Dear Dr. Guenther,

First of all, we would like to thank you and the reviewers for the valuable comments. We appreciate their time and contribution. We have made revisions to reflect all of the comments. We have added more analysis and revised some parts of the manuscript to make it clearer and more accurate.

The revised manuscript is attached, and the responses to the reviewers' comments are listed below.

Responses to comments
Reviewer 1:

There are some revisions suggested mainly to address the uncertainties in the results.

The authors report long term averages of N2O fluxes, including daytime and nighttime averages. However, these averages have very large standard deviations (factor of three larger than the mean) which show that the frequency distribution of the measured fluxes are highly skewed with a small number of high fluxes and a large number of low fluxes. In this case, the uncertainty should be expressed in terms of a 90 or 95% confidence limit derived from the analysis.
We used the nonparametric boot-strapping procedure to obtain the 95% confidence intervals and presented the results in Table 3.

We also added case studies for five selected days for day and night flux comparisons:

Diurnal variations of the N_2O flux were detected (Figures 7 and 8). Figure 7 contains nearly complete diurnal data for each day for five selected days (>20 hours data per day and $u_* \geq 0.2$ m s^{-1}). The peak flux commonly appeared during the daytime, whereas the flux was low at night except for the third sub-period in Figure 8 when soil moisture was high during the night time. The average daytime and night time N_2O fluxes during the five days were 96.4 ± 11.7 μg N_2O-N m^{-2} hr^{-1} and 59.0 ± 13.0 μg N_2O-N m^{-2} hr^{-1}, respectively. The flux was about 63% higher during the daytime than during the night time (Figure 7). The average daytime and night time N_2O fluxes during the whole season were 278.8 ± 47.5 and 99.9 ± 29.8 μg N_2O-N m^{-2} hr^{-1}, respectively. This diurnal response was most likely a temperature response.

The collected data only represented a small fraction of the total measurement period due to filtering of low turbulence and precipitation periods. Regression equations were used to gap-fill the data. Some discussion of the uncertainty in gap-filling is warranted and, in particular, how do uncertainties in gap-filling compare to the other EC measurement uncertainties. Further, how do the uncertainties in gap-filling affect the overall

accumulated N2O fluxes and the conclusion that the N2O flux represents 1.43% of N applied.

We added the following discussion section:

4.5 Uncertainty in the gap-filling

The gap-filling method used in this study may bring uncertainty to the total N_2O flux estimating. However, it is a common practice that regression model is developed using "good" data (with $u_* \geq$ a threshold value); then the regression model is used to gap-fill the missing data and estimate the total value.

We evaluated the uncertainty of the regression equations used in the gap-fillings by comparing the regressed and the measured flux data when ($u_* \geq 0.2$ m s^{-1}) and found the average error ratio was 14%. The regression equations were from the "good" eddy-covariance data($u_* \geq 0.2$ m s^{-1}). The "good" data may have been overestimated about 12-16% (Table 2). Therefore, the total N_2O may be overestimated from the gap-filling by about 27% to 32% [e.g., 27%=(1+14%)(1+12%)-1].

Based on the equation on Figure 11, the seasonal released N_2O should be 3.76 kg N_2O-N Ha^{-1}. However, from this study, it was 6.87 kg N_2O-N Ha^{-1}. Therefore, the gap-filling and the EC measurement uncertainties may have partially contributed to the overestimated N_2O release.

In the same way, since 93% of the good data were collected during daytime, can anything substantive really be said about daytime vs nighttime fluxes? Comparison of the averages with their large uncertainties seems misleading. Perhaps some case study periods where there is more complete data would be useful for addressing day-night changes.

We agree with the reviewer. We did some case studies as mentioned in the response above.

Reviewer 2

Suggestions for technical corrections or reasons for rejection

whether or not the apparent difference between day and nighttime N2O fluxes is actually significant given the large variances for them both and the scarcity of nighttime data that are kept.

We agree with the reviewer. Please see our response to reviewer 1's comment above.

I'd like to see the data used for defining the u* cutoff instead of just using a value from a range in the literature. The approach presented by Barr et al, AGRICULTURAL AND

FOREST METEOROLOGY, 2013, 171 DOI: 10.1016/j.agrformet.2012.11.023) ought to be mentioned and could be included to quantify the uncertainty associated with selecting a cutoff for low-turbulence.

We revised our manuscript and provided the specific values of u* in the revised manuscript as the following:

:

Mammarella (2010) summarizes the appropriate range of the u_* threshold as 0.1 for grassland to 0.3 for forest. In this study we used 0.2 as the threshold for the cornfield. A u_* threshold value (0.15 m s^{-1}) was obtained using the method in Barr et al., 2012. That value was similar to and slightly smaller than our threshold value of 0.2 m s^{-1}. Therefore, our data processing using 0.2 m s^{-1}threshold value was conservative and warranted to exclude all the low-turbulence data and even excluded some data just around the low-to-normal turbulence transition zone (u_* from 0.15 to 0.2 m s^{-1}).

Reviewer #3:

Specific comments
I suggest you re-write the abstract: in its present form it is a dry list of some facts that are reported throughout the paper: it doesn't need to contain any references to other work, but it should synthesise the hypothesis and outcome of your work.

We rewrote the Abstract as instructed synthesizing the outcome of our work.

In the abstract, you mention the fertilisation rate of the field is 217 kg N ha-1. Then in the table, the total N is reported to be 118 kg N ha-1 (39+79). Which one is true?

We clarified this in the revision. 217 kg N ha^{-1} is true. Table 1 only showed the URAN-32-0-0 N during the growing season (April 4 to August 8). An additional 39 kg N ha^{-1} of chicken litter before the growing season was applied on March 10, as presented in the table caption.

Why do you think there is such an abrupt change in N2O concentrations in the period at the beginning of June? (Fig.6). The average shift from the plot seems to be of a bit less than 10 ppb in the level of N2O in the surface layer: this is quite a significant step in concentration, especially looking at the step from one day to the other (roughly on first days of June?): how do you explain it? How did you calibrate the instrument for concentrations? (how regularly, what was used in all instances of calibration). Before the first fertilisation, the levels of N2O seem to be quite consistent with the levels after the fertilisation events (both first and second).
These may have been caused by the high application rates of fertilizer on March 10, April 8, and May 17, and less nitrogen use by the establishing crop before June, which resulted in higher soil N availability and more N_2O emissions during that period, as shown in Figures 5 and 6. In addition, the frequent rain events before June may have leached the nitrogen in deep water and reduced N availability for N emission.

The N_2O analyzer has a standard N_2O chamber inside. We calibrated the instrument to that standard every two weeks and after rainfall events.

I'm not sure of the value of the regression in Fig.10. While it is very useful to show a comparative and summarising plot of other studies combined with this, I am not sure the regression is adding any value. However, I see the authors' point of presenting an overall emission factor.
We basically wanted to show the overall emission factor as the reviewer pointed out.

Generally, the authors report figures with too many digits, regardless of significant figures: albeit this comment may seem pedantic, there is no point in reporting figures that suggest a level of precision that is not actually achieved. Could you modify this throughout?

We modified all these for all the figures.

L440: do you think that the daytime fluxes were higher consistently through the whole season? My impression is that the first two periods did have this behaviour, but afterwards it doesn't look like it from Fig.7. I think it is likely that the first two periods are pushing the overall averages in that direction.
Yes, the reviewer is right. We added one sentence to reflect this fact (after Line 437): "The daytime fluxes were not always higher through the whole season, as shown on Figure 7; i.e., the daytime fluxes were not higher during the third and the fourth periods because the soil moisture was a predominant factor (r_{sm}> 0.4)."
We also conducted case studies to compare day and night flux differences (see our response to reviewer 1's comments above).

Technical corrections: typing errors, etc.
Please revise all references (especially with regards to names), as there are a few spelling errors.

Revised accordingly.

L61-62: remove nitrogen use; "consequently": I think it's wrong, as these are the reason why you get inefficient N use, not the other way round. Correct the sentence.
Removed "nitrogen use" and "consequently" as suggested.

L63: these are some of the forms through which N is lost, not the only ones, so add "e.g."
Revised.

