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## An improved GC-ECD method for measuring atmospheric N<sub>2</sub>O

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### Abstract

Gas chromatography equipped with an electron capture detector (GC-ECD) has been widely used for measuring atmospheric N<sub>2</sub>O, but nonlinear response and the influence of atmospheric CO<sub>2</sub> have been recognized as defects for quantification. An original GC-ECD method using N<sub>2</sub> as carrier gas was improved by introducing a small flow rate of CO<sub>2</sub> makeup gas into the ECD, which could well remedy the above defects. The N<sub>2</sub>O signal of the improved method was 4-fold higher than that of the original method and the relative standard deviation was reduced from > 1% to 0.31%. N<sub>2</sub>O concentrations with different CO<sub>2</sub> concentrations (172.2 × 10<sup>-6</sup>–1722 × 10<sup>-6</sup> mol/mol) measured by the improved GC-ECD method were in line with the actual N<sub>2</sub>O concentrations. However, the N<sub>2</sub>O concentrations detected by the original method were largely biased with a variation range of -4.5%~7%. The N<sub>2</sub>O fluxes between an agricultural field and the atmosphere measured by the original method were greatly overestimated in comparison with those measured by the improved method. Good linear correlation ( $R^2 = 0.9996$ ) between the response of the improved ECD and N<sub>2</sub>O concentrations (93 × 10<sup>-9</sup>–1966 × 10<sup>-9</sup> mol/mol) indicated that atmospheric N<sub>2</sub>O could be accurately quantified via a single standard gas. Atmospheric N<sub>2</sub>O concentrations comparatively measured by the improved method and a high precision GC-ECD method were in good agreement.

**Key words:** N<sub>2</sub>O; GC-ECD; CO<sub>2</sub>; exchange flux; method comparison

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### Introduction

Nitrous oxide (N<sub>2</sub>O) has attracted considerable attention because of its great influence on the global environment. Although the atmospheric concentration of N<sub>2</sub>O is about three orders of magnitude lower than that of CO<sub>2</sub>, the radiative forcing of N<sub>2</sub>O is about 298 times greater than that of CO<sub>2</sub> on the 100 year scale (IPCC, 2007a), and thus N<sub>2</sub>O has been considered as one of the most important greenhouse gases. Additionally, N<sub>2</sub>O plays an important role in ozone depletion in the stratosphere (Crutzen, 1981; Cicerone, 1987). Agricultural fields have been recognized as the most important source for atmospheric N<sub>2</sub>O (Bouwman et al., 1995; Olivier et al., 1998), with an emission strength of 0.11–6.3 Tg N/yr (Mosier et al., 1998; Bouwman et al., 2002; Yan et al., 2003). However, the current global estimation of the flux strength from agricultural fields still possesses great uncertainty, ranging from -61% to 171% of the mean emission (IPCC, 2007b), which is not only derived from the temporal-spatial variations of N<sub>2</sub>O fluxes but also inevitably originates from the limitations of

current flux measurements and analytical methods for N<sub>2</sub>O determination from soil or/and soil-plant systems (Zheng et al., 2008).

The available measurements for N<sub>2</sub>O fluxes from agricultural fields are static chamber and micrometeorological techniques. Static chambers are low-cost and easy-to-operate (Wang, 1999), and have an advantage in N<sub>2</sub>O measurement from small fields with different crops and plots under different treatments (Smith et al., 1994), and have been widely used as N<sub>2</sub>O flux measurements for decades, e.g. the current data of IPCC for N<sub>2</sub>O emission factors mainly originated from static chamber measurements (Bouwman, 1996; Laville et al., 1999). The responses of various GC-ECD instruments are usually assumed to be linearly correlated with N<sub>2</sub>O concentrations, and single point calibration is adopted for quantification (Maljanen et al., 2003; Ding et al., 2007; Ussiri et al., 2009). However, several researchers found a nonlinear correlation between the responses of GC-ECD and N<sub>2</sub>O concentrations (Hall et al., 2007; Fang et al., 2010), and hence this quantification method would result in an underestimation of N<sub>2</sub>O emission. Even so, most studies still use the one point calibration method for measuring

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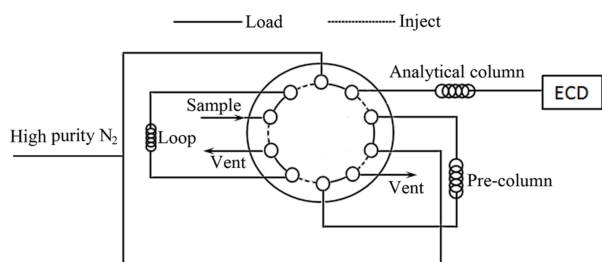
$\text{N}_2\text{O}$  flux because of its convenience for analyzing a large number of samples.

