Applicability of an eddy covariance system based on a close-path quantum cascade laser spectrometer for measuring nitrous oxide fluxes from subtropical vegetable fields

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ABSTRACT

The soil of subtropical vegetable fields is an important source of the atmospheric greenhouse gas nitrous oxide (N2O). In a field study in subtropical China, the authors used an eddy covariance (EC) system based on a close-path quantum cascade laser (QCL) spectrometer to measure N2O fluxes from a vegetable field. During the experimental period from 9 October 2014 to 18 February 2015, the observed half-hourly N2O fluxes ranged from −10.7 to 1077.4 μg N m−2 h−1, with a mean value of 99.3 μg N m−2 h−1. The detection limit (95% confidence level) of the EC system for half-hourly fluxes was estimated at 18.5 μg N m−2 h−1, i.e. smaller than 97.5% of all measured fluxes, and within the range of the lower limit of reported N2O emissions from subtropical vegetable fields. The random uncertainties in the half-hourly fluxes were estimated at 60% on average, of which 62% was due to stochastic variations caused by turbulence and 38% by instrumental noise. The flux systematic uncertainties were estimated at −18% on average, mainly due to the spectral attenuation; however, this negative bias had already been corrected for by calculating half-hourly fluxes. In conclusion, the close-path QCL-based EC technique is capable of measuring the N2O fluxes from the subtropical vegetable fields of China with high reliability and accuracy.

1. Introduction

Nitrous oxide (N2O) is a very important greenhouse gas (IPCC 2007). Agricultural soils have been identified as the dominant source of anthropogenic N2O emissions, contributing approximately 1.7–4.8 Tg N yr−1 on the global scale (IPCC 2006). Emissions from agricultural soils are mainly due to the intensive use of nitrogen fertilizers. However, there are significant uncertainties in estimated N2O emissions at both regional and global scales, mainly due to the lack of flux data for representative crop and management systems.

During the last two decades there has been rapid development in the application of fast response N2O analyzers based on spectroscopic techniques, e.g. the tunable diode laser (TDL) spectrometer and the quantum cascade laser (QCL) spectrometer. Due to the achieved gains in measuring sensitivity, N2O fluxes for different ecosystems can now be measured by the micrometeorological method of eddy covariance (EC) (e.g. Kroon et al. 2007; Wang et al. 2013). As compared to other commonly used techniques, e.g. the static chamber method, the EC technique has the advantage of providing spatially averaged fluxes at the field scale without disturbing the environment of the measured objects, and also produces temporally continuous data (Wang et al. 2013).

The production of vegetables under subtropical climate conditions has been identified as a major source of atmospheric N2O (e.g. Mei et al. 2011; Yao et al. 2015; Zhang et al. 2016). These studies have shown that the lowest level of N2O emissions from subtropical vegetable fields ranges
Therefore, the aims of this study were to evaluate the applicability of the QCL-EC technique for measuring N$_2$O fluxes from vegetable fields in subtropical China, as well as to investigate the characteristics of the N$_2$O emissions during the non-fertilization period and assess flux uncertainties.

2. Field measurements and data processing

2.1. Field site

Field measurements were conducted on a vegetable field located in the suburbs of Yueyang, Hunan, China ((29°30′21.24″N, 112°53′42.95″E), 29 m MSL). The site has a subtropical monsoon climate with a hot and rainy summer and a temperate winter. The mean annual temperature is 17.0 °C, while the mean annual precipitation is 1,260 mm. The soil of the site is classified as sandy loam, with a pH 7.0–8.0 in the top layer of 10 cm. As is usual for this region, the vegetable field was divided into many plots managed by different farmers (Figure 1). Vegetables (cabbage, hot pepper, or pumpkin) are grown in two consecutive seasons, which normally start in March and August, respectively. Nitrogen fertilizers are applied at the beginning of both seasons at a rate of 300–400 kg N ha$^{-1}$. Our measurements began in early October 2014, when all plots were still planted with cabbages (maximum canopy height: 0.35 m), and with nitrogen fertilization having already commenced two months earlier, meaning it was unlikely to have had any substantial effect on N$_2$O emissions during this period. Due to management differences, the date of cabbage harvest for the plots within the EC footprint varied from mid-October to mid-December, which led to spatial heterogeneity in the canopy height from 0.10 to 0.35 m during this period. Following harvest, the fields were left fallow until the end of the measuring campaign.

