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Micrometeorological measurements of nitrous oxide exchange in a cropland

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ABSTRACT

N_2O fluxes in a wheat/maize rotation system were measured using flux gradient methods combined with gas chromatograph (GC) technique. The mean precision of two repeated GC analyses for N_2O concentration achieved to 0.27–0.46 ppbv, which could resolve N_2O concentration differences in a low range of 0.39–0.65 ppbv. To maximize measurable N_2O concentration differences, gradient measurements were conducted only after fertilization or under low wind conditions. During observation period, N_2O flux ranged from −4.41 to 4.84 $mgN_2O\ m^{-2}\ h^{-1}$ for maize field, and from −2.82 to 3.59 $mgN_2O\ m^{-2}\ h^{-1}$ for wheat field. When gradient observation changed from two layers to four layers, the temporal variation of N_2O flux reduced but the mean value changed less. Many negative N_2O fluxes were found in maize and wheat fields even after fertilization. Nearly all of them were caused by negative N_2O concentration differences. During four days' observation in maize field, a mean N_2O flux of −0.75 $mgN_2O\ m^{-2}\ h^{-1}$ was found in the daytime and could not be simply attributed to the temporal variation of N_2O flux. N_2O flux determined by the aerodynamic method (F_a) and the Bowen ratio/energy balance method (F_b) were in a good agreement and statistically significant. The ratio of F_a to F_b increased linearly with energy balance ratio (EBR) obtained by the aerodynamic method in the daytime when EBR is larger than 0.3. It is the first time to give a quantitative description for the impact of energy closure on N_2O flux, and show a possible way to improve the data quality under the condition of poor energy balance.

1. Introduction

Nitrous oxide (N_2O) is a radiatively active trace gas. It not only contributes to global warming but also affects the natural concentration of stratospheric ozone (Crutzen, 1970). Current mixing ratios of N_2O in the atmosphere are around 316 ppbv (parts in 10^9 by volume) and increasing at a rate of 0.2–0.3% per year (IPCC, 2001). Atmospheric N_2O is mainly generated by nitrification and denitrification of microbes in the soil and consumed by photolysis in the stratosphere (IPCC, 2001). The difference between known N_2O sources (17.7 $TgN\ yr^{-1}$) and sinks (12.3 $TgN\ yr^{-1}$) is higher than the known increase of N_2O concentration in the atmosphere (3.9 $TgN\ yr^{-1}$) (IPCC, 2001). For accurate estimation of N_2O photolysis in stratosphere, the large gap of global N_2O budget (1.5 $TgN\ yr^{-1}$) may come from overestimation of N_2O source strength or neglect of some unknown N_2O sinks in the earth's surface. Although there are many uncertainties in the study of N_2O budget, it is evident that human activities improved the unbalance of N_2O source and sink, which result in the increase of atmospheric N_2O. To supply food for the

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growing population, farmers had to apply more and more nitrogen fertilizers to attain high crop productivity. This makes arable soil become the largest anthropogenic source of N_2O (IPCC, 2001). It is significant to determine the contribution of agricultural activity to the atmospheric N_2O.

N_2O flux is generally observed by micrometeorological and chamber methods. Close chambers are easy to operate and widely used in current N_2O flux measurements. However, chambers could only cover a small area (10^{-2}–$10\ m^2$) and always alter the physical status of the observed surface (Mosier and Heinemeyer, 1985). The accuracy and representative of chamber-based measurements are limited by the high spatial variability of soil N_2O emission (Ambus and Christensen, 1994). Micrometeorological techniques could be used to measure the flux at a large scale (10^2–$10^4\ m^2$) and never change the physical condition of observed surface. Since 1990s, with the improvement of the instrument precision and response rate, micrometeorological methods such as eddy covariance, aerodynamic and conditional sampling techniques were successfully used to measure N_2O flux in cropland (Fowler et al., 1995; Hargreaves et al., 1996; Griffith and Galle, 2000; Ding et al., 2004; Pattey et al., 2006), grassland (Hargreaves et al., 1994; Wienhold et al., 1994, 1995; Maggiotto and Wagner-Riddle, 2001; Griffith et al., 2002; Phillips et al., 2007) and forest (Simpson et al., 1997, 1999; Pihlatie et al., 2005). Comparisons among different observation methods and instruments were also carried out in croplands and grasslands (Smith et al., 1994; Christensen et al., 1996; Laville et al., 1999; Li et al., 2002; Pihlatie et al., 2005).

In 1990s, only few negative N_2O fluxes were obtained by micrometeorological approaches (Wagner-Riddle et al., 1996; Skiba et al., 1996; Simpson et al., 1997). Recently, with the development of observation techniques, more and more negative N_2O fluxes were observed (Maggiotto and Wagner-Riddle, 2001; Griffith et al., 2002; Di Marco et al., 2004). Neftel et al. (2007) found a large amount of negative (downward) N_2O flux in grassland using both of the eddy covariance technique and the chamber method, and regarded it as a consequence of soil absorption. However, negative N_2O flux appeared not only under background conditions (Di Marco et al., 2004; Neftel et al., 2007) but also after fertilization (Skiba et al., 1996). The origin of observed negative N_2O fluxes should be investigated carefully because it links with the pattern of terrestrial N_2O sinks and further, the imbalance of global N_2O. On the other hand, energy closure is widely accepted as a method to estimate the availability of eddy fluxes of water vapor and CO_2 (Verma et al., 1986; Mahrt, 1998). The method could be used in N_2O flux measurements also (Wienhold et al., 1995). However, Lacking quantitative analysis of the impact of energy closure on gas flux, energy balance ratio (EBR) is only a reference in the evaluation of data quality and rarely used in the data correction.