L77: oxygen supply within the soil strata.
Revised.

L93: before the references in brackets, put "e.g.", as the articles are all referring to the original source of the Reynolds theory.
Revised.

L97: remove "fluctuations". The covariance is between the variables themselves, not their fluctuations.
Removed.

L99: the vertical wind speed seems an omega; it should be "w" (also in L183).
Revised.

L102: "previous" to when? The laser spectrometers have been available since the early 90s.
Removed "Previous N_2O analyzer instruments lacked the necessary precision and their response times were too slow for use in EC measurements."

L106: The reference needs correction, the author is Di Marco. Correct also in the reference section.
Revised.

L137: it's a wave number.
Revised.

L151: Do you mean NH4+ here?
Yes, revised to NH4+.

L152: can you specify here the working principle of such equipment? Just briefly, but it is useful for the reader who does not normally deal with such system, to identify what detector type is used.
We briefly explained the principle:
The Auto-analyzer mixes sample (liquid state) homogeneously with reagents; the sample and reagents are merged to form a concentration gradient that yields analysis results.

L155: same as line 97.

Removed ‘fluctuations’.

L189: add "applied to trace gas measurements".
Added.

L192: insert “e.g.” before Ferrara.
Added.

L198-199: cospectrum
Revised.

L208: the star in ustar is a subscript, not superscript. correct throughout.
Revised all.

L238:it’s not clear here on what you made the regression/correlation. Does this refer to a figure? If so, include it. If not, then explain more in words what you’ve done, or where you explain it.
Lines 228 to 237 explained some of the regression. We also added the following after Line 237:
“In the regression analysis, soil moisture and temperature were independent variables and N_2O flux was the dependent variable.”
Table 5 shows the regression equations.

L270-1: swap “units” with “points”.
Swapped.

L278-280: this sentence is unclear. Add “that” after “continuous corn canopy”, delete “with”.
Revised.

L280-281: With “these” do you mean the differences? Spell it out, as the sentence is unclear.
We revised “These” to ”These differences”.

L287: using different units of measure through the paper does not help: can you be consistent throughout? You used ng N2O-N m-2 s-1; ug m-2 hr-1; ug ha-1 hr-1. Just settle on one and change throughout.
Changed all flux units to ug m^{-2} hr^{-1} except seasonal cumulative emission, which was changed to kg ha^{-1}.

L315: availability of N
Revised.

L334: what do you mean with N+?
Revised N+ to N.

L363-364: this is a repetition of an earlier sentence.
Removed the repetition.

L368: Delete “a” before vapour cospectra.
Revised.

L375: I don’t understand here: how do you apply the correction?
All the corrections were conducted using the calculated factors by Eddypro using the methods in Ibrom et al. (2007), Horst and Lenschow (2009), and Di Moncrieff et al. (2004).
The corrections were compared with frequency loss calculated from cospectra analysis (Table 2).

L389: delete the comma after Figure 10.
Deleted.

L409-410: you are comparing figures with different units of measure, change that, and as before keep it as much as possible in the same unit.
Revised.

L421: amount is singular in this case
Revised.

L424: change in N2O flux.
Revised.

L426-429: I don’t understand these sentences "monitoring these events.." onwards. Perhaps you can synthetise them in one simpler sentence. How do you mean "apparently caused"? Justify this.
We revised to:
The difference of N_2O emission response after the first and second applications of fertilizer showed the trigger effect of precipitation on the N_2O emission. The other notable feature of Figure 5 was the remarkable increases of N_2O for the days with precipitation. The variations in the increases may have been mainly caused by the changes in soil moisture content due to precipitation.

L430: is it not better to say "is not correlated"?
Revised.

L433: table 4 does not contemplate N application rates, so it is difficult to conclude what you say, perhaps add the information on N application so it is easier to see.
Added the information in Table 4.

L435:delete the double comma. replace "during the diurnal cycles" with "when looking at the diurnal cycles".
Revised.

L442: delete the double dot.
Revised.

L471: N2O-N, not just N.
Revised.

L479-81: i don't fully agree with this, if you specify during the first and second periods it's more correct. The soilT has a diurnal cycle (more or less pronounced) through the year, and this is not driving N_2O emissions at all times (see my comment before).
We removed the following: "although a diurnal variation in flux was in response to the diurnal soil temperature wave. Average daytime emissions were much higher than night emissions (278.8 vs. 100.0 μg N_2O-N m^{-2} hr^{-1})."

Fig4. Caption. "a" and "b" are not visible in the charts, perhaps add them to the plots inside the chart area, otherwise specify in the text what's right/left. Correct "Obukov". Replace "outputted" with "output".
Revised.

Fig 5-6: replace the fertilization asterisk symbols with vertical lines for example, to make it easier to read. These symbols are not easily seen together with the rest of the charts content.
Revised.

Fig 7: the legends, axis, text in the plot areas are too small to be readable. I understand the advantage of having all charts nearby, but I think it would be better to change the format of the written words within the plot areas. I take the regression coefficients are referring to daily values
Revised all accordingly.
In the caption, added 30-min to show the data frequency.

Fig8: again, change the marker for fertilizer events to vertical lines or something that is easier to see. The caption is unclear, you mention data from March were shown, but the graph shows from april onwards?
Added the following in the caption:
"24 days before the experiment (March 10) chicken litter was applied at a rate of 99 kg N ha^{-1} (not shown on the figure)."

Fig.9: need to change the size of the text within the plots, they're difficult to read. Also, in the caption, specify the values time resolution (hourly?). Add in all plots when the fertilisation events occurred (maybe a vertical line).
Revised accordingly. In the caption, added 30-min to show the data frequency.

Fig.10: I suggest to replace the red square with a filled square (red or not) as it will be more visible in the final format.
Revised.

TABLES:
Tab4: In the headers of the table, repeat the units and what does r(p) meaN? Also, SxN, it's an index of some nature, but what information does it add to the paper? If you want to keep it, you need to explain it.
Revised.

Tab6: double parenthesis in the caption, delete it. Replace "swiss" with Switzerland.

Revised.

We thank you and reviewers again for the constructive comments and hope the above mentioned changes are satisfactory for final acceptance of the manuscript.

Sincerely,

Junming Wang

Nitrous oxide emissions from a commercial cornfield (Zea mays) measured using the eddy-covariance technique

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ABSTRACT

Increases in observed atmospheric concentrations of the long-lived greenhouse gas, nitrous oxide (N_2O), have been well documented. However, information on event-related instantaneous emissions during fertilizer applications is lacking. With the development of fast-response N_2O analyzers, the eddy covariance (EC) technique can be used to gather instantaneous measurements of N_2O concentrations to quantify the exchange of nitrogen between the soil and atmosphere. The objectives of this study were to evaluate the performance of a new EC system, to measure the N_2O flux with the system, and finally to examine relationships of the N_2O flux with soil temperature, soil moisture, precipitation, and fertilization events. An EC system was assembled with a sonic anemometer and a fast-response N_2O analyzer (quantum cascade laser spectrometer) and applied in a cornfield in Nolensville, Tennessee during the 2012 corn growing season (April 4–August 8). Fertilizer amounts totaling 217 kg N ha^{-1} were applied to the experimental site. Results showed that this N_2O EC system provided reliable N_2O flux measurements. The cumulative emitted N_2O amount for the entire growing season was 6.87 kg N_2O-N ha^{-1}. Seasonal fluxes were highly dependent on soil moisture rather than soil temperature. This study was one of the few experiments that continuously measured instantaneous, high-frequency N_2O

emissions in crop fields over a growing season of more than 100 days.

1. INTRODUCTION

As the largest corn producer in the world, the United States produces about one-third of the world's corn crop (about 84 million ha in 2011) (http://www.epa.gov/agriculture/ag101/cropmajor.html). Corn is a nitrogen- (N) intensive crop. Every year, large amounts of N are applied to cornfields, but its efficiency is low (30% – 59%) (Halvorson et al. 2005). A large proportion of applied N can be leached to groundwater (e.g., NO_3^-) and/or emitted to the atmosphere (e.g., nitrous oxide , N_2O; nitric dioxide , NO; or nitrogen dioxide, NO_2).

