A relative method for measuring nitric oxide (NO) fluxes from forest soils

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HIGHLIGHTS

- We presented and tested a relative method for measuring NO fluxes from forest soils.
- The soil water samples could be kept in room temperature for several days or more for NO analysis.
- The calculated NO fluxes agreed well with the chamber-based values.
- This method provides a sound methodological basis for interpreting NO flux variations in the field.

GRAPHICAL ABSTRACT

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ABSTRACT

Many forest ecosystems in the world are suffering from high load of nitrogen (N) deposition and acting as potential contributors to atmospheric nitric oxide (NO), which regulates the oxidative capacity of the troposphere. However, the observation of NO flux with traditional dynamic chamber method is laborious in the forest ecosystem, particularly when the electric power generation system is unavailable. In this work, a relative method based on Fick's law of diffusion was developed to measure NO fluxes from forest soils. This method describes the relationship between NO and other trace gases, such as N₂O or CO₂, concerning gas fluxes and gas concentration gradients between the uppermost soil layer and the atmosphere. This relative method can be expressed as two forms: based on the directly obtained soil gas and based on the equilibrium gas at soil water surface. To testify the applicability of this method, both laboratory and field experiments were conducted with soil from an N-saturated subtropical forest in Southwestern China. The results demonstrate that the NO fluxes measured based on the later form agreed well with those observed by chamber method, with the deviation rates of around 9% and 30%, respectively. In conclusion, this relative method provides a sound methodological basis for interpreting NO flux variations in the field, especially in N-saturated forest ecosystems, and allows an improvement of statistical N-budget in the world.

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Nomenclature

C_0	gas concentration in the atmosphere ($\mu\text{g m}^{-3}$)
C_g	gas concentration in the uppermost soil layer ($\mu\text{g m}^{-3}$)
C_i	dissolved gas concentration in the soil water (mol L^{-1})
C_{vg}	gas concentration in the headspace of the soil water sampling vial (mol L^{-1} or atm)
C_{vi}	dissolved gas concentration in the solution collected in the soil water sampling vial (mol L^{-1})
C^*	equilibrium gas concentration upon the soil water surface ($\mu\text{g m}^{-3}$)
C_s	directly obtained soil gas concentration ($\mu\text{g m}^{-3}$)
ΔC	concentration difference between C_0 and C_g ($\mu\text{g m}^{-3}$), expressed as two forms according to the soil gas conditions (ΔC^* or ΔC^s)
D_0	gas diffusion coefficient in the atmosphere ($\text{cm}^2 \text{s}^{-1}$)
ρ_b	dry bulk density of the soil (g cm^{-3})
ρ_d	particle density (g cm^{-3})
D_s	gas diffusion coefficient in the soil ($\text{cm}^2 \text{s}^{-1}$)
F	soil-atmosphere exchange flux ($\mu\text{g m}^{-2} \text{h}^{-1}$)
K_H	Henry's law constant ($\text{mol atm}^{-1} \text{L}^{-1}$)
K_H^0	Henry's law constant at 298.15 K ($\text{mol atm}^{-1} \text{L}^{-1}$)
M	relative molecular mass for observed gas (g mol^{-1})
V_{vg}	final gaseous volume in the soil water sampling vial (L)
V_{vi}	final aqueous volume in the soil water sampling vial (L)
z	soil vertical distance from the soil gas or soil water sampling site to the soil surface (cm)
θ_g	gas-fill porosity in the soil ($\text{cm}^3 \text{cm}^{-3}$)
θ_t	total porosity in the soil ($\text{cm}^3 \text{cm}^{-3}$)
ω	gravimetric water content (mL cm^{-3})

1. Introduction

Nitric oxide (NO), a highly reactive trace gas, plays a crucial role in tropospheric chemistry (Crutzen, 1979; Ludwig et al., 2001; Medinets et al., 2015). Due to the fast chemical conversion between NO and NO₂, which typically occurs within seconds to minutes, NO and NO₂ are commonly considered as the single quantity NO_x. It determines the lifetime of many trace gases and regulates the oxidizing capacity of the troposphere. Soils are a major source of atmospheric NO (Davidson and Kingerlee, 1997; Galbally and Roy, 1978). It is reported that with increasing NH₃-volatilisation from agriculture, many forest ecosystems have received large amounts of N-deposition and acted as potential contributors to the tropospheric NO burden (Buhlmann et al., 2015; Skiba et al., 1998; Venterea et al., 2003).