In this study, we measured N_2O flux in a wheat/maize rotation system using aerodynamic and Bowen ratio/energy balance (BREB) method combined with gas chromatograph (GC) analysis. The objectives are (1) to compare N_2O fluxes between different meteorological methods; (2) to investigate the origin of negative N_2O flux; (3) to research the effect of energy closure on N_2O flux. It is the first time to describe the impact of energy closure on N_2O flux quantitatively. The result may help improve data quality under the condition of energy imbalance.

2. Material and methods

2.1. The experimental site

The experimental site was a large area of even crop field at Luancheng Agro-ecosystem Experimental Station (37°53′N, 114°41′E, 50.1 m elev.), Chinese Academy of Sciences. The station is located in North China Plain within the east monsoon region. It has a semi-humid and warm temperate climate. The soil at the site is typical brown soil with thin humus layer and middle or thick solum, with an organic matter of 12–13 g kg^{-1} and total nitrogen of 0.78 g kg^{-1}. The planting system is summer maize or winter wheat for a rotation in a year. 148 and 172.5 kgN ha^{-1} of urea was applied to summer maize field on July 21, 1995 and July 13, 1997, separately. 109 and 138 kgN ha^{-1} of urea was applied to winter wheat field on October 2, 1995 and October 5, 1997, respectively. After fertilization, the wheat field was plough up and the maize field was irrigated with 60 mm of water immediately.

2.2. Micrometeorological measurements

From 1995 to 1997, six observations were done to measure N_2O flux using the aerodynamic and BREB method in a wheat/maize rotation system. Each observation lasted for several days or a week. Gradients of temperature and humidity were determined by the Bowen ratio instrumentation. It was consisted of two psychrometers attached to a mast in the center of a large even crop field. Near the Bowen ratio apparatus stand, another mast was equipped with two anemometers and a net radiometer (model CN-1, Australia). Net radiation was measured by the net radiometer positioned 2 m above the crop canopy. The heat flux into the soil was measured using two soil heat flux plates buried 2 cm below the soil surface. During two-layer gradient observations in 1995 and 1996, psychrometers and anemometers were positioned at heights of 0.5, 1.6 m or 0.5, 2 m above the maize or wheat canopy, respectively. The positions of two psychrometers were automatically exchanged every 5 min to avoid systematic errors on $\partial\theta$ and ∂W. During four-layer gradient observations in 1997, four psychrometers were positioned immovably at heights of 0.5, 1, 2 and 4 m above the crop canopy. All these sensors were controlled by a datalogger (model DT100, Australia). The measurements were conducted every 15 s and a group of mean values were logged every 5 min. All sensors used in the experiment were strictly calibrated. The resolution of temperature measured by the Bowen ratio instrument was 0.03 °C. The lowest wind velocity measured by anemometers was 0.25 m s^{-1} and the resolution was 0.1 m s^{-1}. During the period of observation, the fetch was in excess of 400 m so that flux measurements using micrometeorological techniques could be achieved above the ground.

2.3. Gas sampling and gas chromatograph analysis

Air samples were collected every two hours in the daytime and every four hours in the nighttime. Air samples at different heights were pumped through pipes into Tedlar bags simultaneously for 10 min. Airflow speeds controlled by flowmeters were approximately 0.5 L min^{-1}. The sampling system was proved to be airtight during the observation period.

Each air sample was sent to laboratory where it underwent at least 2 sequential analyses by gas chromatography (GC). The gas chromatography (HP 5890 Series II Plus) was equipped with a ^{63}Ni electron capture detector (ECD) and a stainless steel separation cylinder (diameter: 1/8 in, length: 6 in) with Porapak Q (80/100 mesh) inside. Argon + 5% CH_4 was used as the carrier gas. The working temperatures of cylinder and detector were 90 °C and 330 °C, respectively. Standard gas, with a concentration of 315 ppbv for N_2O (diluent gas was man-made air), was supplied from Max Planck Institut für Chemie, Germany. The equipment had a good linearity within the range of N_2O concentrations from 250 to 1000 ppbv.

Standard gas was analyzed by GC before and after the measurement of each air sample. In case the analytical error of N_2O concentration was found to be too large, the air sample was measured again until the result was satisfactory. For meteorological measurements, no valid N_2O concentration gradient could be found if the absolute N_2O concentration difference between top and bottom layers were less than their analytical error (see Section 3.2).

2.4. Theory for flux estimation

2.4.1. Aerodynamic technique

In surface layer, energy and mass transfer is restricted by the gradient of temperature, wind speed and gas concentration. According to aerodynamic theory, surface N_2O flux (F_a) could be estimated as follows (Hargreaves et al., 1994; Fowler and Duyzer, 1989):

$$F_a = -\rho_a k^2 (z-d)^2 \frac{\partial u}{\partial z}\frac{\partial C}{\partial z}\frac{k_n}{k_m}(\phi_m \phi_n)^{-1} \tag{1}$$

where ρ_a is dry air density (g m^{-3}); k von Karman's constant (0.42); z the observation height (m); d zero plane displacement (m); C mixing ratio of N_2O (ng g^{-1}). k_m and k_n is transfer coefficient for momentum and N_2O, respectively. ϕ_m and ϕ_n is stability function for momentum and N_2O transfer separately which could be determined by the equation as follows (Pruitt et al., 1973):

$$\phi_n = \phi_m = (1-16R_i)^{-1/3} \quad (R_i < 0) \tag{2}$$

$$\phi_n = \phi_m = (1+16R_i)^{1/3} \quad (R_i > 0) \tag{3}$$

In surface layer, Richardson number is defined as:

$$R_i = \frac{g}{\theta}\frac{\partial \theta}{\partial z}\left(\frac{\partial u}{\partial z}\right)^{-2} \tag{4}$$

where θ is potential temperature (K), g acceleration due to gravity.