A GC-ECD method using high purity  $\text{N}_2$  as carrier gas (hereafter designated as the DN method) has been widely used to measure  $\text{N}_2\text{O}$  both in the field and laboratory (Loftfield et al., 1997; Wang et al., 2005; Lamers et al., 2007; Scheer et al., 2008; Gomes et al., 2009). Besides nonlinear response, large uncertainties in the data from the DN method have recently been found, which was mainly ascribed to the strong influence of  $\text{CO}_2$  concentration on the  $\text{N}_2\text{O}$  signal (Zheng et al., 2008; Wang et al., 2010). The World Meteorological Organization Global Atmosphere Watch (WMO/GAW, 2003) recently reported that the DN method can be greatly improved by introducing  $\text{CO}_2$  as makeup gas into the ECD (hereafter designated as the DN- $\text{CO}_2$  method) and can even provide better precision and stability than a GC-ECD method using an argon-methane mixture (5%  $\text{CH}_4$  in Ar) as carrier gas (the method hereafter designated as the AM method). Hall et al. (2007) also confirmed that the DN- $\text{CO}_2$  method could perform exceptionally well in detecting atmospheric  $\text{N}_2\text{O}$  concentrations in comparison with the AM method over three years. Although the reliability of the DN- $\text{CO}_2$  method has been confirmed for atmospheric  $\text{N}_2\text{O}$  measurements, there are still no reports about the possible influence of extremely high  $\text{CO}_2$  concentrations in the air samples on  $\text{N}_2\text{O}$  flux measurements. The response of the GC-ECD to  $\text{N}_2\text{O}$  concentration for the DN- $\text{CO}_2$  method also needs to be investigated in order to more accurately quantify atmospheric  $\text{N}_2\text{O}$ . Therefore, in this study, a series of comparisons among the DN, AM and DN- $\text{CO}_2$  methods were conducted to verify whether the DN- $\text{CO}_2$  method is reliable for  $\text{N}_2\text{O}$  flux measurements.

## 1 Materials and methods

### 1.1 Instrument introduction

$\text{N}_2\text{O}$  concentrations were analyzed by a GC-ECD system (Model SP3410, Beijing Analytical Instrument Factory, China). The schematic diagram of the GC-ECD system is shown in **Fig. 1**. High purity  $\text{N}_2$  was used as carrier gas with a flow rate of 30 mL/min. The gas sample was loaded into a 2-mL loop connected to a 10-port valve, and was blown into separation columns by switching the 10-



**Fig. 1** Schematic diagram of GC system.

port valve. There were two identical separation columns (2 m × 4 mm) packed with Porapak Q (80–100 mesh) called the pre-column and analytical column, respectively. The pre-column could inhibit  $\text{H}_2\text{O}$  in the air sample from elution into the analytical column and  $\text{H}_2\text{O}$  could be back-flushed when the 10-port valve was switched back. The temperatures for both GC oven and injector port were maintained at 72°C.

### 1.2 Laboratory experiments

#### 1.2.1 Optimizing $\text{CO}_2$ makeup gas flow rate (Exp 1)

A  $\text{CO}_2$  makeup gas ( $979 \times 10^{-6}$  mol/mol  $\text{CO}_2$  in  $\text{N}_2$ ) was introduced into the ECD through downstream of the analytical column with different flow rates (0, 3, 6, 8, 10 and 12 mL/min). The ECD temperature was set at 390°C and  $\text{N}_2\text{O}$  standard gas ( $358 \times 10^{-9}$  mol/mol in air, Center of Standard Reference Materials, China) was analyzed under different  $\text{CO}_2$  makeup gas flow rates.

#### 1.2.2 Optimizing ECD temperature (Exp 2)

The  $\text{N}_2\text{O}$  standard gas was analyzed at different ECD temperatures (250°C, 280°C, 310°C, 340°C, 370°C and 390°C) with fixed  $\text{CO}_2$  makeup gas flow rate.