Previous NO flux measurements from forests were, however, imbalanced in regions under investigation. Most NO flux measurements have been proceeded in Europe and United States (Erickson and Perakis, 2014; Luo et al., 2012; Schindlbacher et al., 2004; van Dijk and Duyzer, 1999); while the studies were limited in Asia (Li et al., 2007; Nishina et al., 2009; Purbopuspito et al., 2006), where most field measurements were centered on croplands (Mei et al., 2009; Zhang et al., 2016a; Zhang et al., 2016b). Given the limited experiments involved, the observed forest NO fluxes in Asia are far from representative of its biome. Previous works have reported that the N-deposition rate in China was higher than those in the United States and Europe, with the average values of 12.89 kg N ha⁻¹ yr⁻¹ (Lu and Tian, 2007). Considering the diverse forest types and the large N-deposition in Asia, especially in China, more observations are undoubtedly needed to form the basis for upgrading NO flux from site scales to regional scales.

To date, the dominant method for NO flux measurements is the dynamic chamber method (Li et al., 2008; Pilegaard et al., 2006; Wolf et al., 2011b; Wu et al., 2010). However, this method proves defective in the

field, especially in the forest ecosystems. Because, in most instances, the electric power generation system for the operation of pump and on-line NO detection instrument is unavailable. Therefore, multiple proxies have been proposed to estimate NO flux in the field, such as laboratory incubation experiments (Bargsten et al., 2010; Schaufler et al., 2010; Yao et al., 2010), empirical models (Stark et al., 2002; Stehfest and Bouwman, 2006; Yan et al., 2005) and diffusion models (Galbally and Johansson, 1989; Remde et al., 1993; van Dijk et al., 2002). Comparing with the in-situ experiment, the laboratory incubation experiment is more suitable for investigating environmental factors regulating soil gas emissions, rather than quantifying the soil gas emission fluxes. Because when the soil cores were collected from the field, the corresponding soil environments would change. The empirical model is developed based on the relationship with NO flux and various environmental factors, such as soil temperature, soil water content and N availability, through large numbers of field measurements. However, due to the imbalanced work done in regions, this method will induce huge discrepancy in NO flux estimation.

As regards the diffusion model, it has been applied for various gases, such as N₂O, CO₂, CH₄ (Kusa et al., 2008; Pihlatie et al., 2007; Pumpanen et al., 2003), HONO (Su et al., 2011) and Hg (Wang et al., 2014; Zhang et al., 2002). This method is developed based on Fick's law of diffusion, concerning soil gas diffusion coefficient and concentration gradient between the uppermost soil layer and the atmosphere. The soil gas diffusion coefficient is related to soil properties, such as soil water content and soil tortuosity, which are spatially and temporally variable (Hutchinson and Livingston, 2002). Thus, this imprecision in estimating soil gas diffusion coefficient will result in large uncertainties in estimations of gas flux.

In this work, we propose a relative method based on gas diffusion principle in soil for measuring NO fluxes from forest soils, especially when the electric power supply system is unavailable. We first derive the formulation of this method, and then test this method through laboratory and field experiments with soil from an N-saturated subtropical forest in Southwestern China.

2. Methods

2.1. The principle of the relative method

2.1.1. Diffusion model

Gas transportation through the soil profile occurs predominantly by diffusion process (Hutchinson and Livingston, 2002). Many reported works assumed that the soil gas diffusion coefficient was constant within the soil profile, and the sources or sinks of the target gas were negligible compared with the quantity of the gas transported by diffusion. Thus, the soil-atmosphere gas exchange flux could be calculated with the diffusion model based on Fick's law:

$$F = -(D_s/z)(C_0 - C_g) = -(D_s/z)\Delta C \quad (1)$$

where F represents the gas exchange flux between soil and atmosphere ($\mu\text{g m}^{-2} \text{h}^{-1}$), D_s means the soil gas diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), which primarily depends on gas properties and the corresponding soil conditions, such as soil air content and soil tortuosity, z is the soil vertical distance (cm), and ΔC represents the gas concentration difference between the atmosphere (C_0 ($\mu\text{g m}^{-3}$)) and the uppermost soil layer (C_g ($\mu\text{g m}^{-3}$)). The gas concentration in the uppermost soil layer (C_g) can be expressed as two forms: the equilibrium concentration upon soil water surface (C^*) (Su et al., 2011) and the directly obtained soil gas concentration (C_s) (Kusa et al., 2008; Wolf et al., 2011a). In most ecosystems, the equilibrium between soil water and soil gas cannot be achieved. When large numbers of gases were produced in the soil, continuous gas emission from soil water to soil gas may occur. In this paper, we will introduce the method based on these two forms.

We assumed that the soil water followed the ideal solution behavior (Su et al., 2011). The equilibrium gas concentration (C^*) upon soil water surface can be calculated according to Henry's law:

$$C^* = C_i/K_H \quad (2)$$

$$K_H(T) = K_H^\circ \exp((1/T - 1/298.15K) \ln(K_H)/d(1/T)) \quad (3)$$

where C_i represents the dissolved gas concentration in soil water (mol L^{-1}), K_H means Henry's law constant ($\text{mol atm}^{-1} \text{L}^{-1}$), K_H° represents the value of K_H at 298.15 K ($\text{mol atm}^{-1} \text{L}^{-1}$), and $\ln(K_H)/d(1/T)$ indicates a temperature related factor.