2.4.2. BREB method

The energy received by natural surfaces from solar radiation is balanced with the energy losing to the atmosphere through the transfer of sensible heat, latent heat and heat storage. The micrometeorological theory for N_2O flux measurements by Bowen ratio/energy balance method (BREB) was described in detail by Denmead (1983) as follows:

$$F_b = \frac{R_n - G}{c_p(\gamma+1)}\frac{\partial C}{\partial T_e} \tag{5}$$

where F_b is the N_2O flux (μg m^{-2} s^{-1}), R_n net radiation (W m^{-2}), G soil heat flux (W m^{-2}), c_p specific heat, γ psychrometric constant, T_e effective temperature (K), which can be given by:

$$T_e = \theta + \frac{\lambda}{c_p}\frac{W}{\gamma+1} \tag{6}$$

where θ is potential temperature, λ latent heat (J kg^{-1}), W mixing ratio of vapor (g g^{-1}).

2.5. Data processing and quality control

For the micrometeorological measurement in uniform croplands, the suitable average sampling time is 10–60 min (Sun et al., 2005). To obtain more available N_2O concentration difference, 10 min was selected as the length of sampling time in our experiment. How to judge the available concentration difference was shown in Section 3.2. The appearance of error data was due to the malfunction of instruments, anthropogenic effects and the extreme weather condition. For instance, if a large positive Bowen ratio were obtained under a very dry weather condition or a negative one was found when advection prevailed in the field, BREB method would lead to great errors in flux estimation. When water vapor and heat flux were more than the normal range (−200–800 W m^{-2}), the corresponding N_2O flux should be eliminated. Some large outlyers remained after primary selection using above criteria will bring to significant influence on the mean flux. For each observation period, N_2O flux outside three standard deviations of the mean was regarded as abnormal one and discarded (Simpson et al., 1997).

3. Results and discussion

3.1. Resolution of GC analysis

When using flux gradient techniques to measure N_2O flux, the accurate observations are needed for the gradients of temperature, humidity, wind speed and N_2O concentration. Since current resolutions of the sensors for temperature, humidity and wind speed are satisfied with the requirement of gradient observations, the precision of N_2O flux is actually determined by the resolution of N_2O concentration analyzed by gas chromatography. To avoid the base line of ECD output shifting with varying temperature, the difference approach (Arah et al., 1994) was used for GC analysis: two repetitions for each gas sample coupled with two repetitions for standard gas, one before the gas sample, the other after. N_2O concentration for each gas sample was calculated using the N_2O peak area of sampling gas and standard gas. Arah et al. (1994) reported that ten to fifteen repeated analyses gave resolutions around 1 ppbv for N_2O. Increasing the replicate injections could decline N_2O analytical errors. However, as the capacity of the instrument was limited by the speed of GC analysis for gas samples, the observation could not last for a long time when the GC analysis for gas samples was slower than the gas sampling. In our experiment, when only two replicate injections were made in GC analysis, the high resolution of N_2O concentration achieved to 0.27–0.46 ppbv, with a mean of 0.36 ppbv. It was able to resolve small N_2O concentration differences ranging from 0.39 to 0.65 ppbv.

To obtain more available N_2O concentration gradients, the observations were done only at low wind speed and/or after fertilization. During observation periods, the average wind velocities were less than 2 m s^{-1} at a height of 2 m above the canopy. The absolute N_2O concentration differences ranged from 0 to 20 ppbv and more than 80% of the absolute values were lower than 2 ppbv, which was very close to the detection limit of GC. Although a high resolution of GC analysis for N_2O was obtained, about 1/3 of the data were rejected because the N_2O concentration differences were too low and within the range of GC analytical errors.

3.2. N_2O concentration gradient

N_2O concentration gradient ($\Delta C/\Delta z$) is defined as the variation of N_2O concentration per unit distance in the vertical direction. It is positive when N_2O concentration decline with the increasing height. For two-layer measurement, N_2O concentration difference is simply calculated as follows:

$$\Delta C = C_2 - C_1 \tag{7}$$

where C_1 and C_2 are the measured N_2O concentrations in high and low layer, respectively. For multi-layer measurement, N_2O concentration difference (ΔC) between top and bottom layer is given by the equation as follows:

$$\Delta C = C_{s,n} - C_{s,1} = \frac{\partial C}{\partial \ln z}(\ln z_1 - \ln z_n) \tag{8}$$

where $\partial C/\partial \ln z$ is the slope of N_2O concentration versus a logarithmic vertical height; $C_{s,1}$ and $C_{s,n}$ are the simulated N_2O concentrations in top and bottom layer, respectively. z_1 and z_n are the heights of top and bottom layer, separately. Fig. 1 give an example of N_2O concentration profiles above the cropland surface. The analytical error for N_2O concentration difference (C_e) is calculated as follows:

$$C_e = \frac{\sum_{i=1}^{n} C_{e,i}}{\sqrt{n}} \tag{9}$$

where $C_{e,i}$ is the analytical error of N_2O concentration in the i layer; n the number of the layer. When absolute N_2O concentration difference between top and bottom layers is higher than its analytical error ($|\Delta C| \geq C_e$), it is available and involved in flux calculation. Conversely, N_2O concentration difference should be rejected and can't be used in analysis.

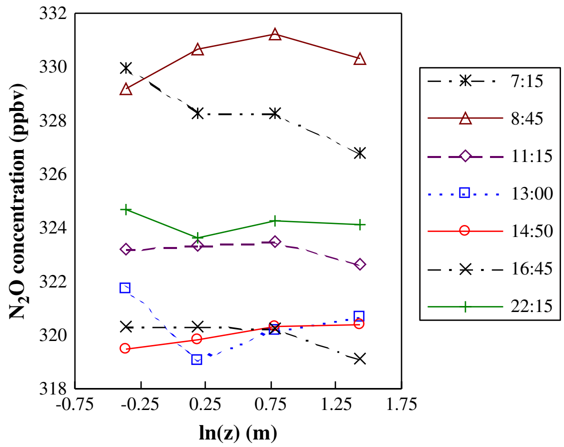

Fig. 1. An example of N_2O concentration profiles above a winter wheat field (October 28, 1997). z: the height above the cropland surface.