N_2O is one of the longest lived greenhouse gases (GHGs) and has an estimated radiative forcing of 0.15 Wm^{-2}, compared to carbon dioxide (CO_2) at 2.43 Wm^{-2} and methane (CH_4) at 0.48 Wm^{-2} (Forster et al. 2007). In addition to its contribution to global warming, N_2O also plays an important role in stratospheric ozone depletion through O (1D) oxidation (Ravishankara et al. 2009). The volume concentration of N_2O in the atmosphere has increased from 273 parts per billion dry air mole fraction (ppbv) in 1950 to 319 ppbv in 2005 (Forster et al. 2007). The major source of anthropogenic N_2O in the atmosphere is believed to be N fertilization accounting for up

to 80% of anthropogenic N_2O emissions (Kroeze et al. 1999; Mosier et al. 1998). N_2O emitted from soil is produced by bacterial processes, mainly through nitrification and denitrification (Davidson and Swank 1986). These processes may be affected by several factors, including the percentage of water-filled pore spaces in soil (WFPS) (Dobbie and Smith 2003; Davidson 1991), mineral N concentrations in the soil (Ma et al. 2010; Bouwman et al. 2002; Bouwman 1996), crop type, soil type, soil moisture, air/soil temperature, and oxygen supply within the soil strata. Therefore, N_2O emissions are typically highly variable both in time and space, and are difficult to quantify.

Significant efforts have been invested in developing reliable tools for measuring instantaneous N_2O emissions from soil to the atmosphere. The two major measurement methods currently available for N_2O fluxes are the chamber method and the eddy covariance (EC) method (Denmead 2008; Molodovskaya et al. 2011). The chambers, either closed (static) or open (dynamic flow), are the traditional tools that have been used in different land management systems (farmland, forest, and grassland) (Tao et al. 2013; Liu et al. 2012; Arnolda et al. 2005; Klemedtsson et al. 1996). The chamber method is simple in concept and operation, as well as low in cost. However, several limitations may affect the data quality, such as small area coverage, called the footprint, (≤ 1 m^2), disturbance of the soil environment, and low sampling frequency (Molodovskaya et al. 2011; Denmead 2008). The EC method calculates the spatial averaged flux from a larger "field scale footprint (10 m^2 $\sim$ 1 km^2) (Denmead 2008). Unlike the chamber method, the EC method does not disturb the soil and crop ecosystem and provides a continuous and real-time flux measurement.

The EC method is based on the Reynolds decomposition theory that a turbulent variable (x) can be represented by a time-averaged component ($\bar{x}$) and a fluctuation component (x') (e.g.,

Famulari et al. 2010; Kaimal and Finnigan 1994; Stull 1988):

$$x = \bar{x} + x' \quad . \tag{1}$$

In the EC method, the vertical flux of a gas is expressed as the covariance between the vertical wind velocity and gas concentration:

$$J = \overline{w'c'} \tag{2}$$

where J is the gas vertical flux, w' and c' are the deviations of vertical wind velocity (w) and gas concentration (c), respectively, and the overbar represents a time average. The EC method requires rapid, simultaneous (or near- simultaneous) measurements of gas concentration and wind velocity at the same point in space. With the developments of fast-response N_2O analyzers in recent years, the EC method has become more common (Jones et al. 2011; Mammarella et al. 2010; Eugster et al. 2007; Pihlatie et al. 2005; Di Marco et al. 2004; Edwards et al. 2003). In this project, an EC system for N_2O measurement was assembled in a commercial cornfield in Nolensville (TN) with a newly available fast-response N_2O analyzer. It was a quantum cascade laser (QCL) spectrometer (model CW-QC-TILDAS-76-CS, Aerodyne Research Inc., Billerica MA).

The objectives of this study were to evaluate the performance of the new N_2O spectrometer in the EC system, to measure the N_2O flux with the system, and finally to examine relationships between the N_2O flux and soil temperature, soil moisture, precipitation, and fertilization events.

2. MATERIALS AND METHODS

2.1. Site description

112 The experimental site was located in a commercial cornfield in Nolensville, Tennessee, 35 km
113 south of Nashville (Figure 1). The field was 300 m (east-west) by 500 m (south-north) with a 2%
114 slope facing west. The soil type was Talbott silty clay loam (fine, mixed, semi-active, thermic
115 Typic Hapludalfs; 32.5% sand, 53.8% silt, 13.8% clay)
116 (http://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx). Soybeans were planted in the
117 previous year's rotation. Corn seeds (Roundup Ready BT Hybrid Corn, P1412 HR, Pioneer Hi-
118 Bred International Inc., Johnston, IA) were sown on April 9, 2012. Measurements were
119 continuous from April 4 to August 8, 2012, covering the entire corn-growing season.

120 The agricultural practice was no-till. A weather station (Vantage PRO2 Plus, Davis
121 Instruments, Vernon Hills, IL) was used to record 30-min precipitation, temperature, pressure,
122 wind speed and direction, relative humidity (RH), and solar radiation. The prevailing wind
123 direction was from the southwest during the growing season.

124

125 *2.2. The EC instruments*

126 A sonic anemometer (CSAT3-A, Campbell Sci, Logan, UT) located in the middle of the field
127 measured three-dimensional wind velocities and virtual air temperatures at a sampling rate of 10
128 Hz. It was positioned 1.3 m above the canopy, and was raised as the corn plants grew taller. N_2O
129 concentrations were measured by a quantum cascade laser (QCL) spectrometer (model CW-QC-
130 TILDAS-76-CS, Aerodyne Research Inc., Billerica, MA). The N_2O analyzer was housed in a
131 trailer where a stable working temperature (293-303 K) was maintained. The pressure of the
132 spectrometer sample cell was 4 kpa (30 Torr). The laser was operated at a wave number of 2193
133 cm^{-1}.

134 The N_2O analyzer was located 50 m from the sonic anemometer. Following the specifications
135 of Eugster et al. (2007), a sampling Teflon tube (6 mm inner diameter, 50 m length) was used to
136 sample the air at the EC sonic anemometer location in the middle of the field and was connected
137 to the N_2O analyzer. The tube intake was 20 cm from the sonic anemometer. Sample air was
138 drawn into the tube intake at a rate of 14 STD L min^{-1}. The analyzer provided 10 Hz
139 measurements of N_2O and water vapor (H_2O) concentrations. The analyzer automatically
140 corrected the H_2O effects on N_2O measurements (WPL and cross-sensitivity of H_2O on N_2O) in
141 real time (Nelson 2002). A Campbell Scientific CR3000 data logger was used to record all the
142 data collected at 10 Hz. The EC measurement footprint ranged from 25 to 90 m upwind, and was
143 calculated using the software EddyPro (version 3.0, LI-COR Biosciences, Lincoln, NE). Soil
144 moisture and soil temperatures were measured with a water content reflectometer (CS616) and an
145 averaging soil thermocouple probe (TCAV, Campbell Sci, Logan, UT), which were buried
146 vertically at a depth of 0-10 cm underground. The mineral NO_3^- and NH_4^+ concentrations in the
147 top 10 cm of soil were measured using a Lachat Flow Injection Auto-analyzer (Loveland, CO).
148 (The Auto-analyzer mixes the sample (liquid state) homogeneously with reagents; the sample and
149 reagents are merged to form a concentration gradient that yields analysis results.)

150 *2.3. N_2O flux calculation and data corrections*

151 The EddyPro version 3.0 was used to process and correct the N_2O flux. EC fluxes were
152 calculated as the covariance of the vertical wind velocity and N_2O concentration over an
153 averaging period:

154 $$J_{N_2O} = \overline{w'c'_{N_2O}} \times \frac{\rho_a}{M_a} \times 3600 \times 28 \times 10^3 \quad , \qquad (3)$$

where J_{N_2O} is the N_2O flux (μg N_2O-N m^{-2} hr^{-1}), c_{N_2O} is the N_2O concentration in air (ppbv), the component prime ($'$) indicates a deviation from the mean, and the overbar denotes a time average, ρ_a is the density of air (kg m^{-3}) and M_a is the molar mass of air (0.028965 kg mol^{-1}), 3600 represents 3600 seconds per hour, and 28 is the molar mass of two N atoms in N_2O (g $mole^{-1}$).