The soil gas diffusion coefficient at certain temperature $D_s(T)$ ($\text{cm}^2 \text{s}^{-1}$) can be calculated as follows: (Heincke and Kaupenjohann, 1999; Jin and Jury, 1996):

$$D_s(T) = [D_0(T_0)(T/T_0)^{1.81}] \theta_g^2 \theta_t^{-2/3} \quad (4)$$

where θ_g and θ_t are the gas-fill porosity and total porosity in the soil ($\text{cm}^3 \text{cm}^{-3}$), and $D_0(T_0)$ represents the gas diffusion coefficient in the atmosphere at standard temperature ($\text{cm}^2 \text{s}^{-1}$). The value of $D_0(T_0)$ for target gas is constant and can be calculated by the CO62 method (Massman, 1998). For example, the D_0 values for N_2O , NO and CO_2 under standard temperature are 0.14, 0.20 and $0.14 \text{ cm}^2 \text{s}^{-1}$, respectively. The air-filled porosity (θ_g) and total porosity in the soil (θ_t) are given by (Davidson and Trumbore, 1995):

$$\theta_t = 1 - \frac{\rho_b}{\rho_d} \quad (5)$$

$$\theta_g = \theta_t - \omega \quad (6)$$

where ω is the gravimetric water content (mL cm^{-3}), ρ_b represents the dry bulk density of the soil (g cm^{-3}), and ρ_d means the particle density (g cm^{-3}). However, these parameters are spatially and temporally variable. Large uncertainties will be induced in estimates of soil gas diffusion coefficient.

2.1.2. The relative method

In this paper, we assumed that the top soil layer was kinetically in steady-state, and the diffusion paths were the same for different soil gases. Thus, the corresponding soil characteristics, such as soil temperature, gas-fill porosity and total porosity, were the same. If we related the diffusion processes of two soil gases, such as NO and N_2O or NO and CO_2 , as follows (Eqs. (7)–(8)), the uncertainty resulted from varying soil properties could be ignored and the gas diffusion coefficients in the soil (D_1^s and D_2^s) would be substituted by those in the air (D_1^0 and D_2^0):

$$\frac{F_1}{F_2} = \frac{-D_1^s(C_1^0 - C_1^*)}{-D_2^s(C_2^0 - C_2^*)} = \frac{D_1^0}{D_2^0} \times \frac{\Delta C_1^*}{\Delta C_2^*} \quad (7)$$

or

$$\frac{F_1}{F_2} = \frac{-D_1^s(C_1^0 - C_1^s)}{-D_2^s(C_2^0 - C_2^s)} = \frac{D_1^0}{D_2^0} \times \frac{\Delta C_1^s}{\Delta C_2^s} \quad (8)$$

where $\frac{F_1}{F_2}$ demonstrates linear correlation with $\frac{\Delta C_1^*}{\Delta C_2^*}$ or $\frac{\Delta C_1^s}{\Delta C_2^s}$, and the slope is

$\frac{D_1^0}{D_2^0}$. This equation can also be represented in the following:

$$\frac{F_1}{F_2} = \left(\frac{D_1^0 M_1 K_{H2}}{D_2^0 M_2 K_{H1}} \times \frac{1 - \frac{C_1^0}{C_1^*}}{1 - \frac{C_2^0}{C_2^*}} \right) \times \frac{C_1^*}{C_2^*} \quad (9)$$

or

$$\frac{F_1}{F_2} = \left(\frac{D_1^0}{D_2^0} \times \frac{1 - \frac{C_1^0}{C_1^s}}{1 - \frac{C_2^0}{C_2^s}} \right) \times \frac{C_1^s}{C_2^s} \quad (10)$$

where M_n represent the relative molecular mass for observed gas. When both gases are largely produced in the soil ($\frac{C_1^0}{C_1^*} < 23\%$ and $\frac{C_2^0}{C_2^*} < 23\%$ or $\frac{C_1^0}{C_1^*} < 3\%$ and $\frac{C_2^0}{C_2^*} < 3\%$, i.e.), gas concentrations in the atmosphere can be neglected and Eqs. (9)–(10) will be further simplified with the deviation rate lower than 30%, which is within an acceptable range reported before for large-scale field experiments (Luo et al., 2012; Stehfest and Bouwman, 2006; van Dijk et al., 2002):

$$\frac{F_1}{F_2} = \frac{D_1^0 M_1 K_{H2}}{D_2^0 M_2 K_{H1}} \times \frac{C_1^*}{C_2^*} \quad (11)$$