One or two weeks after fertilization, absolute N_2O concentration gradient ranged from 0 to 9.96 ppbv m^{-1} in maize field, with a mean of 1.58 ppbv m^{-1}; from 0 to 12.36 ppbv m^{-1} in wheat field, with a mean of 1.78 ppbv m^{-1}. It was higher in the nighttime than in the daytime. Three or four weeks after fertilization, the mean absolute N_2O concentration gradient decreased to two third or half of the former value and its daily difference reduced, too (Table 1 and Fig. 2). During observation periods in maize field, average wind speed was about 1–1.3 m s^{-1} at the height of 2 m above the canopy. The amount of available N_2O concentration difference was mainly affected by fertilization at low wind speed. From one week to one month after fertilization, the proportion of available N_2O concentration difference reduced from 77% to 54%. During observation periods in wheat field, average wind speed was 1.9 m s^{-1} at the height of 2 m above the canopy. The number of measurable N_2O concentration differences was reduced when wind velocity increased. No influence of fertilization on N_2O concentration differences was found under windy conditions.

When gradient observation changed from two layers to four layers, nearly 2/3 N_2O concentration gradients reduced and about 1/3 changed their directions (Fig. 2). It was due to different footprints (source areas) for two-layer and four-layer observations. The mean values and variability of absolute N_2O concentration gradients for four-layer observations were obviously less than two-layer's (Table 1). Considering height difference between top and bottom layers changed from 1.5 to 3.5 m, N_2O concentration differences for two kinds of measurements were similar. Nevertheless, changing from two-layer observation to four-layer's, the analytical errors of N_2O concentration difference enlarged 1.4 times (Eq. (9)), making the proportion of available N_2O concentration difference decrease from 78% to 48%.

In maize and wheat fields, many negative N_2O concentration gradients were obtained for both of two-layer and four-layer observations. Negative N_2O concentration

Table 1
N_2O flux and gradient measured using micrometeorological methods over a wheat/maize rotation system

Plots	Date	Days after fertilization	Measurement method	Observation layers	N_2O flux[a] ($mgN_2O\ m^{-2}\ h^{-1}$)	Absolute N_2O gradient[a] ($ppbv\ m^{-1}$)
Maize field	July 27–August 1, 1995	6–11	Aerodynamic	2	0.359 ± 0.293	1.58 ± 0.31
	July 27–August 1, 1995	6–11	BREB	2	0.299 ± 0.238	1.58 ± 0.31
	August 17–21, 1995	27–31	Aerodynamic	2	0.668 ± 0.339	0.67 ± 0.11
	August 17–21, 1995	27–31	BREB	2	0.305 ± 0.339	0.67 ± 0.11
	August 9–12, 1997	27–30	BREB	2	-0.753 ± 0.393[b]	1.02 ± 0.15[b]
	August 9–12, 1997	27–30		4		0.42 ± 0.07[b]
Wheat field	October 15–20, 1995	13–17	BREB	2	0.778 ± 0.123	1.78 ± 0.47
	May 4–10, 1996		Aerodynamic	2	0.293 ± 0.140	0.53 ± 0.08
	May 4–10, 1996		BREB	2	0.257 ± 0.238	0.53 ± 0.08
	October 27–28 and November 4–5, 1997	22–23 and 30–31	BREB	2	0.276 ± 0.419	0.84 ± 0.13
	October 27–28 and November 4–5, 1997	22–23 and 30–31	BREB	4	0.307 ± 0.280	0.31 ± 0.06

[a] Average ± standard error.
[b] Only daytime.