The averaging period to determine eddy fluxes must be sufficient to adequately sample all the motions that contribute to the fluxes, but an overly long averaging period might affect measurements with irrelevant signals. According to Moncrieff et al. (2004), an averaging period of 30 to 60 minutes is appropriate for gas flux calculations. In this study, a commonly used averaging period of 30 minutes was chosen (Mammarella et al. 2010; Eugster et al. 2007; Aubinet et al. 2000).

EC measurements need several corrections before and after performing a flux calculation. Data spikes can be caused by random electronic spikes in the measuring or recording systems. The de-spike procedure was applied to the raw data (10 Hz) before the calculation of flux. The spike detection and removal method used in this study was similar to that of Vickers and Mahrt (1997). A spike was identified as up to 3 consecutive outliers with respect to a plausible range within a certain time range, and the spike was replaced with the linear interpolation between adjacent data points. The rationale is that if more consecutive values are found to exceed the plausibility threshold, they might be a sign of an unusual yet physical trend (not an outlier). The threshold was set to 3 to 8 times the standard deviation for a given averaging period (3 times for wind velocity and air temperature, and 8 times for N_2O concentrations; these parameters represent the default values in EddyPro).

176 The vertical axis of the sonic anemometer was not always aligned with the local normal to the
177 surface. Therefore, there could be cross-contamination among components of the flux divergence.
178 In order to avoid cross-contamination, an axis rotation was necessary. The EddyPro used a
179 double rotation scheme, in which the u-component was aligned with a local streamline for each
180 30-min interval, and the v-component and w-component were forced to be zero on average.

181 The physical separation of the sonic anemometer and the N_2O analyzer caused a time lag (τ)
182 between the sonic data and N_2O data. Compensation for τ before the covariance calculation is
183 required in the EC technique. In this study, the τ for each 30-min averaging period was obtained
184 by searching for the maximum cross covariance between sonic variables and analyzer
185 measurements.

186 All EC systems applied to trace gas measurements tend to underestimate the true atmospheric
187 fluxes due to physical limitations of the instruments which cause flux losses at high (e.g.,
188 damping effects from long intake tube) and low frequencies. The commonly used methods of
189 addressing spectral attenuation have been described (e.g., Ferrara et al., 2012, and Moncrieff et al.
190 2004). The EddyPro software program provides several options for spectral correction. In this
191 study at the low frequency range, the analytic correction proposed by Moncrieff et al. (2004) was
192 used, and at the high frequency range, the spectral loss was corrected following Ibrom et al.
193 (2007) and Horst and Lenschow (2009).

194 The frequency loss ratio ($\frac{\Delta\emptyset}{\emptyset}$) was calculated as:

195 $$\frac{\Delta\emptyset}{\emptyset} = 1 - \frac{\int_0^{+\infty} CO_M df}{\int_0^{+\infty} CO_T df} \quad (4)$$

where the CO_T is the theoretical N_2O flux cospectrum following Kaimal et al. (1972), CO_M is the N_2O flux cospectra from the measured data, and f is the spectral frequency.

The EddyPro software outputs a frequency correction factor for N_2O (N_2O-cf) as the ratio of the frequency-corrected flux divided by the flux before the frequency correction. Therefore the frequency correction ratio by EddyPro ($\frac{\Delta\emptyset}{\emptyset}(EP)$) is:

$$\frac{\Delta\emptyset}{\emptyset}(EP) = 1 - \frac{1}{N_2O-cf} \quad (5)$$

2.4. Data for weak turbulence and precipitation conditions

It has been found that under weak wind conditions with no surface heating, turbulence may not develop. Friction velocity (u_*) was used to measure the turbulent state of the atmosphere:

$$u_* = (\overline{\omega' u'^2} + \overline{\omega' v'^2})^{\frac{1}{4}}, \quad (6)$$

where u' and v' are the fluctuations in horizontal downwind and crosswind components.

The determination of an adequate u_* threshold for sufficient turbulent mixing was crucial. The common method to determine the u_* threshold is to examine the scatter plot of night time flux versus u_*, and the threshold is located at the point in which the flux begins to level off as u_* increases (Gu et al. 2005). There are also many statistic-based algorithms used to determine u_* thresholds (Papale et al. 2006; Gu et al. 2005; Saleska et al. 2003). Mammarella (2010) summarizes the appropriate range of the u_* threshold as 0.1 for grassland to 0.3 for forest. In this

study we used 0.2 as the threshold for the cornfield. A u_* threshold value (0.15 m s^{-1}) was obtained using the method in Barr et al., 2012. That value was similar to and slightly smaller than our threshold value of 0.2 m s^{-1}. Therefore, our data processing using 0.2 m s^{-1} threshold value was conservative and warranted to exclude all the low-turbulence data and even excluded some data just around the low- to normal-turbulence transition zone (u_* from 0.15 to 0.2 m s^{-1}). During precipitation conditions, the sonic anemometer sensor heads could be wet, causing errors in the instantaneous measurements. Therefore in this study the N_2O flux data were excluded in low turbulence, $u_* < 0.2$ m s^{-1}, and during rainfall.

2.5 Measurement periods

As noted above, continuous measurements were carried out from April 4 to August 8, 2012. The corn was harvested one week after the study period ended. On August 8, the moisture content of the kernels was less than 25%; therefore the study period covered the entire growing season. Prior to planting and before the EC measurements were initiated, chicken litter (99 kg N ha^{-1}) was applied to the field on March 10. Two applications of fertilizers were subsequently supplied on April 10 (URAN-32-0-0 liquid nitrogen, 39 kg N ha^{-1}) and May 14 (URAN-32-0-0 liquid nitrogen, 79 kg N ha^{-1}). The experimental period was divided into four specific periods based on fertilization or precipitation events (Table 1). The first period started 24 days after the application of chicken litter, and the first liquid fertilizer application (URAN-32-0-0, at a rate of 39 kg ha^{-1}) was within this period. The second period was characterized by the second fertilizer application and high precipitation. The third period was without fertilization and significant precipitation, and the fourth period had high relative precipitation but no fertilization. The data were further divided into two groups according to the measurement time: daytime (7 a.m. to 7 p.m.) and night

time (7 p.m. to 7 a.m.). Mean and standard deviations of the N_2O flux, soil moisture, and soil temperature were obtained and regression and correlation analysis were conducted for day and night for different temporal periods. In the regression analysis, soil moisture and temperature were independent variables and N2O flux was the dependent variable. The regression equations were used for filling gaps at the missing data points. The N_2O flux was then integrated for the whole season to obtain the overall N_2O emission.

3. RESULTS

3.1 The performance of the N_2O analyzer

The precision of the N_2O concentration measurements was characterized under field sampling conditions by the Allan variance technique (Figure 2). In the log-log plot, the measurement variance decreased with the integration time (t) with a slope of -1 when $t \leq 10$ s, indicating that there were no correlations between noise sources (pink noise) at time scales of 0.1 to 10 s. The variance had a broad minimum between 10 and 100 s with a minimum corresponding to 0.006 ppbv of standard deviation. The standard deviation was 0.066 ppbv for 10 Hz (integration time 0.1 s), 0.020 ppbv for 1 Hz (integration time 1 s), and 0.006 ppbv for 0.1 Hz (integration time 10 s).

Figure 3 shows the frequency distribution of time lags during the experimental period. The peak value of the distribution appeared at τ = 6.3 s, which represents the air flow time in the sampling tube between the field collection location and the QCL N_2O analyzer.

257 Figure 4 shows sample cospectra of sensible heat and N_2O and the theoretical N_2O
258 cospectra obtained during a windy day (Figure 4.a) and a windy night (Figure 4.b). A rather good
259 performance of the N_2O cospectrum in the low frequencies was demonstrated. The N_2O
260 cospectrum fell off faster at higher frequencies than the theoretical cospectrum and the sensible
261 heat cospectrum. The N_2O flux frequency loss ratios during the daytime and night time were low
262 (1% and 2%). The frequency correction ratios by EddyPro for the daytime and night time were 18
263 and 19%, respectively.