or

$$\frac{F_1}{F_2} = \frac{D_1^0}{D_2^0} \times \frac{C_1^s}{C_2^s} \quad (12)$$

These equations show linear relationships between $\frac{F_1}{F_2}$ and $\frac{C_1^*}{C_2^*}$ or $\frac{C_1^s}{C_2^s}$, with $\frac{D_1^0 M_1 K_{H2}}{D_2^0 M_2 K_{H1}}$ and $\frac{D_1^0}{D_2^0}$ as the slopes of the linear fitting. These theoretical slopes: $\frac{D_{\text{NO}}^0 M_{\text{NO}} K_{\text{HN}_2\text{O}}}{D_{\text{N}_2\text{O}}^0 M_{\text{N}_2\text{O}} K_{\text{HNO}}}$, $\frac{D_{\text{N}_2\text{O}}^0 M_{\text{N}_2\text{O}} K_{\text{HCO}_2}}{D_{\text{CO}_2}^0 M_{\text{CO}_2} K_{\text{HN}_2\text{O}}}$ and $\frac{D_{\text{NO}}^0 M_{\text{NO}} K_{\text{HCO}_2}}{D_{\text{CO}_2}^0 M_{\text{CO}_2} K_{\text{HNO}}}$, can be calculated by empirical constants, and the values are 13.81, 1.36 and 18.84, respectively. Similarly, the theoretical values of $\frac{D_{\text{NO}}^0}{D_{\text{N}_2\text{O}}^0}$, $\frac{D_{\text{N}_2\text{O}}^0}{D_{\text{CO}_2}^0}$ and $\frac{D_{\text{NO}}^0}{D_{\text{CO}_2}^0}$ are calculated as 1.44, 0.98 and 1.42, respectively. Therefore, we can indirectly calculate NO fluxes through the relationship with the flux of N_2O or CO_2 by static chamber method.

2.2. Testing the relative method in the laboratory

The laboratory experiment was conducted with soil samples collected from Tieshanping (29°38'N 104°41'E, TSP, for short), a Masson pine-dominated subtropical forest, in Southwestern China (Fig. 1). TSP has suffered from high load of N-deposition for years ($>5 \text{ g m}^{-2} \text{ yr}^{-1}$). The mean annual temperature and rainfall is 18.2 °C and 1028 mm, with summer being the hottest and wettest period of the year. The soil is acid with the pH value of around 4. For further details about this measurement site, see Zhu et al. (2013). During the laboratory experiment, the water doses applied followed the rainfall in TSP on weekly basis. Thus the soil would experience wetting-drying cycles. The room temperature was kept at around 20 °C, assuring appropriate conditions for microbial activities and enough NO, N_2O and CO_2 production in the soil. In order to establish this relative method, the soil-atmosphere exchange fluxes, dissolved gas concentrations in soil water and soil gas concentrations of NO, N_2O and CO_2 were observed simultaneously.

Fig. 1. Location of the Tieshanping (TSP) forest catchment, Chongqing, China.

2.2.1. Measurements of soil-atmosphere exchange fluxes

During the laboratory experiment, NO, N₂O and CO₂ fluxes were measured by an improved static chamber method (Fig. 2). The chamber is a cylinder made of PVC (20.50 cm in height and the cross-sectional diameter is 26.50 cm). During the whole period, the chamber was treated with light avoidance, and hence any potential photolytic processes, such as OH and VOC production, will not take place in the chamber. Before experiment, the chamber was flushed with dry synthetic air (free from NO and O₃) 10 min with the flow rate of 10 L min⁻¹ to reduce the O₃ concentration level in the chamber (approximately 99.50% lower than that in the ambient air), so as to exclude the potential oxidation process from NO to NO₂ by O₃. Simultaneously, the chamber was shield from the soil with a Teflon cover without disturbing the soil surface. At the top of the chamber, a three-way valve and an inflatable

Teflon bag were installed for gas samples collection and pressure-buffering, respectively. The gas samples were taken with a 50 mL syringe. To mix the chamber air, the syringe should be filled and flushed three times before sampling. During the observation time-period, 40 mL gas was taken for NO analyses at an interval of 5 min and the sampling period lasted 20 min. Another 10 mL gas sample for N₂O and CO₂ analyses was obtained by pre-evacuated 10 mL glass vials at every turn. Our main interest of the laboratory experiment was in verifying the relative method, with no aim to reproduce the gas flux under actual experiment condition.

NO concentration was determined discontinuously by a NO-NO_x analyzer (Thermo Fisher 42i, chemiluminescence detector, USA). Gas samples were injected into the gas stream of NO-free high-purity argon gas to the detector. The detection limit is 1.62 μg m⁻³. The NO-NO_x analyzer

Fig. 2. Schematic of the set-up of improved static chamber, soil gas and soil water samplers.

was calibrated by varying the amount of NO standard gas mixed with purified argon (free of NO). The concentrations of N_2O and CO_2 were analyzed by Agilent 7890 gas chromatography, equipped with an electron capture detector and a flame ionization detector.