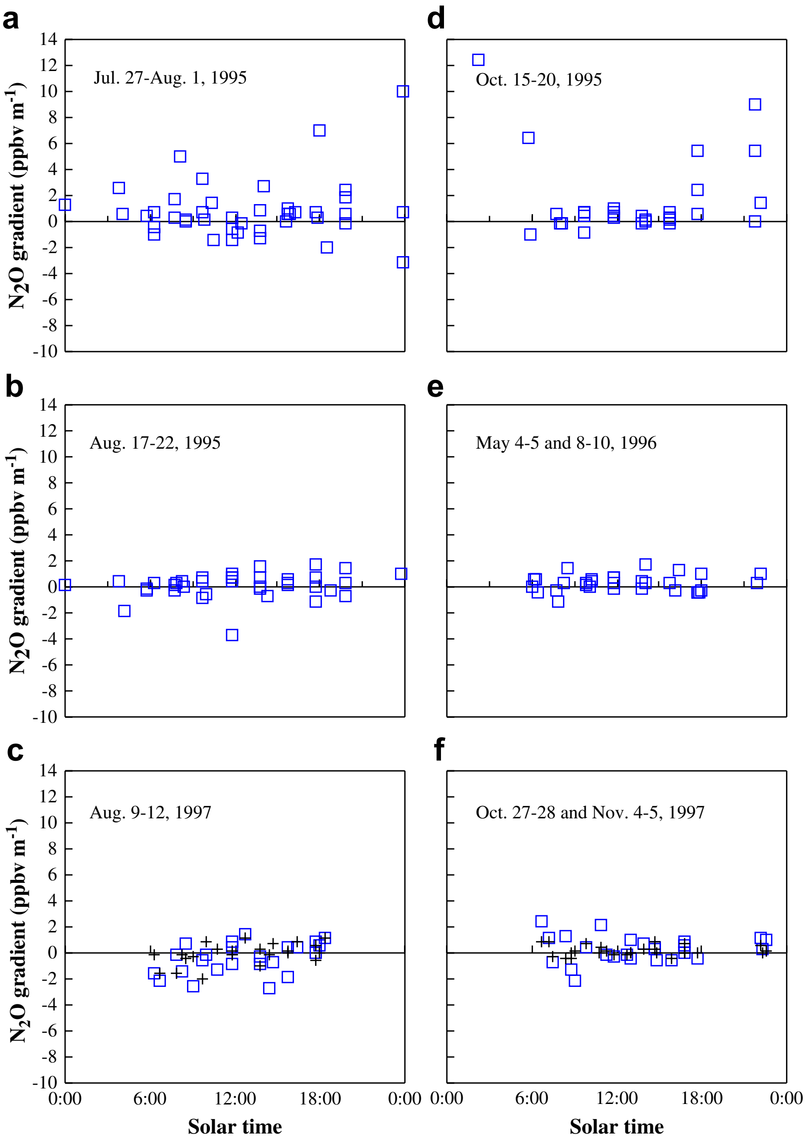

Fig. 2. N_2O concentration gradients above maize (a, b and c) and wheat (d, e and f) fields. Square: 2-layer N_2O gradient; Plus: 4-layer N_2O gradient. Positive sign means N_2O concentration decline with the increasing height.

gradients were often found above the canopy during growing seasons but seldom appeared above the bare soil (Fig. 2). It is implied that negative N_2O concentration gradient may be related to the vegetation.

3.3. N_2O flux

During observation periods, N_2O flux varied from −4.41 to 4.84 $mgN_2O\,m^{-2}\,h^{-1}$ in maize field, from −2.82 to 3.59 $mgN_2O\,m^{-2}\,h^{-1}$ in the wheat field (Figs. 3 and 4). It had a larger range than the results reported by Skiba et al. (1996) (−1.4–3.2 $mgN_2O\,m^{-2}\,h^{-1}$) and Griffith and Galle (2000) (−0.3–0.9 $mgN_2O\,m^{-2}\,h^{-1}$) in wheat fields. Compared to half-hourly mean fluxes presented by Skiba et al. (1996) and Griffith and Galle (2000), 10-min mean fluxes were measured in our experiments. Short average time may lead to a large temporal variation of N_2O flux (Laville et al., 1999).

From middle October to early November, mean N_2O flux obtained by the BREB method in wheat field decreased from 0.778 $mgN_2O\,m^{-2}\,h^{-1}$ two weeks after fertilization to 0.290 $mgN_2O\,m^{-2}\,h^{-1}$ three-four weeks after fertilization (Table 1). Whereas, in maize field, there were more negative N_2O fluxes one week after fertilization than one month after fertilization. This led to higher mean N_2O flux one month after fertilization than one week after fertilization.

On average, N_2O flux determined by aerodynamic method (F_a) was higher than by BREB method (F_b) (Table 1). Nevertheless, Comparing F_a with corresponding F_b, we found they were in agreement statistically (Fig. 5). The frequency of F_a showed a normal distribution with a peak occurred at 0–0.5 $mgN_2O\,m^{-2}\,h^{-1}$. The frequency of F_b showed a double-peak distribution with the maximal peak at −0.5–0.5 $mgN_2O\,m^{-2}\,h^{-1}$ and the second at 1–1.5 $mgN_2O\,m^{-2}\,h^{-1}$. 3/4 of N_2O fluxes obtained by both methods appeared at −1–1.5 $mgN_2O\,m^{-2}\,h^{-1}$ (Fig. 6). 33% of F_a and 44% of F_b were negative. It resulted in a lower mean N_2O flux measured by the BREB method than by the aerodynamic method.

In two-layer measurements in maize field, temporal variation of N_2O flux was large because the distance between two layers was small (1.1 m) (Table 1 and Fig. 3). When gradient observation changed from two layers to four layers, mean N_2O flux changed less, but the temporal variability reduced clearly (Table 1 and Fig. 4). The measured N_2O flux became more stable than before. Although absolute N_2O concentration gradients for four-layer observations were small averagely than two-layer observations, their analytical errors were large. N_2O flux remain high because only large N_2O concentration gradients were kept as the available one and used in flux calculation.

3.4. The impact of energy closure on N_2O flux

To verify the data quality of N_2O flux, energy budget of the aerodynamic measurements was investigated. The turbulence energy flux ($H+\lambda E$) observed by the aerodynamic approach was 73% and 67% of the available energy