2.2. Field measurements

N$_2$O flux measurements were taken from 9 October 2014 to 18 February 2015. We used an EC system consisting of a QCL gas analyzer (QC-TILDAS-DUAL, Aerodyne Research Inc., U.S.A) to measure N$_2$O fluxes from a vegetable field in subtropical China. Compared with the traditional laser spectrometer, this type of laser is more sensitive and carries a number of other advantages such as compactness, high selectivity in operating frequencies, and without using liquid-nitrogen for laser cooling. QCL instruments have been previously used for N$_2$O flux measurements on managed grasslands (Kroon et al. 2007; Neftel et al. 2007, 2010; Merbold et al. 2014) and agricultural fields (Huang et al. 2014; Rannik et al. 2015). However, the performance of the laser in these studies varied due to many factors, such as the wavelength and mode of the laser adopted during operation, the field and environmental conditions, and the manner of the daily maintenance applied by the instrument users, which led to differences in the performance of the QCL-EC system.

Figure 1. Satellite image of the experimental fields on 19 December 2014 (source: Google Earth).
Note: The black triangle indicates the location of the eddy covariance measuring system.
9 October to 15 November 2014, and was then lowered to 2 m until the end of the experiment. The air inlet was installed 12 cm to the east of the sonic anemometer. The vacuum pump was used to draw ambient air to the multi-pass cell via an 11 m-long Teflon tube (inner diameter: 6.4 mm) at a nominal flow rate of 15 l min⁻¹. To avoid water condensation, the tube was heated and coated with heat insulation material. Besides, inlet filters (polycarbonate; pore size: 0.45 μm) were added to prevent contamination of the multi-pass mirrors. The pressure of the sample cell was kept at around 53.2 hPa, and the filters were replaced regularly. Automatic zero calibration was implemented on the QCL every 4 h using pure N₂. We released a standard gas of 380 nmol mol⁻¹ of N₂O in N₂/O₂ into the sample cell at the beginning and the end of the campaign. The measured N₂O differed less than 5% from the standard concentration. Therefore, no further span calibration was performed. Data from the sonic anemometer and the QCL were simultaneously stored in the data logger at a frequency of 10 Hz.

A meteorological station (WS3000, Beijing Techno Solutions, China) was used to observe the environmental conditions every 30 min, including the air and soil (5 cm depth) temperature, precipitation, and solar radiation. The volumetric water content of the soil (0–6 cm) was measured manually every day with a portable probe (ML2x, Delta-T Devices, U.K.). The volumetric records were converted into water-filled pore space (WFPS) using a theoretical particle density of 2.65 g cm⁻³ and the bulk density of the measured soil.

### 2.3. Flux calculation and quality control

In this study, the EddyPro software (Li-COR, U.S.A.) was used for flux calculation and correction. The vertical N₂O flux was calculated as

\[ F_{\text{raw}} = w'c'_{N_2O} \frac{\rho_a}{M_a} \times 3,600 \times 28 \times 10^{-3} \]  

(1)

where \( F_{\text{raw}} \) is the raw turbulent flux (μg N m⁻² h⁻¹); \( w' \) and \( c'_{N_2O} \) represent the instantaneous deviations of the vertical wind velocity (m s⁻¹) and N₂O concentration (nmol mol⁻¹) from the mean values, respectively; the overbar indicates the averaging period of 30 min; \( \rho_a \) is the air density (kg m⁻³); \( M_a \) is the molar mass of air (0.029 kg mol⁻¹), 3,600 denotes 3,600 s h⁻¹, and 28 is the molar mass of two N atoms in N₂O (g mol⁻¹).

The routine schemes proposed by Aubinet et al. (2000) were used to calculate the covariance in Equation (1), which included the steps of spike detection, double rotation of wind components, lag-time compensation, block averaging, and de-trending. The flux correction due to water dilution effect (Webb, Pearman, and Leuning 1980) and water broadening line effect (Neftel et al. 2010) were ignored, because the Aerodyne analyzer simultaneously measured the water vapor and reported the mixing ratio of N₂O with respect to dry air with an empirical algorithm (Rannik et al. 2015). The methods proposed by Moncrieff et al. (2004) and Ibrom et al. (2007) were used to correct the flux losses in the low and high ranges of the spectra, respectively.