#### 1.2.3 Measurements of $\text{N}_2\text{O}$ samples with different $\text{CO}_2$ concentrations (Exp 3)

The experiment was designed to evaluate the possible influence of  $\text{CO}_2$  on the measurement of  $\text{N}_2\text{O}$ . A series of gas samples were prepared by mixing  $\text{CO}_2$  and  $\text{N}_2\text{O}$  standard gases in high purity  $\text{N}_2$  with concentration ranges of  $172.2 \times 10^{-6}$ – $1722 \times 10^{-6}$  mol/mol for  $\text{CO}_2$  and of  $351 \times 10^{-9}$ – $357.3 \times 10^{-9}$  mol/mol for  $\text{N}_2\text{O}$ . The prepared samples (each sample in triplicate) were analyzed by DN and DN- $\text{CO}_2$  methods, respectively.

#### 1.2.4 Responses of the DN and DN- $\text{CO}_2$ methods to $\text{N}_2\text{O}$ concentrations (Exp 4)

The responses of the DN and DN- $\text{CO}_2$  methods to  $\text{N}_2\text{O}$  were checked under 9 concentrations ( $103 \times 10^{-9}$ – $2064 \times 10^{-9}$  mol/mol for DN method;  $93 \times 10^{-9}$ – $1966 \times 10^{-9}$  mol/mol for DN- $\text{CO}_2$  method) prepared by dilution of a standard  $\text{N}_2\text{O}$  gas of  $109.78 \times 10^{-6}$  mol/mol in  $\text{N}_2$  (Center of Standard Reference Materials, China).

#### 1.2.5 Diurnal variation of atmospheric $\text{N}_2\text{O}$ (Exp 5)

Atmospheric  $\text{N}_2\text{O}$  samples were collected from 7:30 to 21:00 at intervals of 1.5 hr by Silonite canister (3.2 L, Entech instruments, Inc. USA) on November 27 and December 9 in 2011, respectively. The  $\text{N}_2\text{O}$  concentrations collected on 27 November were analyzed by the DN and DN- $\text{CO}_2$  methods developed in our laboratory, and the samples collected on 9 December were measured by the DN- $\text{CO}_2$  and AM methods, respectively. The AM method (Agilent 6890N, Agilent Technologies, USA) has been being used to measure the background concentration of atmospheric  $\text{N}_2\text{O}$  in the Key Laboratory for Atmospheric



Chemistry, Chinese Academy of Meteorological Sciences, and the detailed information on the method was described by Fang et al. (2010). The precision of the AM method for atmospheric N<sub>2</sub>O measurement was  $\pm 0.2 \times 10^{-9}$  mol/mol and the coefficient of variation (CV) was about 0.5%.

### 1.3 Flux experiments (Exp 6)

The flux experiments were conducted in a winter wheat (*Triticum aestivum* L.) and summer maize (*Zea mays* L.) rotation field. The field lies in Wangdu County, Hebei Province, China (38°71'N, 115°15'E), and it belongs to a typical region of the North China Plain. The detailed information on the soil properties in this field was described in our previous studies (Zhang et al., 2011, 2012).

Two field measurements were carried out during the winter wheat growing season on 9 March 2010 and during the maize growing season from 30 August to 11 September in 2011. The N<sub>2</sub>O fluxes in these two experiments were both investigated by the static chamber method. N<sub>2</sub>O concentrations were analyzed by the DN and DN-CO<sub>2</sub> methods, respectively. N<sub>2</sub>O fluxes were calculated from the slopes of the linear correlations between the N<sub>2</sub>O concentrations and time accumulated in the static chambers, and the correlation coefficients ( $R^2$ ) were always larger than 0.90 for the DN-CO<sub>2</sub> method.

### 1.4 Statistical analysis

The data analysis was performed using SPSS 13.0 software (SPSS Inc., Chicago, USA) and Origin 8.0 (Origin Lab Corporation, USA).

