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A dual dynamic chamber system based on IBBCEAS for measuring fluxes of nitrous acid in agricultural fields in the North China Plain



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ABSTRACT

A dual dynamic chamber system combined with incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) was first developed to measure nitrous acid (HONO) emission fluxes from agricultural fields in the North China Plain. The concentrations of HONO were measured with two IBBCEAS instruments in the sample and blank chambers, respectively. To ensure the accuracy and reliability of flux measurement, before the dynamic chamber system was deployed in an agricultural field, the correlation and accuracy of the two IBBCEAS instruments were tested, and the mixing uniformity of the gas in the chamber was verified. Within a week after fertilization, the observed HONO flux exhibited a pronounced diurnal variation profile with a maximum of 20.25 ng N m⁻² s⁻¹ at noontime and a minimum of -0.86 ng N m⁻² s⁻¹ in the early morning, one order of magnitude higher than the flux observed in previously reported literature from fields. During this period, the concentrations of HONO in both of the chambers was higher in the daytime than that nighttime, and the concentration. HONO and NO₂ in the sample chambers showed opposite diurnal profiles. The field observation results suggested that the high HONO flux is mainly from the direct emission of soil rather than from the heterogeneous reaction of NO₂. Agricultural fertilization will affect the balance of the HONO budget, and then affect the atmospheric oxidation in the North China Plain.

1. Introduction

Nitrous acid (HONO) plays an important role in the atmospheric chemistry, which is the primary source of the hydroxyl radical (OH). Recent studies have estimated that the photolysis of HONO contributes up to 80% (Elshorbany et al., 2009; Ren et al., 2006) of the OH production in the early morning. Although HONO is readily photolytic during the daytime, many field campaigns showed the high HONO concentrations were observed during daytime (Elshorbany et al., 2009; Ren et al., 2003; Zhou et al., 2002), which could not be explained by the gas-phase reactions, as follows:

$HONO + hv \rightarrow OH + NO$ ((R1)
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$OH + NO \rightarrow 0$	HONO	(R2)

 $HONO + OH \rightarrow NO_2 + H_2O \tag{R3}$

According to pseudo steady state analysis, the daytime missing sources of HONO were 0.06–4.90 ppbv h^{-1} for rural locations (Acker et al., 2006; Kleffmann, 2005; Li et al., 2012; Ren et al., 2010; Su et al., 2008; Zhou et al., 2002, 2007) and 0.75–3.82 ppbv h⁻¹ for urban locations (Hou et al., 2016; Huang et al., 2017; Spataro et al., 2013; Wang et al., 2017). Field measurements of HONO concentrations at different heights in both urban and rural locations suggested that the ground surface may be a potential HONO source (Kleffmann et al., 2003; VandenBoer et al., 2013; Wong et al., 2011, 2013). The most commonly discussed mechanisms are photochemical heterogeneous reduction of nitrogen dioxide (NO₂) by organic material such as aromatics and humic acids (George et al., 2005; Han et al., 2016; Sosedova et al., 2011; Stemmler et al., 2006) and the photolysis of adsorbed nitric acid and nitrate (Laufs and Kleffmann, 2016; Zhou et al., 2003, 2011), although recent evidence suggested that soil can emit HONO directly, including direct emissions from microbes and nitrite in soil (Maljanen

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et al., 2013; Oswald et al., 2013; Scharko et al., 2015; Su et al., 2011; Weber et al., 2015) and the dynamic process of HONO adsorption and desorption on the soil surface (Donaldson et al., 2014; VandenBoer et al., 2013; Vandenboer et al., 2015).

In order to quantitatively estimate the HONO source strength of soil emissions from farmland, it is significant to measure the exchange flux of HONO between the soil and the atmosphere, which can explain the process of HONO production and loss on the soil surface. To date, the gradient method and relaxed eddy accumulation technique have been the main ways of measuring HONO flux measurement (Laufs et al., 2017; Ren et al., 2011; Stutz et al., 2002; Zhang et al., 2012; Zhou et al., 2011). However, these methods require a highly sensitive and fast response HONO measurement system, which are expensive, and can be affected by chemical transformation during the turbulent transport process (Dijk et al., 2002). Dynamic chamber methods are commonly used to measure the gas exchange between the soil and the atmosphere for NO, and NH₃ (Gut et al., 2002; Ni et al., 2015), which is less costly than other technologies and also suitable for long-term observations. However, to date, the dynamic chamber method has only been used to measure HONO flux in a laboratory environment (Maljanen et al., 2013; Oswald et al., 2013; Scharko et al., 2015; Su et al., 2011; Weber et al., 2015). Laboratory conditions are controllable and the temperature in the chamber is almost constant. However, due to considering the effect of water vapor condensation in the chamber on HONO, the existing dynamic chamber method cannot be applied to make field measurements of HONO flux. To overcome this problem, we developed an improved dynamic chamber method combined with IBBCEAS for measurement of HONO flux in the field.