264 Table 2 shows the variation of the frequency loss ratio of N_2O flux under weak to strong
265 wind conditions (u^* is linearly related to wind speed). In general, the mean of flux frequency loss
266 ratios (including all ratios: ≥0 and <0) increased with increased wind speed (u_*) when $u_* \geq 0.2$ m
267 s^{-1}. When $u_* \leq 0.2$ m s^{-1}, the eddies may not have been well enough developed for the
268 measurements to be accurate. Under the night time condition, the frequency loss ratio was larger
269 than under the daytime condition when the u_* values were in the same category. The average
270 EddyPro frequency correction ratio was 15% to 18%.

271 *3.2 Seasonal variations*

272 A total of 5,197 30-min data points were collected. After applying the two filters ($u_* \geq 0.2$,
273 precipitation free), 1,390 data points remained. In general, the concentration and the flux of N_2O
274 had higher values during and after the fertilizer application but gradually decreased with time, as
275 shown in Figure 5 and Figure 6. However, rainfall (soil moisture) was a trigger for N_2O
276 emissions, which is the reason the flux reached peak values on the day of the largest application
277 of URAN-32-0-0 (May 14), and the lack of peak values of N_2O flux just after the first application

with no rainfall. The growing season was characterized by a number of precipitation events which appeared to increase the N_2O concentration as well as the N_2O flux.

Note the two general seasonal concentration levels in Figure 6. One was before a continuous corn canopy was established in early June, and the second, a continuous canopy that extended from mid-June to August 8. These differences may have been caused by the high applications of the fertilizer and less nitrogen use by the establishing crop before June which resulted in higher soil N availability and more N_2O emissions during that period as shown in Figure 5.

3.3 Diurnal variations

Diurnal variations of the N_2O flux were detected (Figures 7 and 8). Figure 7 contains nearly complete diurnal data for each day for five selected days (>20 hours data per day and $u_* \geq 0.2$ m s^{-1}). The peak flux commonly appeared during the daytime, whereas the flux was low at night except for the third sub-period in Figure 8 when soil moisture was high during the night time. The average daytime and night time N_2O fluxes during the five days were 96.4 ± 11.7 μg N_2O-N m^{-2} hr^{-1} and 59.0 ± 13.0 μg N_2O-N m^{-2} hr^{-1}, respectively. The average flux was about 63% higher during the daytime than during the night time (Figure 7). The average daytime and night time N_2O fluxes during the whole season were 278.8 ± 47.5 and 99.9 ± 29.8 μg N_2O-N m^{-2} hr^{-1}, respectively (All the 'mean $\pm$ number' in this paper are 95% confidence intervals unless otherwise noted). This diurnal response was most likely a temperature response.

3.4 Result statistics

299 The N_2O concentrations and fluxes were highly variable with time. The concentration was 322.8
300 $\pm$ 0.3 ppbv with a coefficient of variation (CV) of 1.24%. The N_2O flux ranged from 0.0 to
301 event-related emissions as high as 11,100 μg N2O-N m^{-2} hr^{-1} with a CV of 317.6% and a mean of
302 257.5 $\pm$ 42.9 μg N_2O-N m^{-2} hr^{-1}. As shown in Table 3, nearly 90% of the data were obtained
303 during the daytime. Fluxes were higher during the daytime than during the night (Table 3 and
304 Figure 7). For the whole experimental period, the total emission was 6.87 kg N_2O-N ha^{-1} (Figure
305 9).

306

307 *3.5 Effects of soil moisture, temperature, and N availability on N_2O emissions*

308 Figure 10 presents an overview of the measured concentration and flux for the whole
309 experimental period, together with soil temperature and soil moisture. Generally, the variations of
310 N_2O concentration and flux followed most closely the pattern of variation of soil moisture. As
311 expected, concentrations and fluxes were usually elevated immediately after precipitation events.
312 As shown in Table 1, there was no fertilization event or significant precipitation in the third
313 period, and thus the N_2O flux was constantly low.

314 In previous studies it has been difficult to generalize and interpret the relationships of N_2O
315 emissions with soil temperature or soil moisture quantitatively because in each specific study the
316 determinants are different. In this study, for the entire experimental period, the N_2O flux was
317 positively correlated to soil moisture with a Pearson correlation coefficient r of 0.42 ($p < 0.001$),
318 while the correlation with soil temperature was poor ($r = -0.079$, $p = 0.003$). Table 4 shows the
319 Pearson correlation coefficients for the periods defined in Table 1. The N_2O flux was significantly
320 correlated with soil moisture except for S1N, which was probably limited by the small sample

size. These correlations indicate that on this site the dominant driver of N_2O emissions was soil moisture in addition to substrate N availability.

Although the soil temperature did not positively correlate to the seasonal N_2O emission, it was significantly and positively correlated to the diurnal (hourly) N_2O emission during the first and second sub-periods (correlation coefficient r_{st}=0.76 and 0.56, $p<0.001$) when soil moisture was not strongly predictive ($r_{sm}<0.36$, $p>0.05$) (Figure 8). Therefore, the peak flux during these sub-periods appeared most often during the day when the soil temperature was relatively high compared to the night. However, during times of significant effects of soil moisture ($r_{sm}>0.45$, $p<0.05$) during the third and fourth sub-periods, the temperature effects on the N_2O flux was not significant ($r_{st}<0.2$, $p>0.05$).

Several studies have found that N_2O flux increased exponentially with soil temperature (Dinsmore et al. 2009; Schindlbacher et al. 2004; Smith et al. 2003). At first we regressed the observed N_2O flux with soil temperature and soil moisture following the exponential functions given by Luo et al. (2013). However, for some periods the coefficients of determination (R^2) were low (< 0.4). Then we regressed the N_2O flux with soil temperature and soil moisture using exponential or polynomial functions (Table 5). The values of R^2 ranged from 0.45 to 0.70. For most of the periods, soil moisture explained a significant amount of the variation in N_2O emissions.

N availability was an important factor in N_2O emissions. The fertilizer amount of the second application was more than twice that of the first application; the large amount of fertilizer provided sufficient N. The volume concentration of NO_3^- in the top 10 cm of soil was 5.5 parts per million (ppmv) on April 15, and was 8.5 ppmv on May 16. The concentrations of NH_4^+ were

16 ppmv and 19.5 ppmv for these two days, respectively. The higher mineral N concentration most likely contributed to the dramatic increase in N_2O concentration and flux after the second application.

4. DISCUSSION

4.1. N_2O analyzer performance

Several studies have been performed for N_2O measurements using QCL spectrometers over grassland or forest (Neftel et al. 2010, 2007; Eugster et al. 2007; Kroon et al. 2007; Nelson et al. 2004). Besides experimental locations, seasons, and/or crop types, the instruments utilized in these studies differed from each other in terms of absorption line and precision. For example, in the studies of Kroon et al. (2007) and Neftel et al. (2010), N_2O was measured at wavelengths of 1271.1 cm^{-1} and 1275.5 cm^{-1}, respectively, while in Neftel et al. (2007) and Eugster et al. (2007), N_2O was measured at 2241.0 cm^{-1} and 2243.1 cm^{-1}, respectively. The precision of the instruments in these four studies, at a sampling rate of 1 Hz, was 0.5, 0.7, 0.3, and 0.3 ppbv, respectively. In our study, the precision was 0.02 ppbv at 1 Hz.

The detection limits of the EC flux were calculated as the standard deviations of the cross covariances between vertical wind fluctuations and gas concentration fluctuations far outside of the true time lag ($-200\ s \le \tau \le -50\ s$, and $50\ s \le \tau \le 200\ s$) (Neftel et al., 2010, Wienhold et al., 1995). Thus the EC detection limits derived from this method was not a constant value and was dependent on the instruments and atmospheric conditions. The mean detection limit in this study was 7.56 ug N m^{-2} hr^{-1}, which was less than half of the N_2O flux detection limit of 17.13 ug N m^{-2} hr^{-1} as reported in Neftel et al. (2010) and 21.60 ug N m^{-2} hr^{-1} in Kroon et al. (2007).