## 2 Results and discussion

### 2.1 Influence of CO<sub>2</sub> makeup gas on the ECD signals of N<sub>2</sub>O

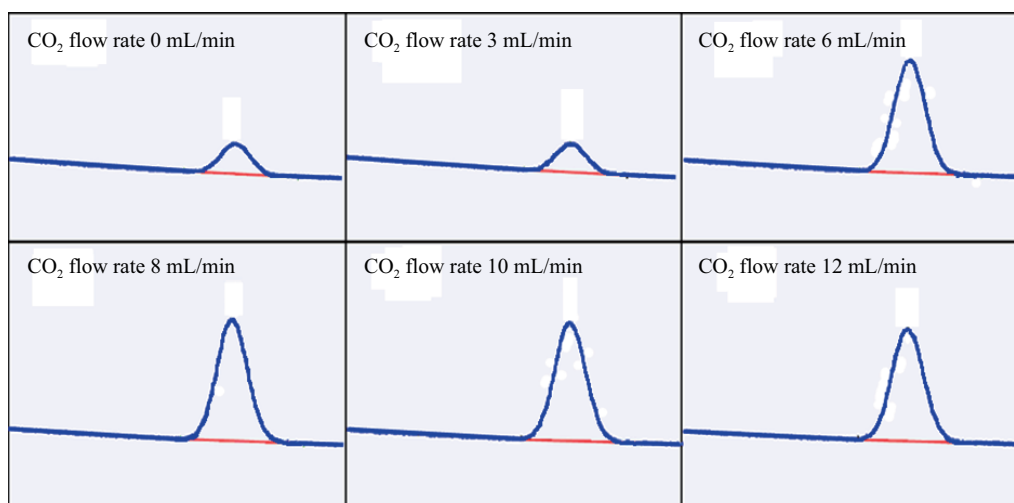
The results of Exp 1 are shown in **Fig. 2**. As illustrated in **Fig. 2**, the N<sub>2</sub>O signal was clearly enlarged when the

CO<sub>2</sub> flow rate increased from 0 to 8 mL/min, and almost remained steady when CO<sub>2</sub> flow rate exceeded 8 mL/min. This phenomenon was similar to that obtained by Wang et al. (2010), who reported that the N<sub>2</sub>O signal remained stable when the CO<sub>2</sub> concentration was larger than  $400 \times 10^{-6}$  mol/mol. The N<sub>2</sub>O signal (peak height) of the DN-CO<sub>2</sub> method with CO<sub>2</sub> flow rate of 8 mL/min was 4-fold higher than that of the DN method (with CO<sub>2</sub> flow rate of 0 mL/min). Based on the negative peak of CO<sub>2</sub>, Wang et al. (2010) ascribed the amplification of the N<sub>2</sub>O signal to the increment of electron abundance induced by introducing CO<sub>2</sub> makeup gas into the ECD. However, we found the ECD baseline voltage increased sharply after introducing CO<sub>2</sub> makeup gas (**Fig. 3**), indicating stronger N<sub>2</sub>O signal with less electron abundance. The specific reason for the increase in N<sub>2</sub>O signal caused by introducing CO<sub>2</sub> makeup gas still needs further investigation.

### 2.2 Influence of ECD temperature on signals of N<sub>2</sub>O and CO<sub>2</sub>

The influence of ECD temperature on signals of N<sub>2</sub>O and CO<sub>2</sub> was also tested under the CO<sub>2</sub> makeup gas flow rate of 8 mL/min (**Fig. 4**). It is evident (**Fig. 4**) that N<sub>2</sub>O signals ( $y$ ) increased with elevated ECD temperature ( $x$ ), exhibiting an exponential correlation relationship between the ECD temperature and the N<sub>2</sub>O signal ( $y = -1731.5 + 2520\exp((x - 240.3)/83.8)$ ,  $R^2 = 0.996$ ,  $n = 6$ ). Considering the ECD upper limit temperature of 400°C, the detector temperature was finally set to 390°C for N<sub>2</sub>O measurements. In contrast, CO<sub>2</sub> signals exhibited a reverse trend compared with N<sub>2</sub>O signals, and negative peak occurred when the ECD temperature was above 370°C (**Fig. 4**), which was in good agreement with the finding of Wang et al. (2010), who pointed out that the electron capture process of N<sub>2</sub>O was an endothermic reaction while the electron capture mechanism of CO<sub>2</sub> was an exothermic reaction.