2.2.2. Measurements of soil gas concentrations

Previous experiments showed that soil gases, such as N_2O and NO, were mostly produced and consumed within the uppermost soil layer (0–0.1 m), which is characterized by high content of organic material (Bargsten et al., 2010; Ludwig et al., 2001; Pihlatie et al., 2007). For this reason, the soil water and soil gas samplers, in this work, were both installed horizontally in triplicate at the depth of 3 cm right below the chamber (Fig. 2). After we installed the samplers, the soil was consolidated for several rain events prior to first gas sampling.

Soil gases were collected from perforated PVC samplers (radius 0.75 cm, height 11 cm) through Teflon tubes, equipped with three-way valves. Our soil gas sampler was a kind of active sampler. During each sampling, the initial 30 mL of the soil gas from the sampling line and sampling tube was rejected, and then another 40 mL soil gas sample was drawn into a 50 mL syringe for NO analysis. In order to avoid photochemical reactions, the gas samples should be covered by aluminum foil. Another 10 mL gas sample for N_2O and CO_2 analysis was transferred to a pre-evacuated 10 mL glass vial.

The appropriate soil gas volume sampled each time should depend on the collecting depth of soil layer and the soil volumetric water content (Nauer et al., 2013). In a homogeneous soil, the shape of the soil from which the soil gas is withdrawn can be simplified as an annular column around the sampler (Fig. S1). When the soil gas sampler was set at the depth of 3 cm, the outer radius of this annular column should not exceed 3.75 cm, otherwise the sampled soil gas would be diluted by air upon soil surface. This corresponded to a maximum volume of 466 mL for the annular column. Hence, when the soil air-filled porosity was $0.5 \text{ m}^3 \text{ m}^{-3}$, the safe gas sampling volume should be <233 mL. During the soil gas sampling period, about 80 mL soil gas was needed. This was within the maximum volume. Besides, our pre-field experiment demonstrated that the measured soil gas concentration was not affected by the ambient gas (Fig. S2).

We have conducted preservation experiment for soil NO concentration analysis in the laboratory. 300 mL soil gas was sampled and preserved in a 1 L Teflon bag for well mix. Then we immediately transferred the soil gas from the Teflon bag into five 50 mL syringes covered by aluminum foil. During the experiment, these gas samples were analyzed after 0, 3, 7, 10 and 15 days, respectively. The results showed that NO gas in the soil could be reserved for 15 days, with the deviation rate of 7.50% (Fig. 3).

2.2.3. Measurements of dissolved gas concentrations in soil water

The dissolved gas concentrations in soil water were analyzed by headspace equilibration technique (Cole and Caraco, 2001; Huang et al., 2013; Moraghan and Buresh, 1977). Soil water was collected by ceramic suction cup lysimeter (P80; Staatliche Porzellanmanufaktur, Berlin) with a three-stopcock assembly. The soil gas were filled out and only the soil water could pass into the sampler. To ensure the accuracy of the dissolved gas concentration in soil water, each soil water sampler should be tested for leakage before installing. Before each sampling, the residual soil water in the sampler was discharged. Then about 25 mL soil water was collected with a 100 mL pre-evacuated glass vial. During the whole sampling period, glass vials were covered by black drawstring bags to avoid direct sunlight.

The weights of the glass vial before and after soil water sampling should be measured to calculate the aqueous (V_{vl} (L)) and gaseous volume (V_{vg} (L)) in the glass vial. After soil water sampling, we use high-purity argon (free from NO, N_2O and CO_2) to equilibrate the glass vial pressure. The glass vial was shaken vigorously for 2 min by hand, allowing fully equilibration of the air and water phase. Then the headspace gas was pushed out by water flowing automatically by gravity, making sure that the headspace gas was under standard atmospheric pressure. A 40 mL gas sample was collected for NO analysis and another 10 mL gas was stored in a 10 mL pre-evacuated glass vial for N_2O and CO_2 analysis. The dissolved gas concentration in soil water (C_l (mol L^{-1})) can be calculated in the following:

$$C_l = (C_{vg}V_{vg} + C_{vl}V_{vl})/V_{vl} \quad (13)$$

$$C_{vl} = C_{vg}K_H \quad (14)$$

where C_{vg} indicates the gas concentration in the headspace of the glass vial (mol L^{-1} or atm) and C_{vl} represents the dissolved gas concentration in the water collected in the glass vial (mol L^{-1}). In this work, Eqs. (13)–(14) can be applied to calculate dissolved CO_2 concentration because the soil pH value in TSP is around 4 with CO_2 as the only existent form in the soil water.

The preservation experiment for NO gas dissolved in soil water has also been conducted. During the experiment, soil water samples were collected into five 100 mL glass vials covered by black drawstring bags, and these samples were analyzed after 0, 3, 7, 10 and 15 days,

Fig. 3. NO concentration variations in soil gas and soil water during preservation experiment.