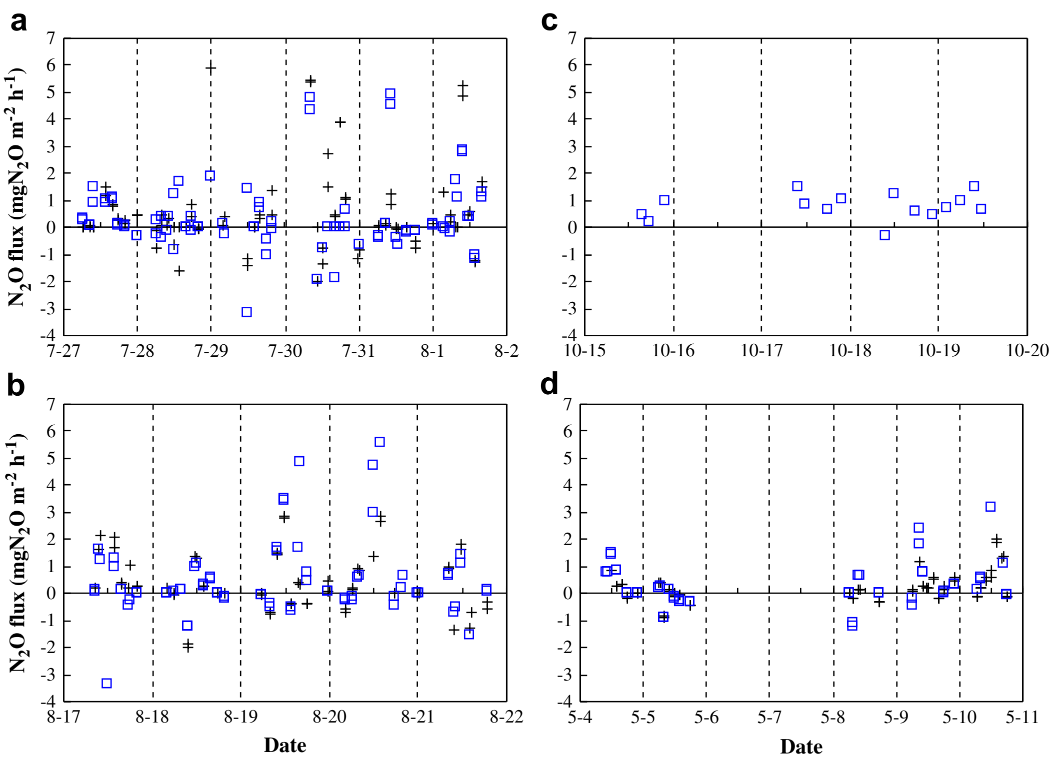

Fig. 3. N_2O fluxes measured using aerodynamic method (plus) and energy balance method (square) in a summer maize field in 1995 (a, b) and in a winter wheat field in 1995 (c) and 1996 (d). Positive sign indicates upward flux, i.e. emission from the cropland. The upright broken line means 0:00.

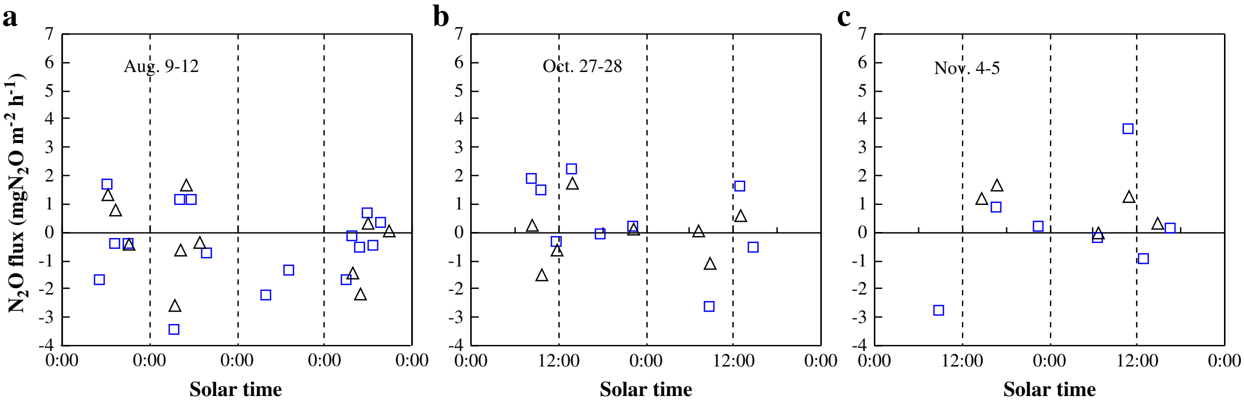

Fig. 4. N_2O fluxes measured by the energy balance method in maize (a) and wheat (b, c) fields in 1997. Square: two layer observation; Triangle: four layer observation. Positive sign indicates upward flux, i.e. emission from the cropland.

flux (R_n-G) in the maize field and the wheat field, respectively (Fig. 7). The difference between F_a and F_b may be caused by the imbalance of energy. The status of energy closure can be described by energy balance ratio (EBR) as follows:

$$\mathrm{EBR} = \frac{H + \lambda E}{R_n - G} \tag{10}$$

Since EBR obtained by the aerodynamic method was unstable in the evening, early morning and late afternoon, the impact of EBR on N_2O flux was only studied in the daytime when solar radiation was larger than 100 W m^{-2}. When EBR was small, the ratio of F_a to F_b changed largely and no obvious relationship between F_a/F_b and EBR could be found (data not shown). When EBR was bigger than 0.3, F_a/F_b increased linearly with EBR in maize and wheat fields. The slope of F_a/F_b to EBR was closed to 1 (Fig. 8a). Good linear relationship between F_a/F_b and EBR showed a possible way to improve the quality of daytime N_2O flux by EBR approach.

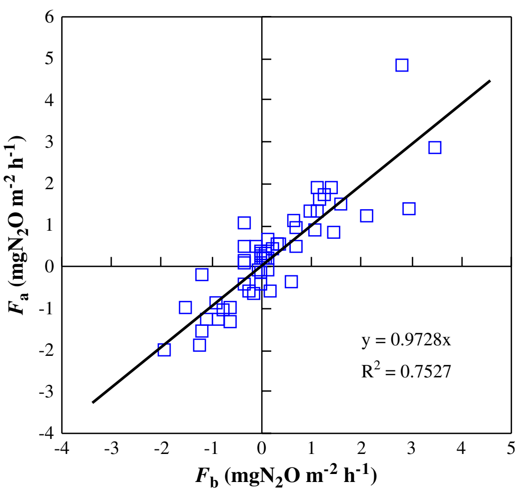

Fig. 5. Comparison between N_2O fluxes measured by the aerodynamic method and the BREB method in wheat and maize fields.