The North China Plain (NCP) is a very important agricultural region in China. The NCP covers approximately $300,000 \text{ km}^2$ and accounts for approximately one-fourth of national grain production (Changming et al., 2001). Recent studies found that the amount of fertilizer applied in the NCP has reached 600 kg N ha⁻¹ yr⁻¹ or even higher (Xiao-Tang et al., 2007; Zhao et al., 2006), but the nitrogen-use efficiency is low, i.e. less than 30% (Jia et al., 2004; Zhao et al., 2006). Liu et al. (2016) reported that the HONO/NO₂ ratios ranged from 1% to 60% at a rural site in the NCP. Such a large ratio range may indicate a unique HONO generation mechanism. Meanwhile, Tan et al. (2017) reported that the HONO concentration reached 2 ppbv at noon in the NCP when the surrounding farmland was fertilized. Therefore, it is urgent to understand the contribution of agricultural production and soil microbial activities to the formation of HONO. Exploration of the HONO emissions from agricultural fields has become a key scientific issue.

Here, we report a dynamic chamber method based on IBBCEAS to measure the emission flux of HONO, which was first applied to the measurement of HONO flux from farmland in the NCP, and quantitatively shows the contribution of farmland HONO emissions to atmospheric HONO sources, revealing that the N-fertilized soil has very strong HONO emission potential.

2. Materials and methods

2.1. Dynamic chamber system

2.1.1. Description of the dynamic chamber system

The schematic of the dynamic chamber system is shown in Fig. 1. In order to determine the concentration of background HONO in the dynamic chamber and eliminate the possible loss and production of HONO within the chamber, the designed flux measurement system used two dynamic chambers of the same size and structure. One dynamic chamber was serves as the sample chamber, which is embedded in the soil to measure the HONO emission. The other dynamic chamber is a blank chamber, with the only difference from the sample chamber being that the bottom of the blank chamber is sealed with FEP film.

In order to avoid the condensation phenomenon caused by the temperature difference inside and outside the dynamic chamber in high humidity environments, an open top design was adopted to reduce the temperature difference inside and outside the chamber. The overall structure of the dynamic chamber was a cylinder with no bottom and top. In order to avoid ambient air entering the chamber, we appropriately reduce the size of the opening at the top of the chamber. The dynamic chamber had a diameter of 0.3 m and a height of 0.8 m. Therefore, the area of soil covered by dynamic chamber is 0.07065 m^2 . The frame material of the whole chamber was stainless steel, which was coated with an inert PFA coating; the sides of the chamber frame were covered with a transparent FEP film (0.1 mm). To adjust the area of the top of the chamber.

In order to ensure the sample chamber and the blank chamber had the same amount of purge flow, the purging flows of the two chambers were controlled by the flowmeters. The ambient air approximately 1 m above the ground was drawn into the three-way valve by the vacuum pump, and one of the airflows entered the blank chamber; the other air flow entered the sample chamber, the purging rate of both chambers was $3.25 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$, which was controlled by the flowmeters. The gas pipes of the flux measurement system were made of PFA material to reduce gas loss.

2.1.2. Calculation of HONO flux

The measured gas flux follows the mass balance principle of the gas in the chamber (Gao and Yates, 1998; Pape et al., 2009), i.e. when the gas in the dynamic chamber system reaches steady state, the flux of HONO was calculated using the following formula:

$$F_N = \frac{Q}{A} \times \frac{M_N}{V_m} \times \left[\mu_{sample} - \mu_{blank}\right]$$

Where, F_N (ng N m⁻² s⁻¹) is the flux of HONO in terms of N. μ_{sample} and μ_{blank} are the mixing ratio in the sample chamber and blank chamber, respectively. Q(m³ s⁻¹) is the purging flow rate, M_N (g mol⁻¹) is the molar mass of nitrogen, V_m (m³ mol⁻¹) is the molar volume of air, and A is the covered area of soil by the chamber.

2.2. Nitrous acid measurements in the chamber

The concentrations of NO_2 and HONO in the chamber were determined by IBBCEAS. IBBCEAS has previously been applied to the measurement of atmospheric HONO and NO_2 (Duan et al., 2018; Min et al., 2016; Nakashima and Sadanaga, 2017; Wu et al., 2014), and is based on Lambert-Beer law. The effective absorption path length is improved by the multiple reflection in the resonator cavity, thus improving the detection sensitivity of the instrument.

Here, the IBBCEAS instrument is based on the research of Duan et al. (2018), and a brief description of the structure of the instrument is given here. The schematic diagram of the IBBCEAS instrument is shown in Fig. 1. The main parts of the IBBCEAS instrument are a light source, achromatic lens, and band-pass filter, optical cavity with high reflective (HR) mirrors at both ends, off-axis parabolic mirror, optical fiber, and spectrometer. A UV LED (365 nm, LZ1-00UV00, LED engin, Osram GmbH, Munich, Germany) with a center wavelength of 365 nm, and a full width at half maximum of 13 nm was used as the light source that emitted 1680 mW of optical power. The optical cavity was composed of two HR mirrors (R = 99.975% @368 nm, Layertec GmbH, Munich, Germany) and a PFA tube with a length of 70 cm and an inner diameter of 22 mm. The surface of the mirrors was purged by dry nitrogen at 0.1 standard liter per minute, and the air flow was controlled by mass flow controller to prevent the surface of the mirror from being contaminated. In order to avoid the drift of the center wavelength of the LED, the temperature of the LED was controlled to be approximately 20 ± 0.05 °C by using a TEC unit. The UV light emitted by the LED was collimated by achromatic lens (f = 60 mm, Edmund) and passed through a band-pass filter (BG3, Newport Corp., Irvine, CA, USA) to suppress the influence of light beyond the measurement band on the

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