Fig. 4. (a)–(c) The relationships between NO, N₂O and CO₂, concerning gas fluxes and gas concentration gradients between the uppermost soil layer and the atmosphere. The data are color coded by the number of watering events. The red solid line denotes the fitted regression line and the red dashed one indicates the line with theoretical slope calculated with empirical constants. (d) NO flux variations measured by the chamber method and the relative method (from N₂O and CO₂, respectively) during laboratory experiment. The black arrows indicate the watering events.

respectively. The results showed that the soil water samples could be reserved for at least 15 days, with the deviation rate of 7.19% (Fig. 3).

2.3. The field experiments

In order to testify the applicability of this relative method in the forest ecosystem, the field experiment was conducted in TSP from July 2014 to June 2015 covering four consecutive seasons. To represent the subtropical forest characteristics in south central China, we selected a 4.6 ha forested head water catchment in TSP, with 96.4% consisted of North-faced hill slopes (HS) and the remainder consisted of ground water discharge zone (GDZ). The dominant soil types in HS and GDZ are clay-rich loamy yellow mountain soil and colluvium soil, respectively. Four sampling plots were selected along these two hydrologically-connected transects, with plot A at the top of HS, plot B at the bottom of HS, plot C at the interface between HS and GDZ, and plot D at GDZ.

In the field experiment, gas flux measurements for N₂O and CO₂ were conducted with traditional static chamber made of stainless steel (40 cm × 40 cm, height 15 cm). During each sampling period, 10 mL gas was taken by pre-evacuated 10 mL glass vial from the chamber at an interval of 5 min after the enclosure of the chamber. The sampling period lasted 20 min. The direct NO flux measurements with dynamic chamber method were only available in A and B sampling plots from July to August 2015, and the details will be shown in a companion paper, supported by Norwegian University of Life Sciences. The soil gas and soil water sampling processes were the same as those described in Section 2.2.

3. Results and discussions

3.1. Testing the relative method in the laboratory

3.1.1. The relative method based on soil gas

During the laboratory experiment, several watering events were conducted, ensuring that the incubated soil experimented several dry-wet cycles. The correlation plot in Fig. 4a shows a poor linear regression between $\frac{F_{N_2O}}{F_{CO_2}}$ and $\frac{\Delta C_{N_2O}^S}{\Delta C_{CO_2}^S}$, with a slope of 1.43 ($R^2 = 0.80$). Note that this relationship varied with different soil conditions, which was induced by watering events. This indicates that when the investigated soil experienced different soil environments, the uncertainty resulted from the changeable soil characteristics could not be overcome. Comparing with this poor relationship, we found better linear correlations between $\frac{F_{NO}}{F_{N_2O}}$ and $\frac{\Delta C_{NO}^S}{\Delta C_{N_2O}^S}$ ($R^2 = 0.87, P < 0.01$), and between $\frac{F_{NO}}{F_{CO_2}}$ and $\frac{\Delta C_{NO}^S}{\Delta C_{CO_2}^S}$ ($R^2 = 0.93, P < 0.01$) in Fig. 4b and Fig. 4c. These slopes of linear fitting were, however, both largely strayed from what should be expected from empirical constants ($\frac{D_{NO}^0}{D_{N_2O}^0} = 1.44$ and $\frac{D_{NO}^0}{D_{CO_2}^0} = 1.42$), with the deviation rates of 164.58% and 245.77%, respectively.

Furthermore, we made a comparison between NO flux measurements made by the chamber method and the relative method based on the relationship between $\frac{F_{NO}}{F_{N_2O}}$ and $\frac{\Delta C_{NO}^S}{\Delta C_{N_2O}^S}$ or between $\frac{F_{NO}}{F_{CO_2}}$ and $\frac{\Delta C_{NO}^S}{\Delta C_{CO_2}^S}$ in Fig. 4d. The NO fluxes measured by the relative method demonstrated similar variation pattern as those by the chamber method: the value dropped to the lowest point after watering events and gradually increased to the top with soil moisture decreasing. Nevertheless,

Fig. 5. (a)–(c) The relationships between NO, N₂O and CO₂, regarding gas emission fluxes and dissolved gas concentrations in soil water. The data are colour coded by the number of watering events. The red solid line denotes the fitted regression line and the red dashed one indicates the line with theoretical slope calculated by empirical constants. (d) NO flux variations measured by the chamber method and the relative method (from N₂O and CO₂, respectively) during laboratory experiment. The black arrows indicate the watering events.

comparing with the chamber-based NO fluxes, the calculated fluxes were both significantly underestimated. The preceding dissatisfactory results, therefore, represented that the feasibility of this method based on soil gas to evaluate NO flux variation was still questionable and we should further conduct field experiments to assess it.

Fig. 6. The relationship between N₂O and CO₂, concerning gas emission fluxes and gas concentration gradients between the uppermost soil layer and the atmosphere in TSP. The red solid line denotes the regression line and the red dash-dotted one indicates the theoretical line calculated by empirical constants. The hollow points represent the data collected during summer campaign.