365 It has been shown that the sensible heat cospectrum calculated from sonic temperatures
366 experiences almost no damping (Neftel et al. 2010; Kroon et al. 2007) (Figure 4.a and 4.b).
367 Therefore, an empirical correction approach can be used, based on a comparison of the sensible
368 heat cospectrum and N_2O cospectrum to correct the high frequency loss (Neftel et al. 2010; Kroon
369 et al. 2007).

370 Neftel et al. (2010), under a wind speed of 0.8 to 2 m s^{-1}, reported a 14 to 30% frequency
371 loss correction ratio compared to a mean correction ratio of 16% by EddyPro in this study
372 (corresponding to u_* =0.2 to 0.5 m s^{-1}). Neftel et al. (2010) used vapor cospectra to correct the
373 frequency loss, whereas, this study used the methods in Ibrom et al. (2007), Horst and Lenschow
374 (2009), and Moncrieff et al. (2004), which may account for the difference in frequency loss
375 correction ratios.

376 About 93% of the valid data ($u_* \geq 0.2$ m s^{-1}) in this study were under wind conditions of
377 0.4 m $s^{-1} > u_* \geq 0.2$ m s^{-1} and were in the daytime, when the corresponding mean frequency loss
378 ratio was low, between 2% and 4%. Therefore, the flux may have been overestimated because the
379 mean frequency correction ratio was 16-18% (Table 2).

380 The mean of the positive frequency loss ratios was greater than 22% and the mean of the
381 negative loss ratios was smaller than -37% (for $u_* \geq 0.2$ m s^{-1}) (Table 2). The negative and the
382 positive ratios cancelled out each other and resulted in the mean 2% to 4% frequency loss ratios.
383 Therefore, for long-term N_2O flux measurements, the mean frequency loss may be low.

384 *4.2. N_2O emission compared with the literature*

A number of studies have been carried out to investigate N_2O emissions from soil to the atmosphere, and the results reported in the literature show tremendous variation (Table 6). Previous studies have shown that the N_2O emission depends on several factors, including precipitation, fertilization, tillage, crop type, soil factor, and instrumentation (Ussiri et al. 2009; Wagner-Riddle et al. 2007). Fertilizer application was a prime factor causing a different N_2O emission in previous studies. Generally, the measured flux and cumulative emission were larger with a larger amount of fertilizer application (Table 6). In order to obtain a gross synthesization of these previous studies, shown in Table 6, and how this study fits into them, we plotted those which reported both fertilizer applied and the integrated amount of N_2O emissions. Figure 11 presents a simple linear plot of emissions (Kg N_2O-N Ha^{-1}) (Table 6, column 9) as a function of fertilizer applied (Kg N Ha^{-1}) (Table 6, column 6). The graph demonstrates a general linear trend (R^2=0.48, $p<0.001$) of increasing emissions with increased amounts of N fertilizer, without regard to soil moisture, crop type, tillage, crop management, measurement techniques, or length of time of the study. The simple linear regression shows the ratio of N_2O emissions to N fertilizer to be 0.0143. Thus, in general, it appears that 1.43% of each unit of N fertilizer applied is emitted to the atmosphere as N_2O.

Corn crops were reported in nine of the studies listed in Table 6. They fit the trends described above. Similar amounts of fertilizers were applied in Lee et al. (2009) and Laville et al. (1999) as in this study; and similar orders of N_2O emission were observed in all three. Where lower applications of fertilizer were reported for corn fields (Molodovskaya et al. 2011, Phillips et al. 2009, Ussiri et al. 2009, Wagner-Riddle et al. 2007, and Grant and Pattey 2003), lower N_2O emissions were measured.

In addition to fertilization, tillage also has played a role in governing N_2O emissions. Lee and colleagues (Lee et al. 2009) showed that with the same amounts of fertilizers for corn, sunflower, and chickpea, different tillage could cause differences in N_2O emissions. And fully tilled fields tended to release less N_2O.

In general, forest N_2O emissions have been lower than those from agriculture, which was probably due to the large amount of fertilizers applied to farmland. For example, compared to the flux rate 257.5 ±42.9 μg N_2O-N m^{-2} hr^{-1} in this study, Mammarella et al. (2010) measured an averaged flux of ~10 μg N_2O-N m^{-2} hr^{-1} during May 2 to June 5, 2003 in a beech forest of Denmark. They showed ~ 5 μg N_2O-N m^{-2} hr^{-1} flux during the spring of 2007 in a forest with pine, small-sized spruce, and birch in southern Finland, using both the EC and chamber methods. Eugster et al. (2007) measured N_2O from a forest mixed with beech and spruce using the EC method. The reported flux was 22.4±11.2 μg N_2O-N m^{-2} hr^{-1}.

4.3 Effects of soil moisture, temperature, and N availability on N emissions

Soil moisture is a major factor for N_2O emissions (Table 4). As indicated by Dobbie and Smith (2003) and Davidson (1991), N_2O emitted from soil is caused principally by the microbial nitrogen transformations during both nitrification and denitrification. These processes are closely related to WFPS since denitrification is an anaerobic process, which depends on the balance between the amount of water entering and leaving the soil. Several studies have confirmed that there are connections between increased N_2O emissions and precipitation (Zona et al. 2011; Jungkunst et al. 2008; Neftel et al. 2007, e.g.). In this study, after the first application of fertilizer, precipitation did not occur immediately and there was no significant change in N_2O flux. On the

429 day of the second application, the total precipitation was 3.02 mm and peak values of N_2O fluxes
430 occurred immediately after the precipitation event (Figure 5). The difference of N_2O emission
431 response after first and second applications of fertilizer showed the trigger effect of precipitation on the
432 N_2O emission. The other notable feature of Figure 5 was the remarkable increases of N_2O for the days with
433 precipitation. The variations in the increases may have been mainly caused by the changes in soil moisture
434 content due to precipitation.
435
436 During the whole season, soil temperature was not positively correlated to N_2O flux ($r=-0.084$,
437 $p<0.01$). Apparently soil temperature generally increased with time during the season, while the
438 N_2O flux did not. Therefore the N_2O flux was correlated mainly with soil moisture (Figure 10
439 and Table 4). Thus compared to the factor of soil moisture, soil temperature had rather weak
440 effects on N_2O emissions at this specific site (Table 4).
441 However, when looking at the diurnal cycles, when soil moisture was not a predominant factor ($r_{sm}<$
442 0.4, $p>0.05$ in the first and second sub-periods), soil temperature was significantly and positively
443 correlated to N_2O emissions ($r_{sm}\geq 0.56$, $p<0.001$) (Figure 8). This indicates if soil moisture is not
444 changed and other factors remain constant, the N_2O emission during the daytime is higher than
445 during the night time. The soil microorganisms were more active during the warmer daytime and
446 produced more N_2O emissions, as pointed out in Maljanen et al. (2002). However, the daytime
447 fluxes were not always higher through the whole season as shown on Figure 7; i.e., the daytime
448 fluxes were not higher during the third and the fourth periods because the soil moisture was a
449 predominant factor ($r_{sm}> 0.4$).
450 As expected, mineral nitrogen availability was an important factor in N_2O emissions. The
451 fertilizer applications before June may have caused higher soil N availabilities and higher N_2O
452 concentrations than after June (Figure 6). The fertilizer amount of the second application was

more than twice that of the first application; it most likely contributed to the dramatic increase in N_2O concentration and flux after the second application (Figure 5).

4.4 Response of N_2O emission to precipitation

Soil moisture was strongly dependent on precipitation events. For most precipitation events during the experimental period, the sonic anemometer sensor heads were wet and could not measure the instantaneous wind velocities precisely. Consequently, estimates of the reaction time of emissions to precipitation are lacking. However, there were two events with low rainfall amounts (< 5 mm for each 30-min measurement period) when the sensor heads were not affected (the diagnostic record from the datalogger showed the instruments functioned normally). During these events, the N_2O emissions increased within 30 minutes after rainfall, indicating soil N_2O emission likely responds to rainfall and a change of soil moisture very quickly, as noted previously by Phillips, et al. (2013) using dynamic chambers. Large emissions immediately after rain events have been shown in emission studies of other gases and vapors, for example, Mercury (Bash and Miller, 2009; Gillis and Miller, 2000), and have been attributed to the evacuation of high concentration gas in soil pores as they fill up with water. The same mechanism may be occurring here. In any case, further examination is necessary because the spikes are large and significant emissions during active rainfall may be missed in this and most other field studies.