The variation coefficient for analyzing N<sub>2</sub>O under the above-optimized conditions (the flow rate of the CO<sub>2</sub>



**Fig. 2** Chromatograph signals of N<sub>2</sub>O standard gas ( $358 \times 10^{-9}$  mol/mol of N<sub>2</sub>O/air) in response to different CO<sub>2</sub> flow rates.

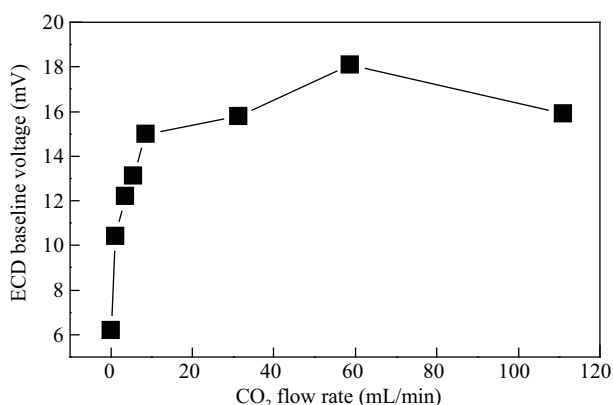


Fig. 3 ECD baselines under different CO<sub>2</sub> makeup gas flow rates.

makeup gas was 8 mL/min and ECD temperature was 390°C) was less than 0.31% based on the reproducibility of a N<sub>2</sub>O standard gas ( $358 \times 10^{-9}$  mol/mol) within 9 hours. The lowest detection limit of N<sub>2</sub>O was about  $8.5 \times 10^{-9}$  mol/mol, and the lowest detectable flux was 0.57 ng N/(m<sup>2</sup>·sec) when chamber height was 90 cm.

### 2.3 Comparisons between the DN and DN-CO<sub>2</sub> methods for measuring N<sub>2</sub>O under different CO<sub>2</sub> concentrations

The results of Exp 3 are shown in Fig. 5. Compared with the actual N<sub>2</sub>O concentration (calculated from dilution), the DN method significantly under- and overestimated the N<sub>2</sub>O concentrations when CO<sub>2</sub> concentrations in the air samples were below and above  $500 \times 10^{-6}$  mol/mol, with a range of -4.5%~7%. The result agreed well with the finding of Zheng et al. (2008), who pointed out that the CO<sub>2</sub> concentration in air samples had an important influence on N<sub>2</sub>O measurement by the DN method. For the DN-CO<sub>2</sub> method, the N<sub>2</sub>O concentrations measured were in good agreement with the N<sub>2</sub>O actual values within a small variation range of -0.73%~0.45%, indicating that the influence of CO<sub>2</sub> in the air samples on the N<sub>2</sub>O signal was negligible. The separation columns used in this study can efficiently separate CO<sub>2</sub> and N<sub>2</sub>O with retention times

of ca. 4.8 min and ca. 5.8 min, respectively. The influence of CO<sub>2</sub> in the air samples on the N<sub>2</sub>O signal measured by the DN method was probably ascribed to the effect of the residual CO<sub>2</sub> component after elution from the column into the ECD. To check the effect of residual CO<sub>2</sub> on the N<sub>2</sub>O measurement, an additional experiment was also conducted using N<sub>2</sub> as a makeup gas for the DN method. In line with the results of the DN-CO<sub>2</sub> method, no influence of CO<sub>2</sub> on the N<sub>2</sub>O signal was found.

Due to soil or plant respiration, CO<sub>2</sub> concentrations in the air samples collected from a static chamber during flux measurements usually vary over a very large range ( $360 \times 10^{-6}$  to  $2000 \times 10^{-6}$  mol/mol, our unpublished data), and N<sub>2</sub>O concentrations measured by the DN method (without makeup gas) must suffer from serious influence by CO<sub>2</sub>, and the fluxes derived should be suspected (Zheng et al., 2008). The lack of influence of CO<sub>2</sub> on the N<sub>2</sub>O signal of the DN-CO<sub>2</sub> method confirmed that the DN-CO<sub>2</sub> method is a reliable method for N<sub>2</sub>O flux measurements.