3.1.2. The relative method based on soil water

In Fig. 5, significant linear correlations were found between $\frac{F_{NO}}{F_{N_2O}}$ and $\frac{C_{NO}^I}{C_{N_2O}^I}$ ($R^2 = 0.97$, $P < 0.01$), $\frac{F_{N_2O}}{F_{CO_2}}$ and $\frac{C_{N_2O}^I}{C_{CO_2}^I}$ ($R^2 = 0.97$, $P < 0.01$), as well as between $\frac{F_{NO}}{F_{CO_2}}$ and $\frac{C_{NO}^I}{C_{CO_2}^I}$ ($R^2 = 0.96$, $P < 0.01$), when investigated soil experienced multiple watering events. These slopes all agreed well with the theoretical ones calculated with empirical constants ($\frac{D_{NO}^0 M_{NO} K_{HN_2O}}{D_{N_2O}^0 M_{N_2O} K_{HNO}} = 13$, $81 \cdot \frac{D_{N_2O}^0 M_{N_2O} K_{HCO_2}}{D_{CO_2}^0 M_{CO_2} K_{HN_2O}} = 1.36$, $\frac{D_{NO}^0 M_{NO} K_{HCO_2}}{D_{CO_2}^0 M_{CO_2} K_{HNO}} = 18.84$), with the deviation rates of 4.63%, 16.91% and 7.38%, respectively. These small deviations indicated that this relative method based on soil water was irrelevant to soil conditions.

In order to examine the capability of this method to evaluate NO flux variations, the comparison between NO fluxes measured by the chamber method and the relative method (based on the relationship between $\frac{F_{NO}}{F_{N_2O}}$ and $\frac{C_{NO}^I}{C_{N_2O}^I}$ or between $\frac{F_{NO}}{F_{CO_2}}$ and $\frac{C_{NO}^I}{C_{CO_2}^I}$) was showed in Fig. 5d.

We found that the calculated NO fluxes agreed well with the observed values, and the variation pattern closely resembled that previously reported in Fig. 4d, with NO flux dropping to the lowest point after watering events and gradually increasing when soil moisture decreased. These differences between NO fluxes measured by chamber method and the relative method from N₂O and CO₂ were both significantly lower (around 9%). This good consistency showed during the wet-dry cycles further identified that this method was suitable for measuring NO fluxes. In the next section, we will investigate the capability of this relative method to interpret NO flux variations in the forest ecosystem.

3.2. Testing the relative method by field measurements

3.2.1. The relative method based on soil gas

The field experiments in TSP have covered multiple seasons and sampling plots. The investigated soil experienced characteristic wet and dry soil conditions, with the soil water filled pore space (WFPS) ranging from 7% to 63%. The average soil temperature value varied from 6.92 °C in winter to 26.19 °C in summer. The correlation plot in Fig. 6 shows a poor relationship between $\frac{F_{N_2O}}{F_{CO_2}}$ and $\frac{\Delta C_{N_2O}^S}{\Delta C_{CO_2}^S}$, with R^2 value of 0.77 ($N = 282, P < 0.01$). Consistent with the dissatisfactory results represented in Fig. 4a, the slope of the linear regression shown here also intensively strayed away from the expected value ($\frac{D_{N_2O}^0}{D_{CO_2}^0} = 0.98$), with the deviation rate of 124.49%. We found that this significant discrepancy happened when the upmost soil layer was extremely unsteady, particularly in summer when intense bacteria activities happened upon the soil gas sampler.

Then, we applied the relative method based on soil gas to measure NO fluxes in TSP from July to August 2014. The average NO fluxes calculated according to the relationship between $\frac{F_{NO}}{F_{N_2O}}$ and $\frac{\Delta C_{NO}^S}{\Delta C_{N_2O}^S}$ ($6.01 \pm 5.52 \mu\text{g N m}^{-2} \text{h}^{-1}$ and $11.08 \pm 1.65 \mu\text{g N m}^{-2} \text{h}^{-1}$) were, as expected, much lower than those measured with chamber method ($12.01 \pm 12.03 \mu\text{g N m}^{-2} \text{h}^{-1}$ and $34.05 \pm 36.17 \mu\text{g N m}^{-2} \text{h}^{-1}$) in A and B two sampling plots. The correlation analysis and the comparison results confirmed that the relative method based on soil gas was unsuitable for NO flux estimation in the field.

Here we attribute these dissatisfactory results to the potential biological activities that happened upon the samplers. When introducing this relative method, we assumed that the upmost soil layer was in steady state, and only considered the physical transportation process in the soil profile. However, even though we can install the soil gas samplers as close as to the soil surface layer, we cannot avoid but only reduce the influence from potential biological activities. If biological activities happened upon soil gas samplers, the time scale of soil gas diffusion process would be larger than that affecting the soil gas concentration difference. Thus, the emission fluxes measured by the relative method will be over- or underestimated. Previous studies that compared flux measurements by the chamber method and the diffusion

model based on the directly obtained soil gas have yielded mixed results. For example, Kusa et al. (2008) found no significant difference between the N_2O fluxes measured by these two methods. However, the comparison results by Pihlatie et al. (2007) represented that the N_2O fluxes measured by the diffusion method were higher and more variable than those by chamber method. Wolf et al. (2011a) found that the differences between these two methods ranged from −3.4% to 20% and from 40.7% to 76.9%, respectively, for CO_2 and N_2O flux measurements.

