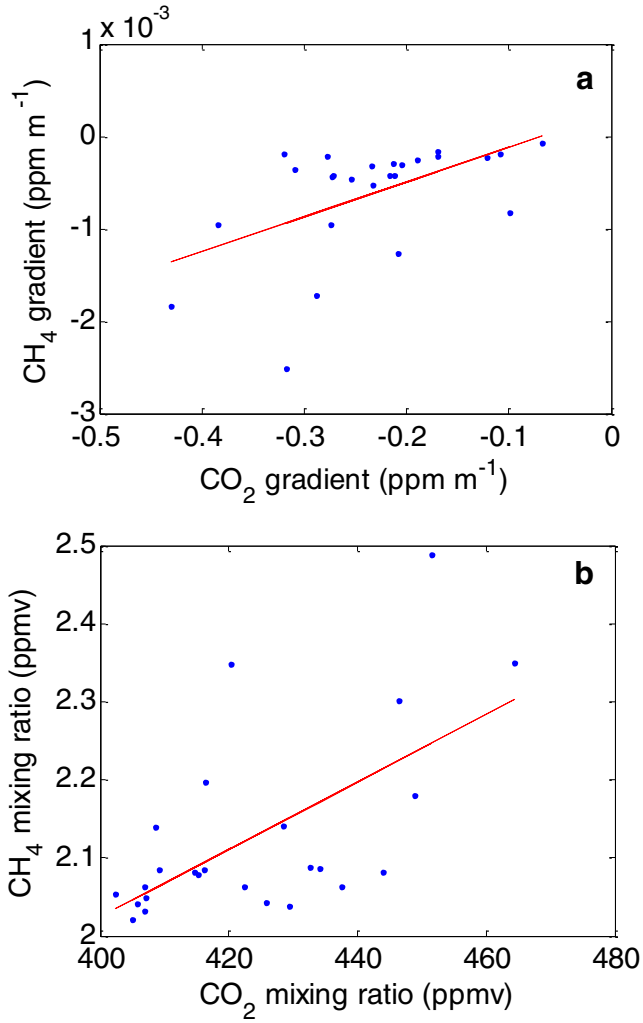

Fig. 9 Linear relationship between the night CH_4 and CO_2 gradients (**a**) and the CH_4 and CO_2 mixing ratios (**b**) at the 3 m height, DOY 243–269, 2009. The results of the linear regression are shown as *red lines*. Each *data point* represents a block average between 22:00 and 04:00 LST

leaves was not significantly different from zero. Vigano et al. (2008) reported that when UV radiation reaches 49 W m^{-2}, fresh corn plant tissues emit CH_4 at a rate of 50 ng CH_4 gdw^{-1} h^{-1}, which is equivalent to 1.4 nmol m^{-2} s^{-1} or about ten times higher than our midday value. This difference could result from the difference in UV exposure. For instance, Vigano et al.'s UV flux intensity was twice as high as the average value in our experiment.

Some of the variations among these studies may have been a consequence of using different measurement methods and experimental conditions. To minimize measurement artifacts, we constructed the chamber system without impacting major physiological processes such as photosynthesis and respiration. In this design, special attention was given to temperature, radiation, and CH_4 and CO_2 background concentrations. The temperature inside the chamber was kept consistent with that of ambient air. The plexiglass chamber material had a transmissivity of 92 % for visible light and 90 % for UV radiation. The CH_4 concentration inside the chamber was within 0.02 ppmv of the ambient value. On average, the CO_2 concentration inside the chamber was 9 and 66 ppmv lower than ambient in the daytime and 4 and 11 ppmv higher than ambient at night during the soybean and corn growing seasons, respectively. The altered CO_2 levels did not have an appreciable effect on plant function, at least from the perspective of CO_2 exchange. For example, the midday CO_2 uptake of unfertilized soybean and fertilized corn (from 10:00 to 16:00 LST) was -12 ± 3 μmol m^{-2} s^{-1} and -39 ± 3 μmol m^{-2} s^{-1}, respectively (Fig. 7). These values were comparable to the plant flux derived from NEE and soil respiration measurements.