### 2.4 Response of the DN-CO<sub>2</sub> method to N<sub>2</sub>O concentrations

Several studies have found a non-linear response for GC-ECD to N<sub>2</sub>O concentrations (Hall et al., 2007; Fang et al., 2010), which would result in large uncertainty for the quantification of atmospheric N<sub>2</sub>O when using a single-point calibration with a standard N<sub>2</sub>O gas, especially for N<sub>2</sub>O flux measurements, because the N<sub>2</sub>O concentration would accumulate from about  $310 \times 10^{-9}$  mol/mol to  $10^{-6}$  mol/mol. To ensure high precision measurements of atmospheric N<sub>2</sub>O, multi-point calibration has been used for global background N<sub>2</sub>O measurements (Hall et al., 2007; Fang et al., 2010), which would result in lower sampling frequency and extra cost for standard gases due to the need for frequent calibration to take into account the fluctuation of the ECD. The responses of the DN method and DN-CO<sub>2</sub> method developed in this study to different N<sub>2</sub>O concentrations were also tested. Considering the frequent fluctuation of the ECD, each N<sub>2</sub>O concentration prepared by diluting the standard N<sub>2</sub>O gas of  $109.78 \times 10^{-6}$  mol/mol

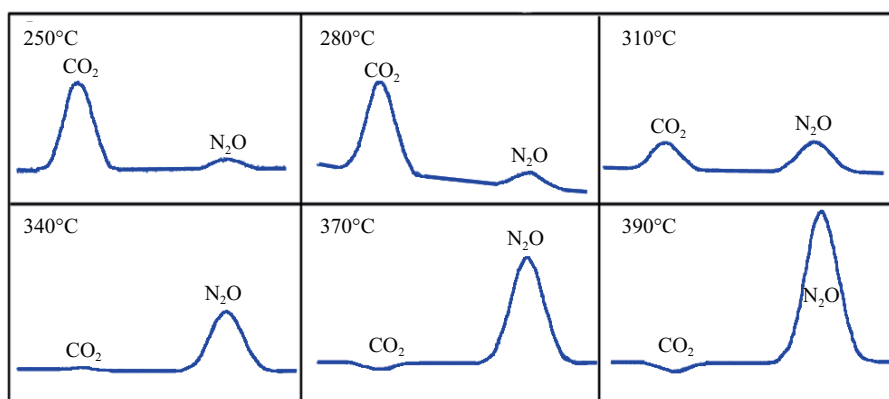
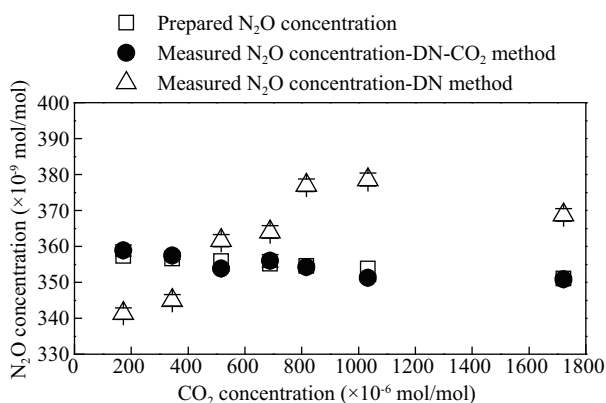
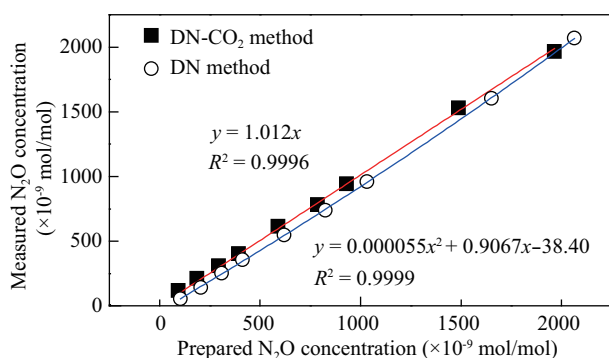


Fig. 4 Chromatograph signals of CO<sub>2</sub> and N<sub>2</sub>O in response to different ECD temperatures for the DN-CO<sub>2</sub> method at CO<sub>2</sub> flow rate of 8 mL/min.



**Fig. 5** Influence of different CO<sub>2</sub> concentrations on N<sub>2</sub>O signals for the DN and DN-CO<sub>2</sub> methods. Error bars given as standard deviations of mean with  $n = 3$ .