3.2.2. The relative method based on soil water

The correlation plot in Fig. 7 represents a remarkable linear relationship between $\frac{F_{N_2O}}{F_{CO_2}}$ and $\frac{C_{N_2O}^I}{C_{CO_2}^I}$, with R^2 value of 0.91 ($N = 344, P < 0.01$). This linear regression agreed well with the theoretically developed one and the deviation rate (4.41%) was unexpectedly lower than that in the laboratory experiment (16.91%). We attributed this lower deviation rate to the larger time and space span covered in the field experiment. Note that this linear correlation can be achieved even in summer, when the upmost soil layer was extremely unsteady: large numbers of soil gases were produced or consumed. The good correlation and consistency further indicated that, with the relative method based on soil water, the proposed hypothesis: if we related the diffusion processes of two soil gases, the uncertainty resulted from varying soil properties could be effectively overcome, can be applicable in the field.

Furthermore, we applied this relative method base on soil water for NO fluxes measurement from July to August 2014. Considering the entire summer campaign, there was good agreement between the chamber-based values ($12.01 \pm 12.03 \mu\text{g N m}^{-2} \text{h}^{-1}$ and $34.05 \pm 36.17 \mu\text{g N m}^{-2} \text{h}^{-1}$) and those calculated based upon the relationship between $\frac{F_{NO}}{F_{N_2O}}$ and $\frac{C_{NO}^I}{C_{N_2O}^I}$ ($10.37 \pm 3.06 \mu\text{g N m}^{-2} \text{h}^{-1}$ and $23.32 \pm 5.86 \mu\text{g N m}^{-2} \text{h}^{-1}$) in A and B two sampling plots, with the deviation rates of 13.66% and 31.54%, respectively. Therefore, we concluded that the relative method based on soil water can act as a promising alternate for NO flux measurements in the field.

In contrast to the directly obtain soil gas, some researchers (Remde et al., 1993; van Dijk et al., 2002) have proposed a theoretically steady-state soil gas, which reached the point when gas-producing and gas-consuming processes balanced each other, to evaluate NO flux variation. Considering the superiority of the relative method based on soil water, we inferred that the equilibrium gas upon soil water surface could better depict the theoretically steady-state soil gas. Biological activities, such as nitrification and denitrification processes, generally take place in the soil water. Thus, the equilibrium gas concentration upon soil water surface is the integrated product of gas production and consumption through serials of biological reactions. Our conclusion was consistent with the work by Su et al. (2011), which found that the theoretically equilibrium HONO concentration in the upmost soil layer could well interpret the HONO soil-atmosphere exchange flux through chamber experiment. However, preceding analysis merely depended upon our experiment results and hypothesis. It is meaningful if more intensive and convincing experiments, such as relating to biological activities, are carried out to disclose further detail about this issue.

4. Conclusions

In this paper we presented and tested a relative method for the measurements of NO flux from forest soils. Our laboratory experiments and the measurements in the field demonstrated that this method based on soil water was suitable for NO flux measurements in the forest ecosystem. During both laboratory and field experiments, the NO fluxes calculated by the relationship between $\frac{F_{NO}}{F_{N_2O}}$ and $\frac{C_{NO}^I}{C_{N_2O}^I}$ agreed well with the chamber-based flux measurements. The good correlation between $\frac{F_{N_2O}}{F_{CO_2}}$ and $\frac{C_{N_2O}^I}{C_{CO_2}^I}$

Fig. 7. The relationship between N_2O and CO_2 , concerning gas fluxes and dissolved gas concentrations in soil water in TSP. The red solid line denotes the regression line and the red dashed one indicates the theoretical line calculated by empirical constants. The hollow points represent the data collected during summer campaign.

found in the field from July 2014 to June 2015 indirectly validated the capability of this relative method to measure NO fluxes over large timescale, for instance to establish seasonal variations within an ecosystem. The preservation experiment showed that the filtered soil water samples could be kept in room temperature for several days or more for NO analysis, so our method was convenient for regional investigation of NO fluxes. In conclusion, the relative method based on soil water acts as a promising proxy to measure NO fluxes in the forest ecosystem, particularly where the power system is unavailable, and then contributes to profile the inventory of NO emission in the world. Additionally, our relative method may provide a methodological basis for the flux measurements of other nitrogen-containing gases, such as nitrous acid (HONO), which has been proven challenging in the world. However, the application of this method should be explored further; more intensive and convincing experiments are needed.

Acknowledgments and data

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.09.012>.

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