Keppler et al.'s (2006) results contrast sharply with ours and other studies. The mean flux of the four studies conducted in normal light levels (Berling et al. 2008; Dueck et al. 2007; Nisbet et al. 2009; this study) is 0.26 ± 0.51 nmol m^{-2} s^{-1} and is one order of magnitude smaller than Keppler et al.'s flux value. Although this is not a new conclusion, the fact that our measurements were made in the field under near-ambient conditions further supports the view that extrapolation of Keppler et al.'s results to the global scale will severely overestimate the role of plants in the atmospheric CH_4 budget (Ferretti et al. 2007; Houweling et al. 2006).

Role of radiation

That both corn and soybean emitted CH_4 during the day and absorbed CH_4 at night (Fig. 7) suggests a role of radiation in regulating plant CH_4 exchange with the atmosphere. The day-to-day variations in CH_4 production were correlated positively with solar radiation (Table 2). McLeod et al. (2008) and Vigano et al. (2008, 2009) found that the CH_4 flux in dark conditions appears lower than if the plant is exposed to UV radiation, implying a photochemical production mechanism. Our results also reveal a negative correlation with the CO_2 flux (Fig. 10, Table 2), raising another possibility that the daytime emission was linked to photosynthesis. The fact that Kirschbaum and Walcroft (2008) did not observe a significant CH_4 flux may be related to the very low light intensity of their experiments (Table 1).

In the absence of solar radiation, the fertilized and unfertilized corn and soybean plants were small sinks of CH_4 (Fig. 7). This uptake phenomenon, although rarely reported, is consistent with reports by Raghoebarsing et al. (2005) and Sundqvist et al. (2012), who suggest that plant CH_4 uptake is an important sink in the global CH_4 budget. In a boreal forest, the CH_4 uptake by plants ranged up to

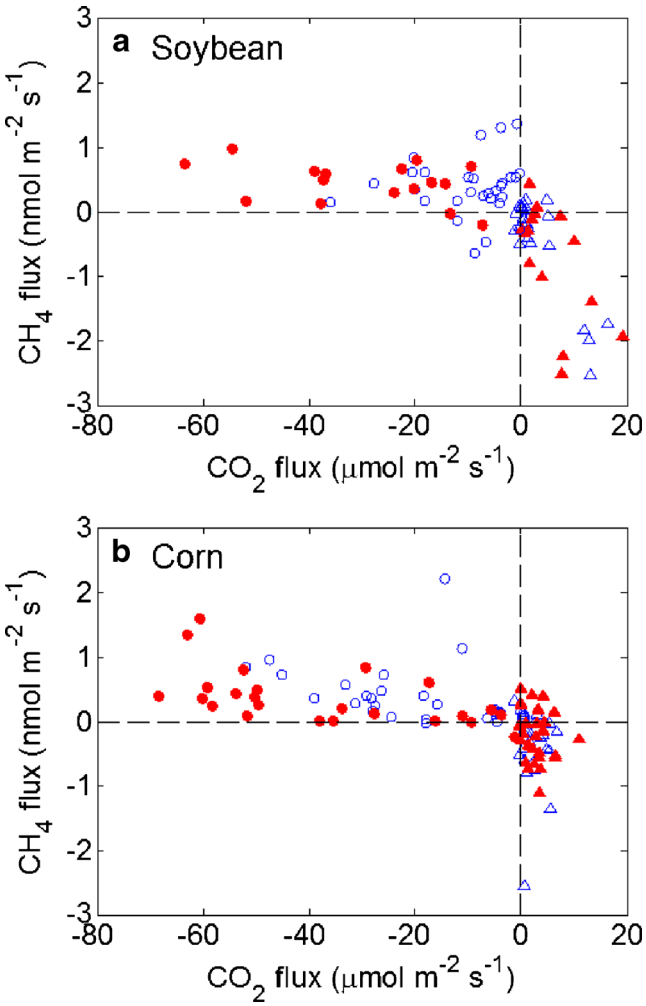

Fig. 10 Relationships between plant CO_2 and CH_4 fluxes. *Red filled circles* Midday fluxes from fertilized plants, *blue open circles* midday fluxes from unfertilized plants, *red filled triangles* midnight fluxes from fertilized plants, *blue open triangles* midnight fluxes from unfertilized plants. **a** Soybean, **b** corn