**Fig. 6** Responses of ECD to different N<sub>2</sub>O concentrations by DN and DN-CO<sub>2</sub> methods.

was quantified by the standard N<sub>2</sub>O gas of  $301 \times 10^{-9}$  mol/mol. As shown in **Fig. 6**, a non-linear response of the DN method was evident, whereas a very good linear correlation ( $R^2 = 0.9996$ , slope = 1.0123) between the response of the DN-CO<sub>2</sub> method and N<sub>2</sub>O concentrations ( $93 \times 10^{-9}$ – $1966 \times 10^{-9}$  mol/mol) was found, indicating that single point calibration is sufficiently reliable to quantify N<sub>2</sub>O concentration by the DN-CO<sub>2</sub> method.

The recovery of our improved method was in the range of 99.5% to 129% when the N<sub>2</sub>O concentrations varied from  $93 \times 10^{-9}$  to  $1966 \times 10^{-9}$  mol/mol, and the mean recovery was 107%.

### 2.5 Comparisons among the DN, DN-CO<sub>2</sub> and AM methods for measuring atmospheric N<sub>2</sub>O concentrations

Atmospheric N<sub>2</sub>O concentrations comparatively measured by the DN and DN-CO<sub>2</sub> methods, as well as the DN-CO<sub>2</sub> and AM methods, are illustrated in **Fig. 7**. Compared with the DN-CO<sub>2</sub> method (**Fig. 7a**), N<sub>2</sub>O concentrations measured by the DN method varied greatly during the one day course, with variation range of  $293.2 \times 10^{-9}$ – $509.6 \times 10^{-9}$  mol/mol. Both the N<sub>2</sub>O concentrations and the error bars measured by the DN method implied that the method is not reliable for atmospheric N<sub>2</sub>O measurements. The atmospheric N<sub>2</sub>O concentrations measured by the DN-CO<sub>2</sub>

method on 9 December (**Fig. 7b**) were in the range of  $322.7 \times 10^{-9}$ – $329.3 \times 10^{-9}$  mol/mol, which was in good agreement with the range ( $324.6 \times 10^{-9}$ – $326.6 \times 10^{-9}$  mol/mol) measured by the AM method. Compared with the AM method, the precision of the DN-CO<sub>2</sub> method developed in this study is still poor for atmospheric N<sub>2</sub>O measurement, exhibiting larger variation and error bars.

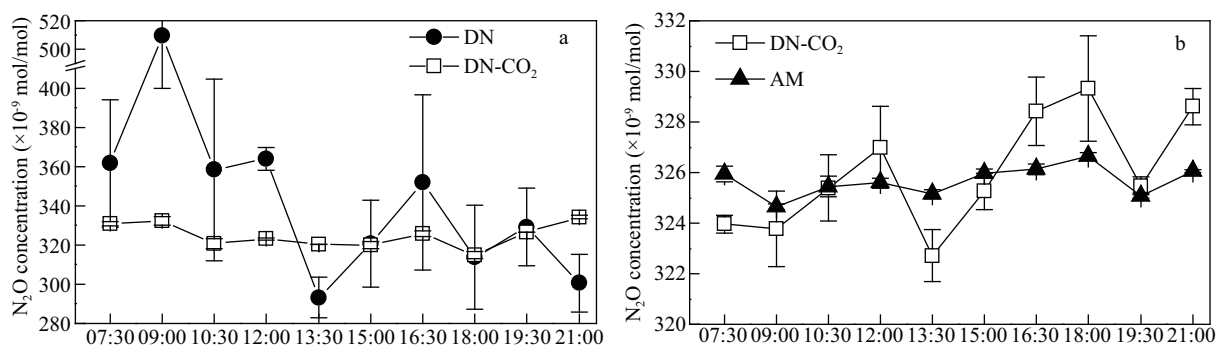
### 2.6 N<sub>2</sub>O flux measurements