4.5 Uncertainty in the gap-filling

The gap-filling method used in this study may bring uncertainty to the total N_2O flux estimating. However, it is a common practice that regression model is developed using "good" data (with $u_* \geq$ a threshold value); then the regression model is used to gap-fill the missing data and estimate the total value.

We evaluated the uncertainty of the regression equations used in the gap-fillings by comparing the regressed and the measured flux data when ($u_* \geq 0.2$ m s^{-1}) and found the average error ratio was 14%. The regression equations were from the "good" eddy-covariance data($u_* \geq 0.2$ m s^{-1}). The "good" data may have been overestimated about 12-16% (Table 2). Therefore, the total N_2O may be overestimated from the gap-filling by about 27% to 32% [e.g., 27%=(1+14%)(1+12%)-1].

Based on the equation on Figure 11, the seasonal released N_2O should be 3.76 kg N_2O-N Ha^{-1}. However, from this study, it was 6.87 kg N_2O-N Ha^{-1}. Therefore, the gap-filling and the EC measurement uncertainties may have partially contributed to the overestimated N_2O release.

5. CONCLUSIONS

A new N_2O analyzer (quantum cascade laser spectrometer, model CW-QC-TILDAS-76-CS, Aerodyne Research Inc., Billerica, MA) was operated continuously for EC flux measurements of N_2O in a cornfield in Nolensville, TN during the period of April 4–August 8, 2012. Based on Allan Variance analysis, the precision of the instrument was 0.066 ppbv for 10 Hz measurements. The seasonal mean detection limit of the N_2O flux measurements was 7.56 ug N_2O-N m^{-2} hr^{-1}. The mean frequency loss ratio of the flux measurements was between 0.02 to 0.04 under the conditions of 0.4 m $s^{-1} > u_* \geq 0.2$ m s^{-1} during the day and 0.42 under the conditions of 0.3 m $s^{-1} > u_* \geq 0.2$ m s^{-1}during the night. We conclude that this N_2O EC system can be used to provide reliable N_2O flux measurements.

497 The cumulative N_2O emission from the experimental site during the entire growing season
498 was 6.87 kg N_2O-N ha^{-1}. This study showed that in addition to N availability in soil, the seasonal
499 and diurnal N_2O emission was highly dependent on soil moisture, and extremely high fluxes
500 appeared after an N fertilization event combined with precipitation. Soil moisture variation was a
501 dominant factor affecting N_2O emissions compared to soil temperature.

502 Combining these results with 9 previous studies in the literature allowed some preliminary
503 synthesization. It appears that approximately 1.43% of each unit of N fertilizer was emitted to the
504 atmosphere as N_2O.

505

506 **6. FUTURE RESEARCH**

507 We recommend that future studies focus on developing precision methods of minimizing N_2O
508 emissions by careful spatial and temporal control of fertilization amounts, water availability, and
509 tilling practices. These should include "mechanism" studies quantifying the N_2O flux rates from
510 various interactions of water and N levels in soils. The effects of reducing the episodic nature of
511 fertilization and water availability should be quantified and methods developed to make such
512 reductions. Complete field-scale experiments designed to test application rates and application
513 timing and yields will likely produce more usable results than even complete monitoring of
514 commercial field operations.

515

516

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Table 1. Overview of four measurement periods characterized by precipitation and fertilization. Two fertilizer application events were on April 10 and May 14, 2012 respectively. Before the experiment 99 kg N ha^{-1} chicken litter was applied on March 10, total precipitation was calculated as the sum of precipitation of each period.

Index	Date	Fertilization kg N ha^{-1}	Total precipitation (mm)
S1D	Apr 4 -- Apr 25, day	39 (URAN-32-0-0)	15.73
S1N	Apr 4 -- Apr 25, night	-	28.68
S2D	Apr 26 -- May 26, day	79 (URAN-32-0-0)	69.82
S2N	Apr 26 -- May 26, night	-	96.23
S3D	May 27 -- Jun 24, day	-	20.32
S3N	May 27 -- Jun 24, night	-	8.62
S4D	Jun 25 -- Aug 8, day	-	74.38
S4N	Jun 25 -- Aug 8, night	-	53.56

877 Table 2. Variation of frequency loss ratio $\frac{\Delta ø}{ø}$ and frequency loss correction ratio by EddyPro $\frac{\Delta \emptyset}{\emptyset}(EP)$

878 with friction velocity (u^*, m s^{-1}) for May 2012. N/A: not available. Numbers in the cells are mean ±

879 standard deviations.

880

u^*	$0 \leq u^* < 0.1$			$0.1 \leq u^* < 0.2$			$0.2 \leq u^* < 0.3$			$0.3 \leq u^* < 0.4$			$0.4 \leq u^* < 0.5$		
Rang of Loss ratio	≥0	<0	all	≥0	<0	all	≥0	<0	all	≥0	<0	all	≥0	<0	all
Daytime															
# of samples	16	18	34	84	65	149	113	140	253	27	22	49	2	N/A	2
$\frac{\Delta \emptyset}{\emptyset}$	0.43 ±0.48	-0.42 ±0.48	0.02 ±0.64	0.33 ±0.55	-0.45 ±1.10	0.01 ±0.91	0.43 ±1.29	-0.39 ±1.64	0.02 ±1.54	0.22 ±0.22	-0.37 ±0.67	0.04 ±0.55	0.31 ±0.29	N/A	0.31 ±0.29
$\frac{\Delta \emptyset}{\emptyset}(EP)$	0.16 ±0.01	0.16 ±0.01	0.16 ±0.01	0.16 ±0.00	0.15 ±0.00	0.16 ±0.01	0.16 ±0.01	0.16 ±0.01	0.16 ±0.01	0.18 ±0.01	0.17 ±0.01	0.18 ±0.01	0.16 ±0.01	N/A	0.16 ±0.01
Nighttime															
# of samples	145	91	236	47	12	59	4	N/A	4	N/A	N/A	N/A	N/A	N/A	N/A
$\frac{\Delta \emptyset}{\emptyset}$	0.76 ±1.35	-0.84 ±1.66	0.14 ±1.67	0.90 ±1.09	-0.23 ±0.26	0.66 ±1.08	0.42 ±0.27	N/A	0.42 ±0.27	N/A	N/A	N/A	N/A	N/A	N/A
$\frac{\Delta \emptyset}{\emptyset}(EP)$	0.16 ±0.01	0.16 ±0.01	0.16 ±0.01	0.16 ±0.01	0.16 ±0.00	0.16 ±0.01	0.16 ±0.01	N/A	0.16 ±0.01	N/A	N/A	N/A	N/A	N/A	N/A

Table 3. Descriptive statistics for 30-min N_2O concentration and flux for the period of experiment, April 4 - August 8, 2012 ($u_* \geq 0.2$ m s^{-1}). Nonparametric boot-strapping procedure was used to obtain the 95% confidence interval.

	Number of samples	Concentration (ppbv)		Flux (μg N_2O-N m^{-2} hr^{-1})	
		Mean	95% Confidence interval	Mean	95% Confidence interval
Daytime	1224	322.9	±0.2	278.8	±47.5
Nighttime	166	322.5	±0.6	99.9	±29.8
Total	1390	322.8	±0.3	257.5	±42.9

Table 4. Statistical results of 30-min soil temperature (°C), soil moisture (%) and N_2O flux (μg N_2O-N m^{-2} hr^{-1}) (mean ±95% confidence interval), as well as Pearson correlation coefficients and p value [r(p)] of N_2O flux with soil temperature or soil moisture ($u_* \geq 0.2$ m s^{-1}). N/A: not available.