0.94 nmol m^{-2} s^{-1}, similar to the CH_4 oxidation rate in soil (Sundqvist et al. 2012). *Sphagnum* mosses, prevalent plants in peat bogs, can uptake CH_4 and the assimilated carbon from CH_4 accounts for 10–15 % of the carbon uptake by the plants (Raghoebarsing et al. 2005).

Three mechanisms have been proposed to explain plant uptake of CH_4, including: (1) methanotrophic bacteria oxidize CH_4 in soil, and plants act as a conduit of the soil flux; (2) the partly endophytic methanotrophic bacteria inside plants consume CH_4 in stems and stem leaves (Raghoebarsing et al. 2005); and (3) the reactive oxygen species generated under environmental stress react with water to produce hydroxyl radicals (OH), which is the major sink of CH_4 (Logan et al. 1981). At this time it is not certain which of these mechanisms accounts for the uptake observed in our study, but an association with plant dark respiration was suggested by the correlation shown in Fig. 10.

Furthermore, all the mechanisms can take place during the daytime when the corn and soybean plants were a net source of CH_4, suggesting that the gross CH_4 production by plants may be much more than observed because part of it was recycled in the plant (Raghoebarsing et al. 2005). This internal recycling mechanism may prevent greater CH_4 release to the atmosphere and lead to a negligible net CH_4 flux from plants.

Impact of fertilization

Fertilization did not significantly affect the plant CH_4 fluxes averaged over daily (24-h), midday, or midnight periods. However, although not statistically significant, the seasonal mean of CH_4 uptake during the midnight periods was smaller in fertilized plots than in unfertilized plots for corn and soybean, and this was consistent with the impact of fertilization on agricultural soil reported in the literature (Jacinthe and Lal 2003; Mosier et al. 2006; Suwanwaree and Robertson 2005). A meta-analysis suggests that CH_4 uptake by soil is inhibited by fertilization at a rate of 0.012± 0.006 kg CH_4-C ha^{-1} $year^{-1}$ per 1 kg N ha^{-1} $year^{-1}$. By multiplying the fertilization rate for corn and soybean, respectively, soil CH_4 uptake should have been reduced by 0.36±0.18 nmol m^{-2} s^{-1} and 1.6±0.8 nmol m^{-2} s^{-1}. In comparison, the reduction in plant CH_4 uptake during the midnight periods in our study was 0.13 nmol m^{-2} s^{-1} and 0.28 nmol m^{-2} s^{-1} for corn and soybean, respectively. Another recent study in the midwest US suggests that fertilization reduces soil uptake of CH_4 by 0.19±0.25 nmol m^{-2} s^{-1} and 0.11±0.08 nmol m^{-2} s^{-1} in fields cultivated with corn and soybean (Johnson et al. 2010). The difference between the reduction in the soil CH_4 uptake reported in the literature and our study suggests that applying the soil inhibition factor to plant CH_4 flux may lead to an overestimation of the fertilization impact of as much as six times.

Landscape-scale flux and uncertainties

Sources and sinks within the tower footprint

To examine the contributions of other sources and sinks in the tower footprint, we conducted a source footprint analysis with the STILT model (Lin et al. 2003). At each time point, 100 air parcels were released at the receptor (44°41′19″N, 93°04′22″W, 200 m) and were transported backward for 2 days. The aggregated distribution of the air parcels defines the footprint of the tall tower. Overlaying this footprint map on the data on the type of land cover from the US Geological Survey, we estimated that 66 % of the footprint during

the observation period was cropland, 11 % was grassland, 11 % was forest, 2 % was wetland, 4 % was water, and 6 % was developed land.