N<sub>2</sub>O fluxes measured by the DN and DN-CO<sub>2</sub> methods are shown in **Fig. 8**. Both the variation trend and values of N<sub>2</sub>O fluxes (**Fig. 8a**) measured by the DN and DN-CO<sub>2</sub> methods were inconsistent during the day with low N<sub>2</sub>O fluxes. The average N<sub>2</sub>O flux measured by the DN method for the day was 8.82 ng N/(m<sup>2</sup>·sec), which was about 153% higher than that ( $3.49$  ng N/(m<sup>2</sup>·sec)) measured by the DN-CO<sub>2</sub> method. Although the variation trends of N<sub>2</sub>O fluxes measured by the DN and DN-CO<sub>2</sub> methods after fertilization (**Fig. 8b**) were similar, the N<sub>2</sub>O fluxes measured by the DN method were irregularly biased from the fluxes measured by the DN-CO<sub>2</sub> method, e.g., the N<sub>2</sub>O flux measured by the DN method was occasionally 5-fold higher than that by DN-CO<sub>2</sub> method on September 6, 2011. The average N<sub>2</sub>O flux measured by the DN method was 113 ng N/(m<sup>2</sup>·sec), which was 49% higher than that by the DN-CO<sub>2</sub> method (76 ng N/(m<sup>2</sup>·sec)). Overestimation of N<sub>2</sub>O emission has been also found using the DN method in comparison with DN-Ascarite and AM methods (Zheng et al., 2008). As mentioned above, the large bias of N<sub>2</sub>O fluxes measured between the DN and the DN-CO<sub>2</sub> methods could be ascribed to the influence of CO<sub>2</sub> concentration on N<sub>2</sub>O measurements for the DN method. Considerable portions of N<sub>2</sub>O flux studies have used the DN method (without makeup gas) and the data obtained should be suspected (Zheng et al., 2008; Wang et al., 2010).

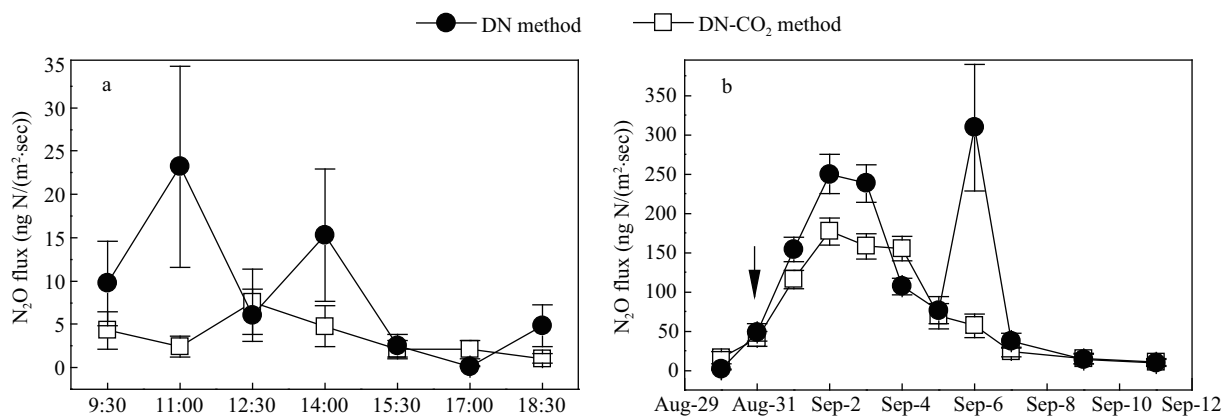
In summary, the influence of CO<sub>2</sub> on N<sub>2</sub>O measurements was found to be very serious for the DN method, but it was negligible for the DN-CO<sub>2</sub> method. Both the atmospheric N<sub>2</sub>O concentrations and N<sub>2</sub>O fluxes measured by the DN method were substantially biased from the values measured by the DN-CO<sub>2</sub> method, whereas the atmospheric N<sub>2</sub>O concentrations comparatively measured using the DN-CO<sub>2</sub> and AM methods were in good agreement. The negligible influence of CO<sub>2</sub> and the good linear correlation between the GC-ECD response and N<sub>2</sub>O concentration confirmed that the DN-CO<sub>2</sub> method is reliable for atmospheric N<sub>2</sub>O measurement.

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**Fig. 7** Atmospheric N<sub>2</sub>O concentrations by DN, DN-CO<sub>2</sub> and AM methods on 27 November (a) and 9 December 2011 (b). Error bars given as standard deviations of mean with  $n = 3$ .



**Fig. 8** N<sub>2</sub>O fluxes measured by the DN and DN-CO<sub>2</sub> methods. (a) diurnal variation of N<sub>2</sub>O fluxes; (b) N<sub>2</sub>O fluxes after fertilization. Arrow shows fertilization. Error bars given as standard deviations.

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