Date	Fertilizer application	Number of samples	Soil temperature	Soil moisture	Flux	Soil temperature r (p)	Soil moisture r(p)
	kg N ha^{-1}		°C	%	μg N_2O-N m^{-2} hr^{-1}		
March 10	99 (chicken litter)	N/A					
Apr 4 -- Apr 25, day	39 (URAN-32-0-0)	274	18.0 ± 0.4	11.8 ±0.3	173.3 ± 27.9	0.18 (0.00)	0.61 (0.00)
Apr 4 -- Apr 25, night		48	18.9 ± 0.6	9.1 ±0.4	62.7 ±20.1	0.45 (0.00)	0.07(0.65)
Apr 26 -- May 26, day	79 (URAN-32-0-0)	392	23.2 ± 0.2	15.0 ±0.4	602.5 ±141.9	-0.20(0.00)	0.49 (0.00)
Apr 26 -- May 26, night		35	21.9 ±0.9	12.0 ±1.1	173.5 ±69.9	0.50 (0.00)	0.64(0.00)
May 27 -- Jun 24, day		326	24.9 ± 0.2	11.1 ± 0.5	60.8 ± 5.6	-0.19(0.00)	0.78 (0.00)
May 27 -- Jun 24, night		36	26.1 ± 0.4	12.0 ±1.7	88.4 ±49.6	0.15 (0.39)	0.61(0.00)
Jun 25 -- Aug 8, day		232	27.1 ± 0.2	10.5 ± 0.5	162.2 ±34.5	-0.25(0.00)	0.57 (0.00)
Jun 25 -- Aug 8, night		47	28.8 ±0.4	8.2 ± 1.1	92.3 ±75.4	-0.49 (0.00)	0.53 (0.00)
Whole experimental period, day		1224	23.2 ±0.2	12.4 ±0.3	279.0 ±48.1	-0.08 (0.00)	0.42 (0.00)
Whole experimental period, night		166	23.9 ±0.7	10.2 ± 0.6	100.1 ± 36.4	0.05 (0.56)	0.50 (0.00)

Table 5. Thirty-min N_2O flux (μg N_2O-N m^{-2} hr^{-1}) regression equations ($p<0.01$) with soil moisture (SM, %) and soil temperature (ST, °C) ($u_* \geq 0.2$ m s^{-1}).

Date	Day Equation	R^2	Night Equation	R^2
April 4 - April 25	$20.16e^{19.398SM}$	0.45	-137.74+5.64SM+564.48ST	0.62
April 26 - May 26	$209037600SM^4-11612160SM^3+2360304SM^2-191720SM+66185.28$	0.68	$18e^{16.48SM}$	0.45
May 27 - June 24	$66154.68SM^3-137696.28SM^2+967.68SM+10.08$	0.71	$6.048e^{16.31SM}$	0.70
June 25 - August 8	$20.16e^{18.35SM}$	0.54	$0.5e^{23.11SM}$	0.54

933 Table 6. Summary of N_2O measurements in literature [mean flux (or flux range) and cumulative emission],
934 EC indicates eddy covariance method, '-' indicates data or information is not available directly from the
935 reference.

936

Reference	Location	Period	Plant	Tillage	Fertilizer, kg N ha^{-1}	Method	Flux, μg N_2O-N m^{-2} hr^{-1}	Cumulative emission, kg N_2O-N ha^{-1}
this study	Williamson, USA	04-08.2012	Corn	No till	217	EC	257.5 ±817.7[a]	6.9
Wang et al. (2013)	Shanxi, China	01--10.2009	Cotton	Till	75	Chamber	1.2--468.8	1.43
		01--12.2009	Cotton	Till	75	EC	-10.8—912.0	3.15
Molodovskaya et al. (2011)	Hardford, New York	06--07.2008	Corn	Till	125	Chamber	30.0±48.0	-
			Alfalfa	Till	750	Chamber	66.0±42.0	-
			Between corn and Alfalfa	-	-	EC	78.0±420.0	
Neftel et al. (2010)	central Switzerland	06--09.2008	Grass	Till	230	Chamber	121.0	3.1
						EC	56.5	1.5[b]
Mammarella et al.(2010)	Sorø, Denmark	05.2003	Beech	-	-	Chamber	9.9±0.12[a]	-
						EC	7.2±0.40[a]	-
	Kalevansuo, Finland	04--06.2007	Pine, spruce, birch	-	-	Chamber	4.5±0.03[a]	-
						EC	4.6±1.0[a]	-
Lee et al. (2009)	Yolo, California	04--09.2004	Corn	Standard till	244	Chamber	0- 100.8[b]	3.8
				minimum tillage	244	Chamber	0- 412.0[b]	8.5
Phillips et al. (2009)	Mandan, North Dakota	04--08.2008	Corn	No till	70 (early spring)	Chamber	210.0[c]	0.6±0.31[a]

					70 (late spring)	Chamber	270.0[c]	0.7±0.22[a]
Ussiri et al. (2009)	Clarleston, USA	11.2004-11.2005	Corn	No till	200	Chamber	12.1	0.9
				Chisel till	200	Chamber	30.8	2.0
				Moldboard till	200	Chamber	27.9	1.8
Li et al. (2008)	Luancheng China	1995--1998	Corn		320.5	Gradient	-4410.0—4840.0	-
			Wheat	-	247	Gradient	-2820.0—3590.0	-
Eugster et al. (2007)	Lägeren mountain, Switzerland	10--11.2005	Beech, spruce	-	-	EC	22.4±11.2[a]	-
Kroon et al. (2007)	Reeuwijk, Netherlands	08--11.2006	Grass	-	337	EC	187.2±284.4[a]	-
Wagner-Riddle et al. (2007)	Ontario, Canada	2000--2001	Corn	Till	150	Gradient	24.0[d]	1.2±0.08[a]
				No till	110	Gradient	17.8[d]	1.0±0.07[a]
		2001-2002	Soybean	Till	-	Gradient	15.0[d]	0.7±0.06[a]
				No till	-	Gradient	10.0[d]	0.5±0.01[a]
		2002--2003	Wheat	Till	90	Gradient	17.4[d]	3.0±0.39[a]
				No till	60	Gradient	8.1[d]	0.7 ±0.11[a]
		2003--2004	Corn	Till	150	Gradient	39.1[d]	1.8±0.20[a]
				No till	110	Gradient	10.1[d]	1.6±0.16[a]
		2004--2005	Soybean	Till	-	Gradient	5.9[d]	0.3±0.08[a]
				No till	-	Gradient	3.6[d]	0.3±0.01[a]
Kitzler et al. (2006)	North Tyrol Limestone Alps, Austria	05.2002--04.2003	Spruce, fir, beech	-	-	Chamber	4.5	0.3±0.11[a]
		05.2003--04.2004	Spruce, fir, beech	-	-	Chamber	4.4	0.4±0.09[a]
Zou et al. (2005)	Nanjing, China	05.2002—10.2002	Rice	-	0	Chamber	48.2	1.38±0.01[a]

					150	chamber	100.0[b]	2.67 ±0.07 [a]
					300	chamber	170.0[b]	4.44 ±0.16 [a]
					450	chamber	215.9	6.17 ±0.42 [a]
		11.2002—06.2003	Winter wheat	-	0	chamber	53.8	2.84 ±0.03 [a]
					100	chamber	91.5	4.83 ±0.06 [a]
					200	chamber	110.0[b]	6.44 ±0.08 [a]
					300	chamber	137.8	7.27 ±0.43 [a]
Grant and Pattey (2003)	Ottawa, Canada	05--07.1998	Corn	Till	155	EC	-	2.2
					99	EC	-	1.2
Laville et al. (1999)	Landes de Gascogne, France	06.1999	Corn	Till	200	Chamber	90—990	-
						EC	72—1440	-
Simpson et al. (1997)	Saskatehewan, Canada	04--09.1994	Aspen	-	-	Gradient	5.04 ±2.5	-

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938 a. Standard deviations.
939 b. Values are not given directly, calculated from known variables.
940 c. The measurements were taken at 10:00-12:00 daily, and used as the daily flux.
941 d. Median, instead of mean.

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