Similar phenomena were found in eddy covariance measurements for CO_2 flux. Since underestimation of CO_2 flux may attribute to lack of energy closure, it was suggested that CO_2 flux could be simply scaled by the proportion of energy imbalance (Yamamoto et al., 1999; Twine et al., 2000; Saigusa et al., 2002). However, not all the causes of energy imbalance will affect trace gas fluxes. Wilson et al. (2002) concluded the reasons for lack of closure of the surface energy budget involved: (1) mismatch of the source areas between turbulence energy flux and available energy flux; (2) neglected energy sinks; (3) instrument bias; (4) high/low frequency loss; and (5) advection. Only the last three reasons may affect trace gas fluxes.

Generally, energy closure was better at high wind velocity (Mahrt, 1998). During observation periods, most of flux measurements were conducted under low wind conditions to get more available N_2O concentration gradient. The imbalance of energy obtained by the aerodynamic method was related to low wind speed. Both EBR and F_a/F_b were small at low friction velocity (u_*). They enhanced with increasing u_* and became more stable when u_* was bigger than 0.3 (Fig. 8b). It was suggested that lack of fully developed turbulence at low u_* was partly

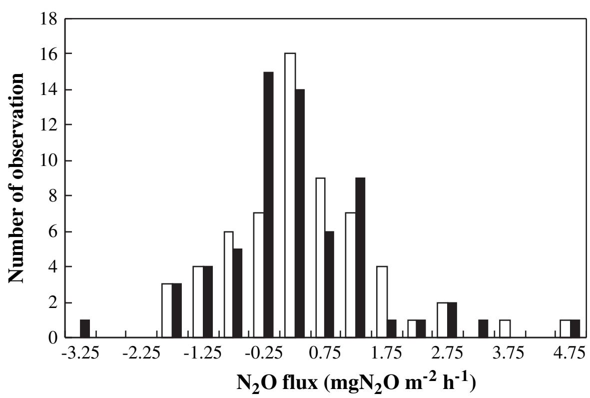

Fig. 6. Frequency distribution of N_2O fluxes measured by the aerodynamic method (empty column) and BREB method (black column) in a wheat/maize rotation system.

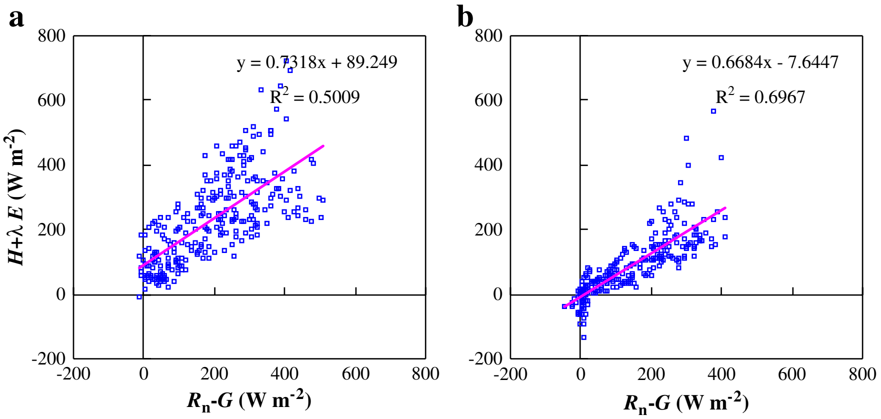

Fig. 7. Closure of available energy ($R_n - G$) and turbulent energy ($H + \lambda E$) measured by aerodynamic method in maize (a) and wheat (b) fields.

responsible for lack of energy closure (Blanken et al., 1997), which result in underestimation of F_a.

On the other hand, when energy imbalance for aerodynamic measurements arise from different source areas between available energy flux and turbulence energy flux, forcing energy closure to estimate turbulence flux (BREB method) may lead to large bias on F_b. Under this situation, we could not consider F_a wrong for its lack closure of energy, and furthermore, revise it by the proportion of energy imbalance. When F_b is used as a reference for F_a, correcting F_a by EBR approach depends on the accurate measurement for available energy flux. Mismatch of the source areas between turbulence energy flux and available energy flux may have little influence on observed energy balance in a homogeneous surface, but have a significant impact on energy closure in a heterogeneous surface. In our experiments, the cropland was a homogeneous surface for most of time. F_b was generally a reliable reference for F_a and the imbalance of energy would lead to large bias in the estimation of F_a.

3.5. Negative N_2O flux

In our study, many negative N_2O fluxes were obtained by aerodynamic and BREB methods in maize and wheat fields even after fertilization (Figs. 3 and 4). It is similar to the phenomenon reported by Skiba et al. (1996). All negative flux by aerodynamic method and most of negative flux by BREB method were due to downward N_2O gradient (Fig. 9), not due to the gradients of temperature, humidity or wind speed. Few negative flux obtained by BREB method may due to advection or storage effects. In gradient observation, the area of footprint varies with the change of wind speed and direction. High spatial variability of soil N_2O emission (Ambus and Christensen, 1994) and variable wind led to a great temporal variability of N_2O flux measured by the micrometeorological methods. To get more available N_2O concentration difference, gas-sampling time in our experiment was 10 min. Short average time would bring to large temporal variation of N_2O flux. Laville et al. (1999) reported that the temporal variation of N_2O flux reduced obviously when average time changed from 15 min to half hour. Average time prolonged from 10 min to 30 min or more might smooth the extreme values away and reduce the temporal variability of N_2O flux. If mean flux were positive, most of negative fluxes would disappear with the reducing temporal variability.