The half-hourly N₂O fluxes were quality controlled using the following steps: First, flux records during instrument maintenance were discarded. Second, fluxes assigned with a quality flag of ‘2’ were rejected after stationarity and integral turbulence characteristic tests (Mauder and Foken 2004). Third, nighttime fluxes with weak wind conditions were filtered out using a friction velocity threshold of 0.12 m s⁻¹, according to the method proposed by Gu et al. (2005). Fourth, flux outliers were removed if they exceeded three times the standard deviation in a window of one day. Finally, fluxes that were more negative than the lower detection limit of the EC system were rejected, based on the assumption that significant N₂O uptake in agro-ecosystems with extensive nitrogen fertilizer input is not well explained by common knowledge; the determination of the detection limit of the EC system is described in the following section.

### 2.4. Estimation of random uncertainty

The random uncertainties in the measured N₂O fluxes (\( \delta_F \)) were mainly produced by the stochastic characteristics of the turbulence (\( \delta_{F,\text{turb}} \)) and the instrumental noise (\( \delta_{F,\text{noise}} \)). In this study, \( \delta_F \) was calculated using Equation (8) in Finkelstein and Sims (2001). The component \( \delta_{F,\text{noise}} \) can also be regarded as the detection limit of the EC system (Rannik et al. 2015), which can be estimated as

\[ \delta_{F,\text{noise}} = 2\sigma_w \times 2\sigma_c \times (Tf)^{-1/2}, \]

where \( f \) is the measurement frequency; \( T \) is the averaging time; \( \sigma_w \) and \( \sigma_c \) represent the noise level of the vertical wind speed and the N₂O concentration, respectively; and the factor of 2 represents the detection limit at the 95% confidence level.

### 3. Results and discussion

#### 3.1. Environmental conditions and N₂O fluxes

The daily mean air temperature ranged from −0.3 to 22.0 °C, with a mean value of 10.2 °C during the campaign. The variation pattern of the daily mean soil temperature was similar to that of the air temperature (Figure 2(a)). During the experiment from 6 October 2014 to 18 February 2015, precipitation totaled 424.6 mm. Changes in WFPS were closely related with rainfall events (Figure 2(b)).
We collected a total of 5944 half-hourly N$_2$O fluxes during the campaign. 3761 of the flux data remained following the first four quality control steps described above, and a further 19 were rejected after the fifth step. This resulted in a final data coverage of 58.2%. The emissions were characterized by bursts of higher fluxes after rainfall and by lower fluxes during other periods; and the minimum, median, mean, and maximum values of the half-hourly fluxes were $-10.7, 60.8, 99.3, \text{ and } 1077.4\ \mu g\ N\ m^{-2}\ h^{-1}$, respectively (Figure 2(c)). The coefficient of variation of the half-hourly fluxes within each day varied between 10% and 169%, with a mean value of 44%. The daily fluxes that averaged over the half-hourly data ranged from 21.8 to 676.0 $\mu g\ N\ m^{-2}\ h^{-1}$ (Figure 2(d)), which were well correlated with the variation of the WFPS (data not shown). According to footprint analysis (Kormann and Meixner 2001), 90% of the fluxes were coming from the area 80–100 m away from the EC mast under unstable conditions. The fetch was long enough even for stable conditions because the borders of the vegetable field in the upwind directions were more than 200 m away.

### 3.2. Performance of the EC measuring system

Using the Allan variance technique (Werle, Miike, and Slemr 1993), we estimated the precision of the QCL spectrometer to be 0.26 nmol mol$^{-1}$ at a sampling rate of 1 Hz under field conditions (Figure 3). This piece of data was collected in the afternoon of 20 December 2014, when turbulence was well developed and N$_2$O emissions were weak. Although the precision may have been even better by taking samples of standard gas, it was very close to the average estimates (0.31 ± 0.29 nmol mol$^{-1}$ at 1 Hz) reported by previous studies that applied this kind of QCL analyzer (Kroon et al. 2007; Neftel et al. 2007, 2010; Huang et al. 2014; Rannik et al. 2015).

The detection limit of the EC system was not a constant value, because $\sigma_w$ and $\sigma_c$ varied with time and were dependent on the performance of instruments and atmospheric conditions. In this study, $\sigma_w$ was determined as the mean value of the standard deviation of $w$ at the half-hourly scale during the campaign, and $\sigma_c$ was regarded as the instrumental precision of QCL at a 10 Hz sampling rate. We noticed the Allan variance of N$_2$O was dominated by white noise when the integration time $t$ was less than 3 s (Figure 3); therefore, $\sigma_c$ was determined by multiplying the QCL precision at 1 Hz by $\sqrt{10}$ which led to a typical instrumental detection limit of 18.5 $\mu g\ N\ m^{-2}\ h^{-1}$ (95% confidence level). This estimate was in the same order of magnitude compared to those in the studies mentioned above in this section, which ranged from 7.6 to 21.6 $\mu g\ N\ m^{-2}\ h^{-1}$. Accordingly, we found 3648 half-hourly fluxes were larger than the detection limit, and 94 fluxes were between the