Even though the landscape is dominated by cropland, the flux from crop plants was negligible in the landscape-scale CH_4 budget, since the plant flux was one to two orders of magnitude smaller than the landscape-scale CH_4 flux. In midday, the (unfertilized) soybean and (fertilized) corn flux was 0.49±0.15 nmol m^{-2} s^{-1} and 0.37±0.18 nmol m^{-2} s^{-1}, respectively, while at midnight, the soybean and corn flux was −1.41±0.40 nmol m^{-2} s^{-1} and −0.23± 0.09 nmol m^{-2} s^{-1}. In comparison, the landscape flux observed at the tall tower during the later growing season was 14.8 nmol m^{-2} s^{-1} at midnight.

Cropland soils in the Midwest US have been investigated intensively for CH_4 flux (Alluvione et al. 2009; Adviento-Borbe et al. 2007; Mosier et al. 2006; Omonode et al. 2007; Ussiri et al. 2009). Divergence exists in the published results due to the complex production and consumption mechanisms of CH_4 by methanogenesis and methanotropic bacteria. These studies show that the soil CH_4 flux in corn or corn-soybean rotation croplands ranges from −0.94 to 0.73 nmol m^{-2} s^{-1}. Adviento-Borbe et al. (2007) reported that the CH_4 soil flux in a soybean-corn rotation field in eastern Nebraska was −0.94 nmol m^{-2} s^{-1}. Ussiri et al. (2009) suggested that tillage may have a significant impact on flux. In a comparative study in Ohio, the soil CH_4 flux ranged from −0.08 nmol m^{-2} s^{-1} under no-till to 0.73 nmol m^{-2} s^{-1} in a field subject to moldboard plowing. Omonode et al. (2007) reported that no-till fields emitted CH_4 at a rate of 0.25 nmol m^{-2} s^{-1} and tilled fields were a net sink of CH_4 at a rate of −0.28 nmol m^{-2} s^{-1} in Indiana. Alluvione et al. (2009) and Mosier et al. (2006), however, found that tillage had a negligible impact on the CH_4 soil flux in cornfields in Colorado, and Bavin et al. (2009) found it extremely difficult to even measure a significant CH_4 flux from bare soils in strip till or conventional managed fields. The difference among these studies may be related to soil properties and to how many years the field has been in no-till or till practice (Mosier et al. 2006). However, all observed fluxes, either positive or negative, were about one magnitude lower than the regional flux.

Native grassland and forest soils seem to have higher CH_4 oxidation rates than cropland soils. In Inner Mongolia, the semi-arid grasslands consume CH_4 at a rate of 0.48 to 0.61 nmol m^{-2} s^{-1} (Wang et al. 2005), while in the southern Rocky Mountains, forest soils take up CH_4 at a rate of 1.2 nmol m^{-2} s^{-1} (Bowling et al. 2009). These findings are consistent with a comprehensive literature review by Le Mer and Roger (2001), which suggested that the CH_4 consumption by upland soils ranges between 0 and 1.74 nmol m^{-2} s^{-1}, depending on the disturbance regime such as tillage and fertilization (Le Mer and Roger 2001). As a result, grassland and forest may contribute mainly to the uptake of CH_4 from the atmosphere, which was very likely offset by the emission from another type of land cover.