Di Marco et al. (2004) found many negative fluxes although the temporal variation of N_2O flux declined after the measurement time scale changed from an hour to

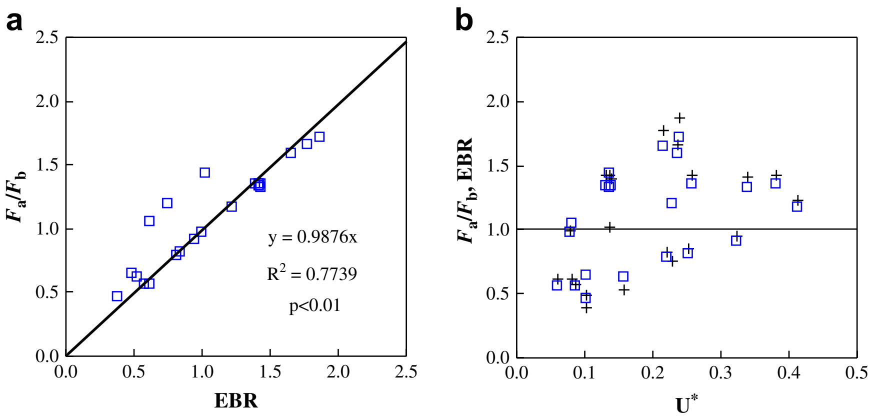

Fig 8. The relationship between F_a/F_b and EBR (a), F_a/F_b and EBR changed with frection velocity (u_*) (b) in wheat and maize fields. F_a/F_b (square) is the ratio of N_2O fluxes measured by aerodynamic method and BREB method. EBR (plus) is energy balance ratio calculated by aerodynamic method.

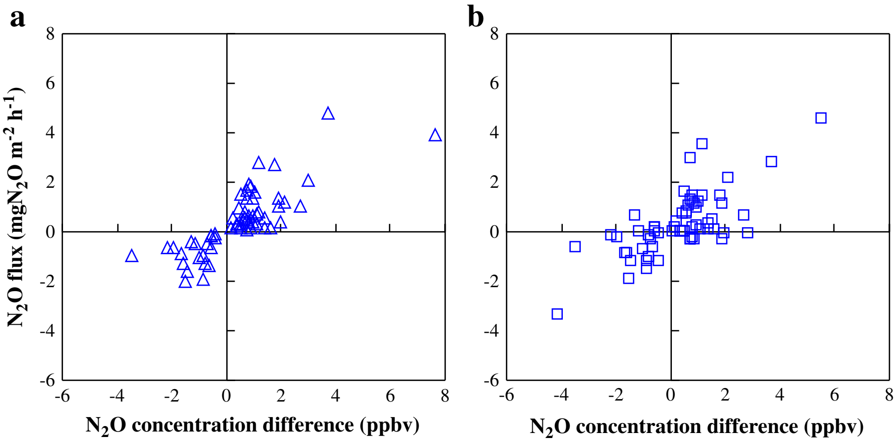

Fig. 9. Relationship between N_2O concentration difference and N_2O flux measured by the aerodynamic (a) and BREB method (b) in wheat and maize fields.

a day. In our study, a mean daytime N_2O flux of $-0.753\ mg\ N_2O\ m^{-2}\ h^{-1}$ was obtained in maize field in August 9–12, 1997 (Table 1). It could not be simply explained by the change of time scale. Based on two years' observation in grassland, Neftel et al. (2007) reported that nearly half of the eddy N_2O flux was negative. It may attribute to soil uptake because negative N_2O flux was also found in corresponding chamber-based measurements. Some chamber-based measurements showed considerable N_2O sinks (-3.2–$-17.4\ \mu gN_2O\ m^{-2}\ h^{-1}$) during sink periods in grassland (Ryden, 1981; Donoso et al., 1993; Flechard et al., 2005) and forest (Donoso et al., 1993; Papen et al., 2001). N_2O absorption by soils is a microbial process involving reduction of N_2O to N_2. It is promoted by anaerobic condition and by organic substances that facilitate growth of soil microorganisms, and it is retarded by nitrate (Blackmer and Bremner, 1976). Wet condition generally benefits to soil N_2O consumption. However, in our study, negative mean N_2O flux was observed in maize field under dry condition. Similar phenomena were found in savannah and bare soil during the dry season (Donoso et al., 1993; Wagner-Riddle et al., 1996). The mechanism of N_2O consumption by dry soils is not fully understood by now.

4. Conclusions

In our experiments, the mean precision of two repeated GC analyses for N_2O concentration achieved to 0.27–0.46 ppbv, which could resolve N_2O concentration differences in a low range of 0.39–0.65 ppbv. This enables us to measure N_2O flux using flux-gradient methods coupled with GC analysis. During observation periods, N_2O flux ranged from -4.41 to $4.84\ mg\ N_2O\ m^{-2}\ h^{-1}$ in maize field, and from -2.82 to $3.59\ mg\ N_2O\ m^{-2}\ h^{-1}$ in wheat field. When gradient observation changed from two layers to four layers, the temporal variation of N_2O flux reduced but the mean value changed less. Many negative N_2O flux was found in wheat and maize fields even after fertilization. Nearly all the negative N_2O fluxes were caused by negative N_2O concentration differences. During four days' observation in maize field, a mean N_2O flux of $-0.753\ mg\ N_2O\ m^{-2}\ h^{-1}$ was found in the daytime and could not be simply attributed to the temporal variation of N_2O flux. N_2O flux determined by the aerodynamic method (F_a) and the Bowen ratio/energy balance method (F_b) were in agreement statistically. The ratio of F_a to F_b increased linearly with EBR obtained by the aerodynamic method in the daytime when EBR was larger than 0.3. It is the first time to describe the impact of energy closure on N_2O flux quantitatively. The results may help improve data quality by EBR approach. Limited by the analytical precision of GC, N_2O flux measured by flux gradient methods were only conducted under low wind conditions or after fertilization. With the development of high-resolution and fast-response trace gas analysis system (e.g. TDLAS and FTIR), the analytical precision and efficiency for N_2O concentration were improved largely and make it possible to carry out long-term N_2O flux measurement at field scales.

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