The sonic data showed that nearly 80% of the winds during the campaign came from northern directions (0$^\circ$–60$^\circ$ and 300$^\circ$–360$^\circ$).
the low and high frequency ranges. We analyzed the co-spectra of N₂O and vertical wind velocity during the periods of 1000–1530 Beijing Time (BT) 2 December 2014 (Figure 4(a)) and 1230–1700 BT 17 February 2015 (Figure 4(b)). The results were averaged to achieve better statistics of the co-spectra, and were obtained under unstable conditions with a Monin–Obukhov length $L$ of less than 0 and a friction velocity $u^*$ of greater than 0.15 m s$^{-1}$. The theoretical undamped co-spectra according to Kaimal et al. (1972) and the temperature co-spectra are also presented in Figure 4. We noticed that the temperature co-spectra were smooth and had almost no damping along the entire frequency range. The pattern of the N₂O co-spectra was almost consistent with the theoretical one, as well as the temperature co-spectra, but disagreed slightly at the high frequency ends, indicating losses of fluxes. According to the methods introduced by Moncrieff et al. (2004) and Ibrom et al. (2007), the final N₂O fluxes were corrected for this systematic underestimation by on average of 18%. The magnitude of the co-spectra correction agreed with the results reported by Huang et al. (2014).

3.4. Random uncertainty of the fluxes

The total relative random uncertainty of the half-hourly N₂O fluxes varied greatly. Most of the estimates were smaller than 150%, and the mean value was 57% (95% confidence level). Meanwhile, the random uncertainties caused by the turbulence characteristics and instrumental noise contributed 62% and 38% to the total, respectively. Rannik et al. (2015) used a similar N₂O gas analyzer, but equipped with only one laser (model CW-TILDAS-CS, Aerodyne Research Inc., U.S.A.) for EC measurements, and used the same method for random uncertainty estimation. They reported that the mean relative random uncertainty was around 120% while applying a confidence level of 95%. Since the relative estimates depend on the flux magnitude, the absolute flux random uncertainty in this study was on average twice as large as the one reported positive and negative detection limits, with six of them negative, indicating that the EC system was capable of measuring 97.5% of the fluxes with high confidence.

During previous field experiments based on chamber measurements, it has been found that the lowest N₂O emissions from subtropical vegetable fields normally occur during winter, with fluxes being in the range of 10–30 μg N m$^{-2}$ h$^{-1}$ (e.g. Mei et al. 2011; Yao et al. 2015; Zhang et al. 2016). The detection limit of our instrument (95% confidence level) was within this range, indicating that the current EC system can reliably measure N₂O fluxes from subtropical vegetable fields all year around, except for a short period in winter in some cases. Moreover, the detection limit can be improved by regular optical alignment and mirror cleaning, as suggested by the manufacturer (Aerodyne), since the current instrumental noise of the QCL was one to two times larger than that in the instrumental specification. This means that in future work the sensitivity and performance of the EC system can be potentially improved.

3.3. Co-spectra

In general, N₂O fluxes measured by the EC system were underestimated due to data acquisition and processing and the non-ideal measuring system (e.g. Moore 1986). This can be illustrated by the co-spectra attenuation in
in Rannik et al. (2015). The difference can be explained by the lower instrumental noise and more homogeneous underlying surface in their study.

4. Conclusions

The close-path QCL-based EC system was running smoothly during the whole experimental period, with a mean detection limit of 18.5 μg N m⁻² h⁻¹ for half-hourly N₂O fluxes. Although this precision was within the range of the lower limit of the N₂O emissions from the subtropical vegetable fields of China reported by previous chamber studies, the EC system detected more than 97% of the half-hourly fluxes from the vegetable fields of the current study, as the magnitude of fluxes was mostly higher than the detection limit. The random and systematic uncertainties in the measured N₂O fluxes were within the same order of magnitude as those reported by other studies that utilized similar QCL gas analyzers. We conclude that the QCL-based EC system is capable of reliably measuring N₂O fluxes from vegetable fields in subtropical China. This useful tool will enable future work related to biosphere–atmosphere exchanges of N₂O in a wide range of agricultural and natural ecosystems.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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