Wetland and developed land, two minor land use categories in the tower footprint, are strong sources of CH_4. In one study, wetland CH_4 emissions were estimated to be 61–87 nmol m^{-2} s^{-1} in Minnesota in September (Shurpali and Verma 1998). A recent field experiment showed that the CH_4 emission is about 20 nmol m^{-2} s^{-1} in a boreal fen in western Canada (Long et al. 2010). In developed areas, CH_4 can be emitted by fossil fuel combustion, landfills, and natural gas leakage (Mosher et al. 1999; Nakagawa et al. 2005; Zimnoch et al. 2010). Nakagawa et al. (2005) reported that automobile exhaust contributed up to 30 % of CH_4 sources in an urban area in Japan. An investigation by Mosher et al. (1999) at nine landfill sites in the northeastern US showed the emission rate of the landfills ranged from 6.6×10^3 to 9.4×10^4 nmol m^{-2} s^{-1}. Regarding natural gas leakage, a study conducted in the urban area of Krakow, Poland, suggests that natural gas led to an emission flux of 14 nmol m^{-2} s^{-1}(Zimnoch et al. 2010). Consequently, even though wetland and developed land account for only 8 % of the tall tower footprint, they may dominate the CH_4 budget.

Uncertainties in the MBR measurement

The MBR method provided a more robust estimate of the CH_4 flux under stable nighttime conditions than under unstable daytime conditions. The high CH_4 concentration near the ground at night indicated that the ground surface was a source of CH_4. Furthermore, the CO_2 and CH_4 vertical gradients were large at night and correlated with each other (Fig. 9a). The nighttime CH_4 flux was 14.8 nmol m^{-2} s^{-1} according to the MBR method. For comparison, the midnight CH_4 flux, obtained by multiplying the slope of the regression shown in Fig. 9b with the nighttime CO_2 flux, was 17.1±9.4 nmol m^{-2} s^{-1}. This latter estimate is independent of the assumption of equal eddy diffusivity between the two gases. Instead, this estimate assumes that the buildup of CO_2 and CH_4 in the stable air layer near the ground resulted from their respective land surface sources so that CO_2 can be used as a tracer to constrain the CH_4 surface flux. The same method was used by Kelliher et al. (2002) to determine the N_2O flux in a grassland landscape affected by animal grazing.

It is not clear whether the regional daytime flux is positive or negative because the small daytime gradients are difficult to resolve. However, it is clear that the daytime CH_4 flux is not large enough to decrease the daily averaged CH_4 flux to the magnitude of the plant flux or even switch the sign of the flux. Zhang (2013) estimated the regional CH_4 flux from the entire observation period with the equilibrium boundary layer method, and the result suggested the

landscape around the tall tower emits CH_4 at a rate of 16.0± 3.1 nmol m^{-2} s^{-1}, on the same magnitude as our MBR estimation at midnight. Based on a continuous gradient measurement on a tall tower in Wisconsin (about 260 km northeast of our tall tower), Werner et al. (2003) reported no diurnal pattern of CH_4 flux and the regional CH_4 emission rate in September was around 10 nmol m^{-2} s^{-1}, similar to our observation. As a result, the nighttime CH_4 flux estimated with the MBR method can provide a reasonable constraint on the CH_4 budget during our observation period. Longer-term measurements and analyses are required to better understand the seasonal variability, annual budget, and source contributions of CH_4 emissions in the upper Midwest.

Conclusions

We observed that soybean and corn plants emitted CH_4 during the daytime (mean midday values 0.49±0.15 nmol m^{-2} s^{-1} and 0.37±0.18 nmol m^{-2} s^{-1}, respectively) and absorbed CH_4 during the nighttime (mean midnight values −1.41± 0.40 nmol m^{-2} s^{-1} and −0.23±0.09 nmol m^{-2} s^{-1}). The strength of the plant flux was at least one order of magnitude smaller than that suggested by Keppler et al. (2006). Fertilization did not have a significant impact on the plant CH_4 flux. The plant CH_4 flux was one to two orders of magnitude smaller than the landscape-scale CH_4 flux measured at the tall tower (14.8±10.3 nmol m^{-2} s^{-1}). Although the plant CH_4 flux was relatively small, it indicates that there is a mechanism for cropland plants to uptake atmospheric CH_4. Cropland plants, therefore, may represent an important sink in the global CH_4 budget.

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